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Microbial Ecology of High Zinc Level Streams

By

Philip J. Say

(B.Sc. Nottingham)

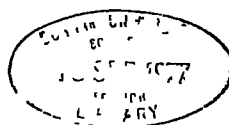
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A Thesis

submitted for the Degree
of Doctor of Philosophy
in the University of Durham

Department of Botany

January, 1977.



This thesis is entirely the result of my own work except for the text references to publications. It has not previously been submitted for any degree or diploma.

P. J. Say

Philip J. Say

January, 1977.

ABSTRACT

A study has been carried out of zinc enrichment in streams draining the Northern Pennine Orefield and the effects of this enrichment on the algae. The sources of the contamination are described and are attributed mainly to continued discharge from adits, and drainage from tailings heaps associated with the disused lead-zinc mines.

Details of surveys performed on 10m reaches situated on 45 streams and an intensive survey of 30 reaches on one stream (Gillgill Burn, Nenthead, Cumbria) are given.

Using factor analysis to evaluate the interrelationships of the inorganic chemical components, the weathering of carbonate minerals was indicated as being an important factor in controlling the ionic composition of the waters.

With increasing levels of zinc, fewer species of algae were represented. Of those species that were present at the higher levels, the genus *Hormidium* was frequently evident. In particular, *H. rivulare* was widespread and often also abundant. A survey of 47 reaches with both high and low levels of zinc was carried out to establish the extent to which populations of *Hormidium* spp. taken from the former were in fact resistant to the zinc. It was demonstrated in the laboratory for *H. rivulare* that this resistance was largely, if not entirely, due to genetic adaptation.

An assessment of the influence of environmental factors in the field on the toxicity of zinc to *H. rivulare* was made by comparing the results of laboratory bioassays with the detailed water chemistry of the sites from which populations were taken. These tentative results were compared with experimental studies in the laboratory. The important factors increasing toxicity are Cd and a rise in pH. Factors leading to a decrease in toxicity are Mg, Ca, and $\text{PO}_4\text{-P}$.

List of abbreviations

°C	degrees Celsius
EDTA	ethylenediaminetetra-acetic acid (disodium salt)
g	gram
h	hour
l	litre
m	metre
M	molar
mg	milligram
min	minute
ml	millilitre
mm	millimetre
µg	microgram
µm	micrometre
nm	nanometre
NTA	nitrilotriacetic acid
O.D.	optical density
P	probability
u.v.	ultra-violet

Glossary

This includes a summary of the words whose usage may lead to ambiguity in the text.

Flush: a watery area around a spring or seepage which may not necessarily have visible flowing water in it.

Groundwater: waters issuing directly from adits and springs or waters primarily influenced by these sources.

Hard water: waters with high levels of hardness producing elements and includes those with levels of calcium exceeding 50mg l^{-1} .

Seepage: very small quantities of water percolating from spring channels creating local marsh or bog areas.

Soft water: waters with low levels of hardness producing elements and includes those with levels of calcium much lower than 50mg l^{-1} , usually less than 20mg l^{-1} .

Spring: water from an underground source issuing at the surface.

Surface water: waters derived more or less totally from atmospheric sources or those primarily influenced by such sources.

Trickle: a small irregular stream.

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1 INTRODUCTION

1.1 General Introduction

In reviewing microbial growth under extreme conditions, Brock (1969) opens his discussion with the question "What is an extreme environment?" He offers an "appropriate" definition as ".... a condition under which some kinds of organisms can grow, whereas others cannot." In accepting this definition he states that the assemblage of species, microbial and multi-cellular living in such environments should be studied, rather than one species. He shows that in this way an idea of the species diversity is obtained, and illustrates this with examples such as saline and thermal lakes, where there are no vascular plants or vertebrates, but which can be rich in microorganisms. He goes on to state that "Such environments are clearly of enormous interest to the microbiologist, especially one interested in the ecological and evolutionary relationships of organisms."

Brock shows that since by definition extreme environments do not support many organisms, two important sets of questions can be asked:

(1) how does the environmental extreme affect organisms which cannot tolerate it?

(11) How is it possible for organisms which are adapted to overcome the effects of the extreme factor?

The waters draining from base metal mining areas can be considered in some cases as extreme environments when carrying elevated levels of a particular heavy metal. This is illustrated by the comments of Carpenter (1924) on the River Ystwyth which drains an area of intense base metal mineralization in West Wales. She describes the Ystwyth as ".... absolutely destitute of fish-life, there is only the slightest coating of moss or liverwort on any of the stones, and algal and phanerogamic vegetation are usually conspicuous by their absence"

Although originally ascribed to the effects of lead, Jones (1940, 1958) later concluded that the continual absence of a typical river flora and fauna was due to the persistently elevated levels of zinc in the streams.

In a recent study of the resistance of microorganisms to the toxic effect of heavy metals, Griffiths *et al.* (1975) were able to conclude that "It is quite clear that the microscopic algae are less sensitive to toxic effects of metal pollution than higher plants and animals."

Although Brock (1969) did not include metal polluted situations in his discussion of extreme environments, it would seem that a detailed study of such habitats and the possible organisms found there would be of immense interest, particularly to the microbial ecologist. Brock recommends that if possible one extreme factor should be isolated for study, and that habitats in which a gradient exists for the factor of interest, from extreme to normal, with all other factors remaining the same, would be most desirable for such an investigation.

Although in metal polluted situations it is sometimes difficult to isolate a single metal, since often there are associated metals and other factors increasing the extreme nature of the habitat, some instances have been found where the toxic effects of the environment can be directed primarily to a particular metal (Jones, 1958; Weatherly *et al.*, 1967). In these studies certain aspects of the toxic nature of zinc were investigated. Weatherly *et al.* were able to conclude from their study of a zinc polluted river in Australia that "Our method of approaching the problem has been to analyse the main chemical aspect of the pollution by means of a geochemical study, and to treat the question of the effects of pollution on the fauna as a kind of bioassay problem, this type of approach can lead to a much clearer understanding of the nature and cause of pollution than a reliance on chemical analyses alone." In this study the photosynthetic flora was not considered,

even though it has been shown to be more tolerant of zinc pollution (Griffiths *et al.*, 1975).

It seems that a geochemical study of streams contaminated with zinc, together with a survey of the photosynthetic flora, backed up by laboratory experiments on the toxicity of zinc, would prove of great value. Such investigations might contribute to an understanding of adaptational, physiological and evolutionary aspects of the tolerance of organisms, and also of the chemical nature of zinc contamination. Fundamental to designing such a study is an understanding of the extent of zinc contamination, the geochemical, physical and chemical controls on zinc availability within the freshwater habitat, and an impression of the information already obtained on the ecology and biochemistry of zinc contamination.

The intention of the following review is to provide the necessary information as a basis on which the study could be made.

1.2 The element zinc

1.2.1 History

It seems widely accepted that the use of zinc in the production of brass began at least 1000 years before the Christian era (Philbrick and Holmyard, 1941), and that the Romans and Greeks were actively producing brass by melting copper with zinc as early as 200 B.C. (Zimmerman, 1972). The identity of zinc as a separate metal was apparently unknown until the Portuguese brought back zinc from China in the sixteenth century. The term zinc and its subsequent use as a name is credited to Paracelsus (1493-1541), by Philbrick and Holmyard. They also state that Henckel prepared metallic zinc comparatively free from impurities in 1720. The discovery of zinc as a separate element is credited by Correns (1969) to Marggraf in 1746.

It is apparent that zinc was discovered as a chemical entity just prior to the development of chemistry as a science, which according to Correns (1969) commenced with the discovery of the more abundant elements such as oxygen (1774) and calcium (1824). But its importance in the context of geochemistry and water chemistry must have started after the development of chemistry as a science in the early 19th century.

1.22 General physical and chemical characteristics

These are summarized in Table 1.1

ion	Zn ²⁺	ionic radius for 6-coordination ("Octahedral")	0.83nm (after Goldschmidt, 1926/34)
atomic number	30		
atomic weight	65.38		
group in the Periodic Table	subgroup IIB		0.74nm (after Ahrens, 1952)
outer electronic configuration	<u>d</u> ¹⁰ <u>s</u> ²	ionization potential (atomic state to X ²⁺)	17.89 eV
		electronegativity	1.7
observed coordination numbers	4,6	approx. ionic character of bond with oxygen, %	63
isotopes	⁶⁵ Zn (half-life, 250 days)	standard free energy of formation in the aqueous form* F ^o	-35.2
	⁶³ Zn (half-life, 38 minutes)	standard free enthalpy of formation* H ^o	-36.4
		entropy (cal/mole/degree S ^o)	-25.5

Table 1.1 General physical and chemical characteristics of zinc (* at 25°C, 1 atmosphere pressure in kcal/mole). (References: Krauskopf, 1967; Mackay and Mackay, 1968; Wedepohl, 1972).

1.3 Geography of zinc

The following brief summary is intended as an introduction to the importance of the Northern Pennine deposits during both the past and present.

1.31 World resources of zinc

Although grouped with a number of other metals (Ni, Mo, Pb) as a "scarce" element (Skinner, 1969), large, localised deposits of zinc ore have been discovered in all of the major continents in the world. From the available information it appears that the United States of America is the largest producer of zinc concentrates in the world, whereas Canada is the largest producer of zinc ores, followed closely by Russia (Zimmermann, 1972).

Although Western Europe once dominated the world in the production of zinc, from the 18th century through to the 19th century (1.4), these reserves (particularly in Britain) were soon more or less commercially exhausted, and with the discovery of large deposits in the Mississippi Valley, Missouri (in the late 19th century), America took over as prime producer from 1900 onwards. Since that time the production of zinc ores has increased up until the present day in other countries such as Australia, Canada, Italy and Ireland.

1.32 Europe

Historically, Europe is probably one of the most important areas in the mining of zinc ores. Notable deposits which were mined in past centuries include those of Liège in Belgium, the Harz Mountains in Germany, the Italian Alps, south-west Sardinia, the Pedrosches Batholith in Spain, the Massif Centrale in France, County Wicklow in Ireland, Cardiganshire and Denbighshire in Wales, and Cornwall and the Pennine districts in England. In nearly all of these areas the production of lead superceded originally that of zinc, although some zinc was taken as a byproduct. It is only since the late

18th Century that zinc became important. Most of the deposits have been exhausted on a commercial basis, particularly those in Britain, and only a few of the original mines operate for zinc in Germany, France, Italy (Sardinia), Spain and Ireland. More recently large scale operations for the production of zinc (from previously mined deposits) have taken place in Ireland (Platt, 1975). Production of zinc also continues in some of the Harz Mountain Mines, notably at the Rammelsberg mine near Goslar (Morrison, 1976), at the mine of the Vieille Montagne Zinc Company, Décaville in the Massif Centrale, and mines in the Iglesias mining region in Sardinia. Deposits of zinc ore discovered recently in Scandinavia are now being worked on the eastern border of the Caledonides in Sweden (Scott, 1976).

1.33 The British Isles

The most important mineralized areas in Britain are illustrated in Fig. 1.1. By far the largest number of workable mineral veins were located in the Northern Pennine Orefield, although significant contributions to British zinc production were obtained from most of the other areas, including the districts of Wales, the Isle of Man, Derbyshire, and South West England. As with other areas of Europe, lead was the prime mineral which was worked in these mineralized zones until the importance of zinc was recognized in the 19th Century. The Northern Pennine mining region is one of the few areas in Britain to have a primary zinc bearing part of the general mineralized zones. In most of the other areas galena is the chief mineral. This region has been called the Alston Moor Zinc Orefield (Fig. 3.3).

Britain was an important producer of zinc concentrates due to the widespread mineralization over a very large number of small deposits, rather than over a few large deposits. Mining of zinc as a primary metal ended in the early 20th Century, but interest has still remained in prospecting for this mineral.

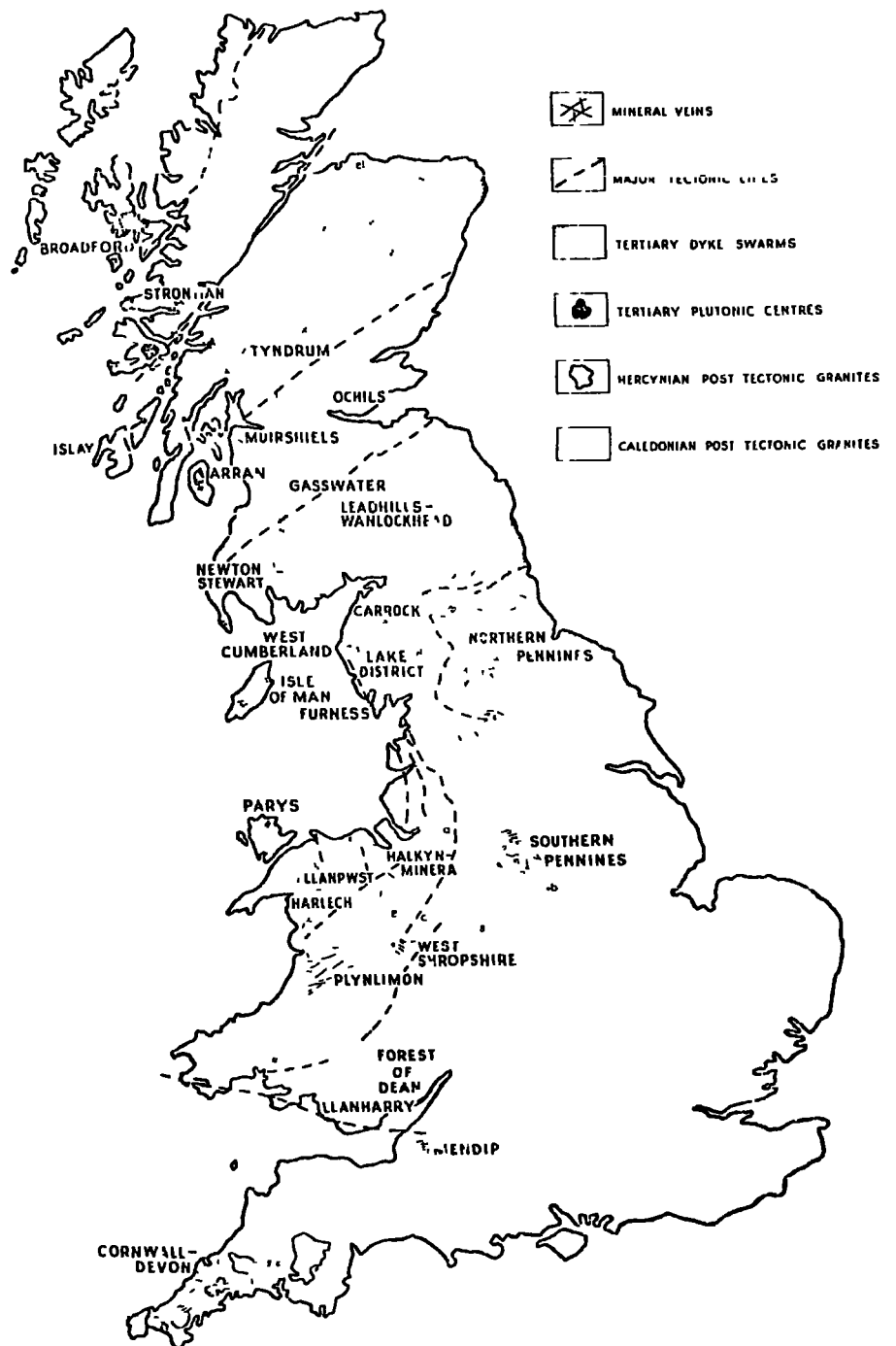


Fig. 1.1 The main mineralized areas in Britain (after Dunham, K.C. (1952) Age-Relations of the Epigenetic Mineral Deposits of Britain. *Trans. Geol. Soc. Glasgow* 21, p. 397.)

Reworking of old deposits is considered to be uneconomic, so interest has been aroused in possible alternatives. Recently a drilling programme has commenced at Vidlin, in Shetland (Garson and May, 1976) after field examination of sulphide mineralization just discovered in 1930 confirmed the possible economic potential of the area. Also suggestions have been outlined by Scott (1976) as to the possible zinc and lead mineralization along the margins of the Caledonian orogen in west Scotland and the Welsh borderland of west England.

1.4 History of zinc mining

Although zinc was used in the production of brass by the ancients in pre-Roman times, metallic zinc was usually obtained by accident since it was extremely rare in the ancient world (Davies, 1935). Some pieces of zinc are known from the early Iron Age in Italy. Brass was unknown in Greece in the 4th Century B.C., but was being manufactured in Bithynia by the 3rd. In Rome, during the time of Augustus, brass was common (Davies, 1935). According to Davies, the first zinc mines to be discovered in the Roman Empire were in A.D. 75 at Stollberg in the Aachen area of Germany. However, as mentioned previously, according to Zimmermann (1972), the separate identity of zinc was not recognized until the Portuguese brought some back from China in the 16th Century. The extent of zinc mining in Roman times is not clear since the mining of lead far overshadowed it, and zinc would often be accidentally taken during the processes of obtaining the former mineral.

It seems well accepted that zinc mining was not important on a commercial scale until the 18th Century when in about 1740 it was produced in England. The Harz Mountain region of the Saxon mining area is recognized as the place where the earliest developments in post-Roman underground mining took place, and where a very large mining industry developed from the late Middle Ages. However zinc was of no commercial importance here either before the 19th

Century (Morrison, 1976). The modern zinc industry dates from about 1806 when zinc smelting was begun at Liège, Belgium. During this century the zinc smelting industry remained mainly in Belgium and the Harz Mountain region of Germany, which together produced approximately 70% of the world's smelter output for the century. In Britain the mining for zinc was again overshadowed by that for lead, but it seems probable that important operations did commence during the middle part of the Nineteenth Century. In the Northern Pennine Orefield the production of zinc took on a new impetus when old lead mines were reworked for zinc between 1890 and 1900. But zinc production on a major scale ceased in Britain between 1920 and 1930.

In America large scale zinc mining operations commenced with the discovery of large reserves in the East Tennessee, the Upper Mississippi Valley Tri-state, and Southeast Missouri districts. Zinc was known to the earliest settlers in Tennessee and mined as early as 1854, but large scale mining of zinc sulphide deposits began only in 1913 (Laurence, 1971). At this stage the other two mining districts mentioned above had long been major zinc producers. In 1909 the United States became the world's largest producer of zinc, a position that it has retained. Although not producing as many zinc concentrates as America, Canada leads the world in the amount of zinc mined.

1.5 The Geology of Zinc

1.51 Origin and abundance

Although there are a large number of countries with workable deposits of zinc (1.31), it has been classified as a "scarce element" (Skinner, 1969). The definition of Skinner is based on the fact that its crustal abundance is below 0.01%. Its relative abundance, when compared with metals such as magnesium, aluminium or iron, is low, but the total amounts in the crust

are quite large, simply because the crust itself is large.

	vol. % of rock type	zinc abundance in rock class	zinc abundance relative to rock abundance
granites, quartz monzonites	44	48.0	21.1
granodiorites, quartz diorites	42	52.4	22
diorites	1	70	0.7
gabbros (basalts)	13	100	13.0
peridotites	0.5	56	0.3
abundance in the upper continental crust:			57.1mg l ⁻¹ Zn

Table 1.2 Zinc abundance in the upper continental crust (after Wedepohl, 1972)

As a percentage of the earth's crust, a figure of 0.004% for zinc has been given (Wedepohl, 1953), which is less than the values estimated for zirconium, vanadium, titanium and strontium.

Wedepohl (1972) has shown from analyses of rock forming minerals that zinc has a tendency to be predominantly incorporated in certain structural positions of silicates and oxides. Because of its similarity in crystal chemical properties with ferrous iron and magnesium, particularly the ionic radii, it replaces these elements favouring positions with coordination numbers 4 and 6; the latter controlled by the presence of certain ligands such as OH⁻. Zinc has been demonstrated in biotite, montmorillonite and serpentine, indicating the stability of the sixfold coordinated positions when several ligands are hydroxide.

Wedepohl (1972) has produced extensive lists of zinc concentrations in rock forming oxides and silicates. He states that the crustal abundance of zinc is far more influenced by its occurrence in those rocks containing ferrous iron and magnesium than in deposits of zinc ore. The abundance of zinc in the more common sediments and sedimentary rocks has been described by Lavery, Barnes and Wedepohl (1971), and summarized in detail by Wedepohl (1972). Zinc would be expected to concentrate in the sedimentary environment via detrital matter deposition and uptake, due to its low solubility in most natural waters (see 1.7). Sedimentary minerals of major importance such as quartz, muscovite and feldspars, being low in structural size, are not as important carriers of zinc as chlorites and magnetites. Colloidal iron oxides and iron oxide coatings on other minerals would be expected to transport large quantities of zinc (1.732).

Of the Arenaceous group of rocks characterized by sandstones, the grey wackes are most abundant and contain an average of $105\text{mg l}^{-1}\text{Zn}$, much of this being present in chlorite and iron minerals (Wedepohl, 1972).

In the Argillaceous group of rocks, characterized typically by clays, shales, mudstones, siltstones and marls and low in bituminous matter, an average zinc concentration computed by Wedepohl is $100\text{mg l}^{-1}\text{Zn}$.

Zinc would also be expected to accumulate in sediments rich in carbon fixed in the degraded organic matter by sulphides and phosphates. Zinc concentrations in black shales of different geologic age and origin have been compiled by Wedepohl (1964). In the presence of degraded organic substances, bacterial microbes can produce sulphide ions and the availability of these will control precipitation of zinc sulphide. Gorham and Swaine (1956) report an average of $800\text{mg l}^{-1}\text{Zn}$ (ZnS) in 13 mud samples from English lakes. Appreciable zinc concentrations would be expected to occur in marine sediments (Rashid and Leonard, 1973).

A classic example which is often cited for the syngenetic sedimentary sulphide precipitation of zinc is that of the "Kupferschiefer" or "Marl Slate" in Europe (see also 1.52). This is a rare example of the coincidence of large volumes of stagnant sea water under reducing conditions, exposure of oxidised sediments which delivered trace metals to be accumulated and precipitated in the sea water, low detrital sedimentation, and thus a limited dilution of the zinc sulphide precipitates in the sediment.

Apart from the sulphide fractions, zinc can accumulate in the phosphate fraction of bituminous sediments (Wedepohl, 1972).

Zinc can accumulate in carbonate rocks, being adsorbed on the clay surfaces during dissolution of the limestones, and can enter the carbonate fraction of limestones and dolomites during diagenesis. The average content of limestones is 30 Zn (Wedepohl, 1972).

1.52 Zinc deposits

Zinc is concentrated in certain areas in the form of localized ore deposits. These can be classified into two main groups, hydrothermal or contact metamorphic deposits, and sedimentary deposits.

1.521 Origin

The former group are thought to have been formed in two possible ways:

(1) By hydrothermal solutions supplied by deep seated magmatic activity.

Thus the often close association of deposits with igneous intrusions would seem to support this hypothesis (Dunham, 1967).

(11) More recent evidence suggests that in some cases the slow escape of hydrothermal solutions of metamorphic rather than magmatic origin was responsible for deposition of the ores (Skinner, 1969). Dunham (1967) presents evidence

which suggests that the Northern Pennine ore deposits were formed by rising hydrothermal waters of magmatic origin. The close association between the intense mineralization and the uplifted dome of Precambrian rocks, the Alston Block, is compared to the association of deposits in Missouri with the Ozark uplift, a similar dome of Precambrian rocks. The deposits of the Mississippi Valley have more recently been recognized as unusual when compared with the normal hydrothermal formations (Skinner, 1969). Isotopic analysis of associated galena, together with the spatial relationships of the zinc ores with the alkaline igneous rocks, have been used to suggest possible magmatic sources of the depositing solutions. However the abundance of zinc as replacement bodies within limestones of various ages in the Valley area causes the genetic implications to be ambiguous.

In describing the large zinc deposits of Iglesias in south western Sardinia, Jensen and Dessan (1966), using isotopes of sulphur, produce evidence which suggests that the northern deposits in the region are not of the same origin as the southern deposits, as was once assumed. The northern deposits are characteristic of magmatic hydrothermal origin, the southern of sedimentary origin.

The nature of the depositing fluids has also been little understood until recently. It is widely accepted now that the solutions were brines. Heyl (1969) states that in the Mississippi Valley deposits, brines enriched with sodium, calcium and potassium chlorides (from adjacent basins), which were heated to temperatures of 70-160°C by magmatic heat, deposited the ores. Evidence from Sawkins (1966) shows that similar concentrated brines with high K/Na ratios deposited the ores in the Northern Pennine Orefield.

Recent investigations have demonstrated that large zinc deposits can be of sedimentary origin. The Rammelsberg deposits in the Harz Mountains, Germany, have been shown by Anger *et al.* (1966) to be of this type. Their results,

using isotopes of sulphur, confirm the origin by syngenetic sedimentation of sulphides precipitated from slowly released solutions. Bacterial reduction of sulphates from the Devonian Ocean is also demonstrated to have contributed to the ore body formation. The large deposits of Broken Hill, Queensland, are now considered to be of exhalative-sedimentary origin, the sedimentation being modified by subsequent metamorphism (Richards, 1966). Studies by Vokes (1966), on the possible modes of origin of the ore deposits associated with the margins of the Caledonian geosyncline in Norway, support a pre-metamorphic or diagenetic emplacement of the sulphides rather than an epigenetic emplacement. More recently Scott (1976) has suggested that ores of zinc may occur, in a similar way, along the margins of a continuation of this feature - the so called Caledonides, in the British Isles.

Perhaps the best known example of a sedimentary deposit of zinc is that of the Kupferschiefer (see 1.51). This stratiform deposit is the least altered by metamorphism. It is known that it was laid down in Permian times in the area now occupied by Central Europe. A shallow sea at that time, now known as the Zechstein Sea, covered an area of approximately 51,800 sq. km., and in it a sedimentary bed of organic-rich muds containing zinc sulphides accumulated. The mud, which consolidated to form shales (termed the "Kupferschiefer"), is not uniformly mineralized. It is uncertain whether the sulphides were introduced diagenetically or precipitated contemporaneously with the muds.

The origin of zinc ore deposits is still not completely understood. There is a wide variety of evidence to support both of the major groups of deposits, but the precise mechanisms of deposition are still under investigation. The importance of understanding the depositional processes of zinc is fundamental to the interpretation of its geology, geochemistry and resultant hydrogeochemistry in the surface waters. An understanding of the depositional

relationships between zinc and associated minerals is also fundamental to an understanding of the controls on its solubility and mobility in surface and ground waters. This finally leads to a better understanding of the relationship between zinc and the organisms present in the stream habitat.

1.522 Age of deposits

It is also not fully understood during which period the deposition took place. It has been proposed by Dunham (1948), in the case of the Northern Pennine deposits, that deposition took place in Hercynian times of Upper Carboniferous to Cretaceous date. More recently Mitchell and Halliday (1976) have proposed that the deposits which include those in the Appalachian region of America, parts of the British Isles, France, Spain and Newfoundland, should be included in one province, the North Atlantic Hydrothermal Province. Throughout this area they propose that analogous hydrothermal circulation existed during late Triassic and lower Jurassic times. Evidence from age-relationships studies in all of these regions is presented to support this hypothesis. The classification of many Western European deposits as exclusively Hercynian in age is questioned by the Mesozoic age obtained for deposits in South West England, and the Pedrosches in Spain, both of which are associated with Hercynian granites.

1.53 Zinc minerals

Wedepohl (1972) lists 102 Zinc minerals. With regard to ore deposits of economic importance, and sources of zinc which can be regarded as environmentally significant, there are eight primary zinc minerals.

Mineral	Formula
Sphalerite (blende)	ZnS (cubic)
Wurtzite	ZnS (hexag.)
Zincite	ZnO
Smithsonite	Zn(CO ₃)
Hydrozincite	Zn ₅ (OH) ₆ (CO ₃) ₂
Willemite	Zn ₂ (SiO ₄)
Hemimorphite	Zn ₄ (OH) ₂ (Si ₂ O ₇) · H ₂ O
Zincosite	Zn(SO ₄)

Sphalerite is by far the most important zinc mineral both economically and in distribution.

A large number of zinc minerals, not listed here, contain hydroxide in structural positions, and this is related to its property of easily substituting for divalent metals with a similar ionic radius in compounds with hydroxide ligands.

1.54 Associated minerals

Sphalerite is frequently associated with galena (lead sulphide) in hydrothermal veins, and can often be found with thin coatings of associated greenockite (cadmium sulphide). When it occurs as replacement bodies in limestone, it is associated with two sulphides of iron, pyrite and pyrrhotine, and an oxide of iron, magnetite. A less frequent associate in hydrothermal veins is the copper ore, chalcopyrite.

Some non-metallic gangue minerals frequently associated with sphalerite are quartz, fluorite, sidente, calcite, and dolomite.

1.6 Geochemistry of zinc

1.61 Weathering of rocks

Chemical weathering which relies on factors such as the mineral composition of the rocks, rock texture, climate, drainage and amount of rock exposure, is a process by which an equilibrium is set up within the system involving rocks, air and water (Krauskopf, 1967). In general it is a slow process and involves the chemical processes of ionization, addition of water plus carbon dioxide, hydrolysis and oxidation. In most rocks, zinc primarily occurs within the structure of silicates and oxides (1.51). During the chemical weathering of these rocks it may pass into solution. The low concentration of zinc in surface waters has been used to indicate a restricted mobility of the element from places of rock weathering (Wedepohl, 1972).

Wedepohl (1972) discusses the weathering of a number of rock types such as basalts and granites. Granite material from the Harz Mountains (Germany), where biotite was the chief host structure, was demonstrated to lose 50% of its original 60mg l^{-1} zinc in leaching, but also locally accumulated 30% by adsorption relative to the primary zinc. Harriss and Adams (1966) demonstrated in granitic rocks from Oklahoma and Georgia (U.S.A.) that in some samples zinc was accumulated during the breakdown from parent material to decomposed rock. Wedepohl (1972) emphasizes that adsorption, rather than solubility, controls the concentration and distance of transport of zinc in weathering solutions. In this respect iron oxides exert a considerable influence on zinc movement (Jenne, 1968), due to their close association with granites. Iron containing minerals such as Horn Blende and Biotite, which are common constituents of igneous rocks, also are important in controlling zinc movement.

Sedimentary rocks, when exposed to the agents of weathering, would be expected to react in a similar manner, in terms of releasing zinc and possibly

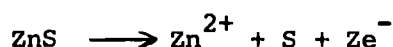
readsorbing it. Krauskopf (1967) discusses chemical weathering in detail. Zinc would be released from limestones when water in combination with carbon dioxide acts on it. However depending on a variety of other factors it could be precipitated as the insoluble carbonate.

The final product of the weathering of rocks is usually soil and the zinc content of the soil is discussed more fully in a later section (1.731 and 1.82).

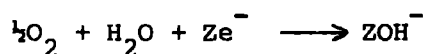
1.62 Weathering of ore deposits of zinc

1.621 General weathering

The aqueous oxidation of sphalerite, zinc sulphide, has been demonstrated to be an electrochemical process (Habashi, 1966). Using kinetic evidence, two main reactions have been established for this process at a temperature below 120°C. These are an anodic reaction represented by:



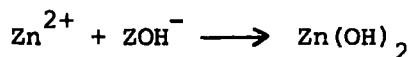
and a cathodic reaction:



Temperature is important since 120°C is the melting point of sulphur and at temperatures above this the sulphur is completely and rapidly oxidized to sulphate. The overall reaction can be simplified to:



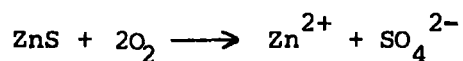
The acid functions by preventing the formation of insoluble zinc hydroxide, which may block the anodic reaction and hence stop the process of dissolution:



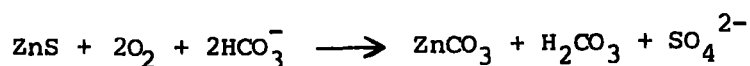
However the weathering of sulphides is a complex process. It normally results in the metal ion entering solution or forming an insoluble compound which is stable under surface conditions, and the sulphur being converted to sulphate. However a variety of environmental conditions control the pathways of the various chemical reactions. In general, a sulphide orebody tends to develop a zonal arrangement of different mineral associations around it when exposed to various weathering processes, which reflect various degrees of oxidation (Sato, 1960). Leaching of zinc from its sulphide ores, under these oxidizing conditions, can lead to a high activity of Zn^{2+} in mine waters, and consequently the production of secondary zinc minerals. If factors controlling the equilibrium of these secondary zinc minerals with their environments become significantly altered, they may undergo further chemical reactions and the resultant reaction products are either removed from the system or form a new mineral which is stable under the new conditions.

The main factors which control the oxidation of sphalerite, and hence the formation of secondary minerals, apart from the presence of an aqueous medium, are pH, total carbon dioxide in solution (or partial pressure of carbon dioxide), concentration of silica, temperature, pressure and Eh (oxidation-reduction potential). The secondary zinc minerals are often termed "supergene" minerals, a term referring to processes involving percolation of water from the surface, and which include solution, hydration and oxidation.

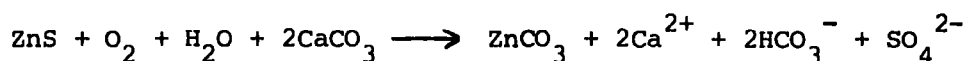
If the pH of the oxidizing aqueous medium is between the values of 6.2 to 8.1 smithsonite, zinc carbonate, is the most stable mineral; and if the conditions also remain stable, this will be the primary supergene mineral in the oxidizing zone around the sphalerite. This can be represented by the following sequence of reactions:



Once the zinc ion moves into the more alkaline environment:



The acidity produced by the initial oxidation of the sulphide is sometimes neutralized if significant calcite is present in the aqueous medium:

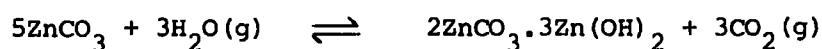


again favouring precipitation of the smithsonite.

Hemimorphite, $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$ has been shown to be the least soluble secondary zinc mineral at pH values below 6.2 (Takahashi, 1960). Its infrequent discovery as the first supergene mineral in the paragenetic sequence can be explained by the following: Firstly, acidic pH values formed by the oxidation of the sulphide would be readily neutralized if any limestone rock is present. Secondly, sufficiently well-circulated groundwaters may remove the possibility of a pH lower than 6.2 around slowly oxidizing sphalerite, since the zinc sulphate concentration may be too low. A 0.01 mole solution of ZnSO_4 has a pH of approximately 5.8 (Takahashi, 1960). Thirdly, since hemimorphite is readily soluble in strongly acidic conditions of pH 3 or less, if values for the aqueous environment remain in this range the mineral will be leached away.

Hemimorphite is more soluble than smithsonite in the pH range of 6.2 - 6.8 but not as soluble as hydrozincite ($2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$). Above pH 6.8, hydrozincite is more soluble than smithsonite, but less soluble than hemimorphite (Takahashi, 1960).

Under certain environmental conditions, hydrozincite can be the most abundant secondary zinc mineral. The most important of these conditions is the requirement of relatively dry conditions. In such a dry environment, the following conversion of smithsonite has been postulated:



The reaction relies mainly on the partial pressure of CO_2 at the respective temperature. Takahashi (1960) has observed that in a zinc mining region in Nevada where hydrozincite abounded, smithsonite became more frequent with an

increase in depth. This was explained by the fact that in the upper horizons, where CO_2 gas could escape freely into the dry air, the partial pressure was maintained at less than the equilibrium value in the above reaction favouring a direction to the right. With increase in depth, CO_2 could be trapped in the interstices between minerals, causing a slow rate of diffusion and consequent escape. This may result in a locally high partial pressure of the CO_2 , causing the reaction to swing to the left.

Hydrozincite is formed freely only when rocks exposed to air do not occur in masses under the water table. Zinc hydroxide has not been observed as a secondary zinc mineral in the oxidation areas around zinc deposits. This is because it is thermodynamically unstable in such environments, since the partial pressure of CO_2 required to convert hydrozincite to the hydroxide at normal atmospheric temperatures, is below the atmospheric CO_2 partial pressure. Under natural weathering conditions the reaction is always driven in favour of hydrozincite formation.

Takahashi determined the stability fields of hemimorphite, smithsonite, hydrozincite and zinc hydroxide from available thermodynamic data at various pH values. The boundaries were in the pH range of 5-8, 5-9, 7-9, and 8-10 respectively. More recently Hem (1972) compared the solubilities of smithsonite and willemite Zn_2SiO_4 , and showed that smithsonite was the least soluble at pH levels below 6.5. He demonstrated that silicate species were the least soluble in the pH range 7.5 - 10.

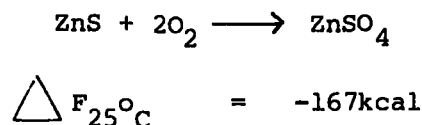
Takahashi was unable to determine the stability field of hemimorphite in terms of the Si-O radical because of insufficient thermodynamic data available on the radicals such as $\text{Si}_2\text{O}_7^{-6}$ and SiO_4^{-4} . The stability fields for willemite were also not computed due to the lack of thermodynamic data. Hem's calculations are based on reliable thermodynamic data for the silicate radicals but were in the absence of carbon dioxide species. Despite these differences

the boundary fields of Takahashi for the zinc minerals in the aqueous oxidation environment around the sulphide ores does have some agreement with the figures of Hemm which are applied to zinc species in surface waters. From both sets of data the overwhelming importance of the concentration of CO_2 , the pH, concentration of silica ions, and concentration of zinc ions can be seen in determining the course of the oxidation, and release of zinc ions from its sulphide ores.

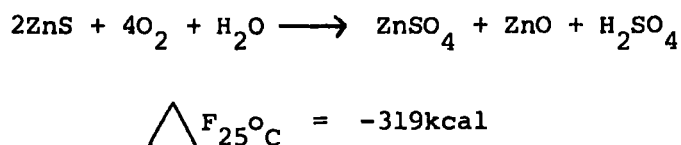
In the oxidation zone around the sulphide ore, zinc is regarded as a comparatively mobile metal (Krauskopf, 1967) since under the assumed conditions occurring in this region the common anions such as SO_4^{2-} , OH^- , CO_3^{2-} and Cl^- permit relatively large amounts to remain in solution. Once the zinc ion enters into solution in the ground water which has reached an ore deposit, and finally enters the surface water from this universal zone, it is subject to interaction with a large number of substances in the new environment such as clay minerals and organics. These factors are dealt with in 1.7.

1.622 Microbial leaching of zinc from ore deposits

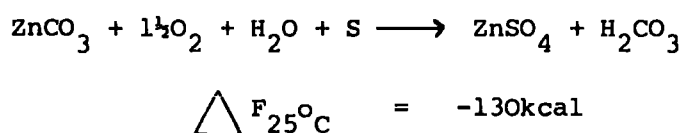
Since zinc does not have several common valency states it does not offer oxidative microorganisms an easily available energy source. However, with sphalerite and wurtzite, under limiting aeration, microbes will oxidize the sulphide moiety to sulphate, forming zinc sulphate in the process.



If a larger supply of oxygen is present, the zinc sulphide can be oxidized to zinc sulphate and sulphuric acid:

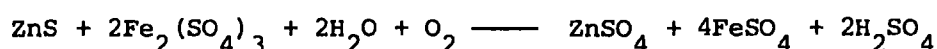


A greater solubilization will be observed where the sulphuric acid is formed. Smithsonite is most easily solubilized by bacteria oxidatively, synthesizing sulphuric or other organic acids:



Zajic (1969) has shown that this process has been performed in the laboratory and addition of elemental sulphur (which is oxidized by the bacterial to H_2SO_4) increases the recovery of zinc.

Thiobacillus ferroxidans has been shown to be capable of oxidizing sphalerite under acidic conditions (Higgins and Burns, 1975). It is assumed that the form of bacterial oxidation would probably be initiated through the generation of ferric sulphate which promotes the dissolution of sulphides, although direct oxidation of sphalerite has not been discounted:



The resulting soluble zinc sulphate can be leached and transported away from the source or deposit.

1.63 Abundance of zinc in natural fresh waters

Because of the similarities in average zinc concentration of most of the common surface rock types, the level of zinc in continental waters is not expected to vary greatly (Wedepohl, 1972). Anomalous concentrations can be produced in two main ways:

- (1) Locally high concentrations can be produced naturally by the leaching processes of sphalerite, the effect of acid water on rocks produced by the oxidation of other sulphides (mainly pyrite), and the leaching of rocks by acid hot springs.

(11) Anthropogenic influences such as mine drainage waters; industrial wastes of certain chemical and metallurgical factories; aerosols of zinc such as dust from smelting processes and coal combustion (for more details see 1.8); and indirectly through contamination of rainwater by zinc aerosols.

In attempting to assess an "average" figure for the zinc concentration in major continental surface waters, factors such as geographic variability, variability due to time, the effect of flow and interaction with the biota should be considered, besides the anomalous values which can occur for the reasons outlined above (Andelman, 1973). However, Wedepohl (1972) concludes that a figure of $10\mu\text{g l}^{-1}\text{Zn}$ would be a suitable average. He suggests that the value of $20\mu\text{g l}^{-1}$ estimated by Turekian (1969) was a little high due to the inclusion of high values from figures given for some Russian streams by Konovalov (1959).

A large number of studies have attempted to produce mean levels for zinc in America. O'Connor *et al.* (1964) review a large amount of data on zinc levels in rivers all over the country and arrive at a mean range between $10\text{--}200\mu\text{g l}^{-1}\text{Zn}$. From their own studies on the Chesapeake Bay area they produce average concentrations for several pH ranges:

pH range	average concentration of zinc in $\mu\text{g l}^{-1}$
6.5 - 6.9	73
7.0 - 7.4	65
7.5 - 7.9	45
8.0 - 8.3	26

Durum *et al.* (1971) sampled 726 river locations throughout America and arrived at an average figure of $20\mu\text{g l}^{-1}$.

If the data of Reeder *et al.* (1972) for 101 streams draining the basin of the Mackenzie River in Canada is considered, it is possible to arrive at an average value of $2.4\mu\text{g l}^{-1}\text{Zn}$.

In Britain few studies have been carried out that are not directly connected with the effects of mining or other forms of pollution. Abdullah and Royle (1972), who studied the effects of the contamination of streams in west Wales by mine waters, compared their findings with the average level of zinc in a "clean" stream water. This was given as $11\mu\text{g l}^{-1}\text{Zn}$.

Other factors which complicate attempts at obtaining an average level of zinc in natural waters is the variation in the methods of collecting and analyzing for zinc. In some cases the figures quoted may be for 'total' zinc, in others for filtered, and quite often the method of filtration is not mentioned.

It is evident that mineralization of the local rock strata can considerably influence 'natural' background zinc concentrations, and this fact is used as part of the method of Geochemical prospecting (extensively reviewed in Hawkes and Webb, 1962). This, together with the other factors previously mentioned, complicates the estimation of an average figure and hence an understanding of the general distribution of zinc in streams and rivers. However an average figure of $10\mu\text{g l}^{-1}$ would seem to be a reasonable estimate when considering the majority of undisturbed stream environments.

1.7 Chemistry of Zinc

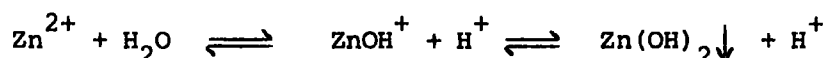
1.71 Factors affecting Zinc solubility

1.711 pH

The importance of pH in controlling the geochemical activity of zinc has already been emphasized (1.62). It is also probably the single most important factor controlling zinc solubility in surface waters, and other

aqueous media. A study made by Elder (1975) in natural water systems on complexation side reactions involving trace metals led him to conclude that "few generalizations can be made about trace metal complexations because they are so highly dependent on pH and anionic concentrations."

In a simplified system and under certain pH conditions, the zinc ion can react with water in the following way (Bachmann, 1961):



This is a generalized mononuclear reaction between zinc and the coordinating ligand, the hydroxyl ion. The traditional equilibrium, or stability constant for the reaction can be expressed in mass action terms by the following:

$$K = \frac{(\text{ZnOH}^+) \cdot (\text{H}^+)}{(\text{Zn}^{2+})}$$

and allows the proportion of zinc, as the different ions, to be determined for different pH values. This model reaction applies only to an ideal system where no competition reactions occur and the zinc and hydroxyl ions exist only in the forms shown. In lake waters Bachmann gave values of zinc for the equilibrium between ionic zinc and zinc hydroxide, of $1.3 \text{ mg l}^{-1} \text{ Zn}$ at pH 8 and $13 \mu\text{g l}^{-1} \text{ Zn}$ at pH 9. From this data he concluded that the complex will not be of importance in lake waters, and that below neutrality the hydroxide complex will be unimportant generally. This statement is supported by the work of Jurniak and Inouye (1962) who demonstrated the solubility of zinc at various pH values in distilled water for a ZnCl_2 -NaOH system. From their data, as the pH rises above 6.8 significant decrease in the level of dissolved Zn occurred and was attributed to the hydroxide formation.

In natural waters, where there may be expected to be a large number of different anions, competing side reactions can exert considerable influence on the main reactions such that the stability constant may be considerably altered. In most natural stream waters the normal range of pH values, together with the presence of other important anions renders the hydroxide complex of zinc of relative unimportance, particularly in the vicinity of weathered zinc areas (Takahashi, 1960). Conversely Zirino and Yamamoto (1972) have shown that at the average pH of seawater (8.1), the hydroxide complex was of considerably more importance, making up 64% of the total zinc, than the zinc itself (17%). Other important complexes were ZnCl^+ (6.4%), ZnCO_3^0 (5.8%), and ZnSO_4^0 and ZnCl_2^0 (together about 4%). The important influence of pH on zinc solubility in seawater can be shown by the fact that at pH 7.0 uncomplexed zinc was found by them to make up 51% of the zinc species present, whilst ZnCl^+ (19%), ZnSO_4^0 (10%) and ZnCl_2^0 (8%), Zn(OH)_2^0 constituted only about 1%. Altering the pH from 7 to 9 increases the hydroxide complex at the expense of the others.

In experimental inorganic media where zinc may be used in high concentrations and alkaline buffers are also used to obtain and maintain pH levels in the upper range, the hydroxide complex might well be produced in significant amounts. Particularly with the addition of NaOH directly to a high zinc media. However, the extent of the complexation will again depend on other factors such as the amount of other ligands present, and the CO_2 concentration of the media.

Hem (1972) has summarized various sources of data on the thermodynamic behaviour and solubility of zinc in various inorganic aqueous environments. With the aid of thermodynamic calculations he was able to predict the activity ratios among various chemical species of zinc for a range of pH values versus Eh values. The method relies on assumptions that the pH and Eh are controlled

by the chemical properties of the predominant reactive substances present, and can be treated in fixed quantities as long as the substances remain dominant or are continually supplied to the system. Rarely in natural fresh waters are systems ever so idealized, being normally far more diverse and complex. However the calculation of such equilibrium constants does help to increase our understanding of trace metal speciation. The data of Hemm indicates a minimum value for zinc concentration at pH 9.5, but the exact point can be influenced by other factors (1.712). It also shows that zinc can remain in solution as the dominant species (Zn^{2+}) up to pH values a little over 7.0, with a dissolved zinc activity of 0.65 mg l^{-1} , and activities of CO_2 and sulphur equal to 0.44 and 0.32 mg l^{-1} respectively.

pH not only influences the reaction between zinc and anions (inorganic complexation), but also exerts a considerable control over organic complexation of zinc (1.72), and the ion exchange reactions between zinc, inorganic colloids, organic colloids, and other solid surfaces (1.73).

1.712 Alkalinity

When CO_2 in the atmosphere dissolves in water it forms an acid which can react with the bases of the rocks. The weathering of calcite and dolomite can thus lead to the formation of HCO_3^- and CO_3^{2-} ions which imparts an 'alkalinity' to the water. These dissolved species participate in homogenous and heterogenous acid-base and exchange reactions, which are significant in regulating the pH and composition of natural waters (Stumm and Morgan, 1970).

It can be seen therefore that although pH has such an overriding influence on the composition of the water and the solubility of trace metals such as zinc, its influence cannot be separated totally from other factors.

The alkalinity of a water can be defined as the capacity of the water to accept protons, or the acid neutralizing capacity of the water (Stumm and

Morgan, 1970) and can be summarized in the following way:

$$(\text{Alk}) = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+)$$

The importance of carbonate radicals in controlling the solubility and hence form of zinc has already been seen in the weathering environment around zinc sulphide ore bodies (1.61). They are of no less importance in controlling zinc solubility once it has entered surface waters.

Solubility curves of zinc in distilled water at alkalinity levels of 10, 50, 100 and 250mg l⁻¹ (CaCO₃) were produced by O'Conner *et al.* (1964), with an increasing pH of 7 to 11. Marked drops in the dissolved zinc level with increasing pH was observed, with the highest alkalinity containing the lowest concentrations of zinc. Ernst, Allen and Mancy (1975) produced solubility curves of zinc for three values of alkalinity. Zinc was shown to be least soluble in the solution with the highest alkalinity (10⁻³ eq. l⁻¹), but all three curves were markedly influenced by the level of pH above pH 7.5, with rapid loss of zinc at all alkalinity levels. Solb  (1974) states that the solubility of zinc, Zn²⁺ is mainly controlled by the solubility of zinc carbonate, which in turn is a function of the pH and total alkalinity. In an idealized system which assumed equilibrium had been reached, no organic complexing occurred and no precipitates of hydroxocarbonates were formed, he calculated that either a 10-fold increase in hardness or unit increase in pH value brought about a 10-fold reduction in the Zn²⁺ concentration.

1.713 Silica

Using thermodynamic calculations, Hem (1972) was able to display graphically the solubility of willemite (Zn₂(SiO₄)₂) as a function of pH. His results indicate a pH range of between 7.5 and 10 where silicate species are less soluble than other forms of zinc. On the basis of these calculations made on idealized, controlled systems he suggests that under the conditions of

most surface waters silicates may exert the most effective control on zinc solubility.

1.714 Phosphate

Jurinak and Inouye (1962) studied the interaction between $ZnCl_2$ and NaOH in the presence of varying amounts of KH_2PO_4 , using a potentiometric titration technique. Initial reactions at the lowest level of phosphate involved precipitation of zinc phosphate, followed by precipitation of excess zinc as the hydroxide. At higher phosphate levels all the zinc was precipitated as zinc phosphate. The increase in pH caused by the introduction of NaOH considerably decreased the levels of both ionic zinc and phosphorous in the range of pH values normally encountered in surface waters.

In most upland streams rising as springs or flushes high phosphate levels would not be expected normally, particularly since they would not receive significant anthropogenic sources such as those from waste water treatment effluents (domestic and industrial), fertilizers and detergents. Dissolved forms of phosphate in these streams would primarily arise from natural weathering and solution of phosphate minerals, soil erosion and transport, and biological transfer involving the biota. Only in nutrient rich waters or inorganic media with excessive phosphate levels would interaction between zinc and this ligand play an effective role in controlling zinc solubility, subject to the influence of other factors including pH. Recently it has been demonstrated (Ramamoorthy and Manning, 1974) that fulvic acid is capable of mobilizing phosphate complexes of zinc.

1.72 Organic Compounds and Zinc

There are a large variety of both natural and synthetic organic materials present in natural surface waters. Included in the former group are the natural degradation products of plant and animal tissue such as amino acids

and humic acids. The latter group is characterized by chemically derived organic species introduced by man, such as detergents, NTA, EDTA, pesticides and synthetic macrocyclic compounds.

Although of equal importance with regard to their interaction with and transport of heavy metals such as zinc, synthetic organic compounds will not be discussed in detail since they are assumed to be of little significance in upland streams, draining mining districts in sparsely populated areas. Some synthetic compounds will be discussed where they are relevant to the solubility of zinc in an experimental laboratory culture medium (viz. EDTA).

On the other hand, natural organic compounds might well be expected to be present in significant amounts where streams have their origin as small channels on the peat covered fells in mining districts.

1.721 Amino Acids

Amino acids are considered to be important constituents of ocean sediments and the sediments of other natural water bodies. The complex, polymeric substances referred to as humic compounds (1.722) are considered to be formed by the reaction of amino acids with polyphenols and ammonias etc., together with biochemical transformations (Rashid, 1972). In the zone of sedimentation, amino acids can chelate or complex zinc, thus influencing its migration, redistribution and concentration within this zone. Rashid (1972) studied the influence of various reagent grade amino acids, together with naturally occurring amino acids present in a humic acid hydrolysate, on the solubility of some metals, which included zinc, from their insoluble carbonates and sulphides. The results showed that up to 75mg l^{-1} zinc was solubilized by the reagent grade amino acids, from its carbonates, but none from its sulphides. However the naturally occurring amino acids were able to solubilize $66\text{mg l}^{-1}\text{Zn}$ from the carbonate and 6.0mg l^{-1} from the sulphide complex. Rashid interpreted

the solubilizing effect as chelation or complexing by the organic substances. Co-ordinate covalent bondings were suggested to occur from the unshared pair of electrons in the nitrogen donor atom of the NH_2 group of the amino functions. Ionic bondings were also suggested with the metal through the oxygen donor atoms of the COOH group also in the amino compound. Comparison of infrared spectra of the original amino acids and their metal complexes confirmed the participation of both oxygen and nitrogen donors in the reactions. The importance of this control over the behaviour of zinc in sediments and the water is obvious since formation of the complexes prevents precipitation, increases its solubility, changes its redox potential, and as a consequence permits it to migrate easily.

1.722 Humic Compounds

Since many of the streams draining the study area collect source waters derived from direct drainage and runoff from peat moss (3.3) and peat has been shown to be a rich source of humic compounds (Rashid, 1974), these waters can be expected to contain a certain amount of these compounds.

A better understanding of the nature and composition of humic compounds and their interactions with metals has come from the work of Broadbent and co-workers with regard to soils (Broadbent, 1957; Lewis and Broadbent, 1961; Randhawa and Broadbent, 1965), Schnitzer and coworkers with regard to soils and water (Schnitzer and Skinner, 1964, 1965, 1966; Schnitzer, 1971), Shapiro with regard to Lake water (Shapiro, 1967) and Christman with regard to fresh waters in general (Christman, 1970).

The recent reviews of Christman (1970) and Schnitzer (1971) have classified and described humic compounds and their interactions with metals. Both emphasize the importance of the fulvic acid component of these substances which together with humic acids and humins have been shown (through solubility studies) to be the chief constituents of humic compounds.

Randhawa and Broadbent (1965), in a study of the metal binding capacity of soil humic acids, were able to show that the species of zinc complexed by the humic acid varied with pH. At pH 7.0, 70% of the zinc retained by the humic acid was shown to be the divalent species, whereas at pH 3.6, 75% of the zinc was monovalent. The total zinc retained increased with increasing pH up to pH 8.5, but showed signs of declining at higher values. Rashid (1971, 1974) has performed many studies characterizing the metal absorption properties of humic acids. Using sedimentary humic acid, zinc was shown to be second only to copper in competing for bonding sites in a metal ion solution containing equal concentrations of CO, Cu, Mn, Ni and Zn. When the absorptive properties of peatmoss were investigated, the order of absorption was found to be $Cu > Ni > CO > Zn > Mn$. Rashid and Leonard (1973) have also been able to show that humic acids can prevent the precipitation of metals as their insoluble sulphides and carbonates.

The role of fulvic acid as a metal binding component of stream and river waters has recently been studied by Ramamoorthy and Kushner (1975). Using extremely fine filters they were able to separate river water samples into four main fractions. A standard fraction using a $0.4\mu m$ membrane filter to separate microorganisms and particulate matter, and three other fractions after passage through filters which retained molecules of molecular weight $>45,000$, $16,000$, and 1400 . Most of the binding capacity was associated with compounds of molecular weight less than $1,400$. Tests were carried out to see how much ions such as CO_3^{2-} , HCO_3^- , and SO_4^{2-} contributed to the complexing of the metals. No contribution to the metal binding capacity of the main river water sampled could be found from these inorganic ions. Further studies revealed that organic molecules were responsible for the metal complexing observed, and that fulvic acid may well have contributed to much of this phenomenon. The metal complexing capacity of fulvic acids has been emphasized by Schnitzer (1971), and associated with the carboxyl, carbonyl

and hydroxyl functional groups. They also have the ability to mobilize metals such as zinc, both at pH levels at which it would normally be insoluble, and in combination with other ligands. Equilibrium studies carried out by Ramamoorthy and Manning (1974) in solutions containing mixtures of phosphate, fulvate, NTA and zinc have demonstrated that fulvic acid not only rapidly complexes and mobilizes the zinc as zinc fulvate, but is also capable of binding the zinc phosphate complex. Phosphate and NTA ions were found to bind more strongly to the zinc fulvate complex than to ionic zinc.

Humic compounds have also been demonstrated to be effective complexing agents for metals often associated with zinc, such as cadmium (Gardiner, 1974).

1.723 EDTA (ethylenediaminetetra-acetic acid)

Although not of importance in the streams considered in this study, this synthetic chelating agent was used in the inorganic medium used in the toxicity tests. Some idea of its potential ability to complex zinc is therefore considered to be of importance.

Gardiner (1976) has produced a detailed study of the capacity of EDTA to complex trace metals in natural waters. Calcium is shown to have a high affinity for EDTA, and in a solution with no other complexing ligands present, a pH value between 5 and 9, and containing only alkali or alkaline earth metals, consideration of stability constants indicates that all the EDTA would be associated with the calcium. Complexation or chelation of zinc by EDTA is dependent on pH and the presence of other complexing ions, and is greatest at high concentrations of EDTA and low levels of calcium.

In an inorganic medium used for growing the moss *Eurynchium riparioides* and testing the effect of metal on its growth, an attempt was made by Lewis (1974) to calculate the ionic concentrations of metals in the medium after chelation with EDTA. The model of the complexing activity was found to be too complicated

to calculate the true ionic concentration of available metal in solution. This was due primarily to the competing side reactions between the metals and other ligands such as CO_3^{2-} , HCO_3^- , and SO_4^{2-} .

A level of $120\mu\text{g l}^{-1}$ EDTA was found by Gardiner to be sufficient to complex most of the important trace metals in the water body under investigation, even with the competitive effect of calcium in hard water.

1.73 Surface chemistry and zinc

When solutions containing zinc ions come into contact with solid phases the concentration of zinc normally decreases through its association with the solid phase (Leckie and James, 1974). Uptake of zinc in this way can be attributed to a number of processes such as adsorption, ion exchange, or coprecipitation. These processes will be affected by the chemical and physical conditions of the system. The importance of solid phases such as stream or lake sediments in controlling trace metal concentrations has long been recognized, and many references to these processes have been given by Bachmann (1961). The most important solid phases which are likely to influence zinc availability in the streams of this study are, besides the biota, inorganic minerals such as clays, hydrous oxides such as those of iron, and organic colloids. Each of these is briefly discussed.

1.731 Inorganic minerals - clays and lime minerals

It has been stated that a major proportion of zinc in soils is probably held there by surface absorption on the colloidal particles instead of in chemical combination (Hibbard, 1940). White (1952) has shown that up to 46% of the total zinc in the soil can be held in the lattice position of the clay minerals. The clay size fraction being classified as $<2\mu\text{m}$.

With regard to the aquatic habitat, Bachmann (1961) has stated that zinc can react with clay particles in two different manners.

The importance of the uptake of zinc by clay types such as illite and montmorillonite is amply demonstrated by its influence on the uptake of zinc by an alga. Keulder (1975) demonstrated this effect on the uptake of ^{65}Zn by *Scenedesmus obliquus*, which was shown to be stimulated by the presence of clays. This was explained by the presence of the clay increasing the exchange positions aiding in the uptake of ions by cation exchange between the algal cells and its surroundings. High calcium levels were shown to have a synergistic effect on zinc adsorption on the clay montmorillonite, leading to the removal of zinc from solution and reduction in its uptake by the alga. The stimulatory effect of the clay was shown to depend on the ionic composition of the medium.

The surface charge that exists along the fracture and cleavage surfaces of most minerals is due to the rupture of bonds and when in contact with water these surface charges respond by adsorbing H_2O molecules which can dissociate (Leckie and James, 1974). The adsorption behaviour of hydrolyzable metal ions such as zinc at the solid/water interface has been shown to be strongly pH dependent. It is also strongly dependent on the hydrolysis of the aqueous metal ion, its enhanced adsorption, charge reversal and coagulated properties (Leckie and James, 1974).

The thermodynamics of zinc adsorption on calcite, dolomite and magnesite-type minerals was compared by Jurinak and Bauer (1956) who demonstrated that zinc was taken up more by dolomite than calcite and that the uptake by Ca-magnesite was considerably increased by the introduction of more MgCO_3 in the mineral. The introduction of Mg^{2+} into the calcite lattice was considered by them to be the cause of the different absorptive properties. Since the ionic radii of magnesium and zinc ions has been shown to be similar (0.83nm and 0.78nm respectively) it was suggested that Zn^{2+} might be better able to fit into the MgCO_3 lattice. Due to the

(1) It can occupy a position within the crystal lattice structure of the mineral.

(11) It can become attached to a negatively charged site on the surface.

In the former state zinc is regarded as unavailable since it is not freely transferred to solution. In the latter case it is considered to be exchangeable since it is in dynamic equilibrium with the ions in solution. The affinity which a clay has for zinc will depend on its structure and the concentration of zinc, together with the relative concentrations of other ions. This ion exchange control on zinc availability will most often be exerted by the stream sediment, where most of the clay, sand and silt tends to accumulate. However under conditions of flood and mixing the colloidal particles may become freely mixed in the main body of stream or river water. Pita and Hyne (1975) have shown that heavy metals such as zinc can be transported in suspended load adsorbed on the clay mineral surfaces.

Zinc was shown to have a strong correlation with percent clay size. It was further demonstrated that most of the zinc present in the sediments of the Fort Gibson Reservoir, Missouri, was deposited as organometallic complexes adhering to the clay particles. The majority of the clay mineral present was of the montmorillonite, illite and kaolinite group, but not all of it was demonstrated to possess surface activity. Most of the zinc absorbing capacity was shown to be associated with that part of the sediment with a specific gravity of 2.0 - 2.9, and it was demonstrated that the organic matter which tends to form metallic complexes would also tend to adhere to the clay mineral surfaces and hence occur in that fraction of the sediment in combination with the zinc.

size of the calcium ion (1.06nm) it would be too small.

1.732 Hydrous oxides

White (1957), in a study of zinc in soils, was able to show a relationship between the zinc content and iron content of many soils. Zinc was particularly associated with limonite, the concentration in this mineral being higher than in the surrounding soils.

Jenne (1968), in a review of the control mechanisms for the concentrations of several ions in both soils and waters, concluded that the hydrous oxides of Mn and Fe were the main controls for the availability of zinc. The sorption and desorption behaviour of the metals was shown to respond to several environmental factors such as pH, and the presence of other complex forming ligands etc. The other controls reviewed included the presence of clays, carbonates and organic matter.

It has already been mentioned that zinc can replace ferrous iron in certain minerals, favouring positions with coordination numbers of 4 and 6, the latter especially if ligands such as OH^- are present. Again the similarity in ionic radius between Zn^{2+} and Fe^{2+} favours zinc substitution for ferrous iron (Wedepohl, 1972). Wedepohl emphasizes the importance of hydrated ferrous oxide (ferric hydroxide) in controlling the solubility of zinc in stream waters.

Further evidence for the importance of Fe and Mn oxides in controlling heavy metal availability has come from the study by Suarez and Langmuir (1976) on a Pennsylvanian soil. Mn oxides identified as todorokite, which occurred chiefly as coatings on quartz grains, were shown to have at least ten fold higher heavy metal percentages (including zinc) than Fe-rich oxides (goethite). Minor amounts of metals occurred in readily exchangeable sites in the organic and clay-poor residual subsoils, the major source of

metals being shown to be hydrous Mn oxides. Of the metals studied (Co, Ni, Cd, Cu, Zn, Pb), zinc was one of the most strongly correlated with soil levels of Mn. Fe oxide contributions of the metal was only important when Fe exceeded the level of Mn in the soil.

1.733 Organic colloids

It is well recognized that organic colloids have varying proportions of the different functional groups, and that these groups may either generate a surface charge that governs electrostatic adsorption or form direct organic-metal bonds (Leckie and James, 1974). These functional groups include hydroxyl, carboxyl, sulfhydryl, amino and imino groups, and depending on the solution pH can be charged or neutral. The formation of organic-metal bonds between zinc and organic substances, such as complexing with fulvic acid, has already been dealt with (1.721).

Bachmann (1961) has summarized early work characterizing the ion exchange properties of organic materials, and has emphasized the importance these might have in the cycle of zinc in lakes.

Nakhshinia and Fel'dman (1972) carried out a detailed study on the effect of certain factors on the bonding of zinc by the bottom organic layer (termed by them "Ooze") in waters. Using concentrations of $0.05 - 1.2 \text{ mg l}^{-1} \text{ Zn}$ the ooze was found to bind 77% of Zn^{2+} added to the water. Mud sand was found to reach an equilibrium at lower concentrations of zinc than the ooze, due to the presence of less organic matter. pH was found to affect significantly the direction of the adsorption process, with higher pH levels favouring the bonding of zinc by the bottom deposits. However it was shown to be a complex process in which it was suggested that intermediate polycyclic compounds could be formed and then subsequently adsorbed. Increases in the concentration of Ca^{2+} were found to reduce the binding

capacity of the ooze by up to 25%. The potential bonding capacity of the bottom sediment was shown to be very high and increased with the content of organic matter.

As mentioned before (1.731), the organic component of the sediments in reservoirs and streams has been shown by Pita and Hyne (1975) to be the most important fraction which absorbs zinc. By fractionating the sediment into that part with a specific gravity (SG) greater than 2.9 (suggested by them to contain metallic precipitates, carbonates and sulphides), with an SG less than 2.0 (suggested to be organic matter plus some attached clay particles) and with an SG between 2 to 2.9 (suggested as being predominantly clay material with attached organic matter), they showed that all of the zinc was in the fraction with SG 2 - 2.9. This led them to conclude that the zinc was bound directly to the clay or to the organic matter which was then absorbed onto the clay material.

1.8 Sources of zinc to the aquatic environment

1.81 The Atmosphere

The atmosphere can contribute zinc to the aquatic environment through a number of agencies. Zinc occurs in the atmosphere mainly in the form of dust, and as a contaminant of rain and snow. These sources originate primarily from pollution. Aerosols containing zinc, which are introduced into the environment, can have a number of origins. The combustion of coal has been sited by Wedepohl (1972) as an important source of zinc to the atmosphere. He has suggested an average concentration of $100\text{mg l}^{-1}\text{Zn}$ for coal, and using approximate figures arrives at a level of $10\mu\text{g l}^{-1}$ average zinc concentration from combustion of coal. He points out that a proportion of zinc will be precipitated in most chimneys (from dust containing usually more than 1% zinc) and as insoluble matter around factories.

Emissions from smelters which have been involved in the refining of sulphide ores is probably one of the most important sources of zinc to the atmosphere. Intensive studies on the effect of such emissions from a complex of smelters in the Sudbury district of Ontario, Canada, have been carried out (Gorham and Gordon, 1960; Nieboer *et al.*, 1972). This large plant deals with the smelting of several different sulphide ores including those for Ni, Fe and to a lesser extent Zn. As well as large amounts of sulphur dioxide, all of these metals were emitted in the fumes in significantly large amounts.

Studies carried out by Jordan (1975) have shown that metal aerosols containing Zn, Cd, Cu, and Pb, as well as SO₂ gas, are incompletely recovered from emissions from a zinc smelter in the Palmerton region of Pennsylvania, America. Such aerosols escape into the atmosphere and can be transported over large distances by winds and air currents. The larger particles would be expected to return to the surface by sedimentation, but smaller particles can be dispersed over wider areas by updraughts and turbulence.

The smelting process, which involves roasting of the sphalerite in air, evolves sulphur dioxide and converts the sulphide to the oxide. It is particles of the oxide which enter the atmosphere in the form of dust from the emissions (together with the SO₂). Once released in this form the oxide might be expected to react with the SO₂ (in the presence of water vapour) to form zinc sulphate which would be soluble in the rain water, and would then be redeposited by wet deposition (through precipitation) as rain or snow.

Pearson *et al.*, (1973) have reviewed the origins of atmospheric trace elements in the vicinity of Lake Windermere. They emphasize the lack of information available for the metal content of rain water in general. The average concentration of zinc in rain water over a period of one year was

given as $85\mu\text{g l}^{-1}$, and in the air 80ng kg^{-1} . The total deposition of zinc was found to be $1\mu\text{g cm}^{-2}$.

A study of precipitation in America by Lazrus *et al.* (1970) was able to demonstrate an average figure of 0.107mg l^{-1} in rain water collected from 32 stations throughout the country. This rather high value was shown by Hem (1972) to be influenced by samples taken in the vicinity of two large airports, from which he states that combustion of fuel would be expected to contribute large amounts to the atmosphere. Hem (1972) concludes that industrial discharges of zinc aerosols are the principal source of zinc in rainfall in Northern America.

A study of the heavy metal content of rainfall in the East Midlands of England by Hallsworth and Adams (1973) demonstrated that flyash emitted from power station chimneys (in combination with rainfall) was an important source of trace metals. Analysis of the flyash gave values of 130 and $530\mu\text{g/g Zn}$.

1.82 Soils

Soils can supply zinc to streams and other surface waters indirectly through the agency of rain and drainage waters. Zinc can occur in soils from several sources. Abnormal zinc concentrations can be expected in soils in the vicinity of ore deposits through the natural processes of weathering (Wedepohl, 1972). Zinc can also be expected to occur naturally in soils from the residual zinc of the weathered rocks on which the soil has been formed (see 1.51 and 1.61). Because of its low mobility and absorption in clay minerals, hydrous ferric oxides, and organic residues, zinc concentration is often slightly higher in soils than in the related undecomposed rocks (Wedepohl, 1972). Anthropogenic influences on zinc levels of soils occur primarily through base metal mining, or deposition of zinc aerosols emitted from the smelting of zinc ores.

1.821 Influence of base metal mining

Abnormal concentrations of zinc in the vicinity of ore deposits and old mine workings are well documented (Ernst, 1966; Alloway, 1969; Alloway and Davies, 1971; Davies, 1971; Bradshaw, 1970; Shimwell and Laurie, 1972). Davies (1971), in a study of soils within a mineralized area in the Tamar Valley in South West England, was able to demonstrate a geographic association between anomalous levels of zinc in the soils and the occurrence of mineralization, mines and tailings heaps. Shimwell and Laurie (1972) record values of zinc in the soils of mining areas in the Southern Pennines, between 1900 - 35000mg l⁻¹Zn, the highest values being intimately associated with mine spoil heaps.

Similar enrichment of lead in soils in the vicinity of weathered quartzite rocks containing the lead ore, galena, were observed by Lag *et al.* (1969) in a mineralized area in Norway. No human activity was observed in this region and the high concentrations of lead were associated with the natural weathering processes on the rocks.

During periods of heavy rainfall soils enriched with zinc in these base metal mining regions might be expected to contribute some of the bound zinc to the drainage waters via the mechanisms (such as leaching) described in 1.62 and 1.7.

1.822 Influence of zinc ore smelting

The contribution of zinc smelter emissions to the enrichment of zinc in the atmosphere has already been discussed (1.81). It is apparent that deposition of such zinc, either through sedimentation from the dry air or through wet deposition by rain will contribute zinc to soils, and hence, eventually, possibly to adjacent water courses. Buchauer (1973) carried out an intensive survey of the contamination of soils near a zinc smelter

by zinc together with cadmium, copper and lead. Within 1km of the smelters, levels of $135,000\text{mg l}^{-1}\text{Zn}$, $1750\text{mg l}^{-1}\text{Cd}$, $2000\text{mg l}^{-1}\text{Cu}$ and $2000\text{mg l}^{-1}\text{Pb}$ were measured in the partially decomposed leaf litter horizon of the soil. In a further study, Jordan and Lechevalier (1975) showed that 13.5% Zn by weight could be measured in the leaf litter horizon, and 8% Zn in the humus horizon of a nearby soil. Comparison between the levels of zinc in soils 2km from the smelter, with those at a site 46km in distance, showed considerable differences. At the nearer site, three soil horizons, the leaf litter, humus, and mineral soil, showed respectively $129,000$, $60,700$, and $1750\text{mg l}^{-1}\text{Zn}$, whereas the distant site showed total zinc levels for these three horizons respectively of 570, 110, and $44\text{mg l}^{-1}\text{Zn}$.

Similar studies on the emissions from smelters in an industrial complex at Avonmouth, on the Severn Estuary, by Burkitt *et al.* (1972) were able to show decreasing concentrations of zinc in the soil along a transect leading away from the smelting works. At a distance of 0.3km, levels were as high as 5000mg l^{-1} , whereas at a distance of 12km, the level had dropped to $90\text{mg l}^{-1}\text{Zn}$.

Leaching of such soils by drainage waters and storm runoff would be expected to contribute significant levels, not only of zinc, but also associated metals such as cadmium, copper and lead, this being dependent on the exchange properties of the soil and the chemistry of the water passing through it.

1.83 Acid mine drainage waters

Acid waters, considerably enriched with heavy metals such as zinc, can originate in two main ways. Springs and streams draining from outcrops of coal bearing strata can become acidic and contain elevated levels of metals through the weathering of exposed sulphide ore bodies. The most

abundant sulphide associated with the rocks of these strata, through which the water percolates, is pyrite, FeS_2 .

Compared with these natural conditions, mining operations expose relatively large areas of rock to the action of the weathering processes, usually resulting in elevated concentrations of water soluble compounds of iron, manganese, zinc etc., contaminating drainage from the mines and eventually sometimes polluting adjacent water courses (Glover, 1975).

There is a voluminous literature concerned with acid mine drainage waters (for reviews see Hargreaves *et al.*, 1975; Glover, 1975; Van Everdingen, 1970), consequently only a brief mention is made here of their contribution of zinc to the stream environment.

Van Everdingen (1970) has described in detail a group of acid springs in British Columbia, Canada, with extreme heavy metal enrichment. One spring with a pH of 2.5 contained up to $177\text{mg l}^{-1}\text{Zn}$. Spring waters from adjacent areas had an average pH of more or less 8.0, and a zinc level of $0.080\text{mg l}^{-1}\text{Zn}$. However, extreme pollution of the relatively alkaline river receiving these springs was not found to occur, attributed by Van Everdingen primarily to the precipitation of metals by the change in pH. An appreciable quantity of zinc was found to enter the river from the springs at low flow periods.

Several studies have been carried out recently on aquatic habitats with respect to the effects of acidic and heavy metal rich discharges from ore smelters. The study of Whitby *et al.* (1976) on the effect of smelter emissions on lakes in Sudbury, Ontario, demonstrated elevated levels of nickel, copper and zinc. These were shown to have caused significant loss in fish, zooplankton and algae.

1.84 Base metal mine drainage waters

Mine waters discharging from old lead and zinc workings, and waters draining the associated tailings heaps, are probably the best documented sources of zinc in the aquatic habitat. A large amount of research, dating from the early accounts of Carpenter (1924), to those of the present day (Jennet *et al.* 1975; Fuge, 1972; Jones and Howells, 1975), provide pertinent information with regard to the enrichment of natural waters with heavy metals from such discharges.

In the early accounts on the effect of mine waters, zinc was often overlooked in preference to lead concentrations which were often high and extremely toxic (Carpenter, 1926). This was stated by Jones (1940) to be because high levels of zinc may not have been suspected. Perhaps the most well known mining region which has been studied for zinc pollution is that of the Cardiganshire area of North Wales. Although Carpenter's original studies (1924) were concentrated primarily on the effects of lead, later research (Jones, 1940, 1958) was directed towards the elevated levels of zinc and their effect on the streams and rivers draining the area. Levels of up to $90\text{mg l}^{-1}\text{Zn}$ were found by Jones (1958) to be discharged from mine adits, and the main river Ystwyth reached levels approaching $1\text{mg l}^{-1}\text{Zn}$. Later studies by Treharne (1962) on mine waters entering an adjacent water course, the River Rheidol, demonstrated similar high zinc concentrations. Streams whose source was derived from adits were cited as the main waters enriched with zinc. Sometimes the pH of these adit streams was extremely acidic, from waters draining associated pyrite ore, and concentrations of zinc were found to reach $187.5\text{mg l}^{-1}\text{Zn}$. A survey of mine waters carried out in the same area by Fuge (1972) showed that even the non-acidic adit waters contained levels of up to $4\text{mg l}^{-1}\text{Zn}$.

An intensive research programme has been carried out on the effect of mine discharges associated with the large lead belt in south east Missouri in America over a period of many years (Wixson, 1968; Wixson and Bolter, 1972; Wixson *et al.* 1972; Jennett *et al.* 1975). Although the main mineral associated with both the mining and research is lead, significant quantities of sphalerite are mined, and discharges have been shown to carry the metal zinc. Because adequate controls have been taken to control contamination of natural water courses by trace metals associated with the mining operations, levels of dissolved zinc were not found to reach levels of extreme toxicity. However problems were experienced with controlling fine particles of ground mineral which escaped flotation and tailings reservoirs, and were transported downstream (Jennett *et al.* 1975). As well as elevated levels of zinc associated with mine waters specifically from lead or zinc mines (where large amounts of sphalerite may be present), high zinc concentrations can also be found in waters associated with mining operations for other metals. Tyler and Buckney (1973) discovered severe metal contamination of two creek waters in north east Tasmania, by discharge of effluents from tin and wolfram mines. The chief contaminants were cited in order as being sulphuric acid, zinc, cadmium, copper, lead, iron and manganese (in both dissolved and particulate form). Levels of zinc in mine effluents rose as high as $105.0 \text{ mg l}^{-1} \text{ Zn}$ in waters of pH 4.9, and $17 \text{ mg l}^{-1} \text{ Zn}$ in waters of pH 6.2.

1.85 Industrial waste

Because of its use in a large number of industries (galvanizing, manufacture of brass, production of zinc pigments used in the manufacture of rubber, paints, pharmaceuticals and chemicals etc.), zinc can be released into the aquatic environment as a contaminant of industrial effluents. Evidence of such zinc contamination is sparingly few, primarily because industrial discharges often take place at variable times which are difficult to

monitor, and often detection of the contamination in the receiving water body may take place some while after the release (Oliver and Cosgrove, 1974) of the discharge. Detection of such contamination usually takes place indirectly through studies of municipal waste water entering sewage treatment plants. A recent study made by Roberts *et al.* (1975) of an effluent in Zurich showed that of the six metals investigated (Cd, Cu, Zn, Ni, Pb and Cu) zinc was found at the highest concentration (0.5mg l^{-1}) in an untreated waste water.

A detailed study carried out by Oliver and Cosgrove (1974) of the efficiency of an activated sludge process in removing zinc from municipal waste water entering Lake Ontario provided interesting information with regard to the passage of zinc through such a plant. Hourly sampling showed that input of zinc was not a continuous process but consisted of "slugs" of metal lasting for discrete time periods, but which were periodic and not predictable. Identical ratios between zinc and lead during the sampling was used as evidence for a similar industrial source. Levels of up to $70 \text{mg l}^{-1} \text{Zn}$ were recorded as entering the plant in the effluent. Although the activated sludge process was shown to be relatively efficient in removing zinc (up to 77% Zn removed), some metal still passed out to enter the river and be transported into the lake. All the zinc removed was shown to be concentrated into the sludge, and the practice of disposing of the sludge onto the land can be seen to be another source of zinc which might find its way into a local watercourse.

1.9 Ecology and Phytosociology of Zinc

1.91 Plant species present under conditions of zinc contamination

1.911 Indicators

An extensive review of heavy metal tolerance in plants carried out by Antonovics *et al.* (1971) contains a large section devoted to the "Ecology of Metal Tolerance". In this section they summarize the systems of classifying metal tolerant plants and indicate some of the more important species. A considerable amount of information has been provided by the work of Ernst (1966, 1968, 1974), particularly with respect to terrestrial communities colonizing the soils around mining complexes and old spoil heaps. Much of the emphasis was directed towards the metal zinc.

Antonovics *et al.* (1971) compiled a table of plants which have been regarded as indicators when prospecting for heavy metals (their general definition of indicator was given as "a plant that in a given area or geographic region has been recognized as associated with a particular metal."). Summarizing the data presented by them for the metal zinc, *Viola calaminaria* is the only terrestrial species universally accepted as an indicator of zinc. In their review of other plant groups, no other species were mentioned as indicative of zinc contamination in the environment.

Ernst (1966) summarized the differential and characteristic species of West and Central European plant communities growing on heavy metal soils, including those contaminated by zinc. Associations of species classified in the Alliance *Thlaspiion calaminariae* (characterized by *Thlaspi alpestre* spp. *calaminare*) within the class *Violetea calaminariae* (characterized by *Viola calaminaria*), are considered to be indicative of zinc contamination of the soil (details of the methods of classification are given by Antonovics *et al.*, 1971, and Shimwell, 1971).

With regard to other plant groups, there is a striking paucity of literature associated with species or genera which by their presence or absence could be considered "indicators" of zinc contamination.

In a review of the toxicity of metals to freshwater algae, Whitton (1970b) summarized some recent literature with regard to the use of algae as indicators of high levels of heavy metals. He was able to conclude that the available information was not adequate enough to decide which species could be considered indicative of high zinc levels. A suggestion was made that if *Stigeoclonium tenue* was found alone in abundant growths in a clear, well illuminated, fast flowing body of water, metal contamination could be suspected at that site.

More recently a study was carried out by Besch *et al.* (1972) on the possible use of benthic diatoms as indicators of the presence of heavy metal contamination. They were unable to establish the presence of reliable indicator species, but obtained an indication of metal contamination by the dominance of species of a corresponding tolerance with simultaneous absence or scarcity of all less tolerant forms. On this basis, diatom species such as *Eunotia exigua* and *Achnanthes microcephala* were regarded as being very resistant to zinc, being frequently abundant at levels in excess of $10\text{mg l}^{-1}\text{Zn}$; and species such as *Diatoma hiemale* and *Cymbella afinis* were regarded as zinc-sensitive, being unable to resist levels greater than $0.1\text{mg l}^{-1}\text{Zn}$. They regard this tentative indicator system as being only applicable to the water conditions in their study area (the north west Miramichi river basin in the Atlantic Provinces of Canada).

In a laboratory study carried out by Williams and Mount (1965) on the influence of zinc on periphytic communities, organisms representing several taxa of freshwater benthos were found to be resistant to levels of zinc up to $8\text{mg l}^{-1}\text{Zn}$. On the basis of their findings a number of

species from these taxa were suggested as being highly tolerant of zinc, such as the bacterium *Sphaerotilus natans*, the fungus *Alternaria tenuis*, the blue-green alga *Schizothrix calcicola*, and the green alga *Spirogyra* sp. However since these species included organisms found to be abundant in a wide variety of habitats, no conclusions could be made as to their use in indicating high zinc concentrations.

Studies carried out on the flora of metal contaminated waters in the mining district of Cardiganshire, Wales, led McLean and Jones (1975) to suggest that abundant growths of the alga *Hormidium rivulare* found growing alone in "clean", flowing waters could be used as an indication of high zinc levels in that water.

From the same study they concluded that streams dominated by the bryophyte *Scapania undulata* on its own, or together with *Hormidium rivulare*, should also be suspected of carrying high levels of zinc. Although there has been much literature accumulated on the reliability of certain bryophyte species to indicate metals such as copper and nickel (Schacklette, 1967), few have been mentioned which are specifically associated with zinc mineralization.

1.912 Tolerant species

Although not necessarily being reliable enough to be regarded as "indicators" of zinc contamination, there are a large number of species which can tolerate and also resist the effects of high zinc concentrations. With regard to terrestrial plant species, the work of Bradshaw and coworkers (Bradshaw, 1952; Bradshaw, McNeilly and Gregory, 1965; Gregory and Bradshaw, 1965), who have carried out extensive studies on the ability of grass species to colonize base metal mine soil heaps, have established species such as *Agrostis tenuis* and *Festuca ovina* as important zinc-tolerant species.

With regard to the aquatic habitat, Whitton (1970a) was able to demonstrate that certain species of Conjugales such as *Spirogyra* sp. and Ulotrichales such as *Ulothrix* sp. were tolerant towards relatively high concentrations of zinc.

1.10 Biochemistry of zinc

The biochemistry of zinc has been the subject of many reviews (Vallee, 1959, 1962; Zajic, 1969), therefore only a brief summary of the more important aspects relevant to photosynthetic organisms in the aquatic habitat will be given here.

1.10.1 Zinc and enzymes, requirements, deficiency

The importance of zinc as a structural component of certain enzymes is well established from its original citation as an active component of the enzyme carbonic anhydrase in both animals (Keilin and Mann, 1944) and plants (Day and Franklin, 1946). Its presence as a functional component of many enzyme systems has been the subject of much research and several reviews (see Vallee and Neurath, 1955; Vallee, 1959).

From the original discovery by Raulin (1869) that zinc was an essential nutrient in the growth of *Aspergillus niger*, it has been found to be an important trace element in the nutrition of both plants and animals. Zajic (1969) has reviewed its importance in microbial metabolism, and Bowen (1966) includes it in a general review of trace element deficiency. Myers (1951) has established its requirement as an inorganic micronutrient in the growth of *Chlorella pyrenoidosa*. Rice (1961) has summarized its importance in the nutrition of terrestrial higher plants, and its subsequent use in fertilizers.

1.10.2 Zinc toxicity

1.10.21 Measurement

The methods often used to assess the toxic effects of zinc to aquatic organisms are similar to those used widely to measure the toxicity of other chemical substances. A large number of reviews have been produced recently which discuss the techniques used for both aquatic flora (Weber, 1973; Mitchell, 1973) and aquatic fauna (Sprague, 1969; Brown, 1973; Eaton, 1973). With regard to the fauna (in particular fish) there are two main types of element toxicity measured:

(1) Acute (where the toxic action of the element e.g. zinc reaches the "crisis" point in a relatively short time period), which is assessed as the LC50, an estimate of the concentration of toxicant in the dilution water which is lethal to 50% of experimental organism (fish). In this assay a standard procedure has developed of monitoring the assay at 24h intervals over a period of 96h (Davies *et al.*, 1976).

(11) Chronic, where the toxic effects of a metal such as zinc are monitored over a much longer time interval such as nine months (Brungs *et al.*, 1976). The effect on many stages in the life cycle can be measured (Davies *et al.*, 1976), and responses are often noted at very low levels of a particular metal.

The toxicity of zinc to photosynthetic organisms can be measured in a variety of ways depending on the type of organism. The effects of zinc on unicellular algae can be measured directly through counts made on the number of cells present after a specified time period (Rachlin and Ferrar 1974). Other methods with such algae include measuring the optical density of the cell suspension (Rana and Kumar, 1974), or variation in the fluorescence of the test cultures (Hannan and Patouillet, 1972). With

regard to filamentous green algae, the toxic effect of substances on growth can be assessed indirectly through the measurement of chlorophyll *a* production (Hargreaves and Whitton, 1976). Recently the toxicity of substance has been assessed by measuring their effect on respiration rate, and specific reactions within the main process of photosynthesis (Overnell, 1975; De Filippis and Pallaghy, 1976b).

1.10.32 Toxic effects of zinc

Although the toxic effects of zinc to plants has been the subject of much research, the precise mechanisms of the toxic effect are still incompletely understood, particularly with respect to algae. It seems that an important mechanism of toxic action is through the alteration of enzymes and resultant disruption of the relevant metabolic reaction (Bowen, 1966). Passow *et al.* (1961) give a review of the interaction between heavy metals, including zinc and enzymic systems. More recent research carried out on extracts of higher plants (Hampp *et al.*, 1976), in addition to algae (De Filippis and Pallaghy, 1976a), have indicated the inhibitory effect of zinc on photosynthesis. Hampp *et al.* were able to show that photosynthetic CO₂-fixation was inhibited in isolated spinach chloroplasts. Zinc was shown to retard the noncyclic electron transport by influencing the electron flow between water oxidation and photosystem II. De Filippis and Pallaghy demonstrated that both photosynthesis and respiration were inhibited by zinc in *Chlorella*. The symptoms of zinc toxicity were shown to be a sharp reduction in pigment content, rates of cell division, and metabolic activity, with a concurrent gain in net C balance due to inhibition of the export of photosynthetic products from the cells.

The toxic effects of zinc on fish seem to be more completely understood and better documented. From the early studies of Carpenter (1927, 1930) and

Jones (1938, 1939) to more recent research carried out by Skidmore and Towell (1972), and Sellers Jr *et al.* (1975), the effects of zinc on the gills, ventilating activity, and blood oxygen have gradually become elucidated. The toxic effect is exemplified by an acute inflammatory action on the gills, with subsequent respiratory collapse (Sellers Jr. *et al.*, 1975).

1.10.4 Tolerance and Resistance to Zinc

There is an extensive literature on the tolerance and adaptation of some terrestrial higher plant species to heavy metals, in particular zinc (Bradshaw, 1952; Jowett, 1958; Ernst, 1969; Bradshaw, 1970). Most of this research has been reviewed by Antonovics *et al.* (1971) and Ernst (1974). The species from heavy metal rich sites which have received critical study have been shown to be metal-tolerant strains of species which have non-tolerant strains growing elsewhere.

In a comparison of the soil microflora of a forest soil rich in zinc with one low in zinc, Jordan and Lechevalier (1975) found that while all the actinomycetes and non-spore forming bacteria isolated from the high zinc soil were zinc-tolerant, some zinc-tolerant forms were also readily isolated from the low zinc soil. Most fungi, regardless of source, were capable of growing in relatively high zinc concentrations.

In a study which included investigations of the possible resistance of aquatic bacteria to heavy metals (in particular zinc) Griffiths *et al.* (1975) were able to show that in general 2% of the bacteria were resistant to zinc. However it was shown that this proportion could rise as high as 16% and even 30% of the total population. It was postulated that the variable distribution of zinc-resistant bacteria might be indicative that the zinc contamination was not uniform, or that other factors (hardness, acidity etc.) were important in the establishment of micro-

environments within a wider sampling area, reducing the relative importance of the zinc contamination. The discovery by them that bacteria associated with the roots of tolerant grasses growing on zinc contaminated spoil heaps possessed a higher level of resistance than those associated with plants on uncontaminated soil, led to the speculation that the bacteria could be important in contributing to the tolerance of the plants.

There are many records of the occurrence of algae at sites with high levels of zinc (Reese, 1937; Jones, 1958; Whitton, 1970b; Besch, Ricard and Cantin, 1972; McLean and Jones, 1975; Gopal, Rana and Kumar, 1975).

However, unlike terrestrial Angiosperms, there have been few studies to investigate whether the algae from these sites are strains possessing greater tolerance than strains of the same species growing elsewhere, or whether they are species which are equally tolerant to heavy metals whether or not they occur at heavy metal rich sites.

A discussion of the evolution of metal tolerance, including that of zinc, has been presented in the review of Antonovics *et al.* (1971). Genetical studies carried out by Gartside and McNeilly (1974a, 1974b) have shown that the genetic control of zinc-tolerance in both the grasses *Anthoxanthum odoratum* and *Agrostis tenuis* is dominant and directional with a high additive genetic variance, and is under polygenetic control. In a review of heavy metal tolerance in plants, Turner (1969) emphasizes the specificity of tolerance in higher plants, particular grasses. However different individual tolerances towards metals can occur together, being correlated to toxic concentrations of several metals being present in the soil of the original habitat at the same time.

Conversely, the study of Griffiths *et al.* (1975) on resistant bacteria has shown that resistance to one particular metal can also confer a measure of

resistance in the same organism to other metals. The resistance was shown to be a stable character since it was retained after growth for a long period of time in the absence of metal ions.

It is apparent that a full understanding of metal tolerance, such as that of zinc, is still incomplete, both with regard to elucidating the precise mechanisms, and understanding the extent to which they are controlled genetically. In summarizing the literature, Antonovics *et al.* (1971) state that "most of the studies on the genetics of metal tolerance have been cursory and rather inconclusive." So it would appear that until more groups of plants are studied with respect to their metal tolerance it is unwise to attempt to generalize on tolerance and resistance in photosynthetic organisms.

1.10.5 Mechanisms of tolerance and zinc accumulation

These two aspects of the biochemical effects of zinc are treated together, since according to Antonovics *et al.* (1971) the possible mechanisms of metal tolerance include many internal processes which involve metal uptake.

Mechanisms of tolerance and accumulation of heavy metals in terrestrial angiosperms are well documented (Turner, 1969; Turner and Marshall, 1971, 1972; Antonovics *et al.*, 1971; Wainwright and Woolhouse, 1975). It is also well documented in terrestrial bryophytes (Ruhling and Tyler, 1970; Gullvag and coworkers, 1973, 1974; Brown and Bates, 1973), fungi (see review of Ross, 1975), and marine algae (Gutnecht, 1963; Bryan, 1969; Parry and Hayward, 1973).

With regard to the freshwater aquatic habitat, fewer studies have been carried out on the tolerance and accumulation of zinc by either algae or bryophytes, particularly from streams considerably enriched by this metal. However some studies have been carried out on the uptake and accumulation

of zinc by aquatic bryophytes. Pickering and Puaa (1969), in a study of zinc uptake by *Fontinalis antipyretica*, showed that a large amount was rapidly accumulated by a passive, mainly exchange, adsorption process involving the donnan -free-space of the cell wall. However two other processes were also demonstrated. A second slightly slower uptake into the protoplast, with the outer layer acting as a diffusion barrier. The final stage, lasting over a period of several days, consisted of an active accumulation within the cells. This third phase was affected by metabolic inhibitors such as the decomplexing agent DNP, and other metabolic influencing factors such as temperature and light. Two uptake mechanisms for zinc were speculated by McLean and Jones (1975) in their study of *Scapania undulata*. An active mechanism at lower zinc levels ($0-10\text{mg l}^{-1}\text{Zn}$) and an uncontrollable passive mechanism at higher levels ($10-25\text{mg l}^{-1}\text{Zn}$). They postulated that when sites for metal combination became saturated in the former, the plant would be swamped by metal uptake via the latter mechanism. They suggested tolerance would exist if an internal protective system was present where the metal is bound to harmless sites which they cite as possibly the cell wall. Once saturated, the metal would be expected to enter the cell, affecting sensitive areas of cell metabolism. During their study they compared uptake between *Fontinalis antipyretica* and *Scapania undulata*, and finding the latter more resistant postulated that *Scapania undulata* might have more internal complexing sites than *Fontinalis antipyretica*. The lower uptake rate for zinc shown by *Scapania undulata* was explained as possibly being due to it being less permeable to zinc at the cell wall.

Some studies with regard to the uptake of zinc have been carried out on freshwater algae. Bachmann (1961) investigated the uptake of Zn^{65} by the algae *Ankistrodesmus* sp. and *Golenkinia paucispina*. He states that a non-metabolic ion-exchange process was demonstrated which was best

represented by the Freundlich adsorption isotherm to describe the relationship between zinc uptake and concentration of zinc in solution. This supported previous findings for the uptake of zinc by *Chlorella* (Knauss and Porter, 1954). The possible existence of an active metabolic process was not excluded from consideration by Bachmann. Matzku and Broda (1970) demonstrated that the uptake of Zn^{65} by *Chlorella fusca* took place in two definite processes. The first was a rapid, but limited, energy- and temperature-independent binding to the cell surface. The zinc taken up in this way was easily removed by washing with non-labelled zinc carrier solution. During the second, zinc was taken up strongly for longer periods and could not be removed completely. The uptake was shown to follow saturation kinetics, and was dependent on energy.

More recently experiments carried out by De Filippis and Pallaghy (1976b) on the uptake of Zn^{65} by *Chlorella* have shown that tolerance of zinc is characterized by the development of a typical exclusion mechanism. A percentage of the zinc taken up was shown to reside in the free space of the cell; the rest was assumed to be compartmented into ionic or bound forms within the cell.

Studies on the uptake of zinc by various species of fungi have provided valuable insight into the possible mechanisms of tolerance and uptake of this metal. Investigations with the filamentous fungus *Neocosmospora vasinfecta* (Paton and Budd, 1972) have indicated an active process which occurred in two phases. In the first phase, zinc was adsorbed onto the surface of the cell and was shown to be associated with the cell membrane rather than the cell wall. In the second phase zinc was transferred across the membrane, a process which was shown to follow carrier-mediated transfer kinetics. Failla *et al.* (1975) demonstrated two similar processes for the yeast *Candida utilis*, with firstly a rapid energy- and temperature-

independent binding to the cell surface. This was followed by a sustained energy- and temperature-dependent translocation across the cell membrane. They discuss the possible involvement of proteins in the translocation process, and since they also demonstrated a regulatory mechanism for the uptake process, discuss the possibility of an intracellular Zn^{2+} -binding protein involved also in this process.

Studies on the accumulation of zinc by *Agrostis tenuis* root homogenates have enabled Turner and Marshall (1971) to show that the cell wall fraction of zinc-tolerant plants was the main site of metal accumulation, but that other particulate fractions accumulated a certain level of zinc which was shown to be significantly more than in similar fractions of non-tolerant clones. A second study (Turner and Marshall, 1972) provided further evidence that accumulation by the cell wall in *Agrostis tenuis* was a major feature of the mechanism of tolerance and also demonstrated a correlation between accumulation of zinc by the subcellular fraction and the index of tolerance. The mitochondrial fraction was identified as being the most important component in the subcellular fraction with regard to zinc accumulation.

A pattern which emerges from the available literature indicates that zinc can be excluded from the metabolic processes within the plant cell by the cell wall. If it does enter the cell it can in some cases be prevented from exerting an influence on enzymes which control 'normal' processes. This can be done by intracellular binding or accumulation at sites away from the main metabolic reactions within the cell. It is clear that the mechanisms of tolerance in any individual might possibly involve a variety of physiological processes which all contribute to the total metal tolerance of the organism.

1.11 Previous studies of Zinc in Freshwater Habitats and its effects on the microflora

1.11.1 Early studies

Perhaps one of the first investigations carried out on the effect of zinc on streams and rivers was that of the Rivers Pollution Commission (1874) in England, which was set up in 1868 to discover the best means of preventing the pollution of rivers by a number of wastes, including those from the mining industries. Even at that time it was noted that zinc was "not infrequently disregarded by the miner, the blende (ZnS) being washed away with the waste slimes from the buddles (an inclined hutch for washing the ore)" and that "Both blende and mundic (Arsenopyrite, FeAsS) contribute in an important degree to river pollution." However attention was directed primarily to the effects of lead (or effects attributed mainly to lead) which was the primary mineral in most of the mines situated in the areas of investigation. The rivers surveyed were situated in most of the main base metal orefields in Britain, such as south west England, the Pennines, west Wales, and the Leadhills district of Scotland. The most obvious effects of lead mining were reported in west Wales on the rivers Rheidol and Ystwyth, where the waters were thick with silt and devoid of benthos for some distance. After the publication of this report the early studies were still directed towards the effect of lead discharged from mining complexes, probably since much of the original mining was carried out for lead, and zinc was either ignored or taken as a secondary product. Thus the work started by Carpenter in Cardiganshire, Wales, in 1919, and reported later (1924, 1925, 1926) was almost exclusively concerned with the effects of lead on the fauna of rivers receiving discharges from lead mines. Although detailed observations on the invertebrate fauna were made by Carpenter, only a mention was made of the flora - "there is only the

slightest coating or moss or liverwort on any of the stones, and algal and phanerogamic vegetation are usually conspicuous by their absence, with the interesting exceptions of the algae *Batrachospermum* and *Saccheria* (Lemniaceae) which often flourish in such situations."

Continuing with studies concerned primarily with the effects of lead, Reese (1937) investigated the microflora of two rivers in Cardiganshire, the Rheidol and its tributary the Melindwr, which were both subjected to discharges from lead mines. Levels of up to $0.15\text{mg l}^{-1}\text{Pb}$ and $0.2\text{mg l}^{-1}\text{Zn}$ were reported in the main rivers below lead mine workings. The microflora was markedly reduced below these sources of metal contamination, but the reduction in the number of macrophyte plants was observed to be even more striking.

The first account of mining pollution to deal exclusively with the problem of zinc enrichment was probably that of Jones (1940). This study was carried out on the River Ystwyth, in Cardiganshire, Wales, and followed the earlier investigations of Carpenter in associated catchment areas. However Jones demonstrates that the pollution by lead is comparatively small when compared to that of zinc in this river. In this account the sources of pollution are defined and described in considerable detail, and in the biological studies emphasis is directed towards the fauna. Adit effluents were shown to contribute up to $38\text{mg l}^{-1}\text{Zn}$ to the main river, and some mine streams reached as high as $57\text{mg l}^{-1}\text{Zn}$. The river Ystwyth itself was shown to reach as high as $1.2\text{mg l}^{-1}\text{Zn}$ below these mining areas. Although detailed lists of invertebrate species were presented, and most of the information was restricted to a description of the fauna, comments were made on the flora of the streams and rivers. *Scapania undulata* was shown to be the only macrophyte which could tolerate the conditions imposed by the mine discharges. Aquatic angiosperms were observed to be completely absent, and algal growths were noted to be "conspicuously absent", when compared with the main stream and its tributaries above the mining areas.

A summary of the research carried out on the pollution of the rivers of west Wales by lead and zinc enriched mine waters (carried out up to this period) was presented by Newton (1944). From this review she was able to conclude that "the presence of zinc is as serious a pollution as the presence of lead, and in the case of plants the former is more deleterious."

The serious nature of metal contamination in these waters of west Wales led Jones to carry out a further study of the river Ystwyth (Jones, 1958). The persistent nature of metal pollution was emphasised by him, and was supported by the fact that the river Ystwyth still remained seriously contaminated with zinc thirty-five years after the cessation of mining activities in its valley.

The second study included more detailed information with regard to the microflora of the river Ystwyth, and repeated analyses of water previously sampled nearly twenty years before. The most significant fact associated with the water analyses was that the levels of lead had significantly dropped in nearly all of the adits and streams, whereas zinc concentrations remained constantly high. Zinc levels in the adit waters were found to reach $30\text{mg l}^{-1}\text{Zn}$, and up to $90\text{mg l}^{-1}\text{Zn}$ in one of the mine streams; whilst the main river carried levels of $0.6\text{mg l}^{-1}\text{Zn}$ before its entry into the sea. The flora, although still noticeably sparse, was found to contain one species which could tolerate levels of $0.6 - 1\text{mg l}^{-1}\text{Zn}$ in the main river, and this was a species of *Lemanea*. However under conditions imposed by one of the more contaminated discharges, even this species was found to be markedly reduced in growth.

1.11.2 Recent studies

More recently, studies concerned specifically with the effects of zinc in stream environments, have become more widespread.

Sprague, Elson and Saunders (1965) describe the effect of mine water discharged into the river Miramichi, in New Brunswick, Canada. The study was mainly concerned with the effect of the mine discharges on the salmon and invertebrate population. Considerable enrichment of the river water by zinc and copper caused a reduction in the population of salmon and the invertebrates. Continued research on this Cu/Zn polluted river system was reported by Besch and Roberts-Pichette (1970) who studied the effect of the base metal mining discharges on the vascular plants in the river. In the most polluted part of the river, levels of copper and zinc could reach as high as 12mg l^{-1} and 65mg l^{-1} respectively. Under extreme conditions of metal contamination, the macrophyte flora was restricted to *Equisetum arvense*. A further study conducted by Besch *et al.* (1972) on the effects of zinc mining in this river system was devoted entirely to a consideration of the benthic flora (see 1.911).

In the base metal mining area of Lake Georgia Mine, on the upper reaches of the river Molonglo, New South Wales, Australia, a detailed investigation was carried out by Weatherly *et al.* (1967) entitled "The Ecology of a Zinc polluted River." Although mining in the area started in 1882, serious metal contamination of the river Molonglo did not occur until the years 1938-1962 (when the mine finally closed). Analysis of the river water in 1961 showed a gradient of zinc ranging from $34.5\text{mg l}^{-1}\text{Zn}$ in the upper reaches immediately below the mine, to $0.9\text{mg l}^{-1}\text{Zn}$ at a site approximately 50km downstream. Although copper was cited as contributing to the pollution of the river during the mining operations, the effect of the mine discharges on the river after closure were attributed solely to the very high zinc levels (since copper concentrations were shown to be negligible). Although ecological studies were almost totally confined to observations on the macroinvertebrate fauna, occasional comments were made on the macrophytic

and algal floras. The upper reaches were found to be devoid of vegetation save for a few scattered patches of *Phragmites communis* and a few algae. As the gradient of zinc declined, macrophyte species such as *Typha angustifolia* and *Juncus* spp. were able to recolonise the river margins.

Recently in west Wales McClean and Jones (1975) have studied the photosynthetic organisms colonizing certain zinc contaminated streams (see 1.911). Continuing with investigations in this area, Griffiths *et al.* (1975) summarize studies carried out which included the effects of high zinc concentrations in the photosynthetic microflora. Species of *Ulothrix*, *Horridium* and *Microspora* were found to be the most abundant algae growing in adit waters.

1.11.3 Environmental implications and conclusions - the problem defined

From this brief review of studies carried out to investigate the effect of zinc in the stream environment, it can be seen that although an awareness of the problem has been long recognized, there are still obvious gaps in the information available on the toxic effects of zinc to photosynthetic communities, particularly the microflora. It is evident from 1.8 and 1.11 that widespread contamination by zinc from a number of sources is still a major problem. The persistence of zinc pollution as established by Jones (1958) would seem to indicate that wherever drainage waters emerge from adits in the vicinity of old disused lead and zinc mine workings, there will be a serious chance of severe zinc pollution of the receiving water body.

It seems from the studies described by Jones and Howells (1975) on the river Rheidol, west Wales, that depending on the main sources of the metal contaminants, the partial recovery of a metal polluted river can occur. The recovery of the water quality of the river Rheidol after the cessation of mining activities was established by them to be a natural process.

However they describe an attempt to prospect for further mineral resources in the area when a bulldozer which was levelling a site for a drilling rig caused the collapse of the front of a sealed adit. The consequent release of underground water caused 230mg l^{-1} soluble Zn and 148mg l^{-1} soluble Pb to enter the main river. It can be seen therefore that even with aquatic environments which have managed to recover from zinc pollution there will always be the possibility of renewed contamination in the vicinity of old mine workings.

From the discussion in 1.6 it can be seen that whenever a sphalerite ore body becomes exposed to the weathering processes, enrichment with zinc of the drainage water will nearly always result.

Because of the continuing contamination of certain rivers with zinc from metal enriched mine drainage waters (derived from old lead/zinc workings), it was felt that the time was right for a more comprehensive study of the effect of zinc on the vegetation of streams carrying high levels of this metal.

The voluminous literature available on the effect of zinc on terrestrial vegetation only serves to highlight the gaps present in the studies on photosynthetic vegetation in aquatic habitats.

1.11.4 Aims

In view of the present state of research with regard to zinc contamination of waters draining base metal mining areas, and its effects on the photosynthetic microflora of such streams, it was felt that a broad approach to the problem, rather than a narrow line, would be profitable and justifiable. The paucity of available literature on the hydrogeochemistry of such waters, particularly in relation to the biological communities they influence, further justifies a broad design to the project.

The approach adopted was of a similar kind to that of Weatherly *et al.* (1967) mentioned in 1.1. Thus zinc "the main chemical aspect of the pollution" would be investigated by means of a hydrogeochemical study and "the effects of the pollution" on in this case the flora would be treated as a "bioassay problem", backed up by laboratory assays on the dominant representative algae.

The precise aims of the thesis can therefore be formulated on the following manner:

- (i) To discover the extent of zinc contamination in streams draining part of the Northern Pennine Orefield.
- (ii) To perform a hydrogeochemical and botanical study on streams contaminated by zinc in an attempt to understand the most important factors influencing the chemistry of the streams, the chemistry of zinc in the streams, and the relationship between the photosynthetic organisms and zinc.
- (iii) To perform a hydrogeochemical and botanical study on one stream demonstrating a gradient of zinc, in an attempt to further understand the chemical relations of zinc and its influence on the organisms present in the stream.
- (iv) By performing studies on a zinc resistant genus of alga, to define the resistance of species within the genus and the factors most important in influencing the toxicity of zinc to these species.

2 METHODS

2.1 Introduction

During the course of this project a large amount of environmental data was collected with regard to the chemistry of streams and their microflora. A recording system designed to deal specifically with large amounts of data on plants in flowing waters was available in the Department of Botany, University of Durham (Whitton, Diaz and Holmes, 1976). The methods adopted during the project make use of part of this recording system.

The approach to this project has been made in four main ways:

(i) The designation of the study area, its reconnaissance and the location of the main sampling sites.

(ii) Implementing a number of intensive surveys to obtain the necessary environmental information commensurate with tackling the aims of the study (1.114).

(iii) The performance of laboratory investigations on selected algal species to complement the field studies.

(iv) Utilizing a computer based approach to handling the data.

2.2 Preliminary studies

2.21 Location of the study area and sampling sites

The main area of study is situated within the Northern Pennine Orefield (Figs. 2.1, 3.1) which has been demonstrated to show a very long history of mining for lead with a shorter period for zinc (Smith, 1923; Dunham, 1948). Studies on tributaries to the Wear in this region have shown levels of zinc which are toxic to certain organisms (B. A. Whitton, pers. comm.).

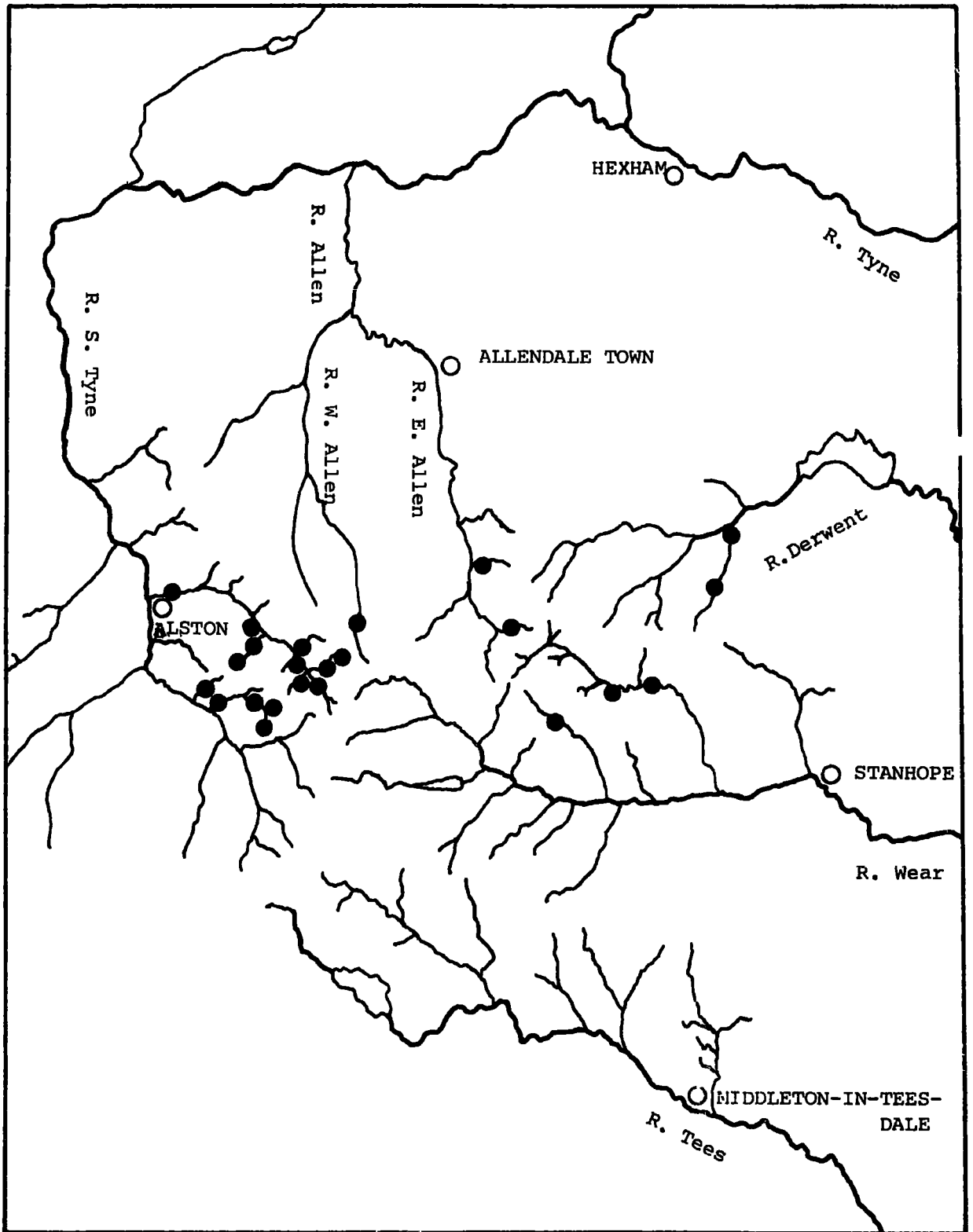


Fig. 2.1 Location of some of the more important sampling sites carrying more than $1\text{mg l}^{-1}\text{Zn}$ in the Northern Pennine Orefield.

The recognition of appropriate sampling sites within this area (Fig. 2.1) was carried out using various methods. It was suspected that streams draining from old lead-zinc mine workings would furnish the main sites, so 1" to the mile Ordnance Survey maps were consulted to locate old mines. Because the upper catchments of the Rivers Tees, Wear and South Tyne contained many old workings, the region was divided into several smaller units. These were characterized by a primary tributary to the three main rivers and each was visited consecutively. These were:

Rookhope Burn
 Kilhope Burn
 River East Allen
 River West Allen
 Nent Valley
 Tyne Head
 Upper Tees and Cow Green
 Tees at Middleton-in-Teesdale

Streams were chosen in the immediate vicinity of an old mine working and during the visits a single water sample was collected for analysis of zinc.

At the time of these reconnaissance trips information on the chemical composition of the sediments of streams draining the Northern Pennine Orefield was supplied by the Applied Geochemistry Group, Imperial College, London (I. Thornton, pers. comm.). This information was part of a general project involving regional geochemical surveys in areas of metalliferous interest in Britain (Nichol *et al.*, 1970a, 1970b, 1971), indicating the distribution of elements such as Zn, Cd, and Pb in stream sediments. Using these data and more detailed maps such as the 6" to the mile Ordnance Survey maps (when these were available) a main area of streams carrying high levels of zinc ($>1\text{mg l}^{-1}$) was located in the Nent Valley coinciding with the primary zinc bearing area of the Orefield (Dunham, 1948).

2.22 Selection of sites

A set of criteria was established for the selection of sites:

(1) The streams must have relative ease of access and not involve a difficult, hazardous or time consuming journey. Thus for speed of sampling sites should be as close to the road as possible.

(11) The stream should not be exposed to prolonged spells of drying out.

(111) Streams should be chosen such that anthropogenic activities are minimized to only those of interest or direct relevance to a study, and should be avoided if major changes in the watercourse are likely to occur frequently.

2.3 Environmental data

2.31 Sampling strategy and selection of reaches

The stream was regarded as the main unit of sampling and this was divided into subunits which were lengths of 10m, referred to as the reach throughout the rest of this account. A reach can be defined as that part of the main current of a stream typically with a length of exactly 10m and never exceeding this length with approximately the same quantity of water leaving it as entering it.

In selecting reaches, the following criteria were observed:

(1) Reaches were chosen such that the water chemistry was comparatively uniform throughout its length.

(11) The entrance of side streams or obvious trickles along their length was avoided. If this was not possible, sampling took place at points away from the vicinity of their entry.

(iii) Reaches were selected such that all water from upstream tributaries had become well mixed. The distance downstream from the entry of a tributary would therefore depend on the size of the stream to be sampled.

(iv) Wherever possible the reach was 10m long. However in some cases, such as the emergence of mine water from adits and its entrance into the stream, or the inclusion of small springs and flushes, occasionally these did not flow for this distance before combining with the larger water body. Exceptions were made in such cases.

(v) Reaches were numbered from 01 to 99, the higher the number the further downstream. 01 was reserved for the source of the stream, springs, emergence of water from adits, or similar sources of water issuing straight from the ground; 99 was used for all reaches which were the last 10m before entry into a larger water body.

The selection of reaches within the stream basin of Gillgill Burn was modified from the procedure used for the selection of all other reaches. The stream and its tributaries were mapped out into a number of 10m reaches at intervals down their lengths. From a preliminary reconnaissance of the area an interval of 50m between each reach was chosen as a convenient distance with regard to the sizes of the streams. Since few, if any, major changes in physiography existed within this distance between reaches, each 10m reach was considered to be representative of the respective 50m interval. Small numbered stakes were used to denote each 10m reach and these were used in future surveys as sampling sites. 29 reaches were marked down the main stream, and between 7-10 on the side tributaries. The stream network was gridded into 60 sampling sites. Thus the source

of Gillgill Burn was designated reach 01 and the last 10m before entry into the River Nent, reach 99. The other 27 reaches were numbered accordingly so that the fifteenth reach, which was approximately halfway down the stream, was reach 50. The same procedure was carried out for the side tributaries.

After two main sampling runs had been carried out on Gillgill Burn, the number of reaches for future surveys was reduced to 30. There were two main reasons for this change:

(1) Where few changes took place down the water course some of the results for the measurement of certain cations were found to be almost identical. Thus by reducing the number of reaches, needless repetition could be avoided and would allow more thorough sampling of the remaining number.

(11) It was found that 60 reaches were too many to sample in one day to allow thorough investigation of a reach.

The position of the main reaches on Gillgill Burn and its tributaries is shown in Fig. 3.10. Of the main tributaries 'Old Mine Gill' was the only one sampled throughout its length. This was due to the very high levels of zinc ($>20\text{mg l}^{-1}$) in this stream. The other tributaries were sampled for the remaining surveys at the last reach (99) before entry into Gillgill Burn.

2.32 Description of reaches

2.321 Geography

After reaches had been located they were allocated numbers, together with the stream, for recording purposes and to act as a unique identifier when entered with other data onto the computer. Streams were given a

four digit number, reaches a two digit number. The following information was recorded for each reach:

- (i) Designated stream and reach number.
- (ii) Stream name - obtained from 2½" or 6" to the mile Ordnance Survey maps. If no name was available, a suitable one was created from the nearest landmark on the map. Such created names are denoted by a single set of inverted commas.
- (iii) Reach name - derived from its position on the stream.
- (iv) Map reference
- (v) Grid reference
- (vi) Tributary records - includes information on which river(s) the stream was a tributary of before reaching the sea.
- (vii) Nearest town or village.
- (viii) County record.
- (ix) Altitude
- (x) A reach guide - notes on finding the site and exact limit of the reach.

Initially this information was entered onto 'reach cards' (Appendix I), but eventually was transferred to computer punch cards and stored in computer files.

2.322 Physical parameters

Whenever a water sample and sample of algal material was removed from a reach, notes were made on the following physical characteristics:

- (1) Width attributes of the reach (m) recorded as maximum, minimum and average, using a metre tape measure.

- (11) Drop (m) along the 10m of the reach including notes on any waterfalls.
- (111) Typical depth when under a medium flow regime (m), using a metre rule.
- (1v) Characteristics of the left and right hand banks (looking downstream) which included notes on height (m), typical angle, and vegetation.
- (v) The immediate environment land use.
- (v1) Direction of flow.
- (v11) Important upstream influences which might be expected to have a major influence on the water chemistry.
- (v111) The substratum. This was coded using the Wentworth (broad size categories) .
- (1x) An indication of the light regime using the following categories : more or less open throughout the year, moderate cover throughout the year, heavy shade throughout the year, moderate shade in summer, and heavy shade in summer.
- (x) The current speed was measured using an OTT current meter.
- Readings were taken wherever possible with the head elevated approximately two thirds of the way between the bed of the stream and the surface of the water to ensure reception of the main course of water. They were made at the fastest point in the reach, chosen from an average of six measurements.
- (x1) Temperature readings were made with a standard laboratory thermometer.

2.33 Chemical analysis

(i) Water collection methods All vessels for collecting water samples were thoroughly washed, including a soak for 24h in 6% HCl and rinsing in distilled water prior to collection. Initially, after the measurements performed in the field for pH, collection of water was divided into five main fractions. The first was unfiltered stream water collected in a 250ml screw top polythene bottle which was filled with the exclusion of air. Measurements for total alkalinity, pH, acidity and conductivity were made on this sample in the laboratory. The remaining four fractions were all filtered through a Sinta No. 2 (sintered glass) filter funnel immediately after collection. Considerable care was taken to standardise the filtration technique. This included a wash of the funnel with HCl whenever there was likelihood of zinc contamination of the pores. The first of these fractions was collected in a 250ml polythene bottle with the walls impregnated with iodine for phosphate analysis. The other two were collected in untreated polythene bottles for the remaining anion analysis. The final fraction was collected in a 100ml pyrex bottle for the measurement of selected cations. During the course of the project it was realised that the collection methods for water analysis would influence greatly the results of the analysis of metals in a given water. This would be because the metals could be present in a number of possible forms such as particulate, colloidal, and dissolved (Stumm and Bilinski, 1973), and different collection methods could include or exclude these different forms. In view of this, a comparison was made between sintered glass funnels and Nuclepore 0.2 μ m membrane filters. The mean values for a wide range of water samples passing through these filters were very similar, but the variability of repeat filtrations on a single sample was greater using sintered glass. Although as a result of this, use of Nuclepore filters for cation surveys has been adopted for more

recent surveys, sintered glass was retained for the early surveys for reasons of comparability. A further modification to later surveys was the inclusion of an unfiltered water sample for cation analysis considered to represent the total fraction of metal in the water. This was acidified with two drops of Aristar grade concentrated HCl. Acid was also added to filtered samples for cation analysis if a long delay was anticipated.

Samples were kept cool in ice cooled containers until arrival at the laboratory. All samples were stored at 2°C prior to analysis. If it was not expedient to carry out anion analysis immediately, samples were stored at -20°C. In the majority of cases analyses were completed within 48h of collection.

(ii) pH This was recorded in the field using a Pye Unicam portable model pH meter No. 293. In the laboratory, readings were taken, using an E.I.L. model 23A direct reading pH meter.

(iii) Electrical conductivity was recorded in mhos using a Lock Portable Transistorized Conductivity Bridge, 3Cl.

(iv) Optical density O.D. measurements made at wavelength 420 were performed on a Hilger and Watts Uvispek photoelectric spectrophotometer.

(v) Total alkalinity was measured as $\text{mg l}^{-1} \text{CaCO}_3$ using the potentiometric titration method recommended by the American Public Health Association (1971).

(vi) Acidity The titration method using phenolphthalein as an indicator, as recommended in the American Public Health Association (1971), was used.

(vii) Hardness Since a fairly complete analysis was performed on water where water hardness was to be determined, the calculation method which included hardness contributed not only by Ca and Mg, but also other

hardness producing cations such as Al, Mn, Fe and Zn, was adopted. In particular, since many of the waters contained high levels of these ions. This method, which is recommended by the American Public Health Association (1971), is reported to be the most accurate method since, unlike titration methods using EDTA, it does not measure hardness exclusively derived from Mg and Ca. Measurements are given as mg l^{-1} equivalent CaCO_3 .

(viii) Cations All cations were measured using a Perkin Elmer 403 Atomic Absorption Spectrophotometer.

(ix) Anions

Cl	argentometric titration)	methods recommended
Si	hetero-polyblue)	by the American
)	Public Health
NH_4 -N	Nesslerization)	Association (1971)
NO_2 -N	method of Crosby (1967)		
NO_3 -N	method of Montgomery and Dymock (1962)		
PO_4 -P	n-hexanol extraction method of Mackereth (1963)		
SO_4 -S	analysed after cation exchange by titration against barium perchlorate using the method of Colson (1963)		

2.34 Biological aggregate information

2.341 Sampling techniques

These involved the collection of two main types of data. Firstly all recognisable vegetation within the reach was recorded. Material in which difficulty was experienced in identification in the field (such as certain grasses and bryophytes) was removed and placed in prelabelled polythene bags (in the case of angiosperms) or dried and placed in paper envelopes (in the case of bryophytes) and identified in the laboratory with the aid of floras and microscopes. Secondly several samples of algal scrapings from all the available microhabitats were collected. Algal material was

scraped from host surfaces or removed from the sediment surface using a micropipette and placed in prenumbered plastic or glass specimen tubes. Duplicate samples were collected for preservation. The preservatives used were either 10% gluteraldehyde in a 50:50 mixture with Caccodilate buffer, or 3% formalin together with 0.1g l^{-1} (of formalin) $\text{Cu}(\text{NO}_3)_2$. The former is especially good for preserving species of Chrysophyte and other gelatinous algae (D. J. Hibberd, pers. comm.). The latter for green algae (N. T. H. Holmes, pers. comm.), because Cu combines with the chlorophyll molecule and helps to maintain chloroplast structure and colour. Live samples were stored in an ice-cooled Thermos flask until identification could take place in the laboratory. Notes were taken on the different microhabitats explored within a reach for material; certain environmental information such as substratum, substratum size and rate of flow was recorded.

Estimates of abundance for species within a reach were made using a scale of one to five related to that used for terrestrial vegetation by Tansley and Crisp (1926):

abundance scale	description
1	rare
2	occasional
3	frequent
4	abundant
5	very abundant

Estimates were also made for algal material on slides under the microscope. Although the estimates were highly subjective it was felt that some indication of the relative abundance of species could be obtained.

2.342 Coding of plant data

During the early part of the project it was anticipated that use would be made of the digital computer to process the semiquantitative plant data.

This necessitated a standardized identification procedure which was carried out as prescribed in detail in section 13 of the Recording System Document (Whitton, Holmes and Diaz, 1976). In essence this involved allocating a six digit figure to each species where the first two digits represented the phylum (or major taxon), the second two the genus, and the third two the species. Where determination to either the species or genus was impossible, the second and third pairs of digits were modified into different categories. Thus with certain blue-green algae and filamentous greens where the genus was determined but species were difficult to establish, different numbers were allocated according to particular width characteristics.

Although a method to process the data involving the computer was not possible due to the restrictions of time, species were allocated numbers so that information could be used in later investigations.

2.343 Taxonomy

Details of the taxonomy of the main organisms in this study are given in 2.41. However brief mention is made here of the taxonomic literature consulted, and the conventions adopted for naming some species of Chrysophyta which were often abundant in reaches but difficult to identify. General works covering all phyla included: West and Fritsch (1927), Bourrelly (1966, 1968, 1970), and the Fritsch collection of algae, Micro-edition by International Documentation Centre.

Myxophyta : Geitler (1932)

Bacillariophyta : Hustedt (1930)

Chlorophyta : For Chaetophorales, Printz (1964); for specifically the Ulotrichales, Ramanathan (1964), and Cox and Bold (1966): desmids, West and West (1904, 1905, 1908, 1911); West, West and Carter (1923):

Chlorococcales and Protococcales, Korshchikov (1953).

In some of the streams a palmelloid chrysophyte was encountered which at different times of the year was very abundant. Three distinct forms of this chrysophyte could be detected, but there was considerable overlap in appearance and habitat, making confident delineation into species difficult. A convention was adopted finally by which the materials were classified as forms A, B and C, and the existing names of the species they most closely resembled were included. Thus form A resembled *Chrysonobula holmesii*, form B *Hydrurus foetidus* and form C *Celloniella palensis*.

2.355 Construction of 'association tables'

Since the lack of time precluded the use of computer techniques to deal with the large amount of primary data accumulated on the distribution of algae within the reaches studied, an alternative method was sought. The method finally chosen was similar to that used by Holmes and Whitton (1975). This method was successful in establishing 'associations' of macrophytes for the River Tweed. By adapting it for use with algae it was hoped that groupings or 'associations' of algae related to increasing levels of zinc might be identified.

The formation of the 'association table' followed the method given by Holmes (1975). Firstly a 'raw table' was compiled with algal species listed in taxonomic order, occurring at the reaches listed in order of decreasing zinc levels. From this table it was noticed that certain combinations of species recurred several times. It was these species with restricted occurrence that were grouped together. The groups of species were then arranged so that those species restricted to the upper levels of zinc were at the top left, and those present only in the lower reaches at the bottom right of the table. Species that occurred throughout the range of zinc levels were placed in the middle, and those

with intermediate distributions placed either side. The algae with similar occurrences were then boxed together giving the final 'associations'. The original ordering of species into groups was done by recording whether a species was present or absent in each reach during each survey. However the use of subjective abundance values (2.355) provided more information, and therefore the tables with the former are not included.

2.356 Abundance values

Although the method of estimating the abundance of species has already been described (2.341), the use of such values in constructing the 'association tables' will be elaborated. The numbers used represent the mean abundance value for species at that reach, for the number of times sampled. The mean value rather than the aggregate was used because in certain cases one or two reaches were not sampled as many times as the majority (6.1). If a species was not consistent in its abundance in a reach, the mean was estimated, based on the highest proportion of values from the samplings. If ambiguity occurred, attempts were made to underestimate rather than over-estimate the abundance. To be recorded as one or above indicates that a species was either present at the reach at every sampling or, if absent from one or more, to be at least recorded as occasional or frequent at others so as to bring the mean of all the samplings to at least one. A plus is used when the mean abundance value for the samplings is less than one. Dots indicate the distribution span across the range of zinc values, but the absence of the species within that particular reach.

The estimation of abundance values was highly subjective. The derivation of mean values also involved subjective estimates incorporating information obtained using the methods described in 2.353 and 2.354. It can be concluded therefore that data collected in such a manner would only be of

limited use when incorporated into an 'association table'. However it was felt that even though it was "limited", such information provided more insight into the distribution of species than merely presence or absence alone.

2.4 Laboratory investigations on selected algal species

2.41 Introduction

All glassware for experimental use was cleaned thoroughly by scrubbing with a brush and detergent, followed by soaking for a minimum period of 24h in 6% HCl. This was followed by rinsing with double distilled water to remove all traces of the acid.

Unless otherwise stated all algae were maintained during long term culture under the following set of standard conditions: 15°C, 6000 lux, in 100ml Pyrex conical flasks with standard media (see below), and moderate shaking in a temperature controlled growth room. All toxicity tests were carried out in 50ml Pyrex boiling tubes with Morton closures; all quantitative experiments were performed in 100ml Pyrex conical flasks.

2.411 The Organisms

The initial experiments where several taxa were screened for their tolerance towards zinc in the laboratory were carried out on a variety of field materials. As it became evident that filamentous green algae were often the predominant macroscopic life form in some of the streams with the higher levels of zinc, attention was directed to a comparison between some of the representatives of this taxa. Further detailed studies revealed that ulotrichalean algae, in particular representative of the genus *Hormidium*, were the most successful organisms at colonizing streams carrying the highest levels of zinc. As a result of this discovery,

attention was more or less exclusively directed towards three species in this genus, *Hormidium rivulare*, *H. flaccidum* and *H. fluitans*.

2.412 Taxonomy of *Hormidium* spp.

Confusion surrounds both the defining of a correct generic name and the separation of species within this genus from extremely similar organisms assigned to the genera *Ulothrix* and *Stichococcus*. To give a detailed account of the taxonomy of these organisms, although of interest, is not commensurate with the aims of this thesis, and therefore for more details the review of Silva, Mattox and Blackwell (1972) should be consulted. The generic name *Hormidium* was changed by Fott (1960) to *Chlorhormidium* because a genus of orchids has priority for the former name. Silva, Mattox and Blackwell (1972) present evidence which they regard invalidates Fott's proposal, and put forward a new name *Klebsormidium*. In spite of this, and the recent critical studies concerning the genus (Pickett-Heaps, 1972; Cain, Mattox and Stewart, 1974), the traditional generic and specific names given in Heering (1914) have been retained. It seems likely that further nomenclatural changes will take place, so it was felt that the use of the well known names will help to minimize later confusion. *Hormidium flaccidum* is in the subgenus *Euhormidium* of Heering, while *H. rivulare* and *H. fluitans* are in the subgenus *Pseudulothrix*. The criteria used to identify the three species of *Hormidium*, and also to differentiate them from a species of *Ulothrix* which was frequently found at *Hormidium* sites, and which often closely resembled *H. rivulare*, are given here in the form of a short key. The key uses as a basis compiled notes from the keys of Heering (1914) and Ramanathan (1964), together with the synopsis of Silva *et al.* (1972), and is extended with personal observations on field material

and notes from laboratory experiments. No attempt is made to include a full key for the differentiation of *Ulothrix* and *Horridium* species or a complete description of all the members of the genus *Horridium* since without personal observations on all of these other organisms or additional cytological characteristics it would merely include reiteration of the already adequate keys of Heering and Ramanathan.

Key

- A Filaments of unlimited length, showing differentiation between apical and basal cells, and no tendency for fragmentation into shorter filaments or unicells to occur. Plastid with more than one pyrenoid. *Ulothrix*
- B Filaments of limited length, basal and apical cells similar in size and shape, clear tendency for some species to fragment into shorter filaments and unicells. Plastid with one pyrenoid. *Horridium*
- B 1. Filaments more or less straight, occasionally spirally twisted in groups to form 'rope-like' strands, not constricted at the crosswalls or sometimes very slightly, readily forming zoospores. *H. flaccidum*
1. Filaments often twisted and geniculately bent, mostly very obviously constricted at the crosswalls, zoospore formation not observed 2
2. Filaments with frequent, very obvious geniculations or knee-joints, sometimes forming a false branch or pseudo-rhizoidal structure, no obvious fragmentation *H. rivulare*

2. Filaments not forming knee joints, very marked tendency to fragment into very short filaments or unicells

..... *H. fluitans*

2.413 Further detailed studies

Hormidium rivulare was chosen for laboratory studies on the effects of environmental factors on zinc toxicity. The main reasons for this choice were as follows:

- (i) It was the most ubiquitous of the three species studied intensively.
- (ii) It showed the greatest range of tolerance towards zinc (Chapter 6).
- (iii) More populations of this species had been studied in the field when compared with the other two species.
- (iv) It was the most easily cultured of the three *Hormidium* species.

2.42 Culture medium

The criteria used in designing the basal medium for zinc toxicity assays were:

- (i) That it would permit relatively rapid growth of all populations (in preliminary tests).
- (ii) That it would favour close agreement between replicate assays.
- (iii) That any precipitation of zinc, when introduced at the higher levels, would be minimized.

This was achieved by using the No. 10 formula of Chu (1942), modified in particular by lowering the final pH and levels of phosphate and carbonate, and by including EDTA as chelating agent (although at a relatively low level ($2 \text{ } \mu\text{g}^{-1}$))

2.421 pH

The importance of pH in controlling the form and toxicity of zinc has been demonstrated (Bachmann, 1961).

Tests were carried out on the effect of pH on concentrations of zinc in the basal medium.

Four replicates of 100ml Pyrex conical flasks and Pyrex boiling tubes (to be used later in assays) were set up at levels of pH increasing by one unit in the range pH 3-10, at two levels of zinc, 10 and 40 mg l^{-1} . The requisite amount of zinc was added from a concentrated stock of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ to 10ml of medium in the boiling tubes and 30ml in the flasks. The medium was previously adjusted to the required pH using 0.1N and 0.02N stocks of H_2SO_4 and NaOH. After addition of the zinc, the pH levels were measured and, if necessary, readjusted. The flasks and tubes were incubated under the same conditions as for the actual assay (2.44) for a period of 24h. The pH levels were measured four times during this period and, where necessary, were readjusted. After this period of time each flask was filtered through a $0.2 \mu\text{m}$ nucleopore membrane filter and the level of zinc measured. The procedure was repeated in the absence of chelating agent (EDTA), and the results are presented in Table 2.1.

The critical range of pH for significant precipitation of zinc in this medium was pH 6-7. Here the level of filtered zinc (from now on referred to as the dissolved fraction) was almost halved through a drop of one

pH	+ IITTA		- EDTA		+ EDTA	
	Level Zn	% dissolved Zn after filtration	Level Zn	% dissolved Zn after filtration	Level Zn	% dissolved Zn after filtration
2	10.0	100	10.0	100		
3	10.0	100	9.8	98	40.0	100
4	9.5	95	9.8	98	40.0	100
5	9.4	94	8.7	87	40.0	100
6	8.9	89	8.5	85	39.0	97.5
7	4.4	44	1.4	14	38.0	95.0
8	0.9	9	0.4	4	23.8	59.5
9	0.6	6	0.6	6	11.7	29.3
10	1.6	16	1.0	10	9.1	22.7
					9.7	24.3

Table 2.1 The effect of pH on zinc solubility in basal medium calculated as a percentage of the original concentrations (10mg l⁻¹Zn and 40mg l⁻¹Zn) after filtration.

pH	Level of Zn = 10mg l ⁻¹ Zn		Level of Zn = 40mg l ⁻¹ Zn	
	original conc.	% dissolved Zn after filtration	original conc.	% dissolved Zn after filtration
6.0	9.0	90	38	95
6.2	9.0	90	38	95
6.4	8.3	83	36	90
6.6	7.2	72	35.2	88
6.8	5.0	50	27.2	68
7.0	4.4	44	22	55

Table 2.2 Zinc solubility in basal medium in the pH range 6.0 - 7.0 measured after filtration.

pH unit. The experiment was repeated between this range with replicate flasks set up at intervals of 0.2 pH unit. The same procedure was carried out and the results are presented in Table 2.2. These results indicate that it is primarily between pH levels of 6.6 and 7.0 that the greatest loss of zinc occurs in the medium. Without the addition of chelating agent there was a greater loss of zinc between the pH levels of 6-7, although its absence did not apparently affect the level of zinc at the lower pH levels.

From the results it seemed evident that to maintain accurate dissolved levels of zinc a pH value of 6.0 was the optimum in this medium before significant precipitation of zinc occurred. This pH value was used in all subsequent experiments. At the highest zinc levels used in assays of resistant organisms only 10% zinc was removed by a 0.2 μ m nuclepore filter.

2.422 Basal medium

The detailed composition of the medium is shown in Table 2.3, together with the concentration of the major elements. In order to provide the necessary trace elements, 0.25ml of the AC microelement stock of Kratz and Myers (1955) was added, modified by the removal of the source of zinc. Analar grade chemicals were used throughout, but although the basal medium was free of added zinc, analysis showed levels of zinc of c. 0.004mg l⁻¹. The traces of zinc present were probably derived from the impurity of the chemicals used.

salt	stock concentration mg l ⁻¹	element	concentration in medium mg l ⁻¹
MgSO ₄ ·7H ₂ O	25.0	Mg	2.47
Ca(NO ₃) ₂	40.0	(Ca (N	9.75 3.40
KH ₂ PO ₄	3.9	(K (P	1.18 0.89
NaHCO ₃	7.9	Na	4.04
Na ₂ SiO ₃	10.9	Si	2.30
Fe/EDTA chelate	0.5	(Fe Na ₂ (EDTA	0.5 2.8
H ₂ SO ₄	4.9		

Table 2.3 Composition of basal medium

The phosphate level was lowered because attempts were to be made at culturing the algae in conditions as close to the natural environment as possible (the majority of reaches had very low levels of phosphate <0.002), and the data of Ernst (1968) suggested that phosphate might antagonize zinc toxicity. A chelating agent was included to avoid any possibility of precipitation of other metals.

2.423 Choice of EDTA as chelating agent

The important influence of chelating agents on heavy metal solubility cannot be overlooked, and numerous authors have shown that certain culture media have the capacity to complex metals, particularly copper (Gächter *et al.*, 1973), thus making their toxicity more difficult to interpret.

An experiment was carried out to investigate the effect of various concentrations of EDTA on the toxicity of zinc to a population of *Horridium rivulare* growing at low concentrations of zinc in the field. The results are listed in Table 2.4. It can be seen that increasing the level of EDTA from 0 - 5mg l⁻¹ has little effect on the T.I.C. ^(P 92) in this

nutrient medium. However, raising the level from 5 - 20mg l⁻¹ EDTA has a marked effect, increasing the resistance of this zinc sensitive population to much higher concentrations of zinc. Since the level of EDTA used in the basal medium was 3.5mg l⁻¹ it was assumed that this concentration would have little effect on the results of the toxicity tests using zinc.. EDTA was therefore continued to be used as the chelating agent.

EDTA (mg l ⁻¹)	J.N.I. \bar{X}	J.L. \bar{X}	T.I.C. \bar{X}	s.d.
0	0.5	1.2	0.77	0.11
0.1	0.8	1.3	1.02	0.19
0.5	0.5	1.2	0.77	0.17
1.0	0.6	1.3	0.88	0.14
1.5	0.5	1.2	0.77	0.10
2.0	0.8	1.3	1.02	0.11
5.0	1.23	3.2	1.98	0.27
7.5	3.2	6.2	4.45	0.33
10.0	3.2	8.2	5.06	0.61
20.0	10.5	20.5	14.67	0.16

Table 2.4 The effect of various concentrations of EDTA on the toxicity of zinc to a zinc-sensitive population of *Horridium rivulare* (n = 4) (all concentrations in mg l⁻¹)

2.424 Addition of zinc

Zinc was added as a solution of ZnSO₄.7H₂O from a 1g l⁻¹ Zn stock solution which has a pH of 5.2. The amounts of zinc added during assays never caused a pH drop of more than 0.2 units, so no attempt was made to improve

the buffering capacity of the basal medium. A range of controls to assess whether the addition of sulphate ion might in any way influence the results of zinc toxicity assays all proved negative.

2.425 Addition of other selected cations and anions

A list of the other metals whose toxicity was compared with that of zinc, together with the factors whose influence on zinc toxicity was studied, is given in Table 2.5, together with the substances added to the medium to bring about the required changes. The basal media lacking particular ions required as controls were obtained by substituting complementary salts.

Table 2.5 Factors whose influence on zinc toxicity was studied

Salt used as source in basal medium	Salt used as source in toxicity test	Complementary salt used for required absence of factor
$MgSO_4 \cdot 7H_2O$	$MgSO_4 \cdot 7H_2O$	Na_2SO_4
$Ca(NO_3)_2$	$CaCl_2 \cdot 2H_2O$	$NaNO_3$
$CuSO_4 \cdot 5H_2O$	$CuSO_4 \cdot 5H_2O$	-
$ZnSO_4 \cdot 7H_2O$	$ZnSO_4 \cdot 7H_2O$	Na_2SO_4
-	$CdSO_4 \cdot 8H_2O$	-
-	$Pb(NO_3)_2$	-
KH_2PO_4	$NaH_2PO_4 \cdot 2H_2O$	KCl
$MgSO_4 \cdot 7H_2O$	Na_2SO_4	-
-	$NaCl$	-
-	NaF	-

Since variation in the levels of the additions to basal medium causes simultaneous variation of the associated ion in the salt (Na^+ , Cl^- , SO_4^{--}), tests were included on the influence of $NaCl$ and Na_2SO_4 on zinc toxicity.

No detectable effect was found over the ranges of Na, Cl and SO_4 used in the other toxicity tests. The initial pH in all experiments testing these factors was kept within the limits 6.0 ± 0.1 pH units. This necessitated addition of NaOH to the solutions with the highest concentrations of calcium and zinc, but never more than one or two drops of 0.02N NaOH were required.

2.426 Experimental procedure for experiments investigating various factors

For practical reasons the experimental procedure for investigating each factor varied slightly.

(1) pH Inocula were obtained from stock maintained at pH 6.0. Experiments were carried out in flasks only, since the daily checks made to monitor and, if necessary, adjust pH required the direct insertion of the electrode into the culture. The shift in pH over one day in the range 3-5 was negligible, never exceeding 0.1 pH units. It ranged up to 0.2 pH units at pH 6, 0.5 pH units at pH 7 and 0.8 pH units at pH 8. These were the maximum values recorded, and they only occurred at the end of the growth period in cultures showing no inhibition.

(11) Magnesium cultures to be used as inocula were incubated in a medium containing 0.2 mg l^{-1} Mg, with no added zinc, for two days prior to the experiment. (The alga degenerated if incubated in a medium free of magnesium.)

(111) Calcium cultures to be used as inocula were incubated in calcium-free/zinc-free medium for two days prior to the experiment. All except one of the populations subjected to the subsequent toxicity test grew well in the absence of any added calcium; the exception was the population taken from the highly calcareous reach 0151/20 which required 1 mg l^{-1} Ca for growth.

(iv) Copper The procedure used for copper closely followed that of zinc but due to the greater toxicity found with copper, a lower range of levels was used in the assays. Addition of copper at the concentrations used caused no shift in the pH of the basal medium.

(v) Cadmium As with copper, the procedure closely followed that used with zinc, but again with a lower range of cadmium concentrations. No pH shifts were encountered. In addition to investigating the toxicity of cadmium when compared to that of zinc, experiments were also carried out to study the possible interaction between cadmium and zinc, and also the influence of calcium on cadmium toxicity, in the absence of zinc.

(vi) Lead An attempt was made to compare the toxicity of lead with that of zinc. The only source of lead which was in any way found to be satisfactorily soluble was $Pb(NO_3)_2$. However a number of complications arose during the course of the bioassays. Firstly precipitation of lead in the form of obvious white 'flakes' with the phosphate in the medium occurred, even at the standard pH used in the toxicity tests and the reduced level of phosphate. Secondly introduction of anomalously high concentrations of nitrate was unavoidable at the higher levels of lead investigated, and it was anticipated that this might considerably affect the toxicity of the lead to the alga investigated. Since the aims of this project did not include a detailed study on the toxicity of lead, further investigations or variations in experimental procedure involving lead were abandoned.

(vii) Phosphate-P Cultures to be used as inocula for the standard toxicity tests were incubated in phosphate-free medium for four days prior to the experiment in an attempt to minimize the reserves of this in the algal material. Quantitative experiments on a zinc tolerant species of *Hormidium rivulare* were carried out using both phosphate-starved and phosphate-rich inocula. In the latter case the alga was incubated in $10\text{mg l}^{-1} \text{PO}_4\text{-P}$ for four days prior to the experiment.

(viii) Fluoride Cultures were maintained for two days in media free of both this ion and zinc prior to the experiment.

Six populations of *Horridium rivulare* were studied during these experiments. These are listed in Table 7.1. Of the two populations which were included in every experiment, the zinc sensitive one was taken from reach 0085/05 and the zinc tolerant one from reach 0093/85. These were chosen because the ionic composition of the stream water chemistries was, with the exception of Zn, Pb and Cd (and also Hydrogen ion content) not too dissimilar.

2.43 Preparation of alga for assay

The alga used for the standard toxicity tests was assayed within 48h from the time of collection in all instances except those collected from reaches outside England. It was stored in water from the reach at which it was collected at 5°C, 500 lux, until 24h before the test, when it was transferred to basal medium at 15°C, 6000 lux (cool white fluorescent light), with moderate shaking for the remaining 24h. Samples of the alga were then removed for microscopy to check that there were no obvious algal contaminants. A small inoculum of alga was added to each of the boiling tubes (with 10ml of medium) used in the assay. This was done manually by pricking out a few short filaments using forceps and a dissecting needle. Prance (1973) has reviewed some of the techniques used for inoculating filamentous algae, but since such a small size was required, none of the methods described were found to be practicable. The inoculum was made as uniform as possible, with only a few short filaments present in each tube. Replication of selected experiments gave good reproducibility using this inoculation method. Checks on similar aliquots of alga to those used for the tests indicated that in most cases the inoculum lay in the range 2.0 - 5.0mg l⁻¹ dry weight.

approximate ratio of inoculum to normal	limits of algal concentration with which inocula were maintained (d. wt.)	J.N.I.		J.L.		T.I.C.	
		\bar{x}	s.d.	\bar{x}	s.d.	\bar{x}	s.d.
x 0.5	1.25 - 2	4.24	0.24	7.7	0.64	5.7	0.48
x 1	2 - 5	4.68	0.44	8.0	0.50	6.2	0.40
x 2	6 - 9	10.2	1.75	20.2	1.20	14.4	1.80
x 4	12 - 17	18.5	2.25	25.5	2.50	21.7	2.50

Table 2.6 Influence of inoculum size on results obtained with otherwise standard assay technique.
(J.N.I. = just non-inhibitory, J.L. = just lethal, T.I.C. = tolerance index concentration:
mean \pm standard deviations. All concentrations in mg l⁻¹)

A study was included on a population of *Horrmidium rivulare* from reach 0093/85 to see what effect the size of inoculum had on the toxicity results obtained. The results (Table 2.6) confirm that the size of inoculum chosen is the most suitable. Use of a larger inoculum led to reduced toxicity and erratic results. It was found with a smaller inoculum that whilst the results were almost identical in terms of the effect of the zinc, standardization of this small size was very difficult.

2.44 Assay Procedure

The assay used was a refinement of that described by Whitton (1970a), and involved incubation of samples of each field population under standard laboratory conditions. At least 25 tubes were used for each test. As it became possible to predict the effects of zinc on a particular population, then the range of zinc concentrations used could be narrowed, and the accuracy of the assay was increased. Inocula were added to media to which zinc had already been added, and the tubes were then incubated under similar conditions to those used during the pre-incubation period: 15°C, 6000 lux, with moderate shaking, the tubes being placed in a rack at an angle.

Growth in the tubes was compared visually on days 2, 4 and 6 both against preserved replicates of the original inocula and also with each tube one against the other. Observations were recorded on each occasion as follows:

- I Maximum concentration of metal causing no lag in algal growth
- II Minimum concentration of metal causing inhibition
- III Maximum concentration at which alga is alive
- IV Minimum concentration of metal required to kill alga

The values recorded for I and II on days 2, 4 and 6 were usually similar, in contrast to observations on some other species studied by Whitton (1970a).

This indicates that any slight indication of growth observed is due mainly to a reduction in rate of exponential growth rather than an increase in lag. However in those cases where slight inhibition was detectable on day 2, but not later, the value for the former was recorded for category II. Where there was any doubt about the results for III and IV, filaments were removed both for microscopic inspection and for re-incubation in basal medium. Live filaments always included some cells with a clearly defined green chloroplast in an otherwise colourless cell. Filaments which failed to grow after subculturing (and were therefore presumed to be dead) frequently had few cells still with a greenish or yellow-green colour, but with the colour diffused throughout the whole cell rather than restricted to just the chloroplast.

The data from the toxicity test were further simplified, and the following empirical formulae were used in making comparison of laboratory and field data:

J.N.I. just non-inhibitory = (I. II) $\frac{1}{2}$

J.L. just lethal = (III. IV.) $\frac{1}{2}$

T.I.C. tolerance index concentration = (I. II. III. IV.) $\frac{1}{4}$

The T.I.C. was chosen simply as an index to integrate as many as possible of the observations made during the assay, and not because of any *a priori* assumptions about the nature of tolerance in a population.

2.45 Quantitative experiments on *Hormidium rivulare*

Following the standard toxicity tests which investigated the toxicity of zinc, and the more elaborate tests which studied the influence of several factors on zinc toxicity to *Hormidium rivulare*, further experiments were in most cases carried out in which the growth of the alga was estimated quantitatively.

Several ways for measuring growth directly were available, but all were found to be unsatisfactory. Cell counts in standard cell chambers as a method is not practicable with a filamentous organism such as *Horrmidium rivulare*. Wet weight measurements have been shown to be unreliable by Vollenweider (1969) due to variability in water content. Dry weight measurements were tested and found to be impracticable in these experiments because the small volume of organism harvested in some cases made accurate determinations very difficult.

An indirect method was finally decided upon using the measurement of chlorophyll α concentration. Several workers (Moul and Mason, 1957; Kobayasi, 1961) have shown a relationship between direct measurement of growth and chlorophyll content, making this a reasonable choice. There are a number of methods available for pigment extraction and estimation. A review of these methods, together with critical assessment, can be found in Vollenweider (1969). No single method is recommended since their accuracy depends very much on the type of material in question and the particular experiment performed. Here the method was modified from that of Talling (1969). The alga was incubated in 30ml medium contained in 100ml conical flasks and shaken gently under conditions otherwise similar to those for the tubes. Samples of alga similar to those used for inocula in this experiment showed a mean value for the chlorophyll α of $60\mu\text{g l}^{-1}$ (S.E. $\pm 5\mu\text{g}$; $n = 6$).

At the end of an experiment, each flask was individually filtered through a Whatman glass fibre paper under reduced pressure to trap the filaments of the organism. The filtrate was discarded and the paper plus extract placed in a McCartney bottle together with 10mls of 90% Methanol. The volume of the solvent used depended on the amount of organism harvested. If the amount was small, 5ml was used, otherwise at all times 10ml was

the volume used. With the lids screwed down, the bottles were placed into a temperature controlled water bath and the temperature brought up to 60°C to boil the methanol. After this the bottles were removed and cooled down. This brief exposure to boiling greatly speeded up the extraction. After cooling to room temperature, the extract was refiltered using a vacuum pump to remove the cell wall tissue and fragmented filter paper. The clear green supernatant was placed into a 5 or 10ml volumetric flask and if any methanol had been lost due to cooling, was made up to volume. After transference to a 4cm spectrophotometer cell, absorbance was read at 665nm and 750nm in a Perkin Elmer 402 Ultraviolet-Visible spectrophotometer using a scan from 510-750nm. The reading at 750nm was subtracted from that at 665nm to correct for any turbidity and the corrected reading substituted into the equation derived from Talling and Driver (1963):

$$\mu\text{g chlorophyll } a \text{ per sample} = 13.9 D_m (V/l)$$

where D_m is the corrected absorbance at 665nm in 90% methanol,

V is the volume of methanol used to extract the sample in ml, and

l is the path length of the spectrophotometer cell in cm.

Several reasons made this the preferred method for the estimation of chlorophyll a in *Hormidium rivulare*. These were:

(i) Methanol was a more suitable solvent than acetone because it was more efficient at penetrating the cells, particularly when boiled for a few seconds.

(ii) The method did not involve lengthy grinding procedures since the solvent penetrated the cells and extracted the pigment most efficiently without the need to disrupt the cell wall.

(iii) The need to correct for interference from chlorophyll degradation products, such as phaeophytin was found unnecessary since the experiments in most cases involved the estimation of growth in uni-algal actively growing cultures. Tests had been made previously and showed that their contribution was negligible, and the time consuming nature of the operation, together with the possible introduction of more errors (i.e. those arising from small absorbances of other pigments such as chlorophylls *b* and *c* and their degradation products at the chosen wavelength) facilitated leaving the extra procedure out.

(iv) The method was swift and easy to perform.

Quantitative experiments were carried out to test the effects of pH, Ca, Mg and PO_4 -P on *Horridium rivulare* (see 2.425).

2.5 Computing and statistics

2.51 Computing techniques

All field and laboratory data were processed by the Northumbrian Universities Multiple Access Computers (NUMAC), based on IBM 360 and 370 main frames and running under the Michigan Terminal System (MTS). All the data collected were coded and punched onto computer cards. The data were processed using various computer programs and stored on computer files. The total environmental information obtained was stored in one large file termed "Chemdata". In order to perform the statistical methods in mind on selected information stored in Chemdata, the requisite data were placed onto several sequential disc files using the "Save File" procedure of the statistical package of the computer program SPSSV6 (Nie *et al.*, 1975). This same package contained all the statistics programs required for the analysis of the data. Three files were set up for the three major series of surveys. The information for each reach was stored as a separate "sub-file" (in the SPSSV6 terminology) within each file. Each sampling of a

particular reach was stored as a separate "case" within each subfile. Each case consisted of the stream and reach number and the measured field variables, together with any transformations (2.523) of the field data.

With regard to the laboratory data performed on the three *Horrmidium* species (6.1), these data were placed on three separate sequential disc files together with the relevant environmental data concerning these species in the same manner as above. The three data files were each set up in an identical manner. Each population was stored as a separate case. The cases were grouped together into subfiles which again corresponded to the relevant reach. Each case consisted of a case number, stream and reach number, the measured field variables, laboratory toxicity data, and the transformations of the data. The pairwise deletion method of treating missing data was used wherever necessary in calculations.

2.52 Statistics applied to environmental data

The steps in the analysis of the environmental data were as follows:

2.521 Descriptive statistics

These were carried out to determine the distributional characteristics of the field variables prior to any subsequent analysis. The means, standard errors, standard deviations, variances, ranges, minima, and maxima for every variable were obtained, subfile by subfile within each file. Although the statistics were referred to, only the mean values are quoted in the summary tables of the data presented in the relevant chapters. The full descriptive statistics are held at the Department of Botany, University of Durham.

2.522 Bivariate correlation analysis

This was performed on the data in an attempt to produce a value which would summarize the relationship between any two of the field variables. The resultant correlation coefficient would indicate the degree to which the variation (change) in one variable is related to the variation (change) in another. Firstly the null hypothesis was proposed which stated that there was no difference between the means between groups of variables or that any two variables were not significantly correlated. Two methods were available to test the null hypothesis; one based on parametric methods, the other on non-parametric methods. Siegel (1956) gives a detailed account of the rationale behind the choice between the two methods. Parametric tests require certain conditions associated with the parameters of the population from which a sample is drawn. These include (i) that the observations must be drawn from normally distributed data, (ii) the observations must be independent, and (iii) that variances are homogenous. Non-parametric tests have been recommended when there are doubts with regard to the normal distribution of the data, and when the data are recorded on a variety of scales (Elliott, 1971; Jones, 1973). Since initial examination of the data caused some doubt with regard to the normal distribution of some of the variables such as Cd, Pb and SO₄-S (partly because determinations were not available for all samples), and because many variables showed several differences in scale, it was considered appropriate to use initially a non-parametric procedure. Non-parametric means that no assumptions are made about the distribution of cases on the variables. The statistic requires only an ordinal level of measurement and a large number of categories or ranks on each of the variables. Using the SPSS subprogram 'Nonparr Corr', Spearman's rank correlation coefficients (r_s) were calculated, together with the appropriate significance value. This procedure was carried out on all of the field data from each of the main surveys.

2.523 Factor analysis

Further examination of the data showed that if logarithmic transformations were performed on the variables showing differences in scale, they were found to conform more closely to the normal distribution pattern. This therefore meant that a parametric correlation analysis could be performed, and the resultant matrix of correlation coefficients used as a basis for a subsequent factor analysis (Rummel, 1968).

Factor analysis is a statistical technique designed to explain complex relations among many variables in terms of a few "factors", which themselves represent simpler relations among fewer variables. The relations are only demonstrated, not explained, this latter being made in the context of known information about the variables. Using the data-reduction capability of this technique, attempts could be made to see if any underlying pattern in the relationships of the water chemistry of the reaches (as demonstrated in a bivariate correlation analysis) existed. This then might be rearranged or reduced to a smaller set of factors or components which could be used as source variables to account for the observed interrelations of the data produced by the bivariate correlation analysis.

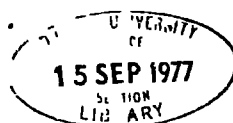
Factor analysis has been used successfully in many geochemical investigations (Dawdy and Feth, 1967; Cameron, 1967; Hitchon *et al.*, 1971; and Reeder *et al.*, 1972) to investigate the chemistry of ground waters, the origin of formation waters and the hydrogeochemistry of surface waters. Detailed explanations of the method of factor analysis when applied to geochemical problems are given by Dawdy and Feth (1967) and Hitchon *et al.* (1971).

The first step in the analysis involved the calculation of appropriate measures of association for the selected variables. The variables chosen for factoring included most of the chemical data. Variables were excluded from a particular analysis only if they demonstrated a reduced number of cases, or failed to exhibit any significant correlations in the intervariable

correlation analysis. The factor analyses were based on product-moment correlation coefficients (Kim, 1975). Pearson correlation coefficients (r) were used to measure the strength of relationship between sets of the interval-level variables (the strength of relationship indicates the goodness of fit of a linear regression line to the data; r^2 gives the proportion of variance in one variable explained by the other). Matrices of the correlation coefficients produced by this method were not presented separately since in many ways they were similar to the tables already produced by the previous intervariable correlation analysis (2.522) and confirmed the results of these; also Rummel (1968) emphasises that it is on the eventual factors that the discussion should focus. These correlation matrices were used as the basic input to the factor analysis.

The second stage involved constructing a set of new variables on the basis of the interrelations exhibited in the data. A principal components analysis was carried out using the SPSSV6 program 'Factor' (Kim, 1975). The initial factor solution was obtained by a principal factoring without iteration. The main diagonal of the correlation matrix was not altered and the extracted principal components were defined as exact mathematical transformations of the original variables. Interpretation of the components was carried out using the method described by Kim (1975).

The final stage involved a principal factor analysis which derived from the principal components a set of factors of as simple structure as possible to explain the interrelations of the original variables (chemical constituents). An R-mode factor analysis, using the above program, was employed. This method employs an iteration procedure for improving the estimates of communality (Kim, 1975). Varimax rotation (Wallis, 1965) of the factors was carried out to produce the terminal solution. Interpretation of the factor matrices was carried out using the methods described by Dawdy and Feth (1967), and Rummel (1968).



With regard to the principal component matrices, loadings for variables on a factor were shown only if they exceeded a value which denoted 15% of the variation of a variable (Rummel, 1968). In the case of the varimax rotated factor matrix, loadings less than 0.3 were omitted from the tables, since they corresponded, approximately, to less than 10% of a variable. The rationale behind further presentation and interpretation of the results of the analysis followed the method given in detail by Hitchon *et al.* (1971) and Reeder *et al.* (1972).

2.53 Statistics applied to laboratory data on *Horridium* species

The toxicity data on zinc to *Horridium* species was combined with the environmental data, and the total data analysed for each species.

2.531 Bivariate correlation analysis

Intervariable correlation matrices were computed for the three species, involving the production of Pearson's product moment correlations (Nie *et al.*, 1975). The correlations included field variables and the measures of toxicity, particularly T.I.C. Logarithmic transformations of field variables with differences of scale again ensured that they conformed to the bivariate normal distribution, and consequently improved the linear relationship with laboratory data (indicated by numerically larger absolute correlation coefficients). Other transformations of the zinc variable were carried out involving the calculated ratios of zinc to possible amelioration factors such as calcium and total hardness. These ratios were included in the correlations.

2.532 Best regression equation

Based on stepwise linear regression analysis (Kim and Kohout, 1975) this was generated using the stepwise forward selection method (Draper and

Smith, 1966), in an attempt to explain the variation in the dependent variable, T.I.C. The independent variables of the regression included all of the field variables together with any of the transformed variables.

The method made use of an equation of the form:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + \dots \dots \dots b_i X_i + \dots \dots b_n X_n + a \quad (1)$$

where Y is the dependent variable (T.I.C.), X_1 and $X_2 \dots X_n$ are the independent variables, $b_0, b_1, \dots b_n$ are the coefficients to be determined, and a is the intercept on the Y ordinate.

As a result of this analysis coefficients are produced which represent the best values for the 'goodness of fit' of the linear regression when the equation is fitted by the specific variables. The goodness of fit was estimated using the F-ratio test (Kim and Kohout, 1975).

The results of this analysis were restricted to presenting the first 6-10 independent variables which enter the equation. The position in descending order from 1-10 determines the degree of importance of that variable in explaining the variation of the dependent variable, T.I.C.

2.533 Principal component analysis

Based on the intervariable correlation matrix, including both laboratory and field data, this analysis was carried out as described in 2.523.

2.534 Pearson correlation coefficients on toxicity data

The results of the experiments investigating the effects of several environmental factors on the toxicity of zinc to *Hormidium rivulare* were analysed in an attempt to obtain the linear relationship between the factor and zinc. The Pearson correlation coefficient r gave an indication of the strength of the relationship. The r^2 value gave the proportion of variance in one variable explained by the other.

3 GENERAL BACKGROUND TO AREA OF STUDY

3.1 Introduction

This chapter presents a general description of the geology of the mining areas through which the streams and rivers to be studied drain. Included in the account are details of the history of mining, which give an indication of the time scale and extent to which anthropogenic influences have affected the region. At the end of the Chapter there is a short section dealing with general aspects of the climate pertinent to the area.

3.2 Introductory notes

According to Pasternak (1971) "Apart from climatic factors, the relief and physico-chemical properties of the substratum of the drainage areas of mountain streams, influence in a high degree the forming of life conditions in these streams." It was felt, therefore, that an investigation of the geological formations in the area, together with a full description of the physiography of the more important streams would provide a basis for the field surveys, in which studies of the biology and water chemistry of the high zinc level streams would be carried out.

The geographical and physical descriptions are based on personal observations, the text of the geological description is taken from the extensive work of Dunham (1948) and Smith (1923), with notes on the history of the mining derived from both of these works, together with those of Wallace (1890) and Sopwith (1833).

The study area is situated in the Pennines (Fig. 3.1), which constitute the dominant feature in the physiography of the North of England (Wray 1948). Described as the "backbone of England", they extend as a central mass of high ground almost from the Cheviots to the Midland Plain. The Pennines show a wide range of geological formations with an equally marked variety of geological structure and physiographical conditions.

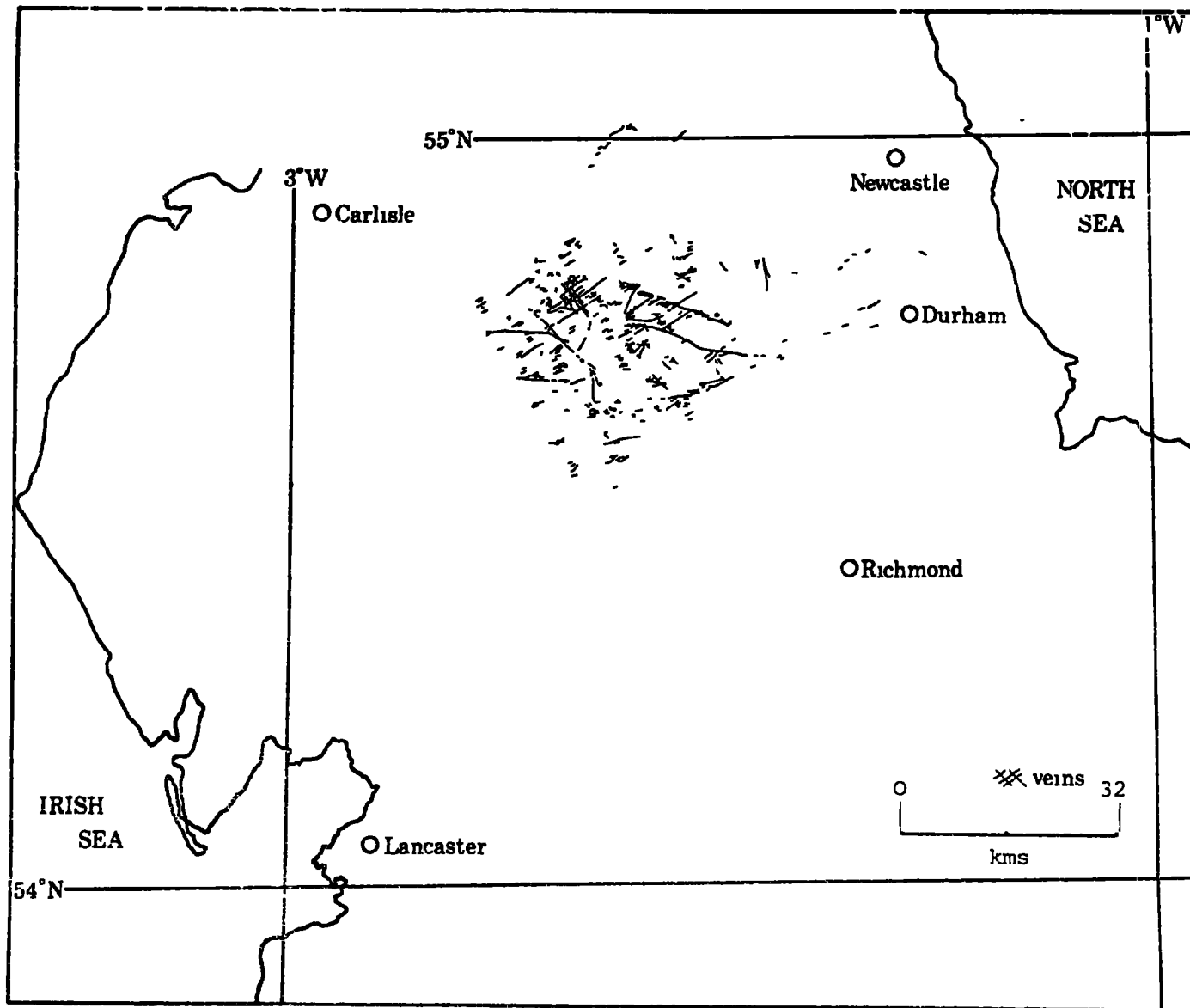


Fig. 3.1 Location of the North Pennine Orefield in Northern England (after Smith, 1974, Fig. 1.1).

They can be divided geologically into three "blocks" (Raistrick and Jennings, 1965) within each of which the structure approximates to a shallow dome. These are the Alston Block, from the Tyne Valley to Stainmore, the Askrigg Block, from Stainmore to the Aire valley; and the Derbyshire Dome, which includes the central area Ashbourne to the Peak. Because mineralisation is extensive within each "block", they have individually been referred to as Orefields. This present account is restricted entirely to a description of the streams and rivers draining the most northerly field associated with the Alston Block (Fig. 3.2).

3.3 Physical characteristics and Geography

The Northern Pennine Orefield covers an approximate $3,885\text{km}^2$ in the counties of Cumbria, Northumberland, Durham and West Yorkshire. It is divided into two complementary halves by the Stainmore Gap, and it is in the northerly half that the area of study is situated. This area is drained by the three principal rivers of North-eastern England, the Tyne, Wear and Tees, and the streams investigated drain the catchment areas of the Tyne and Wear.

The landscape consists primarily of rugged fell and dale country where the bottoms of the main valleys drop to between 240-280m, from the high watersheds which reach average altitudes of approximately 610m. Agriculture is practised in the more fertile valleys with sheep farming being the main preoccupation on the flat, broad topped fells. The higher slopes are covered with hill peat which in most cases has been deeply eroded into "hags". Many of the lower slopes show heaps of exposed rock and chippings forming the characteristic waste tailings heaps, a remnant of the previous mining activities. It is drainage waters from the fells (either produced naturally or from man-made drainage channels), water percolating through the exposed mine waste heaps, mine water from adits, and underground springs, that are the chief sources of the streams studied in the area.

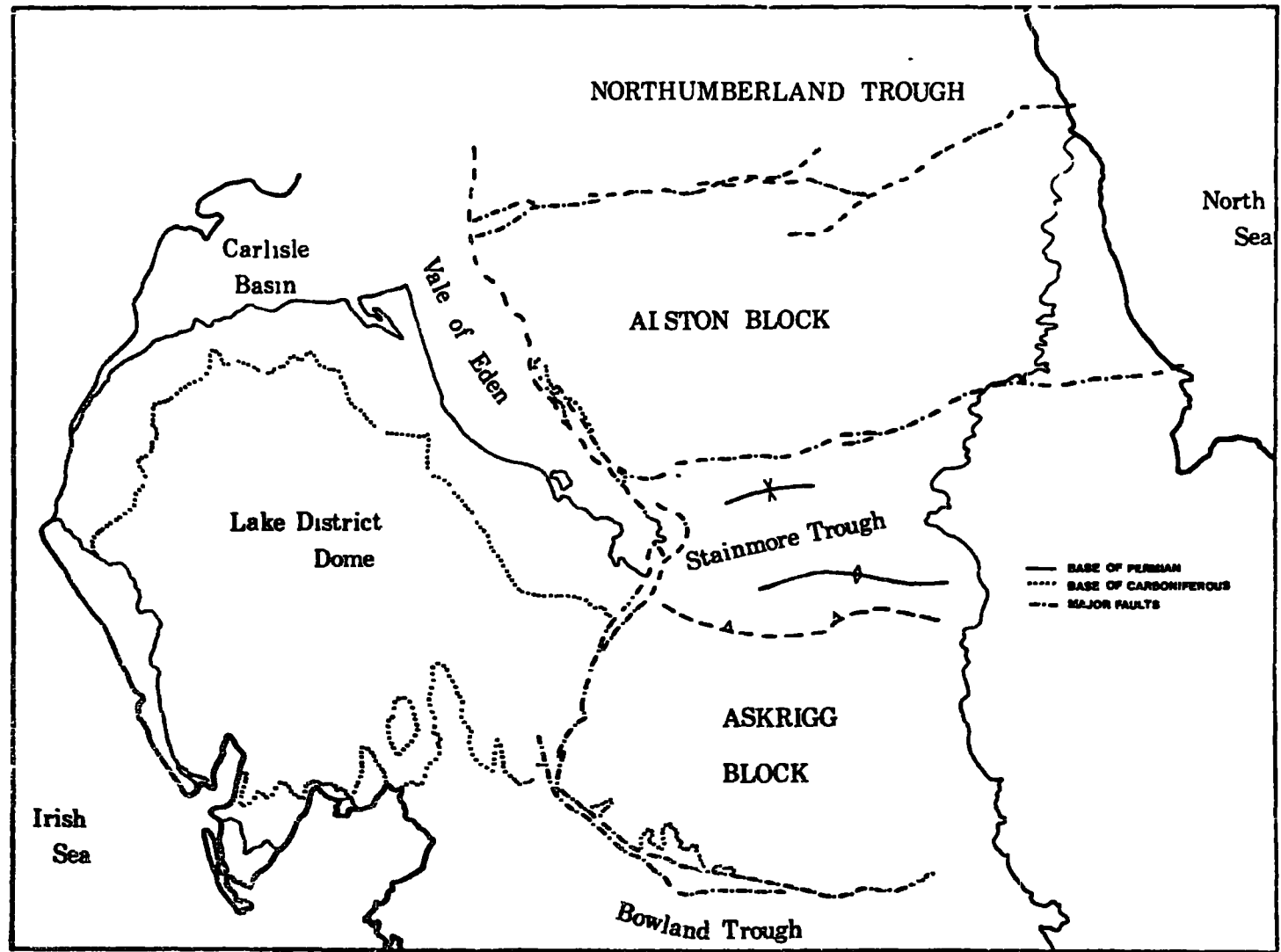


Fig. 3.2 Regional geology of North eastern England (after Smith, 1974, Fig. 2.1).

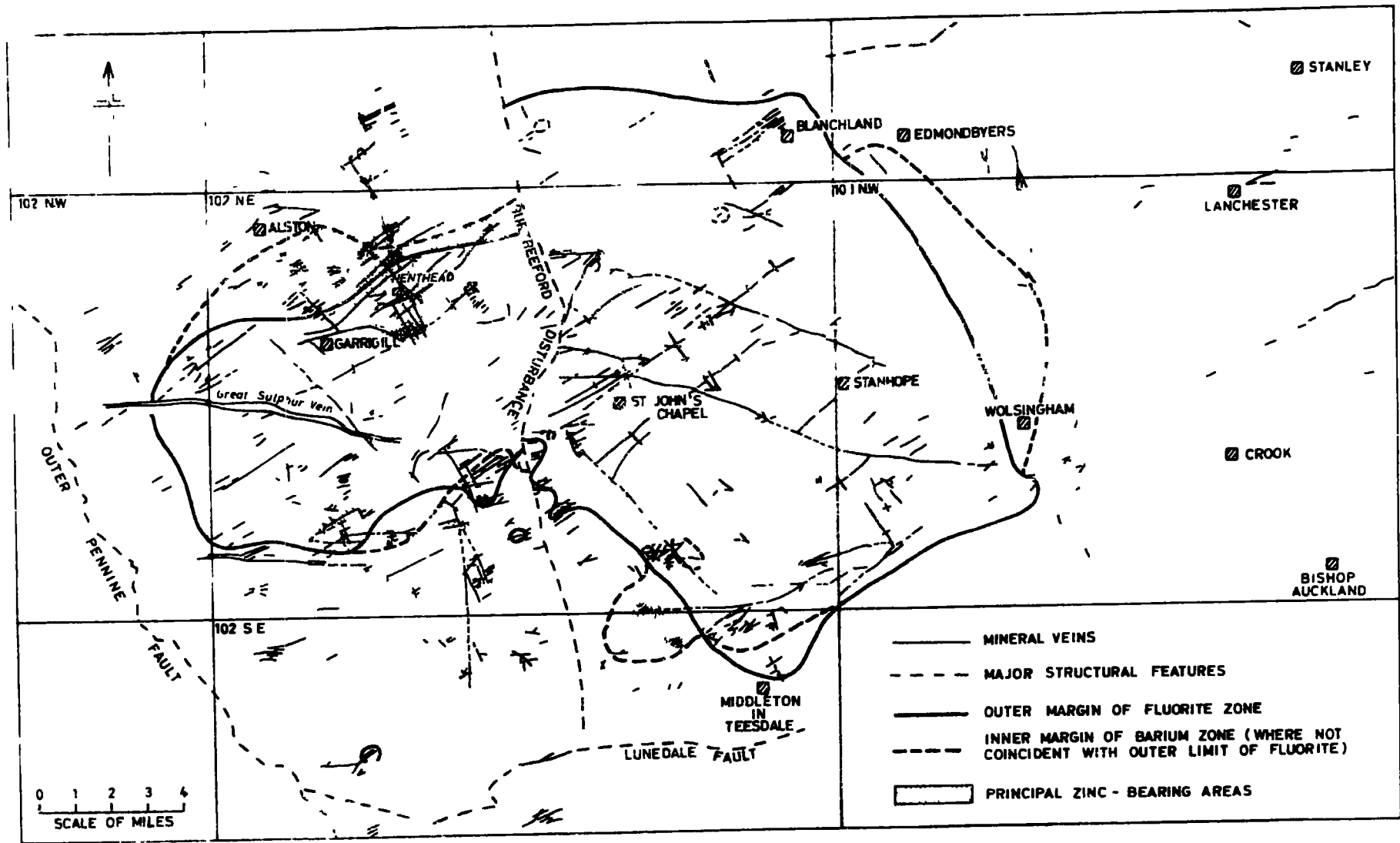


Fig. 3.3 Distribution of mineral veins and main minerals in the Northern Pennine Orefield (after Dunnam, 1948, Plate II).

The South Tyne and its tributary the Allen flow northwards until they reach the main east-west valley, joining the North Tyne near Hexham to form the main River Tyne. The Derwent drains to the North-east until it too joins the Tyne. The Wear drains to the East, and the Tees to the South-east.

The Northern Pennine Orefield together with the distribution of minerals is given in Fig. 3.3. In the present account the Orefield is divided into five main separate areas for descriptive purposes; these are Alston Moor, West Allendale, East Allendale, Weardale and the Derwent Valley.

3.31 Alston Moor

This area lies more or less totally in the county of Cumbria, covering the main South Tyne Valley southwards from Alston and includes the tributary valleys of Black Burn, Cross Gill, Ashgill and the Nent. The whole area contains mineral veins in abundance but, as shown by Dunham (1948), the most productive area lies in the Nenthead district. Here some of the largest lead and zinc deposits in the orfield, and some of the greatest in Britain, have been worked. Consequently most of the streams studied in this area are concentrated in the Nent Valley.

River Nent

The source of the Nent is at 518m. formed by the junction of three small streams, Long Cleugh Burn, Middle Cleugh Burn and Old Carr's Burn. This was formerly an area of intense mining activity, and the upper reaches of the river, bordered on both sides by high heaps of waste tailings (Figs. 3.4 and 3.5), receive drainage waters from these, or direct discharge from old adits. The three formation streams originate from drainage waters fed by springs on the lower slopes of Nag's Head, a peak of 673m in height, three kilometres south-east of Nenthead village. The river flows north-west for about one kilometre, with the bed changing from sheets of exposed sandstone

Fig. 3.4 View of the upper Nent valley above Nenthead village,
showing the many heaps of coarse waste tailings.

Fig. 3.5 View of the Nent looking upstream from Nenthead village
towards Rampgill Mine. To the right of the buildings
is the old Rampgill dressing floor with heaps of fine
tailings in the foreground.



bedrock, with occasional outcrops of limestone, exposed as the river carves its way down through the rock strata through large boulders and cobbles, to a mixture of rock chippings, boulders and gravel as it enters the vicinity of the old smelt mill with its associated tailings heaps. Here it is joined by Rampgill Burn, and a few metres further on receives discharge of mine waters from three of the larger adits in the area, those belonging to Dowgang Level (Fig. 3.6), Rampgill Level (Fig. 3.7) and Scaleburn Level. In this region, at a height of 434m, the river bed is composed of boulders of mineralised limestone and sandstone (the latter predominating), with associated shale chippings and a silty gravel containing fragments of sandstone, limestone, quartz, fluorite and shale derived from the surrounding tailings heaps. In the village of Nenthead, the river is fed by Dowgang Burn, a highly silted stream, originating as a moorland drainage spring on Flinty Fell. This burn receives acid mine drainage waters from two adits associated with an old anthracite mine above the village. As a result of this a yellow ochreous precipitate of ferric hydroxide covers the stream bottom for its remaining length until entry into the Nent. After receiving this burn, the bottom of the Nent becomes silted for several hundred metres downstream.

In the vicinity of the large old dressing floor in the village, Gillgill Burn enters the river. This stream rises on the opposite hillside to Dowgang Burn on the slopes between Black Mill and Kilhope Head. It drops steeply though the valley bordering Fairhill to join the main river.

One kilometre the other side of the village the river enters another mining complex of old workings where it is joined by Gudham Gill. The river passes on through a gently sloping valley bounded by old mine shafts and quarries, and receives further small stream tributaries on its passage to join the South Tyne at Alston. Surface workings became more sporadic away

Fig. 3.6 View across the Ment to show the discharge of mine water from Dowgang adit level. The mine water is directed into the river by the remnants of a water level channel.

Fig. 3.7 View of Rampgill level from which mine water draining Rampgill mine workings is discharged.



from the village, and farming becomes more important in the valley. Cattle grazing in fields in the more fertile areas become a common feature, as do occasional caravan sites bordering the river, indicating an active tourist trade. The fall in height of the valley is uniform and gradual, with the largest drop being at the Nentforce Waterfall, where the large masses of limestone dominating the valley become exposed. In this area there is one of the entrances to the large Nentforce Level, a level used for the discovery of mineral veins and the drainage of mines.

The river flows on westwards to Alston, where at a height of 280m it joins the South Tyne.

River South Tyne

This river rises at a height of 556m, on the slopes of Bellheaver Rigg in the south of Alston Moor. After collecting water from drainage streams on the neighbouring Tynehead Fell, it drops down steeply, flowing northwards towards the village of Garrigill. Approximately two kilometres from Garrigill it receives two large burns, the first being Ash Gill, the second Crossgill. Ash Gill is formed by several streams rising three kilometres to the east on the western slopes of Nag's Head and the eastern slope of Flinty Fell. It passes down a steep valley through the largest coniferous plantation in Alston Moor (Ashgill Wood), which is composed more or less entirely of *Picea abies* (L.) Karst. (Millar, 1964) which was managed principally for the production of mining timber. Crossgill originates on the opposite side of the valley as fell drainage waters.

After the entry of these two large tributaries the river becomes considerably enlarged, and on approaching Garrigill becomes wider, with the river bed composed largely of sandstone boulders with a little limestone, shale and glacial drift. Garrigill Burn, a stream derived from waters mainly draining

from Flinty Fell joins the main river on the other side of the village. This stream is fed by Souther Gill and Bram Gill which both originate as water flowing down the fellside in numerous small channels in the peat. Some of the water drains from old pit heaps near the summit of Flinty Fell. Further down, the stream passes through some disused mine workings where it collects water from spring channels in the exposed limestone, and adits associated with the workings.

From Garrigill village the South Tyne flows for three kilometres collecting drainage waters from the fells of Black Band and Staneshaw Rigg where, in the vicinity of Leadgate, it is joined by Black Burn. This large water course originates as a stream which drains Cross Fell, at 893m, within a few metres of the source of the Tees. It flows northwards down Skirwith and Ousby Fells, increasing in size as small streams feed it, on its passage to join the main river. After entry of this large tributary the river, now considerably larger in volume, passes on towards Alston along a much gentler sloping valley at a height of 274m. As it passes through Alston the river is bordered by farmland with small copses of trees along its banks. Here the bed is completely covered by boulders of various sizes composed almost exclusively of sandstone.

3.32 West Allendale

The West Allen is formed by a large number of springs and seepages which drain over Coalcleugh Moor. The majority of the seepages are composed of water draining through small channels in the peat which eventually become small streams. At this stage the water has eroded through the peat to reach the surface rock strata which is composed mainly of sandstone, shale and some glacial drift. The stream bottoms are stony and subject to flash floods during heavy rain so that they have no rooted vegetation and little moss cover. Old mine workings litter the hillside, being indicated by

dumps of shale. As the main stream passes through Coalcleugh, an extensive area of mine workings, it receives discharge from disused adits, and drainage from the many surrounding tailings heaps.

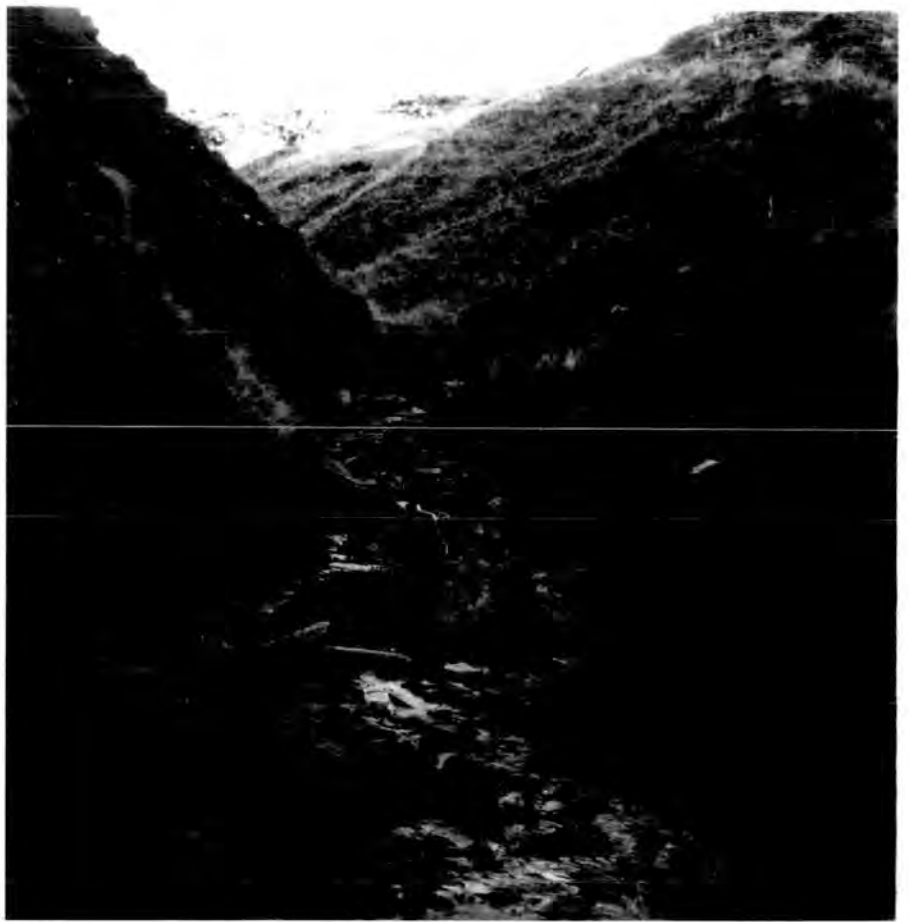
Approximately one kilometre northwards from Coalcleugh it receives Shieldridge Burn formed by the junction of several streams such as Whetstonemea Burn and Quarry Sike, which drain down from the workings of Whetstone Mea and Tindalfell Pits on Coalcleugh Moor. The main stream bottom is composed of large boulders of sandstone, with a gravel consisting of shale and shale dust, blown into the burn from the adjacent tailings heaps. From Coalcleugh to Carr Shield, a distance of three kilometres, it remains a small stream. Its valley is still moderately high (380m) and is bordered by steep banks of exposed shale and mine waste material. The large number of mines in this valley are formed by continuations of mineral veins of the Nent Valley, and the old levels form an interconnected series with those from that area. This has resulted in much of the landscape bordering the river consisting of exposed waste tailings heaps (Fig. 3.8), contrasting markedly with the upper valley of the East Allen (Fig. 3.9). The river continues to flow northward through a steeply banked valley until it joins the East Allen five kilometres north-west of Allendale Town.

3.33 East Allendale

The East Allen is formed by a small stream which flows down the north side of Burtree Fell, at a height of 609m. After receiving seepage waters from flush areas on the fell, it flows northwards towards Allenheads village through a narrow valley which is densely wooded with coniferous trees. Most of the streams in this upper part of the valley originate as flushes on the surrounding fells and mosses. The landscape shows less interference from man in the form of mining activity and is almost entirely used for grazing. In the village of Allenheads, Eastend Burn, a small stream rising

Fig. 3.8 The River West Allen passing through old mine workings. Waste dumps of coarse shale border the stream on each side. On some of these the plant life has recovered sufficiently to form loose mats of vegetation.

Fig. 3.9 In contrast to Fig. 3.8 this view of the upper reaches of the River East Allen shows a river undisturbed by mining activities. The stream banks and emergent boulders display a rich macrophyte flora.



on the south slopes of Quickcleugh Moss joins the main river after flowing down a valley bordered by further coniferous plantations.

Most of the mine workings in this upper part of the East Allen valley can be found to the west of the village of Allenheads where a series of important lead veins were discovered in the area of Middlehope Moor. As the river flows northwards, it is joined by Swinhope Burn, four kilometres north of the village. This larger tributary is formed by a number of small streams draining Swinhope and Carrshield Moors which lie adjacent to Coalcleugh Moor at the head of the West Allen valley. A continuation of the Barneycraig Vein of West Allendale was worked in Swinhope, resulting in the valley being bordered by a large number of tailings heaps and disused mines. The fells surrounding Swinhope Burn can be viewed from the road following this valley and seen to consist of flat topped, gently sloping, broad hills of unenclosed moorland. The East Allen continues to flow through a gently sloping fertile valley of enclosed pastures used for sheep grazing, with occasional old mine workings. After several kilometres it joins the West Allen, the confluence of which forms the River Allen. This enters the South Tyne west of Haydon Bridge. From there the South Tyne flows eastwards to join the North Tyne, forming the Tyne three kilometres west of Hexham.

3.34 Weardale

This is an extensive area which covers most of the Upper Wear Valley and the important side valleys of Sedling and Rookhope in the north, and Burnhope, Swinhope and Bollihope in the south. The Wear is formed by the junction of Kilhope and Burnhope burns at Wearhead. Kilhope Burn originates as a large number of seepages and springs, the majority of the former being formed by direct runoff from the peat covered fells of Wellhope Moor and Kilhope Moor. Most of them occur at heights in excess of 600m. There are a large number

of workings situated down the steep valley of this stream, again indicated by the many heaps of mine tailings and shale. The stream continues to be fed by fell drainage waters in the form of smaller streams, until the first major tributary joins, which is Wellhope Burn. The catchment area of this stream extends over the whole of Wellhope Moor, much of which is now being reforested. In the village of Cowshill, Killhope Burn is joined by Sedling Burn, another large tributary, which drains an area of intensive mining around Burtree pastures. This rises as a small stream at 609m, just north of Sedling Fell. It is fed by small streams draining Burtree and Sedling Fells, many of which follow the course of old disused veins. The valley is steep and the high banks of the tributary streams display the exposed underlying shale. As the stream continues to pass down the valley, drainage waters from nearby tailings heaps and mine waters from old adits increase its volume until it joins Killhope Burn in the village. Active mining (mainly for fluorspar) continues in this tributary valley and the stream receives continual piped discharge of mine water from the settling lagoons of the mine. Killhope Burn flows south for one kilometre to join Burnhope Burn at Wearhead.

The Wear, formed by the confluence of these two streams, flows through a gently sloping valley where agriculture is the chief preoccupation of the inhabitants. It is a comparatively densely populated valley when compared with the other areas described. However, the majority of the tributary valleys are uninhabited. The upper end of the valley shows the most metalliferous mining activity, mainly associated with the tributary valleys, although Stanhope and Frosterley are centres for an extensive limestone quarrying industry, as shown by the large cement factory bordering the river at Eastgate.

At Eastgate, the river is joined by another large tributary, Rookhope Burn. This is one of the larger tributaries in the upper valley of the Wear with an extensive catchment area including Quickcleugh Moss, Risegreen Moss, Wolfcleugh Common and Redburn Common. The whole of the valley contains a large number of disused mine workings, including two old networks being reworked for fluorspar at Groverake and Redburn mines. The burn is formed by three main streams draining from Wolfcleugh Common; these are North Foul Sike, South Foul Sike and South Grain, which are joined by Shorngate Sike running from the south end of Quickcleugh Moss. It flows through an area of old quarries and shafts and is fed by further drainage from the surrounding fells. The stream flows due east for several kilometres through a steep valley. On the surrounding hillsides much of the moorland has been drained and is used for grazing by sheep and cattle. Lower down, nearer the stream margins, tailings heaps are plentiful, particularly in the vicinity of Rookhope village. Passing through the village there is a sharp bend in the stream, after which it flows southwards to join the Wear.

Further tributaries join the Wear as it continues to flow eastwards away from the mining region.

3.35 The Derwent Valley

This is the most north-easterly part of the Orefield, situated in the catchment area of the Derwent, a major tributary to the Tyne. The Derwent is formed at about 260m by the confluence of Beldon and Nookton Burns. These two bodies of water have quite large catchment areas extending over the surrounding fells. Beldon Burn originates from waters draining Byerhope Moss, Quickcleugh Moss and Heatherburn Moor. Nookton Burn is formed by streams draining Hunstanworth Moor, the north side of Redburn Common, and Nookton Fell. The height of most of the surrounding Fells

is approximately 490m. They are more or less totally used for sheep farming. The Derwent passes through a valley with strips of fertile agricultural land bordering it until just before Baybridge, where it is joined by Bolts Burn.

This tributary valley was one of the more intensely mined areas in this region and this can be seen in the large number of tailings heaps, disused mine buildings, chimneys and adit tunnels bordering the stream. Towards the source of the stream is a large mine complex, Whitehops Mine, which is currently in operation for the production of fluorspar. Piped effluent from settling ponds and lagoons, together with ground waters from a network of adits and surface drainage waters from the extensive dumps of tailings and dredged lagoon slurry, all contribute input of water into the stream. This introduces large quantities of silt which is transported into the Derwent. The river passes on through a wooded fertile valley to Blanchland where it is joined by Shildon Burn which originates in the other main area of mine workings in the region. From Blanchland the river flows on to enter the Derwent Reservoir and on north-eastwards to join the Tyne.

3.36 Lower Wear Basin

Included in several surveys (Chapters 4 and 6) was a stream rising on the magnesium limestone of the Coal Measures, in a coalmining area two kilometres south of Pitlington, and seven kilometres west of Durham (see 2.22). The source of the stream is a spring from the magnesium limestone emerging at 137m (the lowest of the streams sampled). After one kilometre it is fed by drainage waters and underground channels from a colliery spoil heap and coal mine complex. In this region the stream bed is composed of limestone boulders over a sandy silt. After receiving piped effluent from the coal mining area, the remaining stream bottom, until it joins Coalford Beck, is covered with a thick precipitate of ferric hydroxide. After feeding several other becks, the water eventually enters the Wear.

3.4 Geology

3.41 Introduction

The geology of the area is dominated by Lower Carboniferous Limestone strata forming outcrops which have become exposed in the ranges of hilly ground to which they give rise. The extensive area of mineral deposits occurs in these rocks, particularly those of the Carboniferous Limestone Divisions. These Carboniferous strata rest on older highly folded Palaeozoic rocks which are exposed in two areas, one as a long narrow strip called the Cross Fell Inlier (lying between the Carboniferous outcrop on the escarpment and the Outer Pennine Fault), the other occurs beneath Cronkley Scar in Upper Teesdale. Dunham (1948) points out that the relations between the rocks and the inlier are structurally complex, but the basement beds of the Carboniferous rocks all along the escarpment rest upon Skiddaw Slates.

3.42 Structure

Three major periods of earth movement have contributed to the tectonic evolution of the Orefield, and by fracturing and folding to deform the rocks have prepared the way for the mineralizing solutions. The earliest was the Caledonian orogeny of Siluro-Devonian date, which imparted to the Lower Palaeozoic rocks a dominant E.N.E. pattern of strong folds. To the west of the orefield the Weardale Granite was implaced as a major batholith towards the end of the period of earth movements. The relatively high ground of the area reflects the buoyant nature of the low density granite, causing the region since Devonian times to remain structurally positive. This positive area is called the Alston Block and is marked by major structural features; the Stablick Fault-system, the Pennine Fault-system and the Stainmore Syncline respectively, in the northern, western and southern margins of the northern half of the Orefield.

The Pennine Fault-system is thought to contain three main groups of faults of different ages. The first, the N.N.W. Inner Pennine Fault downthrowing east, and the second, a series of thrust faults along which the overthrusting was directed E.N.E., are assigned to Hercynian earth-movements, whilst the third, the Outer Pennine Fault (a N.N.W. system, responsible by its westerly downthrowing in bringing the Lower Palaeozoic rocks of the inlier against New Red Sandstone of the Vale of Eden) is attributed to the Tertiary period. The Stublick Fault-system comprises a belt of E. - W. to E.N.E. faults now downthrowing northwards. The Stainmore Syncline in its southerly position may correspond to an early Lower Carboniferous trough of sedimentation lying south of the Swindale Beck Fault and its eastward continuation. The Swindale Beck, Lunedale, Butterknowle and Wigglesworth faults form a linked series of faults running along the north side of the Syncline. The first downthrows north, the rest southwards.

Further faulting along the northern, western and southern margins of the Alston Block was imparted by the Hercynian orogeny during the Carboniferous-Permian interval. Overthrusts in and adjacent to the Cross Fell Inlier were produced by compression directed E.N.E. in this period. Similar earth movements are suspected to have produced the Burtreeford Disturbance, a monocline extending from north to south across the area. It appears that the faults formed in Devonian times act as the basis for hinge-lines to separate (during the Lower Carboniferous period) the stable block from adjacent more rapidly sinking areas. The earliest faulting in this period almost certainly occurred before the intrusion of the Whin Sill. This series of connected or related sills (or phacoliths) of quartz and dolomite was intruded into the Carboniferous sediments in the late Carboniferous early Permian age. Separation of the Alston Block by the faults resulted in uplift characterised by gentle doming with the west elevated to the highest position and the Carboniferous beds dipping north, east and south

away from the centre of the dome in upper Teesdale. A number of small faults are considered to be adjustment fractures associated with the doming, some of which were later mineralised.

The present structural form of the area can be attributed to modifications occurring in the Alpine orogeny of Tertiary date. Establishment of the easterly regional dip of the Carboniferous rocks occurred when normal faulting along margins in a N.N.W. and E. - W. direction caused uplift to the east of the Pennine fault. This elevated the western part of the Alston Block, providing a resultant tilt to the east.

3.43 The Carboniferous Rocks

Four main divisions can be described in the Carboniferous Limestone series (Dunham, 1948). In order, from the lowest to the highest, they are : Basement, Lower, Middle and Upper Limestone Groups. The earliest Carboniferous deposits (basement) probably filled up broad hollows on the pre-Carboniferous floor. They vary in thickness and consist of coarse conglomerates, sandstones and shales, with a few subordinate bands of argillaceous limestone. In areas around Cronkley Fell, on the margins of the Teesdale Inlier, the basement beds are exposed as outcrops. Next in the succession, the Lower Limestone Group follows and is characteristically dominated by the Melmerby Scar Limestone. This is a pale grey to grey coloured limestone exposed in Upper Teesdale above the Whin Sill (by which it was intruded). The upper part of this group is not a continual mass of limestone but consists of alternations of shale, sandstone and limestone. This alternating sequence continues in the next group, the Middle Limestone Group. Here it forms a typical rhythmic series called the Yordale Beds. The complete cycle of strata consists of the following beds in upward succession : limestone, calcareous shale, ferruginous shale, shaley

sandstone, sandstone, gannister or underclay, and coal repeated many times. Changes in sea level and resultant stabilization of the land surface are responsible for the sequences. In Northern England a succession of deltas built up from clastic sediments spread southwards and westwards, laying down mud, then sand up to sea level. The cause of the cycle can be seen to result from the abrupt rise in sea level relative to the plane of deposition at the beginning of individual cycles. Vertical movement of the earth's crust is responsible for the changes producing the cyclothems in this group.

The Upper Limestone Group is indicated by the presence of the Great Limestone at its base, and although the rhythmic alternation of stratas can still be defined, there is a gradual but striking change in conditions. Above the Great Limestone there are only a few very thin limestones, and over much of the area shale predominates over sandstone in this group, although there are some well developed belts of sandstone. This Upper Limestone Group is now regarded as part of the Millstone Grit Series (3.45).

The Great Limestone is grey-blue in colour and fine grained and has been quarried extensively in parts of the district. Its thickness seems to vary, but in much of the area the upper few metres are associated with shale. Above this large band of limestone is a thinner band called the Little Limestone, and between the two are strata of shale and sandstone which vary considerably in detail, markedly influencing the mineral veins in and below these beds. In most of the area pertinent to Alston Moor there is an alternation between first shale next to the Great Limestone, then sandstone followed by coal in three identical cycles, except in the last where sandstone is followed directly by the Little Limestone. The three bands of sandstone consecutively from lower to upper are the Low Coal Sill, High Coal Sill and White Hazle. The sandstones of the series include siliceous and gannister types, with medium to coarse micaceous sandstones.

The Little Limestone is succeeded by shale, although sandstone can occasionally overlie it. The first sandstone above the Little Limestone has been named in the past the Pattinson Sill, although the name has been used for others. Separated from this by a bed of shale is another sandstone, the White Sill, occasionally called the High Pattinson. Overlying this is a shelly sandstone or marine shale, followed by shale of variable thickness above which lies the Firestone Sill. This bed of sandstone is lithologically separated into two types. In Alston Moor, along the Teesdale-Weardale watershed and in the area of Middleton-in-Teesdale, it is a pebbly topped coarse sandstone in places approaching a grit. In the Rookhope and Derwent Valleys it is a hard, brown or white, siliceous, medium-grained sandstone overlaid by gannister. Variation in thickness in the series between the Little Limestone and the top of the Firestone Sill is greater than in preceding groups. Overlying the Firestone there is a coal which has been worked at Coalcleugh and Nenthead. In parts of the area a bed of limestone known as the Crag Limestone lies above the Firestone, although in most of the Alston Moor sections this latter is replaced by 'Ironstone' - a ferruginous, limey sandstone with shells. Following the Crag Limestone are two beds of shelly sandstone interbedded with thick shale beds. The next portion of the Upper Limestone Group comprises the High and Low Slate Sills and interbedded shales. A transgression, markedly unconformable, can be demonstrated at the base of the Low Slate or Grit Gill. Above the Low Grit Sill, and in some places the High Slate Sill, rests a seam of coal. Overlying this is a series of shales, with shelly calcareous sandstones named the Rookhope Shell Beds. These are succeeded by a flaggy sandstone upon which rests a fine-grained, grey limestone, the Lower Felltop Limestone. This is exposed in many sections in Alston Moor but is not present over the whole area. Overlying it is a variable sandstone series named the "Transgression Beds" comprising limonite-stained flaggy sandstones with gannister in places

which are medium to coarse-grained but rarely becoming grits. Dunham (1948) calls these the Coalcleugh Transgression Beds. Next follows a cyclothem of shale with ironstone nodules passing upwards into sandy shale followed by micaceous flaggy sandstone. At the top of the series lies a thin coal overlaid by the Upper Felltop Limestone. This stratum is present widely on the high fells. Main beds extend above this, succeeded by shale over which lies the Grindstone Sill, a flaggy sandstone. This is overlain by gannister, and although little is known about the beds which succeed it, they are assumed to be shaley.

3.44 The Millstone Grit series

The base of this series was originally regarded by early researchers as being at the base of the prominent grit above the Grindstone Sill. This line is however higher than that mapped at the base of the Millstone Grit in the Mid-Pennines, which would coincide with the base of the Upper Limestone Group. The British Carboniferous era is traditionally divided lithologically into Carboniferous Limestone, Millstone Grit and Coal measures. This is now regarded as synonymous to the European Divisions Dinantian, Namurian and Westphalian, based on internationally accepted fossil markers. Although diagnostic fossils are rare in Northern Britain, recent evidence has established the base of the Namurian, now referred to as Millstone Grit. It comprises two facies; the lower division called the Upper Limestone Group (see above) and the upper division, a grit-shale sequence (Johnson, 1970). This Millstone Grit sequence must not, therefore, be confused with the old series which included the Grit-shale sequence only.

This upper division consists of coarse grits with interbedded sandstones, shales and gannisters, together with marine bands and impersistent coals. It represents a continuation of the Upper Limestone Group though the marine influxes were never sufficiently free from clastic sediment to permit the

formation of limestones. Three grits can be defined in the formation with shales underlain by, or containing gannister between the grits.

3.45 Mineral deposits

3.451 General description

The mineral deposits occur as oreshoots, defined by Dunham (1948) as "a continuous body of ore which may be worked with profit, or with hope of profit", a phrase which introduces both geological and economic factors. Mineralized ground can continue beyond the limit of oreshoots since quite often the boundaries of an oreshoot represent workable limits. There are two principal types of oreshoot: (1) Vein oreshoots, developed by mineralizing along fissures which seldom deviate more than 20° from the vertical where they carry orebodies; (11) Metasomatic flats, owing their formation to replacement of flat-lying, favourable beds of limestone. The main difference between the two is in attitude, the former being more or less vertical, the latter horizontal. Both are connected with vein fissures, in the sense that vein fissures carry vein oreshoots (and are able to carry more than one), and flats are invariably associated with vents or fissures by which the mineralizing fluids gained access to the limestone. The orefield exhibits a conjugate pattern of vein fissures with the major trend of productive veins lying in an E.N.E. direction. The larger faults are seldom found strongly mineralized, being blocked by shale brought in at the time of mineralization. The smaller displacements free from blockage produced clean cut fissures in the limestone and sandstone. In softer beds of shale an increase in the hade of the vein results in closing of the fissure, thus restricting passage of the mineralizing solutions to the hard beds. This can cause fissures in an upward course to die out altogether.

This may account for the apparent loss of many veins above the Great Limestone which are often at their best at this horizon. Some vein oreshoots have been termed "ribbon" oreshoots from their appearance in longitudinal section. They are derived from the filling in of laterally extensive channels of no great height. These coincide with the planes of coincidence of a vein fissure with hard beds in the wallrock and are limited above and below by shale which almost closes the fissure. The physical control of these is related to the thin nature of the limestones and sandstones in the Middle and Upper Limestone Groups in which most of the veins have been worked. The height of the oreshoots controlled by these rocks is small compared to their length. The most favourable rocks for the formation of vein oreshoots are respectively limestone, dolerite and hard sandstone. The most unfavourable are soft sandstone and shale. The formation of flats is associated with the thinning of sandstone beds underlying the limestone.

3.452 Minerals

There are two main groups of minerals (Dunham, 1948). These are :

- (1) the Primary minerals which are the original minerals of the deposits which are persistent beyond the reach of surface or near surface agencies;
- (11) the Secondary minerals which occur within the zone of circulating groundwaters but which fail to occur at greater depths. Only some of the minerals included in the Primary group which are thought most to influence the chemistry of streams in the area will be discussed.

Galena PbS is the primary lead mineral occurring as coarsely crystalline bands in the veins and flats. In the latter it may be disseminated through silicified, ankeritised or fluoritised limestone as cubes. It contains a small amount of silver in solid solution and traces of zinc and copper as the separate associated minerals sphalerite and chalcopyrite.

Sphalerite ZnS is the only primary zinc bearing mineral and when found in abundance, as around the Nent and West Allen areas, it occurs as brown to dark brown massive bands in the veins and flats. It contains iron in solution and traces of cadmium.

Chalcopyrite CuFeS₂ is found in very small amounts throughout the orefield.

Pyrrhotite Fe_xS_x, Pyrite FeS₂, and Marcasite FeS₂ are all found associated with the Great Sulphur Vein. Here the massive sulphides consist of an intimate mixture of the three iron sulphides, among which polished surfaces indicate pyrrhotite to have been the earliest.

Fluorite CaF₂ occurs as the most abundant matrix mineral in East Allendale and Weardale and is present in many deposits in Alston Moor (Fig. 3.3).

Quartz and Chalcedony SiO₂ Silica is important as a constituent of the deposits commonly found as milky bands or veinlets of quartz and also as colourless prisms where these have been free to develop. Chalcedony also occurs as delicate bands through the veins in colours of pale brown or pale shades of blue and grey. Both forms replace other constituents of the wallrock during silification which accompanies most veins, especially in limestone. Chalcedonic silica commonly replaces limestone, imparting a black shiny appearance to the rock when freshly broken. Quartz is often found in the replaced rock in microcrystalline form.

Dolomite, Ankerite and Chalybdite An abundance of iron, magnesium, manganese and calcium carbonates is displayed in the orefield. Ankerites have replaced dolomites in being considered the most common in the area. The principal components of this are dolomite, ferrodolomite, mangandolomite, and calcite in solid solution.

3.453 Distribution

Fig. 3.3 shows the distribution of the main minerals in the area. The more important belts of Galena occur towards the outer part of the fluorite area in East Allendale, Nenthead, West Allendale, Burtree Pastures and Bolts Burn. Sphalerite is restricted to that part of the field lying west of the Burtreeford disturbance and is of most practical importance in the outermost part of the fluorite zone, the largest area being in the Nenthead district. Chalybdite is most important in the area east of the Burtreeford disturbance, in the fluorite zone. Quartz is most abundant in the innermost part of the fluorite zone. Ankerites are confined to limestone replacement deposits and appear to bear little relationship to the mineral zones.

3.46 Origin and age of the deposits

Wallace (1861) gave the first comprehensive genetic theory in which he concluded that they were formed from downward moving meteoric waters. Dunham (1948) quotes Goodchild (1889) as concluding that the deposits were emplaced "by the agency of thermal springs rising through pre-existing channels under conditions of great pressure", during the cycle of Tertiary igneous activity. He states that this hydrothermal origin first suggested by Goodchild most adequately explains the primary mineralization of the Northern Pennines. The exact age of the primary mineralization has not been conclusively proven (see 1.52) and Dunham presents evidence for either Hercynian or Tertiary date. It is generally accepted that the deposits originated from aqueous solutions which have been shown (Sawkins, 1966) to be concentrated brines with high ratios of K/Na. The depositing temperatures in the fluorite zone ranged from 100-200°C. The origin of the mineral deposits would therefore appear to be rising hydrothermal waters.

3.5 Mining

From the account given by Wallace (1890) and the detailed outline of the history of mining presented by Dunham (1948), it seems certain that mining did not commence in the area until after the conquest in the 11th century. So although much evidence substantiates the presence of the Romans in or near the area, none has been found which supports the possibility of them having worked any mines. On the other hand, Raistrick (1927) and Raistrick and Jennings (1965) site evidence, from the discovery of a pig of lead in 1735 at Nidderdale inscribed with the Roman Emperor Augustus's insignia, that lead mines in the West Yorkshire region of the lower half of the Pennine Orefield were mined by the Romans, particularly the Greenhow Hill mines which are indicated as being under Roman possession around 81 A.D.

Further evidence to mining in the 12th century in Alston Moor was found in documents from the reigns of Henry II, Richard I and Edward IV; these have been summarized by Wallace (1890) and Smith (1923). Most of the Weardale deposits were discovered during the period up to 1650 but no extensive mining was done in the Alston district before this date.

Mining became particularly important in the 18th century after the acquisition of mines at the end of the 17th century by Sir William Blackett and Family, and the developments made by the London Lead Company soon after in the early 18th century. For 200 years these two firms continued their operations, considerably benefiting the wealth of the district. Raistrick (1938) gives a detailed historical account of the London Lead Company from its founding in 1692 to its decline in 1905. The period of greatest activity of this company in the Northern Pennine area took place between 1790-1882. Just prior to this period, the village of Nenthead was founded

by the company as a mining village in 1753. The Nenthead smelt mill was extended and new mine buildings and cottages were erected at this time. Continued extension of the village and mines occurred during the early 19th century, including the construction of the large Rampgill Low washing floor. Mining operations reached their peak in 1870 and then began to decline, particularly in the early 1890s. The decline was offset by activities continued by the London Lead Company who took over operations in Weardale, maintaining substantial outputs of lead until 1931.

Zinc mining in Alston Moor was developed much later, firstly in a minor way by the London Lead Company until 1882, extended to a more important status by the Nenthead and Tynedale Zinc Company up to 1896, and further developed by the Vieille Montague Zinc Company in 1906. This latter company mined in West Allendale for zinc. The main period for zinc production in the area ended in 1921.

The decline of metalliferous mining has been offset by the development of the non-metallic mineral resources of the field. The mining of Witherite was first developed in the mid to late 19th century, with production being important on a world scale.

By far the most important mining at the present time, which has implications with continued zinc contamination, is that for fluorite in the Weardale and Derwent valley areas of the Northern Pennine Orefield. This industry, which was first begun in 1882 by the Weardale Iron Company and continued by the Weardale Lead Company, is now dominated by two large concerns. The first, run by British Steel, controls two main sets of mine workings, those at Whiteheaps mine situated on Bolts Burn, a tributary to the Derwent, and Groverake Mine in the valley of Rookhope Burn, a tributary of the Wear. The second is the Weardale Lead Company who are now a subsidiary of I.C.I., and who control two main mines. These are Redburn

Mine in the Rookhope Valley, and Burtree Pasture Mine on Sedling Burn, a tributary to Kilhope Burn which at its confluence with Burnhope Burn forms the Wear.

3.6 Gillgill Burn and its drainage basin

3.61 Introduction

This section describes in more detail the physiography and geology of Gillgill Burn on which more intensive studies were carried out (Chapter 5). Details of the physiography are given because of the control exerted by this factor on the type of organism able to colonize the stream, and to act as a guide when incorporated with the map (Fig. 3.10) to relocating reaches which may be of interest in future studies. The geology of the substratum is discussed in detail because of its influence on the hydro-geochemistry of the waters and consequent influence on the flora. A subsection on the mining relevant to Gillgill Burn is included at the end because it gives an impression of the activity and length of duration of such mining activity which has influenced zinc levels in Gillgill Burn.

3.62 Physical characteristics and geography

This tributary to the River Nent rises approximately 1.5km to the east of Nenthead village in the Alston Moor division of the Northern Pennine Orefield, county Cumbria. It emerges at a height of 609m as a small spring at the base of a dump of waste tailings, associated with a large complex of disused mine workings (Fig. 3.11). These old tips lie adjacent to the highest point in the area (644m), Kilhope Head, which is on the county border with Durham. They form connections with the tips in mining areas on Coalcleugh Moor several kilometres into Northumberland.

Gillgill Burn is derived from two source streams, and collects further water from three other main tributaries before joining the Nent in

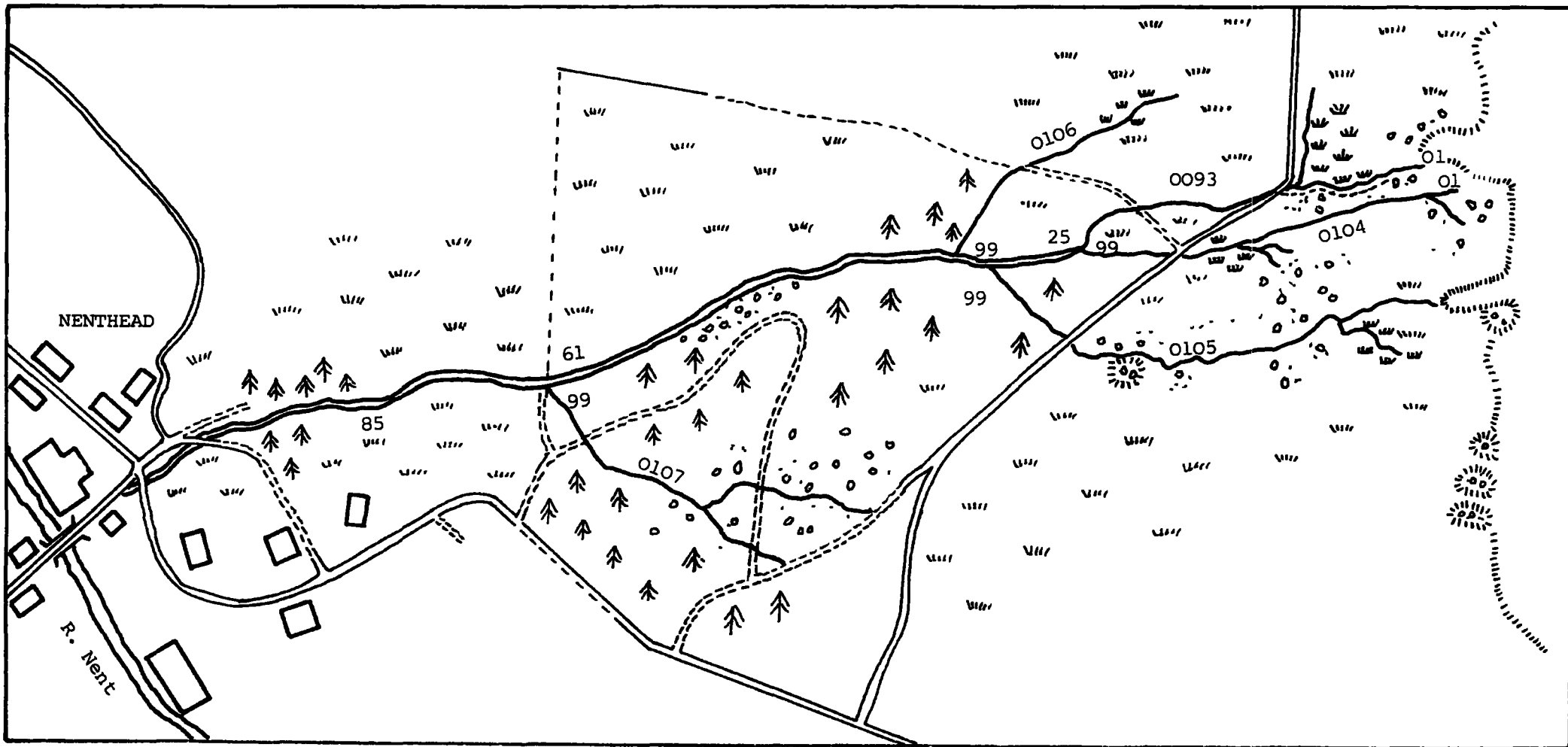


Fig. 3.10 Map to illustrate some of the main reaches on Gillgill Burn and its main tributaries together with some of the more important physiographic features.

coarse tailings and waste dumps
 wet flush areas

Key

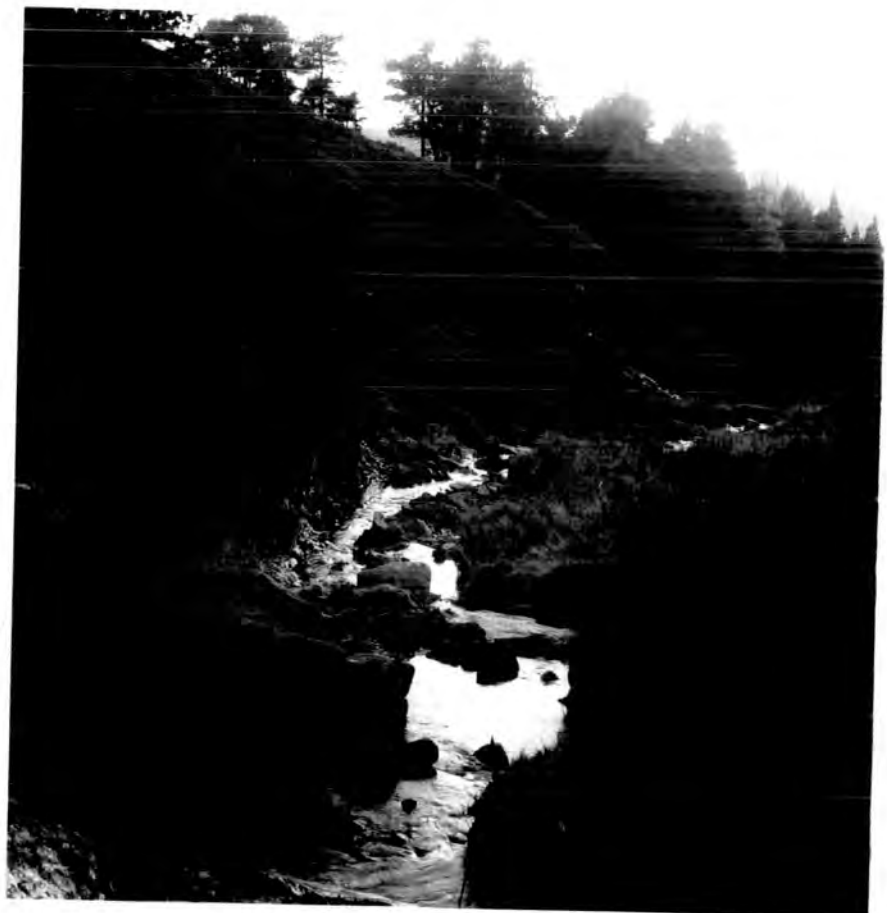
- 0093 Gillgill Burn
- 0104 'Old Mine Gill'
- 0105 'Old Shaft Gill'
- 0106 'Footpath Gill'
- 0107 'Firestone Gill'

in Nenthead village. To avoid confusion in the detailed survey of this basin, one of the sources (which from the old six inch Ordnance Survey map seemed most applicable) was designated as the main stream and the other, together with the three major tributaries, were treated as separate streams (2.321). Since names for these tributaries were not available from the oldest maps consulted, names were derived from the nearest geographical landmark on the map. Fig. 3.10 presents a map which gives the location of the reaches on Gillgill Burn and its tributaries, together with some geographical details concerning the position of the dominant features of the landscape.

Gillgill Burn and 'Old Mine Gill', from their origin a few metres apart in adjacent mine tailings heaps, flow more or less due west as two small streams. Gillgill Burn, after passing for a distance of 50m through a litter of tailings, flows for a short distance over a turf of *Agrostis* spp. before entering a spring mire in the region of reach 08. After seeping through this wetland area, the stream emerges at a point just above the road leading from Nenthead to Allenheads. The stream passes under the road and on appearing at the other side is larger in volume, having received drainage waters from the roadside ditches and flushes bordering the spring mire. This is in the region of reach 11. From here the stream passes through two fields of upland grazing pasture and wet meadow before it plunges fairly abruptly down a steep bank of exposed sandstone boulders to be joined by 'Old Mine Gill' at reach 25. Having now increased both in size and volume, the stream flows over large sandstone boulders, with occasional small waterfalls formed by exposure of the main beds of shale. This is a very steep sided valley with on one side high grassy moorland banks and on the other massive heaps of exposed shale. In the region of reach 32 the main stream receives water from 'Old Shaft Gill'. This is an area where the stream carves a narrow gorge through

Fig. 3.11 The source of Gillgill Burn, as a small spring channel at the base of dumps of coarse tailings and fractured shale.

Fig. 3.12 View of Gillgill Burn in the region of reach 61. Dumps of coarse shale from previous excavations border the stream, as do heaps of tailings (produced by the practice of sorting the ore at the site of removal).



thick beds of shale. Shortly after the bed of the stream becomes littered with flags of sandstone. 'Footpath Gill' joins the main stream several metres above reach 39. Here the height has dropped to 533m and in the sheltered valley coniferous trees (mainly *Picea abies* (L.) Karst) border the stream. The stream continues to flow through a valley bordered sometimes by conifers and grassy banks and at other times exposed tailings heaps (Fig.3.12) or high tips of shale, until it reaches reach 60 where it is joined by 'Firestone Gill'. During this passage the drop is steep, including one high waterfall at reach 50. From here it flows in a series of small pools below waterfalls, alternating with fast flowing stretches over sheets or boulders until reach 85 where it plunges abruptly down a steep waterfall formed by the exposure of the Great Limestone. A small plantation of mature conifers surrounds the burn at this waterfall, providing moderate shade throughout the year. Emerging from this copse the burn enters Nenthead, bordered on one side by a steep bank of meadow and on the other by a number of cottages. It passes under the main road leading from Stanhope to Alston and continues underground for 100 metres beneath an area of rough ground in the village prior to entry into the Nent. The height has dropped here to 430m.

'Old Mine Gill' rises as a small seepage from beneath a heap of mineralized waste in the mining area. It flows due west parallel to the main stream. For the first 150m it rarely forms more than a small trickle between a number of shallow pools under medium to low flow conditions. The bed of the stream consists of fragments of mineralized rock and shale, but for some stretches it flows over a turf of *Agrostis* spp. At reach 71 it enters a flush area from which it emerges with an increased volume due to drainage from this wet area. From here it is bordered by steeper banks of grassland and after passing over exposed sheets of sandstone it enters the main stream.

The source of 'Old Shaft Gill' is a drainage channel on the upper fell above the mine workings. After 100m it reaches the mining complex where it flows around a number of tailings dumps receiving drainage from these. At reach 70 it has considerably increased in volume. From here it drops steeply through a narrow gorge surrounded by high grassy banks. The stream bottom is composed of flags of sandstone. It flows over a stretch of exposed shale bedrock before entering Gillgill Burn. 'Footpath Gill' originates as a spring in an area away from the mine workings 400m west of Gillgill Burn. It flows for 300m due south through upland pasture and wet meadow. From reach 70 it drops steeply through a narrow valley flowing over exposed shale beds and sandstone sheets before entry into the main stream.

The source of 'Firestone Gill' is derived from seepage beneath the base of tailings dumps associated with mine workings to the south of those from which the main stream originates. For 100m the stream percolates through an extensive flush area from which it receives drainage. It emerges from this over a waterfall formed by the exposure of sandstone bedrock. It drops steeply over sandstone boulders before entering Gillgill Burn.

3.63 Geology of Gillgill Burn Area

Gillgill Burn flows through a valley which forms a perfect section through the hillside. Most of the major rock strata become exposed on its passage down to the Nent. The majority of these strata belong to the Upper Limestone Group (or Millstone Grit series - see 3.43). Fig. 3.13 gives an estimated section illustrating the main strata.

Above the source (reach 01), the upper hillside has been subjected to weathering and erosion, exposing layers of coarse sandstone, overlain by thin beds of shale which are covered by thick peat. The sandstone corresponds to the Grindstone, the upper sandstone stratum in the section.

Immediately above and surrounding reach 01 are a number of mine waste dumps composed primarily of shale with mineralized sandstone, and to a lesser extent mineralized limestone. In the original limestone the calcite has been replaced in series by ankerite, siderite and dolomite primarily consisting of magnesium carbonates. Where some of this rock has been exposed to continued weathering it has become dark brown due to the presence of iron oxide. Some of the rocks appear dark where limestone pores which have filled with silica surround the sandstone in a Breccia, becoming cemented by the mineral. The heaps of shale consist of flinty or silicified material, some fractured and enclosing galena and sphalerite. Small fragments of quartz and fluorite lie associated with the mineralized rock.

For the first 150m the stream flows over shale with associated cobbles and chippings of mineralized sandstone and limestone. At reach 11 a change in the oxidation state of ground waters meeting the main stream has caused precipitation of ferric hydroxide so that for the next 200m the stream bed is lined with a coarse silt of shale mixed with this precipitate overlying occasional flags of sandstone. It is not until reach 25 that the passage of the stream begins to reveal large areas of the underlying rock. Here it flows over sheets of sandstone to meet 'Old Mine Gill' at a small waterfall, formed by the exposure of sandstone bedrock which probably corresponds to the High Slate Sill. From here the main stream forms a deep dissection through the rock strata exposing on its way the interbedded shales between the High and Low Slate Sills. From reach 29 to 32 the stream flows over a coarse bedrock of shale and on each side is bordered by extremely high banks of fragmented shale exposed to continual wind erosion. The breaking up and erosion of the shale by the wind, together with occasional land slips, has caused deposits of shale dust to cover the stream bottom. A thin layer of sandstone lies

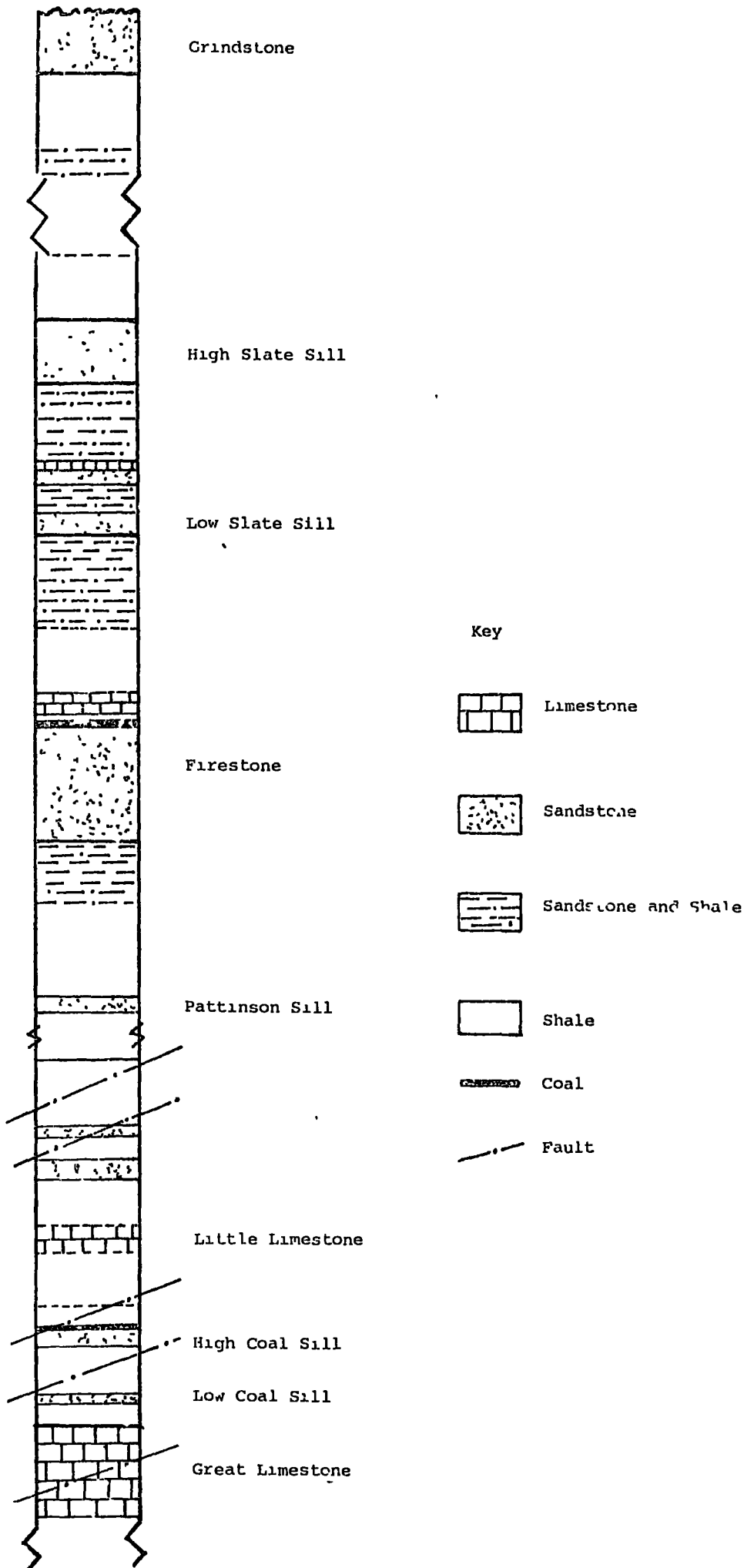


Fig. 3.13 Estimated section of strata for Gillgill Burn.

between the beds of shale corresponding to the Low Slate Sill. 'Old Shaft Gill' enters the stream in this area, flowing down a waterfall over exposed beds of shale. From here the stream bed is littered with boulders of unmineralized sandstone which have broken away from the sandstone bedrock lying above the shale. However the occurrence of occasional mineralized cobbles has increased since the main stream has been fed by 'Old Shaft Gill', presumably by rock brought down by this stream. Within 50m, the third tributary, 'Footpath Gill', joins the main stream. This is just before Gil'gill Burn passes over a small waterfall formed by the exposure of limestone which corresponds to the Crag Limestone. Immediately below the waterfall, associated with the sandstone which follows the limestone, is coal, together with some shale. This overlies sandstone bedrock which continues until reach 50 where it forms a large waterfall plunging deeply down the valley formed by the main stream. The large expanse of sandstone exposed here corresponds to the Firestone Sill. Between reaches 40 and 50 the terrain shows signs of mining activity with at reach 43 the presence of a water leat channel used for washing ore, and indications of a trail crossing the stream, possibly once used by pack horses. Bordering the stream are high tips of shale with some mineralized rock, and an entrance to an old level is evident which may link up with the Coalcleugh level. Below the waterfall at reach 50 for 100m to reach 61 the stream bed consists of sandstone boulders on pebbles and gravels of shale, and this is bordered by heaps of mineralized sandstone, limestone and shale.

At reach 68 a small area of sandstone bedrock is exposed which corresponds to the White Sill or High Pattinson Sill. For 100m this is followed by a bed of shale which at times displays the characteristic dark brown to black colouration of thin seams of coal, or alternatively takes on the bright orange colour of ferric hydroxide where ground waters of different oxidation state meet the main stream. At reach 74 the burn forms a

waterfall over another area of exposed sandstone bedrock which in this case corresponds to the Pattinson Sill. The drop in height to reach 78 is quite sharp and the stream bed again becomes littered with boulders of sandstone lying over a shale substrate. Although not clearly evident, the stream passes over a thin band of limestone rock which is most probably the Little Limestone, since boulders and cobbles of limestone lie amongst the sandstone in this area. Following on to reach 81, and further to 85, the stream flows over slightly thinner bands of sandstone, with at reach 81 a small waterfall being formed at the exposure of one of the bands corresponding to the White Hazle. Interconnecting the bands of sandstone is shale and coal. At reach 85 the stream flows over a large waterfall formed by the exposure of a massive section of limestone strata corresponding to the Great Limestone. After this abrupt drop in height, the burn flows on a flat course to join the Nent. In this region the bed of the stream is composed primarily of shale on which lie varying sizes of sandstone and limestone boulders. By reach 99 the stream has dropped in height from 609m to 432m on entry into the Nent.

'Old Mine Gill' rises from a tip containing strongly mineralized rock. There are cobbles and chippings of mineralized limestone in this waste heap which lies on top of a bed of shale. The stream trickles over this substratum of shale, with tips of waste mine material on each side, with the rocks containing much associated galena and sphalerite. As with the main stream, the valley of this tributary in the upper reaches is very shallow and the drop in height gentle. The first signs of exposed bedrock appear at reach 85 where the stream flows over sheets of sandstone before plunging over a small waterfall formed by the bedrock at reach 99 to meet Gillgill Burn. The sandstone visible here corresponds with the High Slate Sill in the section of Gillgill Burn (Fig. 3.13).

'Old Shaft Gill' in its upper reaches is very similar to 'Old Mine Gill', flowing over a basic substratum of shale bordered on each side by dumps of shale plus mineralized sandstone and limestone. However from reach 70 through to 90 it flows down a steep, abrupt slope where much of the stream bottom is covered with large slabs and boulders of unmineralized sandstone. By reach 99 the exposed bedrock is coarse shale over which the stream flows down to join Gillgill Burn.

The third tributary, 'Footpath Gill', follows the pattern of Gillgill Burn by dissecting deeply into the hillside and revealing a section of the rock strata. From reaches 01 to 70 it forms a 'trickle', with a gentle slope which flows through the upland pasture barely eroding a channel in the hillside. Most of the stream bed is shale, with occasional boulders of sandstone. At reach 70 it plunges steeply, dissecting a narrow valley down the hillside, and on its way exposes various rock strata. The first to appear forms a small waterfall at reach 70, being a bed of sandstone which is a continuation of the High Slate Sill. The stream progresses further down the valley, flowing over beds of sandy shale which in places has a bright orange colour indicating the presence of iron oxides. Lower down, another band of sandstone, the Low Slate Sill, is exposed. A layer of limestone probably connected to the Crag Limestone occurs in the region of reach 90. The stream continues to flow over a shale bed with large slabs and boulders of sandstone until it reaches the main stream.

'Firestone Gill' is formed by seepages from the base of several heaps of coarse shale and mineralized sandstone. At reach 50 it flows over a high waterfall formed by the exposure of a large bedrock of sandstone which corresponds to the Firestone Sill. A short distance from here, in the region of reach 67, the stream drops quite steeply with the whole

of the bottom covered by a thick silt of ferric hydroxide. Again ground waters have reached the surface and entered the main stream where changes in the oxidation state have occurred, causing the iron to precipitate out. This silt covers the stream bed of shale and associated sandstone boulders until it joins the main stream.

3.64 Mining

The mining operations relevant to Gillgill Burn occur in an area designated by Dunham (1948) as Sub Area B - the Nent Valley of Alston Moor, in his original division of the Northern Pennine Orefield. In this valley, particularly surrounding the upper reaches of the Nent, some of the most productive deposits of the orefield have been worked. Most of the early exploitation was carried out in deposits discovered in the higher beds of the Upper Limestone Group, many of which were worked before 1735. After Sir William Blakett discovered rich beds in and around the Great Limestone in West Allendale, the Lords Commissioners of Greenwich Hospital, who owned the royalty to the mines in the Nent Valley, began development. However after 1735 the London Lead Company made the greatest development of the area when the leases of several of the principal mines came into their hands. During this period the adoption of a number of modern methods in mining led to some important changes around Nenthead. The driving of properly engineered horse levels enabled ore to be brought to the surface in wagons. Those at Rampgill, Smallcleugh and Caplecleugh were constructed by the London Lead Company. This meant that instead of dressing the ore at its site of removal, usually a whimsey shaft or opencut, it could be transported to a centralized dressing floor. Two such treatment plants were constructed by the London Lead Company in Nenthead Village to serve the three levels described above. Rampgill level is the main entrance to the workings on the hillside from which Gillgill Burn and its tributaries are derived.

The Nenthead and Tynedale Zinc Company, who took over the leases of mines in Nenthead in 1882 from the London Lead Company, operated the Rampgill dressing floor primarily for zinc concentrates. When the Vieille Montagne Zinc Company succeeded them in 1896, they continued operations and further modified the workings by replacing in 1908 the old dressing floor with a large gravity mill which produced both lead and zinc concentrates. The mill continued to operate until 1921. The modernization of treatment methods and dressing operations at Nenthead has led to the accumulation of large gravel tailings heaps on the slopes bordering the Nent above the village. During the early 1940s, after surveyance of dumps in the area, it was considered economic to rework some of the waste materials for the production of zinc concentrates for war purposes. So in 1942-3 a flotation plant was erected within the earlier mill buildings. The operation, which yielded a reasonable amount of zinc with some lead, has now finished. Where treatment of ore occurred at its site of removal, scattered dumps of coarse rock, some containing much sphalerite, can be seen, as on the surrounding hillsides. These are particularly evident around the upper reaches of Gillgill Burn.

The old mine workings in the area around the source of Gillgill Burn are associated with two main veins which were worked intensively for both lead and zinc ore. These are Rampgill and Scaleburn veins. Rampgill Level forms the main entrance to these two veins, its mouth being situated close to the Nent between the old smelt mill and dressing floor. The level follows a probable continuation of the Scaleburn Vein, but branches before reaching the Smallcleugh Cross Vein, one branch running into Scaleburn Vein, the other into Rampgill.

Rampgill is computed to have been the richest vein in Alston Moor. The working of the mine was carried out during three main periods. The vein was discovered during the first period and was exploited until 1745 from

the Slate Sills, Firestone, White Sill and Pattinson, primarily from surface whimseys. This led to the accumulation of gravel tailings heaps around the area of Gillgill Burn. The London Lead Company acquired the mine in 1745-6 and opened up ground from the Pattinson Sill to the Great Limestone. This proved to be the richest ever worked in Alston Moor. Two main levels were sunk to gain access to the vein, one driven from Firestone bridge in the area of 'Firestone Gill' to command the Firestone Sill, the other was the Rampgill horse level itself. Both commenced soon after 1800. The use of the horse level halted the expansion of waste tips higher up on the hillside around 'Old Mine Gill' and 'Old Shaft Gill', but increased the size of waste dumps on the borders of the Nent in the village next to the dressing floors. The Vieille Montagne Zinc Company were effective in the third period which began in 1896, by reworking a north-easterly part of the mine for zinc ore. They extended workings to the base of the Scar Limestone from which oreshoots were exploited in the Quarry Hazle, Four Fathom Limestone and Slatey Hazle. The sinking of the shaft to the lower Little Limestone discovered no further oreshoots. Rampgill vein, which can be traced from Nunnery Hill south-west of Nenthead to Carrshield Moor in West Allendale, a distance of nearly five kilometres, is continued as the White Wood vein before linking with the Barney Craig Level. Scaleburn Vein is not as rich as Rampgill. It extends from the Great Cross vein to Coalcleugh West Cross vein, a distance of three kilometres, and is continued into West Allendale as the Low Coalcleugh vein. Although productive in the Firestone, the main bearing ground in the vicinity of Patterdale vein was worked from the top of the Great Limestone to the Little Limestone and in the Pattinson Sill. Smith (1923) states that the richest portion of the vein in Cumbria lies 30 fathoms each side of Gillgill, with work carried out in all strata between Pattinson Sill and Quarry Hazle. Much lead was obtained from the Girdle Beds and intervening beds of Plate under the Firestone, but none from the Four Fathom Limestone. The vein has been worked in similar strata in West Allendale.

3.7 The Climate

3.7.1 General background description

The Northern Pennine moorlands have been described by Manley (1936) as comprising "the most consistently elevated and chilly part of England". He describes climatic observations made by him at this time as confirming the "prevailing impression of bleakness associated with a windy and damp upland which correspond well with records at sea level in Southern Iceland". In 1932 a small weather station was established by Manley at Moorhouse, 14.5km S.S.E. of Alston. It was later taken over by the Nature Conservancy and designated as a research station. A climatological station has been maintained there since May 1952, at an elevation of 556m. Since this elevation is close to the height at which many of the streams and reaches are situated in the study area, and since Moorhouse is closely situated to the areas of interest, it was felt that the climatic observations available from this station would be indicative of the general conditions of the whole area at this elevation. Also this was the only station available in the study area with continuous records.

The results of meteorological observations at Moorhouse have been summarized for those made during the period 1906-1935 by Manley (1943), and for the period 1953-62 by Millar (1964). Extracts from these observations have been used in the present study, together with observations made available for the period 1972-75 by the Meteorological office, Bracknell, Berkshire, in an attempt briefly to compare, contrast and evaluate the more important climatic features assumed to be of importance in controlling vegetational growth in the streams, and input of zinc indirectly through their influence on flooding, drainage and weathering of mineral rocks. These latter aspects of climatic importance are discussed later, and only a general impression of the climate is discussed here.

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
1972	-0.1	-0.1	2.1	3.8	6.3	7.3	10.5	10.3	7.2	6.3	1.8	1.8
1973	0.9	-0.1	2.6	2.0	6.8	10.7	11.2	11.3	9.4	5.3	1.7	0.5
1974	1.9	1.5	1.3	3.5	6.5	8.5	10.3	10.5	7.5	3.3	2.7	3.3
1975	2.5	1.3	0.5	3.8	4.7	9.8	12.3	14.2	8.3	6.3	2.4	2.0
average	1.3	0.65	1.6	3.3	6.1	9.1	11.1	11.6	8.1	5.3	2.2	1.9

Table 3.1 Average monthly air temperatures at Moorhouse during the years 1972-1975

3.72 Temperature

Table 3.1 summarizes the mean daily air temperatures at Moorhouse for each month during the years 1972 to 1975. Table 3.2 compares the mean values for each month during this four year period to the mean values of air temperatures given by Manley (1943), and Millar (1964) for the years 1906-1935 and 1953-1962 respectively. Millar states that the average annual temperature of the years 1953-1962 was 5.3°C , which compares to 4.7°C , 5.2°C , 5.1°C and 5.7°C for the years 1972-1975 respectively. He also suggests that from the literature 5.6°C is a temperature at which significant growth of plants takes place. If the data for the mean monthly temperatures (Table 3.1) is regarded, it can be seen that only between the months of May and October does the temperature equal and exceed this value. Clearly, at this elevation the growing season is limited by the duration of low air temperatures. From information provided by Millar it seems that the air temperatures surrounding the reaches lower down in the stream valleys can be on average as much as 2.8°C higher. He also estimates that for terrestrial vegetation, a drop in 180m can add on approximately one month to the growing season. January and February show the lowest mean air temperatures which in 1972 and 1973 fell below freezing point, whilst the warmest months are July and August. Air frosts were recorded in every month except July and August during the years 1972-75, with the exception of one frost which was recorded in July 1972.

At elevations of 548m or more, the climate in this area can be regarded as relatively extreme, and since many of the reaches are as high, or are approaching this height, the colonisation of the streams will be limited to organisms which can also tolerate the extremes of temperature.

years	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	reference
1906-1935	0.56	0.34	1.2	3.4	7.1	10.4	11.6	11.4	9.1	5.7	2.5	1.1	Manley (1943)
1953-1962	-0.28	-0.62	1.5	3.9	7.0	9.7	11.1	11.0	9.5	6.8	3.2	1.2	Millar (1964)
1972-1975	1.3	0.65	1.6	3.3	6.1	9.1	11.1	11.6	8.1	5.3	2.2	1.9	

Table 3.2 Comparison between the mean monthly air temperature at Moorhouse for the years indicated

3.73 Rainfall and Snow

As Millar (1964) observed "the effect of increase of altitude is to increase the frequency and duration of rain as well as adding to its quantity". Thus from Tables 3.3 and 3.4 the mean monthly rainfall figures and yearly averages for the various periods quoted are high. The average annual rainfall of 1,880mm between 1953-1962 at Moorhouse, when compared with 863mm for the annual figure at Newton Rigg, a weather station in the Eden Valley, aptly illustrates this fact. This high annual average is maintained between 1972-1975, ranging from 1,585mm in 1975 to 2,230mm in 1974. Apart from the year 1974, the other three years were well below the long term average rainfall value between 1953-1975 of 2,009mm. During the period from 1972-75 the wettest months were January, November and December, the driest being October. Millar suggests from his data that the upland position of Moorhouse accentuates the seasonal rainfall curve, so that when compared to Newburn Rigg (at 170m) December is disproportionately wetter than May. From this it would seem that sites along the valleys of the Rivers Nent, West and East Allen, and South Tyne were probably drier on the whole than the upper moorland sites. Table 3.5 gives the days of snowfall at Moorhouse for the periods quoted. It can be seen that falls of snow have occurred in every month of the year except for July and August. January, February, and possibly also March, demonstrate on average long periods of snow cover. From personal observations, and those outlined by Millar, it seems that the lower parts of Alston Moor experience at least nearly the same frequency of snowfall as the higher areas such as Moorhouse, but that the snow lies for a markedly longer period at the elevated sites. During the frequent trips made to this area it was often observed during the winter months that snow would persist on the upper slopes bordering the River Nent above 540m, when lower down in the valley no trace of snow remained.

year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
1972	198	92	150	158	223	159	104	97	30	42	328	206
1973	123	129	74	121	131	66	112	179	83	119	116	233
1974	365	215	152	16	75	118	154	92	189	133	272	449
1975	341	32	97	141	43	69	179	120	236	65	150	112
average	257	117	127	109	118	103	137	122	135	90	217	250

Table 3.3 Average monthly rainfall (mm) at Moorhouse during the years 1972-75

year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	reference
1936-1941	165	152	146	102	95	102	152	178	114	190	165	216	Manley (1943)
1953-1962	201	151	98	114	117	100	166	184	158	190	169	226	Millar (1964)
1972-1975	257	117	81	109	118	103	137	122	135	90	217	25	

Table 3.4 Comparison between the mean monthly rainfall (mm) figures at Moorhouse during the years indicated

year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	reference
1972	22	25	10	3	0	0	0	0	0	0	14	7	
1973	9	10	7	11	3	0	0	0	0	4	10	15	
1974	20	11	13	3	3	1	0	0	3	8	11	11	
1975	16	2	19	10	1	2	0	0	1	0	8	8	
1972-75	17	12	12	7	2	0.75	0	0	1	3	11	10	
1936-41	17	17	17	8	1	0.1	0	0	<0.1	2	6	12	Manley (1943)

Table 3.5 Number of days with snow cover per month at Moorhouse for the years indicated

The influence of rainfall on the streams and rivers in this area is discussed in more detail elsewhere (Chapter 9).

3.74 Sunshine

Table 3.6 summarizes the hours of sunshine in average monthly figures for the period of the present study, and also compared to previous measurements made at Moorhouse. The months of May to August demonstrate the longest hours of sunshine, with November, December and January the shortest.

Millar shows that at the higher altitudes of stations such as Moorhouse, the duration of sunshine is naturally reduced by the increased cloudiness when compared with valley sites such as Newton Rigg. The reduction is more marked at higher altitudes and Millar compares Great Dun Fell (847m) to both Moorhouse and Newton Rigg and shows the annual duration of sunshine for the period of the study to be 873h, 1,192h and 1,341h respectively.

It can be concluded that sites such as the source of Gillgill Burn at 609m, although having an open exposure throughout the year, will generally experience less sunshine than much lower sites such as the Nent at Alston (260m).

year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	reference
1972	0.49	1.08	3.22	3.08	3.38	4.75	5.29	5.22	3.76	3.10	0.94	1.16	
1973	1.25	2.66	4.11	3.90	4.93	5.51	4.85	5.14	3.16	2.05	2.50	0.80	
1974	0.45	1.31	2.96	6.44	5.97	5.99	3.80	4.18	2.98	1.25	0.82	0.47	
1975	0.29	2.79	3.28	3.45	7.20	7.91	4.70	7.09	4.08	2.67	1.98	1.20	
1972-75	0.62	1.96	3.40	4.22	5.37	6.04	4.66	5.40	3.50	2.27	1.56	0.90	
1955-62	1.18	1.83	2.71	4.27	5.74	6.16	4.61	4.38	3.49	2.81	1.38	1.03	Millar (1964)

Table 3.6 Average hours of sunshine per day per month for the years indicated at Moorhouse

4 COMPARATIVE STREAM STUDIES

4.1 Introduction

In the first section of this chapter the results from the preliminary reconnaissance trips to the areas listed in 2.21 are presented. These were intended to act as a guide for the choice of the main reaches and to give an indication of the extent of zinc enrichment in streams draining the Orefield. From these results 25 stream sites carrying more than $\text{mg l}^{-1}\text{Zn}$ (at least during one of the surveys) were chosen for more intensive study. The choice of $\text{mg l}^{-1}\text{Zn}$ was made because this level and levels above it had been shown in the literature to be toxic to certain organisms (Williams and Mount, 1965).

Following this in 4.22, the mean values for the parameters measured at the sites are given and the variations in water chemistry are discussed individually for each reach. In 4.23 the results of an intervariable correlation analysis (2.522) are given. This was performed on the data to determine the most significant relationships between variables, with particular emphasis on zinc. The results of a factor analysis (2.523) are presented in 4.24 in which the data were further simplified to indicate the underlying controls on the water chemistry and the possible influences on the availability of zinc.

With regard to the flora, an investigation is made of the extent to which communities of algae may be recognized at the various levels of zinc (4.3) with brief comments made on the distribution of individual species.

4.2 Water chemistry

4.21 Preliminary reconnaissance trips

The results of sampling carried out in the eight sub-areas listed in 2.21 are summarized under the five main areas of the Orefield by the following:

area	counties/ main rivers	no. of streams sampled	no. of streams <0.1mg l ⁻¹ Zn	no. of streams 0.1-1mg l ⁻¹ Zn	no. of streams >1mg l ⁻¹ Zn
Allendale	Northumberland/ E. and W. Allen	25	8	16	1
Alston Moor	Cumbria/S. Tyne and Nent	56	12	29	15
Derwent catchment	Northumberland/ Derwent	16	12	3	1
Teesdale	Durham/Tees	40	22	18	0
Weardale	Durham/Wear	52	25	24	3

The majority of streams carrying more than 1mg l⁻¹Zn were found to be located in Alston Moor. However zinc enrichment is extensive throughout the Orefield if this is judged by the number of streams in each catchment area with more than 0.1mg l⁻¹Zn. The river catchment with the smallest proportion of streams carrying significant levels of zinc was found to be that of the Derwent. From the geological description of the Orefield (Dunham, 1948) it can be seen that this area corresponds with the outer limits of the main lead-zinc bearing strata. The number of mineral veins present is considerably smaller than in the other areas.

From the information obtained during these trips the 25 main reaches for more detailed study were chosen and the results of the surveys are presented in the subsequent sections.

name of stream	stream no.	reach no.	O.D. - 420	conductivity (Micromhos)	pH	total alkalinity	total hardness (mg l ⁻¹ CaCO ₃)	Ca hardness	Mg hardness	Na	K	Mg	Ca	Al	Mn	Fe	Cu	Zn	Cd	Pb	PO ₄ -P	NH ₄ -N	NO ₃ -N	SO ₄ -S	SI	Cl
Rocknape Burn	0012	26	0.018	215	7.5	46.7	145	104	33.8	6.9	3.6	8.2	41.5	0.17	1.29	0.31	0.041	2.80	0.005	0.056	0.010	0.18	0.24	19.0	3.00	15.0
River Nent	0048	12	0.014	301	8.0	91.0	200	134	61.0	7.4	3.4	14.8	53.6	<0.03	0.097	0.19	0.005	2.90	0.009	0.051	0.006	0.07	0.12	20.2	2.13	14.8
River Nert	0041	10	0.007	267	8.8	35.3	133	94.0	35.0	6.9	2.1	8.5	37.5	0.18	0.207	0.86	0.004	1.38	0.003	0.093	0.022	0.14	0.17	24.1	2.18	16.8
River Nert	0048	99	0.008	349	8.2	105	195	150	43.8	8.4	3.3	10.7	60.0	0.03	0.074	0.16	0.003	1.07	0.004	0.075	0.024	0.30	0.18	17.9	2.14	15.1
Boils Burn	0071	95	0.015	293	7.9	81.3	135	97.4	30.8	19.8	5.8	7.5	39.0	0.86	0.430	0.73	0.010	1.24	0.003	0.420	0.007	0.25	0.28	12.9	4.80	17.7
River west Allen	0085	10	0.004	126	6.9	20.6	61.8	41.5	17.3	6.2	1.8	4.2	16.6	0.13	0.142	0.09	0.002	1.41	0.005	0.041	0.010	0.17	0.17	6.9	2.60	15.0
Gudran Gill	0092	20	0.016	87.0	7.3	14.5	39.8	25.5	11.7	3.7	1.0	2.0	10.2	0.05	0.120	0.42	0.003	0.95	0.003	0.038	0.014	<0.01	0.36	1.2	2.50	13.0
Gillgill Burr	0093	01	0.018	133	6.2	8.0	82.6	45.5	20.4	4.4	2.0	4.9	18.2	1.34	0.662	0.20	0.005	6.70	0.042	0.564	0.012	<0.01	0.18	11.3	2.01	12.2
Gillgill Burn	0093	95	0.008	137	7.3	27.8	66.6	46.6	17.6	7.0	1.5	4.3	18.7	<0.03	0.056	0.11	<0.002	1.29	0.006	0.071	0.046	0.28	0.28	11.3	1.96	23.3
Scale Burn	0094	10	0.007	70.0	5.2	-	25.4	7.8	12.5	5.5	0.76	3.0	3.1	0.81	0.198	0.09	0.003	0.94	0.003	0.195	0.007	<0.01	0.08	22.2	1.45	13.8
Pampgill Level	0096	01	0.007	432	8.0	149	300	196	99.4	8.2	4.4	24.2	78.3	<0.03	0.141	0.13	0.002	2.67	0.005	0.027	0.014	0.33	0.21	21.1	3.68	13.2
Do gang Level	0097	01	0.011	559	8.0	176	393	261	121	9.2	6.5	29.4	104.6	<0.03	0.192	0.03	0.003	6.70	0.019	0.005	0.003	0.14	0.14	31.3	3.70	11.2
'Sraie Burn' Level'	0098	01	0.025	200	7.4	95.0	204	146	51.0	14.6	3.5	12.8	58.4	0.05	0.213	0.31	0.005	3.76	0.005	0.106	0.161	0.37	0.55	3.5	3.10	14.2
Garrigall Burn	0102	15	0.021	204	7.5	80.0	127	96.2	28.6	4.3	2.8	7.0	38.5	0.09	0.038	0.32	0.002	0.89	0.003	0.053	0.009	0.02	0.09	7.5	1.79	12.7
Brown Gill	0103	08	0.056	69.5	5.8	2.0	28.3	17.0	6.4	5.9	1.6	1.5	6.8	0.49	0.342	0.69	0.005	0.80	0.002	0.415	0.017	0.06	0.29	4.9	0.73	14.0
'Old Mine Gill'	0104	01	0.002	167	6.0	12.0	95.6	41.4	16.2	3.2	1.2	3.9	16.6	0.86	0.318	0.04	0.004	22.3	0.058	1.60	0.011	0.34	0.24	3.8	1.92	12.5
'Old Mine Gill'	0104	99	0.008	150	6.4	8.5	38.7	20.9	7.4	11.8	1.2	1.8	8.4	0.92	0.153	0.07	0.003	4.37	0.017	0.262	0.016	0.03	0.08	1.2	1.71	22.7
'Old Snaft Gill'	0105	99	0.018	131	6.4	9.5	41.2	22.4	9.5	7.5	1.1	2.3	9.0	0.34	0.092	0.12	0.002	4.96	0.014	0.144	0.011	0.42	0.11	1.84	2.15	16.6
'Firestone Gill'	0107	17	0.005	117	6.3	7.7	41.2	10.7	16.7	8.2	1.3	6.1	6.4	0.40	0.106	0.03	0.005	12.5	0.043	1.44	0.008	0.74	0.33	2.7	1.95	12.6
'Brown Gill Tributary'	0108	08	0.042	86.0	5.4	-	33.1	13.6	6.8	5.4	3.7	1.7	5.4	0.32	0.142	0.30	0.007	7.0	0.029	1.26	0.015	0.06	0.30	10.5	0.58	15.5
'Redburn Fluch'	0111	01	0.012	1593	7.5	153	714	527	180	162	19.1	43.8	211.0	0.07	0.066	0.06	0.010	4.61	0.006	0.057	0.007	0.83	1.35	144.6	2.88	266.0
Ta trace Level	0113	01	0.006	331	7.6	106	336	238	76.0	10.0	7.0	18.4	95.2	0.28	4.59	0.30	0.098	8.20	0.017	0.100	0.005	0.31	0.21	35.0	3.25	15.8
'Cookshold Stream'	0151	20	0.068	1977	7.5	228	284	524	2290	873	24.8	556	210	4.20	4.30	1.20	0.020	0.91	0.005	0.008	0.017	1.10	0.49	600.0	7.40	99.3
'Hudgill Adit' *	0168	01	-	-	6.8	42.0	146	48.4	96.0	4.0	2.5	23.3	19.4	0.08	0.029	0.13	0.006	0.60	0.006	0.065	-	-	-	-	-	-
'Tributary to Hudgill Adit' *	0169	01	-	-	6.7	47.0	179	6.9	170.0	3.2	2.5	41.2	2.8	0.06	0.208	0.11	0.010	1.14	0.008	0.064	-	-	-	-	-	-

Table 4.1 Representative water chemistry for 25 reaches in the comparative stream studies. Values given are the means of four samples taken during low flows between March 1974 to June 1975. (* indicates reaches sampled twice.) Element values are expressed in mg l⁻¹. (- denotes variable not measured.)

4.22 Descriptive account

The mean values from respective surveys for the key chemical parameters measured at each of the reaches is given in Table 4.1. The results for each reach are discussed briefly below.

Rookhope Burn 0012/26

This reach reflects the direct influence of discharge from an adit (Tailrace Level) situated further upstream. The levels of all of the cations measured were elevated considerably, when compared with a reach on the Burn above this adit (see Table 6.1). Of the metals, Mn, Zn and Cd were the most enriched. The effect of this groundwater discharge is also marked by an increase in the concentrations of Mg, Ca, total hardness, pH, SO_4 -S and Si.

River Nent 0048/12, 0048/20, 0048/99

The water chemistries of each of these three reaches illustrate the influence of mine water discharge on a river throughout its length. Reach 0048/12, situated above the village of Nenthead, is directly below the discharge of mine waters from three adits. As a consequence, the levels of pH, total alkalinity, total hardness, Mg and Ca are comparatively high. The heavy metals Zn and Cd are enriched, but Cu and Pb levels remain low. At reach 0048/20, below Nenthead village, total hardness, conductivity, Mg, Ca and Zn have all decreased, whereas the metals Al, Mn, Fe and inorganic P and N have all increased. Further downstream at reach 0048/99, in Alston, just before the confluence of the River Nent with the River South Tyne, changes occur again, reflecting the variable tributary waters. Na, K, Mg, Ca,

total hardness, total alkalinity and conductivity have all increased. The levels of Al, Mn, Fe, Cu and Pb have dropped, whereas Zn and Cd have remained steadily high. Inorganic P and N have continued to rise slightly.

Bolts Burn 0071/99

The chemistry of this tributary to the River Derwent reflects the influence of mine drainage water input from its surrounding catchment area, and from the actively used fluorspar mine situated in its upper reaches. The levels of total alkalinity, total hardness, Na, K, Mg, Ca and Si are all comparatively high, as are the levels of the heavy metals Zn, Cd and Pb.

River West Allen 0085/10

This reach receives some input from groundwater draining from old mine workings which causes increases in total alkalinity, total hardness, pH, and Mg and Ca, particularly when compared with the source water in the upper reaches (cf. Table 6.1) which is derived almost exclusively from atmospheric precipitation draining through peat. The levels of zinc and other heavy metals are also elevated.

Gudham Gill 0092/20

This stream receives very little groundwater input, deriving most of its water from surface runoff, from both the surrounding fells and adjacent old mine waste tailings heaps. The latter source provides the slight total alkalinity and hardness present, and also the elevated Zn levels. This is one of the six sites which does not maintain a consistently high average concentration of Zn above 1mg l^{-1} . This is a result of the

intermittant source of Zn from waste tailings runoff, in which the levels of Zn would rely on factors such as the volume of water supplied as rain.

Gillgill Burn 0093/01, 0093/95

The source of Gillgill Burn at reach 0093/01 is a small spring in which water emerges from a channel in the upper rock strata (which are predominantly sandstone) beneath a waste tailings heap. The strata are heavily mineralised with Zn and Pb and as a result the slightly acid water is enriched with these two metals, together with Cd. The levels of total alkalinity, total hardness, Mg and Ca are relatively low, reflecting the acid nature of the rocks through which the water has percolated.

The lower reach, 0093/95, is situated in the village of Nenthead just prior to the entry of Gillgill Burn into the River Nent. The different water chemistry, when compared with the reach at the source, reflects the entry of various dilution waters. The levels of pH, total alkalinity, inorganic P and N have risen, whereas the metal content has dropped, with the exception of zinc which maintains a comparatively high level.

Scale Burn 0094/10

The source of water for this stream comes from drainage off the peat covered upper fells. As a consequence, the conductivity is low, the pH is acidic, and there is no total alkalinity. The concentrations of Na, K, Mg and Ca are extremely low when compared with the values for other sites on the survey. The elevated levels of Zn and Pb are supplied by runoff from tailings heaps bordering the stream.

Rampgill Level 0096/01, Dowgang Level 0097/01 and Scaleburn Level 0098/01

These three adit waters, although containing minor differences in water chemistry (dependent on local differences in rock strata through which the particular ground waters have filtered) can be discussed together because of the similarity in general source of the waters.

In complete contrast to the previous site, the chemistry of these adit waters is influenced by carbonate-rich ground waters. Much of the water filters through the lower rock strata which are predominantly carboniferous limestones. It also passes over localised metalliferous ore deposits associated with these strata. As a result of these influences the water has high values for pH, total alkalinity, total hardness, Mg and Ca, and also Zn and Cd. Pb levels are low.

Garrigill Burn 0102/15

Although this stream primarily collects its waters from surface drainage over the upper fell areas, it does receive some groundwater input as it passes through an old disused set of mine workings. Consequently the pH, conductivity, total alkalinity and hardness values are high; the levels of Mg and Ca are moderately high; whereas the heavy metal levels, apart from Zn, are all comparatively low.

Brown Gill 0103/08 and 'Browngill Tributary' 0108/08

Because of the similar sources, and proximity of these two stream sites, they are discussed together. The comparatively high O.D., low conductivity and acidic pHs indicate the influence of peat drainage waters, as do the low total alkalinity, total hardness, Mg and Ca values. Conversely, the levels of most of the metals, including Al, Fe, Zn and Pb are all high, indicating the important influence of surface drainage from the old mine waste tailings that border the upper reaches of both streams.

'Old Mine Gill' 0104/01, 0104/99

Although situated on the same stream, these two sites differ in water chemistry. Reach 0104/01 is at the source of the stream and has higher values for conductivity, total alkalinity, hardness, Mg and Ca, reflecting the subterranean origin of the water which seeps out beneath a waste tailings heap. Reach 0104/99 (the last reach on this stream before it joins Gillgill Burn) receives dilution from peat drainage and seepage from surrounding flush areas, and consequently contains lower levels of Mg, Ca and total hardness. The heavy metal content at the source of this stream is the highest encountered of all the sites surveyed.

'Old Shaft Gill' 0105/99

This stream reach demonstrates a similar water chemistry to 0104/99, having very similar influences. The water is relatively soft, with low values for Mg and Ca. The high levels of Zn and Cd reflect seepage from tailings heaps.

'Firestone Gill' 0107/17

This site receives surface drainage from a wide expanse of waste tailings, together with waters seeping continuously from acidic flush areas. As a result of this the water is soft, relatively acid, and enriched with heavy metals, in particular Zn and Pb.

'Redburn Flush' 0111/01

This site contrasts markedly with the last six sites in many respects. It is hard, alkaline and carries high levels of Na, K, Mg and Ca. The origin of this calcareous, base-rich water is seepage from beneath

a large tailings heap of an actively used fluorspar mine. The levels of heavy metals are all relatively low, with the exception of Zn. The very high total ionic concentration is demonstrated by the high conductivity value, and the elevated levels of $\text{SO}_4\text{-S}$ and Cl .

Tailrace Level 0113/01

The adit water flowing from this underground channel receives mine waters from a large number of subterranean shafts and levels. It also receives excess mine water from locally active fluorspar mines. Consequently the water carries elevated levels of Mn, Cu, Zn and Cd, and, because of its calcareous origin, high concentrations of Mg and Ca.

'Cookshold Stream' 0151/20

This is the only stream in this survey not situated in the main study area (see 3.36). It carries high levels of Al, Mn, Fe, Cu, Zn and Cd because of contamination from acid mine drainage waters seeping from beneath a colliery spoil heap associated with an abandoned coal mine. The water which originates as a spring on the magnesium limestone remains very hard and alkaline, with high levels for Na, K, Mg and Ca even after receiving drainage from the mining area.

'Hudgill Adit' 0168/01 and 'Tributary to Hudgill Adit' 0169/01

The two stream waters originate in adjacent areas and are influenced by ground waters, since they both emerge from subterranean channels. They both show higher levels of Mg than Ca, contrasting with other adit waters. Values for total alkalinity, hardness and pH are relatively high, whereas apart from Zn other metal concentrations are low.

4.23 Intervariable correlation analysis

In order to establish the relationships between variables in these waters, in particular those involving Zn, the total data for the 24 key chemical parameters was cross-correlated (for the method and rationale see 2.522). The results of this procedure are given in Table 4.2.

A very strongly cross-correlated group of variables is formed by Na, K, Mg, Ca, conductivity, pH, total alkalinity, the hardness factors, $\text{SO}_4\text{-S}$ and Si . The majority of these positive correlations are highly significant ($P = 0.001$). Another small group of highly cross-correlated variables is formed by Zn, Cd and Pb. Particularly significant is the positive correlation between Zn and Cd ($P = 0.001$). Zn is negatively correlated with Fe ($P = 0.001$) and pH ($P = 0.01$), and weak negative correlations are shown between Zn and $\text{PO}_4\text{-P}$ ($P = 0.05$) and Zn and Cl ($P = 0.05$).

Other significant correlations between variables excluding Zn, but which may be relevant to its chemistry, include the following. Pb shows a series of strong negative correlations with Na, K, Mg, Ca, pH, conductivity and total alkalinity. Cd shows similar trends, but none of the correlations are significant. Pb correlates highly with Al ($P = 0.001$). Al, Mn, Fe and Cu form a small group of inter-correlated metals. Fe correlates highly with O.D. ($P = 0.001$), as does Pb ($P = 0.01$), whereas Zn forms an insignificant negative correlation with O.D. Pb negatively correlates with $\text{SO}_4\text{-S}$ ($P = 0.005$), whereas Zn and Cd form slight positive correlations. All three metals are negatively correlated with Si; however the only significant correlation involves Pb ($P = 0.001$).

	O.D - 420	conductivity	pH	total alkalinity	Na	K	Mg	Ca	Al	Mn	Fe	Cu	Zn	Cd	Pb	PO ₄ -P	NH ₄ -N	NO ₃ -N	SO ₄ -S	Si	Cl	total hardness	Ca hardness	Mg hardness
O.D - 420	1.000			-0.285*					0.237*		0.512***	0.283**			0.264**		-0.324**	0.241*	-0.429**	-0.376**	-0.263**			
conductivity		1.000	0.771***	0.878***	0.564***	0.781***	0.847***	0.852***	-0.344**		-0.221*				-0.558**				0.604**	0.649**	0.333**	0.870**	0.652**	0.843**
pH			1.000	0.790***	0.497***	0.661***	0.792***	0.795***	-0.665**				-0.291**		-0.802**				0.424**	0.597**		0.774**	0.795**	0.792**
total alkalinity				1.000	0.772***	0.846***	0.910***	0.945***	-0.367**						-0.649**		0.361**		0.694**	0.688**	0.361**	0.943**	0.945**	0.910**
Na					1.000	0.635***	0.483**	0.660**		0.272*		0.207*			-0.336**		0.345**		0.616**	0.488**	0.442**	0.574**	0.660**	0.433**
K						1.000	0.783***	0.788***	-0.210*	0.311**		0.339**			-0.468**	-0.287**			0.711**	0.562**	0.260**	0.838**	0.788**	0.783**
Mg							1.000	0.780***	-0.387**			0.243**			-0.609**				0.742**	0.634**		0.951**	0.780**	1.000**
Ca								1.000	-0.361**	0.203*					-0.607**				0.701**	0.631**		0.900**	1.000**	0.780**
Al									1.000	0.404**		0.309**			0.568**						-0.230**	-0.375**	-0.361**	-0.387**
Mn										1.000	0.309**	0.479**									0.229**			
Fe											1.000	0.382**	-0.382**	-0.355**				-0.222**	0.265**					
Cu												1.000						0.426**	0.257**			0.283**		0.243**
Zn													1.000	0.787**	0.376**	-0.203*								
Cd														1.000	0.400**	-0.330*								
Pb															1.000				-0.392**	-0.532**		-0.581**	-0.607**	-0.609**
PO ₄ -P																1.000	0.282**				0.218**			
NH ₄ -N																	1.000		0.477**		0.523**			
NO ₃ -N																		1.000						
SO ₄ -S																			1.000	0.386**	0.516**	0.706**	0.701**	0.742**
Si																				1.000		0.628**	0.631**	0.634**
Cl																					1.000			
total hardness																						1.000	0.904**	0.953**
Ca hardness																							1.000	0.787**
Mg hardness																								1.000

Table 4.2 Interveriable correlation matrix for the chemical data for 25 reaches in the comparative stream survey (* = P<0.05, ** = P<0.01, *** = P<0.001)

4.24 Factor analysis

The results of the intervariable correlation indicated a number of complex interrelations between variables. Factor analysis (Reeder *et al.*, 1972) was used to evaluate relations among the inorganic chemical components. In this way it was hoped that the data might be "reduced" to a smaller set of factors or components that might be taken as "source variables" accounting for the observed interrelations in the data. The first step in re-arranging the data was to find the principal components (eigenvectors) of the correlation matrix.

4.241 Principal component analysis

Using the method outlined in 2.523, a set of principal components was obtained from the total comparative stream data, giving an indication of the eigenstructure of the data. These are presented in Table 4.3. Since this was a preliminary step in 'simplifying' the data, the results will not be discussed at length since it has been emphasized that the results of the subsequent principal factor analysis produce the information which can be interpreted and discussed in terms of controls over the water chemistry (Dawdy and Feth, 1967; Reeder *et al.*, 1972).

From the table it is evident that six principal components have been extracted which account for over 80% of the variance in the correlation matrix. The first principal component is characterised by high positive loadings for K, total hardness, Ca, $\text{SO}_4\text{-S}$ and Si , and a negative loading for Pb. The second features positive loadings for Al, Mn, Cd and Pb together with O.D., opposed by a negative loading for pH. The third is characterised by positive loadings for Zn, Cd, inorganic N and $\text{SO}_4\text{-S}$, opposed by negative loadings for O.D. and Fe. The fourth has positive loadings for Fe and inorganic P, this time opposed by negative loadings

variable	principal component						communality
	I	II	III	IV	V	VI	
O.D. - 420		0.629	-0.401				0.769
conductivity	0.707		0.491				0.886
pH	0.433	-0.746					0.885
total alkalinity	0.815						0.871
Na	0.732						0.912
K	0.959						0.953
Mg	0.878						0.970
Ca	0.916						0.959
Al		0.781					0.808
Mn	0.463	0.419				0.551	0.848
Fe			-0.564	0.483			0.840
Cu						0.704	0.825
Zn			0.574	-0.619			0.877
Cd		0.566	0.443	-0.526			0.866
Pb	-0.598	0.593					0.896
PO ₄ ^{-P}				0.438			0.217
NH ₄ ^{-N}			0.551				0.728
NO ₃ ^{-N}			0.408		0.573		0.799
SO ₄ ^{-S}	0.608		0.462		-0.478		0.941
Si ₄	0.766						0.715
Cl	0.610		0.389		0.520		0.834
total hardness	0.932						0.982
Ca hardness	0.916						0.959
Mg hardness	0.878						0.970
eigenvalue	9.468	3.502	2.612	1.896	1.454	1.379	
per cent of variance explained by principal component							
	39.5	14.6	10.9	7.9	6.1	5.7	
cumulative per cent of variance							
	39.5	54.0	64.9	72.8	78.9	84.6	

Table 4.3 Principal components derived from the correlation coefficient matrix for 25 sites in the comparative stream survey

for Zn and Cd. The fifth principal component has $\text{NO}_3\text{-N}$ and Cl weakly opposed by $\text{SO}_4\text{-S}$. The sixth features positive loadings for Cu and Mn.

4.242 Principal factor analysis

Following the first stage in the 'simplifying' of the data, a principal factor analysis was performed, using the iteration procedure (Kim, 1975) described in 2.524. This was intended to reduce the information to a set of factors which might be interpreted, with reference to the geology of the area, as influencing the chemical relations of the waters.

The R-mode varimax factor matrix (Wallis, 1965) of the chemical data from 90 samples of the 25 streams is shown in Table 4.4. Six factors account for the total variance in the data. The loadings of the ions on these factors are illustrated diagrammatically in Fig. 4.1. The rectangular boxes represent the factors, and the centre line marks the loading equal to zero for the variables. The positive loadings occur above the centre line and the negative loadings below. The further an ion is away from the central line, the higher is its loading.

The first factor accounts for over one half of the variance among the ions. It is represented by high factor scores for total alkalinity, Ca, Cu hardness, followed by Mg hardness, Mg, conductivity, pH and K. High loadings are also demonstrated for $\text{SO}_4\text{-S}$, Si, Na and Cl. This group of positive loadings is opposed by a high negative loading for Pb and to a lesser extent Al. This indicates that there are mutually exclusive components in the system and consequently that some of the ions may be controlled by mineral equilibria (9.211).

The second factor is marked by high loadings for Zn and Cd, with a weak loading for Pb. These are opposed by a negative loading for Fe. The

Variable	factor						communality
	1	2	3	4	5	6	
O.D. - 420					0.757		0.764
Conductivity	0.858						0.837
pH	0.833						0.901
total alkalinity	0.950						0.999
Na	0.594			0.538			0.788
K	0.824						0.819
Mg	0.858			0.359			0.927
Ca	0.943						0.927
Al			0.499	0.386			0.600
Mn			0.807				0.725
Fe		-0.423	0.373		0.670		0.818
Cu			0.674				0.600
Zn		0.880					0.801
Cd		0.872					0.903
Pb	-0.696	0.504					0.818
NH ₄ N						0.721	0.611
NO ₃ N					0.347		0.170
SO ₄ S	0.702			0.364		0.336	0.838
Si	0.657						0.511
Cl	0.396			0.691		0.412	0.844
total hardness	0.931						0.957
Ca hardness	0.947						0.932
Mg hardness	0.860			0.353			0.926
eigenvalue (principal component)	10.164	2.864	2.193	1.463	0.830	0.681	
Per cent of variance explained by factor	55.9	15.7	12.1	8.0	4.6	3.7	
cumulative per cent of variance	55.9	71.6	83.7	91.7	96.3	100.0	

Table 4.4 R-mode varimax factor matrix of chemical data for 25 stream and river sites in the comparative stream survey

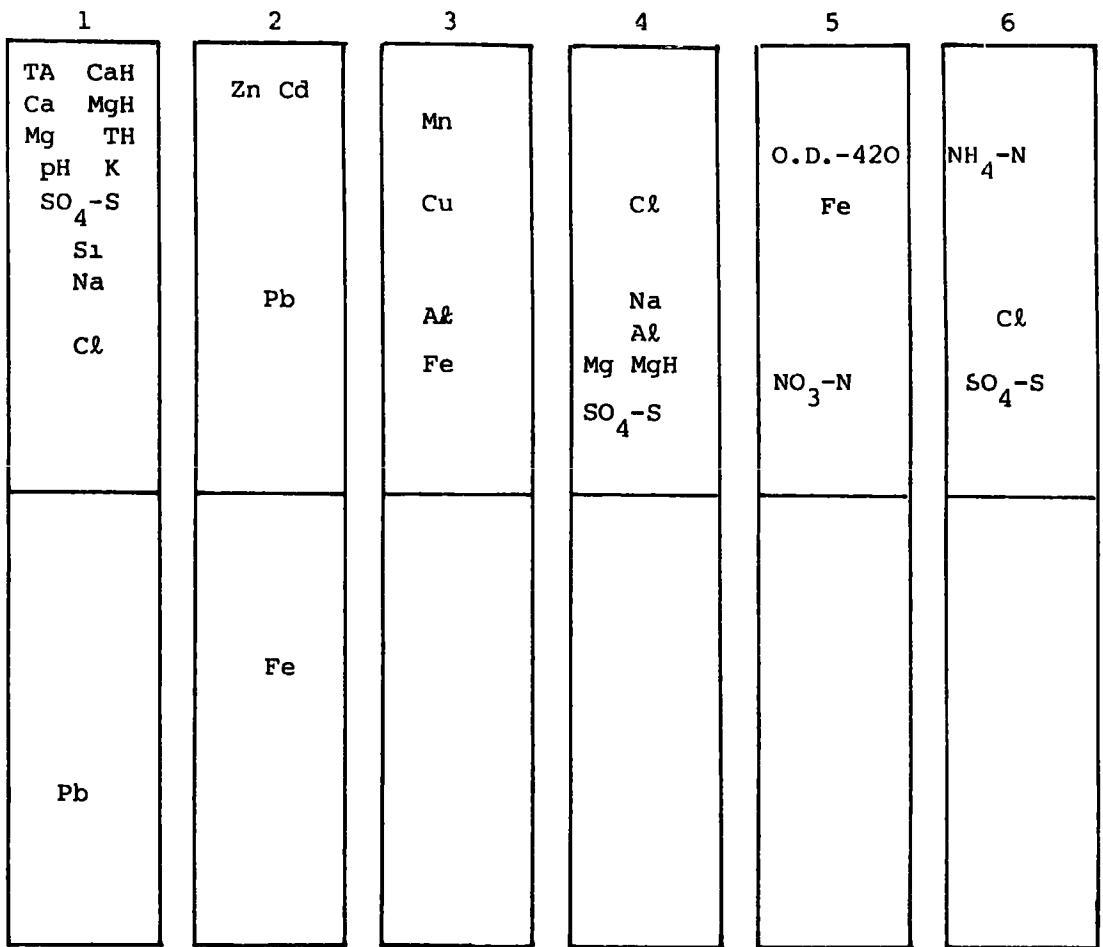


Fig. 4.1 Diagrammatic representation of factors from R-mode varimax solution of chemical data for 25 stream sites in the comparative stream survey.

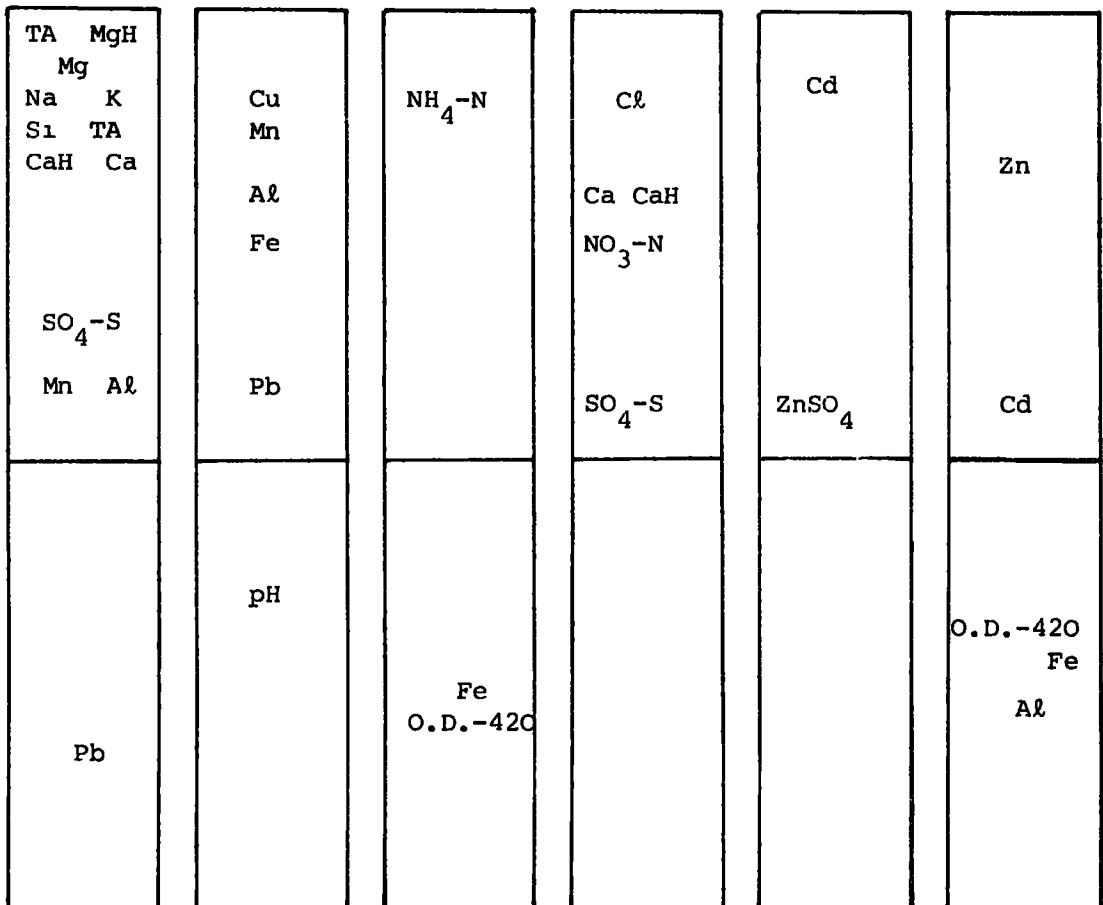


Fig. 4.2 Diagrammatic representation of factors from R-mode varimax solution of chemical data for 14 reaches influenced by ground waters (TA = total alkalinity; TH = total hardness; CaH = calcium hardness; MgH = magnesium hardness.)

factor accounts for 77% of the variance of Zn and 76% of the variance of Cd in the samples studied.

Factor three is represented by the other heavy metals, with particularly high loadings for Mn and Cu.

The fourth factor is primarily a Na-Cl factor, with lower loadings for Al, Mg, Mg hardness and $\text{SO}_4\text{-S}$. The sums of the squares of the coefficients of the cations Al and Mg ($0.387^2 + 0.360^2 = 0.279$) are almost equal to the sums of the squares of the anions $\text{SO}_4\text{-S}$ and Mg hardness ($0.364^2 + 0.354^2 = 0.258$), whereas the coefficients for Na and Cl are very similar, thus indicating that the influence of this factor is primarily controlled by the sources of Na and Cl (Dawdy and Feth, 1967).

Factor five is characterised by high loadings for O.D. and Fe, with a small contribution by $\text{NO}_3\text{-N}$.

The final factor is an 'anionic factor' with high factor scores for the ammonium ion which accounts for over 50% of the variance of this ion, and small contributions from Cl and $\text{SO}_4\text{-S}$.

The occurrence of certain ions in more than one factor implies that multiple controls may be exerted by these factors (Dawdy and Feth, 1967).

Some of the results obtained from this analysis of the total data, pointed towards two broad divisions within which the waters could be classified. These were ground waters (eg. adits) or water courses predominantly influenced by groundwater input, and surface waters which derived their supply almost exclusively from the atmosphere, and surface drainage.

Because of the important difference in the origin and supply of these waters, the data were divided into two groups characterised by the streams considered to be most representative of these divisions, and further analysed to see if any major differences in the controls on the chemistry could be identified.

The first group consisted of the groundwaters and included 14 of the 25 stream sites. The group was characterised by all of the adits, and sites on streams or rivers below input from adits and subterranean channels of deep origin.

The second group included all drainage waters from tailings heaps, and streams whose origin was primarily from surface runoff. Also included in this group were streams whose source was spring water issuing from the upper or surface rock strata.

4.25 Ground waters

4.251 Intervariable correlation analysis

As with the total data, the information on the groundwaters was subjected to a bivariate correlation procedure (2.522), to establish whether any of the previous significant correlations might be altered. The results are presented in Table 4.5. One of the most noticeable differences is a general increase in the correlations between Na, K, Mg, Ca, the hardness factors, total alkalinity, conductivity, Si and $\text{SO}_4\text{-S}$, indicating a stronger interrelationship between these variables in the waters of subterranean origin.

A series of negative correlations occur between Fe and variables in the above cross-correlated group (eg. total alkalinity, K, Mg and Ca).

variable	O.D. - 420	conductivity	pH	total alkalinity	Na	K	Mg	Ca	Al	Mn	Fe	Cu	Zn	Cd	Pb	PO ₄ -P	NH ₄ -N	NO ₃ -N	SO ₄ -S	Si	Cl	total hardness	Ca hardness	Mg hardness		
O.D. - 420	1.000	-0.326*		-0.305*				-0.140*	0.190**		0.455***						0.372**	0.359**	-0.424**	-0.286*			0.290*			
conductivity		1.000		0.865***	0.570**	0.739***	0.875***	0.570**			-0.626**		0.416**	0.629***	-0.567**				0.581***	0.491***	0.453***	0.877***	0.870***	0.875***		
pH			1.000	0.371*					-0.555**		-0.373*	-0.346*														
total alkalinity				1.000	0.588**	0.719***	0.870***	0.891***			-0.481**		0.307*	0.462*	-0.607**				0.518**	0.608**		0.596**	0.631**	0.870***		
Na					1.000	0.770***	0.371**	0.696**	0.305**	0.445**			0.304**				0.355**	0.366**	0.492**	0.605**	0.444**	0.574**	0.696**	0.371**		
K						1.000	0.670**	0.823**	0.424**	-0.297*	0.257*	0.404**	0.364**	-0.343**				0.572**	0.587**	0.365**	0.808**	0.823**	0.670**			
Mg							1.000	0.698**			-0.431**	0.270*	0.418**	-0.441**					0.505**		0.896**	0.698**	1.000**			
Ca								1.000			-0.318**	0.496**	0.354**	-0.490**				0.642**	0.519**		0.932**	1.000**	0.698**			
Al									1.000	0.542**	0.589**	0.553**			0.302*		0.347**				0.302*					
Mn										1.000	0.375**	0.563**								0.481**						
Fe											1.000	0.398**	-0.268*	0.424**					-0.372**			-0.393**	-0.319**	-0.431**		
Cu												1.000			0.373**			0.406**								
Zn													1.000	0.604**					0.349*			0.446**	0.496**	0.271*		
Cd														1.000				0.432**	0.614**		0.479**	0.356**	0.418**			
Pb															1.000					-0.368**		-0.476**	-0.498**	0.441**		
PO ₄ -P																1.000	0.547**									
NH ₄ -N																	1.000	0.534**		0.540**						
NO ₃ -N																		1.000								
SO ₄ -S																			1.000	0.305*	0.587**	0.661**	0.642**	0.677**		
Si																				1.000		0.516**	0.519**	0.505**		
Cl																					1.000					
total hardness																						1.000	0.932**	0.896**		
Ca hardness																							1.000	0.698**		
Mg hardness																									1.000	

Table 4.5 Interveriable correlation matrix for 14 sites in the comparative stream survey influenced by ground waters (* = P<0.05, ** = P<0.01, *** = P<0.001)

Positive correlations between Zn and K ($P = 0.005$) and Ca ($P = 0.001$) became apparent, as do correlations with Ca hardness, and total hardness. Cd shows a similar pattern but with less significant correlations. However Pb still retains highly significant negative correlations with these variables. By separating these ground waters from the other waters, significant correlations between Zn and SO_4-S , and also Cd and SO_4-S , are introduced into the matrix. Cd is highly correlated with Si ($P = 0.005$).

4.252 Factor analysis

As before, the data for the ground waters were further simplified. Principal component analysis was performed to determine the eigenstructure of the data, and this was followed by a principal factor analysis (2.523) to determine an interpretable set of factors which might influence the underlying structure, and relations within the data set.

4.2521 Principal components

Six principal components were obtained to explain the variance in the correlation matrix. These are presented in Table 4.6. The first principal component shows high loadings for K, Mg, total hardness and Mg hardness, moderate loadings for Ca, Ca hardness, Na, Si , Cl, SO_4-S , O.D. and conductivity, and small loadings for Al and Mn. These are opposed by a small negative loading for Pb.

The second is characterised by positive loadings for Fe, O.D. and Al, which are opposed by negative loadings for Cd and to a lesser extent Zn.

The third principal component features positive loadings for Al, Cu, Pb, SO_4-S and inorganic N opposed by the negative loading for pH.

variable	principal component						communality
	I	II	III	IV	V	VI	
O.D. - 420	0.650	0.570					0.855
conductivity	0.626	-0.583	0.464				1.042
pH			-0.594				0.505
total alkalinity	0.753	-0.492					0.904
Na	0.792						0.918
K	0.970						0.964
Mg	0.923						0.970
Ca	0.889						0.953
Al	0.590	0.524	0.428				0.860
Mn	0.521			0.602			0.796
Fe		0.850					0.796
Cu			0.413	0.646			0.806
Zn		-0.421		0.665	0.456		0.896
Cd		-0.537		0.668			0.811
Pb	-0.514		0.573				0.807
PO ₄ ^{-P}						0.803	0.834
NH ₄ ^{-N}			0.585				0.820
NO ₃ ^{-N}			0.556		0.551		0.815
SO ₄ ^{-S}	0.586		0.473		-0.520		0.940
Si ₄	0.753						0.699
Cl	0.594				0.514		0.918
total hardness	0.958						0.981
Ca hardness	0.889						0.953
Mg hardness	0.923						0.970
eigenvalue	9.756	3.455	2.823	2.057	1.713	1.009	
per cent of variance explained by	40.7	14.4	11.8	8.6	7.1	4.2	
cumulative per cent of variance	40.7	55.0	66.8	75.4	82.5	86.7	

Table 4.6 Principal components derived from the correlation coefficient matrix for 14 stream sites in the comparative stream survey, influenced by ground waters

The fourth is characterised by high loadings for the heavy metals Mn, Cu, Zn and Cd.

The fifth principal component contains positive loadings for Zn, $\text{NO}_3\text{-N}$ and Cl which are opposed by a negative loading for $\text{SO}_4\text{-S}$.

The final principal component features a high positive loading for the ammonium ion alone.

4.2522 Principal factors

The R-mode varimax rotated factor matrix of the ground waters is shown in Table 4.7, and the loadings of the ions are diagrammatically represented in Fig. 4.2.

The first factor which accounts for over 50% of the variance in the data is characterised by high loadings for total hardness, Mg, Mg hardness, with smaller contributions from Na, K, Ca, Ca hardness and total alkalinity. The small positive loadings of $\text{SO}_4\text{-S}$, Al and Mn also contribute to this factor. These are all opposed by a moderate negative loading for Pb.

The second factor features positive loadings for Al, Mn, Fe and Cu, with a small contribution from Pb, which are weakly opposed by the negative loading of pH.

The third factor shows $\text{NH}_4\text{-N}$ and $\text{SO}_4\text{-S}$ opposed by negative loadings for O.D. and Fe.

The fourth factor is characterised by positive loadings for Cl, Ca, Ca hardness, conductivity, $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$.

The fifth factor features a high loading for Cd, and to a lesser extent conductivity, with small contributions from Zn and $\text{SO}_4\text{-S}$.

variable	factor						Communality
	1	2	3	4	5	6	
O.D. - 420			-0.627				0.619
conductivity	0.318		0.336	0.437	0.717		0.975
pH		-0.309				0.435	0.361
total alkalinity	0.739						0.835
Na	0.843						0.848
K	0.811			0.503			0.960
Mg	0.933						0.994
Ca	0.725			0.614			0.988
Al	0.357	0.627				-0.448	0.767
Mn	0.390	0.755					0.752
Fe		0.546	-0.473			-0.303	0.708
Cu		0.821					0.728
Zn					0.330	0.737	0.701
Cd					0.853	0.326	0.870
Pb	-0.719	0.378					0.721
NH ₄ N			0.707				0.539
NO ₃ N				0.512			0.354
SO ₄ S	0.438		0.582	0.397	0.347		0.840
Si	0.754						0.671
Cl				0.828			0.811
total hardness	0.936						0.995
Ca hardness	0.725						0.988
Mg hardness	0.933						0.994
eigenvalue (principal component)	3.270	3.310	2.045	1.536	1.058	0.801	
per cent of variance explained by factor	51.4	18.4	11.4	8.5	5.9	4.4	
cumulative per cent of variance	51.4	69.8	81.2	89.7	95.6	100.0	

Table 4.7 R-mode varimax factor matrix of chemical data for 14 stream or river sites influenced by ground waters

The final factor is characterised by positive loadings for Zn and Cd together with pH, opposed by negative loadings for O.D., Al and Fe.

The high communality figures for Mg and Ca indicate that the variance of each is well explained by the factors which have been extracted.

Conversely the low figures for pH and inorganic N indicate that other components are necessary before their variance in these groundwaters is explained satisfactorily. The existence of mutually exclusive components in four of the factors indicates that a number of equilibria control the relationships between ions in these waters (Dawdy and Fith, 1967).

4.26 Surface waters

4.261 Intervariable correlation analysis

The intervariable correlation matrix for waters of surface origin is given in Table 4.8. It is apparent, when comparing this with Table 4.5, that there is a reduction in the number of significant correlations between variables in the surface waters. This is particularly noticeable with respect to Na, K, Mg, Ca, total alkalinity, pH and the hardness factors.

With regard to Zn, a number of correlations that were evident in the groundwaters are lost. Most notable are those between Zn and Ca, Ca hardness and K. However, a strong positive correlation is introduced between Zn and Al ($P = 0.005$). The negative correlation between Zn and Fe is strengthened ($P = 0.001$ cf. $P = 0.05$ for groundwaters). The high correlation between Zn and Cd is increased, and where Zn was uncorrelated with Pb in the ground waters, they become highly positively correlated ($P = 0.001$) in the surface waters.

	O.D. - 420	conductivity	pH	total alkalinity	Na	K	Mg	Ca	Al	Mn	Fe	Cu	Zn	Cd	Pb	PO ₄ -P	NH ₄ -N	NO ₃ -N	SO ₄ -S	Si	Cl	total hardness	Ca hardness	Mg hardness		
O.D. - 420	1.000	0.454**	-0.423**	-0.603**		-0.353*	-0.563**	-0.493**			0.570**	0.426**			0.432**											
conductivity		1.000					0.495**	0.528**			-0.751**	-0.346**	0.470**	0.539**				-0.360*		0.399**			0.626**	0.528**	0.495**	
pH			1.000	0.670**			0.430**	0.416**				-0.336**			-0.638**		0.364*			0.453**	0.469**		0.305**	0.416**	0.430**	
total alkalinity				1.000			0.498**	0.565**	-0.695**						-0.544**		0.577**						0.471**	0.565**	0.497**	
Na					1.000												0.333*				0.558**					
K						1.000		0.301*											0.570**				0.298*	0.301*		
Mg							1.000	0.703**			-0.490**									0.472**			0.830**	0.703**	1.000	
Ca								1.000			-0.321**									0.429**			0.868**	1.000	0.703**	
Al									1.000	0.434		0.351**	0.422**	0.453**	0.580**											
Mn										1.000		0.405**						-0.373**					-0.351*			
Fe											1.000		-0.546**	-0.514**				0.357**					-0.320*	-0.553**	-0.321*	-0.490**
Cu												1.000	0.281*		0.526**			0.380**					-0.392**	-0.434**		
Zn													1.000	0.948**	0.700**								0.538**			
Cd														1.000	0.709**								0.601**			
Pb															1.000								-0.394**	-0.368**		
PO ₄ -P																1.000										
NH ₄ -N																	1.000						0.554**			
NO ₃ -N																		1.000								
SO ₄ -S																			1.000				0.408*			
Si																				1.000			0.402**	0.430**	0.472**	
Cl																					1.000					
total hardness																							1.000	0.678**	0.843**	
Ca hardness																								1.000	0.725**	
Mg hardness																									1.000	

Table 4.8 Interveriable correlation matrix for 11 surface waters in the comparative stream survey
 (* = P<0.05, ** = P<0.01, *** = P<0.001)

Cd shows a similar pattern of correlations to Zn, but with in general, lower orders of significance. Pb also demonstrates a similar pattern with the inclusion of a positive correlation with Cu. The loss of significant negative correlations between Pb and Mg, Cu, the hardness factors and total alkalinity again contrasts with the situation for the groundwaters.

4.262 Factor analysis

4.2621 Principal components

The eigenstructure of these data was found to be determined by seven principal components, compared with six in the results of the previous analysis (Table 4.9).

The first principal component is dominated by high loadings for total alkalinity, the hardness factors, Mg, Ca and pH, opposed by negative loadings for O.D., Fe and Cu. This contrasts with the first principal component of the groundwater matrix which included positive loadings for Na, K, Al and Mn. The high negative loading for Pb has also disappeared.

The second principal component includes positive loadings for Al, Cu, Zn, Cd and Pb, opposed by negative loadings for pH, total alkalinity and Fe. The reverse situation was found with the second principal component for the groundwaters where Al and Fe were opposed by negative loadings for Zn and Cd.

The third principal component for the surface waters is almost exclusively a Na-Cl component with equal loadings for these two ions; with a small contribution from $\text{SO}_4\text{-S}$.

variable	principal component							communality
	I	II	III	IV	V	VI	VII	
O.D. - 420	-0.767							0.804
conductivity	0.718							0.897
pH	0.681	-0.450						0.782
total alkalinity	0.822	-0.469		0.430				1.131
Na			0.754			0.424		0.829
K				0.578				0.513
Mg	0.757						-0.494	0.943
Ca	0.778							0.949
Al		0.702						0.669
Mn					-0.660			0.809
Fe	-0.591	-0.478						0.822
Cu	-0.448	0.405		0.521				0.750
Zn		0.881						0.972
Cd		0.924						0.902
Pb		0.848						0.926
PO ₄ -P						0.782		0.738
NH ₄ -N					0.594			0.736
NO ₃ -N				0.586	0.479			0.751
SO ₄ -S			0.530	0.454			-0.511	0.985
Si ₄	0.554							0.673
Cl								0.888
total hardness	0.756	0.513						0.949
Ca hardness	0.785							0.956
Mg hardness	0.765						-0.487	0.952
eigenvalue	6.750	4.573	2.502	2.093	1.706	1.423	1.263	
per cent of variance explained by principal component	28.1	19.1	10.4	8.7	7.1	5.9	5.3	
cumulative per cent of variance	28.1	47.2	57.6	66.3	73.4	79.4	84.6	

Table 4.9 Principal components derived from the correlation coefficient matrix for 11 surface waters in the comparative stream survey

The fourth principal component shows positive loadings for K, Cu, $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$, contrasting with the same component for the groundwaters which was characterised by positive loadings for Mn, Cu, Zn and Cd.

The fifth principal component shows positive loadings for inorganic N opposed by the negative loading of Mn, where previously for the groundwaters, Zn and $\text{NO}_3\text{-N}$ were opposed by the negative loading of $\text{SO}_4\text{-S}$.

The sixth principal component features $\text{PO}_4\text{-P}$ loading with Na, in contrast to the exclusive ammonium ion component of the groundwaters. The additional seventh principal component shows negative loadings for Mg, Mg hardness and $\text{SO}_4\text{-S}$.

4.2622 Principal factors

Although it was not possible to include one or two variables (such as cadmium and sulphate) in the principal factor analysis, because of a reduced number of cases with these ions (see section 2.522), the R-mode varimax rotated matrix presented in Table 4.10 shows that six factors account for the variance and covariance within the data set on this collection of waters. Fig. 4.3 illustrates the loadings of particular variables on these factors.

Factor one, which accounts for nearly 47% of this variance, is dominated by a high loading for Mg and its respective hardness component, in which 95% of the variances of these variables is explained by this factor. Moderately high loadings are demonstrated by total hardness, Ca, Ca hardness, conductivity and pH. There is a small negative loading of Mn in this factor. When compared with the first factor of the groundwaters, it can be seen that the high contributions of the Na, K and Si have disappeared, as has the high negative loading of Pb.

variable	factor						communality
	1	2	3	4	5	6	
	0.644		0.568		0.393		1.000
pH	0.435	-0.470	0.507				0.757
Na				0.842			0.745
K					0.465		0.286
Mg	0.970						0.987
Ca	0.747	-0.314			0.496		0.971
Al		0.701					0.635
Mn	-0.379	0.308	-0.331				0.380
Fe		-0.528	-0.365	-0.321			0.624
Cu		0.356	-0.517				0.581
Zn		0.894					0.841
Pb		0.874	-0.363				0.944
NO ₃ N						0.825	0.731
Si			0.685				0.533
Cl				0.908			0.848
total hardness	0.853				0.388		0.934
Ca hardness	0.752	-0.313			0.492		0.973
Mg hardness	0.978						1.000
eigenvalue (principal component)							
	6.531	2.740	1.973	1.067	0.986	0.633	
per cent of variance explained by factor							
	40.9	19.7	14.2	7.7	7.1	4.5	
cumulative per cent of variance							
	46.9	66.6	80.7	88.4	95.5	100.0	

Table 4.10 R-mode varimax factor matrix of chemical data for 11 stream or river sites primarily of surface origin

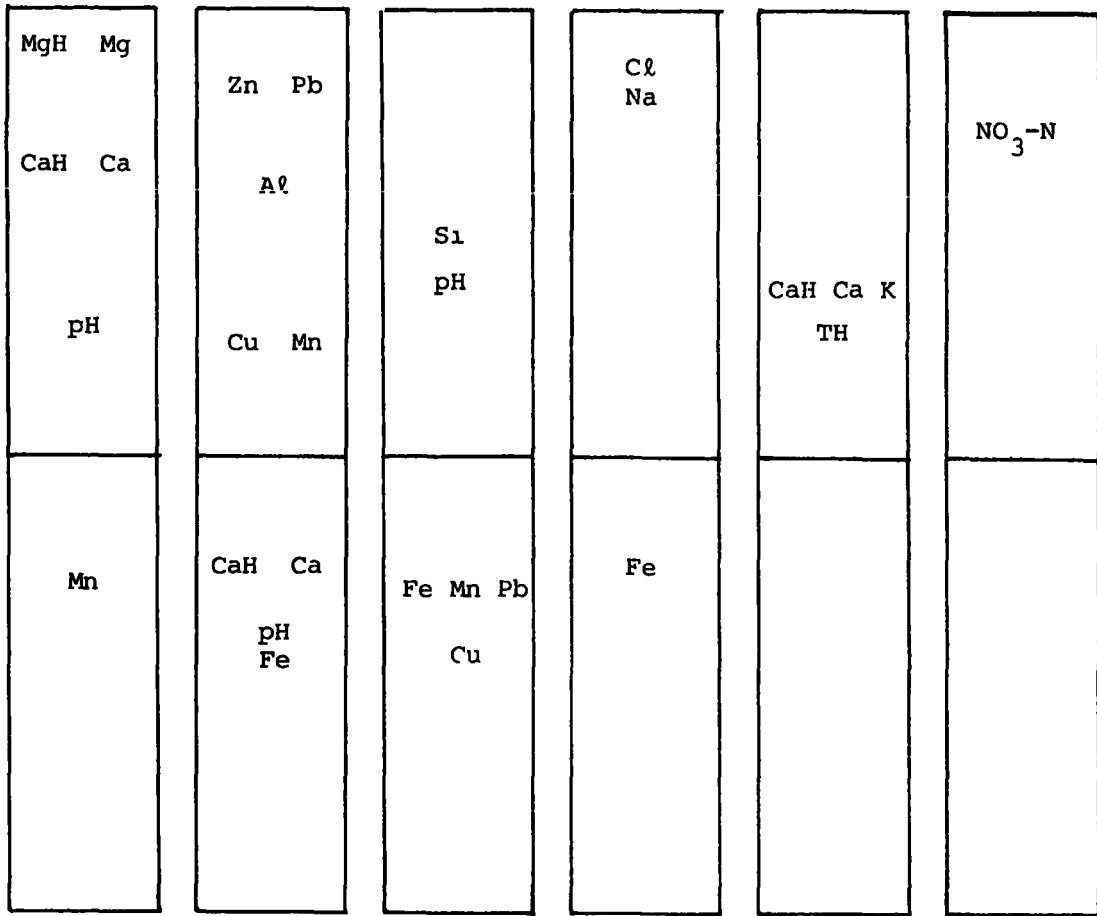


Fig. 4.3 Diagrammatic representation of factors from R-mode varimax solution of chemical data for 11 reaches primarily of surface origin (TA = total alkalinity; TH = total hardness; CaH = calcium hardness; MgH = magnesium hardness.)

The second factor is exclusively a heavy metal factor dominated by high positive loadings for Zn and Pb, and low contributions from Cu and Mn. This contrasts markedly with the situation with the ground waters, where Zn was not featured at all on the second factor, and Cu and Mn had high loadings, with Pb making a small contribution. This factor accounts for 80% of the variance in the zinc ion. Important contributions are given to this factor by moderate negative loadings for Fe, pH, Ca and Ca hardness.

The third factor features moderate positive loadings for Si, conductivity and pH, with moderate negative loadings for the heavy metals. This contrasts with the ammonia-sulphate factor for the groundwaters. The higher proportion of mutually exclusive components in the first three factors for the waters of surface origin would seem to suggest a stronger control exerted by mineral equilibria in these waters than in those of subterranean origin.

The fourth factor is more or less exclusively an Na-Cl factor, accounting for approximately 80% of the variance of both ions in these waters.

The fifth factor features moderate positive loadings for Ca, Ca hardness, K, conductivity and total hardness.

The final factor is exclusively a nitrate factor which accounts for over 60% of the variance in the data of this ion. This contrasts again with the final factor for the groundwaters which featured Zn and Cd, opposed by O.D., Fe and Al.

The generally high communality figures suggest that the majority of the variance exhibited by ions in these waters is adequately explained by the factors extracted. The only ion which stands out is K, which shows a low communality figure, contrasting with the very high figure demonstrated in the groundwaters.

If Figs. 4.1, 4.2 and 4.3 are compared, it can be seen that the major differences between the structure and loadings of the factors justify the division of these waters into two main sorts based on their origin. However, although in each case, including the total data, six factors can be extracted to account for the variance in the respective data it can be seen that the first two factors are dominated by (i) the source of Na, K, Mg, Ca, total alkalinity and the measures of hardness, and (ii) the sources of the primary heavy metals in the area Cu, Zn and Pb.

4.3 Flora of high zinc-level streams

4.3.1 Algae

This section describes the distribution of algal species found at the reaches in terms of the possible 'associations' they might form in relation to increasing levels of zinc. Using the method described in 2.355, an 'association table' was constructed (Table 4.11). The reaches at the top of the table are arranged in order of decreasing zinc from left to right. The delimitation of communities was based on the distribution of species in relation to decreasing zinc levels. The table includes data furnished from subjective abundance values (see section 2.355).

Although there are some species which have a reduced distribution, appearing to be restricted to sites carrying high levels of zinc, these reaches nevertheless display a moderate species diversity with respect to the microflora. A small 'association' is formed by eight species which are almost totally confined to reaches carrying the highest zinc levels. The most abundant of these species are *Phormidium* sp. (>2≤4μm), and *Synechococcus* sp. (>8≤16μm) together with *Caloneis lagerstedtii* and *Achnanthes marginistriata*. The overall communities at these high zinc

Table 4.11 'Association table' of algae sampled during the comparative stream survey. Reaches are arranged from left to right in order of decreasing levels of zinc. Species are arranged to show distribution throughout the range of zinc levels. For more details see text and Section 2.

concentrations are dominated by *Hormidium rivulare*, *Mougetia* sp. ($>8 \leq 12 \mu\text{m}$), and *Cylindrocystis brebissonii*.

Below this are two 'associations' where species are most abundant in the upper ranges of zinc concentrations, but which extend over various lower levels. The upper 'association' is characterised by *Pinnularia viridis* var. *sudetica* and *Eunotia tenella* together with *Euglena mutabilis*. The lower includes *Pinnularia subcapitata*, *P. viridis*, *Mougetia* sp. ($<8 \mu\text{m}$) and *Cosmarium subarctum*. A 'subgroup' of this 'association', which lies directly beneath, contains species which are infrequent or absent from the sites with the extreme zinc levels. However the species do show a tendency to be more abundant to the left of the Table. Species include *Eunotia exigua* and *Hormidium fluitans*.

In the middle of the Table are placed the species which occurred with more or less equal abundance throughout the range of sites; and thus over the range of zinc levels encountered. This 'association' is dominated by *Hormidium rivulare*, *Ulothrix moniliformis*, *Mougetia* sp. ($>8 \leq 12 \mu\text{m}$), *Microthammon strictissimum* and *Cylindrocystis brebissonii*.

Below this 'association' is a group of algae which are characteristic of sites demonstrating the 'middle' range of zinc values encountered during the survey. The group includes Chrysophyta sp. (coded as form 'B' = *Hydrurus foetidus*), with *Phormidium mucicola* (which was always found closely associated with the gelatinous palmelloid growths of the chrysophyte), and *Surirella ovata*, a twisted form of *Fragillaria capucina* and *Synedra rumpens*.

Some species are characteristic of sites carrying the lower levels of zinc but do occur at higher levels. This 'association' includes *Stigeoclonium* sp. (= *S. tenue*), *Phormidium* sp. ($>1 \leq 2 \mu\text{m}$), *Chamaesiphon polymorphus*, *Homoeothrix varians*, *Achnanthes minutissima* and *Cymbella ventricosa*.

A ' subgroup' of the 'association', immediately below, is represented by species which are even more limited to lower levels of zinc, being only scarce or more often absent from the higher levels. These include *Aphanocapsa* sp. ($>1 \leq 2 \mu\text{m}$), *Plectonema boryanum*, *Microspora lauterbornii*, *Diatoma hiemale* var. *mesodon*, *Meridion circulare* and *Gomphonema parvulum*.

At the bottom of the Table is a group of algae which form a small 'association' almost entirely restricted to the lower range of zinc values. These include *Chrysophyta* sp. (coded as form 'A' = *Chrysonobula holmesii*), *Staurastrum punctulatum*, *Ceratoneis arcus* and *Fragillaria intermedia*.

It is clear from the Table that filamentous green algae, in particular *Hormidium rivulare* and *Mougeotia* sp. ($>8 \leq 12 \mu\text{m}$), are the most abundant algae throughout the range of high zinc values in these sites.

4.32 Bryophytes

Table 4.12 presents the distribution of bryophyte species throughout the range of sites, indicated by their presence or absence. Three groups of species emerge from the rearrangement of species in relation to decreasing levels of zinc at the stream sites.

The first group were found only at the sites carrying the higher levels of zinc. The species include *Bryum pallens*, *Pohlia nutans*, and *Dichodontium pellucidum*.

Species in the second group were able to grow throughout the whole range of zinc values encountered. These were *Scapania undulata*, *Philonotis fontana* and *Dicranella varia*.

The third group includes species which were found only in the lower range of zinc concentrations and was most characterized by *Hygrohypnum ochraceum*, *Brachythecium rivulare* and *Bryum pseudotriquetrum*.

computer no.	species	0104/01	0107/17	0113/01	0108/08	0093/01	0097/01	0105/99	0098/01	0104/99	0111/01	0012/26	0048/12	0096/01	0084/10	0151/20	0048/20	0093/95	0071/99	0048/99	0092/20	0102/15	0169/01	0094/10	0103/08	0168/01	
231005	<i>Bryum pallens</i>																										
234304	<i>Pohlia nutans</i>																										
232001	<i>Dichodontium pellucidum</i>																										
222204	<i>Solenostoma triste</i>																										
222102	<i>Scapania undulata</i>																										
234002	<i>Philinotis fontana</i>																										
232106	<i>Dicranella varia</i>																										
231803	<i>Cratoneuron filicinum</i>																										
233202	<i>Hygrohypnum ochraceum</i>																										
230903	<i>Brachythecium rivulare</i>																										
233101	<i>Hygroamblystigeum fluviatile</i>																										
231006	<i>Bryum pseudotriquetrum</i>																										

Table 4.12 Distribution of bryophytes in the comparative stream survey

5 INTENSIVE STUDY OF GILLGILL BURN

5.1 Introduction

During the course of the comparative stream surveys, it became apparent that the study of a single stream network might provide further information with regard to the transport of zinc and its effect on the photosynthetic flora. Gillgill Burn was found to demonstrate a gradient of zinc from very high to low levels and was thus considered to be the most suitable stream for such a study. Further details of the rationale behind the surveys of Gillgill Burn, together with the methods employed, are given in 2.3. Detailed descriptions of the individual sites are presented in Appendix I. Further descriptions of the geology of the area are given in 3.6.

5.2 Water chemistry

5.2.1 Descriptive account

The mean results for the five main surveys carried out on Gillgill Burn and its tributaries are given in Table 5.1. They are formulated in order of increasing stream and reach numbers and do not represent the gradient of zinc values found in this stream system. The difficulties in delineating the main stream at its source, from a tributary (originating in the same area) running parallel to the main stream before joining it, have been discussed previously (see 3.6). Both the main stream (0093) and this second stream (0104), called 'Old Mine Gill', show a gradient of zinc from high to lower levels, from the reaches at their sources, to those just before they join (0093/01 to 0093/25, and 0104/01 to 0104/99 respectively). Gillgill Burn continues to show a slight gradient along its length, with increases in zinc occurring

Stream no.	reach no.	current	temp. °C	O.D. - 420	conductivity (micro-mhos)	pH	total alkalinity (as CaCO ₃)	total hardness (Mg ²⁺ , CaCO ₃)	Ca hardness	Mg hardness	Na	K	Mg	Ca	Al	Mn	Fe	Cu	Zn	Cd	Pb	PO ₄ -P	NH ₄ -N	NO ₃ -N	SO ₄ -S	Si	F	Cl		
Gillgill Burn	0093	01	-	7.4	0.021	163.0	6.2	7.3	84.4	42.6	21.3	3.5	2.2	5.2	17.1	1.41	0.575	0.11	0.012	9.16	0.031	0.932	0.017	<0.01	0.35	2.6	2.61	3.20	11.0	
	0093	04	0.016	8.0	0.015	182.4	6.2	8.0	96.8	52.4	21.3	3.4	2.0	5.2	21.0	1.29	0.719	0.18	0.008	10.8	0.030	1.14	0.018	0.01	0.19	2.5	2.31	2.88	11.3	
	0093	08	0.018	7.3	0.032	146.4	6.3	9.0	71.4	37.4	13.3	3.5	1.1	3.2	15.0	0.92	1.020	1.30	0.003	8.61	0.021	1.23	0.018	0.11	0.13	2.1	1.67	1.55	10.7	
	0093	11	0.022	7.3	0.048	146.5	6.7	31.5	51.3	30.6	8.5	7.6	0.9	2.1	12.3	0.21	0.529	2.94	0.003	3.41	0.009	0.518	0.016	0.13	0.33	1.0	1.51	1.40	15.0	
	0093	25	0.924	9.8	0.06	137.8	6.7	17.5	37.6	27.2	6.8	8.8	0.6	1.7	10.9	0.15	0.111	0.52	0.002	1.23	0.006	0.112	0.015	0.15	0.08	0.7	1.35	1.35	20.7	
	0093	29	0.679	9.8	0.037	125.3	6.8	11.5	38.8	26.1	8.0	8.5	0.8	1.9	10.5	0.9	0.183	0.41	0.002	1.85	0.009	0.148	0.011	0.07	0.11	1.0	1.77	1.80	20.8	
	0093	32	0.560	9.5	0.020	132.9	6.8	12.0	38.7	23.9	9.5	7.5	0.9	2.3	9.6	0.15	0.140	0.27	0.002	2.60	0.014	0.166	0.010	0.02	0.11	1.3	1.90	1.73	16.5	
	0093	40	1.058	10.0	0.020	133.7	6.8	17.0	40.0	25.7	10.3	7.3	1.0	2.5	10.3	0.15	0.053	0.13	0.002	2.0	0.009	0.117	0.016	0.09	0.29	1.1	2.0	1.24	15.2	
	0093	43	0.955	10.3	0.023	135.8	6.9	33.5	52.0	33.7	14.7	7.0	1.2	3.6	13.5	0.13	0.040	0.11	0.002	1.89	0.009	0.114	0.013	0.07	0.30	1.5	2.06	1.20	13.8	
	0093	47	1.131	10.0	0.020	136.9	6.9	32.0	56.4	36.8	16.6	6.8	1.2	4.0	14.8	0.06	0.031	0.12	0.002	1.60	0.009	0.121	0.013	0.05	0.22	2.2	2.16	1.13	14.2	
	0093	50	0.960	9.9	0.021	139.4	6.8	31.5	69.2	46.0	20.5	6.5	1.3	5.0	18.4	0.08	0.031	0.10	0.002	1.46	0.008	0.073	0.013	0.04	0.16	2.0	2.19	1.12	13.7	
	0093	61	1.098	9.9	0.017	140.4	6.9	27.5	67.4	44.8	20.0	6.2	1.5	4.9	18.0	0.04	0.028	0.07	0.003	1.45	0.008	0.068	0.016	0.11	0.11	1.6	2.23	1.08	14.6	
	0093	64	0.930	10.1	0.015	150.2	7.0	25.0	63.2	41.7	18.5	6.1	1.4	4.5	16.7	0.04	0.045	0.07	0.002	1.70	0.007	0.078	0.013	0.11	0.12	1.7	2.17	1.13	14.7	
	0093	68	0.584	10.5	0.015	137.4	7.0	25.0	61.1	40.3	17.7	6.1	1.3	4.3	16.1	0.06	0.051	0.09	0.002	1.67	0.007	0.115	0.008	0.12	0.12	1.7	2.16	1.15	14.8	
	0093	74	0.846	10.5	0.015	139.3	7.1	25.0	60.4	40.2	17.1	5.8	1.3	4.2	16.1	0.04	0.097	0.12	0.002	1.67	0.007	0.094	0.014	0.09	0.12	1.6	2.15	1.17	15.6	
	0093	85	0.895	10.6	0.014	142.3	7.0	25.5	58.1	38.7	16.4	5.7	1.3	4.0	15.5	0.04	0.112	0.14	0.002	1.56	0.007	0.071	0.012	0.08	0.14	1.7	2.12	1.11	15.0	
	0093	88	0.859	10.5	0.014	147.2	7.1	26.0	59.3	40.0	16.4	5.7	1.3	4.0	16.0	0.05	0.081	0.13	0.002	1.52	0.007	0.090	0.011	0.15	0.12	1.7	2.17	1.09	14.9	
	0093	95	0.879	10.8	0.016	159.4	7.3	40.0	69.0	48.0	17.8	6.9	1.4	4.3	19.2	0.05	0.200	0.13	0.004	1.50	0.007	0.067	0.056	0.38	0.75	1.6	2.24	1.06	19.1	
	0093	99	0.716	10.8	0.014	167.4	7.3	41.5	75.8	52.7	18.9	7.6	1.5	4.6	21.1	0.29	0.056	0.15	0.002	1.81	0.008	0.072	0.038	0.43	0.37	1.9	2.29	1.05	22.5	
	'Old Mine Gill'	0104	01	-	10.0	0.002	183.3	6.2	12.0	11.0	48.1	18.8	3.3	1.3	4.6	19.3	1.07	0.403	0.06	0.006	25.60	0.060	2.06	0.007	0.23	0.18	3.9	1.94	2.50	11.7
0104		15	0.016	10.1	0.006	208.4	6.3	11.5	94.0	41.7	15.3	3.3	1.0	3.7	16.7	1.00	0.732	0.11	0.005	20.80	0.059	1.21	0.010	0.17	0.14	3.3	1.78	2.68	13.2	
0104		29	0.016	9.4	0.007	199.4	6.2	16.0	84.2	37.1	12.9	3.2	1.1	3.1	14.8	0.95	0.662	0.31	0.007	18.90	0.057	1.41	0.010	0.12	0.16	2.5	1.74	2.93	12.6	
0104		43	0.06	9.1	0.013	195.8	6.3	7.5	52.5	24.3	8.9	3.6	0.9	2.2	9.7	1.01	0.544	0.36	0.005	9.10	0.017	0.80	0.012	0.15	0.17	6.6	1.72	2.73	11.6	
0104		57	0.223	9.1	0.012	144.3	6.3	6.5	43.6	21.2	7.6	4.4	0.8	1.8	8.5	1.10	0.393	0.24	0.005	6.20	0.027	0.913	0.008	0.21	0.40	2.1	2.14	2.80	12.3	
0104		71	1.397	9.1	0.014	149.1	6.4	6.0	40.7	22.4	7.4	10.5	0.8	1.8	9.0	0.84	0.233	0.09	0.002	4.66	0.021	0.337	0.012	0.16	0.12	1.6	1.97	2.75	19.8	
0104		85	0.219	8.3	0.012	151.5	6.4	7.5	50.1	30.8	8.2	19.6	0.9	2.0	12.3	0.80	0.205	0.23	0.004	4.77	0.019	0.312	0.012	0.13	0.07	2.0	1.97	2.53	21.0	
0104		99	0.926	8.9	0.008	151.3	6.5	8.5	40.3	21.9	7.6	10.9	1.0	1.8	8.8	0.88	0.266	0.07	0.002	4.55	0.017	0.232	0.013	0.03	0.07	1.2	1.67	2.45	20.7	
'Old Shaft Gill'		0105	99	1.009	9.0	0.017	128.9	6.3	9.5	41.0	22.2	9.6	7.0	1.0	2.3	8.9	0.32	0.085	0.14	0.002	5.03	0.014	0.140	0.009	0.36	0.09	1.8	2.20	2.05	14.9
'Footpath Gill'		0106	99	0.892	10.3	0.031	133.6	7.0	12.0	42.8	32.4	9.7	7.0	0.8	2.4	13.0	0.04	0.044	0.20	<0.002	0.024	<0.001	0.031	0.030	0.13	0.39	1.8	1.83	1.32	15.9
'Firestone Gill'	0107	99	0.878	9.9	0.015	121.0	6.5	10.0	41.5	24.4	10.8	5.3	1.1	2.6	9.8	0.11	0.304	0.13	0.002	3.37	0.011	0.196	0.007	0.21	0.09	1.9	2.12	1.57	13.1	

Table 5.1 Representative water chemistry for 30 reaches on Gillgill Burn and its tributaries. Values given are the means of five samples taken during low flows between September 1973 and October 1974. Element values are expressed in mg l⁻¹.

directly below the entry of a tributary carrying higher concentrations of zinc (i.e. reach 0093/32 below the entrance of tributary 0105, 'Old Shaft Gill', reach 0093/64 below the entrance of tributary 0107, 'Firestone Gill'). As was mentioned previously (2.331), a number of reaches were excluded from these surveys (from the original 60 reaches which were marked on the main stream and some of the tributaries) because of the repetition in results. However the gradient of zinc down Gillgill Burn and the total length of the tributaries, for all of the original designated 60 reaches, is shown diagrammatically in Fig. 5.1. 'Old Mine Gill' can be seen to carry the highest zinc levels, with an average of 25.6 mg l^{-1} from the five surveys (at reach 0104/01), and the highest recorded value of 30.2 mg l^{-1} Zn. Comparatively high levels for lead and cadmium are also recorded at this reach, being 2.06 and 0.06 mg l^{-1} respectively. High levels for all of these metals are also recorded for Gillgill Burn at reaches near its source. The streams in general can be regarded as 'soft' waters with calcium rarely exceeding 20 mg l^{-1} Ca, total alkalinity 30 mg l^{-1} CaCO_3 , and total hardness 80 mg l^{-1} CaCO_3 , and more often the values are much lower. The lower reaches of 'Old Mine Gill' are particularly 'soft' with total alkalinity and calcium concentrations rarely exceeding 10 mg l^{-1} CaCO_3 and 10 mg l^{-1} Ca respectively.

The pH range in these waters is 5.9 - 7.2. Gillgill Burn at its source is slightly acidic (pH 5.9) but within 200m the pH climbs to remain more or less neutral throughout its remaining length. 'Old Mine Gill' remains on the acid side of neutrality throughout the whole of its length, generally reflecting more of a superficial runoff from the surrounding peat moorland than does the main stream.

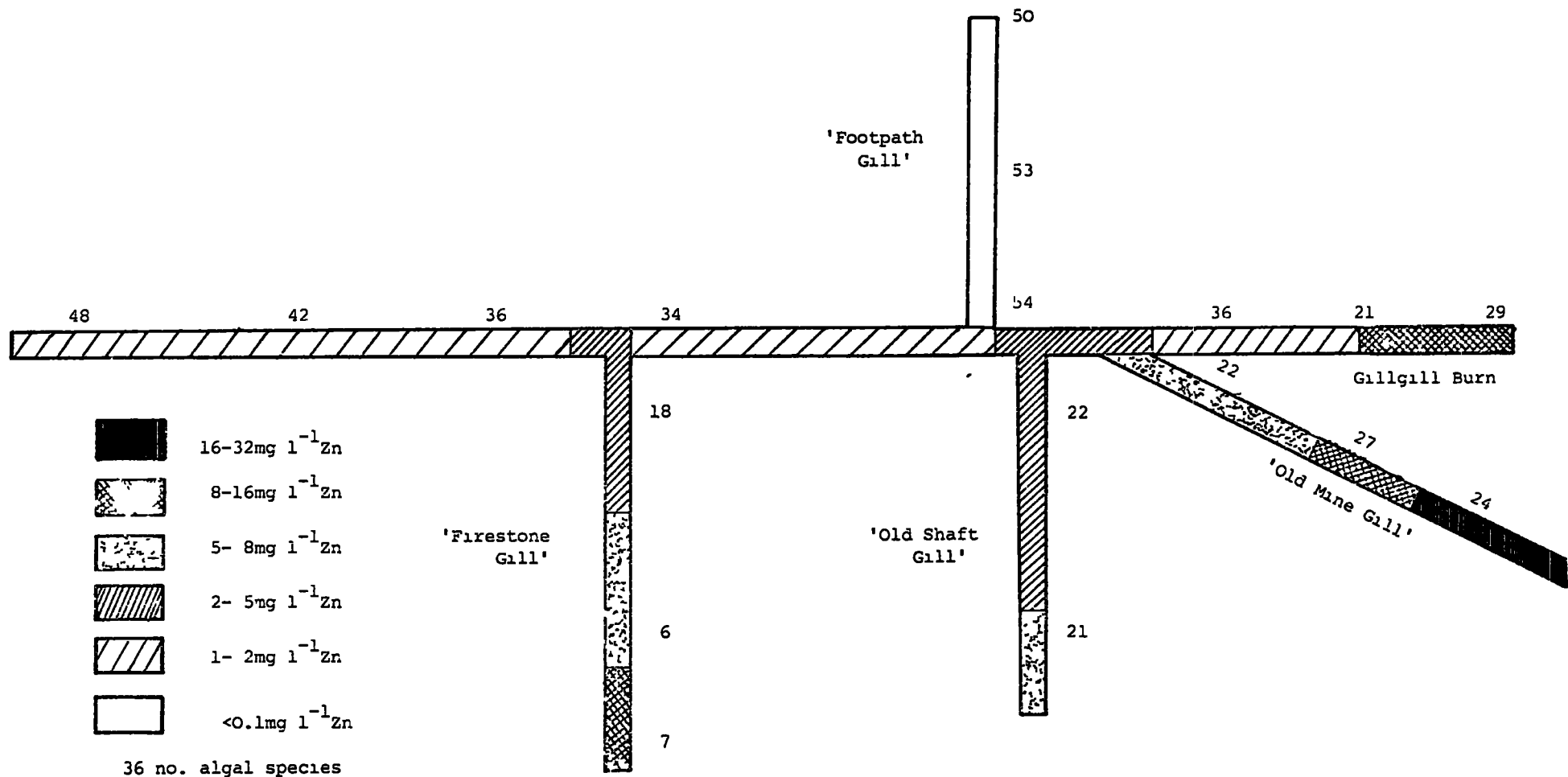


Fig. 5.1 Diagrammatic representation of Gillgill Burn and its tributaries to show the gradient of zinc, and number of algal species at different reaches down this gradient.

The ionic concentration of these waters, as measured by the specific conductance is not high, and shows little variation between 150-200mhos.

The variation in O.D. (section 2.6) throughout these sites is not marked, with the largest differences occurring between sites such as O104/01, which has an extremely low O.D. reflecting the 'purity' of this seepage from beneath a tailings heap, as compared with reach 0093/11 which shows a comparatively high O.D. Most of the contribution to O.D. at this site comes from the yellow-brown colour of the water assumed to be given by the presence of humic substances in the drainage waters received directly from the surrounding peat.

The level of inorganic P and N in these waters is generally low, except for the region of Gillgill Burn which flows through the village of Nenthead. Here some intermittent small discharges of sewage enter the stream, raising the status of ions such as ammonia and nitrate, but this is only for a short stretch before the stream enters the River Nent.

Fluorite, the commonly associated gangue mineral with zinc, shows a very slight gradation of levels down Gillgill Burn, particularly in the early reaches, but for much of the stream's length rarely exceeds 1mg l^{-1} F.

With regard to the other tributaries, both 'Old Shaft Gill' and 'Firestone Gill' strongly resemble 'Old Mine Gill' in both the origin of water and general physiography and chemistry, and this is well illustrated by the similarity in the water chemistry of reach '99' of each of the streams, listed in Table 5.1 (this being the last reach before each tributary joins the main stream). The main differences are associated with the much higher concentrations of zinc and related metals found in the upper reaches of 'Old Mine Gill'.

Included in this survey of the Gillgill Burn stream basin is a tributary to the main stream, called 'Footpath Gill', which is a fairly unique stream due to lack of metal contamination throughout its entire length, before its entry into Gillgill Burn. Although only one of the original seven reaches is included in these five surveys, it is fairly representative of the whole stream in terms of water chemistry. Apart from its inclusion as a main tributary to Gillgill Burn, it can also be considered as a 'control' site because of its freedom from zinc contamination. Apart from the level of zinc, its chemistry is almost identical to the lower reaches of the main stream.

5.22 Intervariable correlation analysis

This procedure was used as described in 4.22 and in more detail in 2.522. A brief glance at the intervariable correlation matrix portrayed in Table 5.2 indicates a widespread set of significant correlations.

However two broad groups of intercorrelated variables can again be defined (cf. 4.25). The first group is characterised by strong positive intercorrelations between Ca, Mg, K, total alkalinity, the hardness-producing factors, pH, with also included in this group Si and $\text{SO}_4\text{-S}$ ($P = 0.001$). Zn, Cd, Pb and F are all significantly negatively correlated with this group of variables ($P = 0.001$). The other highly significant cross-correlated group is formed by the heavy metals Zn, Cd, Cu, Al and Mn, together with F ($P = 0.001$).

As well as correlations with these heavy metals, Zn correlates highly with conductivity and $\text{SO}_4\text{-S}$ ($P = 0.001$). In addition to the negative correlations with Mg and Ca, Zn also negatively correlates with O.D. ($P = 0.001$), Na ($P = 0.001$) and Cl ($P = 0.005$).

O.D. - 240	conductivity	pH	total alkalinity	Na	K	Mg	Ca	Mg	Mn	Fe	Cu	Zn	Cd	Pb	PO ₄ -P	NH ₄ -N	NO ₃ -N	SO ₄ -S	Si	F	Cl	total hardness	Ca hardness	Mg hardness	
O.D. - 420	1.000																								
conductivity	1.000	-0.200**																							
pH		1.000																							
total alkalinity			1.000																						
Na				1.000																					
K					1.000																				
Mg						1.000																			
Ca							1.000																		
Mg								1.000																	
Mn									1.000																
Fe										1.000															
Cu											1.000														
Zn												1.000													
Cd													1.000												
Pb														1.000											
PO ₄ -P															1.000										
NH ₄ -N																1.000									
NO ₃ -N																	1.000								
SO ₄ -S																		1.000							
Si																			1.000						
F																				1.000					
Cl																					1.000				
total hardness																						1.000			
Ca hardness																							1.000		
Mg hardness																								1.000	

Table 3.1: Intercorrelation matrix for 20 variables on Gilligan Run and its tributaries
 (* = P < 0.05, ** = P < 0.01, *** = P < 0.001)

Zn and Pb share common properties within this correlation matrix which were found in previous investigations of surface waters (4.25) but were absent in the ground waters (4.24). A similar pattern of correlations is also demonstrated between Zn and F.

Other correlations which might be of importance in determining the form and mobility of Zn include the following. The negative correlation between Zn and O.D. has already been mentioned. The only ion positively to correlate with O.D. is Fe. The possibility of O.D. giving a measure of the suspended organic matter cannot be overlooked. On the other hand, in view of its close association with Fe, it could indicate suspensions of colloidal precipitates of Fe, such as ferric hydroxide. Deposits of the hydrated oxides of Fe were noticed on the stream bottom in some reaches (see section 9.211). The correlations between $\text{SO}_4\text{-S}$ and Zn, Cu and Pb will reflect the natural weathering of the sulphide ores of these metals during which sulphate ions are released.

5.23 Factor analysis

As described for the comparative stream data (4.23), this analytical procedure was performed on the information collected from the surveys of Gillgill Burn. Cd was excluded from the analysis because of a reduced number of cases (2.523). $\text{PO}_4\text{-P}$ was excluded because of the low communality figure demonstrated during the initial factor runs (2.523). The analysis was performed on the remaining 23 variables.

5.231 Principal components

Using the method outlined in 2.523, six independent principal components were extracted, which accounted for 80% of the variance and covariance within the correlation matrix. The first principal component shows

variable	principal component						communality
	I	II	III	IV	V	VI	
O.D. - 420			-0.425	0.696			0.799
conductivity		0.528				0.648	0.766
pH	0.685	-0.405					0.669
total alkalinity	0.856						0.933
Na			0.726				0.811
K	0.520	0.427	0.412				0.791
Mg	0.793	0.520					0.958
Ca	0.766	0.502					0.920
Al	-0.685	0.532					0.813
Mn	-0.553	0.500					0.673
Fe	-0.423			0.584			0.742
Cu		0.591					0.598
Zn	-0.415	0.765					0.810
Pb	-0.562	0.680					0.843
NH ₄ ^{-N}					0.681		0.654
NO ₃ ^{-N}					0.789		0.664
SO ₄ ^{-S}		0.640				0.476	0.878
Si ⁴	0.482						0.560
Fe	-0.850						0.919
Cl			0.846				0.850
total hardness	0.462	0.814					0.950
Ca hardness	0.766	0.502					0.920
Mg hardness	0.793	0.520					0.958
eigenvalue	6.738	5.433	2.103	1.809	1.379	1.027	
per cent of variance explained by factor	29.3	23.6	9.1	7.9	6.0	4.5	
cumulative per cent of variance	29.3	52.9	62.1	69.9	75.9	80.4	

Table 5.3 Principal components derived from the correlation coefficient matrix for 30 sites on Gillgill Burn and its tributaries

high loadings for total alkalinity, Mg, Ca, the measures of hardness, and pH. These are opposed by a number of negative loadings for the heavy metals, including Zn and Pb, and also a high negative loading for F.

The second principal component combines positive loadings for all the metals excluding Fe, with K, Mg, Ca and $\text{SO}_4\text{-S}$, opposed by a negative loading for pH.

The third component features positive loadings for Na, K, and Cl, opposed by a negative loading for O.D.

The fourth principal component combines positive loadings for O.D. and Fe.

The fifth principal component accounts for the variances of inorganic N in the correlation matrix.

The final principal component features positive loadings for conductivity and sulphate.

5.232 Principal factors

The R-mode varimax factor matrix of the chemical data from 150 samples of the 30 sites is shown in Table 5.4. The loadings on variables within each factor is illustrated diagrammatically in Fig. 5.2. The six extracted factors account for 100% of the variance within the data set. Inspection of factor one shows that most of the covariance in the properties of the system may be accounted for by the variances of Ca and Mg with their respective hardness factors. This is accompanied by a moderate loading for K and a small loading for S₁. This contrasts markedly with the first factor for the matrix of the groundwaters (4.2422, Table 4.7) which loaded predominantly for Mg, with a lower loading for Ca, but which included significant loadings for the Na, K, S₁, $\text{SO}_4\text{-S}$, Al and Mn. This factor accounts for nearly 90% of the variances for

variable	factor						communality
	1	2	3	4	5	6	
O.D. - 420			-0.778				0.643
conductivity		0.375			0.470		0.420
Ph		-0.677					0.638
total alkalinity	0.613			0.471			0.922
Na				0.810			0.674
K	0.480		0.591			0.317	0.724
Mg	0.934						0.986
Ca	0.942						0.919
Al		0.843					0.788
Mn		0.744					0.609
Fe			-0.705				0.623
Cu		0.627					0.440
Zn		0.852					0.794
Pb		0.896					0.835
NH ₄ N						0.583	0.424
NO ₃ N						0.523	0.283
SO ₄ S				-0.392	0.735		0.852
Si	0.366		0.369				0.412
F	-0.422	0.784		-0.303			0.976
Cl				0.827			0.736
total hardness	0.881	0.362					0.945
Ca hardness	0.942						0.918
Mg hardness	0.934						0.986
eigenvalue (principal component)	6.582	5.200	1.784	1.478	0.831	0.676	
percent of variance explained by Factor	39.8	31.4	10.8	8.9	5.0	4.1	
Cumulative per cent of variance	39.8	71.2	82.0	90.9	95.9	100.0	

Table 5.4 R-mode varimax factor matrix of chemical data for 30 sampling sites on Gillgill Burn and its tributaries

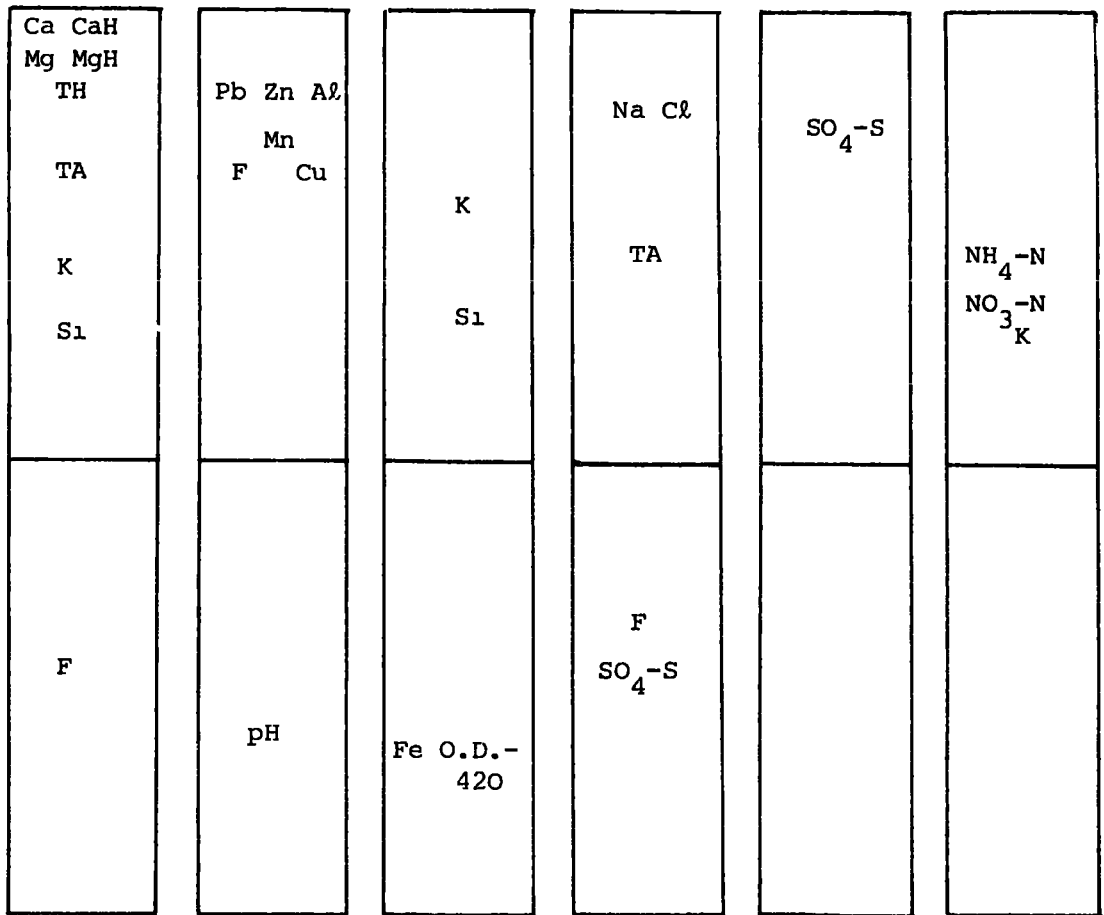


Fig. 5.2 Diagrammatic representation of factors from R-mode varimax solution of chemical data for 30 reaches on Gillgill Burn (TA = total alkalinity; TH = total hardness; CaH = calcium hardness; MgH = magnesium hardness.)

both Mg and Ca. There is a moderate negative loading of fluoride on this factor. In contrast to the situation with the groundwaters, this factor accounts for just over one-third of the variance in the total data (39.8%) compared with over one half of the variance (51.4%) in the data of the groundwaters.

Factor two is a predominantly heavy metal factor, loading highly for Pb, Zn, Al, Mn and Cu. In view of the marked inter-correlation between Cd, Pb, Zn and the other heavy metals, it is not unreasonable to assume that Cd would load highly on this factor.

F also shows a high loading with the heavy metals, which accounts for over 50% of the variance of this ion. There is a moderately high negative loading of pH on this factor indicating the possibility of an equilibrium between mutually exclusive components in these waters (Dawdy and Feth, 1967). Factor three features high negative loadings for O.D. and Fe, combined with moderate positive loadings for K, and to a lesser extent Si. Both Fe and O.D. are only loaded onto this factor, which implies a specific control on both of these variables by this factor.

Factor four is primarily a Na-Cl factor with a moderate positive loading for total alkalinity and negative loadings for $\text{SO}_4\text{-S}$ and F. More than 60% of the variance in both Na and Cl is accounted for by this factor. The negative correlation between the F and Cl components is interesting to note.

Factor five is exclusively a unique $\text{SO}_4\text{-S}$ factor which accounts for over 50% of the variance in this ion.

Factor six is divided more or less equally between positive loadings for the main sources of nitrogen in these waters, the ammonium and nitrate ions. A slight contribution to this factor is given by K. The low communalities for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ suggest that only a small fraction of the variance of each ion is explained by this factor. In fact by squaring the coefficients of each variable, it can be seen that in both cases less than 30% of the variance of these ions is explained by the factor.

The high communality figures for Ca, Mg, Zn, Pb, F and $\text{SO}_4\text{-S}$ indicate that the fraction of the variance of each ion, explained by the extracted factors, is quite high.

5.3 Flora of Gillgill Burn

5.31 Algae

A check list of the species so far distinguished in Gillgill Burn and its tributaries is given in Appendix II.

An 'association table' similar to that constructed for the comparative stream surveys, following the methods outline in 2.355, is given in Table 5.5. The sites have been rearranged in order of decreasing levels of zinc, following the gradient of zinc based on the mean values from the five surveys, and thus do not follow the exact sequence of sampling stations down the respective streams. It was felt that this re-ordering of sites would best demonstrate any pattern in the associations, in relation to zinc concentrations that might exist down the streams.

From Table 5.5 it becomes clear that seven groups or 'associations' between species can be defined in relation to the gradient of zinc in Gillgill Burn and its tributaries. Although the species diversity is

Table 5.5 'Association table' of algae sampled during the survey of Gillgill Burn. Reaches are arranged from left to right in order of decreasing levels of zinc. Species are arranged to show distribution throughout the range of zinc levels. For more details see text and Section 2.

not markedly reduced when compared with the lower zinc sites and control site, it is lower, and there are certain species which are restricted to the upper reaches where the zinc level is markedly higher. This small association at the higher zinc levels is characterised by *Phormidium* sp. ($>2 \leq 4 \mu\text{m}$) and *Synechococcus* sp. ($>8 \leq 16 \mu\text{m}$), *Caloneis lagerstedtii*, *Achnanthes marginistriata*, *Pinnularia appendiculata* and *P. interrupta*. Although these species are specifically associated with the high zinc levels, the actual communities at these upper reaches are dominated by the species such as *Hormidium rivulare*, *Ulothrix moniliformis*, *Cylindrocystis brebissonii*, *Mougetia* sp. ($<8 \mu\text{m}$), and *Mougetia* sp. ($>8 \leq 12 \mu\text{m}$). Also found frequently at sites carrying high zinc levels were the species *Pinnularia viridis* var. *sudetica* and *P. subcapitata*.

The next defineable 'association' is characterised by species which were more abundant in the higher levels of zinc but which did occur at sites lower downstream carrying lower concentrations of zinc. Included in this group are *Euglena mutabilis*, *Microthamnium strictissimum*, *Eunotia tenella*, *Pinnularia viridis* var. *sudetica* and *P. borealis*.

Below this group is an 'association' of species which distinctly clusters towards the centre of the table. Most of the species were not found at the extremely high levels of zinc ($>10 \text{mg l}^{-1} \text{Zn}$) and were not particularly abundant at the lower levels ($<1 \text{mg l}^{-1} \text{Zn}$), but instead demonstrated a greater abundance at the intermediate zinc concentrations in the gradient ($2-6 \text{mg l}^{-1} \text{Zn}$). The predominant species in this 'association' includes the Ulotrichalean species *Hormidium fluitans* and *Microspora lauterbornii*, with *Closterium tumidum*, *Cosmarium undulatum*, *Frustulia rhomboides* var. *saxonica* and *Eunotia exigua*.

In the centre of the table is a large association of algae which are abundant down the whole gradient of zinc levels, but includes some species found throughout most of the sites, but which are more abundant at the higher levels. The 'association' is most characterised by *Horridium rivulare*, *Ulothrix moniliformis*, *Mougeotia* sp. ($>8 \leq 12$), *Mougeotia* sp. ($<8 \mu\text{m}$) and *Pseudanabaena catenata*. Species included in this group which, although present down the whole gradient were more abundant at the higher end, were *Cylindrocystis brebissonii* and *Pinnularia subcapitata*. Conversely species occurring through the gradient, but which were predominant at the lower end, included *Gloeocystis* sp. and *Roya obtusa*. The most abundant species in this group or 'association' also dominated the individual communities at sites down the streams.

Below this central 'association' of algae is a large assemblage of species which can really be subdivided into two 'associations'. Neither includes species which occur at the upper end of the gradient. However the first 'association' includes species more abundant at the lower end, but which do extend some distance up the gradient of zinc, whereas the second includes species which are most abundant at the lower end and which are rarely found out of this lower half of the gradient. The first group, which includes species found up to $8 \text{mg l}^{-1} \text{Zn}$, is characterised by *Chamaesiphon polymorphus*, *Homoeothrix varians* and *Stigeoclonium* sp. The second group, which are rarely found above a zinc concentration of $3 \text{mg l}^{-1} \text{Zn}$ and more often in the range $1-2 \text{mg l}^{-1} \text{Zn}$, includes a Chrysophyte species described previously as 'Form B' (see 2.354V) which most closely resembles *Hydrurus foetidus*, and also a second Chrysophyte species described as 'Form A' which was found most closely to resemble *Chrysonobula holmesii*. Both of these species formed thick gelatinous growths nearly all of the year round, covering large areas of boulders, and always associated with such growths were found the species

Phormidium mucicola, *Plectonema boryanum*, *Aphanocapsa* sp. ($>1\leq 2\mu\text{m}$),
Achnanthes minutissima, *Meridion circulare* and *Staurastrum punctulatum*.

The next 'association' is a small grouping of species which are absent from the upper high zinc-level reaches, are not particularly abundant at the lower end of the gradient, but which tend to cluster in the right hand side of the table (the level of zinc equal to $<1\text{mg l}^{-1}\text{Zn}$). They are primarily diatom species which include *Diatoma hiemale* var. *mesodon*, *Cymbella ventricosa*, a twisted form of *Fragillaria capucina*, and *Gomphonema parvulum*. Also included is the species *Stichococcus bacillaris*.

The final small 'association' is characterised by species which were only found at the 'control site' which was free from zinc contamination but which in all other respects resembled most of the main stream sites. This included the species *Microspora amoena*, *Closterium moniliferum*, *C. rostratum*, *Ceratoneis arcus*, *Gomphonema ventricosum*, *Tabillaria flocculosa* and *Synedra ulna*.

5.32 The Lichens

A check list of the lichen species determined for Gillgill Burn and its tributaries is given in Appendix II. They can broadly be divided into two groups. The first group, although not really relevant to a study of the streams, are important to note because of (i) their occurrence in small boulders and rock chippings in close proximity to the streams, which at flood time were occasionally washed by the stream water, (ii) their occurrence on emergent boulders within the confines of the stream which occasionally received spray even at medium flow, (iii) because of their occurrence on rocks visibly mineralised with sphalerite on the tailings heaps from which drainage water enters the main stream. The more important species to note in this group are

Micarea lignaria, *Lecanora intricata* var. *sonalifera*, *Rhizocarpon obscuratum* var. *reductum*, *Bacidia umbrina* and *Trapelia coarctata* occurring primarily on mineralised sandstone, with *Parmelia saxatilis* on unmineralised sandstone boulders, both on the bank and on emergent boulders within the stream.

The second group includes two truly aquatic species of lichen, *Lecanora lacustris*, and a species of *Verrucaria*, together with species which are mainly terrestrial but which were consistently found in the splash zone of the rocks. These included *Lecidea alvocaerulescens*, *L. macrocarpa* and *L. tumida*.

No attempt was made to relate the lichens to the zinc gradient in the streams since they showed no zonation in their abundance down the streams. The three most common species throughout every site were *Lecanora lacustris*, *Lecidea tumida* and *L. macrocarpa*. It was interesting to note that with *Parmelia saxatilis* these species did show a zonation on boulders within the stream. *Lecanora lacustris* was more or less continually submerged, *Lecidea tumida* was in the zone of most frequent splashing from the stream, *L. macrocarpa* was found in the next zone on the same rock which was more or less dry for most of the time, and *Parmelia saxatilis* was found on top of the boulder away from the water.

An aquatic species of *Verrucaria*, which was not easily observable macroscopically, but was often abundant when samples were investigated with the microscope, was encountered frequently at the lower end of Gillgill Burn. It was often associated with the Chrysophyte algae 'forms A and B' and also *Achnanthes minutissima* and *Phormidium mucicola*.

5.33 Bryophytes

Because of the few species encountered, and their lack of marked zonation down Gillgill Burn, no attempt was made to establish 'associations'.

Instead the occurrence of bryophytes is discussed generally.

From the check list given in Appendix I, it can be seen that there are two main groups of bryophytes. The first group includes aquatic, semi aquatic, or species frequently found associated with the stream waters, and thus subject to their influence e.g. *Scapania undulata*, *Brachythecium rivulare*, *Philonotis fontana*, *Bryum pallens*, *Pellia epiphylla*, *Bryum pseudotriquetrum*.

The second group consists primarily of bank species but ones which intermittently receive washes and spray from the stream waters e.g. *Pohlia nutans*, *Solenostoma triste*, *Sphagnum capillaceum*, *Hygrohypnum luridum*, *Ceratodon purpureus*, *Diplophyllum albicans*.

Of the first group, by far the most abundant species occurring throughout the majority of sites were *Scapania undulata* and *Philonotis fontana*.

However *Scapania undulata*, although abundant where it occurred, was limited to parts of the streams carrying less than $5\text{mg l}^{-1}\text{Zn}$. It occurred at one or two reaches with concentrations of zinc which occasionally exceeded this level (0104/99; 0105/99) and in these cases was restricted to very stunted, black-brown coloured tufts. Up to levels of $2\text{-}3\text{mg l}^{-1}\text{Zn}$, it usually formed lush carpets or hummocks of growth. Downstream from reach 0093/25 this bryophyte was abundant in the whole of the remainder of Gillgill Burn, Its distribution in Gillgill Burn and tributaries is depicted in Fig. 5.3. Although not truly submerged *Philonotis fonata* was often a close associate with *Scapania undulata*, usually growing on or near the 'turfs' of the latter. This species did seem able to grow

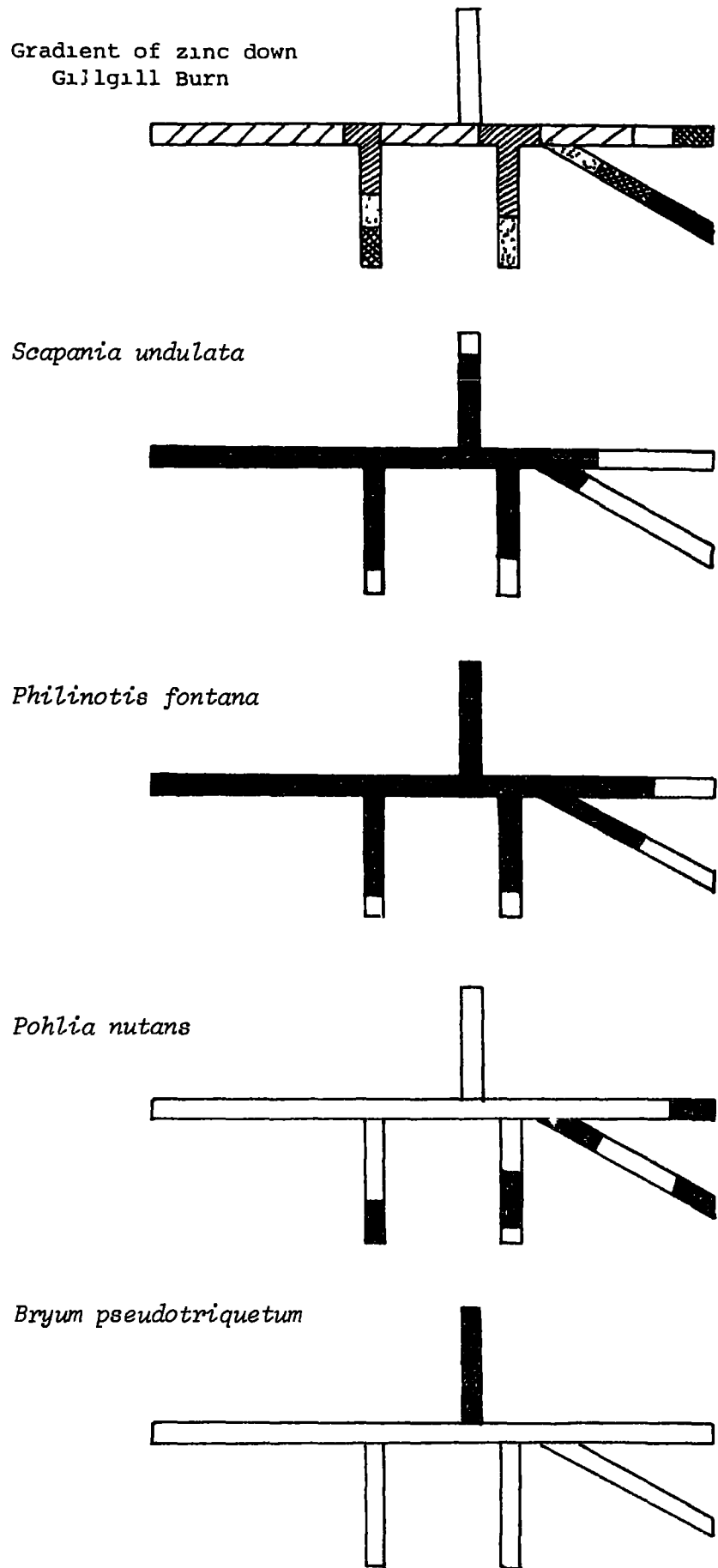


Fig. 5.3 Diagrammatic representation of the distribution of selected bryophytes down the gradient of zinc in Gillgill Burn and its tributaries (for key to zinc gradient see Fig. 5.1).

under higher conditions of zinc contamination than *Scapania*. Thus in reaches O104/57, O104/85 and O104/99 on 'Old Mine Gill' it was able to colonize the stream verges and also areas in midstream since at these reaches during medium to low flow conditions the stream was reduced to a comparatively wide but very shallow 'trickle' over exposed sandstone substratum. The levels of zinc in the water percolating over this substratum were found to vary between 4-8mg l⁻¹Zn. Its distribution in Gillgill Burn and tributaries with regard to the gradient of zinc is given in Fig. 5.3.

Bryum pseudotriquetrum, which can colonize habitats similar to those of *Philmotis fontana* (Watson, 1968), was completely absent from Gillgill Burn and any of the other zinc contaminated tributaries. It was encountered frequently down the whole length of 'Footpath Gill', the control site (Fig. 5.3). *Brachythecium rivulare* was restricted to the lower end of Gillgill Burn.

In contrast, *Solenostoma triste* and *Pohlia nutans* were bank species restricted in occurrence entirely to the upper reaches of Gillgill Burn and the other streams (Fig. 5.3).

6 INFLUENCE OF ZINC ON SELECTED SPECIES IN THE FIELD AND LABORATORY

6.1 Introduction

During the course of the surveys described in 4.2 a number of algae were found capable of growing in reaches with various levels of zinc. The first section of this chapter describes preliminary experiments carried out on material collected from some of these reaches. This was intended to back up observations made in the field on the relative resistance of various algal taxa to zinc. They include therefore material collected from reaches free from contamination by zinc. On the basis of the results of these tests, and from observations made in 4.3 and 5.3 (see also section 2.4), the genus *Horrmidium* was selected for detailed field and laboratory investigations. The results of the field surveys of *Horrmidium* sites is presented in the second section. During these surveys, *Horrmidium* material was collected, and the final section describes the results of the subsequent toxicity tests performed. Included in this section are the results of a statistical analysis (2.52) performed on a combination of the field and laboratory data.

6.21 Comparison between different algal taxa

The results of the toxicity tests carried out on a number of algal species within four taxa are given in Table 6.1. Admittedly a large number of algal species within each of the taxa were not investigated, so generalisations on the relative sensitivities of different taxa need to be treated with caution. However it becomes apparent that filamentous green algae, particularly those in the Ulotrichales, show a distinct resistance towards zinc. But it must be pointed out that although species in this group, particularly in the genus *Horrmidium*, were able to colonise streams with high levels of zinc, and show a resistance to this metal under laboratory conditions (one population of *H. rivulare* with a T.I.C. of

taxon	genus or species	filament width	name of stream	stream no.	reach no.	pH	Zn in water	J.N.I.	J.L.	T.I.C.	order of T.I.C.
Myxophyta	<i>Pseudanabaena catenata</i>	2µm	River West Allen	0085	05	5.2	0.066	1.62	2.22	1.9	21
	<i>Oscillatoria pseudogermnata</i>	2µm	River Nent	0048	12	6.8	0.22	1.22	2.22	1.6	24
	<i>Homoeothrix varians</i>	2µm	River West Allen	0085	10	6.7	1.12	2.73	4.74	3.6	16
Bacillariophyta	<i>Diatoma elongatum</i>		'Cookshold stream'	0151	15	7.2	0.025	0.61	1.22	0.9	30
	<i>Navicula</i> sp.		'Cookshold stream'	0151	15	7.2	0.025	0.14	0.44	0.3	34=
	<i>Nitzschia</i> sp.		'Cookshold stream'	0151	15	7.2	0.025	0.14	0.44	0.3	34=
	<i>Syredra rumpens</i>		'Cookshold stream'	0151	15	7.2	0.025	0.61	0.9	0.7	31
	<i>S. rumpens</i>		Garrigill Burn	0102	15	6.9	0.74	1.22	2.5	1.7	23
	<i>S. ulna</i>		River South Tyne	0055	30	6.8	0.03	1.22	1.87	1.5	26
	<i>Meridion circulare</i>		Gillgill Burn	0093	95	7.3	1.23	3.22	5.22	4.1	14
	<i>Surirelia ovata</i>		River Nent	0048	99	8.3	1.12	3.22	8.22	5.2	13
Xanthophyta	<i>Vaucheria</i> sp.		'Cookshold stream'	0151	15	7.2	0.025	0.35	1.11	0.6	32
Chlorophyta	<i>Ulothrix zonata</i>	25µm	'Lanehead stream'			6.9	0.005	0.16	0.35	0.2	35
	<i>Ulothrix</i> sp.	6µm	'Cookshold stream'	0151	15	7.2	0.025	0.71	3.24	1.5	25
	<i>U. cylindricum</i>	8µm	Whetstoremea Burn	0086	10	6.7	0.007	3.22	12.22	6.3	11
	<i>U. moniliformis</i>	10µm	Gillgill Burn	0093	25	6.4	0.86	1.22	5.47	2.6	18
	<i>Ulothrix</i> sp.	6µm	River West Allen	0085	05	4.3	0.061	0.86	2.24	1.4	28
	<i>hormidium flaccidum</i>	6µm	Bolts Burn	0071	99	7.8	1.43	10.74	20.24	14.7	3
	<i>H. fluitans</i>	8µm	'Browngill Tributary'	0108	08	5.7	9.2	4.74	8.24	6.2	12
	<i>H. fluitans</i>	6µm	Brown Gill	0103	08	5.7	1.21	5.74	16.22	7.7	7
	<i>H. rivulare</i>	6µm	Gillgill Burn	0093	85	6.8	1.38	10.6	23.5	15.7	2
	<i>H. rivulare</i>	7µm	River Nent	0048	99	8.3	1.22	10.5	31.0	18.0	1
	<i>H. rivulare</i>	6µm	Garrigill Burn	0102	15	6.9	0.74	4.24	13.5	7.5	8
	<i>Drapenaldia plumosa</i>		Gillgill Burn	0093	11	6.8	0.89	0.87	4.22	1.9	20
	<i>Microspora lauterbornii</i>	8µm	Long Cleugh Burn			5.8	0.042	1.36	2.22	1.73	22
	<i>M. lauterbornii</i>	8µm	Kilhope Burn	0013	02	5.1	0.031	3.24	5.24	4.1	15
	<i>M. amoena</i>	28µm	Cookhope Burn	0012	25	6.9	0.09	0.61	3.22	1.4	27
	<i>Stichococcus bacillaris</i>	3µm	River Nent	0048	24	7.6	3.3	8.24	10.24	9.2	6
	<i>Stigeoclonium tenue</i>	6µm	Rampgill Level	0096	01	7.4	2.43	4.24	10.24	6.6	10
	<i>S. tenue</i>	6µm	Kilhope Burn	0013	02	5.1	0.031	1.73	4.24	2.7	17
	<i>Rhizoclonium</i> sp.	22µm	'Cookshold stream'	0151	15	7.2	0.025	0.61	2.24	1.2	29
	<i>Mougeotia</i> sp.	8µm	Gillgill Burn	0093	01	5.9	7.9	10.95	18.97	14.4	4
<i>Mougeotia</i> sp.	25µm	Cookhope Burn	0012	25	6.9	0.09	1.22	3.22	2.0	19	
<i>Spirogyra</i> sp.	24µm	Gillgill Burn	0093	25	6.4	1.41	8.94	20.49	13.5	5	

Table 6.1 Results of toxicity tests for species from different taxa collected from a number of different reaches

18mg l⁻¹Zn), one of the species in the genus *Ulothrix*, a population of *U. zonata*, displayed the greatest sensitivity of the 36 populations of algae tested (T.I.C. = 0.24mg l⁻¹Zn). Of the species of Bacillariophyta studied, *Meridion circulare* and *Surirella ovata* showed the greatest resistance towards zinc, both in the field and the laboratory (T.I.C.s respectively = 4.1 and 5.2mg l⁻¹Zn). Both these species were present in streams carrying high levels of zinc, but they never occurred at the highest levels encountered (20-30mg l⁻¹Zn), being always confined to sites where the level of zinc never exceeded 2mg l⁻¹Zn. The two species of *Synedra*, particularly *S. ulna*, appeared to be relatively sensitive (T.I.C. = 1.5mg l⁻¹Zn) in both the field and laboratory, with the latter species never being found at levels of above 0.5mg l⁻¹Zn.

Of the three Cyanophyta studied, *Homoeothrix varians* showed resistance towards zinc with a T.I.C. value of 3.6mg l⁻¹Zn. In the field this species was found in streams with 'intermediate' levels of zinc (ranging from 1.5 to 9mg l⁻¹Zn), but never formed conspicuous growths.

The single Xanthophyta species assayed, *Vaucheria* sp., proved to be sensitive towards zinc (T.I.C. = 0.60mg l⁻¹Zn) and no representative of this taxon was discovered in streams or waters carrying high zinc levels.

Of the Chlorophyta studied, it has already been mentioned that species in the genus *Hormidium* were found to be resistant to zinc toxicity. From Table 6.1 it can be seen that two populations of *H. rivulare* and one of *H. flaccidum* were the first three most resistant species assayed (T.I.C. = 18.0, 15.7 and 14.7mg l⁻¹Zn respectively). From studies in the field (4.3l and 5.3l) they were found to form copious clumps of green threads attached to stones at the highest levels of zinc encountered. Two species of Conjugales, *Spirogyra* sp., and *Mougeotia* sp. were also found to be resistant towards zinc (fifth and fourth respectively in order of tolerance

with T.I.C. = 13.5 and 14.4mg l⁻¹Zn). However the abundance of *Spirogyra* sp. and its distribution in the streams surveyed was markedly reduced when compared with *Mougeotia* sp. and the Ulotrichales. It became apparent therefore that a comparative study of several species in the Ulotrichales, and the genus *Mougeotia*, would establish the most resistant organisms to zinc in the laboratory, and the organisms on which the main study would concentrate.

6.22 Comparison within the Ulotrichales and the genus *Mougeotia*

Six populations of the species *Ulothrix zonata*, *U. moniliformis*, *Hormidium rivulare*, and the genera *Microspora* and *Mougeotia* were obtained from sites showing a wide range of zinc concentrations and assayed using the toxicity test. The results are presented in 6.2. The small number of populations sampled permit only general comments to be made.

From these assays it was evident that species tested from streams carrying high levels of zinc showed an increased resistance when compared to those from low levels. *Hormidium rivulare*, *Ulothrix moniliformis* and a species of *Mougeotia* (filament width = >8<12µm) demonstrated the most resistant populations from streams contaminated by zinc. It was difficult with the small number of samples to separate the relative resistances of these three species, but it was evident in the surveys carried out in 4.3 that *Hormidium rivulare* was the most abundant organism of the three at a variety of different streams in the study area. On this basis the genus *Hormidium* and in particular *H. rivulare* was chosen for more detailed study. With regard to the other two species, both were quite common at a variety of different stream sites, but were never as ubiquitous as *H. rivulare*.

Species of *Microspora* showed a mixed response towards zinc, with the two populations of *M. amoena* being zinc-sensitive, whilst *M. lauterbornii*,

Genus or species	filament width	site description	stream no.	reach no.	pH	Zn in water	J.N.I.	J.L.	T.I.C.
<i>Mougeotia</i> sp.	>8<12µm	Kilhope Burn	0013	02	4.9	0.047	10.24	12.24	11.2
<i>Mougeotia</i> sp.	>8<12µm	Dowgang level	0097	01	8.3	4.69	20.25	39.0	28.1
<i>Mougeotia</i> sp.	>8<12µm	'Old Mine Gill'	0104	01	6.0	22.8	17.0	20.5	18.7
<i>Mougeotia</i> sp.	>8<12µm	'North Grain Sike'	0115	10	4.2	0.022	1.24	2.24	1.7
<i>Mougeotia</i> sp.	30µm	Rookhope Burn	0012	25	7.6	0.067	0.62	2.24	1.2
<i>Mougeotia</i> sp.	30µm	'Footpath Gill'	0106	99	6.8	0.068	0.87	1.73	1.2
<i>Hormidium rivulare</i>	6µm	Gillgill Burn	0093	47	6.9	1.41	3.73	11.0	6.4
<i>H. rivulare</i>	6µm	Eastend Burn	0082	10	5.9	0.060	1.12	2.22	1.6
<i>H. rivulare</i>	6µm	River Nent	0048	20	7.2	1.37	8.25	16.25	11.6
<i>H. rivulare</i>	6µm	'Old Mine Gill'	0104	01	6.0	22.4	14.5	25.5	
<i>H. rivulare</i>	8µm	'Firestone Gill'	0107	17	6.0	9.8	10.75	28.7	17.6
<i>H. rivulare</i>	8µm	'Cooksoold stream'	0151	20	7.1	0.022	1.12	2.22	1.57
<i>Microspora lauterbornii</i>	8µm	Kilhope Burn	0013	02	4.9	0.047	2.24	5.74	3.6
<i>M. lauterbornii</i>	8µm	Eastend Burn	0082	10	5.9	0.060	0.87	2.24	1.4
<i>M. lauterbornii</i>	8µm	Gillgill Burn	0093	85	6.7	1.57	6.24	10.24	8.0
<i>M. lauterbornii</i>	8µm	'Rake Sike B'	0120	01	3.9	0.051	1.24	1.73	1.5
<i>M. amoena</i>	24µm	Rookhope above	0012	25	7.6	0.067	0.87	1.73	1.2
<i>M. amoena</i>	24µm	'Footpath Gill'	0106	99	6.8	0.068	0.62	1.11	0.8
<i>Ulothrix moniliformis</i>	8µm	River East Allen	0081	06	6.8	0.010	0.61	1.11	0.8
<i>U. moniliformis</i>	8µm	Eastend Burn	0082	10	5.9	0.060	0.16	0.87	0.4
<i>U. moniliformis</i>	10µm	Gudham Gill	0092	20	6.9	0.91	1.37	2.22	1.7
<i>U. moniliformis</i>	10µm	Gillgill Burn	0093	01	5.9	8.2	2.22	15.0	5.8
<i>U. moniliformis</i>	10µm	'Old Mine Gill'	0104	01	6.0	22.4	20.5	23.5	22.0
<i>U. moniliformis</i>	10µm	Sipton Burn	-	-	5.8	0.030	0.6	1.11	0.8
<i>U. zonata</i>	25µm	'Lanehead stream'	-	-	6.8	0.005	0.07	0.35	0.2
<i>U. zonata</i>	25µm	Foreshield Burn	0091	30	8.4	0.012	0.27	2.73	0.9
<i>U. zonata</i>	25µm	River South Tyne	0055	30	7.7	0.051	0.35	0.9	0.6
<i>U. zonata</i>	25µm	Rookhope Burn	0012	25	7.6	0.067	0.22	1.11	0.5
<i>U. zonata</i>	30µm	'Sipton Bridge Sike'	-	-	6.4	0.008	0.87	1.11	0.9
<i>U. zonata</i>	30µm	Wnet-tonemea Burn	0086	10	6.9	0.008	0.87	1.62	1.2

Table 6.2 Results for toxicity tests on species in the Ulotrichales, and the genus *Mougeotia*

although showing some resistance to zinc in populations from high zinc levels in the field, never reached the level of tolerance shown by *H. rivulare*. *M. amoena* was never found at sites with zinc contamination.

Ulothrix zonata proved to be zinc-sensitive in all six populations tested and was never found in the field at sites showing more than $0.08 \text{ mg l}^{-1} \text{ Zn}$.

Of the populations of *Mougeotia* spp. studied, it was evident that species with the filament width of $>8 \leq 12 \mu\text{m}$ were more resistant to zinc than species with the filament width of $30 \mu\text{m}$. *Mougeotia* spp., with a filament width greater than $24 \mu\text{m}$, were never found in streams with a mean level of zinc above 0.08 mg l^{-1} . Conversely, at two sites demonstrating consistently high levels of zinc, 0104/01 and 0097/01 (Table 4.1), *Mougeotia* sp. ($>8 \leq 12 \mu\text{m}$) formed copious growths throughout the spring and summer.

6.3 Field Surveys

6.3.1 Introduction

These surveys were designed to sample a number of reaches where species in the genus *Hormidium*, particularly *H. rivulare*, formed a conspicuous part of the flora. This genus was chosen for intensive study for reasons discussed fully in 2.4.1. The reaches were selected to cover a wide range of zinc levels.

The surveys were performed originally on 42 reaches chosen from earlier surveys, including those described in 4.2.

Towards the end of the study an opportunity was made available to include five sites from continental mining areas in which *Hormidium* species were found. The advantages of including these four sites would be that a comparison could be made with populations from a geological region far removed from the main study area.

In all, samples of algal material were collected from 47 sites, of which 42 were in North-east England, one in France, three in Germany, and one in Ireland.

This part of the chapter presents the results of these surveys in a manner similar to that described in 4.1.

6.32 Water chemistry

The key field descriptive statistics are summarized in Tables 6.3 and 6.4. The mean values for chemical parameters measured at each of the reaches is given in Table 6.3. The range from minimum to maximum, together with the mean figures for the variables for each of the three *Horridium* species, is given in Table 6.4. It can be seen from Table 6.3 that these sites display a marked variation in water chemistry. Parameters such as pH range from 3.8 (reach 0120/01) to 8.0 (reach 0091/30) and total hardness from 4.9 (reach 0120/01) to 2978 (0151/20) $\text{Mg l}^{-1}\text{CaCO}_3$. The levels of certain cations also vary considerably, with Ca and Mg ranging from 0.6 and 0.9mg l^{-1} respectively (reach 0120/01) to 212 and 585mg l^{-1} (reach 0151/20).

Of the heavy metals, Zn shows one of the most extensive ranges from 0.005mg l^{-1} (reach 0118/07) to 22.8mg l^{-1} (reach 0104/01). The levels of Cd and Pb range from <0.0001 and <0.001 to 0.088 and 1.78mg l^{-1} respectively.

It Table 6.4 is referred to, it can be seen that both *Horridium rivulare* and *H. flaccidum* were present at the sites, with the highest level of zinc included in the survey (maximum of $26.8\text{mg l}^{-1}\text{Zn}$). Throughout most of the year at this site they were found to form copious tufts of green threads attached to stones and silt. The maximum level of zinc at which *H. fluitans* was found was $7.0\text{mg l}^{-1}\text{Zn}$.

variable	<i>H. rivulare</i>		<i>H. flaccidum</i>		<i>H. fluitans</i>	
current	0.749	(<0.333 - 2.310)	0.809	(0.253 - 1.40)	0.747	(0.135 - 1.769)
temperature	11.0	(0.5 - 22.5)	9.8	(3.5 - 18.0)	9.4	(0.5 - 19.0)
O.D. - 420	0.027	(0.001 - 0.189)	0.011	(0.001 - 0.037)	0.046	(0.001 - 0.189)
conductivity	244	(29 - 3480)	199	(47.5 - 970)	83.8	(6.0 -172)
pH	6.5	(3.7 - 8.4)	6.4	(4.2 - 7.9)	5.3	(6.9 - 3.6)
total alkalinity	53.4	(0 - 250)	62.4	(4.0 - 227)	10.2	(0 - 24)
total hardness	208	(4.0 - 5321)	171	(13.0 - 692)	26.5	(6.6 - 53.4)
Ca hardness	79.7	(1.3 - 831)	86.6	(4.3 - 312)	14.5	(1.3 - 37.7)
Mg hardness	116	(2.6 - 4424)	57.0	(5.0 - 391)	6.7	(2.5 - 13.6)
Na	36.8	(0.1 - 2750)	8.8	(2.7 - 32.0)	7.2	(1.9 - 27.2)
K	2.8	(0.1 - 43.5)	3.5	(0.30 - 25.0)	0.9	(0.1 - 2.1)
Mg	28.3	(0.6 - 1075)	13.8	(1.2 - 95.0)	1.6	(0.6 - 3.3)
Ca	32	(0.5 - 333)	34.7	(1.7 - 125)	5.8	(0.5 - 15.1)
Al	0.34	(<0.03 - 4.2)	0.28	(<0.03 - 4.2)	0.30	(<0.03 - 1.20)
Mn	0.406	(0.005 - 8.2)	0.46	(0.010 - 4.3)	0.20	(0.040 - 0.72)
Fe	0.32	(<0.01 - 4.8)	0.67	(<0.01 - 4.8)	0.59	(0.02 - 1.73)
Cu	0.010	(<0.002 - 0.100)	0.016	(<0.002 - 0.100)	0.005	(<0.002 - 0.032)
Zn	2.14	(0.005 - 26.8)	5.4	(0.015 - 26.8)	1.78	(0.005 - 7.0)
Cd	0.010	(<0.0001- 0.088)	0.011	(<0.0001- 0.073)	0.0060	(<0.0001- 0.0390)
Pb	0.065	(<0.001 - 2.20)	0.112	(<0.001 - 1.78)	0.204	(0.005 - 1.82)
PO ₄ -P	0.038	(<0.002 - 0.50)	0.011	(0.005 - 0.041)	0.012	(<0.002 - 0.036)
NH ₄ -N	0.30	(<0.01 - 2.10)	0.25	(<0.01 - 1.0)	0.21	(<0.01 - 1.90)
NO ₃ -N	0.3	(0.01 - 4.5)	0.22	(<0.01 - 0.66)	0.25	(<0.01 - 1.14)
SO ₄ -S	32.4	(0.54 - 1115)	21.5	(2.9 - 135)	7.2	(0.54 - 48.0)
Si ₄	2.61	(0.04 - 9.8)	3.4	(1.0 - 7.4)	1.0	(0.011 - 3.35)
Cl	28.8	(8.5 - 212.5)	21.6	(10.0 - 112.5)	20.6	(8.4 - 60.0)

Table 6.4 Mean values (and ranges) of physical and chemical parameters in waters from which the three *Hormidium* species were collected. (Concentrations of elements in mg l⁻¹)

H. rivulare demonstrates the widest range of all of the variables included in the study. Thus pH ranges from 3.7 to 8.4, total hardness from 4.0 to 5321mg l⁻¹CaCO₃, and Zn from 0.005 to 26.8mg l⁻¹.

H. flaccidum shows a similar range in values.

H. fluitans is confined to a much narrower range of values for all the parameters listed. Particularly evident is pH where it shows an acid preference (mean of 5.3), and Mg and Ca, which range from 0.6 to 3.3, and 0.5 to 15.1mg l⁻¹ respectively.

6.33 Intervariable correlation analysis

Using the method outlined in 2.522, a matrix of correlation coefficients was produced for the main chemical parameters measured during the surveys. This is presented in Table 6.5. If reference is made to this table, there are two main groups of cross-correlated variables, as was established for the streams studied in the previous surveys (4.3, 5.3). The largest and most obvious group is formed by the variables which include Na, K, Mg, Ca, pH, total alkalinity, the measures of hardness, Si and SO₄-S.

The other group is characterized by positive correlations (P = 0.001) between Zn, Cd and Pb, and to a lesser extent Al and Cu. Another small positively intercorrelated group is formed by Fe, Mn, Al and Cu.

Other important correlations between Zn and the other variables include the following. It is negatively correlated with both O.D. and Fe (P = 0.001) which are themselves highly positively correlated (P = 0.001). It is also negatively correlated with pH (P = 0.01). It correlates highly with K and conductivity (P = 0.01). Cd resembles Zn in the pattern of correlations within the matrix, apart from the correlation with O.D. Pb also shows similarities, but demonstrates high negative correlations with Mg and Ca.

	O.D - 420	conductivity	pH	total alkalinity	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	PO ₄ -P	NH ₄ -N	NO ₃ -N	SO ₄ -S	Si	Cl	total hardness	Ca hardness	Mg hardness	
O.D - 420	1.000	0.481	-0.184	-0.170	-0.261	0.401	-0.409	-0.366	0.298		0.754	0.309	-0.395					0.290	-0.343	-0.444		-0.402	-0.365	-0.108	
conductivity		1.000	0.638	0.800	0.350	0.731	0.851	0.886	-0.215		-0.443	0.300				0.411			0.427	0.494	0.218	0.510	0.826	0.851	
pH			1.000	0.819	0.361	0.545	0.740	0.791	-0.583				-0.299		-0.495				0.319	0.538		0.753	0.791	0.740	
total alkalinity				1.000	0.554	0.710	0.788	0.920	-0.417		-0.320				-0.232				0.485	0.411	0.320	0.893	0.940	0.766	
Na					1.000	0.466	0.329	0.452		0.320						0.192	0.231		0.504	0.374	0.592	0.371	0.452	0.330	
K						1.000	0.792	0.744			-0.300	0.306	0.249	0.266					0.639	0.547	0.298	0.832	0.744	0.792	
Ca							1.000	0.797	-0.273		-0.349	0.210			0.235				0.577	0.091		0.952	0.797	1.000	
Mg								1.000	-0.314		-0.228				-0.256				0.538	0.566	0.210	0.981	1.000	0.797	
Al									1.000	0.407	0.212	0.264	0.195	0.331	0.438	0.224					-0.191		-0.306	0.311	-0.273
Mn										1.000	0.248	0.179							0.342	0.238	0.252				
Fe											1.000	0.187	-0.453	-0.358				0.276	-0.216	-0.205		-0.371	-0.228	-0.349	
Cu												1.000	0.170	0.233	0.209			0.278				0.239		0.210	
Zn													1.000	0.766	0.739		-0.249	-0.232							
Cd														1.000	0.686		-0.274								
Pb															1.000			-0.243	-0.423	-0.279	-0.181	-0.256	-0.235		
PO ₄ -P																1.000					0.298				
NH ₄ -N																	1.000		0.257		0.263				
NO ₃ -N																		1.000							
SO ₄ -S																			1.000	0.317	0.453	0.551	0.577	0.577	
Si																				1.000	0.187	0.608	0.508	0.692	
Cl																					1.000	0.210			
total hardness																						1.000	0.884	0.851	
Ca hardness																							1.000	0.802	
Mg hardness																								1.000	

Table 6.5 Intervariable correlation matrix for the chemical data from 42 *Hormium* sampling sites
(* = P<0.05; ** = P<0.01; *** = P<0.001)

6.34 Factor analysis

The steps previously established for the factor analysis of the chemical data (2.523, 4.23) were performed on the information collected during the present surveys.

6.341 Principal components

The matrix of principal components derived from the correlation matrix for the *Hormidium* site surveys is given in Table 6.6. Five principal components were extracted which accounted for 80% of the variance in the correlation matrix.

Over one third of the variance was accounted for by the first principal component which showed heavy loadings for Na, K, Mg, Ca and the measures of hardness, with a negative loading for Pb.

The second principal component loads heavily for the heavy metals, in particular Al, Pb, Cd and Zn. A moderate negative loading is shown by pH.

The third component features negative loadings for O.D. and Fe, opposed by positive loadings for Zn and Cd.

The fourth principal component is dominated by $\text{SO}_4\text{-S}$, with a moderate contribution from conductivity.

The fifth principal component is exclusively a $\text{PO}_4\text{-P}$ component.

6.342 Principal factors

The R-mode varimax factor matrix of the chemical data is given in Table 6.7, and the loadings of the various ions in these factors are illustrated in Fig. 6.1. Five factors account for the total variance in the data, with the first factor accounting for over 50% of this variance in the ions. High loadings on this factor occur for Na, K, Mg, Ca, total alkalinity

variable	Principal component					communality
	I	II	III	IV	V	
O.D. - 420			-0.774			0.787
conductivity	0.659			0.618		0.919
pH		-0.653				0.697
total alkalinity	0.740					0.752
Na	0.726			-0.522		0.879
K	0.969					0.963
Mg	0.936					0.937
Ca	0.947					0.945
Al		0.808				0.805
Mn	0.510					0.559
Fe			-0.864			0.767
Cu		0.429				0.424
Zn		0.608	0.685			0.884
Cd		0.630	0.431			0.702
Pb	-0.403	0.720				0.832
PO ₄ ^{-P}					0.827	0.827
SO ₄ ^{-S}	0.612			0.704		0.931
Si ₄	0.783					0.683
Cl	0.697					0.591
total hardness	0.959					0.964
Ca hardness	0.947					0.944
Mg hardness	0.936					0.937
eigen value	9.206	3.227	2.586	1.514	1.193	
per cent of variance explained by principal component						
	41.8	14.7	11.8	6.9	5.4	
cumulative per cent of variance						
	41.8	56.5	68.3	75.2	80.6	

Table 6.6 Principal components derived from the correlation coefficient matrix for 42 *Horridium* sites

and the measure of hardness, with low contributions from SO_4 -S and Mn.

Factor two is characterized by high loadings for Zn, Cd and Pb, with over 70% of the variance in Zn accounted for by this factor. These positive loadings are opposed by the negative loading of Fe. Al offers a small positive contribution to this factor.

The third factor is exclusively a unique SO_4 -S factor which accounts for 84% of the variance of SO_4 -S in the samples studied. It is associated with a high positive loading for conductivity.

Factor four is primarily an O.D./Fe factor accounting for nearly 100% and 42% of the variance of these two variables in the waters respectively. Cu shows a small positive loading, illustrating its connection with the other two variables. There are small but significant negative loadings of Zn and pH on this factor.

The fifth factor shows moderate loadings for pH and total alkalinity, opposed by negative loadings for Al and Mn. This again demonstrates the existence of mutually exclusive components in the system.

The low communality figures for Mn and Cu suggest that smaller fractions of their variances are explained by the factors extracted. This is evident, particularly when compared with the values for K, Mg, Ca and Zn.

6.4 Algal communities associated with *Horrmidium* species

During the interpretation of the data on the microflora associated with the three *Horrmidium* species, attempts were made to discover if any 'associations' of species with *Horrmidium* populations could be defined by constructing a table in which the *Horrmidium* sites were arranged in order of decreasing zinc concentration. This method therefore closely follows that used in sections 4.31 and 5.31 and outlined in 2.354.

variable	factor					communality
	1	2	3	4	5	
O.D. - 420				0.994		0.995
conductivity	0.375		0.875			0.948
pH				-0.376	0.522	0.578
total alkalinity	0.604				0.495	0.775
Na	0.860					0.810
K	0.949					0.972
Mg	0.938					0.942
Ca	0.900					0.972
Al		0.372			-0.616	0.746
Mn	0.466				-0.389	0.448
Fe		-0.354		0.659		0.597
Cu				0.310		0.290
Zn		0.865		-0.340		0.911
Cd		0.718				0.527
Pb		0.857				0.863
SO ₄ ^{-S}	0.327		0.926			0.967
Si	0.717					0.682
Cl	0.605					0.446
total hardness	0.959					0.973
Ca hardness	0.900					0.972
Mg hardness	0.938					0.942
eigen value (principal component)						
	9.068	2.950	2.382	1.401	0.677	
percent of variance explained by Factor						
	55.0	17.9	14.5	8.5	4.1	
cumulative per cent of variance						
	55.0	72.9	87.4	95.9	100.0	

Table 6.7 R-mode varimax factor matrix of chemical data for 42 *Horrmidium* sampling sites

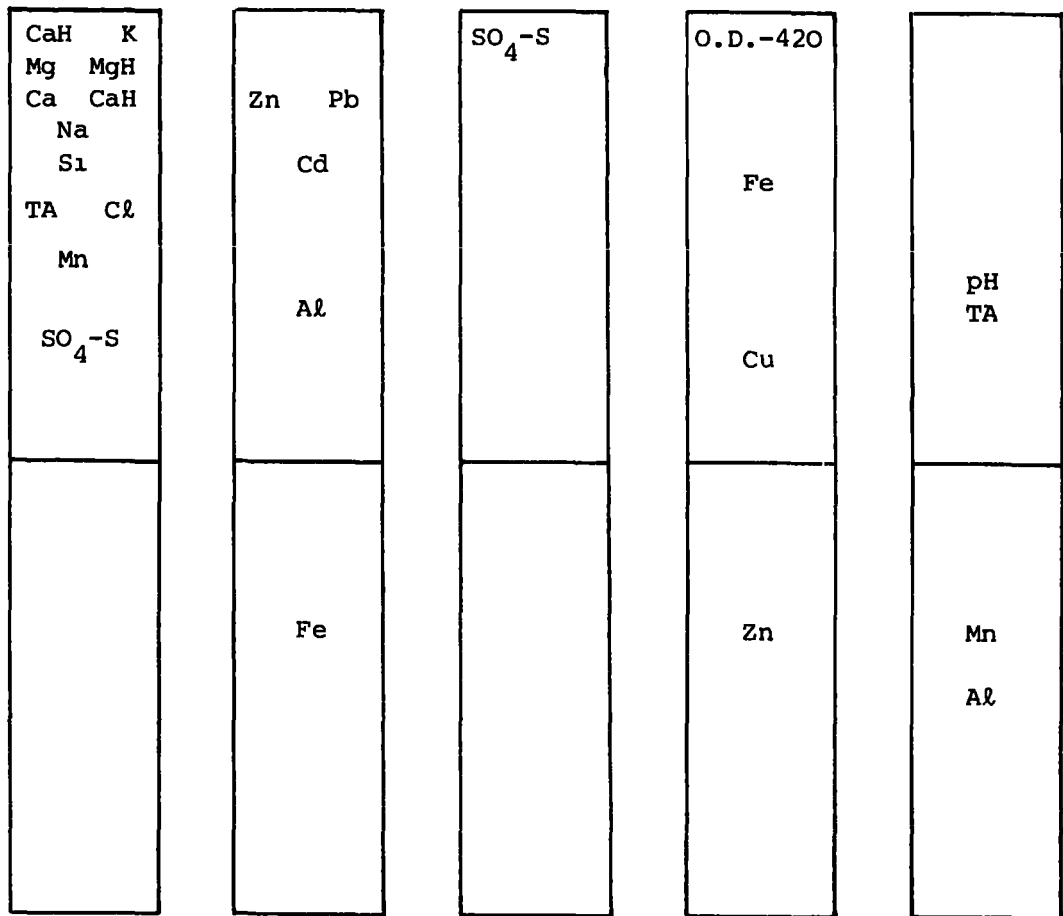


Fig. 6.1 Diagrammatic representation of factors from R-mode varimax solution of chemical data for 42 *Hormidium* sites (TA = total alkalinity; TH = total hardness; CaH = calcium hardness; MgH = magnesium hardness.)

The final 'association table' extracted from the data is given in Table 6.8. It can be seen that *Hormidium rivulare* and *H. flaccidum* have an extensive range, particularly the former which occurs abundantly more or less throughout the sites. *H. fluitans* is less abundant than the other species throughout the range of sites, being more restricted to the right hand side of the table. However within individual sites it can be abundant.

Distinct clusters of species do occur when the sites are arranged in order of decreasing levels of zinc. These can be defined into five main 'associations'. If comparisons are made with the two previous tables which illustrate 'associations' of species down a gradient of zinc levels (Tables 4.11 and 5.5), similar patterns in the 'associations' occur, even though a large number of different sites, with some containing lower levels of zinc, are included in the present surveys. A small 'association' occurs on the left hand side of the table at the higher concentrations of zinc. The communities here are dominated by *Hormidium rivulare* and *H. flaccidum*. The 'association' is formed by *Phormidium* sp. and *Synechococcus* sp., together with *Pinnularia borealis*, *P. appendiculata*, *Caloneis lagerstedtii*, *C. bacillum*, *Achmanthes marginistriata*, *Eunotia tenella* and *Euglena mutabilis*.

Following this is an 'association' of species found at 'intermediate' to 'low' levels of zinc ($0.5 - 8 \text{ mg l}^{-1} \text{ Zn}$), but which were found to be more or less absent from either the very high levels or extremely low levels of zinc. All three species of *Hormidium* (when present in the case of *H. fluitans*) were abundant in the communities at the sites where the species in this 'association' were found. Prominent members include *Plectonema boryanum*, *Phormidium mucicola*, *Schizothrix* sp., *Cymbella ventricosa*, *Amphora veneta*, *Diatoma hiemale* var. *mesodon*, *Frustulia rhomboides* var.

Table 6.8 'Association table' of algae sampled during the survey of *Horrmidium* sites. Reaches are arranged from left to right in order of decreasing levels of zinc. Species are arranged to show distribution throughout the range of zinc levels. For more details see text and Section 2.

saxonica, Chrysophyta sp. form 'A' (*Chrysonebula holmesii*) and Chrysophyta sp. form 'B' (*Hydrurus foetidus*).

The middle of the table is dominated by a large 'association' of algae both relatively abundant within the 'association', and prominent components of the flora within each community at the various sites. It is dominated by *Hormidium rivulare* and also characterized by *Ulothrix moniliformis* and *Mougeotia* sp. ($>8 \leq 12 \mu\text{m}$). Other prominent members include *Cylindrocystis brebissonii*, *Cosmarium subarctum*, *Pseudanabaena catenata*, *Pinnularia subcapitata*, *P. viridis*, *P. viridis* var. *sudetica* and *Achnanthes minutissima*.

Below this large assemblage of algae is an 'association' which includes species more abundant to the right hand side of the table in the sites carrying 'moderate' to very low levels of zinc ($< 2 \text{mg l}^{-1} \text{Zn}$). Some of the species do occur at the higher zinc levels but are predominantly present (sometimes in abundance) at the lower levels. The 'association' is characterized by *Stigeoclonium* sp. (= *S. tenue*), *Homoeothrix varians*, *Chamaesiphon polymorphus*, *Gomphonema parvulum*, *Surirella ovata*, *Staurastrum punctulatum*, *Roya obtusa* and *Microspora lauterbornii*. At the sites where it occurs, *Hormidium fluitans* is a dominant member of this 'association'. In the next 'association', species are more or less absent from the upper zinc concentrations, being more associated with the lower zinc sites or those free of zinc contamination. It is characterized by *Gongrosira incrustans*, *Stichococcus bacillaris*, *Meridion circulare*, *Navicula cryptocephala* and *Synedra rumpens*.

The final 'association' of algae includes species which are more or less confined to the very low levels of zinc ($< 0.1 \text{mg l}^{-1}$). It features a large number of species which includes *Phormidium autumnale*, *Lyngbya martensiana*,

Navicula radiosa, *Diatoma elongatum*, *Tabellaria flocculosa*, *Synedra ulna*, *Lemanea fluviatilis*, *Cladophora glomerata*, *Microspora amoena* and *Ulothrix zonata*.

6.5 Laboratory investigations on *Hormidium* species

6.51 Introduction

During the course of the surveys carried out on *Hormidium* sites, material of the three species was brought into the laboratory for assay. This was intended to balance the observations on resistance to zinc in the field with tests on the comparative resistance to zinc under laboratory conditions.

The materials and methods adopted for carrying out the assays on populations, and the subsequent statistical analysis of the data, are given in 2.4 and 2.5. Since the resistance of populations to zinc was found to be so closely associated with the level of zinc in the field and other aspects of the water chemistry, the results of the laboratory investigations are presented with the relevant aspects of the environmental data, and the subsequent analyses are devoted to comparisons between the two sets of data.

6.52 Assays

The results for the toxicity tests carried out on 35 populations of *Hormidium rivulare*, 12 populations of *H. fluitans* and 9 populations of *H. flaccidum* are presented, together with the mean field level of zinc at each site in Table 6.9. Included with the data on the field zinc levels is a column of figures giving the maximum level of zinc recorded at that site. In most cases this occurred during the respective number of surveys carried out during this investigation, but with the figures marked with an asterisk higher levels of zinc were recorded at these sites during further surveys. The figures are included because they later form

reach from which population taken	field Zn			<i>H. rivulare</i>				<i>H. fluitans</i>				<i>H. flaccidum</i>			
				J.N.I.	J.L.	T.I.C.		J.N.I.	J.L.	T.I.C.		J.N.I.	J.L.	T.I.C.	
	\bar{x}	s.d.	max.	\bar{x}	\bar{x}	\bar{x}	s.d.	\bar{x}	\bar{x}	\bar{x}	s.d.	\bar{x}	\bar{x}	\bar{x}	s.d.
0012/25	0.079	0.034	0.115	4.68	6.00	6.2	2.18								
0012/29	1.13	0.854	1.94	4.24	8.62	6.0	1.89								
0013/02	0.100	0.094	0.940*	7.19	7.00	3.9	4.52	1.46	4.72	2.5	0.66				
0048/20	1.38	0.535	1.94	6.05	16.3	9.9	2.10								
0048/99	1.04	0.395	1.40	11.9	24.6	17.0	3.28								
0055/30	0.037	0.021	0.14	0.89	4.67	1.9	0.07								
0071/99	1.21	0.232	1.48									7.2	21.1	12.0	3.09
0077/05	0.26	0.385	0.710	4.73	8.05	6.2	1.13					5.2	10.2	7.3	0.70
0081/06	0.020	0.008	0.030	1.14	1.02	1.5	0.27								
0082/10	0.072	0.014	0.090	1.12	1.68	1.4	0.27	1.12	2.36	1.6	0.08				
0085/05	0.063	0.066	0.066	0.92	1.68	1.2						0.74	1.43	1.0	0.28
0086/10	0.018	0.013	0.033	6.75	10.0	8.2	1.72								
0089/05	0.018	0.009	0.025	0.90	0.74	1.3	0.36								
0091/30	0.012	0.001	0.014	1.06	3.97	2.0	0.31								
0092/20	0.953	0.228	1.20					1.46	5.24	2.7	1.78				
0093/01	8.22	1.284	13.70*									8.15	15.2	10.9	6.67
0093/85	1.52	0.157	1.80	10.6	23.4	15.7	2.35								
0094/10	0.871	0.265	1.10									9.00	20.4	13.5	1.69
0098/01	3.70	1.145	4.58	2.64	4.48	3.4	0.28								
0101/05	0.654	0.500	1.27	4.14	13.3	7.4	1.76								
0102/15	0.90	0.0298	1.15	4.30	13.2	7.1	5.40								
0103/08	0.70	0.074	1.00					5.30	18.4	9.5	3.42				
0104/01	22.34	4.404	30.20*	13.7	25.8	17.7	8.03					7.62	20.4	14.5	3.07
0104/99	4.66	1.247	6.82*					7.00	12.2	9.0	1.68				
0105/99	5.00	1.074	6.40*					3.99	8.86	6.0	1.90				
0107/17	11.40	2.972	14.80	10.5	24.2	15.9	2.93								
0108/08	5.59	1.442	9.20					12.7	21.4	16.5	13.0				
0115/10	0.044	0.008	0.052					0.88	3.48	1.7	0.38				
0116/10	0.039	0.012	0.050	1.5	2.24	1.6	0.04	1.09	2.36	1.6	0.24				
0118/08	0.007	0.004	0.010	1.23	2.25	1.7		1.73	2.49	2.1	0.58				
0120/01	0.032	0.019	0.051	1.23	2.24	1.7	0.00								
0124/50	0.028	0.028	0.028	0.22	1.23	0.50									
0147/30	0.104	0.044	0.161	0.91	1.3	0.27									
0151/15	0.022	0.005	0.027									0.75	1.48	1.0	0.14
0151/20	0.57	0.667	1.970	1.11	2.14	1.5	0.47								
0167/10	0.093	0.019	0.107	2.59	6.73	4.0									
0168/01	7.58		21.60	7.24	20.4	11.9	3.30					10.2	28.9	17.2	0.05
0169/01	1.14	1.173		3.24	10.4	5.8	1.29					3.86	15.4	7.7	4.07
0170/07	0.039	0.052						3.74	4.74	4.2	0.00				
0171/08	0.048	0.052		0.53	3.60	1.3	0.02								
0172/04	0.026	0.026						0.70	5.48	2.0	0.00				
2008/50	1.05			3.24	7.25	4.9									
3001/99	1.34			14.7	49.0	26.9									
4005/05	8.40			30.5	49.0	3E.7									
4006/01	6.80			5.48	18.7	10.1									
4013/92	9.00			8.94	28.7	1E.0									

Table 6.9 Mean field zinc levels of *Horndium* sampling sites, together with mean results for four toxicity tests J.N.I. = just non-inhibitory, J.L. = just lethal, T.I.C. = tolerance index concentration. Maximum zinc levels collected during further surveys but not included in estimate of mean levels of zinc are marked*. All species were sampled each time water was collected, with the exception of *H. flaccidum* which was not detectable once at each of sites 0104/01 and 0168/01. (all concentrations in mg l⁻¹)

part of an analysis on the data (6.531). Higher levels of zinc were needed to inhibit the growth of some populations when compared with others, and these populations also required higher concentrations of zinc to cause death by the end of the 6-day culture period. This is well illustrated by comparing populations of *Hormidium rivulare* from reaches 0048/99 with 0089/05, and 0104/01 with 0085/05. A similar pattern of results was found for all three species.

Further tests carried out were able to show that repeat experiments on the same population gave similar results, whether repeated within a few days of collection, or after long term subculturing either in 'low' or 'high' zinc concentrations. A comparison was made between two sensitive and two resistant populations of *Hormidium rivulare*, as determined from Table 6.9, with the toxicity of zinc at the beginning and end of a six month period of weekly subculturing; each assay was based on four experiments. Table 6.10 gives the results of these tests and includes data for one population which was assayed eight times at intervals over a period of 18 months. The larger standard deviations shown for some of the populations when first studied were found to be a reflection of the assay technique. No attempt was made at quantitatively assessing the number of somatic changes in the filaments, or generations that occurred with these populations during the six month period. However it does not seem unreasonable to suggest that the results shown in this table indicate that differences in response to zinc by different populations in short-term tests may be a reflection of genetic and not environmental adaptation. The ratio J.L./J.N.I., expressed as a percentage, ranged from 14.7 - 79.2, with a mean of 45.2 (S.D. = 15.5). There was no detectable trend in this ratio with populations from increasing field zinc levels.

reach from which population taken	field Zn	pretreatment	J.N.I.		J.L.		T.I.C.	
			\bar{x}	s.d.	\bar{x}	s.d.	\bar{x}	s.d.
0081/06	0.020	fresh	1.14	0.17	1.92	0.37	1.50	0.27
		6 months at 0 mg l ⁻¹ Zn	1.25	0.11	1.85	0.12	1.52	0.11
		6 months at 1 mg l ⁻¹ Zn	1.20	0.22	1.90	0.24	1.51	0.24
0085/05	0.063	fresh	0.919	0.43	1.68	0.79	1.24	0.58
		6 months at 0 mg l ⁻¹ Zn	1.70	0.23	1.82	0.64	1.41	0.32
		6 months at 1 mg l ⁻¹ Zn	1.20	0.42	1.60	0.22	1.38	0.27
0093/85	1.52	fresh	10.6	0.37	23.5	5.26	15.7	2.35
		6 months at 0 mg l ⁻¹ Zn	10.5	0.25	24.5	0.86	16.0	0.84
		6 months at 15 mg l ⁻¹ Zn	10.0	0.37	25.0	0.94	15.8	0.68
		mean of 8 assays at 0 mg l ⁻¹ Zn	10.6	0.31	24.4	4.31	16.0	1.68
0104/01	22.8	fresh	13.7	7.55	25.8	7.63	18.7	8.02
		6 months at 0 mg l ⁻¹ Zn	12.5	0.84	27.5	0.86	18.5	0.94
		6 months at 20 mg l ⁻¹ Zn	10.5	0.42	31.5	2.64	18.2	4.48

Table 6.10 Comparison for two sensitive and two tolerant populations of *Horrmidium* of the toxicity of zinc at the beginning and end of a 6 month period of weekly subculturing; each assay is based on four experiments. Data are also included for one population which was assayed 8 times at intervals over a period of 18 months. (J.N.I. = just non-inhibitory; J.L. = just lethal; T.I.C. = tolerance index concentration; all concentrations in mg l⁻¹.)

6.53 Analysis of the data

6.531 Intervariable correlations

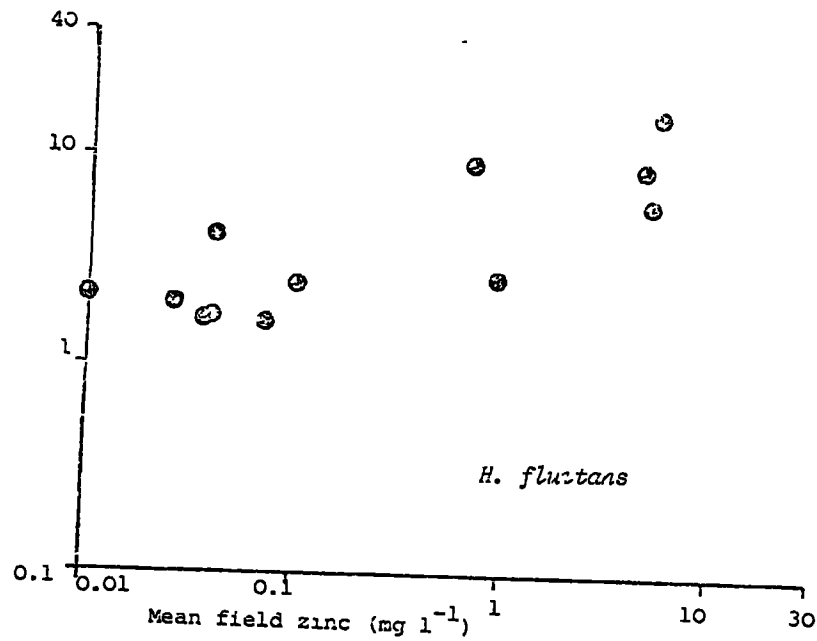
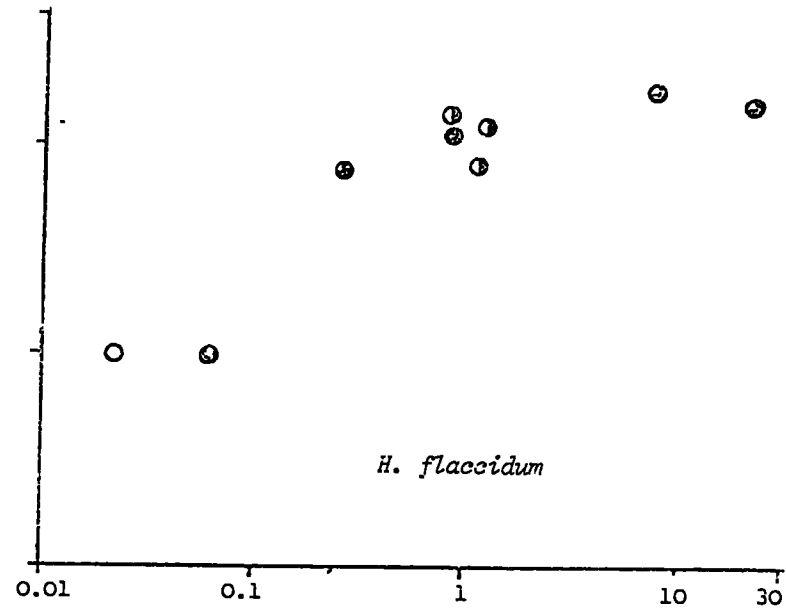
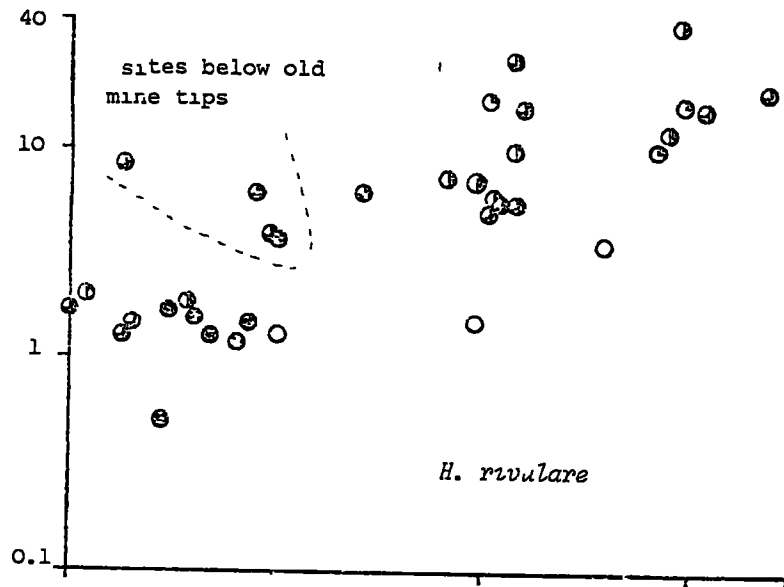
Table 6.11 summarizes the correlations found between the T.I.C. and a selection of the measured field variables (or their transformations) for the three different *Horneridium* species. No significant correlation could be found between variations in T.I.C. among populations from the sites collected on different days, and variations in water chemistry collected on those same days. From Table 6.11 it can be seen that the T.I.C. correlates positively with Cd, Zn and Pb (more or less in order of significance) for all three species. The most consistently significant correlations between T.I.C. and these metals is shown with *H. fluitans*. Negative correlations are demonstrated between T.I.C. and Na, K, Mg, Ca and the measures of hardness in *H. rivulare* and *H. flaccidum*, but are most marked in the latter species. The most significant negative correlation occurs with Mg and its contribution to the measure of hardness.

The logarithmic transformations of the Zn and Cd values show numerically higher correlations with T.I.C., as do some of the crude ratio transformations of Zn, suggesting that an improvement in the linear relationship is obtainable. There are improved correlations between T.I.C. and \log Zn, \log Cd and \log Zn/ \log total hardness ratio in the case of *H. rivulare*.

The correlation between T.I.C. and the maximum Zn ever recorded at a site is slightly better than the correlation with mean Zn for *H. rivulare* and *H. flaccidum*, but approximately the same for *H. fluitans*.

A scatter diagram of T.I.C. plotted against mean field zinc for the three species is shown in Fig. 6.2. In the case of *H. rivulare*, if certain anomalous points are removed, a discontinuity becomes apparent in the otherwise linear relationship. Although there are considerably less

F.I.C (mg l⁻¹ Zn)



- ⊙ <5 mg l⁻¹Ca
- ⊗ 5 - 25mg l⁻¹Ca
- ⊕ 25 - 50mg l⁻¹Ca
- ⊖ 50 - 75mg l⁻¹Ca
- >75 mg l⁻¹Ca

Fig. 6.2 Scatter diagram showing mean T.I.C. plotted against mean field zinc.

	<u><i>Hormidium rivulare</i></u>	<u><i>H. flaccidum</i></u>	<u><i>H. fluitans</i></u>
	n = 98	n = 38	n = 28
	T.I.C.	T.I.C.	T.I.C.
conductivity	0.184	-0.125	0.197
pH	0.198	0.151	0.173
Na	-0.115	-0.352	-0.054
K	-0.024	-0.192	0.495 *
Mg	-0.083	-0.556 *	0.006
Ca	0.096	-0.446 *	0.104
Zn	0.536 *	0.220	0.640 *
Pb	0.458 *	0.222	0.810 *
Cd	0.594 *	0.467 *	0.831 *
total hardness	0.008	-0.506 *	0.225
Mg hardness	-0.083	-0.556 *	0.006
Ca hardness	0.096	0.446 *	0.104
<u>logarithmic transformations</u>			
log Zn	0.706 *	0.581 *	0.602 *
log Cd	0.643 *	0.611 *	0.624 *
log total hardness	0.281	-0.200	0.230
<u>ratio transformations</u>			
Zn/Cd	0.536 *	0.224	0.709 *
Zn/total hardness	0.581 *	0.258	0.692 *
log Zn/log total hardness	0.667 *	0.553 *	0.590 *

Table 6.11 Summary of correlations of tolerance index concentration (T.I.C.) for the three *Hormidium* species v. measured field variables and their transformations (* P = <0.05)

populations for *H. flaccidum*, there are signs of a similar discontinuity. In the case of *H. fluitans*, the relationship is more linear, but again these suggestions are made on a reduced number of populations when compared with *H. rivulare*. Differences between the responses of the three species were difficult to establish because of the fewer populations of *H. flaccidum* and *H. fluitans*. The tendency of *H. fluitans* to fragment into short filaments or unicells made interpretation of the assays more complicated with this species.

6.532 Multiple stepwise linear regression

Using the T.I.C. as the dependent variable (Y), a stepwise linear regression was carried out for the three species in order to establish an equation which would best describe the response (T.I.C.) in terms of the independent or predictor variables (X). Table 6.12 lists the variables in order of their inclusion in the equation (2.532). Bearing in mind the fact that for *H. flaccidum* and *H. fluitans* there are a reduced number of populations when compared with *H. rivulare*, the following points seem worthy of comment. There is some similarity between the three species in their placing of Cd, first for *H. fluitans* first as the logarithmic value for *H. flaccidum* and fourth for *H. rivulare*. Zn or Zn transformations are highly placed for all three species, and in particular as the log Zn value for *H. rivulare*. In contrast, the high placing of Mg and Ca for *H. flaccidum* is not mirrored in the other two species. Of special interest is the high placing of PO_4 -P and Si for *H. rivulare*. These results tend to point to two different trends in the data, which have different prominence, depending on the species. The heavy metal influence is seen more clearly in *H. rivulare* and *H. fluitans*, while the influence of amelioration factors is seen more clearly in *H. flaccidum*.

	position (z)	variable (X_z)	b_z	cumulative multiple correlation coefficient r^2	analysis of variance	D F.	sum of squares	mean square	F
<u>H. rivulare</u>	1	log Zn	79.719	0.498					
	2	PO ₄ -P	35.573	0.549					
	3	log Zn/log Mg hardness	396.804	0.571	due to the regression	10	1636.3442	168.6344	657.606
	4	Cd	-75.692	0.555	residual	39	10.0010	0.2564	
	5	Si	-16.060	0.609					
	6	log Mg hardness	11.312	0.634					
	7	log Zn/log total hardness	201.930	0.662					
	8	log Zn/log Ca	57.576	0.727					
	9	conductivity	0.061	0.847					
	10	K	4.342	0.994					
		regression constant a	=	7.813					
<u>d. flaccidum</u>	1	log Cd	9.657	0.373					
	2	Mg	0.179	0.507	due to the regression	6	279.5936	38.2056	422.407
	3	NH ₄ -N	15.940	0.656	residual	1	0.0906	0.0906	
	4	Zn/Mg hardness	-13.349	0.845					
	5	Ca	-0.229	0.975					
	6	log Zn/total hardness	49.842	0.999					
		regression constant a	=	42.248					
<u>h. fluitans</u>	1	Cd	1399.267	0.691					
	2	NO ₃ -N	-30.603	0.794	due to the regression	8	348.4179	43.5522	171.320
	3	Zn/total hardness	-125.804	0.928	residual	1	0.2542	0.2542	
	4	Cl	-0.132	0.994					
	5	log Zn/log Ca	-0.090	0.996					
	6	Fe	-0.104	0.998					
	7	K	0.526	0.998					
	8	Mn	0.963	0.999					
		regression constant a	=	15.103					

Table 6.12 Multiple stepwise linear regression equations where the tolerance index concentration (T.I.C.) is the dependent variable Y and the set of possible independent variables $X_{(1,2,\dots,i,\dots,n)}$ are conductivity, pH, Na, K, Mg, Ca, Zn, Cu, Mn, Fe, Al, Pb, Cd, Cl, Si, PO₄-P, NH₄-N, NH₂-N, NO₃-N, total hardness, Ca hardness, Mg hardness, log Na, log K, log Mg, log Ca, log Zn, log Cd, log total hardness, log Ca hardness, log Mg hardness, Zn/Ca, Zn/Ca hardness, Zn/Mg hardness, Zn/total hardness, Zn/log Ca, Zn/log Ca hardness, log Zn/log Mg hardness, log Zn/log total hardness. Only those variables included up to the tenth position in the equation are shown.

6.533 Principal component analysis*Horrmidium rivulare*

The matrix of principal components is given in Table 6.13 and shows that over 90% of the variances in the correlation matrix are explained by the eight extracted.

The first principal component is dominated by the measures of toxicity together with the three heavy metals Zn, Cd and Pb. It also includes the crude ratio transformations of zinc. Nearly 60% of the variance of all of these variables is accounted for by this component.

The second component features high loadings for Na, K, Mg, Ca and the measures of hardness, with moderate contributions from Cl, Si and $\text{PO}_4\text{-P}$.

The third component includes no very high loadings, but a number of moderate loadings for the metals Al, Mn, Cu and Pb, opposed by a negative loading for pH. Included in this component are small loadings for the crude ratio transformations of zinc.

The fourth principal component features high loadings for Cu and Fe, with over 60% of the variance of the former in the correlation matrix explained by this component.

The fifth component includes a moderate loading for conductivity opposed by negative loadings for Na and Cl.

The sixth is exclusively a manganese component accounting for over 50% of the variance of this variable in the correlation matrix.

The seventh component features the sources of inorganic N with both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ loading on this component.

Principal components

variable	Factor I	Factor II	Factor III	Factor IV	Factor V	Factor VI	Factor VII	Factor VIII	communality
conductivity		0.777			0.450				0.892
pH		0.540	-0.501						0.735
Na		0.729			-0.467				0.954
K		0.884							0.960
Mg		0.843							0.956
Ca		0.878							0.960
Zn	0.392		0.692						0.941
Cu			0.470	0.812					1.020
Mn						0.742			0.780
Fe			0.459	0.796					0.980
Al			0.687						0.962
Pb	0.721		0.413						0.792
Cd	0.300		0.710						0.807
Cl	-0.420	0.672			-0.416				0.843
Si		0.698							0.741
PO ₄ -P		0.577						0.497	0.674
NH ₄ -N							0.672		0.900
NO ₃ -N		0.461					0.432		0.883
total hardness		0.951							0.961
J.N.I.	0.838								0.948
J.L.	0.818								0.950
T.I.C.	0.954								0.997
Ca hardness		0.878							0.961
Mg hardness		0.843							0.956
Zn/Ca	0.824		0.425						0.969
Zn/Ca hardness	0.824		0.425						0.969
Zn/Mg hardness	0.817		0.401						0.959
Zn/total hardness	0.857								1.004
eigen value	10.708	8.442	3.584	2.555	1.343	1.310	1.143	1.004	
per cent of variance explained by principal component	32.4	25.6	10.9	7.7	4.1	4.0	3.5	3.0	
cumulative per cent of variance	32.4	58.0	68.9	76.6	80.7	84.7	88.1	91.2	

Table 6.13 Principal components derived from the correlation coefficient matrix for 31 *Horradium rivulare* sites, including laboratory and field data

The final principal component includes a moderate loading for $\text{PO}_4\text{-P}$ only.

The generally high communality figures indicate that a high fraction of the variance of each variable within the correlation matrix is explained by the extracted components.

H. fluitans

Six principal components were extracted for this species to explain the variance of the correlations between the variables in the correlation matrix (Table 6.14). In general they followed the same pattern as that of *H. rivulare*.

The first component loads highly for the measures of toxicity, Zn, Cd and lead, together with the crude ratio transformation of zinc. But also included in this component are loadings for K, Al, $\text{PO}_4\text{-P}$, total hardness, conductivity and pH. These are opposed by negative loadings for Fe and $\text{NH}_4\text{-N}$. Nearly 80% of the variance of Zn and T.I.C. are explained by this component.

The third principal component features moderate loadings for Na, Mn and Cl, opposed by a negative loading for Si.

The fourth includes loadings again for Na and Cl, together with Al. These are opposed by a weak negative loading for $\text{NO}_3\text{-N}$.

The fifth features weak loadings for Cd and $\text{NO}_3\text{-N}$, opposed by weak negative loadings for pH and Mn.

The sixth includes a weak loading for $\text{NH}_4\text{-N}$, opposed by a moderate loading for Cu.

Principal components

variable	Factor I	Factor II	Factor III	Factor IV	Factor V	Factor VI	communality
conductivity	0.471	0.604					0.765
pH	0.414	0.588			-0.404		0.869
Na		0.581	0.465	0.475			0.872
K	0.703						0.630
Mg		0.855					0.950
Ca		0.866					0.960
Zn	0.422		0.883				0.959
Cu		-0.410				-0.610	0.603
Mn			0.614		-0.413		0.638
Fe	-0.490						0.594
Al	0.438			0.630			0.708
Pb	0.768	-0.431					0.803
Cd	0.833		0.439				1.034
Cl		0.534	0.545	0.468			0.907
Si		0.520	-0.595				0.816
PO ₄ -P	0.617						0.605
NH ₄ -N	-0.462	-0.431				0.438	0.706
NO ₃ -N				-0.440	0.460		0.517
total hardness	0.585	0.784					0.970
J.N.I.	0.883						0.923
J.L.	0.800						0.923
T.I.C.	0.885						0.976
Ca hardness		0.866					0.961
Mg hardness		0.855					0.950
Zn/Ca	0.856						0.942
Zr/Ca hardness	0.856						0.942
Zn/Mg hardness	0.906						0.977
Zn/total hardness	0.881						0.966
eigen value	13.093	7.11	2.68	2.13	1.56	1.18	
per cent of variance explained by principal component	39.7	21.6	8.1	6.5	4.7	3.6	
cumulative per cent of variance	39.7	61.2	69.4	75.8	80.6	84.1	

Table 6.14 Principal components derived from the correlation coefficient matrix for 12 *Horridum frutans* sites including laboratory and field data

Over 80% of the variances in the correlations between these variables is explained by these six principal components. Some of the communality figures are low, such as those for Fe, Cu, $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$, indicating that the components explain only a small proportion of the variances of these elements.

H. flaccidum

The six principal components extracted from the correlation matrix for this species (Table 6.15) contrast with the other two species in the placing of variables or components.

The first principal component which accounts for over 40% of the variances in the correlation matrix includes high positive loadings for Mg, Ca, Si, Cl and the measures of hardness, with moderate loadings for conductivity, Na, K, pH, $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$. These are all opposed by moderate negative loadings for Zn, Cd, Pb, the measures of toxicity and the crude ratio transformations of Zn.

The second component features high loadings for Zn and its transformations, accounting for over 60% of the variance of these variables in the correlation matrix. Included in this component are moderate loadings for conductivity, Cd, Pb and $\text{PO}_4\text{-P}$.

The third component includes moderate loadings for the measures of toxicity, pH and conductivity.

The fourth features high loadings for Al, Fe, Cu and Pb, together with $\text{NO}_3\text{-N}$.

The fifth includes a moderate loading for $\text{NH}_4\text{-N}$, opposed by a high negative loading for Mn.

variable	Principal component						communality
	Factor I	Factor II	Factor III	Factor IV	Factor V	Factor VI	
conductivity	0.679	0.462	0.556				1.038
pH	0.403		0.763				0.916
Na	0.776						0.897
K	0.640		0.524				0.940
Mg	0.895						0.982
Ca	0.887						0.992
Zn	-0.519	0.827					0.999
Cu				0.762			0.728
Mn					-0.802		0.734
Fe				0.815			0.865
Al				0.820		0.400	0.858
Pb	-0.450	0.416		0.651			0.853
Cd	-0.576	0.714					0.955
Cl	0.853						0.870
Si	0.809						0.939
PO ₄ -P	0.583	0.520					0.755
NH ₄ -N					0.590	-0.490	0.805
NO ₃ -N	0.428			0.647			0.735
total hardness	0.887						1.002
J.N.I.	-0.672		0.619				0.942
J.L.	-0.708		0.637				0.943
T.I.C.	-0.720		0.656				0.995
Ca hardness	0.887						0.992
Mg hardness	0.895						0.982
Zn/Ca	-0.549	0.808					0.990
Zn/Ca hardness	-0.549	0.808					0.990
Zn/Mg hardness	-0.531	0.814					0.984
Zn/total hardness	-0.573	0.798					0.991
eigen value	13.757	5.482	4.848	3.408	1.795	1.241	
per cent of variance explained by principal component	41.7	16.6	14.7	10.3	5.4	3.8	
cumulative per cent of variance	41.7	58.3	73.0	83.3	88.8	92.5	

Table 6.15 Principal components derived from the correlation coefficient matrix for 9 sites sampled for *Horridium flaccidum*, including laboratory and field data.

The sixth includes a weak loading for Al opposed by a weak negative loading for $\text{NH}_4\text{-N}$.

The six principal components cumulatively account for over 90% of the variances in the correlations of these variables. The generally high communality figures indicate that the extracted principal components account for a high proportion of the variances within the correlation matrix of individual variables.

7 ENVIRONMENTAL FACTORS AFFECTING THE TOXICITY OF ZINC TO *HORMIDIUM RIVULARE*

7.1 Introduction

There were indications from the results presented in 6.53 that certain environmental factors might be influencing the toxicity of zinc to *Hormidium* spp. The aim of the following series of experiments was to examine in the laboratory some of these factors with reference to *H. rivulare*.

7.2 Factors influencing the toxicity of zinc

7.21 pH

The effect of pH on the toxicity of zinc (using chlorophyll α to estimate total growth) is shown in Fig. 7.1. It can be seen that for both the zinc sensitive population (0085/05) and the zinc tolerant (0093/85), zinc toxicity decreases markedly with a fall in pH. The only pH value to affect growth of the control material was that of pH 3 where for population 0093/85 no growth occurred, and for 0085/05 only slight growth took place. Apart from this, the pH at all other values had no detectable influence on growth in controls lacking added zinc. The pH values of 4 and 5 were the most effective at reducing zinc toxicity to both populations, particularly the zinc resistant one, with the effect diminishing above pH 6.

7.22 Calcium

The influence of this element on the toxicity of zinc to six populations, four zinc tolerant, and two zinc sensitive, is shown in Fig. 7.2. The marked ameliorating effect is evident in almost all of the population up to the highest level ($200\text{mg l}^{-1}\text{Ca}$) investigated. The responses of both

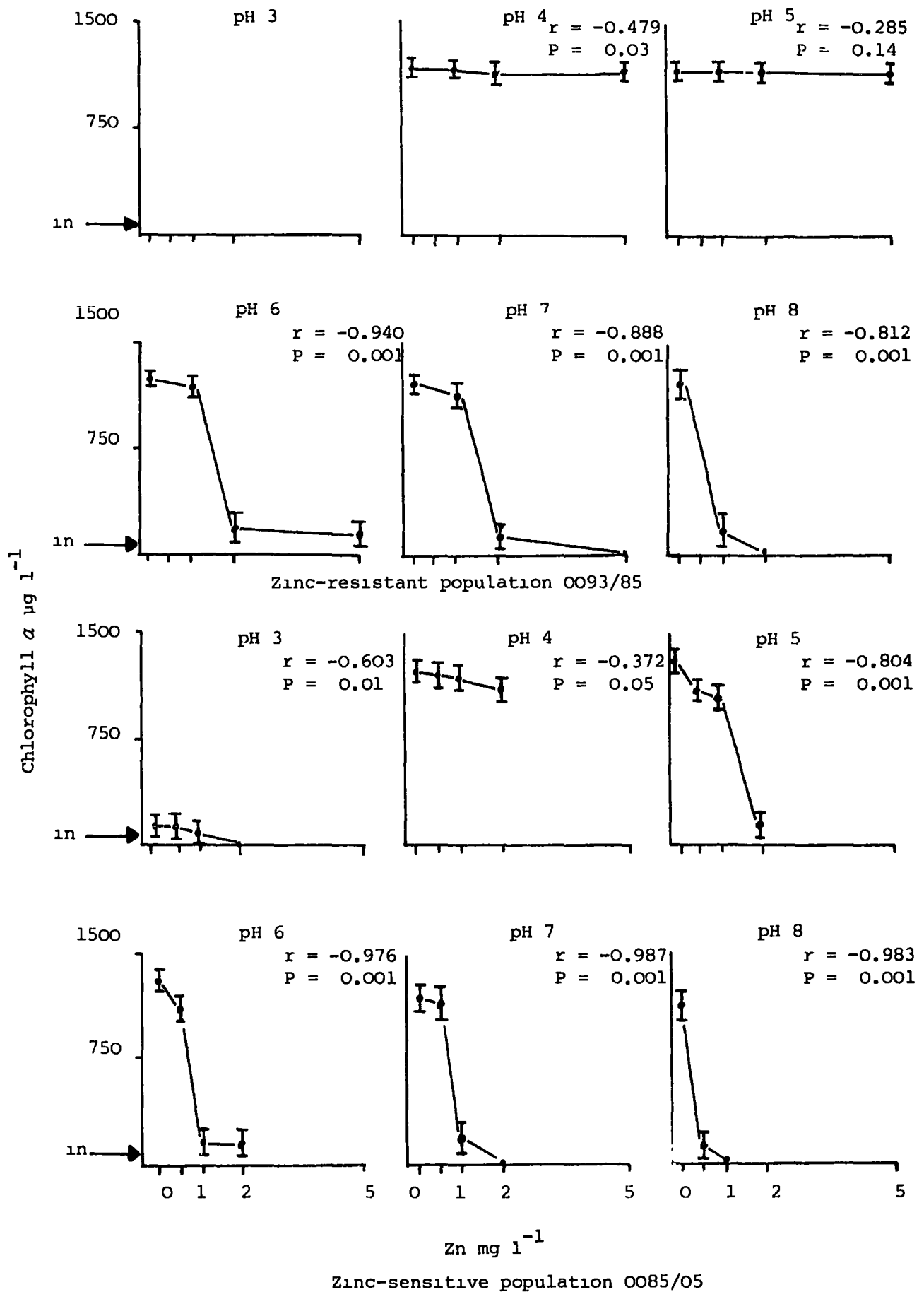


Fig. 7.1 Effect of pH on toxicity of zinc to a zinc-sensitive population (0085/05) and a zinc-resistant one (0093/85), as measured by the total growth over six days. (1n = initial inoculum; vertical lines indicate standard errors.)

tolerant and sensitive populations was similar, particularly at the higher calcium levels, with the exception of one sensitive population (0124/50) in which the effect was not as marked. The main difference between the two population types was that calcium levels up to 20mg l^{-1} were not as effective at increasing the resistance of zinc sensitive material as they were of zinc tolerant. The correlation coefficients between T.I.C. and calcium were highly significant in each case, with the lowest significance value being for population 0124/50 ($P = 0.01$) and the highest for populations 0104/01 and 0085/05 ($P = 0.001$). If the results of the quantitative experiment carried out on population 0093/85 are referred to (Fig. 7.3), they further support the ameliorating effect of calcium on zinc toxicity to *H. rivulare*.

7.23 Magnesium

The influence of this element is shown in Fig. 7.4. In contrast to the effect of calcium there is a marked difference in the ameliorating effect of magnesium between tolerant and sensitive populations. The influence is most marked in population 0104/01, one of the most zinc-resistant populations, and is least evident for 0085/05, the only zinc-sensitive population tested. In all cases the effect approaches an asymptotic value by $75\text{mg l}^{-1}\text{Mg}$. Reference to Fig. 7.5 further supports the ameliorating effect of magnesium on zinc toxicity to the zinc-resistant population.

7.24 Phosphate

The effect of phosphate on zinc toxicity is shown in Fig. 7.6. It can be seen that phosphate had a very marked influence, especially with the two zinc-tolerant populations (high correlation coefficients between level of phosphate and T.I.C. ($P = 0.001$)). The effect on the zinc-sensitive population was very slight as is demonstrated by the lower significance of

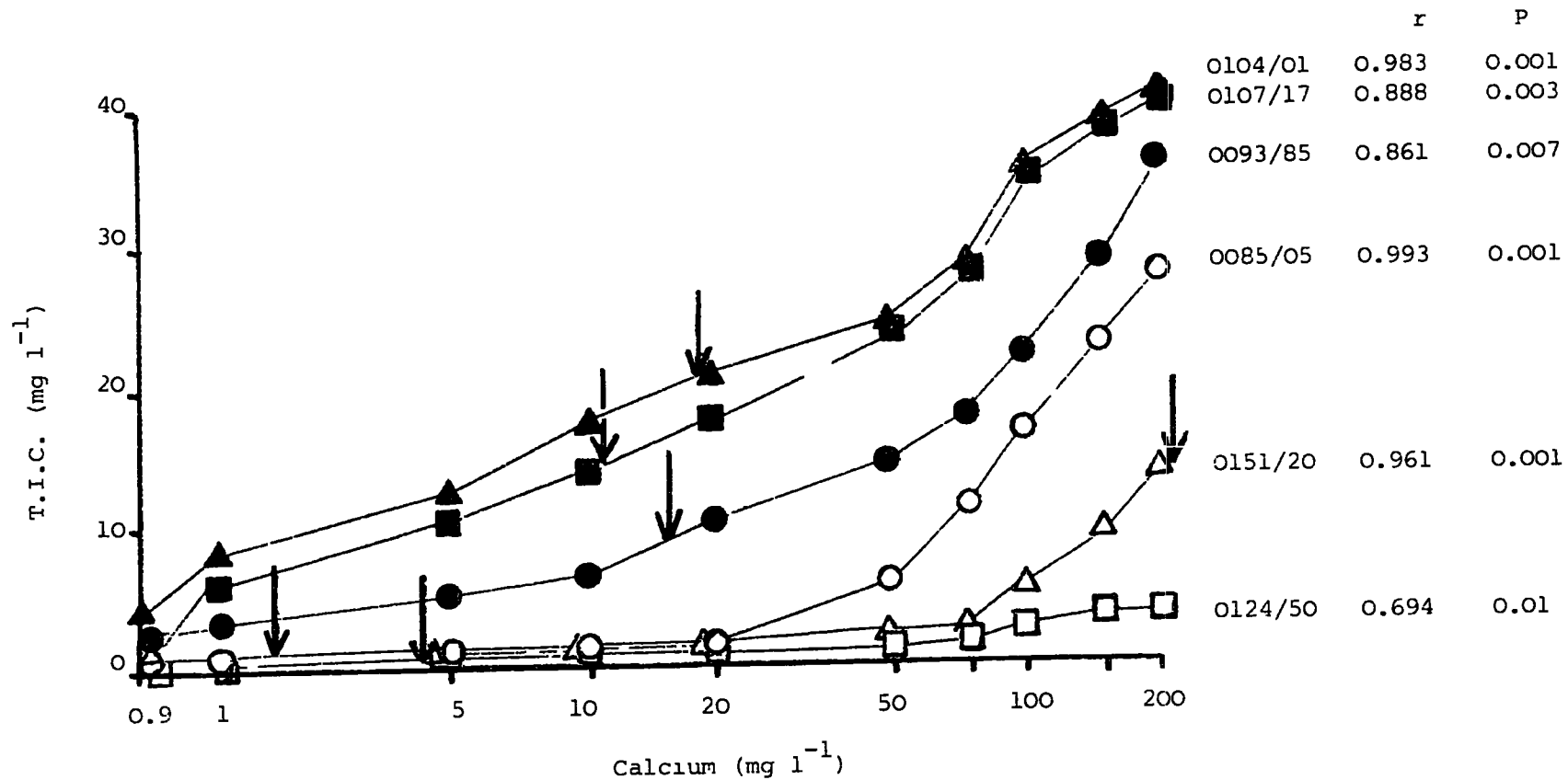


Fig. 7.2 Effect of calcium on toxicity of zinc to three sensitive populations and three zinc tolerant populations. (T.I.C. = tolerance index concentration; arrows indicate mean field levels of calcium; for clarity, standard errors have been omitted.)

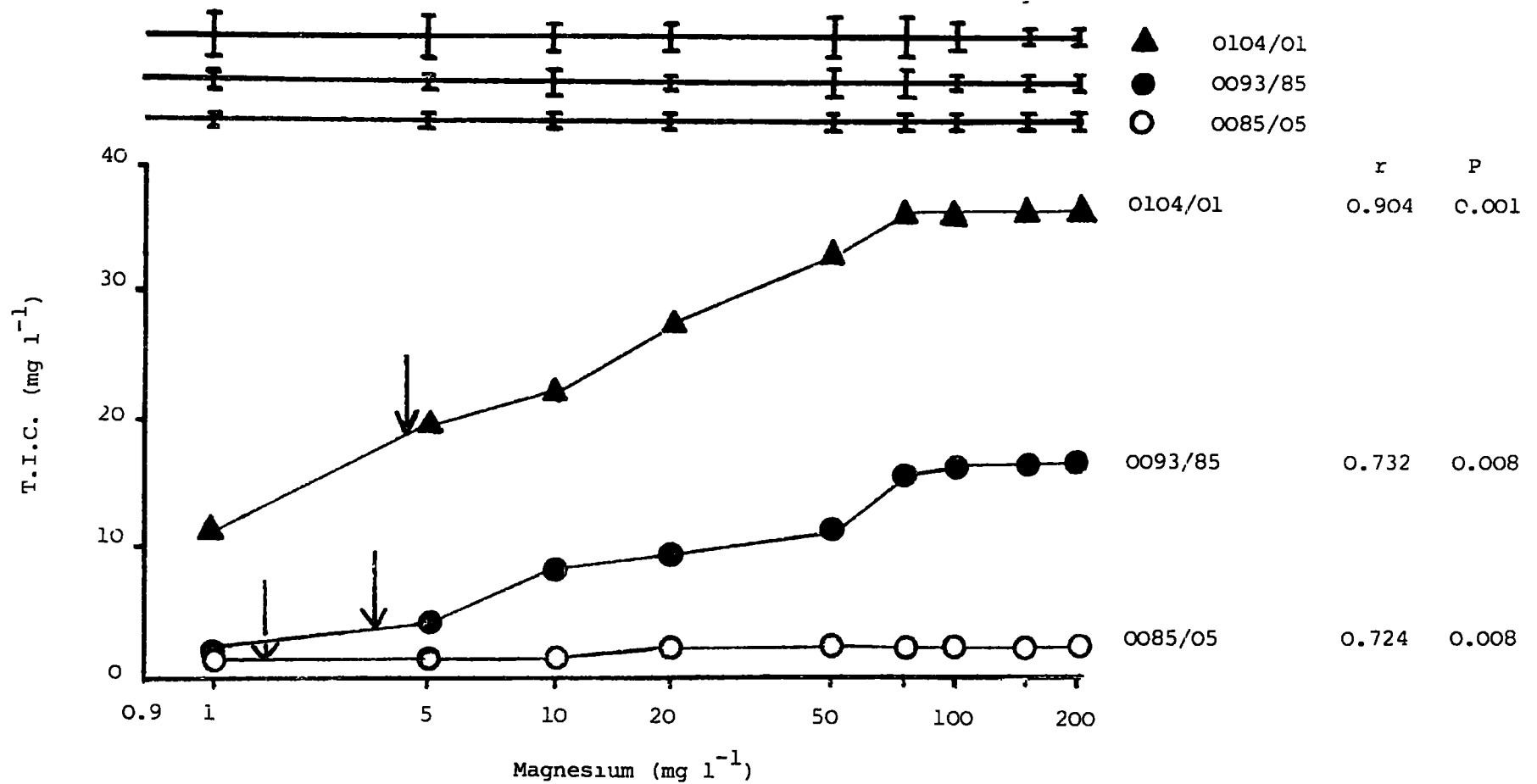


Fig. 7.4 Effect of magnesium on toxicity of zinc to a zinc sensitive population and two zinc resistant ones. (T.I.C. = tolerance index concentration; vertical lines standard errors; arrows indicate field levels of magnesium.)

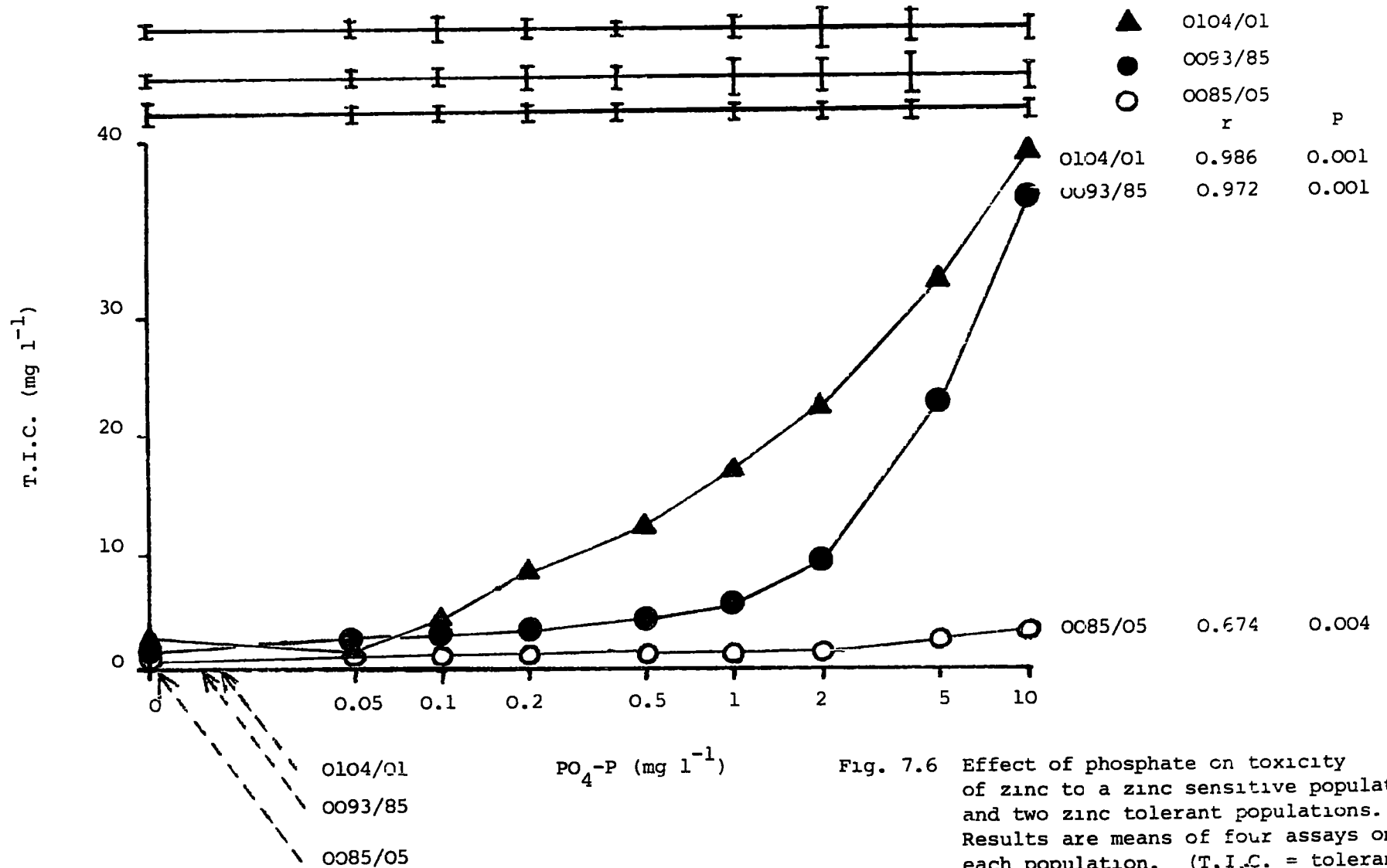


Fig. 7.6 Effect of phosphate on toxicity of zinc to a zinc sensitive population and two zinc tolerant populations. Results are means of four assays on each population. (T.I.C. = tolerance index concentration; vertical lines indicate standard errors, arrows indicate mean field levels of PO_4-P .)

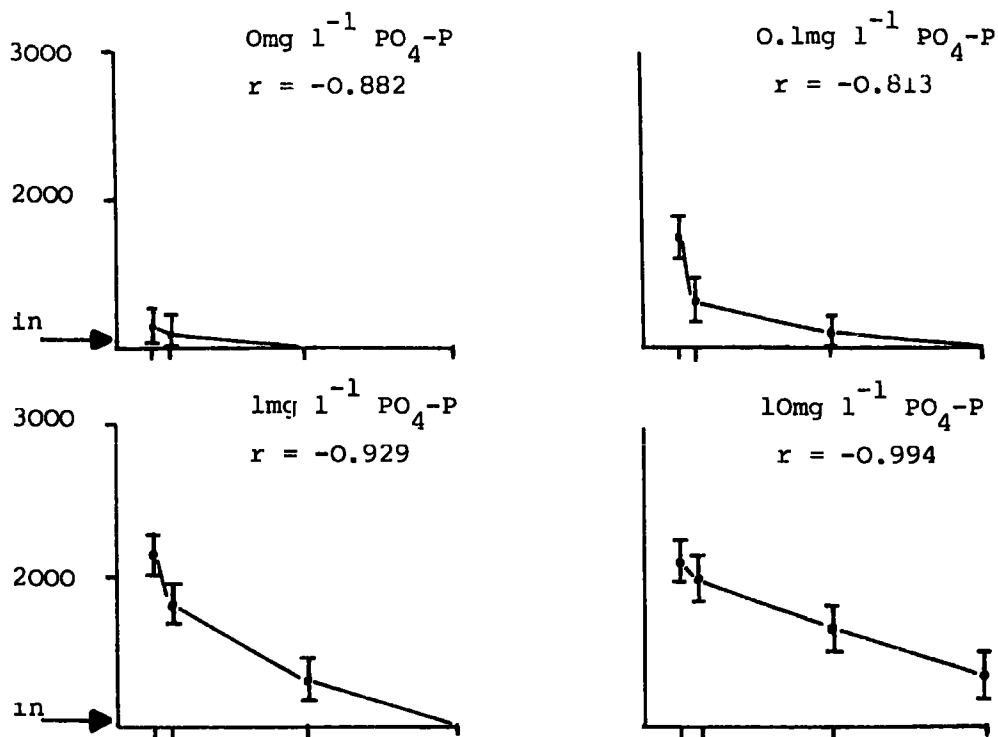


Fig. 7.7 Effect of phosphate on toxicity of zinc to a phosphate-starved population (0093/85) as measured by total growth over six days (in = initial inoculum; vertical lines indicate standard errors; in all cases P = 0.001.)

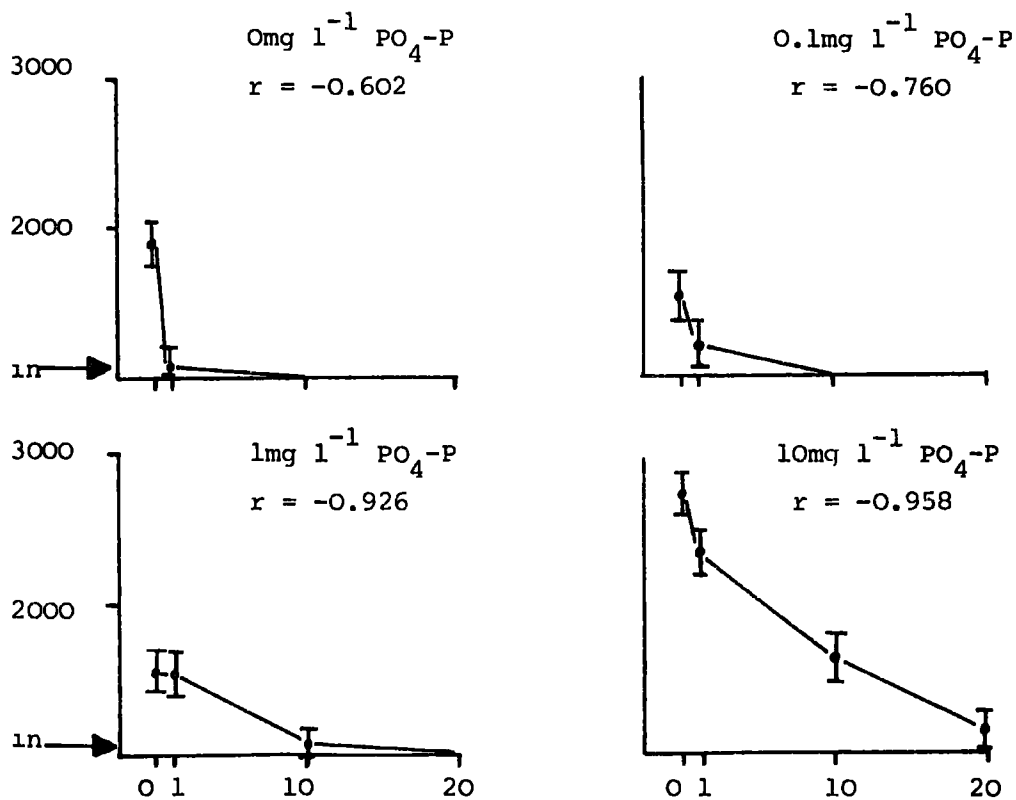


Fig. 7.8 Effect of phosphate on toxicity of zinc to a phosphate-rich population (0093/85) as measured by total growth over six days (in = initial inoculum; vertical lines indicate standard errors; in all cases P = 0.001.)

the smaller correlation coefficient ($P = 0.01$). It was evident from these experiments that the level of phosphate also had a marked influence on the growth rate of the alga. Thus the controls of the assays with the lowest levels of phosphate grew less well than some of the cultures incubated at higher phosphate levels with added zinc. However these latter nevertheless showed partial inhibition by zinc in comparison with controls at these higher phosphate levels. The quantitative experiment, which was performed to support the results of the toxicity tests, was carried out on phosphate starved and phosphate rich cultures of the resistant population 0093/85 (2.425). The results, diagrammatically presented in Figs. 7.7 and 7.8, confirm the ameliorating effect of phosphate on toxicity. The generally higher values for the quantity of chlorophyll *a* harvested in these experiments, when compared to the other quantitative studies, supports the visually assessed higher growth rates. There was considerable difference between the results of the two different cultures of this population. The phosphate-rich culture, as might be expected, grew better in the controls at the lowest level of external phosphate, but generally did not perform as well in the presence of zinc as the starved culture. With increasing phosphate levels the starved culture picked up quickly so that the results at the highest level of phosphate were similar for both cultures.

7.25 Cadmium

This element was one of the two factors studied in the laboratory which were shown to be closely correlated with zinc in the field studies (4.22, 5.22). The toxicity of cadmium has been established (see 7.31), and the combinations of zinc and cadmium were found to be more toxic than either element applied individually (Table 7.1).

Zn (mg l ⁻¹)	Cd (mg l ⁻¹)	'indicated' toxicity of Cd: Zn
0	0.335	x 15.5
0.1	0.335	x 15.2
0.5	0.237	x 19.8
1.0	0.162	x 25.9
1.5	0.136	x 27.2
2.0	0.047	x 68.1
2.5	0.034	x 79.4
3.0	0.034	x 64.7
5.0	0.010	x 20
5.2	0	-

Table 7.1 Levels of cadmium required to be added to various levels of zinc in order to produce the standard toxicity response (T.I.C., tolerance index concentration). A further column indicates how much more toxic cadmium would have to be than zinc in order to produce the standard toxicity response in the presence of lower levels of zinc. In order to be able to make the calculations, it has been assumed that a fixed amount of zinc contributes a fixed component to the toxicity response; however, the data are interpreted as evidence of synergism.

7.26 Fluoride

The effects of various levels of fluoride on zinc toxicity to the zinc-sensitive population 0085/05 are summarized in Table 7.2. No obvious alteration in the response towards zinc was observed at the levels of fluoride investigated (0.5 - 30mg l⁻¹ F). In addition to observing the possible effects on zinc toxicity, duplicate sets of tubes were set up to establish the possible effects of fluoride on its own at high concentrations. The range of fluoride concentrations assayed were from 0 - 30mg l⁻¹. There was no apparent inhibitory effect of fluoride at the highest level (30mg l⁻¹) studied.

F (mg l ⁻¹)	J.N.I.	J.L.	T.I.C.
0	1.1	2.2	1.56
0.5	1.1	2.2	1.56
1	1.0	2.1	1.49
2	1.1	2.2	1.56
5	1.2	2.2	1.62
10	1.2	2.2	1.62
15	1.6	2.2	1.88
20	1.2	2.2	1.62
25	1.1	2.2	1.56
30	1.1	2.2	1.56

Table 7.2 Summary of the effect of fluoride on zinc toxicity for population 0085/05 (level of fluoride at site = 0.44mg l⁻¹ F)

7.3 Toxicity of other heavy metals

A brief attempt was made to compare the toxic effects of three other heavy metals, lead, cadmium, and copper, to that of zinc. The results for all three are presented in the following table.

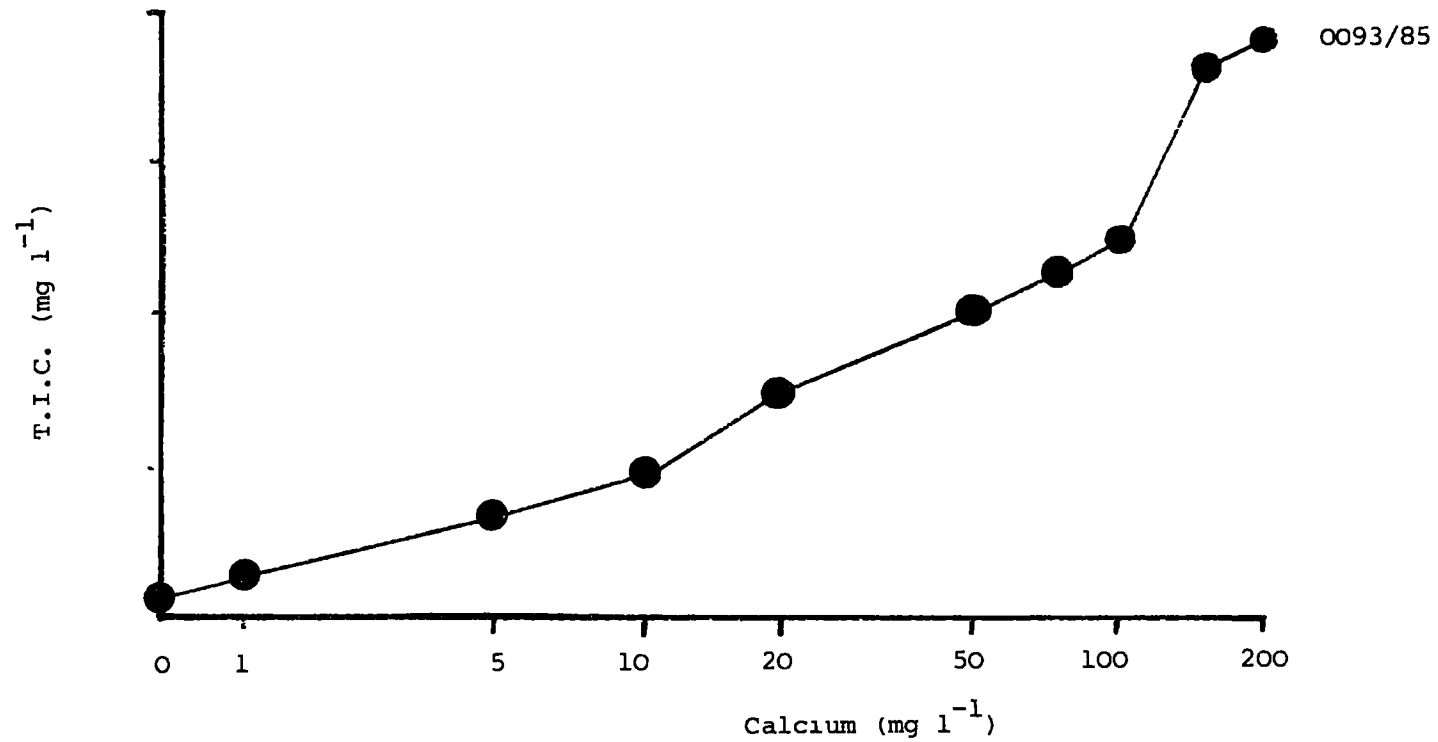


Fig. 7.9 Effect of calcium on toxicity of cadmium. (T.I.C. = tolerance index concentration.)

	zinc-sensitive		zinc-resistant	
	0085/05		0093/85	
	\bar{x}	s.d.	\bar{x}	s.d.
lead	22.5	4.58	35.5	6.36
copper	0.03	0.01	0.15	0.04
cadmium	0.04	0.01	0.20	0.05
zinc	1.2	0.26	15.7	1.60

7.31 Lead

The results for lead on both zinc-resistant and zinc-sensitive populations of *H. rivulare* were found to be the most erratic and unreliable of the comparisons. Difficulties were found in preventing flocculent precipitates from forming, even at pH 6.0. Also the large additions of the accompanying nitrate ion from the salt used as its source ($\text{Pb}(\text{NO}_3)_2$) would complicate any interpretation of the effects observed.

7.32 Copper

This element was found to be consistent in its effect, as interpreted from the low standard deviations (Table 7.3). It was found to be more toxic than zinc when comparisons were made on the two populations. However a measure of increased resistance to the toxic effects did seem to be indicated by the zinc-resistant population.

7.33 Cadmium

Cadmium was also found to be more toxic than zinc to both a zinc-resistant and a zinc-sensitive population of *H. rivulare* (Table 7.3). The influence of calcium on the toxicity of cadmium was also investigated to compare its effect with that on zinc. The results are presented in Fig. 7.9. The ameliorating effect was found to be more marked than with that of zinc.

8 MORPHOLOGICAL RESPONSES OF *HORMIDIUM* SPECIES TO ZINC

8.1 Introduction

This chapter brings together the key microscopical observations made on the three *Hormidium* species. Such observations were made on materials both taken directly from the field, and grown in the laboratory at different levels of zinc. They include more detailed morphological studies on the responses of *H. rivulare* to the interaction between certain environmental factors and the toxic effects of zinc.

8.2 Field material

The distinguishing features of the three *Hormidium* species, described for material removed from streams with less than 0.1 mg l^{-1} Zn are summarised in Table 8.1, and illustrated in Figs. 8.1 to 8.6.

8.2 *Hormidium rivulare*

Table 8.2 summarises observations made on 40 populations of *H. rivulare* taken from various zinc levels. The most noticeable differences with increasing levels of zinc are :

- (i) The general reduction in filament width, and overall increase in the cell lengths (Fig. 8.7).
- (ii) An increase in the frequency and size of geniculations, and also an increase in the amount of associated mucilage (Figs. 8.8 and 8.9).
- (iii) A thickening of the cell wall.

	filament width in μm	length of cells in μm	geniculations	chloroplast description	cell wall	fragmentation of filament	production of zoospores
<i>H. rivulare</i>	5-8	6-15	frequent	elliptical in shape	thick; constricted at the crosswalls	no	no
<i>H. flaccidum</i>	5-7	6-15	few	elliptical in shape	thin; not obviously constricted at the crosswalls	no	yes
<i>H. fluitans</i>	5-8	5-24	rare	elliptical in shape, sometimes double	thin; constricted at the crosswalls	yes	no

Table 8.1 A summary of the main distinguishing characters of *Hormidium* populations observed in field material

- Fig. 8.1 A typical filament of *Hormidium rivulare* showing the elliptical shape of the chloroplast. The cell wall is comparatively thick, and cells are constricted at their cross walls (x 4950)
- Fig. 8.2 Filament of *H. rivulare* showing the circular envelope of mucilage surrounding a small geniculation (x3150)
- Fig. 8.3 Filament of *H. rivulare* demonstrating a thick cell wall and longer cells than those of Fig. 8.1. The chloroplast is still typically elliptical in shape (x 3150).
- Fig. 8.4 Typical filaments of *H. flaccidum* showing empty cells after release of zoospores through the ruptured cell wall. In the lower filament two zoospores have not quite escaped (x 3150).
- Fig. 8.5 Single filament of *H. flaccidum* showing cells rounding off to form zoospores which are in the process of rupturing the cell wall prior to escaping from the filament (x 4500).
- Fig. 8.6 Low power view of filaments of *H. fluitans* anchored to a pad of mucilage by which they are attached to boulders in the fast flowing parts of the streams (x 350).

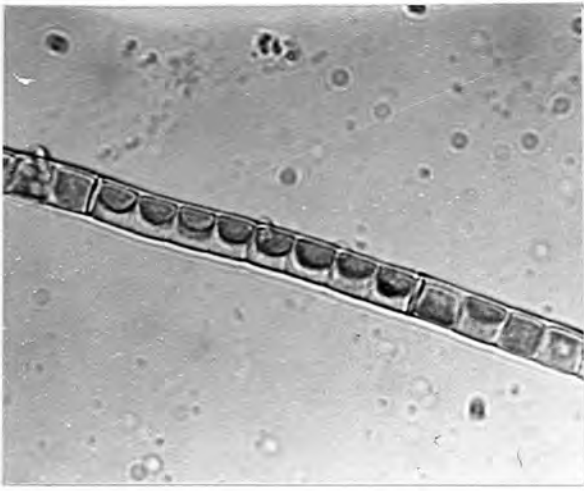


Fig.8.1

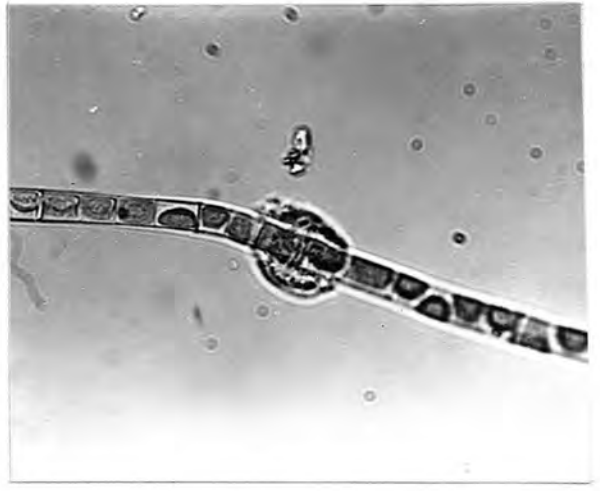


Fig.8.2

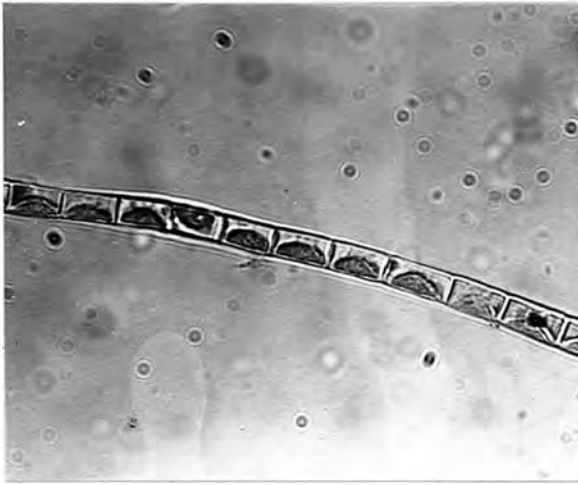


Fig.8.3

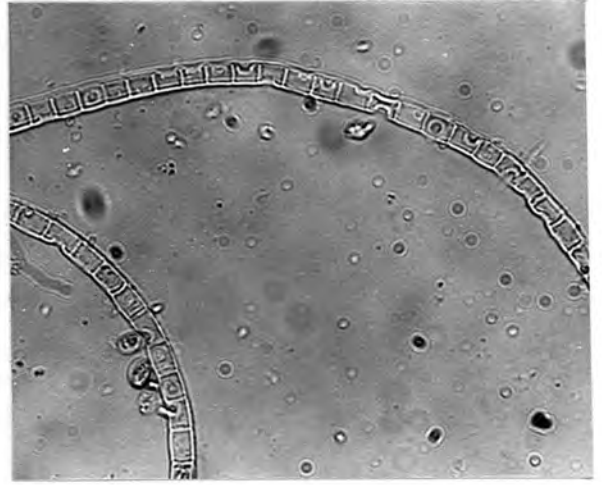


Fig.8.4



Fig.8.5

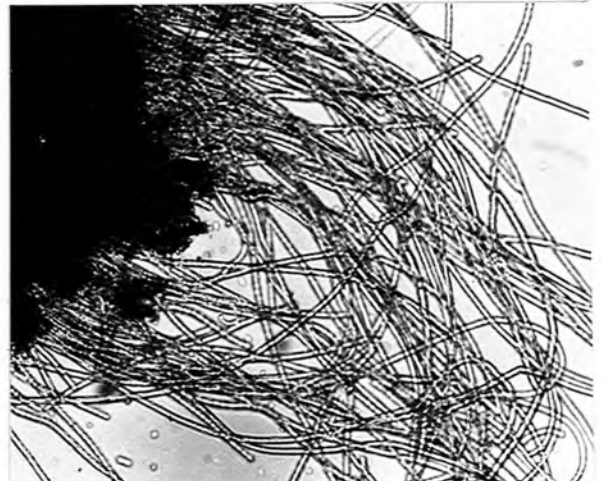


Fig.8.6

- Fig. 8.7 Filament of *H. rivulare* showing the reduction in filament width coupled with an increase in cell length as the level of zinc is increased in the culture medium (x 3150).
- Fig. 8.8 The large exaggerated geniculations of *H. rivulare* produced naturally in the field at high concentrations of zinc, and also occurring under high concentrations of zinc in basal medium (x 3915).
- Fig. 8.9 Filaments of *H. rivulare* showing copious amounts of mucilage accompanying the geniculations under increasing levels of zinc (x 2880).
- Fig. 8.10 At very high concentrations of zinc discrete particles are evident adhering to the outside of a filament of *H. rivulare* (x 3780).
- Fig. 8.11 At concentrations of zinc either side of the T.I.C. healthy filaments accompany those 'smothered' with the particles. Beneath the covering of particles filaments still appear to be quite healthy as can be seen by the obvious full chloroplasts (x 3780).
- Fig. 8.12 Fragmentation of *H. fluitans* into short filaments of unicells as a response to merely being transferred from the field to basal medium, or in basal medium as a response to increased zinc concentrations (x 4230).

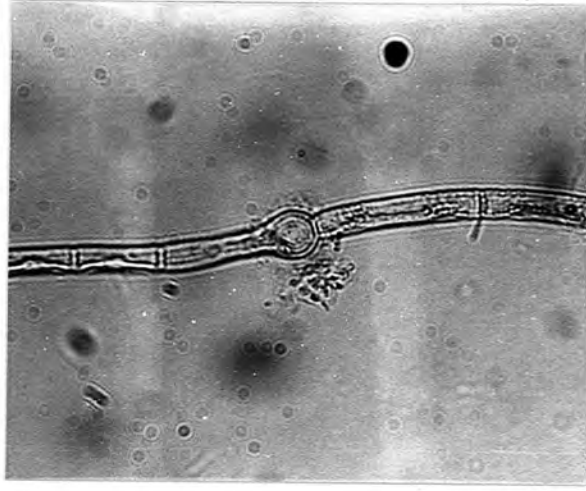


Fig.8.7



Fig.8.8

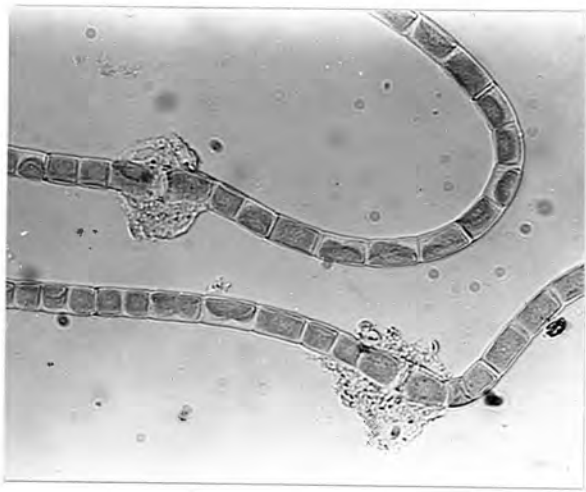


Fig.8.9

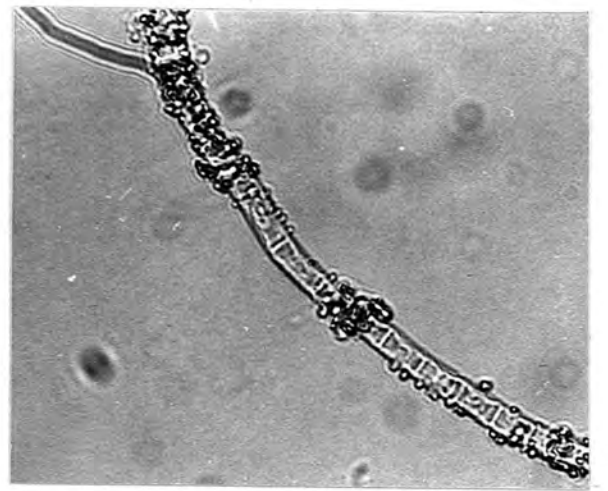


Fig.8.10

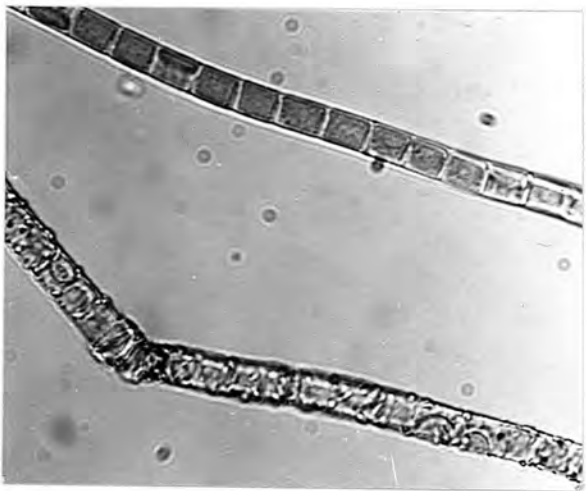


Fig.8.11

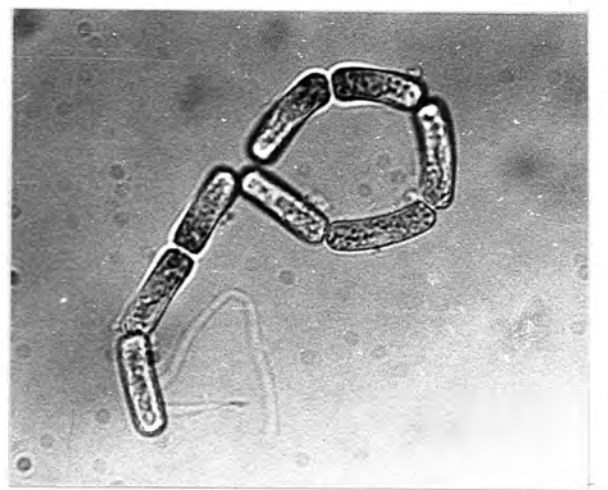


Fig.8.12

- Fig. 8.13 Clumps of fragmented filaments of *H. fluitans* produced in response to increasing zinc levels in the basal medium (x 3150).
- Fig. 8.14 Considerable increase in the length of cells of *H. rivulare* produced under extremely low levels of phosphate even in the absence of zinc (x 2700).
- Fig. 8.15 The granular appearance of the long cells of *H. rivulare* is evident under low phosphate conditions and with increases in the level of zinc (x 3060)
- Fig. 8.16 A filament of *H. rivulare* under higher levels of phosphate showing an increase in filament width, reduction in cell length, an increase in the incidence of geniculations and obvious constrictions at the cross walls of cells when compared to those under conditions of reduced phosphate levels (x 2700)

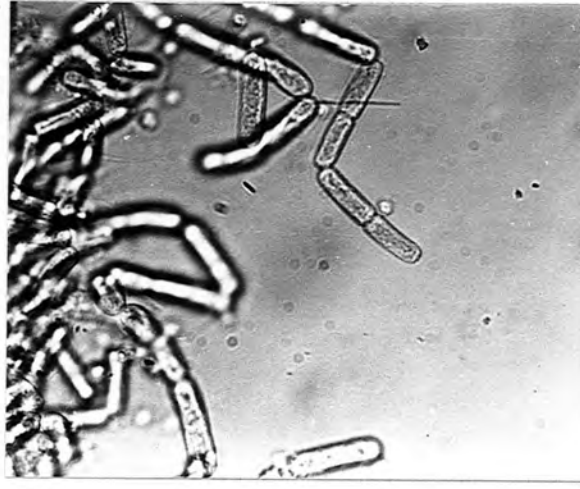


Fig. 8. I3

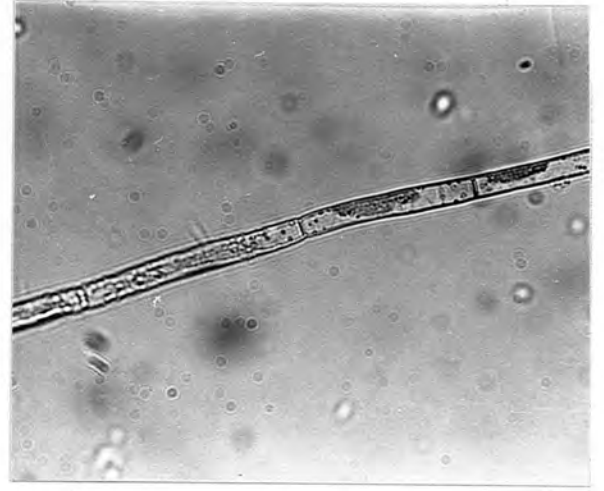


Fig. 8. I4

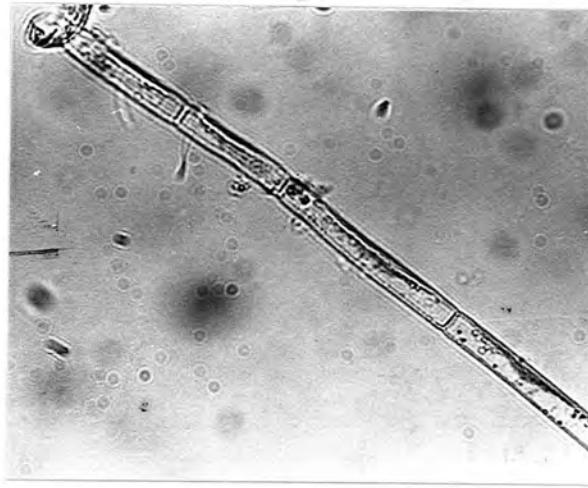


Fig. 8. I5



Fig. 8. I6

8.22 H. flaccidum

Populations from both high and low levels of zinc did not differ markedly in morphology. Observations made on 20 populations can be summarised by the following :

- (1) Irrespective of the zinc level, zoospores are produced readily (Fig. 8.4).
- (11) Geniculations are not obvious and are found only very occasionally.
- (111) Cell walls remain thin and there are no constrictions at the cross walls.

8.23 H. fluitans

At all zinc levels at which this species was found the cells and filaments were more or less identical.

8.3 Observations made on material in culture and during the toxicity test8.31 H. rivulare

Material taken from reaches with various zinc levels, and cultured in zinc-free media, retained the frequency of geniculations observed in the field (Table 8.2).

Under the conditions of the toxicity test, an increase in the concentration of zinc was found to produce a similar type of morphological response with both zinc-tolerant and zinc-sensitive populations. An increase in the level of zinc up to the J.N.I. concentration was accompanied normally by an increase in the frequency

mg l ⁻¹ Zn	filament width in μm		length of cells in μm		geniculations	chloroplast description	cell wall
	range	mean	range	mean			
0-1	5-9	6	6-15	8	present; plus mucilage	sharply demarcated; elliptical shape, filling half of the cell	constricted at the crosswalls
1-5	5-9	6	6-20	12	frequent; plus large amounts of attached mucilage	elliptical, filling less than half of the cell	thickened; constricted at the crosswalls
5-15	5-8	6	6-20	12	frequent; with prominent round shape plus mucilage	elliptical, filling less than half of the cell	thickened; constricted at the crosswalls
>20	4-6	5	6-30	20	abundant; plus attached mucilage	shape not easily defined, but sometimes elliptical. Fills considerably less than half of the cell	thickened; constricted at the crosswalls

Table 8.2 The main morphological differences in *H. rivulare* with increasing levels of zinc

of geniculations, and also in the thickness of the cell wall. When the level of zinc was taken up to the J.L. concentration, an effect was produced on most of the filaments where discrete particles could be seen adhering to the outside of the cell wall (Fig. 8.10). There were often intensely clustered around the mucilage covering a geniculation. At zinc levels either side of the T.I.C., filaments without such attached particles often accompanied filaments 'smothered' by such particles (Fig. 8.11). Cells often appeared to be quite healthy under this 'coating' of particles. With further increases in the level of zinc, cell walls became considerably thicker, cells became swollen and misshapen, and the chloroplasts diffuse and yellow-green in colour. At levels of zinc above the J.L. concentration, filaments were composed mainly of colourless, swollen cells.

8.32 *H. flaccidum*

During the course of the toxicity test, a pattern similar to that shown by *H. rivulare* was observed. At zinc levels above the J.N.I. concentration, filaments showed signs of attached 'particles' adhering to the mucilage, covering the outside of the cell. The mucilage often took on a 'crinkled' appearance. Still further increases in the level of zinc produced swollen cells with diffuse yellow-green chloroplasts which were difficult to distinguish. Eventually cells became colourless.

8.33 *H. fluitans*

Although forming long interwoven filaments in the field, *H. fluitans* frequently fragmented into unicells when transferred to basal medium without added zinc (Fig. 8.12). This made experiments on zinc toxicity more difficult to interpret.

In filaments which remained intact, an increase in zinc levels above the J.N.I. concentration caused immediate fragmentation of the filaments, which formed tight clumps of unicells at the bottom of the flask (Fig. 8.13). A further increase caused the unicells to become long and misshapen, with the interior of the cell becoming diffuse and granulate, until they degenerated to become colourless.

8.4 Further responses observed in *H. vulgare*

8.41 Ca_cium

In the absence of zinc, and at levels of calcium ranging from 0-5mg l⁻¹, filaments were narrow (5.6µm), with the cells appearing more vacuolate. At levels of calcium ranging from 50-200mg l⁻¹, filaments were wider (8-9µm), and the chloroplast was larger. As the levels of zinc were increased, a similar pattern of events as those described for the ordinary toxicity test were observed.

8.42 Magnesium

The responses were similar to those for calcium, except that at the lower levels of magnesium the chloroplast appeared more diffuse and yellow-green in colour.

8.43 Phosphate

At low levels of phosphate (<0.05mg l⁻¹ PO₄-P) in the absence of added zinc, filaments were narrow (4-5µm), and the length of the cells was observed to reach in some cases up to eight times the width (Fig. 8.14). In such cases the chloroplast filled considerably less than half of the cell and became longer and flatter, but still retained the elliptical shape. The occurrence of geniculations was reduced at low phosphate

levels and the cells appeared granular inside (Figs. 8.14, 8.15). When the level of phosphate was increased to 0.5mg l^{-1} filament width increased (6-8 μm), whilst cell length generally decreased to at most three times the width. The granular appearance to the cells also disappeared. At high phosphate levels (10mg l^{-1}) cells remained short (rarely exceeding two times their width) and wide (8 μm) with pronounced constrictions at their crosswalls (Fig. 8.16).

As the concentrations of zinc were increased, a similar pattern as that shown in the standard toxicity test was observed at all phosphate levels.

9. DISCUSSION

9.1 Introduction

As might have been expected from a knowledge of the geology of the Northern Pennine Orefield (Dunham, 1948), many streams in this area were found to carry high levels of zinc. The extent of this zinc contamination and its primary sources are discussed in 9.2. In 9.3 a comparison is made with surveys carried out on zinc rich streams elsewhere (1.11).

A discussion of the factors indicated as controlling both the inorganic chemistry of some of the mine waters and also the availability of zinc is given in 9.4. Because of the large quantity of chemical information collected, factor analysis was employed to interpret the data (2.5). The applicability of this method is shown by Kramer (1969) who states that "initially factor analysis isolates empirically and objectively groupings of chemical variables to be considered further." Because of its widespread use in hydrogeochemical studies (Hitchon *et al.*, 1971; Reeder *et al.*, 1972) the method discussed by Dawdy and Feth (1967) was used in the present study (see 2.523). Since no specific geological analyses were performed during the study, the interpretation of the factor analysis is based largely on the works of Dunham (1948, 1967). Although it is not possible to reach definitive conclusions on the factors controlling the overall chemistry of the streams, it is however possible to postulate the likely underlying factors (9.4). Emphasis is directed towards the initial factors in the factor matrix which are of most importance, and those directly involving zinc. All the field surveys (4.2, 5.2, 6.4) are discussed together.

In view of the fact that manual treatment was employed when analysing the information on the distribution of algae and bryophytes in the streams, caution is exercised when discussing the results (9.5). However, even in

the absence of quantitative measures of algal abundance and distribution, some important observations can be made.

At high zinc levels the genus *Horridium* proved to be most widespread and often the most abundant alga (6.4), and experimental studies on it (6.5) are discussed in 9.6.

It has often been stressed that the isolation of any one factor in determining the distribution of species is not only very difficult, but also a simplistic approach (Griffiths *et al.*, 1975). However an extreme environment (Brock, 1969) such as the streams carrying the higher zinc levels studied in this survey may provide an example of a situation where a single factor becomes of paramount importance. The isolation of zinc as a factor for consideration has been achieved during the present study both in a comparison of sites on different streams (4.2) and of different reaches down a single stream (5.2). However it is clear that other factors do interact with zinc in influencing its toxicity (6.53, 7.2), and these are discussed in 9.7.

9.2 The extent of zinc contamination in the Northern Pennine Orefield

In this section an indication of the magnitude of zinc contamination of waters draining the Orefield is given. This is followed by an appraisal of the chief sources of this contamination.

9.21 The situation during 1972-1975

Zinc contamination of streams draining the Northern Pennine Orefield has been shown to be extensive (4.2, 4.3) even though at least 40 years have passed since the remaining lead-zinc mines were closed down. A number of streams carrying more than $1 \text{ mg l}^{-1} \text{ Zn}$ occurred in the five main areas of the Orefield (Figs. 2.1, 3.3) and these are all associated with old mine workings (4.22).

From the results given in 4.21 it can be seen that the most serious zinc enrichment was found in the Alston Moor region of the Orefield. Here 15 reaches located on different streams were found to carry in excess of $1 \text{ mg l}^{-1} \text{ Zn}$. The position of these streams all coincided with the primary zinc-bearing area around Nenthead and along the Nent valley. The other main areas where streams were found to carry high levels of zinc are Weardale and Allendale, if this is judged by the proportion of streams sampled carrying more than $0.1 \text{ mg l}^{-1} \text{ Zn}$.

9.22 Sources of zinc contamination

The chief sources of zinc contamination in the Northern Pennine Orefield are summarized in Fig. 9.1. They apply both to past mining activities for lead and zinc, and to current mining operations which are reworking some of the old mines for fluorspar.

(1) Natural weathering of sulphide ore bodies

This contribution of zinc has been previously discussed in 1.62.

(11) Quarries

In certain mines large amounts of rock have been removed to obtain the ore, leaving large expanses of bare rock in the form of small quarries. Seepages occur on the rock faces which can join along fractures in the weathered rock to form small streams. Sometimes the quarry intersects the water table and seepages arise from the escaping ground water. In the more mineralized areas such seepages can contain the weathered products of sphalerite.

(111) Tailings heaps

Large heaps of coarse tailings from the milling and concentrating processes are evident near the location of mines, particularly those in the Nent Valley at Nenthead (Figs. 3.4, 3.5). Seepages emanate from the base of such heaps and these have been shown to be the source of some of the streams in the area

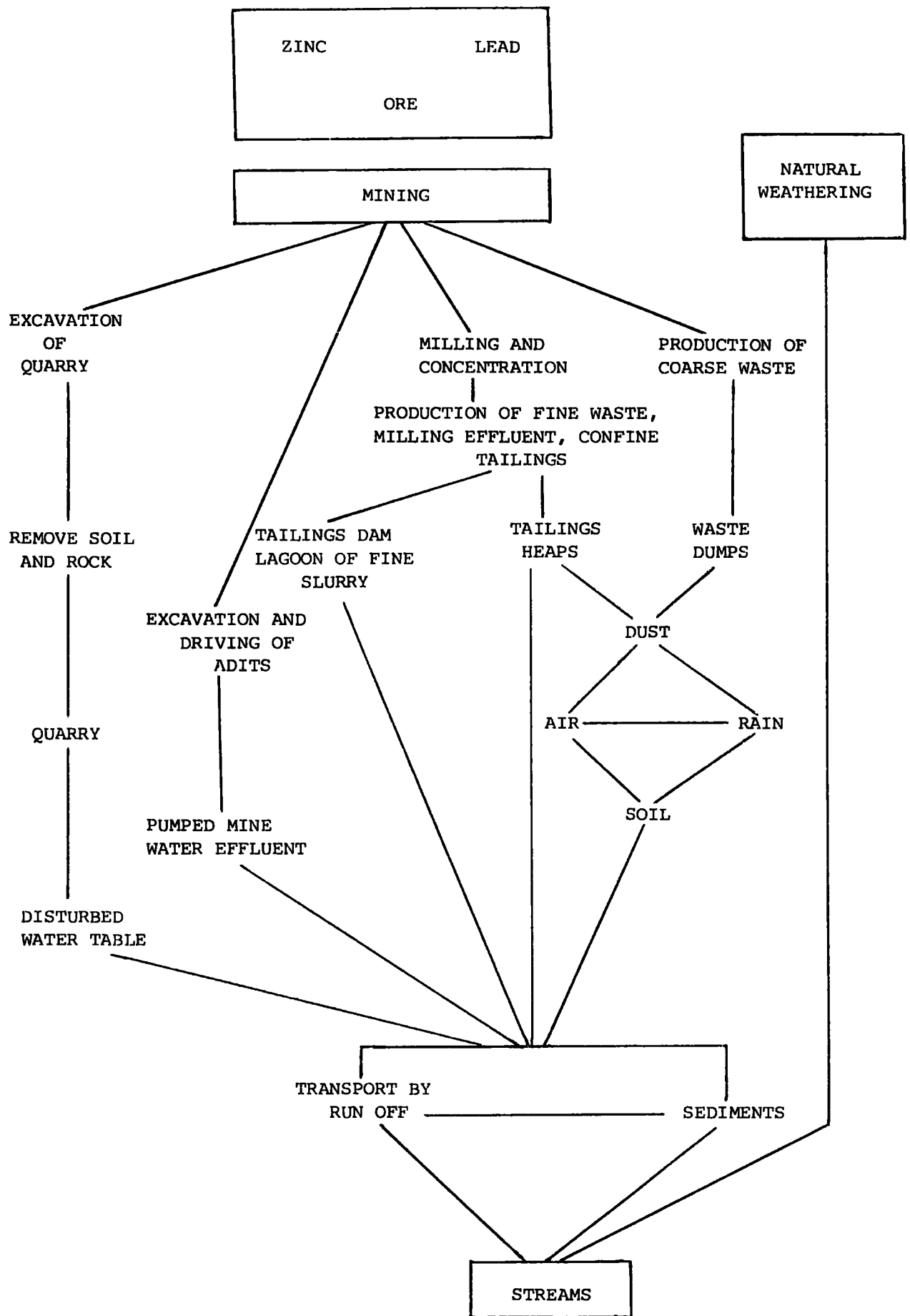


Fig. 9.1 Main sources of zinc to the aquatic environment in the Northern Pennine Orefield

(e.g. 'Brown Gill Tributary' 0108/08, and 'Redburn Flush' 0111/01). The supply of water is provided mainly from atmospheric precipitation and by surface drainage through and around these heaps.

Dunham (1948) has shown from the analysis of material removed from a dump of coarse tailings that these can be extremely rich in zinc. The highest level of zinc encountered during the present study was in 'Old Mine Gill' 0104/01, which originates as a seepage from the base of coarse tailings.

(iv) Waste dumps

Coarse rock waste produced during the excavation of mines and the driving of adit levels are a further source of zinc contamination (Fig. 3.12). This again comes from seepages emanating from the base of dumps of this material. Gudham Gill 0092/20 derives in part some of its water from such sources. In general the concentrations of zinc, as shown by the results of surveys including Gudham Gill are lower than those found in seepages from tailings heaps due to the smaller amount of mineralized rock in the dumps.

Both the heaps of tailings and dumps of waste rock (more often shale) were frequently found to contain finer material, which was shown as in the case of Gillgill Burn to be subject to wind erosion (3.63). The transportation of this dust into the streams may provide another source of zinc if fine particles of sphalerite are present.

(v) Adit levels and pumped mine water

Water emerging from adits can be a source of high zinc levels as shown by the results of surveys presented in 4.2. From the description of mines given in Dunham (1948) it is evident that adit levels in mining regions such as Nent-head link up to form a network of underground levels covering wide areas. Where these reach the water table, ground waters collect, and some of the larger adits act as discharge points for a continuous supply of water from

these underground channels. The majority of adit levels were driven primarily to promote direct drainage of the mine workings, thus extending the working depth of the mine below the natural water table. The continued discharge of water from some of these is probably related to the depth to which they were sunk. Some adits have been known to discharge waters underground which drain into cavern systems as described by Dunham (1948) for Hudgill Mine. The interconnection of adits discharging at the surface with these underground cavern systems which act as 'reservoirs' for the ground waters could also in part account for the continued discharge at the present time. The high levels of zinc are most probably derived from the oxidizing effects of meteoric waters passing over fissures of rock containing sphalerite. When active mining was still carried out these adits were used to carry away mine water pumped from the areas of ore extraction. In present mining operations for fluorspar old adits are still used for discharge of excess ground water.

The most characteristic examples of this source of zinc in the present study are Tailrace level O113/O1 which discharges into Rookhope Burn, and Dowgang level O097/O1 which discharges into the River Nent (Fig. 3.6).

9.3 Comparison with surveys of other streams contaminated by zinc

It was stated in 1.11.3 that few detailed studies appear to have been carried out in the past, particularly in England, of the chemistry of streams draining base metal mining regions in relation to the algae. However as mentioned in 1.93, a number of studies have been performed on certain aspects of the chemistry of mine waters. In the following section comparisons are made with these studies, dealing first with those in Britain and then those elsewhere.

9.31 Britain

Studies carried out in other lead and zinc mining areas in England include those reported for Cornwall by the Cornish River Authority (Purves, 1975). Similar sources of zinc contamination to those of the Pennine Orefield are described from some of the old mine workings. However in contrast to the present study, adit waters were shown in general to be highly acidic (the lowest value reaching pH 3.2), containing high levels of arsenic (0.3mg l^{-1}) and copper (3.6mg l^{-1}) in addition to zinc (34mg l^{-1}). In the present study analysis was not carried out for arsenic, but the levels of copper were never as high (rarely exceeding 0.09mg l^{-1} e.g. in Tailrace level 0113/01). The pH of adit waters in the present study was rarely found to drop below 7.0. The differences between these waters are related to the fact that some of the adit waters discussed for the Cornwall region originate from areas where oxidation of pyrite occurred. As discussed in 1.83, such resultant acidic water can carry extremely high levels of zinc.

In a hydrogeochemical investigation of waters draining the lead-zinc mining area of Derbyshire, Edmunds (1971) describes a number of different mine waters. Some of these are shown to have been enriched with zinc and have similar sources to those of the present study. Drainage of the mining area is shown to have been similarly carried out by the driving of tunnels which in this region are locally termed "soughs". The water from this source resembles the water issuing from adits in the present study area. The chemical composition of a typical zinc contaminated sough given by Edmunds includes some of the following measurements: pH 7.10, total hardness $330\text{mg l}^{-1}\text{CuCO}_3$, $107\text{mg l}^{-1}\text{Ca}$, $15\text{mg l}^{-1}\text{Mg}$, $2.52\text{mg l}^{-1}\text{Zn}$. This compares with pH 8.0, total hardness $393\text{mg l}^{-1}\text{CaCO}_3$, $104.6\text{mg l}^{-1}\text{Ca}$, $29.4\text{mg l}^{-1}\text{Mg}$, and $6.7\text{mg l}^{-1}\text{Zn}$ for the adit Dowgang Level in the Nent area. No mention is made by Edmunds of the contribution of zinc from drainage emanating from waste tailings. He relates the majority of high zinc values to waters issuing from soughs and seepages from quarry areas.

As with the present study, high values for zinc correspond with the main area of occurrence of zinc ores.

From the literature it appears that the most documented area in connection with the contamination of streams by zinc is that of west Wales (1.11). In this area there are no records of water quality for the period when mining was at its peak (Jones and Howells, 1975). The first analyses are quoted by Carpenter (1924) for the period when the mining industry was in its final stage of decline. In the present area of study there also appear to be no records for the chemistry of waters when mining was at its peak (1870-1921), particularly those associated with the zinc mining area in the Nent Valley. The earliest available documentation of water chemistry in this area appears to be that carried out by the Department of Botany, University of Durham, in 1969 (B. A. Whitton, pers. comm.) for reaches on the River Nent. Since no earlier analyses are available, a comparison is made between information collected during the present study on waters draining the Northern Pennine Orefield, and both past and present surveys carried out in west Wales.

A comparison of zinc and lead contents for reaches on the River Ystwyth is given in Table 9.1. In Table 9.2 a comparison of these two elements is given for reaches on the River Nent. Additional information is also given on levels of pH and calcium, where available. From Table 9.1 it can be seen that there is little change in the levels of zinc or lead in the Ystwyth over the 35y period in which analyses were made. Thus it continues to receive contamination by zinc below the workings of the Cwm Ystwyth mine. If a comparison is made between Tables 9.1 and 9.2 it can be seen that the two rivers are similar in several respects. Analyses of zinc and lead were not available for the Nent for a similar span of years as shown for the Ystwyth. However little fluctuation in the levels of these elements was shown for the 3y sampling period. Both rivers demonstrate the persistent nature of zinc contamination as suggested by Jones (1958), since they both carry high levels of zinc at least 40y after the cessation of mining

Sites on the river Ystwyth	pH	Zn	Pb	Ca	Year and author
Above Cwm Ystwyth mine	6.4	ND	ND	3.0	Jones, 1940
	6.3	ND	-	-	Alloway, 1967
	6.9	ND	ND	1.26	McLean and Jones, 1975
Below Cwm Ystwyth mine	6.0	0.9	0.05	-	Jones, 1940
	6.15	1.35	-	-	Alloway, 1967
	6.4	0.88	0.032	2.0	McLean and Jones, 1975
At Llanfarian	6.4	0.8	Trace	4.4	Jones, 1940
	6.8	0.6	-	-	Jones, 1958
	6.7	0.43	-	-	Alloway, 1967
	7.0	0.59	ND	17.0	McLean and Jones, 1975

Table 9.1 Historical comparison of zinc and lead analysis for sites on the river Ystwyth (all elements in mg l^{-1} ;

ND = not detectable)

reach	reach no.	pH	Ca	Zn	Pb	year
Source	01	6.2	6.3	0.08	0.012	1972
		6.2	7.7	0.07	0.011	1973
Above Dowgang Level	11	6.8	15.0	0.75	0.041	1973
		6.9	24.2	0.83	0.071	1974
		6.8	23.5	0.89	0.047	1975
Below Dowgang Level	12	7.1	57.0	2.7	0.038	1973
		7.1	54.0	3.2	0.052	1974
		7.0	48.0	2.1	0.041	1975
At Alston	99	7.9	58.0	1.22	0.021	1973
		8.1	64.0	1.02	0.011	1974
		7.8	49.0	1.31	0.024	1975

Table 9.2' Comparison of zinc and lead analyses for sites on the river Nent (elements in mg l⁻¹)

activity in their valleys. In Tables 9.3 and 9.4 similar comparisons are made between the waters issuing from two adits from the two respective areas. The summary in Table 9.3 demonstrates the continuing discharge of high levels of zinc from the adit in the Cwm Ystwyth mine over the 35y period. Table 9.4 illustrates the consistent discharge of zinc from the adit Tailrace level (0113/01) over a four year period. Additional data given by Jones (1940, 1958) and McLean and Jones (1975) on the chemistry of streams draining from heaps of tailings, and adits of the Cwm Ystwyth mine show similar ranges in parameters to streams in the Nent Valley. Thus in some of the contaminated streams bordering the Ystwyth, levels of zinc ranged from $0.31-15.35\text{mg l}^{-1}$, lead from $0.20-3.35\text{mg l}^{-1}$, and cadmium up to 0.10mg l^{-1} . This compares with typical ranges of $0.7-22.8\text{mg l}^{-1}\text{Zn}$, $0.23-1.82\text{mg l}^{-1}\text{Pb}$, and $0.0055-0.09\text{mg l}^{-1}\text{Cd}$ (see Table 4.1) in some of the zinc enriched streams bordering the Nent (4.2).

In a study of mine waters in the Rheidol Valley, an adjacent mining area to that bordering the Ystwyth, Treharne (1962) describes sources of zinc contamination similar to those found for the Northern Pennine Orefield. Adit waters were again shown to be the chief source of high zinc levels, but as with those in the Cornish mining area, they contrasted with those in the present study by being highly acid. Such adits were shown by Treharne to be associated with areas of rotting pyrite and contained up to $187.5\text{mg l}^{-1}\text{Zn}$ and $212\text{mg l}^{-1}\text{Fe}$. Drainage from waste tailings was also demonstrated to be a serious source of zinc contamination. A sample of run-off taken during a period of heavy rain was found to contain $34.2\text{mg l}^{-1}\text{Zn}$ and $4.36\text{mg l}^{-1}\text{Pb}$. In a later study of mine waters in the same area Fuge (1972) showed that the acid waters issuing from adits were still considerably enriched with magnesium, calcium, aluminium, iron and zinc. Other mine waters were shown to have a higher pH range from 6-8, and although enriched with zinc, the levels were lower than the acid waters. Table 9.5 gives some average analyses of the mine waters in the Rheidol Valley. These are from adits containing non-acid waters with a similar pH range to those of the present study. They are compared with a

pH	Zn	Pb	
6.4	38.0	8.0	Jones, 1940
6.6	30.0	Trace	Jones, 1958
6.8	27.5	-	Alloway, 1967
-	15.4	0.25	McLean and Jones, 1975

Table 9.3 Historical comparison of zinc and lead analyses for an adit discharging into the Ystwyth

pH	Zn	Pb	Ca	
7.3	8.7	0.051	95.5	1972
7.4	7.6	0.085	90.0	1973
7.4	9.0	0.085	93.6	1974
7.4	7.1	0.090	88.8	1975

Table 9.4 Comparison of zinc and lead for the adit Tailrace Level, O113/O1, which discharges into Rookhope Burn

	Average composition of water from 6 adits in the Rheidol valley mining area	Average composition of water from 6 adits in the Nent valley mining area
pH	7.23	7.5
Na	7.2	9.2
K	0.98	4.8
Mg	4.1	21.6
Ca	13.7	71.2
Al	n.d.	0.08
Mn	0.30	1.03
Fe	0.04	0.18
Cu	0.03	0.023
Zn	3.69	4.38
Cd	n.d.	0.010
Pb	n.d.	0.060
Si	3.16	3.46
Cl	9.83	13.6

Table 9.5 Comparison between the average composition of water from 6 adits in the Nent valley compared with 6 in the Rheidol valley (reference Fuge, 1972)

corresponding set for the Nent Valley. In general the chemistry of the water is similar except for the levels of potassium, magnesium and calcium which in the case of the adits in the Nent Valley are much higher. The difference is related to the lack of limestone strata in the Rheidol Valley area. This point is discussed in more detail in 9.4.

9.32 Mining areas in other parts of the world

It seems evident from the review of the sources of zinc contamination given in 1.8, and from some of the above discussion, that areas of copper-zinc-lead mineralization, often referred to as 'base-metal deposits' can have associated acid mine waters. These are derived from the oxidation of other sulphide minerals frequently associated with them, characterized principally by pyrite. In the Northern Pennine Orefield, pyrite mineralization is not extensive and is only predominant in one series of deposits associated with the Great Sulphur Vein (Dunham, 1948). Since the mining areas studied did not coincide with this vein, no highly acid waters were encountered.

In a study of a copper-lead-zinc mining region in New South Wales, Australia, Weatherly *et al.* (1967) showed that the chief sources of zinc contamination were from drainage waters emanating from waste tailings and those from a slurry pond. Because much of the fine tailings consisted of pyrite in addition to sphalerite, most of the water was acid. The levels of zinc in the main river receiving this drainage water rose as high as 34.5mg l^{-1} . Although the pH had risen to 7.3 at a reach approximately 50km downstream from the mine, the level of zinc was still 1.5mg l^{-1} . This further emphasizes the persistent nature of zinc contamination in waters receiving various forms of mine drainage.

In the study of Besch *et al.* (1972) of mine waters in the New Brunswick region of Canada there are fewer data given for the chemistry. However

the data given on ranges of zinc, pH and hardness show similarities with those of the present area. Thus the average values for zinc in the contaminated streams ranged from 0.107 to 10.94mg l^{-1} , for pH from 3 - 7.8 and for total hardness from 13 - $445\text{mg l}^{-1} \text{CaCO}_3$. The higher values for total hardness were caused when liming of the mine effluents was carried out. The more common range of hardness values given for contaminated streams which were not limed was 13 - $62\text{mg l}^{-1} \text{CaCO}_3$. It is evident that these waters too are relatively soft and therefore comparable to some of the surface waters draining the present study area. The source of the highly acidic nature of some of the waters (which again contrasts with those of the present study) is similar to other areas described above i.e. oxidation of pyrite. The most acid mine waters of the present study were only 'mildly' acidic, the lowest pH reaching 5.8 for the source of Gillgill Burn (0093/01). The most acidic waters overall are shown by the results to be derived from surface drainage through thick peat on the upper fells above the mine sites.

From the studies made by Jennett *et al.* (1971, 1975) in the mining region of south eastern Missouri it is evident that the zinc contamination of streams comes from the more recent mining operations for lead (in contrast to activities in the present area which ended between 1920-1930), and has been minimized by active controls. The levels of zinc quoted rarely exceed 0.2mg l^{-1} . Part of the reason for the low levels of zinc is attributed by them to the "slightly basic" nature of the pH (7.8 - 8.3). These values for pH are shown by them to be characteristic of surface streams in the region. They are accompanied by levels of total hardness which range from 30 - $360\text{mg l}^{-1} \text{CaCO}_3$. The higher range in these latter values shows contrasts with those of surface drainage waters in the Northern Pennine Orefield. All the sources of zinc contamination were shown to be derived principally from surface drainage over tailings, and seepage from tailings

dams and slurry ponds. Much of the zinc was shown to be transported in suspensions of colloidal material which had escaped from flotation and tailings reservoirs, to be deposited downstream in the receiving body of water.

9.33 General comments

It is difficult to assess the influence of the atmosphere in providing zinc to the present area of study, since no analyses of rainwater were carried out.

Emissions from zinc smelters were shown to be an important source of zinc to the atmosphere and ultimately the soil and stream environments (1.81). Since the closure of zinc smelters took place in the present area of study at least 40 years ago, the importance of this source will be negligible. Nevertheless analysis of rainwater in areas away from immediate industrial activity (Pearson *et al.*, 1973) does indicate that zinc can be present in relatively high quantities.

Transportation of zinc concentrates within and away from the Orefield has virtually ceased since the closure of dressing plants and flotation mills. Thus the incidence of the distribution of zinc through disturbance, accidental spills and other agencies connected with the transportation methods will also be minimized. The only significant contribution of zinc in this way might come indirectly from the active mining and processing of fluorspar.

9.4 Chemical relations of zinc in mine drainage waters of the Northern Pennine Orefield

During the preceding discussion the extent of zinc contamination of waters in the Northern Pennine Orefield and the primary sources have been described, and subsequently compared with lead and zinc mining areas elsewhere. Certain similarities have been demonstrated and, where appropriate, the contrasting features have been indicated. From the review of the geological and geochemical aspects of zinc mineralization in 1.5 and 1.6, and also from the results of the factor analysis performed on the inorganic chemical components measured during the present surveys (4.23, 5.23, 6.34), it becomes apparent that such differences can be related to the underlying geology.

This section continues the discussion by outlining the main controls on the composition of the mine drainage waters (as indicated by the factor analysis), and relating these to possible controls on the availability of zinc.

9.41 Hydrogeochemical controls on the chemical composition of mine drainage waters in the Northern Pennine Orefield

From the account presented in Chapter 3 it is evident that some of the reaches surveyed in 4.2 and 6.3 are representative of differing hydrological and geological conditions. Included are waters from springs, seepages, surface run-off and adits. At least three main rock groups, differing fundamentally in their geochemistry, will have potential influence on the chemistry of these waters: relatively pure limestone, chiefly from the great limestone stratum, lead-zinc-fluorite mineralization; rocks of the Upper Millstone Grit series. In a study of groundwaters in the Derbyshire Dome, Edmunds (1971) was able to demonstrate almost identical influences.

In his study waters draining more than one rock group were termed "hybrid" waters. In the area of the present study certain situations occur where water draining over the upper sandstone/shale strata of the Millstone Grit mixes with waters discharged from adits receiving drainage from the lower limestone rock, thus forming "hybrid" waters.

The results of the factor analysis presented in 4.232 support the hydrological observations that the mine drainage waters can be divided into two main groups based on their sources. These were previously stated to be ground and surface waters (4.232).

If the factor analyses performed on the data from all of the field surveys are considered together, some general observations can be made. In spite of the hydrogeological complexity of the Orefield, there appear to be certain regularities in the hydrogeochemical controls of the mine drainage waters. The first factor in the analyses, which in most cases explained up to 50% of the variance among the ions in the waters, accounted for essentially all of the variance of Mg, Ca, and carbonate, together with a proportion of the variance of Na, K, Si, $\text{SO}_4\text{-S}$ and Cl. This factor is interpreted as representing the weathering products of carbonate minerals of the limestone rock, particularly in the case of the ground waters. Ca would be contributed primarily from the calcite. Mg may be derived from weathering of the limestone wallrock in which much of the calcite has been replaced by dolomite. It is possible that a contribution of Mg and Ca may come from the weathering of ankerites which form dominant gangue minerals associated with the mineral veins (Dunham, 1948). Dunham has given these minerals the general formula $(\text{MgCO}_3 \cdot \text{CaCO}_3)$. $(\text{FeCO}_3 \cdot \text{CaCO}_3)$. $(\text{MnCO}_3 \cdot \text{CaCO}_3)$. (CaCO_3) , showing the principal components to be dolomite, ferrodolomite, mangandolomite and calcite.

In the case of Gillgill Burn, whose source water is predominantly derived from the upper sandstone/shale strata (and surface drainage over sandstone tailings and dumps of loose, fractured shale) there may be additional sources of Mg and Ca. A contribution may well come from the weathering of sandstone since the cementing agents of the quartz can be dolomitic (Dunham, 1948). Thus in the surface waters in general, carbonate components of the arenaceous and argillaceous rocks might be expected to contribute to this factor.

Edmunds (1971) included a section on the "major" elements in his study of groundwaters. In this group he included Na, K, Mg, Ca, HCO_3 , SO_4 -S and Cl. As in the present study, irrespective of the source of water, limestone (or carbonate minerals) was shown to be the dominant control on the chemistry of these elements.

The second factor most influencing the inorganic composition of the mine drainage waters in the present study was in all cases a factor dominated by the sources of the heavy metals, which were primarily Zn, Cd, and Pb. In some cases loadings for these ions were opposed by negative loadings for either Fe, Fe and pH or pH. This suggested that controls on the solubility of these metals, in particular zinc (see 9.32), might involve mineral equilibria controlled by pH or ion exchange reactions involving Fe. The factor is interpreted as representing the weathered products of the metallic ores, in particular sphalerite and galena. The association of F with this factor in Fig. 5.2 for Gillgill Burn (F was only analysed for the data on Gillgill Burn and its tributaries) substantiates this suggestion. This is because fluorite has been shown to be the prime gangue mineral accompanying the ores of Zn and Pb in the area (Dunham, 1948).

In most of the factor analyses performed, Fe and O.D. were found to load together forming either a separate factor or in opposition to Zn and Cd.

Occasionally they were accompanied by positive loadings for K, Al and Si. It is tempting to suggest that this might represent an inorganic colloidal factor with a high proportion of Fe-rich colloids such as limonite or illite. The inclusion of K, Al and Si might be interpreted as further evidence for this suggestion since clay minerals present in shales contain all of these elements. The opposition on these factors by Zn would fit such a hypothesis since the important control of zinc availability by clays, and hydrated Fe oxides, has been discussed (1.73; see also 9.4).

In the case of the surface waters there is a possibility that the loading of Fe and O.D. might represent a control exerted by humic substances leached from the peat. There are several reasons behind this possible interpretation:

(i) A number of streams in the surveys were shown to originate from drainage channels in thick peat and demonstrated a relatively high measurement for O.D. and also a high level for Fe (e.g. reaches 0115/10, 0116/10, and 0083/10).

(ii) Peat contains humic substances (Schnitzer, 1971), and these can chelate Fe (Shapiro, 1967).

(iii) Since Zn can participate in ion exchange reactions with humic substances (1.733), its negative loading on the factor may indicate this control on its availability.

Na and Cl were found in some cases to form a unique factor (5.232). Since this occurred primarily with the analysis of data for the surface waters, it might represent a source of these elements from the atmosphere. Alternatively it might result from contamination by road salt since the catchments of some of the streams included roadside ditches which at time of flood from melting snows might receive substantial quantities of these elements.

SO_4 -S was found frequently to factor separately or in combination with Zn, Cd, and to a lesser extent Ca. Dunham (1948) has shown that meteoric waters carrying oxygen and carbon dioxide circulate above the permanent water table converting, during the secondary processes, sulphides to sulphates and carbonates. If large amounts of sulphate are present in the meteoric water, calcite can be converted to gypsum. This factor might well represent the products of such reactions.

The results of the factor analysis confirm the hypothesis made at the beginning of this section that at least three major rock groups in the Orefield influence the inorganic composition of both ground and surface waters. In 9.31 it was shown that certain features of mine waters in the Rheidol Valley (as described by Fuge, 1972) were different from those in the Nent Valley. In particular the non-acidic adit waters were shown to carry much lower levels of Mg and Ca. As with the present study, it seems possible to relate the disparity to differences in the geology of the two areas. Smith has given a detailed account of the geological successions associated with the mining area of Cardiganshire. In contrast to the Nent area, none of the mineral lodes are associated with limestone strata. Limestone is shown to be absent from the successions of strata traced from surface workings to the lowest subterranean workings. The formation with which the lower workings are found to be associated is shown by Smith to consist of massive beds of grey grit alternating with shales. The succession continues to alternate between ferruginous shales, sandstones, grey shales with flags and mudstones to the upper grits known as the "Aberystwyth grits". Some of the shales are shown to contain large amounts of pyrite which might account for the occurrence of many highly acidic adit waters. The absence of limestone strata would seem to account for the low levels of Mg and Ca in the adit waters and the characteristic "soft" waters of the area (Griffiths *et al.*, 1975.

9.42 Factors indicated as most influencing the chemistry of zinc

Although Zn was found to show many correlations in these waters (Tables 4.2, 5.2), by simplifying the data using factor analysis techniques the more important controls on Zn concentration are indicated.

With regard to the groundwaters it appears that colloids rich in iron may exert an influential control of the concentration of Zn. This is indicated by the presence of only one factor where Zn is opposed by other variables. This is factor six (Fig. 4.2) where O.D., Fe and Al are the mutually exclusive components with Zn. Although pH is indicated as exerting a specific control on equilibria involving the majority of the other heavy metals (by its placing on factor two), Zn is notable for its absence on this factor. This would seem to imply that pH is possibly secondary in its influence on zinc concentration when compared with iron colloids. Jenne (1968) has proposed that the hydrous oxides of Fe and Mn furnish the principal control on the fixation of Zn in freshwater sediments. The results here indicate that in the ground waters this control may be of equal importance. Since Zn negatively correlates with Fe, this implies that the control exerted by the Fe-rich colloids might be through ion-exchange or adsorption processes. The importance of such mechanisms in controlling heavy metal concentrations has been reviewed by Leckie and James (1974), and discussed in 1.73. In many of the adit waters such as reaches 0113/01, 0097/01, and reaches receiving direct discharge from these, such as 0151/20, suspensions of colloidal material were often noted, and the stream bottoms were always covered by a thick deposit of silt. The high correlation between Zn and Cd, and their association on factors, suggest the possibility that similar controls are exerted on Cd in these waters. The equal loading of Zn and $\text{SO}_4\text{-S}$ on factor five implies the possibility of an equilibrium control of Zn concentration through the

oxidation of sphalerite. This supports the weathering processes of ore deposits as outlined in 1.62.

In contrast to the situation with ground waters the results of the surface waters including Gillgill Burn (Figs. 4.3, 5.2) indicate that pH might be the most influential factor controlling the behaviour of Zn in these waters. In Table 4.10, which lists the factors for the surface waters, it can be seen that Zn occurs on only one factor, the second one which accounts for 80% of its variance. It loads highly with Pb, Al and to a lesser extent with Mn and Cu which suggests common sources of these ions from weathered mineral deposits. In addition to being opposed by pH on this factor there are negative loadings for Fe, Ca, and Ca hardness.

This suggests that the control of pH may operate through a solubility relationship involving Fe, perhaps as the precipitated hydrous oxide, and Ca perhaps in the form of calcite. The level of pH would then not only control the mineral equilibria, but also possible ion exchange processes between the heavy metals and the surfaces of the insoluble hydrous oxide and carbonate.

If the data on Gillgill Burn are considered (Fig. 5.2), Zn again loads highly on factor two with the other heavy metals and F, but is only opposed by a negative loading for pH. This infers the important influence of pH in these waters in controlling solubility reactions involving zinc.

9.43 General comments

In making attempts to interpret the first factor extracted from each of the factor analyses it is evident that difficulty will be experienced in separating the contribution made from carbonate minerals (chiefly dolomite) of the limestone bedrock and those of the ankerites, and cementing agents

of the argillaceous and arenaceous rocks. The possible importance of the latter should not be overlooked since the control of carbonate minerals was shown to operate in both ground and surface waters. In a hydro-geochemical study of surface streams draining the Mackenzie River basin, Canada (a non-metalliferous mining area), Reeder *et al.* (1972) were able to show that the weathering of carbonate minerals exerted the main control on the inorganic composition of the streams. The conclusion was based on the results of an R-mode factor analysis performed on their data. Included in their interpretation of the factor was a contribution from calcareous material in the argillaceous and arenaceous rocks of the region, as well as from limestone.

The possible importance of Fe-rich colloids such as limonite and illite in controlling the availability of zinc in the ground waters shows agreements with the comments made by Wedepohl (1972) which were included in 1.61. Here Wedepohl emphasizes that adsorption rather than solubility controls the concentration and distance of transport of zinc in weathering solutions. Also numerous authors have shown how zinc can concentrate in the mineral limonite (White, 1957; Jenne, 1968; Wedepohl, 1972). In the surface waters pH was indicated as being of most importance in controlling zinc availability. However Fe-rich colloids were also indicated as being of possible importance. On certain factors Fe and pH loaded together (Fig. 4.3) indicating the possible control of pH over ion exchange reactions involving Fe minerals and zinc (1.73).

However it must be emphasized that these speculations are based purely on interpretation of the factor analysis and are not supported by analysis of the waters for their colloidal/clay content. The suggestions are considered to represent a reasonable interpretation of the possible factors controlling the availability of zinc from the available geological information.

9.5 The distribution of species with special reference to levels of zinc

In the previous sections the sources of zinc contamination and their relationship with the local geology have been discussed. Particular emphasis has been made on the geochemical controls of the mine water chemistry and consequent influence on the availability of zinc.

Comparisons were made with mining areas elsewhere.

In this section the distribution of algal species and bryophytes is discussed in relation to the levels of zinc in waters contaminated by the drainage from mines. Caution is exercised when generalisations on the distribution of species and comments on their relative resistance towards zinc are made. This is because no quantitative assessment was made of the seasonal abundance of species in the area. Comparisons are made, where appropriate, with studies made on the flora of zinc contaminated streams elsewhere.

9.51 Algae

In the results presented in 4.31, 5.31, and 6.4 it was suggested from arranging the data into 'association tables' that certain 'associations' of species could be defined in relation to increasing levels of zinc. A similar pattern is demonstrated by the data from the three surveys even though Tables 5.5 and 6.8 include additional species from reaches free from zinc contamination. The 'association' restricted to reaches carrying high zinc levels ($>10\text{mg l}^{-1}$) shows a high proportion of species of diatom (reaches 0104/01, 0104/15, 0107/17). The species were shown to include *Caloneis lagerstedtii*, *Pinnularia borealis* and *Achnanthes marginistriata*. Although these species shared a restricted occurrence to the high zinc reaches, other species of diatom which were distributed throughout the ranges of zinc levels were generally more abundant at these reaches.

This group includes *Pinnularia subcapitata*, *P. viridis* and *Eunotia exigua*.

Besch *et al.* (1972) carried out a detailed investigation of the benthic diatom communities present in streams contaminated by zinc in New Brunswick, Canada. Their data for the distribution of species of diatom in relation to zinc levels is summarized in Table 9.6. A similar set of data for the present study is summarized in Table 9.7 using the calibration of Besch *et al.* There is some agreement between the information but this is also coupled with slight contrasts. Thus in both cases *Eunotia exigua* and *Pinnularia interrupta* are shown to be very resistant and *Tabellaria flocculosa* is shown to have a low resistance. However there is disagreement in the placing of *Synedra ulna*, *S. rumpens* and *Achnanthes minutissima*. Besch *et al.* place these respectively as resistant, moderately resistant, and low resistant, whereas in the present study they were found to be respectively low resistant, resistant and resistant. Even though Besch *et al.* emphasize that their data are only calibrated for the situation of zinc contamination in New Brunswick, the similarities with the present data are worth noting.

From the results presented in 4.31 it was established that filamentous green algae were the most abundant species at reaches with high zinc levels. However they were shown not to be restricted to the "associations" but were equally abundant throughout the range of zinc levels encountered. It is clear from all three 'association tables' that species in the genus *Hormidium*, particularly *H. rivulare*, are the most abundant in the 'associations' in the middle of the tables, signifying their ability to colonize reaches with a wide range of zinc levels. Other species included in these 'associations' are *Ulothrix moniliformis* and *Mougeotia* sp. (>8<12µm).

Very resistant	resistant	moderately resistant	low resistant	very low or no resistance
>10mg Zn/l	1-2mg Zn/l	~1mg Zn/l	0.1-0.2mg Zn/l	<0.1mg Zn/l
<i>Achnanthes microcephala</i>	<i>Synedra ulna</i>	<i>Synedra rumpens</i>	<i>Achnanthes minutissima</i>	<i>Diatoma hiemale</i>
<i>Eunotia exigua</i>		<i>Fragillaria intermedia</i>	<i>Achnanthes linearis</i>	<i>Eunotia arcus</i>
<i>Pinnularia interrupta</i> var. <i>biceps</i>		<i>Fragillaria</i> <i>crotonensis</i>	<i>Anomoeoneis serians</i>	<i>E. venensis</i>
<i>Fragillaria virescens</i>			<i>Tabellaria flocculosa</i>	<i>Gomphonema intricatum</i> var. <i>pumila</i>
			<i>T. fenestrata</i>	<i>G. augur</i>
				<i>G. angustatum</i>
				<i>Cymbella microcephala</i>
				<i>C. affinis</i>
				<i>Achnanthes deflexa</i>

Table 9.6 Tolerance of zinc of some common species of Bacillariophyta in the N.W. Miramichi area, New Brunswick, Canada. After Besch *et al.* (1972) Table 8.

very resistant $>10\text{mg l}^{-1}\text{Zn}$	resistant $1-2\text{mg l}^{-1}\text{Zn}$	moderately resistant $\sim 1\text{mg l}^{-1}\text{Zn}$	low resistant $0.1-0.2\text{mg l}^{-1}\text{Zn}$	very low or no resistance $<0.1\text{mg l}^{-1}\text{Zn}$
<i>Achnanthes marginistriata</i>	<i>Amphora veneta</i>	<i>Ceratoneis arcus</i>	<i>Synedra ulna</i>	<i>Diatoma elongatum</i>
<i>Caloneis lagerstedtii</i>	<i>Achnanthes minutissima</i>	<i>Fragillaria intermedia</i>		<i>D. vulgare</i>
<i>Eunotia tenella</i>	<i>Cymbella ventricosa</i>	<i>Gomphonema parvulum</i>	<i>Nitzschia linearis</i>	<i>Gomphonema ventricosum</i>
<i>E. exigua</i>	<i>Surirella ovata</i>	<i>Meridion circulare</i>	<i>Navicula cryptocephala</i>	<i>G. olivaceoides</i>
<i>Pinnularia interrupta</i>	<i>Synedra rumpens</i>		<i>N. radiosa</i>	<i>Tabellaria flocculosa</i>
<i>P. borealis</i>				
<i>P. subcapitata</i>				
<i>P. viridis sudetica</i>				

Table 9.7 Tolerance of zinc of some common species of Barillariophyta in the streams draining the North Pennine

Orefield

The 'associations' depicted in Tables 4.11, 5.5, and 6.8 are summarized in Table 9.8 in terms of the most abundant species in particular ranges of zinc. An indication of the relative resistance of species is also given. If a comparison is made between this table and a summary made of the results from studies carried out on streams in other mining regions (Table 9.9), there is clear agreement between them, particularly in the placing of *Horridium rivulare*, *Ulothrix* sp. and *Microthamnion* sp. as being notably zinc tolerant.

Although Reese (1937) confined her studies primarily to the main river Rheidol, observations were made on a highly zinc contaminated stream issuing from an adit. The only algal species given for this stream was a species identified as *Ulothrix* sp. Species which were able to colonize the main river below the mine workings included *Diatoma hiemale*, *Meridion circulare*, *Gomphonema parvulum* and *Ulothrix* sp. These species tend to correspond to the 'association' in the present study characteristic of 'lower' levels of zinc in the range $0.5 - 2.0 \text{ mg l}^{-1} \text{ Zn}$ (Table 9.3). This includes the species Chrysophyta sp. 'A' (= *Chrysonobula holmesii*) together with *Aphanocapsa* sp. ($>1 \leq 2 \mu\text{m}$) and *Meridion circulare*. Although found at reaches with higher levels of zinc *Chamaesiphon polymorphus* and *Achnanthes minutissima* were often found in abundant numbers associated with these species.

Griffiths *et al.* (1975) have carried out more recent investigations of streams in the same mining area as that of Reese (1937). They included in their studies observations made on streams draining through mine tailings and those emerging from adits. These were found to be highly contaminated by zinc (c.f. 9.31) but contained abundant growths of the green filamentous algae *Ulothrix* sp., *Horridium* sp. and *Mougeotia* sp. Similar findings were made by McLean and Jones (1975) for streams draining adjacent areas in the

very resistant >10mg l ⁻¹ Zn	resistant 2.0 - 5.0mg l ⁻¹ Zn	moderately resistant 0.5 - 2.0mg l ⁻¹ Zn	low resistant 0.1 - 0.5mg l ⁻¹ Zn	very low or no resistance <0.1mg l ⁻¹ Zn
<i>Euglena mutabilis</i>	<i>Chamaesiphon polymorphus</i>	<i>Chrysophyta</i> sp. 'A' =	<i>Navicula radiosa</i>	<i>Diatoma vulgare</i>
<i>Caloneis lagerstedtii</i>	<i>Phormidium mucicola</i>	<i>Chrysonobula holmesii</i>	<i>Synedra ulna</i>	<i>Tabellaria flocculosa</i>
<i>Pinnularia subcapitata</i>	<i>Chrysophyta</i> sp. 'B' =	<i>Ceratoneis arcus</i>	<i>Drapenaldia plumosa</i>	<i>Microspora amoena</i>
<i>P. viridis</i> var. <i>sudetica</i>	<i>Hydrurus foetidus</i>	<i>Fragillaria intermedia</i>		<i>Ulothrix zonata</i>
<i>Cylindrocystis</i> <i>brebissonii</i>	<i>Diatoma hiemale</i> var. <i>mesodon</i>	<i>Gomphonema parvulum</i>		
<i>Mougeotia</i> sp. (>8≤12μm)	<i>Microspora</i> sp. (>8≤12μm = <i>M. lauterbornii</i>)	<i>Meridion circulare</i>		
<i>Horridium rivulare</i>		<i>Staurastrum punctulatum</i>		
<i>Microthamnion</i> <i>strictissimum</i>				
<i>Ulothrix moniliformis</i>				

Table 9.8 Tolerance towards zinc of some of the more abundant species in the study area, as determined by field observations.

Location of mining region	Species indicated as being tolerant of zinc	Reference
Cardiganshire, west Wales	<i>Ulothrix</i> sp.	Reese, 1937
New Brunswick, Canada	<i>Achnanthes microcephala</i> } - - <i>Eunotia exigua</i> <i>Pinnularia interrupta</i> var. <i>biceps</i> <i>Fragillaria virescens</i> <i>Microthamnion</i> sp. <i>Mougeotia</i> sp., <i>Ulothrix</i>	Besch <i>et al.</i> , 1972
Cardiganshire, west Wales	<i>Hormidium</i> spp. <i>H. rivulare</i> <i>Ulothrix</i> sp.	McLean and Jones, 1975
Cardiganshire, west Wales	<i>Hormidium</i> sp. <i>Microspora</i> sp. <i>Ulothrix</i> sp.	Griffiths <i>et al.</i> , 1975

Table 9.9 Algal species tolerant of zinc as indicated by field studies carried out in mining areas other than that of the Northern Pennines

same mining region. *Hormidium rivulare* was noted particularly in highly contaminated streams. Table 9.3 shows the similarities in species colonising streams in the present study area containing high levels of zinc.

Species whose distribution was restricted to very low levels of zinc being rarely, if ever, found at levels above $0.1 \text{ mg l}^{-1} \text{ Zn}$, formed a large 'association' which was dominated by *Ulothrix zonata*, *Microspora amoena*, *Mougeotia* sp. ($>16 \leq 24 \mu\text{m}$) and *Synedra ulna*. When considering species in this 'association' it is important not to exclude the possibility of other factors contributing to the restricted occurrence. Zinc was established in the laboratory under standard conditions to be toxic to species such as *Ulothrix zonata* and *Synedra ulna*. However, as suggested by Griffiths *et al.* (1975), there might be other factors which could limit the diversity of algal species in addition to the high levels of zinc. Discharge of highly calcareous water from adits into otherwise 'soft' surface waters might impose new conditions which could modify the indigenous microflora. There was a suggestion from the present study that species such as *Hormidium fluitans*, *Eunotia exigua*, *Cylindrocystis brebissonii*, *Penium navicula* and *Diatoma hiemale* var. *mesodon* were able to colonise softer, more acidic, waters contaminated by zinc; whereas *Stigeoclonium* sp. (= *S. tenue*) *Amphora veneta*, *Surirella ovata*, *Synedra rumpens* and *Cymbella ventricosa* favoured harder waters with a pH range of 7 - 8. This aspect is taken up later (9.63, 9.7) where the results of studies investigating the influence of environmental factors on the toxicity of zinc to *Hormidium* spp. will be considered.

9.52 Bryophytes

From Table 4.12 and Section 5.33 it is evident that *Scapania undulata* and *Philonotis fontana* showed a wide distribution in the study area and a general tolerance towards a wide range of zinc levels. However there were indications that both species showed a preference for soft, acidic waters, including those contaminated by zinc. They were found associated most frequently with waters showing a pH range of 3.8 - 6.8, with the total hardness ranging from 10 - 55mg l⁻¹CaCO₃. In such streams *Scapania undulata* formed 'turfs' of growth over the lip of small waterfalls, or on exposed rock surfaces where the current was fast. In all cases the substrate was either sandstone or shale. *Philonotis fontana* was usually found at the stream margins or in wet flush areas formed by surface drainage. *Dicranella varia*, which showed a similar tolerance to ranges in the levels of zinc, contrasted in its habitat preference. It was found most often growing on silt trapped between boulders of limestone in the streams emerging from adits. This is indicated in Table 4.12 by its presence in reaches such as 0097/01, 0098/01 and 0113/01. It was also found growing on a fine silt or slurry bordering reach 0111/01, a small stream emerging from the base of a tailings heap associated with a fluorspar mine.

Pohlia nutans was found to be a 'bank' species associated with reaches carrying the higher levels of zinc. In such reaches it was often growing in positions in which it received continual washing or spray from the stream water. It was found most characteristically in the upper reaches of surface drainage of streams, particularly where these were bordered by banks of peat. The waters were soft and acidic, containing up to 10mg l⁻¹Zn.

Bryum pallens and *Dichodontium pellucidum* were placed in the same 'association' as *Pohlia nutans* (characteristic of higher zinc levels), but were found

growing in different habitats. Reaches colonized by them included mine waters emerging from adits. *Dichodontium pellucidum* was emergent primarily, growing attached to silt trapped between boulders of limestone. In such positions it was washed by intermittent spray from the adit water.

Bryum pallens was found mostly submerged in the mine water, often with much silt attached to it. The ranges of pH and total hardness favoured by these two species were 6.9 - 7.6, and 190 - 390mg l⁻¹CaCO₃ respectively.

Cratoneuron filicinum, *Hygrohypnum ochraceum*, *Brachythecium rivulare* and *Hygroamblystegium fluviatile* were all found associated with relatively hard waters carrying 'intermediate' levels of zinc (1 - 4mg l⁻¹Zn). They were all found to be semi-emergent, attached usually to sand or gravel trapped between boulders, or in some cases growing midstream attached to a boulder.

Bryum pseudotriquetrum was the main species found to be relatively intolerant of zinc. It was found in one reach (0168/01) with a mean level of 0.6mg l⁻¹Zn in a flush area fed by the stream, but this water was relatively hard (total hardness of 179mg l⁻¹CaCO₃). It was found most frequently in uncontaminated reaches (0106/99) which were relatively soft (total hardness 43mg l⁻¹CaCO₃), attached usually to sandstone boulders or turfs of *Scapania undulata*.

The best documented area for studies made on species of bryophyte colonizing streams contaminated by zinc is that of west Wales.

The early studies of Carpenter (1924) in this area make only brief mention of the bryophytes of polluted streams. In the streams classed as "barren" it is stated that there is "only the slightest coating of moss or liverwort." This gives an indication of the ability of bryophytes to colonize zinc polluted streams. Reese (1937) mentions in her study of the microflora

that a stream highly contaminated with zinc was devoid of vegetation apart from *Ulothrix* sp. and a vegetative portion of a leafy liverwort. Although no name is given, this may well have been *Scapania undulata*. Jones (1940) describes briefly the flora of the zinc contaminated Ystwyth and shows that it was limited to occasional tufts of *Scapania undulata*. The observations made in the present study support these findings which confirm the ability of *Scapania undulata* to colonize soft waters enriched with zinc. Recently more detailed studies have been carried out on the resistance of *Scapania undulata* to the toxicity of zinc by McLean and Jones (1975). The highest level of zinc at which they found *S. undulata* in the field was 4.1 mg l^{-1} . The water at this site was soft, with $6.9 \text{ mg l}^{-1} \text{ Ca}$ and a total hardness of $37.0 \text{ mg l}^{-1} \text{ CaCO}_3$. The highest level of zinc at which *Scapania undulata* was found in the present study occurred at reach O108/08 with a mean of $7.0 \text{ mg l}^{-1} \text{ Zn}$. This too was soft water with a mean value of $5.4 \text{ mg l}^{-1} \text{ Ca}$ and a total hardness figure of $33.1 \text{ mg l}^{-1} \text{ CaCO}_3$. *Hormidium rivulare* was found frequently to accompany *Scapania undulata* by McLean and Jones.. This was similarly found in streams such as Gillgill Burn and Gudham Gill. Other species were also found to accompany *Scapania undulata* (9.33) in these streams, including *Microspora* sp. ($>8 \leq 12 \mu\text{m} = M. lauterbornii$) and *Hormidium fluitans*.

It seems evident that *Scapania undulata* is one of the few aquatic bryophytes capable of resisting the toxic effects of zinc. There is no apparent need for the presence of possible ameliorating factors such as high levels of pH, total hardness or calcium at reaches in which it grows. These factors seem necessary for aquatic species such as *Brachythecium rivulare*.

9.6 The resistance of *Horneridium* species to zinc

This Section discusses the resistance to zinc of the three *Horneridium* species as indicated by the field and laboratory observations. Comments made on the morphological observations carried out on field and laboratory material are included at the end of the section.

9.61 Field and laboratory observations

The present survey includes data from sites with very low to very high levels of zinc, and with a relatively wide range of water chemistries associated with them (6.4). *Horneridium rivulare* and *H. flaccidum* were abundant at the site with the highest zinc level (mean of 22.8, maximum of 30.2mg l⁻¹Zn), but *H. fluitans* was found at sites only up to a mean of 5.59mg l⁻¹Zn (6.5). All populations taken from the highest zinc levels appeared quite healthy, so it is uncertain whether the species may occur elsewhere at even higher zinc levels in the pH range dealt with here. *H. fluitans* is more restricted to situations with relatively fast current speeds, and these were less common in the streams with the highest zinc levels. *H. rivulare* has been found in highly acidic streams with zinc levels even higher than in the present survey (Hargreaves *et al.*, 1975), but at low pH values, zinc is much less toxic to *H. rivulare* (Hargreaves & Whitton, 1976; also see section 9.71).

The results of the assays show that populations of the three *Horneridium* species growing in streams carrying high levels of zinc are adapted forms, being more tolerant of high zinc levels than populations of the same species isolated from unpolluted streams. It has been shown for populations of *H. rivulare* (Table 6.10) that the level of resistance does not change with long-term subculture, thus indicating that adaptation is genetic. It is difficult to state exactly from the scatter diagrams (Fig. 6.2) of the T.I.C. plotted against mean field zinc what is the

threshold above which populations become adapted to higher levels of zinc, and below which they remain comparatively sensitive. This threshold would in any case be expected to vary with the levels of the other factors influencing zinc toxicity (9.62). In the case of *H. rivulare* however it does seem reasonable to conclude that if seven sites are excluded from consideration, then the threshold lies within the discontinuity indicated in Fig. 6.2, 0.2 - 0.8mg l⁻¹ mean field zinc. For most sites the threshold is probably nearer the lower than the higher of these values. The seven sites excluded consist of the three with the highest calcium levels, together with the only four sites which, although they have low mean field zinc levels (<0.1mg l⁻¹), nevertheless lie downstream of old mine tips, and so are almost certainly subject to much higher zinc levels at times of flood. This phenomenon has in fact been demonstrated for site 0013/02 (Table 6.9), the only one of the four sites which has been studied in detail elsewhere (B. A. Whitton, pers. comm.).

In a study of the effect of zinc smelter waste on selected laboratory cultures of algae, Rana and Kumar (1974) were able to show that strains of *Chlorella vulgaris* and *Scenedesmus* sp. were more tolerant of zinc than strains of other test algae. The tolerance towards zinc was shown to be retained with long term subculturing and led them to conclude that genetic adaptation was responsible, a conclusion similar to that reached here for *Horridium rivulare*.

A study was carried out by Stokes *et al.* (1973) on the heavy metal tolerance of algae from contaminated lakes in the Sudbury mining area of Ontario. Whilst not giving clear evidence for genetic adaptation of species of *Chlorella* and *Scenedesmus* to the toxicity of the metals copper and nickel, they did show that strains isolated from the contaminated lakes were more tolerant than closely related laboratory strains of species in the same

genera. In discussing their results they postulate that the two genera may be inherently more adaptable to the toxic effect of the metals than most other algae.

9.62 Morphological observations

The key morphological observations on the *Horridium* species have been presented in Chapter 8.

There was some evidence with *H. rivulare* that a morphological as well as a physiological response may be involved. An increased frequency of geniculations with high zinc levels was observed both as a response to the environment with populations from sites with low zinc levels and as an inherent response with populations from sites with very high zinc levels. It is tempting to suggest that the response in the zinc resistant populations is under genetic control. It is of course uncertain whether geniculations have any direct functional significance in reducing zinc toxicity, but it is worth noting their association with mucilage (Figs. 8.8, 8.9). Ramanathan (1964) has credited their formation as a response to the scouring effect of the current on filaments. However it was observed in the present study that they were abundant on material collected from seepages with little current speed, and that their numbers were increased in material cultured in flasks under various levels of zinc, including experiments where the flasks were not shaken.

9.63 Factors indicated as influencing most the toxicity of zinc to *Horridium* species

Comments on the relationship between laboratory and field observations on zinc are made difficult by two aspects of the field results. The levels of some of the chemical parameters which might perhaps influence the toxicity of zinc (Cd, Pb) are also correlated with the levels of zinc.

All the relationships investigated are based on laboratory experiments where most, if not all, of the zinc is in solution, yet this is not so with all the heavy metals present in the field. The influence of pH in the field, on the percentages of Zn, Cd and Pb which are 'soluble' (pass through a 0.2 μ m Nuclepore filter) at various total metal concentrations (Fig. 9.2) emphasizes this point. From the results of the intervariable correlation carried out on the levels of metals present, both cadmium, and to a slightly lesser extent, lead, were highly positively correlated with zinc ($P = 0.001$). In the stepwise regression analysis, lead was not shown to be an important independent variable. It is clear that from the field data alone it is not possible to separate any influence of cadmium from that of zinc, and that it is also difficult to separate lead. It is therefore possible that cadmium and also lead may contribute to part of the observations ascribed to zinc (9.64).

Comparison of the laboratory and field results strongly suggests that certain chemical factors reduce the toxicity of zinc to these *Horridium* species. For example, from the plot of T.I.C. against log field zinc level (Fig. 6.2), a number of points clearly deviate from the possible fitted regression line. In these cases the populations show a lower T.I.C. than would be expected from the level of zinc in which they grow. These sites all have very high levels of calcium, total hardness and total alkalinity, which are themselves correlated (in the present survey). It is suggested that these populations are growing at higher levels of zinc than they would otherwise have done because of the presence of the ameliorating factors. The importance of calcium and total hardness, but not total alkalinity, is supported by the results of the stepwise linear regression and the principal component analysis.

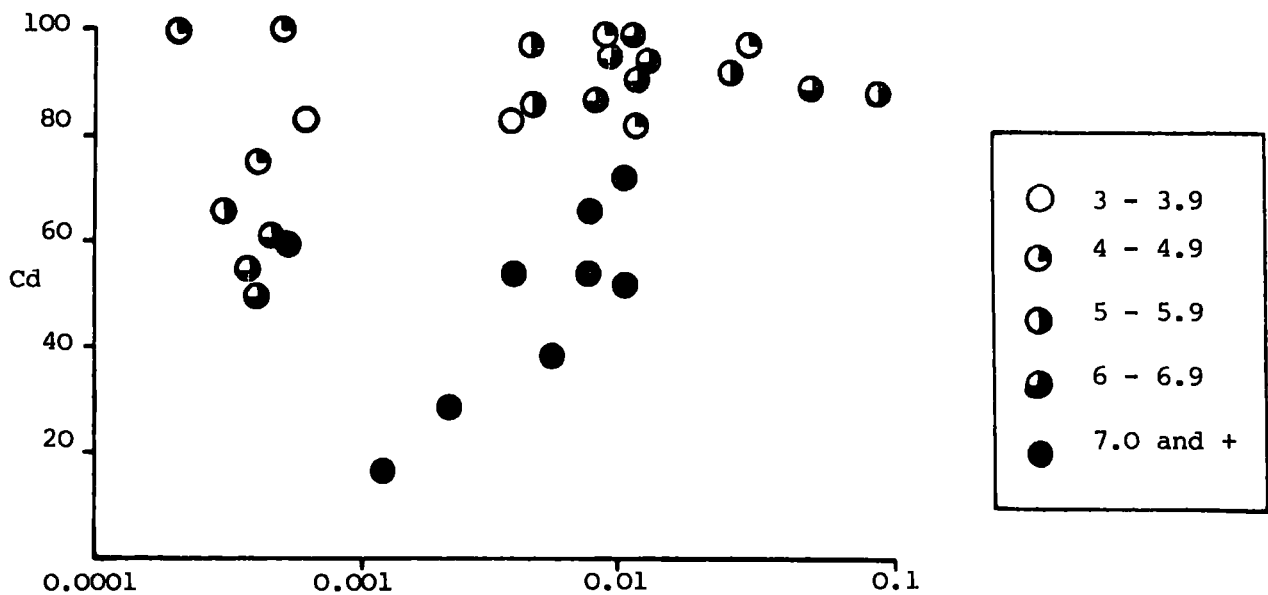
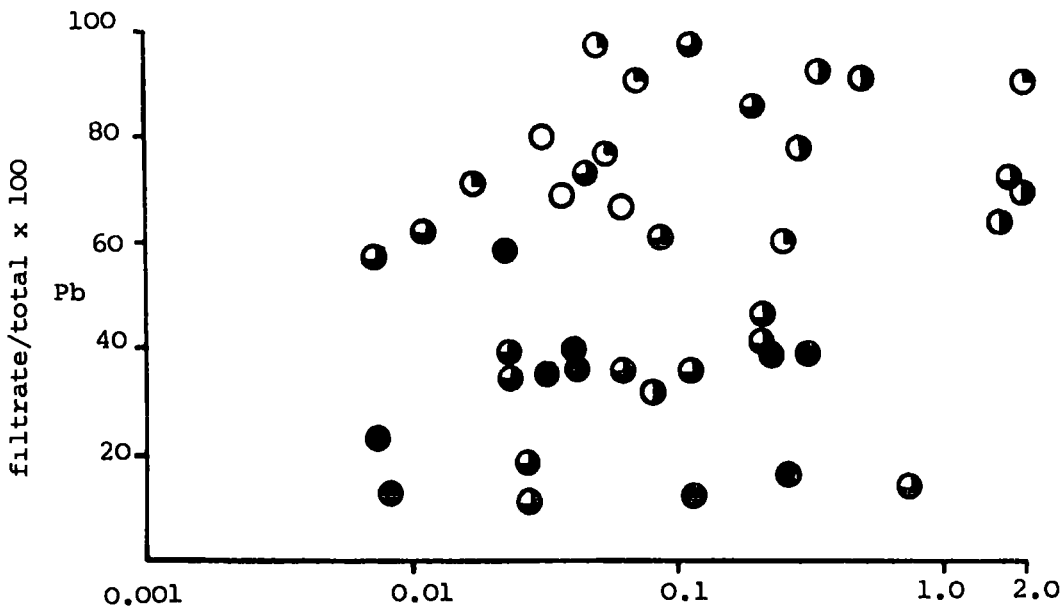
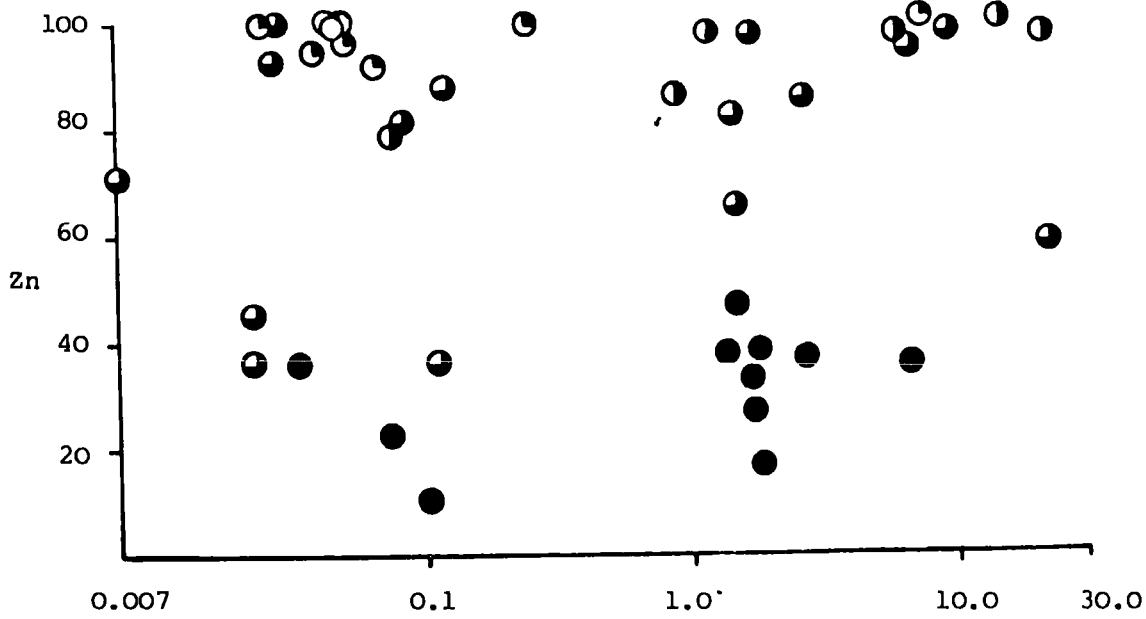
It must be emphasized that the T.I.C. is an empirical formula chosen initially because it made use of the maximum number of observations from an assay. In contrast to results with *Stigeoclonium tenue* (J.P.C. Harding & B.A. Whitton, unpublished), the T.I.C. values obtained for *Horridium* species show no improved correlation with the mean field zinc level in comparison with the J.N.I. (just non-inhibitory) values. Fig. 6.2 shows that, under the conditions used, the populations usually have much higher T.I.C. values than the mean field zinc levels from which they were taken, but that at the uppermost field levels, the results tend to be more similar, a result resembling that found for *Stigeoclonium tenue* (Harding & Whitton, 1976). The difference between laboratory and field results still holds for the lower and intermediate zinc levels even if sites with high levels of 'ameliorating factors' such as Ca are excluded from consideration. Use of the J.N.I. rather than T.I.C. gives a better correspondence between laboratory and field results over the intermediate field levels, but would tend to underestimate the zinc toxicity at the upper field zinc levels and still overestimate it at the lower ones. The underestimation at the upper field zinc levels would become even more marked if total, rather than 'soluble', zinc is considered, since the amount of insoluble zinc increases at high zinc levels (Fig. 9.2).

9.64 Comparison between the factors most influencing zinc toxicity to *Horridium* species

Although fewer populations of *H. flaccidum* and *H. fluitans* were studied, than of *H. rivulare*, some comparisons can nevertheless be made.

9.641 *H. rivulare*

The summary of the correlations between T.I.C. and selected field variables and some of their 'crude' transformations (Table 6.11) show some results



total metal concentration (mg l^{-1})
 Fig. 9.2 Relationship between filtered and total metal concentration at various values of pH

worthy of mention. As might be expected, the most significant correlations ($P = <0.05$) are between T.I.C. and Zn with some of its transformations, although Cd and Pb also correlate highly with T.I.C. The most significant correlation is between T.I.C. and log Zn. Of the untransformed variables, Cd correlates most highly. In the stepwise regression analysis, log Zn was ranked as the most important variable influencing T.I.C. Further support for the importance of Zn in influencing T.I.C. comes from the principal component analysis. Here it showed a moderate loading on the first principal component, together with a very high loading for T.I.C., and also featured very highly on the third component. In the regression analysis 'crude' ratio transformations of log Zn were ranked third, sixth, seventh and eighth. They were ratios associated primarily with the measures of hardness.

Although PO_4 -P showed few correlations with other chemical parameters in the field data (Table 6.5), it was ranked as the second most important variable influencing T.I.C. Its presence on two principal components indicates further the importance of this variable (see 9.73). Cd ranks highly in its influence on T.I.C. (fourth), and is closely associated with Zn on principal components one and three (Table 6.13).

9.642 H. flaccidum

The summary of correlations in Table 6.11 for *H. flaccidum* contrasts with those of *H. rivulare* and *H. fluitans*. The main significant positive correlations were found between T.I.C. and log Zn, log Cd, and Cd. However, in contrast to *H. rivulare* and *H. fluitans*, T.I.C. showed significant negative correlations with Mg, Ca and the measures of hardness.

Further evidence which might be used to indicate the importance of Cd in possibly influencing Zn toxicity is given by its high ranking (first) in the stepwise regression analysis. However unlike the other two species,

possible amelioration factors (9.7) such as Mg and Ca are also placed highly (second and fifth respectively). Comparisons between the principal component matrices (Tables 6.13, 6.14, 6.15) further emphasize the contrast between this and the other two species.

9.643 H. fluitans

Similarities are shown between this species and *H. rivulare* in the correlations of T.I.C. (Table 6.11). However the absolute values for the coefficients, particularly for Zn, Cd, and Pb, are higher.

In the stepwise regression analysis, Cd is again ranked first in importance for influencing T.I.C. Crude ratio transformations of Zn are also ranked highly. This is the only species to show high rankings for Fe and Mn (sixth and eighth respectively), which have been shown to influence the availability of Zn (1.732 and 9.22). The importance of these two variables is further confirmed by their presence with negative loadings on two principal components. The importance of Cd is substantiated further by its high loading on the first component and moderate loading on the third in comparison to Zn which showed a small loading on the first and higher loading on the third component.

9.644 General comments

It is clear that over most of the field zinc range, the algae are much more sensitive in the field than in the laboratory. It is difficult to compare culture conditions with long term exposure to zinc in the field, but a few of the many obvious factors which might play a role are considered.

(i) In the field, a population might possibly be eliminated at zinc concentrations bringing about only a very slight inhibition in growth rate owing to competition with a slightly more tolerant population. However if this explanation were to be applied over the whole zinc range, the presence (Table 6.3) of populations in very high zinc sites at levels above the J.N.I. of these populations would imply that at these levels increased adaptation for zinc tolerance brings about a marked reduction in growth rate.

(ii) Tolerance to zinc might be lower during a particular growth stage such as the attachment and development of zoospores. Zoospore production (and attachment) has been observed only in *H. flaccidum*, but there is no evidence that *H. flaccidum* is more sensitive than the other two species.

(iii) If the T.I.C. is related to maximum rather than mean field zinc level, the two quantitative values become slightly closer, and there is a slight improvement in the correlations for *H. rivulare* and *H. flaccidum*. It seems likely that most of the English sites with field zinc levels showing the large standard deviations (Table 6.9) will at times be subject to even higher levels than those included in the table. These reaches are below superficial mine workings whose contribution to stream zinc levels is markedly dependent on rainfall.

(iv) The presence of a chelating agent in the medium is probably in part responsible for the lack of sensitivity with populations at the lowermost field zinc levels, though it seems most unlikely that it is entirely responsible.

(v) As mentioned above, part of the observed laboratory tolerance to zinc might in fact be a result of other toxic substances playing a role in the field. Although cadmium was always present at much lower levels than zinc, nevertheless the present data suggest that this is the element most likely to be involved.

The levels of zinc in the rainfall of industrial countries are known often to be considerably higher than in the stream water of many of the 'low' zinc sites included in the present study. Lazarus, Lorange & Lodge (1970) recorded a mean value of $0.107 \text{ mg l}^{-1} \text{ Zn}$ in the rain at 32 sites in the United States, while Pearson *et al.* (1973) recorded a mean of $0.085 \text{ mg l}^{-1} \text{ Zn}$ at a site in the English Lake District. The assay technique used in the present studies would probably not be sensitive enough to show adaptation to zinc if this should occur at even lower levels than suggested in the interpretation of Fig. 2 given above.

However even if there is no variation in zinc tolerance among the populations from lower field zinc levels, it is still worth pointing out that the level of field zinc which does appear to result in adaptation in some populations is probably not so much higher than that which sometimes occurs in rain.

9.7 Environmental factors influencing zinc toxicity to *Horrmidium rivulare*, as determined in the laboratory

The results presented in Chapter 7 show clearly that a range of factors may influence the toxicity of zinc to *Horrmidium rivulare*. In all cases the experimental results confirm the significance of factors suggested by the analysis of the field data.

9.71 pH

The toxicity of zinc decreased with a fall in pH (Fig. 7.1) for both a zinc sensitive and zinc tolerant population of *Horrmidium rivulare*. This agrees with the observations of Hargreaves and Whitton (1976) on a population of *H. rivulare* isolated from a highly acidic stream. There was however an apparent slight contrast in the behaviour of *H. rivulare* populations reported in the study of Hargreaves and Whitton and those described here. The former study showed that populations of *H. rivulare*,

which are resistant to zinc, are also especially resistant to low pH values, although they may come from sites which are unlikely ever to encounter such values naturally. Of the two populations on which the influence of pH was tested in the present study, the zinc-sensitive one did show slight growth at pH 3.0, but the zinc-tolerant one did not do so. However it seems probable that this may reflect differences in adaptation to environmental pH in the two populations, since the sensitive population came from a reach with a mean field pH of 4.4, and the zinc-tolerant one from a reach with a mean field pH of 6.8 (Table 6.1).

Zinc was most toxic at pH values of 7 and 8, which is above the critical level for significant precipitation of zinc as $\text{Zn}(\text{OH})_2$ in basal media (3). It has been shown that a rise in external pH increases the uptake of zinc (Bachmann, 1961; Paton and Budd, 1972). In contrast to this, Failla *et al.* (1975) demonstrated that the uptake of zinc by *Candida utilis* was increased by a reduction in the level of external pH. This was attributed to the increased solubility and effective concentration of Zn^{2+} at low pH levels. However above pH 6.8 there was a sharp increase in the uptake of zinc by *Neocosmospora vasinfecta* (Paton and Budd, 1972), but it was suggested that much of this might represent precipitation of insoluble $\text{Zn}(\text{OH})_2$ at the mycelial surface. It is tempting to suggest that the large number of 'particles' observed during the present study (Fig. 8.10) to be attached to the mucilage of *Hormidium rivulare*, particularly at pH values of 7 and 8, could be localised deposits of precipitated $\text{Zn}(\text{OH})_2$. The toxic effects of zinc under high pH values could be attributed to the increased uptake causing saturation of available internal binding sites leading to the alteration of metabolic processes.

9.72 Calcium and magnesium

Both calcium and magnesium reduce the toxicity of zinc and in most cases this effect is marked. With the two zinc-tolerant populations, the effect of magnesium was greater at several lower concentrations than that of calcium, but the influence of calcium increased over a much greater range of concentrations. The influence of magnesium was relatively small on the zinc-sensitive population (0085/05), in agreement with the observation of Harding and Whitton (1977) on *Stigeoclonium tenue*. The quantitative effects of calcium varied between populations, but in general the more tolerant the population, the more effective was added calcium in reducing the toxicity of zinc. A further complication in the interpretation of the influence of calcium is that the alga may vary in its response to calcium even in the absence of zinc. The population from the highly calcareous reach 0151/20 did not grow in laboratory culture at $1 \text{ mg l}^{-1} \text{ Ca}$, whereas the other five populations grew in the absence of calcium.

The effectiveness of calcium at higher levels in reducing the toxicity of zinc to both zinc sensitive and zinc tolerant populations would fit the hypothesis that a mechanism exists whereby the zinc is initially bound passively. With such a mechanism, calcium might compete with zinc for these sites. It is well documented that the presence of calcium around roots may greatly reduce heavy metal toxicity (Wyn-Jones and Lunt, 1967). A number of studies have shown that the uptake of zinc can involve two phases (Paton and Budd, 1972; Failla *et al.*, 1975) in which the first includes rapid uptake by a temperature and energy dependent binding process to the cell wall. Such a mechanism has been shown to resemble a cation uptake mechanism involving ion exchange modified by metal-complex formation (Puckett *et al.*, 1973). This supports the possible competitive role of calcium when influencing the toxicity of zinc.

The effect of magnesium could be by way of the same process, particularly since this element shares some similar ionic properties with zinc (ionic radii almost identical, 0.83nm and 0.78nm (after Goldschmidt, 1926) respectively). However the reduced effectiveness of magnesium in ameliorating the toxicity of zinc to a zinc sensitive population of *H. rivulare* would not be explained by considering this mechanism alone.

9.73 Phosphate

The influence of phosphate in reducing zinc toxicity to *Horridium rivulare* is striking. Its quantitative importance is also demonstrated by the results illustrated in Figs. 7.7 and 7.8. It seems probable that the level of $\text{PO}_4\text{-P}$ present in the assay medium is a major factor in the reduction of zinc toxicity in the laboratory compared with the field, even though the level of P in the assay medium had been reduced from 2.23mg l^{-1} in the No. 10 medium of Chu (1942) to 0.89mg l^{-1} .

Rana and Kumar (1974) were able to demonstrate the effectiveness of phosphate in reducing the toxicity of zinc to *Chlorella vulgaris* and *Plectonema boryanum*. They also showed that an increase in phosphate content improved the growth of both algae. They attributed the underlying mechanism for the ameliorating effect to the possible interference of zinc absorption at the membrane. This was not suggested to be through competitive antagonism (since they are not structural analogues), but by the formation of complexes between phosphate and zinc ions rendering the zinc less mobile. However in the present study, the differences in the influence of phosphate between zinc sensitive and tolerant populations suggest the possibility of a second mechanism for their ability to withstand zinc. The marked decrease in the toxicity of zinc to the zinc tolerant populations may be associated with some active mechanism.

Such a mechanism has been reported by McLean (1975) for *H. rivulare* growing in streams with high levels of zinc, and also for other filamentous green algae growing in streams with low levels of zinc. Silverberg (1975) has shown that in *Stigeoclonium tenue* some lead is deposited in cytoplasmic vacuoles, thus suggesting that these may be important binding sites for 'excess' metal ions entering the cell. He also cites evidence for the translocation of lead through the cytoplasm.

More recently the experiments of De Filippis and Pallaghy (1976) on the possible resistance mechanism of *Chlorella* sp. to zinc toxicity demonstrated that tolerance was characterized by the development of an exclusion mechanism. Approximately 33% of the zinc taken up was shown to be associated with the cell wall and the remainder was suggested by them to be compartmented into ionic and bound forms (phosphates) within the cell.

These mechanisms of transporting and compartmenting zinc within the cell might be expected to require energy. It is tempting to suggest that the increased effectiveness of phosphate in reducing zinc toxicity to a zinc tolerant population of *H. rivulare* might be associated with an active mechanism. Thus in addition to possibly preventing toxicity by complexing the zinc in the medium, it might provide increased energy for those organisms with an active mechanism of transporting any zinc that enters the cell away from sensitive metabolic areas.

9.74 Cadmium

Cadmium is highly toxic, but the antagonistic influence of calcium on cadmium toxicity to the population studied was proportionately greater than that on zinc toxicity to either this same population or any of the other five studied. Cadmium (in the absence of any zinc) was 34 times more toxic than zinc to the zinc + cadmium sensitive population studied (0085/05) and 15.5 times more toxic to the zinc + cadmium tolerant

population (0093/85). As cadmium was itself present at reach 0093/85 at a level sufficiently high to influence *H. rivulare* (compare Table 6.3 and Fig. 7.9), it is uncertain how much of the zinc resistance detectable in this population is a response to field cadmium, and how much of the cadmium resistance is a response to field zinc. The data in Table 7.1 indicate that the toxic effects of zinc and cadmium are synergistic, thus resembling the response found by Hutchinson and Czyrska (1972) for *Lemna valdiviana*. The present results on cadmium suggest that any level of cadmium above 0.01mg l^{-1} must be suspected of producing a significant increase in the toxicity of any zinc present.

9.75 Fluoride

This element which was shown in the surveys of Gillgill Burn to be highly correlated with zinc (5.22) did not demonstrate a significant influence on the toxicity of zinc. This was judged from experiments on a zinc sensitive population removed from a reach with low levels of fluoride in the water. Fluoride itself was not found to be toxic with this population up to levels of 30mg l^{-1} .

9.76 The toxicity of other heavy metals to *H. rivulare*

(1) Lead

Since the field data did not indicate that this is one of the principal factors involved in influencing the toxicity of zinc, and since critical experimental studies on lead were found to be more complicated than any of the other factors (7.32), only a brief mention is made of lead. Investigation of lead is difficult due to the problem of producing laboratory media with levels as high as those found in the field (Table 4.1). The results of Whitton (1970) suggest that when lead is added (as $\text{Pb}(\text{NO}_3)_2$)

to cultures of filamentous algae, it is much less toxic than zinc. However under these circumstances little of the lead is in solution, and the effects are complicated by the addition of high levels of $\text{NO}_3\text{-N}$.

In a study of the toxicity of lead to the marine flagellate *Platymonas subcordiformis*, Hessler (1974) measured the actual levels of lead in solution, and even this soluble lead was relatively low in toxicity, requiring 2.5mg l^{-1} Pb to produce a sub-lethal response. These results do however contrast with those of Davies *et al.* (1976) for rainbow trout, where lead was found to be highly toxic.

(11) Copper

Copper was found to be more toxic than zinc to both zinc tolerant and zinc sensitive populations of *H. rivulare*. The possibility of the slight increased resistance of the zinc tolerant population when compared with the zinc sensitive was suggested by the data (Table 7.3). These results confirm the observations made by Whitton (1970) on other filamentous green algae where copper was demonstrated to be more toxic than zinc.

9.8 Concluding remarks

During the present study it has been shown that zinc contamination of waters draining from old mine workings in the Northern Pennine Orefield is still a serious problem. This is despite the fact that the majority of mines in the area ceased their major activity more than 40 years ago. However the contaminated streams have been shown to support relatively diverse communities of algae. The most abundant algae at the highest levels of zinc were found to be filamentous green algae, in particular representatives of the genera *Hormidium*, *Ulothrix* and *Mougeotia*.

Populations of *Horridium* species growing in reaches carrying high levels of zinc were shown to be adapted forms and the results of further experiments with *H. rivulare* suggested that this adaptation might be genetic. A precise threshold level of zinc at which adaptation might take place was not found during the present experiments. There was some indication that a critical value might be in the range $0.1 - 0.8 \text{mg l}^{-1} \text{Zn}$ being possibly nearer the lower figure. However it was difficult to judge whether adaptation to lower levels of zinc might also occur. There was no reason to suggest this latter possibility from the results of bioassays, but the assay technique might not be sufficiently sensitive to indicate adaptation to lower levels of zinc. It is to be hoped that further work using a larger number of populations of *Horridium* spp., in particular *H. rivulare*, taken from streams carrying levels of zinc in the range $0.1 - 0.8 \text{mg l}^{-1} \text{Zn}$ would lead to a more complete understanding of the adaptation to zinc in this species.

The indication that factors such as calcium, magnesium and phosphate play a role in the tolerance of *H. rivulare* to zinc fit the hypothesis that more than one tolerance mechanism might be present. A passive binding of zinc to exchange sites in the region of the cell wall might be subject to competition from other ions such as Ca^{2+} and Mg^{2+} . Phosphate might be important if complexes are formed with zinc which exclude the zinc from the binding sites. From the morphological observations made on *H. rivulare* it was only possible to speculate on the functional role of the cell wall and accompanying mucilage in protecting the cell against the toxic effects of zinc. A suggestion was made that the mucilage may act as a binding site for zinc, particularly complexed forms such as the hydroxide. Zinc was observed to concentrate at the mycelial surface of *Neocosmospora vasinfecta* as the hydroxide complex by Paton and Budd (1972). It is clear that more detailed study of the cell wall of *H. rivulare* would clarify the possible role it may have in the tolerance to zinc of this species.

An active mechanism for zinc tolerance, as described by McLean (1975) and Paton and Budd (1975) might involve magnesium as a cofactor or possibly phosphate as a source of energy. Further experimentation is required to determine the precise role of these factors, but their influence on the toxicity of zinc to *H. rivulare* is clearly shown by the results of the present study.

SUMMARY

A study was made of zinc-enriched streams in the Northern Pennine Orefield to show the range of zinc levels and distribution of algae. The most important sources of high zinc concentrations were examined and shown to be continued discharge of mine waters from adits and drainage from exposed heaps of tailings. Both were shown to be associated with old mine workings which have not been active for at least 40 years. The highest levels of zinc (up to 30mg l^{-1}) were found in water emanating from the base of coarse tailings heaps (O104/O1). The streams carrying the highest levels of zinc were situated in the valley of the river Nent which coincides with the location of the primary zinc bearing area of the Orefield.

Details of two field surveys are given which were designed to provide information on the chemistry of mine waters in the area, and to establish the possible presence of tolerant algae. The first survey was carried out on 25 stream reaches which during one of the four samplings carried more than $1\text{mg l}^{-1}\text{Zn}$. The second survey involved five samplings of 30 reaches on one stream which showed a gradient of zinc. Factor analysis was used to evaluate relations among the inorganic chemical components in the waters, and also the possible factors playing a significant role in controlling the availability of zinc. The results of this analysis justified dividing the waters into two major groups based on differences in their source and water chemistry. These were ground and surface waters. The former were found to be influenced by water draining from fissures in the lower limestone strata. In general, ground waters demonstrated a relatively constant composition of Na, K, Mg, Ca, Zn, Si and values for hardness, particularly those discharging from adits.

The levels of Al, Fe and Pb were found to be low. The surface waters (influenced primarily by atmospheric precipitation) showed a mixed ionic composition in general, related in part to variation in their proximity to areas of mineralization. The levels of Mg, Ca, Al, Fe, Zn, Pb and SO_4 -S were found to vary much more than in ground waters and the levels of Al, Fe and Pb were higher. The results of the factor analysis suggested several factors which might be of importance in controlling the ionic composition of both groups of waters. In both cases the most important factor appeared to be associated with the weathered products of carbonate minerals including those of the limestone rock, and ankerite minerals. A second important factor was found to be associated with the weathering of the sulphide ores, in particular sphalerite.

Even the most heavily zinc contaminated streams were found to be capable of supporting communities of algae. The number of algal species was often considerably lower than was found in nearby streams free from zinc enrichment. The most resistant algae were shown to be species of *Hormidium*, *Ulothrix*, *Mougeotia* and *Microspora*. These organisms formed abundant growths at the highest levels of zinc, with species of *Hormidium* being the most obvious. *Hormidium rivulare* was the most widespread and abundant of the *Hormidium* spp. encountered. On this basis the genus *Hormidium* was chosen for more detailed studies.

A survey was carried out of 47 reaches showing a wide range of zinc levels where species in the genus *Hormidium* were found to be abundant. The three representatives of this genus studied were *H. rivulare*, *H. flaccidum* and *H. fluitans*. In addition to the field surveys, laboratory experiments were performed in which the resistance to zinc of the three species was assessed. The results of the experiments showed that populations removed from higher levels of zinc were more resistant to the toxic effects than

those removed from lower levels. The critical range of field zinc levels above and below which the responses in the laboratory differed markedly was $0.1 - 0.4 \text{ mg l}^{-1} \text{ Zn}$.

The results of long term culture experiments with *H. rivulare* suggested that the increased resistance in this species might be largely, if not entirely, due to genetic adaptation.

The application of various statistical analyses to a combination of the field and laboratory data has suggested that two main groups of chemical factors may be influencing the toxicity of zinc in the field. The first group which appears to increase the toxicity of zinc includes Cd and Pb, while the second group, which includes Mg, Ca and various hardness factors, appears to reduce the toxicity. As the occurrence of Zn, Cd and Pb in the field are all strongly intercorrelated, it is not possible to distinguish clearly the effects of one from the other, although the data do suggest that Cd is more likely than Pb to influence zinc toxicity. The 'amelioration' factors are also strongly intercorrelated in the field, so it is difficult to comment on their relative importance. There was some indication for *H. rivulare* that an increase in $\text{PO}_4\text{-P}$ and a decrease in pH may also reduce zinc toxicity.

The indications from the analysis of these data were confirmed by the results of laboratory experiments on *H. rivulare*. The toxicity of zinc to *Horndium rivulare* was shown to decrease by rises in the levels in the culture medium of magnesium, calcium and phosphate, and increase by rises in pH and cadmium. The effects of all these are sufficiently marked so that they may be expected to have considerable importance in the field. In contrast, assays with sodium, chloride and sulphate showed no detectable influence of these ions on zinc toxicity.

Calcium always appeared to be more effective than magnesium at reducing zinc toxicity, particularly at the higher concentrations of these elements. This was found for both zinc-tolerant and zinc-sensitive populations. However at lower concentrations magnesium was sometimes more effective, particularly with the zinc-tolerant populations. Both magnesium and phosphate were more effective in reducing zinc toxicity with zinc-tolerant populations than with zinc-sensitive ones. Cadmium and copper were found to be highly toxic. A combination of zinc and cadmium proved also to be highly toxic, with indications that the effect was synergistic. There was a suggestion that the presence of cadmium at levels of 0.01 mg l^{-1} and above, at a reach, might lead to a significant increase in the toxicity of any zinc also present. Calcium was effective in reducing the toxicity of cadmium to *H. rivulare* and there were indications that the reduction was proportionately greater than with zinc.

The study calls attention to the persistent nature of zinc contamination of streams in the metalliferous mining area of the Northern Pennines. It gives an indication of the main sources of this contamination and its consequent effect on the algal flora.

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APPENDIX I

Background information for the more important reaches in the field surveys.
Other reach data held at the Department of Botany, University of Durham.

OO12

25

ROOKHOPE BURN 10m above entry of Tailrace level
Rookhope, Co. Durham
Wear Basin. tributary to R. Wear joining R. Wear at Eastgate
Grid ref. NY917428
Map ref.: 54°47'N 2°8'W
Nearest village: Rookhope
Altitude: 366m Direction of flow: East
Length: 10m; width: max. 3.2m; min. 1.8m; av. 2.2m; drop 0.2m
Depth: 24cm
LH bank: 10° gravel, stones, leading to gently rising ground of
Agrostis turf
RH bank: 30° up to grassland bank
Immediate environmental land use: grazing pasture for sheep
Upstream area description: drains old mine workings in Rookhope Valley,
including tailings from Groverake mine which
is still operating. Also receives drainage
from upper Fells

Substratum:	20	20%	50	5%
	30	30%	60	5%
	40	40%		

Notes: Rock type mainly sandstone with some shale pebbles
Light: 1 100%

OO12

26

ROOKHOPE BURN 100m below Entry of Tailrace level
Rookhope, Co. Durham
Wear Basin: tributary to R. Wear joining R. Wear at Eastgate
Grid ref.: NY917428
Map ref.: 54°47'N 2°8'W
Nearest village: Rookhope
Altitude: 366m Direction of flow: East
Length: 10m; width: max. 5.5m; min. 2.8m; av. 3.6m; drop 0.2m
Depth. 12cm
LH bank: 10° gravel stones leading to gently rising ground of
Agrostis turf
RH bank: 90° earth with above *Agrostis* turf
Immediate environmental land use: sheep grazing
Upstream area description: drains old mine workings in Rookhope Valley
including tailings from Groverake mine which
is still operating. Also receives drainage
waters from upper Fells

Substratum:	20	20%
	30	30%
	40	40%
	50	5%
	60	5%

Notes: Rock type mainly sandstone, some shale pebbles
Light: 1 100%

0012

29

ROOKHOPE BURN

Above Rookhope Village

Rookhope, Co. Durham

Wear basin: tributary to R. Wear joining it at Eastgate

Grid ref.. NY922429

Map ref.: 54°47'N 2°8'W

Nearest village: Rookhope

Altitude: 354m

Direction of flow: East

Length: 10m; width: max. 4m; min. 1.8m; Av.: 3.4m; Depth: 30m

Drop: 0.2m

LH bank: 60° soil up to *Agrostis* turf plus other upland grassland speciesRH bank: 90° soil or earth up to *Agrostis* turf plus other upland grassland species

Immediate environmental land use: sheep grazing land

Upstream area description: drains old mine workings, receives drainage waters from upper Fells

Substratum:	20	30%
	30	30%
	40	30%
	50	5%
	60	5%

Notes: Rock type sandstone plus some shale material

Light: 1 100%

0013

02

KILHOPE BURN

Kilhope, Co. Durham

Wear basin: joins Burnhope Burn to form R. Wear at Wearhead 10 metres below road crossing it

Grid ref.. NY809432

Map ref.. 54°46'N 2°17'W

Nearest village: in Co. Durham Cowshill but nearer Nenthead in Co. Cumbria

Altitude: 520m

Direction of flow: East

Length: 10m width: max. 4.5m; min. 2.0; av.: 3.0; depth: 10cm; drop: 1.3m

LH bank: 0.2 - 0.5m, 45° moorland grassland

RH bank: 0.2 - 1.0m, 80° moorland grassland

Immediate environmental land use: moorland, upland sheep grazing

Upstream area description: mainly drainage waters from Fells - acid, organic-rich waters.

Substratum:	10	50%
	20	20%
	30	20%
	40	10%

Notes. Rock type sandstone boulders and bedrock; small amount of shale

Light: 1

0048

20

RIVER NENT

Nenthead, Cumbria

Below Nenthead, 10m above main road
bridge which crosses

Tyne Basin . joins S. Tyne at Alston

Grid ref.. 767448

Map ref.: 54°47'N 2°20'W

Nearest village: Nenthead

Altitude: 384m

Direction of flow: W

Length: 10m; width: max. 5m, min. 3.5m; av.: 4m; depth: 20-30cm;

Drop: 0.3m

LH bank: 60° herbs, *Luzula sylvatica*; some trees sycamore further back

RH bank: 30° grasses; herbs, some trees further back

Immediate environmental land use: agricultural land above bank area to river

Upstream area description: fed by streams draining old mine workings;
further up mining complex of Nenthead village

Substratum:	20	40%
	30	30%
	40	20%
	50	5%
	60	5%

Notes: rock type limestone boulders amongst sandstone; small amounts
of shale

Light 1

0048

99

RIVER NENT

Alston, Cumbria

20m above entry into River South Tyne

Tyne basin: joining S. Tyne at Alston

Grid ref.: NY716467

Map ref.: 54°48'N 2°26'W

Nearest town: Alston

Altitude. 259m

Direction of flow: N

Length: 10m; width: max. 4.4m; min. 3.6m; av.: 4m; depth: 20-30cm;

Drop: 0.2m

LH bank. 90° Herbs, Grasses, further back some trees

RH bank: 90° Herbs, Grasses, further back clump of Willows bordering
railway embankment

Immediate environmental land use: Caravan site nearby

Upstream area description: has passed through part of Alston expected
to have received some effluent further up
Nent Valley intermittently passing old mine
workings

Substratum:	20	30%
	30	30%
	40	20%
	50	10%
	60	10%

Notes: Mixture of sandstone and limestone; small amount of shale

Light 1

0055

30

RIVER SOUTH TYNE a 10m stretch 30m above entry of R. Nent
 Alston, Cumbria
 Tyne Basin: joins N. Tyne to form Tyne
 Grid ref.: NY716467
 Map ref.: 54°48'N 2°26'W
 Nearest town: Alston
 Altitude: 262m Direction of flow: N
 Length: 10m; width: max. 8m; min. 4m; av.: 6m; depth: 30-60cm; drop: 0.3m
 LH bank: 60° Herbs, *Luzula* sp., *Salix* sp. further away meadow pasture
 RH bank: 60° Herbs, *Salix* sp.
 Immediate environmental land use: one side caravan park, the other grazing
 pasture for sheep and cattle
 Upstream area description: large catchment area including some streams
 draining mining areas and some the upper fells.
 The majority drain moorland and upper grassland
 and meadows

Substratum:	20	40%
	30	40%
	40	10%
	50	5%
	60	5%

Notes: Rock type sandstone with occasional limestone boulders; little
 shale

Light 1

0055

31

RIVER SOUTH TYNE
 Alston, Cumbria
 Tyne Basin: joins N. Tyne to form R. Tyne
 Grid ref.: NY716469
 Map ref.: 54°48'N 2°26'W
 Nearest town: Alston
 Altitude: 259m Direction of flow: N
 Length: 10m; width: max. 10m; min. 6m; av.: 8m; depth: 40-60cm; drop:
 0.3m
 LH bank: 30° grasses and herbs
 RH bank: 80° bank of grasses, herbs, some *Salix* sp. forms railway
 embankment
 Immediate environmental land use: on one side railway line, on other
 pasture mainly for sheep and some cattle
 Upstream area description: mainly fed by streams draining fells. Some mine
 workings present in certain areas

Substratum:	10	10%
	20	30%
	30	30%
	40	20%
	50	5%
	60	5%

Notes: Rock type mainly sandstone, very occasional limestone boulders;
 little shale

Light 1

0061

05

RIVER DERWENT

Blanchland, Northumberland

Tyne Basin: tributary to R. Tyne

Grid Ref.: NY956498

Map ref.: 54°50'N 2°4'W

Nearest village: Blanchland

Altitude: 247m

Direction of flow: E

Length: 10m; width: max. 8m; min. 4m; av.: 6m; depth: 30cm; drop: 0.2m

LH Bank: 90° earth with Bryophytes, some *Luzula sylvatica*; herbs; Beech and Birch treesRH Bank: 30° herbs; *Luzula sylvatica*; trees Birch and mainly Beech

Immediate environmental land use: mainly wood on one side, some pasture and meadow further across on the other

Upstream area description: mainly drainage from upper fells

Substratum:	20	30%
	30	40%
	40	15%
	50	10%
	60	5%

Notes: Rock type sandstone; little shale

Light 2/5

0061

06

RIVER DERWENT

10m below Bridge at Baybridge

Blanchland, Northumberland

Tyne Basin: tributary to R. Tyne

Grid ref.: NY958499

Map ref.: 54°50'N 2°4'W

Nearest village: Blanchland

Altitude: 247m

Direction of flow: E

Length: 10m; width: max. 20m; min. 8m; av.: 15m; depth: 30cm; drop: 0.3m

LH Bank: 10°, herbs, *Luzula sylvatica*, *salix* sp. further back Willow ScrubRH Bank: 10° herbs, *Luzula sylvatica*, *salix* sp. further back Pine and Beech wood

Immediate environmental land use: wooded and forestry

Upstream area description: receives entry of Bolts Burn bringing mine effluent from working fluorspar mine and drainage from old lead mine workings.

Further up mainly drainage from upper fells

Substratum:	20	30%
	30	30%
	40	20%
	50	10%
	60	10%

Notes: Rock type sandstone

Light 2

0071

99

BOLTS BURN 10m above the confluence with R. Derwent
 Tyne Basin: tributary of R. Derwent which joins R. Tyne
 Grid ref.: NY958499
 Map ref.: 54°50'N 2°4'W
 Nearest village: Blanchland, Northumberland
 Altitude: 247m Direction of flow: N
 Length: 10m; width: max. 4m; min. 2.5m; av.: 3m; depth: 12cm; drop: 0.2m
 LH Bank: 0° stones; some earth and leaf mould; small amount herbage
 (*Luzula*) wooded - Beech
 RH Bank: 90° earth with on top Herbs (mainly *Luzula sylvatica*) wooded - Beech
 Immediate environmental land use: mainly wood and forest in nearby vicinity
 Upstream area description: source from upper fells drains through old lead
 mine workings now re-opened for fluorspar by
 British Steel. Many drainage waters from
 tailings heaps and settling ponds enter below
 mine; also receives direct effluent from adit.

Substratum:	20	20%
	30	30%
	40	30%
	50	10%
	60	20%

Notes: Rock type cobbles mainly of sandstone; odd small pieces of
 limestone; grit and silt composed of powdered quartz, fluorspar,
 sandstone plus a little limestone
 Light: 2/5

0077

01

SIPTON SIKE small seepage on exposed tailings heap
 adjacent to Sipton Burn
 Tyne Basin: joins Sipton Burn which is tributary of R. E. Allen which
 eventually joins R. S. Tyne
 Grid ref.: NY851499
 Map ref.: 54°50'N 2°14'W
 Nearest village or town: Allendale Town, Northumberland
 Altitude: 450m Direction of flow: W
 Length: 3m; width: max. 12cm; min. 2cm; av.: 4cm; depth <1cm; drop: 1m
 LH Bank: 0° chippings and grit of spoil heap
 RH Bank: 0° chippings and grit of spoil heap
 Immediate environmental land use: sheep grazing
 Upstream area description: it originates from percolation from tailings heap

Substratum:	40	40%
	50	30%
	60	30%

Notes: Rock type shale with quartz and fluorspar grit
 Light: 1

0081

06

RIVER EAST ALLEN Upper reach in wooded area above Allenheads
 Allenheads, Allendale, Northumberland
 Tyne Basin: joins R. S.Tyne
 Grid ref.: NY858448
 Map ref.: 54°47'N 2°13'W
 Nearest village: Allenheads
 Altitude: 430m Direction of Flow: N
 Length: 10m; width: max. 4m; min. 2.5m; av: 3m; depth: 15cm; drop: 0.3m
 LH Bank: 90° earth with on top thick cover of *Luzula sylvatica* and bracken;
 wooded
 RH Bank: 90° earth with on top Nettles, Herbs, some *Luzula*; wooded
 Immediate environmental land use: wooded
 Upstream area description: drains down from upper fells and receives
 tributaries from meadow pastures

Substratum:	20	10%
	30	40%
	40	20%
	50	20%
	60	10%

Notes: Rock type sandstone and a little shale gravel
 Light: 2/5

0081

16

RIVER EAST ALLEN LOWER 10m below wooden footbridge
 Allenheads, Allendale, Northumberland
 Tyne Basin: joins R. S.Tyne after merging with R. W.Allen to form R. Allen
 Grid ref.: NY856458
 Map ref.: 54°48'N 2°13'W
 Nearest village: Allenheads
 Altitude: 396m Direction of flow: N
 Length: 10m; width: max. 6m; min. 4m; av.: 5m; depth: 20cm; drop: 0.3m
 LH Bank: 90° Herbs, *Luzula*, *Salix* sp.
 RH Bank: 90° Herbs and grasses
 Immediate environmental land use: adjacent to road through Allenheads;
 village houses nearby
 Upstream area description: British Steel mine complex in village; one or
 two vegetatively recolonized spoil heaps dotted
 around

Substratum:	20	10%
	30	20%
	40	30%
	50	30%
	60	10%

Notes: Rock type mainly sandstone boulders; one or two limestone rocks
 present; gravel mainly sandstone
 Light: 1

0082

10

EASTEND BURN 10m above where road crosses it,
 Allenheads, Allendale, Northumberland above village
 Tyne Basin: tributary of R. E.Allen which eventually joins R. S.Tyne
 Grid ref.: NY867454
 Map ref.: 54°48'N 2°13'W
 Nearest village: Allenheads
 Altitude: 481m Direction of flow: W
 Length: 10m; width: max. 60cm; min. 20cm; av.: 30cm; depth: 4cm; drop
 0.5m
 LH Bank: 0° Herbs and Grass immediately border - further back high
 bank of exposed shale and slabs of sandstone
 RH Bank: 0° Herbs and Grasses - further back high bank of grassland and
 meadow species
 Immediate environmental land use: meadow pasture for sheep and cattle
 Upstream area description: drains upper fells and moorland
 Substratum: 20 10%
 30 20%
 40 40%
 50 20%
 60 10%
 Notes: Rock type mainly sandstone with some shale
 Light: 1

0085

05

RIVER WEST ALLEN 10m stretch 20m above where road crosses it in
 Allendale, Northumberland bend
 Tyne Basin: joins R. E.Allen to form R. Allen which later joins
 R. S.Tyne
 Grid ref.: NY802449
 Map ref.: 54°47'N 2°18'W
 Nearest village: Carr Shield
 Altitude: 549m Direction of flow: N
 Length: 10m; width: max. 1m; min. 20cm; av.: 60cm; depth: 12cm; drop: 1.2cm
 LH Bank: 90° exposed shale bank and some sandstone debris and peat
Nardus grassland cover on top
 RH Bank: 80° exposed earth, shale and sandstone boulders and peat
 moorland plants and *Nardus* grassland
 Immediate environmental land use: upland sheep grazing pasture
 Upstream area description: areas drain from top of fells and moorland
 Substratum: 10 10%
 20 20%
 30 30%
 40 20%
 50 15%
 60 5%
 Notes: Rock type sandstone boulders and shale with some exposed shale
 bedrock
 Light: 1

0085

10

RIVER WEST ALLEN 10m stretch 50m below broken down walls of mine complex
Allendale, Northumberland

Tyne Basin: joins R. E.Allen to form R. Allen which later joins R.S.Tyne

Grid ref.: NY802453

Map ref.: 54°48'N 2°18'W

Nearest village: Carr Shield

Altitude: 510m

Direction of Flow: N

Length: 10m; width: max. 2m; min. 1.2m; av.: 1.5m; depth: 12cm; drop: 0.8m

LH Bank: 60° Grasses (*Agrostis/Festuca*) set back a little is very high
tailings heap of mainly fractured shale

RH Bank: 60° Grassland (*Agrostis/Festuca*) set back is somewhat less steep
series of spoil heaps of mainly shale, most now grassed over
with *Agrostis/Festuca* community

Immediate environmental land use: immediate surroundings of old mine
workings, area now mainly sheep grazing

Upstream area description: old mine buildings, river flows right through
these, waters from adits enter, also drainage
from spoil heaps

Substratum:	20	10%
	30	30%
	40	25%
	50	30%
	60	50%

Notes: Rock type sandstone boulders; much shale

Light: 1

0086

10

WHETSTONEMEA BURN

Allendale, Northumberland

Tyne Basin: tributary to R. W.Allen which eventually enters R. S.Tyne

Grid ref.: NY807455

Map ref.: 54°48'N 2°17'W

Nearest village: Carr Shield

Altitude: 500m

Direction of Flow: NW

Length: 10m; width: max. 3m; min. 0.4cm; av.: 1.8m; depth: 10cm; drop: 0.8m

LH Bank: 0.3 - 0.5m, 80°, *Nardus* grassland

RH Bank: 0.3 - 0.5m, 80°, *Nardus* grassland

Immediate environmental land use: upland sheep grazing

Upstream area description: mainly drainage from upper fells; occasional
seepage from very old spoil heap

Substratum:	20	20%
	30	30%
	40	30%
	50	15%
	60	5%

Notes: Rock type sandstone plus a little shale

Light: 1

0089

05

TINDALFELL SIKE

Allendale, Northumberland

Tyne Basin: joins R. W. Allen which eventually enters R. S. Tyne

Grid ref.: NY808457

Map ref.: 54°48'N 2°17'W

Nearest village: Carr Shield

Altitude: 510m

Direction of Flow: NW

Length: 10m; width: max. 2m; min. 0.8m; Av.: 1.3m; depth: 12cm; Drop: 1m

LH Bank: 0.2 - 0.4m, 60°, *Nardus* grasslandRH Bank: 0.2 - 0.4m, 60°, *Nardus* grassland

Immediate environmental land use: sheep grazing

Upstream area description: drainage waters from disused Tindalfell Pits
and associated spoil heaps

Substratum:	20	20%
	30	30%
	40	20%
	50	5%
	60	5%

Notes: Rock type sandstone plus some shale

Light: 1

0091

30

FORESHIELD BURN

10m above entry into R. Nent

Alston Moor, Cumbria

Tyne Basin: tributary to R. Nent which later joins R. S. Tyne

Grid ref.: NY749467

Map ref.: 54°48'W 2°23'W

Nearest town: Alston

Altitude: 343m

Direction of Flow: S to SW

Length: 10m; width: max. 1.5m, min. 1.0m; av.: 1.2m; depth: 30cm; drop: 0.2m

LH Bank: 0.4m, 90°, Herbs and Grasses a little set back is stone wall

RH Bank: 0.4m, 80°, Herbs and Grasses

Immediate environmental land use: Farm

Upstream area description: drains from upper fells; draining through
farmland also and suspected of receiving some
effluent from this

Substratum:	20	10%
	30	40%
	40	30%
	50	15%
	60	5%

Notes: Rock type sandstone mainly, with some limestone and some shale

Light: 1

0092

20

GUDHAM GILL

Nenthead, Cumbria

Tyne Basin: joins R. Nent which is tributary to R. S.Tyne

Grid ref.: NY778448

Map ref.: 54°47'N 2°20'W

Nearest village: Nenthead

Altitude: 442m

Direction of Flow: SW

Length: 10m; width: max. 3m; min. 1.2m; av.: 1.6m; depth: 10cm; drop: 1.5m

LH Bank: 0.2m, 45°, grasses, herbs

RH Bank: 0.4m, 30°, grasses, herbs

Immediate environmental land use: sheep grazing

Upstream area description: drainage from derelict mine spoil heaps and associated adits

Substratum:	10	50%
	20	10%
	30	20%
	40	10%
	50	5%
	60	5%

Notes: Rock type sandstone plus small amount of shale

Light: 1

0093

01

GILLGILL BURN

10m after source

Nenthead, Cumbria

Tyne Basin: enters R. Nent which joins R. S.Tyne

Grid ref.: NY795440

Map ref.: 54°47'N 2°19'W

Nearest village: Nenthead

Altitude: 609m

Direction of Flow: W

Length: 10m; width: max. 0.4m; min. 0.1m; av.: 0.2m; depth: 4cm; drop: 0.5m

LH Bank: 0.2m, 90°, grasses mainly *Agrostis* spp.RH Bank: 0.2m, 80°, grasses mainly *Agrostis* spp.

Immediate environmental land use: originates as spring from old waste tailings tip, receives drainage and percolations from surrounding tips

Substratum:	30	10%
	40	30%
	50	40%
	60	20%

Notes: Rock type mainly mineralized sandstone plus some shale; grit and sand of sandstone, plus fractured shale, quartz, some fluorspar, shale dust

Light: 1

0093

04

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: joins R. Nent which feeds R. S.Tyne

Grid ref.: NY795440

Map ref.: 54°47'N 2°19'W

Nearest village: Nenthead

Altitude : 594m

Direction of Flow: W

Length: 10m; width: max. 0.16m; min. 0.1m; av.: 0.2 depth: 2cm; drop 0.6m

LH Bank: Om, O^o, pebbles and rock chippings further back grassland
mainly *Agrostis* spp.)

RH Bank: " " " " "

Immediate environmental land use: grazing

Upstream area description: originates from spoil heaps and receives
drainage from surrounding tips

Substratum:	30	10%
	40	30%
	50	40%
	60	20%

Notes: Rock type mineralized sandstone; fluorspar, quartz, some shale

Light: 1

0093

08

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: joins R. Nent which feeds R. S.Tyne

Grid ref.: NY794440

Map ref.: 54°47'N 2°19'W

Nearest village: Nenthead

Altitude: 579m

Length: 10m; width: max. 0.6m; min. 0.1m; Av.: 0.4m; depth: 2cm; drop: 0.5m

LH Bank: Om, O^o, *Agrostis* grassland plus bog vegetationRH Bank: Om, O^o, *Agrostis* grassland plus bog vegetation

Immediate environmental land use: grazing

Upstream area description: derived from spoil heaps and drainage from
surrounding tips; in immediate vicinity
receives some bog percolations

Substratum:	40	50%
	50	40%
	60	10%

Notes: Rock type mineralized sandstone and some shale

Light: 1

0093

11

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: joins R. Nent which feeds R. S.Tyne

Grid ref.: NY793440

Map ref.: 54°47'N 2°19'W

Nearest village: Nenthead

Altitude: 571m

Direction of Flow: W

Length: 10m; width: max. 0.4m; min. 0.1m; av.: 0.2m; depth: 4cm; drop: 0.3m

LH Bank: 0m, 0°, grasses plus *Juncus* sp.RH Bank: 0m, 0°, grasses (*Agrostis* sp.) plus *Juncus* sp.

Immediate environmental land use: grazing for sheep

Upstream area description: drainage waters from ole mine spoil heaps
plus moorland and bog

Substratum:	20	10%
	30	10%
	40	20%
	50	20%
	60	40%

Notes: Rock type sandstone; shale; plus thick deposit of Ferric Hydroxide
ppt. as silt

Light: 1

0093

15

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: joins R. Nent which feeds R. S.Tyne

Grid ref.: NY793440

Map ref.: 54°47'N 2°19'W

Nearest village: Nenthead

Altitude: 560m

Direction of Flow: W

Length: 10m; width: max. 0.4m; min. 0.2m; av.: 0.3m; depth: 8cm; drop: 0.5m

LH Bank: 20cm, 90°, clay/shale, topped by *Juncus/Nardus* vegetation

RH Bank: 0.2m; 90°, " " " "

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from mine spoil heaps and moorland

Substratum:	40	20%
	50	20%
	60	30%
	70	30%

Notes: Rock type shale, iron ppt. clay

Light: 1

0093

25

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent, a tributary to R. S.Tyne

Grid ref.: NY792439

Map ref.: 54°47'N 2°19'W

Altitude: 552m

Length: 10m; width: max. 0.6; min. 0.2; Av. 0.3; depth: 4cm; drop: 2m
 waterfall at end of reach; last 3m water trickles down fairly
 steep surface of exposed sandstone boulders

LH Bank: 0m, 0°, herbs, grasses, bog vegetation for part of reach;

Agrostis/Heather/Vacc. myrt/*Nardus* community bordering rest of reach

RH Bank:

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from old mine tips and moorland
and wet meadow

Notes: Rock type sandstone plus some shale

Substratum:	20	50%
	30	20%
	40	20%
	50	5%
	60	5%

Light: 1

0093

29

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent, a tributary to R. S.Tyne

Grid ref.: NY791439

Map ref.: 54°47'N 2°19'W

Altitude: 543m

Direction of Flow: SW

Length: 10m; width: max. 0.8m; min. 0.3; av.: 0.5; depth: 4cm; drop: 1.6m

LH Bank: immediately non-existent, with grass/herbage next to water;
 mainly *Deschampsia cespitosa*, however within 0.5m steep grassland
 bank overlooks stream 60-80° - *Nardus/Agrostis* moorland species
 cover the bank

RH Bank:

Immediate environmental land use: sheep grazing

Upstream area description: drainage from waste tailings heaps and upper
 moorland area also received first major
 tributary, 'Old Mine Gill', which drains from
 adjacent spoil heaps to upper Gillgill Burn area

Substratum:	10	10%
	20	30%
	30	20%
	40	20%
	50	10%
	60	10%

Notes: Rock type large sandstone blocks, intermittent exposed shale bedrock
 - gravel = shale/sandstone

Light: 1

0093

32

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent, a tributary to R. S.Tyne

Grid ref.: NY791439

Map ref.: 54°47'N 2°19'W

Altitude: 536m

Direction of Flow: SW

Length: 10m; width: max. 1.5m; min. 0.8m; av.: 1.0m; depth: 8cm; drop: 1.6m

LH Bank: 1m, 90°, exposed shale topped by *Nardus* grasslandRH Bank: 1m, 90°, exposed shale with slightly further back very high
exposed shale spoil heap

Immediate environmental land use: sheep grazing

Upstream area description: receives principal drainage waters from old
mine workings

Substratum:	10	20%
	20	30%
	30	20%
	40	15%
	50	10%
	60	5%

Notes: Rock type shale with some blocks of sandstone

Light: 1

0093

36

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent, a tributary to R. S.Tyne

Grid ref.: NY790439

Map ref.: 54°47'N 2°19'W

Altitude: 527m

Direction of Flow: W

Length: 10m; width: max. 1.2m; min. 0.8m; av.: 1m; depth: 8cm; drop: 0.8m

LH Bank: 0.20m, 45°, *Deschampsia cespitosa* grassland plus *Nardus*; further back
grassy high bankRH Bank: 0.1m, 30°, *Deschampsia cespitosa* grassland plus *Nardus*; further
back exposed shale waste heap

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from mine workings; receives input
from tributary rising in adjacent mine workings
and tips

Substratum:	20	20%
	30	30%
	40	30%
	50	15%
	60	5%

Notes: Rock type sandstone plus shale

Light: 1

0093

40

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent, a tributary to the R. S. Tyne

Grid ref.: NY790439

Map ref.: 54°47'N 2°19'W

Altitude: 521m

Direction of Flow: W

Length: 10m; width: max. 1.2m; min. 0.7m; av.: 0.8m; depth: 8cm; drop: 2.4m

Waterfall in reach over exposed limestone strata

LH Bank: 0.3m, 80°, shale covered by grasses and herbs (*Agrostis/Nardus/*
*Deschampsia/*Occ. *Juncus*)

RH Bank: " " " " " "

Immediate environmental land use: grazing for sheep

Upstream area description: immediately above entry of low Zn level
tributary originating as spring from upper
pasture land. Further up Gillgill Burn drainage
from mine workings

Substratum:	10	30%
	20	20%
	30	20%
	40	20%
	50	10%

Notes: Rock type some exposed limestone bedrock; sandstone boulders;
sandstone and shale gravel

Light: 1

0093

43

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent, a tributary to R. S. Tyne

Grid ref.: NY789439

Map ref.: 54°47'N 2°19'W

Altitude: 512m

Direction of Flow: W

Length: 10m; width: max. 1.6m; min. 0.8m; av.: 1.2m; depth: 4cm; drop: 1.2m

LH Bank: 0.2m, 90°, grasses and herbs (*Agrostis/Deschampsia/Nardus*)

RH Bank: " " " " " "

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from old tips and upland moorland
and pastures : small waterfall over sandstone
bedrock

Substratum:	10	60%	bedrock
	20	20%	
	30	5%	
	40	10%	
	50	5%	

Notes: Rock type mainly sandstone plus a little shale

Light: 1

0093

47

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent, a tributary to R. S.Tyne

Grid ref.: NY788439

Map ref.: 54°47'N 2°19'W

Altitude: 506m

Direction of Flow: W

Length: 10m; width: max. 1.8m; min. 0.8m; av.: 1.2m; depth: 6cm; drop: 2.5m
high waterfall over exposed sandstone bedrockLH Bank: 80°, 0.3m, grasses and herbs (*Agrostis/Deschampsia/Nardus*)

RH Bank: " " " " "

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from old tips and upper pasture

Substratum:	10	60%
	20	20%
	30	5%
	40	10%
	50	5%

Notes: Rock type sandstone plus some shale

Light: 1

0093

50

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which joins R. S.Tyne

Grid ref.: NY788438

Map ref.: 54°47' 2°19'W

Altitude: 503m

Direction of Flow: W

Length: 10m; width: max. 1.8m; min. 0.8m; av.: 1.2m; depth: 6cm; drop: 1.8m

LH Bank: 0.2m, 60°, grasses and herbs (*Agrostis/Nardus/Deschampsia*)

RH Bank: " " " " "

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from upper mine areas and pastures

Substratum:	20	40%
	30	30%
	40	15%
	50	10%
	60	5%

Notes: Rock type sandstone plus a little shale

Light: 1

0093

61

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which joins R. S.Tyne

Grid ref.: NY785438

Map ref.: 54°47' 2°19'W

Altitude: 480m

Direction of Flow: W

Length: 10m; width: max. 1.5m; min. 0.17; av.: 1.2m; depth: 6cm; drop: 1.2m

LH Bank: 0.1-0.3, 45-60°, grasses and herbs (*Agrostis/Deschampsia/Nardus*)

RH Bank: " " " " "

Immediate environmental land use: sheep grazing

Upstream area description: drainage from upper mine areas and pastures

Substratum:	20	30%
	30	30%
	40	20%
	50	10%
	60	10%

Notes: Rock Type sandstone plus some shale

Light: 1

0093

64

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which joins R. S.Tyne

Grid ref.: NY785438

Map ref.: 54°47' 2°20'W

Altitude: 472m

Direction of Flow: W

Length: 10m; width: max. 1.5m; min. 0.7; av.: 1.2m; depth: 6cm; drop: 1.2m

LH Bank: 0.1-0.3, 30°, grasses and herbs (*Agrostis/Deschampsia/Nardus*)

RH Bank: 0.3m, 90°, grass and herbs on top (" ")

Immediate environmental land use: sheep grazing

Upstream area description: drainage from upper mine areas and pastures including entry of new side tributary from further mining area heaps

Substratum:	20	20%
	30	30%
	40	30%
	50	10%
	60	10%

Notes: Rock Type sandstone plus some shale

Light: 1

0093

85

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which eventually joins R.S. Tyne

Grid Ref: NY783437

Map ref: 54°47'N 2°20'W

Nearest village: Nenthead

Altitude: 457m

Direction of flow: W

Length: 10m; width: max. 1.5m; min. 0.6m; Av: 1.2m; Depth: 4cm; Drop: 3m

High waterfall cascading down exposed Great Limestone Bedrock

LH Bank: 0.2-0.8m, 90°, Grasses, some herbs with trees mainly fir and sycamore above bank on higher grassy bank

RH Bank: 0.4-0.8m, 90°, Grasses/herbs immediately with trees fir and mainly sycamore behind, also continuation of stone wall separating stream from path through small wood which stream is now entering

Immediate environmental land use: Wooded; further back surrounded by pasture for grazing.

Upstream area description: Drainage from Upper Mine workings plus drainage waters from pasture land

Substratum:	10	50%
	20	20%
	30	20%
	40	5%
	50	5%

Notes: Rock type limestone and sandstone, little if any shale.

Light: 2/5

0093

95

GILLGILL BURN

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which enters R.S. Tyne

Grid ref: NY781436

Map ref: 54°47'N 2°20'W

Direction of flow: W

Nearest village: Nenthead

Altitude: 434m

Length: 10m; width: max. 2m; min. 0.6m; Av: 1.7m; Depth: 12cm; Drop: 0.5m

LH Bank: 0.2-0.4m, 60°, Herbs and Grasses little way back, high hilly bank of wet meadow species

RH Bank: 0.2-1.2m, 60°-90°, part of reach bordered by stone wall, lower part bordered by grasses and herbs

Immediate environmental land use: pasture for cattle and horses on left side, bordered by horses on right

Upstream area description: immediately upstream receives sewage waste and piped drainage from road, also effluent from boiler (cinders) and occasional waste tips from houses, further up influenced by mine drainage waters from upper mining area and drainage from pasture areas

Substratum:	20	20%
	30	30%
	40	30%
	50	15%
	60	5%

Notes: Rock type sandstone and limestone

Light: 1

0093

99

GILLGILL BURN

Last 10m before entry into R. Nent

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which enters R.S. Tyne

Grid ref: NY780436

Map ref: 54°47'N 2°20'W

Nearest village: Nenthead

Altitude: 427m

Direction of Flow: W

Length: 12m; width: max. 0.7m; min. 0.5m; Av: 0.6m; Depth: 5cm; Drop: 0.2m

LH Bank: 0.3m, 90°, concrete bordered

RH Bank: 0.3m, 90°, concrete bordered

This reach passes along man-made concrete channel emerging from a long tunnel before entering Nent

Immediate environmental land use: rough ground formerly part of adjacent dressing mill now grassed over and used by locals to graze ponies

Upstream area description: influence of waste from houses in village and upper mining area drainage waters and waters draining upper pasture land

Substratum: 10 100%

Notes: Rock type concrete/cement, plus some stones (sandstone/brick)

Light: 2

0096

01

RAMPGILL LEVEL

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which eventually joins R.S. Tyne

Grid ref: NY781434

Map ref: 54°47'N 2°20'W

Nearest village: Nenthead

Altitude: 434m

Direction of Flow: S

Length: 2m; width: max. 0.3m; min. 0.2; av: 0.2; depth: 6cm; drop: 1m

LH Bank: 0.1-0.2m, 30-80°, grasses/herbs

RH Bank: " " "

Reach consists of 2m of water emerging from adit, tumbling abruptly out of tunnel down waterfall to join R. Nent

Immediate environmental land use: relic mine buildings nearby (smelting, dressing floors) now converted to chicken farm. Occasional seepage from this enters the water. Farmer spreads chicken dung on rough ground surrounding the adit.

Upstream area description: drainage from old level

Substratum: 20 10%

30 20%

40 40%

50 20%

60 10%

Notes: Rock type sandstone, little limestone shale

Light: 1

0097

01

DOWGANG LEVEL

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which eventually joins R.S. Tyne

Grid ref: NY781434

Map ref: 54°47'N 2°20'W

Nearest village: Nenthead

Altitude: 434m

Direction of Flow: N

LH Bank: Om, O^o, bordered by grasses (mainly *Deschampsia cesp.*)RH Bank: Om, O^o, " " " "

Immediate environmental land use: water emerges from obvious tunnel of adit and cascades down over rock forming a waterfall before entering R. Nent on opposite side to Rampgill Level. Some larch trees nearby, above adit mainly grassland for sheep grazing

Upstream area description: drains through long level receiving waters from many other adits

Substratum:	20	10%
	30	20%
	40	10%
	50	10%
	60	60%

Notes: Rock type limestone and some sandstone

Light: 1

0098

01

'SCALEBURN LEVEL'

Nenthead, Cumbria

Tyne Basin: feeds R. Nent which eventually joins R.S. Tyne

Grid ref: NY781434

Map ref: 54°47'N 2°20'W

Nearest village: Nenthead

Altitude: 434m

Direction of Flow: S

Length: 3m; width: max. 0.2m; min. 0.1m; av: 0.1m; depth: 5cm; drop: 0.2m

LH Bank: Om, O^o, bordered by grasses and herbs (*Desch. cesp./Holcus/Cochlearia sp.*)

RH Bank: " " " " " "

Immediate environmental land use: surrounded by old mine buildings (mainly behind) converted to chicken farm receives effluent from this - above it track leading to mine complex; rough ground around used by farmer to dump effluent mainly grassed over.

Upstream area description: drainage waters through old mine levels emerge from this level or adit

Substratum:	30	10%
	40	30%
	50	20%
	60	40%

Notes: Rock type sandstone plus a little limestone, little shale

Light: 1

0102

15

GARRIGILL BURN

Garrigill, Cumbria

Tyne Basin: tributary to R.S. Tyne

Grid ref: NY752425

Map ref: 54°46'N 2°23'W

Nearest village: Garrigill

Altitude: 434m

Direction of Flow: W

Length: 10m; width: max. 2.4m; min. 0.8m; av: 1.4m; depth: 6cm; drop: 1.2m

small waterfall over exposed sandstone bedrock

LH Bank: 0.2m, 80°, grasses

RH Bank: " " "

Immediate environmental land use: Nearby grazing pasture for sheep and cattle

Upstream area description: drainage from upper mine workings

Substratum:	10	40%
	20	20%
	30	20%
	40	15%
	50	5%

Notes: rock type sandstone plus a little shale

Light: 1

0103

08

BROWN GILL

Garrigill, Cumbria

Tyne Basin: tributary to R.S. Tyne

Grid ref: NY764423

Map ref: 54°46'N 2°22'W

Nearest village: Garrigill

Altitude: 548m

Direction of Flow: W

Length: 10m; width: max. 0.5m; min. 0.2m; depth: 4cm; drop: 2m

Steep waterfall down stone/brick ramparts beneath road bridge

LH Bank: 0m, 0°, grasses (*Agrostis/Festuca/Nardus*)

RH Bank: " " "

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from old waste tailings heaps

Substratum:	10	30%
	20	20%
	30	10%
	40	20%
	50	15%
	60	5%

Notes: Rock type sandstone plus some shale

Light: 1

0104

01

'OLD MINE GILL'

Nenthead, Cumbria

Tyne Basin: feeds Gillgill Burn which joins R. Nent, a tributary to
R.S. Tyne

Grid ref: NY795440

Map ref: 54° 47'N 2° 19'W

Nearest village: Nenthead

Altitude: 594m

Direction of Flow : W

Length: 10m; width: max. 0.2m; min. 0.05m; av: 0.1m; depth: 2cm; drop: 1.2m

LH Bank: 0°, 0m, grasses and rock chippings, gravel (*Agrostis* spp.)

RH Bank: " " " " "

Immediate environmental land use: open moorland, grazing for sheep

Upstream area description: originates as percolation or drainage from
tailings heap

Substratum:	30	10%
	40	30%
	50	40%
	60	20%

Notes: Rock type mineralized sandstone, plus a little mineralized limestone,
a little shale; fluorspar, quartz and sandstone grit

Light: 1

0104

99

'OLD MINE GILL'

Nenthead, Cumbria

Tyne Basin: feeds Gillgill Burn which enters R. Nent, a tributary to
R.S. Tyne

Grid ref: NY782439

Map ref: 54° 47'N 2° 19'W

Nearest village: Nenthead

Altitude: 549m

Length: 10m; width: max. 1.2m; min. 0.1m; av: 0.2m; depth: 1cm; drop: 3m.

Drops down steadily in 10m over series of small waterfalls over exposed
sandstone bedrock to join Gillgill BurnLH Bank: 0.1m; 60°, grasses (*Agrostis* community)

RH Bank: 0m, 0°, " " "

Immediate environmental land use: moorland, grazing for sheep

Upstream area description: direct drainage from old mine workings

Substratum: 10 100%

Notes: Rock type sandstone

Light: 1

0105

99

'OLD MINE GILL'

Nenthead, Cumbria

Tyne Basin: feeds Gillgill Burn which enters R. Nent, a tributary to
R.S. Tyne

Grid ref: NY791438

Map ref: 54°47'N 2°19'W

Nearest village: Nenthead

Altitude: 541m

Direction of Flow: N

Length: 10m; width: max. 1.2m; min. 0.8m; av: 1.0; depth: 4cm; drop: 2.4cm
waterfall down exposed shale bedrockLH Bank: 0.2m; 80°, grasses (*Agrostis/Festuca* community)

RH Bank: 0.1m; 80°, " " " "

Substratum:	10	60%	"	"
	20	10%		
	30	10%		
	40	10%		
	50	5%		
	60	5%		

Immediate environmental land use: moorland, grazing for sheep

Upstream area description: drainage from old mine tips

Notes: Rock type shale plus a little sandstone

Light: 1

0106

99

'FOOTPATH GILL'

Nenthead, Cumbria

Tyne Basin: feeds Gillgill Burn, a tributary of the R. Nent which
eventually joins the R.S. Tyne

Grid ref: NY790439

Map ref: 54°47'N 2°19'W

Nearest village: Nenthead

Altitude: 533m

Direction of Flow: S

Length: 10m, width: max. 0.5m; min. 0.1m; av: 0.3m; depth: 4cm; drop: 0.5m

LH Bank: 0m, 0°, herbs and grasses (wet meadow species)

RH Bank: " " " "

Immediate environmental land use: sheep grazing pasture

Upstream area description: drainage from upland wet meadow pastures

0107

17

'FIRESTONE GILL'

Nenthead, Cumbria

Tyne Basin: feeds Gillgill Burn, a tributary to R. Nent which later joins
the R.S. Tyne

Grid ref: NY788436

Map ref: 54° 47'N 2° 19'W

Nearest village: Nenthead

Altitude: 511m

Direction of Flow: W

Length: 10m; width: max. 0.2m; min. 0.1; depth: 2cm; drop: 0.2m

LH Bank: Om, O°, grasses (*Agrostis* spp.)

RH Bank: " " "

Immediate environmental land use: grazing for sheep

Upstream area description: direct runoff from waste tailings heaps

Substratum:	40	20%
	60	40%
	50	40%

Notes: Rock type mineralized sandstone, a little shale

Light: 1

0107

99

'FIRESTONE GILL'

Nenthead, Cumbria

Tyne Basin: feeds Gillgill Burn which joins the R. Nent, a tributary to
the R.S. Tyne

Grid ref: NY786437

Map ref: 54° 47'N 2° 19'W

Nearest village: Nenthead

Altitude: 480m

Direction of Flow: N

Length: 10m; width: max. 0.4m; min. 0.1m; av: 0.2m; depth: 5cm; drop: 0.4m

LH Bank: Om, O°, grasses and *sphagnum* sp.

RH Bank: " " "

Immediate environmental land use: grazing for sheep

Upstream area description: drainage from spoil heaps of upper mine workings
plus seepage from acidic (bog type) flushes

Substratum:	20	10%
	30	10%
	40	10%
	50	10%
	60	60%

Notes: Rock type sandstone covered by iron deposit (ferric hydroxide)

Light: 1

0108

08

'BROWN GILL TRIBUTARY'

Garrigill, Cumbria

Tyne Basin: feeds Brown Gill which joins Gillgill Burn, a tributary
to the R.S. Tyne

Grid ref: NY764423

Map ref: 54° 46'N 2° 22'W

Nearest village: Garrigill

Altitude: 548m

Direction of Flow: W

Length: 10m; width: max. 0.3m; min. 0.1m; av: 0.2m; depth: 2cm; drop: 1.2m

LH Bank: 0m, 0°, grasses (*Agrostis/Festuca/Nardus* grassland)

RH Bank: " " " "

Immediate environmental land use: sheep grazing

Upstream area description: direct runoff from spoil heaps of old mine
workings

Substratum:	20	20%
	30	30%
	40	30%
	50	15%
	60	5%

Notes: Rock type sandstone plus a little shale

Light: 1

0113

01

TAILRACE LEVEL

Rookhope, Co. Durham

Wear Basin: feeds Rookhope Burn, a tributary to the R. Wear

Grid ref: NY917428

Map ref: 54° 47'N 2° 8'W

Nearest village: Rookhope

Altitude: 366m

Direction of Flow: N

Length: 4m; width: max. 0.4m; min. 0.2m; av: 0.3m; depth: 6cm; drop: 0.8m

LH Bank: 0.2m, 60°, grasses (*Agrostis* community)

RH Bank: 0.4m, 80°, " " " "

Immediate environmental land use: sheep grazing

Upstream area description: derived from adit waters from many old mine
workings in the area

Substratum:	20	20%
	30	50%
	40	10%
	50	10%
	60	10%

Notes: Rock type sandstone plus a little shale; sometimes much silt;
deposit of calcite on rocks

Light: 1

Check list of algae (* indicates those species for Gillgill Burn)

* 010531	<i>Aphanocapsa</i> sp. >1<2µm	Nägeli
* 010911	<i>Calothrix parietina</i>	Thuret
011203	<i>Chamaesiphon fuscus</i>	(Rostaf.) Hansg.
011205	<i>C. incrustans</i>	Grun,
* 011211	<i>C. polymorphus</i>	Geitler
* 011602	<i>Clastidium setigerum</i>	Kirchner
* 013313	<i>Homoeothrix varians</i>	Geitler
014208	<i>Lyngbya kutsingii</i>	Schmidle
014211	<i>L. martensiana</i>	Menegh
014232	<i>Lyngbya</i> sp. >1<2µm	Agardh
* 014852	<i>Microcoleus</i> sp. >2<4µm	Desmazières
* 015535	<i>Oscillatoria irrigua</i>	Kütz.
015523	<i>O. pseudogeminata</i>	G. Schmid
* 015551	<i>Oscillatoria</i> >1<2µm	Vaucher
015533	<i>Oscillatoria</i> >4<6µm	Vaucher
015703	<i>Phormidium autumnale</i>	(Ag.) Gom.
* 015708	<i>P. mucicola</i>	Hub.-Pestalozzi et Naum
015710	<i>P. subfuscum</i>	Kütz.
* 015731	<i>Phormidium</i> sp. >1<2µm	Kütz.
* 015732	<i>Phormidium</i> sp. >2<4µm	Kütz.
* 015802	<i>Plectonema boryanum</i>	Gomont
* 015902	<i>Pleurocapsa polonica</i>	Raciborski
* 016101	<i>Pseudanabaena catenata</i>	Lauterb.
* 016607	<i>Schizothrix delicatissima</i>	W. et G.S. West
* 016650	<i>Schizothrix</i> sp.	Kütz
* 017435	<i>Synechococcus</i> sp. >8<16µm	Nägeli
017611	<i>Tolypothrix distorta</i> var. <i>penicillata</i>	(Ag.) Lemm.
020650	<i>Batrachospermum</i> sp.	Roth.
021902	<i>Lemanea fluviatilis</i>	C. Ag.
021950	<i>Lemanea</i> sp.	Bory
030202	<i>Euglena gracilis</i>	Klebs
* 030203	<i>E. mutabilis</i>	Schmitz
061931	<i>Vaucheria</i> sp. <64µm	D.C.
* 08013	<i>Chromulina ovalis</i>	Klebs
* 080301	<i>Chrysonobula holmesii</i>	Lund
* 080701	<i>Hydrurus foetidus</i>	(Vill.) Kirchn.
* 081402	<i>Synura sphagnicola</i>	Korch.
081403	<i>S. uvella</i>	Ehrenb.
081601	<i>Celloniella palensis</i>	Pascher
090404	<i>Melosira varians</i>	C.A. Ag.
* 100170	<i>Achmanthes marginistriata</i>	
* 100171	<i>Achmanthes minutissima</i>	Kütz.
100269	<i>Amphora veneta</i>	Kütz.
100349	<i>Amphiprora</i> sp.	Ehrenb.
100501	<i>Ceratoneis arcus</i>	Kütz.
100549	<i>C. arcus</i> var. <i>amphioxys</i>	(Rabh.)
100602	<i>Cocconeis placentula</i>	Ehrenb.
100869	<i>Cymbella parva</i>	(W. Smith) Cleve
* 100870	<i>Cymbella ventricosa</i>	Kütz.
101001	<i>Diatoma hiemale</i>	(Lyngbye) Heiberg
101002	<i>D. vulgare</i>	Bory
* 101069	<i>D. hiemale</i> var. <i>mesodon</i>	(Ehrenb.) Grun.
* 101301	<i>Eunotia exigua</i>	(Bréb.) Grun.
* 101369	<i>E. tenella</i>	(Grun.) Hustedt
101401	<i>Fragillaria crotonensis</i>	Kitton
101449	<i>F. intermedia</i>	Grun.
101449	<i>F. capucina</i>	Desmazières

101505	<i>Gomphonema olivaceum</i>	(Lyngbye) Kütz.
101506	<i>G. ventricosum</i>	Gregory
101569	<i>G. olivaceoides</i>	
* 101570	<i>G. parvulum</i>	Kütz.
* 101701	<i>Meridion circulare</i>	Agardh
101802	<i>Navicula cryptocephala</i>	Kütz.
* 101869	<i>N. cryptocephala</i> var. <i>veneta</i>	(Kütz) Grun.
* 101870	<i>N. minima</i>	Grun.
101905	<i>Nitzschia sigmoidea</i>	(Grun.) Hust. erw.
101974	<i>N. amphibia</i>	Grun.
101975	<i>N. linearis</i>	W. Smith
* 102070	<i>Pinnularia appendiculata</i>	(Agardh) Cleve
* 102071	<i>P. borealis</i>	Ehrenb.
102072	<i>P. maior</i>	Kütz.
* 102073	<i>P. subcapitata</i>	Gregory
* 102074	<i>P. viridis</i>	(Nitzsch) Ehrenb.
* 102075	<i>P. viridis</i> var. <i>sudetica</i>	(Hilse) Hust.
102201	<i>Rhoicosphenia curvata</i>	(Kütz) Grun.
* 102369	<i>Surirella ovalis</i>	Brébisson
* 102370	<i>S. ovata</i>	Kütz.
* 102402	<i>Synedra rumpens</i>	Kütz.
102403	<i>S. ulna</i>	(Nitzsch) Ehrenb
102502	<i>Tabellaria flocculosa</i>	(Roth) Kütz.
* 109969	<i>Neidium alpinum</i>	
* 109970	<i>N. minutissimum</i>	
* 109971	<i>Caloneis bacillum</i>	
* 109972	<i>C. lagerstedtii</i>	(Grun.) Mereschkowsky
109973	<i>Anomoeoneis exilis</i>	(Kütz.) Cleve
109974	<i>Frustulia rhomboides</i>	(Ehr.) de Toni
* 109975	<i>F. rhomboides</i> var. <i>saxonica</i>	(Rabh.) de Toni
120210	<i>Closterium leibleinii</i>	Kütz.
120214	<i>C. moniliferum</i>	(Bory) Ehrenb.
120216	<i>C. peracerosum</i>	Gay
120218	<i>C. ralfsii</i>	Breb.
* 120305	<i>Cosmarium punctulatum</i>	Bréb.
* 120307	<i>C. subarctoum</i>	(Lagerh.) Racib.
* 120501	<i>Cylindrocystis brebissonii</i>	Menegh.
* 121431	<i>Mougeotia</i> sp. <8µm	Agardh
* 121432	<i>Mougeotia</i> >8<12µm	Agardh
121749	<i>Penium navicula</i>	Bréb.
* 122002	<i>Roya obtusa</i>	(Bréb.) West and G.S. West
* 122140	<i>Spirogyra</i> sp. >16<24µm	Link
* 122405	<i>Staurastrum punctulatum</i>	Bréb.
* 122732	<i>Zygnema</i> sp. >16<24µm	Agardh
* 130431	<i>Chlamydomonas</i> sp. <8µm	Ehrenb.
* 130432	<i>Chlamydomonas</i> sp. >8µm	Ehrenb.
* 130050	<i>Gloeocystis</i> sp.	Nägeli
* 140206	<i>Ankistrodesmus falcatus</i>	(Coroa) Ralfs
140432	<i>Characium</i> sp.	A. Braun.
140450	<i>Characium</i> sp.	A. Braun.
143508	<i>Scenedesmus obliquus</i>	(Turp.) Kg.
143510	<i>S. quadricauda</i>	(Turp.) Bréb.
* 152803	<i>Gongrosira incrustans</i>	Schmidle
* 152901	<i>Hormidium fluitans</i>	Heering
* 152902	<i>H. rivulare</i>	Kütz.
* 152903	<i>H. subtile</i>	Heering

* 152904	<i>Hormidium flaccidum</i>	A. Br.
* 153232	<i>Microspora</i> sp. $>8 < 12 \mu\text{m}$ = <i>M. lauterbornii</i>	Schmidle
153235	<i>Microspora</i> sp. $>20 < 24 \mu\text{m}$ = <i>M. amoena</i>	Rabenh.
* 153303	<i>Microthamnion strictissimum</i>	Rabenh.
* 154150	<i>Raphidonema</i> sp.	Lagerh.
* 154435	<i>Stichococcus bacillaris</i>	Nageli
* 154433	<i>Stichococcus</i> sp. $>2 \mu\text{m}$	Gay
* 154532	<i>Stigeoclonium</i> sp. = <i>S. tenue</i>	Kütz.
154703	<i>Ulothrix zonata</i>	Kütz.
* 154704	<i>U. moniliformis</i>	Kütz.
160302	<i>Cladophora glomerata</i>	(L.) Kütz.
160731	<i>Oedogonium</i> sp. $<8 \mu\text{m}$	Link
161050	<i>Rhizoclonium</i> sp.	Kütz. emend Brand

Check list of lichens for Gillgill Burn

(for authorities see James, P.W. (1967) *A New Check List of British Lichens. Lichenologist* 3, 95-153.

Bacidia umbrina
Lecanora intricata var. *sonalifera*
L. lacustris
Lecidea alvocaerulescens
L. macrocarpa
L. tumida
Micarea lignaria
Parmelia saxatilis
Rhizocarpon obscuratum var. *reductum*
Trapelia coarctata
Verrucaria sp.

Check list of bryophytes for Gillgill Burn

(for authorities see Warburg, E.F. (1963) *Census Catalogue of British Mosses*, 3rd edition. *Brit. Bryol. Soc.*, Ipswich.

Acrocladium stramineum
Brachythecium rivulare
Bryum pallens
B. pseudotriquetrum
B. sp.
Camptothecium lutescens
Ceratodon purpureus
Cratoneuron commulatum
Ctenidium molluscum
Dichodontium pellucidum
Dicranella heteromalla
D. squarrosa
Dicranium bonjeani
Hygroanthystepium tenox
Hygrohypnum luridum
Philonotis fontana
Pohlia nutans
P. sp.

Paton, J.A. (1965) *Census Catalogue of British Hepatics*, 4th edition. *Brit. Bryol. Soc.*, Ipswich.

Polytrichum aciculare
P. aloides
P. commune
P. piliferum
Rhytidiadelphus squarrosus
Sphagnum capillaceum
S. girgensohnii
S. palustre
S. squarrosum
S. subsecundum var. *inundatum*
Calypogeia muellerana
Cephaloziella sp.
Diplophyllum albicans
Lophorolea cuspidata
Lophozia ventricosa
Pellia epiphylla
Plagiochila asplenioides
Scapania undulata
S. gracilis
Solenostoma triste

