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BARIUM AND HEAVY METALS IN THE WATERS AND AQUATIC PLANTS
OF THE CATCHMENT OF BLEABERRY GILL, NORTH YORKSHIRE

A dissertation submitted for the Degree of Master of
Science in Ecology in the University of Durham, 1982.

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This dissertation is the result of my own work and has not been presented in candidature for any other degree or diploma.

C. M. OWEN

November 1982.

ABSTRACT

Ca, Zn, Ba and Pb concentrations were measured in the waters and plants of Bleaberry Gill, North Yorkshire. Ba concentrations were compared with those of other streams in Arkengarthdale, considered to be non-contaminated by mining activity. Ba concentrations in bryophytes from Bleaberry Gill were an order of magnitude greater than those from streams uncontaminated with Ba, though aqueous concentrations were only 2 - 3 X greater. Zn was not present in particularly elevated concentrations, though Pb concentrations were elevated. Concentrations of these elements in bryophytes were not particularly high compared to other mining areas. In a series of experiments Hygrohypnum ochraceum was transplanted between streams with different aqueous metal concentrations. Uptake of Ba was rapid in populations of moss previously exposed to low and medium concentrations of Ba in water. The population from the lower Ba site achieved a lower maximum concentration than the population from the medium Ba site. Loss of Ba was rapid after a short exposure to elevated concentrations but took longer after prolonged exposure. The behaviour of Zn was similar, though both uptake and loss were slower than for Ba. Possible effects of proposed mining developments in the catchment of Bleaberry Gill are considered.

LIST OF ABBREVIATIONS

| | |
|---------------|--|
| ° | |
| C | degrees celsius |
| cm | centimetre |
| cv | coefficient of variation |
| EEC | European Economic Community |
| g | gramme |
| h | hours |
| km | kilometre |
| l | litre |
| m | metre |
| M | molar |
| min | minute |
| ml | millilitre |
| n | number of observations |
| OD | ordnance datum |
| O.S. | Ordnance Survey |
| ppb | parts per billion |
| ppm | parts per million |
| rpm | revolutions per minute |
| sd | standard deviation |
| T | time in hours from start of experiment |
| \bar{x} | arithmetic mean |
| μg | microgramme |
| μS | micro Siemens |

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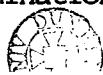
1 INTRODUCTION

1.1 General introduction

In recent years there has been much interest in the effect of mining for heavy metals on natural waters. Studies in the Northern Pennines (e.g. papers in Say and Whitton 1981), Wales (e.g. Carpenter 1924, McLean and Jones 1975) and South-West England (e.g. Foster 1982) have demonstrated accumulation and toxic effects of heavy metals in freshwater systems, but have tended to ignore other elements which may reach abnormally high concentrations as a result of mining activity. One such element is barium, which occurs as barium sulphate (barytes) and barium carbonate (witherite) among the 'gangue' of mineral veins in the Swaledale orefield, in the Lunehead-Teesdale-East Cumbria (Westmorland) mineral province (Wilson et al. 1922), in Derbyshire and in small quantities in other areas of mineralisation.

Mining for heavy metals has ceased in the Northern Pennines but extraction of gangue minerals, particularly fluorspar and barytes, has taken its place. Fluorspar is used as a flux in the steel industry and demand for the product has declined in parallel with the demand for steel (Meek, 1981). Barytes is a primary constituent and weighting agent (specific gravity 4.2) of muds used in offshore oil drilling operations (Tagatz and Tobia 1978). Demand is increasing and extraction of barytes is likely to replace fluorspar production as the major mining activity in the Northern Pennines.

The interest in barytes shown by mining companies has drawn attention to barium as a contaminant of streams and rivers of mining areas. None of the studies of metal contamination of streams in the Northern



Pennines have included consideration of barium, and little information exists about barium in either the waters or plants of natural waters. This study has a dual aim. First, to assess the concentration of barium in the waters and aquatic plants of an area where barium is the major gangue mineral and in which the extraction of barium minerals may begin in the near future. Second, it was hoped to investigate the dynamics of barium in populations of plants in an attempt to assess some of the possible effects of the proposed mining development. As the area was formerly important for the mining of lead it was also necessary to look at the behaviour of heavy metals such as zinc and lead. This study ran concurrently with a parallel study on the fauna of Bleaberry Gill, conducted by Miss J. A. Palmer. Water chemistry data collected for the preliminary survey are common to the two projects.

1.2 Heavy metals and plants in freshwaters

An abundant literature has developed on the relationships between heavy metal concentrations in the aquatic environment and those in plants. It is beyond the scope of this study to review that literature fully but some brief consideration is relevant.

Metal accumulation by plants has been considered both for limnic and flowing water environments. Welsh and Denny (1980) found correlations between concentrations of copper and lead in the shoots of submerged aquatic macrophytes and concentrations in the sediments of Ullswater. No correlations were found between concentrations in shoots and lake water.

For flowing waters many studies have demonstrated that bryophytes accumulate metals such that increased concentrations in water are reflected in increased concentrations in plant tissues. Studies in the

River Derwent catchment (Harding 1978, Burrows 1981) and in the Welsh ore field (Ystwith and Rheidol valleys) by Burton and Peterson (1979) have shown that bryophytes from stream reaches contaminated by metals had higher concentrations of metal in their tissues than plants from uncontaminated reaches.

Various studies have pointed to the potential use of aquatic plants as monitors of water pollution (Whitton 1979). Dietz (1973) found that enrichment factors for minor elements were greater for mosses than for higher plants. Empain (1976a, 1976b) found close correlations between concentrations of zinc in river water and those in the bryophytes Rhynchostegium riparioides (Hedw.) C. Jens (= Eurhynchium riparioides (Hedw.) Rich.), Cinclidotus nigricans (Brid.) Loeske (= C. riparius (Web. and Mohr) Arnott), and Fontinalis antipyretica. Empain indicated the possible value of these species as monitors of zinc pollution. These ideas have been developed towards the goal of making quantitative estimates of unknown concentrations of metals in water from known concentrations in plants (Say et al. 1981). So far this goal has not been reached because of inadequate knowledge of the effect of water chemistry parameters such as the presence of other cations and nutrient content on uptake of particular metals.

The moss Hygrohypnum ochraceum and the liverwort Scapania undulata have figured prominently in studies of metal contamination. McLean and Jones (1975) found that Scapania was the only bryophyte at three sample sites on the Rivers Ystwith and Magwr, where aqueous zinc concentrations reached 4.1 mg l^{-1} . Whitton et al. (1982) found Scapania growing in sites with a range of aqueous zinc concentration of $0.005 \text{ to } 7.0 \text{ mg l}^{-1}$ (total and filtrable) and a range of lead concentrations of $0.003 \text{ to } 1.82 \text{ mg l}^{-1}$ (total). Moreover the authors suggested that the absence of Scapania from sites with higher concentrations of heavy metals could be explained, at least in part, by

other factors. Shacklette (1965) found Scapania growing on iron and copper minerals and in close proximity to zinc and lead minerals.

1.3 Barium in natural waters

1.3.1 Chemical speciation and solubility

BaSO_4 and BaCO_3 are the only two barium compounds which can control the barium content of natural waters (Puchelt 1972). Jenne et al. (1980) found that barium activity in waters of various origins was limited by barytes solubility. All waters analysed were under saturated with barium carbonate. The solubilities of BaSO_4 and BaCO_3 in water are given below. Solubility of both compounds increases in acids and in electrolyte solutions. Solubility of BaCO_3 in water depends on the partial pressure of CO_2 in the atmosphere.

| T °C | BaSO_4 g l ⁻¹ sat. sol. | BaCO_3 g l ⁻¹ |
|------|---|-----------------------------------|
| 0 | 0.00115 | |
| 8.8 | | 0.016 |
| 10 | 0.0020 | |
| 18 | 0.00226 | 0.022 |
| 20 | 0.0024 | |
| 25 | 0.00223 | 0.0180 |
| 30 | 0.00285 | 0.034 |
| 40 | | 0.0241 |
| 50 | 0.0039 | |

Data from Linke (1958).

1.3.2 Concentration in freshwater

Published data on concentrations of barium in freshwater are sparse compared to those for other metals. Bowen (1979) gives a mean value of 0.01 mg l^{-1} for the concentration in world freshwaters. Durum and Hafty (1963) quote a range of $9 - 152 \text{ ug l}^{-1}$, with a median of 45 ug l^{-1} , for large rivers of the USA. Barium concentrations ranged from $6.8-22 \text{ ug l}^{-1}$ in the Neuse River North Carolina, USA, (Turekian, 1967). Benes et al. (1976) found 13.0 ug l^{-1} in Lake Trehorningen, Baerum, Norway and Salbu et al. (1975) measured a range of $10.8 - 13.5 \text{ ug l}^{-1}$ in four aliquots of a sample from the Skien River, also in Norway. Lutwein and Weise (1962) investigated the elemental concentration of waters of the River Mulde and its tributaries some of which drained mineral mining areas. The main river carried 5-100 ppb barium in true solution but some minor tributaries carried up to 730 ppb. Havlik et al. (1980) found concentrations of $0.1 - 5.0 \text{ mg l}^{-1}$ in fresh and waste waters of a uranium ore mining area of Czechoslovakia.

A study of seepages in the Arkengarthdale mineral area (Say and Whitton 1982) found a range of barium concentrations from $0.25 - 23.5 \text{ mg l}^{-1}$. Concentrations of barium in water samples from Bleaberry Gill and Arkengarthdale collected in that survey are given in Table 1.3.1.

1.4 Barium in plant tissues.

Barium is non-essential to plants (Bowen 1979) but may have a function in some species as a structural component. Schröter et al. (1975) reported crystallites of barium sulphate in the rhizoids of Chara fragilis and suggested that these may have a role in graviperception. Brook (1981) reports the presence of barium sulphate crystals in several species of desmids. The function of these is not

-1

TABLE 1.3.1 Concentration (mg l⁻¹) of Ba in waters of stream sites in the Bleaberry Gill and Arkengarthdale areas on 16 March 1982. From Say and Whitton (1982).

| site name | Durham stream reach | Ba |
|---------------------------|---------------------|------|
| Fourth Whim upper seepage | 0329-05 | 5.2 |
| Fourth Whim flush a | 0330-05 | 4.6 |
| Fourth Whim flush b | 0331-05 | 4.7 |
| Fourth Whim Gill | 0326-50 | 4.9 |
| Fourth Whim Spring | 0327-01 | 5.3 |
| Fourth Whim lower seepage | 0333-01 | 23.5 |
| Fourth Whim drainage | 0325-20 | 7.4 |
| Moor Intake Tips seepage | 0334-01 | 4.65 |
| Moor Intake Sike | 0335-50 | 0.25 |
| Moor Intake Gill | 0336-20 | 1.00 |
| Moor Intake flush a | 0337-02 | 7.4 |
| Moor Intake flush b | 0338-10 | 7.3 |
| Moor Intake Gill | 0336-30 | 1.50 |
| Moor Intake Gill | 0336-50 | 3.45 |
| Black Mires Gill | 0339-40 | 0.35 |
| Black Mires track flush | 0340-10 | 0.20 |
| CB Smelter drainage ditch | 0341-10 | 5.8 |
| CB Smelter sike | 0342-20 | 0.25 |
| CB roadside ditch | 0343-01 | 1.15 |
| Cocker House spring | 0344-01 | 0.25 |
| Moulds old road ditch | 0345-90 | 0.50 |
| Moulds Old Level | 0328-05 | 0.30 |
| Moulds Old Sike | 0346-80 | 0.40 |
| Moulds Old Flush | 0347-90 | 0.25 |
| Bleaberry Gill | 0212-20 | 1.43 |
| Bleaberry Gill | 0212-25 | 1.24 |
| Bleaberry Gill | 0212-49 | 0.66 |
| Wetshaw Bottom | 0322-99 | 0.28 |
| Fourth Whim Sike | 0323-99 | 2.86 |
| Moulds Old Level | 0328-10 | 0.19 |

clear, though they may act as statoliths or have an excretory function.

Available data for bryophytes and aquatic plants from the literature are limited. Rastorfer (1974) reported concentrations of 31 and 30 ppm Ba in Polytricum hyperboreum, 38 ppm in Polytricum commune var. jensenii and 34 ppm in Campylum stelatum all from Barrow, Alaska (dry weight). Cowgill (1973) analysed several species of aquatic macrophyte from Linsley Pond, Connecticut USA, for all elements. Unfortunately barium data are given for Pontedaria cordata (48 ppm) only. The author does not explain her failure to include barium data for other species nor are concentrations in the plant related to concentrations in water.

Boyd and Lawrence (1967) found 200 and 7 ppm Ba in single samples of the algae Microcystis and Euglena respectively. No data on concentrations of the element in the water from which the samples were collected are given. Fjerdingsstad et al. (1981) found 127 and 177 ppm Ba in two samples of Chlamydomonas nivalis from Spitzbergen, with 0.02 mg l⁻¹ in snow from which the sample was collected. A sample of the same species from East Greenland yielded 173 ppm with 0.13 mg Ba l⁻¹ in snow.

1.5 Toxicity of barium

Barium as an element is slightly toxic. The toxicity of its compounds depends on their solubility; the chloride, nitrate, carbonate and sulphide are toxic to man (Havlik et al. 1980). The concentration of barium in drinking waters is regulated in several countries. The EEC Directive on the quality of surface waters intended for abstraction as drinking water indicates a limit of 0.1 - 1.0 mg l⁻¹ (Directive 80/778/EEC). The respective standards for Czechoslovakia and the USA are 1.5 mg l⁻¹ (Havlik et al. 1980) and 1.0 mg l⁻¹ (Brenniman et al. 1981).

Havlik et al. (1980) found no toxic effect of barium concentrations up to 100 mg l^{-1} on strains of the green algae Scendesmus obliquus, Ankistrodesmus falcatus or Chlorella kessleri. Chaudhry et al. (1977) determined the level of barium in plants necessary to cause yield depression. Barium (as $\text{Ba}(\text{NO}_3)_2$) was applied to soil media to give concentrations of 0, 500, 1000, 2000, $\mu\text{g Ba g}^{-1}$. At the $500 \mu\text{g g}^{-1}$ level bush beans (Phaseolus vulgaris) had $2030 \mu\text{g Ba g}^{-1}$ in leaves and yields were decreased by 14%. At $2000 \mu\text{g Ba g}^{-1}$ soil bush beans had $22,200 \mu\text{g g}^{-1}$ and yields were depressed by 63%. For barley (Hordeum vulgare) $500 \mu\text{g Ba g}^{-1}$ gave $2060 \mu\text{g g}^{-1}$ in plants and depressed yields by 38%. At $2000 \mu\text{g Ba g}^{-1}$ soil barley had only $9970 \mu\text{g g}^{-1}$ in tissues but yields were depressed by 81%.

2 AREA DESCRIPTION

2.1 Introduction

The main area of study was the catchment of Bleaberry Gill (0212) including Old Gang Beck (0374). A number of streams in Arkengarthdale were investigated, in addition, and Moor Intake Gill (0336-50) was used for experimental purposes. Figure 2.1.1 shows the position of streams sampled during the study. Figures in brackets after stream names are Durham Stream Reach Code numbers. The first four figures give the stream code and the last two digits (where given) refer to designated 10 m reaches numbered from 1 - 99, starting upstream (Say et al, 1977).

2.2 Geographical

Bleaberry Gill rises at approximately 550 m OD and flows for approximately 4 km before joining Old Gang Beck, to form Barney Beck (0198) at approximately 320 m OD. Figure 2.2.1 shows the major features of the catchment. From a topographical point of view the course of Bleaberry Gill can be divided into three sections:

i) Upper; on the millstone grit plateau overlain by peat. It is in this section that the major inputs of metals from ephemeral drainage and seepage from mine tips are likely to occur. The major tributaries (Figure 2.2.1), Wetshaw Bottom (0322), and 'Surrender Moss Gill' (0348), draining peat bog also join the stream in this section. The bed of the stream consists of peaty deposits, silts, and in places bedrock, a generally unsuitable substrate for macro-algae and bryophytes.

FIGURE 2.1.1 The study area, showing streams and sample sites investigated in Survey II and used in experiments. Greater detail of the Bleaberry Gill system (inset box) is given in FIGURE 2.2.1.

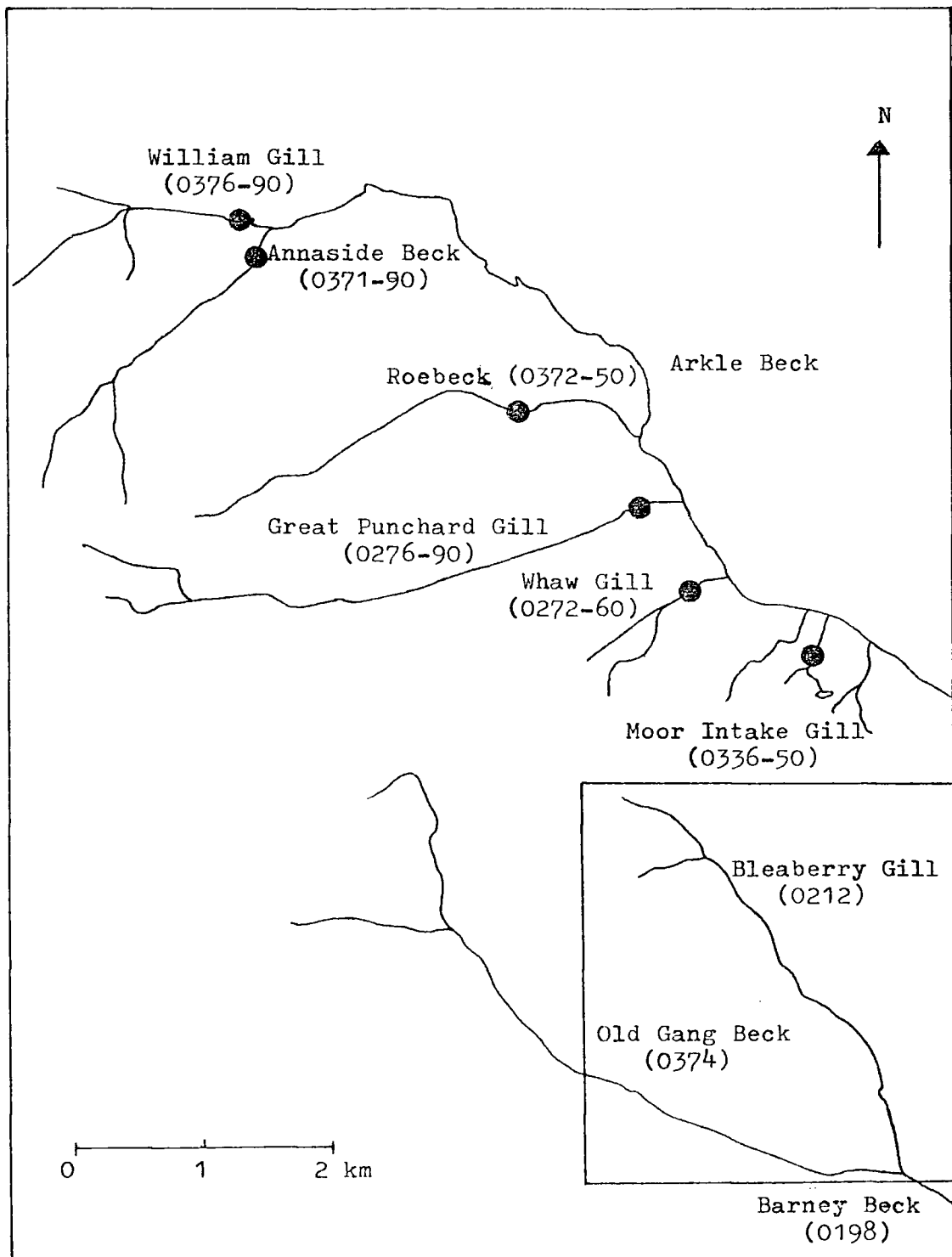


FIGURE 2.2.1 Bleaberry Gill, showing major tributaries and features of the catchment mentioned in the text. Sampling and experimental sites are shown in FIGURE 2.2.2.

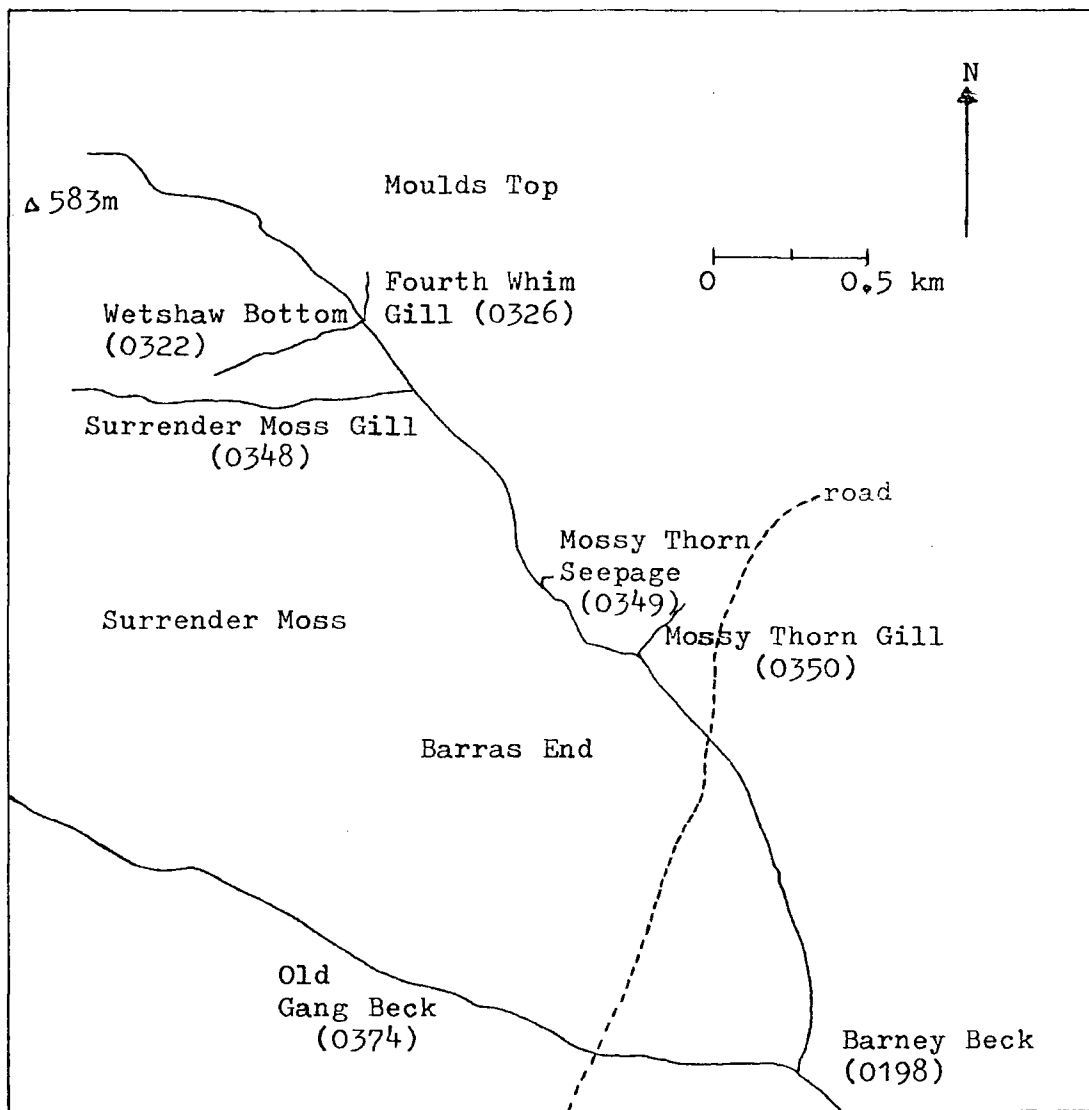
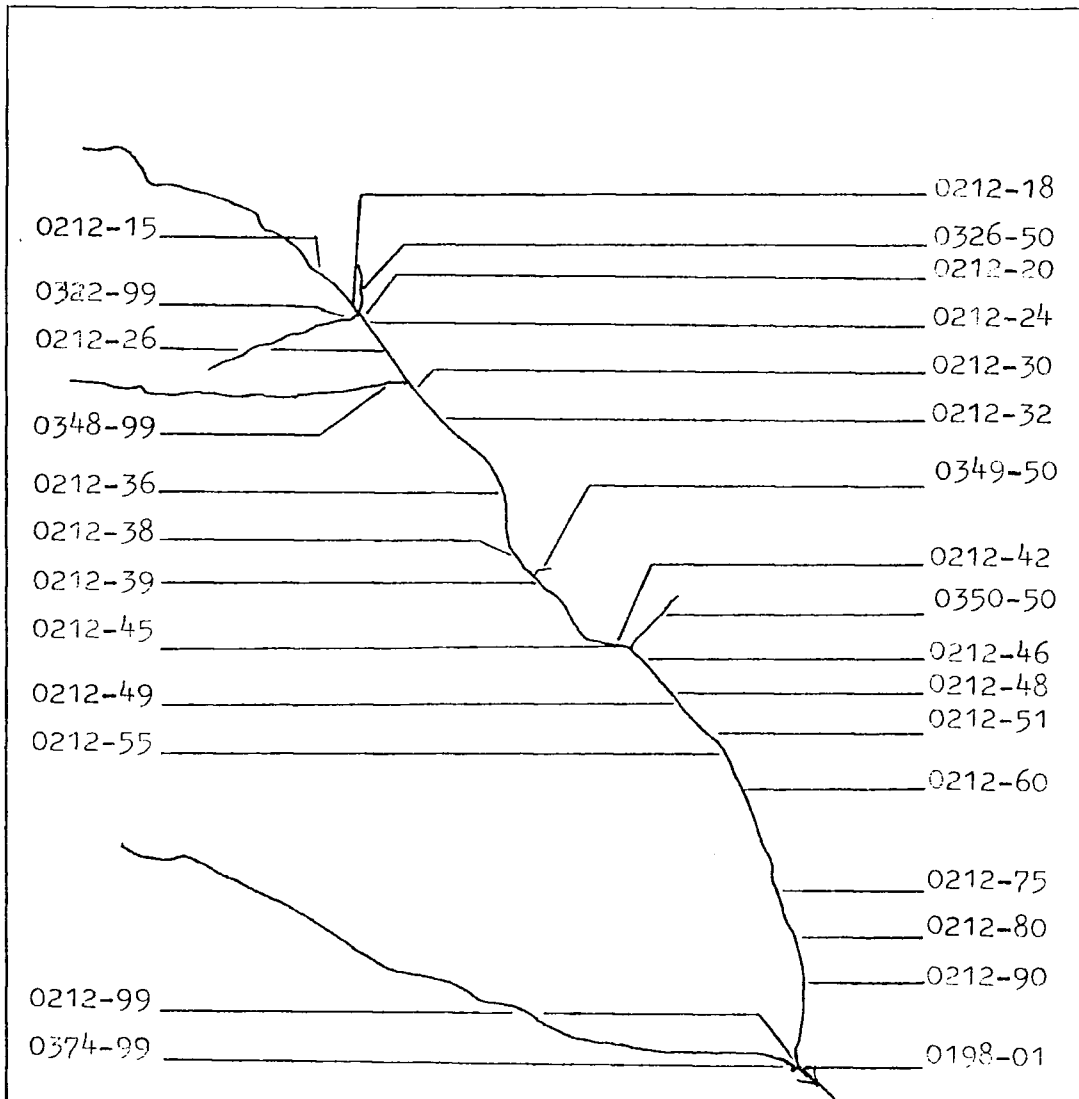


FIGURE 2.2.2 Bleaberry Gill, showing the position of stream reaches sampled in this study.



ii) Middle; the 'gorge' section. Here the rate of vertical descent increases markedly after the upper plateau as the stream crosses the complex strata of sandstones, grits, cherts and limestones of the lower Millstone Grit Series. In this section the stream bed is, in places, blocky and plants are more common than above.

iii) Lower; consisting of a stretch of low gradient and a final stretch of increased gradient as the stream traverses the upper beds of the Carboniferous Limestone Series. There are no permanent surface tributaries in this section.

Streams studied in Arkengarthdale originate in a variety of topographical situations. Moor Intake Gill (0336) originates as springs among mine waste tips at the foot of the south slope of Arkengarthdale. Whaw Gill (0277) and Great Punchard Gill (0276) originate at altitude on the valley side and both have old mine workings in their headwaters. William Gill (0376) rises in moorland at the head of Arkengarthdale. Roebeck (0372) and, in particular, Annaside Beck (0371) drain peat land and appear to be little influenced by mine drainage or from mineralised rock.

2.3 Geology

Swaledale and Arkengarthdale lie on the Askrigg Block of the Carboniferous formation, consisting of strata of the Millstone Grit and Carboniferous Limestone Series. The Millstone Grit outcrops on the fell top plateaux. This series consists of coarse and fine grained sandstones with intercalated shale formations. The lower strata of the millstone grit contain beds similar to those of the Upper Limestone Group, i.e. limestones, cherts, shales and sandstones. Each valley has cut through both the millstone grits and the upper strata of the limestone such

that a complex of strata are exposed on each valley side.

2.4 Mining

Figure 2.4.1 shows the position of Bleaberry Gill in the context of the major mineral veins and mining centres of the North Yorkshire orefield. Bleaberry Gill forms the boundary between the mining setts of the Old Moulds group in Arkengarthdale and the Surrender sett of Swaledale. The catchment of the stream is littered with workings and waste heaps from former lead mines.

Moulds Level was opened in 1674, though mining in the area predates this. Two smelt mills were constructed on the north bank of Bleaberry Gill shortly after 1674 and seem to have been important until the building of the New Mill in Langthwaite c.1824 (Raistrick 1975b). The O.S. map of 1847 depicts only the sites of mills along Bleaberry Gill indicating that the mills had fallen into disuse before then.

Lead mining operations declined in the Northern Pennines generally in the late 19th century and Swaledale/Arkengarthdale were no exception. Some small scale operations continued into this century; Arkengarthdale mines were worked until 1902 and the Old Gang Mines until 1914. Since the 1940's the principal mining activity in the Pennines as a whole has been the extraction of gangue minerals, principally fluorspar and barytes, with some sporadic re-working of heaps (Raistrick and Jennings 1965).

The principal gangue mineral of the Friarfold vein is barytes with some witherite. Some of the latter was won from the Old Gang Mine in 1892 (Wilson et al. 1922) and the Barras End Mines re-opened for a few years in the 1920's for the production of witherite (Raistrick 1975a).

Otherwise the gangue seems to have been extracted only to allow access to the metalliferous ores. Some of the tips of the Old Gang Mines are currently being re-worked for barytes.

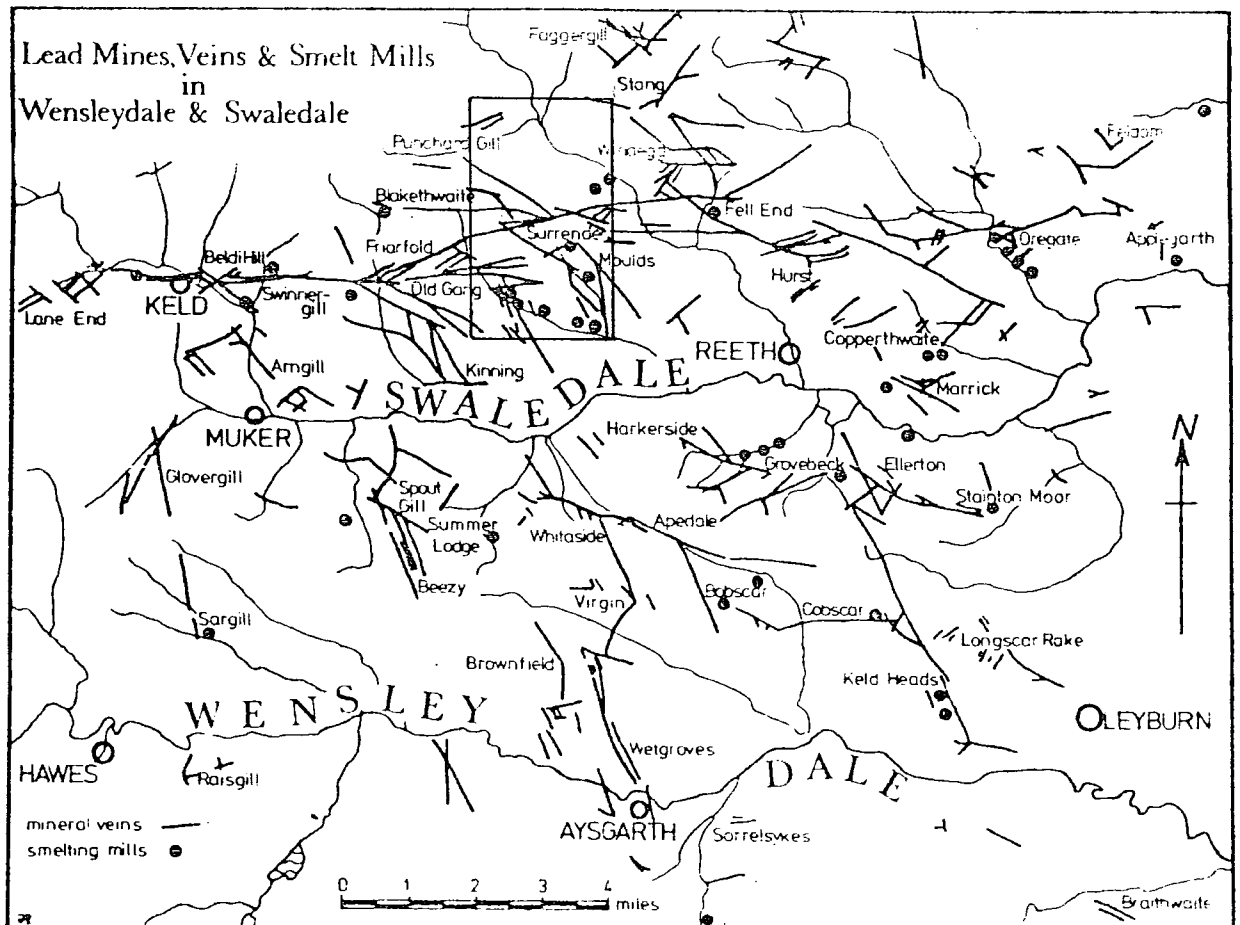
The proposed development in the area of Bleaberry Gill is for the extraction of barytes, fluorspar and galena from existing mine waste dumps. The operating company hope to remove 30000 tonnes of material from Fourth Whim heaps which consist of 48.3% barytes, 15.2% fluorspar, 7.1% witherite, 1.5% lead and 0.5% zinc, plus 150000 tonnes of dump material from other waste tips in Arkengarthdale. Processing by the wet gravity method will be conducted on site. A series of settling ponds will be filled at first with water abstracted from Bleaberry Gill below Wetshaw Bottom (0322). The plant will re-cycle water and under normal conditions there will be no discharge to Bleaberry Gill. The plant is expected to lose up to 10% water volume per week through percolation, evaporation and entrainment in concentrate removed from the site. Once in steady operation the plant water will probably become saturated with metals. Should the pond impoundments fail or the processing water be flushed from the plant by a flood, then Bleaberry Gill may be expected to receive a discharge of such contaminated water.

2.5 Other landuse

The catchment of Bleaberry Gill is used as extensive sheep grazing and is managed as a grouse moor. The stream sites in Arkengarthdale drain land used in an essentially similar manner.

FIGURE 2.4.1 Mineral veins and smelting mills of the Swaledale and Wensleydale area. Source: Raistrick (1975a) frontispiece.

The position of the study area is given by the inset box.



3 MATERIALS AND METHODS

3.1 Equipment preparation

All glassware and plastics used in the collection and analysis of waters and plant materials were acid washed. Apparatus was soaked in 4% (by volume) HNO_3 (reagent grade) for a minimum of 20 minutes. Each item was then rinsed six times in distilled water and three times in deionized water. Glassware was oven dried plastics were air dried. All materials were acid washed unless otherwise stated.

3.2 Collection and storage of water samples

Water samples for metal analysis were collected in boro-silicate glass snap-cap vials and stored in an icebox for transport to the laboratory. In the preliminary survey, survey II, and when collecting plant material for analysis, total water samples were taken direct from the main flow of the stream. During experiments 1 - 4 total water samples were collected as follows: Water was taken from the main flow of the stream in a 2 l polypropylene beaker and left to stand for five minutes to allow coarse suspended particles to settle out. From this 25 ml was decanted direct into a snap-cap vial. This sample is termed the total sample. A further 25 ml was collected after being passed through a polycarbonate Nuclepore filter (0.2 μm), mounted in a Swinnex plastic holder, from a glass syringe. This sample is referred to as the filtrable sample (American Public Health Association, 1971). The first 10 ml of water passed through the filter was discarded. In some cases

filtrable samples had to be collected in two stages because of blocking of the filter by suspended matter in the water. Back in the laboratory water samples were acidified with two drops of HNO_3 (Fison's 'Primar Grade'). Acidification reduced the pH below 1, reduced precipitation of inorganic chemical species and reduced microbial activity. Samples were stored in the refrigerator at 3°C .

Water for sulphate analysis was passed through a No. 2 Sinta funnel (sintered glass) and 250 ml collected in 300 ml polypropylene bottles. On return to the laboratory these samples were deep-frozen and stored at -20°C .

3.3 Physico-chemical analysis in the field

Water temperature was measured with a laboratory thermometer previously calibrated against a thermometer of known accuracy. pH was measured with an Orion Ionalyser/Model 407 probe calibrated against appropriate buffers. Conductivity was measured with an Electronic Instruments Ltd Model MCl Mk V electrolytic measuring set.

3.4 Collection and processing of plant materials

3.4.1 Collection

Bryophytes and algae were collected from parts of the stream reach at which current speeds were greatest. (A reach is defined as a 10 m length of stream having no tributaries, Say *et al.* 1977.) Only totally submerged plants were sampled. Material was collected using stainless steel forceps and stored in glass vials or plastic bottles.

In the laboratory plant material was stored in the collection vessel
at 3 C until processing.

3.4.2 Fractionation

a) Selection of material. For bryophytes 1 cm shoot tips were chosen for metal analysis. 30 - 50 tips were collected to give a dry weight of approximately 30 mg dry weight, where possible. For Lemanea both 2 cm tips and whole plants were analysed. Approximately 100 - 150 tips gave 20-25 mg dry weight.

b) Processing. Material was fractionated as soon as possible after collection. The maximum delay was 10 days. Possible change in metal composition of bryophytes under storage conditions was investigated for samples of Scapania undulata and Hygrohypnum ochraceum. Samples of each species collected from different sites on 17 June were divided into two sub-samples one of which was fractionated on 18 June, the other on 29 June. Results are presented in Table 3.4.1. Means of the sub-samples of Scapania show no significant difference in metal concentration. Ca, Zn and Ba concentrations are not different in the samples of Hygrohypnum but Pb is significantly more concentrated in the samples fractionated on 29 June ($p = <.05$). No explanation is offered to explain this and no account of it was taken in analysis of results.

Material for fractionation was washed twice in distilled water before tips or filaments were selected. Material for analysis was washed a third time before being dropped onto laboratory roll to remove excess moisture. The fractionation process was conducted in a series of acid washed glass petri dishes using a scalpel and stainless steel forceps.

In field experiments material was fractionated on site immediately after collection. Here glass petri dishes had to be re-used and were

TABLE 3.4.1 Results of fractionation study: Concentration of metals
⁻¹
 (µg g) in samples of plant material collected on 17 June 1982 and
 processed on 18 and 29 June.

| species / date | Ca \bar{x} | sd | Zn \bar{x} | sd | Ba \bar{x} | sd | Pb \bar{x} | sd |
|----------------------------|--------------|-----|--------------|-----|--------------|-----|--------------|-----|
| <u>Scapania</u> 18 June | 7240 | 315 | 3450 | 306 | 5970 | 578 | 2690 | 170 |
| <u>Scapania</u> 29 June | 6990 | 10 | 3440 | 535 | 6690 | 766 | 2380 | 377 |
| <u>Hygrohypnum</u> 18 June | 7870 | 422 | 99 | 11 | 386 | 153 | 9 | 3 |
| <u>Hygrohypnum</u> 29 June | 7650 | 386 | 62 | 75 | 226 | 29 | 29 | 19 |

rinsed three times in distilled water before each use. To reduce the amount of moss needed and to facilitate rapid processing of material in field conditions only 20 one cm moss tips were collected per sample.

3.4.3 Drying

Fractionated material was transferred to acid washed snap-cap vials and dried for 48 hours at 105 C. Dry material was cooled in a desiccator for 15 minutes and either weighed at once or stored. Stored material was re-dried for 24 hours before being cooled and weighed as above.

3.4.4 Acid digestion

Acid digestion is the process by which the metal content of solid matter is brought into solution. A known dry weight of plant material, weighed to 0.1 mg, was boiled in 5 ml 2 M HNO₃ (Primar Grade) in pyrex boiling tubes, using a Tecam 3D BH heating mantle at 150 C. Digestion was terminated when the boiling mixture became unstable, which was taken as indicative that digestion was complete, or after a maximum of 45 minutes.

After digestion the resulting solution was allowed to cool. The supernatant was poured off into a 25 ml volumetric flask and the remainder poured into a centrifuge tube with one deionized water rinse of the boiling tube. The whole was then centrifuged for 5 minutes at 3500 rpm. The resulting supernatant was added to the volumetric flask, a second rinse of the boiling tube added to the centrifuge tube, in which the precipitate was re-suspended, and centrifuging repeated. The supernatant was again added to the volumetric flask and the whole made up to volume (25 ml) with deionized water.

With each set of digests one blank, prepared as above but without plant material, was included. A full block of digests, then, consisted of 23 samples plus one acid blank.

3.5 Metal analysis

The metals Ca, Zn, Fe, Ba and Pb were measured using either a Perkin-Elmer 403 or 5000 atomic absorption spectrophotometer. Concentrations of Pb $> 0.1 \text{ mg l}^{-1}$ and all concentrations of other metals were analysed by direct aspiration using an acid resistant nebuliser. Ba required a nitrous oxide/acetylene flame other metals an air/acetylene flame. Pb at concentrations $< 0.1 \text{ mg l}^{-1}$ was determined with a Perkin-Elmer heated graphite atomizer HGA 74 (graphite furnace).

Water samples were shaken thoroughly before analysis, while digest solutions were not. Ca standards for digest determinations were made up in 0.4 M HNO_3 (acid matched).

Metal concentrations are expressed to the number of decimal places to which they could be measured, in mg l^{-1} (see below). Digest results are derived from the equation:

$$\frac{\text{concentration } \text{mg l}^{-1} \times \text{volume sample ml}}{\text{dry weight mg}} \times 1000 \text{ } \mu\text{g g}^{-1}$$

Results are expressed to three significant figures with the exception that only whole numbers are presented. Mean and standard deviations are given to one more significant figure than the values from which they were calculated.

3.6 Atomic absorption spectroscopy errors and detection limits

There are three sources of error, which were considered to be important, when analysing waters by atomic absorption spectroscopy:

- 1) heterogeneity within the sample;
- 2) contamination in collection, filtering and from glassware;
- 3) atomic absorption spectroscopy errors;

These errors are not necessarily cumulative, for example errors introduced through instrument noise may obscure variation introduced through 1) and 2).

Detection limits can be defined as the concentration of an element which will produce a signal/noise ratio of 2. This considers both the signal amplitude and the base line noise and constitutes the lowest concentration that can be significantly differentiated from zero.

Detection limits for analyses by direct aspiration were as follows:

Ca 0.05 mg l^{-1}

Zn 0.005 mg l^{-1}

Fe 0.02 mg l^{-1}

Ba 0.1 mg l^{-1}

Pb 0.1 mg l^{-1} (0.003 mg l^{-1} using the graphite furnace)

Concentrations in digest solutions are subject to additional errors from contamination due to greater handling, the addition of acid and deionized water, and interference to absorption by the more complex matrix by comparison to water samples.

Detection limits in digest solutions are a function of both atomic absorption spectroscopy limits, dry weight, and the volume to which the digest solution is diluted. Dry weights varied between samples though volume did not.

The number of significant figures to which the concentration of a metal can be measured varies with the instrument range into which the samples fall. For example, Ca concentrations were frequently in the range $10.0 - 100.0 \text{ mg l}^{-1}$, and could be measured to one decimal place. Zn at concentrations between 0.005 and 0.2 mg l^{-1} could be measured to three decimal places. Digest solutions were usually more concentrated than waters and measureable to fewer decimal places.

3.7 Anion analysis

Sulphate was determined only for waters collected on 14 May. Samples were removed from storage 24 hours before analysis and allowed to thaw at room temperature. Sulphate was determined by the turbidimetric method in which the sulphate ion is precipitated in a hydrochloric acid medium with barium chloride (American Public Health Association, 1971). Turbidity was determined with a Shimadzu digital double beam spectrophotometer model UV 150 02. Results are expressed as sulphate-sulphur.

3.8 Sampling programme

In a preliminary survey, conducted on 27 April 1982, total water samples were collected from sites in the catchment of Bleaberry Gill (0212), plus one sample from Old Gang Beck (0374-99) and Barney Beck (0198-99) (Table 4.1.1). In order to obtain a profile of concentration

of metals in the plants of Bleaberry Gill, plant samples were collected from 7 reaches on the stream, from Mossy Thorn Gill (0348-50) and from the lowest reach on Old Gang Beck (0374-99). These sites were selected, on the basis of results from the preliminary survey, to give the widest range of aqueous metal concentrations possible, within the constraints of the distribution of plant material. Plant samples were collected on 14 May 1982 (except material from Bleaberry Gill site 0212-80 which was sampled on 18 May). Total and filtrable water samples as well as samples for sulphate analysis were collected from each site on 14 May. Temperature, conductivity and pH were measured on site at the time of collection of samples (Table 4.2.1).

Because of the limited range of ambient aqueous metal concentrations in Bleaberry Gill, a second investigatory survey of five stream sites in Arkengarthdale was undertaken (termed survey II). The primary aim of this survey was to locate potential sites for transplant experiments. In addition it was hoped that plant samples could be collected from sites with a wider range of aqueous metal concentrations than available within the Bleaberry Gill system. Results from this survey are given in Tables 4.3.1 (waters) and 4.3.2 (plant analyses).

3.9 Transplant experiments

In a series of four experiments boulders with populations of Hygrohypnum ochraceum were transplanted between streams to assess loss or uptake of metals.

3.9.1 Selection of sites

For uptake experiments Hygrohypnum populations were obtained from

Annaside Beck (0371-90) and Bleaberry Gill (0212-51). Annaside Beck was shown to have low concentrations of the heavy metals Zn and Pb and had the lowest concentration of Ba of any stream sampled in this study. The Bleaberry Gill site was chosen because of its ease of access. The site selected to receive the moss transplants was Moor Intake Gill (0336-50) which was shown to have elevated concentrations of metals, especially Ba, by the survey conducted by Say and Whitton (1982). Reach 50 was selected for its ease of access. Moor Intake Gill was also used in the experiments on loss of metals. In this case populations of Hygrohypnum from Bleaberry Gill were transplanted to the stream and allowed to equilibrate with the elevated concentrations of metals there before being returned to Bleaberry Gill. The site on Bleaberry Gill, 0212-48, chosen for the experiments was selected as a compromise between ease of access and avoidance of possible human interference.

3.9.2 Methods

Boulders with moss were carried between streams in plastic buckets or baths containing stream water. Moss samples were collected for analysis according to the schedule illustrated in Table 3.9.1. A shorter and more intensive (i.e. over 27 hours) period of sampling was selected for uptake experiments than for metal loss experiments as loss was expected to be slower than uptake (J.D. Wehr pers. comm.).

Replicates (4 or 5) were taken on four sampling times per experiment and control material collected at suitable times. (See Table 3.9.1). Water samples were collected at the same time as each moss sample and pH, water temperature and conductivity were monitored throughout the experiments.

TABLE 3.9.1 Timing of sample collection in transplant experiments.

| Time (h) | Experiment | | | |
|----------|------------|---|---|---|
| | 1 | 2 | 3 | 4 |
| 0.0 | + | + | + | + |
| 0.5 | + | | | |
| 1.0 | + | + | | + |
| 1.5 | + | + | | |
| 2.0 | + | + | + | + |
| 3.0 | + | + | | |
| 4.0 | + | + | + | + |
| 6.0 | + | + | + | |
| 8.0 | | | + | |
| 9.0 | + | + | | + |
| 12.0 | + | + | + | + |
| 24.0 | | | + | |
| 25.0 | | | | + |
| 27.0 | + | + | | + |
| 48.0 | | | + | |
| 96.0 | | | + | |
| 144.0 | | | + | |

* denotes collection of replicates

3.10 Taxonomy

Nomenclature follows Smith (1978) for mosses and Watson (1968) for liverworts. Lemanea samples were referred to L. fluviatilis (L.) Ag.

The following species were encountered in this study:

Hygrohypnum ochraceum (Turn. ex Wils.) Loeske

Rhynchostegium riparioides (Hedw.)

Bryum pallens Sw.

Drepanocladus exannulatus (Hedw.) Warnst.

Drepanocladus uncinatus (Hedw.) Warnst.

Scapania undulata L. (Dum.)

Lemanea fluviatilis (L.) Ag.

4 RESULTS OF SURVEYS

Concentrations of metals in plants, total and filtrable water samples are referred to by the subscripts as in the example: Zn_p , Zn_t and Zn_f .

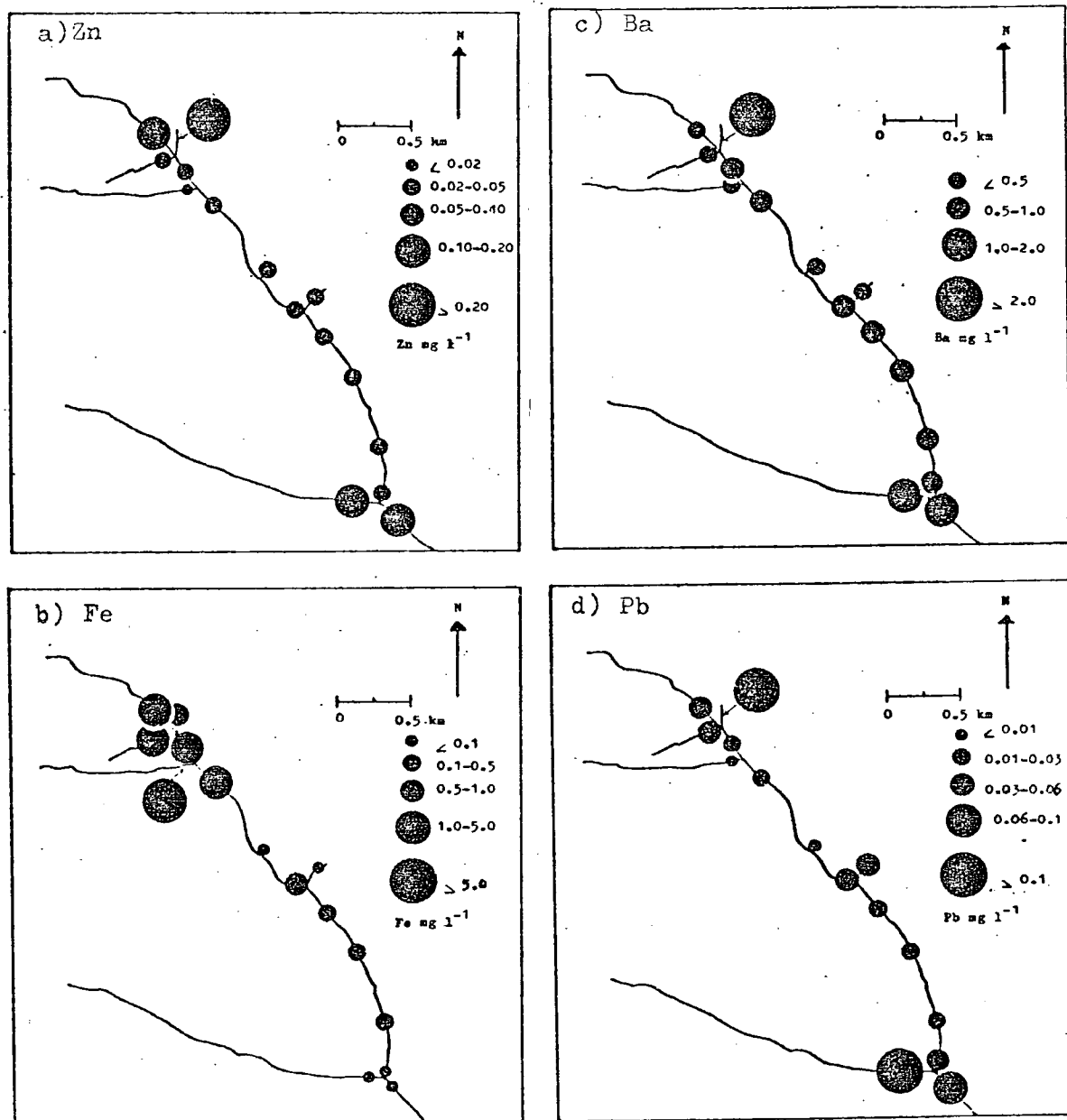
4.1 Preliminary survey, 27 April 1982

Figure 4.1.1 shows concentrations of Zn, Fe, Ba, and Pb for selected reaches in the Bleaberry Gill catchment (full data for all reaches are given in Appendix 1). Metal concentrations in the waters of Bleaberry Gill followed the series;

$$Ca < Ba < Zn + Pb$$

Ca concentrations increase downstream on Bleaberry Gill and are particularly low in the upper reaches below the confluence with Wetshaw Bottom (0322). Zn concentrations are highest in small streams draining mine heaps in the upper catchment, including Bleaberry Gill above Wetshaw Bottom, but show no trend of increase or decrease in the main stream. Fe concentrations were greater than those of Ba in the upper reaches of Bleaberry Gill, but decreased downstream. The major source of Fe appeared to be drainage from peat, for example 'Surrender Moss Gill' (0348). Such inflows clearly raised the concentration of Fe in Bleaberry Gill for some way below the confluences. Ba concentrations, like Zn, are highest in small streams draining mine wastes (e.g. Fourth Whim Gill, 0326) but increase downstream in the main river. Pb levels shown no trend to increase or decrease downstream. None of the metals analysed showed any significant correlations with each other within the main stream of Bleaberry Gill (at $p = < .05$).

FIGURE 4.1.1 Concentration of a); Zn, b); Fe, c); Ba, d); Pb, for representative sites in the catchment of Bleaberry Gill on 270482.



Concentrations of Ca, Zn, Ba and Pb were higher in Old Gang Beck (0374-99) than in Bleaberry Gill but Fe concentration was lower.

4.2 Profile of metal concentrations in plants, 14 May 1982

4.2.1 Waters

Water chemistry data collected on 14 May concurrently with plant samples are presented in Table 4.2.1. Concentrations of Ca and Pb were similar to those of the preliminary survey, while concentrations of Zn and Ba were generally higher. Fe concentrations were lower than on 27 April. Total and filtrable samples show minor differences only for Ca, Zn, Fe and Ba, but Pb total and filtrable samples are quite different. Ca (total and filtrable) is positively correlated ($p = < .01$) with pH, SO_4^{2-} and conductivity. Of the metals, Zn and Ba are positively correlated and Ca and Fe are negatively correlated (both $p = < .01$). Fe is negatively correlated with pH, conductivity and SO_4^{2-} .

4

4.2.2 Plants

Four species of moss (Drepanocladus exannulatus, Bryum pallens, Hygrohypnum ochraceum, Rhynchostegium riparioides), the liverwort Scapania undulata and the macro-alga Lemanea fluviatilis were collected from sampling sites on Bleaberry Gill. Summary data for concentrations of Ca, Zn, Ba and Pb in plant tissues from each sampling site are presented in Table 4.2.2. The concentration of elements in the plants followed the same order as the concentration in waters, i.e:

$$Ca < Ba < Zn + Pb$$

| SITE NAME | CODE | T °C | pH | Con | Ca | | Zn | | Fe | | Ba | | Pb | | SO ^{-S} ₄ |
|------------------------|----------|------|-----|-----|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------------------------------|
| | | | | | t | f | t | f | t | f | t | f | t | f | |
| BLEABERRY GILL | 0212-99 | 12.0 | 7.6 | 195 | 30.3 | 30.1 | 0.051 | 0.049 | 0.133 | 0.075 | 1.100 | 1.080 | 0.018 | 0.009 | 3.485 |
| BLEABERRY GILL | 0212-80* | | | | 28.1 | | 0.039 | | 0.158 | | 1.000 | | 0.016 | | |
| BLEABERRY GILL | 0212-75 | 16.0 | 7.5 | 179 | 26.0 | 26.3 | 0.051 | 0.044 | 0.181 | 0.083 | 0.940 | 0.960 | 0.022 | 0.015 | 3.459 |
| BLEABERRY GILL | 0212-49 | 15.0 | 7.2 | 153 | 21.6 | 21.5 | 0.042 | 0.045 | 0.249 | 0.183 | 0.780 | 0.730 | 0.020 | 0.011 | 3.194 |
| BLEABERRY GILL | 0212-46 | 13.4 | 7.3 | 154 | 20.5 | 20.5 | 0.038 | 0.037 | 0.249 | 0.116 | 0.630 | 0.590 | 0.019 | 0.011 | 3.300 |
| BLEABERRY GILL | 0212-36 | 14.6 | 6.5 | 99 | 9.9 | 9.8 | 0.047 | 0.032 | 1.295 | 0.300 | 0.780 | 0.780 | 0.043 | 0.019 | 2.850 |
| BLEABERRY GILL | 0212-26 | 14.0 | 5.8 | 60 | 4.0 | 4.3 | 0.048 | 0.039 | 1.112 | 0.315 | 0.530 | 0.490 | 0.016 | 0.009 | 2.532 |
| BLEABERRY GILL | 0212-20 | 12.0 | 6.6 | 121 | 20.2 | 19.7 | 0.108 | 0.103 | 0.488 | 0.232 | 2.000 | 2.000 | 0.032 | 0.012 | 3.194 |
| WETSHAW BOTTOM | 0322-99 | 14.1 | 5.8 | 49 | 1.6 | 1.7 | 0.047 | 0.037 | 1.179 | 0.739 | 0.140 | 0.120 | 0.008 | 0.008 | 2.452 |
| SURRENDER MOSS GILL | 0348-50 | 8.3 | 7.7 | 285 | 47.9 | 47.8 | 0.033 | 0.037 | N Det | N Det | 0.390 | 0.310 | 0.008 | 0.008 | 5.074 |
| OLD GANG BECK | 0374-99 | 14.0 | 7.2 | 292 | 57.5 | 57.6 | 0.181 | 0.181 | N Det | N Det | 1.840 | 1.800 | 0.078 | 0.067 | 7.134 |

* data collected 18 May 1982

TABLE 4.2.1 Water chemistry data collected on 14 May 1982.

Metal concentrations in mg l⁻¹, conductivity in μS cm⁻¹ (at 25 C).

| SITE NAME | CODE | SPECIES | Ca | | | Zn | | | Ba | | | Pb | | |
|------------------|---------|------------------------------------|-----------|-----|----|-----------|------|----|-----------|------|----|-----------|------|----|
| | | | \bar{x} | sd | cv | \bar{x} | sd | cv | \bar{x} | sd | cv | \bar{x} | sd | cv |
| BLEABERRY GILL | 0212-20 | <u>Scapania undulata</u> | 5458 | 390 | 7 | 556 | 107 | 19 | 2538 | 449 | 18 | 1551 | 317 | 20 |
| | | <u>Drepanocladus exannulatus</u> | 6325 | 347 | 6 | 524 | 116 | 22 | 2750 | 425 | 15 | 819 | 271 | 33 |
| | | <u>Bryum pallens</u> | 7765 | 318 | 4 | 752 | 144 | 19 | 3180 | 693 | 22 | 1188 | 399 | 34 |
| BLEABERRY GILL | 0212-26 | <u>Scapania undulata</u> | 4400 | - | - | 572 | - | - | 1860 | - | - | 1960 | - | - |
| BLEABERRY GILL | 0212-36 | <u>Scapania undulata</u> | 3074 | 516 | 17 | 234 | 102 | 44 | 2820 | 488 | 21 | 914 | 107 | 12 |
| BLEABERRY GILL | 0212-46 | <u>Hygrohypnum ochraceum</u> | 7118 | 619 | 9 | 1034 | 89 | 9 | 2863 | 1038 | 21 | 1197 | 104 | 9 |
| BLEABERRY GILL | 0212-49 | <u>Hygrohypnum ochraceum</u> | 9016 | 461 | 6 | 1098 | 139 | 13 | 4557 | 2139 | 47 | 1079 | 202 | 19 |
| | | <u>Scapania undulata</u> | 5214 | 622 | 12 | 1329 | 294 | 22 | 2289 | 988 | 43 | 1623 | 734 | 45 |
| | | <u>Lemanea fluviatilis (whole)</u> | 793 | 22 | 3 | 651 | 15 | 2 | 185 | 8 | 4 | 421 | 38 | 9 |
| BLEABERRY GILL | 0212-75 | <u>Hygrohypnum ochraceum</u> | 10070 | 406 | 4 | 2057 | 179 | 9 | 4024 | 733 | 18 | 1997 | 326 | 16 |
| | | <u>Scapania undulata</u> | 6063 | 848 | 14 | 2184 | 177 | 8 | 3984 | 876 | 22 | 2659 | 327 | 12 |
| | | <u>Lemanea fluviatilis (tips)</u> | 414 | 199 | 48 | 457 | 131 | 27 | 228 | 58 | 29 | 206 | 88 | 42 |
| | | <u>Lemanea fluviatilis (whole)</u> | 570 | 88 | 15 | 544 | 67 | 12 | 209 | 30 | 12 | 348 | 51 | 15 |
| | | <u>Scapania undulata</u> | 5582 | 408 | 7 | 1596 | 87 | 5 | 2478 | 644 | 26 | 1788 | 268 | 16 |
| BLEABERRY GILL | 0212-99 | <u>Rhynchostegium riparioides</u> | 13940 | 288 | 2 | 2748 | 220 | 8 | 6770 | 1448 | 21 | 6264 | 2126 | 40 |
| | | <u>Scapania undulata</u> | 5850 | 193 | 3 | 1366 | 48 | 4 | 1968 | 186 | 10 | 1180 | 290 | 25 |
| | | <u>Lemanea fluviatilis</u> | 164 | 32 | 20 | 207 | 43 | 21 | 223 | 26 | 11 | 183 | 25 | 14 |
| | | <u>Lemanea fluviatilis</u> | 608 | 425 | 70 | 490 | 80 | 16 | 258 | 241 | 93 | 266 | 148 | 56 |
| MOSSY THORN GILL | 0350-50 | <u>Rhynchostegium riparioides</u> | 13600 | 283 | 2 | 650 | 20 | 3 | 5850 | 2390 | 41 | 1160 | 274 | 23 |
| OLD GANG BECK | 0374-99 | <u>Hygrohypnum ochraceum</u> | 13900 | 173 | 1 | 3413 | 1473 | 43 | 15330 | 6731 | 44 | 8303 | 3550 | 43 |

-1
TABLE 4.2.2 Concentration of Ca, Zn, Ba and Pb ($\mu\text{g g}^{-1}$) in plant samples collected on 14 May.

The alga Lemanea contains much less metal than the bryophyte material analysed. Both 2 cm tips and whole plant material was analysed from two sites, 0212-75 and 0212-99. At neither site was Ba concentration significantly different in samples of tips and whole plant. Zn and Pb were significantly ($p = <.01$) more concentrated in whole plant material at one site each but not at the same site. Ca attained higher concentrations in whole plant material at both sites ($p = <.01$ and $p = <.05$).

At sites where both occurred concentrations of Ca were greater in Hygrohypnum than Scapania, but Pb concentrations were lower (significance $p = <.01$). At site 0212-49 concentrations of Zn and Ba in Hygrohypnum were greater than in Scapania, but at site 0212-75 Zn and Ba were at similar concentration in both species. At site 0212-80 Rhynchostegium contained significantly greater concentrations of all metals analysed than Scapania ($p = <.01$). Rhynchostegium was also present in 'Mossy Thorn Gill' (0350-50) where it contained similar concentrations of Ca and Ba to the material from 0212-80 despite the differences in aqueous concentration of those metals. Zn and Pb were at lower concentration in Rhynchostegium from Mossy Thorn Gill compared to reach 0212-80. Hygrohypnum collected from Old Gang Beck (0374-99) contained significantly higher concentrations of metals than the same species from any site on Bleaberry Gill (Table 4.2.2).

Only Scapania was found at sufficient sites to facilitate correlation between water chemistry variables and metal concentrations in plant tissues. Ca concentrations in the plant are significantly positively correlated with both C_a and C_a . Zn, Ba and Pb in plant material are not correlated with the concentration of the respective metal in the water. Zn in the plant is significantly negatively correlated with both Fe_t and Fe_f but aqueous Zn shows no correlation with Fe_f . A regression

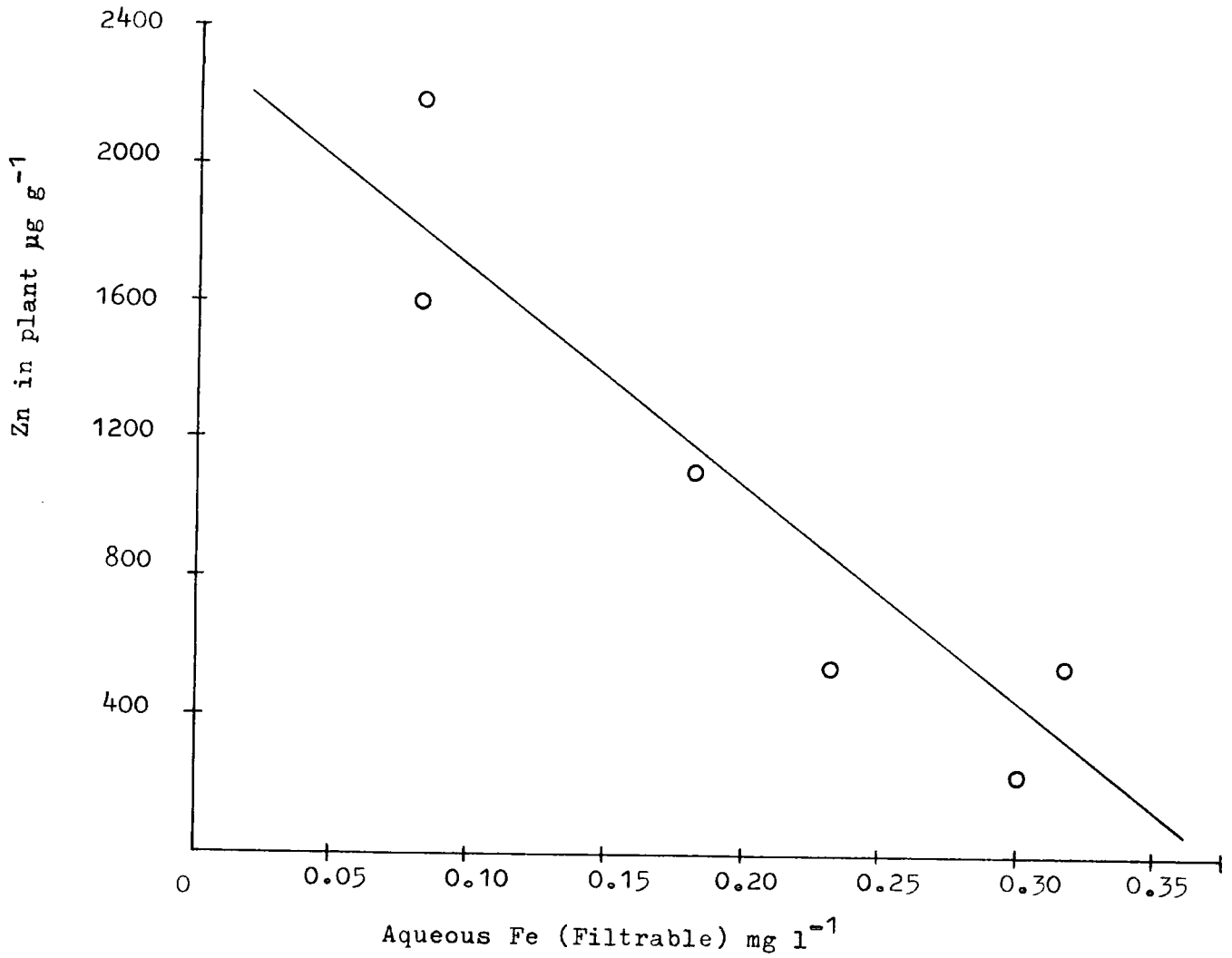
| | Cap | Znp | Bap | Pbp | Cat | Caf | Znt | Znf | Fet | Fef | Bat | Baf | Pbt | Pbf | pH | SO -S |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cap | 1.000 | | | | | | | | | | | | | | | |
| Znp | | 1.000 | | | | | | | | | | | | | | |
| Bap | | | 1.000 | | | | | | | | | | | | | |
| Pbp | | | | 1.000 | | | | | | | | | | | | |
| Cat | | | | | 1.000 | | | | | | | | | | | |
| Caf | | | | | | 1.000 | | | | | | | | | | |
| Znt | | | | | | | 1.000 | | | | | | | | | |
| Znf | | | | | | | | 1.000 | | | | | | | | |
| Fet | | | | | | | | | 1.000 | | | | | | | |
| Fef | | | | | | | | | | 1.000 | | | | | | |
| Bat | | | | | | | | | | | 1.000 | | | | | |
| Baf | | | | | | | | | | | | 1.000 | | | | |
| Pbt | | | | | | | | | | | | | 1.000 | | | |
| Pbf | | | | | | | | | | | | | | 1.000 | | |
| pH | | | | | | | | | | | | | | | 1.000 | |
| SO -S | | | | | | | | | | | | | | | | 1.000 |

P= <.01 R=.917
P= <.05 R=.811

TABLE 4.2.3 Correlation matrix relating metal composition of Scapania and water chemistry data.

Only significant correlations and non-significant correlations thought to important are included.

FIGURE 4.2.1 Relation of Zn in Scapania 1 cm tips to aqueous Fe (filtrable). $r = .8806$, $y = -6122.9x + 2252.8$. $n = 6$.



of Zn (Figure 4.2.1) against Fe gave an R-Square value of 0.7755 ($p = < .05$). Ba and Pb show no significant correlations with any water chemistry parameter measured. Correlation coefficients are presented in Table 4.2.3.

4.3 Survey II: Survey of Arkengarthdale sites, 17 June 1982

Results of analyses for Ca, Zn, Ba and Pb for the waters of five sites in Arkengarthdale are presented in Table 4.3.1. Plant material was analysed from three sites; data are presented in Table 4.3.2.

The Arkengarthdale sites show a range of aqueous metal concentration. Ba concentrations of Annaside Beck (0371-90), Roebeck (0372-50) and William Gill (0376-90) are lower than any site on Bleaberry Gill. Annaside Beck had the lowest metal concentrations of all sites sampled.

Concentration of metals in plant tissues followed the same order as in samples from Bleaberry Gill but only Ca values are of similar magnitude to those found from Bleaberry Gill. As at sites on Bleaberry Gill, Hygrohypnum from William Gill (0376-90) contained more Ca than Scapania but less Pb. Ba levels were also significantly greater in Hygrohypnum but Zn concentrations were similar. There were no significant differences in Ca, Zn, Ba or Pb concentrations in Hygrohypnum from William Gill and Annaside Beck.

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TABLE 4.3.1 Concentration of Ca, Zn, Ba and Pb (mg l⁻¹) in total water samples from stream sites in Arkengarthdale on 17 June (Survey II).

| SITE NO. | NAME | Ca | Zn | Ba | Pb |
|----------|------------------|------|-------|-------|-------|
| 0276-90 | Gt Punchard Gill | 39.9 | 0.035 | 0.818 | 0.090 |
| 0277-60 | Whaw Gill | 62.4 | 0.041 | 1.590 | 0.194 |
| 0371-90 | Annaside Beck | 11.2 | 0.041 | 0.081 | 0.005 |
| 0372-50 | Roebeck | 20.2 | 0.034 | 0.311 | 0.014 |
| 0376-90 | William Gill | - | 0.113 | 0.245 | - |

All samples were total water samples.

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TABLE 4.3.2 Concentration ($\mu\text{g g}^{-1}$) of Ca, Zn, Ba and Pb in plants collected from stream sites in Arkengarthdale on 17 June (Survey II).

| SITE NO. | SPECIES | Ca | | Zn | | Ba | | Pb | |
|----------|--------------------|-----------|-----|-----------|----|-----------|-----|-----------|----|
| | | \bar{x} | sd | \bar{x} | sd | \bar{x} | sd | \bar{x} | sd |
| 0371-90 | <u>Scapania</u> | 8100 | 273 | 99 | 9 | 252 | 60 | 47 | 52 |
| 0376-90 | <u>Hygrohypnum</u> | 7870 | 422 | 99 | 11 | 386 | 153 | 9 | 3 |
| 0376-90 | <u>Scapania</u> | 4900 | 89 | 98 | 3 | 167 | 26 | 63 | 8 |

5 RESULTS OF EXPERIMENTS

5.1 Introduction

It could be anticipated that commercial extraction of barium minerals in the Bleaberry Gill catchment would have an effect on the chemistry of the stream and thus affect the biota. To assess what these effects might be a series of transplant experiments, between streams of various aqueous Ba concentration were designed to examine the dynamics of Ba in the moss Hygrohypnum ochraceum. Four experiments were conducted, two on each of uptake and loss of Ba (see p35 for methods). As the metals Zn and Pb had been shown to be at elevated concentrations in the stream waters, data were also collected on uptake and loss of those metals as well as for Ca. For the sake of brevity the experiments are referred to as 1 - 4 as indicated:

Experiment 1 Transplant of Hygrohypnum from Annaside Beck (0371-90) to Moor Intake Gill (0336-50);

Experiment 2 Transplant of Hygrohypnum from Bleaberry Gill(0212-51) to Moor Intake Gill (0336-50);

Experiment 3 Transplant of Hygrohypnum from Bleaberry Gill to Moor Intake Gill for 14 days and replacement in Bleaberry Gill (0212-46) to assess loss of metals;

Experiment 4 Transplant of Hygrohypnum as above but replaced in Bleaberry Gill after 12 hours.

Summary data only are presented here; full data for each experiment are given in Appendix 2. Variation in aqueous concentration of metals in experiments was minor compared to between site variation. Mean aqueous metal concentrations at experimental sites are given in Table 5.1.1.

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TABLE 5.1.1 Mean metal concentrations (mg l⁻¹) for total water samples collected from donor and recipient sites in experiments 1 - 4.

| EXPT | SITE | | pH | Ca | Zn | Fe | Ba | Pb |
|------|------------------|---------|-----|------|-------|-------|-------|-------|
| 1 | ANNASIDE BECK | 0371-90 | 6.2 | 7.57 | 0.017 | 0.245 | 0.120 | 0.008 |
| | MOOR INTAKE GILL | 0336-50 | 7.5 | 55.5 | 0.235 | 0.061 | 4.81 | 0.011 |
| 2 | BLEABERRY GILL | 0212-51 | 7.7 | 17.2 | 0.029 | 0.043 | 0.078 | 0.029 |
| | MOOR INTAKE GILL | 0336-50 | 7.8 | 72.5 | 0.151 | 0.230 | 17.2 | 0.007 |
| 3 | MOOR INTAKE GILL | 0336-50 | 8.0 | 71.4 | 0.120 | 0.439 | 24.9 | 0.015 |
| | BLEABERRY GILL | 0212-48 | 8.0 | 16.4 | 0.033 | 0.762 | 0.603 | 0.035 |
| 4 | MOOR INTAKE GILL | 0336-50 | 8.0 | 70.7 | 0.115 | 0.503 | 25.2 | 0.016 |
| | BLEABERRY GILL | 0212-48 | 7.9 | 16.0 | 0.035 | 0.750 | 0.656 | 0.034 |

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TABLE 5.2.1 Concentrations ($\mu\text{g g}^{-1}$) of Ca, Zn, Ba and Pb in control samples collected in uptake experiments. Samples from Moor Intake Gill (0336-50) were of Drepanocladus uncinatus and from Bleaberry Gill (0212-48) Hygrohypnum ochraceum.

| SITE | | EXPT | TIME | Ca \bar{x} | Zn \bar{x} | Ba \bar{x} | Pb \bar{x} |
|------------------|---------|------|-------|--------------|--------------|--------------|--------------|
| MOOR INTAKE GILL | 0336-50 | 1 | T 3.5 | 19220 | 2349 | 10530 | |
| | | | T 27 | 18640 | 2522 | 10680 | |
| MOOR INTAKE GILL | 0336-50 | 2 | T 0 | 17820 | 2324 | 12540 | 775 |
| | | | T 27 | 18490 | 2160 | 11020 | 633 |
| BLEABERRY GILL | 0212-48 | 2 | T 0 | 11830 | 1322 | 5330 | 1658 |
| | | | T27 | 13240 | 1354 | 8507 | 1840 |

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TABLE 5.3.1 Concentration ($\mu\text{g g}^{-1}$) of Ca, Zn, Ba and Pb in control samples collected in loss experiments. All samples were of Hygrohypnum ochraceum.

| SITE | | EXPT | TIME | Ca \bar{x} | Zn \bar{x} | Ba \bar{x} | Pb \bar{x} |
|----------------|---------|------|------|--------------|--------------|--------------|--------------|
| BLEABERRY GILL | 0212-48 | 3 | T 0 | 9034 | 933 | 2563 | 911 |
| | | | T 48 | 9768 | 835 | 2588 | 794 |
| | | | T144 | 8458 | 961 | 2445 | 845 |
| BLEABERRY GILL | 0212-48 | 4 | T-12 | 8129 | 858 | 2392 | 1046 |
| | | | T 25 | 9758 | 835 | 2588 | 794 |

5.2 Experiments 1 and 2: Uptake of Ba by Hygrohypnum ochraceum

In the first uptake experiment (experiment 1), conducted on 1 and 2 July, a population of Hygrohypnum ochraceum was transplanted from Annaside Beck (0371-90) to Moor Intake Gill (0336-50). The object of this experiment was to demonstrate uptake of Ba by a population of the moss assumed to be unadapted to elevated concentrations of Ba and other metals in water. The second experiment (experiment 2) involved a transplant of Hygrohypnum from Bleaberry Gill (0212-51) to Moor Intake Gill, (0336-50) in order to assess the uptake of Ba by a population representative of that stream. It was hoped that transplanting moss to Moor Intake Gill, with higher aqueous Ba concentrations than Bleaberry Gill, would simulate a pulse of contaminated flow such as might occur due to mining development. In addition this experiment would demonstrate uptake of metals by a population of Hygrohypnum from a site with relatively elevated aqueous metal concentrations.

Figure 5.2.1 (a - g) show changes in concentration of the metals Ca, Zn, Ba and Pb through experiments 1 and 2 (change in Pb concentration was not assessed in experiment 1 because aqueous concentrations of the element were similar at both sites). A series of t-tests were conducted to test the significance of differences between replicate samples collected at various times through the experiments. In both experiments Ba uptake was rapid, complete within about two hours, though the results of experiment 2 were more variable and less clear. The Annaside Beck population of moss experienced a 3-4 fold increase in concentration of Ba, from $684 \mu\text{g g}^{-1}$ to $2600 \mu\text{g g}^{-1}$. The Bleaberry Gill population experienced an increase from 9000 to $11000 - 11500 \mu\text{g g}^{-1}$.

Ca uptake appeared to be as rapid as that for Ba, reaching a peak concentration in the Annaside Beck population of Hygrohypnum after 2

hours, with an increase from 7700 to approximately 9000 $\mu\text{g g}^{-1}$. Figure 5.2.4 d shows that the Bleaberry Gill population of the moss appears to accumulate Ca, but t-tests suggest that this is not significant. In both experiments Zn had reached a peak by 9 hours after which there was no further significant change. As with Ba, both Ca and Zn reached higher concentrations in the population of moss from Bleaberry Gill than in the population from Annaside Beck. Peak Ca concentrations for Annaside Beck and Bleaberry Gill populations were approximately 9000 and 13500 $\mu\text{g g}^{-1}$ respectively, and the corresponding Zn concentrations were 900 - 1000 and approximately 1650 $\mu\text{g g}^{-1}$. In experiment 2 Hygrohypnum appeared to lose Pb after being transplanted between Bleaberry Gill and Moor Intake Gill.

As Hygrohypnum was not present in Moor Intake Gill (0336-50) samples of Drepanocladus uncinatus were collected on two occasions during each experiment (1 and 2) to check that levels of metals in moss native to the stream did not change during the experiments. Metal concentrations in these samples are given in Table 5.2.1. Hygrohypnum from Annaside Beck did not acquire concentrations of metals comparable with those in controls. The Bleaberry Gill population of Hygrohypnum accumulated Ba, to a concentration similar to that of Drepanocladus but Ca and Zn concentrations remained lower than those of the moss native to Moor Intake Gill. Control material collected at T0 and T27 from Bleaberry Gill (0212-51) showed no significant change occurred in concentration of any metal analysed during the period of the experiment (Table 5.2.1).

5.3 Experiments 3 and 4: Loss of Ba from Hygrohypnum ochraceum

Populations of Hygrohypnum were transplanted from Bleaberry Gill to Moor Intake Gill (0336-50) and allowed to equilibrate there for 14 days (experiment 3) and 12 hours (experiment 4) before being returned

to Bleaberry Gill (0212-48) for assessment of loss. In experiment 3 moss was transplanted to Moor Intake Gill on 23 July and returned to Bleaberry Gill on 5 August. For experiment 4 the moss population was transplanted to Moor Intake Gill at 6.45 pm on 5 August. Between 23 July and 5 August concentrations of Ba in the water of Moor Intake Gill had increased from approximately 17 mg l^{-1} to 24 mg l^{-1} (Table 5.1.1).

Figures 5.3.1 to 5.3.8. show change of concentration of metals through the experiments. In experiment 3 Ba was lost rapidly at first, but then more slowly. At the end of the experiment, after 144 hours, Ba may not have regained equilibrium with aqueous concentrations in Bleaberry Gill. Concentrations in experimental material, at $4000 \text{ } \mu\text{g g}^{-1}$ compared to $2500 \text{ } \mu\text{g g}^{-1}$, were significantly different from controls ($p = <.01$) (Table 5.3.1). In experiment 4 after only 12 hours equilibration in Moor Intake Gill, Hygrohypnum lost Ba very rapidly, within two hours. The concentration of Ba in the moss at the start of experiment 4 was only $7492 \text{ } \mu\text{g g}^{-1}$, lower than at the start of experiment 3 ($11000 - 11500 \text{ } \mu\text{g g}^{-1}$).

Ca and Zn each decreased in concentration through both experiments. As with Ba both metals were lost more rapidly after only short exposure than after 14 days exposure to elevated concentrations. In experiment 3 Ca and Zn had reached concentrations comparable to those of controls within 144 hours. In experiment 4 Ca had reached a concentration not significantly different from controls within 25 hours, Zn within 9 hours, but, like Ba, concentrations of Ca and Zn in Hygrohypnum were lower at the start of experiment 4 than at the start of experiment 3. Pb concentrations in Hygrohypnum appeared to decline in experiment 3, regaining a level comparable to controls within 48 hours. In experiment 4 there was no obvious pattern of change in Pb concentration.

FIGURE 5.2.1 Experiments 1 and 2: Change in concentration of the metals Ca, Zn, Ba and Pb in Hygrohypnum ochraceum after transplanting from Annaside Beck (0371-90) to Moor Intake Gill (0336-50) (a - c) and after transplanting from Bleaberry Gill (0212-51) to Moor Intake Gill (d - g). Bars represent standard deviation (where replicate samples were taken). Standard deviations are not given for Pb because variation between replicates was great.

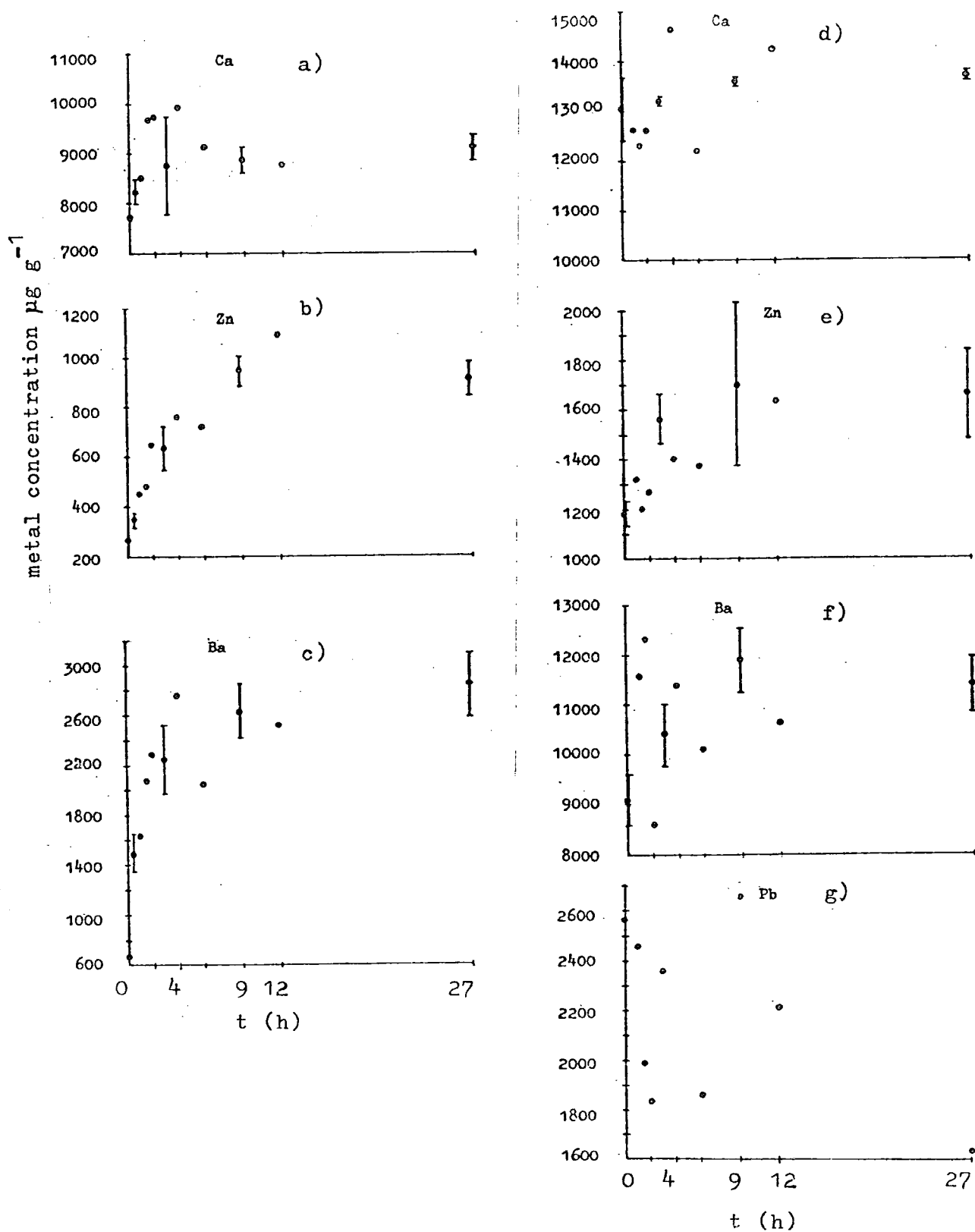
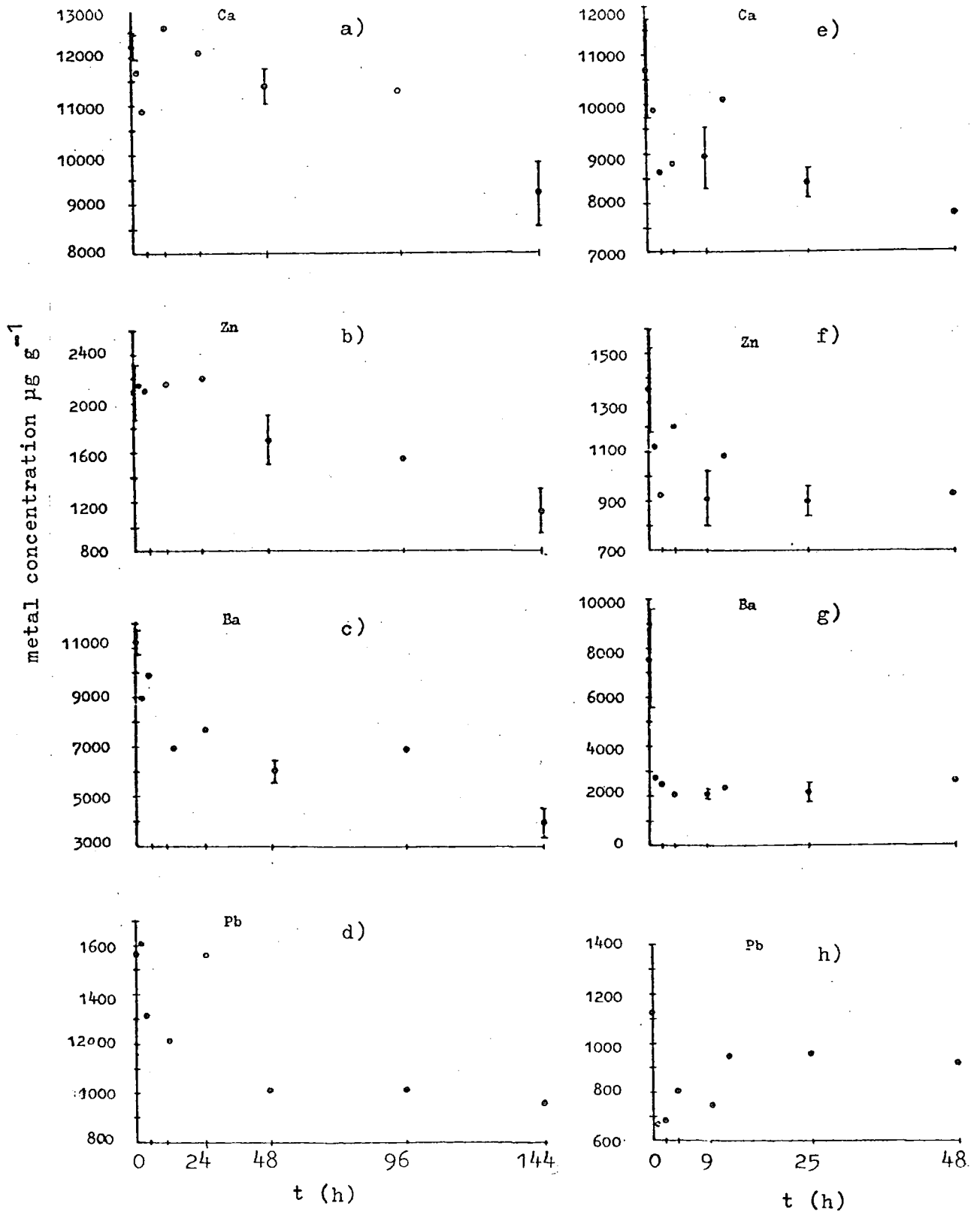


FIGURE 5.3.1 Experiments 3 and 4: Change in concentration of the metals Ca, Zn, Ba and Pb in *Hygrohypnum ochraceum* after 14 days equilibration in Moor Intake Gill (O336-50) and return to Bleaberry Gill (O212-48) (a - d) and after 12 hours equilibration in Moor Intake Gill and return to Bleaberry Gill (e - h). Bars represent standard deviation (where replicate samples were taken). Standard deviations are not given for Pb because variation between replicates was great.



6 DISCUSSION

6.1 Waters

Comparison of aqueous metal concentrations with those measured by other workers is complicated by the fact that different methods of collection and analysis are adopted. Moreover concentrations of metals may change both in the short term and seasonally (Grimshaw et al. 1976). Nevertheless a comparison with some metal concentrations reported in the literature is attempted in order to assess the extent of contamination by metals in Bleaberry Gill.

Abdullah and Royle (1972) and Dowling et al. (1981) each present data which they consider to represent chemical conditions in 'clean' streams. The former authors suggest that representative Zn and Pb concentrations for uncontaminated streams in North Wales might be $11 \mu\text{g l}^{-1}$ and $0.7 \mu\text{g l}^{-1}$. Dowling et al. investigated the chemistry of the River Caragh in West Ireland in an attempt to provide 'baseline' conditions with which to compare polluted streams in the rest of Europe. Zn and Pb in the Caragh were in the range $17.4 - 42.4 \mu\text{g l}^{-1}$ and $2.4 - 4.8 \mu\text{g l}^{-1}$ respectively. Neither study included analyses for Ba. Concentrations of Zn in Bleaberry Gill are higher than those in the Welsh streams but overlap with those from the Caragh. Clearly then Zn concentrations in Bleaberry Gill may be considered to be not elevated. Pb concentrations however are an order of magnitude greater than those of the uncontaminated streams.

By comparison with other streams in mining areas, Zn in particular, is relatively low in concentration. The River Derwent (Co. Durham) has been monitored frequently above and below the entry of Bolts Burn, a

tributary contaminated by mine and processing plant effluent. Mean Zn and Pb values for two reaches on the Derwent and for Bolts Burn are given by Harding et al. (1981):

| stream | n | Zn | Pb |
|-----------------------------|-----|--------------------------|--------------------------|
| R. Derwent above Bolts Burn | 41 | 0.020 mg l ⁻¹ | 0.007 mg l ⁻¹ |
| Bolts Burn | 100 | 1.453 | 0.276 |
| R. Derwent below Bolts Burn | 100 | 0.317 | 0.062 |

Zn concentrations in Bleaberry Gill are only a little greater than those of the Derwent above Bolts Burn, but Pb concentrations are similar to those in the Derwent below Bolts Burn. Neither element reaches the levels observed in Bolts Burn.

Ba concentrations in Bleaberry Gill are high compared to all values for freshwaters discussed in the Introduction, except those quoted by Lutwein and Weise (1962) and Havlik et al. (1980) for mineral mining areas. However many of these values are for large streams which may not be comparable with Bleaberry Gill. It would be more profitable to assess concentrations of Ba in Bleaberry Gill in comparison to other sites sampled in this study and in the study by the University of Durham Botany Department (Say and Whitton 1982) (see Table 1.3.1).

The range of aqueous Ba concentrations from sites in this study is 0.081 - 25.4 mg l⁻¹. This range encompasses that found in the survey conducted on 16 March 1982 by the University of Durham Botany Department. Concentrations of Ba in Bleaberry Gill clearly fall into the lower end of this range but it must be borne in mind that many of the sites with Ba concentrations in excess of 1 mg l⁻¹ are small spring or flush sites, and have a discharge much lower than that of Bleaberry Gill. The results of analysis of water samples collected on 27 April

and 14 May indicate that concentrations of Ba in Bleaberry Gill are low primarily because most of the water in the stream originates in peat and not among mine spoil. Wetshaw Bottom (0322) and 'Surrender Moss Gill' (0348) together contribute most of the flow from the upper valley, in summer at least. Thus water from mine waste heaps is diluted by water carrying relatively low levels of metals.

Streams such as Roebeck (0372), William Gill (0376), Wetshaw Bottom and Surrender Moss Gill draining peat and, 'Mossy Thorn Gill' (0350), a ground water flow, carry Ba concentrations in the range 0.2 - 0.5 mg l⁻¹. It is suggested that this can be regarded as the 'normal' Ba concentration of uncontaminated waters in the Swaledale/Arkengarthdale area. Against this standard Bleaberry Gill can be regarded as only slightly contaminated by Ba.

The origin of Ba causing an increase in concentration downstream in Bleaberry Gill is obscure. There are no surface tributaries which could account for this but there may be sub-surface seepage from groundwater or from mine spoil. In addition Ba may be taken into solution from mineralised rock in the bed of the stream.

Moor Intake Gill (0336-50), at concentrations up to 25 mg l⁻¹, is clearly grossly contaminated with Ba. Concentrations increased during the course of this study from 4.809 to a maximum of 25.4 mg l⁻¹. Some of this increase can be attributed to decreases in discharge but during July and August there were engineering works in progress on waste heaps above the stream and this is thought to be responsible for the majority of the effect.

Old Gang Beck (0374-99) carried higher concentrations of Ca, Zn, Ba and Pb but less Fe than Bleaberry Gill. The higher concentrations of Zn, Ba and Pb can be explained by three factors: The stream is eroding waste heaps from old processing works, receives drainage from old mine

workings and there is active re-working of tips in progress in the river valley.

The metal concentration of streams studied in Arkengarthdale is related to their origin. Whaw Gill (0277) originates in an area of old lead workings and may receive mine drainage. Thus high Ba and Pb concentrations may be expected. Streams draining predominantly peat, Roebeck (0372) and Annaside Beck (0371), as already discussed, have low metal concentrations, probably due to lack of contact with mineralised rock.

6.2 Metals in plants

Concentration of a particular metal in plants shows no correlation with that metal in water with the exception of Ca. Plant metal concentrations must be explained by factors other than aqueous metal levels for individual elements. Figure 4.2.1 shows the relationship between Zn and Fe for Scapania. Fe accounts for 77% of the variation in Zn_p ; high concentration of Fe_f in the water appears to reduce accumulation of Zn_p. This supports the suggestion of Whitton et al. (1981); 'the largest component of variation within the sites is a situation with high levels of iron in the water versus low levels of zinc in both water and plant.' In the present study no significant effect of Fe on aqueous Zn was noted, there was no significant correlation between aqueous Zn and Fe. The presence of high levels of Fe may account for the relatively low amounts of Zn in samples of Drepanocladus exannulatus and Bryum pallens from site 0212-20. Fe does not appear to affect concentrations of Ca, Ba or Pb.

Whitton et al. (1981) suggested that there was a correlation between the logarithm of metal concentration in the water and the logarithm of

metal concentration in Scapania, from a large number of sites. No such correlation was found in this study, though a much narrower range of sites and, therefore chemical conditions, were examined.

Comparison of plant metal concentrations reported in different studies is fraught with difficulty because of the different methods of collection, processing and analysis adopted by different authors. Wehr et al. (in press) compared several methods of analysis and found that not only did concentration of metals vary according to method used but the effect of particular treatments varied between elements.

There are few data presented in the literature with which to compare data on concentration of Ba in plants presented here. Rastorfer (1974) gives Ba concentrations of 30 - 38 ppm for terrestrial bryophytes. Forty eight ppm Ba were found in the aquatic macrophyte Pontedaria cordata by Cowgill (1973). Fjerdingstad et al. (1978) found up to 177 ppm Ba in Chlamydomonas from Spitzbergen and Greenland. The minimum Ba concentration found at any site in this study was $167 \mu\text{g g}^{-1}$ (H. ochraceum from William Gill, 0376-90), and the range of concentrations from low aqueous Ba sites was $167 - 386 \mu\text{g g}^{-1}$. It is not possible to say, without comparisons from other areas, whether even these concentrations are greater than normal. However these sites may be taken as representative of 'background' conditions for the study area. Plant material from Bleaberry Gill has a concentration of Ba an order of magnitude greater than this background level.

Chaudhry et al. (1977) found that 1% Ba in leaves of barley had toxic effects and reduced yields. Ba in excess of 1% was present in H. ochraceum from Old Gang Beck (0374-99) and in Drepanocladus uncinatus from Moor Intake Gill (0336-50). Hygrohypnum transplanted to Moor Intake Gill from Bleaberry Gill accumulated Ba to levels in excess of 1%. It is impossible to say whether such concentrations are toxic to these bryophytes. Conversely Havlik et al. (1980) found no toxic effect

of 100 mg Ba l⁻¹ to laboratory strains of species of green algae.

Maximum values of Zn and Pb concentration ($\mu\text{g l}^{-1}$) for Scapania and Hygrohypnum reported by various authors are given below. These can be regarded as representative of contaminated sites.

| author | <u>S. undulata</u> | | <u>H. ochraceum</u> | |
|----------------------------|--------------------|-------|---------------------|------|
| | Zn | Pb | Zn | Pb |
| McLean and Jones (1975) | 1950 | 14825 | | |
| Burton and Peterson (1979) | 3558 | 8902 | 780 | 2450 |
| Harding (1978) | 2992 | 2387 | 1438 | 993 |
| Burrows (1981) | 7700 | 2650 | 3100 | 1040 |
| This study: | | | | |
| i) Bleaberry Gill | 2184 | 2658 | 2057 | 1997 |
| ii) All sites | 2184 | 2658 | 3413 | 8303 |

Zn and Pb in Scapania and Hygrohypnum were not at particularly high concentration in Bleaberry Gill. The maximum concentration of Pb found in the present work, from Old Gang Beck (0374-99), is higher than any recorded in the literature reviewed here.

A comparison with the study of Bleaberry Gill conducted by Say and Whitton (1982) is perhaps valid though in that project plant samples were digested in concentrated nitric acid rather than 2 M acid as in this study. Monthly samples collected between November 1981 and March 1982 gave the following range of metal concentrations ($\mu\text{g l}^{-1}$) in Scapania from Bleaberry Gill site 0212-49:

| | |
|----|-------------|
| Ca | 3660 - 9340 |
| Zn | 544 - 1191 |
| Ba | 940 - 4090 |
| Pb | 1740 - 9010 |

Results presented here fall within the ranges above for Ca, Ba and Pb though Zn concentrations were higher in material analysed here. It is apparent that there is considerable variation in metal levels in the plants of Bleaberry Gill and it is impossible to say whether the Zn

concentrations in plant material sampled on 14 May represent a significant increase over those measured earlier or whether they fall within the range of normal variation.

6.3 Experiments

Uptake experiments have shown that Ba can be taken up rapidly (to a maximum within 2 hours) by Hygrohypnum ochraceum populations previously exposed to low and medium concentrations of Ba in water. The difference in concentration between waters of Annaside Beck (0371-90) and those of Moor Intake Gill (0336-50) represents a 40 fold increase but concentration in the plants increased by only 4 fold. The results of experiment 2, involving a transplant of Hygrohypnum from Bleaberry Gill (0212-51) to Moor Intake Gill, were less clear than the results of the first experiment because of greater variability between samples (Figure 5.2.1). The Bleaberry Gill population of Hygrohypnum increased its Ba concentration by only 1/3 though the change in water concentration on transplant represented an increase of almost 20 fold. The Bleaberry Gill population took up approximately $2000 - 2500 \mu\text{g g}^{-1}$ Ba, about the same in total as the Annaside Beck population. It seems likely that the fact that the two populations had a different percentage increase in concentration is of some biological significance. Though the Bleaberry Gill population achieved a far higher maximum concentration of Ba, it appears that proportionally fewer cation binding sites remained available in that population than in the Annaside Beck population.

Maximum concentrations of Ba achieved by the Annaside Beck population of Hygrohypnum were approximately $2600 \mu\text{g g}^{-1}$, far lower than the maximum reached by the Bleaberry Gill population ($11000 - 11500 \mu\text{g g}^{-1}$). It appears that the two populations had a differential ability to accumulate Ba. Hygrohypnum samples collected from Old Gang Beck

(0374-99) on 14 May had a mean Ba concentration of $15330 \mu\text{g g}^{-1}$, indicating that the maximum observed for the Bleaberry Gill population was not a maximum for the species. Presumably the Old Gang Beck population, exposed to a consistently higher concentration of Ba in water, has naturally more cation binding sites available than the Bleaberry Gill population. It is tentatively suggested that Hygrohypnum populations exposed to different ambient Ba concentrations will have the ability to take up Ba to different maxima. It is significant that by the start of experiment 3 aqueous Ba concentrations in Moor Intake Gill (0336-50) had increased to 24 mg l^{-1} . Concentrations in the moss transplanted to Moor Intake Gill on 23 July were no greater 14 days later, at the start of experiment 3, than those reached by the moss during experiment 2 (i.e. $11000\text{--}11500 \mu\text{g g}^{-1}$). Thus it appears that the transplanted moss had accumulated as much Ba as possible, irrespective of aqueous concentration.

Experiments 3 and 4 demonstrate how Hygrohypnum loses Ba on return to normal aqueous Ba concentrations. Figure 5.3.3 shows the pattern of Ba loss after 14 days in an elevated Ba environment. There is a relatively rapid initial loss but even after 144 hours Ba concentration in transplanted material had not reached that of controls. In experiment 4 Hygrohypnum exposed to elevated Ba for only 12 hours demonstrated a rapid rate of loss (Figure 5.3.1). The peak Ba level in this experiment was only $7500 \mu\text{g g}^{-1}$, lower than that attained in other experiments. Moreover control material collected during experiment 4 had lower concentrations of Ba than control material from experiment 2. This may be because material for experiment 4 came from a different sub-population to that from experiment 2, or may be due to some change in the Bleaberry Gill population as a whole. The first possibility raises the question as to whether there are different maxima of Ba concentration that can be achieved by various sub-populations of Hygrohypnum within Bleaberry Gill.

The uptake experiments (1 and 2) demonstrated that Zn was taken up by both Annaside Beck and Bleaberry Gill populations of Hygrohypnum. As aqueous Fe may have a negative effect on Zn uptake and increased in Moor Intake Gill between the two experiments (Table 5.1.1) the results may not be strictly comparable. The Bleaberry Gill population accumulated more Zn than the Annaside Beck population, but maxima were reached after approximately the same time. Hygrohypnum transplanted back to Bleaberry Gill in experiments 3 and 4 lost Zn. Unlike Ba more Zn was present in the moss at the start of experiment 3 than at the end of experiment 2 ($2100 \mu\text{g g}^{-1}$ as opposed to $16-1700 \mu\text{g g}^{-1}$), indicating that further Zn accumulation had occurred. Aqueous Zn in Moor Intake Gill was at lower concentration during experiment 3 than during experiment 4, but may have increased in the intervening period to account for the further increase in Zn in the plant. In experiment 3 Zn reached a concentration comparable to that of controls after 144 hours. Zn loss in experiment 4 was more rapid and complete within 48 hours. This suggests that Zn, like Ba, becomes more firmly bound to plant material after long periods of exposure to higher concentrations.

Ca was accumulated by the Annaside Beck population in experiment 1 but not (to a significant degree) by the Bleaberry Gill population in experiment 2. Uptake of Ca in experiment 1 was complete within 3 hours. As for other metals loss of Ca was more rapid in experiment 4 than during Experiment 3. Loss was complete after 48 hours in experiment 4 but only after 144 hours in experiment 3.

Pb accumulation was not assessed in experiment 1 because aqueous concentrations of the metal were similar in both streams. As Pb concentrations were lower in Moor Intake Gill than Bleaberry Gill it is to be expected that transplanted moss lost Pb in experiment 2 (Figure 5.2.1 g) It does seem anomalous, however, that Pb concentrations appear to decrease in experiment 3 after replacement in Bleaberry Gill. The results for experiment 4 show an apparent increase of Pb on transplant

back to Bleaberry Gill, though statistical tests do not bear this out.

The results of experiment 3 suggest that no more Ba is accumulated by moss, above the maximum concentration observed after 2-3 hours, during long exposure to high Ba concentrations. This is also the case for Ca but not for Zn, which increased in concentration over the long period of exposure to elevated aqueous concentrations. All three metals were less easily lost on return to 'normal' concentrations after long exposure than after short exposure to elevated metal concentrations. Pickering and Puia (1969) suggested that there were three phases of Zn uptake by the moss Fontinalis antipyretica; two relatively rapid passive phases and a slower active phase lasting several days. The accumulation of Zn noted between experiments 2 and 3 can possibly be attributed to such active accumulation. The lack of increase in Ca or Ba in this period may suggest that active uptake of these metals does not occur or occurs at a much slower rate, so as not to be detectable in this type of experiment. On the other hand there must be some process of cation binding in operation to account for the slower rate of loss of metals after long exposure to high metal concentrations in water. Clearly 12 hours is insufficient time for such binding to occur.

Experiments 2, 3 and 4 were intended to elucidate the effects of contaminated discharge in Bleaberry Gill. A brief outline of the proposed mining operation was given in Chapter 2. There will be no discharge of contaminated water under normal operational conditions but if for some reason, e.g. a flash flood, water is lost from the plant it is likely to be saturated with metals. Thus a pulse of contaminated water will pass down Bleaberry Gill, though this is likely to be of short duration. The experiments have shown that under such conditions there would be rapid uptake of Ba and other metals by Hygrohypnum and

equally rapid loss once the contaminated discharge has passed. Say et al. (1982) point to the value of mosses as environmental monitors suggesting that they may allow the detection of short duration pollution discharges. As Hygrohypnum loses Ba rapidly this species may not be an effective monitor of Ba, at least. If other bryophyte species respond in a similar way to Ba then these plants can be of little value as monitors of possible Ba contamination. It appears that only if there is a sustained period of discharge contaminated by Ba will increased concentrations remain in the plant for more than a few hours.

6.4 Concluding remarks.

The experiments were designed to demonstrate the dynamics of Ba in populations of the moss Hygrohypnum. It has also been possible, however, to make comments about the dynamics of other metals. For Ca, Ba and Zn the different populations of moss each seem to have maximum concentrations to which they accumulate metals. Ca and Ba are taken up more rapidly than Zn, within 2-3 hours rather than within 9 hours. All three elements are lost more rapidly after short exposure to elevated concentrations than after long exposure. For Ba, 144 hours may not be sufficient to allow return to normal concentration in tissue. Results for Pb are inconclusive, but this can be expected because the experiments were not designed to assess Pb dynamics.

The results presented here suggest what might occur in Hygrohypnum if there were a contaminated discharge of water in Bleaberry Gill. Ba would be accumulated and lost rapidly while Zn would be accumulated more slowly and lost more slowly. Ca, Ba and Zn would be accumulated to a maximum for individual populations irrespective of aqueous metal concentration. There is some evidence to suggest that different sub-populations of Hygrohypnum might have different maxima, this may

help to explain the variability of metal concentrations in material collected from different sites and on different occasions.

In the way of all science this study has posed more questions than it has answered. In particular there are three areas which deserve further study:

i) Concentrations of Ba have been found in species of bryophytes which have been shown to be toxic to higher plants. Are such levels of Ba in any way toxic to these bryophytes?

ii) This study has indicated that there may be differences in the capacity for uptake of Ba and Zn by Hygrohypnum. Does Ba uptake occur by active processes and if so at what rate?

iii) There appear to be differences in the uptake capacity of populations of Hygrohypnum ochraceum growing in different ambient Ba concentrations. Are these differences genetic and do they confer tolerance of elevated Ba concentrations on different Hygrohypnum populations?

SUMMARY

1) This study was an attempt to assess the concentration of Ba and the heavy metals, Zn and Pb, in the water and plants of the Bleaberry Gill catchment, N. Yorkshire. Analyses of waters and plants from other streams in the area were included in order to allow comparisons between Bleaberry Gill and streams uncontaminated by metals.

2) Bleaberry Gill is a tributary of the River Swale (via Barney Beck). The area was formerly important for lead mining and there are current proposals to extract barium minerals from existing spoil heaps.

3) Bleaberry Gill was found to contain only moderate concentrations of Zn and Ba, though Pb concentrations were relatively high. Typical concentrations of these elements were: Zn; $0.03 - 0.05 \text{ mg l}^{-1}$, Ba; $0.6 - 0.9 \text{ mg l}^{-1}$, Pb; $0.02 - 0.05 \text{ mg l}^{-1}$.

4) Concentrations of Ba in plants from Bleaberry Gill were an order of magnitude greater than in plants from uncontaminated streams. The most abundant species, Scapania undulata and Hygrohypnum ochraceum, had concentrations of 2537 and $3114 \text{ } \mu\text{g Ba l}^{-1}$, respectively. Zn and Pb concentrations in plants from Bleaberry Gill were not high compared to other mining areas reported in the literature. Mean Zn and Pb concentrations in Scapania were 1120 and $1668 \text{ } \mu\text{g l}^{-1}$ and for Hygrohypnum were 1396 and $1425 \text{ } \mu\text{g l}^{-1}$. Concentrations of Zn in Scapania were found to be negatively correlated with aqueous Fe.

5) Uptake of Ba and other metals by populations of Hygrohypnum ochraceum from Annaside Beck (0371-90) and Bleaberry Gill (0212-51) was investigated in transplant experiments between those sites and

Moor Intake Gill (0336-50), a stream with elevated aqueous Ba concentrations. The Annaside Beck population, previously exposed to low Ba, accumulated Ba to a maximum within 2 - 3 hours. The Bleaberry Gill population accumulated Ba more slowly, took up less Ba than the Annaside Beck population, but achieved a higher maximum concentration (11000 - 11500 $\mu\text{g g}^{-1}$ compared to approximately 2600 $\mu\text{g g}^{-1}$). There appears to be a maximum concentration to which Ba accumulation proceeds, possibly related to 'normal' aqueous concentrations to which the plant is exposed.

6) Loss of Ba from populations of Hygrohypnum from Bleaberry Gill was assessed after short (12 hours) and long (14 days) periods of exposure to elevated Ba concentrations in Moor Intake Gill (0336-50). After short exposure to elevated concentrations Ba was lost within 2 hours of being replaced in Bleaberry Gill (0212-48). After 14 days exposure there was a rapid initial loss but 144 hours after replacement in Bleaberry Gill loss of Ba may not have been complete.

7) In uptake experiments maximum concentrations of Zn were reached approximately 9 hours after placement in the site with higher aqueous Zn concentration for both Annaside Beck (0371-90) and Bleaberry Gill (0212-51) populations of Hygrohypnum. The Bleaberry Gill population achieved a greater maximum concentration than the Annaside Beck population. Loss of Zn was more rapid after short exposure to elevated concentrations than after long exposure. 'Normal' tissue concentrations of Zn were reached within 144 hours following long exposure and after 25 hours following short exposure. No conclusive results were achieved in transplant experiments with regard to Pb.

8) Possible effects of mining developments within the catchment of Bleaberry Gill were considered. Because of the nature of the proposed processing plant any contaminated flows are likely to be of short

duration. The experiments have indicated that uptake of metals will occur if aqueous concentrations of metal rise but that Bleaberry Gill populations of Hygrohypnum have a limited capacity for metal uptake. Once aqueous metal concentrations have returned to normal, loss of metals from plants will occur, at a rate dependent on the length of exposure to elevated concentrations of metals in water.

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APPENDIX

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APPENDIX 1: Preliminary survey: Concentration of metals (mg l⁻¹) in
total water samples collected on 27 April 1982.

| SITE NAME | SITE CODE | Ca | Zn | Fe | Ba | Pb |
|---------------------|-----------|------|-------|-------|-------|-------|
| BLEABERRY GILL | 0212-15 | 17.1 | 0.108 | 1.662 | 0.496 | 0.034 |
| BLEABERRY GILL | 0212-18 | 15.1 | 0.085 | 1.820 | 0.443 | 0.067 |
| WETSHAW BOTTOM | 0322-50 | ND | 0.045 | 1.186 | 0.449 | 0.034 |
| FOURTH WHIM GILL | 0326-50 | 37.3 | 0.490 | 0.770 | 3.250 | 0.113 |
| BLEABERRY GILL | 0212-20 | 19.9 | 0.105 | 0.668 | 1.583 | 0.048 |
| BLEABERRY GILL | 0212-24 | 1.92 | 0.033 | 1.296 | 0.153 | 0.011 |
| BLEABERRY GILL | 0212-26 | 4.44 | 0.045 | 1.150 | 0.739 | 0.023 |
| SURRENDER MOSS GILL | 0348-99 | 18.9 | 0.014 | 11.2 | 0.372 | 0.007 |
| BLEABERRY GILL | 0212-30 | 12.2 | 0.043 | 7.135 | 0.697 | 0.021 |
| BLEABERRY GILL | 0212-32 | 12.8 | 0.038 | 4.820 | 0.723 | 0.029 |
| BLEABERRY GILL | 0212-36 | 12.3 | 0.038 | 2.310 | 0.644 | 0.044 |
| BLEABERRY GILL | 0212-38 | 8.70 | 0.040 | 1.116 | 0.697 | 0.058 |
| MOSSY THORN SEEPAGE | 0349-50 | 4.80 | 0.050 | 0.046 | 0.264 | 0.006 |
| BLEABERRY GILL | 0212-39 | 6.20 | 0.043 | 0.586 | 0.475 | 0.031 |
| BLEABERRY GILL | 0212-42 | 8.60 | 0.030 | 0.570 | 0.818 | 0.037 |
| BLEABERRY GILL | 0212-45 | 9.90 | 0.033 | 0.490 | 0.882 | 0.034 |
| MOSSY THORN GILL | 0350-50 | 45.0 | 0.030 | 0.050 | 0.342 | 0.047 |
| BLEABERRY GILL | 0212-46 | 23.2 | 0.035 | 0.330 | 0.523 | 0.028 |
| BLEABERRY GILL | 0212-49 | 22.1 | 0.035 | 0.260 | 0.686 | 0.027 |
| BLEABERRY GILL | 0212-55 | 23.0 | 0.043 | 0.210 | 0.768 | 0.023 |
| BLEABERRY GILL | 0212-60 | 25.2 | 0.035 | 0.186 | 0.717 | 0.021 |
| BLEABERRY GILL | 0212-75 | 26.4 | 0.050 | 0.132 | 0.778 | 0.040 |
| BLEABERRY GILL | 0212-80 | 28.8 | 0.045 | 0.114 | 0.717 | 0.022 |
| BLEABERRY GILL | 0212-90 | 28.6 | 0.036 | 0.110 | 0.799 | 0.043 |
| BLEABERRY GILL | 0212-99 | 29.2 | 0.035 | 0.076 | 0.717 | 0.042 |
| OLD GANG BECK | 0374-99 | 55.0 | 0.145 | 0.036 | 1.523 | 0.116 |
| BARNEY BECK | 0198-01 | 46.0 | 0.130 | 0.044 | 1.290 | 0.093 |

ND = not determined.

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APPENDIX 2: Mean concentrations ($\mu\text{g g}^{-1}$) of metals in samples of Hygrohypnum ochraceum collected during transplant experiments.

a) Experiment 1

| Time (h) | Ca | Zn | Ba |
|------------------------|-------|------|-------|
| 0.0 | 7720 | 265 | 684 |
| 0.5 | 8244 | 352 | 1481 |
| 1.0 | 8550 | 455 | 1638 |
| 1.5 | 9720 | 484 | 2090 |
| 2.0 | 9750 | 651 | 2290 |
| 3.0 | 8705 | 637 | 2246 |
| 4.0 | 9920 | 761 | 2760 |
| 6.0 | 9120 | 719 | 2150 |
| 9.0 | 8872 | 949 | 2640 |
| 12.0 | 8820 | 1090 | 2510 |
| 27.0 | 9130 | 914 | 2843 |
| 3.5 control | 19220 | 2349 | 10530 |
| 27.0 (0366) | 18640 | 2522 | 10680 |
| 11.0 control (0371) | 6753 | 174 | 379 |

b) Experiment 2

| Time (h) | Ca | Zn | Ba | Pb |
|-------------|-------|------|-------|------|
| 0.0 | 13100 | 1187 | 9071 | 2357 |
| 1.0 | 12600 | 1330 | 11600 | 2260 |
| 1.5 | 12300 | 1200 | 12300 | 1790 |
| 2.0 | 12700 | 1270 | 8600 | 1640 |
| 3.0 | 13180 | 1563 | 10850 | 2159 |
| 4.0 | 14700 | 1400 | 11400 | 2900 |
| 6.0 | 12200 | 1370 | 10100 | 1660 |
| 9.0 | 13630 | 1696 | 11920 | 2465 |
| 12.0 | 14300 | 1360 | 10600 | 2100 |
| 27.0 | 13740 | 1664 | 10840 | 1400 |
| 0.0 control | 11830 | 1322 | 5330 | 1658 |
| 27.0 (0212) | 13240 | 1354 | 8507 | 1840 |
| 0.0 control | 17820 | 2324 | 12540 | 775 |
| 27.0 (0366) | 18490 | 2160 | 11020 | 633 |

c) Experiment 3

| Time (h) | Ca | Zn | Ba | Pb |
|-------------|-------|------|-------|------|
| 0.0 | 12200 | 2094 | 11310 | 1575 |
| 2.0 | 11800 | 2140 | 9000 | 1610 |
| 4.0 | 11900 | 2100 | 9970 | 1310 |
| 6.0 | 8900 | 1100 | 3040 | 1160 |
| 8.0 | 14400 | 3020 | 13300 | 6500 |
| 12.0 | 12600 | 2160 | 6970 | 1220 |
| 24.0 | 12100 | 2180 | 7700 | 1560 |
| 48.0 | 11450 | 1699 | 6033 | 1085 |
| 96.0 | 11300 | 1550 | 6900 | 1086 |
| 144.0 | 9190 | 1116 | 3924 | 959 |
| 0.0 control | 9034 | 933 | 2563 | 911 |
| 48.0 (0212) | 9768 | 835 | 2588 | 794 |
| 144.0 | 8458 | 961 | 2445 | 845 |

d) Experiment 4

| Time (h) | Ca | Zn | Ba | Pb |
|---------------|-------|------|------|------|
| 0.0 | 10760 | 1355 | 7492 | 1126 |
| 1.0 | 9880 | 1120 | 2780 | 688 |
| 2.0 | 8610 | 923 | 2480 | 677 |
| 4.0 | 8790 | 1200 | 2030 | 809 |
| 9.0 | 8933 | 909 | 2100 | 745 |
| 12.0 | 10200 | 1080 | 2320 | 949 |
| 25.0 | 8424 | 896 | 2148 | 956 |
| 48.0 | 7760 | 932 | 2570 | 917 |
| -12.0 control | 8129 | 858 | 2393 | 1046 |
| 25.0 (0212) | 9768 | 835 | 2588 | 794 |

