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ACCUMULATION OF HEAVY METALS BY ORGANISMS IN THE DERWENT CATCHMENT

By

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(B. Sc. Reading)

A thesis submitted for the degree of
Master of Science
in the University of Durham

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This thesis results entirely from my own work and has not previously been offered in candidature for any other degree or diploma.

I G Burrows

I. G. Burrows
October 1981

ABSTRACT

The distribution of Zn, Cd and Pb in water, sediments, plants and animals from the River Derwent and Derwent Reservoir was studied during four periods of intensive survey between October 1978 and November 1979.

Elevated concentrations of Zn, Cd and Pb were found in all components from the river below the entry of a polluted tributary, Bolts Burn. Concentrations of Zn in river sediments from above Bolts Burn and Zn and Cd from below were found to show significant positive correlations with the organic content of sediments. It is suggested that autumn shed leaves may exert considerable influence on the metal composition of river sediments during decomposition and may cause an increase in the amount of metal potentially available to detritivorous invertebrates in their food.

Marked variations were observed in concentrations of Zn, Cd and Pb in plants and animals from the river between reaches and surveys. Among the animals, mayflies as a group had especially high concentrations of metals and Zn, Cd and Pb were frequently higher in samples of these from the river above Bolts Burn than in many other animals from below this stream.

Metal pollution was shown to extend into the Derwent Reservoir. Elevated concentrations of Zn and Pb evident in water, sediments and submerged plants near the entry of the river were found to decrease on passing towards the dam.

Comparisons between metal concentrations in the biota and those in their environment made it possible to assess possible importance of water and sediments as sources from which metals may be accumulated.

ABBREVIATIONS

min	minute
h	hour
My	million years
nm	nanometres
µm	micrometre
mm	millimetre
cm	centimetre
m	metre
km	kilometre
ha	hectare
ml	millilitres
l	litre
µg	microgramme
mg	milligramme
g	gramme
°C	degrees Celcius
n	number of measurements
$\bar{x}$	mean value
s.d.	standard deviation
c.v.	coefficient of variation
P	probability
r.p.m.	revolutions per minute
cond.	conductivity
tot. alk.	total alkalinity
V/V	volume for volume
T and 'total'	water sample decanted from 2 l beaker after standing for 5 min
F and 'filtrable'	water sample capable of passing through Nuclepore filter of pore size 0.2 µm

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CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Previous studies have shown that the River Derwent below the entry of Bolts Burn carries elevated levels of Zn, Cd and Pb (Harding, 1978; Harding and Whitton, 1978; 1981). The metals are transported by the river and influence the chemistry of the water and sediments in the Derwent Reservoir. Deposition of metals takes place on passing down the reservoir, with Pb entering the sediments most rapidly and Zn least rapidly. Concentrations of metals in water leaving the reservoir are similar to those in the 'unpolluted' section of the R. Derwent upstream of its confluence with Bolts Burn. Thus, the reservoir acts as a 'trap' for the metals. The alga *Lemanea* and several species of bryophyte growing in the river, and the alga *Nitella flexilis* and the grass *Glyceria fluitans* growing in the reservoir are all known to concentrate heavy metals to high levels.

The reservoir is used as a 'put and take' trout fishery and is stocked with brown and rainbow trout. Following the previous studies there was increased concern about the possibility that trout in the reservoir might accumulate heavy metals from their food. It was with this in mind that the Northumbrian Water Authority and the Sunderland and South Shields Water Company jointly commissioned an investigation to determine the levels of metals in invertebrates which may constitute the food organisms of trout in the R. Derwent and Derwent Reservoir and to compare the levels of environmental contamination with the earlier studies.

Examples of such broad studies published in the literature have involved large research teams *e.g.* that of the 'New Lead Belt' of

Missouri (see Wixson, 1977) or the Melimex project on heavy metals in Lake Baldegg (summarized by Gächter, 1979). Harding (1978), discussing such investigations noted that "Even comprehensive studies ... may fail to present sufficient detail regarding certain essential considerations" and "... analyses of water are often of limited value because they refer to a single collection and take no account of temporal variations caused by discharge, seasonal or diurnal fluctuations or changing inputs from artificial sources." The present study was commissioned for the period September 1978 to December 1979. It was a challenge to review previous research and to consider the best ways of combining the approach necessary to fulfil the requirements of the water management project with the one to carry out more fundamental research.

1.2 HEAVY METALS IN THE AQUATIC ENVIRONMENT

1.21 General Introduction

Interest in heavy metals in aquatic systems has increased rapidly in recent years and this has resulted in a substantial volume of literature on numerous aspects of heavy metals in the aquatic environment. Only a small portion of the literature can be reviewed here and only that most relevant to the present study has been considered. Many areas have as a consequence been left uncovered but reference has been made to papers containing further detailed information.

The hydrogeochemistry of heavy metals has been investigated by many workers. One of the most recent and comprehensive reviews on heavy metals in the aquatic environment is that of Förstner and Wittmann (1979). Although this deals especially with hydrogeochemistry, information on the toxicity and bioaccumulation of heavy metals in freshwater and marine environments is given and an extensive bibliography included.

1.22 Plants

It is not within the scope of the present work to review the many aspects of the relationship between heavy metals in plants and their environment and so discussion here will be limited to brief consideration of heavy metal accumulation by aquatic macrophytes.

The literature abounds with evidence that increased concentrations of heavy metals in the environment result in elevated concentrations in plants. Many of the studies have been carried out on streams and rivers and have focused on bryophytes. For example, Harding (1978) reported that levels of Zn, Cd and Pb in the moss *Hygrohypnum ochraceum* and the liverwort *Scapania undulata* collected from a heavy metal contaminated reach on the R. Derwent were higher than in samples collected from an 'unpolluted' reach. Similar observations were made by Burton and Peterson (1979) who investigated the levels of Zn and Pb in aquatic bryophytes from upland streams of a lead-zinc mining area in Dyfed, Wales. They found that plants growing in streams carrying effluent from old mine workings had higher levels of both metals than plants collected from uncontaminated streams in the same area. Several authors have examined the relationship between metal concentrations in the environment and in bryophytes more closely. McLean and Jones (1975) found metal extracts (especially Pb) of *Scapania undulata* from contaminated reaches on the rivers Ystwyth and Clarach, Wales, mirrored variations in metal concentrations of the water. They suggested the possible value of this plant as a monitor of metal concentrations in water. Perhaps the most detailed studies of this kind are those of Empain (1976a, 1976b) who analyzed bryophytes from three rivers in Belgium. He reported good correlations between concentrations of Zn in water and the bryophytes *Rhynchostegium (Platyhypnidum) riparioides*, *Cinclidotus nigricans* and *Fontinalis antipyretica*. His data indicate that these plants may be of use as monitors of zinc pollution. It has been shown that metal concentrations in other river plants are influenced by concentrations in their environment. For example, concentrations of Ni, Co and Cu in *Myriophyllum verticillatum* from the Moira River, Canada, were shown to be related to those of the sediment (Mudroch and Capobianco, 1979) and Harding and Whitton (1981) found linear relationships between the logarithm of the concentrations of Zn, Cd and Pb in 2 cm tips of the alga *Lemanea fluviatilis* and the logarithm of the metal concentrations in water. Studies such as these have led to consideration of the use of plants as indicators of river water quality with respect to heavy metals (Whitton, 1979).

Some interesting reports on heavy metal accumulation by plants from contaminated lakes have also been published. The sediments and the surrounding water are frequently considered as the sources from which plants may accumulate heavy metals. Roots are thought to be important in metal uptake from sediments while shoots are favoured for uptake from water. Harding and Whitton (1978), for example, investigated Zn, Cd and Pb in water, sediments and the submerged plants *Nitella flexilis* and *Glyceria fluitans* in the Derwent Reservoir. They considered that *N. flexilis*, which has no proper root system, probably accumulated almost all of its metal content from the water while sediments were likely to be a source of at least some of the heavy metals accumulated by rooted plants of *G. fluitans*.

Welsh and Denny (1980) found positive correlations between Pb and Cu concentrations in submerged shoots of aquatic macrophytes and in the underlying sediments collected from a number of sites on Ullswater and Coniston Water in the English Lake District, but were unable to demonstrate similar correlations between shoots and lake water. It was suggested that water must be the primary or only source of metals for non-rooted plants. High levels of Pb in the shoots of rooted plants were attributed to adsorption from the surrounding water and a loss of Pb from sediments to the immediately-overlying water was suggested to be part of this process. High levels of Cu in shoots were considered to be caused in part by the same mechanism but it was considered that a translocation pathway from roots to shoots was also involved.

The mechanisms thought to be involved in metal uptake and loss by aquatic plants have been discussed in a number of the studies outlined above including that of Harding and Whitton (1981) in which the influence of various substances on the loss of Zn from *Lemanea* filaments was also considered. Many aspects of metal uptake, loss and movement by submerged angiosperms have been considered by Denny (1980) in a review which '... attempts to assemble the information which may contribute to a clearer understanding of absorption, translocation, accumulation and excretion of solutes by submerged rooted aquatic vascular plants.'

Several authors have discussed the role of plants in cycling metals within lake systems. The release of metals to water from sediments by plants was considered by both Harding and Whitton (1978) and Welsh and Denny (1976, 1980) but neither presented data to indicate what effects such release might have on the concentration of metal in the lake water. McIntosh, Shephard, Mayes, Atchison and Nelson (1978) measured the levels of Cd in *Potamogeton crispus* in Lake Palestine, Indiana, and also estimated the quantity of plant material and the volume of water in the lake. They calculated that if all the Cd bound up in all the plants in the lake was to be released simultaneously during a sudden plant 'die-off' the concentration of Cd in the lake water would increase by between 0.3 and 1.0 $\mu g\ l^{-1}$. During the study Cd levels in the water ranged from 0.5 - 2.5 $\mu g\ l^{-1}$ and as the possibility of such a release occurring was very slight, the problem was not considered serious. Nevertheless, the authors point out the possibility that significant effects might occur locally during rapid decay of highly contaminated plant material, especially in sheltered areas with very little mixing of the water. In such an event both the flora and fauna could be seriously affected.

1.23 Animals

1.231 Introduction

The interactions between heavy metals and freshwater aquatic invertebrates have been studied for many years. Early studies were concerned with the effects of metals on the distribution of invertebrates, but present-day interests range from surveys of the mineral composition of animals in different environments to detailed investigations of the mechanisms involved in metal uptake and loss and the factors which influence them. All of these are considered below, but heavy metal toxicity is not discussed as this subject has been dealt with in two early reviews (Doudoroff and Katz, 1953; Skidmore, 1964) and more recent research papers with useful comments in the literature (Bengtsson, 1978; Benoit, Leonard, Christensen and Fiandt, 1976; Cearley and Coleman, 1974; Clubb, Gaufin and Lords, 1975a; Eisler, 1977; Khangarot and Rajbanshi, 1979; Rao and Saxena, 1981; Rehwoldt, Lask, Shaw and Wirhowski, 1973; Solbé and Flook, 1975; Spehar, 1976; Warnick and Bell, 1969).

1.232 Mechanisms of heavy metal uptake and loss

Aquatic invertebrates living in a heavy metal contaminated environment may be exposed to metals in their food, the surrounding water and the sediments. Each represents a potential source from which metals may be taken up and the mechanisms of uptake are likely to differ according to the source of the metal and the species of animal considered.

Detailed investigations into the mechanisms of metal uptake and loss by freshwater invertebrates have been few, although marine species have received more attention (see reviews of Bryan, 1976; Förstner and Wittmann, 1979). The majority of investigations involving freshwater invertebrates have been restricted to demonstration of metal uptake or loss by an active or passive process. Metal exchange with the surrounding water has received most attention which is perhaps not surprising in view of the following considerations:

i) water is usually the primary contaminated medium in polluted aquatic environments

ii) water-borne metals are potentially a source common to all invertebrates

iii) the chemistry of metals in water is better understood and may be more readily manipulated in a controlled manner than other potential sources

One of the earliest laboratory investigations into the accumulation of metals by freshwater invertebrates is that of Getsova and Valkova (1962). Using solutions of radioisotopes maintained at 16°C and 22°C, they exposed larvae of Odonata, Trichoptera and Diptera to various metals, including ^{59}Fe, ^{65}Zn, ^{115}Cd. Different species accumulated a given element in different amounts and different elements accumulated to different levels by a given species. The authors recognized the possibility that uptake mechanisms may differ between insect species and suggested that metal uptake from solution may be related, at least in part, to metabolic activity. They urged that future research be directed towards identifying the nature of sorption, mineral exchange and the mechanisms of accumulation.

Kormondy (1965) studied the uptake and loss of ^{65}Zn by the dragonfly *Plathemis lydia* in a static exposure system. Equilibrium between ^{65}Zn in solution and larvae was attained within 24 - 48 hours and 95% of the initial activity associated with contaminated larvae remained on the cast exuvium at moulting. It was concluded that metal uptake was by surface adsorption or cation exchange. A comparison was made between the rate of loss of ^{65}Zn from live and dead larvae; rates were found to be the same under laboratory and field conditions indicating that metal was lost by a passive process.

More recently, Dodge and Theis (1979) reported that when larvae of the midge *Chironomus tentans* were exposed to solutions containing copper, mainly in the form of cupric ions, live and dead larvae both took up the metal, although the level was always lower in the latter. The authors suggested that uptake of copper from solution by *C. tentans* was largely passive, involving chemical interactions between ionic copper and sorption sites at the surface or interior of the organism but did not discount the possibility that another mechanism, in some way connected with metabolic activity, may also be involved in metal uptake.

Indirect evidence that metal uptake by aquatic insects may at least in part be an active process was produced by Clubb, Gaufin and Lords (1975b). These workers exposed larvae of the mayfly *Emphemerella grandis*, the stonefly *Pteronarcella badia* and the caddisfly *Brachycentrus americanus* to 5.0 mg l^{-1} Cd at three different oxygen concentrations in a continuous flow bioassay. The concentration of Cd in larvae harvested after four days exposure related positively to the oxygen concentration at which they had been maintained. The authors explained that oxygen consumption by the larvae of mayflies and stoneflies had been shown by other workers to increase as the dissolved oxygen concentration was increased and that increased oxygen consumption is accepted as being indicative of increased metabolic activity; they concluded that absorption of Cd from solution by larvae of aquatic insects may be coupled to the organism's metabolic activity.

In perhaps the most critical study of metal uptake and loss so far reported for an aquatic insect, Carter and Nicholas (1978) demonstrated metabolism to be important in the uptake of zinc by larvae of the midge *Simulium ornatipes*. Passive ion exchange was unimportant in the loss of zinc by this organism and the authors suggested that the metal must be lost by an active process such as excretion. Having fractionated larvae into three components based on their solubility in water and 80% (V/V) ethanol the distribution of zinc within the fractions was examined using larvae exposed to ^{65}Zn under different conditions. The fractions were as follows: water insoluble constituents - the 'cuticle' fraction (cuticle, gut contents and cellular debris); water soluble-ethanol soluble constituents - the 'low molecular weight' fraction (low molecular weight compounds, *e.g.* amino acids, simple sugars, simple fatty acids); water soluble-ethanol insoluble constituents - the 'high molecular weight' fraction (high molecular weight compounds, *e.g.* proteins, polysaccharides, high molecular weight lipids). Two zinc pools were identified within the cuticle and high molecular weight fractions, one in which zinc was held weakly and exchanged rapidly with zinc in solution and another in which zinc was more firmly held and exchanged slowly. The results of washing samples with a series of buffers indicated that zinc was bound by phenolic groups in the cuticle fraction and by phosphoric acids in the high molecular weight fraction. Results of experiments carried out at different temperatures and zinc concentrations led the authors to suggest that absorbed zinc may be associated initially with the low molecular weight fraction and then later transferred to the cuticle and high molecular weight fractions as tissue synthesis progresses. It seems likely that larvae living in a stream receiving intermittent discharges of zinc would retain metal in their tissues long after the pollutant had been carried downstream and thus represent a continued source of zinc for predators.

Although investigations into mechanisms of metal uptake in freshwater invertebrates have concentrated on insects, several workers have considered other invertebrate groups. Freshwater snails have been studied by several workers. Yager and Harry (1964) investigated the uptake of radioactive zinc, cadmium and copper by *Taphius glabratus*. Their data indicate adsorption to be important in the uptake and loss of metal by the shell in this organism and they suggest several routes for metal absorption from solution:

i) through the epithelium of the exposed soft tissue
ii) through the wall of the digestive tract from fluid which entered through the mouth
iii) through the shell, or under the shell and into the animal through the underlying mantle epithelium

Metal absorption by the first route was considered to be the most probable; it is however not possible to assess the importance of each route from the data presented. Wier and Walter (1976) reported that *Physa gyrina* took up cadmium from solution at almost twice the rate at which the metal was eliminated when contaminated animals were transferred to clean water. They suggested that the difference between the two rates may be due to binding mechanisms similar to those discovered in mammals, *e.g.* the bonding of metal ions to sulphydryl groups of proteins.

A study of cadmium uptake by the amphipod *Gammarus pulex* has recently been reported by Wright (1980), who exposed intermoult specimens to ^{109}Cd in artificial stream water. Metal uptake was reduced by 80% when the animals were exposed to the metabolic inhibitor 2:4 dinitrophenol prior to cadmium exposure and adsorption of cadmium to the exoskeleton contributed only a small proportion of the metal taken up by the animal as a whole. Thus it appears the uptake of cadmium in this species is largely an active process. The author suggested that cadmium accumulation may be accounted for by a process of 'accidental' active cadmium uptake associated with the calcium regulatory mechanism in which cadmium substitutes for calcium.

The uptake of heavy metals by aquatic oligochaetes has been considered by several workers; nevertheless the mechanisms of uptake still remain largely unexplained. Dean (1974) demonstrated the uptake of ^{65}Zn by (unidentified) tubificid worms from solutions prepared in the laboratory. He also exposed worms to river water contaminated by radionuclides from reactor effluent and found that ^{51}Cr, ^{60}Co, ^{65}Zn and ^{195}Zr - Nb had been taken up from the water after 30 days. In a further experiment tubificids were exposed to radionuclide contaminated river sediments for 70 days, when the worms were removed and divided into two groups, with and without gut contents. The former were contaminated with ^{65}Zn and ^{59}Fe but, surprisingly, no radionuclides were detected in the latter, thus indicating that metals had not been transferred to the worms from the sediment in spite of the long exposure period. Dean concluded that metal uptake from sediments was unimportant and suggested that the direct uptake of dissolved radionuclides from water by physical or biological mechanisms was the only significant route of metal accumulation in aquatic oligochaetes. Nevertheless, tubificid worms have been demonstrated to take up heavy metals from their food. Patrick and Loutit (1976) carried out experiments in which worms were fed bacteria cultured in either a medium enriched with Cr, Cu, Mn, Fe, Pb and Zn, or in an uncontaminated medium. Worms were fed contaminated or uncontaminated bacteria for seven days, after which time the worms were collected, allowed to empty their intestinal tracts and analysed. The concentrations of all the metals added to the bacteria culture medium were higher in worms fed on contaminated bacteria, indicating the passage of metals from the bacteria to the worms. The uptake of the metals is likely to have involved their passage across the wall of the gut by active or passive processes but details of such mechanisms have not yet been reported. However, Say and Giani (1981) examined the distribution of zinc in Oligochaetes collected from several zinc polluted rivers and found localized deposits of this metal in the region of the chloragogen tissue surrounding the intestinal tract. The chloragogen cells in oligochaetes play an important role in intermediary metabolism, similar to the role of the liver in vertebrates, and their close association with the gut highlights the possibility that chloragogen tissue may be intimately involved in processes such as metal uptake, storage, detoxification and excretion.

1.233 Factors affecting heavy metal uptake and loss

In the previous section (1.232) the mechanisms by which freshwater invertebrates exchange heavy metals with their environment were discussed briefly and it was noted that only a few species have been studied in detail. Some of these studies report data on the influence of environmental and biological factors on metal uptake and loss. These and other studies are described below.

1.2331 Physical and chemical factors

This section is concerned only with metal uptake and loss from solution, but it seems likely that some of the principles outlined may apply to metal accumulation from other sources.

Nature and duration of exposure

Many studies have been documented on the uptake and loss of heavy metals by aquatic invertebrates and from these it is clear that the duration of exposure to solutions of heavy metals influences the levels to which they are concentrated by animals. The general pattern of metal accumulation observed is one of an increasing concentration of metal in the test organism as exposure proceeds, with the metal level increasing by successively smaller amounts per unit time. Accordingly some workers have reported that metal concentrations in experimental animals ceased to increase after a given time and that equilibrium was reached. For example, Kormondy (1965) reported that equilibrium was attained after 24 - 48 hours in experiments on ^{65}Zn uptake and loss by nymphs of the dragonfly *Plathemis lydia*. Similarly Kinkade and Erdman (1975), in a study of Cd uptake by organisms in a simulated freshwater ecosystem, found that concentrations of Cd in the snail *Ampullaria paludosa*, the catfish *Corydoras punctatus* and the guppy *Lebistes reticulatus* tended towards equilibrium as the experiment progressed. Both studies were carried out in closed systems where the dosing solutions were not replenished. The latter authors noted a rapid initial loss of metal from solution with the concentration tending towards a constant level as the experiment progressed. Thus the equilibria reported for the metal levels in the animals appear to represent the limit of uptake within the exposure systems employed rather than the limit of the metal concentrating capacity of the experimental animals.

Experiments in which dosing solutions have been renewed have shown that following a rapid initial increase in the concentration of metal in the test organism the rate accumulation settles to a near constant rate. For example, Gillespie, Reisine and Massaro (1977) exposed the crayfish *Oreonectes propinquus* to solutions of 100 and 1000 μg l^{-1} ^{109}Cd which were renewed after 96 hours. They found that the rate of accumulation decreased during the first 20 hours exposure whereafter the rate remained constant with no indication of further reduction when the experiment was terminated after 200 hours. Dean (1974) found little reduction in the rate of ^{65}Zn from contaminated well water by tubificid worms after 216 hours exposure. In his experiments, solutions were changed every other day and the volume of the exposure system was such that there was little change in zinc concentration between solution changes.

Dean's results appear to differ from the general pattern of accumulation outlined earlier. It is possible that the pattern of metal accumulation differs between organisms or perhaps some take longer to reach equilibrium than others, if they reach equilibrium at all. In order to answer this, experiments would need to be carried out over longer periods of time with different organisms exposed to metals under the same conditions. Nevertheless, the data reported in the literature give an indication of the pattern of metal concentration one might expect to observe in organisms exposed to intermittent metal discharges.

Concentration of metal to which invertebrates are exposed

The concentrations of metals in freshwater invertebrates have been shown by many workers to be related positively to metal levels in the solutions to which the animals have been exposed and it has been established as a general principle that increased metal levels in solution give rise to higher concentrations in the invertebrates. However, the relationship is not a simple one, and may be affected by many environmental and biological factors.

Gillespie *et al.* (1977) found that the rate of accumulation of

^{109}Cd by the crayfish *Oreonectes propinquus*, after 190.5 hours of exposure to solutions of 0.01, 0.1 and 1.0 µg g^{-1} was higher for the more concentrated solutions. The 190.5 hours tissue concentrations of Cd for 10 and 1,000 µg l^{-1} solutions were reported as 18.4 µg g^{-1} and 534.4 µg g^{-1} (both wet weight) respectively. The authors reported a significant ($P < 0.01$) difference in the final tissue concentration of Cd in crayfish from the 1,000 µg l^{-1} solution compared with crayfish from the two lower concentration solutions but found no such differences between animals from these two solutions. Successive 10 fold increases in metal concentration in the dosing solutions did not give rise to corresponding changes in metal concentrations in the exposed animals. Spehar, Anderson and Fiandt (1978) have shown that this applies also to the uptake of Cd by the stonefly *Pteronarcys dorsata* and the caddisfly *Hydropsyche betteni*. Nehring (1976) found that accumulation of Cu, Zn, Pb and Ag by nymphs of the mayfly *Ephemerella grandis* and the stonefly *Pteronarcys californica* increased as the concentration of the dosing solution was increased. Similarly, Thorp, Giesy and Wineriter (1979) reported a positive relationship between levels of Cd in the crayfish *Cambarus latimanus* and the solutions in which they had been exposed.

In most reports on the accumulation of heavy metals by aquatic invertebrates, the metal concentration given for the solutions to which the animals were exposed refers to the total concentration of the metal dissolved in the dosing solution and takes no account of the chemical form of the metal. Data reported by Dodge and Theis (1979) suggest that knowledge of the chemical form of a metal in solution may be of greater importance than the total concentration of the metal. These workers exposed larvae of the midge *Chironomus tentans* to five solutions of Cu all having the same concentration of soluble Cu and arranged that the chemical speciation of the metal in each solution differed. Cu was concentrated most readily by the larvae when free cupric ions and a copper-hydroxy complex were the dominant forms of the metal and no significant uptake took place when copper-glycine and copper nitrilotriacetic acid were dominant. Although the importance of chemical speciation of metals in solution has been recognised in toxicity studies where it has frequently been demonstrated that the ionic form of metals is the most toxic to aquatic invertebrates, investigators have been slow to appreciate the importance of chemical speciation in work on metal accumulation. The study of Dodge and Theis appears to be the only one of its kind reported in the literature and their results clearly indicate the need for further investigations to be carried out on this aspect of metal uptake by aquatic invertebrates.

Temperature and oxygen

The body temperature of aquatic invertebrates is dependent on the temperature of their environment and the rate at which their metabolic processes continue is related positively to their body temperature. Thus, the higher rates of metal uptake at elevated temperatures noted by several workers have been used as evidence that metal uptake may be, at least in part, a biologically active process (see Section 1.232).

Dean (1974) found that tubificid worms maintained in ^{65}Zn solutions at 15°C had higher body concentrations of the metal after 9 days exposure than animals kept at 6°C and lower body concentrations than worms maintained at 25°C even though the concentration of Zn was the same at each temperature. He concluded that a biological mechanism was involved in metal uptake by tubificid worms. Similarly, larvae of the blackfly *Simulium ornatipes* maintained at 20°C concentrated ^{65}Zn to a higher level than larvae maintained at 0°C (Carter and Nicholas, 1979).

Oxygen has been linked to metal accumulation by aquatic invertebrates in both field and laboratory studies. The laboratory study of Clubb *et al.*

(1975b) was described in Section 1.232. Karbe, Antonacopoulos and Schnier (1975) reported a field study on the influence of water quality on accumulation of heavy metals by three species of mussels and found a tentative correlation between oxygen saturation and metal accumulation.

The information available thus suggests that both elevated temperatures and increased levels of oxygen cause an increase in the level to which aquatic invertebrates accumulate heavy metals; however the extent to which the two factors interact under natural conditions is uncertain.

Other metals

It has been known for many years that increased water hardness confers protection against heavy metal toxicity and it has become clear in more recent years that it also influences heavy metal uptake and loss. Kinkade and Erdman (1975) investigated the influence of hardness components (Ca^{2+} and Mg^{2+}) in water on the uptake and concentration of ^{115}Cd in a simulated freshwater ecosystem which included infusoria snails *Ampullaria poludosa*, catfish *Corydoras punctatus* and guppies *Lebistes reticulatus*. Two systems were set up in 1 litre plastic containers at an initial concentration of 0.1 mg l^{-1} Cd, one as a soft water system (total Mg^{2+} and Ca^{2+} of 0 mg l^{-1}) the other as a hard water system (total Mg^{2+} and Ca^{2+} approximately 150 mg l^{-1}). Initial uptake of Cd was generally faster in hard water than in soft water but after 21 days Cd levels were highest in animals cultured in soft water. The hardness component influenced both the rate of uptake and the total residues of Cd in the test organisms. Wright (1980) also investigated Cd and Ca interactions, in this case on the amphipod *Gammarus pulex*; he was unable to find any clear relationship between the rate of whole body Cd uptake and the external concentration of Ca.

Carter and Nicholas (1978) reported that Ca^{2+} at concentrations of 50 mg l^{-1} and 100 mg l^{-1} did not affect the accumulation of Zn by larvae of the blackfly *Simulium ornatipes* from 0.1 mg l^{-1} Zn^{2+} over a 24 hour period. They also found that Ca^{2+} had no effect on the loss of Zn from blackfly larvae. These workers also investigated the effect of Zn^{2+} on the loss of Zn from blackfly larvae and found that Zn loss was not influenced by the presence of Zn^{2+} in the surrounding medium. They suggested that loss of Zn must be an active process.

1.2332 Biological factors

It is evident from 1.2331 that physical and chemical factors influence the uptake and loss of metals by affecting a biological mechanism or function such as metabolic activity. Other, more strictly biological factors may also influence uptake and loss, as, for instance, the stage in the life cycle. Getsova and Volkova (1962) exposed 4th instar larvae and pupae of the midge *Culex pipiens* to ^{35}S, ^{45}Ca, ^{60}Co, ^{65}Zn, ^{90}Sr, ^{106}Ru, ^{137}Cs and ^{144}Ce. After 3 days exposure the concentrations of S, Co, Zn, Ru, Cs and Ce in larvae were higher than in pupae while the reverse was true for Ca and Sr. *Gammarus pulex* which has moulted recently, takes up Cd at a much faster rate than intermoult specimens (Wright, 1980). The author suggested that the calcium status of the organisms strongly influenced Cd uptake in this species. Anderson and Brower (1978) found no difference between males and females in the levels of Cd, Cu, Pb and Zn in three natural populations of the crayfish *Oreonectes virilis*. Similarly, Thorp, Giesy and Wineriter (1979) found no difference in the tissue concentrations of Cd in males and females of the crayfish *Cambarus latimanus*, which had been exposed to the metal for five months.

Accumulation of Cu and Pb by the crustacean *Asellus meridianus* is influenced by the tolerance of the animal to these metals (Brown, 1977a: 1978). Having previously (Brown, 1976) demonstrated Cu and Pb tolerance in one population of these organisms and lead tolerance only in a second population, she used these,along with animals from a third population which showed no tolerance to either metal, and investigated the uptake of Cu and Pb from water and food. All populations accumulated both metals from solution. Uptake of Pb by non-tolerant animals proceeded faster than in those from Pb tolerant populations. Pb tolerant animals accumulated Pb from Pb enriched food and Cu tolerant animals accumulated Cu from Cu enriched food, while non-tolerant animals showed no evidence of accumulating metals to which they were susceptible and died during the course of investigations. The rate or level of Pb accumulation from water or food were not different for animals tolerant to Cu and Pb and those tolerant to Pb only. It was suggested that metal tolerance may be associated with improved metal storage capability.

1.234 Observations on heavy metals and invertebrates in natural systems

Many of the early studies on heavy metals in aquatic systems were concerned with the effects of these pollutants on the composition of the invertebrate fauna (see Section 1.231). Streams draining moorland in (then) Cardiganshire (now Dyfed), Wales, received considerable attention, as many were polluted by base-metal mining operations.

Carpenter (1922, 1924) studied the River Rheidol and River Ystwyth and found that the fauna in reaches highly polluted by effluent from lead mines was limited to the larvae of a few species of aquatic insects. In surveys carried out before 1922 she found that even the fauna in the lower reaches of these rivers was severely reduced and noted the complete absence of Platyhelminths, Mollusca, Trichoptera, Crustacea, Oligochaeta and Hirudinea. Up to this time 14 species of insect larvae had been recorded from the lower Rheidol and only 9 species from the lower Ystwyth. By 1924, following the cessation of mining and ore dressing operations the fauna of both streams showed signs of recovery; 29 species were present in the Rheidol and 26 species in the Ystwyth. Carpenter recognized that the impoverished fauna of these streams was related to pollution by lead mining and ore dressing operations within their catchment areas and concluded that the presence of lead salts in a diffusable form was the causative factor. A further recovery by the fauna of the Rheidol up to 1932 was reported by Laurie and Jones (1938) who recorded 103 species in the lower reaches and in a survey carried out during 1947 and 1948 Jones (1949) found 191 species to be present including representatives of those groups previously noted by Carpenter as being absent.

Jones also documented the recovery of the fauna of the R. Ystwyth. He recorded 44 species in surveys carried out during 1939 and 1940 (Jones, 1940) and suggested that soluble zinc was probably more important than lead in limiting the fauna. By 1953, even though mine workings in the catchment had been inoperative for 35 years, the river still showed signs of pollution; levels of Zn in the water ranged from 0.2 - 0.7 mg l^{-1} while levels of Pb were negligible. The fauna was composed of at least 45 species and although, qualitatively, it compared favourably with unpolluted streams, the Oligochaeta, Hirudinea, Mollusca and Crustacea remained unrepresented and Trichoptera were rare (Jones, 1958). Jones also noted the absence of the small dytiscid beetles *Deronectes* and *Oreodytes*.

Recovery from heavy metal pollution would thus appear to be a slow process. However, observations made by Carpenter (1926) indicate that when adverse conditions no longer prevail, complete recovery of the fauna is possible in a relatively short period. She reported that in

1924, only six years after mining operations in the catchment area ceased, the previously polluted Marchant Brook had a fauna characteristic of a Cardiganshire moorland stream. This recovery was only short lived because mining activities recommenced in 1924 and a survey carried out during 1925 revealed that the fauna of the stream had been seriously affected; the mollusc *Ancylus fluviatilis*, which was common in unpolluted streams in the area but very sensitive to metal pollution, and all Trichoptera larvae had disappeared although the occurrence of Plecoptera and Ephemerid nymphs was unaffected.

Carpenter regarded the disappearance of molluscs from the fauna as the first index to the pollution of a stream by lead-mining while that of Trichoptera larvae marked the second phase. Carpenter's conclusions were similar to those of Ortmann (1909) who recognized the disappearance of molluscs and then crustacea as successive stages in the pollution of Pennsylvanian streams by mining operations.

The effects of heavy metal pollution on the composition of the invertebrate fauna of rivers continue to be reported. For example, Wurtz (1962) documented the elimination of mollusc populations from streams in the catchment of the Northwest Miramichi River, New Brunswick, Canada, during the dewatering operations of a base-metal (Zn, Pb, Cu) mine. Nicholas and Thomas (1978) found that heavy metal wastes from abandoned mines entering the Molonglo River, New South Wales, had almost eliminated the fauna from the river for many kilometres downstream. Occhiogrosso, Waller and Lauer (1979) investigated the effects of heavy metal contaminated sediments on the distribution of oligochaetes and chironomids in Foundry Cove on the Hudson River, New York; densities of these organisms were reduced in areas where contamination was greatest. In a study of the River Hayle, Cornwall, Brown (1977b) found that the number of taxa in the fauna was reduced at heavy metal polluted sites and Armitage (1980) recorded similar observations during his study of the River Nent in the Northern Pennines but was not always able to distinguish between the effects of heavy metal pollution and organic enrichment at some of the sites examined.

The effects of heavy metals on the composition of the fauna of lakes have received much less attention than that of rivers. This may be on account of the difficulties involved in separating the effects of metals from the influence of such variables as substratum, wave exposure, organic enrichment and the mixing profile of the water column during different seasons. In a study of the comparative effects of sediment and water contamination on the benthic invertebrates of four lakes in the Canadian subarctic, Moore, Beaubien and Sutherland (1979) found that the numbers of species of both molluscs and insects were lowest in those lakes where sediments were most highly contaminated by heavy metals. However, the authors did not attribute the observed distribution to heavy metal contamination alone but suggested that water hardness and winter mortality of organisms due to freezing were also involved.

Wentsel, McIntosh and Anderson (1977) investigated the effects of heavy metal contaminated sediments on the distribution of benthic invertebrates in Palestine Lake, Indiana. In general, densities of an oligochaete (*Limnodrilus* sp.) increased as the level of sediment contamination increased, while chironomid density decreased. The distribution of *Limnodrilus* was attributed to the elimination of competitors and predators by heavy metals, while the toxic effects of contaminated sediments were thought to determine chironomid distribution. Indeed contaminated sediments have been shown to influence the growth, emergence and distribution of chironomids from this lake in other studies (Wentsel, McIntosh and Atchison, 1977; Wentsel, McIntosh and McCafferty, 1978; Wentsel, McIntosh, McCafferty, Atchison and Anderson, 1977).

Field studies have also added to the laboratory information on environmental factors and metal composition described above (1.232, 1.233). Several species have been studied in detail, especially with a view to using the particular animal as a monitor of heavy metal pollution. Such use of an organism as a 'monitor' by virtue of metal levels in its tissues is based on the assumption that metal levels in the organism reflect environmental contamination. The approach has perhaps been used more often for plants than animals. Whitton (1975) in discussing the use of algae in studies of low level heavy metal pollution stated that "... analyses of plant material are of more value than that of the water, as the plants integrate events in the environment over long periods." There are advantages in using organisms as monitors where intermittent effluent discharges are involved because spot checks based on chemical analysis of single water samples may fail to detect contamination whereas elevated levels of metals are likely to persist in the biota long after the pollutants have been carried downstream. Before a plant or animal can be used as a monitor it is essential to have detailed information about the dynamic aspects of metal exchange between the organism and its environment.

The use of mussels as monitors of heavy metal pollution has received the attention of several workers who between them have discussed the advantages, disadvantages and associated problems at length (Clarke, Clarke and Wilson, 1976; Foster and Bates, 1978; Jones and Walker, 1979; Manly and George, 1977; Merlini, Cadario and Oregioni, 1978).

The use of aquatic insects as monitors of heavy metal pollution was investigated by Nehring (1976). Caged nymphs of the mayfly

Ephemerella grandis and the stonefly *Pteronarcys californica* concentrated metals in relative proportion to the occurrence of the metals in a stream by some predictable, reproducible factor and Nehring concluded that these insects may serve as effective biological monitors of heavy metal pollution. His data suggest that Zn levels in these organisms was very dependent on the levels in the surrounding water and support the view of Förstner and Wittmann (1979) that 'The heavy metal content of an organism should by no means be regarded as a constant value but rather as a factor subject to the influence of varying biotic and abiotic environmental conditions.'

Studies on heavy metal accumulation by natural populations of invertebrates from ponds and lakes have been fewer than for rivers but a series of investigations dealing with the levels of various pollutants, including As,Cd, Cu, Mn, Pb, Zn and Hg, in different components of several lentic systems in South Africa have been documented (Greichus, Greichus, Amman, Call, Hamman and Pott, 1977; Greichus, Greichus, Draayer and Marshall, 1978; Greichus, Greichus, Amman and Hopcraft, 1978). Concentrations of each metal were lower in water than any other component analysed, while metal concentrations in sediments were generally higher than in oligochaetes, chironomids and composite samples of other aquatic insects. Gommes and Muntau (1975) reported similar findings for the concentrations of Cu, Zn, Cr, Ni and Mn in water, sediments and oligochaetes collected from the littoral zone of southern Lake Maggiore. Here, highest concentrations of Cu and Zn were recorded in gastropods while concentrations of Mn in lamellibrancs were higher than in samples of any other material. Concentrations of other metals in these two groups of organisms were lower than in the sediments but higher than in water. In a later study of the distribution of Cd in the same lake, Gommes and Muntau (1976) reported metal concentrations in the sediment to be higher than in the water and found that Cd was accumulated to higher concentrations in the soft tissues of the molluscs *Unio* and *Viviparus* than in the shells of these animals.

Namminga, Scott and Burks (1974) studied the distribution of Cu, Pb and Zn in a pond ecosystem and found concentrations of all three metals in water samples to be lower than other components analysed. Concentrations of Cu and Zn were higher in the benthos than in the sediments while the opposite was true for Pb. There was no increase in the amount of metals associated with increasing trophic levels.

Of the rivers on which similar studies have been carried out, many have been slow flowing and contaminated by domestic and agricultural effluents as well as heavy metals. Investigations of such environments which have included metal analyses of invertebrates and other components of the river are those of Mathis and Cummings (1973), Namminga and Wilhm (1977), Anderson and Brower (1978) and Eyres and Pugh-Thomas (1978). As with the studies carried out on ponds and lakes the results of these investigations show that metal concentrations in water are exceeded by those in both invertebrates and sediments while the exact relationship between these components differs according to the organisms and metals considered. For example, Mathis and Cummings (1973) found higher concentrations of Zn in clams than in tubificid worms but observed that the opposite was true for Cr, Co, Ni, Cd and Pb. Namminga and Wilhm (1977) showed that concentration factors for Cu, Pb and Zn in chironomids exceeded factors for sediments (both compared with water) while Cr was less concentrated in the animals. Eyres and Pugh-Thomas (1978) studied the relationship between substrate and tissue concentrations of Pb, Cu and Zn in the leech *Erpobdella octoculata* and the crustacea *Asellus aquaticus*. They found that although metal concentrations were higher in *Asellus*, both organisms exhibited similar trends in the way tissue concentrations changed with increasing substrate concentrations of each metal.

Anderson (1977) reported the concentrations of Cd, Cu, Pb and Zn in 35 genera of freshwater invertebrates from the Fox River, Illinois and Wisconsin, but data were not given for the environmental levels of these metals. In general the order of the concentrations of metals in the animals was Zn $>$ Pb $>$ Cd. Mayflies had the highest concentrations of Zn, Cd and Pb although high Zn concentrations were also observed in caddisflies and clams. The highest concentrations of Cu occurred in crustaceans.

Few studies on the metal composition of the fauna of fast flowing streams have been reported possibly because such streams tend to be restricted to the upland parts of catchment areas where industrial pollution is less common. Enk and Mathis (1977) investigated the distribution of Cd and Pb in Jubilee Creek, Illinois, which drains a rural area and is unaffected by industrial effluents, though herbicide and pesticide run-off from farmland in the catchment probably occurs. Mayflies and damselflies contained the highest concentrations of Cd, while lower concentrations occurred in caddisflies. The concentrations of Cd in all the aquatic insects were higher than in sediments, which in turn had higher concentrations than the water. The distribution of Pb was different: all the insects had higher concentrations than the water but concentrations in the sediments were higher than in mayflies and one of the caddisflies. Pb concentrations in snails of the genus *Physa* were higher than in any other component analysed.

Fast flowing streams polluted by effluent from abandoned base-metal mines were studied by Brown (1977b) and Nicholas and Thomas (1978). The latter authors reported Zn concentrations in animals collected from the Molonglo River, New South Wales, over a three year period but did not include data on the environmental levels of Zn at the time samples of invertebrates were collected. Caddisflies were found to have the highest concentrations of Zn of any larvae examined although those in dragonfly pupal cases were the highest recorded for all the tissues analysed. Brown measured the concentrations of Cu, Zn and Fe in water, sediments and invertebrates from the River Hayle, Cornwall, at three different times of year. Metal concentrations were presented only for the higher taxonomic categories. In general, the highest metal concentrations were found in 'free-living' caddisfly larvae and significant correlations were found between levels of Cu and Zn in these animals and in the surrounding water. No comparisons were made between metal concentrations in animals collected at different times of year.

1.3 AIMS

The brief review of the literature presented in Section 1.2 reveals several areas where further research would be rewarding. The investigation commissioned by the Northumbrian Water Authority and the Sunderland and South Shields Water Company (Section 1.1) provided an opportunity to study a fast flowing nutrient poor river and an oligotrophic reservoir contaminated by heavy metals derived from mining operations.

It was decided that the aims of the project should be:

i) To examine the distribution of zinc, cadmium and lead in water, sediments, plants and benthic macroinvertebrates from the R. Derwent and Derwent Reservoir during 3 different seasons with a view to comparing the level of contamination with that reported in earlier studies of the same area.

ii) To determine and compare the concentrations of zinc, cadmium and lead in the more abundant invertebrate taxa from the river and the reservoir and to examine the relationship with metal concentrations in other components of the environment in an attempt to discover their importance as sources from which invertebrates may accumulate metals.

iii) To perform a similar study on zinc and lead in submerged macrophytes in the Derwent Reservoir.

CHAPTER 2

BACKGROUND TO AREA OF STUDY

2.1 INTRODUCTION

This chapter deals mainly with the Derwent Catchment, but reference is also made to the Northern Pennines as a whole. Geographical and geological aspects are described followed by a brief history of mining operations. The final section is a summary of the state of the River Derwent and Derwent Reservoir during the period of study (September 1978 - December 1979). The account is based largely on that given by Harding (1978) but draws also on Dunham (1948; 1972) and Johnson (1972). Additional information was obtained by discussion or by personal observation.

2.2 GEOGRAPHICAL ASPECTS

2.21 Derwent catchment

2.211 Introduction

The term Derwent catchment as used here refers to the area which drains directly into the Derwent Reservoir. It is made up of moorland, woodland and pasture around the R. Derwent, its tributaries and the reservoir; it covers an area of 8721 ha, much of which lies above an altitude of 400 m. The annual rainfall within the catchment is 935 mm, of which 546 mm leaves the area as surface run-off (Anon., 1976).

2.212 Derwent Reservoir

2.2121 Water supply

The Derwent Reservoir is situated near the town of Consett, County Durham, and lies in the valley of the River Derwent along the boundary between County Durham and Northumberland (Fig. 2.1). The reservoir was formed by the construction of an earth dam across the Derwent valley in accordance with the Derwent Water Order of 1957.

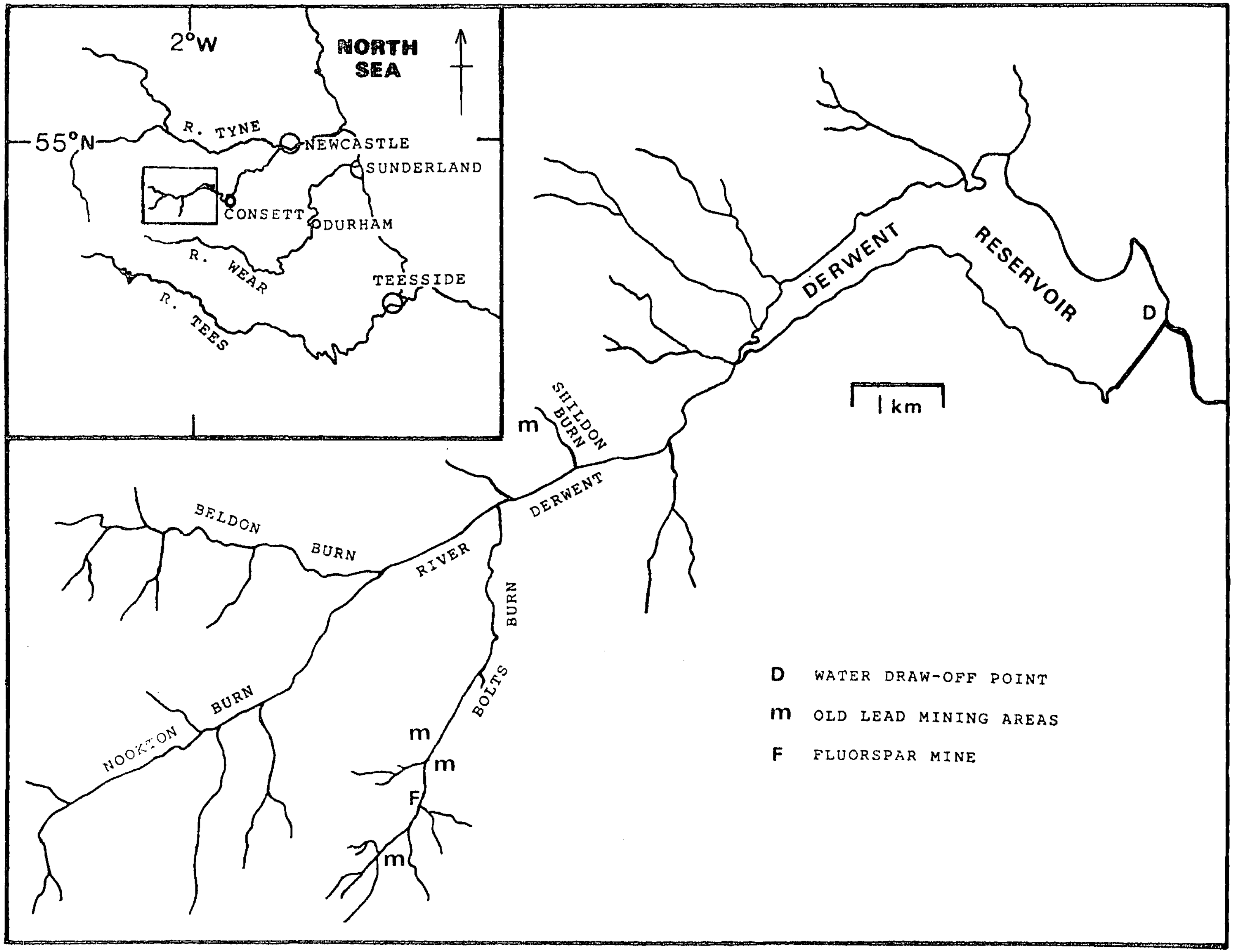


Fig. 2.1 Map of Derwent Reservoir catchment (redrawn from Harding, 1978)

Work on the dam commenced in 1960 and water was first taken into supply in 1966. One of the largest inland waters in England, the reservoir, when full to capacity (50.06×10^6 m^3) has a surface area of 405 ha, a maximum depth of 30 m, a length of 5.6 km and a maximum width of 1.6 km (Fig. 2.2). It was constructed for the joint use of the Durham County Water Board (now the Wear Division of the Northumbrian Water Authority) and the Sunderland and South Shields Water Company. The latter manage the reservoir and the associated treatment works situated 4 km down the valley at Mosswood. Water for public supply is drawn from near the dam and passed to Mosswood for treatment. From here, treated water for the Authority is pumped to a service reservoir at Castleside whence onward distribution is gravitational. The Company's share of the water gravitates from Mosswood to a major control point at Washington. During this study water was fed from the reservoir into the public supply at an average rate of 1.08×10^5 m^3 day^{-1} (D. W. Forster, pers. comm.)

2.2122 Recreation facilities

Recreational use of the reservoir includes a game fishery stocked with hatchery reared rainbow and brown trout on a 'put and take' basis. A sailing club is established on the north shore and three picnic sites have been laid out near the reservoir. A further attraction is the wildfowl, gulls and waders which can be observed from vantage points near the shoreline.

2.2123 Nature reserve

The western end of the reservoir is a nature reserve to which there is no public access. It comprizes 60 ha of water and 33 ha of surrounding land. The area, managed by a committee including representatives from the Durham County Conservation Trust, the Nature Conservancy Council, the Northumberland Wildlife Trust, the Sailing

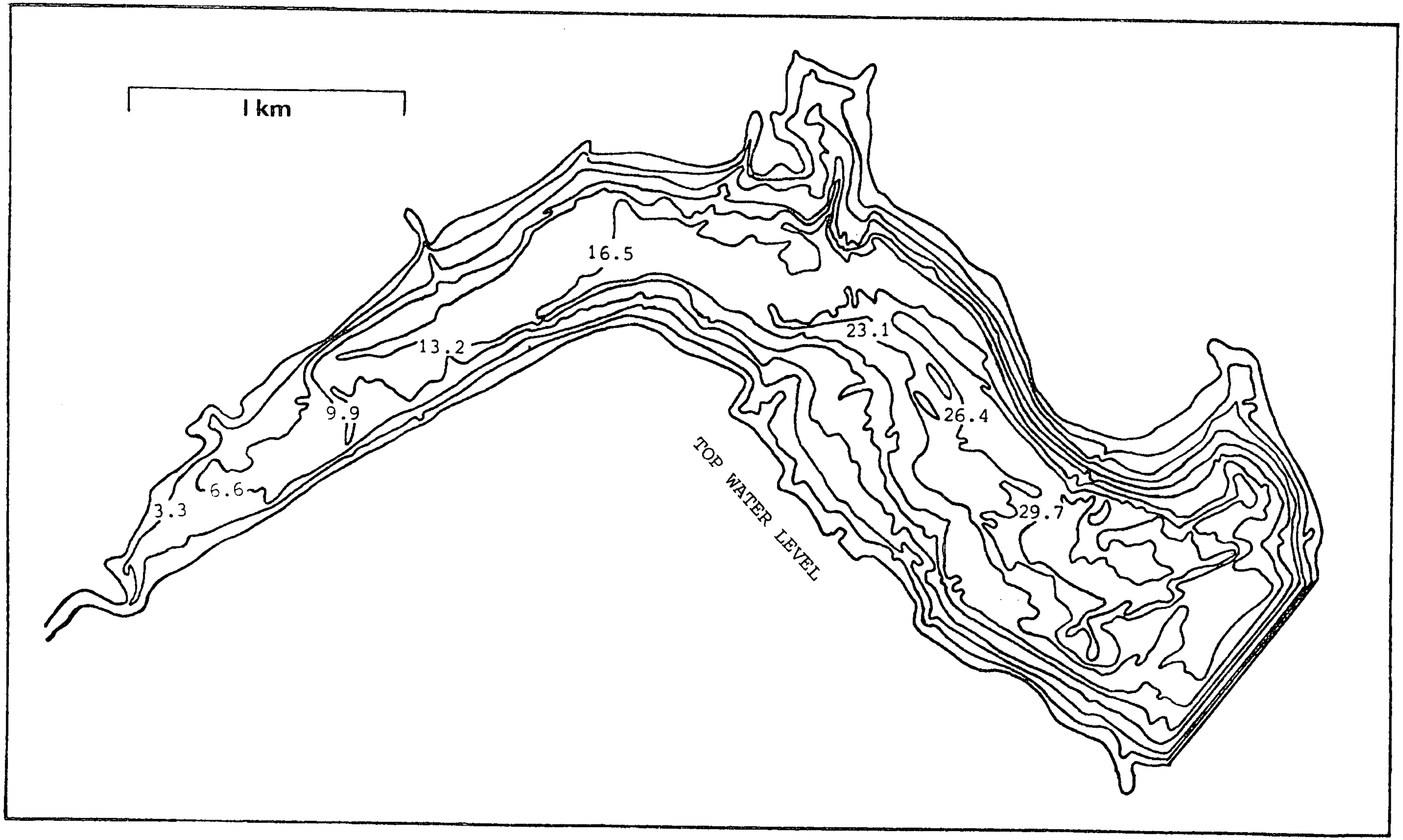


Fig. 2.2 Depth contour map of Derwent Reservoir (redrawn from Harding, 1978)

Club and the Water Company, has proved to be very attractive to birds; 10 different species of waterfowl and waders have nested in the reserve and 140 species have been recorded in the reservoir area.

2.213 River Derwent and its tributaries

The R. Derwent is the main feeder stream of the Derwent Reservoir, entering it at the western end through the nature reserve (Fig. 2.1). The river is formed 5 km south-west of the reservoir at an altitude of approximately 260 m by the confluence of Nookton and Beldon Burns (NY 944492).

Nookton Burn rises at over 550 m and drains Nookton Fell, Nookton West Fell and Hunstanworth Moor. Beldon Burn lies to the north of Nookton Burn and is formed by streams draining Heatheryburn Moor, Quickcleugh Moss, Byerhope Moss and Halleywell Fell. The remains of old mine workings are evident in the catchment areas of both streams.

The largest tributary of the R. Derwent upstream of the reservoir is Bolts Burn. It rises to the east of Hunstanworth Moor as a series of flushes and enters the river on the south bank 3.5 km from the reservoir. It is evident that the valley of Bolts Burn has been the site of considerable mining activity as the stream is bordered by old lead workings and spoil heaps along its middle reaches. In this region, 3.5 km from its confluence with the R. Derwent, Bolts Burn flows through the workings associated with the Whiteheaps fluorspar mine where it receives effluent from the mine adit and fluorspar treatment plant.

The second largest tributary is Shildon Burn. This stream joins the river 2.5 km from the reservoir, near the village of Blanchland. Shildon Burn drains Blanchland Moor and flows through a wooded valley towards the village. Abandoned mine workings can be seen in the valley and the stream receives water from an adit associated with the mines.

From Blanchland, the R. Derwent flows in a north-easterly direction towards the reservoir. The surrounding fell land is used mainly for forestry or grazing sheep. The river receives sewage effluent from each of the treatment works serving the small villages of Hunstanworth and Blanchland situated 4.5 km and 2.5 km upstream of the reservoir respectively.

All the streams in the catchment are shallow and fast flowing, with substratum composed mainly of sandstone boulders and cobbles. The streams are prone to flash flooding which frequently occurs following heavy rain or snow melt. During high flow the water in Nookton Burn, Beldon Burn and the R. Derwent carries increased levels of brown humic material washed down from the extensive areas of peat which occur on the surrounding fells.

2.3 GEOLOGICAL ASPECTS

2.31 Stratigraphy

2.311 Northern Pennine Orefield

The northern Pennine Orefield, described by Dunham (1948) as the country extending southwards from the Tyne valley to the Craven district in Yorkshire, is divided into two complementary parts by the Stainmore gap. The northern half forms a single physiographic unit known as the Alston Block; a plateau uplifted along its western margin and tilted to the east. Earth movements during the Carboniferous and Carboniferous-Permian interval of the Hercynian orogeny caused widespread uplifting, doming, folding, thrusting and faulting. The region is dissected by the rivers Tees, Wear and Tyne. The R. Derwent is a major tributary of the latter and its catchment falls within the area described.

2.312 Derwent catchment

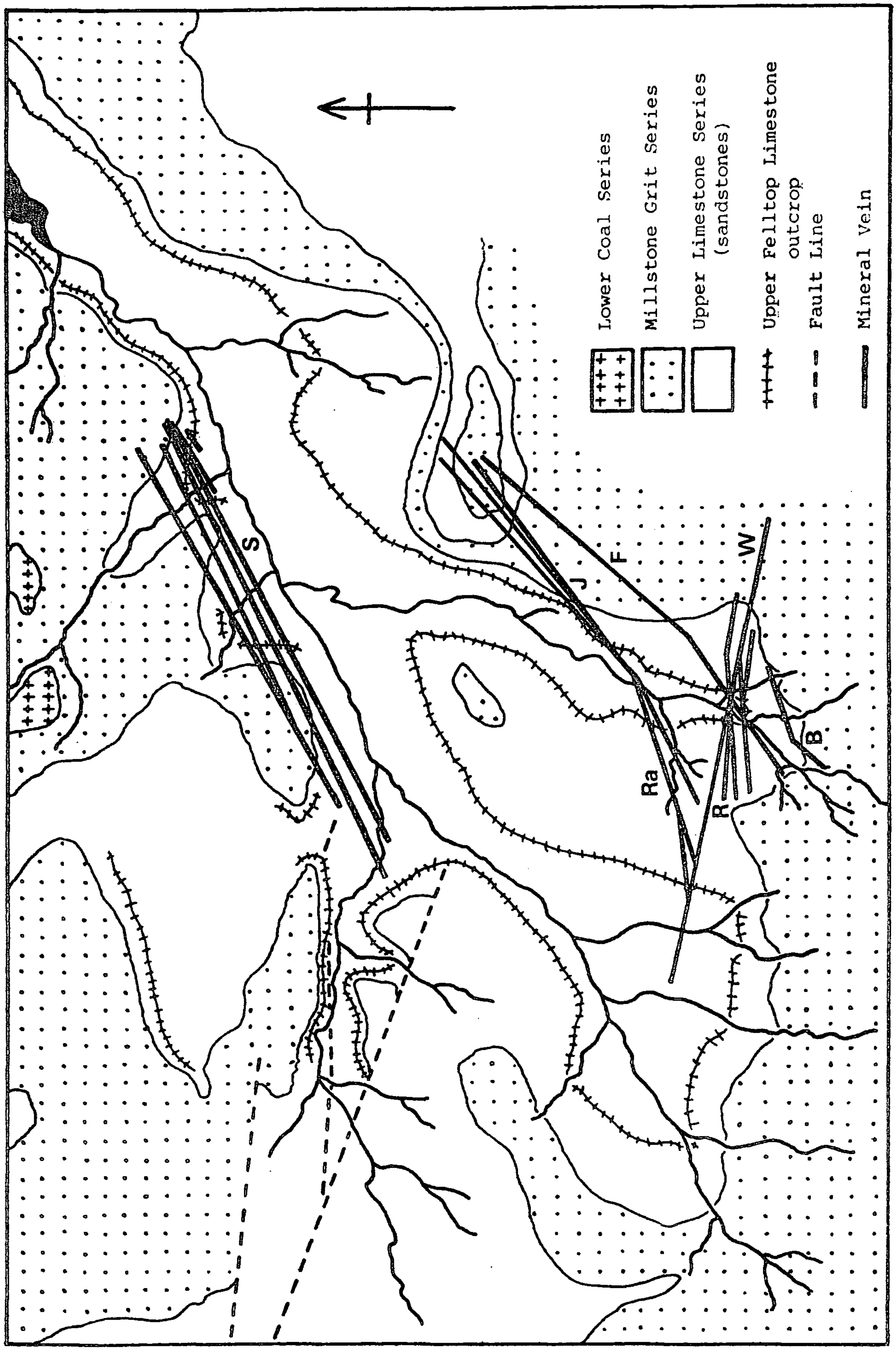
Surface rock formations within the Derwent catchment belong in the main to the Upper Carboniferous Limestone Group (Namurian) of the Upper Carboniferous age, here represented by sandstone beds which occur between the Crag and Upper Felltop Limestones. On high ground the Limestone Series is overlain by the Millstone Grit series, while formations over the whole area are underlaid by the Great Limestone (Fig. 2.3). Hard brittle beds (limestones and sandstones) alternate with soft yielding strata (shales, 'grey beds' and some weakly cemented sandstones). The sandstones in the catchment were laid down in deltaic channels during the deposition of the Rogerley and Coalcleugh transgression beds and have given rise to brittle strata of greater than usual thickness at high stratigraphical levels, particularly in the Hunstanworth area (Fig. 2.4). The importance of the sandstones and their associated strata with regard to mineralization and mining is outlined below.

2.32 Mineralization

The following outlines mineralization within the study area and again is based on Dunham (1948; 1972). The first section deals with general aspects of mineral deposition and is followed by a section relating to mineral deposits within the Derwent catchment.

2.321 Deposition

Mineral deposits were lain down as a result of precipitation from hot aqueous solutions rich in minerals during a period of activity spread over at least 100 My. Minerals of economic value laid down in this way include galena (PbS), sphalerite (ZnS) and the associated spar minerals fluorspar (CaF_2) and barytes ($BaSO_4$). Workable deposits are known as 'oreshoots', defined by Dunham (1948) as, 'a continuous body of ore which may be worked with profit or hope of profit'. Oreshoots can be classified into two principal types:


Lower Coal Series
Millstone Grit Series
Upper Limestone Series (sandstones)
Upper Felltop Limestone outcrop
Fault Line
Mineral Vein
S
J
F
W
Ra
R
B

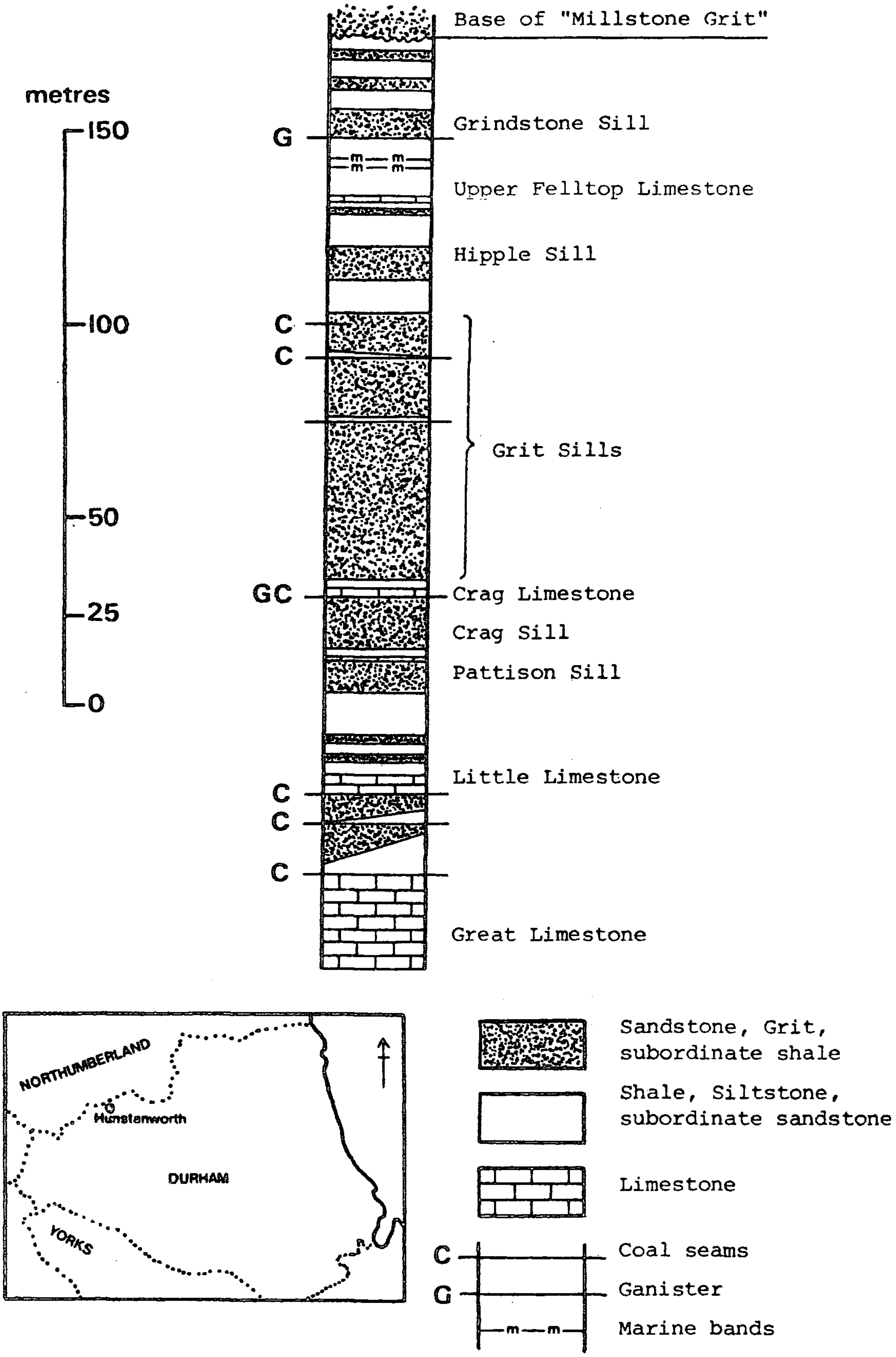


Fig. 2.4 Stratigraphical section at Hunstanworth (after Bott and Johnson, 1972; Dunham, 1948)

i) metasomatic 'flats', formed by the replacement of flat-lying favourable beds of limestone

ii) vein or ribbon oreshoots, developed by mineralization along fissures

While flats only occur within limestone, veins are found in association with limestone and other hard brittle strata (*e.g.* sandstone).

It was once thought that fissure veins were widened joints in the brittle strata into which mineralizing fluids had migrated but examination of veins has shown them to follow the line of small normal faults with downthrows ranging from less than 1 m to about 10 m. Earth movements during an earlier age (Section 2.311) created, within the hard beds, natural structural 'channels' along which mineralizing fluids could flow. The vertical dimensions of the veins were controlled by the thickness of the brittle strata and the presence of the overlying softer shales (Fig. 2.5).

The height of oreshoots is thus small in comparison to their length which may reach several thousand metres. Note also that mineral veins may carry more than one oreshoot and extend for many kilometres although mineralization may not be continuous within each oreshoot.

2.322 Deposits within the Derwent catchment

Although analysis of the horizons at which mineralization occurs reveals a striking concentration in and near the Great Limestone, mineral deposits are by no means confined to strata at this level. Mineralizing fluids frequently forced their way upwards from one hard bed to the next giving rise to deposits at higher stratigraphical levels. The Hunstanworth and Shildon vein groups in the Derwent catchment were formed in this way. At Hunstanworth the deep sandstone beds had an important effect upon mineralization, giving rise to oreshoots over 30 m high.

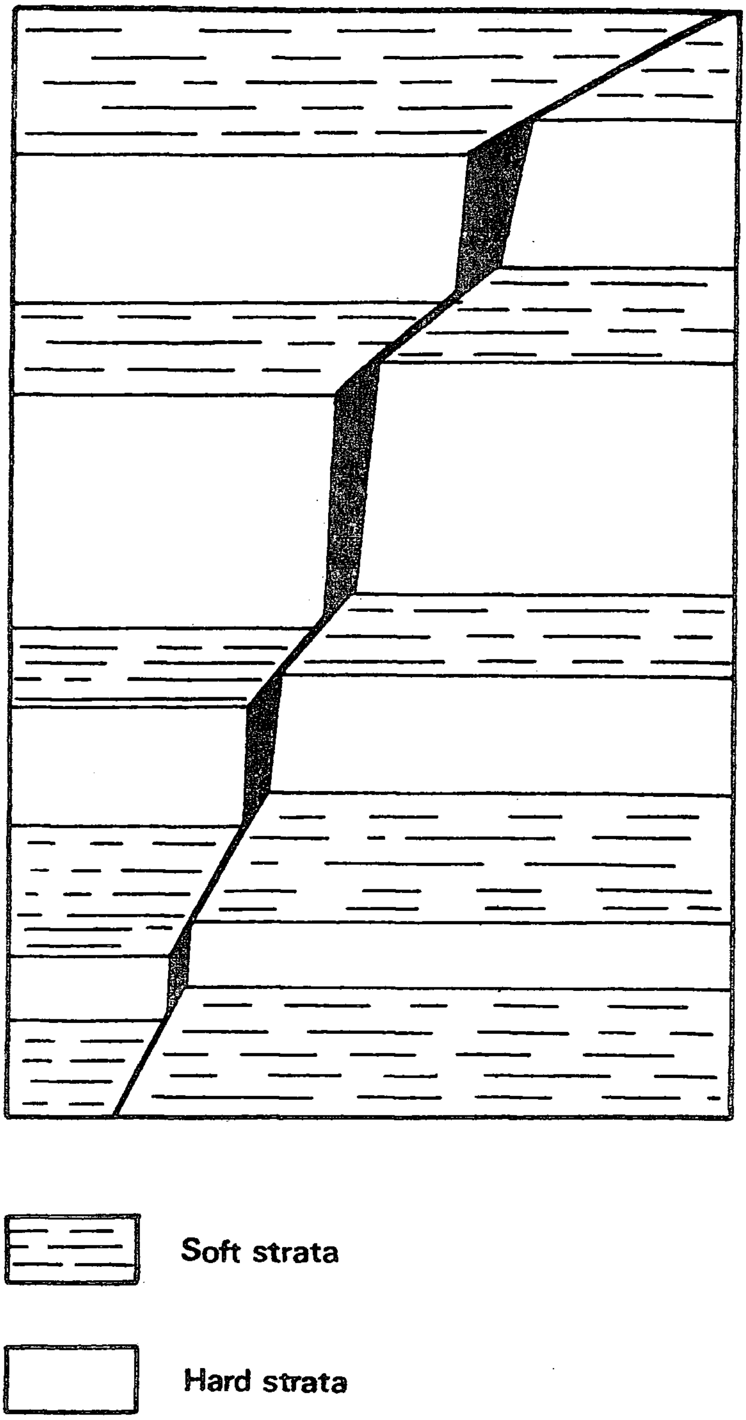


Fig. 2.5 Idealized cross-section of a fissure-vein (after Dunham, 1948)

All the veins in the Shildon group along with Fernygill vein, Boltshead vein and Jefferies veins in the Hunstanworth group coincide in direction with one of the principal directions of the regional joint system (N. 65° W.). The White vein and Red vein at Hunstanworth follow a direction near to W. N. W. (Fig. 2.3). They carry the widest oreshoots in the area, reaching 7 - 8 m in places. Unlike the other veins in the Hunstanworth group, the White and Red veins are subject to abrupt changes in direction and are more highly mineralized where their direction most nearly approaches E. - W. In the Hunstanworth group of veins as a whole the minerals are dominated by fluorite (CaF_2) not metals, a feature which has caused the veins to be worked long after other sites in the area were abandoned (Section 2.4).

2.4 MINING OPERATIONS

2.41 Northern Pennine Orefield

Mineral deposits were known to exist soon after the Norman conquest and may even have been discovered in Roman times although there is no evidence that the Romans worked this orefield. Mining has been continuous since the 12th century when it is known that deposits were worked for silver and lead. Documents dating from the 15th century name lead mines that can be identified as Blackdene and Allercleugh and also an iron mine north of Stanhope Park. The list of mines named in the documents relating to the case of W. Blackett *v.* Isaac Basire in 1666 shows that most of the deposits in Weardale had then been discovered. Up to this time ore had been extracted from bell pit workings and by hushing.

The 18th century saw the development of underground mining carried out by the family concern of the Blacketts and Beaumonts which operated workings in Weardale from 1666 to 1884, and the London Lead Company which between 1692 and 1906 worked mines in Teesdale, Weardale and the Derwent catchment. The fall in the price of lead during 1876 discouraged these companies; the London Lead Company surrendering its Alston Moor leases in 1882 and the Weardale leases of the Beaumonts being surrendered in 1884.

Mining for lead was continued in Weardale by the Weardale Lead Company which introduced fluorspar mining into the area before the turn of the century. The Weardale Lead Company was purchased by Imperial Chemical Industries (ICI) who sold the total assets of Weardale Lead to Swiss Aluminium (U.K.) Ltd (Samuk) in 1977. Samuk hold mining rights over an area of approximately 600 km^2 and own seven mines at which they are concentrating on fluorspar production (Anon., 1978). The only other fluorspar producer in the orefield is the British Steel Corporation which owns the Groverake and West Blackdene mines in Weardale and the Whiteheaps mine at Ramshaw in the Derwent catchment.

2.42 Derwent catchment

2.421 Outline of mining activities

The oldest mining operations were undoubtedly open-cast in places where veins were exposed. Mining for lead and silver was carried out during the 16th and 17th centuries. The London Lead Company acquired the mines in the Derwent catchment around 1725 and worked them until the end of the century. No records for lead production from the mines during this period now exist. In the only surviving mine report book of the company, Thomas Dodd, writing in 1806, urged that all the mines in the Derwent area should be given up "as there are no encouraging prospects in that country." However, the London Lead Company was followed by several other undertakings; these include Easterby, Hall and Company (1807 - 1810), the Derwent Mining Company (1810 - 1883) and

Hunstanworth Mines Ltd who worked Whiteheaps mine for fluorspar between 1924 and 1931. Blanchland Fluor Mines Ltd continued to mine fluorspar in 1938. This company was acquired by Colvilles Ltd which became part of the British Steel Corporation on renationalization of the steel industry.

A description of the principal veins and abandoned mines which have been worked in the Derwent catchment has been given by Harding (1978).

2.422 Whiteheaps mine and recent developments

The only active mine in the Derwent catchment during the present study (September 1978 - December 1979) was the British Steel Corporation's Whiteheaps mine near Ramshaw. Situated on the Hunstanworth group of veins (Fig. 2.3) and previously worked for lead ore, the mine was until recently (see below) worked for fluorspar which has been won from all the major veins in the group. The fluorspar is used as a catlyst in the steel making process.

During early operations at Whiteheaps much of the gangue in the White vein was considered too siliceous to be of use but the installation of a treatment plant in the mine complex allowed increased production from the vein. Although production of fluorspar from the mine has been interrupted during recent years when new levels have been driven to reach further deposits, the treatment plant has been active continuously, being used to process fluorspar from other British Steel mines in the area and was in use throughout the duration of this study.

Fluorspar treatment of Whiteheaps involves screening follwed by crushing and separation of fluorspar by flotation. Effluent from the treatment plant consists of a thick sludge of finely ground particulate matter (mostly fluorspar and siliceous material with small quantities of galena), which is piped to a series of three settling ponds before discharge into Bolts Burn. A concentrated solution of ferrous sulphate is added to the effluent before it enters the first settling pond. Sacks of lime are added to the uppermost pond to maintain high pH values and precipitate a 'blanket' of ferric hydroxide. Both these conditions are induced to bring down heavy metals by precipitation and absorption, followed by settling out before the effluent is finally discharged into Bolts Burn. Sludge is dredged from the ponds at intervals and deposited onto surface tips within the mine complex.

Apart from the treatment plant effluent, only one other significant input of water to Bolts Burn is directly connected with workings within the mine. This is the Whiteheaps adit level, which carries pumped drainage water from the underground workings into the stream via a tunnel and a small pond. Operation of the underground pump is completely automatic depending on the level of water within the workings, and water from the adit may be passing into Bolts Burn when the effluent is not flowing and *vice versa*.

The fall in demand for steel during recent years and the associated fall in demand for flourspar have caused the British Steel Corporation to streamline its operations in the orefield with the effect that both Whiteheaps mine and treatment plant were closed during 1980. A British Steel spokesman was quoted by Meek (1979) as saying, "Whiteheaps will be retained on a care and maintenance basis", so that, "As soon as the situation does improve we can open up straight away." The treatment plant is last known to have been in operation during the final week of June 1980 when, a breakdown of the treatment works at West Blackdene mine, where all the fluorspar produced by British Steel in this area is now treated, made it necessary to reopen the Whiteheaps plant. At the time of writing (January 1981) the fluorspar treatment plant at Whiteheaps mine is again idle, the mine is not being worked for fluorspar, the 'skeleton' work force are 'on short time' (D. W. Forster, pers. comm.) and it seems unlikely that production of fluorspar from the mine will be resumed in the near future.

2.5 POLLUTION IN THE DERWENT CATCHMENT

Previous studies by Harding (1978) and Harding and Whitton (1978) show that the Derwent catchment is contaminated with heavy metals (especially Zn, Cd and Pb). Bolts Burn, a major tributary of the R. Derwent receives effluent from a fluorspar treatment plant and water from an adit level as it flows through the Whiteheaps mine complex (Section 2.422). Both inputs are contaminated with heavy metals; the adit water is characterized by high concentrations of Zn and Cd (mainly soluble) while the effluent carries high concentrations of Pb and particulate matter. During wet weather particulate material derived from spoil heaps within the mine complex also enters Bolts Burn as surface run-off and contributes to the concentration of particulate Pb.

The R. Derwent upstream of Bolts Burn carries very low levels of Zn, Cd and Pb and is unaffected by old lead workings in the valleys of Nookton Burn and Beldon Burn. Below Bolts Burn the R. Derwent is contaminated with Zn, Cd and Pb and elevated levels of these metals persist in the river at its junction with the Derwent Reservoir. Shildon Burn which joins the R. Derwent at Blanchland (Section 2.422), is contaminated by Zn, Cd and Pb derived from an adit level draining old mine workings in the valley but does not have a major effect on heavy metal concentrations in the river as the water of both streams has a similar metal composition. Although inputs of small quantities of treated domestic sewage occur at Hunstanworth and Blanchland the

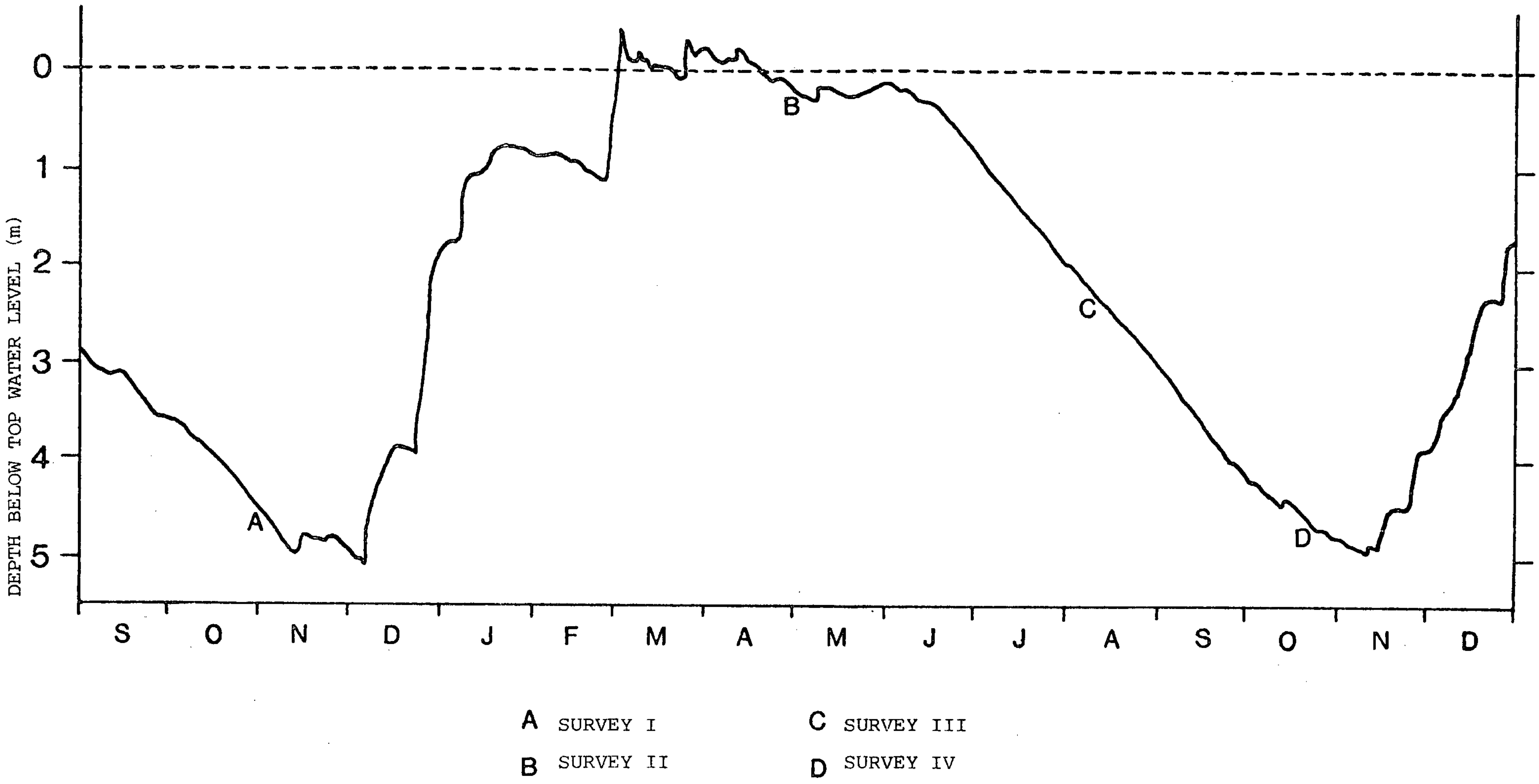


Fig. 2.6 Water level in Derwent Reservoir during present study (September 1978 - December 1979)

R. Derwent carries only low levels of soluble reactive inorganic phosphate and combined nitrogen and is otherwise unaffected by anthropogenic organic enrichment.

2.6 STATE OF RIVER AND RESERVOIR DURING PRESENT STUDY

There were several features of the environment and biota during the period (September 1978 - December 1979) which differed from the period (September 1974 - August 1977) of the previous study reported by Harding (1978). Although some of these are dealt with in more detail later, they are summarized here for clarity.

(i) It is probable that activities at the Whiteheaps Mine were decreased.

(ii) Moderate growths of the liverwort *Scapania undulata* occurred in the lowest reach of Bolts Burn, whereas they were absent altogether during the previous study.

(iii) The winter of 1978/79 was exceptionally severe, with long periods of snow and with ice on the reservoir. Very high river flows occurred at the time of snow melt.

(iv) Spring growths of the alga *Lemanea* in the R. Derwent were much reduced.

(v) Reservoir levels were unusually high during the first part of 1979, but dropped to more typical levels in the summer (Fig. 2.6).

(vi) Wind action in the reservoir was especially marked throughout summer 1979.

(vii) The alga *Nitella* was more abundant in the reservoir during summer 1979 than the summers of 1975 and 1976 (B. A. Whitton, pers. comm.).

(viii) Trout fishing in the reservoir "got off to a slow start" in 1979 compared with previous years (R. W. Hunter, pers. comm.).

CHAPTER 3

MATERIALS AND METHODS

3.1 APPARATUS AND CHEMICALS

All glassware, with the exception of snap-top vials, was made of Pyrex glass. Snap-top vials were made of boro-silicate glass. Polypropylene bottles were used for the storage of water samples for anion analysis.

Most chemicals were of 'Analar' grade, but reagent grade acid was used for washing apparatus and 'Trace metals analysis' grade acid (FISONS) was used for acid digestion and for acidifying water samples. Glass stills were used to produce single and double distilled water, the latter being passed through a Houseman Hegro deionizer when deionized water was required.

3.2 ROUTINE LABORATORY PROCEDURES

3.21 Acid washing

Apparatus to be acid washed was soaked in 10% (V/V) hydrochloric acid for a minimum of 30 min., rinsed six times with single distilled water, twice with double distilled water and then air dried. Apparatus was acid washed unless otherwise stated.

3.22 Acid digestion

Determination of the metal composition of solid materials required that the metals be brought into solution. This was achieved by boiling a known weight of the solid with 5 ml of concentrated nitric acid for 1 h. The resulting solution was cooled to $20^{\circ}C$. Digest solutions were made up to the required volume with double distilled water.

Digestion of samples collected during Survey I was carried out in 100 ml Kjeldahl flasks heated by an Electro-thermal heating rack; 18 mm diameter test tubes and a Tecam DB 3H heating block were used for all other digestions.

3.23 Atomic absorption spectrophotometry

The concentrations of the metals Na, K, Mg, Ca, Mn, Fe, Zn, Cd, Pb in water samples and acid digest solutions were determined by flame atomic absorption using a Perkin-Elmer 403 atomic absorption spectrophotometer. Determinations of Cd and Pb were made by direct aspiration into an air/acetylene flame or by the Tm sampling boat procedure (Kahn, Peterson and Schallis, 1968). The other metals were determined by direct aspiration. An acid resistant nebulizer was used for the aspiration of acid digest solutions. All samples were shaken immediately before analysis.

The concentrations of the elements in each sample were corrected for background and blank determinations.

3.3 WATER

3.31 Collection, fractionation and storage

Stream water was collected from the main flow of the designated sampling reach. Water from the reservoir was collected by wading at all sites. All water samples were collected from immediately below the surface using a 2 l polythene beaker.

Water for metal analysis was left to stand in the beaker for 5 min to allow large suspended particles to settle. A 'total' (T) sample was then obtained by pouring approximately 25 ml of water from the beaker into a snap-top vial. Collection of a 'filtrable' (F) sample was achieved by passing approximately 25 ml of water through a Nuclepore membrane filter of pore size 0.2 µm. Water was passed through the filter using a disposable plastic syringe. The first 5 ml of water passed through a filter was discarded. Filters were held in plastic Swinnex filter holders during filtration and were transferred to the holders using stainless steel forceps. It was necessary occasionally to use more than one membrane filter in order to obtain a 25 ml sample, because of the presence of especially high levels of suspended materials. Membrane filters were not acid washed but were rinsed with double distilled water before use. After collection of 'total' and 'filtrable' samples sufficient 'Trace metal grade' concentrated nitric acid was added to each to reduce the pH below 1.0. In practice this was usually two drops from a '50 dropper' pipette.

Water for anion analysis was passed through a No. 2 Sinta funnel and approximately 250 ml was collected in a 300 ml screw top polypropylene bottle.

Unfiltered water for laboratory determination of pH, conductivity and optical density was collected by filling a 300 ml screw top polypropylene bottle under water. The lid was secured while the bottle was submerged thus eliminating bubbles and reducing gaseous exchange during transportation to a minumum.

All water samples were placed in the dark in an ice box for transportation to the laboratory. Samples for metal analysis were stored in the dark at 4°C. Those for anion analysis were deep frozen at -20°C until required.

3.32 Physico-chemical analysis

3.321 Field

Water temperature was measured by immersing a laboratory thermometer, previously cross calibrated against a thermometer of known accuracy, just under the water surface until a steady reading was obtained. Current speed was measured at the fastest accessible point in a sampling reach using an OTT current meter. A portable meter supplied by Lakes Instruments Ltd was used to take field measurements of dissolved oxygen and Pye-Unicam 293 portable meters were used to measure Eh and pH. Electrodes were calibrated against appropriate standards. Total alkalinity was determined following the potentiometric method recommended in Standard Methods for Examination of Water and Wastewater (American Public Health Association, 1971). A subjective estimate of river flow was made on a 1 to 5 scale.

3.322 Laboratory

The concentrations of nine metals (Na, K, Mg, Ca, Mn, Fe, Zn, Cd, Pb) were determined in each of the 'total' and 'filtrable' samples by atomic absorption spectrophotometry.

Determinations of Cl and Si were carried out following the colorimetric methods described in Standard Methods for Examination of Water and Wastewater (American Public Health Association, 1971). Fluoride (F) was measured using an Orion fluoride specific ion electrode. Soluble reactive inorganic phosphorus (PO_4 - P) was determined using the antimony acid molybdate colorimetric method described by Stainton, Capel and Armstrong (1977).

Immediately upon return to the laboratory pH, conductivity and optical density were measured. Laboratory pH measurements were made simultaneously with an Electronic Instruments 23A pH meter and the portable meter used in the field. Both meters were calibrated with the standards used in the field and then checked against freshly made standards. On one occasion the two sets of standards differed and a second batch of fresh standards was made up. The sets of freshly made standards gave similar readings and so were used to calibrate the pH meters. Conductivity was measured with an Electronic Instruments MC-1 conductivity bridge. Optical density measurements were made at wavelengths of 240, 254 and 420 using a Uvispek spectrophotometer. Samples were filtered through a membrane filter of pore size 0.2 μm before measurements were made.

3.4 SEDIMENTS

3.41 Collection, fractionation and storage

Collection of sediment from the R. Derwent was carried out within the boundaries of 10 m sampling reaches. Care was taken to avoid areas of algal growth, or areas where material washed from the bank of the reach might contribute significantly to the bottom sediment. Collections were made from at least four locations within a reach and pooled. When sufficient material was present collections were made from as many as 10 locations within a reach.

Samples were collected from the reservoir by removing the top 1 cm layer of sediment from 10 locations within the boundaries of a site.

Excess water was drained from the sediment after collection from each location at a sampling station and was then transferred to a closeable, heat resistant, heavy-duty paper soil sample bag for transportation to the laboratory.

All sediment samples were dried at 105°C for 72 h, cooled, passed through a 210 μm mesh nylon sieve and collected in vials. The sediment was stored in the vials until required for digestion and determination of organic content.

3.42 Acid digestion and analysis

Samples were redried at 105°C for 24 h and then cooled in a desiccator. Acid digestion was carried out as previously described (Section 3.22) using 50.0 mg of dried sediment. The digest was then poured into a centrifuge tube, the digestion vessel rinsed out with double distilled water and the washings poured into the same centrifuge tube. The suspension was centrifuged at 3500 r.p.m. for 5 min., the supernatant decanted into a 50 ml volumetric flask and made up to volume with double distilled water. The digest solution was finally poured into a snap-top vial and stored at 4°C.

Digest solutions prepared from samples collected during Surveys I - IV were analysed for Na, Mg, Ca, Mu, Fe, Zn, Cd and Pb; those from samples collected during the survey of the reservoir were analysed for Zn and Pb. All analyses were made by atomic absorption spectrophotometry (Section 3.23). Following analysis, the nitric acid extractable concentration of each element, expressed as $\mu g\ g^{-1}$ dry wt, was calculated for each sample.

Organic content of sediments was determined by placing approximately 1 g of sieved sediment into a dry, pre-weighed (W_1) Vitreosil crucible. The sediment was dried at 105°C for 24 h, removed from the oven and cooled in a desiccator. Crucible and sediment were weighed (W_2), placed in a muffle furnace at 550°C for 48 h, removed, cooled and weighed again (W_3). The loss of weight upon ignition $W_2 - W_3$ was corrected for carbonate loss and the resulting value (W_4) used in the calculation of the percentage organic content of the dry sediment as follows:

$$\frac{W_2 - W_1}{W_4} \times 100 = \text{\% organic content on dry weight basis}$$

3.5 LEAVES AND DETRITUS

3.51 Collection, fractionation and storage

Leaves were collected from trees growing on the banks of the river. Terminal leaves were collected from at least 20 branches of each species; the leaves from different trees of the same species at the same site were pooled, placed in a polythene bag, put in an ice-box and returned to the laboratory. The leaves were not cleaned in any way.

Detrital material of two types was taken from the river. These were:

i) leaves that had hardly started to decay

ii) a mixture of sediment and decaying organic material which had lost almost all recognizable inclusions

Samples of each type were obtained by pooling material collected from at least four locations within a reach. No attempt was made to wash the material in the field. Each sample was put in a polythene bag which was placed in an ice-box and returned to the laboratory. Leaves of sample type i) above were separated into individual species in the laboratory and each species was then further divided into two fractions; one fraction was washed in distilled water, the other remained unwashed. The decaying organic material, sample type ii) above, was also divided into washed and unwashed fractions.

Samples of leaves and detrital material were dried in beakers at 105°C for 72 h, cooled in a desiccator and then ground with a pestle and mortar. Each sample was passed through a 210 µm mesh nylon sieve, collected in a snap-top vial and stored until required for digestion.

3.52 Acid digestion and analysis

Samples were redried at 105°C for 24 h and then cooled in a desiccator. Acid digestion was carried out as previously described (Section 3.22) using 50.0 mg of dried material. Digests of detrital material were then treated in the same manner as a sediment digest but were made up to a volume of 25 ml. Finally the solution was transferred to a snap-top vial and stored at 4°C until analysis.

All digest solutions were analysed for Na, K, Mg, Ca, Mn, Fe, Zn, Cd and Pb as previously described (Section 3.23) and the concentration of each element as $\mu g\ g^{-1}$ dry wt computed for each sample.

3.6 AQUATIC PLANTS

3.61 Collection, fractionation and storage

In the case of river bryophytes collections of the species under study were made from four to ten locations within a sampling reach and pooled. Only completely submerged material was collected. The pooled sample was washed thoroughly in stream water, shaken and transferred to a polythene bag which was then placed in an ice-box. After returning to the laboratory fifty 2 cm shoot tips were removed from the sample. The tips were rinsed in a series of dishes of distilled, double distilled and finally deionized water. Washed tips were lightly blotted dry with filter paper and transferred to a snap-top vial for drying.

Aquatic macrophytes were collected from within 10 m transects of shallow water accessible by wading near the edge of the reservoir. Samples of *Glyceria fluitans* comprised ten leaves. Only the flat laminae of healthy floating leaves were taken (these correspond to the fraction described as 'old leaves' by Harding, 1978). *Nitella flexilis* was collected as whole plants; five plants constituted a sample. Care was taken when handling the plants to avoid damaging the long internodal cells. Macrophytes were washed in reservoir water to remove loosely attached debris, shaken dry, placed in polythene bags and transported to the laboratory in an ice-box. In the laboratory samples were washed in a similar manner to bryophytes and then the rhizoids were removed from *Nitella* with stainless steel scissors.

Bryophyte and macrophyte samples were dried in snap-top vials at 105°C for 72 h, cooled in a desiccator and stored until digestion.

3.62 Acid digestion and analysis

Samples were redried at 105°C for 24 h and then cooled in a desiccator. Bryophyte samples were removed from the snap-top vials, weighed to the nearest 0.1 mg and digested as previously described (Section 3.22). *Glyceria* and *Nitella* were removed from the snap-top vials, ground with a pestle and mortar, passed through a 210 µm mesh nylon sieve to remove coarse fragments and then redried. Acid digestion was carried out using 25.0 mg of dried material as already described (Section 3.22). All plant digests were made up to 25 ml decanted into snap-top vials and stored at 4°C until analysis.

Bryophyte digests were analysed for Zn, Cd and Pb and macrophyte digests for Zn and Pb as described above (Section 3.23). The concentration of the elements in each sample was calculated and expressed as $\mu g\ g^{-1}$ dry wt of plant material.

3.7 ANIMALS

3.71 Collection, storage and identification

Animals were collected from the R. Derwent by a standard kick-sampling method (Macan, 1958; Hynes, 1961) using a net of mesh size 1.0 mm. Collections made in this way were supplemented by picking animals from stones and bryophytes. The number of locations at which kick-samples were taken within the boundaries of a reach varied and was determined by the abundance of animals within the reach.

The material collected was placed in the top of a stack of two sieves (upper sieve mesh size 5.6 mm, lower sieve mesh size 1.0 mm) and washed with stream water to remove fine organic and inorganic material and separate many of the animals from the coarse material which remained in the uppermost sieve. The contents of the sieves were put into white enamel trays, a small amount of stream water added and the animals removed from the remaining debris, using stainless steel forceps, into glass petri dishes containing stream water. Taxa were sorted into separate petri dishes and the organisms from several collections were pooled until there were sufficient to form a sample for acid digestion. The required number of individuals was removed from the petri dish, rinsed in double distilled water, carefully blotted with filter paper to remove excess water and placed in a vial. Only whole, living individuals sharing the same macroscopic morphological features were included in a sample.

group	author	
Tricladida	Reynoldson	1978
Gastropoda	Macan	1960
Hirudinea	Mann	1964
Malacostraca	Gledhill, Sutcliffe & Williams	1976
Ephemeroptera	Macan	1979
Plecoptera	Hynes	1977
Elminthidae	Holland	1972
Megaloptera	Elliot	1977
	Elliot, O'Connor & O'Connor	1979
Trichoptera	Boon	1978
	Hickin	1967
	Hildrew & Morgan	1974
	Hiley	1976
	Mackereth	1954
Diptera	Brindle	1960, 1967
	Bryce & Hobart	1972
	Davies	1968
general	Macan	1959

Table 3.1 Keys used for identification of invertebrates.

In addition to the samples of each taxa collected for metal analysis a further sample was taken for identification purposes and was stored in suitable preservative. Even when there were too few individuals to form a sample for metal analysis the organisms were placed in preservative and later identified.

Samples of animals were collected from sites along the shore of the reservoir in much the same way as for the river.

Animals collected during Survey I were sorted in the laboratory while those collected during Surveys II, III and IV were sorted in the field.

All animal samples for metal analysis were transported to the laboratory in an ice-box. In the laboratory samples were dried at 105°C for 72 h and then stored until required for digestion.

Animals were identified according to the keys listed in Table 3.1. It was assumed that a sample taken for identification purposes would contain the same species of organisms as the corresponding sample(s) taken for metal analysis. Identification of all digested samples is based on this assumption.

For some species only those individuals within a given size range were sampled *e.g. Perla bipunctata*. Individuals were measured to the nearest mm by placing them on graph paper graduated in 1 mm increments. Measurements were made from the anterior of the head to the posterior of the abdomen. Antennae, circi and other appendages were not included in measurements of body length.

3.72 Acid-digestion and analysis

Samples were redried for 24 h at 105°C, cooled in a desiccator and weighed. Digestion was carried out as previously described (Section 3.22) and the liquid digest poured into a 25 ml volumetric flask. The digestion vessel was rinsed twice with double distilled water and the washings decanted into the flask. The solution was made up to volume and transferred to a snap-top vial. Samples were stored at 4°C until analysis.

Determinations of Mg, Ca, Mn, Fe, Zn, Cd and Pb were made as previously described (Section 3.23) and the concentration of each element as $\mu g\ g^{-1}$ dry wt of tissue computed for each sample.

3.8 PRESENTATION OF RESULTS

3.81 Water

Physico-chemical variables are reported to the number of significant figures and the limit of detection consistent with the method by which they were determined.

Mean concentrations of metals and anions in water samples are reported as described below:

i) Mean concentrations of all anions and metals, with the exception of Cd and Pb, are reported to the same number of significant figures as the individual values from which they were calculated unless these fell into more than one instrument concentration range, in which case the mean value is quoted according to the range into which it falls.

ii) All mean concentrations of Cd and Pb are quoted to one more significant figure than the individual sample, *e.g.* the mean of the sample values 0.0004, 0.0004, 0.0003, 0.0004, 0.0004 is reported 0.000038 rather than 0.0003.

iii) In some instances concentrations of Cd, Pb and PO_4-P are reported as being <0.0003, <0.003 and <0.005 respectively. When calculating the mean of a series of sample values including such values the average of the appropriate value and zero (*i.e.* Cd 0.00015, Pb 0.0015, PO_4-P 0.0025) was used. The mean value obtained for the series is reported as described in i) and ii) above or as <0.0003, <0.003 or <0.005 for Cd, Pb and PO_4-P respectively.

iv) Mean values were not rounded up.

Standard deviations are reported to one more significant figure than the individual values from which they were calculated. They are however not reported at all for Cd, Pb and PO_4-P when mean values fall below 0.0003, 0.003 and 0.005 respectively.

3.82 Digests

The limit of detection for metals in solid samples (μg g^{-1}) is a function of the dry weight of material digested and the minimum concentration of the metal which can be detected in the digest solution. As the former varied between samples and the latter with the instrument concentration range into which the sample fell, metal concentrations in samples (μg g^{-1}) are reported to the number of significant figures consistent with the limit of detection down to the level of integers. The concentration of Cd is reported in the same manner to the level of one place of decimals.

For all metals, the values for the mean and standard deviations of a series of concentrations were derived and are presented in the same way as described for water samples (Section 3.81).

CHAPTER 4

SAMPLING SITES AND PROGRAMME OF INVESTIGATION

4.1 SAMPLING SITES

4.11 Streams

Samples from streams were taken from within defined 10 m lengths termed reaches. Streams and reaches sampled were coded in accordance with the computer orientated recording system in use at Durham University. Stream numbers, reach numbers and reach locations are given in Table 4.1, while reach locations are also depicted in Fig. 4.1.

Five reaches were established on the R. Derwent, two (03, 05) upstream of the entry of Bolts Burn and three (08, 23, 27) below it. Reaches 03, 05, 08 and 23 were in fast flowing 'riffle' areas and reach 27 was situated on a slower flowing stretch of the river (Fig. 4.2a, b, c, d, e). One sampling reach was established on Bolts Burn (99) near its confluence with the R. Derwent (Fig. 4.2f).

4.12 Derwent Reservoir

Sampling points on the reservoir (termed sites) were chosen both for routine survey (R3,R7, R9, R10) and a special study of water, sediments and plants (R1 - R22). Locations are given in Table 4.2 and depicted in Fig. 4.3. Samples were collected at the shore from within 10 m wide transects running into the reservoir perpendicular to the shoreline at top water level. Thus the exact position of the sites varied according to the reservoir water level and may be determined by referring to Tables 4.2 and 4.3 and Figs 2.2 and 4.3.

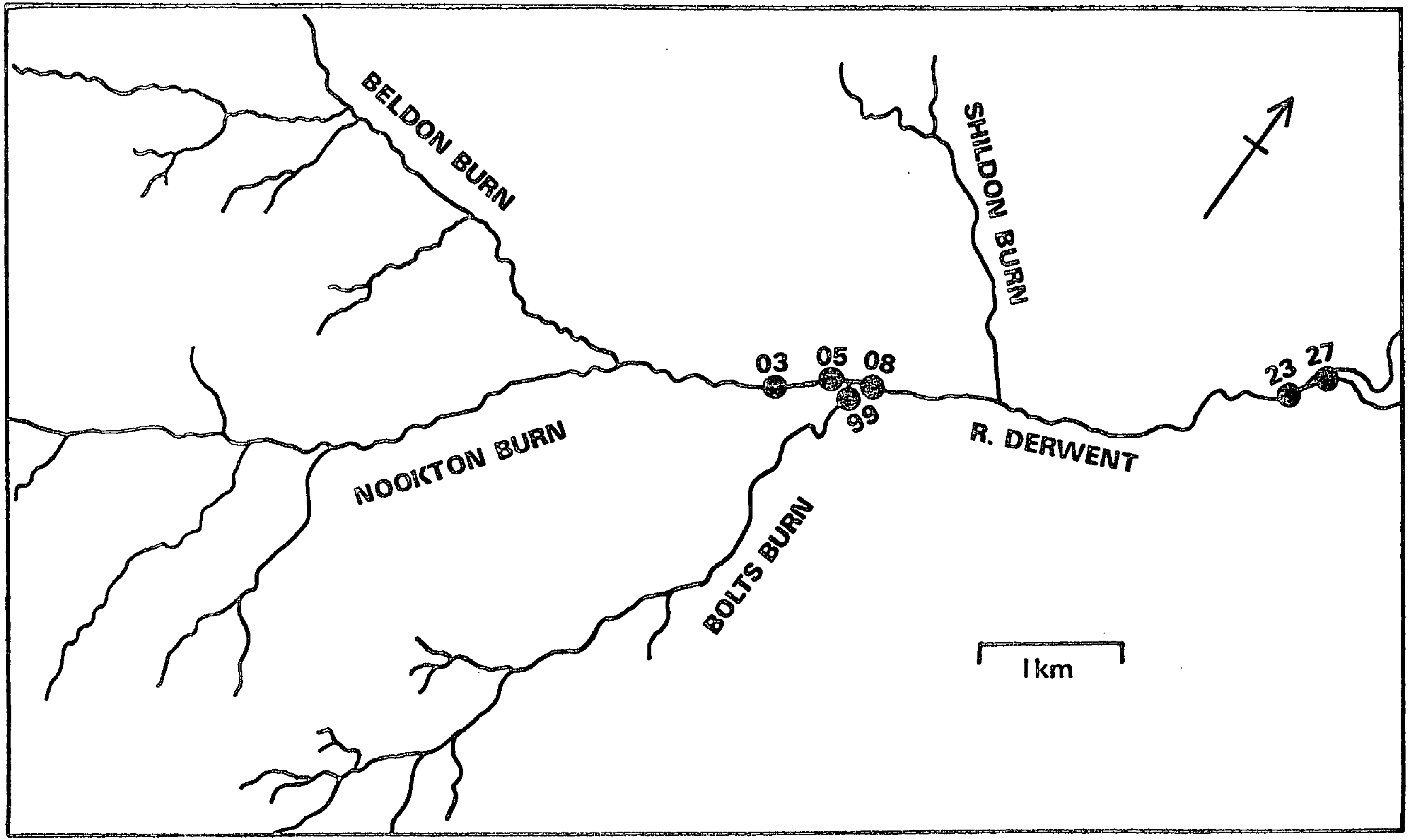


Fig. 4.1 R. Derwent and Bolts Burn, showing locations of sampling reaches

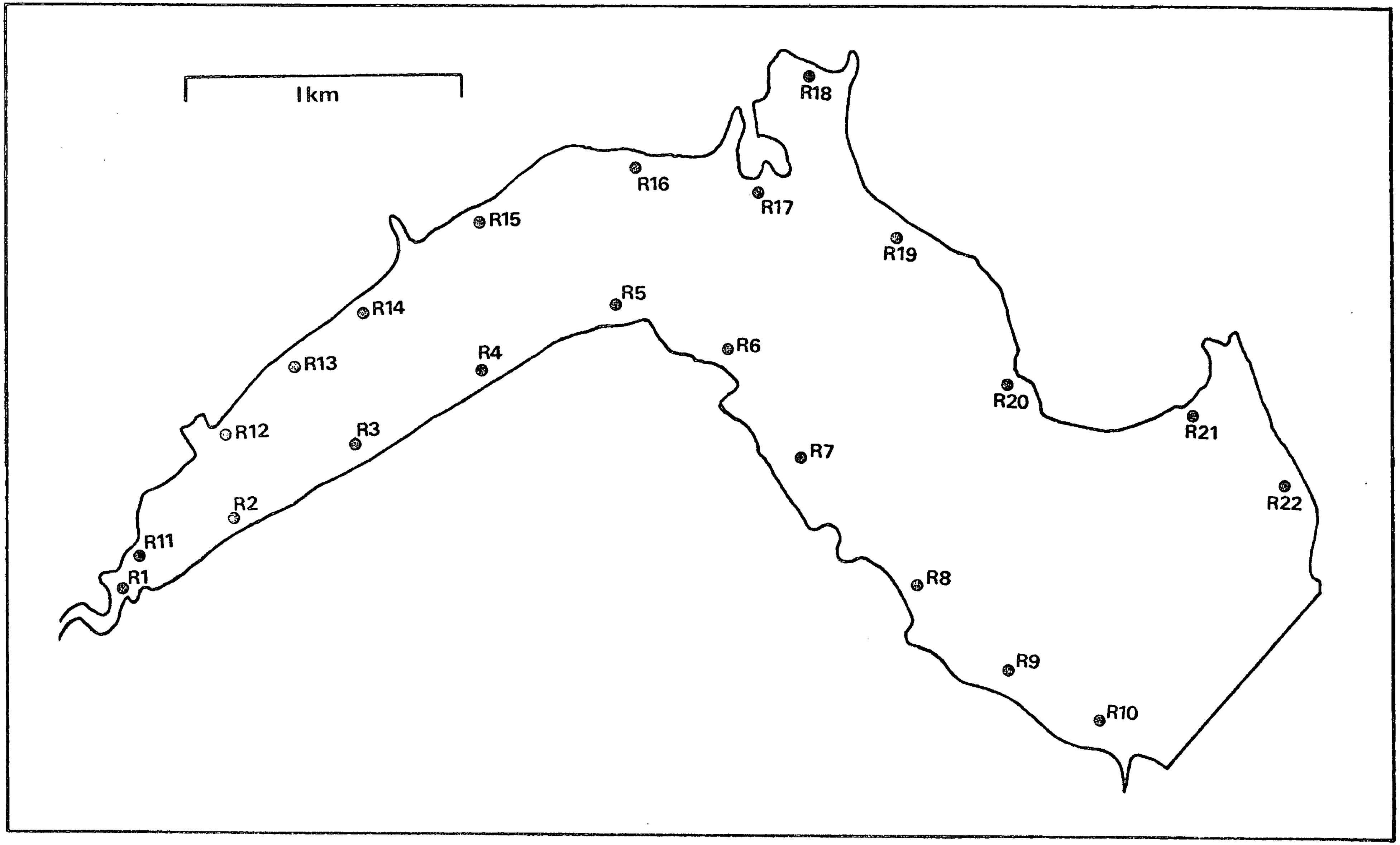


Fig. 4.3 Derwent Reservoir showing locations of sampling sites

Table 4.1 Locations of sampling reaches on R. Derwent and Bolts Burn

stream no.	reach no.	grid ref.	
0061	03	NY 954496	R. Derwent
0061	05	NY 957498	R. Derwent above entry of Bolts Burn
0061	08	NY 959499	R. Derwent below entry of Bolts Burn
0061	23	NY 983513	R. Derwent at Carrick's picnic site
0061	27	NY 984516	R. Derwent downstream of bridge at Carrick's picnic site
0071	99	NY 957498	Bolts Burn at confluence with R. Derwent

Table 4.2 Locations of sampling sites on Derwent Reservoir (grid references correspond to locations at top water level)

south shore		north shore	
site	grid ref.	site	grid ref.
R1	NY 987515	R11	NY 986518
R2	NY 995521	R12	NY 992523
R3	NY 995521	R13	NY 995524
R4	NY 999524	R14	NY 995526
R5	NZ 003526	R15	NY 999530
R6	NZ 007525	R16	NZ 005532
R7	NZ 009522	R17	NZ 009531
R8	NZ 015515	R18	NZ 011535
R9	NZ 017514	R19	NZ 013531
R10	NZ 022511	R20	NZ 020523
		R21	NZ 025524

Survey I

date	rainfall	reservoir level below top
25.10.78	0.02 mm	4.24 m
26.10.78	1.50	4.28
27.10.78	0	4.31
28.10.78	0	4.35
29.10.78	0	4.38
20.10.78	0	4.42
31.10.78	0	4.46
01.11.78	2.8	4.50
02.11.78	0.2	4.53
03.11.78	0	4.56
04.11.78	1.9	4.63
05.11.78	0	4.67

Survey II

date	rainfall	reservoir level below top
26.04.79	0.8 mm	0.08 m
27.04.79	6.1	0.09
28.04.79	1.0	0.12
29.04.79	0.9	0.13
30.04.79	1.1	0.17
01.05.79	0.8	0.21
02.05.79	1.6	0.23
03.05.79	2.0	0.25
04.05.79	0.7	0.27

Survey III

date	rainfall	reservoir level below top
08.08.79	9.3 mm	2.17
09.08.79	1.4	2.21
10.08.79	3.7	2.24
11.08.79	1.1	2.27
12.08.79	tr.	2.30
13.08.79	0.4	2.36
14.08.79	9.8	2.38
15.08.79	3.1	2.41
16.08.79	0.3	2.45

Survey IV

date	rainfall	reservoir level below top
22.10.79	0 mm	4.56 m
23.10.79	0	4.60
24.10.79	0	4.64
25.10.79	07	4.67
26.10.79	15.5	4.67
27.10.79	1.2	4.66
28.10.79	tr.	4.68
29.10.79	tr.	4.71
30.10.79	1.9	4.74
31.10.79	2.7	4.80

Table 4.3 Rainfall and reservoir levels during Surveys I - IV

(Readings are usually taken (by D. W. Forster or staff) early in the morning, so rainfall values refer to the 24 hours finishing at 0800 h on the date listed.)

4.2 SAMPLING PROGRAMME

Most of the data collected during this study result from four periods of intensive survey, the remainder coming from a series of special studies.

4.21 General Surveys

4.211 Introduction

Four surveys were carried out, the first three during different seasons (autumn, spring and summer respectively) followed by a fourth one year after the first. An attempt was made to collect a relatively standard package of information during each survey. Further, it was hoped to carry out each survey during a period of stable weather (and hence river conditions). This was accomplished during the first three surveys but unfortunately a storm occurred during the final survey causing a marked increase in river flow. The dates over which the surveys were carried out are given in Table 4.4. Rainfall and river flow during each survey are summarised in Table 4.5

After the first survey of the present study, the unpolluted reach 05 was replaced by one about 400 m upstream (03) to minimize any possibility of sampling animals which had migrated from the polluted section of the river. For general presentation of data and discussion, no distinction is made between the two reaches. The details of all the stations sampled during each general survey are given in Table 4.6 and Sections 4.212 - 4.215 below.

To allow comparisons to be drawn between each survey and also between the present study and that of Harding (1978), a substantial number of samples yielding 'background' environmental information were collected. Thus a considerable part of the sampling effort during each survey was directed towards the abiotic components of the system.

Table 4.4 Dates on which Surveys I - IV were carried out

day	Survey I	Survey II	Survey III	Survey IV
1	25.10.78	26.04.79	08.08.79	22.10.79
2	26.10.78	27.04.79	09.08.79	23.10.79
3	27.10.78	28.04.79	10.08.79	24.10.79
4	28.10.78	29.04.79	11.08.79	25.10.79
5	29.10.78	30.04.79	12.08.79	26.10.79
6	30.10.78	01.05.79	13.08.79	27.10.79
7	31.10.78	02.05.79	14.08.79	28.10.79
8	01.11.78	03.05.79	15.08.79	29.10.79
9	02.11.78			30.10.79
10	03.11.78			
11	04.11.78			

Table 4.5 Summary of rainfall and river flow during Surveys I - IV (for rainfall, see Table 4.3)

survey	rainfall	river flow
I	negligible	low
II	low	medium
III	moderate	medium
IV	negligible then storm day 4	medium until storm then very high for two days returning to medium

4.212 Collection of water samples

The days on which sampling stations were visited during Surveys I - IV are given in Table 4.6. A 'total' and a 'filtrable' sample for metal analysis were collected every time a sampling station was visited. On the first day of each survey four samples for anion analysis were collected from each station chosen for general survey. During Survey I four samples were also collected from 05 and 08 on days 2 - 4.

4.213 Collection of sediment samples

On day 1 of each survey five samples were collected from every sampling station included in the survey (Table 4.6).

4.214 Collection of plants

The only aquatic plants sampled during the general surveys were bryophytes collected from 03/05 and 08 on the R. Derwent. Five species were collected during the study although it was not always possible to include each species on every sampling occasion. Single samples of each species were collected during Surveys I and II while five samples of each species were taken during Surveys III and IV wherever possible. The details of the days on which each species was sampled and the number of samples collected are given in Table 4.7.

4.215 Collection of animals

Samples of benthic macroinvertebrates for metal analysis were collected during each of Surveys I - IV. The days on which stations were sampled are given in Table 4.8. At each station, the choice of species and the extent to which samples were replicated depended largely on the number of individuals that could be found. Samples were collected either as single samples or in replicates of five. The taxa and number of samples collected from the R. Derwent are given in Tables 4.9 and 5.17 while details for the reservoir can be found in Tables 4.10 and 6.9.

	Bolts Burn reach 99	R. Derwent all* reaches	R. Derwent 'additional' samples from reaches				Derwent Reservoir Sites	
			03/05	08	23	27	R3, R7, R10	Rp
Survey I days		1 2 3 4 5			6	6	1 3 6 9, 11	
Survey II days	1 2 3 4 5	1 2 3 4 5	6 7 8	6	6 7		1 2 3 4 5	1 2 3 4 5
Survey III days	1 2 3 4 5	1 2 3 4 5	6 7		6		1 2 3 4 5	1 2 3 4 5
Survey IV days	1 2 3 4 5 6 7	1 2 3 4 5 6 7		8	8 9		1 2 3 4 5	1 2 3 4 5

* reach 27 sampled during Survey I only

Table 4.6 Days on which sampling stations were visited during Surveys I - IV

(For dates, see Table 4.4)

code	name	reach	survey							
			I		II		III		IV	
			day	n	day	n	day	n	day	n
220400	*Chiloscyphus* sp.	03							7	5
		08					5	5	8	1
222102	*Scapania undulata* (L.) Dum.	03			7	1	6	5	7	5
		08			6	1	5	5	8	5
232501	*Rhynchostegium riparioides* (Hedw.) C. Jens	03					6	5		
		08					5	5	8	5
232703	*Fontinalis squamosa* Hedw.	03/05	5	1	7	1	6	5	7	5
		08								
233202	*Hygrohypnum ochraceum* (Turn. ex Wils.) Loeske	03			7	1	6	5	7	5
		08	5	1	6	1	5	5	8	5

Table 4.7 Days on which bryophytes were collected from R. Derwent during Surveys I - IV

Code as used at Durham. n = number of replicates (For dates, see Table 4.4)

survey	reach on R. Derwent				site on Derwent Reservoir			
	03/05	08	23	27	R3	R7	R9	R10
I	5	5	6	6	11	11		11
II	8	6	7					
III	7	5	6		5	5	5	5
IV	7	8	9		5	5	5	5

Table 4.8 Days on which animals were collected from R. Derwent and Derwent Reservoir during Surveys I - IV

(For dates, see Table 4.4)

35 03 08 02	*Oreodytes sanmarki* Sahlberg	in Maitland, this is under *O. rivalis* (Gyllenhal)	?	beetle
35 11 03 01	*Limnius volckmari* (Panzer)	only species recorded	D	beetle
38 01 01 01	*Rhyacophila dorsalis* (Curtis)	only species recorded	C	caddisfly
38 03 03 01	*Polycentropus flavomaculatus* (Pictet)	only species recorded	F	caddisfly
38 05 01 01	*Hydropsyche pellucidula* (Curtis)	only species recorded	F	caddisfly
38 08 00 00	Limnephilidae	larvae identified only to family	?	caddisfly
40 01 00 00	Tipulidae (excluding *Dicranota)*	larvae identified only to family	D	cranefly
40 01 35 00	*Dicranota* sp(p).	2 spp. occur in Britain, but situation not known for R. Derwent	D	cranefly
40 14 02 00	*Chironomus* sp(p).	17 spp. occur in Britain but situation not known for R. Derwent	D H	midge
40 15 05 00	*Simulium* sp(p).	13 spp. occur in Britain but situation not known for R. Derwent	F	blackfly

Table 4.9 Invertebrates collected from R. Derwent for metal analysis

Code according to Maitland (1977). D, detrivore: F, filter-feeder: H, herbivore: P, parasite.

code	name	popular name	notes	feeding habit
13 07 01 07	*Lymnaea peregra* (Muller)	snail	only species recorded	H
17 02 03 02	*Glossiphonia complanata* (L.)	leech		P
28 07 03 05	*Gammarus pulex* (L.)	shrimp	only species recorded	D
35 03 00 00	Dytiscidae	beetle	two species: see note below	C
40 14 02 00	*Chironomus* sp(p).	midge	17 species occur in Britain situation not known for Derwent Reservoir	DH

Note: Two species of beetle identified: *Potamonectes depressus* (Fab.) agg in Maitland as *Deronectes depressus* (Fabricius) = 35 03 07 03 *Stictotarsus duodecimpustulatus* (Fab.): formerly *Deronectus* but not included in Maitland's checklist.

Table 4.10 Invertebrates collected from Derwent Reservoir for metal analysis

4.3 SPECIAL STUDIES

4.31 Introduction

In addition to the general surveys described above, a number of studies were carried out to investigate selected components of the R. Derwent and Derwent Reservoir. These are outlined below.

4.32 Leaves and detritus from R. Derwent

Samples of leaves from trees growing on the river bank and leaf detritus from the river bed were collected from reaches 05 and 08 on 29.10.78 and from reaches 23 and 27 on 30.10.78. Details of the fractions collected can be found in Section 3.61 and Table 5.19.

4.33 Water, sediment and submerged plants from Derwent Reservoir

Samples of water, sediment, *Nitella flexilis* L. (alga) and *Glyceria fluitans* L. (submerged grass) were collected from all sites with the exception of R1, R2 on the south shore and R11, R19, R20, R22 on the north shore. Wherever possible five samples of each plant were collected but if insufficient material was present then only one large sample was taken. Details of the number of plant samples collected at each site are given in Table 6.12.

CHAPTER 5

COMPOSITION OF WATER, SEDIMENTS, PLANTS AND ANIMALS FROM RIVER DERWENT

5.1 INTRODUCTION

The results from all the general surveys (I - IV) and a special study of the River Derwent are presented here. Summaries of water chemistry and sediment data are reported in Sections 5.21 and 5.22, respectively. Data for plants and animals are given in 5.23 and 5.24 while the results of a special study of leaves and detritus (described in Section 4.32) are given in Section 5.3. All data are presented as described in Section 3.81. Brief comments on the results are made here but discussion and comparison of metal levels in different components is left until Chapter 7.

5.2 GENERAL SURVEYS

5.21 Water

Data are reported for the following variables: Na, K, Mg, Ca, Mn, Fe, Zn, Cd, Pb, F, Cl, Si, PO_4-P, conductivity, pH and total alkalinity. These are summarized in Tables 5.1 and 5.2 for the first five sampling occasions in each survey and are the only summaries of water chemistry which are strictly comparable between reaches. Raw data are given in Appendix 1 (metals) and Appendix 2 (anions).

5.211 Bolts Burn at confluence with R. Derwent (0071-99, Fig. 4.2f)

This reach was sampled on 17 occasions during the present study. Mean levels of Zn, Cd and Pb for the whole study are given below (n = 17).

	Zn	Cd	Pb
'total' (mg l^{-1})	1.25	0.0020	0.070
'filtrable' (mg l^{-1})	1.20	0.0018	0.050

Table 5.1 Summary of data on all water chemistry variables for each reach based on first five sampling occasions in each survey (concentrations in mg l^{-1} where appropriate)

stream	reach	n	conductivity ($\mu S\ cm^{-1}$)		pH		total alkalinity ($mg\ l^{-1}\ CaCO_3$)			Na						K					
										T			F			T			F		
			min	max	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
0071	99	15								30.1	14.7	42.6	29.8	15.1	43.5	7.4	3.2	11.6	7.1	3.2	10.5
0061	03/05	20	82	225	6.4	7.7	37	5	79	6.0	4.0	7.9	6.0	4.3	8.0	1.66	1.12	2.5	1.63	0.45	2.2
0061	08	20	126	391	6.2	8.0	57	8	116	12.4	5.6	21.8	12.2	5.7	21.6	3.0	1.42	5.0	2.9	1.37	4.9
0061	23	20	126	370	6.4	8.3	54	7	108	11.9	5.8	20.1	11.7	5.7	20.3	3.0	1.44	4.7	2.9	1.41	4.7
0061	27	5	170	245	6.5	7.9	50	44	56	10.5	8.5	13.0	10.2	8.0	12.6	2.7	2.3	3.2	2.5	2.2	3.0

stream	reach	n	Mg						Ca						Mn					
			T			F			T			F			T			F		
			mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
0071	99	15	4.6	0.72	10.0	4.5	0.68	9.4	41.4	22.5	55.2	40.4	22.4	55.3	0.30	0.150	0.47	0.30	0.148	0.46
0061	03/05	20	3.45	1.74	5.1	3.39	1.72	5.0	13.9	6.12	21.4	13.5	6.00	20.1	0.048	0.015	0.240	0.047	0.016	0.230
0061	08	20	4.55	2.26	7.0	4.45	2.20	7.2	21.0	8.32	32.2	20.4	8.20	31.8	0.110	0.052	0.240	0.107	0.046	0.220
0061	23	20	4.52	2.20	6.8	4.38	2.16	6.7	20.2	7.73	30.8	19.6	7.42	30.9	0.079	0.029	0.240	0.071	0.024	0.220
0061	27	5	4.29	3.73	4.80	3.95	3.58	4.40	20.4	17.7	23.1	18.8	16.5	21.4	0.041	0.032	0.047	0.035	0.028	0.039

stream	reach	n	Fe						Zn						Cd					
			T			F			T			F			T			F		
			mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
0071	99	15	0.12	0.04	0.39	0.07	0.04	0.21	1.22	0.77	2.38	1.17	0.75	2.36	0.0019	0.0012	0.0028	0.0018	0.0012	0.0030
0061	03/05	20	0.71	0.17	1.78	0.57	0.12	1.41	0.020	0.010	0.070	0.020	0.007	0.060	<0.0003	<0.0003	0.0005	<0.0003	<0.0003	0.0006
0061	08	20	0.55	0.11	1.46	0.45	0.06	1.30	0.30	0.126	0.62	0.29	0.126	0.58	0.0006	0.0003	0.0013	0.0006	0.0004	0.0012
0061	23	20	0,50	0.10	1.50	0.39	0.05	1.20	0.25	0.141	0.61	0.223	0.132	0.35	0.0006	0.0004	0.0010	0.0006	0.0005	0.0008
0061	27	5	0.89	0.66	1.25	0.68	0.49	0.98	0.226	0.116	0.27	0.213	0.204	0.223	0.0005	0.0004	0.0006	0.0005	0.0005	0.0006

stream	reach	n	Pb						F			Cl			Si			PO_4-P		
			T			F														
			mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
0071	99	15	0.071	0.024	0.146	0.051	0.024	0.096												
0061	03/05	20	0.007	<0.003	0.018	0.005	0.003	0.018	0.40	0.22	0.72	6.7	5.9	7.2	2.16	0.96	2.77	0.013	<0.005	0.023
0061	08	20	0.021	0.018	0.038	0.016	0.007	0.027	1.12	0.65	1.81	7.5	6.9	8.2	3.18	1.56	4.08	0.011	<0.005	0.020
0061	23	20	0.020	0.006	0.042	0.015	0.003	0.035	1.23	0.74	1.88	8.4	6.6	10.6	3.11	1.06	4.08	0.016	0.005	0.032
0061	27	5	0.028	0.016	0.049	0.018	0.012	0.025	0.74	0.74	0.74	7.2	7.2	7.2	3.36	3.36	3.36	0.010	0.010	0.010

		pH	total alkalinity (mg l^{-1} $CaCO_3$)			Ca		Mn		Fe		Zn		Cd		Pb	
survey	reach	min max	$\bar{x}$	min	max	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
I	0061-05	6.8-7.7	38	27	46	14.2	1.71	0.021	0.0051	1.01	0.307	0.029	0.0066	0.00037	0.00017	0.011	0.0050
	0061-08	6.8-7.8	54	41	64	20.1	3.59	0.084	0.0249	0.84	0.268	0.28	0.089	0.00070	0.00014	0.021	0.0050
	0061-23	6.7-8.0	53	46	60	18.5	2.15	0.032	0.0074	0.67	0.168	0.217	0.0210	0.00068	0.00013	0.019	0.0057
	0061-27	6.5-7.9	50	44	56	18.8	1.94	0.035	0.0041	0.68	0.211	0.213	0.0077	0.00058	0.00004	0.018	0.0046
II	0061-03	6.4-7.2	14	9	21	7.5	1.12	0.082	0.0208	0.40	0.092	0.016	0.0036	<0.0003		0.005	0.0019
	0061-08	6.2-7.2	22	19	25	11.5	2.26	0.103	0.0150	0.32	0.113	0.156	0.0309	0.00054	0.00021	0.019	0.0060
	0061-23	6.8-7.3	23	16	32	11.9	1.95	0.084	0.0144	0.27	0.101	0.150	0.0247	0.00052	0.00016	0.021	0.0077
III	0061-03	7.4-7.7	66	54	79	18.7	1.66	0.021	0.0022	0.23	0.065	0.016	0.0089	<0.0003		<0.003	
	0061-08	7.5-8.0	100	90	116	29.4	2.28	0.120	0.0196	0.13	0.050	0.39	0.0506	0.00076	0.00021	0.010	0.0040
	0061-23	8.0-8.3	90	75	108	28.3	2.71	0.075	0.0136	0.13	0.062	0.238	0.0363	0.00064	0.00005	0.006	0.0033
IV	0061-03	6.5-7.2	32	5	42	13.8	4.41	0.064	0.0924	0.67	0.259	0.021	0.0217	<0.0003		0.006	0.0043
	0061-08	6.4-7.4	53	8	75	20.8	7.12	0.121	0.0582	0.53	0.319	0.36	0.152	0.00066	0.00031	0.017	0.0036
	0061-23	6.4-7.5	50	7	64	19.8	6.97	0.094	0.0720	0.50	0.388	0.29	0.075	0.00054	0.00008	0.016	0.0048

Table 5.2 Summary of selected water chemistry variables (pH, alkalinity, Ca, Mn, Fe, Zn, Cd, Pb) for each reach sampled during main surveys of R. Derwent (metals are for 'filtrable' samples on first five days of collection; concentrations in mg l^{-1} where appropriate)

Comments

i) The 'total' metal concentrations in water from this reach were the highest of any stream sampled during this study. (Zn = 2.38 mg l^{-1}, Cd = 0.0028 mg l^{-1}, Pb = 0.146 mg l^{-1}).

ii) The concentrations of Na, K, Mg, Ca, Mn, Zn and Cd did not differ substantially between 'total' and 'filtrable' samples on any sampling occasion. Fe and Pb were not found to behave in this way.

iii) For all samples the concentrations of metals fall into the following series:

$$Zn > Mn > Fe > Pb > Cd$$

5.212 R. Derwent upstream of Bolts Burn (0061-03 and 0061-05, Fig. 4.2a and b)

The R. Derwent upstream of Bolts Burn was sampled at two reaches (03 and 05) during this study (see Section 4.211). An analysis of water samples collected from each reach at approximately the same time is given in Table 5.3. Even though the data for metals are based on single samples, it can be seen by comparing the two reaches that the physical and chemical variables measured are not markedly different. Thus, for the purposes of data presentation and discussion no distinction is made between the two reaches.

Mean concentrations of Zn, Cd and Pb for the whole study are given below (n = 27).

	Zn	Cd	Pb
'total' (mg l^{-1})	0.020	<0.0003	0.007
'filtrable' (mg l^{-1})	0.019	<0.0003	0.005

reach	conductivity ($\mu S\ cm^{-1}$)	pH	total alkalinity ($mg\ l^{-1}\ CaCO_3$)	Na		K		Mg		Ca		Mn	
				T	F	T	F	T	F	T	F	T	F
03	150	7.2	36	6.7	6.4	1.64	1.62	3.34	3.38	1.59	1.60	0.029	0.026
05	152	7.1	38	6.5	6.4	1.60	1.60	3.28	3.26	1.70	1.68	0.030	0.032

reach	Fe		Zn		Cd		Pb		F	Cl	Si	PO_4-P
	T	F	T	F	T	F	T	F				
03	0.67	0.54	0.011	0.010	0.0003	<0.0003	0.007	0.004	0.29	6.9	2.77	<0.005
05	0.71	0.65	0.011	0.008	0.0004	<0.0003	0.005	0.005	0.31	6.1	2.52	<0.005

Note: all concentrations in mg l^{-1} where appropriate.

Table 5.3 Results of analysis of two water samples collected at approximately the same time (22.10.79) from reaches 03 and 05 in the R. Derwent

survey	reach	Zn		Cd		Pb	
		T	F	T	F	T	F
I	05	0.027	0.027	0.0003	<0.0003	0.011	0.006
	08	0.41	0.38	0.0008	0.0008	0.021	0.017
	23	0.250	0.225	0.0007	0.0007	0.016	0.012
	27	0.239	0.217	0.0005	0.0007	0.015	0.012
II	03	0.013	0.022	0.0003	0.0003	0.008	0.009
	08	0.150	0.145	0.0003	0.0004	0.020	0.016
	23	0.185	0.186	0.0006	0.0004	0.022	0.019
III	03	0.016	0.017	0.0003	0.0003	0.003	0.003
	08	0.40	0.40	0.0011	0.0011	0.008	0.007
	23	0.30	0.30	0.0009	0.0008	0.015	0.013
IV	03	0.014	0.016	0.0004	0.0004	0.010	0.009
	08	0.35	0.34	0.0007	0.0007	0.014	0.014
	23	0.27	0.27	0.0004	0.0003	0.016	0.015

Table 5.4 Concentrations of Zn, Cd, Pb (mg l^{-1}) in water from R. Derwent at time animals were collected. (For details of sampling days and concentrations of other metals, see Sections 4.212, 4.215 and Appendix 1)

survey	reach	Zn		Cd		Pb	
		T	F	T	F	T	F
I	05	0.027	0.027	0.0003	0.0003	0.011	0.006
	08	0.41	0.38	0.0008	0.0008	0.021	0.017
II	03	0.021	0.016	0.0004	0.0003	0.007	0.006
	08	0.150	0.145	0.0003	0.0004	0.020	0.016
III	03	0.020	0.018	0.0003	0.0003	0.003	0.004
	08	0.40	0.40	0.0011	0.0011	0.008	0.007
IV	03	0.014	0.016	0.0004	0.0004	0.010	0.009
	08	0.35	0.34	0.0007	0.0007	0.014	0.014

Table 5.5 Concentrations of Zn, Cd, Pb (mg l^{-1}) in water from R. Derwent at time bryophytes were collected. (For details of sampling days and concentrations of other metals see Sections 4.212, 4.214 and Appendix 1.)

Comments

i) 'Total' metal concentrations were lower at this reach than at any other stream site sampled during this study. (Zn 0.010 mg l^{-1}, Cd $<$ 0.0003 mg l^{-1}, Pb $<$ 0.003 mg l^{-1}).

ii) In general there were no clear differences between the concentrations of metals in 'total' and 'filtrable' samples. However, under conditions of increased flow such as occurred during Survey IV it was apparent that the concentrations of K and Fe were higher in 'total' samples (see Appendix 1, Survey IV).

iii) Concentrations of Zn, Cd and Pb were similar during each survey; Fe was higher during Surveys I and IV than during II and III; other metals showed no clear trends.

iv) The concentrations of metals in samples fell into the following series:

$$\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Cd}$$

5.213 R. Derwent downstream of Bolts Burn (0061-08, Fig. 4.2c)

Samples were collected from this reach on 24 occasions. The mean concentrations of Zn, Cd and Pb are given below (n = 24).

	Zn	Cd	Pb
'total' (mg l^{-1})	0.28	0.0006	0.020
'filtrable' (mg l^{-1})	0.28	0.0006	0.016

Comments

i) In general concentrations of Na, K, Mg, Mn, Zn and Cd were similar in 'total' and 'filtrable' samples. Levels of Ca, Fe and Pb tended to be higher in 'total' samples.

ii) Concentrations of Na,K, Mg, Ca, Mn, Zn, Cd and Pb were found to be higher than in the R. Derwent upstream of Bolts Burn on all sampling occasions while the levels of Fe were found to be lower. The opposite was true when compared with Bolts Burn.

iii) The concentrations of metals in samples fell into the following series:

$$\text{Fe} > \text{Zn} > \text{Mn} > \text{Pb} > \text{Cd}$$

5.214 R. Derwent at entrance to Derwent Reservoir (0061-23, Fig. 4.2d)

Water was collected from this reach on 28 occasions during the present study. Mean levels of Zn, Cd and Pb are given below (n = 28).

	Zn	Cd	Pb
'total' (mg l^{-1})	0.244	0.0006	0.019
'filtrable' (mg l^{-1})	0.226	0.0006	0.015

Comments

i) The comments made about reach 08 in Section 5.213 also apply here.

ii) Comparisons between samples collected at 08 and 23 on the same day show no apparent trends but mean concentrations (Tables 5.1, 5.2) reveal that Mn, Fe and Zn in 'total' and 'filtrable' were lower at 23 while only slight decreases in concentrations of Na, Mg and Pb occurred. K, Ca and Cd generally remained unchanged.

5.22 Sediments

The composition of the sediments in the R. Derwent was studied in order to establish their possible importance as sources of heavy metals for detritivorous invertebrates. Both metal composition and organic content were determined. The methods of collection and analysis have already been described (Section 3.4) and involved pooling material collected from different locations within a reach, followed by extraction of metals with concentrated HNO_3. Determinations of metal composition and organic content were made on all samples collected. Sediment was not collected from Bolts Burn at any time during this study.

5.221 Metal composition

The mean metal composition of sediments collected from each reach for Surveys I - IV are given in Tables 5.6 - 5.9 respectively. The standard deviations given in these tables refer to replicate samples collected from each reach. The overall mean values for the whole study are given in Table 5.10.

Comments

i) When the overall mean values for the whole study are considered, the concentrations of all metals were lower at 03/05 than at reaches below Bolts Burn.

ii) The same was true of each sampling occasion with the exception of the following where metal levels at 08, 23 and 27 were lower than at 03/05: Survey I, Mg at 27; Survey II, Na at 08 and 23; Survey III, Mn at 23, Fe at 08 and 23.

iii) The large standard deviations found for all metals suggest there may be marked variations in the composition of sediments from different locations within each reach.

iv) No clear pattern of the distribution of Zn, Cd and Pb between 08 and 23 is apparent.

5.222 Organic content

Determination of the organic content of sediments was carried out on the same samples as metal analysis. The results for Surveys I - IV

reach	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
05	330	84	1070	132	2100	361	870	177	19400	860	122	17	3.8	2.0	110	10
08	340	54	1160	107	9870	1050	1330	155	23600	830	1740	890	8.7	4.0	2620	740
23	470	59	1310	127	16100	2560	2260	384	25100	1670	2720	548	13.8	2.3	2230	616
27	510	55	1030	67	17700	1520	1110	171	19700	1840	1230	221	9.2	2.2	2240	695

Table 5.6 Metal composition of sediments at all river sites during Survey I (25.10.78; μg g^{-1}; n = 5)

reach	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
03	570	295	920	81	1110	154	670	189	18100	1770	82	14	0.6	0.3	120	23
08	340	156	1120	156	9980	2340	960	386	18600	1870	550	223	3.1	2.0	1740	524
23	430	325	1220	103	11900	1080	770	96	18700	1230	486	137	3.5	1.3	1800	294

Table 5.7 Metal composition of sediments at all river sites during Survey II (26.04.79; μg g^{-1}: n = 5)

reach	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
03	860	239	910	167	1210	170	1890	752	24800	5970	244	57	1.1	0.2	96	20
08	1530	228	1090	144	6850	995	1990	385	21400	2880	1540	335	7.2	1.8	1600	404
23	1230	85	1000	112	6710	402	1640	186	23400	1140	2240	969	12.4	2.9	1810	236

Table 5.8 Metal composition of sediments at all river sites during Survey III (08.08.79; μg g^{-1}: n = 5)

reach	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
03	270	59	820	214	760	238	930	574	18200	4320	170	43	0.8	0.3	104	20
08	360	36	2410	397	6810	1590	3010	908	34400	6800	2760	935	11.4	4.1	3120	704
23	380	77	1570	428	6050	1595	1610	420	26000	4949	1790	576	7.5	2.1	1690	400

Table 5.9 Metal composition of sediments at all river sites during Survey IV (22.10.79; μg g^{-1}; n = 5)

reach	n	Na	Mg	Ca	Mn	Fe	Zn	Cd	Pb
03/05	20	500	930	1290	1090	20100	154	1.5	107
08	20	690	1440	8370	1820	24500	1640	7.6	2270
23	20	620	1270	10190	1570	23300	1800	9.3	1880
27	5	510	1030	17700	1110	19700	1230	9.2	2240

Table 5.10 Mean metal composition of sediments from R. Derwent for whole study (µg g^{-1})

reach	survey							
	I		II		III		IV	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
03/05	3.15	0.714	2.63	0.381	4.16	0.951	2.70	1.263
08	3.51	0.877	0.83	0.666	2.73	0.617	3.50	0.757
23	3.69	0.682	0.75	0.283	3.98	1.214	3.46	0.595

Table 5.11 Mean % organic content of sediments collected from R. Derwent during Surveys I - IV (dry wt basis: n = 5)

are given in detail in Appendix 3 while the mean values for each survey are presented in Table 5.11. The results are expressed as a percentage of the sample dry weight. The standard deviations refer to replicate samples collected from within each reach.

Comments

i) It is apparent that the mean organic content of sediments was not appreciably different at 03/05, 08 and 23 either during or between Surveys I, III and IV.

ii) During Survey II the organic content of sediment from 03/05 was significantly higher than at 08 or 23 while the latter did not differ appreciably from one another.

5.23 Plants

Samples of bryophytes were collected from reaches 03/05 and 08 during each survey. The methods of collection and analysis have been described in Section 3.6 and involved pooling material taken from different locations within a reach. Samples of plant material were not collected from Bolts Burn, even though *Scapania undulata* was present in this stream during the present study. The levels of Zn, Cd and Pb in the bryophytes collected during Surveys I - IV are given in Tables 5.12 - 5.15 respectively. Standard deviations refer to replicate samples collected from within each reach.

Comments

i) *Fontinalis squamosa* was not found at any reach in the R. Derwent downstream of Bolts Burn although it was always present at 03/05.

ii) Concentrations of Zn, Pb and Cd were greater in plants collected from 08 than in samples from 03/05 upstream of Bolts Burn.

iii) Metal concentrations in *Fontinalis squamosa* were the lowest recorded for each survey with the exception of Cd in *Rhynchostegium riparioides* at 03/05 during Survey III.

iv) Concentrations of metals in *Hygrophypnum ochraceum* at 03/05 were generally the same for each survey. The highest levels of Zn, Cd and Pb at reach 08 occurred during Survey III while the levels for Surveys I, II and IV were lower and similar to one another.

v) The concentrations of Pb in *Scapania undulata* from 03/05 were similar on each sampling occasion while Zn levels were similar during Surveys II and III and highest during Survey IV. Cd levels differed between each survey. High levels for all three metals were found in samples collected from 08 especially during Surveys III and IV.

vi) The order of concentrations of the three metals was the same in all samples from both reaches:

$$Zn > Pb > Cd$$

5.24 Animals

A considerable part of the sampling effort during each survey was devoted to the collection of animals. Sampling was purely qualitative and no attempt was made to determine the numbers of organisms present at each reach. Nevertheless it was still possible to discern which species were most abundant and comments are made in Section 5.241 below Data on the metal composition of the animals sampled during each survey are presented in Section 5.242. Further discussion and comparison with metal analyses made on other components of the environment is left until Chapter 7.

5.241 Species composition and relative abundance

Samples of benthic invertebrates were collected from the R. Derwent during each survey and the more abundant taxa taken for metal analysis. Representatives of these and the less abundant taxa were stored in

reach	taxon	n	Zn	Cd	Pb
0061-05	*Fontinalis squamosa*	1	740	10.7	330
0061-08	*Hygrohypnum ochraceum*	1	2050	42.7	360

Table 5.12 Concentrations of Zn, Cd, Pb in pooled 2 cm tips of bryophytes collected from R. Derwent (05, 08) during Survey I ($\mu g\ g^{-1}$)

reach	taxon	n	Zn	Cd	Pb
0061-03	*Scapania undulata*	1	365	9.6	204
	Fontinalis squamosa	1	200	8.1	110
	Hygrohypnum ochraceum	1	437	12.1	120
0061-08	*Scapania undulata*	1	1760	21.1	680
	Hygrohypnum ochraceum	1	2030	34.3	450

Table 5.13 Concentrations of Zn, Cd, Pb in pooled 2 cm tips of bryophytes collected from R. Derwent (03, 08) during Survey II ($\mu g\ g^{-1}$)

reach	taxon	n	Zn		Cd		Pb	
			$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
0061-03	*Scapania undulata*	5	334	36.0	31.5	4.34	202	83.9
	Rhynchostegium riparioides	5	381	57.9	11.6	2.58	103	13.4
	Fontinalis squamosa	5	299	81.7	13.4	5.09	69	17.4
	Hygrohypnum ochraceum	5	341	19.0	14.6	6.27	104	20.9
0061-08	*Chiloscyphus* sp.	5	3020	856	56.0	24.80	1220	388
	Scapania undulata	5	7700	1744	45.1	5.78	2650	537
	Rhynchostegium riparioides	5	4610	672	78.1	11.00	1700	310
	Hygrohypnum ochraceum	5	3100	312	67.5	7.62	1040	337

Table 5.14 Concentrations of Zn, Cd, Pb in pooled 2 cm tips of bryophytes collected from R. Derwent (03, 08) during Survey III (μg g^{-1})

reach	taxon	n	Zn		Cd		Pb	
			$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
0061-03	*Chiloscyphus* sp.	5	636	41.9	20.8	4.84	518	119.7
	Scapania undulata	5	700	254.7	14.3	6.98	291	56.1
	Fontinalis squamosa	5	145	15.4	6.9	1.48	70	17.3
	Hygrohypnum ochraceum	5	424	58.4	12.8	4.25	245	60.3
0061-08	*Chiloscyphus* sp.	1	6150		27.7		1570	
	Scapania undulata	5	7270	893.0	34.1	3.53	1800	294
	Rhynchostegium riparioides	5	2100	70.5	12.8	1.35	808	43.2
	Hygrohypnum ochraceum	5	1670	152.0	18.0	3.70	515	64.9

Table 5.15 Concentrations of Zn, Cd,Pb in pooled 2 cm tips of bryophytes collected from R. Derwent (03, 08) during Survey IV (µg g^{-1})

suitable preservative and identified. The combined results from all four surveys for reaches 03/05, 08, 23 and 27 on the R. Derwent and reach 99 on Bolts Burn are presented as a list in Table 5.16. Identification was not always made to the same level for all representatives of a particular group. Many of the organisms belonging to the more difficult taxonomic groups such as Trichoptera and Diptera have been grouped together and are listed under these major group headings. Thus Table 5.16 is not a comprehensive list of species.

Reaches 03/05, 08 and 23 were all fast flowing (Fig. 4.2 a, b, c, d) and were sampled during each survey whereas reach 27 which was slower flowing (Fig 4.2e) and formed part of the reservoir when this was near top water level was sampled during Survey I only.

Comments

i) No invertebrates were found in Bolts Burn on any sampling occasion.

ii) With the exception of the Nematoda, Oligochaeta and Hydracarina which were represented by only a few individuals at each reach where they occurred, the invertebrate fauna was found to consist entirely of insect larvae predominated by the groups Ephemeroptera and Plecoptera.

iii) No major differences were found in the species present at reaches above and below Bolts Burn.

iv) *Baetis rhodani* was the most numerous of the three species recorded for this genus.

v) The mayflies *Rithrogena* sp(p). and *Ecdyonurus venosus* were equally abundant at 08 and 23 during Survey II but *Ecdyonurus venosus* was the more numerous on all other occasions.

vi) *Ephemerella ignita* was common at 03/05, 08 and 23 during Survey III.

vii) *Amphinemura sulcicollis* was the most numerous stonefly during Survey II. The stoneflies *Brachyptera risi* and *Isoperla grammatica* were common at o3/05, 08 and 23 during Survey II while the two species of *Protonemura* recorded were present in fewer numbers. *Chloroperla torrentium* was more common than *C. tripunctata*, both were recorded at 03/05, 08 and 23 during Survey II but were less abundant at 03/05 than the other reaches.

viii) *Leuctra fusca* was the most common stonefly during Survey III and the most numerous of the three species recorded for this genus. *Dinocras cephalotes* was recorded at 03/05, 08 and 23 during Survey III but was not found at any other time.

ix) *Perla bipunctata* was the only stonefly found during all four surveys. It was equally abundant at 03/05 and 08 during each survey but was only recorded from reach 23 during Survey III.

x) *Perlodes microcephala* was recorded at 03/05, 08 and 23 during each of Surveys I, II and IV. During Survey II it was as abundant at 03/05 and 08 as *Perla bipunctata*.

The abundance of other groups was not recorded in detail, but an indication of the abundance of some of the remaining organisms may be obtained by referring to Tables 5.17 and 5.18.

5.242 Metal composition

The detailed results of the metal composition of animals collected from the R. Derwent during each general survey are given in Table 5.17, which also includes data on the number of samples collected, the number of organisms per sample and the dry weight of each sample (average dry weight where $n > 1$). The results for Zn, Cd and Pb are summarized in

code	taxon	reach			
		03/05	08	23	27
10 00 00 00	Nematoda	+	+	+	
16 00 00 00	Oligochaeta	+	+	+	+
19 00 00 00	Hydracarina	+	+	+	
30 02 01 02	*Baetis scambus* Eaton	+	+		
30 02 01 05	*Baetis rhodani* (Pictet)	+	+	+	
30 02 01 07	*Baetis muticus* (L.)	+	+	+	
30 03 01 00	*Rithrogena* sp(p).	+	+	+	
30 03 04 01	*Ecdyonurus venosus* (Fabricius)	+	+	+	
30 05 01 01	*Ephemerella ignita* (Poda)	+	+	+	
31 01 03 02	*Brachyptera risi* (Morton)	+	+	+	
31 02 01 01	*Protonemura praecox* (Morton)	+	+	+	
31 02 01 03	*Protonemura meyeri* (Pictet)	+	+	+	
31 02 02 02	*Amphinemura sulcicollis* (Stephens)	+	+	+	
31 02 04 03	*Nemoura avicularis* Morton	+	+	+	
31 02 04 04	*Nemoura cambrica* (Stephens)	+	+		
31 03 01 03	*Leuctra hippopus* (Kempny)	+	+	+	
31 03 01 05	*Leuctra fusca* (L.)	+	+	+	
31 03 01 06	*Leuctra moselyi* Morton	+	+	+	
31 05 02 01	*Perlodes microcephala* (Pictet)	+	+	+	+
31 05 04 01	*Isoperla grammatica* (Poda)	+	+	+	
31 06 01 01	*Dinocras cephalotes* (Curtis)	+	+	+	
31 06 02 01	*Perla bipunctata* Pictet	+	+	+	
31 07 01 01	*Chloroperla torrentium* (Pictet)	+	+	+	
31 07 01 02	*Chloroperla tripunctata* (Scopoli)	+	+	+	
35 03 08 02*	*Oreodytes sanmarki* Sahlberg	+	+	+	
35 05 00 00	Hydrophilidae		+		
35 11 01 01	*Elmis aenea* (Muller	+		+	
35 11 03 01	*Limnius volckmari* (Panzer)	+	+	+	
36 01 01 02	*Sialis fuliginosa* Pictet	+	+	+	
38 00 00 00	Trichoptera	+	+	+	+
38 01 01 01	*Rhyacophila dorsalis* (Curtis)	+	+	+	
38 03 03 01	*Polycentropus flavomaculatus* (Pictet)	+	+	+	+
38 05 01 01	*Hydropsyche pellucidula* (Curtis)	+	+	+	+
38 08 00 00	Limnephilidae	+	+	+	+
40 00 00 00	Diptera	+	+	+	+
40 01 35 00	*Dictanota* sp(p).	+	+	+	+
40 14 02 00	*Chironomus* sp(p).				+
40 15 05 00	*Simulium* sp(p).	+	+	+	

Note: *In Maitland under *O. rivalis* (Gyllenhal)

Reach 27 sampled during Survey I only

Table 5.16 Invertebrates collected from R. Derwent and their occurrence at different reaches

Table 5.17 Metal composition ($\mu g\ g^{-1}$) of invertebrates from R. Derwent during Surveys I - IV

Survey I 29.10.78 (day 5) R. Derwent reach 05: metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg	Ca	Mn	Fe	Zn	Cd	Pb
Ecdyonurus venosus	1	30	37.2	1176	1976	632	1781	1229	17.8	22
Leuctra spp.	1	18	23.0	1440	1160	217	1250	250	11.7	27
Perla bipunctata 0.5 - 1.0 cm	1	3	12.0	1060	1600	354	850	250	10.9	12
Perla bipunctata 1.5 - 2.0 cm	1	4	70.0	1785	3464	371	1089	232	2.5	8
Dicranota sp(p).	1	50	12.0	970	2120	708	1450	347	8.1	27

Survey I 29.10.78 (day 5) R. Derwent reach 08: metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg	Ca	Mn	Fe	Zn	Cd	Pb
Ecdyonurus venosus	1	35	24.7	1180	2870	506	1360	2446	18.8	128
Leuctra spp.	1	18	18.0	970	3160	1097	2360	833	14.1	113
Perlodes microcephala	1	10	32.0	1313	2531	477	1289	812	3.7	56
Perla bipunctata 1.5 - 2.0 cm	1	2	110.0	2682	4909	191	273	522	2.7	20

Table 5.17 (con.) Survey I 30.10.78 (day 6) R. Derwent reach 23: metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg	Ca	Mn	Fe	Zn	Cd	Pb
Ecdyonurus venosus	1	40	27.0	1240	2820	518	1850	4259	24.9	58
Perlodes microcephala	1	8	78.2	1535	3037	291	927	856	4.8	33
Rhyacophila dorsalis	1	6	40.0	1150	775	181	356	493	11.5	12
Polycentropus flavomaculatus	1	10	18.0	1020	900	292	910	805	5.1	32
Hydropsyche pellucidula	1	7	52.0	779	861	529	1288	634	3.7	73
Oreodytes sanmarki	1	11	11.0	2270	1060	773	2090	345	20.5	127
Tipulidae, excluding *Dicranota*	1	3	63.0	1349	4048	2056	7381	2262	12.9	381
Dicranota sp(p).	1	50	34.0	1346	1500	154	846	1286	10.7	59

Survey I 30.10.78 (day 6) R. Derwent reach 27: metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg	Ca	Mn	Fe	Zn	Cd	Pb
Polycentropus flavomaculatus	1	10	13.3	1120	840	320	820	1879	7.6	45
Tipulidae, excluding *Dicranota*	1	4	53.0	1462	5047	2400	11132	2485	15.2	530
Chironomus sp(p).	1	220	127.6	1215	2371	1009	4240	1504	58.7	305

Table 5.17 (con.) Survey II 03.05.79 (day 8) R. Derwent reach 03 : metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
Ecdyonurus venosus	1	10	69.2	1044		830		299		2481		812		4.4		19	
Brachyptera risi	5	10	19.3	990	57	600	21	88	12	1450	499	122	12	3.1	1.4	13	2
Amphinemura sulcicollis	5	25	8.1	1250	43	960	162	263	47	5542	1028	203	13	5.1	1.0	68	19
Leuctra spp.	5	10	6.4	1160	121	1050	90	194	64	3310	746	212	21	2.7	1.0	47	15
Perlodes microcephala	5	1	32.6	2370	153	5356	414	106	22	1386	318	316	41	1.2	0.1	11	4
Isoperla grammatica	5	10	16.1	1430	134	1470	298	113	40	1242	281	304	71	2.4	2.2	22	21
Perla bipunctata 1.5 - 2.0 cm	5	1	33.7	2152	256	2394	662	578	100	1792	410	277	43	0.8	0.3	10	2
Limnius volckmari (adults)	1	20	20.0	2070		550		287		770		137		0.7		18	
Rhyacophila dorsalis	1	4	44.7	1152		324		212		430		234		0.7		6	
Hydropsyche pellucidula	1	2	17.4	910		410		1738		3990		359		1.0		86	
Limnephilidae larvae	1	5	54.3	1441		465		962		3236		244		0.8		23	
Limnephilidae cases	1	5	302.0	488		452		2500		6970		3500		5.7		198	
Simulium sp(p).	1	10	11.3	1320		2010		110		1570		143		1.9		33	

Table 5.17 (con.) Survey II 01.05.79 (day 6) R. Derwent reach 08 : metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
Baetis spp.	1	10	24.3	1300		1300		202		1560		2458		7.8		102	
Rithrogena sp(p).	5	10	21.9	1520	99	1540	86	187	42	2300	308	2368	143	11.4	2.0	171	24
Ecdyonurus venosus	5	5	40.9	1332	44	1456	106	270	58	2620	203	1333	70	6.1	0.6	171	23
Brachyptera risi	5	10	22.5	970	97	760	113	191	90	1780	331	337	46	5.7	1.8	87	15
Amphinemura sulcicollis	5	42	12.7	1400	69	1910	141	400	67	7930	352	855	54	6.7	0.8	293	32
Leuctra spp.	1	20	11.8	1220		1220		95		1525		381		1.9		315	
Perlodes microcephala	5	1	36.5	2370	235	5500	1334	61	7.8	1015	581	504	98	2.4	1.1	70	35
Isoperla grammatica	5	9	13.2	1450	139	1560	157	126	20	2870	1060	675	117	3.6	0.8	271	138
Perla bipunctata 1.0 - 1.5 cm	1	5	46.0	1141		771		195		1255		309		0.5		100	
Perla bipunctata 1.5 - 2.0 cm	5	1	47.8	2284	780	2366	1302	385	100	1544	384	406	27	0.8	0.2	128	37
Chloroperla spp.	1	10	18.8	625		611		99		1010		226		0.9		101	
Limnius volckmari (adults)	1	18	17.0	2470		1110		1190		1330		382		0.7		180	
Limnephilidae (larvae)	1	5	57.1	1619		1055		893		3371		910		3.1		372	
Limnephilidae (cases)	1	10	447	866		6430		2673		1521				9.6		2210	
Simulium sp(p).	1	25	18.8	1270		1460		66		1170		226		1.8		160	

Table 5.17 (con.) Survey II 02.05.79 (day 7) R. Derwent reach 23 : metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg $\bar{x}$	Mg s.d.	Ca $\bar{x}$	Ca s.d.	Mn $\bar{x}$	Mn s.d.	Fe $\bar{x}$	Fe s.d.	Zn $\bar{x}$	Zn s.d.	Cd $\bar{x}$	Cd s.d.	Pb $\bar{x}$	Pb s.d.
Rithrogena sp(p).	5	8	21.1	1270	147	1160	167	272	203	2190	888	3920	446	16.7	7.7	169	71
Ecdyonurus venosus	5	5	27.2	1492	52	1340	115	351	113	2340	917	2300	69	11.6	1.8	164	51
Brachyptera risi	5	10	23.0	1270	158	1000	142	105	33	1350	338	345	63	4.5	1.1	90	24
Amphinemura sulcicollis	5	25	8.6	2090	150	2690	170	587	38	8040	763	1059	74	3.7	1.7	596	83
Leuctra spp.	1	10	12.6	1130		1170		115		2260		476		2.3		214	
Perlodes microcephala	5	1	45.3	2560	352	5810	913	60	35	588	332	608	293	2.4	1.4	70	28
Isoperla grammatica	5	10	18.4	1760	76	2110	709	56	23	1500	458	689	123	2.9	1.6	108	27
Chloroperla spp.	1	10	6.0	1620		2750		166		2000		750		3.7		295	
Limnius volckmari (adults)	1	20	18.2	2550		782		315		700		673		2.0		103	
Rhyacophila dorsalis	1	4	15.3	1650		750		130		833		620		0.9		94	
Hydropsyche pellucidula	1	2	39.7	787		497		390		1320		428		1.4		117	
Limnephiladae (larvae)	1	2	27.2	1562		781		716		2426		845		2.4		208	
Limnephilidae (cases)	1	2	39.4	1522		10970		736		17000				2.9		671	
Tipulidae	1	2	29.0	1551		1181		646		6550		1215		7.9		122	
Simulium sp(p).	1	10	10.3	1500		2010		109		2660		461		4.8		213	

Table 5.17 (con.) Survey III 14.08.79 (day 7) R. Derwent reach 03 : metal concentrations in animals (µg g^{-1})

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
Baetis spp.	5	25	14.6	1680	97	1420	141	504	96	2270	474	1797	174	7.5	0.8	20	5
Ecdyonurus venosus	1	25	40	1687		1512		668		3310		2750		16.6		30	
Ephemerella ignita	5	10	16.9	2430	263	1130	122	910	140	1830	327	1734	543	6.0	1.9	20	7
Leuctra spp.	5	20	8.9	1620	170	1620	317	930	454	5060	2147	414	62	1.2	0.1	85	30
Perla bipunctata 1.5 - 2.0 cm	1	3	107	1770		1028		182		420		233		0.8		4	
Limnius volckmari (larvae)	1	10	5.5	2720		1040		1000		3860		72		1.8		45	
Limnius volckmari (adults)	5	10	8.4	2390	176	1170	79	1490	694	1250	591	170	7	1.5	0.5	32	11
Rhyacophila dorsalis	1	4	37.4	1470		427		254		334		561		2.4		5	
Limnephilidae (larvae and cases)	1	60	50.7	719		922		912		11830		138		0.5		42	
Dicranota sp(p).	1	15	23.5	980		560		8		10		179		0.8		4	

Table 5.17 (con.) Survey III 12.08.79 (day 5) R. Derwent reach 08 : metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
Baetis spp.	6	25	14.3	1550	67	2290	134	408	70	1170	128	10520	760	35.1	6.9	320	72
Ecdyonurus venosus	1	6	4.6	2060		5320		706		4340		15050		79.3		1625	
Ephemerella ignita	5	10	16.7	2970	335	2060	348	1347	107	2340	757	8158	1052	18.5	4.1	704	140
Leuctra spp.	5	25	13.0	1370	79	2190	292	673	95	3340	653	1293	153	20.7	2.4	391	48
Perla bipunctata 1.5 - 2.0 cm	1	3	29.0	1181		775		137		431		482		5.3		93	
Oreodytes sanmarki	1	10	9.2	1300		1440		163		815		1114		10.0		149	
Limnius volckmari (larvae)	1	15	10.2	3280				1490		2690		1250		5.8		504	
Limnius volckmari (adults)	5	20	14.3	2310	171	1040	192	1474	372	1230	359	824	132	3.7	0.8	404	130
Rhyacophila dorsalis	1	8	149	1275		350		125		134		687		3.8		32	
Limnephilidae (larvae and cases)	1	50	34.5	1130		8985		1000		14490		1811		7.1		789	
Dicranota sp(p).	1	10	15.6	1000		785		28		400		304		5.2		76	
Simulium sp(p).	1	30	15.7	1670		3400		652		3820		1194		29.1		617	

Table 5.17 (con.) Survey III 13.08.79 (day 6) R. Derwent reach 23 : metal concentrations in animals ($\mu g\ g^{-1}$)

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
Baetis spp.	5	25	18.4	1460	112	1820	200	393	53	1170	270	7954	731	36.3	2.3	102	33
Ecdyonurus venosus	1	15	15.8	1690		2530		727		2680		14550		57.7		231	
Ephemerella ignita	5	10	17.5	3080	679	1980	323	2055	172	2510	515	10660	1821	23.1	4.7	281	47
Leuctra spp.	5	30	17.5	1280	163	1820	259	739	108	2780	456	1294	140	17.2	1.6	291	54
Limnius volckmari (larvae)	1	15	11.0	2950		1310		750		2500		1060		7.9		231	
Limnius volckmari (adults)	1	20	17.8	2450		955		716		912		1060		4.4		115	
Rhyacophila dorsalis	5	4	77.7	1198	94	368	41	177	38	179	30	976	9	5.8	0.6	9	1
Dicranota sp(p).	1	10	15.4	1070		714		29		640		357		3.5		24	

Table 5.17 (con.) Survey IV 28.10.79 (day 7) R. Derwent reach 03; metal concentrations (µg g^{-1})

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.
Ecdyonurus venosus	1	30	35.5	1230		1410		478		3090		1220		26.3		18	
Brachyptera risi	1	40	27.3	1080		1700		531		2560		183		29.6		25	
Perlodes microcephala	1	6	15.5	1400		1800		320		2770		403		50.0		53	
Perla bipunctata 1.5 - 2.0 cm	5	1	56.8	1476	762	1485	1412	91	11.3	406	103	239	32	12.4	4.7	5	1
Polycentropus flavomaculatus	1	5	13.1	1060		640		477		530		515		52.4		28	
Limnephilidae	1	20	38.0	671		1177		1243		21050		131		1.0		34	
Dicranota sp(p).	1	40	18.7	1470		880		106		900		185		31.4		22	

Survey IV 28.10.79 (day 8 R. Derwent reach 08; metal concentrations (µg g^{-1})

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.
Ecdyonurus venosus	1	20	15.5	1300		2410		345		2400		2000		60.3		120	
Brachyptera risi	1	40	35.6	696		2450		351		2240		498		23.8		179	
Perlodes microcephala	1	4	19.0	1440		1970		113		710		328		32.8		69	
Perla bipunctata 1.5 - 2.0 cm	1	3	102.0	1225		745		61		264		325		6.21		18	
Limnius volkmari (adults)	1	15	17.2	2340		970		436		850		392		45.7		90	
Hydropsyche pellucidula	1	3	17.2	1090		2180		311		2510		581		50.7		261	
Limnephilidae	1	10	30.2	1030		14980		1481		26490		1374		24.0		529	
Tipulidae, excluding *Dicranota*	5	4	83.8	1293	196	2321	393	961	168	5390	1130	918	121	15.6	3.1	363	128
Dicranota sp(p).	1	25	13.0	1400		1230		142		1230		557		73.0		96	

Table 5.17 (con.) Survey IV 30.10.79 (day 9) R. Derwent reach 23: metal concentrations in animals (µg g^{-1})

taxon	n	animals per sample	sample dry wt (mg)	Mg	Ca	Mn	Fe	Zn	Cd	Pb
Baetis spp.	1	50	17.5	1340	1780	400	1050	2770	71.8	128
Rithrogena sp(p).	1	30	10.0	1450	2750	500	1970	5920	88.2	190
Ecdyonurus venosus	1	10	5.0	1450	3100	365	1950	5000	150.5	140
Brachyptera risi	1	40	27.6	1114	2390	615	2350	579	28.1	226
Perlodes microcephala	1	10	62.1	1743	2673	523	3860	962	14.2	161
Limnius volckmari (larvae)	1	20	18.6	2280	1190	1470	2040	900	52.9	318
Hydropsyche pellucidula	1	8	47.0	898	973	691	2230	659	19.8	127
Tipulidae, excluding *Dicranota*	1	5	43.6	1433	1932	625	2860	951	21.7	252
Dicranota sp(p).	1	40	21.4	1670	1190	142	820	590	37.6	114

Table 5.18 Summary of metal composition ($\mu g\ g^{-1}$; Zn, Cd, Pb) of invertebrates from R. Derwent during Surveys I - IV

		Survey I			Survey II						Survey III						Survey IV					
		Zn	Cd	Pb	Zn		Cd		Pb		Zn		Cd		Pb		Zn		Cd		Pb	
					$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
Baetis spp.	03										1797	174	7.5	0.8	20	5						
	08				2458		7.8		102		10520	760	35.1	6.9	320	72						
	23										7954	731	36.3	2.3	102	33	2770		71.8		128	
Rithrogena sp(p).	03																					
	08				2368	143	11.4	2.0	171	24												
	23				3920	446	16.7	7.7	169	71							5920		88.2		190	
Ecdyonurus venosus	03	1229	17.8	22	812		4.4		19		2750		16.6		30		1220		26.3		18	
	08	2446	18.8	128	1333	70	6.1	0.6	171	23	15050		79.3		1625		2000		60.3		120	
	23	4259	24.9	58	2300	69	11.6	1.8	164	51	14550		57.7		231		5000		150.5		140	
Ephemerella ignita	03										1734	543	6.0	1.9	20	7						
	08										8158	1052	18.5	4.1	704	140						
	23										10660	1821	23.1	4.7	281	47						
Brachyptera risi	03				122	12	3.1	1.4	13	2							183		29.6		25	
	08				337	46	5.7	1.8	87	15							498		23.8		179	
	23				345	63	4.5	1.1	90	24							579		28.1		226	
Amphinemura sulcicollis	03				203	13	5.1	1.0	68	19												
	08				855	54	6.7	0.8	293	32												
	23				1059	74	3.7	1.7	596	83												
Leuctra spp.	03	250	11.7	27	212	21	2.7	1.0	47	15	414	62	1.2	0.1	85	30						
	08	833	14.1	113	381		1.9		315		1293	153	20.7	2.4	391	48						
	23				476		2.3		214		1294	140	17.2	1.6	291	54						
Perlodes microcephala	03				316	41	1.2	0.1	11	4							403		50		53	
	08	812	3.7	56	504	98	2.4	1.1	70	35							328		32.8		69	
	23	856	4.8	33	608	293	2.4	1.4	70	28							962		14.2		161	

Table 5.18 (con.)

		Survey I			Survey II						Survey III						Survey IV					
		Zn	Cd	Pb	Zn		Cd		Pb		Zn		Cd		Pb		Zn		Cd		Pb	
					x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.
Isoperla grammatica	03				304	71	2.4	2.2	22	21												
	08				675	117	3.6	0.8	271	138												
	23				689	123	2.9	1.6	108	27												
Perla bipunctata	03	232	2.5	8	277	43	0.8	0.3	10	2	233		0.8		4		239	32	12.4	4.7	5	1
	08	522	2.7	20	406	27	0.8	0.2	128	37	482		5.3		93		325		6.2		18	
	23																					
Chloroperla spp.	03																					
	08				226		0.9		101													
	23				750		3.7		295													
Oreodytes sanmarki	03																					
	08										1114		10.0		149							
	23	345	20.5	127																		
Limnius volckmari (larvae)	03										72		1.8		45							
	08										1250		5.8		504							
	23										1060		7.9		231		900		52.9		318	
Limnius volckmari (adults)	03				137		0.7		18		170	7	1.5	0.5	32	11	392		45.7		90	
	08				382		0.7		180		824	132	3.7	0.8	404	130						
	23				673		2.0		103		1060		4.4		115							
Rhyacophila dorsalis	03				234		0.7		6		561		2.4		5							
	08										687		3.8		32							
	23	493	11.5	12	620		0.9		94		976	9	5.8	0.6	9	1						
Polycentropus flavomaculatus	03																515		52.4		28	
	08																					
	23	1805	5.1	32																		
	27	1879	7.6	45																		

Table 5.18 (con.)

		Survey I			Survey II						Survey III						Survey IV					
		Zn	Cd	Pb	Zn		Cd		Pb		Zn		Cd		Pb		Zn		Cd		Pb	
					x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.	x̄	s.d.
Hydropsyche pellucidula	03				359		1.0		86													
	08																581		50.7		261	
	23	643	3.7	73	428		1.4		117								659		19.8		127	
Limnephilidae (larvae)	03				244		0.8		23													
	08				910		3.1		372													
	23				845		2.4		208													
Limnephilidae (cases)	03				3500		5.7		198													
	08				32870		9.6		2210													
	23				1640		2.9		671													
Limnephilidae (larvae + cases)	03										138		0.5		42		131		1.0		34	
	08										1811		7.1		789		1374		24.0		529	
	23																					
Tipulidae, excluding *Dicranota*	03																					
	08																918	121	15.6	3.1	363	128
	23	2262	12.9	381	1215		7.9		122								951		21.7		252	
	27	2485	15.2	530																		
Dicranota sp(p).	03	347	8.1	27							179		0.8		4		185		31.4		22	
	08										304		5.2		76		557		73.0		96	
	23	1286	10.7	59							357		3.5		24		590		37.6		114	
Chironomus sp(p).	03																					
	08																					
	23																					
	27	1504	58.7	305																		
Simulium sp(p).	03				143		1.9		33													
	08				226		1.8		160		1194		29.1		617							
	23				461		4.8		213													

Table 5.18 with the exception that only one of the size ranges of *Perla bipunctata* (15 - 20 mm) is included. The standard deviations refer to replicate samples collected as described in Section 3.71.

Comments

i) It was possible to sample only two taxa (*Ecdyonurus venosus* and *Perla bipunctata*) from 03/05 and 08 during all four surveys; *Ecdyonurus venosus* was also sampled from 23 during each survey.

ii) The levels of metals were higher in samples from 08 than from 03/05 in all cases for Pb, all but one case for Zn (*Perlodes microcephala*, Survey IV) and all but four cases for Cd (*Leuctra* spp., Survey II; *Perlodes microcephala*, Survey IV; *Perla bipunctata*, Survey IV; *Simulium* spp., Survey II).

iii) There is no obvious pattern as to whether the levels of metals are higher at 08 or 23.

iv) It is apparent that the mayflies as a group (*Baetis* spp., *Rithrogena* sp(p)., *Ecdyonurus venosus*, *Ephemerella ignita*) tend to accumulate Zn, Cd and Pb to higher levels than other animals.

v) The three taxa of mayfly sampled during Survey III all showed especially high levels of metals; the concentrations in these organisms at reach 03/05 were in many instances higher than in other taxa sampled from 08 and 23.

vi) Concentrations of Zn, Cd and Pb in caddisflies were similar to those in stoneflies.

vii) The results for the concentrations of Zn, Cd and Pb in the seven taxa of stonefly were all reasonably similar with the exception that *Leuctra* spp. showed much higher levels of Zn and Cd (but not Pb) in Survey III than in Survey II. However, the other stonefly sampled during Survey III, *Perla bipunctata*, showed similar results to those for Survey II.

(viii) The levels of Zn, Cd and Pb in *Perla bipunctata* were similar for all four surveys and were either the lowest or near lowest recorded for any taxa during each survey.

5.3 SPECIAL STUDY

In addition to the samples collected during the four general surveys an additional study was made on the R. Derwent as described in Section 4.32.

5.31 Metal composition of leaves and detritus from the river bed

The banks of the R. Derwent below Bolts Burn receive a deposit of heavy metal-rich sediment whenever there is a major flood. It is possible therefore that terrestrial plants might be subject to metal enrichment here in comparison with sites upstream of Bolts Burn. The alder also has some roots reaching directly into the river water, so in the case of this tree there is a further possibility for metal uptake. If bankside trees do accumulate metals they may in turn add metals to the river at leaf-fall. The possibility also exists that decaying leaf matter may bind heavy metals from the water thus making them available to detritivorous insect larvae.

Details of the samples of leaves and detritus collected are shown in Table 5.19. The methods of collection and analysis have been described in Section 3.5. As the study took place in November, the leaves of alder and sycamore taken from the trees were old (though still more or less green). The leaves taken from the river bed had probably mostly fallen within the previous four weeks. Flows had been low in the period prior to sampling so many of the leaves on the river bed had probably come from trees overlying the stretch of the river

P, leaves picked from tree growing on river bank: U, unwashed materials from river bed; W, washed leaves from river bed

material	site	code	Na	K	Mg	Ca	Mn	Fe	Zn	Cd	Pb
detritus	0061-05	W	205	1300	1250	20400	832	2270	180	5.7	17
		U	260	1700	1320	18000	2300	8400	240	4.9	85
	0061-08	W	420	1250	1200	22100	920	2270	1900	9.1	95
		U	620	2800	1600	22700	4100	15000	2780	14.2	402
	0061-23	W	730	1650	1200	23900	130	1720	1340	6.8	87
		U	850	2650	1400	21700	880	6100	1820	9.7	250
	0061-27	W	570	5500	1800	15300	690	1000	1620	13.5	45
		U	590	5600	1900	15100	1730	6150	2260	14.2	295
alder	0061-05	P	560	8400	2100	12400	530	190	90	3.8	10
		W	490	4700	1600	13300	510	620	115	3.0	17
		U	570	4500	2050	15900	1430	1860	220	14.6	21
	0061-08	P	1020	7000	2400	14700	1450	220	275	1.9	41
		W	340	2000	1360	19700	660	720	705	4.3	62
		U	600	4100	1600	16600	1760	5070	1020	5.7	197
	0061-23	W	450	2000	1410	22500	676	1270	1250	6.8	91
		U	440	2400	1500	18300	1430	3900	1550	6.8	166
sycamore	0061-05	P	370	11100	1150	9950	240	135	170	6.8	15
		W	465	6050	1670	24000	475	725	125	0.4	16
		U	545	4100	1420	22200	890	1950	120	0.4	22
	0061-08	P	440	15600	1700	18800	380	135	390	2.1	15
		W	575	4200	1600	20800	520	300	415	5.9	31
		U	490	4850	1850	25800	1720	4700	1280	5.7	208
oak	0061-08	W	315	1250	825	14900	1790	675	472	6.8	54
		U	460	1400	1120	18600	1230	2100	475	4.9	133

Table 5.19 Metal composition (μg g^{-1}) of aerial leaves and river bed detritus from R. Derwent during Survey I

from where the samples were taken.

It is unfortunate that there was no replication of the different types of samples at any site but nevertheless the following are apparent:

i) Levels of Mn and Zn in leaves from trees below Bolts Burn are higher than those from trees above Bolts Burn. The difference is sufficiently large that it is unlikely to be due to analytical error.

ii) The percentage increase between reach 05 and reach 08 is more for alder than sycamore, though the absolute level of Zn at reach 08 is higher for sycamore. It is therefore doubtful whether the presence of roots directly in the river water is of quantitative importance in determining the levels in leaves.

iii) The detritus, which included a lot of highly degraded leaves, had much higher levels of Zn and Pb than the recently fallen leaves.

iv) The levels of Zn, Cd and Pb in washed alder leaves were all higher at reach 23 than reach 08, suggesting that possibly some leaves at 08 had floated from sites above Bolts Burn.

v) The ratio, metal in unwashed leaves from river bed : level in washed leaves from river bed, in general falls into the following series:

$$\mathrm{Fe} > \mathrm{Mn} > \mathrm{Pb} > \mathrm{Zn} > \mathrm{Cd}$$

CHAPTER 6

COMPOSITION OF WATER, SEDIMENTS, PLANTS AND ANIMALS FROM THE DERWENT RESERVOIR

6.1 INTRODUCTION

The Derwent Reservoir was sampled during each of the four general surveys and during a special study of the macrophytes in the reservoir as described in Chapter 4. The results of these investigations are presented below. Summaries of the water chemistry and sediment analyses for each general survey are reported in Sections 6.21 and 6.22 respectively while animal data are considered in Section 6.23. The results of the macrophyte study are presented in Section 6.3 All data are presented as described in Section 3.81 and discussed further in Chapter 7.

6.2 GENERAL SURVEYS

Reservoir sites sampled during the four general surveys were R3, R7, R9 and R10 (see Section 4.12).

6.21 Water

Data are reported for the following variables: Na, K, Mg, Ca, Mn, Fe, Zn, Cd, Pb, F, Cl, Si, PO_4-P, conductivity, pH and total alkalinity. Summaries for the first five sampling occasions of each survey are given in Tables 6.1 and 6.2. Raw data may be found in Appendix 1 (metals) and Appendix 2 (anions).

Comments

i) Levels of Cd in reservoir water were frequently undetectable (<0.0003 mg l^{-1}) and will not be considered further.

ii) The mean concentrations of Na, K, Mg and Ca do not differ substantially between sites and show no marked differences between 'total' and 'filtrable' samples.

site	n	conductivity ($\mu s\ cm^{-1}$)		pH		total alkalinity ($mg\ l^{-1}\ CaCO_3$)			Na						K					
										T			F			T			F	
		min	max	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
R3	20	103	150	6.3	7.4	14	9	23	7.3	5.6	8.2	7.3	5.5	8.9	1.66	1.26	1.86	1.62	0.66	1.81
R7	20	104	140	6.3	7.3	12	6	21	7.4	6.5	8.2	7.2	5.4	8.8	1.67	1.53	1.95	1.59	1.09	1.81
R9	15	106	130	6.7	7.5	12	6	15	7.1	6.4	7.8	7.2	6.4	8.0	1.63	1.48	1.82	1.62	1.49	1.80
R10	20	103	142	6.0	7.4	13	6	18	7.4	6.6	8.4	7.1	6.2	8.0	1.67	1.44	1.90	1.60	1.40	1.91

site	n	Mg						Ca						Mn					
			T			F			T			F			T			F	
		mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
R3	20	2.44	1.99	2.82	2.38	1.75	2.64	8.99	6.72	11.4	8.72	6.60	10.8	0.072	0.041	0.120	0.058	0.015	0.105
R7	20	2.48	2.21	2.84	2.37	1.78	2.68	8.90	6.68	11.1	8.51	6.24	10.4	0.081	0.035	0.290	0.059	0.023	0.169
R9	15	2.39	2.19	2.74	2.37	2.14	2.70	8.04	6.36	9.8	7.95	6.28	9.5	0.080	0.045	0.200	0.057	0.023	0.124
R10	20	2.45	2,16	2,88	2.35	2.13	2.60	8.77	6.28	11.4	8.53	6.24	10.2	0.072	0.022	0.304	0.041	0.020	0.095

site	n	Fe						Zn						Cd					
			T			F			T			F			T			F	
		mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
R3	20	0.36	0.25	0.59	0.20	0.14	0.39	0.048	0.026	0.074	0.046	0.024	0.070	<0.0003	<0.0003	0.0011	<0.0003	<0.0003	0.0010
R7	20	0.50	0.20	1.84	0.21	0.14	0.33	0.046	0.020	0.074	0.040	0.012	0.067	<0.0003	<0.0003	0.0005	<0.0003	<0.0003	0.0006
R9	15	0.48	0.22	2.00	0.21	0.12	0.52	0.039	0.024	0.067	0.033	0.018	0.067	<0.0003	<0.0003	0.0004	<0.0003	<0.0003	0.0004
R10	20	0.44	0.21	0.97	0.19	0.13	0.57	0.039	0.022	0.087	0.034	0.019	0.078	<0.0003	<0.0003	0.0012	<0.0003	<0.0003	0.0005

site	n	Pb						F			Cl			Si			PO_4-P		
			T			F													
		mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
R3	20	0.012	0.003	0.033	0.006	<0.003	0.015	0.78	0.60	0.95	10.4	9.0	11.2	1.02	0.78	1.13	0.010	<0.005	0.020
R7	20	0.014	0.005	0.055	0.007	<0.003	0.020	0.76	0.60	0.96	10.9	9.6	11.9	1.04	0.68	1.50	0.010	<0.005	0.023
R9	15	0.011	<0.003	0.025	0.005	<0.003	0.011	0.76	0.56	0.95	11.5	10.9	12.8	1.01	0.68	1.26	0.020	0.008	0.032
R10	20	0.009	<0.003	0.028	0.004	<0.003	0.011	0.74	0.59	0.95	10.6	8.8	12.1	0.87	0.65	1.10	0.011	<0.005	0.018

		pH		total alkalinity			Ca		Mn		Fe		Zn		Cd		Pb	
survey	site	min	max	(mg l^{-1} $CaCO_3$)			$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
				$\bar{x}$	min	max												
I	R3	6.5 -	7.4	18.8	16	23	9.8	1.01	0.031	0.0146	0.29	0.057	0.046	0.0039	<0.0003		0.008	0.0048
	R7	6.5 -	7.3	16.4	14	21	9.6	1.42	0.036	0.0083	0.25	0.043	0.033	0.0032	0.00031	0.00010	0.007	0.0016
	R10	6.5 -	7.4	17.0	15	18	10.0	0.12	0.029	0.0084	0.22	0.018	0.029	0.0067	<0.0003		0.005	0.0011
II	R3	6.7 -	7.4	11.0	9	14	7.84	0.140	0.083	0.0086	0.18	0.023	0.061	0.0069	0.00044	0.00031	0.0098	0.0021
	R7	6.3 -	7.1	9.0	6	11	7.66	0.126	0.074	0.0104	0.15	0.017	0.057	0.0057	<0.0003		0.0104	0.0058
	R9	6.9 -	7.4	8.6	6	10	7.65	0.198	0.065	0.0096	0.19	0.077	0.043	0.0107	<0.0003		0.0072	0.0022
	R10	6.0 -	7.1	10.0	6	16	7.54	0.305	0.070	0.0158	0.17	0.033	0.050	0.0182	<0.0003		0.0082	0.0016
III	R3	6.7 -	7.4	14.2	12	16	7.67	0.628	0.069	0.0191	0.18	0.027	0.050	0.0174	<0.0003		<0.003	
		6.5 -	7.3	11.6	10	13	7.28	0.600	0.050	0.0061	0.20	0.050	0.054	0.0131	<0.0003		0.0036	0.0008
		6.8 -	7.5	13.0	12	15	7.13	0.522	0.054	0.0198	0.20	0.054	0.035	0.0145	<0.0003		0.0038	0.0025
		6.7 -	7.3	14.0	13	15	7.15	0.550	0.058	0.0299	0.24	0.186	0.038	0.0122	<0.0003		<0.003	
IV	R3	6.7 -	7.0	15.4	14	16	9.58	0.350	0.051	0.0317	0.18	0.039	0.029	0.0033	<0.0003		0.064	0.0011
	R7	6.6 -	7.0	13.0	12	14	9.50	0.315	0.077	0.0547	0.26	0.055	0.017	0.0054	<0.0003		0.0080	0.0037
	R9	6.7 -	7.0	15.0	13	16	9.09	0.732	0.054	0.0403	0.24	0.152	0.021	0.0031	<0.0003		0.0057	0.0031
	R10	6.8 -	7.0	14.6	12	16	9.46	0.110	0.009	0.0034	0.16	0.043	0.022	0.0027	<0.0003		0.0056	0.0016

Table 6.2 Summary of selected water chemistry variables (pH, alkalinity, Ca, Mn, Fe, Zn, Cd, Pb) for each reach during main surveys of Derwent Reservoir (metals are for 'filtrable' samples on first five days of collection; concentrations in mg l^{-1} where appropriate)

iii) Mean levels of Fe, Zn and Pb generally decrease on passing down the reservoir (R3 - R10) while mean levels of Mn do not differ substantially between sites. Concentrations of these metals were found to be higher in 'total' than in 'filtrable' samples, the difference being greatest for Mn.

iv) Levels of Ca and Fe were lower during Surveys II and III than at other times. Zn concentrations were lower during Survey IV than other surveys and levels of Pb were lower during Survey III. Concentrations of other metals were generally the same between surveys.

v) On all sampling occasions the order of the concentrations of metals was as follows:

$$Fe > Mn > Zn > Pb > Cd$$

6.22 Sediments

Collection of sediments involved the pooling of material collected from different locations within the boundaries of a site as described in Section 3.4. Determinations of metal composition and organic content were made on all samples collected.

6.221 Metal composition

The mean metal composition of sediments collected during Surveys I - IV are given in Tables 6.3 - 6.6 , respectively. Standard deviations in these tables refer to replicate samples collected from each site. Mean values for the whole study are given in Table 6.7 .

Comments

i) Mean levels of Na, Mn, Zn, Cd and Pb were higher at R9 than at other sites.

ii) In general the order of the concentrations of metals in sediments at all sites was as follows:

$$Fe > Mn > Zn > Pb > Cd$$

site	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
R3	340	23	760	106	890	185	360	45	19000	1460	80	18	1.7	1.4	48	6
R7	360	90	300	76	1090	382	120	34	6800	1750	120	30	1.5	1.1	147	39
R10	320	53	610	108	600	189	230	58	11200	1970	70	8	0.7	0.3	87	46

Table 6.3 Metal composition of sediments at reservoir sites (R3, R7, R10) during Survey I (25.10.78; $\mu g\ g^{-1}$; $n = 5$)

site	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
R3	600	266	840	153	1250	231	440	152	15500	2130	148	79	0.9	0.4	140	75
R7	550	106	230	92	260	37	75	33	5100	2370	39	36	0.6	0.3	25	6
R9	540	105	390	32	940	197	520	386	7200	2500	960	51	1.1	0.5	39	10
R10	600	94	440	63	830	150	430	155	9400	2670	62	27	<0.3		43	10

Table 6.4 Metal composition of sediments at reservoir sites (R3, R7, R9, R10) during SUrvey II (27.04.79; $\mu g\ g^{-1}$; $n = 5$)

site	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
R3	910	124	820	248	1560	286	550	70	20400	2070	340	46	1.3	0.3	220	19
R7	100	82	870	247	470	90	380	175	9000	3180	244	57	1.5	0.6	120	67
R9	760	251	1090	213	1320	433	1400	682	20600	6760	776	310	5.3	2.3	240	76
R10	340	223	540	125	280	86	610	347	12000	2820	107	43	0.8	0.3	54	10

Table 6.5 Metal composition of sediments at reservoir sites (R3, R7, R9, R10) during Survey III (08.08.79; $\mu g\ g^{-1}$; n = 5)

site	Na		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
R3	280	40	400	79	180	24	160	24	11700	974	540	11	0.4	0.1	34	13
R7	290	47	350	45	500	70	150	32	8600	1310	142	71	0.7	0.2	82	28
R9	450	301	310	74	360	76	410	257	8500	1460	137	48	0.5	0.1	72	16
R10	448	186	1500	393	460	23	710	110	30000	7030	162	68	0.6	0.2	97	22

Table 6.6 Metal composition of sediments at reservoir sites (R3, R7, R9, R10) during Survey IV (22.10.79; $\mu g\ g^{-1}$; n = 5)

site	n	Na	Mg	Ca	Mn	Fe	Zn	Cd	Pb
R3	20	530	700	970	370	15400	270	1.0	100
R7	20	320	430	580	180	7370	136	1.0	93
R9	15	580	590	870	770	12100	620	2.3	117
R10	20	420	770	540	490	15600	100	0.5	70

Table 6.7 Mean metal composition of sediments from Derwent Reservoir (sites R3, R7, R9, R10) for whole study ($\mu g\ g^{-1}$)

site	survey							
	I		II		III		IV	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
R3	2.48	0.233	4.55	0.683	5.94	0.950	1.33	0.262
R7	4.91	0.917	1.90	0.929	9.48	2.075	2.83	1.558
R9			7.12	3.460	15.37	5.182	1.61	0.558
R10	3.72	0.977	4.01	0.899	3.25	0.561	3.86	0.484

Table 6.8 Mean % organic content of sediment collected during Surveys I - IV (dry wt basis; n = 5)

differing on only two occasions (Survey II R9 and Survey IV R3) when Zn $>$ Mn.

iii) Levels of metals differed markedly between surveys and sites and were sometimes very variable within sites making further interpretation difficult.

6.222 Organic content

Organic content analysis was carried out on all sediment samples collected from the reservoir during Surveys I - IV. The data are summarized in Table 6.8 and are given in detail in Appendix 3. Results are expressed as a percentage of the sample dry weight. Standard deviations refer to replicate samples.

Comments

i) Organic content of sediments varied considerably between samples, sites and surveys making detailed comparisons unjustified.

ii) No trends were obvious between sites but on two out of three surveys (II and III) the organic content of sediments was highest at site R9.

6.23 Plants

Plant material was not collected from the Derwent Reservoir during the general surveys but was the subject of a special study, the results for which are reported in Section 6.3.

6.24 Animals

Animals were collected from the Derwent Reservoir during each of the four general surveys but during Survey II no organism or group of organisms was found in sufficient abundance to provide enough material for metal analysis. Sampling was purely qualitative. No attempt was made to determine either the numbers of organisms present at each site or the relative abundance of the different taxa. Data on the metal composition of animals collected during Surveys I, III and IV are presented in Section 6.242 and are discussed in relation to metal levels in other components of the environment in Chapter 7.

6.241 Species composition

During each of the four general surveys, invertebrates were collected from the reservoir, stored in suitable preservative and later identified. The combined results for all sites from each of the four general surveys are presented as a list in Table 6.9. As with invertebrates collected from the river, identification was not always made to the same level for all the organisms collected. Many of the organisms belonging to the more difficult taxonomic groups were placed together under a major group heading, *e.g.* Oligochaeta, Trichoptera, etc. Table 6.9 is not therefore a comprehensive list of species occurring in the Derwent Reservoir.

Comments

i) Although organisms were not sampled quantitatively it was apparent that the benthic organisms occurred in only low numbers at all sites (R3, R7, R9, R10).

ii) The organisms found are not unusual for a body of water such as the Derwent reservoir.

6.242 Metal composition

The results of metal analysis of invertebrates collected from the reservoir during Surveys I, III and IV are given in Table 6.10; details of the numbers of samples collected, numbers of organisms per sample and the dry weight of each sample (average dry weight where $n > 1$) are also included. Standard deviations refer to replicate samples collected as described in Section 3.7.

code	taxon
03 12 02 00	*Polycelis* sp.
12 07 01 07	*Lymnaea peregra* (Muller)
16 00 00 00	Oligochaeta
17 01 01 01	*Piscicola geometra* (L.)
17 02 03 02	*Glossiphonia complanata* (L.)
24 03 02 05	*Daphnia hyalina* Leydig
24 03 06 02	*Bosmina coregoni* Baird
26 02 01 03	*Diaptomus gracilis* (Sars)
26 13 07 01	*Cyclops strenuus* Fischer
28 07 03 05	*Gammarus pulex* (L.)
30 02 02 01	*Centroptilum luteolum* (Muller)
30 02 02 02	*Centroptilum pennulatum* Eaton
30 07 01 02	*Ephemera danica* Muller
33 11 00 00	Corixidae
35 03 00 00*	Dytiscidae
35 05 00 00	Hydrophilidae
38 08 00 00	Limnephilidae
40 00 00 00	Diptera
40 14 02 00	Chironomus sp(p).

Note: *Two species identified: *Potamonectes depressus* (Fabricius) Agg., in Maitland as *Deronectes depressus* (Fabricius) = 35 03 07 03; *Stictotarsus duodecimpustulatus* (Fabricius), formerly *Deronectes* but not included in Maitland's checklist.

Table 6.9 Invertebrates collected from Derwent Reservoir during present study

Table 6.10 Metal composition (μg g^{-1}) of invertebrates from Derwent Reservoir during Surveys I - IV

Survey I 02.11.78 (day 7) Derwent Reservoir: metal concentrations in animals (μg g^{-1})

taxon		n	animals per sample	sample dry wt (mg)	Mg	Ca	Mn	Fe	Zn	Cd	Pb
SITE R7											
Lymnaea peregra	0.5 - 1.0 cm	1	15	158.0	1455	213608	516	1424	253	14.5	65
Lymnaea peregra	1.0 - 1.5 cm	1	15	466.3	1367	227858	375	1139	206	10.3	52
Lymnaea peregra	1.5 - 2.0 cm	1	3	388.3	953	251094	553	1803	234	13.0	52
Gammarus pulex	0.5 - 1.0 cm	1	10	79.0	1456	80696	101	522	88	7.1	8
Gammarus pulex	1.0 - 1.5 cm	1	10	114.0	1667	84430	70	373	87	9.0	25
Dytiscidae		1	60	175.2	771	771	21	164	69	0.5	2
Chironomus sp(p).		1	60	132.0	1079	1004	477	5455	265	4.3	75
SITE R10											
Gammarus pulex	0.5 - 1.0 cm	1	7	54.6	1511	84707	101	435	96	9.5	4

Table 6.10 (con.) Survey IV 26.10.79 (day 5) Derwent Reservoir: metal concentrations in animals (µg g^{-1})

taxon	n	animals per sample	sample dry wt (mg)	Mg	Ca	Mn	Fe	Zn	Cd	Pb
SITE R3										
Gammarus pulex 0.5 - 1.0 cm	1	12	102.0	1610	84300	149	1340	107	11.9	66
SITE R7										
Glossiphonia complanata	1	5	46.0	1043	570	119	1730	2559	49.0	113
Gammarus pulex 0.5 - 1.0 cm	1	10	66.5	1635	75100	101	900	93	13.0	16
SITE R10										
Gammarus pulex 0.5 - 1.0 cm	1	10	44.0	1727	90900	176	1640	119	16.1	20
Dytiscidae	1	10	27.7	776	1335	60	397	63	24.8	13

Table 6.10 (con.) Survey III 12.08.79 (day 5) Derwent Reservoir: metal concentrations in animals (μg g^{-1})

taxon	n	animals per sample	sample dry wt (mg)	Mg		Ca		Mn		Fe		Zn		Cd		Pb	
				$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
SITE R3																	
Gammarus pulex 0.5 - 1.0 cm	1	20	123.5	1780		78100		127		738		137		13.1		36	
Dytiscidae	5	15	45.9	656	16	407	15	15	4	164	72	68	3	12.8	1.9	3	0
SITE R7																	
Gammarus pulex 0.5 - 1.0 cm	1	7	63.7	1850		53300		192		686		137		17.3		6	
Dytiscidae	1	15	43.0	715		476		20		290		63		18.8		2	
SITE R9																	
Gammarus pulex 0.5 - 1.0 cm	1	25	185.0	1743		70200		182		1120		136		18.9		20	
Dytiscidae	5	13	39.8	686	64	368	34	24	5	186	105	77	6	17.3	3.5	5	1
SITE R10																	
Gammarus pulex 0.5 - 1.0 cm	1	7	35.8	1820		55800		104		907		132		25.9		5	

Comments

i) It was not possible to collect samples of any taxon from every site on all sampling occasions, consequently the data are fragmentary; nevertheless, *Gammarus pulex* was taken on 10 out of a possible 15 times.

ii) Levels of Zn and Cd in *Gammarus pulex* were similar at all sites on all sampling occasions but levels of Pb varied between sites and surveys.

iii) There is no obvious pattern to the distribution of metals in the Dytiscidae although the levels were consistently lower than in other organisms.

iv) Highest levels of Zn, Cd and Pb recorded for any animal from the reservoir were found in the leech *Glossiphonia complanata* collected from R7 during Survey IV, while *Lymnaea peregra* was found to have the highest levels of Mn and *Chironomus* sp(p). the highest Fe.

v) The metal concentrations in the different size classes of *Lymnaea peregra* and *Gammarus pulex* were in general similar for all metals. As it was not possible to collect replicate samples of each size class critical comparison is not justified.

6.3 SPECIAL STUDY

Macrophytes were not collected from the reservoir during the general surveys but were the subject of a special study. During this study samples of plant material, water and sediment were collected from various sites around the shore of the reservoir. Details of the locations of sites, the numbers of each type of sample taken and the dates of collection are given in Section 4.33. All the samples were analysed for Zn and Pb, while determinations of the concentrations of Na, K, Mg, Ca, Mn, Fe and Cd were also made on the water samples.

The results of this special study are presented below and brief comment made on the metal composition of each component sampled. Comparisons between the different components are also made. The results are discussed further in Chapter 7.

6.31 Metal composition of water

The concentrations of metals in the water samples are given in Table 6.11.

Comments

i) Sites nearest the river (R1, R11) have higher levels of all metals ('total' and filtrable) except Pb than sites nearest the dam (R10, R22).

ii) The concentration of Pb is much higher at R1 than R10 and somewhat higher at R11 than R22. The value for R10 is however higher than for R11. This is almost certainly due to wind action on the southern shore.

iii) The levels of many metals were found to be exceptionally high at R2 with, for instance 'total' Pb at 0.60 mg l^{-1}. This is the highest concentration of Pb found in any water sample collected during the present study. The following were at least 50% higher at R2 than R1: 'total' Mn, 'total' Fe, 'total' Zn, 'total' Cd, 'total' Pb. The order in which R2 exceeds R1 is.

$$Fe > Pb > Cd > Zn > Mn$$

The water column was especially shallow here (Fig. 2.2, Fig. 4.3) and overlies beds of *Nitella*. On the day that samples were collected substantial amounts of suspended material were present in the water at this site.

iv) Elevated levels of 'total' Mn, Fe and Pb were apparent at sites R4 and R10. (It is not clear from the data that Zn behaves in the same manner.)

Table 6.11 (con.)

	Na		K		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
site	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F
R11	8.9	7.9	2.2	2.2	3.0	3.1	9.00	9.36	0.180	0.175	0.44	0.26	0.080	0.088	0.0010	0.0004	0.013	0.011
R12	7.4	7.1	1.84	1.76	2.7	2.5	6.92	6.36	0.145	0.180	0.45	0.33	0.059	0.054	0.0010	0.0003	0.009	0.006
R13	7.1	6.6	1.68	1.82	2.8	2.4	7.24	6.48	0.055	0.040	0.35	0.14	0.052	0.043	0.0003	0.0003	0.010	0.003
R14	7.1	6.9	1.76	1.78	2.4	2.5	6.48	6.64	0.060	0.040	0.27	0.19	0.047	0.043	<0.0003	<0.0003	0.003	0.003
R15	7.4	6.9	1.76	1.76	2.4	2.4	6.40	6.60	0.045	0.035	0.28	0.16	0.048	0.046	0.0007	0.0003	0.007	0.003
R16	7.2	6.9	1.76	1.84	2.5	2.5	6.88	6.84	0.055	0.060	0.36	0.12	0.051	0.045	0.0004	0.0003	0.008	0.003
R17	8.0	7.8	1.78	1.68	2.3	2.4	6.64	6.44	0.055	0.045	0.23	0.13	0.055	0.050	0.0003	0.0004	0.005	0.003
R18	8.1	7.4	1.74	1.68	2.5	2.3	6.56	6.48	0.115	0.080	0.39	0.19	0.051	0.052	0.0004	0.0004	0.005	0.004
R19	8.0	7.7	1.90	1.68	2.4	2.2	6.32	6.28	0.055	0.035	0.27	0.14	0.047	0.043	0.0004	0.0003	0.006	0.003
R20	8.2	7.6	1.70	1.76	2.5	2.3	6.52	6.24	0.055	0.035	0.23	0.19	0.053	0.046	0.0004	0.0004	0.005	<0.003
R21	8.4	7.6	1.66	1.68	2.5	2.3	6.40	6.00	0.060	0.055	0.28	0.15	0.051	0.051	0.0003	0.0003	0.003	0.003
R22	8.4	7.5	1.82	1.70	2.3	2.3	6.32	6.24	0.050	0.050	0.23	0.19	0.053	0.047	0.0004	0.0003	0.004	0.003

v) Levels of filtered Mn are also higher at R4, R6, R9 and R10. If there is any increase in filtered Fe and Pb it is not as obvious as with Mn. This suggests that particles influenced by water turbulence and small enough to pass through a 0.2 µm filter contribute more to the concentration of Mn in the filtrable fraction than the concentration of other elements.

vi) In general along both shores the concentrations of all metals in the water decrease on passing away from the entrance of the river towards the dam although this trend may be interrupted locally.

vii) The ratio of Zn : Pb increases on passing down the reservoir away from the mouth of the river suggesting that Pb is lost from the water column more rapidly than Zn.

6.32 Concentrations of Zn and Pb in sediments

The concentrations of Zn and Pb in sediment samples are given in Table 6.12. Standard deviations refer to replicate samples. The data are also expressed pictorially in Figs 6.1 and 6.2.

Comments

i) The levels of both metals decrease on passing down the reservoir along both shores but, as was found with the water samples, this trend may be interrupted locally. While the levels of Zn appear to be similar along both shores the data suggest that Pb levels may be higher along the northern shore.

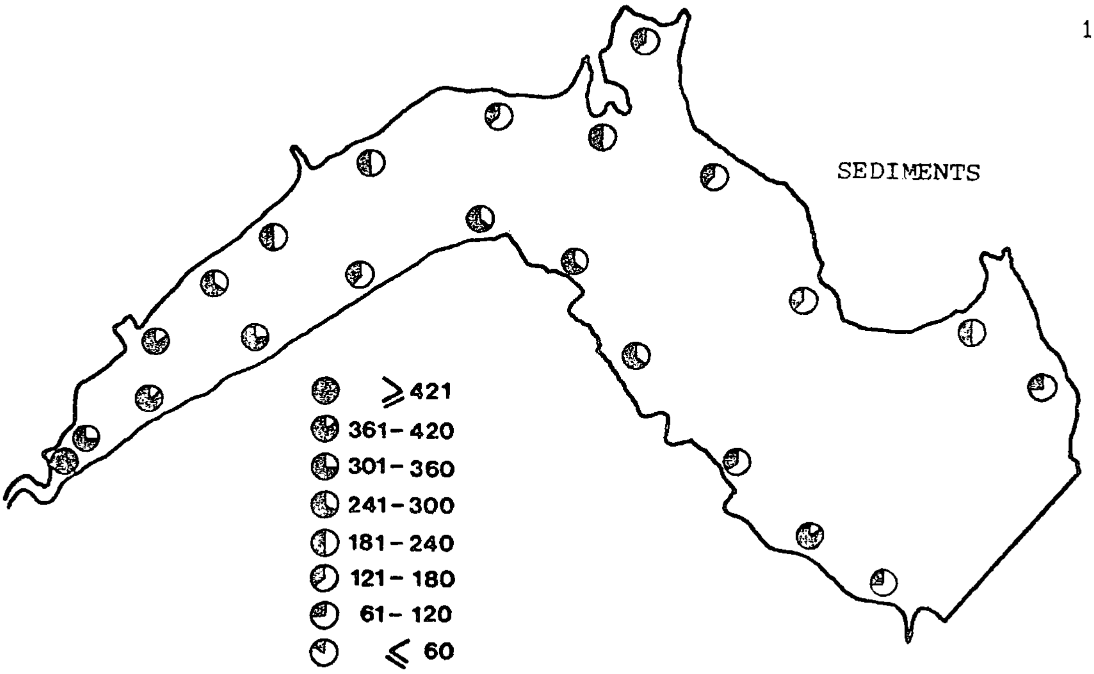
ii) The ratio of Zn : Pb in sediments increases on passing down the reservoir away from the mouth of the river and may be lower along much of the northern shore than along the southern shore.

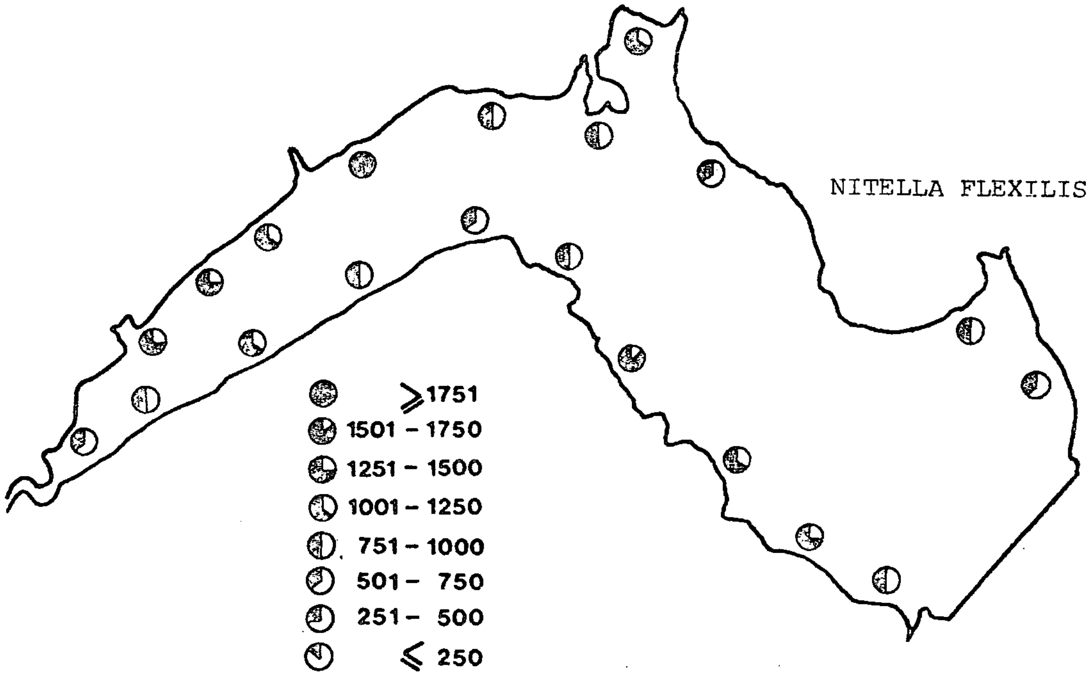
		Zn		Pb				Zn		Pb	
site	n	$\bar{x}$	s.d.	$\bar{x}$	s.d.	site	n	$\bar{x}$	s.d.	$\bar{x}$	s.d.
R1	5	570	48	870	71	R11	5	330	43	380	78
R2	5	390	16	590	41	R12	5	400	55	510	96
R3	5	340	46	228	19	R13	5	250	76	480	144
R4	5	179	14	95	26	R14	5	181	17	156	20
R5	5	290	17	126	33	R15	5	189	14	430	104
R6	5	268	50	105	18	R16	5	177	22	250	22
R7	5	244	57	125	67	R17	5	180	19	175	83
R8	5	124	7	108	24	R18	5	168	18	200	29
R9	5	390	328	240	76	R19	5	163	15	165	23
R10	5	107	43	54	10	R20	5	131	48	34	4
						R21	5	250	82	64	8
						R22	5	102	5	101	6

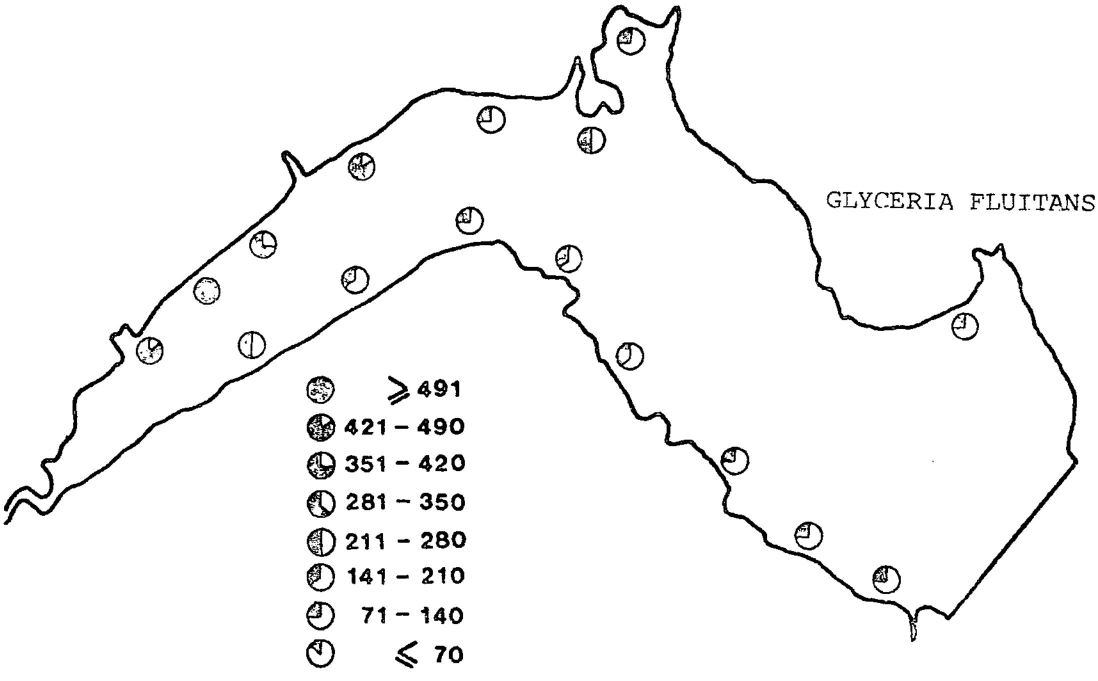
Table 6.12 Metal composition (μg g^{-1}; Zn, Pb) of reservoir sediments at sites sampled during special study

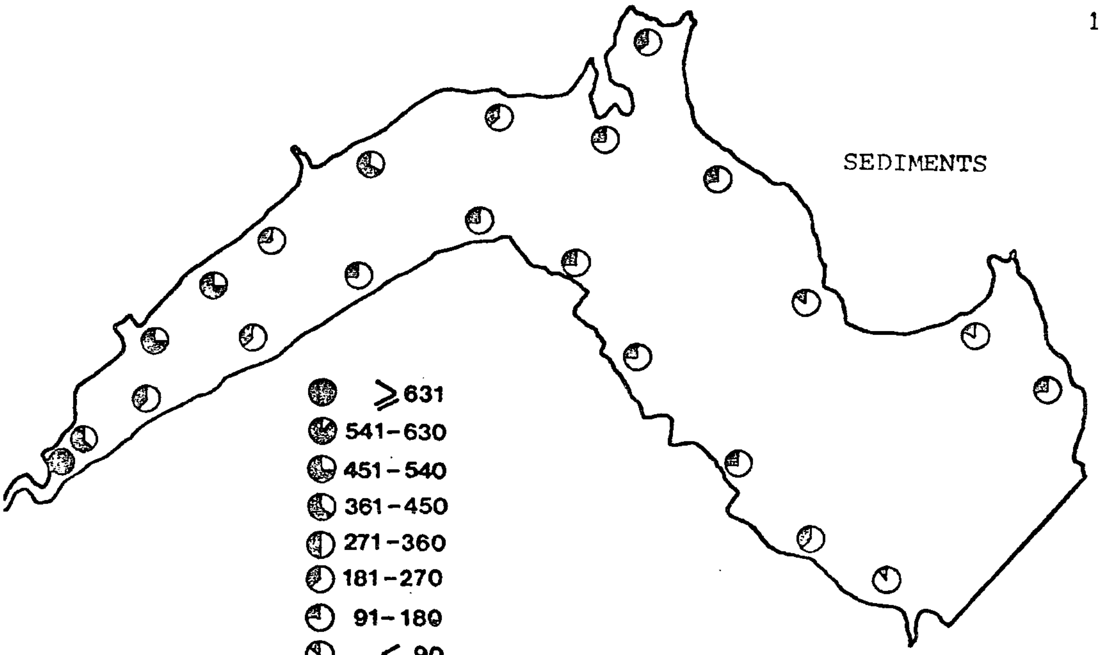
	Glyceria fluitans					*Nitella flexilis*				
		Zn		Pb			Zn		Pb	
site	n	$\bar{x}$	s.d.	$\bar{x}$	s.d.	n	$\bar{x}$	s.d.	$\bar{x}$	s.d.
R1										
R2						5	930	39	530	95
R3	1	220		45		5	1020	57	110	26
R4	5	140	30	22	6	5	900	50	120	43
R5	5	130	16	15	3	5	690	47	99	30
R6	5	185	29	16	3	5	850	52	120	7
R7	5	156	11	15	4	5	1600	66	94	4
R8	5	131	8	14	1	5	1120	91	73	10
R9	5	111	15	22	7	5	1340	56	95	18
R10	5	89	14	14	2	5	870	45	72	13
R11						5	610	158	490	79
R12	1	440		106		5	1310	178	330	73
R13	1	500		83		5	1450	107	200	59
R14	5	350	16	76	21.0	5	1140	110	127	20
R15	5	440	203	95	95.0	5	1980	56	184	36
R16	5	123	5	13	2.1	5	840	116	76	10
R17	5	270	41	24	3.4	5	560	72	41	6
R18	5	93	9	12	3.0	5	1120	82	78	6
R19						5	620	49	76	9
R20										
R21	5	133	26	10	2.7	5	930	38	51	10
R22						1	570		29	

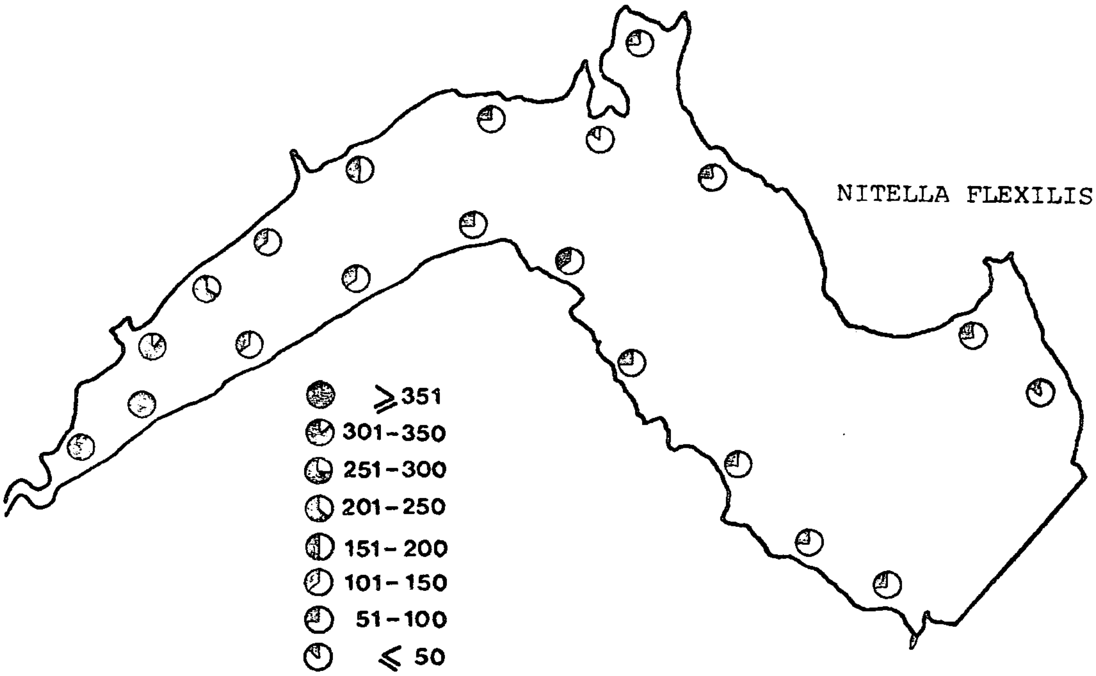
Table 6.13 Metal composition (μg g^{-1}; Zn, Pb) of *Glyceria fluitans* and *Nitella flexilis* at reservoir sites during special study

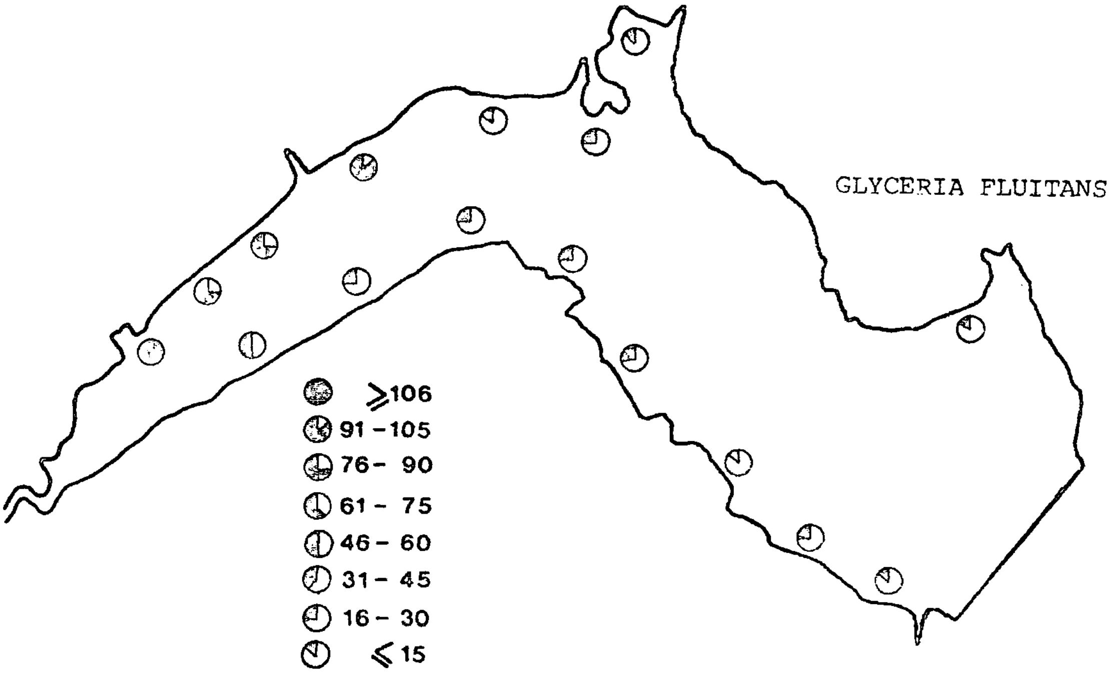

SEDIMENTS
≥421
361-420
301-360
241-300
181-240
121-180
61-120
≤60


NITELLA FLEXILIS
≥1751
1501-1750
1251-1500
1001-1250
751-1000
501-750
251-500
≤250


GLYCERIA FLUITANS
≥491
421-490
351-420
281-350
211-280
141-210
71-140
≤70


SEDIMENTS


NITELLA FLEXILIS


GLYCERIA FLUITANS

6.33 Concentrations of Zn and Pb in plants

The concentrations of Zn and Pb in samples of the aquatic macrophytes *Nitella flexilis* and *glyceria fluitans* are given in Table 6.13. Standard deviations refer to replicate samples. The data are also expressed pictorially in Figs 6.1 and 6.2.

Comments

i) There was a wide range in the concentrations of both Zn (560 - 1980 μg g^{-1}) and Pb (12 - 530 μg g^{-1}) in *Nitella flexilis*.

ii) The concentrations of Pb in *Nitella flexilis* appear to decrease on passing down the reservoir rowards the dam but no such pattern is evident for Zn, *i.e.*the Zn:Pb ratio increases on passing down the reservoir.

iii) Although the concentrations of Zn in *Nitella flexilis* are similar for both shores there is some indication that Pb levels may be higher in plants collected from the northern shore.

iv) There was a wide range in the concentrations of both Zn (93 - 500 μg g^{-1}) and Pb (10 - 106 μg g^{-1}) in *Glyceria fluitans*.

v) In general the concentrations of Zn and Pb in *Glyceria fluitans* both decreased on passing down the reservoir towards the dam.

vi) The concentrations of both metals in *Glyceria fluitans* are generally higher along the northern shore than along the southern shore.

vii) Zn and Pb concentrations were much lower in *Glyceria fluitans* than in *Nitella flexilis* at sites where both species were present.

CHAPTER 7

DISCUSSION

7.1 INTRODUCTION

This study was designed to examine the distribution of heavy metals (Zn, Cd, Pb) in the R. Derwent and Derwent Reservoir. Such a study was inevitably very broad and its limitation to one year meant that many components could only be represented by a few samples. Nevertheless, the results reported in Chapters 5 and 6 allow detailed comparisons to be made between metal concentrations in water, sediments and selected plants and animals.

The metal composition of the water is considered first (section 7.2) followed by the sediments (section 7.3) where comparisons between these two components are made. The importance of organic matter in binding metals to river sediments is also considered.

Sections 7.4 and 7.5 deal with plants and animals respectively. Here, metal concentrations in the various taxa are compared at different sampling stations, during different surveys and with one another; detailed comparisons with metal concentrations in water and sediments are also made and their possible importance as sources of metals for selected organisms is also considered.

7.2 WATER

7.21 Bolts Burn

This stream is considered first as the previous study of Harding (1978) showed that after passing through the Whiteheaps mine complex it carried elevated concentrations of Zn, Cd and Pb and was the main input of these metals to the R. Derwent upstream of the Derwent Reservoir. Bolts Burn was sampled in order to establish similarities in metal input to the R. Derwent during the two studies.

Comments on the metal composition of water from Bolts Burn were made in Section 5.211 where it was pointed out that concentrations of Zn and Cd did not suffer substantially between 'total' and 'filtrable' samples while Pb did not behave in this way. This indicates that the proportion of Pb in the water associated with particulate material was greater than for Zn and Cd. Such a difference in the behaviour of these metals was also apparent during the previous study and was shown to be related to their source in the Whiteheaps mine complex (Harding, 1978; Section 2.5). The similarity between the two studies suggests a common source of metal contamination.

A more detailed comparison with Harding's results shows that while metal concentrations in Bolts Burn were generally lower during the present study, especially 'total' Pb and 'total' Cd, 'filtrable' Pb was higher. Harding reported that occasionally Bolts Burn carried a high load of suspended material and under such conditions higher concentrations of Pb associated with particulate material were found compared to when the stream was running clear. Similar conditions *i.e.* high levels of suspended material, were observed during the present study (P. A. Russell, pers. comm.) but did not occur on any sampling occasion during Surveys I - IV. Although it is not possible to make further comparisons without more detailed information, it seems likely that the data summarized above for 17 sampling occasions during this study do not represent conditions in Bolts Burn as adequately as those

	stream and reach no.	n	Zn T	Zn F	Cd T	Cd F	Pb T	Pb F
Harding 1978	0071-99	100	1.45	1.18	0.0055	0.0064	0.276	0.023
present study	0071-99	17	1.25	1.20	0.0020	0.0018	0.070	0.050

of the previous study based on 100 samplings.

7.22 R. Derwent

Water was collected from reach 03/05 on the R. Derwent upstream of Bolts Burn to determine the chemical composition of a 'pollution free' reach. Harding (1978) found no evidence of any influence of old mine workings in the valleys of Nookton Burn and Beldon Burn on the metal composition of water in the R. Derwent and considered that reach 05,'.........provided an example of a reach where 'natural' factors might be expected to be almost the only ones affecting the composition of the water'. Nevertheless, as reach 03/05 was important in establishing the 'background' metal concentrations to which the biota were exposed, it was considered necessary to confirm the findings of the previous study by collecting samples during each general survey.

It was found that concentrations of Zn, Cd and Pb at 03/05 did not differ substantially between surveys (Section 5.212) and mean values for the whole study are similar to those reported by Harding (1978).

	stream and reach no.	n	Zn T	Zn F	Cd T	Cd F	Pb T	Pb F
Harding 1978	0061-05	48	0.026	0.021	0.0005	0.0022	0.007	0.009
present study	0061-03/05	27	0.020	0.019	<0.0003	<0.0003	0.007	0.005

Bolts Burn was found to influence the chemistry of the R. Derwent at reaches 08 and 23 (Table 5.1). Brief comparison was made with reach 03/05 (Sections 5.213, 5.214) and it was noted in particular that concentrations of Zn, Cd and Pb were higher at reaches 08 and 23. The magnitude of the increases in Zn, Cd and Pb at 08 and 23 for 'total' and 'filtrable' samples calculated from the data in Table 5.1 are given below. The implications with regard to metal accumulation by the biota are considered in Sections 7.4 and 7.5.

	Zn		Cd		Pb	
reach	T	F	T	F	T	F
08	X 15.0	X 14.5	X 2.0	X 2.0	X 3.0	X 3.2
23	X 12.5	X 11.1	X 2.0	X 2.0	X 2.8	X 3.0

It can be seen from the figures above and the data in Table 5.1 that although elevated concentrations of Zn, Cd and Pb persisted at reach 23, mean concentrations of both Zn and Pb were lower than at reach 08. It seems unlikely that the observed decrease is a dilution effect caused by water from Shildon Burn as this stream carries similar concentrations of metals to the R. Derwent (Harding 1978) but may instead result from an association of Zn and Pb with the sediments as water passes downstream from Bolts Burn. This is considered further in Section 7.321.

In addition to causing changes in the concentrations of metals, Bolts Burn also influences the anion composition of water in the R. Derwent, giving rise to higher concentrations of F, Cl and Si but lower po$_4$-P at reach 08. Further increases in F and Cl and an increase in PO$_4$-P at 23 are probably caused by inputs of sewage effluent at Blanchland (Section 2.5, Table 5.1).

Detailed comparison of the chemical composition of water from each site between surveys is made difficult by the variability of the data, caused mainly by intermittent effluent discharge from Whiteheaps mine. However it seems likely that flow may be an important factor influencing seasonal changes as Zn, Cd and Pb concentrations tended to be lower during spring when the river was at its highest, and higher during summer and autumn when low flow was observed.

7.23 Derwent Reservoir

As with the R. Derwent, water samples were collected from the reservoir in order to examine seasonal changes and determine the concentrations of metals to which the biota were exposed.

In general concentrations of metals were similar between surveys and a trend of decreasing metal concentrations was apparent on passing down the reservoir from the mouth of the river towards the dam (Tables 6.1, 6.2, 6.11; Sections 6.21, 6.31).

During the summer of 1979 wind action on the reservoir was especially marked (Section 2.6); the resulting waves frequently caused an increase in levels of suspended material in the water along the shore and occasionally large differences were observed between metal concentrations in 'total' and 'filtrable' water samples (Section 6.31). The data for site R2 (Table 6.11) provide an example of the effects of wave action on metal concentrations in reservoir water. At the time water samples were collected from this site a strong N.E. wind was blowing. Although the sampling technique included a period of five minutes to allow for sedimentation of larger particles, the 'total' water sample carried high levels of suspended material and substantial differences in concentrations of Ca, Mn, Fe, Zn, Cd and Pb between 'total' and 'filtrable' samples were recorded. The difference was most striking for Pb; the concentration in the 'filtrable' sample was 0.018 mg l^{-1} while the 'total' was 0.600 mg l^{-1} and was the highest concentration of Pb recorded in any water sample during the entire study.

Although it is not clear from Table 6.11 to what extent wave action influences the release of metals from the sediments to the overlying water, it is evident that not all metals behave in the same way as can be seen by comparing 'total' and 'filtrable' Mn at R3, R4, R6, R9, R10 and R18 with for example 'total' and 'filtrable' Pb. A detailed investigation of the effects of turbulence on the distribution of metals between water and sediments may elucidate the situation and would aid comparisons with metal concentrations in the biota.

Samples of water collected from the shore of the reservoir during windy conditions are unlikely to be representative of the main body of the reservoir, however, no attempt was made to collect samples further from the shore where the effects of the wave action may have been less evident as it was intended that the water samples should be representative of the conditions to which plants and invertebrates were exposed.

The effects of collecting water samples from the shore as opposed to open water sites sampled by Harding (1978) and Harding and Whitton (1978) prevent detailed comparisons with this study. However, one feature, the decrease in metal concentrations in the water on passing down the reservoir is common to all the investigations and is considered in Section 7.33.

7.24 Comparison with the literature

This section briefly compares the concentrations of Zn, Cd and Pb recorded in water samples during the present study with those reported by other workers (Table 7.1) and the terms 'low', 'moderate' and 'high' are introduced to describe the levels of pollution in the Derwent catchment.

Abdullah and Royle (1972) reported metal concentrations for several rivers in Wales and suggested that concentrations of Zn, Cd and Pb in water from a 'clean' stream for the area they studied might be 0.011, 0.00041 and 0.00070 mg l^{-1} respectively. These concentrations are similar to those recorded in the 'unpolluted' R. Caragh, Ireland, by Dowling, O'Connor, O'Grady and Clynes (1981) (See Table 7.1). Although the concentrations of Zn, Cd and Pb at reach 03/05 on the R. Derwent are slightly higher, they are similar to those reported by other workers for streams in the Northern Pennines at reaches unaffected by mining activities (Table 7.1) and may be considered as low. In contrast, the concentrations of Zn, Cd and Pb

author(s)	year	water course	filtration	Zn	Cd	Pb
Abdullah & Royle	1972	R. Twymyn (Wales)	?	0.300 - 0.600		
		R. Rheidol (Wales)	?	0.050 - 0.130	0.0010 - 0.0034	0.0013 - 0.0024
		R. Ystwyth (Wales)	?	0.200 - 0.270		0.002 - 0.006
		R. Mawddach (Wales)	?	0.014 - 0.050		
Adams *et al.*	1980	Palestine Lake (Indiana)	0.45μ membrane filter	0.032 - 0.636	0.0006 - 0.0433	
		Williamson Ditch (Indiana)	0.45μ membrane filter	0.624 - 0.894		
		Trimble Creek (Indiana)	0.45μ membrane filter	0.0125- 0.0356		
Brooker & Morris	1980	R. Rheidol (Wales)	unfiltered	0.104 - 0.327	0.0008 - 0.0013	0.009 - 0.012
		R. Ystwyth (Wales)	unfiltered	0.015 - 0.565	0.0007 - 0.0015	0.005 - 0.067
Burton & Peterson	1979	R. Rheidol (Wales)	0.5μ Millipore filter	0.05 -27.5		0.1 - 0.5
		R. Ystwyth (Wales)	0.5μ Millipore filter	0.01 - 0.66		0.1 - 0.4
Davison	1980	Windermere (England)	0.4μ Nucleopore filter	0.0021	< 0.00005	< 0.0001
Dowling *et al.*	1981	R. Caragh (Ireland)	unfiltered	0.0024- 0.0220	< 0.0005	0.0008 - 0.0048
Gale *et al.*	1973	Streams in New Lead Belt (Missouri)	unfiltered	$<$0.010 - 0.280	< 0.01	0.002 - 0.830
Gommes & Muntau	1976	Lake Maggiore (Italy)	unfiltered		0.0005 - 0.0056	
Harding	1978	Bolts Burn above Whiteheaps Mine	'total'	$\bar{x} = 0.021$	$\bar{x} = 0.0006$	$\bar{x} = 0.015$
		Bolts Burn reach 99	'total'	$\bar{x} = 1.453$	$\bar{x} = 0.0055$	$\bar{x} = 0.276$
		R. Derwent reach 05	'total'	$\bar{x} = 0.026$	$\bar{x} = 0.0005$	$\bar{x} = 0.007$
		R. Derwent reach 07	'total'	$\bar{x} = 0.317$	$\bar{x} = 0.0018$	$\bar{x} = 0.051$
		R. Derwent reach 25	'total'	$\bar{x} = 0.217$	$\bar{x} = 0.0018$	$\bar{x} = 0.061$
		R. Tyne upstream of R. Nent	'total'	0.031	< 0.0001	0.006
		R. Tyne downstream of R. Nent	'total'	0.187	0.0015	0.021
Kronfield & Navrot	1974	Qishon River (Israel)	Whatman GF/C filter	0.2 - 0.8	< 0.01	0.13
McLean & Jones	1975	R. Ystwyth (Wales)	unfiltered	$<$ 0.50 - 3.50	$<$0.01 - 0.076	0.003 - 0.032
Moore *et al.*	1979	Four lakes in Canadian subarctic	?			0.002 - 0.91
Namminga *et al.*	1974	Theta Pond Oklahoma university	unfiltered	$\bar{x} = 0.016$		$\bar{x} = 0.013$
Paul & Pillai	1978	R. Peryar (Indiana)	Whatman 42 filter	0.015 - 0.40	0.002 - 0.20	
Sakino *et al.*	1980	Murasaki River (Japan)	?		< 0.0001	0.020
		Wariko River (Japan)	?		< 0.0001	0.060
Say	1977	R. Nent near source	No. 2 Sinta filter	0.080		0.012
		R. Nent at Nenthead	No. 2 Sinta filter	2.70		0.038
Tyler & Buckney	1973	Storys Creek (Tasmania)	0.5μ filter	0.10 - 105	0.03 - 6.10	
Valdez	1975	R. Mersey at Warrington	?		0.003 - 0.19	
		R. Tame at Stockport	?		0.004 - 0.13	
		Nant-y-fendrod at Swansea	?		0.05 - 1.29	
Vivian & Massie	1977	T. Tawe (Wales)	Whatman GF/C filter	0.012 - 6.800	0.0009 - 0.160	0.0041 - 0.150
Welsh & Denny	1976	Ullswater (England)	?			0.002 - 0.005
		Red Tarn Beck (England)	?			0.040
Present Study		Bolts Burn reach 99	'total'	0.77 - 2.38	0.0012 - 0.0028	0.024 - 0.146
				$\bar{x} = 1.24$	$\bar{x} = 0.0019$	$\bar{x} = 0.070$
		R. Derwent reach 03/05	'total'	0.010 - 0.070	$<$ 0.0003 - 0.0005	$<$0.003 - 0.018
				$\bar{x} = 0.019$	$\bar{x} < 0.0003$	$\bar{x} = 0.007$
		R. Derwent reach 08	'total'	0.126 - 0.62	$<$ 0.0003 - 0.0013	0.014 - 0.038
				$\bar{x} = 0.28$	$\bar{x} = 0.0006$	$\bar{x} = 0.020$
		R. Derwent reach 23	'total'	0.141 - 0.61	0.0004 - 0.0010	0.006 - 0.049
				$\bar{x} = 0.25$	$\bar{x} = 0.0005$	$\bar{x} = 0.019$
		Derwent Reservoir	'total'	0.020 - 0.32	$<$ 0.0003 - 0.0014	$<$0.003 - 0.600

<u>Table 7.1</u> Comparison between concentrations of Zn, Cd and Pb in R. Derwent and Derwent Reservoir during present study with those reported in the literature for other bodies of water (concentrations in mg l^{-1})

recorded for Bolts Burn at reach 99 were frequently higher than many of those tabulated and must be considered'high'. The R. Derwent at reaches 08, 23 and 27 is also contaminated but to a less extent than Bolts Burn. Comparison with Table 7.1 reveals that metal concentrations in the R. Derwent are similar to those reported for many other polluted streams and contamination may be classed as 'moderate' for Zn, and Pb while Cd falls between 'moderate' and 'low'.

It is important to remember that such terms are merely convenient labels based on comparisons with the results of other workers and bear no relation to the possible effects of metals on the biota.

7.3 SEDIMENTS

7.31 Introduction

Heavy metals in sediments may be available for uptake by rooted aquatic plants (see Section 1.22) and it was suggested in Section 1.232 that sediments represent a potential source from which invertebrates may accumulate metals. Analyses of sediments were carried out during this study with a view to assessing their possible importance as a source of metals to the biota.

7.32 R. Derwent

The metal composition of river sediments for each survey were given in Tables 5.6 - 5.9 and the mean values for the whole study presented in Table 5.10. Comments on these data were made in Section 5.221 and the more important points are summarized below for convenience.

i) Mean concentrations of all metals for the whole study were lower at 03/05 than other reaches and with a few minor exceptions (see Section 5.221) the same was true of each survey.

ii) Replicate samples showed high variability and no clear pattern of the distribution of Zn, Cd and Pb could be distinguished between reaches 08 and 23 or between surveys.

The high variability found within each reach does not facilitate detailed comparisons between reaches and surveys and suggests that there may be marked differences in metal concentrations of sediments from locations close to one another within a reach. Unfortunately, it was outside the scope of this study to investigate such variation but it is obviously an area where more critical studies need to be carried out if seasonal changes in the metal concentrations of sediments are to be assessed accurately.

A comparison with the previous study of Harding (1978) reveals that concentrations of some metals (*e.g.* Fe) differ considerably but as his data are based on single samples from each reach detailed comparison is not justified.

7.321 Relation between metals in water and sediments from R. Derwent

It was suggested earlier (Section 7.22) that river sediments may play a part in removing metals from the overlying water; indeed, the higher concentrations found at reaches below Bolts Burn suggest the passage of metals from water to the sediments. Comparison of the mean concentrations of Zn, Cd and Pb during each survey with concentrations in the water at the time sediment samples were collected (Tables 5.6-5.9; Appendix 1, day 1 Surveys I-IV) indicates that in general, high metal concentrations in sediments coincide with higher concentrations in water. This is more apparent for Zn and Pb than for Cd (Table 7.2) which suggests the exact relationship between metal concentrations in water and sediments may differ for each metal. A factor which may

Zn	Cd	Pb
0.7840^{**}	0.3713	0.6891^{*}

* $P<0.05$

** $P<0.01$

Table 7.2 Correlation coefficients for concentrations of Zn, Cd and Pb in sediment with the corresponding metal in water (T) for the R. Derwent

Reach	Zn	Cd	Pb
03/05	0.4685^{*}	- 0.0393	- 0.0763
08	0.5697^{**}	0.7064^{***}	0.3114
23	0.8189^{***}	0.7108^{***}	0.0119

* $P<0.05$

** $P<0.01$

*** $P<0.001$

Table 7.3 Correlation coefficients for concentration of Zn, Cd and Pb in sediment with the organic content of sediments from the R. Derwent influence the observed relationships is the intermittent nature of effluent discharge from Whiteheaps mine; a change in the concentration of metals in the water need not be reflected immediately in the metal composition of the sediments. Unfortunately, there is no way of telling from the data how stable conditions in the river were at the time of sampling.

7.322 Organic matter and metals in sediments

Work reported in other studies (see review of Förstner and Wittmann, 1979) has shown the organic component of sediments to be important in binding heavy metals. The relationships between the organic content of sediments and the concentrations of Zn Cd and Pb were examined by computing the correlation coefficients (Table 7.3). Zn in sediments shows a significant positive correlation with the organic content of sediments at the 'uncontaminated' reach 03/05 as well as reaches 08 and 23 downstream of Bolts Burn while Cd is positively correlated with the organic content of sediments at 08 and 23 (but not 03/05). In contrast, Pb concentrations in sediments show no significant correlation with organic matter at any reach.

The primary contaminating medium in the R. Derwent is water and as most of the Zn and Cd in the river water existed in a non-particulate form (Section 5.212, 7.21) it seems likely that contamination of the sediments by these metals occurs when they become adsorbed to material already present in the sediments rather than by deposition of contaminated particles from the water. The data suggest organic matter may be involved in this process.

Further evidence that organic material in the sediments may be important in binding Zn and Cd comes from the special study of the metal composition of leaves and detritus from the river bed. The data were presented in Table 5.19 and although the results are based on single samples of material, suggest detritus, which consisted largely of decomposing organic material (mainly leaf fragments), contained proportionately higher concentrations of Zn and Cd than Pb in comparison with leaves which were intact and had been in the river for a shorter time. Further, washed samples of leaves and detritus retained Zn and Cd in greater proportions than Pb when compared with unwashed samples.

The larger proportion of Pb lost when samples were washed suggests that it was only loosely bound or present in an unbound particulate form. The latter seems more likely as Harding (1978) and Harding and Whitton (1978) consider that effluent from the fluorspar treatment plant at Whiteheaps mine contains discrete particles of lead ore which become deposited on the river bed. Such deposition may also account for the slightly higher levels of Pb observed at reach 08 in comparison with reach 23 (Table 5.10) and could explain the poor correlations observed between Pb in water and sediments (Table 7.3).

Comparison of the metal composition of detritus with that of sediment samples (Tables 5.6, 5.19) shows that while concentrations of Zn and Cd are similar, concentrations of Pb are much higher in sediment. This may be explained by the presence of particulate Pb in greater quantities in the sediments than detritus and supports the suggestion that binding by organic material is less important in the case of Pb than it is for Zn and Cd. It seems that while the leaves themselves do not constitute a major input of heavy metal at polluted reaches they may exert considerable influence on the metal composition of river sediments as they decompose and may cause an increase in the amount of metal potentially available to detrivores in their food.

7.33 Derwent Reservoir

It was pointed out in Section 6.221 that the metal and organic composition of sediments collected during Surveys I-IV(Tables 6.3-6.8;

Appendix 3) differed markedly between sites and surveys and were frequently subject to considerable intra site variability, making it difficult to detect any clear pattern of distribution. However, a clearer picture of the distribution of Zn and Pb in reservoir sediments can be gained from the results of the special study (Table 6.12; Figs 6.1, 6.2). Comments of the data were made in Section 6.32 and are summarized below:

i) Highest concentrations of Zn and Pb (570 $\mu g\ g^{-1}$ and 870 $\mu g\ g^{-1}$ respectively) occurred at site R1 near the mouth of the river but were lower than at reach 23 on the R. Derwent (2240 $\mu g\ g^{-1}$ and 1810 $\mu g\ g^{-1}$ respectively).

ii) Concentrations of both metals decreased on passing down the reservoir towards the dam although the pattern was found to be interrupted locally and Pb concentrations decreased more rapidly than Zn.

iii) Zn concentrations were similar along both shores while concentrations of Pb tended to be lower along the south shore.

The pattern of decreasing metal concentrations on passing towards the dam is similar to that observed for water and cannot be readily accounted for by the present data. However, it may be explained by the observations of Harding and Whitton (1978) who suggested that a greater association of Pb with particulate material caused the metal to enter the sediments more rapidly than Zn.

At the time the special study was undertaken the south shore was more affected by wave action than the north shore, as can be seen by comparing 'total' with 'filtrable' water samples from along each shore

(Table 6.12). This, coupled with an association of Pb with particulate material, may explain the tendency for Pb concentrations to be lower along the south shore; water turbulence may act to reduce concentrations of Pb in sediments at exposed sites either by keeping particles in suspension thus preventing them settling out of the water column or by resuspending particles which had previously settled and redepositing them elsewhere perhaps in deeper water or at less exposed sites.

Metal concentrations in reservoir sediments collected during this study were lower than reported in the previous studies of Harding (1978) and Harding and Whitton (1978). This may be because samples were collected from the shore during the present study and were taken when reservoir levels tended to be higher.

7.4 PLANTS

7.41 R. Derwent

Five bryophytes (*Chiloscyphus* sp., *Scapania undulata, Rhynchostegium riparioides, Fontinalis squamosa, Hygrohypnum ochraceum*) were present in sufficient amounts to be sampled from above (03/05) and below (08) the entry of Bolts Burn. Interpretation of the results is difficult because not every species was present during each survey and the variability of metal concentrations within populations was measured only during Surveys III and IV.

Bryophytes from reach 08 always contained much higher concentrations of Zn, Cd and Pb than those from reach 03/05 (Tables 5.12 - 5.15): they reflect the elevated levels of metals in their environment. The order of the concentrations of the three metals was the same in all samples from both reaches (Zn$>$Pb$>$Cd) reflecting the order observed for water but not sediments. This is perhaps not surprizing as bryophytes, having no proper root system, presumably absorb most of their nutrients and other substances from the surrounding water rather than the sediments.

The results indicate that metal concentrations vary from survey to survey at each reach. For instance, in the case of *Fontinalis squamosa*, the only species samples from reach 03 in all four surveys, the ranges of concentrations ($\mu g\ g^{-1}$) are: Zn, 145 - 740; Cd, 6.9 - 13.4; Pb, 69 - 330. Similarly, for *Hygrohypnum ochraceum* the only species samples from reach 08 in all four surveys, the ranges of concentrations are: Zn, 1670 - 3100; Cd, 18.0 - 67.5; Pb, 360 - 1040. There are significant differences between Surveys III and IV in the concentrations of Zn, Cd and Pb in *Fontinalis squamosa*, Zn and Cd in *Scapania undulata* and Zn and Cd in *Hygrohypnum ochraceum* at reach 03 (Tables 5.12 - 5.15, 7.4). At reach 08 there are significant differences in the concentrations of Zn, Cd and Pb in *Rhynchostegium riparioides* and *Hygrohypnum ochraceum*, and Cd and Pb in *Scapania undulata* (Table 7.4) with those for Survey III being higher. Ambient water chemistries at the time of sampling indicate higher Zn, similar Cd and lower Pb during Survey III at both reaches (Table 5.5).

The enrichment ratios (compared to 'filtrable' water) for Zn, Cd and Pb in *Scapania undulata, Fontinalis squamosa* and *Hygrohypnum ochraceum* differ considerably for each metal, plant, reach and survey (Table 7.5). It is unwise to attach too much importance to these values without knowledge of how conditions in the river were changing at the time of sampling and how rapidly metal concentrations in the plants respond to such changes. While conditions at 08 could have changed markedly only a short time before sampling owing to the intermittent nature of discharges from Whiteheaps mine, it is reasonable to expect that conditions at 03/05 would have been more stable. Thus, the enrichment ratios recorded at 03/05 are likely to give the best indication of the abilities of different bryophytes to accumulate Zn, Cd and Pb. However, the large differences in enrichment ratios between surveys

Reach 03 Survey III v Survey IV

taxon	Zn	Cd	Pb
Scapania undulata	2.834*	4.679**	1.971
Fontinalis squamosa	4.141**	2.741*	5.559***
Hygrohypnum ochraceum	3.022*	0.531	4.940**

Reach 08 Survey III v Survey IV

taxon	Zn	Cd	Pb
Scapania undulata	0.490	3.631**	3.104*
Rhynchostegium riparioides	8.306***	13.175***	6.372***
Hygrohypnum ochraceum	9.213***	13.066***	3.420**

* $P < 0.05$

** $P < 0.01$

*** $P < 0.001$

Table 7.4 't' statistic for comparison between Surveys III and IV in concentrations of Zn, Cd and Pb in bryophytes at reaches 03 and 08

taxon	reach	survey											
		I			II			III			IV		
		Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
Scapania undulata	03				22812	32000	34000	18555	105000	50500	43750	35750	72750
	08				12137	52750	42500	19250	41000	378571	21382	48714	128571
Fontinalis squamosa	03	27407	35666	55000	12500	27000	18333	16611	44666	17250	9625	17250	17500
Hygrohypnum ochraceum	03				27312	40333	20000	18944	48666	26000	26500	32000	61250
	08	5394	53375	21176	14000	86000	28125	7750	61363	148570	4911	25714	36785

Table 7.5 Enrichment ratios for Zn, Cd and Pb in *Scapania undulata*, *Fontinalis squamosa* and *Hygrohypnum ochraceum* from reaches 03/05 and 08 on R. Derwent during Surveys I-IV (enrichment ratio = concentration in plant divided by concentration in 'filtrable' water; for details of each see Tables 5.12-5.15 and Appendix 1)

author(s)	bryophyte					
	Scapania undulata		*Fontinalis squamosa*		*Hygrohypnum ochraceum*	
	Zn	Pb	Zn	Pb	Zn	Pb
McLean and Jones (1975)	1950	14825	1283	7600		
Burton and Peterson (1979)	3558	8902	2841	1385	780	2450
Harding (1978)	2992	2387			1438	993
present study	7700	2650	740	330	3100	1040

Table 7.6 Comparison of the maximum concentrations of Zn and Pb found in *Scapania undulata*, *Fontinalis squamosa* and *Hygrohypnum ochraceum* during present study with those reported by other workers

for each species at 03/05 indicate that metal uptake by bryophytes may be governed by factors other than metal concentrations in the surrounding water.

The maximum concentrations of Zn and Pb found during this study in *Scapania undulata, Fontinalis squamosa* and *Hygrohypnum ochraceum* are compared with those reported in the literature in Table 7.6. The higher Pb concentrations reported by McLean and Jones (1979) may be explained at least in part by higher metal concentrations in the stream water. The higher concentrations of Zn during this study cannot be explained in terms of higher metal concentrations in water as the concentrations recorded here were lower than in the studies with which the present data are compared.

7.42 Derwent Reservoir

The results of a special study designed to investigate the distribution of Zn and Pb in the submerged macrophytes *Nitella flexilis* and *Glyceria fluitans* from the Derwent Reservoir (Table 6.11) show that elevated concentrations of Zn and Pb occurred in each species, indicating that the metals were present in a form available for uptake by both non-rooted and rooted plants. The possible sources of metals and mechanisms of uptake by submerged macrophytes have been considered briefly in Section 1.22, where it was seen that both water and sediments may be involved. In an attempt to assess the importance of water and sediments as sources of Zn and Pb for *Nitella flexilis* and *Glyceria fluitans*, metal concentrations in the environmental components were compared with those in the plants. In order that the condition of normality required for correlation was fulfilled, data for Site R2 on the south shore was not included in the comparisons for *Nitella flexilis*. The north and south shores are considered separately on account of the differences observed along each in the behaviour of Zn and Pb in water and sediments.

Along the south shore a significant positive correlation was found between Zn in water and Zn in *Glyceria fluitans*. Strong positive correlations also occurred between Pb in *Glyceria fluitans* and Pb in 'filtrable' (but not 'total') water and sediments. No significant correlations were found between Zn and Pb in *Nitella flexilis* and the corresponding metals in the environmental components (Table 7.7). The relationships for the north shore were different; significant positive correlations were found between concentrations of Pb in *Glyceria fluitans* and sediments, *Nitella flexilis* and water ('total' and 'filtrable') and *Nitella flexilis* and sediments, while no significant correlations were found between concentrations of Zn in either plant and Zn in the environmental components (Table 7.8).

The results for both shores suggest that sediments may be a source of Pb for *Glyceria fluitans* and that water may be a source of Pb for *Nitella flexilis*. There is also an indication that along the south shore at least water may be a source of Zn for *Glyceria fluitans*. Further, the data suggest that sediments may be a source of Pb for *Nitella flexilis* which is a little surprizing as this plant has no proper root system and therefore no means of taking up metals directly from the sediment. However, Welsh and Denny (1980) proposed that a loss of Pb from Ullswater sediments to the overlying water caused by turbulence and/or lowered redox potentials coupled with adsorption of particulate material to the surface of submerged leaves were important factors in the occurrence of high Pb levels in submerged shoots of *Potamogeton pectinatus*. Similarly, Wixson (1977) suggested that discrete particles of lead ore entrapped by filaments of algae may be acted upon by strongly negative groups on the surface of the cells resulting in the disassociation of Pb from the particles and subsequent binding to the exterior and interior of the plants. Similar processes may be involved in Pb uptake

taxon	water				sediments	
	Zn		Pb		Zn	Pb
	T	F	T	F		
Nitella flexilis	-0.0604	-0.2461	0.1992	0.5694	0.2104	0.1952
Glyceria fluitans	0.4900	0.8366***	0.2144	0.6468	0.3982	0.6945

* $P < 0.05$

** $P < 0.01$

*** $P < 0.001$

Table 7.7 Correlation coefficients between concentrations of Zn and Pb in *Nitella flexilis* and *Glyceria fluitans* from the south shore of the Derwent Reservoir and concentrations of the same metals in water and sediments

taxon	water				sediments	
	Zn		Pb		Zn	Pb
	T	F	T	F		
Nitella flexilis	-0.3188	-0.2919	0.8422**	0.8922***	0.2098	0.7399**
Glyceria fluitans	0.1306	-0.3236	0.4836	0.3894	0.4218	0.7948*

* $P < 0.05$

** $P < 0.01$

*** $P < 0.001$

Table 7.8 Correlation coefficients between concentrations of Zn and Pb in *Nitella flexilis* and *Glyceria fluitans* from the north shore of the Derwent Reservoir and concentrations of the same metals in water and sediments by *Nitella flexilis*.

The earlier study of the Derwent Reservoir (Harding and Whitton, 1978) indicated that water, but not sediment, may be important as a source of Zn and Pb for *Nitella flexilis* while for *Glyceria fluitans*, Pb was thought to be derived from both water and sediment. The present study confirms the previous observations for Pb but the situation for Zn is unclear and requires further investigation.

The concentrations of Zn and Pb recorded here for *Nitella flexilis* are similar to those reported by Harding and Whitton (1978). The lowest concentration of Zn found during the present study was 570 $\mu g\ g^{-1}$ in a sample collected from the north shore near the dam (Site R22) and may be compared with 470 $\mu g\ g^{-1}$ in a sample of material taken from the R. Tees by Harding (1978) and 240 $\mu g\ g^{-1}$ reported in *Nitella* sp. from an un-named source by Boyd and Lawrence (1967). The only metal analyses in the literature for *Glyceria fluitans* appear to be those of Harding and Whitton (1978); concentrations of Zn and Pb found during the present study are similar to the ones reported by these workers.

The possibilty of metals being released from plants to water was considered briefly in Section 1.22 and several authors have expressed concern about the effects of such release on the biota. For example, Welsh and Denny (1976) discussing Pb in Ullswater concluded that the release of Pb from sediments by rooted submerged plants'..plays a key role in the deleterious cycling of metals in the lake which could give rise to faunistic abnormalities', while McIntosh, Shephard, Mayes, Atchison and Nelson (1978) considerd that release of metals from decaying plant material could'..be of some significance (to the biota) if a rapid die-off of highly contaminated plants were to take place in a small area with little mixing'. The possibility that such localized effects could occur in the Derwent Reservoir cannot be discounted; at

Sites R7, R18 and R21 the beds of *Nitella flexilis* and *Glyceria fluitans* are very dense and occur in areas sheltered from the effects of wave and wind action.

7.5 ANIMALS

7.51 Introduction

It was pointed out in Section 1.234 that few published accounts of heavy metal accumulation by aquatic invertebrates from natural systems include data on environmental concentrationts of metals even though such information may be important for interpreting the results. As with plants, it was hoped to assess the importance of water and sediments as possible sources of metals by comparing concentrations in these environmental components with metal concentrations in the animals.

7.52 Species composition

7.521 River Derwent and Bolts Burn

While no animals were recorded from Bolts Burn on any sampling occasion, reach 03/05 on the R. Derwent above Bolts Burn and reaches 08 and 23 below were found to be populated by representatives of at least 36, 36 and 34 different species respectively (Table 5.16). No major differences are evident in the species composition of these sampling stations suggesting that polluted water from Bolts Burn does not have a qualitative effect on the riffle fauna of the R. Derwent after the two streams become mixed. As no attempt was made to determine the numbers of animals at each reach it is not possible to evaluate quantitative effects. However, in a recent study of the rivers Ystwyth and Rheidol which carry similar levels of metals to the R. Derwent, Brooker and Morris (1980) were unable to demonstrate any simple relationship between metal concentrations in water and the number of taxa or total invertebrate densities at each site for either river. The fauna of the R. Derwent is dominated by the insecta and is in general similar to those reported for other rivers in the area by Armitage, MacHale and Crisp (1975) and Armitage (1977a, 1980).

7.53 Metal composition

7.531 R. Derwent

A total of 212 samples of invertebrates representing 21 taxonomic categories at least 12 of which are distinct species were collected (Table 5.17). But in spite of the large number of samples, the results are difficult to interpret for the same reasons already expressed for bryophytes (Section 7.41).

Detailed comparison between surveys for individual taxa is limited to *Perla bipunctata* at reach 03 in Surveys II and IV; concentrations of Cd and Pb (but not Zn) are significantly higher ($P < 0.001$ and $P < 0.01$ respectively) during Survey IV although concentrations of the two metals in water and sediments were similar on each occasion (Tables 5.4, 5.7, 5.9). The results suggest that metal concentrations in other taxa may vary from survey to survey at a reach (Table 5.18). For example, in *Ecdyonurus venosus* which was collected from reach 23 in each survey, the ranges of metal concentrations ($\mu g\ g^{-1}$) are: Zn, 2300 - 14550; Cd, 11.6 - 150; Pb, 51 - 231.

Where detailed comparisons between reaches above and below Bolts Burn were possible metal concentrations were usually significantly higher at reaches below Bolts Burn (Table 7.9), suggesting that elevated concentrations of metals in the environment give rise to higher concentrations in the fauna. However, the data indicate that the exact relationships between metal concentrations of Zn, Cd and Pb in animals with those in water and sediments differ from one taxon to another (Table 7.10). The significant positive correlations observed suggest that water may be a source of Zn for *Brachyptera risi*, *Leuctra* spp. and *Perla bipunctata*, Cd for *Leuctra* spp. and Pb for *Ecdyonurus venosus* while sediments may be a source of Zn for *Brachyptera risi*, *Ecdyonurus venosus*, and *Leuctra*

taxon	survey	reach	Zn	Cd	Pb
Baetis spp.	III	08	25.017^{***}	8.884^{***}	9.294^{***}
		23	18.321^{***}	26.445^{***}	5.493^{***}
Ephemerella ignita	III	08	12.133^{***}	6.185^{***}	10.911^{***}
		23	10.503^{***}	7.542^{***}	12.281^{***}
Brachyptera risi	II	08	10.112^{***}	2.549^{*}	10.934^{***}
		23	7.775^{***}	1.758	7.149^{***}
Amphinemura sulcicollis	II	08	26.248^{***}	2.793^{*}	13.518^{***}
		23	25.475^{***}	1.587	13.865^{***}
Leuctra spp.	III	08	11.906^{***}	18.15^{***}	12.088^{***}
		23	12.851^{***}	22.317^{***}	7.456^{***}
Perlodes microcephala	II	08	2.448^{*}	2.429^{*}	3.744^{**}
Isoperla grammatica	II	08	6.061^{***}	1.146	3.988^{**}
		23	6.061^{***}	0.410	5.621^{***}
Perla bipunctata	II	08	5.681^{***}	0.000	7.120^{***}
Limnius volkmari	III	08	11.063^{***}	5.214^{***}	6.375^{***}

* $P<0.05$

** $P<0.01$

*** $P<0.001$

note: significant differences indicate higher concentrations than at reach 03

Table 7.9 't' statistics for comparison of concentrations of Zn, Cd and Pb in invertebrates from reaches 08 and 23 with those from reach 03

taxon	water (F)			sediment		
	Zn	Cd	Pb	Zn	Cd	Pb
Ecdyonurus+ *venosus*	0.5783	-0.1859	0.9321***	0.6838*	0.3349	0.7074*
Brachyptera risi	0.9385**	0.2626	0.5163	0.8487*	0.4370	0.7665
Leuctra spp.	0.8739**	0.9777***	0.3364	0.9321***	0.8227**	0.6001
Perlodes microcephala	0.5235	-0.0523	0.5131	0.4716	-0.1508	0.2538
Perla bipunctata	0.8606**	0.1950	0.3538	0.5814	0.0976	0.3450
Limnius volkmari (adults)	0.8797**	-0.1135	0.0393	0.9129**	-0.2608	0.6039
Rhyacophila dorsalis	0.6707	0.4736	0.6507	0.5106	0.8904*	0.3928
all'free-living' Trichoptera	0.3224	0.0147	0.4770	0.3855	0.0389	0.4989
Dicranota sp(p).	0.3119	-0.1817	0.5963	0.6900	0.1831	0.7221*
Gammarus pulex++	0.8269**		0.4986	0.4332	0.2345	-0.0892

* $P < 0.05$
** $P < 0.01$
*** $P < 0.001$

\+ data from Survey III not included
++ Cd concentrations in water below detection limit (< 0.0003 mg l^{-1})

Table 7.10 Correlation coefficients for concentrations of Zn, Cd and Pb in animals when compared with concentrations of the same metals in water and sediments from R. Derwent and Derwent Reservoir spp., Cd for *Leuctra* spp. and *Rhyacophila dorsalis* and Pb for *Ecdyonurus venosus* and *Dicranota* sp(p).

When data from reach 03/05 were excluded from the comparisons given in Table 7.10, concentrations of Pb in *Leuctra* spp. were found to show a significant ($P < 0.05$) negative correlation with Pb in sediments. Eyres and Pugh-Thomas (1978) found negative correlations for Cu and Zn when they compared concentrations in *Erpobdella octoculata* and *Asellus aquaticus* with those in sediments at polluted reaches on the R. Irwell and suggested this may indicate the animals had the ability to exclude these metals from their tissues. It seems possible that *Leuctra* spp. may regulate tissue concentrations of Pb by the same mechanism but further investigation would be required to confirm this.

Ecdyonurus venosus provided an opportunity to examine metal concentrations in an invertebrate which passes through two generations a year. There appears to be a winter generation of nymphs which emerge in early summer and a fast growing summer generation which emerge in late summer and early autumn. Similar observations have been made for the R. Alyn (Clwyd) by Rawlinson (1939). Concentrations of metals, especially Zn, were much higher during Survey III than the previous two surveys (Table 5.18). Examination of the average metal content of nymphs collected at each reach reveals that those belonging to the summer generation (collected during Survey III) contained similar amounts of Zn and Cd as nymphs from the winter generation (collected during Survey II) even though the dry weights of the latter were more than four times greater at reach 03/05, 10 times at reach 08 and 3 times at reach 23 (Table 7.11). Clearly, metal accumulation differs between the two generations although further investigation is required to determine the causal factors. These observations show the importance of having a thorough knowledge of the biology of organisms used as

survey	reach	dry weight of nymph (mg)	weight (µg) of metals in nymph		
			Zn	Cd	Pb
	05	1.24	1.52	0.0220	0.027
I	08	0.70	1.72	0.0132	0.090
	23	0.67	2.87	0.0168	0.039
	03	6.92	5.61	0.0304	0.131
II	08	8.18	10.9	0.0498	1.39
	23	5.44	12.5	0.0631	0.892
	03	1.60	4.40	0.0265	0.048
III	08	0.76	11.5	0.0607	1.24
	23	1.05	15.3	0.0607	0.243
	03	1.18	1.44	0.0311	0.021
IV	08	0.77	1.55	0.0467	0.093
	23	0.50	2.50	0.0752	0.070
	max	8.18	15.3	0.0132	1.39
	min	0.50	1.44	0.0752	0.021

Table 7.11 Average metal content of single *Ecdyonurus venosus* nymphs during Surveys I - IV (calculated from data in Table 5.17)

monitors of metal pollution if data are to be interpreted meaningfully.

As aquatic invertebrates may accumulate metals from their food (Sections 1.232, 1.2332), it seems likely that those with different feeding habits may concentrate metals to different levels. The data for stoneflies in Survey II allows metal concentrations in the two carnivorous species, *Perlodes mocrocephala* and *Perla bipunctata*, to be compared with those in the non-carnivorous *Brachyptera risi*, *Amphinemura sulcicollis* and *Leuctra*. Although the relationships differ according to which species are compared, concentrations of Cd and Pb at 03/05 and Zn, Cd and Pb at 08 were generally lower in the carnivorous species while Zn at 03/05 was higher. Comparison of metal concentrations in these two carnivorous stoneflies and the carnivorous free living caddisfly *Rhyacophila dorsalis* with those found in other animals, all of which probably represent potential prey, suggests that metal concentrations do not increase up the food chain. Indeed, for reach 03/05 and 08, concentrations in *Perla bipunctata* are the lowest or near lowest recorded for any taxa during each survey. Similar results have been reported for other aquatic systems. For example, Namninga, Scott and Burks found no increase in the Cu, Zn and Pb associated with increasing trophic levels in a pond ecosystem and the concentrations of Cu Fe and Zn found in carnivorous animals from the R. Hale by Brown (1977b) were lower than those for other taxa.

Upstream migration and drift of benthic invertebrates have frequently been reported (*e.g.* Armitage, 1977a; Ball, Wojtalik and Hooper, 1963; Dendy, 1944; Elliott, 1971; Harker, 1953; Lehmkuhl and Anderson, 1972; Neave, 1930) and although observations on such movements were not made for the R. Derwent during this study it seems likely that they took place.

It is possible that the concentrations of metals recorded in animals from reach 03/05 would tend to be increased by upstream migration of individuals from the polluted section of the river, while concentrations of metals in samples from reach 08 would tend to be decreased by individuals drifting from the unpolluted section of the river upstream of Bolts Burn. Further, concentrations of metals in animals from reach 23 would tend to be affected very little, by drift or migration. While it is not possible to determine whether the concentration of metals in a single animal sample has been affected by drift or migration, comparison of the variation observed in replicate samples from 03/05 and 08 with the variation in replicate samples from reach 23 would indicate such effects if they were substantial.

Members of the genus *Baetis* are particularly susceptible to drift (Armitage, 1977a) and so the effects described above ought to be most obvious in this group. Examination of replicate samples collected during Survey III (Table 5.18) reveals that only Cd at reach 08 was more variable than for reach 23; Zn showed similar variability at all reaches while that for Pb was lower at 03/05 and 08 than 23. With the exception of *Ephemerella ignita* for which the variability in concentrations of all three metals at 03/05 suggests the possibility of upstream migration, data for other taxa do not point to drift or migration having had any substantial effects on the metal concentrations recorded. This may be because little or no movement of animals occurs or concentrations of metals in the animals change very rapidly and take only a short time to reach equilibrium with the new environmental conditions.

7.532 Derwent Reservoir

Invertebrates from five taxa were present in sufficient quantities to be used for metal analysis. No animals were analysed during Survey II. The amphipod *Gammarus pulex* was taken most frequently but unfortunately it was not possible to determine variation in metal concentrations on any occasion which makes detailed comparisons between sites and surveys unjustified. Metal concentrations in this animal were in the following ranges (µg g^{-1}): Zn, 88 - 137; Cd, 7.1 - 25.9; Pb, 4 - 66. No consistent trends were apparent on passing down the reservoir. Comparison with metal concentrations in water and sediments shows a significant positive correlation with Zn in water (Table 7.10)and suggests water may be a source of this metal for *Gammarus pulex.*

The highest concentrations of Zn, Cd and Pb were found in the leech *Glossiphonia complanata* from site R7 during Survey IV and were 2559, 49.0 and 113 µg g^{-1} respectively. The only taxon sampled from both the reservoir and the river was *Chironomus*; metal concentrations were much lower in the sample from the reservoir (Tables 5.18, 6.10). With the exception of *Glossiphonia complanata*, concentrations of Zn, Cd and Pb in animals from the reservoir were much lower than those in animals from the R. Derwent below Bolts Burn and in many cases were also lower than at 03/05 above Bolts Burn. This is probably due at least in part to the lower concentrations of metals in reservoir water and sediments at the sites from which the animals were collected.

7.533 Comparison with the literature

The previous studies in the literature which are most relevant to the present one are those of Anderson (1977) and Brown (1977). Anderson reported on the levels of Cu, Zn, Cd and Pb in 35 genera of invertebrates in the Fox River in Illinois and Wisconsin. No environmental levels of metals were given, but it seems probable that they were much lower than reported in the present study as concentrations in the animals were in general much lower. The order of concentration of metals in animals was generally $Zn > Pb > Cd$. This also applies to the present study. Anderson concluded that the levels of Zn in mayflies and caddisflies were relatively high. The following are some examples of metal levels found by Anderson:

taxon	metal concentrations (μg g^{-1})		
	Zn	Cd	Pb
Gammarus	101		
Hexagenia	177		
Baetis	206		
Hydropsyche	220	1.52	18.8
Chironomidae	144	2.17	29.7
Simulium	102	2.53	24.0

Brown (1977) studied the influence of mine drainage on the R. Hayle in Cornwall, where the water and sediments are enriched with Cu as well as Zn (and probably other heavy metals). The levels of Zn were however generally lower than found in the polluted stretch of the R. Derwent. For the animals she analysed, the highest levels were found in 'free-living' Trichoptera, the lowest in adult Coleoptera with Plecoptera intermediate. No details were given for individual species. One mayfly, *Baetis rhodani*, was recorded from the river, but no analyses were included. Although Brown collected samples at three different times of year, a comparison of Zn concentrations between the three groups mentioned above is reported only for a survey carried out during March. In order to present some comparison, the data from the R. Derwent (Survey II, April) have been 'pooled' and unweighted mean values are given together with the data reported by Brown.

Concentrations of Zn (μg g^{-1})

	Brown 1977		present study		
	site 4	site 11	03	08	23
Plecoptera	410	404	239	558	663
'Free-living' Trichoptera	625	774	296	382	524
Adult Coleoptera	63	175	137		673

It is evident that, using these data, the order in which the different taxa concentrate Zn is similar in reach 03 of R. Derwent to that found in the R. Hayle. However the order at reach 23 on R. Derwent is completely reversed. It is probable that pooling the results from many species within a site gives results of only limited value as the relative contribution of each species remains unknown.

Brown also reported a significant positive correlation between Zn in 'free-living' Trichoptera and Zn in sediments. No significant correlations were apparent when concentrations of Zn, Cd and Pb in all 'free-living' Trichoptera were compared with those in water and sediments for this study although when one species, *Rhyacophila dorsalis*, was considered by itself a significant correlation was observed with Cd in sediments (Table 7.10). This again suggests that information may be lost by pooling data for different species.

7.6 CONCLUDING REMARKS

It has been shown that during the period October 1978 to November 1979 the water, and sediments of the R. Derwent from below its confluence with Bolts Burn as far as the Derwent Reservoir were contaminated with Zn, Cd and Pb. Elevated concentrations of these metals were found in the water and sediments of the reservoir and were highest in the area set aside as a nature reserve.

Where comparisons with the previous studies of Harding (1978) and Harding and Whitton (1978) have been possible there was no evidence to suggest that the levels of pollution in the Derwent Catchment had increased. Indeed, in the case of water from the R. Derwent and Bolts Burn, metal concentrations were in general lower during the present study but not to the extent where contamination could no longer be considered serious. Following the closure of Whiteheaps mine (Section 2.422) effluent discharge to Bolts Burn from the fluorspar treatment plant has ceased although the adit which drains the mine still flows.

This will have reduced the amounts of metals, especially Pb, entering Bolts Burn and may allow the stream to be colonized by benthic invertebrates.

The results for metal composition of plants and animals show that at any one place at any one time the various taxa accumulated metals to different levels. Substantial differences were also found for the same taxa at different sampling stations and during different surveys. Comparison of metal concentrations in organisms with those in water and sediments revealed that the exact relationship between these components differed for each metal plant and animal indicating that interaction may be complex.

Even though metal concentrations in water from the R. Derwent were subject to rapid change due to the intermittent effluent discharge from Whiteheaps mine, significant positive correlations were found between concentrations of Pb in *Ecdyonurus venosus,* Zn in *Brachyptera risi,* Zn and Cd in *Leuctra* spp., Zn in *Perla bipunctata* and the corresponding metals in river water. This indicates that concentrations of these metals in the animals also change rapidly. It is suggested that these animals may be useful as monitors of metal pollution. The poor correlations observed in the case of other animals from the river suggest either that water is not an important source from which metals are accumulated or that metal concentrations in their tissues do not respond rapidly to changes in the surrounding water.

SUMMARY

1. A study on the distribution of Zn, Cd and Pb in water, sediments, plants and animals from the R. Derwent and Derwent Reservoir was carried out between October 1978 and November 1979 during four periods of intensive survey.

2. The R. Derwent had elevated concentrations of Zn, Cd and Pb in water and sediments at its junction with the Derwent Reservoir. The mean concentrations of these metals in 'total' water samples from the river near its point of entry into the reservoir were (mg l^{-1}): Zn, 0.25; Cd, 0.0006; Pb, 0.020; concentrations for sediments were ($\mu g\ g^{-1}$): Zn, 1800; Cd, 9.3; Pb, 1880.

3. Metals were carried into the R. Derwent 3.5 km upstream from the reservoir by a polluted tributary, Bolts Burn, which receives effluent from a fluorspar mine. Mean concentrations of metals in 'total' water samples from this stream were (mg l^{-1}): Zn, 1.25; Cd, 0.0020; Pb, 0.070.

4. The R. Derwent upstream of Bolts Burn was sampled to establish 'background' metal concentrations. Mean concentrations for 'total' water samples were (mg l^{-1}): Zn, 0.020; Cd, $<$0.0003; Pb 0.007. There was a large increase in concentrations of these metals in water below the entry of Bolts Burn, with a gradual fall-off on passing downstream towards the reservoir. Mean concentrations of metals in sediments from the R. Derwent above Bolts Burn were ($\mu g\ g^{-1}$): Zn, 154; Cd, 1.5; Pb, 107; concentrations below Bolts Burn were much higher, but unlike the water no fall-off was apparent on passing towards the reservoir.

5. Comparison of metal concentrations in sediments with their organic content suggests that organic matter may be involved in

binding Zn and Cd to sediments. Leaves shed in autumn may influence the metal composition of sediments by binding Zn and Cd during decomposition.

6. Concentrations of Zn, Cd and Pb in R. Derwent bryophytes were always higher below Bolts Burn. The highest concentrations recorded for Zn and Pb occurred in *Scapania undulata* (7700 and 2650 $\mu g\ g^{-1}$, respectively) and for Cd in *Rhynchostegium riparioides* (78.1 $\mu g\ g^{-1}$). The enrichment ratios (compared with 'filtrable' water) were different for each metal and species considered; there were also obvious differences between surveys, even at the 'unpolluted' reach upstream of Bolts Burn.

7. Analyses were made on 212 samples of animals from the river, representing 21 taxa. Two species, *Ecdyonurus venosus* and *Perla bipunctata*, were sampled from above and below Bolts Burn during each of the four surveys. The concentrations of Zn, Cd and Pb were higher in animals below Bolts Burn than above in all cases for Pb, all but one for Zn and all but four for Cd. The mayflies as a group tended to accumulate Zn, Cd and Pb to higher levels than other animals. Concentrations in mayflies from above Bolts Burn were frequently higher than in other taxa from below this stream. In general, concentrations of metals in stoneflies and caddis were similar. As with bryophytes, marked differences were found for metal concentrations in each species between reaches and surveys.

8. Comparison of metal concentrations in 'filtrable' water with those in animals suggests that water may be an important source of Zn for *Brachyptera risi*, *Leuctra* spp., *Perla bipunctata* and *Limnius volckmari*, Cd for *Leuctra* spp. and Pb for *Ecdyonurus venosus*. Similar comparisons with sediments suggested these as a source of Zn for *Ecdyonurus venosus*, *Brachyptera risi* and *Leuctra* spp. and

Limnius volckmari, Cd for *Leuctra* spp. and *Rhyacophila dorsalis* and Pb for *Ecdyonurus venosus* and *Dicranota* sp(p).

9. Investigation of the distribution of metals in the water and sediments of the Derwent Reservoir showed that elevated concentrations of Zn and Pb occurred near the mouth of the river. A trend of decreasing metal concentrations on passing away from the river towards the dam was apparent, although this pattern was interrupted locally.

10. Elevated concentrations of Zn and Pb occurred in the macrophytes *Nitella flexilis* and *Glyceria fluitans* from the reservoir. Comparison with metal concentrations in water and sediments indicated that water and sediments may be a source of Pb for *Nitella flexilis* and sediments may be important as source of Pb for *Glyceria fluitans*.

11. Concentrations of Zn, Cd and Pb in animals from the reservoir were in general lower than for the river. The highest concentrations of these metals were found in the leech *Glossiphonia complanata* which had the following composition ($\mu g\ g^{-1}$): Zn, 2559; Cd, 49.0; Pb, 113. Comparison of the concentrations of Zn, Cd and Pb in water and sediments with those in *Gammarus pulex* indicated that water may be an important source of Zn for this animal.

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APPENDIX 1

Water chemistry: primary data for metals during Surveys I - IV

Na K Mg Ca Mn Fe Zn Cd Pb

Survey I Na (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	5.8	5.7	5.5	5.4	5.9	5.6	6.5	6.1	7.0	6.2	6.1	0.60	5.8	0.33
08	9.2	9.6	8.8	9.4	8.9	8.1	14.4	13.3	14.1	13.5	11.8	2.89	10.7	2.46
23	8.7	8.2	8.6	8.1	10.0	9.0	13.0	12.9	13.4	11.5	10.7	2.31	9.9	2.15
27	8.5	8.0	8.7	8.8	9.6	9.0	12.7	11.7	13.0	12.6	10.5	2.18	10.2	2.00

	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	6.7	6.7	7.4	7.5	5.6	5.5	7.9	7.5	8.4	8.4	7.2	1.09	7.1	1.08
R7	6.8	6.4	7.9	7.4	7.3	5.4	8.0	7.8	8.4	7.6	7.6	0.63	6.9	1.00
R10	6.7	6.6	7.9	7.0	7.4	7.0	7.9	7.6	7.8	7.6	7.5	0.51	7.1	0.43

<u>Survey I K (mg l^{-1}) water</u>

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	1.61	1.49	1.40	1.54	1.69	1.40	1.70	1.70	1.77	1.68	1.63	0.142	1.56	0.127
08	2.7	2.7	2.2	2.2	2.3	2.1	2.9	2.8	3.4	3.3	2.7	0.49	2.6	0.48
23	2.6	2.3	2.3	2.1	2.5	2.2	3.1	3.3	3.2	2.7	2.7	0.38	2.5	0.47
27	2.4	2.4	2.3	2.3	2.4	2.2	3.1	2.8	3.2	3.0	2.7	0.43	2.5	0.34
	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	1.66	1.73	1.70	1.65	1.26	0.66	1.78	1.60	1.44	1.36	1.56	0.213	1.40	0.436
R7	1.65	1.52	1.67	1.53	1.53	1.09	1.58	1.57	1.57	1.49	1.60	0.058	1.44	0.197
R10	1.63	1.49	1.70	1.49	1.60	1.41	1.61	1.44	1.60	1.46	1.62	0.042	1.45	0.034

Survey I Mg (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	3.76	3.21	2.88	2.71	3.33	3.01	3.83	3.76	3.93	3.67	3.54	0.437	3.27	0.442
08	4.58	4.41	3.51	3.23	4.02	3.53	4.91	4.43	4.91	4.71	4.38	0.609	4.06	0.642
23	4.57	4.00	3.78	3.29	4.09	3.60	4.61	4.50	4.83	3.85	4.37	0.428	3.84	0.453
27	4.41	3.90	3.73	3.58	4.04	3.75	4.49	4.15	4.80	4.40	4.29	0.415	3.95	0.324

	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	2.77	2.61	2.82	2.64	1.99	1.75	2.62	2.52	2.60	2.57	2.56	0.332	2.41	0.376
R7	2.76	2.51	2.71	2.63	2.45	1.78	2.64	2.47	2.84	2.52	2.68	0.147	2.38	0.341
R10	2.73	2.52	2.88	2.41	2.57	2.39	2.63	2.40	2.67	2.36	2.69	0.118	2.41	0.061

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey I Ca (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	16.4	14.2	12.7	12.2	14.3	13.0	16.8	15.4	17.6	16.4	15.5	2.01	14.2	1.71
08	21.8	21.7	17.9	16.2	18.4	16.3	25.4	22.8	25.0	23.6	21.7	3.53	20.1	3.59
23	21.2	18.7	17.9	15.9	18.6	17.2	22.1	21.6	23.9	19.2	20.7	2.48	18.5	2.15
27	20.9	18.4	17.7	16.5	18.5	17.7	21.9	20.1	23.1	21.4	20.4	2.27	18.8	1.94

	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	11.0	10.4	11.4	10.8	8.20	8.41	10.8	10.5	10.8	9.21	10.4	1.27	9.8	1.01
R7	11.0	10.1	11.1	10.4	9.90	7.12	10.9	10.4	10.6	10.3	10.7	0.48	9.6	1.42
R10	10.9	10.2	11.4	10.0	10.7	9.84	10.4	10.0	10.2	10.0	10.7	0.46	10.0	0.12

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey I Mn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	0.031	0.022	0.035	0.028	0.023	0.016	0.015	0.019	0.023	0.018	0.025	0.0077	0.021	0.0051
08	0.097	0.102	0.087	0.075	0.052	0.046	0.104	0.088	0.112	0.109	0.090	0.0233	0.084	0.0249
23	0.051	0.042	0.047	0.027	0.029	0.024	0.040	0.038	0.036	0.032	0.040	0.0087	0.032	0.0074
27	0.047	0.036	0.047	0.036	0.032	0.028	0.040	0.039	0.043	0.036	0.041	0.0062	0.035	0.0041
	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	0.044	0.030	0.069	0.050	0.043	0.015	0.044	0.042	0.041	0.020	0.048	0.0116	0.031	0.0146
R7	0.071	0.041	0.062	0.043	0.035	0.031	0.043	0.024	0.080	0.042	0.058	0.0188	0.036	0.0083
R10	0.044	0.027	0.064	0.037	0.037	0.020	0.048	0.025	0.082	0.040	0.055	0.0180	0.029	0.0084

Survey I Fe (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	1.10	0.71	1.78	1.41	1.38	1.25	1.07	0.96	0.99	0.75	1.26	0.323	1.01	0.307
08	0.83	0.74	1.46	1.30	1.21	0.88	1.01	0.68	0.87	0.64	1.07	0.261	0.84	0.268
23	0.73	0.74	1.21	0.85	0.97	0.73	0.70	0.66	0.69	0.40	0.86	0.226	0.67	0.168
27	0.66	0.49	1.25	0.98	0.96	0.84	0.80	0.55	0.78	0.58	0.89	0.227	0.68	0.211
	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	0.59	0.39	0.56	0.28	0.32	0.25	0.59	0.25	0.43	0.30	0.49	0.119	0.29	0.057
R7	0.73	0.31	0.61	0.27	0.74	0.19	0.48	0.26	0.60	0.26	0.63	0.107	0.25	0.043
R10	0.57	0.24	0.75	0.21	0.59	0.25	0.81	0.22	0.64	0.21	0.67	0.104	0.22	0.018

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey I Zn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	0.028	0.025	0.019	0.030	0.021	0.040	0.023	0.023	0.027	0.027	0.023	0.0038	0.029	0.0066
08	0.238	0.36	0.200	0.188	0.229	0.197	0.35	0.28	0.41	0.38	0.28	0.090	0.28	0.089
23	0.25	0.227	0.239	0.200	0.235	0.202	0.239	0.209	0.27	0.25	0.246	0.0142	0.217	0.0210
27	0.25	0.215	0.116	0.223	0.27	0.208	0.244	0.204	0.25	0.219	0.226	0.0622	0.213	0.0077

	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	0.044	0.046	0.048	0.047	0.044	0.046	0.039	0.053	0.032	0.042	0.041	0.0061	0.046	0.0039
R7	0.046	0.038	0.051	0.035	0.047	0.034	0.034	0.031	0.030	0.030	0.041	0.0090	0.033	0.0032
R10	0.041	0.025	0.039	0.029	0.034	0.041	0.040	0.024	0.038	0.029	0.038	0.0027	0.029	0.0067

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey I Cd (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	<0.0003	<0.0003	<0.0003	0.0005	<0.0003	0.0006	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	0.00037	0.00017
08	0.0007	0.0006	0.0005	0.0008	0.0005	0.0005	0.0007	0.0008	0.0008	0.0008	0.00064	0.00013	0.00070	0.00014
23	0.0005	0.0005	0.0006	0.0008	0.0006	0.0007	0.0006	0.0006	0.0006	0.0008	0.00058	0.00004	0.00068	0.00013
27	0.0006	0.0006	0.0005	0.0006	0.0004	0.0006	0.0006	0.0005	0.0006	0.0006	0.00054	0.00008	0.00058	0.00004

	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	<0.0003	0.0003	0.0007	<0.0003	0.0004	0.0003	0.0003	0.0004	0.0003	0.0003	0.00037	0.00020	<0.0003	-
R7	0.0003	<0.0003	<0.0003	0.0003	0.0004	0.0004	<0.0003	0.0004	0.0003	0.0003	<0.0003	-	0.00031	0.00010
R10	0.0003	0.0003	0.0003	0.0003	<0.0003	<0.0003	0.0003	<0.0003	0.0003	<0.0003	<0.0003	-	<0.0003	-

Survey I   Pb (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	25.10.78		26.10.78		27.10.78		28.10.78		29.10.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
05	0.015	0.018	0.012	0.012	0.018	0.013	0.008	0.006	0.011	0.006	0.012	0.0038	0.011	0.0050
08	0.032	0.025	0.027	0.027	0.020	0.015	0.037	0.021	0.021	0.017	0.027	0.0072	0.021	0.0050
23	0.042	0.028	0.031	0.019	0.022	0.019	0.023	0.017	0.016	0.012	0.026	0.0100	0.019	0.0057
27	0.049	0.020	0.029	0.025	0.024	0.018	0.023	0.019	0.016	0.012	0.028	0.0125	0.018	0.0046

	1		3		6		9		11					
	25.10.78		27.10.78		30.10.78		02.11.78		04.11.78					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
R3	0.018	0.015	0.017	0.010	0.009	0.004	0.011	0.008	0.006	0.003	0.012	0.0051	0.008	0.0048
R7	0.010	0.009	0.017	0.008	0.012	0.005	0.009	0.007	0.017	0.009	0.013	0.0038	0.007	0.0016
R10	0.009	0.007	0.012	0.006	0.008	0.005	0.007	0.004	0.007	0.005	0.008	0.0020	0.005	0.0011

Survey I   Additional water chemistry: R. Derwent, day 6

			Na		K		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
DAY	DATE	SITE	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F
6	30.10.78	0061 - 23	11.3	9.9	2.65	2.48	3.75	3.57	18.1	16.9	0.044	0.022	0.51	0.39	0.250	0.225	0.0007	0.0007	0.016	0.012
6	30.10.78	0061 - 27	13.4	12.0	3.01	2.99	4.49	4.49	21.9	21.9	0.044	0.033	0.63	0.46	0.239	0.217	0.0005	0.0005	0.015	0.012

Survey II Na (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	$s.d._T$	$\bar{x}_F$	$s.d._F$
03	4.0	4.3	4.3	4.6	4.5	4.5	4.0	4.4	5.9	5.5	4.5	0.78	4.7	0.48
08	5.6	5.7	7.0	7.2	7.2	7.4	6.4	6.1	9.1	9.3	7.1	1.29	7.1	1.40
23	6.0	6.1	7.1	7.0	7.0	7.3	6.9	7.0	9.2	8.6	7.2	1.18	7.2	0.90
R3	6.4	6.4	6.4	6.5	6.5	6.7	6.5	6.5	7.4	8.8	6.6	0.42	6.9	1.02
R7	6.5	6.7	7.1	7.0	7.2	7.9	7.1	7.0	8.2	8.8	7.2	0.61	7.4	0.86
R9	6.6	6.9	6.4	6.8	7.0	7.0	6.6	6.4	7.9	8.0	6.9	0.60	7.0	0.59
R10	6.6	6.5	6.6	6.6	6.7	6.2	6.7	6.6	7.9	8.0	6.9	0.56	6.7	0.70

Survey II K (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	1.12	1.06	1.16	1.18	1.25	1.19	1.19	1.14	1.42	1.40	1.22	0.117	1.19	0.126
08	1.42	1.51	1.74	1.77	1.82	1.87	1.65	1.63	2.1	2.1	1.75	0.262	1.79	0.256
23	1.57	1.58	1.98	1.97	1.82	1.99	1.78	1.80	2.1	2.1	1.86	0.228	1.89	0.211
R3	1.67	1.68	1.60	1.57	1.60	1.57	1.61	1.60	1.69	1.64	1.63	0.042	1.61	0.047
R7	1.64	1.65	1.63	1.62	1.56	1.58	1.55	1.48	1.66	1.66	1.60	0.049	1.59	0.072
R9	1.64	1.63	1.55	1.56	1.57	1.59	1.58	1.62	1.60	1.69	1.58	0.034	1.61	0.048
R10	1.70	1.81	1.57	1.56	1.44	1.40	1.66	1.62	1.69	1.67	1.61	0.108	1.61	0.150

Note: Numbers of decimal places differ because of sensitivity of range used for measurement.

Survey II Mg (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	1.74	1.72	2.00	1.97	1.87	1.88	2.00	1.94	2.50	2.42	2.02	0.288	1.98	0.261
08	2.27	2.28	2.74	2.74	2.69	2.61	2.71	2.63	3.36	3.36	2.75	0.389	2.72	0.394
23	2.42	2.45	2.86	2.88	2.84	2.80	2.86	2.90	3.42	3.36	2.88	0.355	2.87	0.324
R3	2.28	2.23	2.23	2.25	2.28	2.21	2.28	2.28	2.22	2.24	2.25	0.030	2.24	0.025
R7	2.23	2.21	2.28	2.21	2.31	2.31	2.32	2.31	2.21	2.19	2.27	0.048	2.24	0.058
R9	2.22	2.25	2.20	2.23	2.24	2.19	2.25	2.27	2.19	2.14	2.22	0.025	2.21	0.051
R10	2.32	2.26	2.25	2.23	2.20	2.18	2.29	2.24	2.16	2.13	2.24	0.065	2.20	0.052

Survey II Ca (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	6.29	6.25	7.55	7.31	7.16	7.25	7.61	7.46	9.61	9.35	7.64	1.218	7.52	1.127
08	8.96	8.95	11.5	11.5	11.4	11.4	11.3	10.9	15.8	15.2	11.7	2.47	11.5	2.26
23	9.46	9.40	11.5	11.6	11.8	11.8	11.9	12.0	15.6	14.9	12.0	2.21	11.9	1.95
R3	7.74	7.69	7.65	7.69	7.98	7.96	7.95	7.91	7.99	7.96	7.86	0.156	7.84	0.140
R7	7.58	7.46	7.67	7.64	7.68	7.75	7.76	7.78	7.78	7.69	7.69	0.079	7.66	0.126
R9	7.55	7.51	7.58	7.58	7.71	7.50	7.68	7.70	8.01	7.98	7.70	0.182	7.65	0.198
R10	8.13	7.70	7.78	7.69	7.00	7.00	7.80	7.69	7.70	7.64	7.68	0.415	7.54	0.305

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey II Mn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.105	0.108	0.097	0.092	0.064	0.090	0.064	0.056	0.056	0.067	0.077	0.0221	0.082	0.0208
08	0.116	0.116	0.120	0.117	0.102	0.104	0.078	0.080	0.091	0.099	0.101	0.0174	0.103	0.0150
23	0.104	0.106	0.094	0.088	0.089	0.077	0.063	0.067	0.088	0.083	0.087	0.0151	0.084	0.0144
R3	0.090	0.082	0.092	0.080	0.106	0.099	0.097	0.078	0.080	0.080	0.093	0.0095	0.083	0.0086
R7	0.096	0.081	0.060	0.062	0.080	0.082	0.083	0.065	0.083	0.084	0.080	0.0129	0.074	0.0104
R9	0.100	0.074	0.064	0.058	0.076	0.063	0.089	0.076	0.065	0.054	0.078	0.0155	0.065	0.0096
R10	0.304	0.094	0.054	0.052	0.080	0.072	0.088	0.060	0.134	0.072	0.132	0.1003	0.070	0.0158

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey II Fe (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.63	0.56	0.46	0.40	0.40	0.34	0.43	0.33	0.53	0.41	0.49	0.091	0.40	0.092
08	0.53	0.49	0.37	0.40	0.36	0.26	0.31	0.25	0.30	0.23	0.37	0.092	0.32	0.113
23	0.51	0.44	0.34	0.29	0.27	0.22	0.27	0.20	0.24	0.20	0.32	0.109	0.27	0.101
R3	0.42	0.17	0.25	0.17	0.39	0.16	0.39	0.18	0.29	0.22	0.34	0.073	0.18	0.023
R7	0.31	0.14	0.23	0.14	0.23	0.14	0.29	0.18	0.20	0.15	0.25	0.046	0.15	0.017
R9	0.43	0.17	0.22	0.20	0.22	0.14	0.47	0.33	0.23	0.15	0.31	0.125	0.19	0.077
R10	0.97	0.20	0.23	0.13	0.23	0.16	0.43	0.21	0.41	0.15	0.45	0.303	0.17	0.033

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey II Zn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	$s.d._T$	$\bar{x}_F$	$s.d._F$
03	0.022	0.020	0.015	0.014	0.024	0.015	0.017	0.013	0.032	0.021	0.022	0.0066	0.016	0.0036
08	0.126	0.126	0.149	0.152	0.172	0.167	0.140	0.132	0.211	0.203	0.159	0.0332	0.156	0.0309
23	0.141	0.132	0.154	0.139	0.144	0.143	0.151	0.146	0.187	0.194	0.155	0.0184	0.150	0.0247
R3	0.070	0.062	0.073	0.068	0.059	0.050	0.074	0.065	0.069	0.064	0.069	0.0059	0.061	0.0069
R7	0.074	0.060	0.056	0.058	0.052	0.047	0.063	0.060	0.065	0.060	0.062	0.0085	0.057	0.0056
R9	0.054	0.053	0.043	0.032	0.036	0.032	0.055	0.054	0.054	0.044	0.048	0.0085	0.043	0.0107
R10	0.087	0.078	0.034	0.037	0.033	0.031	0.058	0.055	0.054	0.050	0.053	0.0220	0.050	0.0182

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey II Cd (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.0005	0.0005	<0.0003	<0.0003	0.0003	0.0005	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
08	0.0007	0.0009	0.0005	0.0004	0.0006	0.0006	0.0003	0.0004	0.0005	0.0004	0.00052	0.00012	0.00054	0.00021
23	0.0009	0.0008	0.0005	0.0005	0.0005	0.0005	0.0004	0.0004	0.0004	0.0004	0.00054	0.00020	0.00052	0.00016
R3	0.0011	0.0010	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	<0.0003	0.0003	0.00043	0.00038	0.00044	0.00031
R7	0.0005	0.0006	0.0003	0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
R9	0.0004	0.0004	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
R10	0.0012	0.0005	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.0003	<0.0003	<0.0003	0.00036	0.00046	<0.0003	-

Survey II Pb (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	26.04.79		27.04.79		28.04.79		29.04.79		30.04.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.010	0.008	0.007	0.005	0.006	0.006	0.005	0.003	0.007	0.004	0.0070	0.0018	0.0052	0.0019
08	0.029	0.027	0.038	0.024	0.021	0.015	0.018	0.013	0.026	0.017	0.0264	0.0077	0.0192	0.0060
23	0.038	0.035	0.028	0.020	0.017	0.015	0.026	0.019	0.027	0.019	0.0272	0.0074	0.0216	0.0077
R3	0.017	0.008	0.015	0.009	0.033	0.013	0.021	0.011	0.010	0.008	0.0192	0.0086	0.0098	0.0021
R7	0.010	0.005	0.013	0.009	0.017	0.011	0.029	0.020	0.009	0.007	0.0156	0.0081	0.0104	0.0058
R9	0.015	0.005	0.010	0.007	0.013	0.007	0.017	0.011	0.008	0.006	0.0126	0.0036	0.0072	0.0022
R10	0.028	0.008	0.012	0.007	0.011	0.008	0.020	0.011	0.009	0.007	0.0160	0.0079	0.0082	0.0016

Survey II Additional water chemistry: (a) Bolts Burn, days 1 - 5; (b) R. Derwent, days 6 - 8

			Na		K		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
DAY	DATE	SITE	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F
1	26.04.79	0071 - 99	14.7	15.1	3.29	3.25	4.5	4.5	22.5	22.4	0.220	0.214	0.16	0.08	0.77	0.75	0.0027	0.0024	0.145	0.087
2	27.04.79	0071 - 99	17.3	17.2	3.74	3.73	5.0	5.0	24.9	24.5	0.216	0.210	0.12	0.07	0.81	0.78	0.0018	0.0018	0.103	0.092
3	28.04.79	0071 - 99	18.6	18.2	3.96	3.98	5.2	5.1	26.4	26.3	0.282	0.265	0.12	0.07	0.84	0.78	0.0016	0.0016	0.064	0.052
4	29.04.79	0071 - 99	16.5	16.9	3.94	3.91	5.3	5.1	26.8	26.4	0.150	0.148	0.20	0.07	0.91	0.86	0.0015	0.0012	0.096	0.066
5	30.04,79	0071 - 99	20.2	19.5	4.42	4.29	5.9	5.7	29.7	28.9	0.323	0.320	0.12	0.07	0.99	0.93	0.0012	0.0014	0.058	0.036
6	01.05.79	0061 - 03	4.8	4.7	1.20	1.19	2.00	1.96	7.61	7.48	0.060	0.058	0.50	0.48	0.016	0.014	0.0004	0.0004	0.007	0.004
		0061 - 08	6.6	6.8	1.64	1.65	2.72	2.69	11.3	11.3	0.076	0.074	0.46	0.34	0.150	0.145	0.0003	0.0004	0.020	0.016
		0061 - 23	6.7	6.6	1.80	1.76	2.80	2.71	10.9	11.2	0.072	0.071	0.41	0.37	0.144	0.140	0.0004	0.0004	0.024	0.002
7	02.05.79	0061 - 03	4.6	4.5	1.32	1.34	1.98	2.00	7.42	7.44	0.058	0.054	0.42	0.39	0.021	0.016	0.0004	0.0003	0.007	0.006
		0061 - 23	8.9	8.5	2.29	2.34	3.58	3.52	15.8	15.7	0.088	0.086	0.40	0.35	0.185	0.186	0.0006	0.0004	0.022	0.019
8	03.05.79	0061 - 03	4.9	5.0	1.27	1.34	2.14	2.20	8.69	8.70	0.070	0.070	0.55	0.47	0.023	0.022	0.0003	0.0003	0.008	0.009

Survey III Na (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	7.4	7.3	7.4	7.5	7.9	8.0	7.8	7.8	7.8	7.7	7.6	0.24	7.6	0.27
08	17.9	18.1	18.1	18.2	18.9	18.6	21.8	21.6	18.2	18.5	18.9	1.62	19.0	1.46
23	16.9	17.0	18.4	18.2	17.3	18.1	20.1	20.3	18.5	18.3	18.2	1.24	18.3	1.19
R3	8.2	8.9	7.8	7.6	8.0	7.4	7.7	7.7	7.4	7.4	7.8	0.30	7.8	0.62
R7	8.0	8.0	7.6	7.0	7.8	8.0	7.7	7.7	7.0	7.2	7.6	0.37	7.5	0.46
R9	7.9	7.9	7.6	7.4	7.5	7.0	7.4	7.7	7.0	7.1	7.4	0.32	7.4	0.38
R10	8.4	7.8	7.5	7.5	7.9	7.2	7.7	7.7	7.0	7.0	7.7	0.51	7.4	0.33

Survey III K (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	2.3	2.4	2.2	2.2	2.2	2.1	2.3	2.2	2.5	2.4	2.3	0.12	2.2	0.13
08	4.4	4.4	4.5	4.4	4.4	4.2	5.0	4.9	4.5	4.6	4.5	0.25	4.5	0.26
23	4.4	4.2	4.3	4.4	4.0	3.9	4.6	4.8	4.7	4.7	4.4	0.27	4.4	0.36
R3	1.76	1.76	1.59	1.59	1.58	1.59	1.58	1.60	1.59	1.56	1.62	0.078	1.62	0.079
R7	1.74	1.66	1.59	1.59	1.61	1.62	1.58	1.60	1.56	1.56	1.61	0.071	1.60	0.037
R9	1.78	1.70	1.60	1.58	1.53	1.51	1.55	1.61	1.48	1.49	1.58	0.115	1.57	0.084
R10	1.74	1.70	1.70	1.53	1.54	1.54	1.63	1.59	1.47	1.48	1.61	0.111	1.56	0.083

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey III Mg (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	4.76	4.78	4.81	4.70	4.91	5.0	5.0	4.90	5.1	4.86	4.91	0.138	4.84	0.114
08	6.4	6.5	6.4	6.4	6.7	6.5	7.0	7.2	6.7	6.6	6.6	0.25	6.6	0.32
23	6.5	6.4	6.2	6.3	6.3	6.4	6.8	6.7	6.4	6.6	6.4	0.23	6.4	0.16
R3	2.43	2.41	2.40	2.40	2.31	2.40	2.36	2.29	2.30	2.31	2.36	0.056	2.36	0.057
R7	2.31	2.30	2.46	2.38	2.50	2.48	2.46	2.37	2.32	2.34	2.41	0.088	2.37	0.066
R9	2.43	2.26	2.39	2.40	2.26	2.23	2.35	2.34	2.49	2.31	2.38	0.086	2.30	0.066
R10	2.40	2.40	2.34	2.37	2.30	2.20	2.28	2.32	2.20	2.21	2.30	0.074	2.30	0.091

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey III Ca (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	$s.d._T$	$\bar{x}_F$	$s.d._F$
03	15.8	15.9	19.2	19.5	18.8	19.5	19.8	18.8	21.4	20.1	19.0	2.04	18.7	1.66
08	27.2	26.2	30.0	29.0	30.2	28.8	32.2	31.8	31.2	31.5	30.1	1.87	29.4	2.28
23	24.8	23.9	27.9	28.5	27.8	28.2	30.8	30.9	29.7	30.1	28.2	2.28	28.3	2.71
R3	6.72	6.60	7.65	7.90	7.70	7.72	7.82	7.90	8.18	8.24	7.61	0.540	7.67	0.628
R7	6.68	6.24	7.50	7.35	7.60	7.50	7.65	7.70	7.56	7.64	7.39	0.405	7.28	0.600
R9	6.36	6.28	7.40	7.15	7.50	7.20	7.62	7.38	7.16	7.68	7.20	0.503	7.13	0.522
R10	6.28	6.24	7.55	7.10	7.28	7.28	7.60	7.65	7.23	7.49	7.18	0.532	7.15	0.550

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey III Mn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.030	0.020	0.020	0.020	0.025	0.020	0.025	0.020	0.030	0.025	0.026	0.0041	0.021	0.0022
08	0.150	0.150	0.125	0.125	0.105	0.105	0.125	0.120	0.100	0.100	0.121	0.0198	0.120	0.0196
23	0.105	0.085	0.110	0.090	0.080	0.075	0.080	0.070	0.075	0.055	0.090	0.0162	0.075	0.0136
R3	0.080	0.080	0.120	0.095	0.055	0.045	0.080	0.060	0.085	0.065	0.084	0.0232	0.069	0.0191
R7	0.080	0.055	0.055	0.050	0.060	0.050	0.070	0.055	0.065	0.040	0.066	0.0096	0.050	0.0061
R9	0.070	0.050	0.145	0.085	0.050	0.040	0.070	0.060	0.045	0.035	0.076	0.0402	0.054	0.0198
R10	0.060	0.035	0.130	0.095	0.055	0.045	0.100	0.085	0.045	0.030	0.078	0.0358	0.058	0.0299

Survey III Fe (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.33	0.29	0.28	0.26	0.31	0.25	0.29	0.24	0.17	0.12	0.27	0.062	0.23	0.065
08	0.22	0.19	0.20	0.15	0.19	0.17	0.13	0.12	0.11	0.06	0.17	0.047	0.13	0.050
23	0.21	0.19	0.15	0.17	0.43	0.17	0.13	0.08	0.10	0.05	0.20	0.132	0.13	0.062
R3	0.27	0.23	0.54	0.18	0.26	0.16	0.27	0.20	0.26	0.17	0.32	0.123	0.18	0.027
R7	0.30	0.28	0.29	0.22	0.27	0.15	0.28	0.21	0.25	0.17	0.27	0.019	0.20	0.050
R9	0.40	0.25	0.84	0.24	0.24	0.17	0.34	0.22	0.22	0.12	0.40	0.252	0.20	0.054
R10	0.29	0.13	0.68	0.25	0.46	0.57	0.48	0.14	0.26	0.15	0.43	0.169	0.24	0.186

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey III Zn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.010	0.007	0.009	0.013	0.010	0.010	0.024	0.028	0.020	0.023	0.014	0.0069	0.016	0.0089
08	0.35	0.34	0.44	0.43	0.36	0.34	0.46	0.45	0.40	0.40	0.402	0.0481	0.392	0.0506
23	0.234	0.200	0.31	0.28	0.28	0.26	0.27	0.25	0.23	0.200	0.264	0.0333	0.238	0.0363
R3	0.049	0.036	0.043	0.033	0.040	0.047	0.065	0.068	0.063	0.070	0.052	0.0114	0.050	0.0174
R7	0.045	0.039	0.037	0.041	0.038	0.059	0.064	0.067	0.067	0.064	0.050	0.0143	0.054	0.0131
R9	0.041	0.028	0.044	0.021	0.028	0.027	0.045	0.042	0.058	0.057	0.043	0.0107	0.035	0.0145
R10	0.039	0.032	0.038	0.024	0.033	0.034	0.056	0.046	0.053	0.055	0.043	0.0100	0.038	0.0122

Note: Numbers of decimal places differ because of sensitivity of range used for measurement.

Survey III Cd (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
08	0.0007	0.0008	0.0008	0.0007	0.0005	0.0005	0.0007	0.0007	0.0011	0.0011	0.00076	0.00021	0.00076	0.00021
23	0.0007	0.0007	0.0007	0.0006	0.0005	0.0006	0.0010	0.0006	0.0007	0.0007	0.00072	0.00017	0.00064	0.00005
R3	0.0003	0.0006	<0.0003	0.0004	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
R7	0.0003	0.0003	0.0004	0.0003	0.0003	0.0003	0.0004	<0.0003	<0.0003	<0.0003	0.00031	0.00010	<0.0003	-
R9	0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
R10	<0.0003	0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-

Survey III Pb (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	08.08.79		09.08.79		10.08.79		11.08.79		12.08.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	-	<0.003	-
08	0.016	0.015	0.021	0.015	0.009	0.009	0.007	0.007	0.008	0.007	0.0122	0.0060	0.0106	0.0040
23	0.019	0.011	0.013	0.009	0.008	0.006	0.007	0.004	0.006	0.003	0.0106	0.0054	0.0066	0.0033
R3	0.006	0.004	0.025	0.006	0.004	<0.003	0.003	<0.003	<0.003	<0.003	0.0079	0.0096	<0.003	-
R7	0.018	0.005	0.008	0.004	0.008	0.003	0.005	0.003	0.005	0.003	0.0088	0.0053	0.0036	0.0008
R9	0.017	0.007	0.025	0.006	0.004	0.003	0.003	0.003	0.003	0.003	0.0101	0.0103	0.0038	0.0025
R10	0.007	0.003	0.016	0.005	0.003	<0.003	0.004	<0.003	<0.003	<0.003	0.0063	0.0057	<0.003	-

Survey III Additional water chemistry: (a) Bolts Burn, days 1 - 5; (b) R. Derwent, days 6 - 7

			Na		K		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
DAY	DATE	SITE	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F
1	08.08.79	0071 - 99	42.6	41.4	9.8	9.2	10.0	9.4	51.6	52.0	0.47	0.46	0.04	0.04	1.14	1.13	0.0017	0.0017	0.041	0.043
2	09.08.79	0071 - 99	41.8	41.0	9.4	9.2	9.2	9.2	50.5	50.5	0.36	0.36	0.06	0.04	1.34	1.29	0.0021	0.0022	0.058	0.041
3	10.08.79	0071 - 99	42.1	41.4	8.9	8.8	9.2	9.2	50.5	49.5	0.31	0.29	0.04	0.04	1.03	0.98	0.0019	0.0017	0.038	0.034
4	11.08.79	0071 - 99	44.1	43.5	9.6	9.5	9.6	9.3	53.0	49.0	0.31	0.31	0.04	0.04	1.21	1.20	0.0018	0.0015	0.024	0.026
5	12.08.79	0071 - 99	40.1	39.7	9.2	9.1	9.4	9.4	55.2	55.3	0.26	0.26	0.04	0.04	1.25	1.20	0.0028	0.0030	0.027	0.024
6	13.08.79	0061 - 03	7.8	7.9	2.4	2.3	4.98	4.90	20.6	20.0	0.031	0.027	0.19	0.16	0.020	0.018	0.0003	0.0003	0.003	0.004
		0061 - 23	19.1	18.3	4.6	4.6	6.9	6.7	30.3	30.6	0.09	0.095	0.14	0.18	0.30	0.30	0.0009	0.0008	0.015	0.013
7	14.08.79	0061 - 03	7.6	7.6	2.3	2.3	4.86	4.90	19.7	19.8	0.028	0.026	0.22	0.22	0.016	0.017	0.0003	0.0003	0.003	0.003

Note: Numbers of decimal places differ because of sensitivity of range used for measurement

Survey IV   Na (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	6.7	6.4	6.4	6.5	6.4	6.7	6.0	6.3	4.9	5.1	6.0	0.70	6.2	0.63
08	14.1	14.0	13.2	13.2	12.7	12.8	13.4	13.8	6.5	6.2	11.9	3.10	12.0	3.27
23	13.3	13.5	13.5	13.6	12.2	12.3	12.7	12.7	5.8	5.4	11.5	3.22	11.5	3.45
R3	8.1	7.7	8.0	7.4	7.5	7.6	7.6	7.3	7.5	7.6	7.7	0.28	7.5	0.16
R7	7.4	7.4	7.4	7.5	7.4	7.2	7.3	7.0	7.5	7.6	7.4	0.07	7.3	0.24
R9	7.3	7.7	7.3	7.5	7.8	7.6	7.0	7.0	6.7	6.4	7.2	0.40	7.2	0.54
R10	7.8	7.7	7.7	7.0	7.4	7.5	7.2	7.2	7.5	7.4	7.5	0.23	7.3	0.27

Survey IV K (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	1.64	1.62	1.92	2.25	1.72	1.78	1.91	1.93	1.12	0.45	1.51	0.347	1.60	0.686
08	3.6	3.6	3.6	3.5	3.4	3.2	3.70	3.70	1.45	1.37	3.1	0.95	3.0	0.97
23	3.7	3.7	3.7	3.7	3.1	3.0	3.2	3.3	1.44	1.41	3.0	0.93	3.0	0.94
R3	1.86	1.87	1.86	1.83	1.84	1.81	1.83	1.90	1.84	1.84	1.84	0.013	1.85	0.035
R7	1.87	1.76	1.90	1.75	1.83	1.76	1.81	1.76	1.95	1.81	1.87	0.055	1.76	0.023
R9	1.76	1.74	1.75	1.80	1.74	1.70	1.82	1.74	1.64	1.52	1.74	0.064	1.70	0.106
R10	1.84	1.78	1.80	1.76	1.90	1.91	1.86	1.81	1.82	1.79	1.84	0.038	1.81	0.058

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey IV Mg (mgl^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	$s.d._T$	$\bar{x}_F$	$s.d._F$
03	3.34	3.38	3.72	3.74	3.90	4.00	3.80	3.82	2.04	1.96	3.36	0.767	3.38	0.825
08	4.71	4.69	5.1	5.0	5.2	5.0	5.1	5.3	2.26	2.20	4.47	1.251	4.43	1.269
23	4.67	4.64	5.2	5.1	5.1	5.1	5.1	5.1	2.20	2.16	4.45	1.276	4.42	1.278
R3	2.60	2.52	2.64	2.52	2.64	2.51	2.54	2.60	2.63	2.57	2.61	0.042	2.54	0.039
R7	2.44	2.29	2.64	2.68	2.56	2.42	2.60	2.52	2.72	2.60	2.59	0.103	2.50	0.152
R9	2.42	2.44	2.74	2.70	2.74	2.63	2.54	2.68	2.54	2.66	2.59	0.140	2.62	0.104
R10	2.48	2.36	2.68	2.50	2.60	2.52	2.58	2.60	2.62	2.50	2.59	0.072	2.49	0.086

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey IV   Ca (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	15.9	16.0	15.3	15.3	15.9	16.0	15.8	16.1	6.12	6.00	13.8	4.30	13.8	4.41
08	22.7	23.5	23.7	23.7	23.7	23.8	25.3	25.2	8.32	8.20	20.7	7.00	20.8	7.12
23	22.7	22.4	24.2	24.0	22.7	22.4	23.3	23.0	7.73	7.42	20.1	6.95	19.8	6.97
R3	10.2	10.1	10.0	9.76	9.80	9.20	9.96	9.42	11.0	9.44	10.1	0.47	9.58	0.350
R7	9.60	9.19	9.84	9.80	9.50	9.40	10.2	9.88	10.1	9.26	9.84	0.304	9.50	0.315
R9	9.64	9.46	9.50	9.46	9.72	9.24	9.80	9.52	7.54	7.80	9.24	0.956	9.09	0.732
R10	9.70	9.50	9.40	9.50	9.50	9.31	9.46	9.40	9.60	9.60	9.53	0.118	9.46	0.110

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey IV Mn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.029	0.026	0.017	0.022	0.023	0.023	0.023	0.022	0.240	0.230	0.066	0.0971	0.064	0.0924
08	0.132	0.120	0.100	0.092	0.068	0.070	0.115	0.103	0.240	0.220	0.131	0.0653	0.121	0.0582
23	0.071	0.071	0.081	0.083	0.042	0.038	0.077	0.061	0.240	0.220	0.102	0.0785	0.094	0.0720
R3	0.064	0.041	0.051	0.024	0.058	0.034	0.051	0.051	0.110	0.105	0.066	0.024	0.051	0.0317
R7	0.290	0.169	0.078	0.054	0.106	0.070	0.040	0.023	0.093	0.071	0.121	0.0974	0.077	0.0547
R9	0.065	0.042	0.051	0.050	0.058	0.032	0.060	0.023	0.200	0.124	0.086	0.0634	0.054	0.0403
R10	0.036	0.015	0.030	0.008	0.023	0.008	0.022	0.006	0.023	0.008	0.026	0.0060	0.009	0.0034

Survey IV Fe (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.67	0.54	0.67	0.55	0.61	0.53	0.62	0.54	1.70	1.20	0.85	0.473	0.67	0.295
08	0.50	0.41	0.49	0.41	0.45	0.37	0.45	0.36	1.20	1.10	0.61	0.326	0.53	0.319
23	0.45	0.39	0.40	0.33	0.42	0.32	0.38	0.30	1.50	1.20	0.63	0.487	0.50	0.388
R3	0.29	0.19	0.28	0.14	0.30	0.16	0.30	0.21	0.43	0.24	0.32	0.062	0.18	0.039
R7	1.84	0.33	0.82	0.28	0.81	0.21	0.32	0.20	0.55	0.29	0.86	0.581	0.26	0.055
R9	0.40	0.17	0.63	0.20	0.33	0.16	0.40	0.19	2.00	0.52	0.75	0.706	0.24	0.152
R10	0.21	0.15	0.28	0.13	0.22	0.13	0.24	0.22	0.29	0.21	0.24	0.035	0.16	0.043

Survey IV Zn (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.011	0.010	0.016	0.015	0.011	0.008	0.013	0.014	0.070	0.060	0.024	0.0256	0.021	0.0217
08	0.62	0.58	0.42	0.40	0.37	0.36	0.35	0.34	0.150	0.152	0.38	0.168	0.36	0.152
23	0.61	0.35	0.36	0.34	0.34	0.32	0.31	0.29	0.174	0.165	0.35	0.158	0.29	0.075
R3	0.040	0.033	0.035	0.028	0.026	0.030	0.026	0.024	0.029	0.030	0.031	0.0061	0.029	0.0033
R7	0.063	0.012	0.031	0.016	0.026	0.014	0.020	0.019	0.023	0.026	0.032	0.0174	0.017	0.0054
R9	0.024	0.019	0.028	0.022	0.026	0.018	0.025	0.026	0.032	0.020	0.027	0.0031	0.021	0.0031
R10	0.026	0.024	0.025	0.024	0.022	0.025	0.022	0.020	0.022	0.019	0.023	0.0019	0.022	0.0027

note: numbers of decimal places differ because of sensitivity of range used for measurement

Survey IV Cd (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.0005	0.0004	<0.0003	-	<0.0003	-
08	0.0013	0.0012	0.0007	0.0006	0.0005	0.0005	0.0006	0.0006	0.0007	0.0004	0.00076	0.00031	0.00066	0.00031
23	0.0006	0.0007	0.0008	0.0005	0.0005	0.0005	0.0007	0.0005	0.0004	0.0005	0.00060	0.00015	0.00054	0.00008
R3	0.0003	<0.0003	<0.0003	<0.0003	0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
R7	0.0004	0.0005	<0.0003	<0.0003	<0.0003	<0.0003	0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-
R9	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	0.0003	<0.0003	<0.0003	0.0003	<0.0003	<0.0003	-	<0.0003	-
R10	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	-	<0.0003	-

Survey IV Pb (mg l^{-1}) water

SITE	DAY													
	1		2		3		4		5					
	22.10.79		23.10.79		24.10.79		25.10.79		26.10.79					
	T	F	T	F	T	F	T	F	T	F	$\bar{x}_T$	s.d.$_T$	$\bar{x}_F$	s.d.$_F$
03	0.007	0.004	0.008	0.004	0.008	0.004	0.008	0.007	0.016	0.014	0.0094	0.0037	0.0066	0.0043
08	0.020	0.017	0.020	0.016	0.027	0.018	0.017	0.013	0.024	0.023	0.0216	0.0039	0.0174	0.0036
23	0.015	0.011	0.021	0.019	0.018	0.015	0.019	0.013	0.025	0.023	0.0196	0.0037	0.0162	0.0048
R3	0.010	0.005	0.013	0.006	0.014	0.006	0.011	0.007	0.015	0.008	0.0126	0.0020	0.0064	0.0011
R7	0.055	0.014	0.020	0.008	0.023	0.006	0.008	0.004	0.011	0.008	0.0234	0.0187	0.0080	0.0037
R9	0.010	0.005	0.015	0.005	0.008	<0.003	0.006	0.007	0.023	0.010	0.0124	0.0068	0.0057	0.0031
R10	0.006	0.005	0.006	0.006	0.006	0.007	0.006	0.003	0.008	0.007	0.0064	0.0008	0.0056	0.0016

Survey IV Additional water chemistry: (a) Bolts Burn, days 1 - 7; (b) R. Derwent, days 6 - 9

			Na		K		Mg		Ca		Mn		Fe		Zn		Cd		Pb	
DAY	DATE	SITE	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F	T	F
1	22.10.79	0071 - 99	36.1	35.9	11.6	10.5	0.81	0.78	47.8	47.4	0.42	0.44	0.07	0.06	2.38	2.36	0.0028	0.0027	0.067	0.039
2	23.10.79	0071 - 99	36.9	36.5	10.2	9.8	0.87	0.86	51.4	51.0	0.40	0.40	0.013	0.04	1.92	1.81	0.0023	0.0019	0.088	0.047
3	24.10.79	0071 - 99	32.6	32.8	8.3	8.00	0.81	0.76	46.0	42.0	0.40	0.40	0.15	0.04	1.42	1.31	0.0014	0.0015	0.065	0.053
4	25.10.79	0071 - 99	36.8	36.3	10.2	9.2	0.82	0.80	51.2	48.2	0.26	0.25	0.15	0.04	1.36	1.27	0.0013	0.0013	0.058	0.039
5	26.10.79	0071 - 99	22.4	22.3	7.1	6.4	0.72	0.68	39.8	37.0	0.29	0.24	0.39	0.21	1.22	1.09	0.0023	0.0013	0.146	0.096
6	27.10.79	0071 - 99	30.1	29.5	7.5	7.0	0.82	0.80	41.2	41.3	0.31	0.32	0.14	0.08	1.43	1.39	0.0015	0.0017	0.057	0.043
7	28.10.79	0071 - 99	19.5	19.4	5.4	5.4	0.75	0.76	36.6	36.6	0.22	0.23	0.22	0.23	1.38	1.28	0.0020	0.0018	0.065	0.045
6	27.10.79	0061 - 03	8.5	5.7	2.00	1.03	0.35	0.25	12.3	7.9	0.135	0.126	1.00	0.90	0.021	0.021	0.0004	0.0004	0.012	0.010
		0061 - 08	8.6	5.6	1.91	1.84	0.34	0.34	12.4	12.4	0.153	0.151	0.90	0.75	0.190	0.185	0.0006	0.0004	0.015	0.014
		0061 - 23	8.4	8.4	1.72	1.86	0.25	0.34	12.1	9.0	0.135	0.125	0.90	0.70	0.210	0.200	0.0005	0.0004	0.016	0.016
7	28.10.79	0061 - 03	6.3	5.7	1.57	1.56	0.33	0.32	11.4	11.0	0.058	0.058	0.92	0.82	0.014	0.016	0.0004	0.0004	0.010	0.009
		0061 - 08	8.1	8.6	2.2	2.1	0.40	0.40	15.6	15.1	0.087	0.084	0.79	0.70	0.250	0.230	0.0007	0.0007	0.016	0.014
		0061 - 23	8.7	8.8	2.3	2.2	0.41	0.41	15.4	15.4	0.074	0.070	0.65	0.66	0.27	0.28	0.0007	0.0007	0.019	0.020
8	29.10.79	0061 - 08	10.1	10.4	2.6	2.6	0.45	0.45	18.1	18.0	0.080	0.082	0.88	0.63	0.35	0.34	0.0007	0.0007	0.014	0.014
		0061 - 23	10.5	10.9	2.7	2.7	0.46	0.46	18.8	18.0	0.069	0.058	0.57	0.51	0.28	0.27	0.0005	0.0005	0.013	0.013
9	30.10.79	0061 - 23	10.0	9.7	2.8	2.8	0.56	0.51	24.0	23.1	0.072	0.069	0.44	0.44	0.27	0.27	0.0004	0.0003	0.016	0.015

APPENDIX 2

Water chemistry: primary data for anions during Surveys I - IV

F Cl Si PO_4-P

Surveys I and II Anions (mg l^{-1}) n=4

Survey I 25.10.78 (day 1)

SITE	ANION							
	F		Cl		Si		PO$_4$-P	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
05	0.22	0.029	5.9	0.34	2.19	0.130	0.007	0.0014
08	0.65	0.037	6.9	0.92	3.06	0.134	0.005	0.0005
23	0.74	0.028	6.6	0.19	3.26	0.103	<0.005	-
27	0.74	0.052	7.2	0.71	3.36	0.168	0.010	0.0014
R3	0.60	0.040	9.0	0.41	1.13	0.071	<0.005	-
R7	0.60	0.023	9.6	0.26	1.18	0.062	0.007	0.0012
R10	0.59	0.012	8.8	0.05	1.08	0.023	0.009	0.0015

Survey II 26.04.79 (day 1)

	F		Cl		Si		PO$_4$-P	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
03	0.40	0.014	6.9	0.15	0.96	0.184	0.021	0.0014
08	0.75	0.009	7.1	0.23	1.56	0.143	0.018	0.0017
23	0.80	0.009	8.0	0.10	1.06	0.354	0.028	0.0009
R3	0.85	0.008	11.1	0.49	1.10	0.243	0.019	0.0017
R7	0.81	0.011	11.9	0.20	1.50	0.204	0.023	0.0012
R9	0.79	0.005	12.8	1.23	1.26	0.289	0.032	0.0025
R10	0.77	0.014	12.1	0.11	1.10	0.147	0.015	0.0005

Surveys III and IV   Anions (mg l^{-1}) n=4

Survey III 08.08.79 (day 1)

SITE	ANION							
	F		Cl		Si		PO_4-P	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
03	0.72	0.010	7.2	0.55	2.73	0.188	0.023	0.0014
08	1.81	0.085	8.2	0.86	4.08	0.143	0.020	0.0012
23	1.88	0.085	10.6	0.49	4.08	0.314	0.032	0.0005
R3	0.95	0.010	11.2	0.15	1.10	0.470	0.020	0.0008
R7	0.96	0.022	11.4	0.40	0.80	0.135	0.021	0.0016
R9	0.95	0.008	11.0	0.78	0.70	0.005	0.021	0.0012
R10	0.95	0.008	10.6	0.25	0.65	0.057	0.018	0.0018

Survey IV 22.10.79 (day 1)

	F		Cl		Si		PO_4-P	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
03	0.29	0.005	6.9	0.28	2.77	0.150	<0.005	-
08	1.27	0.012	7.8	0.17	4.05	0.163	<0.005	-
23	1.51	0.018	8.5	0.52	4.07	0.119	<0.005	-
R3	0.74	0.005	10.4	0.20	0.78	0.062	<0.005	-
R7	0.68	0.005	11.0	0.10	0.68	0.085	<0.005	-
R9	0.56	0.005	10.9	0.63	1.08	0.047	0.008	0.0012
R10	0.67	0.005	11.1	0.47	0.67	0.104	<0.005	-

Anions (mg l^{-1}) in water samples (n=4) collected from R. Derwent reach 05 and reach 08 on four consecutive days

ANION	SITE	DAY							
		1		2		3		4	
		25.10.78		26.10.78		27.10.78		28.10.78	
		$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
F	05	0.22	0.027	0.19	0.016	0.19	0.026	0.24	0.036*
	08	0.65	0.037	0.53	0.012	0.52	0.037	0.80	0.025*
Cl	05	5.9	0.34	5.0	0.45	5.7	0.48	6.1	0.42
	08	6.9	0.92	6.0	0.53	6.1	0.42	7.1	0.43
Si	05	2.19	0.130	1.33	0.112	1.75	0.081	2.06	0.063
	08	3.06	0.134	2.22	0.292	2.34	0.220	3.14	0.105
PO_4-P	05	0.007	0.0014	0.005	0.0005	<0.005	-	0.006	0.0008
	08	0.005	0.0008	<0.005	-	<0.005	-	0.005	0.0008

* n=3 for these samples only

APPENDIX 3

Organic content of sediments during Surveys I - IV

Organic content of sediments collected during Surveys I and II (% dry wt)

Survey I 25.10.78 (day 1)

SITE	SAMPLE 1	2	3	4	5	$\bar{x}$	s.d.
05	2.04	3.88	3.06	3.67	3.14	3.15	0.714
08	4.22	4.25	2.11	3.69	3.32	3.51	0.877
23	4.69	2.96	3.44	4.06	3.33	3.69	0.682
27	1.70	0.63	1.69	1.71	0.97	1.34	0.507
R3	2.31	2.84	2.57	2.26	2.43	2.48	0.233
R7	4.34	5.11	4.13	4.57	6.42	4.91	0.917
R10	4.72	4.10	4.28	2.25	3.27	3.72	0.977

Survey II 26.04.79 (day 1)

SITE	SAMPLE 1	2	3	4	5	$\bar{x}$	s.d.
03	2.84	2.71	3.08	2.08	2.47	2.63	0.381
08	0.32	1.15	0.47	0.38	1.87	0.83	0.666
23	0.61	1.09	0.36	0.78	0.93	0.75	0.283
R3	4.72	4.71	4.62	3.42	5.28	4.55	0.683
R7	1.31	2.81	1.13	3.02	1.24	1.90	0.929
R9	11.14	6.81	9.85	5.25	2.57	7.12	3.46
R10	4.71	5.00	3.96	2.72	3.69	4.01	0.899

Organic content of sediments collected during Surveys III and IV (% dry wt)

Survey III 08.08.79 (day 1)

SITE	SAMPLE 1	2	3	4	5	$\bar{x}$	s.d.
03	4.63	2.81	3.77	4.25	5.33	4.16	0.951
08	2.85	1.85	3.34	2.41	3.24	2.73	0.617
23	4.96	4.98	3.77	2.02	4.21	3.98	1.214
R3	4.38	5.88	6.24	6.30	6.92	5.94	0.950
R7	12.12	10.61	9.78	7.83	7.05	9.48	2.075
R9	12.17	7.92	17.91	18.44	20.45	15.37	5.182
R10	3.83	3.01	2.53	3.10	3.82	3.25	0.561

Survey IV 22.10.79 (day 1)

SITE	SAMPLE 1	2	3	4	5	$\bar{x}$	s.d.
03	1.91	2.95	2.04	1.80	4.81	2.70	1.263
08	4.23	3.36	3.23	2.44	4.24	3.50	0.757
23	3.02	4.50	3.27	3.40	3.14	3.46	0.595
R3	1.55	0.91	1.22	1.45	1.52	1.33	0.262
R7	4.75	2.78	0.75	2.02	3.85	2.83	1.558
R9	1.59	1.35	1.57	2.52	1.02	1.61	0.558
R10	3.14	3.62	4.05	4.17	4.34	3.86	0.484