# Pollution in the river team and invetigations of zinc toxicity to elected algal species

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## TABLE OF CONTENTS

Page

ABSTRACT

# LIST OF TABLES

# LIST OF FIGURES

# ABSTRACT

The River Team is a 26.8 km tributary of the River Tyne; it enters the Tyne at Newcastle. Aspects of pollution were studied in the River Team over a five month period from April to August 1979. Sources of pollution included sewage effluents, mining and industrial discharges.

Nine sampling sites were chosen above and below various sources of input in order to obtain a representative profile of the river. Water and sediment samples were collected for analysis from the nine sites throughout the five month period. Particular attention was given to zinc as this was one of the pollutants in the river. Levels up to 28.60 mg $l^{-1}$ total Zn were recorded below one industrial drain which discharges effluent from Durham Chemicals. This firm produces a variety of zinc-based products which are used by other industries. A survey was conducted below the major sources of mining and industrial input to determine the discharge variations occurring throughout a 24 h period.

Organisms found at the nine sites were identified. Laboratory experiments were conducted to determine the toxicity of various zinc concentrations on selected species of algae collected at the sites. Experiments conducted on *Stigeoclonium tenue* Kütz, revealed that zinc-sensitive strains occurred in the upper stretch of the river which was relatively uncontaminated in comparison with the highly polluted lower stretch where zinc-tolerant strains of *S. tenue* survived.

A species of *Ulothrix* collected from the mouth showed relatively poor resistance to zinc. This result was very unusual as the tolerance index concentration (T.I.C.) was much lower than the field concentration of zinc at this site. Various explanations are suggested to account for this unusual phenomenon.

# CHAPTER 1

# INTRODUCTION

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# INTRODUCTION

## 1.1 GENERAL INTRODUCTION TO STUDY

The biota of many streams, lakes and rivers have changed drastically since man began using these waters to carry away domestic and industrial wastes. The Team is an example of such a river; it forms a 26.8 km tributary of the River Tyne, entering the latter at Newcastle. Attention was drawn to this highly polluted river, parts of which were graded as class 3 and 4 quality (Northumbrian Water Authority Report, July 1977) by J.W.Hargreaves of the N.W.A. The Team was therefore considered to be an interesting river on which to conduct a survey. As zinc was one of the sources of pollution, it was decided that the effects of zinc selected organisms should be studied in further detail. The detailed aims of this project are listed in section 1.8 at the end of this review of some of the literature.

## 1.2 HEAVY METALS

The most thorough studies of the effects of poisons on river have been concerned with pollution by metals. The term "heavy metal" generally refers to those metals having a density greater than five, so includes approximately 40 elements altogether (Passow et al., 1961). Some of these, such as Cu, Mn, Fe, and Zn are essential in small amounts for the growth of all organisms. Wilson (1976) defines "trace" metals as those present at concentrations of $<1$ mg $l^{-1}$, but the concentration of certain heavy metals are often higher than this in polluted waters and they can be toxic to many forms of life. Elevated levels of heavy metals can therefore lead to a decreased species diversity, and hence an "extreme" environment as termed by Brock (1969).

Organisms remaining in the stream might still be affected in various ways, for instance they might accumulate heavy metals and be unable to complete a certain stage in their life history, or their growth rates might be affected. Consequently much interest has been generated to investigate these factors and study the sensitive organisms as well as discover the means by which the tolerant organisms can survive.

## 1.3 SOURCES OF HEAVY METALS ENTERING FRESHWATER ENVIRONMENT

Natural sources of metals are introduced into freshwater systems by the erosion of rocks, minerals and the sediments carried in the water. Most streams have also been contaminated by artificial sources throughout the years, receiving heavy metals from mining, agriculture, industry and domestic pollution. These aspects are reviewed extensively by Harding (1977) who notes that concentrations of Zn, Pb, Cd of >0.1 mg $l^{-1}$, 0.05 mg $l^{-1}$, and 0.001 mg $l^{-1}$ respectively, are generally the result of artificial pollution. With the exception of thermal or acid streams, streams carrying >1 mg $l^{-1}$ Zn, 0.1 mg $l^{-1}$ Pb or 0.005 mg $l^{-1}$ Cd are usually restricted to areas affected by past or present mining activities or industry.

### 1.31 Input from mining activities

For long it has been known that waters draining the surface or underground workings of zinc or lead mines may carry elevated concentrations of heavy metals. Many of the streams on the Northern Pennine Orefield are affected by inputs of metals derived from past or present mining activities. In a study of this area, Say (1977) recorded levels up to 22.3 mg $l^{-1}$ Zn in the water of "Old Mine Gill" near Nenthead. In West Wales seepages from dumps have for many years given rise to complaint, and a long series of papers have been published on the subject by members of Univerity College Aberystwyth (Carpenter, 1924, 1925, 1926; Reese, 1937; Laurie and Jones, 1938; Newton, 1944). Most of the mines had ceased to operate before these investigations began, and Jones (1958) who has written many papers on this area, reports that zinc has continued to leach out of some dumps for at least 35 years after mining operations ceased.

### 1.32 Input from industry

There are many examples in the literature of pollution attributed to industrial sources; for example, Oliver (1973) attributed elevated concentrations of 846 $\mu g\ g^{-1}$ Zn and 390 $\mu g\ g^{-1}$ Pb in sediment from the Ottawa River to local industries; Jaffe and Walters (1975) working on the Humber estuary, reported that high titanium content (up to 12000 $\mu g\ g^{-1}$) and vanadium (up to 2030 $\mu g\ g^{-1}$) were most likely derived from local titanium dioxide processing plants. There is little precise data, however, on the composition of the actual discharges from industries, because in the United Kingdom the water authorities are prevented from disclosing to the public any information on the concentration of heavy metals in industrial effluents because of prohibition under the Rivers (Prevention of Pollution) Act 1961. Concentrations of pollutants may therefore only be disclosed once the pollution has been diluted in river water (Valdez, 1975).

## 1.4 BEHAVIOUR OF HEAVY METALS IN THE FRESHWATER ENVIRONMENT

De Greef (1976) states that, "once metals are in the surface water, within a short time there grows up a complicated and still not fully understood relationship between the dissolved fraction and the complex fraction".

The distribution of a heavy metal between different fractions in freshwaters is influenced by many factors such as pH, alkalinity and phosphate content of the water; these factors are briefly reviewed by Harding (1977). The state in which a particular metal is in, can profoundly influence its transportation, sedimentation, its availability and toxicity to organisms.

In a study of metal distribution in streams, Perhac (1972) classified the solids into:

(i) coarse particulates ( $>150$ nm)
(ii) colloidal particulates ( $<150$ nm, $>10$ nm)
(iii) dissolved solids ( $<10$ nm)

He found that although the heavy metals were generally most concentrated in the colloids, the greatest total quantity of each element typically occurred in the dissolved state simply because the dissolved solids comprise most of the total solid in the water. Fe and Mn were found to be notable exceptions, both occurring most abundantly in the particulate fraction. This may be due to the ease with which the divalent forms are oxidised to the relatively insoluble $Fe^{3+}$ hydroxide and $Mn^{4+}$ oxide.

Several authors, for instance Jenne (1968), Murray et al. (1968), have suggested that inorganic precipitates such as ferric hydroxide and hydrous manganese oxide can act as efficient agents for adsorption and co-precipitation of dissolved metals. Organic solids can also be a very important adsorbent for metals (Williams et al. 1973).

## 1.5 TOXICITY OF HEAVY METALS TO AQUATIC ORGANISMS

It has been reported by many authors from observations based on field studies and laboratory experiments, that elevated levels of heavy metals can lead to a decreased species diversity.

### 1.51 Fauna

Out of all the organisms studied in research on heavy metal toxicity, fish have received the most attention. Carpenter (1924) reports that most upland reaches in the area she studied in Wales, had a high stock of fish; but in rivers such as the Ystwyth and Rheidol where they received washings from lead mine tailings, no fish occurred, and she attributed this to the toxicity of dissolved lead. However, in the earlier stages of the work in this area, no distinction was made between the effects of lead and zinc, and Jones (1940) later concluded that it was zinc rather than lead that was the responsible factor.

Carpenter (1924) also found that the invertebrate fauna was very much reduced in contaminated streams, and in many cases there was a complete absence of Crustacea, Hirundinea, Platyhelmia, Oligchaeta, Mollusca and Trichoptera; the fauna in places being limited to a few insect larvae.

### 1.52 Flora

Visually, the marked effects that heavy metals have on reducing the variety of species are perhaps initially seen in the changes of vegetation. Jones (1958) reported that downstream of the Cwm Ystwyth mine at Pontrhydroes the whole appearance of the River Ystwyth had changed as the normal flora of mosses and green algae had been eliminated and growths of Lemanea were abundant. Carpenter (1924) in her studies on the River Rheidol, found that the reaches downstream of the lead mines had a vegetation limited to slight coatings of bryophytes and some growths of the red algae Batrachospermum and Lemanea. In a study by Say (1978) on the heavily polluted and aptly named Riou-Mort, marked changes were observed in the benthic algal flora below the sources of pollution which were mainly suspended solids, Zn, Cd, Cu, $H_2SO_4$ and Mn. Under extreme heavy metal pollution at certain sites no algal species were found, whilst at others the flora was reduced to two species.

Although pollution reduces the diversity of species, there frequently remains some organisms capable of surviving. Griffiths, Hughes and Thomas (1974), in a study of the rivers in Cardiganshire, found that the filamentous green algae *Hormidium*, *Ulothrix* and *Microspora* were strikingly tolerant to metal pollution as they were especially abundant where the streams emerged from mines. These three species, including *Mougeotia*, were also listed by Say (1977) as algae showing the most resistance to heavy metal pollution in the high zinc level streams of the Northern Pennine Orefield.

As a result of such observations, biologists have attempted to use the sensitive and tolerant organisms to judge the degree and severity of pollution by analysing changes in the species composition.

## 1.6 BIOLOGICAL INDICATORS

As long ago as 1913 Forbes emphasised the use of organisms as environmental indicators when he suggested that,"it is quite possible to arrange the plants and animals of a stream in the order of their preference for, and tolerance of, organic impurities, in such a way that a graded list of them may serve as an index to grades of contamination". Ten years later, Purdy (1923) also commented on the use of biological indicators, "If it be true that the biological life of a stream is distinctly and profoundly affected by the numerous factors which form the environment, it follows that the organisms in a stream constitute in a general way a reflection of the prevailing environmental condition of the stream". Consequently a large number of the laboratory studies carried out on the toxicity of different heavy metals to different species of algae have been concerned with the possible uses of algae as monitors of pollution, or with the toxic effects of metal-containing algicides (Whitton and Say, 1975). Although some tentative generalisations can be made for some species, results from other studies may reveal conflicting data.

Numerous authors have suggested that Stigeoclonium demonstrates some tolerance to metal pollution. S. tenue was listed by Weimann (1952) among the species of algae that were very resistant to metallic poisons in the Nordrhein-Westfalen region; Palmer (1959) quoted the alga as an indicator of pollution by copper and chromium; Butcher (1955) found that alga within a five mile recovery zone below a copper waste effluent on the River Churnet; Whitton (1970 b) suggested that abundant growths of Cladophora indicate that the waters are not subject to repeated pollution of heavy metals in solution, but that "well illuminated flowing water sites with abundant growths of Stigeoclonium but no Cladophora at all should be treated as suspect for metal pollution".

Observations by McLean (1974) are in apparent contrast to these and he suggested that its tolerance to heavy metals was due to its tolerance and affinity for organic pollution, and that in the absence of organic pollution it would not tolerate zinc or lead. Other authors such as Fjerdingstad (1950) and Hynes (1960) have reported that the organism can tolerate pollution by organic matter, and Stigeoclonium has in consequence also been used as an indicator of organic pollution. However it has also been found in regions which could not be described as being polluted with organic matter, so to use it as an indicator in this sense should also be questioned. McLean and Benson-Evans (1974) describe S. tenue as a fairly tolerant organism which is not restricted to an environment of organic pollution.

It is also possible that different strains of individual species of algae might differ in tolerance to forms of pollution, and that such strains may occur naturally in polluted environments. There are indications in the literature that this is so in the case of heavy metal pollution. For instance Say, Diaz and Whitton (1977) carried out detailed laboratory investigations of the tolerance of species of Hormidium to zinc. It was found that at sites with higher concentrations of zinc on the water, populations of H. flaccidum and H. rivulare had increased resistance to zinc, and this was probably a result of genetic adaptation.

## 1.7 ENVIRONMENTAL FACTORS AFFECTING THE TOXICITY OF HEAVY METALS TO ORGANISMS

Field and laboratory observations have shown that there are various features of the environment that may have pronounced effects on the level at which a heavy metal is toxic to an organism. The distribution and various forms in which a metal can exist in an aquatic system has already been briefly reviewed in section 1.4, and these states may have different effects on the organisms.

Say and Whitton (1977) for example, found that the toxic effects of Zn on Hormidium rivulare were reduced by increases in the concentrations of Mg, Ca, and $PO_4$. Similar observations were reported by Say, Diaz and Whitton (1977) who also worked on species of Hormidium. They found that Pb and Cd however, acted in the opposite way by increasing the toxicity of Zn.

The effects that Mg and Ca have in reducing the toxicity of Zn also apply to Stigeoclonium tenue (Harding and Whitton, 1977). However, effects were found to be more marked in the zinc-tolerant population than in the zinc-sensitive population, so there are further distinctions between the strains.

pH is another factor which can affect the toxicity of heavy metals; Hargreaves and Whitton (1976) have shown that the toxicity of zinc to a population of Hormidium rivulare isolated from an acid mine drainage was least at the optimum pH range for the growth of the algae, pH 3.5-4.0; but toxicity increased markedly at higher pH values.

Rana and Kumar (1974), in a study of the toxicity of zinc to Chlorella vulgaris and Plectonema boryanum, suggest that a plausible mechanism underlying the phosphate protection of zinc toxicity seems to operate at the membrane levels, possibly by interfering with the absorption of one another. They suggest that the phosphate ions form complexes with zinc ions and render them non-toxic, thereby blocking the entry of zinc into the cell. Other hypotheses to explain the effectiveness of calcium in reducing zinc toxicity suggest that a mechanism exists whereby the zinc is initially bound passively, and that calcium might compete with zinc for these sites (Say and Whitton, 1977).

## 1.8 AIMS OF THIS STUDY

In view of the past literature summarized in this chapter and the correspondence with J.W.Hargreaves who drew attention to the polluted River Team (section 1.1), it was decided that the aims of this study should include:

(i) a series of physical and chemical analyses of water and sediment samples to assess the factors and concentrations of metals polluting the river, determining the most polluted stretches of water and giving indications as to the likely sources of pollution.

(ii) a 24 h survey to determine any variations in the discharge of effluents that might occur throughout the day.

(iii) a survey to identify the types of organisms found at various sites along the length of the river.

(iv) laboratory experiments designed to test the toxicity of various zinc levels on selected species of algae found growing in the river.

The first three aspects formed the basis of a joint project by the author and S.C.Taverner, who conducted a parallel study investigating the accumulation of zinc in algae and bryophytes found growing in the river.

The study was conducted over a period of five months from April to August 1979.

# CHAPTER 2

# MATERIALS AND METHODS

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# MATERIALS AND METHODS

## 2.1 WATER CHEMISTRY

### 2.11 FIELD METHODS

### 2.111 General Comments

Fine days were chosen for sampling the river in order to avoid water specimens being contaminated by rainwater, and days immediately following periods of heavy rainfall were avoided as levels of metals in the river would be diluted to a greater extent than at times when the water level was at an average height.

Water at the mouth of the Team was sampled at low tide in order to avoid further complications and dilution caused by an inflow of sea water. One sample on the 25 April was taken at high tide, but these results have not been used in the calculation of mean values for this site.

Exact locations for water collection were chosen such that any effluent or discharge received immediately above the sampling point would be well mixed with the river water. Water was collected, and field recordings were taken from the middle of the river wherever possible, just below the water surface. The sampler faced upstream at all times, in order to avoid collections being disturbed and contaminated by currents stirring up bottom sediments.

Samples for the 24 h survey carried out on the 26 and 27 June 1979, were collected by the methods outlined below; samples were taken every hour exactly on the hour from 1200h on the 26 June through the night until 1100h the following day.

### 2.112 Field Records

The weather conditions, state of depth, colour and current speed of water were noted on each sampling day and at each site; the latter three factors are included in the description of sampling sites (see section 3.32).

Temperature of the water was measured directly in the river by holding a thermometer just below the surface of the water and waiting until the reading remained at a constant value.

Oxygen levels were recorded by holding a Mackereths oxygen probe in the water and noting the percentage saturation directly from the meter (Lakes Instruments Ltd ) when the needle settled at a constant value. This reading was converted into mg $l^{-1}$ $O_2$ in the laboratory by the use of a standard calibration chart.

The pH and total alkalinity were recorded in the field by measuring 100 ml of river water into a plastic beaker that had been rinsed several times with river water at that site. The Pye Unicam pH probe previously rinsed with distilled water, was agitated in the sample until a constant value could be read from the meter (Pye Unicam model 293) which had been calibrated using buffers of pH 4 and pH 7 made by dissolving the appropriate pH tablets in 100 ml of distilled water. Total alkalinity was estimated from this sample by titrating 0.02 N $H_2SO_4$ from a 2 ml plastic syringe into the 100 ml of river water contained in the plastic beaker. The volume of $H_2SO_4$ needed to alter the pH of the sample to pH 4.5 was noted, and a further quantity of acid was carefully added until the sample reached pH 4.2. The total volume of acid used in the titration was recorded. Total alkilinity was calculated as follows:

$$\begin{array}{l}\text{Total alkalinity} \\ \text{mg } l^{-1}\ CaCO_3\end{array} = \frac{(2A - B) \times N \times 50{,}000}{\text{ml sample}}$$

where A = ml titration for sample to reach pH 4.5

B = total ml titration for sample ro reach pH 4.2

N = normality of acid.

### 2.113 Collection of water samples

As previously mentioned in the general comments (2.111), water was collected upstream of the sampler and immediately below the water surface

(i) Cation sample, Total water.

A 2000 ml plastic beaker was rinsed several times with water from the sampling site and then filled with river water. This was allowed to stand for 5 minutes so that larger particles of sediment would settle to the bottom. Water from just below the surface was drawn into a 10 ml plastic syringe which had previously been acid washed by soaking for at least 0.5h in 10% HCl, thoroughly rinsed six times with distilled water, and allowed to dry naturally in the air. The sample of river water was transferred into a plastic snap top glass phial which would hold up to 30 ml of water; the phial having previously been acid washed by the method already stated, although glassware was dried in an oven at 105°C. A drop of conc. $HNO_3$ A.A.S. grade for trace metal analysis, was added to the sample in order to keep the metal ions in solution. The tube was appropriately labelled and stored in an ice box whilst in the field.

(ii) Cation sample, Filtered water

The 10 ml plastic syringe was refilled from the 2000ml beaker, and the water was slowly filtered through a 25 mm diameter 0.2μm porous polycarbonate Nuclepore filter fitted into a Swinnex holder; the Nuclepore filter having previously been acid washed for 0.5h in a 10% solution of HCl and thoroughly rinsed six times in distilled water. The filters were stored in a beaker of distilled water, and placed on the acid washed Swinnex filter holder carefully with tweezers to lessen the chance of contamination. The filtered water was collected in another acid washed plastic snap top glass tube, and a drop of conc. $HNO_3$ A.A.S. grade for trace metal analysis was added to it. The tube was labelled and placed in the ice box.

(iii) Anion samples

Two samples for choride and phosphate analysis were taken by filtering river water through two grade 2 Sinta glass funnels which were rinsed with water from the site before use. The Sinta glass funnels were supported on tripods and the filtered water was collected in two dry, acid washed polythene bottles. The bottles, which could hold 250 ml, were two-thirds filled in order to provide sufficient space for the water to expand when the samples were placed in the laboratory's deep freeze. Until then, the anion samples were temporarily stored in the ice box.

The filtering process was occasionally impeded by suspended materials such as sediments and diatoms, blocking and discolouring the white filter. If this occurred in the field, a piece of rubber tubing was attached to the filter and distilled water blown back through the filter in an attempt to dislodge the blockages. The Sinta glass funnels were frequently cleaned and acid washed between sampling trips.

(iv) Water collected for physico-chemical analyses.

A further sample of water was collected directly from the river in a wide necked plastic bottle with a screw-on lid. The container was thoroughly rinsed twice with river water from the site and then held at an angle to the surface so that the river water flowed into the bottle rather than bubbling in and introducing more air. The bottle was manoeuvred and the lid screwed on under the water surface so as to exclude all air bubbles from the sample. This extra bottle was labelled and placed in the ice box, and on return the laboratory this water was analysed immediately for pH, conductivity and optical density.

## 2.12 LABORATORY METHODS

### 2.121 Storage of samples

Cation samples were stored in the refrigerator at 4°C until required for analysis. The anion samples were placed in the deepfreeze, ensuring that there was sufficient space in the polythene bottles for the water to expand on freezing, and when required, were allowed to thaw completely before use. The extra bottle of water collected for the determinations of pH, conductivity, and optical density, was analysed immediately on return to the laboratory; if a short delay was envisaged, the samples were placed in the refrigerator.

### 2.122 Physico-chemical analysis of water samples

(i) Lab. pH

Lab. pH was determined by a pH meter made by Electronic Instruments Ltd pH meter 7020 which had previously been calibrated using pH buffers of pH 4 and 7. The Pye Unicam probe was rinsed with distilled water between samples, and the meter frequently rechecked against the buffers. Values were compared with those obtained in the field.

(ii) Conductivity

A sample of water was tipped into a conductivity cell which had previously been cooled in the refrigerator so that it was at the same temperature as the water; this procedure facilitated the precise determination of readings on the conductivity meter, as the recorder needle moved less erractically. Conductivity was measured on a Gallemkamp conductivity meter Model MC1 Mark V.

### (iii) Optical density

The water samples in the wide necked polythene bottles were allowed to settle and water was drawn into a 10 ml plastic syringe that had previously been rinsed with distilled water, and placed in a 4 cm optical cell, which had also previously been rinsed with distilled water. Samples were measured in a Uvispek spectrophotometer at wavelengths of 240 and 254 nm, against a control cell containing distilled water.

## 2.123 Chemical analysis of water samples

### (i) Cations

Analyses for the metals, Zn, Fe, Mn, were determined directly from the total water samples and the filtered water samples using a Perkin-Elmer 403 Atomic Absorption Spectrophotometer. The determination of Ca and Mg involved the addition of a lanthium chloride solution. 4 ml of sample were placed in an acid washed glass tube and 6 drops of a 10% w/v $La\ Cl_3$ solution were added, and the solution stirred with a clean glass rod. Lanthium controls the effects of Si, Al, $PO_4^{3-}$, $SO_4^{3-}$ and also makes the absorption independent of pH. The spectrophotometer is calibrated against a blank of distilled water and standard solutions of known concentrations of the appropriate metal; although in the case of Ca and Mg, these will have $LaCl_3$ added.

The A.A.S. grade conc. $HNO_3$ for trace metal analysis, a drop of which was used to keep metals in the sample in solution, was tested on occasions to determine whether it had been contaminated at any stage.

### (ii) Anions

Chloride content was determined by the Argenometric method listed in "The Chemical Analysis of Fresh Water". This method was slightly adapted as follows:

A 0.0141 N solution of $AgNO_3$ was titrated against 10 ml of sample to which had been added 10 drops of potassium chromate indicator, made by dissolving 1g of $K_2CrO_4$ in 100 ml of distilled water. Sufficient $AgNO_3$ solution was added to the sample until a pinkish-orange end point was reached. The Chloride concentrations of the samples were determined from a standard graph previously constructed by titrating the $AgNO_3$ against different known concentrations of a standard 0.0141 N solution of NaCl, 1 ml of which was equivalent to 500μg Cl.

Soluble Reactive Phosphorus was determined by the Acid Molybdate-antimony analysis listed in "The Chemical Analysis of Fresh Water". The concentrations of $P - PO_4$ in the final solutions were determined by use of a Uvispek spectrophotometer, and exact values read from a graph constructed by plotting the volumes of appropriate reagents used in the titration against various known concentrations of a standard phosphate solution.

## 2.2 SEDIMENTS

### 2.21 Introduction

Samples of sediment were analysed for zinc content in order to investigate the amount of this metal adsorbed on particles, and to determine whether there was any difference in this respect between sites, as well as compare the relative proportions of the metal contained in the sediment with the levels occurring in the water at the nine chosen sites.

### 2.22 Collection

Four samples of sediment were collected from each site and placed in polythene bags. Sediment samples were also taken from above the point where Kibblesworth mine water is pumped into the river, between sites

5 and 6 (see Fig. 3.2).

### 2.23 Preparation and analysis

#### (i) Preparation of sediment for digestion

The sediments were removed from the polythene bags, placed in acid washed glass beakers and dried in an oven at 105°C for 48h. Material was then sieved through a fine mesh, the netting having 210μm wide holes; the particles which passed through the sieve were collected in an acid washed glass tube. The sieved material was redried for a further 12h in the oven, and the tubes then transferred to a desiccator until required.

#### (ii) Digestion

50mg of sediment were weighed and placed in a Kjeldahl flask. 5 ml of conc. $HNO_3$ A.A.S. grade for trace metal analysis were added, and the contents of the Kjeldahl flask were boiled for 0.5h. The solution was allowed to cool, and was then transferred to a 25ml volumetric flask; distilled water was added until the diluted solution reached the 25ml mark. The contents of the volumetric flask were then transferred into an acid washed snap top glass tube and stored in the refrigerator at 4°C until required for analysis. The digested sediment was analysed for zinc content on a Perkin-Elmer 403 Atomic Absorption spectrophotometer.

## 2.3 RESISTANCE OF SELECTED ALGAL SPECIES TO ZINC

### 2.31 INTRODUCTION

The filamentous green alga, Stigeoclonium tenue Kütz. was the principal species chosen for toxicity tests involving various concentrations of the heavy metal zinc. It was present at virtually all sampling sites with the exception of site 9, at the mouth, where a species of Ulothrix was collected for toxicity tests as this was the only species of filamentous algae observed to grow there.

## 2.32 COLLECTION OF MATERIAL

Algae were identified in the field using a Nikon field microscope.

Wherever possible, clean samples uncontaminated by sediment, diatoms or other species of algae, were collected. If the cover of Stigeoclonium tenue was dense, the algae covering an area approximately $1cm^2$ were removed with dissecting tweezers and placed in a 250ml glass bottle containing sufficient river water from that site to cover the bottom of the container to a depth of 0.5-1cm. Wherever possible, the species were collected from as small an area as would allow, to reduce the chance of slightly different populations being collected. The specimens collected were therefore assumed to have similar genetic material. Bottles were placed in an ice box whilst in the field.

## 2.33 METHODS FOR ASSAY IN THE LABORATORY

### 2.331 Acclimation of Algae in the culture medium

A suitable culture medium of Chu 10 E, modified by Durham University, was used for the assays. The stock solutions listed below, were made and stored in acid washed glass bottles kept in a refrigerator, with the exception of $Na_2SiO_3$ which was stored in an acid washed plastic beaker. The bottle containing Fe EDTA was covered with foil in order to keep the solution in the dark.

A solution of Chu 10 E was made by adding the listed amounts of stock solutions to a 1 l acid washed volumetric flask nearly filled to the mark with distilled water. The distilled water had been allowed to stand open to the atmosphere in order for it to become saturated with carbon dioxide, necessary for plant growth. After each separate stock solution was introduced, the phosphate solution being the final addition, the flask was shaken to ensure complete mixing of the different solutions in order to reduce the possibility of any metals precipitating, and the Chu 10 E solution was brought to the 1 l mark with distilled water, and thoroughly mixed.

To make 1 l of Chu 10 E solution the following quantities of stock solutions are required:

| | |
|---|---|
| 0.5 ml of 7.820 g $l^{-1}$ | K $H_2PO_4$ solution |
| 1.0 ml of 25.0g $l^{-1}$ | $MgSO_4.7H_2O$ solution |
| 1.0 ml of 40.0g $l^{-1}$ | Ca $(NO_3)_2$ solution |
| 1.0 ml of 7.925 g $l^{-1}$ | $NaHCO_3$ solution |
| 0.25 ml of 43.5 g $l^{-1}$ | $Na_2SiO_3$ solution |
| 0.25 ml of 2.0 g $l^{-1}$ | Fe EDTA solution |

0.25 ml of AC microelements + Zinc (low Mn) stock solution.

The AC microelements + Zinc solution contained the following chemicals:

| | |
|---|---|
| 2.86 g $l^{-1}$ | $H_3BO_3$ |
| 0.181 g $l^{-1}$ | $MnCl_2.4H_2O$ |
| 0.079 g $l^{-1}$ | $CuSO_4.5H_2O$ |
| 0.042 g $l^{-1}$ | $CoSO_4.7H_2O$ |
| 0.027 g $l^{-1}$ | $Na_2MoO_4.2H_2O$ |
| 0.222 g $l^{-1}$ | $ZnSO_4.7H_2O$ |

The solution of Chu 10 E therefore contained a zinc concentration of 0.05 mg $l^{-1}$.

Fresh solutions of Chu 10 E were made as required, and were kept no longer than five days.

50 ml of the Chu 10 E culture medium were measured into 250 ml

conical flasks that had previously been acid washed with 10% $H_2SO_4$, and carefully stoppered with cotton wool, trying to avoid any fibres of cotton wool falling into the solution, as this would provide a surface on which metals might adsorb, and would therefore slightly alter the composition and concentration of the Chu 10 E medium.

Tufts of algae were removed with tweezers from the river water and rinsed in some separate Chu 10 E solution to remove any material loosely adhering to the filements, and the algae were then transferred into the conical flask containing the Chu 10 E medium. The flasks were placed in a Gallenkamp "shake tank" situated in a cold room, and were secured in a rack suspended just above the water surface, so that the bottom 3-5 cm of the flasks were in contact with the water. The algae were thus kept at a constant 14°C and at a light intensity of 5500 lux, illuminated by means of fluorescent strip lights at the bottom of the tank. The samples were shaken by a motor which was connected to the rack by means of a rubber belt. The moderate movement ensures the circulation of solution around the algae and so reduces the possibility of metal adsorbing to the filaments and forming a barrier around them. The algae were left to acclimate in the Chu 10 E medium for 36h before the toxicity experiments commenced.

### 2.332 Toxicity tests

#### (i) Preparation of material

A series of boiling tubes, having been previously acid washed by soaking for at least 0.5h in 10% $H_2SO_4$ and then rinsed thoroughly eight times with distilled water, dried in an oven at 105°C, and carefully plugged with cotton wool, were assembled and labelled with various predetermined concentrations of zinc that the culture medium was to contain.

A litre solution of Chu 10 E medium was prepared as in the manner already described in section 2.331, but the AC microelements solution added in this instance contained no zinc, and the amounts of stock solutions added were increased in order to make the final solution of Chu 10 E 10% more concentrated.

9.5 ml of the 110% Chu 10 E medium were pipetted into each of the boiling tubes, a minimum of thirty tubes were used for each assay to cover a range of zinc concentrations. The medium then required a further 0.5 ml of liquid to be added in order to alter the concentration of Chu 10 E to that experienced by the acclimating algae in the shake tank. Appropriate calculated volumes of both distilled water and a $ZnSO_4.7H_2O$ solution of known concentration were added to the solutions in the boiling tubes by means of acid washed 0.5ml and 0.1 ml pipettes, such that a series of tubes each containing 10 ml of Chu 10 E medium covered a range of different zinc concentrations. Control tubes which contained no zinc were duplicated. Filaments of algae were introduced into the solutions after the appropriate volume of distilled water had been added, but before the addition of the zinc solution.

The algae acclimating in the shake tank were tipped into clean petri dishes, checked under the microscope to ensure that their condition was satisfactory, and strands of uniform size were tweezed out with dissecting equipment, checked visually for a standard size, and rinsed briefly in Chu 10 E medium. They were introduced into the solution contained in the boiling tubes by using an inoculating needle which was regularly flamed, as were the necks of the tubes in order to reduce the possibility of microbial contamination occurring. The appropriate volumes of zinc solution were finally added, and the tubes shaken to prevent the algal filaments being subjected to temporary high concentrations of the zinc solution. The labelled tubes were then placed in the rack of the shake tank at an angle so that the contents would be agitated, under the conditions previously stated in section 2.331.

### (ii) Assessment of growth

Growth was checked visually on days 3, 5 and 7 (the toxicity tests commencing on day 0), and the tubes moved to alternative areas in the shake tank so that any differences in local effects such as slight variations in temperature or light intensity resulting from tubes being in the middle of the rack or at the edges of the rack for example, would be averaged out.

The algae were scored visually on a 0-5 scale, taking into account the colour and healthy appearance of the algae as well as the amount of material growing in the tube. Comparisons were made between tubes and also with the control tubes. A score of 0 indicated dead material which was easily identified as the filaments lost their green colour and became white; a mark of 5 indicated good, healthy growth. Scoring was therefore as follows:

5 - healthy appearance of algae, with excellent growth
4 - healthy appearance of algae, with good growth
3 - healthy appearance of algae, with reduced growth
2 - signs of dead filaments occurring; restricted growth
1 - some green filaments left amongst dead material
0 - dead filaments, having a white appearance.

Final assessments of growth were taken on day 7, as scores were found to be constant after this period of time had elapsed. Filaments of algae were also checked under the microscope.

## 2.34 EVALUATION OF TOXICITY TESTS

Figures for various algal tolerance values were calculated according to the method listed by Harding and Whitton (1976).

The following figures were determined from the scores in the assays:

I - maximum concentration causing no inhibition.

II - minimum concentration causing slight inhibition.

III - maximum concentration at which the alga is alive.

IV - minimum concentration at which the alga is killed.

These values were multiplied as follows to provide a numerical estimation for the concentrations of zinc at which the alga is killed, and the level at which the alga can grow without inhibition. The tolerance index concentration (T.I.C.) is calculated from these derived values.

| | |
|---|---|
| Just non-inhibitory | $(\mathrm{I.II})^{1/2}$ |
| Just lethal | $(\mathrm{III.IV})^{1/2}$ |
| Tolerance index concentration (T.I.C.) | $(\mathrm{I.II.III.IV})^{1/4}$ |

# CHAPTER 3

# AREA OF STUDY AND LOCATION OF SAMPLING SITES

# CHAPTER 3

# AREA OF STUDY AND LOCATION OF SAMPLING SITES

## 3.1 GEOLOGY

Coal seams in the area occur mainly in the upper strata of the carboniferous rocks, and in general dip gently in an easterly direction from their outcrops in the west and, after crossing a central north-to-south syncline, rise over domes, especially in the Whitley Bay and Whitburn areas, before resuming their easterly dip. Apart from these gentle fold structures, the coalfield is crossed by faults tending mainly W.S.W. to E.N.E. and from west of north to east of south. The former are in general bigger, occasionally moving the rocks up to 300 m vertically.

As the coal measures fall towards the east, they pass under Permian strata composed of basal poorly cemented sandstones or, in some areas, thin cemented breccias, overlain by thick magnesium limestones. The latter rocks form cliffs extending from South Shields just south of the River Tyne to beyond Blackhall at the southernmost extremity of the coalfield. Outcrops of limestone also occur around Stanley, the River Team flows round the northern side of this town (see fig 3.1). A limestone outcrop also occurs on the eastern side of the river following a line just west of north and east of south through Newcastle.

## 3.2 MINING IN THE REGION

### 3.21 Historical aspects

Coal has been associated with the north-east of England since Roman times, but it was the medieval coal merchants and shippers of Newcastle who founded the coal trade and initiated the industrial fame for Tyneside. Shipments from the Tyne date from the thirteenth century, but most coal was still burned in households near the outcrops. The great expansion of the coal industry in the region began about 1550; by 1770 the region's coal output exceeded a million tonnes a year, and by the nineteenth century coal gained further impetus.

Development of railways revolutionised the transport system and together with improved shipping facilities, contributed to the mining industry's expansion. In the present century the National Coal Board (N.C.B.) report that output rose from 46 million tonnes in 1900 to a peak of 56 million tonnes in 1911. In the 1920's and 1930's yearly output varied between 40 and 50 million tonnes and in 1946, the last year before nationalisation, the region produced 33 million tonnes.

### 3.22 Recent mining activities affecting the river

Four major collieries affect the River Team either by pumping minewater directly into the river, or by tip water draining naturally into the water (see Fig. 3.2).

East Tanfield colliery occurs near the source of the river; this mine was closed in January 1965 but a small volume of water draining from the tips will eventually go to the East Tanfield sewage station and will have some effect on the river. (J.L. Carslake, N.C.B. pers. comm.).

Mine water from Marley Hill colliery and Blackburn Fell colliery will also enter the river at Causey Burn via Bobgins Burn which is a tributary of the River Team. Blackburn Fell colliery only recently closed on 20 March 1979, prior to this study beginning. Marley Hill colliery is still functional, and until 1976 discharged mine water directly into Bobgins Burn. In 1976 however, the procedure was altered, both minewater and the coal itself are pumped into the River

Derwent. There is therefore only a small amount of minewater affecting Bobgin's Burn mainly through natural tip drainage, although very small volumes are occasionally still pumped from Marley Hill colliery into this tributary.

The remaining mine which affects the Team to a greater extent than those already mentioned is at Kibblesworth. Kibblesworth mine was closed in October 1974, but large volumes of water are still pumped into the Team (see Fig. 3.14), principally at night when electricity rates are cheaper, although some pumping may occur during the day in order to keep the level of water down, especially after periods of heavy rainfall (J.L. Carslake, N.C.B. pers. comm.).

## 3.3 SAMPLING SITES ON THE RIVER TEAM

### 3.31 General comments

Nine sites were chosen along the length of the river where samples of water and collections of algae could be taken for analysis and assay.

The sites were well spaced along the course of the river in order to obtain a fair representation of the state of water in the particular stretches above and below the various effluents discharging into the river. Choice of sites was also limited by points of access to the river, so sites were restricted to areas where the water ran alongside the road or at bridges, where equipment did not have to be carried over long distances. Certain sites, namely Tantobie Bridge, Beamish, and Team Valley Trading Estate (T.V.T.E.) 3rd Avenue, were selected as they are regularly sampled by the Northumbrian Water Authority, so results of water analysis could be compared.

The total number of possible sites meeting the above criteria was restricted to nine, as this was found to be the maximum able to be visited and investigated in one day.

## 3.32 Description of the sampling sites

### SITE 1. KYO

Map reference : NZ 174528

(taken from Ordnance Survey, 1:50000 second series
Tyneside Sheet 88)

Distance downstream from source : 1.1 km

At this point the river is known as Kyo Burn and is approximately 0.5 m - 1.5 m wide and 10-50 cm deep, so could best be described as a stream. The site is easily accessible as the stream runs alongside the road, and water samples were taken just before it passes under the bridge (see Figs 3.3 and 3.4). Vegetation on the banks include species of grasses, *Urtica dioica* L., *Rubus fruticosus* agg., *Impatiens glandulifera* Royle, species of Umbelliferae and thistles, and a small clump of a few willow trees.

The water at this site is usually very clear, and the stream bed visible. The flow is often at a moderate speed, though it can become quite rapid at times, especially after periods of heavy rainfall when the water becomes turbid. The stream bed consists of gravel covered by large stones so there is a suitable substrate on which algae can become attached, and niches for animals to inhabit. The mosses *Brachythecium rivulare*, *Fontinalis antipyretica* Hedw. and *Rhynchosegium ripariodes* (Hedw.) C.Jens., grew on stones in the stream, and dense amounts of the alga *Stigeoclonium tenue* Kütz. and a species of *Ulothrix* covered many stones. In June the stream had extremely dense growths of *Ulothrix* species, although these, along with *Stigeoclonium tenue*, died away in July, whilst chains of various diatoms remained. Some sewage fungus was present.

There are no major effluents coming into the stream at this point; but there will be some runoff from agricultural land and possibly a little sewage from farms.

SITE 2 TANTOBIE

Map reference : NZ 194547

Distance from source : 4.8 km

Between sites 1 and 2 Kyo Burn has drained into a marshy area just to the northeast of Tanfield Lea and reemerges about 0.5 km later (see Fig. 3.1). The exact location chosen for sampling was 20 m upstream of Tantobie Road Bridge, where the stream is about 2 m wide and 50 cm deep. The surrounding area is open wasteland, and the dominant plant on the stream banks is *Impatiens glandulifera* growing to a height of 2-2.5 m in August.

The water is usually slow flowing at this site and is often clear, revealing a sandy bottom. However, at times of high flow after heavy rainfall the water becomes very murky, as also occurs when the stream bed is deliberately disturbed, unsettling mud and silty material by the sides of the bank and also under the sand. The nature of the substrate probably accounts for the reduced number of plant and animal species at this site; very small amounts of *Stigeoclonium tenue* and *Cladophora glomerata* (L.) Kütz. were attached to various pieces of rubbish such as tyres and tin cans lying in the stream (see Figs 3.5 and 3.6), although dense strands of diatoms occurred near the sides of the stream. Sewage fungus was also present.

Armstrong Corks Ltd , and Everready are the two firms nearby this site; the former does not discharge effluent into the stream (J.W. Hargreaves, Northumbrian Water Authority, pers.comm.), and the latter also does not affect the water at this site, but drainage from Everready tips enter the water further downstream. This site is regularly sampled by the Northumbrian Water Authority.

## SITE 3 BEAMISH

Map reference : NZ 205547
Distance from source : 7.8 km

At this point the river is known as Beamish Burn and is approximately 4-5 m wide and 10-70 cm deep. The exact location for obtaining water samples was 50 m downstream of the bridge, just before the river bends to the left handside; the land is privately owned at this point, but access was kindly granted by the owners. Vegetation on either side of the banks included species of grasses, as well as a few herbaceous species such as *Endymion non-scriptus* (L.) Garcke and *Allium ursinum* L. Trees such as sycamore , elm, elder and hawthorn shaded the river in places.

The water was often turbid at this site (see Figs 3.7 and 3.8) and had a moderate and occasionally rapid flow. The river bed comprised of large stones and a gravelly substrate, which provided suitable means of attachment for algae and habitats for animals. The liverwort *Lunularia cruciata*, and the mosses *Brachythecium rivulare* and *Rhynchostegium riparioides*(Hedw.) C.Jens. grew on the larger stones, and there were dense growths of *Cladophora glomerata* and *Stigeoclonium tenue* at this point in the river, although *Stigeoclonium* had disappeared by July. Sewage fungus was also present.

In the last 3 km stretch between sites 2 and 3 the river has received various effluents apart from surface run off from both agricultural land and mining areas (see Fig. 3.2) initially, there is tip drainage from the Everready works, which discharges just below site 2; the river then receives effluent from East Tanfield sewage works, and also mine water from the disused East Tanfield colliery. Bobgins Burn is a large tributary joining the river near Causey, and will carry some minewater drainage from the recently disused Blackburnfell colliery, and Marley Hill colliery which is still functional. This site is regularly sampled by the Northumbrian Water Authority.

## SITE 4 URPETH

Map reference : NZ 235542

Distance from source : 12.4 km

The river near High Urpeth is about 4 m wide and 10-80 cm deep, although at the exact sampling location 10 m upstream of the bridge, it is 1.5 m in a few places. The valley on one side is covered with trees including sycamore and willows which shade the water at various times. Plants growing under this canopy include *Endymion non-scriptus*, *Allium ursinum* and *Myrrhis odorata* (L.) Scop.; by the water's edge *Impatiens glandulifera* is very common.

The water is generally quite clear at this site and has a moderate rate of flow over a stony substrate. Substantial amounts of *Stigeoclonium* and *Cladophora glomerata*, were observed, along with *Rhynchostegium riparioides* and *Brachythecium rivulare*; small amounts of sewage fungus were also present.

No major effluents have entered the river between sites 3 and 4 other than surface run off from the land and possibly small amounts of sewage from Beamish Park. There are numerous gravity feeds in this stretch of the river which introduce some mine water, as will the small colliery in Beamish Park Museum (J.L. Carslake, N.C.B. pers.comm.) although levels of metals introduced are virtually insignificant.

## SITE 5 ABOVE BIRTLEY

Map reference : NZ 255561

Distance from source: 15.9 km

At this point the river is 3-4 m wide and 20-60 cm deep. The site is easily accessible and samples of water were collected from about 30 m upstream of the bridge. The immediate area has vegetation typical of wasteland, including species of grasses, *Rumex* sps , *Urtica dioica*, *Impatiens glandulifera*; there are also a few willow trees along the banks.

The water is generally clear at this site, although on occasions it has appeared murkier, and the flow is moderate. A few large boulders and stones occur in places on the sandy, gravelly bottomed stream bed, and bryophytes and algae can also find a source of attachment on various pieces of rubbish thrown into the stream such as car tyres, metal road signs, and numerous bricks; the latter indicating the presence of the nearby brick works. *Rhynchostegium riparioides*, *Brachythecium rivulare*, *Fontinalis antipyretica* Hedw., *Cladophora glomerata* and *Stigeoclonium tenue* and sewage fungus occur at this site.

No major effluents have been discharged into this part of the river, so the stretch from site 3 at Beamish (see Figs 3.7 and 3.8) to this point (see Fig. 3.10) allows the water to recover naturally to some extent from Everready surface water, mine seepage water, and East Tanfield sewage works.

### SITE 6 BELOW BIRTLEY

Map reference : NZ 258570
Distance from source : 17.4 km

Although this location is only 1.5 km downstream of the previous site (see Figs 3.1 and 3.2), the river has changed dramatically during this period. For a while it runs parallel with the railway embankment, and the ground has a vegetation typical of this type of area and open waysides. The grassy banks dip down to a river that is now 5-6 m wide and approximately 20-60 cm deep (see Fig. 3.15).

The water is constantly turbid and oily patches can often be seen on the surface; raw sewage has also occasionally been noted. An obnoxious chemical odour can be frequently detected which was found to be characteristic of this site. The river bed is composed of small stones, sand and gravelly material, and although the substrate material is suitable, there was little indication of life other than a mucilaginous unicellular green alga of unidentified species. A band of Stigeoclonium tenue was found on the sides of the bridge just above the water level, although its appearance was totally different from at the previous sites as it was restricted to the basal filament form. Protonema occurred on the sides of the bank just above the water level. This was cultured by S.C.Taverner in the laboratory and identified as Pohlia delicatula (Hedw.) Grout.

In the 1.5 km between sites 5 and 6 the river has received four major effluents (see Fig. 3.2). Rowletch Burn is a tributary of the Team used as a drain for discharges from various industries, notably British Oxygen Company (B.O.C.), Picon, Century Aluminium, and Ready Mixed Concrete (see Fig. 3.2). Below this effluent, a large drain carries discharge from Durham Chemicals and the Royal Ordnance Factory (see Figs 3.11 and 3.12). The third major input to the river is from Birtley Sewage works (see Fig. 3.13); and finally there is pumped mine water principally from Kibblesworth mine which is now disused, already mentioned in section 3.22 (see Fig. 3.14).

SITE 7 LAMESLEY

Map reference : NZ 251 579

Distance from source : 18.6 km

Water samples were taken immediately downstream of the bridge, where the river is about 5-6 m wide and 10-80 cm deep. Vegetation on the banks is grassy with various herbaceous species and a few willow trees (see Fig. 3.18).

The river water is usually turbid and often has traces of the characteristic odour associated with the previous site. Broken concrete slabs and pieces of rubbish have accumulated underneath the bridge, otherwise the substrate is of sand and gravel. Virtually no plants or animals inhabit this area, although Stigeoclonium tenue occurred in places in its basal form only, and the moss protonema of Pohlia delicatula grew on the sides of the bank just above the water level. Sewage fungus was present.

No further effluents have been discharged into the river between sites 6 and 7.

## SITE 8 TEAM VALLEY TRADING ESTATE (T.V.T.E.)

Map reference : NZ 245605
Distance from source : 22 km

After the river has passed through Lamesley, it is directed for a distance of about 1.5 km in a channel which runs in the centre of the dual carriageway of the Team Valley Trading Estate, below road level. However, the water can still be seen through wire netting which covers the channel, and this is overgrown by rambling roses. The river is then redirected from the middle of the dual carriageway, and runs through the back of the trading estate parallel to the road. It is 6 m wide and is between 30-60 cm deep throughout this straight stretch. Water samples were collected immediately upstream of the Third Avenue Bridge (see Figs 3.19 and 3.20).

Water at this site is slow flowing and constantly murky, carrying vast quantities of clearly visible suspended solids. Raw sewage has been noted on occasions from storm sewage overflow, and there are often oily patches on the water surface. An assortment of debris including branches, car bumpers, oil drums, drainpipes and metal road works signs, has accumulated just before the bridge, and these provide a source of attachment for some healthy populations of Stigeoclonium tenue. The algae died away for a period in June, although the species reappeared for a short time in July.

Numerous effluents are discharged into the Team as it passes through the industrial trading estate; many of the overflows can be seen above or at water level, although others discharge from below so are not visible. The situation in the Team Valley Trading Estate is therefore very complex and no attempt has been made to distinguish between the various factories at this point. This site is regularly sampled by the Northumbrian Water Authority.

## SITE 9 THE MOUTH

Map reference : NZ 232625

Distance from source : 25.3 km

The River Team continues flowing through Gateshead until it enters the Tyne, 19 km from the mouth of the River Tyne. Tides affect the lower 1.7 km of the River Team, so the tidal stretch starts from about 24 km downstream from the source. At low tide the river is approximately 7 m wide (see Figs 3.21 and 3.22), but becomes 23 m wide at high tide.

The water is turbid and large amounts of suspended solids are clearly visible. Raw sewage is frequently observed at this site, and oily patches are common on the water surface. The banks of the river are muddy and black with oily deposits, the surface being colonised by vast quantities of Englena mutabilis. The only filamentous alga noted at this site was Ulothrix sp., a small amount being observed in June only.

Various effluents have been discharged into this lower stretch of the river since the previous sampling site, and this again complicates the situation. Possibly one of the major polluters at this point (of the atmosphere as well as the river) is the National Coal Boards Norwood Coking Plant.

| | Sites | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| fauna | | | | | | | | | |
| Ephemeroptera | + | + | + | + | + | | | | |
| Plecoptera | + | | | | + | | | | |
| Trichoptera | + | | + | + | + | | | | |
| Simulidae | + | | + | + | + | | | | |
| Chironomids | + | + | + | + | + | | + | + | |
| *Limnea pereger* | | + | + | + | + | | | | |
| Platyelmintha | | | | | | + | | | |
| Dipteran larvae | + | | + | + | + | | | | |
| Oligochaeta | | + | | | | | | | |
| flora | | | | | | | | | |
| *Brachythecium rivulare* | + | | + | + | + | | | | |
| *Rhynchostegium ripariodes* | + | | + | + | + | | | | |
| *Fontinalis antipyretica* | + | | | | + | | | | |
| *Ulothrix* sp. | + | | | | | | | | + |
| *Stigeoclonium tenue* | + | + | + | + | + | + | + | + | |
| *Cladaphora glomerata* | | | + | + | + | | | | |
| Sewage fungus | + | + | + | + | + | + | + | + | |

Table 3.1 - Types of organisms found in River Team

Figure 3.1 Map of River Team

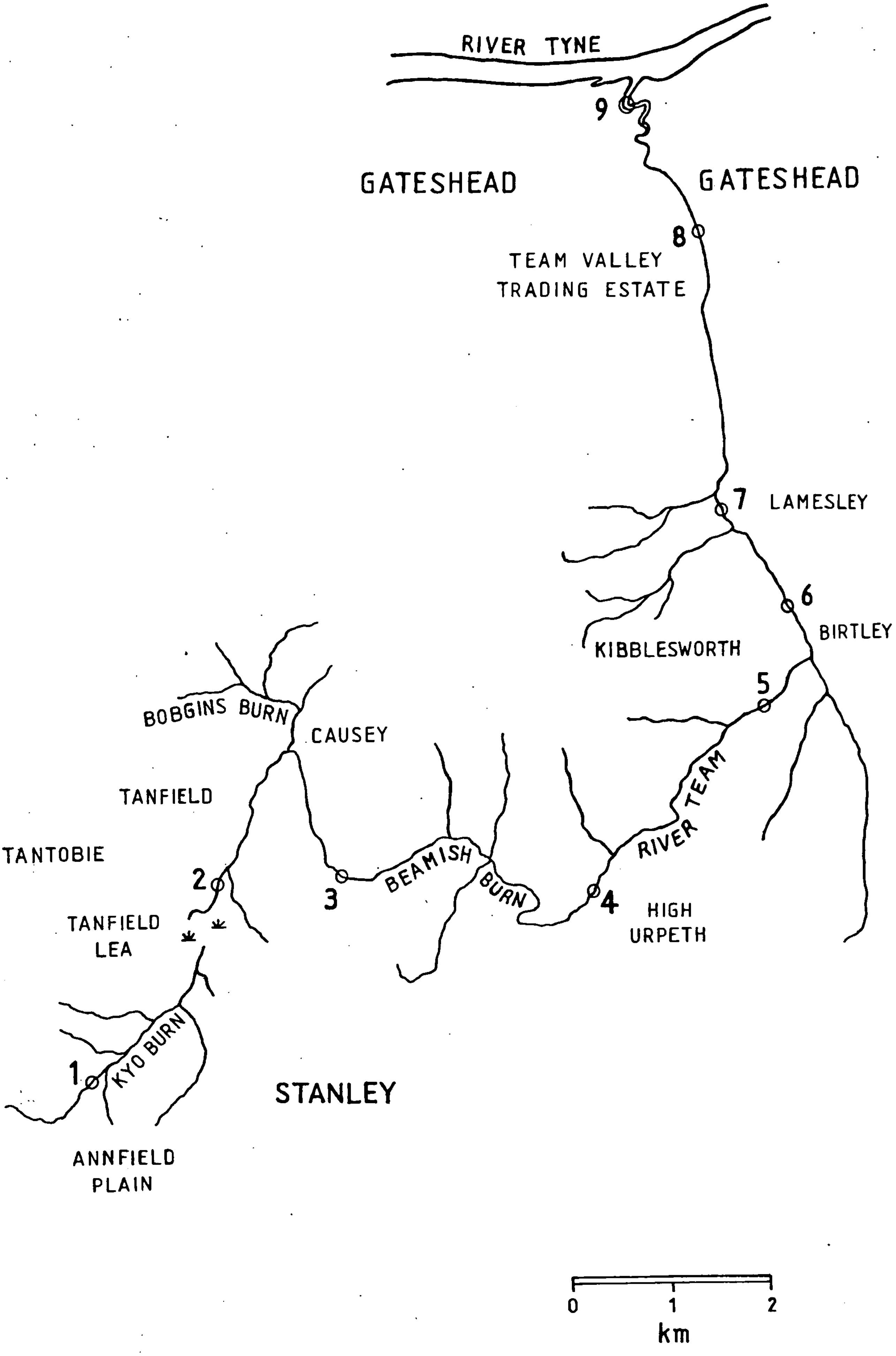

RIVER TYNE
9
GATESHEAD
GATESHEAD
8
TEAM VALLEY
TRADING ESTATE
7
LAMESLEY
6
BIRTLEY
KIBBLESWORTH
5
BOBGINS BURN
CAUSEY
TANFIELD
TANTOBIE
2
3
BEAMISH
BURN
RIVER TEAM
4
HIGH
URPETH
TANFIELD
LEA
1
KYO BURN
STANLEY
ANNFIELD
PLAIN
0
1
2
km

Figure 3.2 Plan showing mining and industrial influences on River Team

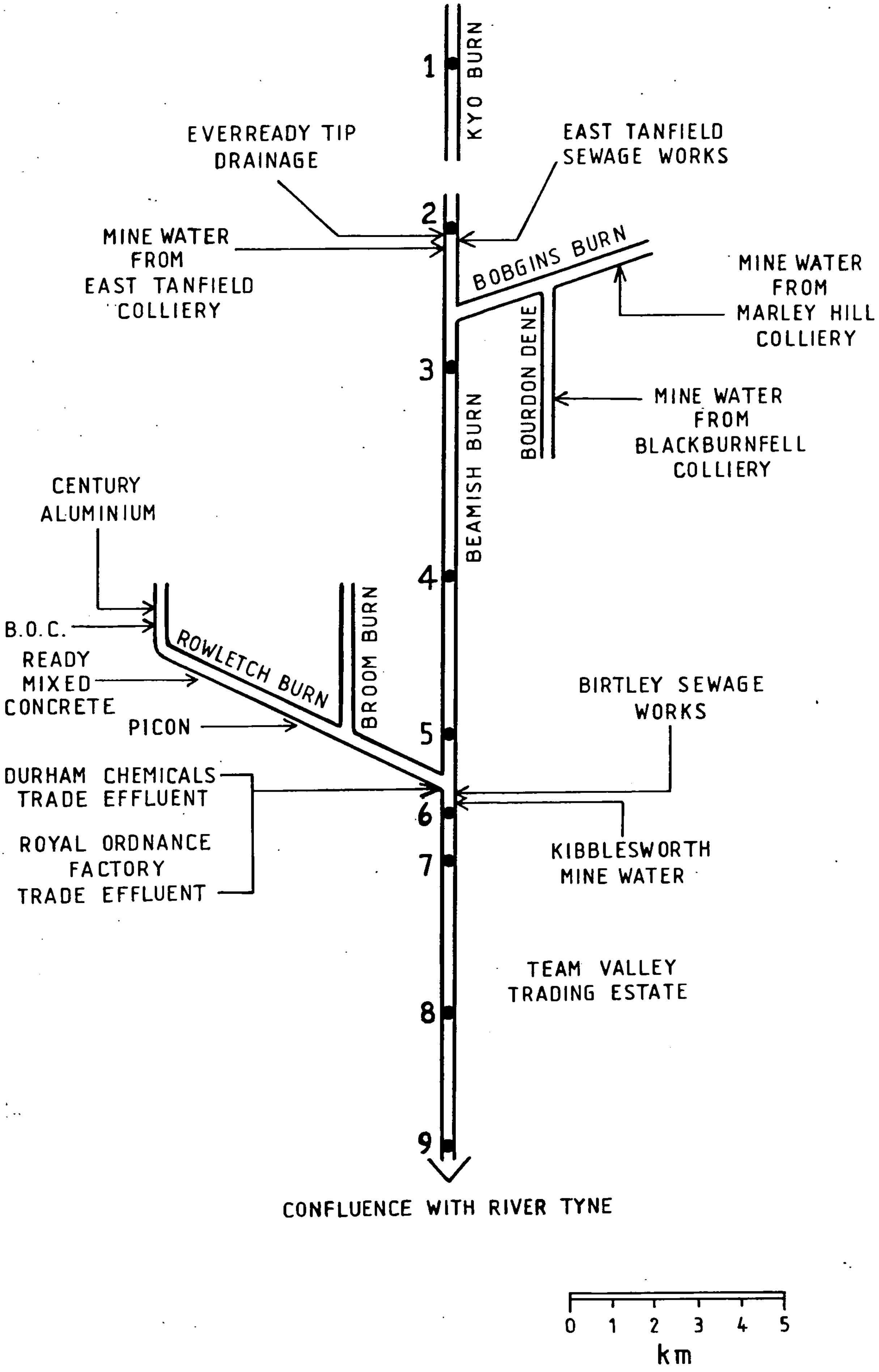

KYO BURN
1
EVERREADY TIP DRAINAGE
EAST TANFIELD SEWAGE WORKS
2
MINE WATER FROM EAST TANFIELD COLLIERY
BOBGINS BURN
MINE WATER FROM MARLEY HILL COLLIERY
BOURDON DENE
3
MINE WATER FROM BLACKBURNFELL COLLIERY
BEAMISH BURN
CENTURY ALUMINIUM
4
B.O.C.
READY MIXED CONCRETE
ROWLETCH BURN
BROOM BURN
PICON
5
BIRTLEY SEWAGE WORKS
DURHAM CHEMICALS TRADE EFFLUENT
6
ROYAL ORDNANCE FACTORY TRADE EFFLUENT
7
KIBBLESWORTH MINE WATER
TEAM VALLEY TRADING ESTATE
8
9
CONFLUENCE WITH RIVER TYNE
0
1
2
3
4
5
km

Fig. 3.3 SITE 1. KYO

View upstream immediately onto the sampling site just before Kyo Burn passes under the road bridge.
(Photograph taken mid June.)

Fig. 3.4 SITE 1. KYO

View of Kyo Burn immediately below site 1, looking upstream just after it has passed beneath the bridge. Note the dense algal cover of *Stigeoclonium tenue* and *Ulothix* sp.
(Photograph taken mid June).

Fig. 3.5 SITE 2 TANTOBIE

View downstream immediately onto site 2. The stream passes under the road via the two large drainage holes below the bridge.

(Photograph taken mid June).

Fig. 3.6 SITE 2 TANTOBIE

Closer view of the stream bed. The water is often clear, revealing the sandy substrate. Note the virtual absence of algae, other than that attached to rubbish such as a few car tyres.

(Photograph taken mid June).

Fig. 3.7 SITE 3 BEAMISH

View upstream of Beamish Burn after it has passed under the bridge. The sampling site is 50 m downstream of the bridge. The water is often murky here, and the algae attached to the stones are Stigeoclonium tenue and Cladophora glomerata.

(Photograph taken mid June).

Fig. 3.8 SITE 3 BEAMISH

View immediately downstream of the sampling site.

(Photograph taken mid June).

Fig. 3.9 SITE 4. URPETH

View looking downstream onto sampling site just before bridge.
(Photograph taken mid June).

Fig. 3.10 SITE 5. ABOVE BIRTLEY

View looking upstream from the sampling position.
(Photograph taken mid June).

Fig. 3.11 EFFLUENT FROM DURHAM CHEMICALS AND THE ROYAL ORDNANCE FACTORY

This effluent is discharged into the River Team between sites 5 and 6; colour contrast between the two bodies of water is rather striking. An obnoxious chemical odour accompanies the discharge, and the same smell can still be detected at sites 6 and 7 further downstream.

(Photograph taken mid June, in the afternoon).

Fig. 3.12 EFFLUENT FROM DURHAM CHEMICALS AND THE ROYAL ORDNANCE FACTORY

Photograph taken beside the drain, looking downstream.

Fig. 3.13 BIRTLEY SEWAGE WORKS AND ITS DISCHARGE

This effluent is discharged into the river between sites 5 and 6, further downstream from Durham Chemicals and the Royal Ordnance Factory. The bottom surface of the drain outlet is completely covered by a Filamentous green alga; however, algae are not found in the river itself at this point.

(Photograph taken mid June).

Fig. 3.14 PUMPED WATER FROM KIBBLESWORTH MINE

This effluent is pumped into the river between sites 5 and 6, further downstream from Birtley Sewage Works.
Pumping occurs mainly at night when the electricity rate is cheaper; however some does occur in the day, especially after periods of heavy rainfall.
Note the boulders stained bright orange from deposits of Ferric hydroxide.

(Photograph taken mid June, in the afternoon).

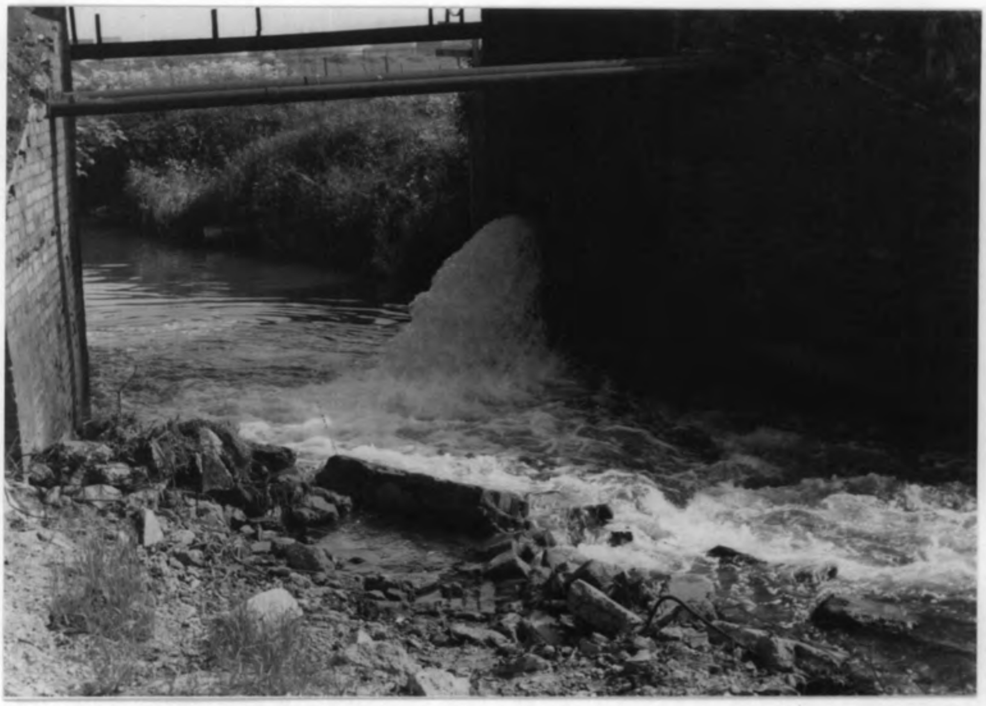


Fig. 3.15 SITE 6 BELOW BIRTLEY

View looking downstream onto the sampling site which is immediately upstream of the bridge. Note the murky colour of the water.

(Photograph taken mid June).

Fig. 3.16 SITE 6 BELOW BIRTLEY

View looking immediately upstream. The dense algal cover on the L.H.S. is a species of Ulothrix growing below a drainage effluent. Note that the alga does not grow into the river.

(Photograph taken mid June).

Fig. 3.17 DRAIN JUST BELOW SITE 6 CHOKED WITH
<u>ULOTHRIX</u> SP.

Note that the alga does not extend into the river water.
The species died away in July.

(Photograph taken mid June).

Fig. 3.18 SITE 7 LAMESLEY

View looking upstream onto sampling site which is immediately downstream of the bridge.

(Photograph taken mid June).

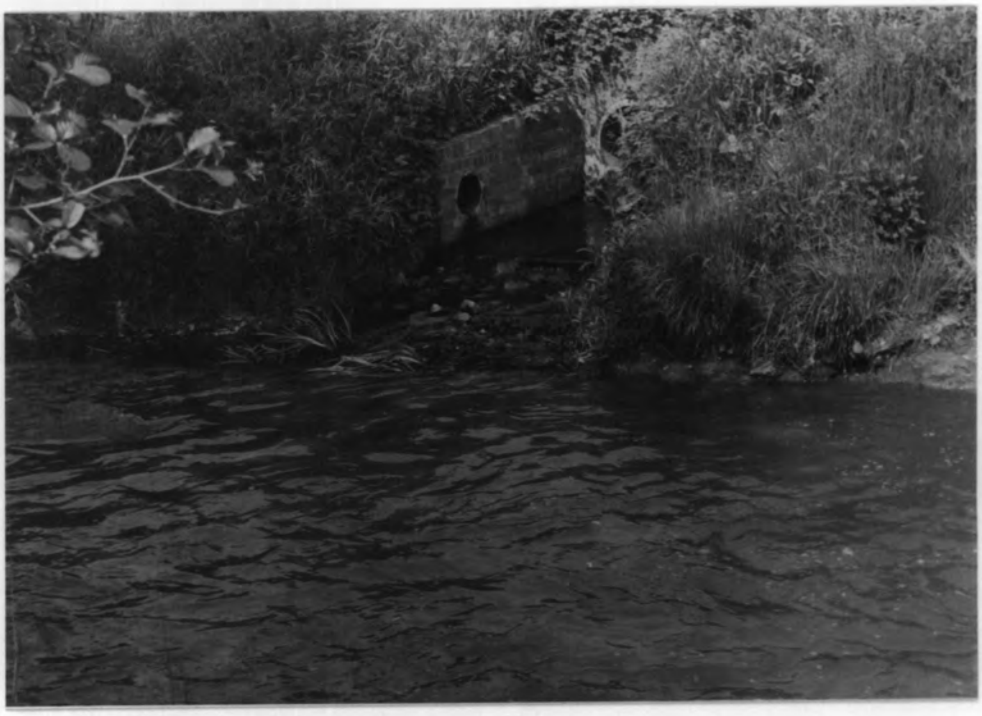


Fig. 3.19 SITE 8 T.V.T.E.

View looking downstream onto the sampling site which is immediately upstream of the bridge.

(Photograph taken mid June).

Fig. 3.20 COLLECTING SAMPLES OF *STIGEOCLONIUM TENUE* AT SITE 8

This was virtually the only part of the river in the trading estate where filamentous algae could be found. A suitable substrate for attachment was provided by accumulated rubbish by the bridge. Note the murky colour of the water.

(Photograph taken mid June).

Fig. 3.21 SITE 9 THE MOUTH

View looking upstream onto the sampling site. The photograph is taken at low tide, revealing boulders and muddy banks. Vast amounts of *Euglena mutabilis* were found on the mud surface.

(Photograph taken mid June).

Fig. 3.22 SITE 9 THE MOUTH

View looking downstream from the sampling site. Note the assorted rubbish and debris thrown into the river.

(Photograph taken mid June).

# CHAPTER 4

# RESULTS

# CHAPTER 4

# RESULTS

## 4.1 WATER ANALYSIS

### 4.11 Presentation of results

Data are collected from water samples taken on six days in April,May and June and are presented in tabular form (see Tables 4.1, 4.2, 4.3, 4.4, 4.5 and 4.6). Results are also listed in the appendix under site headings, so that variations occurring in water chemistry at a particular site are more easily discernible. Mean and standard deviations for variables are listed in the tables of the appendix. In a few instances, a measurement has been omitted deliberately when calculating means; such measurements are enclosed in brackets. The figures obtained at site 9, the mouth, on 25 April for example, were recorded at high tide rather than at low tide when the effects of sea water complicate the issue. In a few cases there is obvious contamination of the water sample, such as occurs with the filterable zinc at site 3 on 19 June; the value measured was approximately five times higher than that for total zinc.

Graphs have been constructed using the mean values to provide a visual representation of changes occurring throughout the river. The maximum and minimum results obtained at each site have been included on the graphs (Figures 4.1 - 4.20) to show the range experienced at each site rather than plotting the standard deviations, as environmental extremes are often more important to organisms in determining their survival in an environment. A second reason for plotting the range of variation rather than the standard deviations from the mean values is that in some instances there are insufficient data for the standard deviations to be meaningful. For instance, samples taken on 9 May (Table 4.5) and 25 April (Table 4.6) do not include data for all of the nine sites as some were not visited.

## 4.12 Comments on results

(i) Temperature (see Figure 4.1).

The minimum temperature recorded in the river was 7.75°C and the maximum was 21°C. The temperature of the water in the upper stretch of the river from sites 1 - 5, had an average value of about 12°C; in the lower stretch from sites 5 - 9, this had increased to just over 14°C. The temperature at the five lower sites varied more, by generally fluctuating from 10-20°C in comparison to the upper sites whence a smaller range over approximately 6°C was experienced.

(ii) Oxygen levels (see Figure 4.2)

The percentage saturation of $O_2$, and the level of $O_2$ expressed as mg $l^{-1}$ are relatively constant in the upper stretch of the river from sites 1 - 4 where mean values of $O_2$ are approximately 11-12 mg $l^{-1}$ and are over the 100% saturation point. A slight rise occurs at site 5, and then the levels drop quite considerably from a mean value of 13 mg $l^{-1}$ to 9.4 mg $l^{-1}$ at Lamesley, and eventually further still to 5.72 mg $l^{-1}$ at the mouth where the water on 19 June was recorded as containing only 2 mg $l^{-1}$.

(iii) pH (see Figures 4.3 and 4.4)

Field pH an laboratory pH do vary slightly, but overall tend to follow the same trend. Field values in the upper stretch of the river at site 1 begin with a mean value of pH 7.6 and gradually increase to a mean of pH 8.3 at site 5. The pH values are relatively stable at each site, generally not fluctuaing much more than 0.5 pH unit overall. There is then a rapid decrease to pH 7.4 at site 6 after which the pH remains relatively steady in the lower stretch of the river.

(iv) Total alkalinity (see Figure 4.5)

Mean values for total alkalinity are approximately 100 mg $l^{-1}$

$CaCO_3$ at sites 1 and 2; this figure doubles at site 3 and remains at a constant value of approximately 200 mg $l^{-1}$ $CaCO_3$ until another sharp increase occurs at site 6 which increases the total alkalinity to approximately 300 mg $l^{-1}$ $CaCO_3$; the level again remains relatively stable at the lower sites. The range of variation recorded at each site increases with each "step-like" progression along the length of the river, such that the smallest variations occur at Kyo and Tantobie, and the largest variations occur at the four lower sites.

(v) Conductivity (see Figure 4.6)

Records are relatively constant at 1000 μmhos at sites 1 and 2, slightly increasing to 1500 μmhos at sites 3,4 and 5. A large increase occurs between sites 5 and 6 to a mean value of 3608 μmhos at site 6, and slightly declines to 2712 μmhos at the mouth. There is a wider range of variability at these lower four sites.

(vi) Optical density (see Figures 4.7 and 4.8)

Values determined at 240 nm are slightly higher than those determined at 254 nm, but the overall trend is very similar as can be seen from the two graphs. An increase in optical density occurs between sites 1 and 2, the values then remain relatively constant, or decline very slightly until site 5. A sharp increase occurs between sites 5 and 6, followed by a decrease after the peak at site 6, and a more gradual increase throughout the lower stretch. Values of optical density are therefore higher in the lower reaches of the river.

(vii) Cl (see Figure 4.9)

Cl values are relatively constant at approximately 55 mg $l^{-1}$ from sites 1-5. Figures after this site vary from about 50 mg $l^{-1}$ to approximately 600 mg $l^{-1}$, mean values dramatically increasing to about 400 mg $l^{-1}$ at sites 6, 7 and 8 and decreasing to 246 mg $l^{-1}$ at the mouth at low tide.

(viii) $P\text{-}PO_4$ (see Figure 4.10)

The mean value for $P\text{-}PO_4$ peaks at site 3 at 0.87 mg $l^{-1}$, gradually declining to 0.26 mg $l^{-1}$ at site 5 and fractionally increasing along the remaining stretch of river. The variation noted at site 3 is considerable, figures range from a minimum value of 0.14 mg $l^{-1}$ to a maximum of 2.5 mg $l^{-1}$.

(ix) Ca (Figures 4.11 and 4.12)

Mean values for total Ca and filtered Ca are virtually identical, the filtered values generally being up to 5 mg $l^{-1}$ smaller than the total values. The trend is therefore similar in the two graphs. Mean values for Ca are high, between 100-120 mg $l^{-1}$ at most sites, although values around 80 mg $l^{-1}$ occur at Kyo and Tantobie.

(x) Mg (see Figures 4.13 and 4.14)

The profile for Mg along the length of the river is much the same as Ca; total and filtered values are similar and the mean values are generally high, between 35-40 mg $l^{-1}$. A slightly lower value occurs at Tantobie.

(xi) Fe (see Figures 4.15 and 4.16)

The levels of Fe present in the total water sample are of a different order of magnitude from that determined from the filtered water samples, although the overall trend of the two graphs is similar. Levels of Fe at the upper sites from Kyo to above Birtley are virtually constant, at approximately 0.5 mg $l^{-1}$ in the total water samples, whereas the mean value for the filtered Fe is about five times lower, at approximately 0.1 mg $l^{-1}$. The concentration of Fe in the water is greater in the lower stretch of the river, a dramatic increase occurs between sites 5 and 6 when the concentration rises to a mean value of about 2 mg $l^{-1}$ for total Fe, and 0.2 mg $l^{-1}$ for filtered Fe. Total Fe concentration decreases at the mouth to a mean value of 1.32 mg $l^{-1}$. There is a greater range of variation at the lower sites, especially in the case of total Fe, in comparison to the upper sites where the level is virtually stable.

(xii) Mn (see Figures 4.17 and 4.18)

Levels of Mn in the total water samples and in the filtered water samples are virtually identical, and the two graphs follow a similar pattern. The level is approximately 0.4 mg $l^{-1}$ at Kyo, this drops slightly at Tantobie, and eventually increases to a mean value of about 0.5 mg $l^{-1}$ at Urpeth (site 4), after which there is another slight drop in concentration before higher values around 0.5 - 0.6 mg $l^{-1}$ are reached at sites 6, 7, 8 and 9.

(xiii) Zn (see Figures 4.19 and 4.20)

Levels of Zn are relatively stable at the upper five sites, about 0.06 mg $l^{-1}$ at Kyo, slightly lower at Tantobie, after which there is an increase to a mean value of 0.21 mg $l^{-1}$ at Beamish. The levels then drop until site 6, where the graph peaks at a mean value of 7.18 mg $l^{-1}$ total Zn and 5.96 mg $l^{-1}$ filtered Zn. The concentrations gradually decline after this peak where the levels can be extremely variable, although still remains high.

## 4.2 ZINC LEVELS IN SEDIMENT

### 4.21 Presentation of results

Zinc levels determined in the sediments collected in July are presented in Table 4.7, and a graphical representation of changes occurring throughout the course of the river (in Figure 4.21). The mean and range of values for each site has been plotted rather than the standard deviations which were based on four samples taken from each site, for reasons previously stated in section 4.11.

### 4.22 Comments on results

Levels of zinc found in the sediment collected from sites 1-5 are relatively constant, containing approximately 500 μg $g^{-1}$, although a slightly higher mean level of 967 μg $g^{-1}$ was found at Beamish. The level of zinc in the sediment after site 5 increases after each subsequent site until a mean concentration of 6140 μg $g^{-1}$ was found at the mouth. Extra samples of sediment taken just upstream of Kibblesworth mine water discharge contain an average concentration of zinc at 3642 μg $g^{-1}$, this point forming a peak in the graph between sites 5 and 6.

## 4.3 24 h SURVEY

### 4.31 Presentation of results

Data collected from water samples taken at site 6 from 1200 h on 26 June throughout the night until 1100 h the following day,are presented in table 4.8. Graphs have been constructed to provide a visual representation of changes occurring throughout the 24 h period.

### 4.32 Comments on results

(i) Temperature (see Figure 4.22)

Temperature throughout the afternoon and evening was relatively constant at approximately 16°C. The temperature dropped by about 1°C during the night and following morning.

(ii) Oxygen (see Figure 4.23)

The oxygen level remained relatively stable throughout the 24 h survey, between 9-10 mg $l^{-1}$ in the afternoon and 10-10.5 mg $l^{-1}$ throughout the night.

(iii) pH (see Figure 4.24)

pH readings taken in the laboratory were stable at about pH 7.25, readings only varying by 0.1 pH unit either side of this value. In comparison, the field recordings followed a cyclic path, the minimum pH 6.9 occurring at 2200 h and the maximum pH 7.9 occurring eight hours later at 0600 h.

(iv) Total alkalinity (see Figure 4.25)

Initial values of approximately 430 mg $l^{-1}$ $CaCO_3$ were detected for the first eight samplings but at 2000 h a large increase was observed and the higher values around 550 and 600 mg $l^{-1}$ were maintained until 0600 h after which the total alkalinity returned to its original level.

(v) Conductivity (see Figure 4.26)

Conductivity was recorded around 4000 µmhos for the first eight samplings and a dramatic increase was noted at 2000 h peaking to a maximum value of 5500 µmhos at 2100 h. The increased level of conductivity was maintained around 5000 µmhos until 0600 h after which the level dropped.

(vi) Optical density (see Figure 4.27)

These graphs do not show any notable changes throughout the 24 h period. Optical density measured at 240 nm generally ranges from between 0.3 - 0.4 in comparison to that measured at 254 nm which generally ranges between 0.2 - 0.3.

(vii) Cl (see Figure 4.28)

Cl concentration was recorded at about 600 mg $l^{-1}$ for the first eight samplings, and then rose dramatically at 2000 h, peaking at 950 mg $l^{-1}$ at 2100 h and eventually stabilizing around 750 mg $l^{-1}$ until 0600 h, adter which the level dropped back to the original level.

(viii) $P\text{-}PO_4$ (see Figure 4.29)

$P\text{-}PO_4$ levels were relatively high at about 0.3 mg $l^{-1}$ at the beginning of the 24 h period, and gradually dropped throughout the afternoon to reach a concentration of approximately 0.1 mg $l^{-1}$ through the night. A notable peak occurs the following morning at 0900 h, reaching 0.43 mg $l^{-1}$.

(ix) Ca (see Figure 4.30)

Levels of total and filtered Ca generally vary between 120-140 mg $l^{-1}$ throughout the 24 h period, although there are no dramatic peaks, increases or decreases.

(x) Mg (see Figure 4.31)

Concentrations of total and filtered Mg generally vary between 40-55 mg $l^{-1}$ throughout the 24 h survey, although no dramatic peaks, increases or decreases can be noted.

(xi) Fe (see Figure 4.32)

Levels of total and filtered Fe are different in that the filtered values are often up to 1 mg $l^{-1}$ less than the total values, although the trend in each case is virtually identical. The total Fe concentration was recorded at approximately 2.3 mg $l^{-1}$ for the first eight samplings, and then rose rapidly to a peak at 3.9 mg $l^{-1}$ at 2000 h, after which the concentration gradually declined but remained high until 0600 h and then dropped to the original level.

(xii) Mn (see Figure 4.33)

Levels of total Mn are slightly higher than levels of filtered Mn, varying between 0.64 and 0.73 mg $l^{-1}$ for the first eight samplings, and increasing to 0.85 mg $l^{-1}$ at 2000 h after which the level gradually returns back to an average original concentration of 0.7 mg $l^{-1}$.

(xiii) Zn (see Figure 4.34)

Levels of Zn are high; the concentration determined from the total water sample was 2.2 mg $l^{-1}$ at 1200 h; filtered values are generally about 0.3 mg $l^{-1}$ lower in most cases. The concentrations gradually decline to about 1 mg $l^{-1}$ at 0600 h, and at 0700 h there is a sharp peak reaching a maximum total value of 3.6 mg $l^{-1}$ which declines equally as quickly to about 2.0 mg $l^{-1}$ for the remaining four hours of the survey.

## 4.4 ALGAL TOXICITY TESTS

### 4.41 Presentation of results

Results from toxicity tests with Stigeoclonium tenue and Ulothrix sp. and zinc are presented in tabular form. Scores allocated to the species from the nine sampling sites under various zinc concentrations are listed in Table 4.9. Table 4.10 contains the values used in the calculations of the tolerance index concentrations. The T.I.C values estimated for Stigeoclonium tenue are plotted against the mean field values of total zinc concentrations occurring at each site; the latter values are listed in the appendix.

### 4.42 Comments on results

T.I.C. estimations of Stigeoclonium tenue to zinc were between 1.10 - 2.06 mg $l^{-1}$ for algae collected from sites 1-5 in the upper stretch of the river, but were higher for algae collected from sites 6, 7 and 8 where the T.I.C. ranged from 2.43 - 4.02 mg $l^{-1}$ Zn. The sample of Ulothrix sp. collected from the mouth had a very low T.I.C. of 0.61 mg $l^{-1}$ Zn.

| Site | time (h) | temp. ($^{o}C$) | $O_2$ (% sat.) | $O_2$ ($mg\ l^{-1}$) | field pH | lab. pH | tot. alk. ($mg\ l^{-1}\ CaCO_3$) | cond. (μmhos) | O.D. 240nm | O.D. 254nm |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. Kyo | 1030 | 12.0 | 117 | 12.4 | 7.5 | 7.8 | 126 | 1140 | 0.04 | 0.03 |
| 2. Tantobie | 1100 | 17.0 | 148 | 14.0 | 8.1 | 8.0 | 114 | 1160 | 0.15 | 0.14 |
| 3. Beamish | 1145 | 15.0 | 107 | 10.6 | 7.7 | 8.1 | 254 | 1650 | 0.14 | 0.11 |
| 4. Urpeth | 1215 | 15.0 | 112 | 10.9 | 8.2 | 8.1 | 282 | 2050 | 0.09 | 0.08 |
| 5. Above Birtley | 1300 | 18.5 | 158 | 14.4 | 8.5 | 8.7 | 240 | 1600 | 0.14 | 0.11 |
| 6. Below Birtley | 1345 | 20.0 | 122 | 10.8 | 8.0 | 8.1 | 197 | 2250 | 0.34 | 0.25 |
| 7. Lamesley | 1430 | 20.0 | 96 | 8.5 | 7.8 | 7.9 | 203 | 2250 | 0.26 | 0.21 |
| 8. T.V.T.E. | 1515 | 20.0 | 75 | 6.6 | 7.8 | 7.7 | 210 | 2250 | 0.26 | 0.21 |
| 9. Mouth | 1615 | 21.0 | 23 | 2.0 | 8.6 | 8.3 | 323 | 2800 | 0.32 | 0.31 |

| Site | Cl ($mg\ l^{-1}$) | P-$PO_4$ ($mg\ l^{-1}$) | Ca ($mg\ l^{-1}$) tot. | Ca ($mg\ l^{-1}$) fil. | Mg ($mg\ l^{-1}$) tot. | Mg ($mg\ l^{-1}$) fil. | Fe ($mg\ l^{-1}$) tot. | Fe ($mg\ l^{-1}$) fil. | Mn ($mg\ l^{-1}$) tot. | Mn ($mg\ l^{-1}$) fil. | Zn ($mg\ l^{-1}$) tot. | Zn ($mg\ l^{-1}$) fil. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Kyo | 60 | 0.01 | 95.2 | 87.8 | 46.0 | 40.8 | 0.36 | 0.15 | 0.53 | 0.48 | 0.08 | 0.10 |
| 2. Tantobie | 47 | 0.03 | 77.6 | 73.2 | 33.8 | 31.6 | 0.59 | 0.09 | 0.32 | 0.32 | 0.02 | 0.04 |
| 3. Beamish | 63 | 2.50 | 118.6 | 108.4 | 41.8 | 39.4 | 0.47 | 0.10 | 0.34 | 0.31 | 0.14 | (0.71) |
| 4. Urpeth | 55 | 1.06 | 138.8 | 115.6 | 47.8 | 43.0 | 0.36 | 0.10 | 0.45 | 0.39 | 0.07 | 0.09 |
| 5. Above Birtley | 65 | 0.10 | 113.2 | 104.0 | 40.6 | 37.6 | 0.45 | 0.14 | 0.36 | 0.32 | 0.06 | 0.04 |
| 6. Below Birtley | 62 | 0.78 | 108.0 | 93.0 | 33.4 | 31.0 | 0.39 | 0.08 | 0.38 | 0.31 | 3.67 | 0.66 |
| 7. Lamesley | 65 | 1.00 | 111.6 | 98.8 | 34.4 | 29.8 | 0.44 | 0.10 | 0.46 | 0.38 | 3.40 | 0.77 |
| 8. T.V.T.E. | 63 | 1.10 | 106.0 | 101.2 | 32.6 | 30.8 | 0.46 | 0.16 | 0.41 | 0.41 | 2.13 | 1.00 |
| 9. Mouth | 145 | 0.75 | 98.0 | 96.4 | 34.8 | 34.4 | 1.00 | 0.14 | 0.41 | 0.36 | 1.60 | 0.20 |

Table 4.1 date : 19 June 1979

| Site | time | temp. | $O_2$ | | field | lab. | tot. alk. | cond. | O.D. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (h) | ($^{o}$C) | (% sat.) | (mg $1^{-1}$) | pH | pH | (mg $1^{-1}$ $CaCO_3$) | (μmhos) | 240nm | 254nm |
| 1. Kyo | 1215 | 12.0 | 120 | 12.5 | 7.7 | 7.4 | 100 | 1180 | 0.12 | 0.09 |
| 2. Tantobie | 1130 | 13.0 | 115 | 11.8 | 7.6 | 7.4 | 91 | 1070 | 0.17 | 0.14 |
| 3. Beamish | 1045 | 13.0 | 95 | 9.7 | 7.9 | 7.6 | 199 | 1650 | 0.19 | 0.13 |
| 4. Urpeth | 1330 | 14.0 | 109 | 10.9 | 8.1 | 7.7 | 215 | 1800 | 0.17 | 0.11 |
| 5. Above Birtley | 1430 | 15.7 | 136 | 13.1 | 8.3 | 6.8 | 203 | 1750 | 0.16 | 0.10 |
| 6. Below Birtley | 1515 | 17.0 | 103 | 9.4 | 7.2 | 6.9 | 382 | 4850 | 0.35 | 0.26 |
| 7. Lamesley | 1615 | 17.0 | 82 | 7.7 | 7.5 | 7.1 | 345 | 4600 | 0.31 | 0.27 |
| 8. T.V.T.E. | 0930 | 15.0 | 77 | 7.4 | 7.3 | 7.1 | 416 | 5000 | 0.31 | 0.27 |
| 9. Mouth | 1800 | 17.5 | 44 | 4.1 | 7.6 | 7.2 | 231 | 3800 | 0.39 | 0.33 |

| Site | Cl | $P\text{-}PO_4$ | Ca (mg $1^{-1}$) | | Mg (mg $1^{-1}$) | | Fe (mg $1^{-1}$) | | Mn )mg $1^{-1}$) | | Zn (mg $1^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (mg $1^{-1}$) | (mg $1^{-1}$) | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. |
| 1. Kyo | 55 | 0.04 | 86.0 | 76.6 | 34.0 | 34.8 | 0.42 | 0.10 | 0.39 | 0.40 | 0.06 | 0.04 |
| 2. Tantobie | 52 | 0.08 | 66.0 | 67.6 | 26.2 | 26.0 | 0.46 | 0.10 | 0.31 | 0.31 | 0.02 | 0.02 |
| 3. Beamish | 73 | 0.86 | 105.4 | 104.6 | 37.6 | 36.6 | 0.49 | 0.18 | 0.50 | 0.44 | 0.24 | 0.17 |
| 4. Urpeth | 65 | 0.39 | 112.8 | 110.6 | 42.8 | 40.6 | 0.48 | 0.12 | 0.57 | 0.56 | 0.10 | 0.02 |
| 5. Above Birtley | 65 | 0.36 | 105.0 | 112.8 | 37.4 | 40.4 | 0.38 | 0.14 | 0.51 | 0.50 | 0.05 | 0.03 |
| 6. Below Birtley | 550 | 0.10 | 118.0 | 114.6 | 41.4 | 40.2 | 2.40 | 0.12 | 0.66 | 0.66 | 28.60 | 25.90 |
| 7. Lamesley | 522 | 0.20 | 128.0 | 125.6 | 45.0 | 40.6 | 2.25 | 0.26 | 0.72 | 0.70 | 7.40 | 6.30 |
| 8. T.V.T.E. | 622 | 0.18 | 110.0 | 128.0 | 35.8 | 42.8 | 2.70 | 0.28 | 0.77 | 0.74 | 1.65 | 1.40 |
| 9. Mouth | 425 | 0.36 | 118.4 | 108.8 | 38.4 | 40.0 | 1.70 | 0.21 | 0.63 | 0.63 | 1.95 | 1.50 |

Table 4.2 date : 5 June 1979

| Site | time (h) | temp. ($^oC$) | $O_2$ (% sat.) | $O_2$ (mg $l^{-1}$) | field pH | lab. pH | tot. alk. (mg $l^{-1}$ $CaCO_3$) | cond. (μmhos) | O.D. 240nm | O.D. 254nm |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. Kyo | 1200 | 12.0 | 104 | 11.0 | 7.4 | 7.3 | 86 | 1060 | 0.04 | 0.04 |
| 2. Tantobie | 1245 | 14.0 | 109 | 11.0 | 7.3 | 7.2 | 82 | 920 | 0.14 | 0.11 |
| 3. Beamish | 1315 | 13.0 | 112 | 11.6 | 8.0 | 7.9 | 200 | 1530 | 0.13 | 0.08 |
| 4. Urpeth | 1415 | 14.0 | 109 | 11.0 | 7.9 | 7.7 | 180 | 1510 | 0.15 | 0.08 |
| 5. Above Birtley | 1745 | 14.0 | 115 | 11.5 | 8.2 | 7.9 | 196 | 1510 | 0.17 | 0.08 |
| 6. Below Birtley | 1715 | 15.5 | 103 | 10.5 | 7.2 | 7.0 | 360 | 4400 | 0.32 | 0.19 |
| 7. Lamesley | 1645 | 15.5 | 98 | 9.5 | 7.2 | 7.0 | 352 | 4180 | 0.23 | 0.16 |
| 8. T.V.T.E. | 1600 | 15.5 | 102 | 9.7 | 7.3 | 7.1 | 318 | 3900 | 0.24 | 0.19 |
| 9. Mouth | 1430 | 16.5 | 67 | 6.4 | 7.2 | 7.2 | 314 | 3750 | 0.32 | 0.25 |

| Site | Cl (mg $l^{-1}$) | P-$PO_4$ (mg $l^{-1}$) | Ca (mg $l^{-1}$) tot. | Ca (mg $l^{-1}$) fil. | Mg (mg $l^{-1}$) tot. | Mg (mg $l^{-1}$) fil. | Fe (mg $l^{-1}$) tot. | Fe (mg $l^{-1}$) fil. | Mn (mg $l^{-1}$) tot. | Mn (mg $l^{-1}$) fil. | Zn (mg $l^{-1}$) tot. | Zn (mg $l^{-1}$) fil. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Kyo | 41 | 0.01 | 63.0 | 69.4 | 25.6 | 28.4 | 0.40 | 0.08 | 0.36 | 0.33 | 0.04 | 0.01 |
| 2. Tantobie | 40 | 0.07 | 62.0 | 77.6 | 21.2 | 23.2 | 0.50 | 0.10 | 0.27 | 0.24 | 0.01 | 0.01 |
| 3. Beamish | 57 | 0.38 | 105.0 | 100.0 | 39.4 | 34.2 | 0.43 | 0.10 | 0.33 | 0.34 | 0.10 | 0.06 |
| 4. Urpeth | 60 | 0.32 | 102.0 | 102.0 | 39.2 | 34.6 | 0.55 | 0.09 | 0.50 | 0.43 | 0.06 | 0.04 |
| 5. Above Birtley | 57 | 0.25 | 102.0 | 104.0 | 34.2 | 35.2 | 0.57 | 0.13 | 0.42 | 0.41 | 0.04 | 0.04 |
| 6. Below Birtley | 560 | 0.11 | 135.0 | 114.2 | 44.4 | 39.0 | 2.10 | 0.14 | 0.64 | 0.60 | 2.65 | 2.23 |
| 7. Lamesley | 475 | 0.10 | 130.0 | 118.0 | 41.4 | 35.8 | 1.75 | 0.10 | 0.65 | 0.61 | 12.10 | 10.20 |
| 8. T.V.T.E. | 377 | 0.09 | 128.6 | 119.2 | 43.4 | 39.2 | 3.40 | 0.13 | 0.73 | 0.60 | 2.47 | 1.77 |
| 9. Mouth | 380 | 0.22 | 109.0 | 112.0 | 36.4 | 39.0 | 1.75 | 0.30 | 0.58 | 0.50 | 1.70 | 1.33 |

TABLE 4.3 date : 1 June 1979

| Site | time (h) | temp. ($^oC$) | $O_2$ (% sat.) | $O_2$ (mg $l^{-1}$) | field pH | lab. pH | tot. alk. (mg $l^{-1}CaCO_3$) | cond. (µmhos) |
|---|---|---|---|---|---|---|---|---|
| 1. Kyo | 1130 | 9.0 | 105 | 11.8 | 7.8 | 7.4 | 102 | 950 |
| 2. Tantobie | 1200 | 9.5 | 82 | 8.9 | 7.7 | 7.2 | 104 | 810 |
| 3. Beamish | 1245 | 10.5 | 117 | 12.2 | 8.3 | 8.0 | 237 | 1280 |
| 4. Urpeth | 1400 | 10.2 | 121 | 13.2 | 8.4 | 8.1 | 190 | 1450 |
| 5. Above Birtley | 1500 | 11.5 | 138 | 14.6 | 8.5 | 8.3 | 183 | 1480 |
| 6. Below Birtley | 1530 | 14.0 | 115 | 10.4 | 7.3 | 7.1 | - | 4400 |
| 7. Lamesley | 1615 | 14.0 | 98 | 9.9 | 7.6 | 7.3 | - | 4400 |
| 8. T.V.T.E. | 1815 | 14.0 | 94 | 9.3 | 7.6 | 7.4 | - | 4100 |
| 9. Mouth | 1730 | 13.0 | 68 | 6.9 | 7.6 | 7.3 | - | 1800 |

| Site | Cl (mg $l^{-1}$) | $P\text{-}PO_4$ (mg $l^{-1}$) | Ca (mg $l^{-1}$) tot. | Ca (mg $l^{-1}$) fil. | Mg (mg $l^{-1}$) tot. | Mg (mg $l^{-1}$) fil. | Fe (mg $l^{-1}$) tot. | Fe (mg $l^{-1}$) fil. | Zn (mg $l^{-1}$) tot. | Zn (mg $l^{-1}$) fil. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. Kyo | 54 | 0.02 | 106 | 106 | 41 | 40 | 1.07 | 0.23 | 0.07 | 0.08 |
| 2. Tantobie | 75 | 0.45 | 80 | 70 | 25 | 22 | 0.55 | 0.18 | 0.06 | 0.04 |
| 3. Beamish | 78 | 0.14 | 134 | 130 | 44 | 43 | 0.36 | 0.07 | 0.25 | 0.22 |
| 4. Urpeth | 76 | 0.49 | 128 | 128 | 42 | 43 | 0.36 | 0.07 | 0.12 | 0.08 |
| 5. Above Birtley | 59 | 0.32 | 114 | 112 | 39 | 38 | 0.45 | 0.11 | 0.08 | 0.05 |
| 6. Below Birtley | 600 | 0.20 | 136 | 136 | 42 | 46 | 2.60 | 0.90 | 1.68 | 1.35 |
| 7. Lamesley | 632 | 0.17 | 134 | 124 | 44 | 40 | 2.60 | 0.32 | 1.85 | 1.30 |
| 8. T.V.T.E. | 530 | 0.13 | 122 | 134 | 41 | 43 | 2.10 | 0.18 | 1.67 | 1.20 |
| 9. Mouth | 108 | 0.43 | 102 | 98 | 32 | 29 | 0.84 | 0.16 | 1.90 | 1.18 |

Table 4.4 date: 19 May 1979

| Site | time<br>(h) | temp.<br>($^{o}C$) | $O_2$<br>(% sat.) | $O_2$<br>(mg $l^{-1}$) | field<br>pH | lab.<br>pH | tot. alk.<br>(mg $l^{-1}$ $CaCO_3$) | cond.<br>(μmhos) |
|---|---|---|---|---|---|---|---|---|
| 3. Beamish | 1900 | 9.0 | 103 | 11.6 | 7.7 | 7.6 | 146 | 910 |
| 4. Urpeth | 1830 | 9.0 | 103 | 11.6 | - | 7.8 | 136 | 790 |
| 5. Above Birtley | 1750 | 9.2 | 104 | 11.6 | 7.9 | 7.4 | 118 | 760 |
| 6. Below Birtley | 1515 | 11.0 | 98 | 10.5 | 7.4 | 7.3 | 253 | 2250 |
| 7. Lamesley | 1445 | 10.0 | 90 | 9.8 | 7.3 | 7.3 | 240 | 2050 |
| 8. T.V.T.E. | 1300 | 10.0 | 103 | 11.4 | 7.6 | 7.4 | 224 | 1800 |
| 9. Mouth | 1115 | 10.0 | 84 | 9.2 | 7.3 | 7.3 | 185 | 1410 |

| Site | Cl<br>(mg $l^{-1}$) | $P\text{-}PO_4$<br>(mg $l^{-1}$) | Ca (mg $l^{-1}$)<br>tot. | Ca (mg $l^{-1}$)<br>fil. | Mg (mg $l^{-1}$)<br>tot. | Mg (mg $l^{-1}$)<br>fil. | Zn (mg $l^{-1}$)<br>tot. | Zn (mg $l^{-1}$)<br>fil. |
|---|---|---|---|---|---|---|---|---|
| 3. Beamish | 39 | 0.49 | 102 | 92 | 29.0 | 27.6 | 0.31 | 0.29 |
| 4. Urpeth | 54 | 0.30 | 92 | 84 | 28.0 | 25.4 | 0.29 | 0.23 |
| 5. Above Birtley | 30 | 0.20 | 86 | 78 | 24.4 | 23.0 | 0.24 | 0.27 |
| 6. Below Birtley | 227 | 0.12 | 110 | 104 | 30.6 | 29.2 | 2.60 | 2.01 |
| 7. Lamesley | 295 | 0.15 | 106 | 98 | 29.8 | 27.4 | 1.95 | 1.30 |
| 8. T.V.T.E. | 550 | 0.19 | 106 | 98 | 27.2 | 25.6 | 1.50 | 1.15 |
| 9. Mouth | 173 | 0.18 | 94 | 90 | 23.6 | 21.2 | 9.73 | 2.08 |

Table 4.5 date : 9 May 1979

| Site | time | temp. | $O_2$ | | lab. | cond. | O.D. | |
|---|---|---|---|---|---|---|---|---|
| | (h) | ($^oC$) | (%sat.) | (mg $l^{-1}$) | pH | (μmhos) | 240nm | 254nm |
| 5 Above Birtley | 1500 | 7.8 | 110 | 12.8 | 7.8 | 1210 | 0.09 | 0.02 |
| 6 Below Birtley | 1445 | 11.0 | 109 | 11.8 | 7.0 | 3500 | 0.23 | 0.12 |
| 7 Lamesley | 1415 | 11.0 | 101 | 11.0 | 6.9 | 3400 | 0.17 | 0.08 |
| 8 T.V.T.E. | 1600 | 11.0 | 102 | 11.0 | 6.8 | 3310 | 0.36 | 0.15 |
| *9 Mouth (high tide) | (1730) | (10.5) | ( 78) | ( 8.4) | (7.0) | (6000) | (0.19) | (0.14) |

| Site | Cl (mg $l^{-1}$) | $P\text{-}PO_4$ (mg $l^{-1}$) | Ca (mg $l^{-1}$) | | Mg (mg $l^{-1}$) | | Zn (mg $l^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | | tot. | fil. | tot. | fil. | tot. | fil. |
| 5 Above Birtley | 57 | 0.30 | 128 | 114 | 42.0 | 40.0 | 0.15 | 0.13 |
| 6 Below Birtley | 230 | 0.21 | 130 | 130 | 39.6 | 40.0 | 3.90 | 3.62 |
| 7 Lamesley | 575 | 0.17 | 118 | 140 | 36.8 | 42.6 | 2.57 | 2.20 |
| 8 T.V.T.E. | 490 | 0.24 | 144 | 132 | 41.0 | 40.0 | 3.02 | 4.12 |
| *9 Mouth (high tide). | (>1000) | (0.13) | - | - | - | - | (4.66) | (3.39) |

TABLE 4.6 date: 25 April 1979

|  | Site | (i) | (ii) | (iii) | (iv) | mean | s.d. |
|---|---|---|---|---|---|---|---|
|  |  | Zn ($\mu g\ g^{-1}$) |  |  |  |  |  |
| 1 | Kyo | 400 | 708 | 364 | 550 | 505 | 158 |
| 2 | Tantobie | 655 | 500 | 400 | 364 | 480 | 130 |
| 3 | Beamish | 1083 | 950 | 750 | 1083 | 967 | 157 |
| 4 | Urpeth | 750 | 550 | 542 | 450 | 573 | 126 |
| 5 | Above Birtley | 625 | 450 | 542 | 550 | 542 | 72 |
| 6a | Above Kibblesworth | 2136 | 2318 | 2750 | 7364 | 3642 | 2495 |
| 6 | Below Birtley | 1542 | 917 | 3100 | 2773 | 2083 | 1027 |
| 7 | Lamesley | 2200 | 2050 | 3150 | 2800 | 2550 | 515 |
| 8 | T.V.T.E. | 1875 | 1550 | 2950 | 5650 | 3006 | 1861 |
| 9 | Mouth | 6500 | 8167 | 4591 | 5300 | 6140 | 1565 |

Table 4.7

**Concentration of zinc in sediments**

| time | temp. | $O_2$ | | field | lab. | tot. alk. | cond. | O.D. | | Cl | $P\text{-}PO_4$ | Ca ($mg\ l^{-1}$) | | Mg ($mg\ l^{-1}$) | | Fe ($mg\ l^{-1}$) | | Mn ($mg\ l^{-1}$) | | Zn ($mg\ l^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (h) | (°C) | (% sat.) | ($mg\ l^{-1}$) | pH | pH | ($mg\ l^{-1}\ CaCO_3$) | (µmhos) | 240nm | 254nm | ($mg\ l^{-1}$) | ($mg\ l^{-1}$) | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. |
| 1200 | 16.0 | 98 | 9.4 | 7.4 | 7.35 | 432 | 4300 | 0.31 | 0.25 | 630 | 0.32 | 130.0 | 128.0 | 43.6 | 41.8 | 2.35 | 1.25 | 0.73 | 0.70 | 2.20 | 1.75 |
| 1300 | 16.0 | 102 | 9.7 | 7.25 | 7.35 | 432 | 4000 | 0.40 | 0.27 | 545 | 0.25 | 135.6 | 121.6 | 44.6 | 41.0 | 2.35 | 1.60 | 0.71 | 0.60 | 2.00 | 1.65 |
| 1400 | 16.2 | 101 | 9.6 | 7.25 | 7.3 | 412 | 4200 | 0.33 | 0.26 | 634 | 0.25 | 133.0 | 119.0 | 48.0 | 40.4 | 2.30 | 1.35 | 0.70 | 0.62 | 2.00 | 1.60 |
| 1500 | 16.2 | 96 | 9.2 | 7.4 | 7.3 | 435 | 4200 | 0.35 | 0.30 | 593 | 0.30 | 126.0 | 125.0 | 42.0 | 40.6 | 2.30 | 1.30 | 0.67 | 0.60 | 1.70 | 1.20 |
| 1600 | 16.5 | 96 | 9.1 | 7.4 | 7.3 | 427 | 4000 | 0.40 | 0.32 | 630 | 0.24 | 128.0 | 133.2 | 43.6 | 43.0 | 2.30 | 1.50 | 0.66 | 0.65 | 1.70 | 1.40 |
| 1700 | 16.45 | 98 | 9.3 | 7.35 | 7.35 | 429 | 3900 | 0.37 | 0.29 | 630 | 0.17 | 128.0 | 120.0 | 44.0 | 43.2 | 2.40 | 1.45 | 0.70 | 0.64 | 1.75 | 1.45 |
| 1800 | 16.0 | 97 | 9.3 | 7.25 | 7.35 | 430 | 4100 | 0.32 | 0.22 | 605 | 0.13 | 126.0 | 120.0 | 48.0 | 41.4 | 2.40 | 1.55 | 0.74 | 0.69 | 1.80 | 1.50 |
| 1900 | 16.0 | 100 | 9.5 | 7.1 | 7.35 | 442 | 3900 | 0.38 | 0.32 | 637 | 0.17 | 122.0 | 114.0 | 45.8 | 42.0 | 2.25 | 1.60 | 0.64 | 0.60 | 1.60 | 1.30 |
| 2000 | 16.0 | 105 | 10.1 | 7.1 | 7.2 | 565 | 5200 | 0.35 | 0.29 | 910 | 0.06 | 140.0 | 128.0 | 50.0 | 47.0 | 3.90 | 2.70 | 0.85 | 0.80 | 1.40 | 1.15 |
| 2100 | 16.0 | 104 | 10.0 | 7.0 | 7.2 | 546 | 5500 | 0.34 | 0.30 | 950 | 0.04 | 134.0 | 127.0 | 47.6 | 47.0 | 3.75 | 2.60 | 0.79 | 0.78 | 1.20 | 0.98 |
| 2200 | 16.0 | 105 | 10.1 | 6.9 | 7.25 | 550 | 4600 | 0.29 | 0.27 | 845 | 0.09 | 136.0 | 129.4 | 55.0 | 46.0 | 3.65 | 2.40 | 0.82 | 0.75 | 1.20 | 1.10 |
| 2300 | 15.5 | 104 | 10.1 | 7.0 | 7.2 | 567 | 4600 | 0.30 | 0.28 | 725 | 0.10 | 134.0 | 141.6 | 49.2 | 46.2 | 3.40 | 2.40 | 0.84 | 0.77 | 1.30 | 1.10 |
| 2400 | 15.0 | 107 | 10.4 | 7.2 | 7.2 | 564 | 4800 | 0.35 | 0.29 | 755 | 0.10 | 142.0 | 144.4 | 49.6 | 49.6 | 3.30 | 2.40 | 0.84 | 0.82 | 1.15 | 1.00 |
| 0100 | 15.0 | 105 | 10.3 | 7.25 | 7.25 | 573 | 5000 | 0.35 | 0.28 | 749 | 0.13 | 140.0 | 132.0 | 49.8 | 49.6 | 3.25 | 2.10 | 0.78 | 0.77 | 1.20 | 1.00 |
| 0200 | 15.0 | 104 | 10.2 | 7.25 | 7.2 | 580 | 4800 | 0.32 | 0.29 | 749 | 0.07 | 139.8 | 133.0 | 50.0 | 49.6 | 3.15 | 2.15 | 0.84 | 0.79 | 1.40 | 1.20 |
| 0300 | 15.0 | 106 | 10.3 | 7.5 | 7.25 | 596 | 5100 | 0.35 | 0.27 | 749 | 0.12 | 140.0 | 129.0 | 47.2 | 43.8 | 3.10 | 2.15 | 0.85 | 0.81 | 1.20 | 1.05 |
| 0400 | 15.0 | 107 | 10.4 | 7.4 | 7.2 | 608 | 4800 | 0.32 | 0.26 | 755 | 0.07 | 142.0 | 128.0 | 49.4 | 44.4 | 3.25 | 2.25 | 0.78 | 0.82 | 1.25 | 1.10 |
| 0500 | 15.0 | 106 | 10.3 | 7.6 | 7.25 | 586 | 5000 | 0.28 | 0.27 | 745 | 0.04 | 138.0 | 125.0 | 53.2 | 43.2 | 3.10 | 2.20 | 0.79 | 0.80 | 1.10 | 0.90 |
| 0600 | 15.0 | 105 | 10.3 | 7.9 | 7.15 | 604 | 5100 | 0.30 | 0.24 | 780 | 0.08 | 133.4 | 126.0 | 47.4 | 45.0 | 3.10 | 2.25 | 0.80 | 0.80 | 1.15 | 0.98 |
| 0700 | 14.5 | 103 | 10.4 | 7.8 | 7.2 | 492 | 4300 | 0.30 | 0.23 | 660 | 0.11 | 131.4 | 120.0 | 43.2 | 44.0 | 2.35 | 1.40 | 0.76 | 0.70 | 3.60 | 3.00 |
| 0800 | 14.75 | 103 | 10.4 | 7.6 | 7.25 | 482 | 4300 | 0.32 | 0.25 | 610 | 0.13 | 125.2 | 137.0 | 50.0 | 44.0 | 2.40 | 1.60 | 0.75 | 0.74 | 2.20 | 1.90 |
| 0900 | 15.0 | 102 | 9.9 | 7.6 | 7.25 | 428 | 4200 | 0.31 | 0.27 | 575 | 0.43 | 116.4 | 114.0 | 40.0 | 43.0 | 2.25 | 1.70 | 0.68 | 0.68 | 1.90 | 1.50 |
| 1000 | 15.0 | 107 | 10.4 | 7.6 | 7.35 | 454 | 4200 | 0.31 | 0.26 | 630 | 0.23 | 132.0 | 115.2 | 44.0 | 40.0 | 2.40 | 1.60 | 0.74 | 0.69 | 2.10 | 1.70 |
| 1100 | 16.0 | 97 | 9.3 | 7.55 | 7.25 | 452 | 4600 | 0.37 | 0.27 | 620 | 0.28 | 128.0 | 112.4 | 43.2 | 44.8 | 2.60 | 1.40 | 0.70 | 0.68 | 1.90 | 1.50 |
| mean | 15.55 | 102 | 9.9 | 7.36 | 7.26 | 504 | 4529 | 0.33 | 0.27 | 696 | 0.16 | 132.5 | 130.0 | 47.0 | 44.2 | 2.82 | 1.87 | 0.76 | 0.72 | 1.67 | 1.38 |
| s.d. | 0.61 | 4 | 0.5 | 0.25 | 0.06 | 72 | 459 | 0.03 | 0.03 | 105 | 0.10 | 6.7 | 8.4 | 3.7 | 2.9 | 0.55 | 0.46 | 0.06 | 0.08 | 0.55 | 0.45 |

Table 4.8 Water chemistry results, 24 h survey.

|  | 1 |  | 2 |  | 3 |  | 4 |  | 5 |  | 6 |  | 7 |  | 8 |  |  |  |  | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | KYO |  | TANTOBIE |  | BEAMISH |  | URPETH |  | ABOVE BIRTLEY |  | BELOW BIRTLEY |  | LAMESLEY |  | T.V.T.E. |  |  |  |  | MOUTH |
| Zn (mg $l^{-1}$) date | 250579 | 200679 | 070679 | 150679 | 200579 | 210679 | 230579 | 250579 | 070679 | 210679 | 150679 | 290679 | 200779 | 200779 | 230579 | 060679 | 200679 | 120779(i) | 120779(ii) | 060679 (*Ulothrix* sp.) |
| 0.00 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 0.05 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 0.10 | 5 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |  | 5 | 5 | 5 | 5 | 4 |
| 0.25 | 4 | 4 | 5 | 5 | 5 | 4 | 5 | 4 | 4 | 4 | 5 | 5 | 5 | 5 |  | 5 | 5 | 5 | 5 | 4 |
| 0.50 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 5 | 5 | 5 |  | 5 | 5 | 5 | 5 | 3 |
| 0.75 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |  | 4 | 4 | 4 | 5 | 3 |
| 1.00 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 5 | 4 | 4 | 4 | 4 | 3 |
| 1.25 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |  | 4 | 4 | 4 |  | 3 |
| 1.50 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |  | 4 | 4 | 4 | 4 | 3 |
| 1.75 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |  | 4 | 4 | 4 |  | 3 |
| 2.00 | 3 | 4 | 4 | 4 | 3 | 4 | 3 | 4 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 3 |
| 2.25 | 3 | 3 | 4 | 4 | 3 | 3 | 3 | 3 | 3 | 3 |  |  |  |  |  | 4 |  |  |  | 3 |
| 2.50 | 3 | 3 | 4 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 4 | 4 | 4 |  | 4 | 4 | 3 | 4 | 3 |
| 2.75 | 3 | 3 | 4 | 4 | 3 | 3 | 3 | 3 | 3 | 3 |  |  |  |  |  | 4 |  |  |  | 3 |
| 3.00 | 2 | 3 | 4 | 3 | 3 | 3 | 2 | 3 | 3 | 3 | 4 | 4 | 4 | 4 | 3 | 4 | 4 | 3 | 4 | 2 |
| 3.25 |  | 3 | 3 | 3 |  | 2 |  | 3 | 3 | 3 |  |  |  |  |  | 4 |  |  |  | 1 |
| 3.50 | 0 | 2 | 3 | 3 | 3 | 2 | 2 | 3 | 3 | 3 | 4 | 4 | 3 | 4 |  | 4 | 4 | 3 | 4 | 1 |
| 3.75 |  | 2 | 3 | 3 |  | 2 |  | 2 | 3 | 3 |  |  |  |  |  | 4 |  |  |  | 1 |
| 4.00 | 0 | 2 | 3 | 3 | 2 | 2 | 2 | 2 | 3 | 3 | 4 | 4 | 3 | 4 | 3 | 4 | 3 | 3 | 4 | 0 |
| 4.25 |  | 1 | 3 | 3 |  | 1 |  | 2 | 3 | 3 |  |  |  |  |  | 4 |  |  |  | 0 |
| 4.50 | 0 | 1 | 3 | 2 | 2 | 0 | 2 | 2 | 2 | 3 | 4 | 3 | 3 | 3 |  | 4 | 3 | 3 | 4 | 0 |
| 4.75 |  | 1 |  | 2 |  | 0 |  | 2 |  | 2 |  |  |  |  |  | 4 |  |  |  | 0 |
| 5.00 | 0 | 1 | 1 | 2 | 1 | 0 | 1 | 1 | 1 | 2 | 3 | 3 | 3 | 3 | 2 | 3 | 3 | 2 | 3 | 0 |
| 5.25 |  |  |  | 0 |  | 0 |  | 1 |  | 2 |  |  |  |  |  | 3 |  |  |  | 0 |
| 5.50 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 2 | 3 | 3 | 3 | 3 |  | 3 | 3 | 2 | 1 | 0 |
| 5.75 |  |  |  | 0 |  | 0 |  | 0 |  | 2 |  |  |  |  |  | 3 |  |  |  | 0 |
| 6.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 2 | 3 | 3 | 3 | 3 | 1 | 3 | 3 | 1 | 1 | 0 |
| 6.25 |  |  |  |  |  | 0 |  | 0 |  | 1 |  |  |  |  |  | 3 |  |  |  | 0 |
| 6.50 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 3 | 3 | 3 | 3 | 1 | 3 | 3 | 1 | 1 | 0 |
| 6.75 |  |  |  |  |  | 0 |  | 0 |  | 0 |  |  |  |  |  | 3 |  |  |  | 0 |
| 7.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 3 | 3 | 3 | 3 | 1 | 3 | 3 | 1 | 0 | 0 |
| 7.25 |  |  |  |  |  |  |  |  |  | 0 |  |  |  |  |  |  |  |  |  | 0 |
| 7.50 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 3 | 3 | 3 | 3 | 0 | 3 | 3 | 0 | 0 | 0 |
| 7.75 |  |  |  |  |  |  |  |  |  | 0 |  | 3 | 3 | 3 | 0 |  |  |  |  | 0 |
| 8.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 3 | 3 | 3 | 3 | 0 | 3 | 2 | 0 | 0 | 0 |
| 8.50 | 0 | 0 |  |  | 0 | 0 | 0 |  |  | 0 | 3 | 3 | 2 | 3 | 0 | 3 | 2 | 0 | 0 |  |
| 9.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 3 | 2 | 2 | 0 | 2 | 1 | 0 | 0 | 0 |
| 9.50 | 0 | 0 |  |  | 0 | 0 | 0 |  |  | 0 | 2 | 3 | 1 | 2 | 0 | 2 | 1 | 0 | 0 |  |
| 10.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 3 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 |
| 10.50 |  |  |  |  |  |  |  |  |  |  | 0 | 2 | 1 | 1 |  |  | 0 | 0 |  |  |
| 11.00 |  |  |  |  |  |  |  |  |  |  | 0 | 2 | 1 | 1 |  |  | 0 | 0 | 0 | 0 |
| 11.50 |  |  |  |  |  |  |  |  |  |  | 0 | 2 | 0 | 1 |  |  | 0 | 0 |  |  |
| 12.00 |  |  |  |  |  |  |  |  |  |  | 0 | 2 | 0 | 0 |  |  | 0 | 0 | 0 | 0 |
| 12.50 |  |  |  |  |  |  |  |  |  |  | 0 | 1 | 0 | 0 |  |  | 0 | 0 |  |  |
| 13.00 |  |  |  |  |  |  |  |  |  |  | 0 | 0 | 0 | 0 |  |  | 0 | 0 | 0 | 0 |
| 13.50 |  |  |  |  |  |  |  |  |  |  | 0 | 0 | 0 | 0 |  |  |  | 0 |  |  |
| 14.00 |  |  |  |  |  |  |  |  |  |  | 0 | 0 | 0 | 0 |  |  | 0 | 0 | 0 | 0 |
| 14.50 |  |  |  |  |  |  |  |  |  |  | 0 | 0 | 0 | 0 |  |  |  | 0 |  |  |
| 15.00 |  |  |  |  |  |  |  |  |  |  | 0 | 0 | 0 | 0 |  |  | 0 | 0 | 0 | 0 |

Table 4.9 Scores designated to algae in toxicity tests

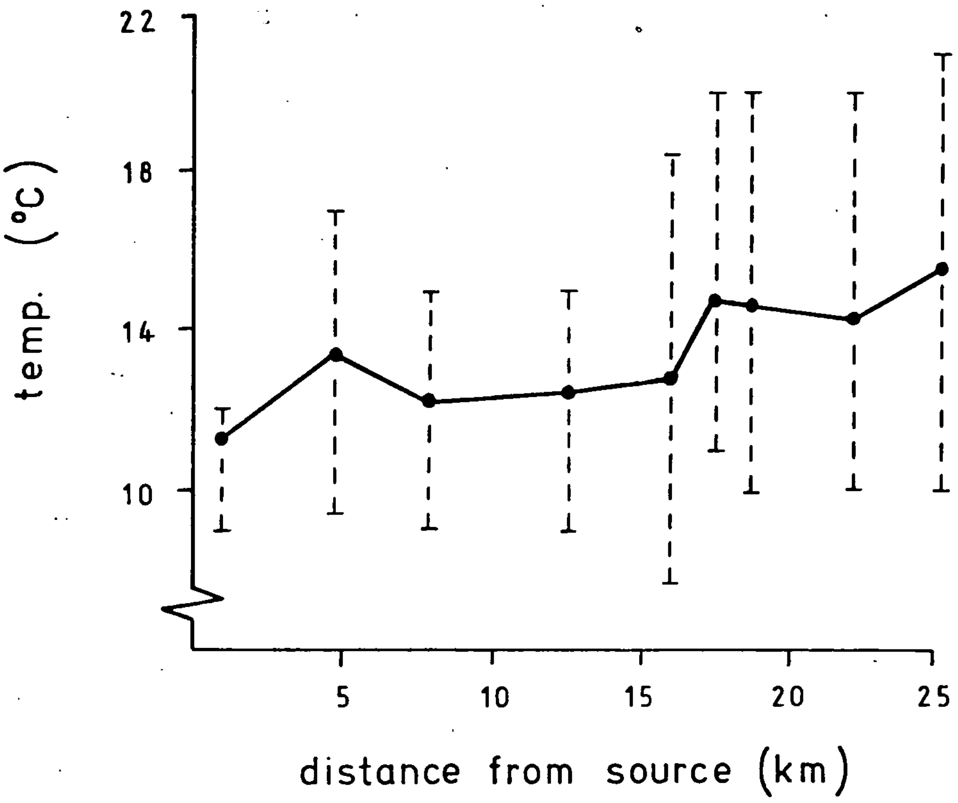
| Site | date | I | II | Just non-inhibitory | III | IV | Just lethal | T.I.C. |
|---|---|---|---|---|---|---|---|---|
| 1 Kyo | 250579 | 0.1 | 1.5 | 0.39 | 3.25 | 3.0 | 3.12 | 1.10 |
|  | 200679 | 0.05 | 2.0 | 0.32 | 5.0 | 3.5 | 4.18 | 1.16 |
| 2 Tantobie | 070679 | 0.25 | 3.0 | 0.87 | 5.0 | 4.75 | 4.87 | 2.06 |
|  | 150679 | 0.25 | 2.75 | 0.83 | 5.0 | 4.5 | 4.74 | 1.98 |
| 3 Beamish | 200579 | 0.25 | 1.75 | 0.66 | 5.0 | 4.0 | 4.47 | 1.72 |
|  | 210679 | 0.1 | 2.0 | 0.45 | 4.25 | 3.25 | 3.72 | 1.29 |
| 4 Urpeth | 230579 | 0.25 | 1.75 | 0.66 | 5.0 | 3.0 | 3.87 | 1.60 |
|  | 250579 | 0.1 | 2.0 | 0.45 | 5.25 | 3.75 | 4.44 | 1.41 |
| 5 Above Birtley | 070679 | 0.1 | 1.75 | 0.42 | 8.0 | 4.5 | 6.0 | 1.58 |
|  | 210679 | 0.1 | 2.0 | 0.45 | 6.5 | 4.75 | 5.56 | 1.58 |
| 6 Below Birtley | 150679 | 0.25 | 4.5 | 1.06 | 10.0 | 9.5 | 9.75 | 3.21 |
|  | 290679 | 0.5 | 4.0 | 1.41 | 12.5 | 10.5 | 11.46 | 4.02 |
| 7 Lamesley | 200779 | 0.5 | 3.0 | 1.22 | 11.0 | 8.5 | 9.67 | 3.43 |
|  | 200779 | 0.5 | 4.0 | 1.41 | 11.5 | 9.0 | 10.17 | 3.79 |
| 8 T.V.T.E. | 230579 | 1.0 | 2.0 | 1.41 | 7.0 | 5.0 | 5.92 | 2.89 |
|  | 060679 | 0.5 | 4.75 | 1.54 | 10.0 | 9.0 | 9.49 | 3.82 |
|  | 200679 | 0.5 | 3.5 | 1.32 | 9.5 | 8.0 | 8.72 | 3.39 |
|  | (i)120779 | 0.5 | 2.0 | 1.00 | 7.0 | 5.0 | 5.92 | 2.43 |
|  | (ii)120779 | 0.75 | 4.5 | 1.84 | 6.5 | 5.25 | 5.84 | 3.28 |
| 9 Mouth | 060679 | 0.05 | 0.25 | 0.11 | 3.75 | 3.0 | 3.35 | 0.61 |

Table 4.10

Results of toxicity tests

Figure 4.1 Mean water temperatures at sampling sites along the river.
Dotted lines indicate the range of values recorded at each site.

Figure 4.2 Mean values for $O_2$ levels, expressed as mg $l^{-1}$, along the river.
Dotted lines indicate the range of values recorded at each of the nine sites.


22
18
14
10
temp. (°C)
5
10
15
20
25
distance from source (km)

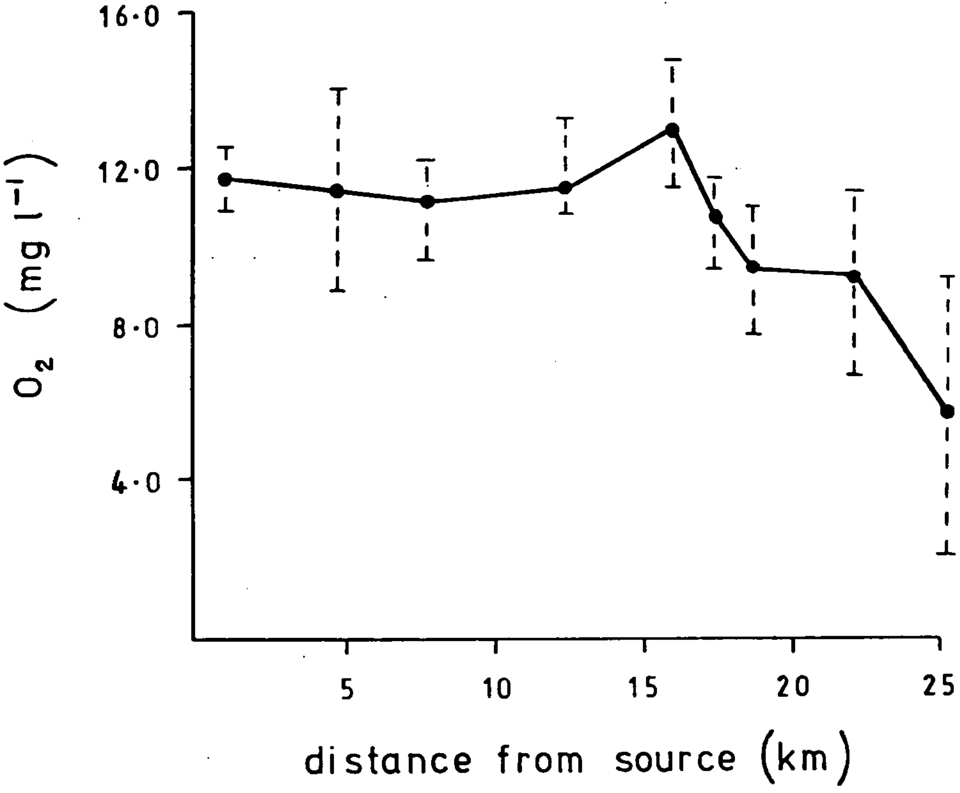
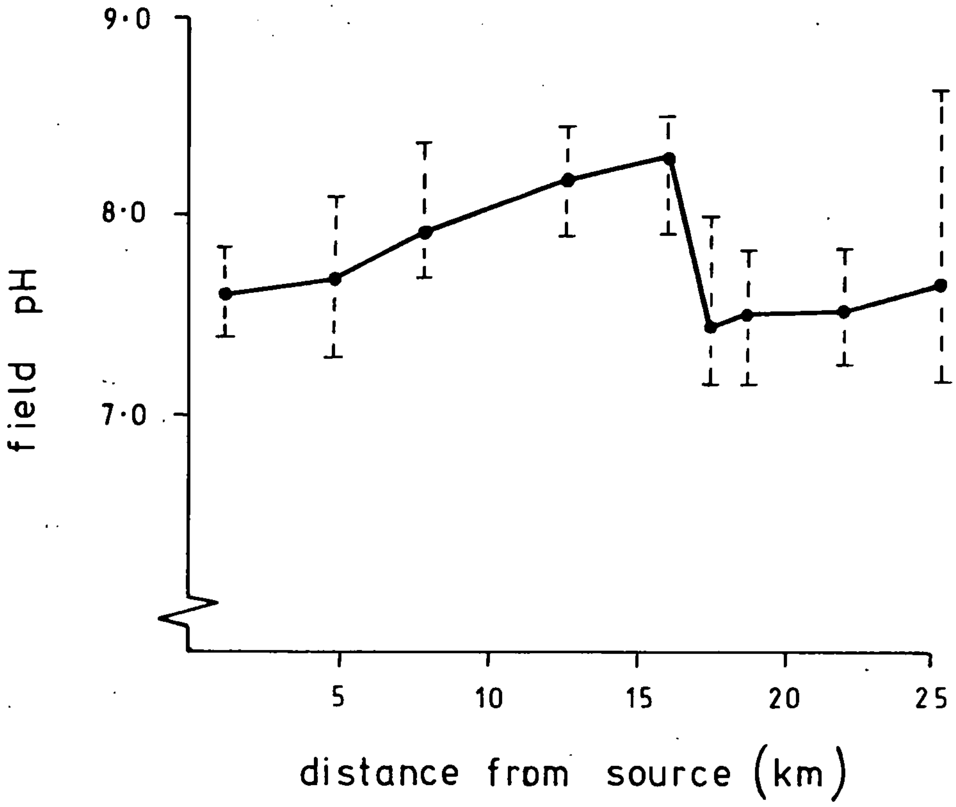

16·0
12·0
8·0
4·0
$O_2$ (mg $l^{-1}$)
5
10
15
20
25
distance from source (km)

Figure 4.3 Mean pH values recorded in the field at sites along the river.
Dotted lines indicate the range of values recorded at each site.

Figure 4.4 Mean pH values obtained in the laboratory from water samples collected at the nine sites along the river.
Dotted lines indicate the range of values recorded at each site.


9·0
8·0
7·0
field pH
5
10
15
20
25
distance from source (km)

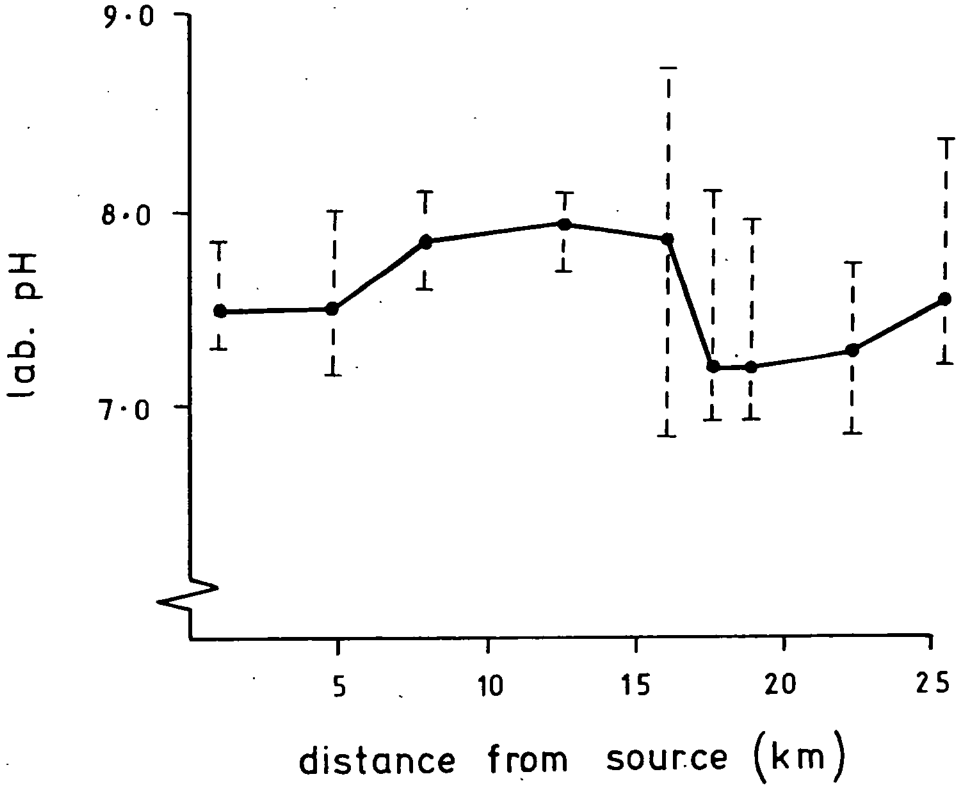
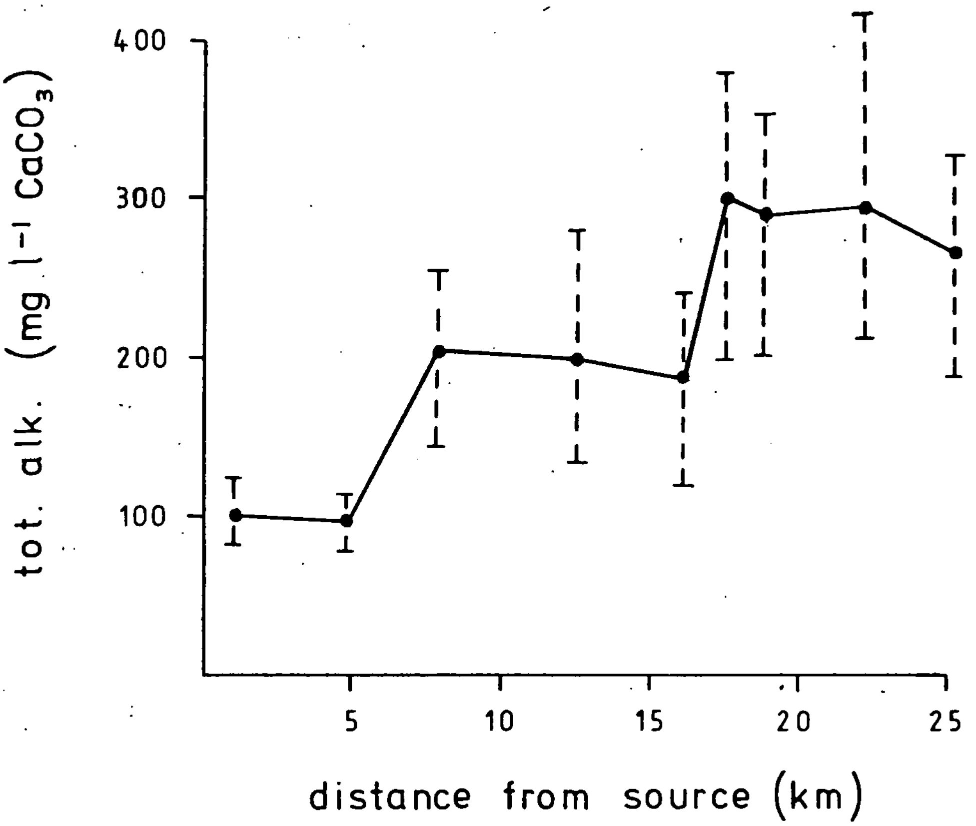

9·0
8·0
7·0
lab. pH
5
10
15
20
25
distance from source (km)

Figure 4.5 Changes in the mean values of total alkalinity along the river.
Dotted lines indicate the range of values recorded at each site.

Figure 4.6 Mean conductivity values obtained in the laboratory from water samples collected at the nine sites along the river.
Dotted lines indicate the range of values recorded at each site.


tot. alk. (mg l⁻¹ CaCO₃)
400
300
200
100
5
10
15
20
25
distance from source (km)

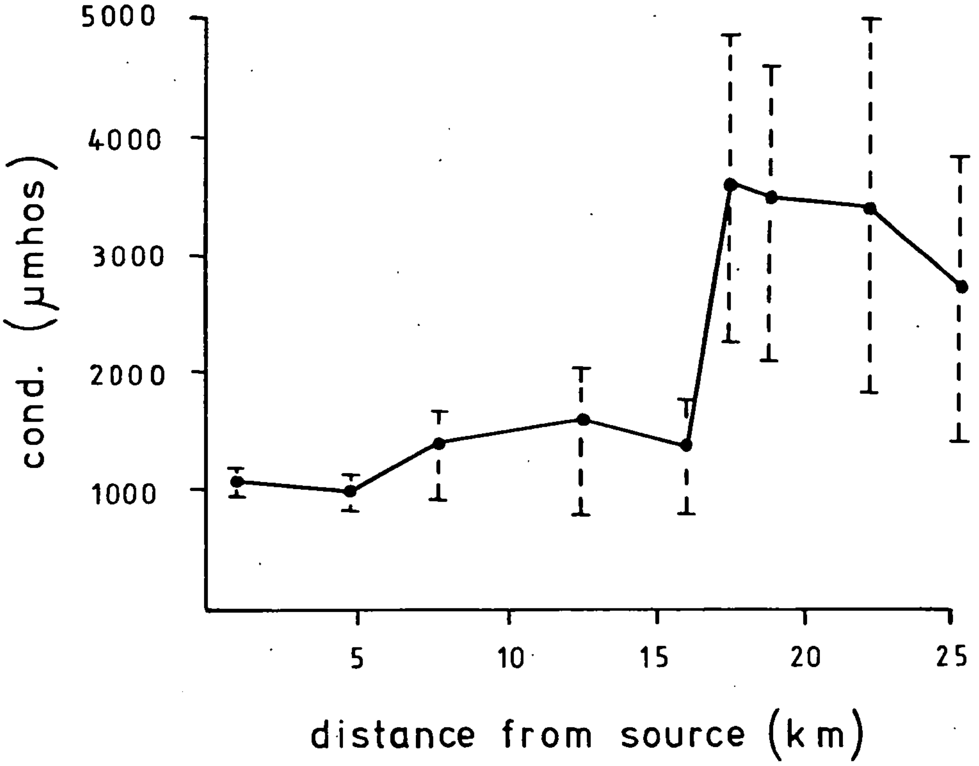
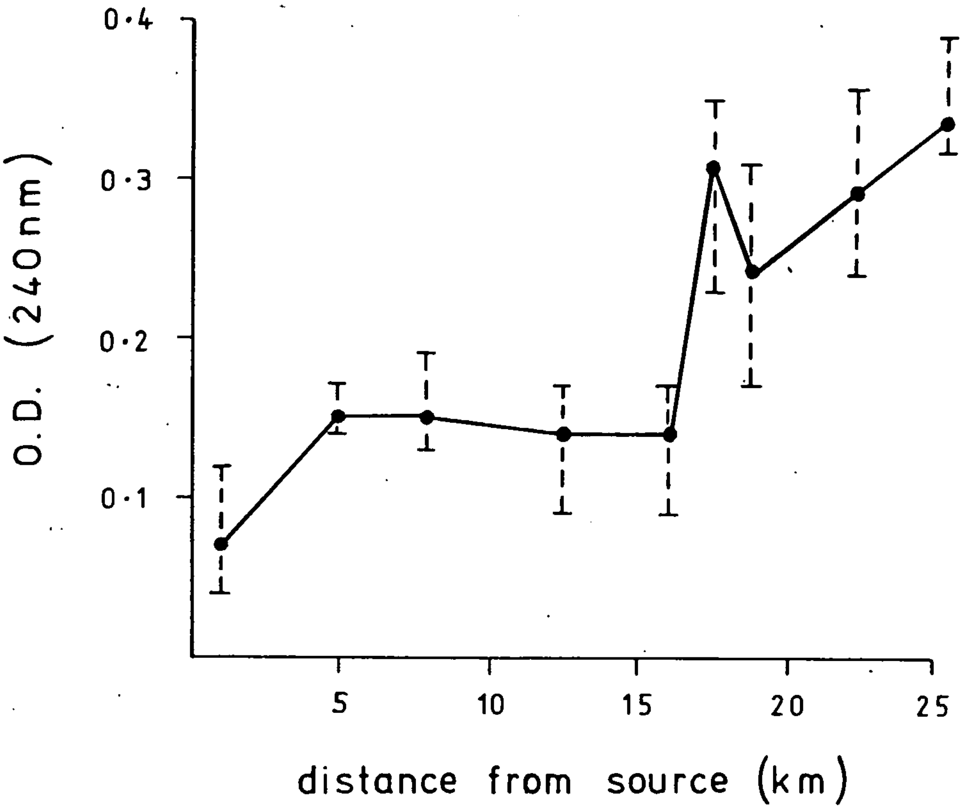

cond. (μmhos)
5000
4000
3000
2000
1000
5
10
15
20
25
distance from source (km)

Figure 4.7 Mean values of optical density measured at 240nm on a Uvispek spectrophotometer.
Dotted lines indicate the range of values recorded at each site.

Figure 4.8 Mean values of optical density measured at 254 nm on a Uvispek spectrophotometer.
Dotted lines indicate the range of values recorded at each site.


0·4
0·3
0·2
0·1
O.D. (240nm)
5
10
15
20
25
distance from source (km)

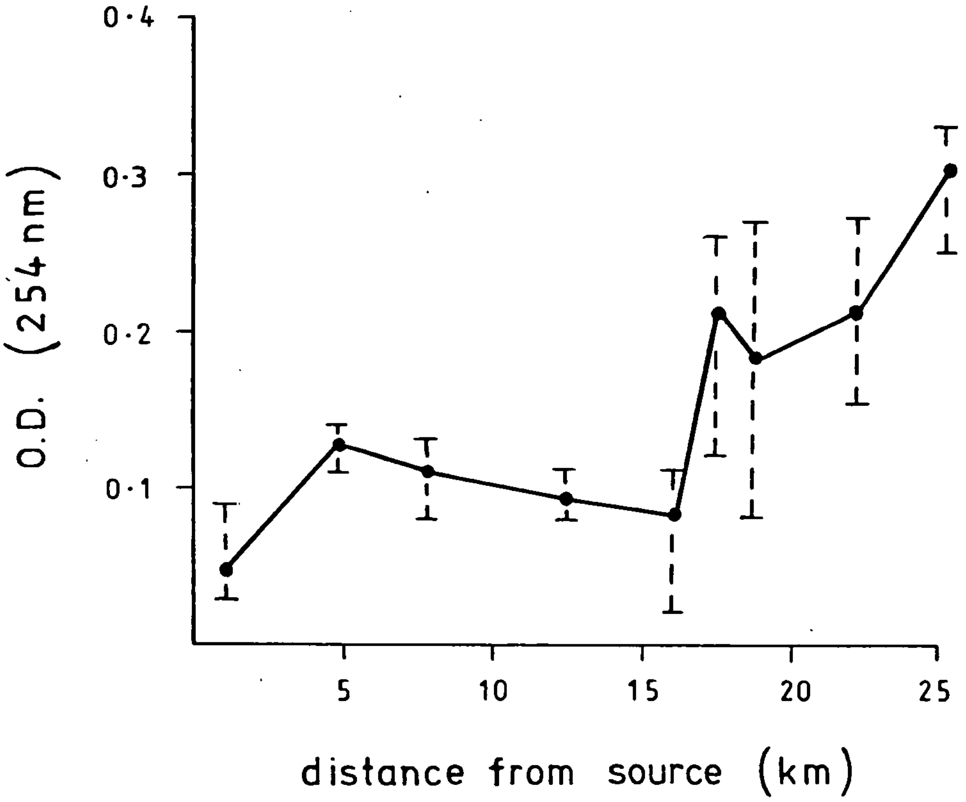
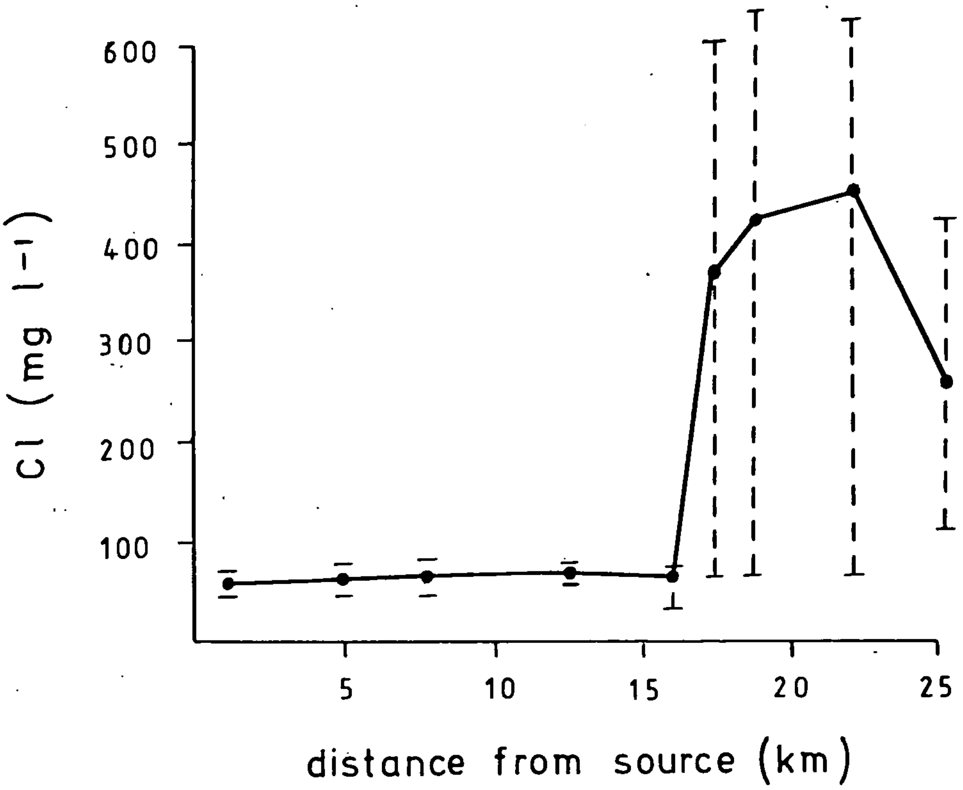

0·4
0·3
0·2
0·1
O.D. (254nm)
5
10
15
20
25
distance from source (km)

Figure 4.9 Changes in the mean value of Cl levels along the river.
Dotted lines indicate the range of values recorded at each site.

Figure 4.10 Changes in the mean value of $P\text{-}PO_4$ levels along the river.
Dotted lines indicate the range of values recorded at each site.


Cl (mg l⁻¹)
600
500
400
300
200
100
5
10
15
20
25
distance from source (km)

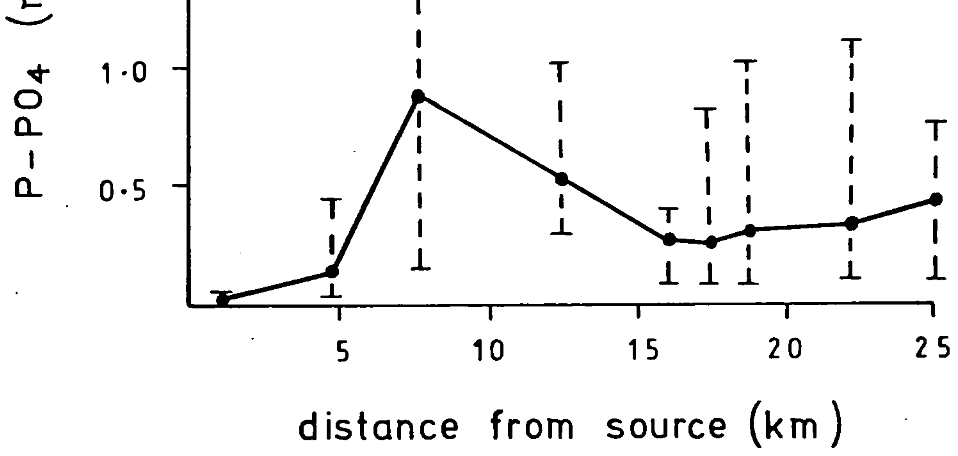
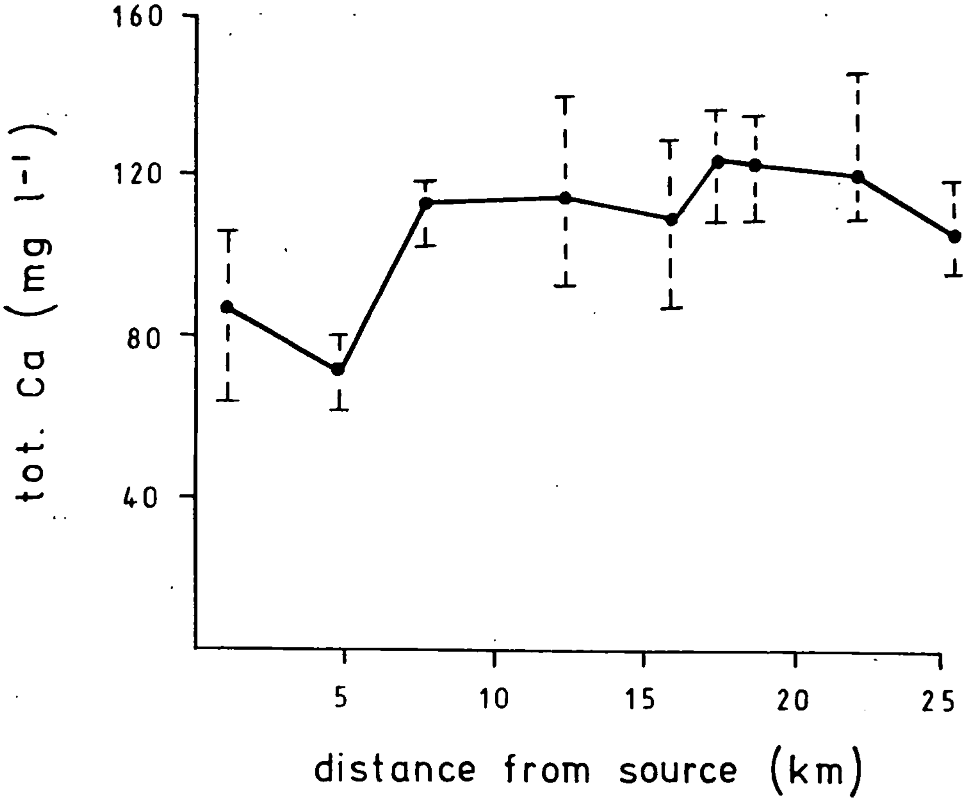

P-PO4 (mg l⁻¹)
2·5
2·0
1·5
1·0
0·5
5
10
15
20
25
distance from source (km)

Figure 4.11 Mean Ca concentrations determined from total water samples taken at nine sites along the river. Dotted lines indicate the range of values recorded at each site.

Figure 4.12 Mean Ca concentrations determined from filtered water samples taken at nine sites along the river. Dotted lines indicate the range of values recorded at each site.


160
120
80
40
tot. Ca (mg l⁻¹)
5
10
15
20
25
distance from source (km)

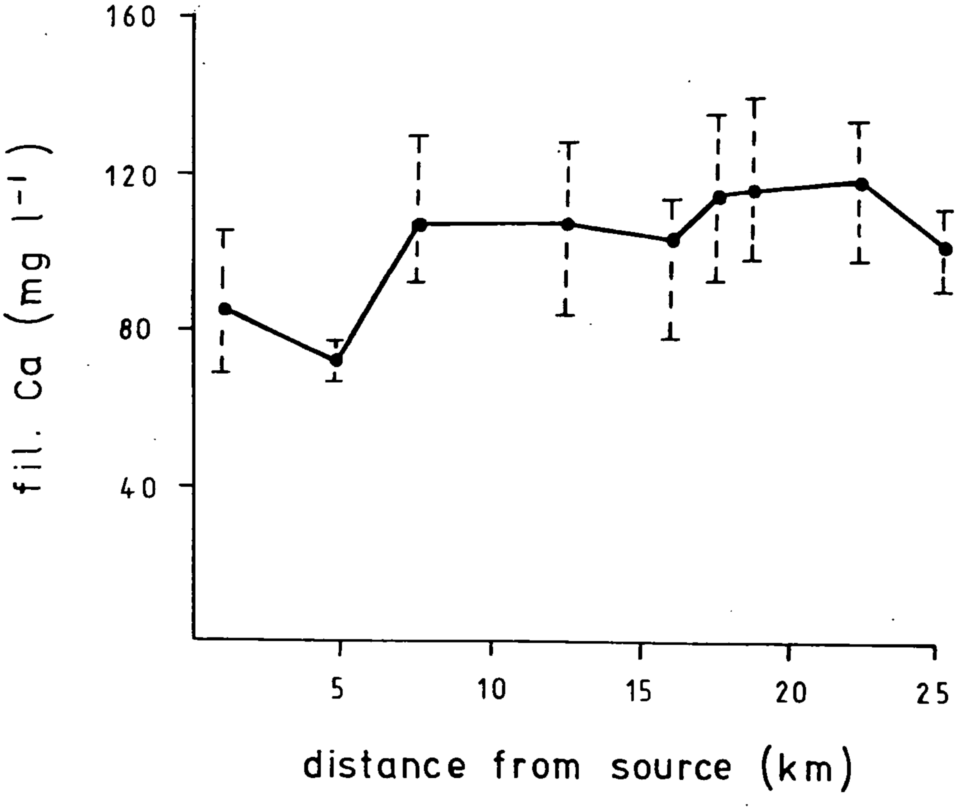
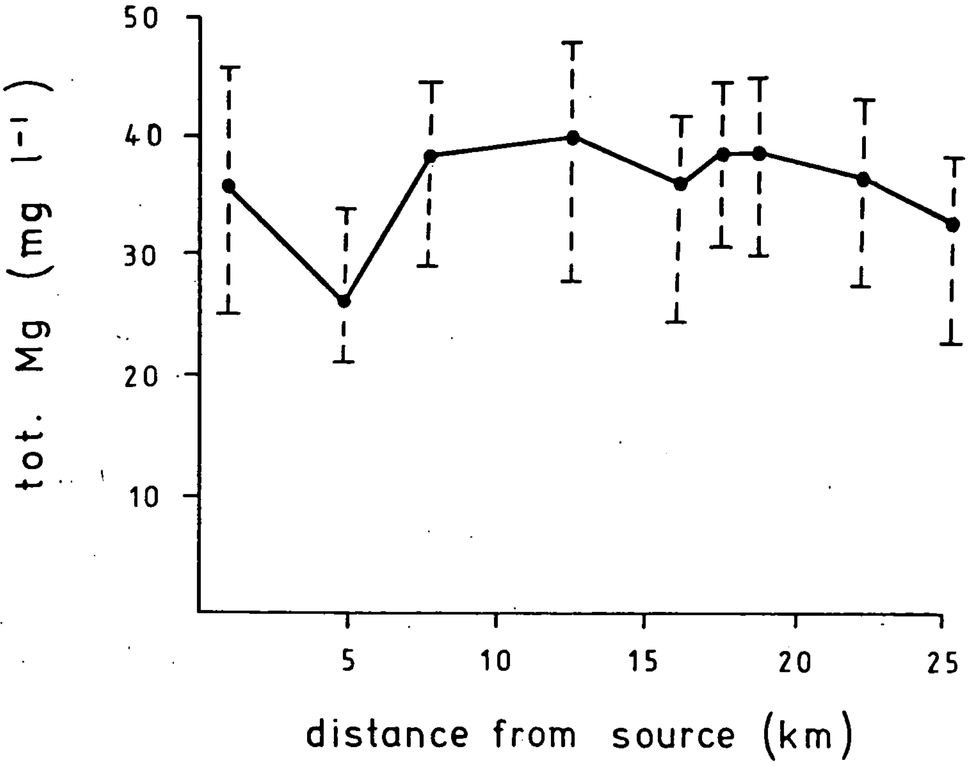

160
120
80
40
fil. Ca (mg l⁻¹)
5
10
15
20
25
distance from source (km)

Figure 4.13 Mean Mg concentrations determined from total water samples taken at the nine sites along the river. Dotted lines indicate the range of values recorded at each site.

Figure 4.14 Mean Mg concentrations determined from filtered water samples taken at nine sites along the river. Dotted lines indicate the range of values recorded at each site.


tot. Mg (mg l⁻¹)
50
40
30
20
10
5
10
15
20
25
distance from source (km)

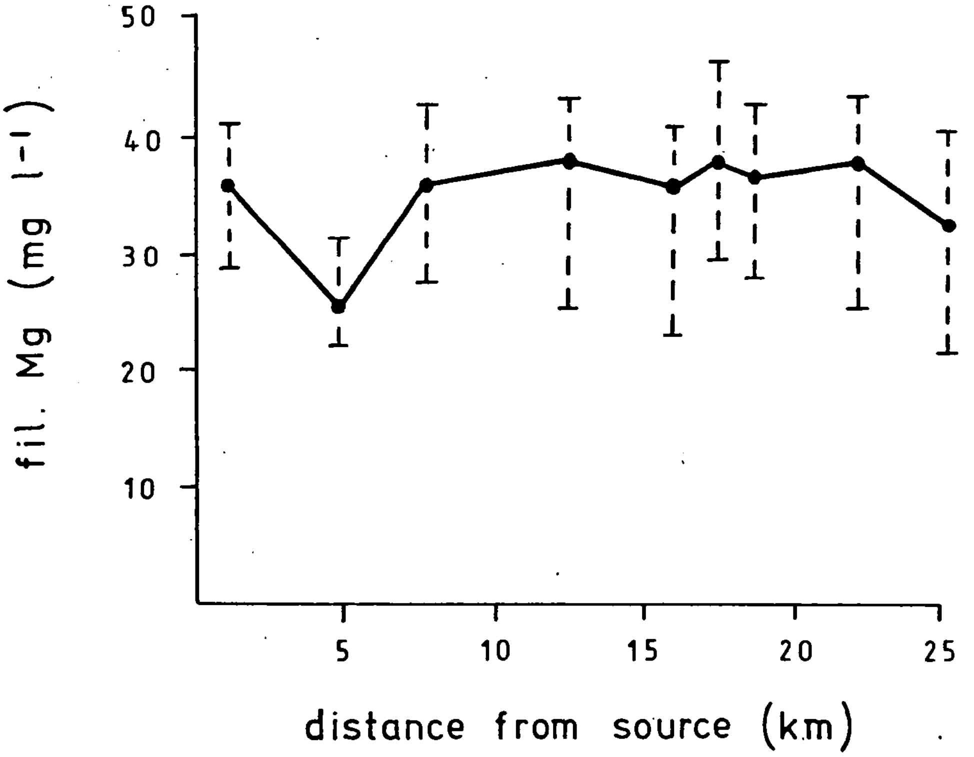
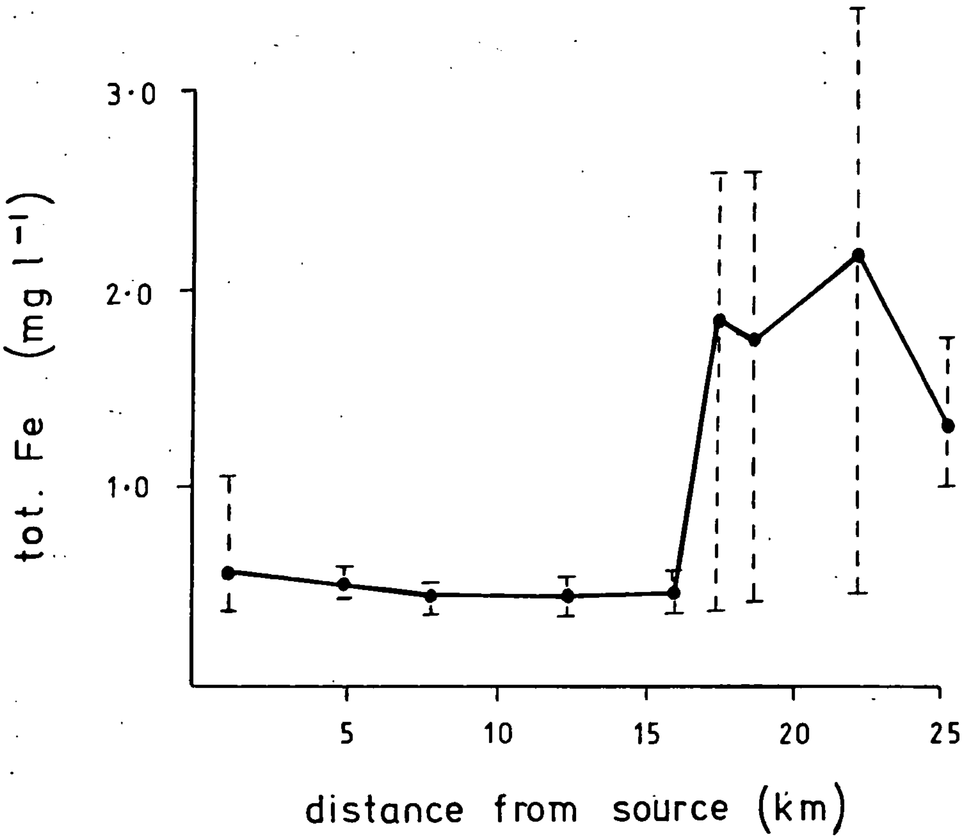

fil. Mg (mg l⁻¹)
50
40
30
20
10
5
10
15
20
25
distance from source (km)

Figure 4.15 Mean Fe concentrations determined from total water samples taken at the nine sites along the river.
Dotted lines indicate the range of values recorded at each site.

Figure 4.16 Mean Fe concentrations determined from filtered water samples taken at the nine sites along the river.
Dotted lines indicate the range of values recorded at each site.


3·0
2·0
1·0
tot. Fe (mg l⁻¹)
5
10
15
20
25
distance from source (km)

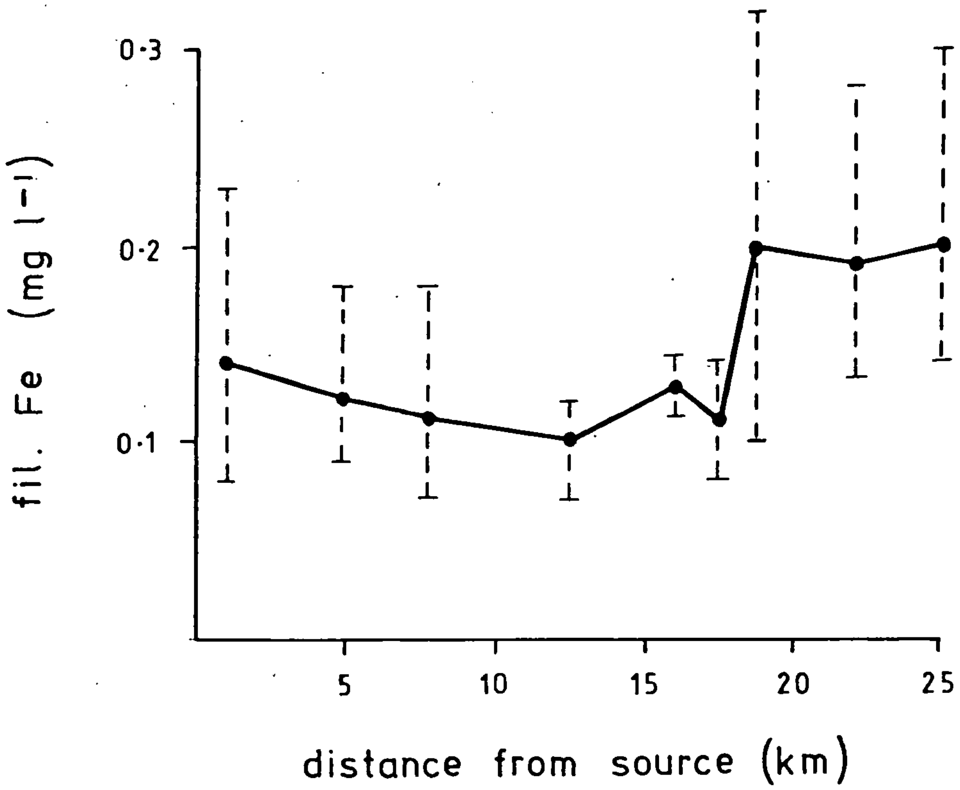
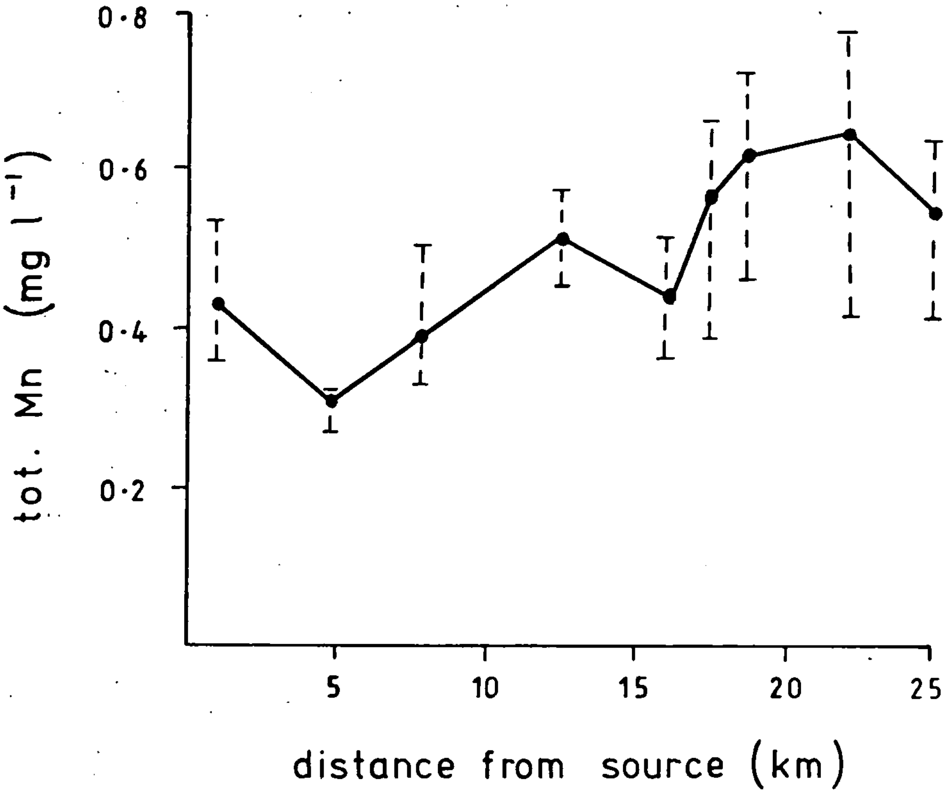

0·3
0·2
0·1
fil. Fe (mg l⁻¹)
5
10
15
20
25
distance from source (km)

Figure 4.17 Mean Mn concentrations determined from total water samples taken at nine sites along the river. Dotted lines indicate the range of values recorded at each site.

Figure 4.18 Mean Mn concentrations determined from filtered water samples taken at nine sites along the river. Dotted lines indicate the range of values recorded at each site.


0·8
0·6
0·4
0·2
tot. Mn (mg l⁻¹)
5
10
15
20
25
distance from source (km)

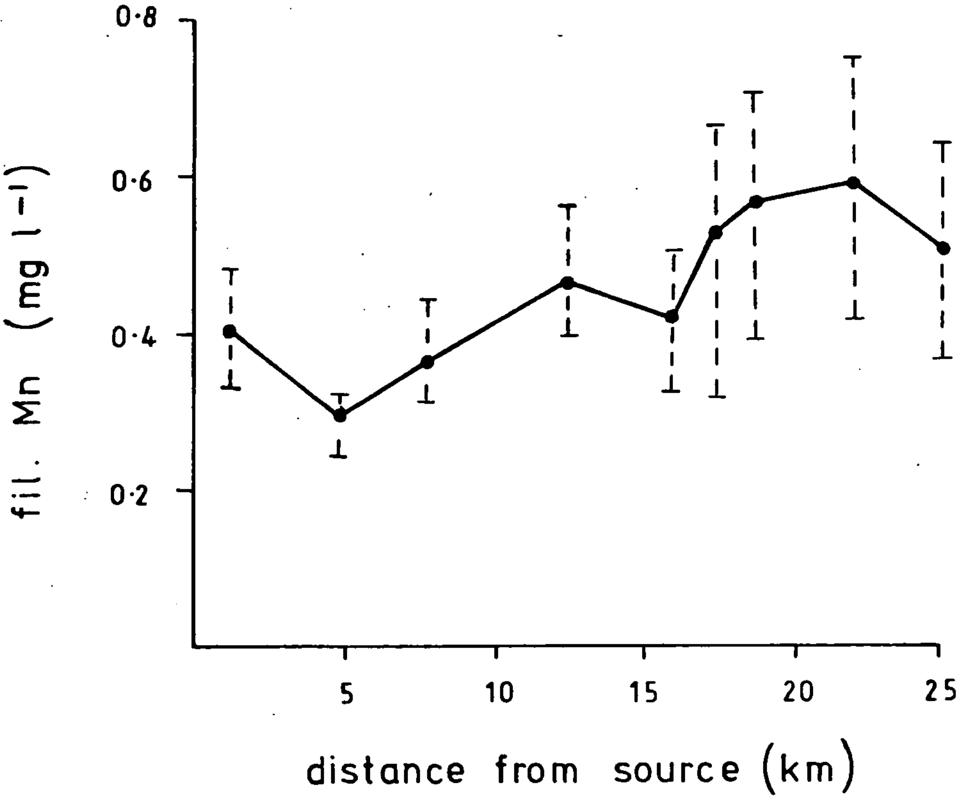
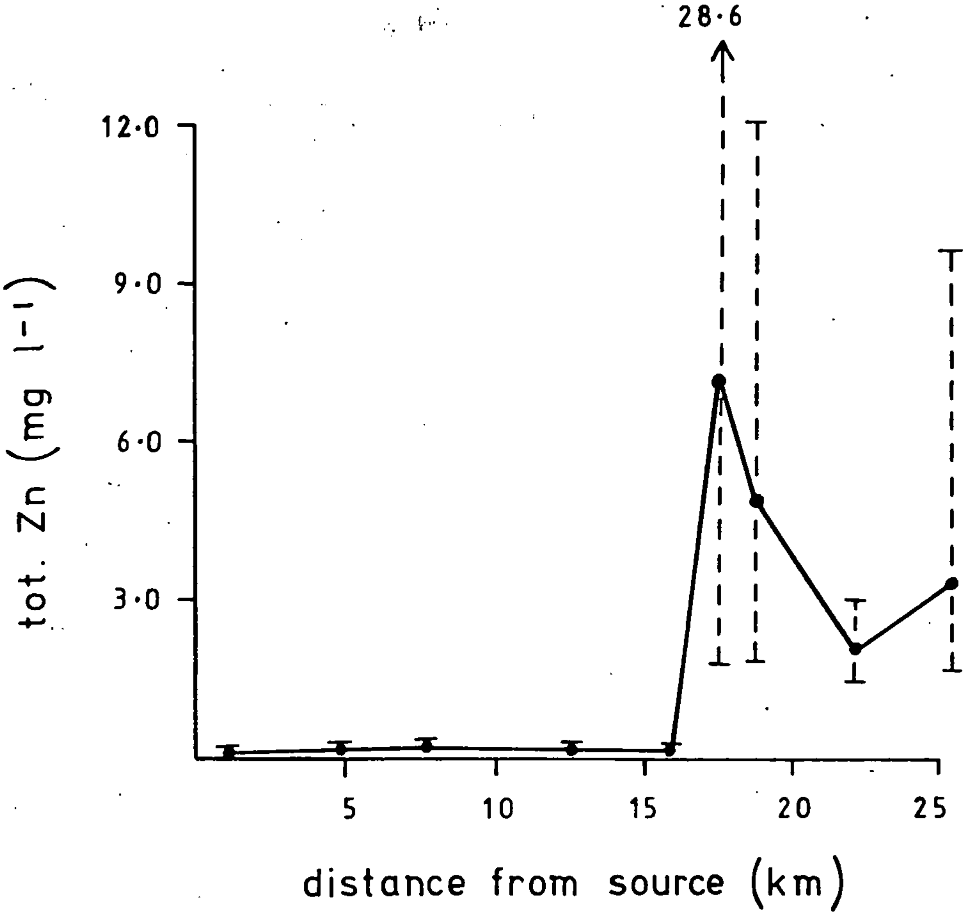

0·8
0·6
0·4
0·2
fil. Mn (mg l⁻¹)
5
10
15
20
25
distance from source (km)

Figure 4.19 Mean Zn concentrations determined from total water samples taken at nine sites along the river. Dotted lines indicate the range of values recorded at each site.

Figure 4.20 Mean Zn concentrations determined from filtered water samples taken at nine sites along the river. Dotted lines indicate the range of values recorded at each site.


28·6
12·0
9·0
6·0
3·0
tot. Zn (mg l⁻¹)
5
10
15
20
25
distance from source (km)

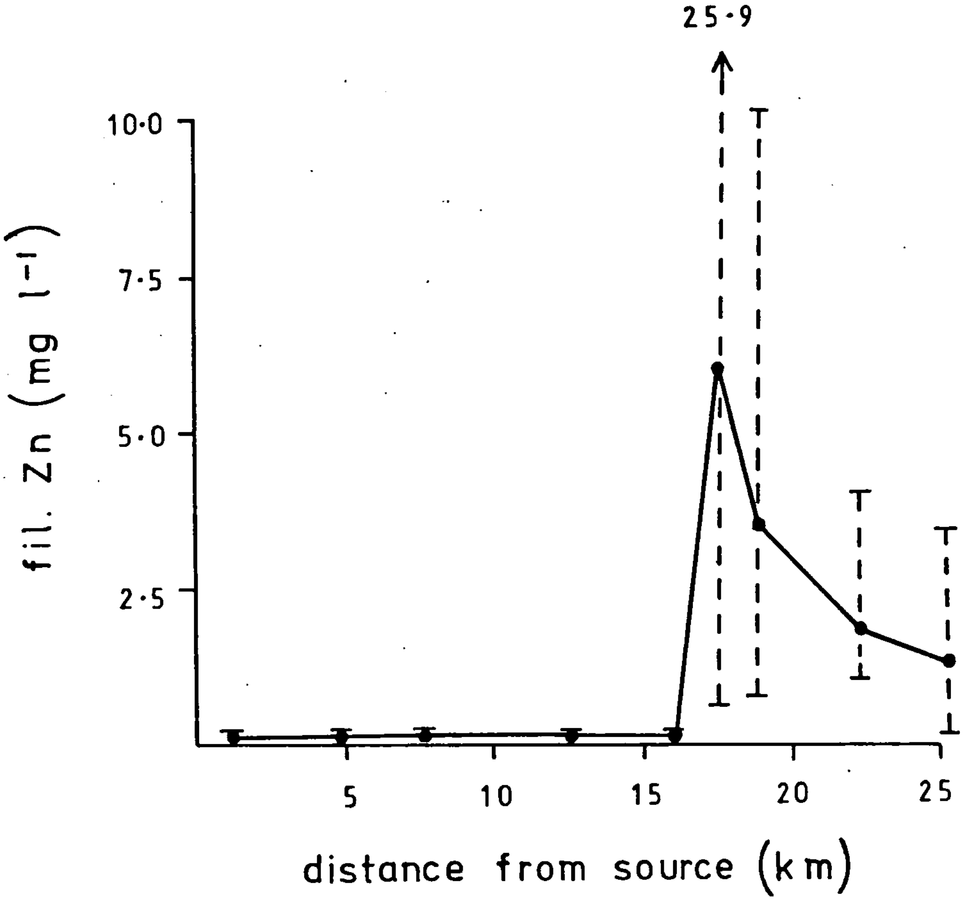

25·9
10·0
7·5
5·0
2·5
fil. Zn (mg l⁻¹)
5
10
15
20
25
distance from source (km)

Figure 4.21 Mean values of Zn content in sediment samples taken along the river.
Dotted lines indicate the range of values recorded at each site.

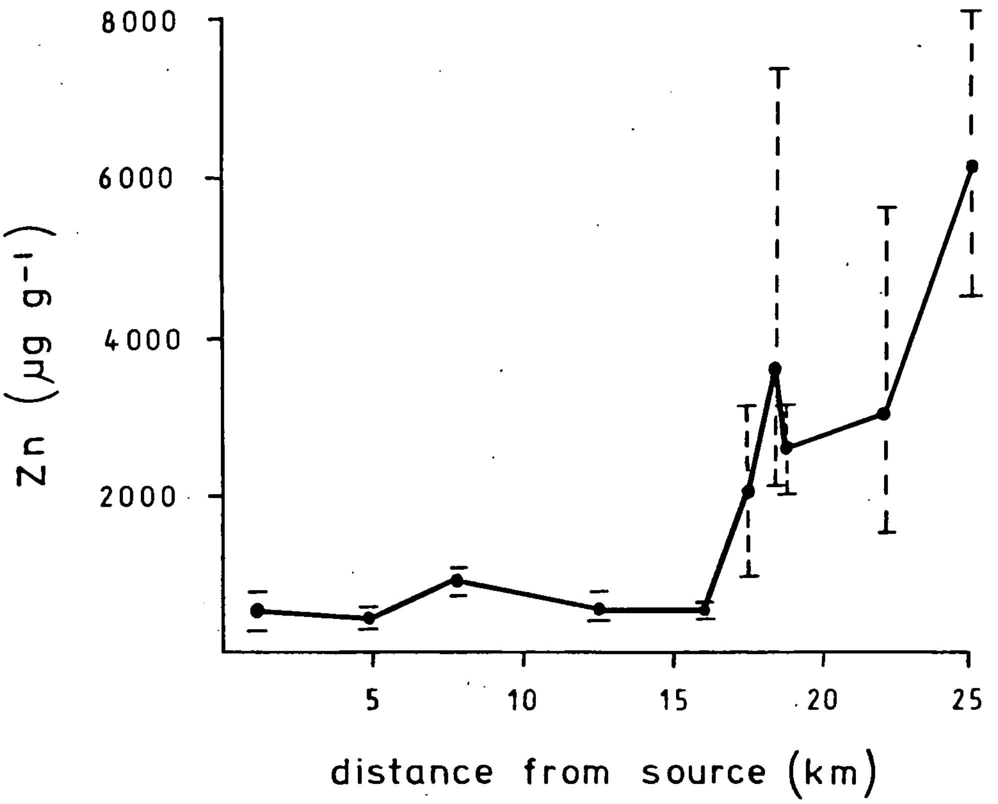
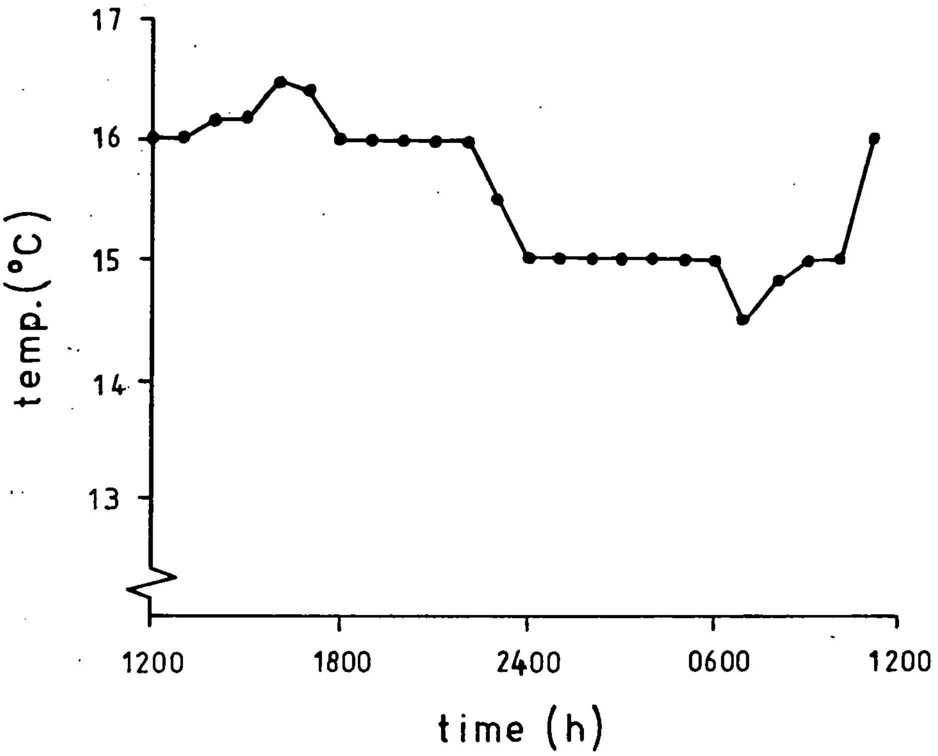

8000
6000
4000
2000
Zn (μg g⁻¹)
5
10
15
20
25
distance from source (km)

Figure 4.22 Temperature variations occurring throughout a 24 h period at site 6.

Figure 4.23 Variations in the $O_2$ level over a 24 h period at site 6.


17
16
15
14
13
temp. (°C)
1200
1800
2400
0600
1200
time (h)

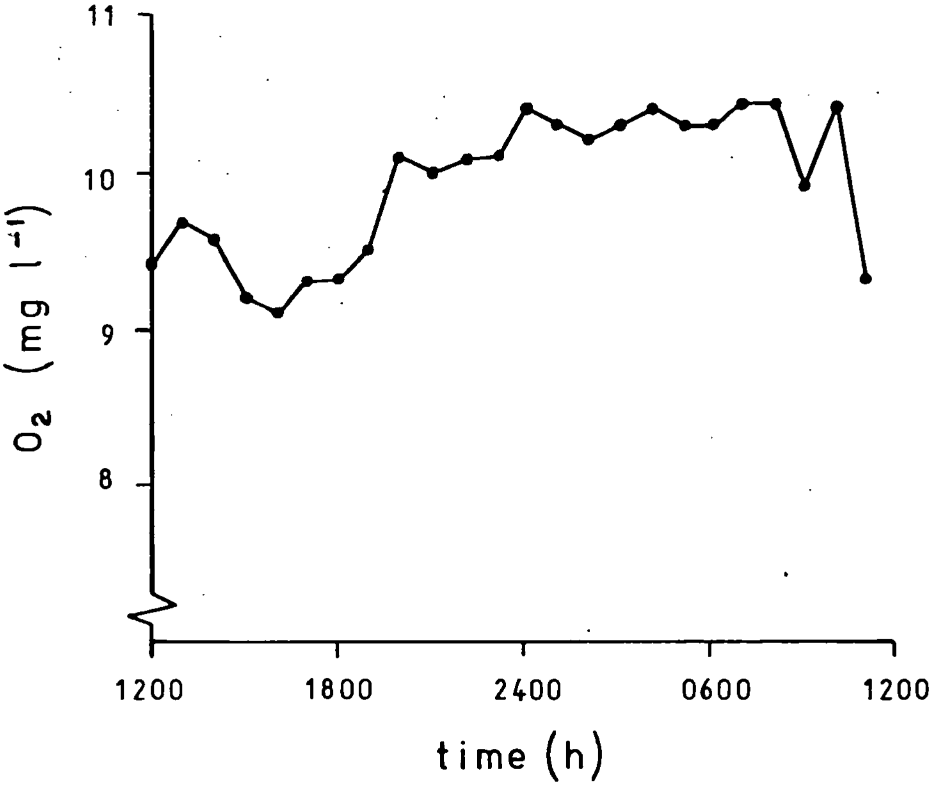
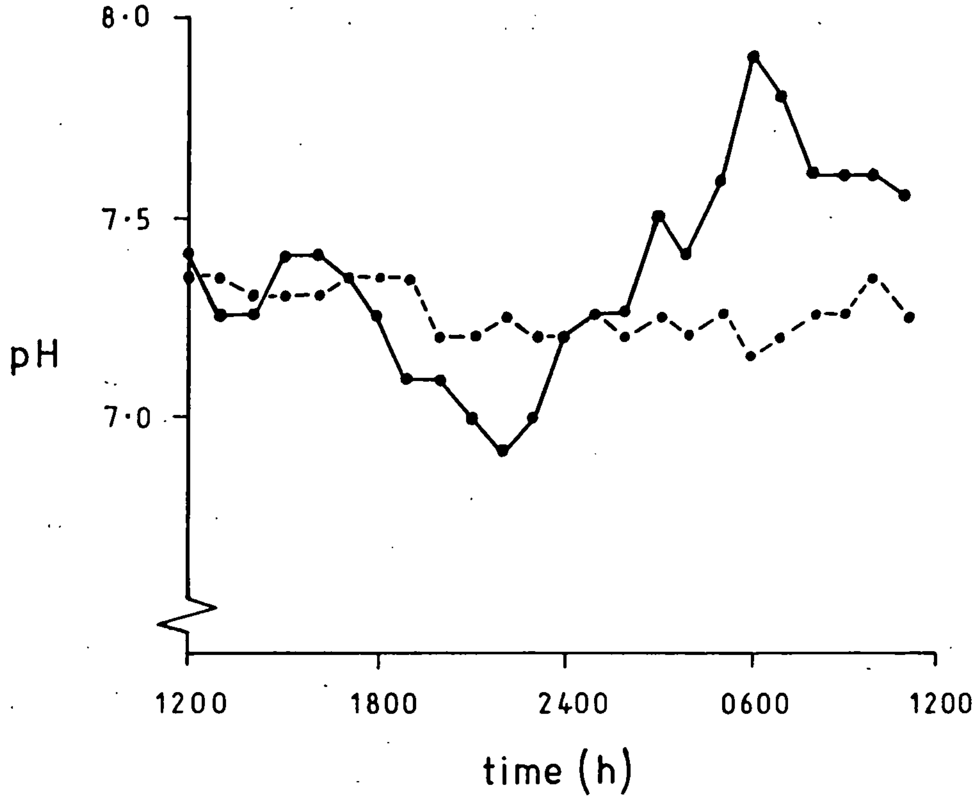

11
10
9
8
$O_2$ (mg $l^{-1}$)
1200
1800
2400
0600
1200
time (h)

Figure 4.24 Changes in pH values recorded in the 24 h survey at site 6.
Solid line indicates pH values determined in the field.
Dotted line indicates pH values obtained from water samples taken to the laboratory.

Figure 4.25 Values of total alkalinity recorded in the 24 h survey at site 6.


8·0
7·5
7·0
pH
1200
1800
2400
0600
1200
time (h)

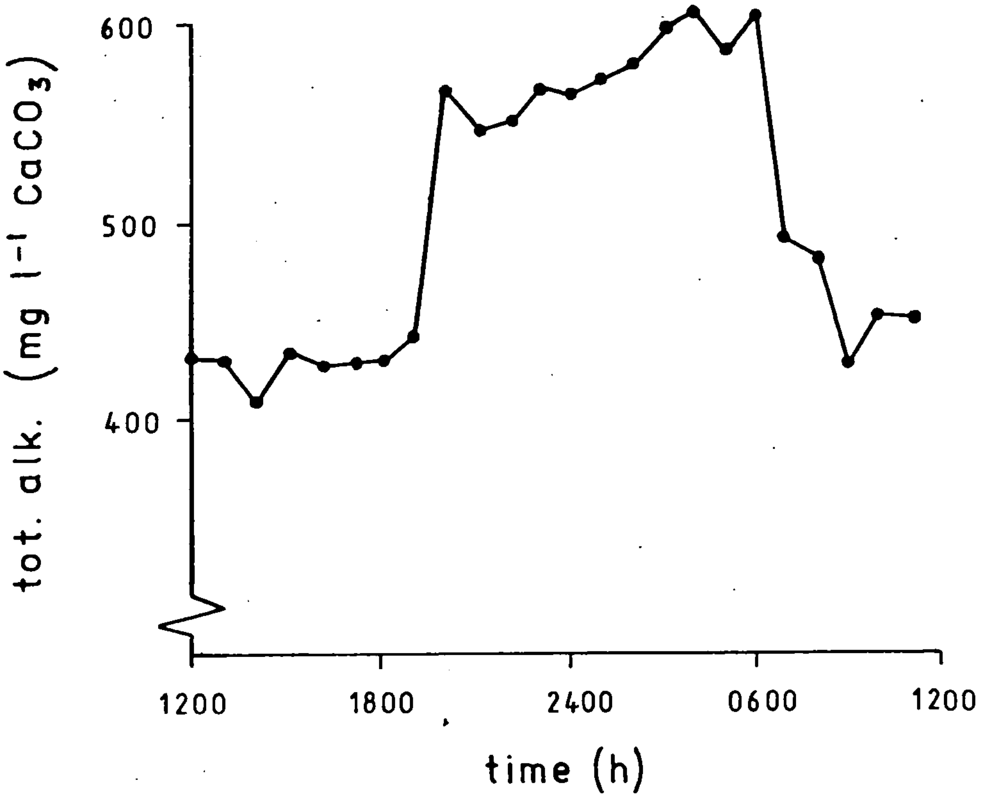
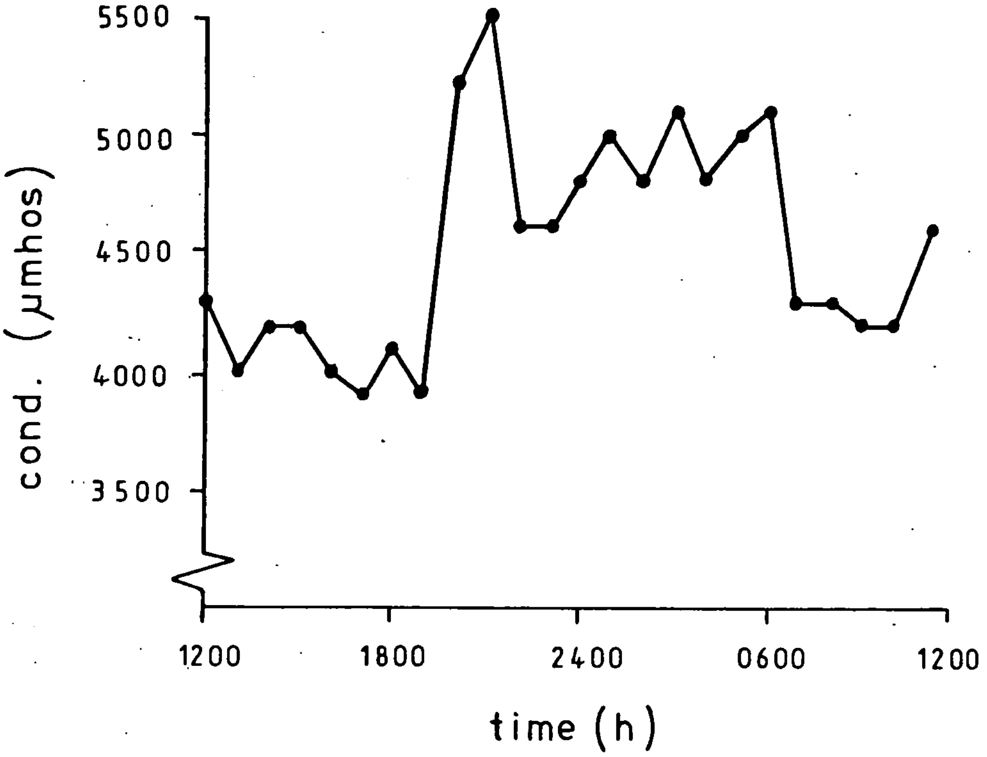

600
500
400
tot. alk. (mg l⁻¹ CaCO₃)
1200
1800
2400
0600
1200
time (h)

Figure 4.26 Changes in the conductivity of the water at site 6 over a 24 h period.

Figure 4.27 Variations in the optical density of the water at site 6 over a 24 h period.
Solid line indicates O.D. measured at 240 nm.
Dotted line indicates O.D. measured at 254 nm.


5500
5000
4500
4000
3500
cond. (μmhos)
1200
1800
2400
0600
1200
time (h)

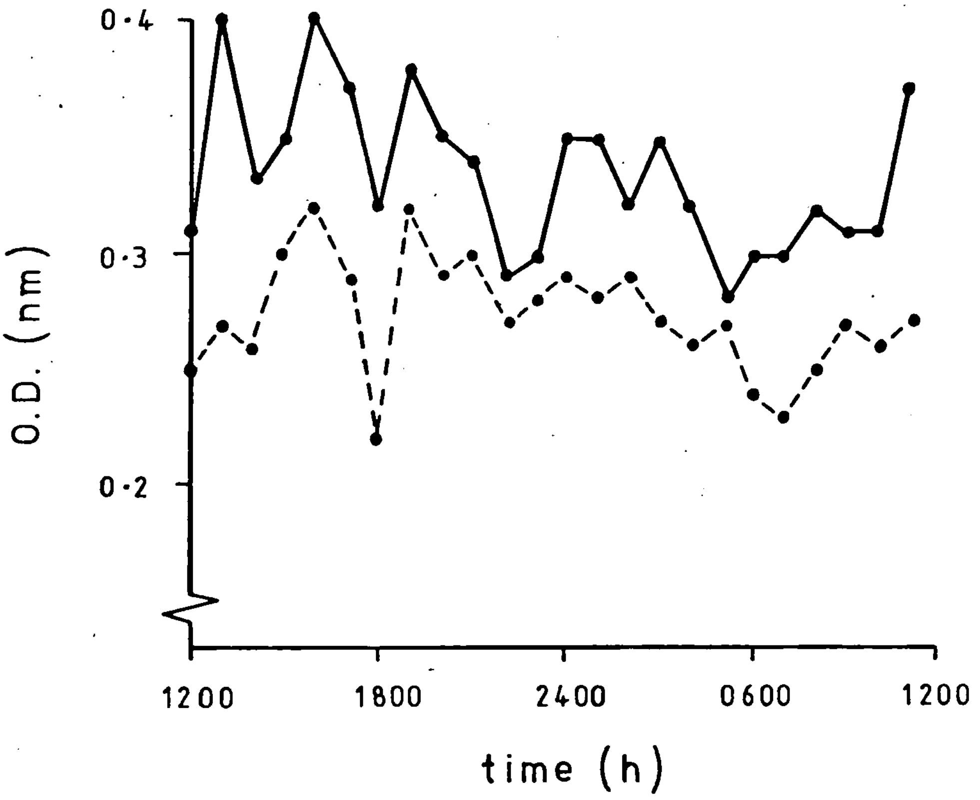
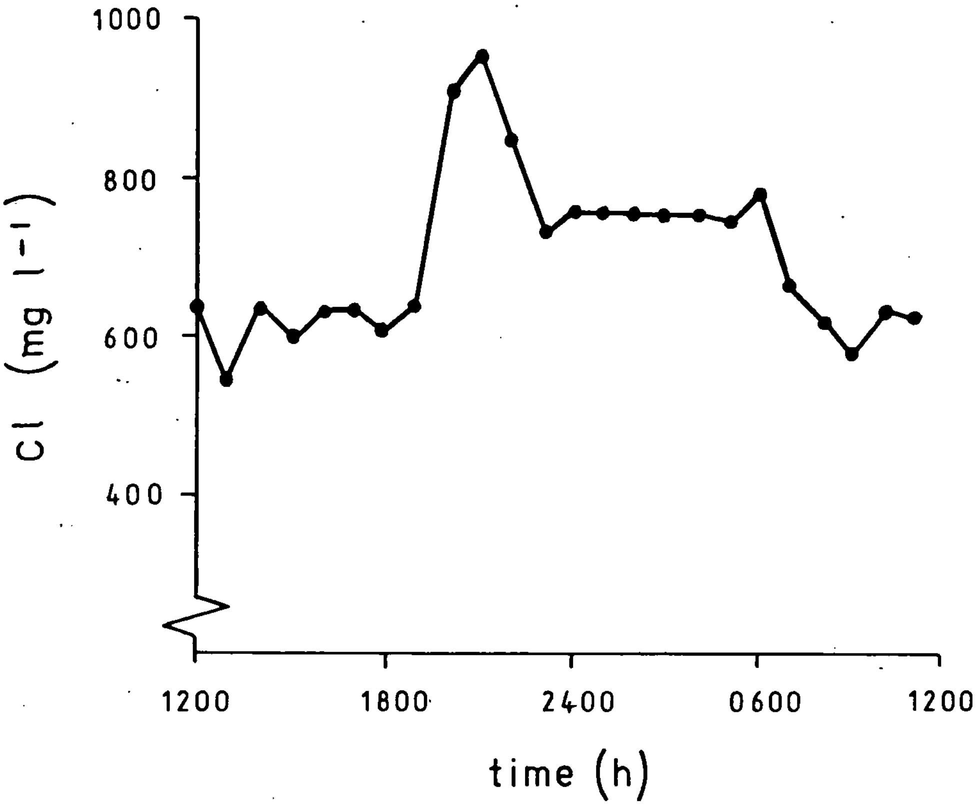

0·4
0·3
0·2
O.D. (nm)
1200
1800
2400
0600
1200
time (h)

Figure 4.28 Changes in Cl concentrations over a 24 h period at site 6.

Figure 4.29 Variations in the $P\text{-}PO_4$ concentration recorded in the 24 h survey at site 6.


1000
800
600
400
Cl (mg l-1)
1200
1800
2400
0600
1200
time (h)

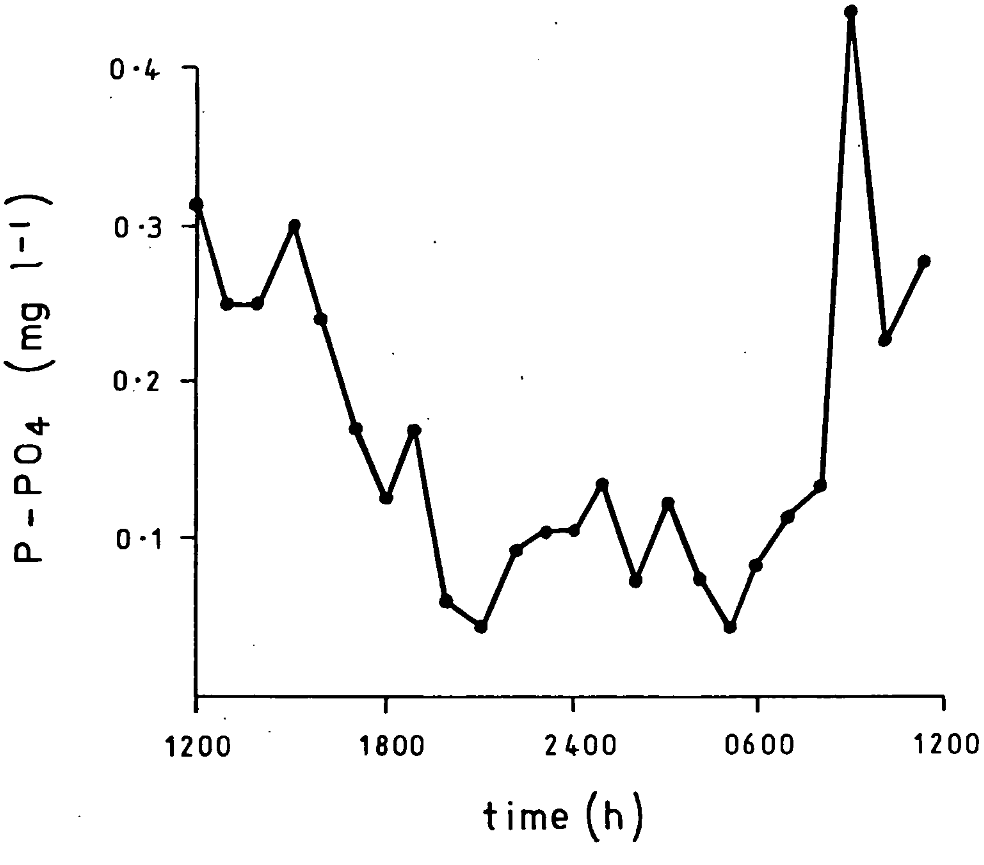
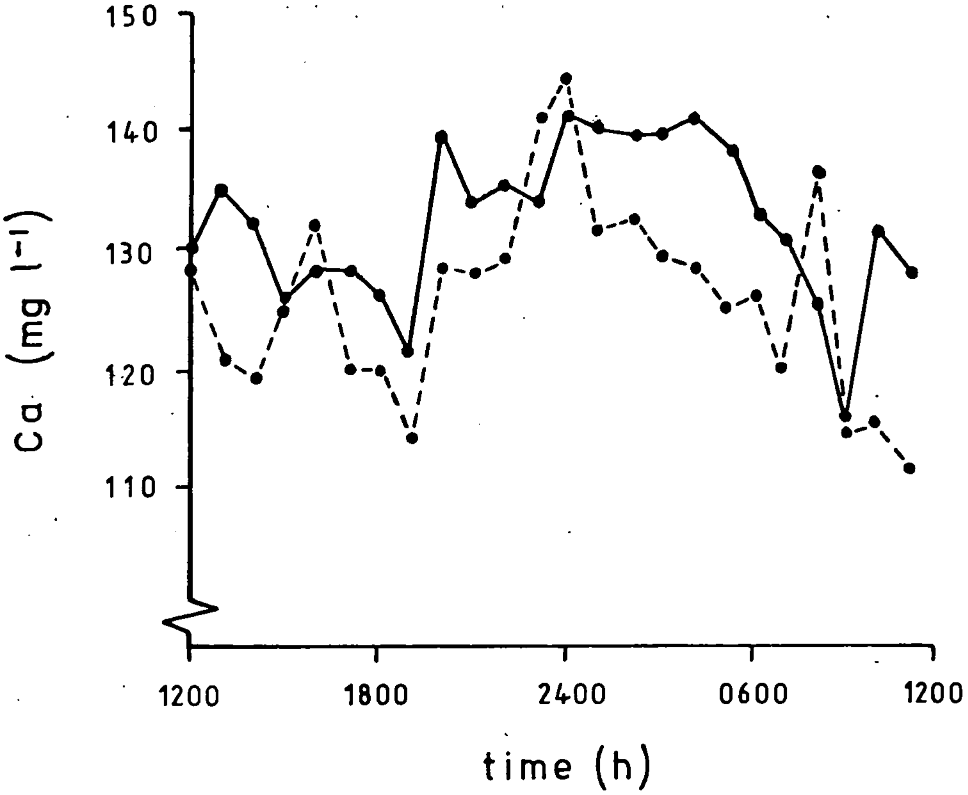

0·4
0·3
0·2
0·1
P-PO4 (mg l-1)
1200
1800
2400
0600
1200
time (h)

Figure 4.30 Levels of Ca recorded in the 24 h survey at site 6. Solid line indicates Ca concentrations determined from total water samples.
Dotted line indicates Ca concentrations determined from filtered water samples.

Figure 4.31 Levels of Mg recorded in the 24 h survey at site 6. Solid line indicates Mg concentrations determined from total water samples.
Dotted line indicates Mg concentrations determined from filtered water samples.


Ca (mg l⁻¹)
150
140
130
120
110
1200
1800
2400
0600
1200
time (h)

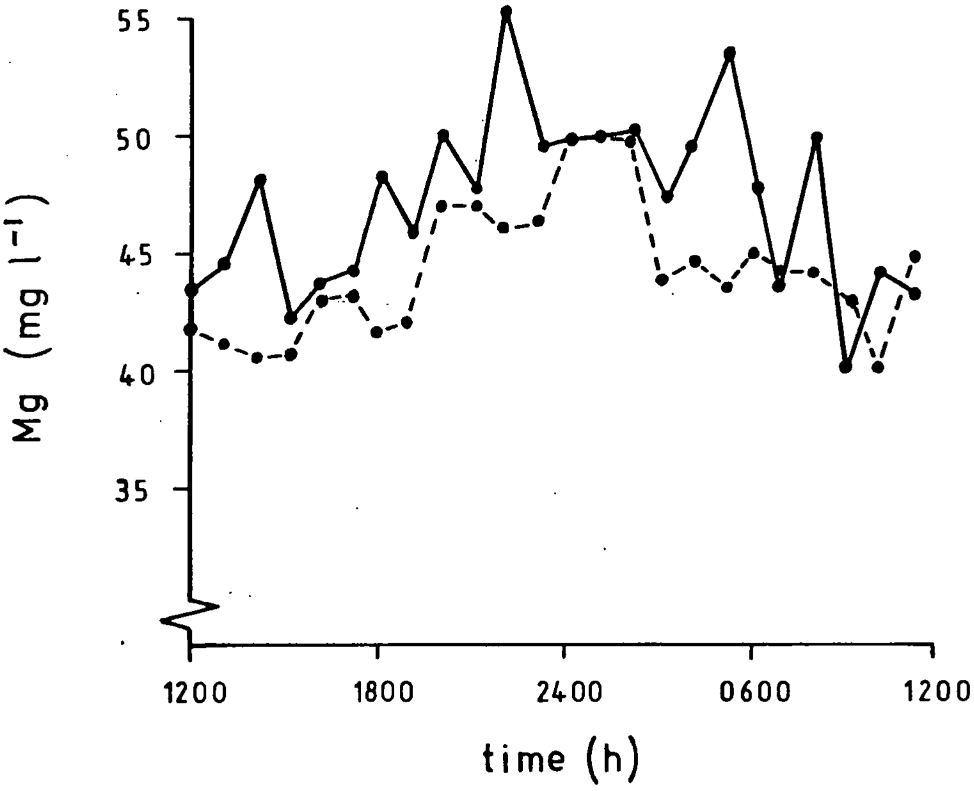
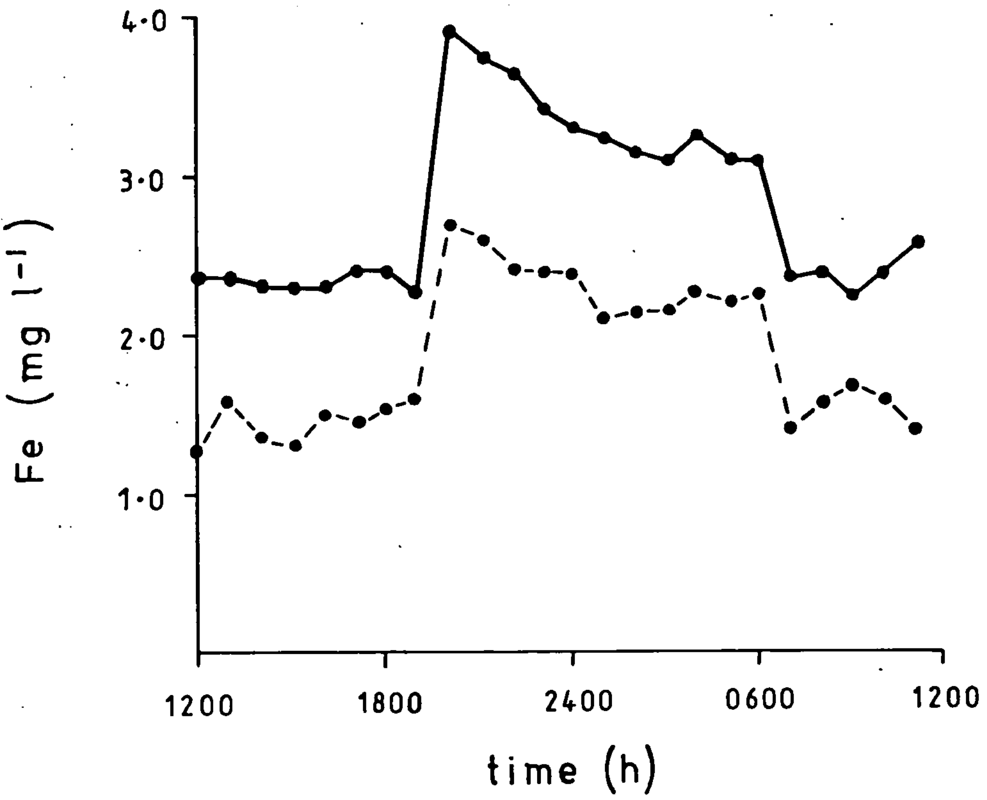

Mg (mg l⁻¹)
55
50
45
40
35
1200
1800
2400
0600
1200
time (h)

Figure 4.32 Levels of Fe recorded in the 24 h survey at site 6. Solid line indicates Fe concentrations determined from total water samples.
Dotted line indicates Fe concentrations determined from filtered water samples.

Figure 4.33 Levels of Mn recorded in the 24 h survey at site 6. Solid line indicates Mn concentrations determined from total water samples.
Dotted line indicates Mn concentrations determined from filtered water samples.


4·0
3·0
2·0
1·0
Fe (mg l⁻¹)
1200
1800
2400
0600
1200
time (h)

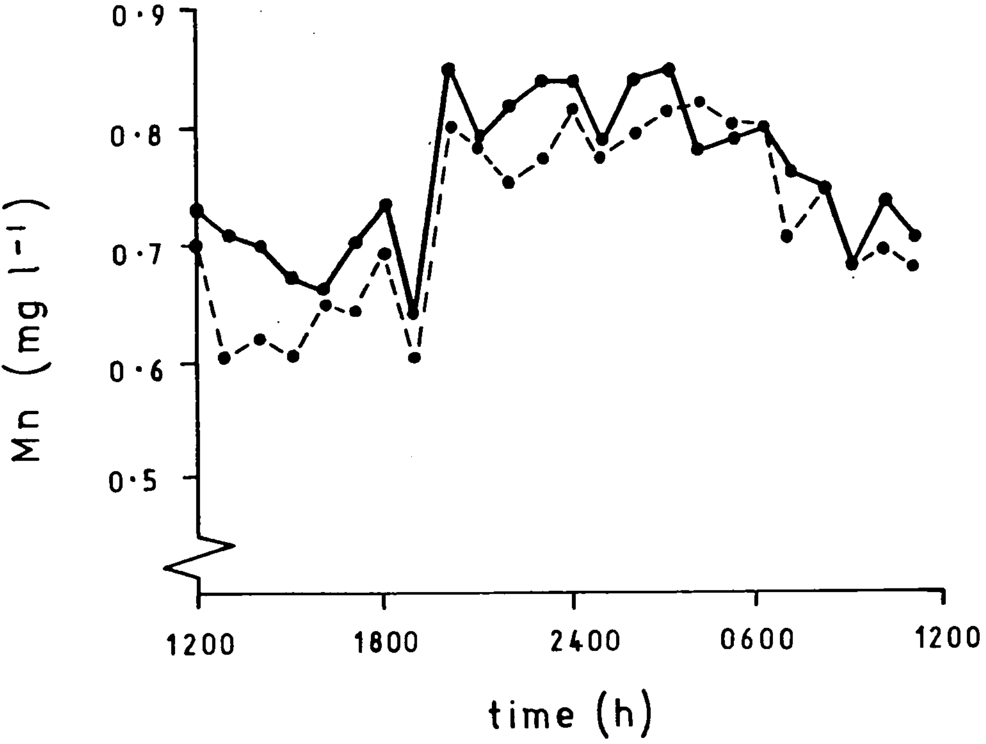

0·9
0·8
0·7
0·6
0·5
Mn (mg l⁻¹)
1200
1800
2400
0600
1200
time (h)

Figure 4.34 Levels of Zn recorded in the 24 h survey at site 6. Solid line indicates Zn concentrations determined from total water samples.
Dotted line indicates Zn concentrations determined from filtered water samples.

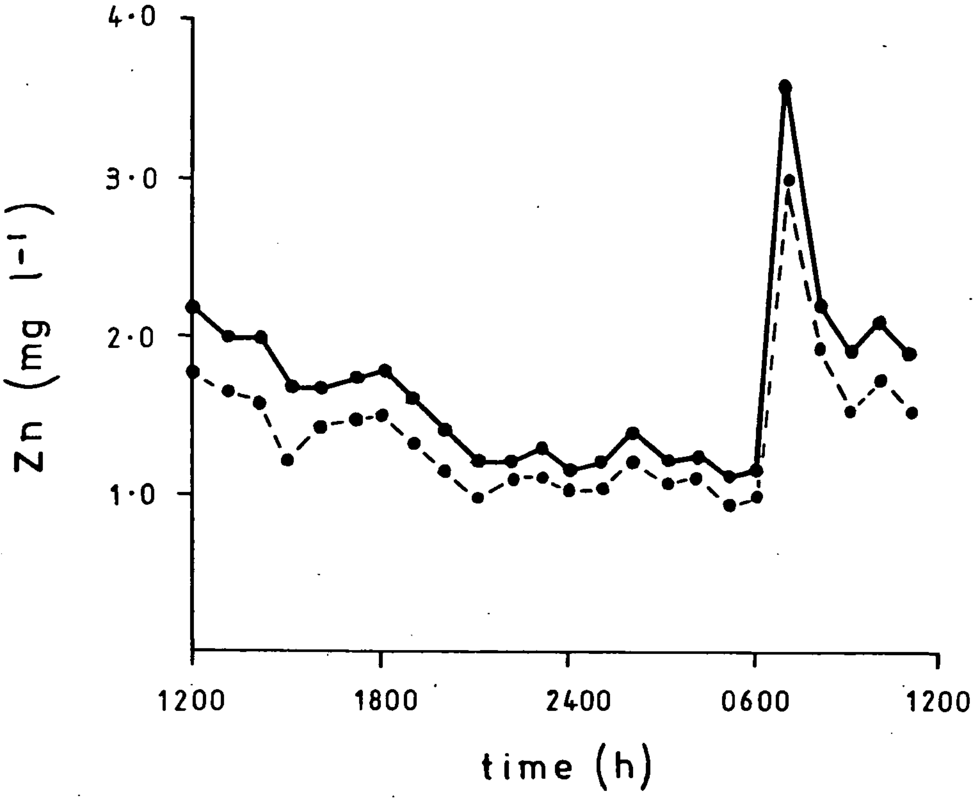
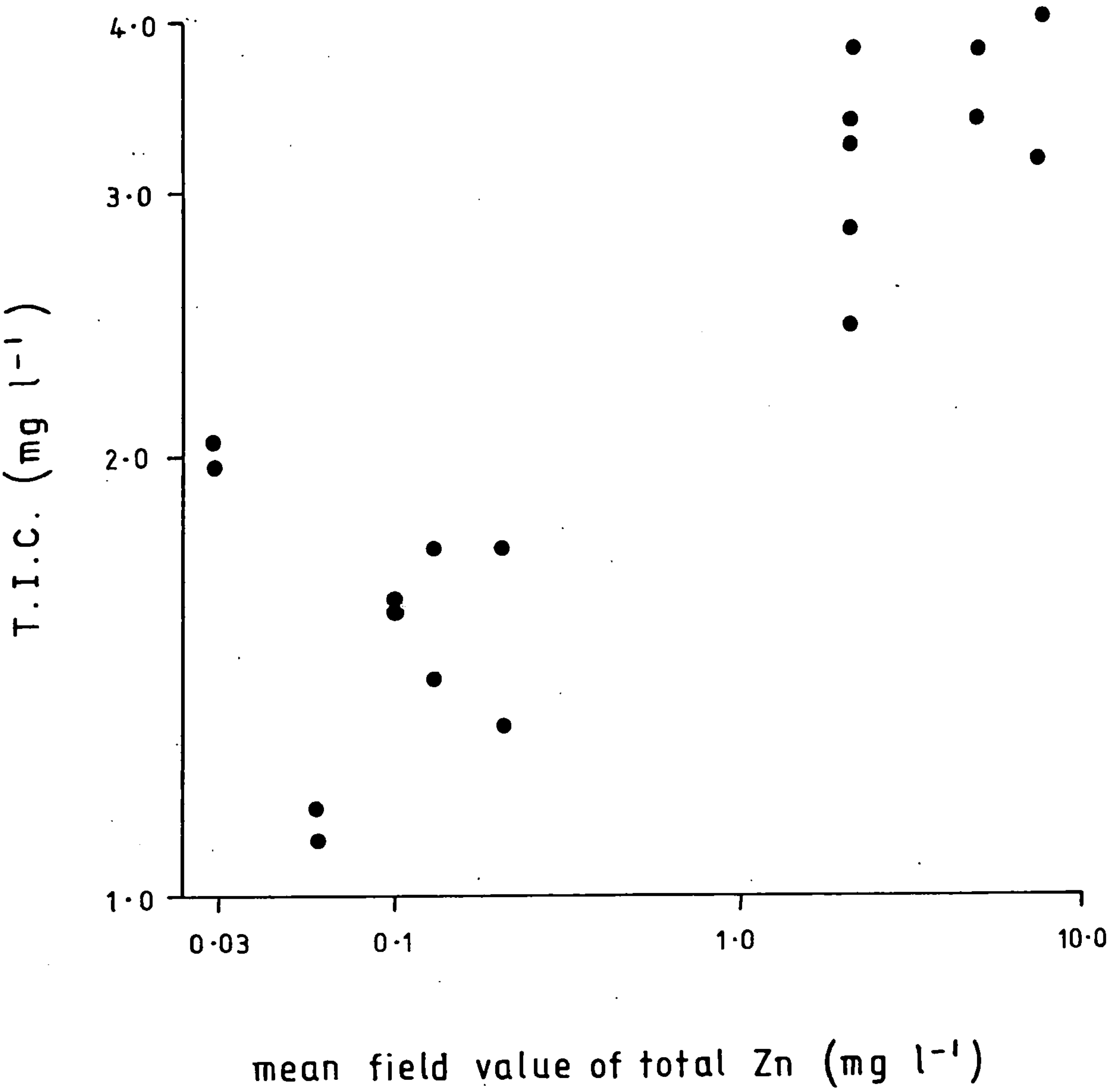

4·0
3·0
2·0
1·0
Zn (mg l⁻¹)
1200
1800
2400
0600
1200
time (h)

Figure 4.35 T.I.C. values for Stigeoclonium tenue plotted against mean total field Zn levels



4·0
3·0
2·0
1·0
T.I.C. (mg l⁻¹)
0·03
0·1
1·0
10·0
mean field value of total Zn (mg l⁻¹)

# CHAPTER 5

# DISCUSSION

# CHAPTER 5

# DISCUSSION

In the course of this study, water samples were collected along the length of the river on six separate occasions. Data obtained from their analysis provide an indication of the state of water at the chosen sites and the variation that can occur. In the months available for this project it was only possible to devote a limited amount of time to this aspect of water chemistry. Ideally, the river should be monitored regularly throughout all seasons and at various times of the day and night to detect variations.

Many papers have reported large variations of metal concentrations when a series of samples from a particular site on a river have been analysed. Downing and Edwards (1969) quote results for copper in a river that shows quite regular diurnal fluctuations with a maxima and minima of approximately 250 and 60 $\mu g\ l^{-1}$ Cu respectively; they do not state the reason for this behaviour, but it seems likely that an effluent discharge was involved. Grimshaw _et_ _al_. (1976) monitored the levels of dissolved zinc in the River Ystwyth and noted a range from 0.17 to 0.88 mg $l^{-1}$ and related this to discharge variation. They point out that the bulking of samples, infrequent sampling, and sampling without regard to the recording of discharges are inadvisable in such situations.

Several authors have also reported seasonal effects on the concentrations of trace metals (Silker, 1964; Pasternak and Antoniewicz, 1971), when, for example, concentrations would be highest at low flows (a "dilution" effect) and for brief periods during the initial stages of storm run off which Grimshaw _et_ _al_. (1976) term a "flushing" effect. Griffiths (1919) and Carpenter (1925) also note that metals may be weathered to a soluble form and "flushed" from spoil tips into rivers by rainfall after warm dry spells. Abdullah and Royle (1972), in a study of rivers and lakes in Wales, report that the concentrations of heavy metals could vary up to 60% from month to month.

Since the number of water surveys in this project on the River Team was limited, samples were not taken on days of heavy rainfall or when the river was in flood in order to avoid these effects and so obtain representative figures under conditions of moderate flow.

Analyses of water samples generally reveal that the river can be divided into two distinct stretches, at some point between sites 5 and 6. Concentrations of Cl, Fe, Mn, Zn and also values for conductivity and optical density are relatively stable from sites 1 - 5 but notably increase below Birtley where there is a far greater range in variability (see Chapter 4 Results). Corresponding changes can also be seen in the percentage saturation and concentration of $O_2$, the levels of which decrease markedly below Birtley as do the field pH and laboratory pH values. Phenomena such as these reflect the industrial and mining activity which both directly and indirectly affect the river. Although interactions between all variables in the system are extremely complex (as outlined in section 1.4) and over-simplification should be avoided, there are some over-riding influences from industrial works and mines mentioned in Chapter 3 and summarized in Figure 3.2, and attention is drawn to these.

Main influences in the upper stretch of the river from mine water, tip drainage and East Tanfield sewage works occur between sites 2 and 3 and these effects are reflected in increases in the pH (see Figures 4.3 and 4.4), the total alkalinity (see Figure 4.5) and the conductivity (Figure 4.6) caused by the addition of ions and suspended material to the water. The optical density has already increased at Tantobie prior to the effluents mentioned above joining the river (Figures 4.7

and 4.8), but this is most likely due to the nature of the sandy substrate at this site overlying dark silty material which is easily disturbed.

A distinguishing feature in the concentration of phosphate along the river, is the very marked increase and peak at Beamish where the greatest variability and the maximum concentration of 2.5 mg $l^{-1}$ P-$PO_4$ was detected (see Figure 4.10). This higher concentration can be attributed to effluent from the East Tanfield sewage works. Furthermore there are no notable increases in the metal concentrations in the upper stretch of the river, other than a slight rise in the concentration of manganese, suggesting that effects from the minewater and tip drainage are negligible. However it is not known whether samples were taken at times when pumping did not occur. It is possible that discharge from the sewage works might physically dilute the elements introduced from tip and mine water, as well as having some chemical effect by causing metals to form complexes with organic compounds present in the sewage water and being precipitated out in the sediments, so reducing the amount actually dissolved in the water, (see Section 1.4). It has however, been confirmed (J.L.Carslake, N.C.B., pers.comm.) that the effects of minewater on the River Team from East Tanfield, Marley Hill, and Blackburn Fell collieries are virtually negligible, especially when compared to that pumped from Kibblesworth where iron staining is very obvious (see Figure 3.14) and the effects that industrial effluents have on the chemistry of the water in the lower stretch of the river.

Levels of calcium and magnesium are very high at all sites, approximately 80-120 mg $l^{-1}$ and 25-40 mg $l^{-1}$ respectively (there is little difference in each case between the filtered values and the total values), because of the magnesium limestone occurring in this area (Section 3.1). The graphs of calcium and magnesium (Figures 4.11, 4.12, 4.13 and 4.14) follow much the same trend and mean values are relatively stable for the length of the river. Slight increases between sites 2 - 3 and sites 5 - 6 might be a result of mining activity exposing greater amounts of magnesium limestone and leaching of this rock will introduce more magnesium and calcium into the water.

In the case of other metals, for example, iron and zinc (Figures 4.15 and 4.16, 4.19 and 4.20 respectively), there are greater differences between the concentrations of metal found in the filtered water samples and those determined from the total water samples, suggesting that a larger proportion of these metals may have formed complexes with other compounds, many of which may be unable to pass through the 0.2 μm Nuclepore filter (Section 2.113). However, it should be noted that there may be drawbacks in the use of filters which may lead to inaccuracies in the determination of metal concentrations:

(i) Water passed through the filter may become contaminated by impurities leached from the filter, or the filter could absorb ions or particles that are smaller than the pores (Marvin, Proctor and Neal, 1972).

(ii) The filter could gradually become blocked and this might result in changing rates of retention of particles during the filtering process (Hem, 1972).

(iii) Filters even with a small pore size may permit the passage of finely suspended particles (Kennedy, Zellweger and Jones, 1974).

(iv) Filtration may disturb equilibrium existing between types of metals present in the original sample of water (Wilson 1976).

When reviewing literature, it should also be noted that in addition to the above problems, authors have used different types of filter which may affect samples and results in some way and make comparisons more difficult (Standridge, 1976).

Between sites 5 and 6 there are often dramatic changes in the monitored factors of the river. The amount of oxygen present in the water declines from a mean of 13.0 mg $l^{-1}$ $O_2$ at site 5 to a mean of 5.7 mg $l^{-1}$ at the mouth because of industrial effluents released into the river and the effect they have on drastically reducing the amounts and types of photosynthetic organisms in the lower stretch.

Both laboratory and field pH's are the other factors which show a very marked decrease between sites 5 and 6 (see Figures 4.3 and 4.4), largely as a result of the minewater pumped at Kibblesworth. Water passes through mines and spoil heaps with a high content of $FeS_2$ (pyrite, marcasite or pyrrhotite), and these minerals are oxidised by the action of air, water and bacteria to produce $H_2SO_4$ which lowers the pH of the drainage water; (these phenomena have been noted by many authors, for example, Galbraith, Williams and Siems, 1972). The chemical reactions involved in the production of acid and the occurrence of acid streams have been reviewed by Hargreaves, 1977. Low pH may cause serious pollution problems in some rivers, but the water may carry high concentrations of heavy metals in solution which may subsequently pollute other bodies of water. Where oxygen is sufficient, $Fe^{2+}$ is oxidised to $Fe^{3+}$ which forms an insoluble hydroxide; this is clearly visible on the rocks below Kibblesworth mine discharge (Figure 3.14). Concentrations of iron in the water increase below site 5 as a result of mine drainage, (Figures 4.15 and 4.16), and the rise in manganese is also associated with this (Figures 4.17 and 4.18).

Concentrations of zinc in the minewater may contribute to the dramatic increase and peak of zinc at site 6 (Figures 4.19 and 4.20), but most of this heavy metal will come from industrial effluents being discharged into the river. Northumrian Water Authority quote concentrations of approximately 100 mg $l^{-1}$ Zn from Durham Chemical tip drainage. Durham Chemicals make a variety of products including both organic and inorganic chemicals, the chief products being zinc compounds, metal soaps and plasticisers. In a leaflet issued by the Durham Chemical Group, Birtley, Co. Durham (August, 1968), the principal products are listed as: zinc oxide, zinc dust and flake, zinc sulphate, zinc carbonate, Calamine, metal soaps, PVC stabilisers and plasticisers, lead silicate, cadmium-sulphide carbonate, antimony sulphide, "Chemlock" Adhesive and Bonding agents, Polytetrafluroethylene Unsintered Tape. Almost the entire output is used as raw materials by other manufacturing industries; principally the paint, rubber and plastic industries.

It would have been interesting to sample the water immediately below the Durham Chemicals and Royal Ordnance factory drain before the river receives inputs from Birtley sewage works and Kibblesworth minewater, as the latter two additions probably benefit the river by diluting the foul smelling industrial discharge which pollutes the water. Difficulties would have arisen in transporting the necessary sampling equipment to this area though, as it is away from the road.

Phosphate levels do not markedly increase at site 6 which is below Birtley sewage works as would initially be suspected, possibly because of the over-riding effects from industrial effluents and the interactions that could take place between the inorganic and organic compounds released into the water. Notable increases in the total alkalinity (Figure 4.5), the conductivity (Figure 4.6) and optical density (Figures 4.7 and 4.8) occur between sites 5 and 6 as would be expected as a result of the sewage effluent, industrial discharge and minewater input into the river at this point. The Team then has a short recovery period, receiving no further major effluents until it flows through the Industrial Trading Estate.

The range of concentrations of metals etc. is generally far greater in the lower stretch of the river than in the upper stretch where levels are usually steady, seen for instance in the cases of zinc (Figures 4.19 and 4.20), total iron (Figure 4.15), and chloride concentrations (Figure 4.9). This mainly results from the times at which the water samples are taken in relation to the times at which various industries discharge their effluent, although the amount of effluent released and the concentration of its components are also important factors. The former consideration was investigated at site 6 in a 24 h survey.

A notable increase in such factors as total alkalinity, conductivity, Cl, Fe, Mn and total Ca concentrations occurred at 2000 h. These elevated values remained well above the respective background levels which occurred at the beginning and end of the 24 h period. Generally, rapid decreases in the levels were observed ten hours later between 0600 and 0700 h, well shown for example in the cases of filtered and total Fe (Figure 4.32), the conductivity (Figure 4.26) and the total alkalinity (Figure 4.25). These corresponding trends indicate a period of time during which mine water was added to the river. It was observed that Kibblesworth was pumping mine water for the whole of the 24 h period, so presumably increased pumping took place between 2000 h and 0600 h when electricity rates would be cheaper.

A sharp peak appears in the zinc concentration (Figure 4.34) at 0700 h which is most probably caused by the release of industrial effluent from Durham Chemicals. The marked increase in zinc concentration immediately follows the decline in pumping at Kibblesworth, so it is plausible that the mine water had a diluting effect on industrial effluent that was probably already being discharged. However, the concentration of total zinc rapidly drops from 3.60 mg $l^{-1}$ at 0700 h to 2.20 mg $l^{-1}$ at 0800 h, and there was a gradual and progressive decline from 2.20 mg $l^{-1}$ Zn the previous afternoon when the survey commenced. If the minewater was to have a diluting effect at some stage, a sudden drop in the concentration of zinc would probably have been expected in the ten hour period of increased pumping, but this does not occur. It is therefore more likely that industrial effluent containing zinc was released at some time between 0600h - 0700 h.

A dramatic peak similarly occurs in the concentration of phosphate, but at 0900 h (Figure 4.29). Assuming that the sample had not been contaminated, the result is quite feasible, as one would expect a greater pressure on household water resources in the morning. Pressure is placed on sewage works when people are active and this is reflected in the levels of phosphate which are higher throughout the day when the majority of the population are working, and gradually declines to the lower levels recorded in the night.

Monitoring at regular periods throughout a day therefore shows changes that take place within the system and reveals the wide range of metal concentrations etc. that can be experienced within a short time period. This should be borne in mind when quoted values are based on a few or only single collections, which take no account of temporal variations caused by discharge, seasonal or diurnal fluctuations or changing inputs from artificial sources.

Thornton and Webb (1973) have suggested that the analysis of stream sediments may provide a more stable index of the long term trace element status of a catchment than can be obtained by periodic sampling of the water itself.

The zinc content of the sediment samples taken from the river bed are higher at sites 6, 7, 8 and 9 than those collected from the upper sites. A sudden increase occurs between sites 5 and 6 (see Figure 4.21)

The difference between zinc content of the water and sediments is that in the case of the latter, the zinc content continues to increase from site 6 to the mouth, whereas the zinc content of the water peaks at site 6 (Figures 4.19 and 4.20). The major input of zinc occurs between sites 5 and 6, and as it forms complexes and gradually precipitates further downstream onto the river bed increasing the proportion present in the sediment, so the amount actually present in the water will be reduced.

The size of particles in sediments may have a marked effect on the binding of heavy metals, and this consideration is stressed by several authors such as Perhac (1972); Oliver (1973) reported that higher concentrations of zinc and lead were accumulated by fine grained sediments in the Ottawa River than by coarser particles, and this was also found by Jaffe and Walters (1975) working on the Humber estuary. Results might therefore have been slightly different if other sieves had been used in this project (Section 2.23).

Results from this study indicate that the distribution and types of species present in the Team also support the observation based on water analysis, that the upper section of the river is relatively uncontaminated when compared to the more polluted stretch below Birtley. The use of specific organisms as indicators of pollution was proposed by Forbes in 1913, who remarked that biological observations are more dependable in certain ways than chemical determinations since they show cumulative effects of the past and present conditions, while chemical tests apply only to the moment of sampling (Section 1.6).

A greater variety of plants and animals were found in the upper stretch (see Table 3.1). Although these results are not quantitative it was apparent that the number of individuals were more abundant in this section. Stonefly and mayfly nymphs for example, were restricted to the upper five sites, and they are taken by the Northumbrian River Authority Annual Report 1973, to be indicative of water classified as "clean" by chemical analysis. It is felt that mayflies can be excellent indicators of water quality because of their relatively long life cycle and their low mobility which does not enable them to escape toxic materials. Thus their presence in otherwise suitable habitats reflects the quality of the water which flows over them.

It should be noted however, that there may be some populations of a species which may be able to tolerate forms of pollution to a greater extent than other strains within the species (Section 1.6). Jones (1940) for instance found that stoneflies, mayflies and some chironomids were resistant to both lead and zinc pollution, and were found living in water containing nearly 60 mg $l^{-1}$ Zn. Observations of this kind immediately incite suspicions as to the reliability of organisms used in classifying the state of an environment and make the concept of biological indicators rather questionable. Therefore if organisms are to be used as indicator species a great deal of knowledge is obviously required about the ecological tolerances and requirements of the species on a seasonal and diurnal basis as well as adaptations for resisting acute and chronic pollutants. Different stages in an lifecycle may possibly have varying degrees of tolerance; for instance, Anderson (1950) found Daphnia magna to be most sensitive to heavy metals at the moulting stage, and suggested that this might apply to arthropods generally as the body is more permeable then. Alternatively, the organism may have its development suppressed and be restricted to a certain stage in its life cycle, as occurs for instance in the case of bryophytes being restricted to the protonema stage and Stigeoclonium tenue existing in the basal filament form only; (this latter point will be discussed later in more detail). This may cause confusion and difficulty in the identification of species. Another feature which may also cause problems in using organisms as indicators of pollution, is that the phenotype may be plastic and the actual morphology of the organism may alter appreciably under different environmental conditions so that a single species could assume alternative characteristics causing its appearance to be distinct from the more usual form. Confusion might therefore arise in identification as the phenotype may perhaps more closely resemble an alternative species described by taxonomic keys and consequently be incorrectly named.

Indicator species of particular biotypes should be widespread and numerous, possibly more so than in any other biotypes. In many cases species may be absent not because of the direct effects of pollution, but because the habitat is unfavourable or suitable food is absent. For instance the reduced amount and variety of plant and animal species at Tantobie (see Table 3.1) is most probably caused by the lack of suitable habitats. The sandy streambed forms an unstable substrate which is unfavourable for plant attachment and there is little protective cover for animals, so the fauna comprises mostly of burrowing types.

The tolerance that various species of algae show to heavy metal pollution has already been discussed in section 1.52; and attention has been drawn to the use of Stigeoclonium tenue as an indicator species (Section 1.6). This species was found at all sites with the exception of the mouth, indicating its tolerance of heavy metal pollution and organic pollution. Results obtained from the toxicity tests on S. tenue to zinc indicate that the populations found growing below Birtley could tolerate higher concentrations of zinc than those living in the upper stretch of the river where the environmental concentration of zinc was lower (Table 4.10 and Figure 4.35). There therefore appears to be different strains of S. tenue in the River Team. The mean tolerance index concentration determined for the zinc-sensitive populations growing in the upper stretch was 1.55 mg $l^{-1}$ Zn, compared to 3.36 mg $l^{-1}$ Zn calculated for the zinc-tolerant populations found in the lower stretch of the river. The phenomenon of tolerant and sensitive strains occurring within a single species has also been reported by many authors. Whitton (1970a) compared the tolerance to zinc in laboratory cultures of populations of _S. tenue_ isolated from several freshwater environments and noted apparently slightly greater resistance to the metal in a population from an effluent rich in zinc. Rajendran (1975) demonstrated further examples of enhanced resistance to zinc in populations of this alga collected from zinc-polluted streams draining the Northern Pennine Orefield. Tolerant and sensitive strains of _S. tenue_ were also found by Harding (1977) who suggested that the enhanced tolerance was the result of genetic adaptation as the level of tolerance remained unchanged in both a zinc-sensitive and a zinc-tolerant population after six months of culturing in media with different concentrations of zinc. Attention has also been drawn to investigations of a similar nature into other species, especially _Hormiduim_ spp., in sections 1.6 and 1.7.

The only filamentous alga found at the mouth was _Ulothrix_ sp., a small amount of which occurred for a short time only. The T.I.C. determined for this population was low, 0.61 mg $l^{-1}$ Zn; yet for a short time the alga survived at the mouth where the mean concentration of total zinc was 3.38 mg $l^{-1}$ Zn and the mean concentration of filtered zinc was 1.26 mg $l^{-1}$. The T.I.C. determined for this population is therefore unusual in that it is much lower than the field concentrations of zinc. Research previously mentioned in the discussion and sections 1.6 and 1.7 generally reveals that the T.I.C. is often greater than the field concentrations of zinc. This study for example, has shown that the populations of _Stigeoclonium tenue_ growing in the upper sites had T.I.C.s between 1.10 - 2.06 mg $l^{-1}$ Zn. These values are considerably higher than the mean field concentrations of total zinc which ranged from 0.03 - 0.21 mg $l^{-1}$ Zn in the upper stretch. Possible suggestions to explain this peculiar phenomenon of such a low T.I.C. shown by a population of Ulothrix sp. living in a zinc polluted environment are considered.

(i) The small amount of alga survived only for a short time at the mouth. It is therefore possible that it had grown when the environmental concentration of zinc was lower than that indicated from water surveys.
It has previously been stressed both earlier in the discussion and in Chapter 1 that periodic sampling of the water for chemical analyses often do not take into account seasonal and diurnal fluctuations or the variations in discharge from industries. The mean concentrations of zinc were based on samples of water collected from the mouth on only six separate occasions. It is feasible that these samples may have been collected when the zinc concentration was relatively high. There could therefore be periods of time when the level was lower and the population of Ultothrix sp. had an opportunity to become established.

(ii) Another consideration to explain the extremely low T.I.C. of the population of Ulothrix sp. is that the experimental culture medium is not identical to the field environment. The alga is therefore subjected to different conditions. The organic content and phosphate concentrations are higher in the field for instance. Levels of calcium are also high in the Team. In a study of the resistance of Stigeoclonium tenue to zinc, Harding and Whitton (1976) found that for sites with high calcium levels, the species were less tolerant to a particular level of zinc than were populations from sites with low calcium levels. This factor may therefore influence the level at which zinc can no longer be tolerated by the alga. Field and laboratory studies have shown that the level of other metals etc. may influence the toxicity of any particular metal (Sections 1.4 and 1.7).

In the field, the alga at the mouth is also subjected to tidal influences, so regularly experiences great changes in the environment when sea water mixes with the river water. The chemistry of the water therefore changes considerably. The alga also experiences physical changes in the field environment, for example the depth at which it is submerged. Such changes obviously do not occur in the laboratory.

Another consideration is that the concentration of zinc in the culture medium will decrease from its original level as the algal filaments may accumulate a proportion of the zinc and some may also be bound to the cell membranes. At the end of the seven day incubation period the culture medium in a few tubes was analysed for zinc content on the atomic absorption spectrophotometer, and the reduced zinc concentration was verified.

The fact that the alga is subjected to different conditions is probably the more likely consideration.

However, filaments of Ulothrix sp. in the control tubes did appear to be healthy and showed some growth at the end of the seven day incubation period. Unfortunately assessment of growth was not quantitative since methods involved in the measurement of growth would have been excessively time consuming and impractical under the circumstances. Therefore scores were awarded by visually assessing the appearance and the amount of alga present, and making comparisons between tubes controls (Section 2.332). Although this is subjective it seems to be a suitable and practical method of assessing the degree of tolerance shown by the algae.

Further observations on *S. tenue* revealed that at the end of the seven day incubation period (Section 2.332), long branched erect filaments predominated in the controls, whereas the algae capable of surviving at the higher zinc levels had a greater proportion of twisted basal filaments composed of swollen cells with a few short branches, having a "knobbly" appearance. Concentrations of zinc that brought about a marked reduction in total growth during assay therefore had a greater effect on the erect part of the thallus than on the basal system. This fact is in accordance with observations made by Harding (1977). In the field at sites 6 and 7 it was observed that *S. tenue* was virtually restricted to this basal form; only occasionally did very short erect filaments develop. At the lower levels of zinc some release of zoospores occurred from the erect filaments, followed by settling and germination on the walls of the tubes. Harding (1977) reported that the maximum levels at which settling of zoospores occurred were rather similar to the T.I.C. This was in agreement with populations found in the upper stretch of the river, but for the more tolerant populations zoospores tended to settle and develop at higher levels.

# SUMMARY

# SUMMARY

Chemical analyses of the water and sediments at nine sites on the River Team revealed that the upper stretch of the river was relatively uncontaminated in comparison with the highly polluted lower stretch below Birtley.

Concentrations of total zinc between 0.01 - 0.31 mg $l^{-1}$ were recorded in the upper stretch, compared with concentrations of 1.5 - 28.6 mg $l^{-1}$ in the lower stretch. Sediments contained zinc concentrations between 364 - 1083 µg $g^{-1}$ for samples collected at the upper sites, whereas those collected from the lower sites had zinc concentrations between 917 - 8167 µg $g^{-1}$. Durham Chemicals was the main source of pollution. This firm produces a variety of zinc-based products which are used by other industries.

Although very high levels of zinc do occur in the River Team, it is not the only important form of pollution. Other forms include pumped mine water and also organic pollution from sewage works. Up to 2.5 mg $l^{-1}$ P-$PO_4$ was recorded at Beamish and is attributed to effluent from East Tanfield sewage works. Levels of P-$PO_4$ for the rest of the river were between 0.01 - 1.10 mg $l^{-1}$.

It was observed that the variety of organisms found in the lower stretch of the river below the major sources of pollution, was very much reduced. Biological evidence therefore supports the observation that the upper stretch is relatively uncontaminated when compared to the lower stretch below Birtley. Attention is drawn to the effects that pollution, especially that caused by heavy metals, can have on organisms. The use of organisms as biological indicators of pollution is discussed, and their advantages and disadvantages are considered.

The results of toxicity tests performed in the laboratory demon-

strated that *Stigeoclonium tenue* growing at the higher concentrations of zinc found in the field had a greater resistance to the metal than populations growing in the lower concentrations of zinc. At the lower sites where mean values of total zinc ranged from 2.07 - 7.18 mg $1^{-1}$ Zn, the tolerance index concentrations (T.I.C. ) of populations of *S. tenue* were found to be between 2.43 - 4.02 mg $1^{-1}$ Zn. In the upper sites where mean values of total zinc ranged from 0.03-0.21 mg $1^{-1}$ Zn, the T.I.C. of populations of *S. tenue* were found to be 1.10 - 2.06 mg $1^{-1}$ Zn. Concentrations of zinc that brought about a marked reduction in growth during assay had a greater effect on the erect part of the thallus than on the basal form at the two sites below the major sources of pollution.

A species of *Ulothrix* collected from the mouth and assayed was found to show relatively poor resistance to zinc, having a T.I.C of only 0.61 mg $1^{-1}$ Zn. The mean concentration of total zinc at this site was 3.38 mg $1^{-1}$ Zn and the mean concentration of filtered zinc was 1.26 mg $1^{-1}$. The T.I.C. determined for this population is therefore unusual in that it is much lower than the field concentrations of zinc. Various explanations are suggested to account for this pe~~r~~culiar phenomenon.

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# APPENDIX

| Date | time | temp. | $O_2$ |  | field | lab. | tot. alk. | cond. | O.D. |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | (h) | ($^{o}C$) | (% sat.) | (mg $1^{-1}$) | pH | pH | (mg $1^{-1}$ $CaCO_3$) | (μmhos) | 240nm | 254nm |
| 190579 | 1130 | 9.0 | 105 | 11.8 | 7.8 | 7.4 | 102 | 950 | - | - |
| 010679 | 1200 | 12.0 | 104 | 11.0 | 7.4 | 7.3 | 86 | 1060 | 0.04 | 0.04 |
| 050679 | 1215 | 12.0 | 120 | 12.5 | 7.7 | 7.4 | 100 | 1180 | 0.12 | 0.09 |
| 190679 | 1030 | 12.0 | 117 | 12.4 | 7.5 | 7.8 | 126 | 1140 | 0.04 | 0.03 |
| mean |  | 11.3 | 112 | 11.9 | 7.6 | 7.5 | 104 | 1083 | 0.07 | 0.05 |
| s.d. |  | 1.5 | 8 | 0.7 | 0.2 | 0.2 | 17 | 101 | 0.05 | 0.03 |

| date | Cl | $P-PO_4$ | Ca (mg $1^{-1}$) |  | Mg (mg $1^{-1}$) |  | Fe (mg $1^{-1}$) |  | Mn (mg $1^{-1}$) |  | Zn (mg $1^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | (mg $1^{-1}$) | (mg $1^{-1}$) | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil |
| 190579 | 54 | 0.02 | 106.0 | 106.0 | 41.0 | 40.0 | 1.07 | 0.23 | - | - | 0.07 | 0.08 |
| 010679 | 41 | 0.01 | 63.0 | 69.4 | 25.6 | 28.4 | 0.40 | 0.08 | 0.36 | 0.33 | 0.04 | 0.01 |
| 050679 | 55 | 0.04 | 86.0 | 76.6 | 34.0 | 34.8 | 0.42 | 0.10 | 0.39 | 0.40 | 0.06 | 0.04 |
| 190679 | 60 | 0.01 | 95.2 | 87.8 | 46.0 | 40.8 | 0.36 | 0.15 | 0.53 | 0.48 | 0.08 | (0.10) |
| mean | 53 | 0.02 | 87.6 | 85.0 | 36.7 | 36.0 | 0.56 | 0.14 | 0.43 | 0.40 | 0.06 | 0.04 |
| s.d. | 8 | 0.02 | 18.3 | 16.0 | 8.9 | 5.7 | 0.34 | 0.07 | 0.09 | 0.08 | 0.02 | 0.03 |

SITE 1 - KYO

| Date | time (h) | temp. ($^{o}C$) | $O_2$ (% sat.) | $O_2$ (mg $l^{-1}$) | field pH | lab. pH | tot. alk. (mg $l^{-1}$ $CaCO_3$) | cond. (µmhos) | O.D. 240nm | O.D. 254nm |
|---|---|---|---|---|---|---|---|---|---|---|
| 190579 | 1200 | 9.5 | 82 | 8.9 | 7.7 | 7.2 | 104 | 810 | - | - |
| 010679 | 1245 | 14.0 | 109 | 11.0 | 7.3 | 7.2 | 82 | 920 | 0.14 | 0.11 |
| 050679 | 1130 | 13.0 | 115 | 11.8 | 7.6 | 7.4 | 91 | 1070 | 0.17 | 0.14 |
| 190679 | 1100 | 17.0 | 148 | 14.0 | 8.1 | 8.0 | 114 | 1160 | 0.15 | 0.14 |
| mean | | 13.4 | 114 | 11.4 | 7.7 | 7.5 | 98 | 990 | 0.15 | 0.13 |
| s.d. | | 3.1 | 27 | 2.1 | 0.3 | 0.4 | 14 | 156 | 0.02 | 0.02 |

| Date | Cl (mg $l^{-1}$) | $P-PO_4$ (mg $l^{-1}$) | Ca (mg $l^{-1}$) tot. | Ca (mg $l^{-1}$) fil. | Mg (mg $l^{-1}$) tot. | Mg (mg $l^{-1}$) fil. | Fe (mg $l^{-1}$) tot. | Fe (mg $l^{-1}$) fil. | Mn (mg $l^{-1}$) tot. | Mn (mg $l^{-1}$) fil. | Zn (mg $l^{-1}$) tot. | Zn (mg $l^{-1}$) fil. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 190579 | 75 | 0.45 | 80.0 | 70.0 | 25.0 | 22.0 | 0.55 | 0.18 | - | - | 0.06 | 0.04 |
| 010679 | 40 | 0.07 | 62.0 | 77.6 | 21.2 | 23.2 | 0.50 | 0.10 | 0.27 | 0.24 | 0.01 | 0.01 |
| 050679 | 52 | 0.08 | 66.0 | 67.6 | 26.2 | 26.0 | 0.46 | 0.10 | 0.31 | 0.31 | 0.02 | 0.02 |
| 190679 | 47 | 0.03 | 77.6 | 73.2 | 33.8 | 31.6 | 0.59 | 0.09 | 0.32 | 0.32 | 0.02 | 0.04 |
| mean | 54 | 0.16 | 71.4 | 72.1 | 26.6 | 25.7 | 0.53 | 0.12 | 0.30 | 0.29 | 0.03 | 0.03 |
| s.d. | 15 | 0.20 | 8.8 | 4.3 | 5.3 | 4.3 | 0.06 | 0.04 | 0.03 | 0.04 | 0.02 | 0.02 |

SITE 2 - TANTOBIE

| Date | time | temp. | $O_2$ | | field | lab | tot. alk. | cond. | O.D. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (h) | ($^oC$) | (% sat.) | (mg $l^{-1}$) | pH | pH | (mg $l^{-1}$ $CaCO_3$) | (μmhos) | 240nm | 254nm |
| 090579 | 1900 | 9.0 | 103 | 11.6 | 7.7 | 7.6 | 146 | 910 | - | - |
| 190579 | 1245 | 10.5 | 117 | 12.2 | 8.3 | 8.0 | 237 | 1280 | - | - |
| 010679 | 1315 | 13.0 | 112 | 11.6 | 8.0 | 7.9 | 200 | 1530 | 0.13 | 0.08 |
| 050679 | 1045 | 13.0 | 95 | 9.7 | 7.9 | 7.6 | 199 | 1650 | 0.19 | 0.13 |
| 190679 | 1145 | 15.0 | 107 | 10.6 | 7.7 | 8.1 | 254 | 1650 | 0.14 | 0.11 |
| mean | | 12.1 | 107 | 11.1 | 7.9 | 7.8 | 207 | 1404 | 0.15 | 0.11 |
| s.d. | | 2.4 | 8 | 1.0 | 0.2 | 0.2 | 42 | 315 | 0.03 | 0.03 |

| Date | Cl | $P-PO_4$ | Ca (mg $l^{-1}$) | | Mg (mg $l^{-1}$) | | Fe (mg $l^{-1}$) | | Mn (mg $l^{-1}$) | | Zn (mg $l^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (mg $l^{-1}$) | (mg $l^{-1}$) | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. |
| 090579 | 39 | 0.49 | 102.0 | 92.0 | 29.0 | 27.6 | - | - | - | - | 0.31 | 0.29 |
| 190579 | 78 | 0.14 | 134.0 | 130.0 | 44.0 | 43.0 | 0.36 | 0.07 | - | - | 0.25 | 0.22 |
| 010679 | 57 | 0.38 | 105.0 | 100.0 | 39.4 | 34.2 | 0.43 | 0.10 | 0.33 | 0.34 | 0.10 | 0.06 |
| 050679 | 73 | 0.86 | 105.4 | 104.6 | 37.6 | 36.6 | 0.49 | 0.18 | 0.50 | 0.44 | 0.24 | 0.17 |
| 190679 | 63 | 2.50 | 118.6 | 108.4 | 41.8 | 39.4 | 0.47 | 0.10 | 0.34 | 0.31 | 0.14 | (0.71) |
| mean | 62 | 0.87 | 113.0 | 107.0 | 38.4 | 36.2 | 0.44 | 0.11 | 0.39 | 0.36 | 0.21 | 0.19 |
| s.d. | 15 | 0.95 | 13.4 | 14.2 | 5.8 | 5.8 | 0.06 | 0.05 | 0.10 | 0.07 | 0.09 | 1.00 |

SITE 3 - BEAMISH

| Date | time (h) | temp. ($^{o}$C) | $O_2$ (% sat.) | $O_2$ (mg $l^{-1}$) | field pH | lab. pH | tot. alk. (mg $l^{-1}$ $CaCO_3$) | cond. (μmhos) | O.D 240nm | O.D 254nm |
|---|---|---|---|---|---|---|---|---|---|---|
| 090579 | 1830 | 9.0 | 103 | 11.6 | - | 7.8 | 136 | 790 | - | - |
| 190579 | 1400 | 10.2 | 121 | 13.2 | 8.4 | 8.1 | 190 | 1450 | - | - |
| 010679 | 1415 | 14.0 | 109 | 11.0 | 7.9 | 7.7 | 180 | 1510 | 0.15 | 0.08 |
| 050679 | 1330 | 14.0 | 109 | 10.9 | 8.1 | 7.7 | 215 | 1800 | 0.17 | 0.11 |
| 190679 | 1215 | 15.0 | 112 | 10.9 | 8.2 | 8.1 | 282 | 2050 | 0.09 | 0.08 |
| mean | | 12.4 | 111 | 11.5 | 8.2 | 7.9 | 201 | 1520 | 0.14 | 0.09 |
| s.d. | | 2.7 | 7 | 1.0 | 0.2 | 0.2 | 54 | 474 | 0.04 | 0.02 |

| Date | Cl (mg $l^{-1}$) | $P-PO_4$ (mg $l^{-1}$) | Ca (mg $l^{-1}$) tot. | Ca (mg $l^{-1}$) fil. | Mg (mg $l^{-1}$) tot. | Mg (mg $l^{-1}$) fil. | Fe (mg $l^{-1}$) tot. | Fe (mg $l^{-1}$) fil. | Mn (mg $l^{-1}$) tot. | Mn (mg $l^{-1}$) fil. | Zn (mg $l^{-1}$) tot. | Zn (mg $l^{-1}$) fil. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 090579 | 54 | 0.30 | 92.0 | 84.0 | 28.0 | 25.4 | - | - | - | - | 0.29 | 0.23 |
| 190579 | 76 | 0.49 | 128.0 | 128.0 | 42.0 | 43.0 | 0.36 | 0.07 | - | - | 0.12 | 0.08 |
| 010679 | 60 | 0.32 | 102.0 | 102.0 | 39.2 | 34.6 | 0.55 | 0.09 | 0.50 | 0.43 | 0.06 | 0.04 |
| 050679 | 65 | 0.39 | 112.8 | 110.6 | 42.8 | 40.6 | 0.48 | 0.12 | 0.57 | 0.56 | 0.10 | 0.02 |
| 190679 | 55 | 1.06 | 138.8 | 115.6 | 47.8 | 43.0 | 0.36 | 0.10 | 0.45 | 0.39 | 0.07 | 0.09 |
| mean | 62 | 0.51 | 114.7 | 108.0 | 40.0 | 37.3 | 0.44 | 0.10 | 0.51 | 0.46 | 0.13 | 0.09 |
| s.d. | 9 | 0.32 | 19.0 | 16.4 | 7.4 | 7.5 | 0.09 | 0.02 | 0.06 | 0.09 | 0.09 | 0.08 |

SITE 4 - URPETH

| Date | time (h) | temp. ($^{o}C$) | $O_2$ (% sat.) | $O_2$ ($mg\ l^{-1}$) | field pH | lab. pH | tot. alk. ($mg\ l^{-1}\ CaCO_3$) | cond. ($\mu$mhos) | O.D. 240nm | O.D. 254nm |
|---|---|---|---|---|---|---|---|---|---|---|
| 250479 | 1500 | 7.8 | 110 | 12.8 | - | 7.8 | - | 1210 | 0.09 | 0.02 |
| 090579 | 1750 | 9.2 | 104 | 11.6 | 7.9 | 7.4 | 118 | 760 | - | - |
| 190579 | 1500 | 11.5 | 138 | 14.6 | 8.5 | 8.3 | 183 | 1480 | - | - |
| 010679 | 1745 | 14.0 | 115 | 11.5 | 8.2 | 7.9 | 196 | 1510 | 0.17 | 0.08 |
| 050679 | 1430 | 15.7 | 136 | 13.1 | 8.3 | 6.8 | 203 | 1750 | 0.16 | 0.10 |
| 190679 | 1300 | 18.5 | 158 | 14.4 | 8.5 | 8.7 | 240 | 1600 | 0.14 | 0.11 |
| mean |  | 12.8 | 127 | 13.0 | 8.3 | 7.8 | 188 | 1385 | 0.14 | 0.08 |
| s.d. |  | 4.1 | 21 | 1.3 | 0.2 | 0.7 | 45 | 354 | 0.04 | 0.04 |

| Date | Cl ($mg\ l^{-1}$) | $P-PO_4$ ($mg\ l^{-1}$) | Ca ($mg\ l^{-1}$) tot. | Ca ($mg\ l^{-1}$) fil. | Mg ($mg\ l^{-1}$) tot. | Mg ($mg\ l^{-1}$) fil. | Fe ($mg\ l^{-1}$) tot. | Fe ($mg\ l^{-1}$) fil. | Mn ($mg\ l^{-1}$) tot. | Mn ($mg\ l^{-1}$) fil. | Zn ($mg\ l^{-1}$) tot. | Zn ($mg\ l^{-1}$) fil. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 250479 | 57 | 0.30 | 128.0 | 114.0 | 42.0 | 40.0 | - | - | - | - | 0.15 | 0.13 |
| 090579 | 30 | 0.20 | 86.0 | 78.0 | 24.4 | 23.0 | - | - | - | - | 0.24 | 0.27 |
| 190579 | 59 | 0.32 | 114.0 | 112.0 | 39.0 | 38.0 | 0.45 | 0.11 | - | - | 0.08 | 0.05 |
| 010679 | 57 | 0.25 | 102.0 | 104.0 | 34.2 | 35.2 | 0.57 | 0.13 | 0.42 | 0.41 | 0.04 | 0.04 |
| 050679 | 65 | 0.36 | 105.0 | 112.8 | 37.4 | 40.4 | 0.38 | 0.14 | 0.51 | 0.50 | 0.05 | 0.03 |
| 190679 | 65 | 0.10 | 113.2 | 104.0 | 40.6 | 37.6 | 0.45 | 0.14 | 0.36 | 0.32 | 0.06 | 0.04 |
| mean | 56 | 0.26 | 108.0 | 104.1 | 36.3 | 35.7 | 0.46 | 0.13 | 0.43 | 0.41 | 0.10 | 0.09 |
| s,d, | 13 | 0.09 | 14.1 | 13.5 | 6.4 | 6.5 | 0.08 | 0.01 | 0.08 | 0.09 | 0.08 | 0.09 |

SITE 5 - ABOVE BIRTLEY

| Date | time (h) | temp. ($^oC$) | $O_2$ (% sat.) | $O_2$ (mg $l^{-1}$) | field pH | lab. pH | tot. alk. (mg $l^{-1}$ $CaCO_3$) | cond. (μmhos) | O.D. 240nm | O.D. 254nm |
|---|---|---|---|---|---|---|---|---|---|---|
| 250479 | 1445 | 11.0 | 109 | 11.8 | - | 7.0 | - | 3500 | 0.23 | 0.12 |
| 090579 | 1515 | 11.0 | 98 | 10.5 | 7.4 | 7.3 | 253 | 2250 | - | - |
| 190579 | 1530 | 14.0 | 115 | 10.4 | 7.3 | 7.1 | - | 4400 | - | - |
| 010679 | 1715 | 15.5 | 103 | 10.5 | 7.2 | 7.0 | 360 | 4400 | 0.32 | 0.19 |
| 050679 | 1515 | 17.0 | 103 | 9.4 | 7.2 | 6.9 | 382 | 4850 | 0.35 | 0.26 |
| 190679 | 1345 | 20.0 | 122 | 10.8 | 8.0 | 8.1 | 197 | 2250 | 0.34 | 0.25 |
| mean | | 14.8 | 108 | 10.6 | 7.4 | 7.2 | 298 | 3608 | 0.31 | 0.21 |
| s.d. | | 3.5 | 9 | 0.8 | 0.3 | 0.4 | 88 | 1140 | 0.05 | 0.06 |

| Date | Cl (mg $l^{-1}$) | $P-PO_4$ (mg $l^{-1}$) | Ca (mg $l^{-1}$) tot. | Ca fil. | Mg (mg $l^{-1}$) tot. | Mg fil. | Fe (mg $l^{-1}$) tot. | Fe fil. | Mn (mg $l^{-1}$) tot. | Mn fil. | Zn (mg $l^{-1}$) tot. | Zn fil. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 250479 | 230 | 0.21 | 130.0 | 130.0 | 39.6 | 40.0 | - | - | - | - | 3.90 | 3.62 |
| 090579 | 227 | 0.12 | 110.0 | 104.0 | 30.6 | 29.2 | - | - | - | - | 2.60 | 2.01 |
| 190579 | 600 | 0.20 | 136.0 | 136.0 | 42.0 | 46.0 | 2.60 | 0.90 | - | - | 1.68 | 1.35 |
| 010679 | 560 | 0.11 | 135.0 | 114.2 | 44.4 | 39.0 | 2.10 | 0.14 | 0.64 | 0.60 | 2.65 | 2.23 |
| 050679 | 550 | 0.10 | 118.0 | 114.6 | 41.4 | 40.2 | 2.40 | 0.12 | 0.66 | 0.66 | 28.60 | 25.90 |
| 190679 | 62 | 0.78 | 108.0 | 93.0 | 33.4 | 31.0 | 0.39 | 0.08 | 0.38 | 0.31 | 3.67 | 0.66 |
| mean | 372 | 0.25 | 122.8 | 115.3 | 38.6 | 37.6 | 1.87 | 0.11 | 0.56 | 0.52 | 7.18 | 5.96 |
| s.d. | 226 | 0.26 | 12.5 | 15.9 | 5.4 | 6.3 | 1.01 | 0.03 | 0.16 | 0.19 | 10.50 | 9.82 |

SITE 6 - BELOW BIRTLEY

| Date | time | temp. | $O_2$ | | field | lab. | tot. alk. | cond. | O.D. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (h) | (°C) | (% sat.) | (mg $l^{-1}$) | pH | pH | (mg $l^{-1}$ $CaCO_3$) | (μmhos) | 240nm | 254nm |
| 250479 | 1415 | 11.0 | 101 | 11.0 | - | 6.9 | - | 3400 | 0.17 | 0.08 |
| 090579 | 1445 | 10.0 | 90 | 9.8 | 7.3 | 7.3 | 240 | 2050 | - | - |
| 190579 | 1615 | 14.0 | 98 | 9.9 | 7.6 | 7.3 | - | 4400 | - | - |
| 010679 | 1645 | 15.5 | 98 | 9.5 | 7.2 | 7.0 | 352 | 4180 | 0.23 | 0.16 |
| 050679 | 1615 | 17.0 | 82 | 7.7 | 7.5 | 7.1 | 345 | 4600 | 0.31 | 0.27 |
| 190679 | 1430 | 20.0 | 96 | 8.5 | 7.8 | 7.9 | 203 | 2250 | 0.26 | 0.21 |
| mean | | 14.6 | 94 | 9.4 | 7.5 | 7.2 | 285 | 3480 | 0.24 | 0.18 |
| s.d. | | 3.7 | 7 | 1.2 | 0.2 | 0.4 | 75 | 1110 | 0.06 | 0.08 |

| Date | Cl | $P-PO_4$ | Ca (mg $l^{-1}$) | | Mg (mg $l^{-1}$) | | Fe (mg $l^{-1}$) | | Mn (mg $l^{-1}$) | | Zn (mg $l^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (mg $l^{-1}$) | (mg $l^{-1}$) | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil. |
| 250479 | 575 | 0.17 | 118.0 | 140.0 | 36.8 | 42.6 | - | - | - | - | 2.57 | 2.20 |
| 090579 | 295 | 0.15 | 106.0 | 98.0 | 29.8 | 27.4 | - | - | - | - | 1.95 | 1.30 |
| 190579 | 632 | 0.17 | 134.0 | 124.0 | 44.0 | 40.0 | 2.60 | 0.32 | - | - | 1.85 | 1.30 |
| 010679 | 475 | 0.10 | 130.0 | 118.0 | 41.4 | 35.8 | 1.75 | 0.10 | 0.65 | 0.61 | 12.10 | 10.20 |
| 050679 | 522 | 0.20 | 128.0 | 125.6 | 45.0 | 40.6 | 2.25 | 0.26 | 0.72 | 0.70 | 7.40 | 6.30 |
| 190679 | 65 | 1.00 | 111.6 | 98.8 | 34.4 | 29.8 | 0.44 | 0.10 | 0.46 | 0.38 | 3.40 | 0.77 |
| mean | 427 | 0.32 | 121.3 | 117.5 | 38.6 | 36.0 | 1.76 | 0.20 | 0.61 | 0.56 | 4.88 | 3.68 |
| s.d. | 212 | 0.39 | 11.1 | 16.4 | 5.9 | 6.2 | 0.95 | 0.11 | 0.13 | 0.17 | 4.09 | 3.78 |

SITE 7 - LAMESLEY

| Date | time | temp. | $O_2$ | | field | lab. | tot. alk. | cond. | O.D. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (h) | (°C) | (% sat.) | (mg $l^{-1}$) | pH | pH | (mg $l^{-1}$ $CaCO_3$) | (μmhos) | 240nm | 254nm |
| 250479 | 1600 | 11.0 | 102 | 11.0 | - | 6.8 | - | 3310 | 0.36 | 0.15 |
| 090579 | 1300 | 10.0 | 103 | 11.4 | 7.6 | 7.4 | 224 | 1800 | - | - |
| 190579 | 1815 | 14.0 | 94 | 9.3 | 7.6 | 7.4 | - | 4100 | - | - |
| 010679 | 1600 | 15.5 | 102 | 9.7 | 7.3 | 7.1 | 318 | 3900 | 0.24 | 0.19 |
| 050679 | 0930 | 15.0 | 77 | 7.4 | 7.3 | 7.1 | 416 | 5000 | 0.31 | 0.27 |
| 190679 | 1515 | 20.0 | 75 | 6.6 | 7.8 | 7.7 | 210 | 2250 | 0.26 | 0.21 |
| mean | | 14.3 | 92 | 9.2 | 7.5 | 7.3 | 292 | 3393 | 0.29 | 0.21 |
| s.d. | | 3.6 | 13 | 1.9 | 0.2 | 0.3 | 96 | 1199 | 0.05 | 0.05 |

| Date | Cl | P-$PO_4$ | Ca (mg $l^{-1}$) | | Mg (mg $l^{-1}$) | | Fe (mg $l^{-1}$) | | Mn (mg $l^{-1}$) | | Zn (mg $l^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (mg $l^{-1}$) | (mg $l^{-1}$) | tot. | fil. | tot. | fil. | tot. | fil. | tot. | fil | tot. | fil. |
| 250479 | 490 | 0.24 | 144.0 | 132.0 | 41.0 | 40.0 | - | - | - | - | 3.02 | 4.12 |
| 090579 | 550 | 0.19 | 106.0 | 98.0 | 27.2 | 25.6 | - | - | - | - | 1.50 | 1.15 |
| 190579 | 530 | 0.13 | 122.0 | 134.0 | 41.0 | 43.0 | 2.10 | 0.18 | - | - | 1.67 | 1.20 |
| 010679 | 377 | 0.09 | 128.6 | 119.2 | 43.4 | 39.2 | 3.40 | 0.13 | 0.73 | 0.60 | 2.47 | 1.77 |
| 050679 | 622 | 0.18 | 110.0 | 128.0 | 35.8 | 42.8 | 2.70 | 0.28 | 0.77 | 0.74 | 1.65 | 1.40 |
| 190679 | 63 | 1.10 | 106.0 | 101.2 | 32.6 | 30.8 | 0.46 | 0.16 | 0.41 | 0.41 | 2.13 | 1.00 |
| mean | 439 | 0.32 | 119.4 | 118.7 | 36.8 | 36.9 | 2.17 | 0.19 | 0.64 | 0.58 | 2.07 | 1.77 |
| s.d. | 201 | 0.38 | 15.1 | 15.7 | 6.2 | 7.1 | 1.25 | 0.07 | 0.20 | 0.17 | 0.59 | 1.18 |

SITE 8 - T.V.T.E.

| | Date | time (h) | temp. ($^oC$) | $O_2$ (% sat.) | $O_2$ (mg $l^{-1}$) | field pH | lab. pH | tot.alk. (mg $l^{-1}$ $CaCO_3$) | cond. (µmhos) | O.D. 240nm | O.D. 254nm |
|---|---|---|---|---|---|---|---|---|---|---|---|
| * | 250479 | 1730 | (10.5) | (78) | (8.4) | - | (7.0) | - | (6000) | (0.19) | (0.14) |
| | 090579 | 1115 | 10.0 | 84 | 9.2 | 7.3 | 7.3 | 185 | 1410 | - | - |
| | 190579 | 1730 | 13.0 | 68 | 6.9 | 7.6 | 7.3 | - | 1800 | - | - |
| | 010679 | 1430 | 16.5 | 67 | 6.4 | 7.2 | 7.2 | 314 | 3750 | 0.32 | 0.25 |
| | 050679 | 1800 | 17.5 | 44 | 4.1 | 7.6 | 7.2 | 231 | 3800 | 0.39 | 0.33 |
| | 190679 | 1615 | 21.0 | 23 | 2.0 | 8.6 | 8.3 | 323 | 2800 | 0.32 | 0.31 |
| | mean | | 15.6 | 57 | 5.7 | 7.7 | 7.5 | 263 | 2712 | 0.34 | 0.30 |
| | s.d. | | 4.2 | 24 | 2.8 | 0.6 | 0.5 | 67 | 1095 | 0.04 | 0.04 |

| | Date | Cl (mg $l^{-1}$) | $P-PO_4$ (mg $l^{-1}$) | Ca (mg $l^{-1}$) tot. | Ca (mg $l^{-1}$) fil. | Mg (mg $l^{-1}$) tot. | Mg (mg $l^{-1}$) fil. | Fe (mg $l^{-1}$) tot. | Fe (mg $l^{-1}$) fil. | Mn (mg $l^{-1}$) tot. | Mn (mg $l^{-1}$) fil. | Zn (mg $l^{-1}$) tot. | Zn (mg $l^{-1}$) fil. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * | 250479 | (>1000) | (0.13) | - | - | - | - | - | - | - | - | (4.66) | (3.39) |
| | 090579 | 173 | 0.18 | 94.0 | 90.0 | 23.6 | 21.2 | - | - | - | - | 9.73 | 2.08 |
| | 190579 | 108 | 0.43 | 102.0 | 98.0 | 32.0 | 29.0 | 0.84 | 0.16 | - | - | 1.90 | 1.18 |
| | 010679 | 380 | 0.22 | 109.0 | 112.0 | 36.4 | 39.0 | 1.75 | 0.30 | 0.58 | 0.50 | 1.70 | 1.33 |
| | 050679 | 425 | 0.36 | 118.4 | 108.8 | 38.4 | 40.0 | 1.70 | 0.21 | 0.63 | 0.63 | 1.95 | 1.50 |
| | 190679 | 145 | 0.75 | 98.0 | 96.4 | 34.8 | 34.4 | 1.00 | 0.14 | 0.41 | 0.36 | 1.60 | 0.20 |
| | mean | 246 | 0.39 | 104.3 | 101.0 | 33.0 | 32.7 | 1.32 | 0.20 | 0.54 | 0.50 | 3.38 | 1.26 |
| | s.d. | 145 | 0.23 | 9.6 | 9.1 | 5.8 | 7.8 | 0.47 | 0.07 | 0.12 | 0.14 | 3.55 | 0.68 |

SITE 9 - MOUTH