Bioaccumulation of zinc and cadmium in two stream systems

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BIOACCUMULATION OF ZINC AND CADMIUM IN TWO STREAM SYSTEMS

by

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Tables

Page

INTRODUCTION

1. INTRODUCTION

Many streams are subjected to a persistent form of pollution brought about by drainage from the remains of mining activities - heavy metal pollution. These areas are likely to have small but significant amounts of theses elements present that may cause severe deterioration of the water quality and possible poison contamination throughout the food chain. The biological effects of an increasing amount of these metals in aquatic systems has been in recent years the concern of a large number of environmentalists. Zinc and cadmium are two such heavy metals discussed in this dissertation.

Zinc has been shown to be an almost universal constituent of living matter and is recognized to be an essential element for the growth and development of micro-organisms, (Myers 1951) plants (Arnon 1958) and animals (Underwood 1956). Contrastingly, there is no evidence that cadmium is biologically essential or beneficial as the literature only implicates the various deleterious effects on all living organisms including man (McKee and Wolf 1963; Ball 1967; Shuster and Pringle 1969).

There is considerable information available to show that aquatic organisms accumulate high levels of heavy metals and this accumulation is dependent to a large degree on environmental factors. Literature pertaining to this subject is reviewed in Section 1.2.

The purpose of this study was to look at the effect of one such parameter, pH on the accumulation rates of zinc and cadmium for the organisms of two different streams. An acidic and an alkaline stream of past mining history was chosen for this investigation. Also, since the alkaline stream had a natural concentration gradient of zinc and cadmium (Section 3.1,4), attention was focused on the accumulation rates of the species concerned along the gradient. For convenience, the results and discussion have been separated into different sub-sections.

By way of introduction it would be useful to first look at zinc and cadmium in the stream environment.

1.1 Zinc and Cadmium in the Stream Environment

Zinc and cadmium occur in all three phases of a stream environment - water, sediment and biota. The chemical and physical conditions of the water help determine the metal's state and its availability to the sediment and organisms. Physical - chemical sorption phenomena allow the sediments to concentrate high levels of these elements. The rate of exchange of metals from the sediment to the water column may also control the amount of heavy metal available to the biota. Three mechanisms have been suggested by which aquatic organisms can accumulate heavy metals: absorption through membranes, accumulation of particulate matter, and adsorption through cell-wall interfaces (Duke et al. 1966).

1.2 Bioaccumulation - Dependence on the Environment

Bioaccumulation of zinc and cadmium have been reported by a number of investigators both using direct techniques (Dietz 1972; Leeder 1972; Hutchinson and Czyrska 1972) and radioactive tracers (Davis and Foster 1958; Osterberg 1964; Polikarpov 1966). The capacity of an organism to accumulate elements is usually expressed by the enrichment (concentration) ratio which is the concentration of heavy metal in the organism and in the aqueous solution:

$$K = \frac{C}{C_1}$$

where C and C are respectively the concentration of heavy metal in the aquatic organism and in the aqueous medium (Polikarkov 1966).

A stream organism may accumulate heavy metals to a point where it becomes deleterious or toxic to the individual species. This bioaccumulation of these elements depends not only on the concentration in solution but is also influenced by such environmental factors such as temperature, light, dissolved oxygen and pH. It can also be modified by salts of the alkaline earths and of the heavy metals (Skidmore 1964).

A great deal of the literature pertaining to these variables and accumulation concerns toxicity effects and are discussed below.

(a) Temperature

It is evident that temperature affects the uptake of heavy metals from the aqueous medium through its effects on biological processes. Lloyd (1960) reports that a rise in temperature from 12° to 22°C reduced the survival rate of rainbow trout (*Salmo gairnerii*) by a factor of 2.5 in media containing relatively high zinc concentrations. Accordingly, Eisler (1971) and Gardner and Yevich (1969) both showed that mummichogs (*Fundulus heteroclitus*) were more sensetive to Cd at higher temperatures than at lower ones.

Temperature has even a more pronounced effect on the concentration of heavy metals in natural conditions. During the winter months, the vertebrate and invertebrate fauna of the Columbia River consumed little food material and consequently contained lower levels of radioactive elements as compared to the warmer months (Davis and Foster 1958).

However, Lloyd and Herbert (1962) suggest that the effect of temperature on the threshold concentration of a heavy metal will usually be small as compared with the effects the other environmental factors can have.

(b) Light

Light has a great influence on the concentration of many elements by most plants. Bachman and Odum (1960) reported that Zn^{65} is taken up by six benthic algal species proportional to the photosynthetic and growth rates. Gutknecht (1961, 1963) found similar results also investigating marine benthic algae. The element zinc is so intimately related to photosynthesis that the present radiocarbon method of assessing primary production is being augmented by development of a new technique using radioactive zinc (Bachman and Odum 1960; Polikarkov 1966). Polikarkov (1966) studied other trace elements (Co, St, Cs, Ce) and observed higher enrichment ratios in Ulva in the presence of light than without it. To the best of the author's knowledge no information concerning accumulation of cadmium under various light conditions has been shown. It is suggested that since cadmium is not essential or beneficial light would not be an important factor.

(c) Dissolved Oxygen

The dissolved oxygen content of a river can fluctuate appreciably due to time of day, rate of flow, amount of oxidizable material entering it and other factors. It should be emphasized that the levels of dissolved oxygen present in the water need not be low in order to become an important variable when heavy metals are present. Lloyd (1960) exposed rainbow trout (Salmo gardnerii) to various concentrations of zinc sulphate in media containing different concentrations of dissolved oxygen. He found that half the fish population was reduced by a zinc level that was four times greater at an oxygen concentration of 8.9ppm. than it was at 3.8ppm. Similarly, Westfall (1945) working on goldfish (Caprinus auratus) found lead more toxic in water at low oxygen levels.

Lloyd and Herbert (1962) offer an hypothesis to account for the increased accumulation and toxicity. They suggest that trout increase the rate of flow over their gills as the oxygen content of the water is reduced. Since the gill is one of the main sites for the sorption of heavy metals, the increased flow of water over them allows more poison to become in contact with the fish in a given time.

(d) pH

Heavy metal ions can react with water in the following manner (Bachman 1963):

$$X^{2+} + H_2O = XOH + H^+ = X(OH)_2 + H^+$$

X = Zn or Cd

As the pH of the medium is shifted towards the acidic side an increasing amount of the metallic ion is in solution whereas as the pH rises towards neutrality precipitation of the metal occurs. Smith (1973) reports that a pH of 1.5 or less was necessary to ensure that all of the zinc remained in solution. Furthermore, Alloway (1969) states that increasing the pH allows heavy metals to be more readily sorbed on soil particles and also form complexes with organic matter.

Very little research has been performed concerning the effect of pH on uptake and accumulation. Since acid environments favor most of the heavy metals to be in solution, low enrichment ratios would be expected due to poor accumulation rates via sorption phenomena.

(e) Effects of Salts of the Alkaline Earth Metals

As early as 1897, Ringer discovered that toxicity of some metal cations to aquatic organisms is reduced in the presence of other metal cations, notably calcium. This basic phenomenom is known as antagonism.

Lloyd (1960) reports that hardness is the most important single factor governing the toxicity of zinc ions to rainbow trout (Salmo gardnerii). He noted a ten-fold difference between the toxicities of zinc in the hardest and softest water over a two and a half day exposure. Similarly, Jones (1938) observed that sticklebacks (Gasterosteus aculeatus) had a higher survival rate in waters containing more calcium. More recently, Bryan (1967, 1969) showed that the absorption of zinc is reduced in the presence of calcium in the freshwater crab (Austropotamobius pallipae) and by manganese in the brown seaweed (Laminaria digitata).

Two theories have been put forth to explain the mechanism of antagonism by the alkaline earth metals. According to the permeability theory (Jones 1939), the alkalai-earths antagonize heavy metal compounds by reducing the permeability of the cell membranes, thus decreasing the penetrability of the metal into the tissues.

The second theory concerns the inhibition of coagulation between the heavy metals and protoplasm by calcium ions since it is believed that toxicity of most metal ions is due to this coagulation inside the cell (Heilbrunn 1937). These mechanisms are poorly understood and further research is needed to evaluate them.

(f) Effects of Heavy Metal Salts

If an aquatic organism is exposed to two different poisons, the effect may be additive, synerginistic, or antagonistic. Brandt (1949), after exposing trout (*Salmo gairnerii*) to sulphates of different metals found zinc and cadmium to be additive whereas zinc and copper was strongly synergistic. Contrastingly, Hutchinson and Czynska (1972) report that zinc and cadmium acted synergistically together with two aquatic plants they investigated. Obviously, more evidence is needed on this topic. Still, Corner and Sparrow (1956) have offered a possible explanation to explain synergism. They suggest that uptake and accumulation is increased due to one metal increases the permeability of the body surface for the other metal.

MATERIALS AND METHODS

2. MATERIALS AND METHODS

2.1 Water Analysis

Monthly water analyzes were taken from each site for the determination of sodium, potassium, magnesium, calcium, zinc and cadmium. Samples were filtered in the field with a Sinta glass funnel (Grade 2) into 100ml pre-acid washed bottles. Only one sample was taken from each location since previous workers have shown no significant deviation between samples (Robinson 1970, Leeder 1972). The filtrate (X (aq).) was then taken directly to the atomic absorption spectrophotometer (Perkins-Elmer Model 403) for metal analysis. In some element determinations, preparation of the water sample was needed:

(a) Potassium

A 0.15ml solution of 15,000 mg/1 Na was added to 5 ml of the water sample. Blanks and standards were prepared in the same way.

(b) Magnesium and Calcium

A 4 ml aliquot of the water sample was pipetted into a tube and 6 drops of lanthanum chloride was added. The tubes were then assayed for magnesium and calcium. Blanks and standards also had the above additions.

(c) Sodium, Zinc and Cadmium

No additional preparation of the sample was needed for these elements.

Temperature and pH were also recorded monthly in the field with a thermometer and portable pH meter.

2.2 Collection and Preparation of Biotic Material

Biological material was collected randomly at all stations. Invertebrate sampling presented the most problem in collection, especially the chironomid Tendipes sp., which had to be separated from the mats of Drepanocladus fluitans from which it was attached. Collection of the ephemeropteran, Ephemerella sp. was also tedious since it was difficult to find enough material for analysis.

A survey of the fauna and flora of both sites is outlined in Tables III and IV. This limited survey shows both streams to be floristically poor and only two bryophytes, Drepanocladus fluitans and Scapania undulata, an angiosperm Juncus effusus, and an alga ~~e~~ Hormidium sp. were in sufficient quantities for analysis for heavy metals. Similarly, only six species of insects from the acid stream (Section 3.1) and five species from the Nenthead stream (Section 3.2) were in large enough numbers for analysis. The only vertebrate form, Rana temporaria was sparcely distributed.

Most of the plant material collected was cut into different sections to determine whether zinc or cadmium concentrated in one particular area. The species concerned were the bryophytes and the angiosperm.

In preparation, all plant material was easy to clean with the exception of Hormidium sp. This filamentous algae presented problems since detrital material was inseparable from it. Therefore, faulty enrichment ratios could have arisen. Animal samples were clean and easy to work with. After preparation, biological material was analysed either by dry or wet-ashing techniques.

2.3 Plant Analysis

The plant samples concerned were dry ashed according to the method outlined by Ulrich and Johnson (1959), and Baker et al. (1964). After comparing dry-ashing with two other techniques, Adrian (1973) concluded that dry-ashing is an acceptable method with high precision and is an easy technique to follow.

Specimens brought back to the laboratory were washed several times with demineralised, distilled water before being placed in a drying oven at 103°C for 24 hours. The material was then ground up with a porcelain mortar and pestle and samples between 0.1-0.3g were weighed in pre-acid washed, dust free, silica crucibles. The crucibles were next placed in a lead-lined electric muffle furnace at 490°C for 24 hours. This type of furnace was used since Baker et al. discovered that clay lining of the sides and surface was a source of zinc and aluminium contamination. The plant material was then removed, and weighed again to obtain the inorganic ash content. After the ash material was dissolved in a certain volume of 2N HCl, it was filtered through Whatman's # 1 filter paper into pre-acid washed 25 ml volumetric flasks. Demineralised, distilled water made up the rest of the volume. Usually, as in most plant samples, an insoluble silica fraction remained; however, the amount of trace elements lost was negligible. Blanks were also prepared with the same volume of hydrochloric acid used since even double distilled hydrochloric acid contains appreciable amounts of heavy metals (Robertson 1968).

2.4 Animal Analysis

Both dry and wet-ashing techniques were employed depending on the species concerned.

(a) Dry-Ashing

All invertebrate material was digested for metals following the procedure outlined in Section 2.3. Size of samples varied from 0.02-0.15g.

(b) Wet-Ashing

Vertebrate specimens were digested according to the methods described by Ullrich and Johnson (1957) and Preston *et al.* (1971). The material was placed in a drying oven overnight at 103°C. After the samples were ground with mortar and pestle and weighed, 20ml of nitric acid was added to it and the soution was allowed to stand overnight. A small quantity (5ml) of perchloric acid and hydrochloric acid was then added. The solution was next placed on a warming plate and was left to evaporate. When 1-2 ml remained in the flask, the contents were filtered with Whatman's # 42 filter paper into pre-acid washed glass bottles and the solution was diluted to 100 ml with demineralised, distilled water. The samples were then taken to the atomic absorption spectrophotometer for metal analysis. Blanks were also made up with reagents only.

2.5 Sediment

Analysis of sediment was performed following a modification of the technique outlined by Cross *et al.* (1970). Sediments (2.0g) from both areas were placed in a drying oven at 103°C for 24 hours. Particles used in this method were $\angle$ 1.17 mm. After weighing the particles, 50 ml of 0.1 N HCl acid was added and the solution was left alone undisturbed overnight. The sediment was next ground with a mortar and pestle and diluted to 100 ml using 0.1 N HCl acid. Two hours later, the remaining sediment was filtered with Whatman's 42 filter paper. The resulting filtrate was made up to a volume of 150 ml with 0.1 N HCl acid and the concentration of metals was then determined by atomic absorption spectrophotometry. Blanks were also prepared with reagents only.

2.6 Particulate Matter

Particulate matter was defined as all foreign material that was not passable through a 0.45 μ Millipore membrane filter. The method used is described by Preston <u>et al</u>. Three to four litres of water were filtered from each site. The filters were then placed in a wide mouthed beaker which had previously been added 100 ml of 0.1 N HCl and 1 ml of hydrogen peroxide. A large watch glass was placed over each beaker to prevent foreign matter from entering. The contents were next heated gently until the liquid had evaporated to about 20 ml, and the solution was then transferred to a 50 ml pre-acid washed volumetric flask with some help with demineralised, distilled water. Samples were then taken to the atomic absorption spectrophotometer for analysis. Blank samples were also prepared.

2.7 Broad Band Matrix Interference

The elements sodium, potassium, magnesium and calcium have been known to produce considerable "noise" at all wavelengths and therefore positive interference in the determination of heavy metals (Preston <u>et al</u>. 1970). Table I below indicates the various absorbances of certain metals on the zinc and cadmium wavelengths.

Table I Interference of Various Metals on the Zinc and Cadmium Wavelengths

Metal Conc. (mg/l)	Interference on Zn wavelength (mg/l)				Interference on Cd wavelength			
	Na	K	Mg	Ca	Na	K	Mg	Ca
500	0.002	un	un	0.008	un	un	un	0.011
1000	0.004	0.001	0.001	0.016	0.0035	0.001	0.001	0.024
2000	0.010	-	-	-	0.0075	-	-	0.051
3000	0.015	-	-	-	0.011	-	-	-
5000	-	0.009	-	0.069	0.023	0.006	-	0.162
10000	0.209	0.018	-	0.127	0.047	0.012	-	0.246

*un - undetectable

This table shows that high concentration of these elements can create substantial interference in the determination of zinc and cadmium. For this reason, metal analysis was preformed on all plant and animal digestions to evaluate the amount of interference present for each species tested. However, interference was negligible. Values for concentrations of sodium, potassium, magnesium and calcium were always less than 150 mg/l of element! For example, the case of the hemipteran, Gerris lacustris (Table II). Referring back to Table I, interference at these levels is undetectable.

Table II Interference on the Zinc and Cadmium Wavelengths for the hemipteran, Gerris lacustris

Element	Conc. (mg/l) in 25 ml flask	Interference on Zn wavelength (mg/l)	Interference on Cd wavelength (mg/l)
Na	2.9	undetectable	undetectable
K	7.1	undetectable	undetectable
Mq	1.05	undetectable	undetectable
Ca	2.1	undetectable	undetectable

Table III. Flora and Fauna Survey of the Acid Stream

SPECIES

FLORA

1. Angiosperms

Juncus effusus

2. Bryophytes

Drepanocladus fluitans

FAUNA

1. Insects

or Hemiptera

Gerris lacustris

Sigara sp.

or Diptera

Tendipes sp.

Dipteran Flies

or Coleoptera

Gyrinus sp.

or Odonata

Enallagma cyathigerum

Table IV Flora and Fauna Survey of the Nenthead Stream

	SPECIES	
	FLORA	Station(s)
1.	Angiosperms	
	Juncus effusus	2, 3, 4, 5, 7.
2.	Bryophytes	
	Scapania undulata	3, 4, 5, 7.
3.	Algae	
	Hormidium sp.	6.
	FAUNA	
1.	Insects	
or.	Hemiptera	
	Velia caprai	2, 3, 5, 6, 7, 8.
or.	Ephemeroptera	
	Ephemerella sp.	3, 4, 5, 8.
or.	Coleoptera	
	Hydrophilus sp.	1, 2, 3, 4, 5, 6, 7, 8.
or.	Tricoptera	
	Potamophylax latipennis	5, 6.
	Hydropsyche instabilis	3, 5, 6, 7.
2.	Vertebrates amphibia	
	Rana temporaria	2, 4, 5, 7.

AREAS SELECTED

3. AREA SELECTED

3.1 Acid Stream

(a) Location and Introduction

The acid stream studied was located near the town New Brancepeth in County Durham (Fig. 1). The stream arises from an underground spring fixed near the top of coal heaps and flows for about 1.5 kilometres before entering Red Burn and eventually the River Wear. Figure 2 is a more detailed map of the stream itself. The sampling site chosen was a small reservoir where the stream enters and leaves (Fig. 3). Stream flow is negligible. Bottom sediment was characterised by a fine, silty material. The water depth does not exceed 1.5 metres. Physical and chemical features are itemized in Section 4. The reservoir area recorded the highest diversity of aquatic life. A survey of the flora and fauna has been outlined in Table III (Section 2).

(b) Mining History

Drift mining in the coal seams surrounding the stream began in the 18th century and terminated in 1948. Later, shafts were erected to reach the deeper seams (1926) and it was not until 1966 that mining in the area finally ceased. (Robinson 1970). The coal mined contained appreciable amounts of pyrite and marcasite. Consequently, the mine drainage invariably contains sulphuric acid and accounts for the low pH (3) of the stream. Literature pertaining to the formation of acid wastes is given by Parsons (1957), and Koryak *et al*. (1972).

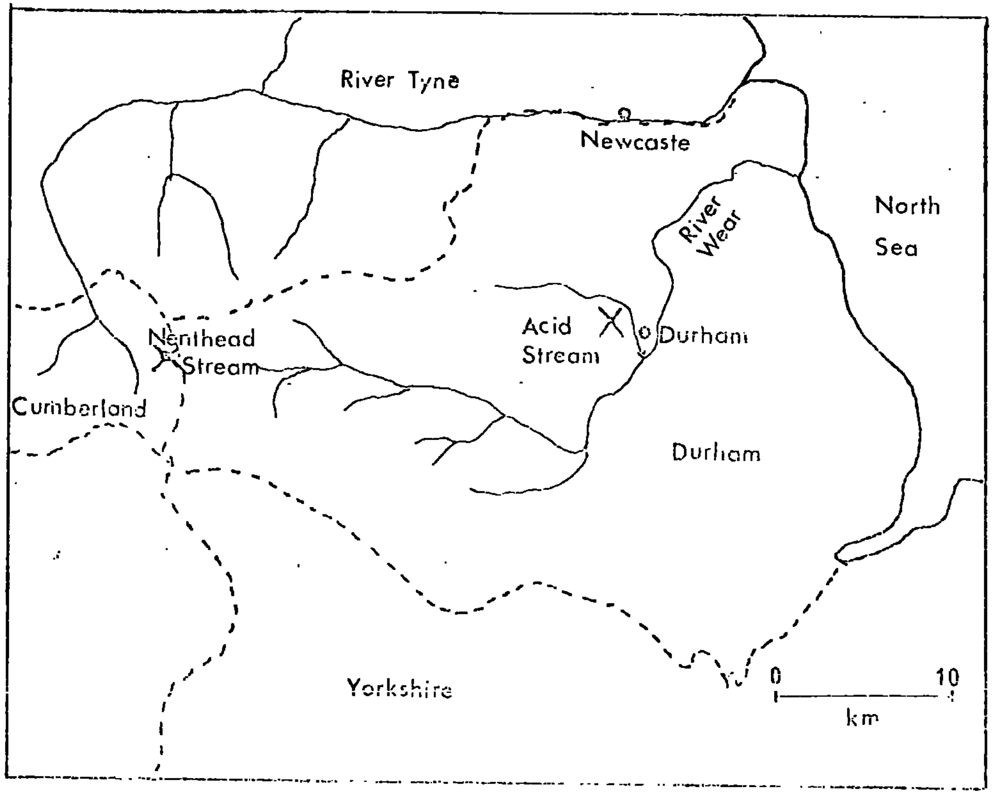

FIG.1 MAP SHOWING LOCATION OF ACID STREAM AND NENTHEAD STREAM

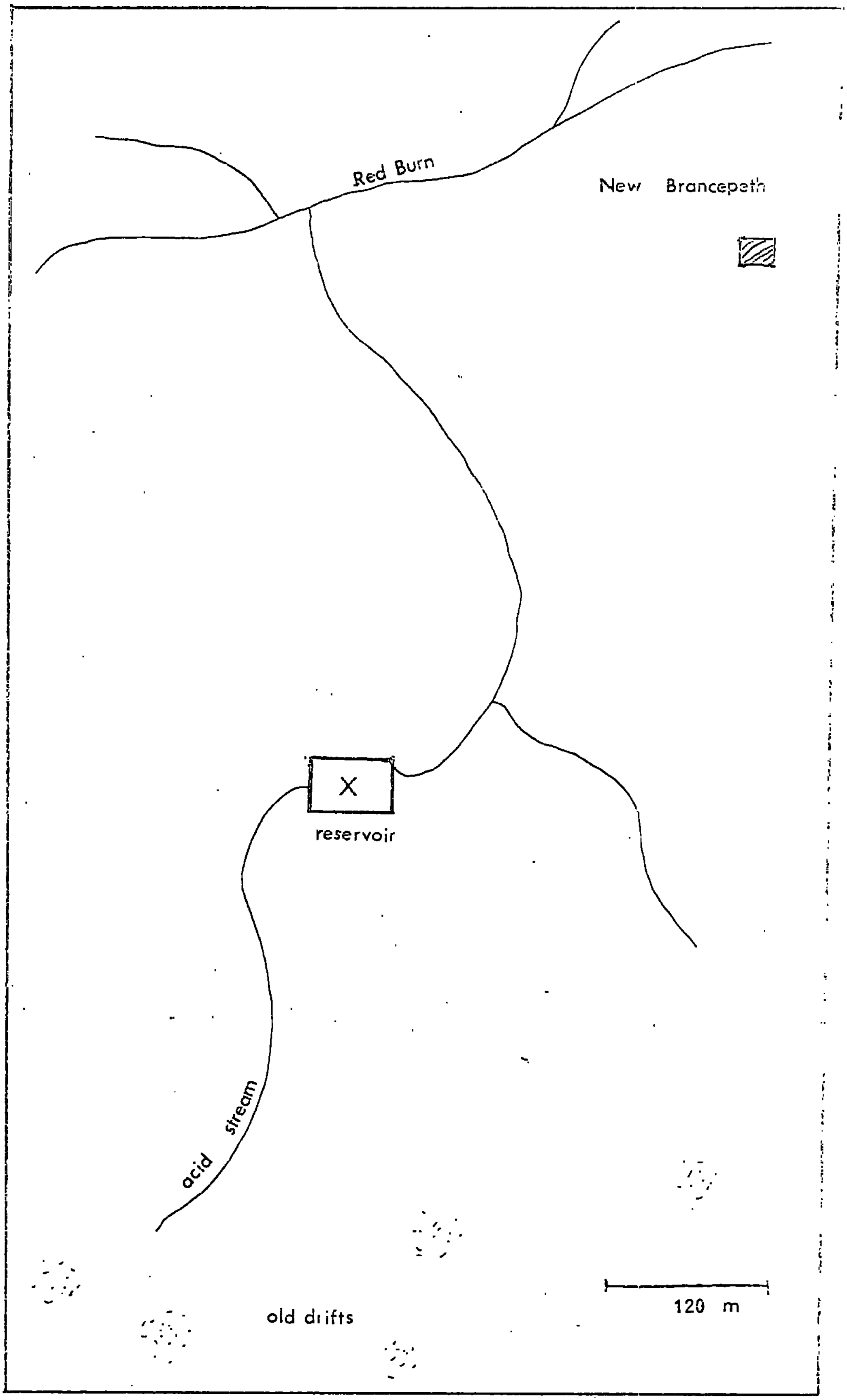

FIG. 2 MAP SHOWING RESERVOIR SITE OF THE ACID STREAM

FIG. 3 RESERVOIR STATION OF THE ACID STREAM

3.2 Nenthead Stream

(a) Location and Introduction

The alkaline stream investigated was located at Nenthead village in the Alston district in East Cumberland (Fig. 1). The beginning of the stream seeps from the side and toe of an old mine heap and flows south west for 2.5 kilometres before entering the River Nent which later empties into the Tynet River. The main stream and many of its tributaries are heavily polluted by heavy metal drainage derived from abandoned zinc and lead mines. As already indicated (Section 1), the Nenthead stream provided a natural concentration gradient of zinc and cadmium. Consequently, eight sampling sites were chosen. Figure 4 outlines these stations. The stream is characterized by swift running water (Fig. 5) except at station 2 where the flow is slow and sluggish. Sediment varies from a gravel type at most stations to a muddy type at station 2. Physical and chemical data for the various stations are discussed in Section 4. A flora and fauna list has been presented in Table IV (Section 2). Station 2 was used as a comparison to the acid stream because of similar sediment types, heavy metal contents and flow rates.

(b) Mining History

The Nenthead district has had an intensive mining history. Ironstone was worked in this region as early as the 12th century and by 1917 the output of the Weardale was about 300 tons weekly (Contril *et al*. 1919). The principle zinc bearing region of this area is positioned at Nenthead (Fig. 6). Sphalerite is the only primary zinc material of the field.

Analysis of sphalerite concentrates in this region reveals 59.9% zinc and 0.26-0.40% cadmium (Dunham 1948).

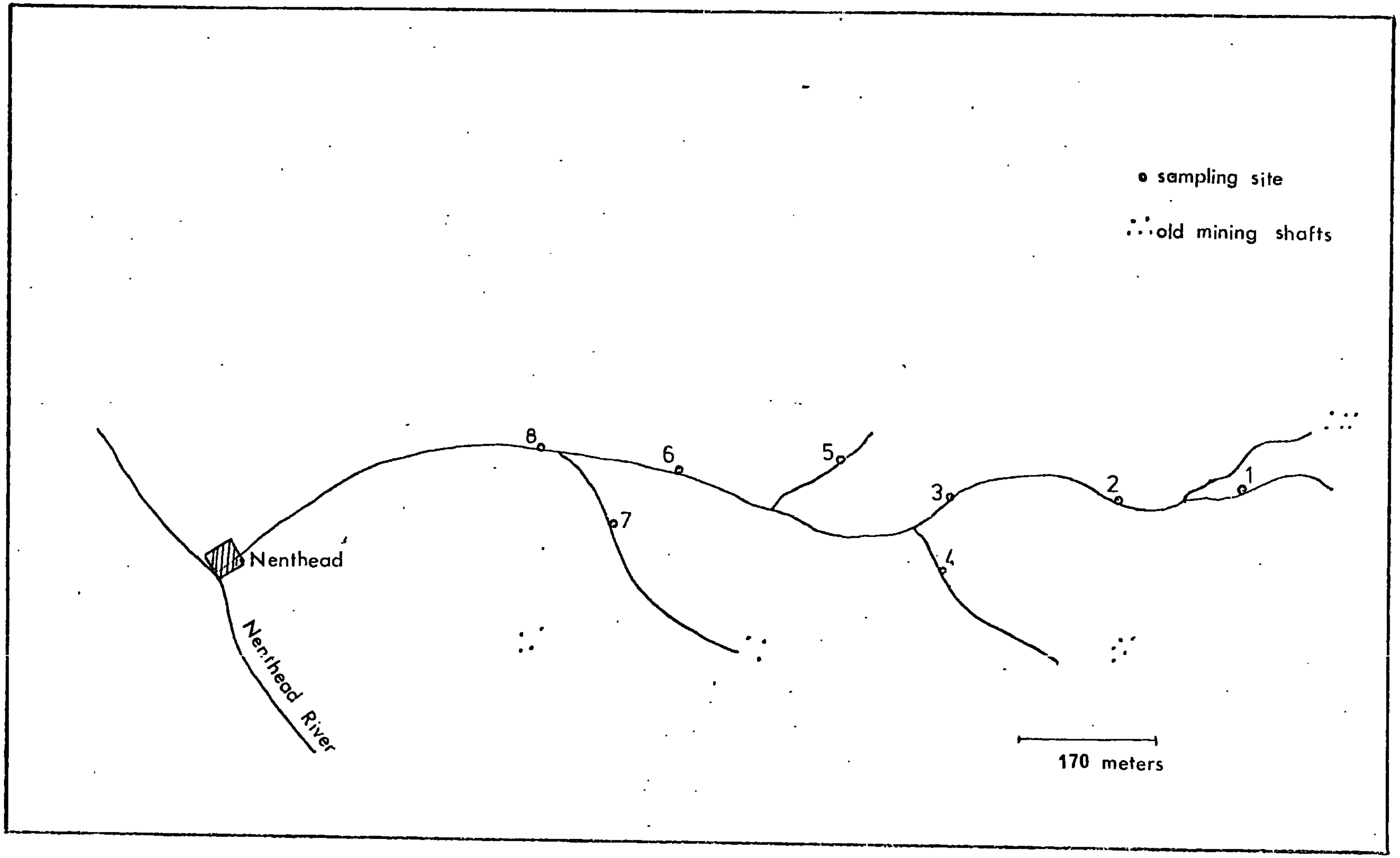

FIG. 4 MAP SHOWING SAMPLING SITES OF THE NENTHEAD STREAM

FIG. 5 NENTHEAD STREAM AT STATION 5

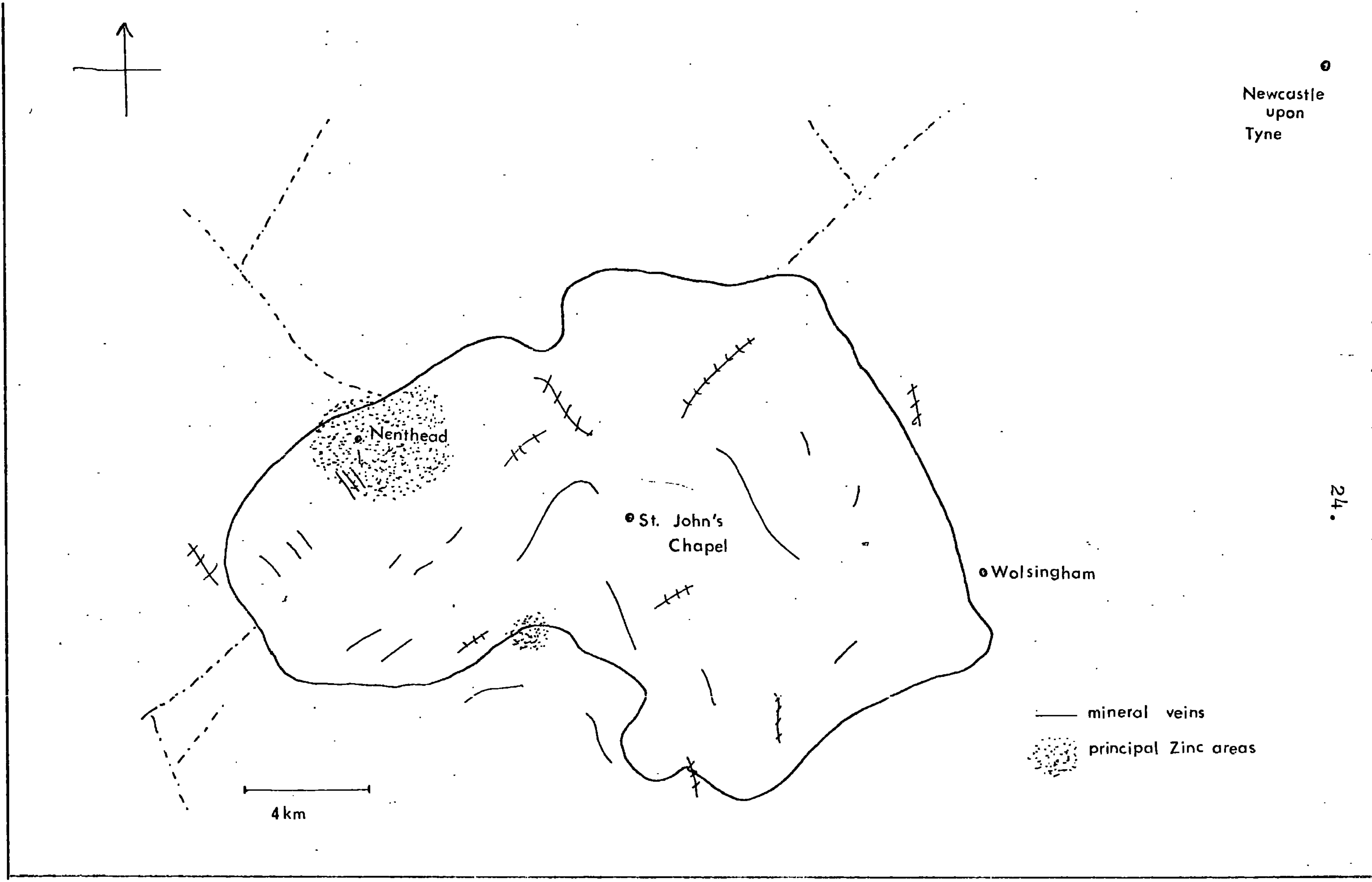

FIG. 6 MAP SHOWING PRINCIPAL ZINC-BEARING AREAS

RESULTS

4. RESULTS

4.1 Water Analysis

(a) Acid Stream and Station 2 Nenthead Stream

The pH readings recorded at the acid stream ranged from 2.49 to 2.71 throughout the study. The pH values determined at station 2 were also fairly stable, varying from 6.6 to 6.7 (Table V, VII-IX).

Tables V-IX show the results of four water collections carried out during May, June, July and August at each site. Zinc and cadmium levels at both stations ranged as follows: (mg/l)

	Zn	X	Cd	X
Acid Stream	0.965-1.027	1.007	0.0085-0.017	0.0118
Station 2	0.90-3.40	1.62	0.0075-0.021	0.014

Monthly variation of each element from both sites is shown graphically in Figs. 7, 9, 10.

The cations sodium, potassium, magnesium and calcium all showed higher levels in the acid stream than station 2 (Tables V-IX). These elements also indicated less monthly variation in the acid stream (Figs.8, 12-15)

(b) Nenthead Stream

Tables VI-X and Figs. 9,10 point out the natural concentration gradient of heavy metals found at the different stations. Mean zinc values ranged from 28.6^{o} mg/l at station 1 to 4.84 mg/l and finally dropped to 0.153 mg/l at station 5. Similarly, mean cadmium levels varied from 0.065 mg/l at station 1 to 0.003 mg/l at station 5. A direct correlation (r = 0.9920) between the aqueous zinc and cadmium concentrations was found along the stream (Table XI and Fig. 11).

Each station showed different concentrations of the cations sodium, potassium, magnesium and calcium (Tables VI-X). Mean sodium values ranged from 8.66 mg/l at station 4 to 3.22 mg/l at station 1. Contrastingly, mean potassium levels were found lowest at station 4 and highest at station 1. Mean magnesium and calcium levels were recorded highest at station 5 (7.93 mg/l Mg, 28.85 mg/l Ca) whereas the lowest values were noted at station 3 (1.47 mg/l Mg, 8.14 mg/l Ca).

4.2 Plant Analysis*

(a) Acid Stream and Station 2 Nenthead Stream

Tables XII-XIV and XVII show the actual values of zinc and cadmium accumulated and their enrichment (concentration) ratios expressed in both dry and ash weights. Acid stream flora showed extremely low enrichment values. The bryophyte, Drepanocladus fluitans recorded concentration ratio of only 44.8 for zinc and 148 for cadmium. Enrichment ratios for the angiosperm, Juncus effusus were also low. Contrastingly, J. effusus collected at station 2 registered a much enrichment of both heavy metals. Chi-square distribution for this angiosperm from both sites revealed that both zinc and cadmium concentration values are significantly p 0.001) higherat station 2. Bioaccumulation of each element by the different sectioned parts of the plant species varied considerably. This is shown in Tables XII-IV and XVII and graphically in Figs. 16 and 17.

[*] For convenience, the results listed below are stated in dry weight figures only.

(b) Nenthead Stream

Tables XIV-XXI indicate the actual heavy metal concentration and the enrichment ratios of each species studied. Enrichment ratios varied for each station. The bryophyte, Scapania undulata registered zinc enrichment ratios which ranged from 828 at station 4 to 19281 at station 5. Similarly, ratios for cadmium varied greatly, extending from 819 at station 7 to 2433 at station 5. Accordingly, highest enrichment ratios for Juncus effusus were recorded at station 5 and the lowest values were noted at station 7.

The only algal species analyzed, Hormidium sp. had a zinc concentration ratio of 516 at station 6. However, as indicated in Section 2.2, this enrichment result may be misleading dure to errors in preparation.

Accumulation gradients were also found in the sectioned parts of Scapania undulata and Juncus effusus (Figure 17).

4.3 Animal Analysis*

(a) Acid Stream and Station 2 Nenthead Stream

The actual heavy metal accumulation value and the enrichment ratios for each species is shown in Tables XII-IV and XVII.

The most abundant invertebrate present in the acid stream was the chironomid Tendipes sp. The larval form of this species recorded enrichment levels of 85.9 for zinc and 139 for cadmium. Ratios of both elements for the emerging adults were similar. However, values for the empty moults of the pupal state were notably higher!

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* For convenience, the following results are expressed in dry weight figures only.

A Zinc concentration ratio of 136 for the hemipteran, *Gerris lacustris*, was the highest value recorded for all the adult forms of the acid stream's truly aquatic insects. Contrastingly, cadmium levels were highest in the hemipteran, *Sigara sp*. It is interesting to note that in both elements, enrichment ratios were greater in the young than the adult stage of *Gerris lacustris*. A dragonfly in the area, *Enallagma cyathegerum* had a concentration ratio of 269 for zinc and 441 for cadmium.

In comparison, the hemipteran *Velia caprai* (adult) from station 2 registered an enrichment ratio of 453 for zinc and 429 for cadmium. Similar to *Gerris lacustris*, the younger stage of *Velia caprai* recorded a higher enrichment value than the adult stage. Concentration ratios for the coleopteran *Hydrophilus sp*. were 262 for zinc and 364 for cadmium.

Chi-square distribution on similar insect orders from both sites showed that both heavy metals were significantly (p 0.001) higher at station 2 (Table XXII). Not too much should be taken from this test since these comparisons were done with similar orders of insects and not the actual species itself.

(b) Nenthead Stream

The actual heavy metal accumulation value and the enrichment ratios for each species is outlined in Tables XIV-XXI. Enrichment values varied enormously for the species concerned. Concentration ratios for *Velia caprai* range from 174 for zinc and 181 for cadmium at station 7 to 1873 for zinc and 967 for cadmium at station 5. Similarly, enrichment ratios of both elements for the coleopteran *Hydrophilus sp*.

and the tricopteran *Hydropsyche instabilis* were highest at station 5 and lowest at station 7.

The tricopteran *Potamophylax latipennis* and the empheropteran *Ephemerella sp.* recorded the highest enrichment ratios of all the insects analyzed.

The only invertebrate investigated, *Rana temporaria*, registered zinc concentration ratios which ranged from 367 at station 7 to 3242 at station 5. Cadmium levels varied from 341 at station 4 to 1653 at station 5.

Correlations between the enrichment ratios and the actual aqueous heavy metal concentration were attempted for each element on each species. Correlation coefficients are shown in Table XXIII and significant relationships are expressed graphically in Figs.18-20. Plant and animal material investigated for zinc showed significant negative correlations (p 0.05) for each species. Contrastingly, only *Juncus effusus* and *Ephemerella sp.* showed significant correlations for cadmium.

4.4 Particulate Matter and Sediment

(a) Acid Stream and Station 2 Nenthead Stream

Zinc incorporated as particulate matter at station 2 was 380 greater than the values recorded in the acid stream. Similarly, the cadmium level in suspended matter at station 2 was 32 higher than the figure noted in the acid stream (Table XXIV).

Both sites had a characteristic muddy bottom sediment. Sediment values at station 2 had 352 more zinc and 510 more cadmium than sediment from the acid stream (Table XXV).

Chi-square distribution showed significant differences (p 0.001) for the concentration of zinc and cadmium in particulate matter and sediment for both sites (Table XXVI).

(b) Nenthead Stream

Particulate matter readings were not attempted for each station. Sediment values varied enormously between the stations. No significant correlation was found to suggest a gradient (Table XXVII).

Table V Water Analysis Acid Stream

	15/V/73	22/VI/73	20/VII/73	5/VIII/73	Mean
Temp.°C	9.4	21.8	16.1	17.0	
pH	2.71	2.49	2.65	2.68	
Na	12.98	11.6	17.3	17.5	14.8± 4.6
K	1.21	0.40	13.3	14.0	7.2 ± 2.3
Mg	60.80	85.0	53.5	54.4	63.4 ± 7.9
Ca	59.57	55.6	70.0	70	63.8 ± 7.9
Zn	1.026	1.027	1.01	0.965	1.007±0.08
Cd	0.01	0.017	0.012	0.0085	0.0118±0.003

N.B. All results in mg/l

Table VI Water Analysis Nenthead Stream 15/V/73

Station	Na	K	Mg	Ca	Zn	Cd
1	-	1.09	3.9	16.3	20.2	0.065
2	-	0.64	2.1	12.1	3.34	0.013
3	-	0.73	1.55	3.7	2.94	0.002
4	-	0.61	1.33	5.1	4.22	0.024
5	-	-	-	-	0.15	0.001
6	-	0.65	2.1	9.0	1.63	0.015
7	-	1.17	2.9	9.8	4.71	0.010
8	-	0.76	2.4	9.8	1.59	0.006

Table VII Water Analysis Nenthead Stream 13/VI/73

Station	Temp. (°C)	pH	Na	K	Mg	Ca	Zn	Cd
*1	17.9	6.45	3.3	1.47	5.1	23.5	27.6	-
2	18.0	6.6	5.90	1.04	1.73	13.4	0.90	0.015
3	18.3	6.7	6.5	0.17	1.60	10.8	0.810	0.0055
4	18.1	5.63	7.7	0.077	1.73	9.65	6.09	0.015
5	16.5	6.4	8.9	0.65	2.3	16.4	0.140	0.003
6	17.4	6.5	5.6	1.11	7.4	27.6	2.0	0.006
7	17.6	6.10	4.4	1.24	3.5	11.7	3.8	0.011
8	17.8	6.3	5.0	1.16	6.5	25.7	2.0	0.015

* Water analysis 25/VI/73

Table VIII Water Analysis Nenthead Stream 4/VII/73

Station	Temp. (°C)	pH	Na	K	Mg	Ca	Zn	Cd
1	19.1	6.5	-	-	-	-	37.5	-
2	19.2	6.7	6.0	0.26	2.12	16.4	1.30	0.021
3	19.5	6.65	5.8	0.33	1.34	8.3	0.50	0.015
4	19.5	5.65	9.9	0.32	2.17	10.7	5.38	0.022
5	17.5	6.4	8.3	0.24	2.34	15.2	0.140	0.008
6	18.5	6.75	5.7	0.68	12.13	36.5	1.55	0.015
7	19.25	6.15	4.6	0.82	3.81	12.2	2.38	0.016
8	20.25	6.35	5.5	0.86	3.81	26.5	1.38	0.020

Table IX **Water Analysis Nenthead Stream 4/VIII/73**

Station	Temp. (^oC)	pH	Na	K	Mg	Ca	Zn	Cd
2	19.3	6.75	5.3	0.43	6.9	18.1	0.970	0.0075
3	19.4	6.7	6.5	0.31	1.4	10.1	0.690	0.006
4	19.6	5.5	8.4	0.47	1.3	7.1	3.66	0.0095
5	18.3	6.4	7.8	0.15	2.1	14.9	0.183	0.001
6	18.6	6.4	6.0	0.42	10.1	22.3	1.75	0.0065
7	18.7	6.0	6.4	0.45	3.0	10.1	3.17	0.0095
8	19.50	6.25	5.55	0.15	4.9	18.2	1.65	0.006

Table X. **Mean Element Values for each Site** (4 collections)

Site	Sodium mg/1	Potassium mg/1	Magnesium mg/1	Calcium mg/1	Zinc mg/1	Cadmium mg/1
1	3.32	1.28	4.53	19.92	28.4±6.0	0.065
2	5.71	0.593	3.22	15.00	1.62±0.781	0.014±0.005
3	6.26	0.422	1.47	8.23	1.23±0.654	0.007±0.0008
4	8.66	0.369	1.63	8.14	4.84±1.94	0.0176±0.008
5	5.76	0.715	7.93	28.85	0.153±0.04	0.003±0.009
6	8.33	0.380	2.45	15.50	1.73±0.680	0.0106±0.0033
7	5.13	0.920	3.33	10.95	3.51±1.7	0.0116±0.003
8	5.35	0.732	4.4	20.05	1.66±0.71	0.0117±0.004

Table XI **Correlation Coefficient between Zinc and Cadmium Distribution in the Nenthead Stream**

r	sig
0.99207	0.001

Table XII Enrichment Ratio for the Flora and Fauna of the Acid Stream

- ZINC -

Zn (aq) 1.007 mg/l

SPECIES	No of Samples	Zinc (mg/kg) dry wt	ash wt	Enrichment Ratio dry wt	ash wt
FLORA					
Angiosperms					
Juncus effusus (0–150 mm)	1	37.5	457.5	34.7	454
(150–300 mm)	1	35	432.5	34.7	430
(300 mm)	1	30	380	29.8	377
Bryophytes					
Drepanocladus fluitans	3	45.3±7	414±24	44.8	411
(stems)	1	44.6	297	44.3	295
(leaves)	1	42.4	658	42.1	653
(0–50 mm)	1	52	486	51.6	483
(50–100 mm)	1	48	448	47.6	445
(100 mm)	1	33	308	32.7	306
(detritus)	3	42.5±2.3	357	41.2	354
FAUNA					
Insects					
Tendipes sp. (larva)	4	86.5±8.2	1025±64	85.9	1018
(moults)	1	139.7	2342	139	2325
(adults)	3	91.6±10.2	1086±83	90.9	2072
Dipteran flies	1	157.5	1955	156	1941
Gerris lacustris (young)	3	182.5±31	2700±94	181	2681
(adults)	3	137.3±20	2065±65	136	2051
Sigara sp.	1	110	1430	109	1420
Gyrinus sp.	3	90.2±4.6	89.6	1193±4	1185
Enallagma cyathigerum	1	271	1030	269	1023

Table XIII Enrichment Ratios for the Flora and Fauna of the Acid Stream

- CADMIUM -

Cd(aq) 0.0118 mg/l

SPECIES	No of Samples	Cadmium mg/kg		Enrichment Ratio	
		dry wt	ash wt	dry wt	ash wt
FLORA					
Angiosperms					
Juncus effusus (0-150 mm)	1	1.68	31.8	227	2695
(150-300 mm)	1	2.20	26.8	186	2271
(300 mm)	1	0.9	10.7	77	907
Bryophytes					
Drepanocladus fluitans	1	1.75	16.3	148	1379
(stems)	1	1.76	11.7	149	992
(leaves)	1	1.67	26.5	142	2246
(0.50 mm)	1	5.0	45	424	3815
(50-100 mm)		-	-	-	-
(100 mm)	1	1.25	11.6	106	983
(detritus)	1	1.25	8.1	106	686
FAUNA					
Insects					
Tenedipes sp. (larva)	1	1.64	19.6	139	1661
(moults)	1	1.98	31.7	168	2685
(adults)	1	1.60	37.3	136	3179
Dipteran flies	1	3.1	37.5	263	3179
Gerris lacustris (young)	1	2.5	37.3	212	3158
(adults)	1	2.4	36	203	3051
Sigara sp.	1	2.51	32.6	213	2763
Gyrinus sp.	1	2.3	30.4	195	2576
Enallagma cyanthigerum	1	5.2	19.8	441	1678

Table XIV Enrichment Ratio for the Flora and Fauna of Stations 1 and 2

- ZINC -

	Station 1 ZN(aq) 28.4 mg/1					Station 2 ZN(aq) 1.62 mg/1				
SPECIES	No of samples	Zinc (mg/kg) dry wt	ash wt	Enrichment Ratio dry wt	ash wt	No of samples	Zinc (mg/kg) dry wt	ash wt	Enrichment Ratio dry wt	ash wt
FLORA										
Angiosperms										
Juncus offusus (0-150 mm)	-	-	-	-	-	3	530±28	7133±97	327	4403
(150-300 mm)	-	-	-	-	-	3	457±32	5964±110	282	3681
(300 mm)	-	-	-	-	-	3	403±30	4834±95	249	2984
FAUNA										
Velia caprai (young)	-	-	-	-	-	1	850	12750	527	7870
(adults)	-	-	-	-	-	3	734±40	11187±150	453	6905
Hydrophilus sp.	1	450	5635	9.26	120	1	425	5610	262	3463
Vertebrates										
Rana temporaria	-	-	-	-	-	1	1183	-	730	-

Table XV

Enrichment Ratios for the Flora and Fauna of Stations 3 and 4

- ZINC -

SPECIES	Station 3 ZN(aq) 1.23 mg/1					Station 4 ZN(aq) 4.84 mg/1				
	No of samples	Zinc (mg/kg) dry wt	Zinc (mg/kg) ash wt	Enrichment Ratio dry wt	Enrichment Ratio ash wt	No of samples	Zinc (mg/kg) dry wt	Zinc (mg/kg) ash wt	Enrichment Ratio dry wt	Enrichment Ratio ash wt
FLORA										
Angiosperms										
Juncus effusus (150-300 mm)	1	448	5168	364	4201	1	565	6800	117	1405
Bryophytes										
Scapania undulata	3	4820±79.3	21678±170	3919	17624	3	4109±73	18381±162	828	3798
(0-30 mm)	1	13217	59616	10746	48468		-	-	-	-
(30-60 mm)	1	4550	20450	3699	16626		-	-	-	-
(top 20-30 mm)	3	4389±76	19748±168	3568	16055		-	-	-	-
FAUNA										
Insects										
Velia caprai (adults)	1	664	9954	539	8093		-	-	-	-
Ephemerella sp.	1	1219	11867	991	9648	1	1700	16490	351	3407
Hydrophilus sp.	1	329	4426	267	3529	1	488	6387	101	1320
Hydropsyche instabilis	3	769±32	6915±99	625	5622		-	-	-	-
Vertebrates										
Rana temporaria		-	-	-	-	1	2050	-	424	-

Table XVI Enrichment Ratios for the Flora and Fauna of Stations 5 and 6

- ZINC -

SPECIES	Station 5 Zn(aq) 0.153 mg/l No of samples	Zinc (mg/kg) dry wt	ash wt	Enrichment Ratio dry wt	ash wt	Station 6 ZN(aq) 1.73 mg/l No of samples	Zinc (mg/kg) dry wt	ash wt	Enrichment Ratio dry wt	ash wt
FLORA										
Angiosperms										
Juncus effusus (150-300 mm)	1	195	2360	1274	15426		-	-	-	-
Bryophytes										
Scapania undulata	3	2950±61.6	13269±133	19281	86726		-	-	-	-
Algae										
Hormidium sp.		-	-	-	-	3	892±34	2791±133	516	1613
FAUNA										
Insects										
Velia caprai (young)	1	403	6038	2631	39464		-	-	-	-
(adults)	1	285	4275	1863	27941	1	770	11550	445	6676
Ephemerella sp.	1	540	5184	3542	34080		-	-	-	-
Potamorphylax latipennis (body)	3	1989±59.6	7063±138	12993	46164	3	7772±102	31333±250	4493	18112
"house"	1	685	-	4477	-	1	2361	-	1364	-
Hydropsyche instabilis	3	446±25	4150±85	2915	27124	3	799±30	7240±93	462	4185
Hydrophilus sp.	1	153	1980	993	12941	1	440	5808	254	3357
Vertebrates										
Rana temporaria	1	496	-	3242	-		-	-	-	-

Table XVII Enrichment Ratio for the Flora and Fauna of Stations 7 and 8

- ZINC -

	Station 7 ZN(aq) 3.5 mg/kg					Station 8 ZN(aq) 1.66 mg/kg				
SPECIES	No of samples	Zinc (mg/kg) dry wt	Zinc (mg/kg) ash wt	Enrichment Ratio dry wt	Enrichment Ratio ash wt	No of samples	Zinc (mg/kg) dry wt	Zinc (mg/kg) ash wt	Enrichment Ratio dry wt	Enrichment Ratio ash wt
FLORA										
Angiosperms										
Juncus offusus (150-300 mm)	1	243	2903	69.2	827		-	-	-	-
Bryophytes										
Scapania undulata	3	3906±72	17538±162	1113	4997		-	-	-	-
FAUNA										
Insects										
Velia caprai (adults)	1	610	9150	174	2607	1	773	11752	472	7080
Hydrophilus sp.	1	260	3410	74	972	1	450	5635	259	3395
Ephemerella sp.		-	-	-	-	1	1564	15020	942	9048
Hydropsyche instabilis	3	507±42	4748±120	144	1353		-	-	-	-
Vertebrates										
Rana temporaria	1	1287	-	367	-		-	-	-	-

Table XVIII   Enrichment Ratios for the Flora and Fauna of Stations 1 and 2

- CADMIUM -

	Station 1	Cd(aq) 0.065 mg/l				Station 2	Cd(aq) 0.014 mg/l			
SPECIES	No of samples	Cadmium (mg/kg) dry wt	ash wt	Enrichment Ratio dry wt	ash wt	No of samples	Cadmium (mg/kg) dry wt	ash wt	Enrichment Ratio dry wt	ash wt
FLORA										
Angiosperms										
Juncus effusus (0-150 mm)	3	6.0±2.0	80.1±14.8	429	5721		-	-	-	-
(150-300 mm)	3	3.65±1.1	45.8±15.1	261	3271		-	-	-	-
(300 mm)	3	2.2±0.7	26.8±8.8	157	1914		-	-	-	-
FAUNA										
Insects										
Velia caprai (young)	1	6.3	128	450	6750		-	-	-	-
(adults)	1	6.0	92.6	429	6614		-	-	-	-
Hydrophilus sp.	1	5.1	67.8	364	4843	1	5.85	77.2	108	1400
Vertebrates										
Rana temporaria	1	18.7	-	1336	-		-	-	-	-

Table XIX Enrichment Ratios for the Flora and Fauna of Stations 3 and 4

- CADMIUM -

Station 3 Cd(aq) 0.007 mg/l

Station 4 Cd(aq) 0.0176 mg/l

SPECIES	Station 3 No of Samples	Station 3 Cadmium (mg/kg) dry wt	Station 3 Cadmium (mg/kg) ash wt	Station 3 Enrichment Ratio dry wt	Station 3 Enrichment Ratio ash wt	Station 4 No of samples	Station 4 Cadmium (mg/kg) dry wt	Station 4 Cadmium (mg/kg) ash wt	Station 4 Enrichment Ratio dry wt	Station 4 Enrichment Ratio ash wt
FLORA										
Angiosperms										
Juncus effusus (150-300 mm)	1	3.60	42.8	514	6114	1	4.2	53.8	238	3057
Bryophytes										
Scapania undulata		-	-	-	-	3	15.0±4	62.1±9.1	852	3528
(0-30 mm)	1	51.7	236	7386	33714		-	-	-	-
(30-60 mm)	1	33	152	4714	21714		-	-	-	-
(top20-30 mm)	1	14.5	66	2071	9428		-	-	-	-
FAUNA										
Insects										
Velia casrai (adults)	1	5.9	88.9	843	12700		-	-	-	-
Ephemerella sp.	1	10.25	97.6	1464	13943	1	12	122	682	6932
Hydrophilus sp.	1	5.09	67.1	727	9586	1	5.5	80.8	312	4591
Hydropsyche instabilis	3	14.7±1.6	136±13.2	2100	19429		-	-	-	-
Vertebrates										
Rana temporaria		-	-	-	-	1	22.68	-	341	1

Table XX Enrichment Ratios for the Flora and Fauna of Stations 5 and 6

- CADMIUM -

	Station 5 Cd(aq) 0.003 mg/1					Station 6 Cd(aq) 0.0106 mg/1				
SPECIES	No of samples	Cadmium (mg/kg)		Enrichment Ratio		No of samples	Cadmium (mg/kg)		Enrichment Ratio	
		dry wt	ash wt	dry wt	ash wt		dry wt	ash wt	dry wt	ash wt
FLORA										
Angiosperms										
Juncus effusus (150-300 mm)	1	1.65	20	550	666		-	-	-	-
Bryophytes										
Scapania undulata	1	7.3	40	2433	13333		-	-	-	-
FAUNA										
Insects										
Velia caprai (young)	1	3.3	49.5	1100	16500		-	-	-	-
(adults)	1	2.9	44.1	967	14700	1	5.5	96.3	518	9085
Petamorphylax latipennis (body)	3	2.5±0.3	8.75±1.6	833	2866	3	29±3.0	103±	2736	9717
(house)	1	5.7	-	1906	-	1	11.3	-	1066	-
Hydropsyche instabilis	3	4.2±0.9	57.3±7.4	1400	19100	1	21	206	1981	19434
Ephemerella sp.	1	3.5	34.2	1166	11400		-	-	-	-
Hydrophilus sp.	1	1.75	22.8	583	5733	1	5.78	75.2	488	7094
Vertebrates										
Rana temporaria	1	4.96	-	1653	-		-	-	-	-

Table XXI Enrichment Ratio for the Flora and Fauna of Stations 7 and 8

- CADMIUM -

SPECIES	Station 7 Cd(aq) 0.0116 mg/kg					Station 8 Cd(aq) 0.0117 mg/kg				
	No of samples	Cadmium (mg/kg) dry wt	Cadmium (mg/kg) ash wt	Enrichment Ratio dry wt	Enrichment Ratio ash wt	No of samples	Cadmium (mg/kg) dry wt	Cadmium (mg/kg) ash wt	Enrichment Ratio dry wt	Enrichment Ratio ash wt
FLORA										
Angiosperms										
Juncus effusus (150-300 mm)	1	2.09	23.5	181	2026		-	-	-	-
Bryophytes										
Scapania undulata	1	9.5	42.1	819	2629		-	-	-	-
FAUNA										
Insects										
Velia caprai (adults)	1	5.05	75.25	434	6488		-	-	-	-
Ephemerella sp.		-	-	-	-	1	11.8	118.2	1008	10103
Hydropsyche instabilis		-	-	-	-	1	8.07	75.6	690	6466
Hydrophilus sp.	1	2.42	32.4	209	2793	1	5.19	75.6	444	6462
Vertebrates										
Rana temporaria	1	6.02	-	367	-		-	-	-	-

Table XXII Chi-square Distribution Comparing Biological Material, Particulate Matter and Sediment from the Acid Stream and Station 2 Nenthead Stream

Comparison	χ^2 Value Zn	sig	χ^2 Value Cd	sig
Juncus effusus (150-300 mm)	193	0.001	12.6	0.001
Hemiptera (young)	169	0.001	85.6	0.001
(adult)	170	0.001	80	0.001
Coleoptera	84.6	0.001	51	0.001
Particulate Matter	20	0.001	69.8	0.001
Sediment	3654	0.001	122	0.001

Table XXIII Correlation coefficients for Organisms of the Nenthead Stream

	Zinc		Cadmium	
Species	r	sig	r	sig
FLORA				
Juncus effusus (150-300 mm)	-0.8847	0.02	-0.8077	0.05
Scapania undulata	-0.9517	0.05	-0.7481	Not sig
FAUNA				
Velia caprai	-0.9687	0.001	-0.7318	Not sig
Hydrophilus sp.	-0.8946	0.001	-0.6540	Not sig
Ephemerella sp.	-0.9217	0.05	-0.8218	0.05
Hydropsyche instabilis	-0.9719	0.01	-0.8106	Not sig
Rana temporaria	-0.8875	0.05	-0.7231	Not sig

Table XXIV **Concentration of Zn and Cd in Particulate Matter from the Acid Stream and Station 2 Nenthead Stream**

Particulate Matter	Zinc mg/kg	Enrichment Ratio	Cadmium mg/kg	Enrichment Ratio
Acid Stream	0.516±0.21	0.512	0.039±0.007	3.30
Station 2	196±32	21	1.25±0.35	89

Table XXV **Concentration of Zn and Cd in Sediment from the Acid Stream**

	Zinc mg/kg dry wt	Enrichment Ratio	Cadmium mg/kg dry wt	Enrichment Ratio	Type of Sediment
Sediment	16.8±4.1	16.7	0.40±0.10	33.9	muddy

Table XXVI Concentrations of Zn and Cd in sediments from the Nenthead Stream

Station	Zinc mg/kg dry wt	Enrichment Ratio	Cadmium mg/kg dry wt	Enrichment Ratio	Type of sediment
1	-	-	11.9±3.5	183	gravel
2	6004±82	3706	1.86±0.49	204	muddy
3	543±93	442	2.5±1.0	351	gravel sand
4	-	-	-	-	-
5	42.2±6.8	276	0.0215±0.0009	7	gravel
6	1067±38	617	4.6±0.8	434	gravel
7	1241±58	354	6.6±2.3	569	gravel
8	1603±75		3.11±1.1		gravel

Table XXVII Correlation Coefficient for Sediment of the Nenthead Stream

	Zinc		Cadmium	
	r	Sig	r	Sig
Sediment	0.13637	not sig	0.13640	not sig

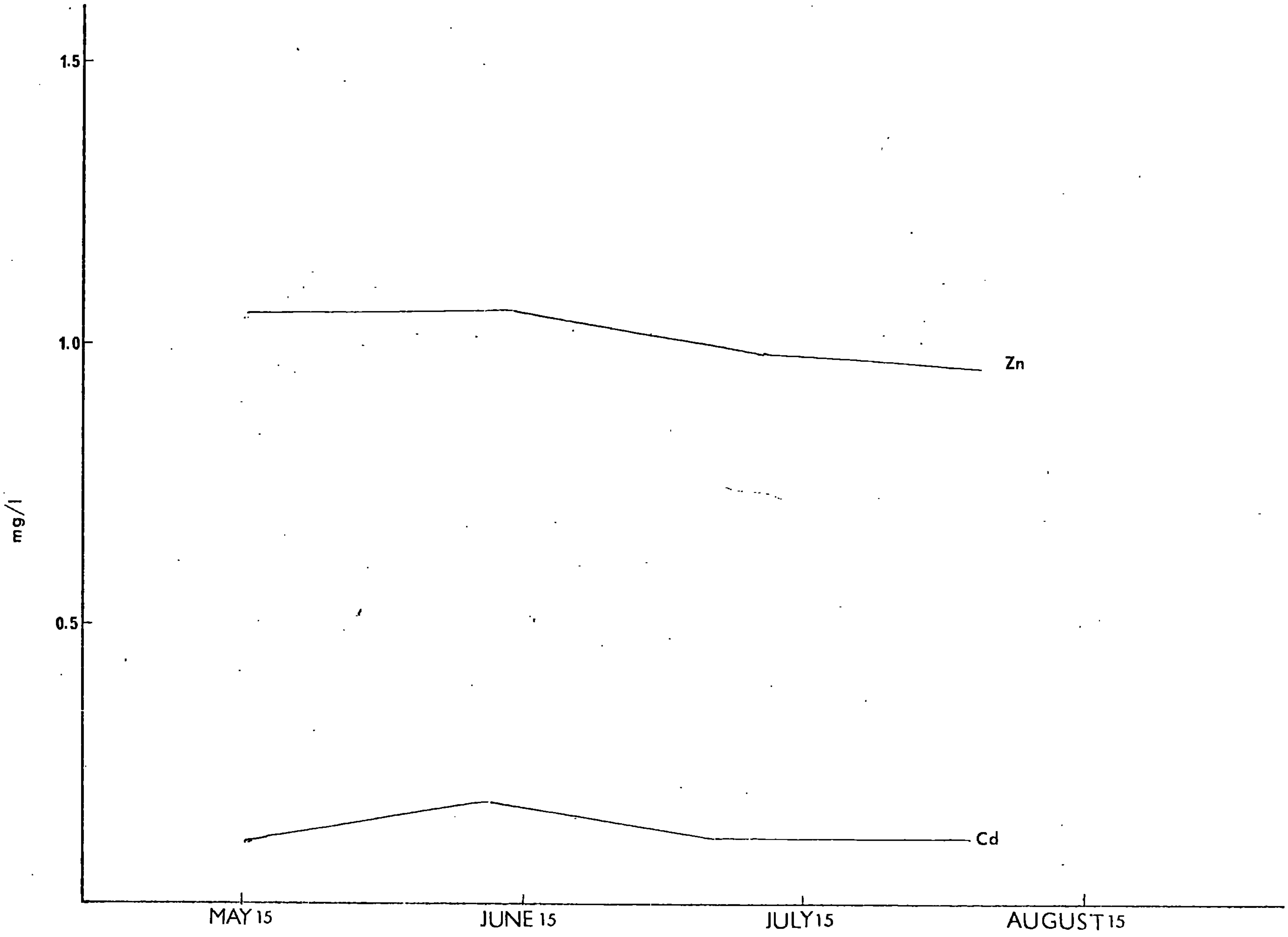

FIG. 7 MONTHLY VARIATION OF HEAVY METALS IN THE ACID STREAM

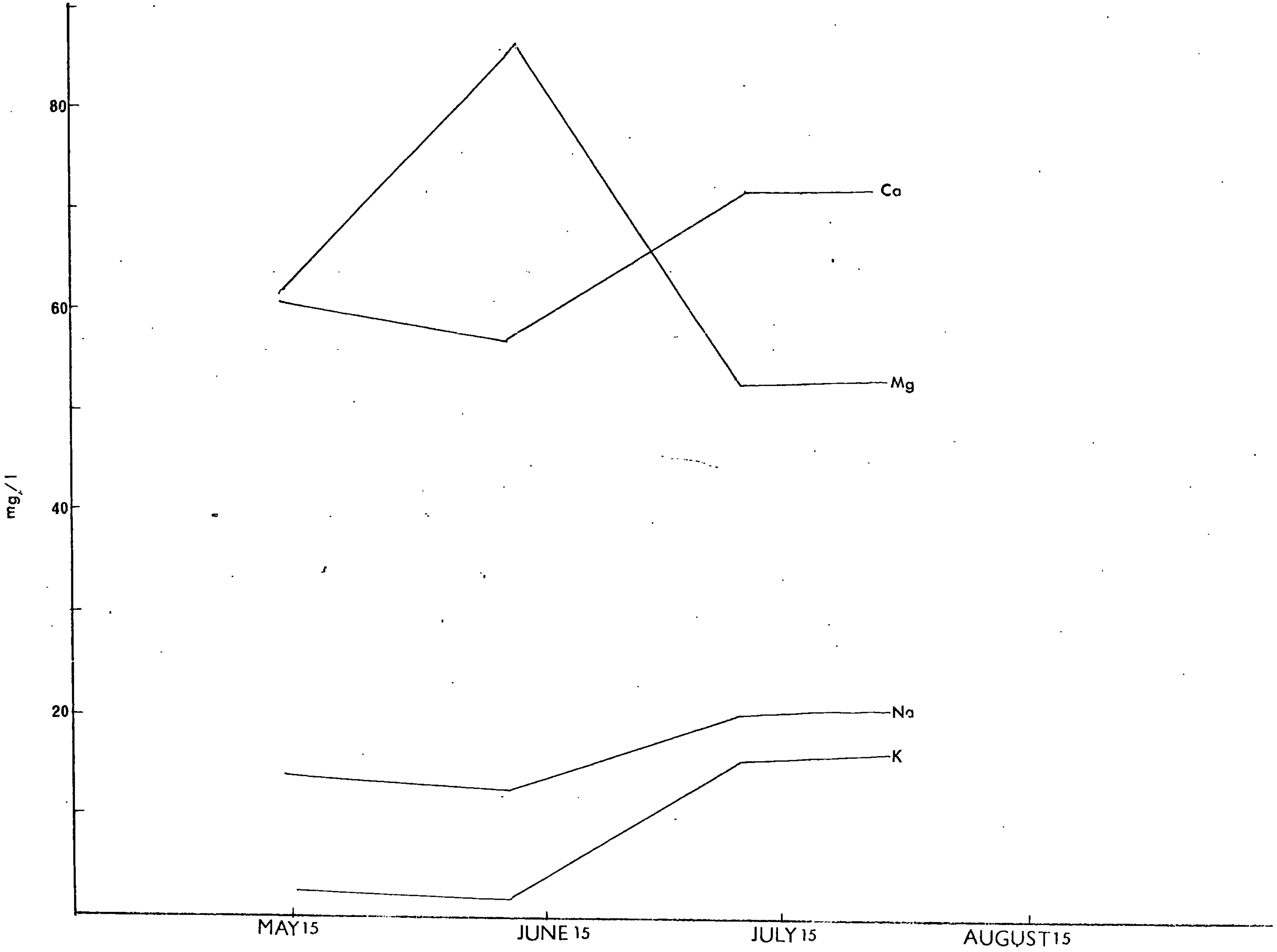

FIG. 8 MONTHLY VARIATION OF METAL-CATIONS IN THE ACID STREAM

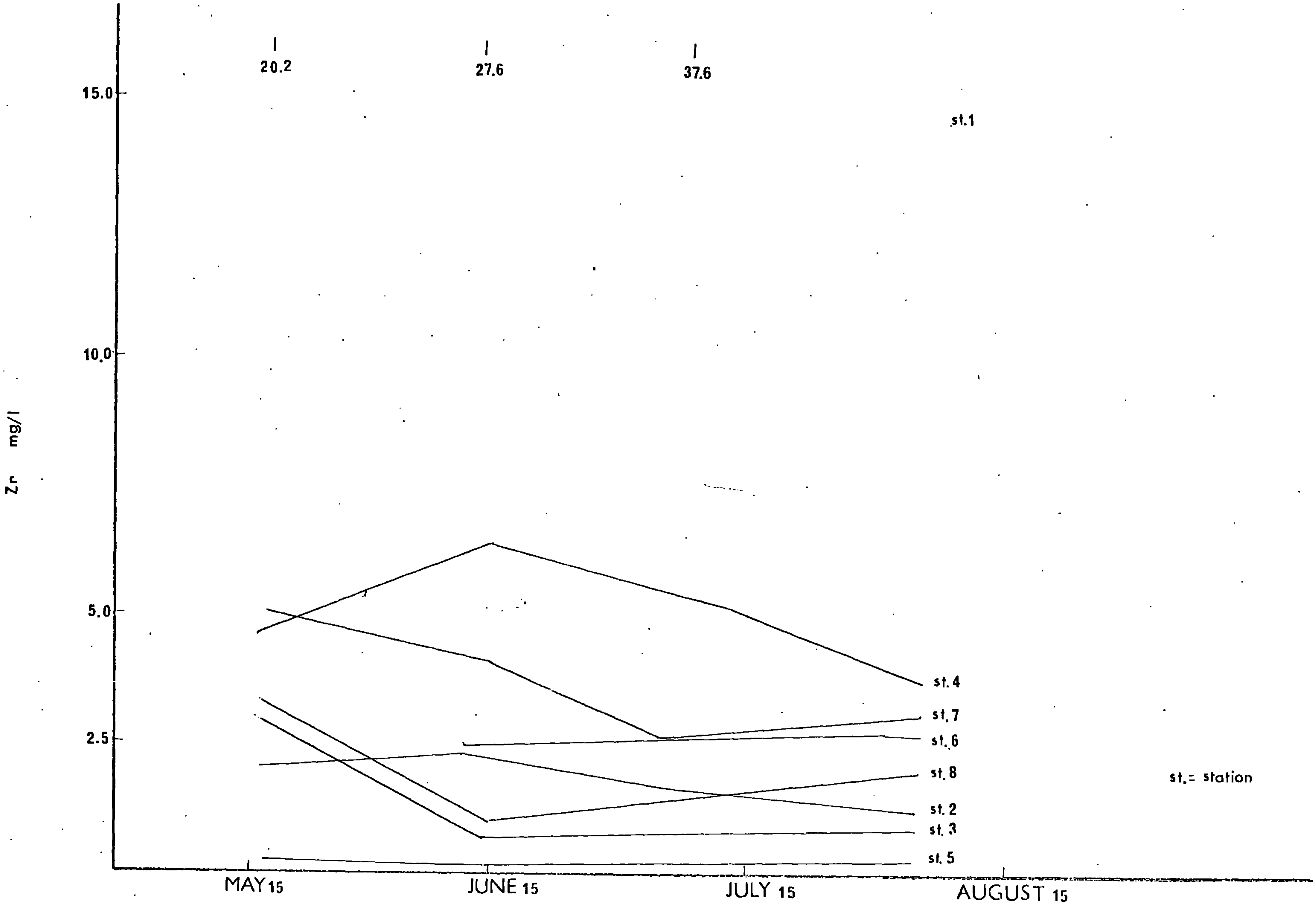

FIG. 9 MONTHLY VARIARATION OF ZINC IN THE NENTHEAD STREAM

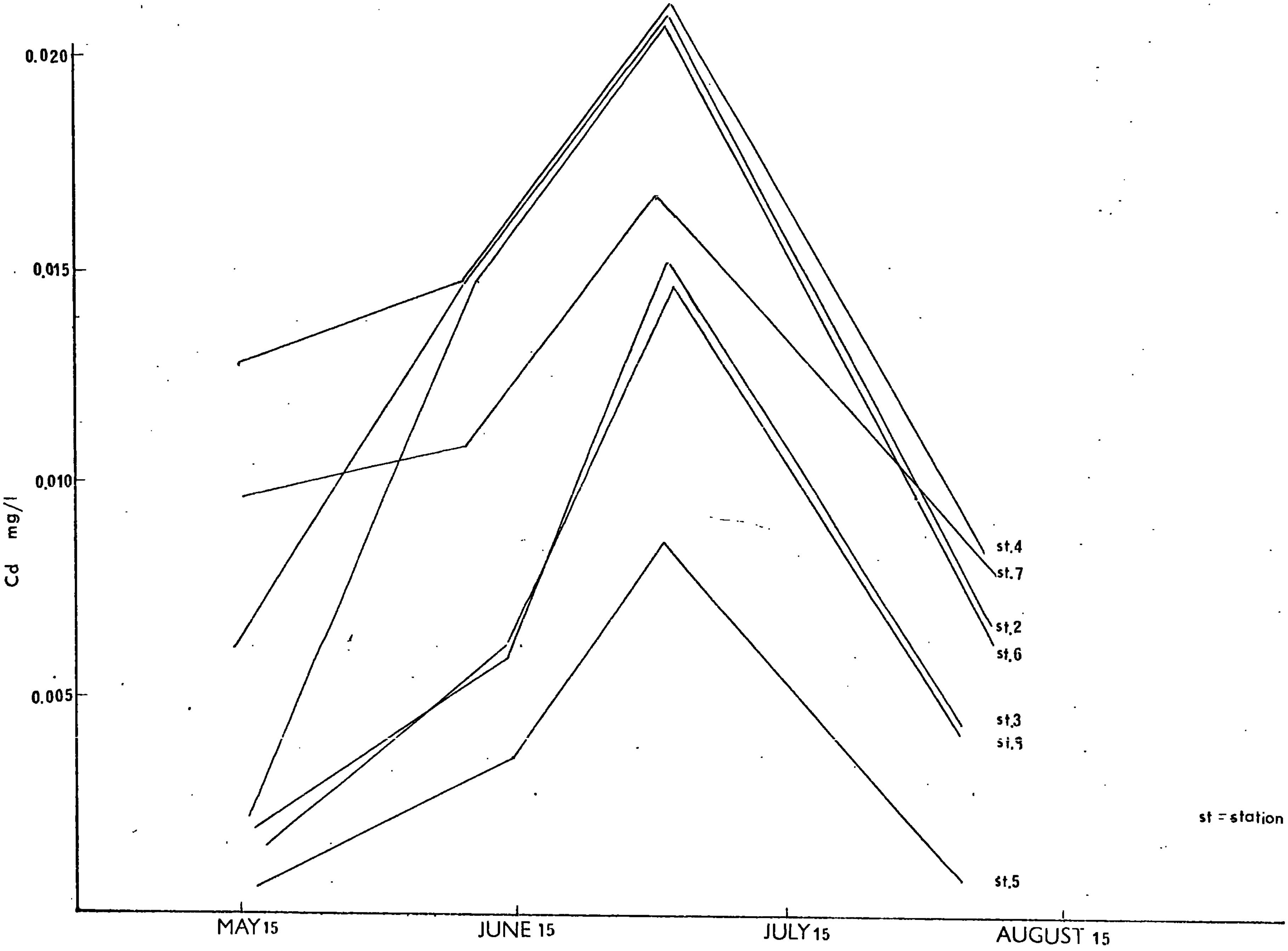

FIG.10 MONTHLY VARIATION OF CADMIUM IN THE NENTHEAD STREAM

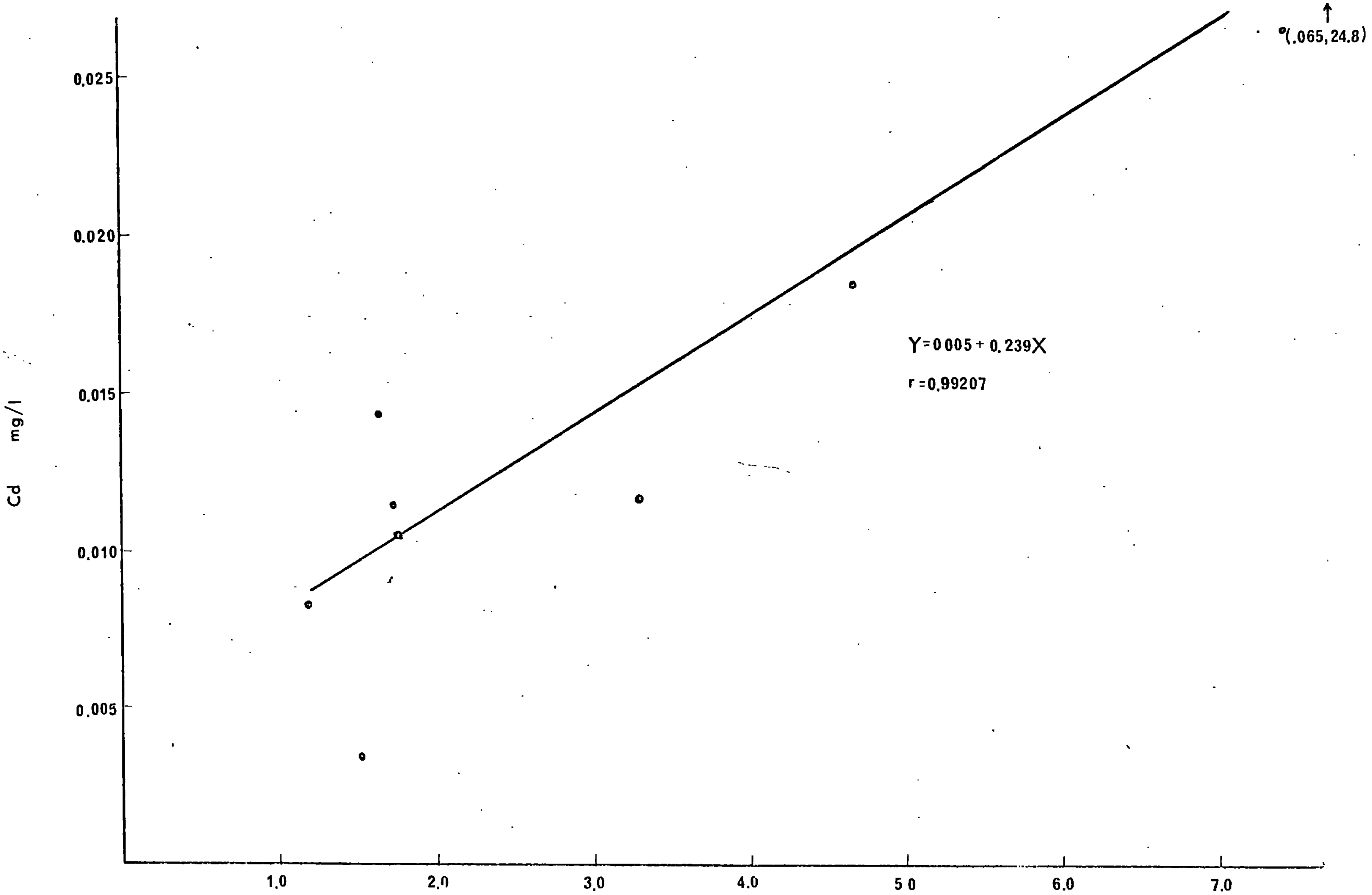

FIG. 11 RELATION BETWEEN CADMIUM(AQ) AND ZINC(AQ) CONCENTRATION

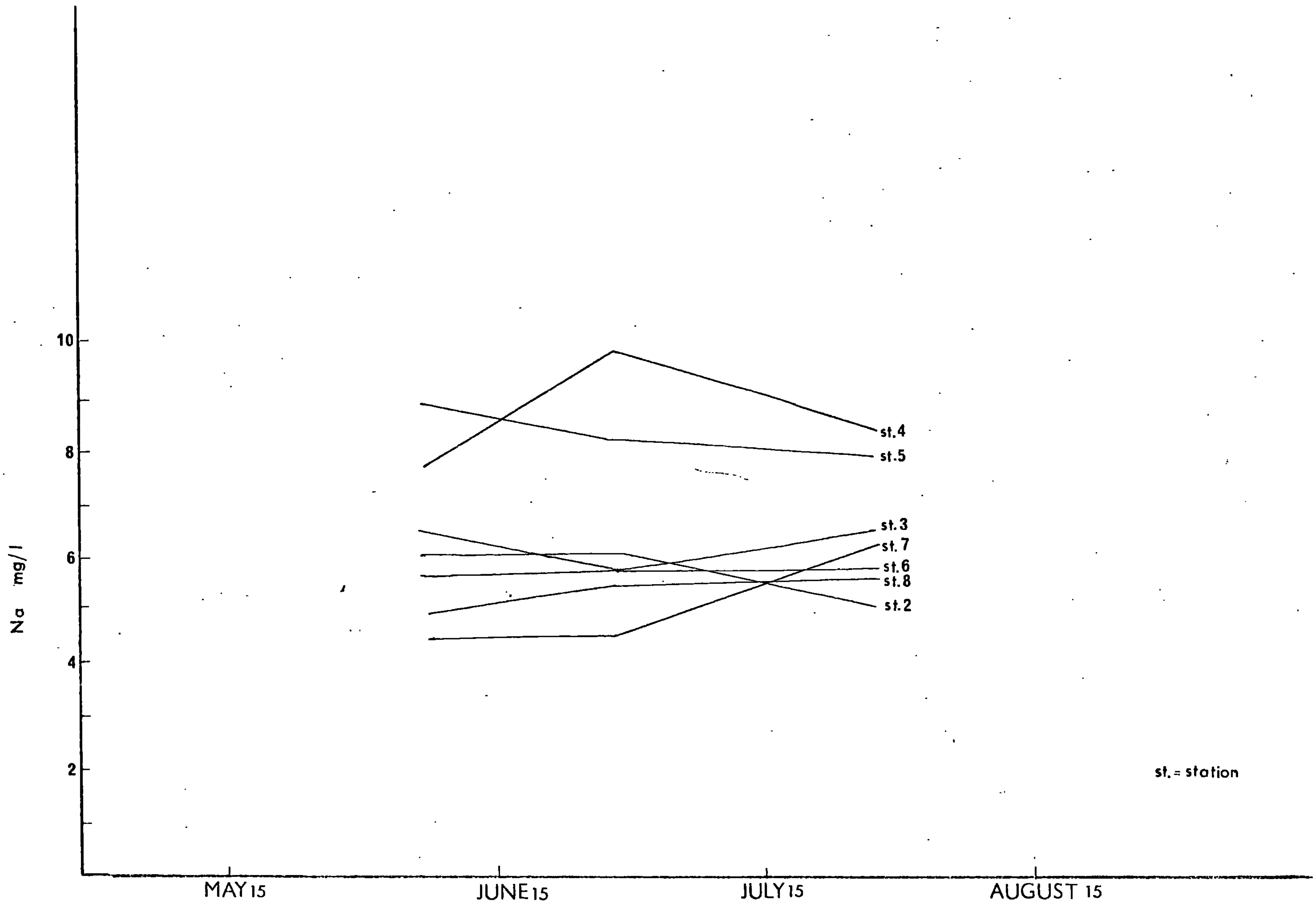

FIG.12 MONTHLY VARIATION OF SODIUM IN THE NENTHEAD STREAM

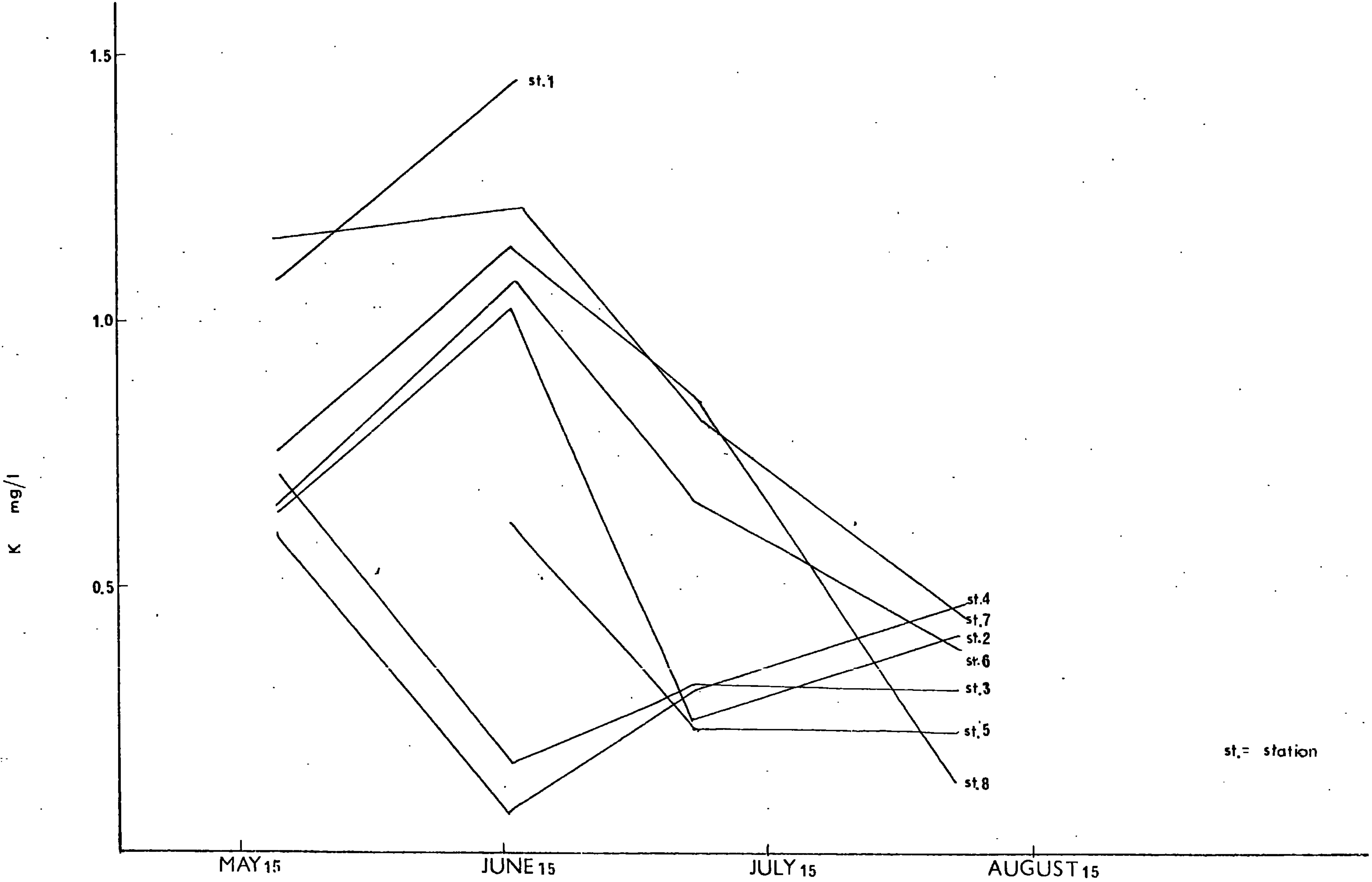

FIG.13 MONTHLY VARIATION OF POTASSIUM IN THE NENTHEAD STREAM

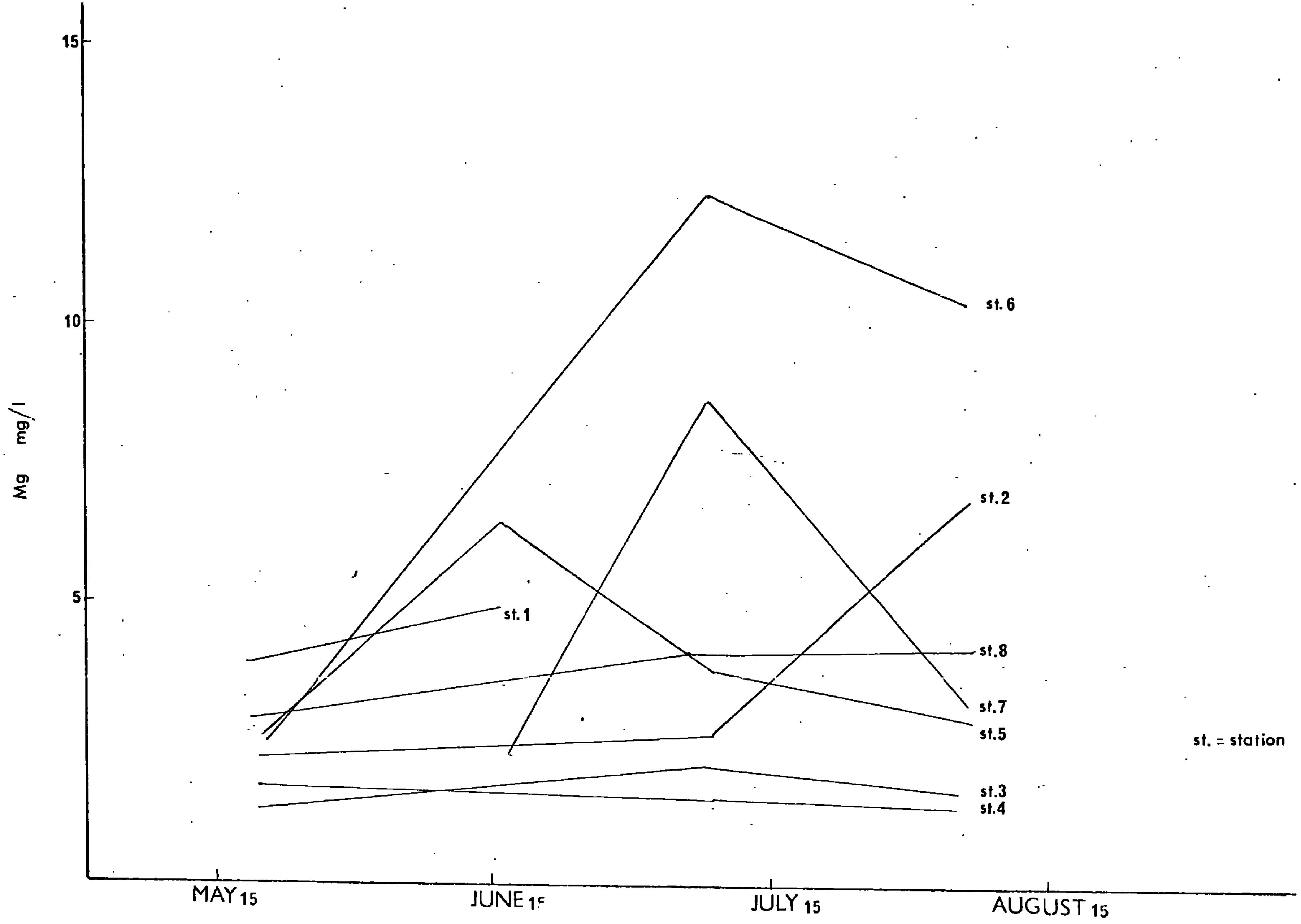

FIG. 14 MONTHLY VARIATION OF MAGNESIUM IN THE NENTHEAD STREAM

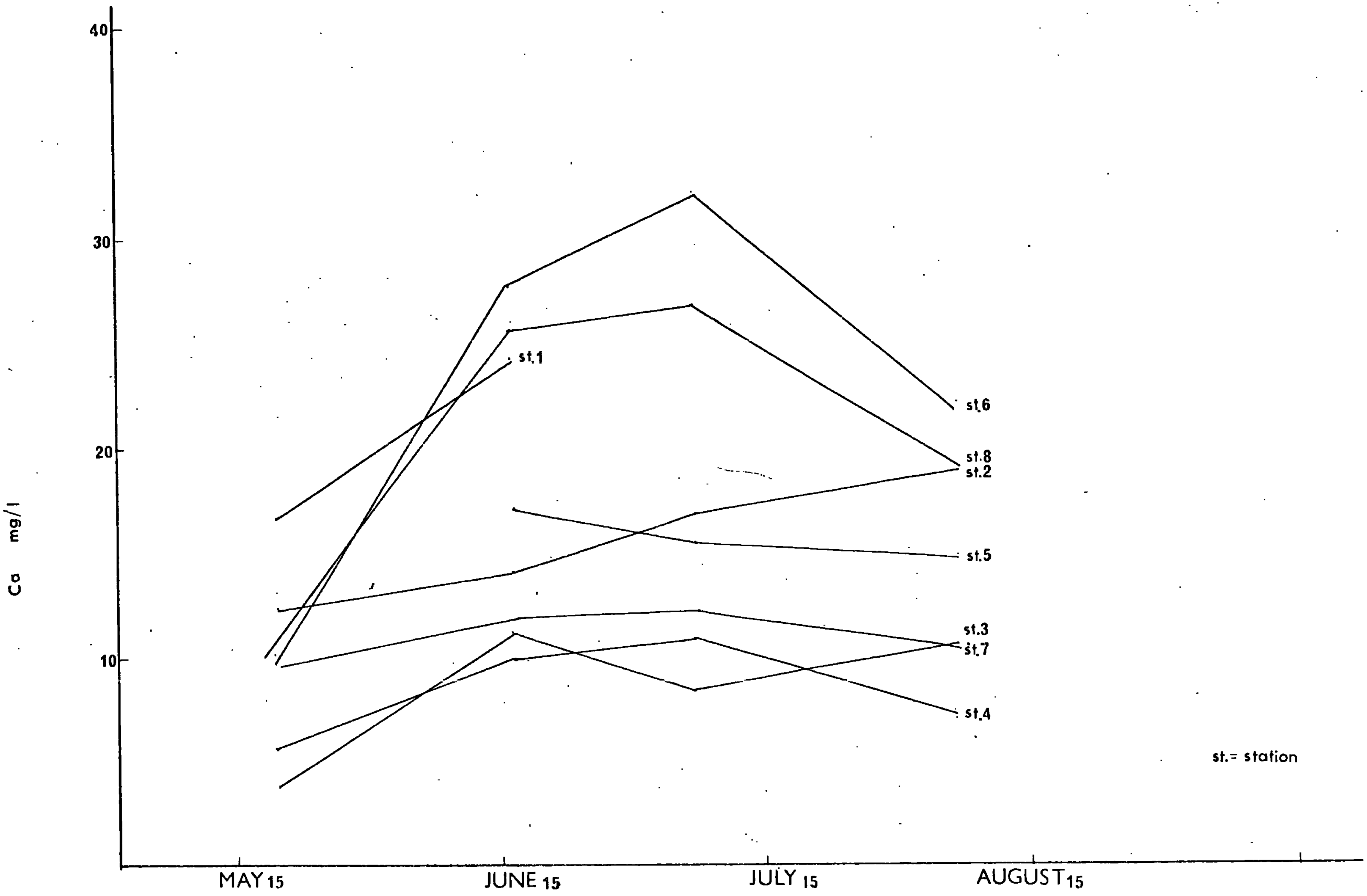

FIG.15 MONTHLY VARIATION OF CALCIUM IN THE NENTHEAD STREAM

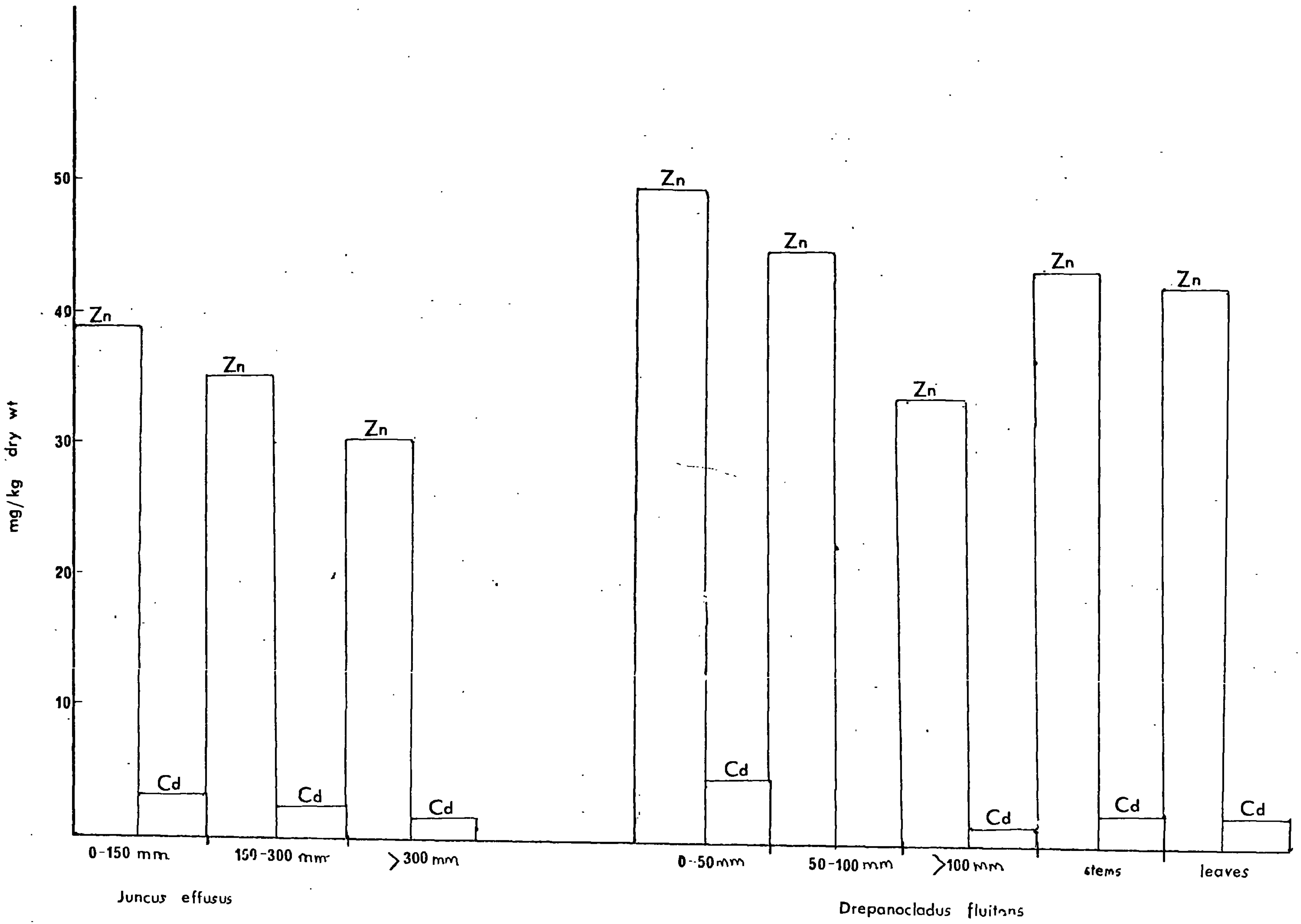

FIG.16 CONCENTRATION OF ZINC AND CADMIUM IN DIFFERENT SECTIONS OF JUNCUS EFFUSSUS AND DREPANOCLADUS FLUITANS FROM THE ACID STREAM

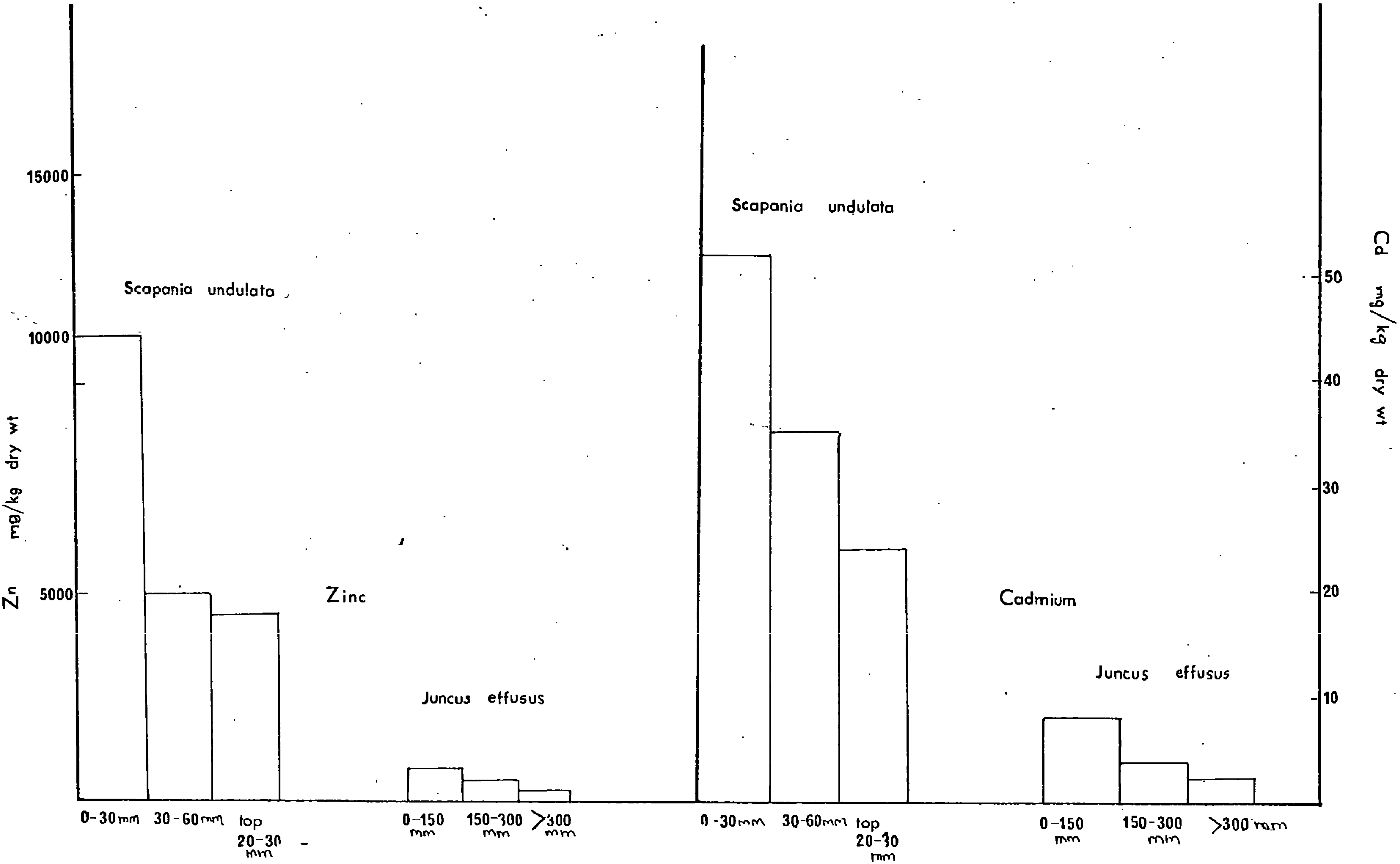

FIG. 17 CONCENTRATION OF ZINC AND CADMIUM IN DIFFERENT SECTIONS OF SCAPANIA UNDULATA AND JUNCUS EFFUSUS FROM THE NENTHEAD STREAM

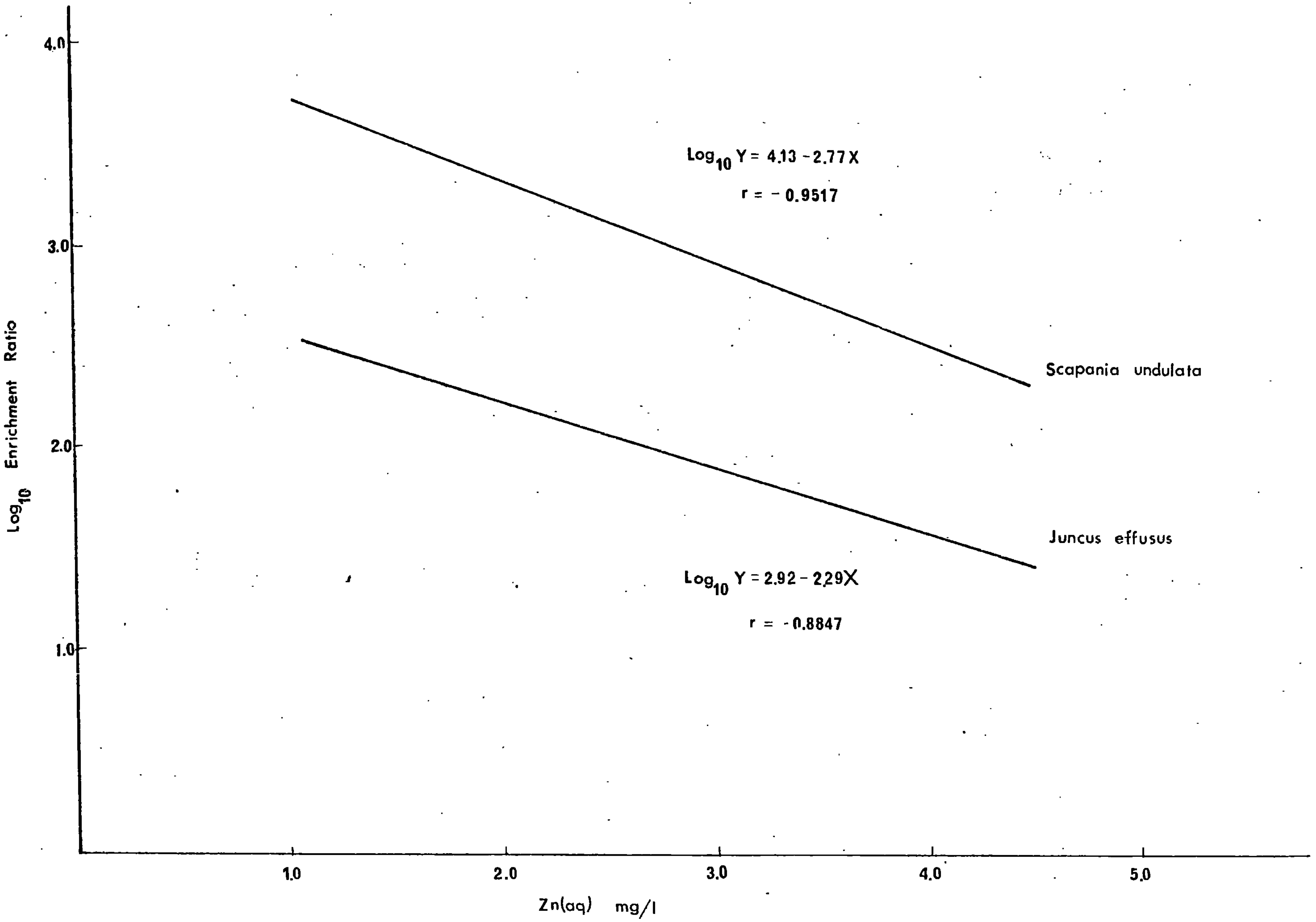

FIG.18 RELATION BETWEEN LOG_{10} ENRICHMENT OF FLORA AND ZINC(AQ) CONCENTRATION RATIOS

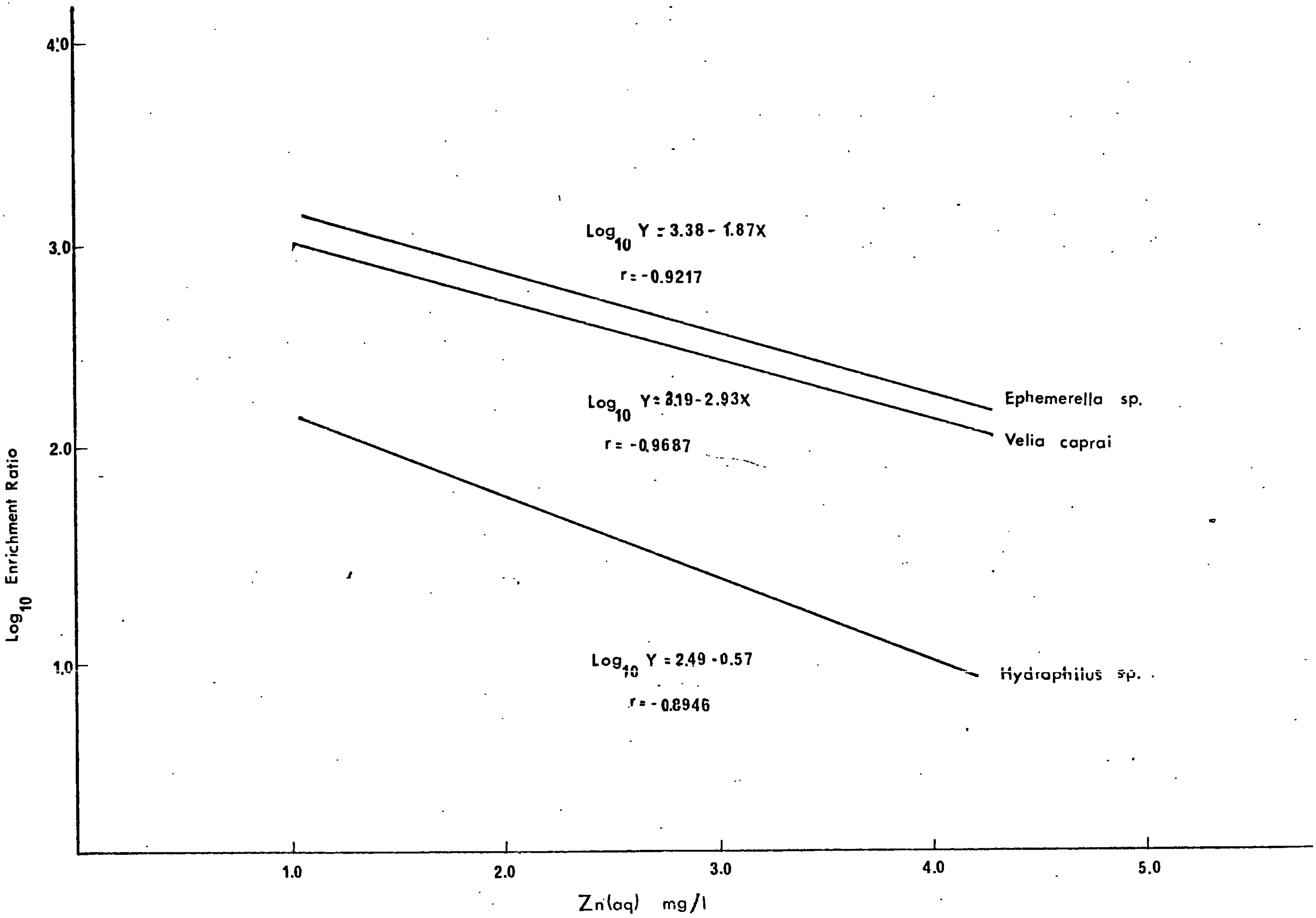

FIG.19 RELATION BETWEEN LOG$_{10}$ ENRICHMENT RATIOS OF FAUNA AND ZINC(AQ) CONCENTRATION

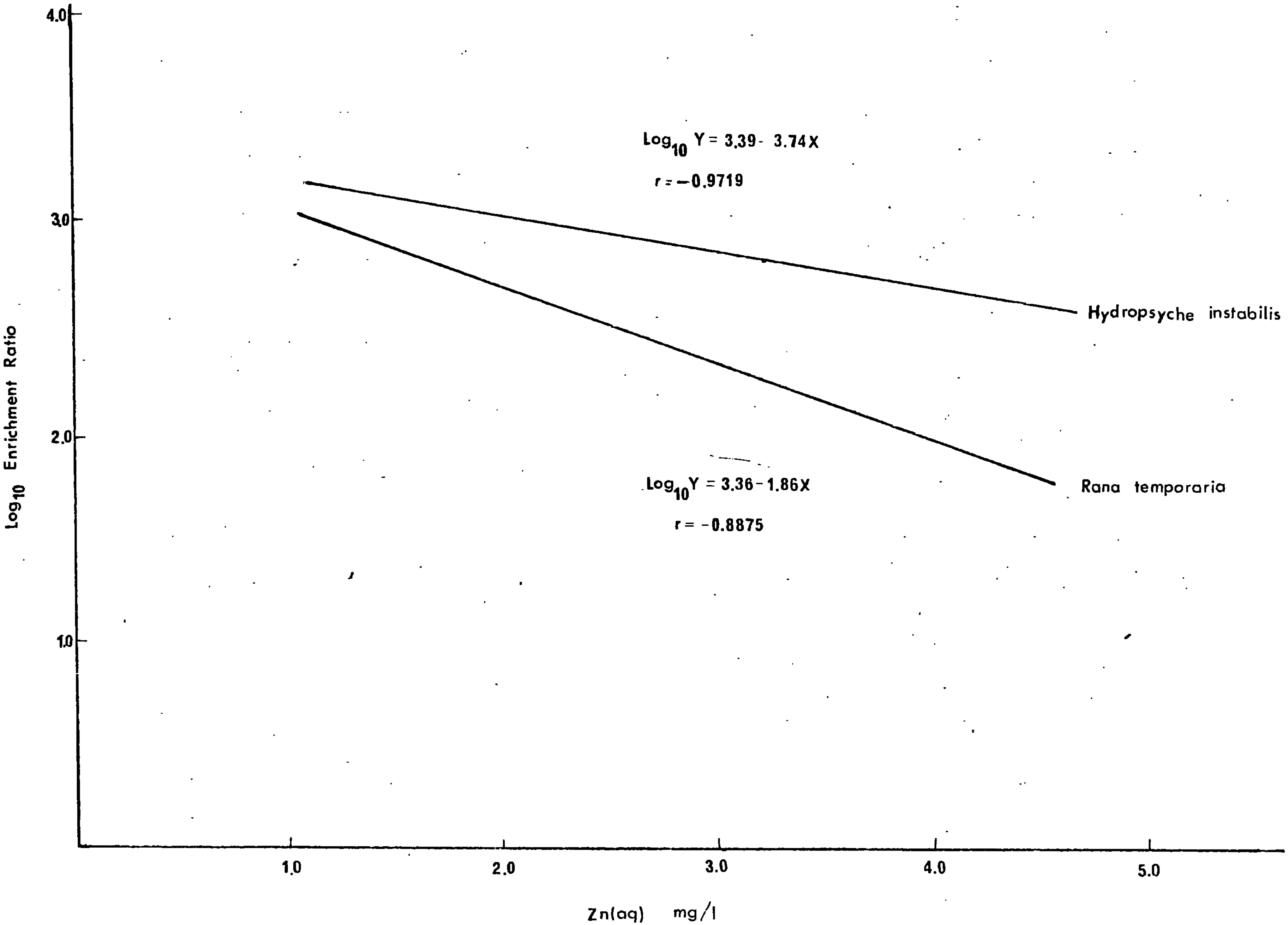

FIG.20 RELATION BETWEEN LOG_{10} ENRICHMENT RATIOS OF FAUNA AND ZINC(AQ) CONCENTRATION

5. DISCUSSION

5.1 Acid Stream and Station 2 Nenthead Stream

Zinc and cadmium concentrations in the acid water remained relatively constant throughout this study. The lower mean standard error for these elements suggest their distribution to be more stable and fluctuate less than the heavy metals present at station 2. High variations at station 2 (and the rest of the Nenthead Stream stations) causes some uncertainty about the mean heavy metal concentration, and this could seriously affect the enrichment ratios (Section 2.1) of the biotic material concerned. Water samples should have been taken more regularly.

Chi-square distribution has suggested that enrichment ratios of similar species or orders are significantly lower in the acid stream than station 2. The uptake and accumulation of zinc and cadmium are affected by the acid nature of the water.

Mechanisms by which heavy metals can become associated with stream flora are by adsorption and ion-exchange processes. The situation in the acid stream is unique. Adsorption of these elements by adhesion to the plant's surface would be negligible since most heavy metals tend to stay in solution in acidic environments. VanEverdingen (1970) reports that three-quarters of all available zinc was in solution in the acid streams (pH2.5-3.8) he investigated. Values of this nature would probably have been obtained from a more detailed study of the acid stream since very little zinc or cadmium was incorporated in particulate matter or sediment (Section 4.4).

Like adsorption, absorption through the leaf and root systems would also be minimal. This could be attributed to the type of cation exchange components in the cell wall. Ion exchange capacities of Fucus and Ulva were found to be pH sensitive (Gutknecht 1963). Poor uptake and accumulation rates probably account for the flora's low enrichment values.

Concentration ratios for the plant species of the more alkaline station 2 are much higher since more material could be derived from solution and sediment.

Invertebrate forms have many pathways for sorption of heavy metals. Not only can these elements be absorbed on the surface (Duke et al. 1966) or absorbed through the membrane (Bryan 1971) but a large quantity can be absorbed either directly or indirectly through the food chain (Cross et al. 1970). Lowman et al. (1966) states that probably the total amount of heavy metal passed between trophic levels is related to the amount associated with the food. Most energy in aquatic ecosystems passes through the detritus food chain rather than the herbivore food chain (Saunders 1972). The invertebrate fauna of the acid stream has fit into Cummins (1973) classification as basically detritivores with the exception of Enallagma cyathigerum, a carnivore. Food sources of these detritus feeders would be mainly derived from particulate matter and sediment. However, concentrations of zinc and cadmium in particulate matter and sediment show extremely low levels. Also, as in the acid stream flora, absorption through membranes and adsorption on the animal's surface would also be negligible. As a result, low enrichment levels would be expected.

High concentration ratios would obviously be the case for the insect fauna of station 2. Energy flow is probably also based on a detritus system. Mean levels of zinc and cadmium in particulate matter and sediment were several magnitudes higher than in the acid stream.

The high levels of sodium, potassium, magnesium and calcium in the acid stream could also modify the uptake and accumulation of heavy metal ions (Section 1.2a). With similar levels of calcium, Bryan (1967) demonstrated that zinc absorbance is reduced in the fresh water crab, Austropotamobius pallipes. Nilsson (1970) noted low accumulation and reduced toxic of cadmium at these high calcium levels in several plant species. High concentrations of these cations in the acid stream could therefore act as a secondary factor to account for the low enrichment values obtained.

The hydrogen ion concentration is an important variable affecting enrichment of zinc and cadmium. Still, the actual physiological modes of uptake and accumulation and how these are affected by variables such as pH is not known. A deeper more integrated knowledge is needed on this topic. Also, little attention has been given to the question of mixtures of environmental parameters (e.g. pH and alkaline earth metal slats) in uptake and accumulation processes.

5.2 Nenthead Stream

The natural concentration gradient was due to dilution by the various tributaries interlocking with the main stream. As already indicated (Section 5.1), heavy metal concentration at each site varied considerably during the study period and more water samples should have been taken. Also data concerning stream flow, precipitation and erosion should have been recorded to understand these fluctuations more carefully.

The direct relationship between zinc and cadmium levels in the stream coincide with the report by Hutchinson and Czyrska (1972) that cadmium is usually found associated with zinc.

The low levels of sodium, potassium, magnesium and calcium at the different stations show the stream to be only slightly calcareous and alkaline, offering little protection from heavy metals.

Poor correlation of sediment values suggest that zinc and cadmium sorption is perhaps related to the actual particle size distribution. For instance, Cross et al. (1970) observed low zinc concentration rates in sediment with a higher percentage of sand component than silt or clay.

Juncus effusus concentrated more zinc and cadmium in the root section and since this is the main uptake site one would expect this. Gregory (1964) and Leeder (1972) also report that heavy metals concentrated in the terminal parts of angiosperms. Similarly, both Scapania undulata and Drepanocladus fluitans (from the acid stream) accumulated more zinc and cadmium away from the tips. Both plant groups could perhaps reduce any toxic build-up in the "root" region by binding the heavy metals internally, a process like chelation, as suggested by Jowett (1958) for tolerant populations of Agrostis.

Enrichment ratios depend on the species concerned and their role in the community. The enrichment of zinc and cadmium in water plants is relatively higher in the mosses. This was also noted in the acid stream. Dietz (1972) and Leeder (1972) also found enrichment ratios for mosses much higher than for angiosperms. This suggests that mosses would be more effective as indicator organisms of heavy metal pollution. Enrichment of the detritivore *Velia caprai* is much lower than that of the carnivore *Hydropsyche instabilis*. The filter feeding nature of *Potamorphylax latipennis* and *Ephemerella sp*. accounts for their high concentration ratios. Chipman *et al*. (1958) and Cross *et al*. (1966) also observed the most intense enrichment for filter feeders. Even an organism of the third trophic level, *Rana Temporaria* registered lower zinc enrichment ratios than the filter feeders. Concentration ratios also vary with the life-history stage, as in the case of *Velia caprai* and *Tendipes sp*. (acid stream). Pyefinch and Mott, (1948) reported similar findings.

The inverse relation for enrichment of zinc demonstrates that the log-zinc accumulation is directly proportional to the amount of heavy metal concentration in the water. The poor relationship found for cadmium suggests that this element is not readily accumulated and this is in general aagreement with the literature.

This study has shown that enrichment ratios of zinc is a useful criteria to predict the average concentrations of zinc in the water column. It would be desirable for similar investigations to be carried out for other heavy metals in order to obtain a clear picture for enrichment.

SUMMARY

6. SUMMARY

An investigation was carried out to compare the enrichment ratios of biota found in an acid and alkaline environment. Both streams selected were located in areas of past mining activities and regular water analysis were carried out to ascertain the levels of zinc and cadmium.

Since the Nenthead stream provided a natural heavy metal concentration gradient, attention was also focused on the enrichment ratios of the flora and fauna concerned along this gradient.

Two species of bryophytes an angiosperm and an algae consisted of the flora analysed from both sites. Six species of insects from the acid stream and five species from the Nenthead stream made up the invertebrate fauna. One vertebrate species, Rana temporaria was also sampled.

Enrichment ratios of biological matter, particulate matter and sediment were much lower in the acid stream than station 2 of the Nenthead stream. These lower accumulation levels recorded were due to the acidic nature of the water.

Enrichment levels of the flora were highest in the mosses from both areas.

More accumulation took place away from the tip for the mosses and nearer the root for the angiosperms.

The filter-feeding tricopteran Potamorphylax latipennis and ephemeropheran Ephemerella sp. had the highest enrichment ratios of all species investigated.

Inverse correlations of enrichment ratios revealed that log-zinc bioaccumulation is directly apportional to the

aqueous zinc concentration. These correlations also suggested that cadmium is not readily accumulated.

Enrichment ratios are a useful "tool" for studying environmental effects on accumulation and predicting the average amount of heavy metals (zinc) in the water column.

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