

Durham E-Theses

An investigation of heavy metal ion concentrations in littoral and sub-littoral marine ecosystems

Starkie, Alan

How to cite:

Starkie, Alan (1970) *An investigation of heavy metal ion concentrations in littoral and sub-littoral marine ecosystems*, Durham theses, Durham University. Available at Durham E-Theses Online: <http://etheses.dur.ac.uk/9159/>

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.

AN INVESTIGATION OF HEAVY METAL ION CONCENTRATIONS IN
LITTORAL AND SUB-LITTORAL MARINE ECOSYSTEMS

Alan Starkie

The University of Durham,
formerly at the University College of North Wales, Bangor.

A dissertation submitted to the University of Durham
as part of the requirement for the degree of Master
of Science (Advanced Course in Ecology),
September, 1970.



I N D E X

Summary	iii
Introduction	1.
Site selection and the pollution gradient	3.
Literature review	5.
Materials and methods	12.
Results	17.
Discussion	18.
Bibliography	25.
Appendices.	

S U M M A R Y

Some common littoral and sublittoral marine organisms have been analysed, using atomic absorption spectrophotometry, to determine the concentration of copper, iron, lead, zinc and mercury they contained.

The results show that there is variation in the concentration of these elements, (1) in given species taken from different sites, (2) in different species taken from the same site, and often (3) with age in a given species.

The geographical variation, seen in all species analysed, is correlated with the concentration heavy metal ions in the water the organism lives in.

It is suggested that analysis of heavy metal ion concentrations in organisms is a good means of monitoring this type of pollution.

The variation between species may, in some cases, be correlated with an accumulation of heavy metal ions up the food chain, but in polluted waters there is evidence of the breakdown of the natural food webs and/or regulation of heavy metal ions.

Suggestions for future research strategy are included.

An Investigation of heavy metal ion concentrations in littoral and sub-littoral ecosystems.

Introduction

The President of the United States' advisory committee has stated:-

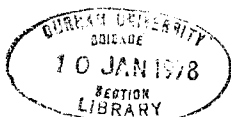
"Environmental pollution is the unfavourable alteration of our surroundings, wholly or largely as a by-product of men's action, through direct or indirect effects of changes in energy patterns, constitution and abundance of organisms."

In the marine environment this includes such activities as dredging, the introduction of sewage, domestic and industrial liquid wastes, coal washings and other solid wastes into the sea directly, or indirectly via the rivers.

Pollution can, however, be classified into two main types; the first involves the introduction of completely new substances into the environment and the second involves an increase in the level of a naturally occurring substance which is already present.

In recent years technological advances have lead to the production of many new chemicals. For example, more than 90% of the pesticides in use today are synthetic compounds. The introduction of such novel toxic substances as these into an ecosystem often has comparatively straightforward effects. The organisms that are susceptible to the toxin and absorb a lethal dose are eliminated whilst those that have a natural resistance, or receive sub-lethal doses, survive.

This can also be the consequence of the second type of pollution, which involves a faster cycling of naturally occurring biogeochemicals. This, however, is often complicated by the fact that organisms have evolved over many years in the presence of these chemicals, and had the opportunity to undergo further evolution as the concentration of these chemicals has increased. Often these elements are even involved in metabolic processes.

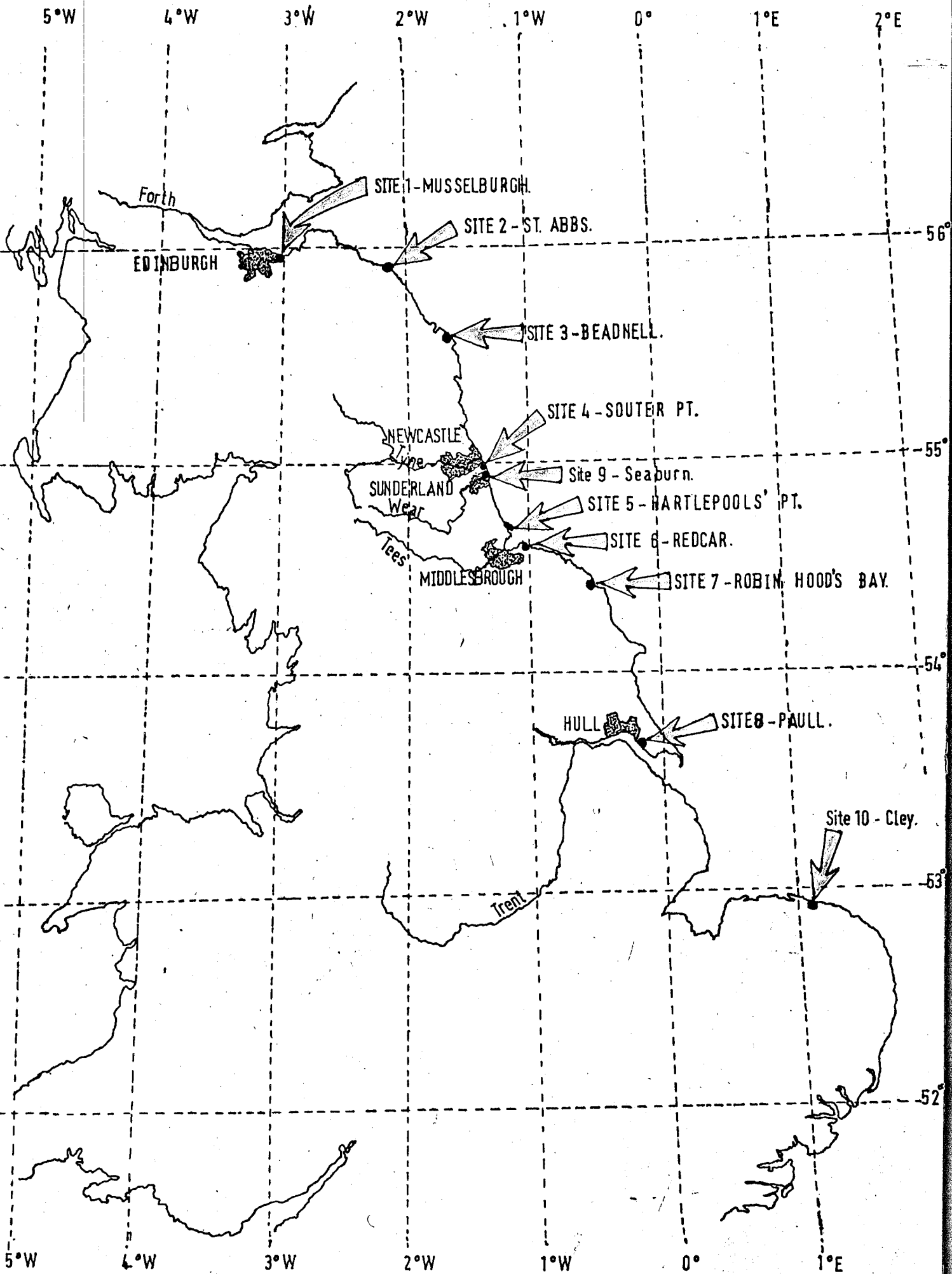


Nature has an enormous capacity to recover from minor modifications of the environment, and these have been characteristic of the development of civilisation during most of recorded history. One therefore might be lead to expect a more complex or more subtle reaction to this second type of pollution than that resulting from the first.

Although one of the proper uses of the marine environment is in its capacity to dilute and disperse the waste products of society, care must be taken to ensure that this use does not exclude other equally valuable activities. The latter include such things as food production and recreation. It is equally important that we do not poison the system by adding to it more waste than it can accept. For man's future well-being it would therefore be beneficial to be able a) to define 1) the extent of polluted water, and 2) the extent to which it is polluted, and b) to monitor the effects this pollution is having within the ecosystem. It was thought that a study of the concentrations of some of these biogeochemicals, namely the heavy metal ions, in the ecosystem might assist us in defining the degree and extent of pollution and might also help us towards a deeper understanding of its effects. This would allow more accurate prediction of future trends.

Site Number	Major Sites	Location		Suspended Solids Mg / l	SITE DATA	
		Lat.	Long.		Faecal Bacteria per litre	P04 ug / l
1.	Musselburgh, Midlothian.	55°57'N	3°02'W	30	100,000	50
2.	St. Abbs, (Petticoe Wick), Berwickshire.	55°55'N	2°09'W	12.1	200	0.37
3.	Beadnell Bay, Northumberland	55°33'N	1°37'W	18	9,000	1.74
4.	Souter Point, County Durham	54°58'N	1°20'W	58	100,000	2.78
5.	Hartlepool's Point, County Durham	54°41'N	1°11'W	70	160,000	71.9
6.	Redcar, North Riding, Yorkshire.	54°37'N	1°04'W	n.d.	n.d.	3.3
7.	Robin Hood's Bay, North Riding, Yorkshire.	54°26'N	0°31'W	52.5	n.d.	2.48
8.	Paull, East Riding, Yorkshire	53°42'N	0°13'W	n.d.	n.d.	n.d.
ADDITIONAL SITES						
9.	Seaburn, County Durham	54°56'N	1°22'W	n.d.	n.d.	5.3
10.	Cley, Norfolk	52°57'N	1°03'E	n.d.	n.d.	n.d.

FIGURE I. MAP SHOWING THE LOCATION OF THE SAMPLING SITES



Scale 1:2,500,000 (40 miles = 1 inch).

Site Selection and the pollution gradient

I chose the major sites which are listed in table I and shown in the map (figure I) because they appear to belong to a series differing in the degree of pollution of the water. Two additional sites which were not studied in detail are also included in the table. These are Seaburn, where samples of Mytilus edulis, the mussel, and Nucella lapillus, the whelk, were collected on a sewage pipe close to its outlet and Cley where Asterias rubens, the starfish, were collected after a large kill had occurred and thousands of individuals had been washed up on the shore.

Current research has shown that, as one might expect, there is a difference between the unpolluted water off the coast of North Northumberland and South-East Scotland and the heavily polluted waters off the Durham coast. These waters are polluted because the valleys of the Tyne, Wear and Tees are occupied by large urban populations (190,000 people in the Tyneside, and 170,000 people in the Teesside conurbations) and are the site of heavy engineering, shipbuilding, chemical and other industries. This also applies to the Firth of Forth and Humber Estuaries.

The parameters shown in table I are figures that are available (Bellamy et al, 1967, John, 1968, Jones, 1970) as indicators of the extent of pollution. The number of faecal bacteria, estimated by a Standard Method, A.P.H.A., (1965) indicates the extent of pollution by sewage. Phosphate and nitrate, two biologically important compounds, are nutrients that are usually in short supply in the open sea and such high values therefore probably indicate the extent of nutrient enrichment by eutrophicated river water - the nutrients having been derived from land drainage and sewage effluent. A report just published ("Taken for Granted 1970") points out that up to half the water of the Tyne, Wear and Tees is treated sewage effluent. All the sewage of the City of Edinburgh is discharged raw into the estuary. A recent report ("The Scotsman," August 10th, 1970) states that there were at least 10,000 square yards of untreated sewage lying at low tide mark at Seafield. Pollutants also include domestic and

industrial liquid wastes, the products of agricultural and engineering erosion, and solid wastes, such as coal washings and fly ash (from electricity generators). Jones (1970) points out that up to five hundred thousand tons of fly ash and over one million tons of coal washings and silt were deposited in the sea adjacent to Tynemouth each year.

It has been found that the macrophyte flora of the Durham coast is restricted, both in diversity and performance. This is thought to be caused by suspended matter reducing the light available to the plants. (Bellamy et al., 1967, Bellamy, 1968, Bellamy et al., 1968).

The tidal wave on the coast moves from North to South. There is also a residual current from North to South (Admiralty Tide Tables, 1970), both of which cause movement of the water in a southerly direction. Thus polluted water from the Tyne, Wear, and Tees will be dispersed southwards, but south of Redcar the sea water becomes less polluted due to mixing. It contains, however, high levels of inorganic material in suspension generated by fresh water erosion of the boulder clay cliffs, which are characteristic of the region.

It was my hope that by collecting and analysing various species from each site for heavy metal ion concentrations it would be possible to define the degree and extent of the pollution described above. As a subsidiary study various age groups of the species to be analysed were also collected in an attempt to gain some insight into the effect this pollution is having in the ecosystem.

Literature review

Sea water probably contains every chemical element but some have not yet been detected. Much information is available on the occurrence of various elements in marine plants and animals, but it is not yet comprehensive. Some of the earliest analyses for heavy metal ions in marine organisms seem to have been made by Philips (1917), Cornée (1919), Bodensky (1920) and Severy (1923). With the development of improved analytical techniques more work has been done on the minor constituents of sea water and their concentration by marine organisms.

The term 'minor constituents' can be misleading, as Harvey (1955) points out, in that even at exceedingly great dilution of an element the number of its atoms in a small volume of water is very great. As an example he quotes the fact that a sea water sample containing 0.004 u. g. gold per litre will contain 2 million atoms per mm³. It follows that many atoms of even these very dilute elements, will make contact with the surface of organisms in the sea, allowing absorption and adsorption to occur.

Concentrations of trace metals in sea water are usually in the region of 1 - 10 u g/l (Bryan 1969) but it is difficult to generalise as variation is seen both from element to element and with geographical location, especially in coastal waters. Tables giving the trace elements which have been determined in sea water have been compiled by Sverdrup, Johnson and Fleming (1942 pp 176-177) Harvey (1945 pp 31-32), Legendre (1947) and Harvey (1955 pp 140-141).

A survey of the literature suggested that it is possible, on the one hand to find marine organisms that regulate the internal concentration of heavy metal ions almost completely and are not appreciably affected by the external concentration (e.g. Bryan 1966) and, on the other, to find organisms which are unable to regulate the concentration at all. (Black and Mitchell, 1952, Young and Langille, 1958, Gutnecht, 1965). Other organisms fall between these two extremes, e.g., zinc regulation in the oyster, Crassostrea virginica, is only partial. (Chipman, Rice and Price, 1958).

Discussion of this problem in general terms is limited and so the literature concerning the concentration of the various ions investigated is now discussed separately.

Copper

Sea water has been analysed for copper by a number of people. Chow and Thompson (1952) have tabulated the results of various observers and show a wide variation in its concentration. Values ranged from less than 1 $\mu\text{g}/\text{l}$ in oceanic water to as much as about 25 $\mu\text{g}/\text{l}$ in certain estuarine waters.

Copper is essential for plant growth. It occurs in several enzymes and in the chloroplasts. It is also important to many animals occurring, for example, in haemocyanin, the respiratory pigment of many invertebrates.

Cornec (1919) carried out the first spectrographic analyses of marine plants and found copper present. The analyses, however, were qualitative and the species investigated were not given.

In 1940 ^Hby discussed the physiological importance of certain elements, including copper, in several species of algae and determined the concentration of copper to be 1.1 - 1.4 $\mu\text{g}/\text{g}$ of dry matter in Ascophyllum nodosum, 4 $\mu\text{g}/\text{g}$ in Laminaria and 3.4 - 8.4 $\mu\text{g}/\text{g}$ in Fucus vesiculosus.

Black and Mitchell in 1952 analysed for trace elements in algae and found a seasonal variation with June values (taken as being representative of the summer metabolic state) reaching 10 $\mu\text{g}/\text{g}$ in oven dried Fucus vesiculosus, 21 $\mu\text{g}/\text{g}$ for the stipe and 6 $\mu\text{g}/\text{g}$ for the frond of Laminaria digitata. Values for the sea water were put at less than 3000 $\mu\text{g}/\text{l}$. with the method used which is clearly far above the concentration that one would expect to be present. Harvey (1955) quotes the concentration of cupric ions (the typical form in sea water as cuprous ions are rapidly oxidized to cupric) which is poisonous to marine plants and animals to vary around 1000 $\mu\text{g}/\text{l}$.

Young and Langille (1958) analysed algae from the Atlantic coast of Canada and found copper concentrations ranging from 6 - 62 p.p.m. (equivalent to $\mu\text{g}/\text{g}$) occasionally with exceptionally large amounts of about 100 p.p.m. in Ulva and Laminaria.

Bryan (1964 and 1968) measured copper concentrations in decapod crustaceans and found there was from 20 - 35 $\mu\text{g}/\text{g}$ of fresh weight of copper, and suggested this constancy was due to the regulation of the concentration in the body fluids and tissues.

Iron

Natural sea water contains from 1 - 60 $\mu\text{g} / \text{l}$ of iron (Harvey 1955). The quantity of iron in true solution in sea water is however very small, owing to the insolubility of ferric hydroxide in the alkaline pH (8.1 - 8.3) of natural sea water. Iron is associated with land drainage and is normally present at higher concentrations in coastal waters than in the open sea. (Schaeffer and Bishop, 1958).

Harvey (1937), Goldberg (1952) and others have presented evidence that the algae can, and do, utilize particulate iron as their major source of this element, presumably by hydrolysing particles adsorbed on their surfaces.

Ryther and Kramer (1961) investigated the relative iron requirements of some coastal and offshore plankton algae and found that the oceanic species required less iron than coastal species. Oceanic species attained maximum populations at levels of iron capable of supporting either no growth or a small fraction of the potential growth of the coastal species under the conditions of the experiment. The oceanic species attained maximum growth with no additional iron to 20 $\mu\text{g} / \text{l}$ of additional iron whilst the coastal species required 65 - 1300 $\mu\text{g} / \text{l}$ for maximum growth.

Oy, in his study in 1940, estimated the concentration of iron to be between 120 and 1330 $\mu\text{g} / \text{g}$ of dry matter in several species of algae.

Black and Mitchell (1952) found the summer concentration of iron to reach 730 $\mu\text{g} / \text{g}$ in Fucus vesiculosus and about 1500 $\mu\text{g} / \text{g}$ in the stipe of Laminaria digitata, whilst values for the frond remained lower at 410 $\mu\text{g} / \text{g}$ of dry weight.

Lead

Harvey (1955) quotes the concentration of lead in sea water, according to two authors, Bowy (1938) and Noddack (1940) as being 4 - 5 $\mu\text{g} / \text{l}$. Black and Mitchell (1952) quote values of less than 8 $\mu\text{g} / \text{l}$ to less than 5 $\mu\text{g} / \text{l}$ for the samples they analysed.

Little data is available on the concentration of lead in marine organisms. Figures for lead are included by Webb (1937) in his studies on the ultimate

comparison of biological material. Black and Mitchell (1952) found the concentrations of lead to reach 7 $\mu\text{g/g}$ of dry weight in Fucus vesiculosus, 7 - 16 $\mu\text{g/g}$ in the stipe and 4 - 7 $\mu\text{g/g}$ of dry weight in the lamina of Laminaria digitata in summer. A concentration of 8 p.p.m. is reported for Chondrus crispus by Young and Langille (1958). This was based on only two estimations.

Mercury

There seem to be only a few references in the literature concerning the concentration of mercury in sea water and marine organisms. This may be because concentrations are usually very low making the element difficult to detect.

An analysis of the concentration in sea water by Stock and Gucael (1934) gave a value of 0.03 n.g / g (1 n.g = 10^{-9} g) equivalent to 0.03 parts per billion.

The only other analysis of marine material for mercury appears to be that of sea fish, carried out by Raeder and Snekvik (1941). They quote values of 25 - 155 n.g / g.

Recently, when the Swedes anticipated problems being caused by the use of methyl and ethyl mercury compounds as seed dressings certain animals and plants were analysed for mercury content (e.g. Johnels et al., 1967, Linnell and Stenmark 1967, Tejning 1967). Pheasants (Phasianus colchicus L.) are quoted as containing up to 0.93 $\mu\text{g/g}$ in the musculature (Tejning, 1967) and pike, (Esoc lucius L.) in contaminated water up to 3 $\mu\text{g/g}$ in the axial musculature.

Zinc

Atkins (1936) estimated zinc in sea water to have a concentration of less than 8 $\mu\text{g/l}$, Black and Mitchell (1952) quote the slightly higher concentration of 9 - 12 $\mu\text{g/l}$ for Atlantic water whilst Gutknecht (1963) found between 2 $\mu\text{g/l}$ and 18 $\mu\text{g/l}$ for Woods Hole Harbour water and Parker (1962) 8 $\mu\text{g/l}$ in the water of a Texas Bay.

Zinc, like iron and copper is metabolically important (Malstrom, 1956; Wessner, 1962, and Vallec, 1962) but low concentrations in water are reported

to be toxic to higher plants. Chipman et al (1958) tested marine phytoplankton for zinc toxicity and found the lowest concentration which reduced the division rate of Nitzschia to be 250 $\mu\text{g} / \text{l}$. This was approximately ten times the concentration found in the sea-water samples they collected.

In his study Parker (1962) analysed the sediments in the bay for zinc content and found concentrations of 10 - 18 p.p.m. These values are at the lower end of the range of those reported by Ishibashi et al (1959).

Black and Mitchell (1952) have reported summer concentrations of up to 105 $\mu\text{g} / \text{g}$ in dried Fucus vesiculosus and values of 90 $\mu\text{g} / \text{g}$ in the dried stipe of Laminaria digitata compared with approximately 65 $\mu\text{g} / \text{g}$ in the dried lamina.

Young and Langille (1958) found a similar range of concentrations of zinc from 35 - 97 p.p.m. in the various species of algae they analysed, as did Parker (1962) who quotes 60 - 100 p.p.m.

The behaviour of Zn-65 in waters containing nuclear reactor wastes has been investigated by Davis et al (1958). They found that although the Zn-65 concentration was the lowest of eight isotopes detected in the diluted effluent it was among the most highly concentrated by algae, and was readily transferred upward through the food chain.

Gutknecht (1963) investigated Zn-65 uptake by four species of benthic marine algae and found that Fucus vesiculosus showed the highest retention of this isotope. Freshly collected samples of the four species were then analysed for ordinary zinc. Fucus vesiculosus was found to have the highest zinc concentration (829 $\mu\text{g} / \text{g}$ dry weight) which is consistent with the fact that it showed the highest retention of the isotope.

Bryen (1969) studied the absorption of zinc in Laminaria digitata with the use of radionuclide Zn-65 and atomic absorption analysis. He found no evidence for the regulation of zinc by the plant. Absorption of zinc or Zn-65 he concluded, is a gradual process of accumulation and is not accompanied by the exchange of zinc. Therefore, once absorbed, zinc or Zn-65 shows little tendency to be lost from the plant.

Analysis of zinc in animals of the principal marine phyla has shown that this

element is nearly always present (Philips, 1917, Bodansky, 1920, Severy, 1923), concentrations varying from barely detectable amounts to values of several hundred $\mu\text{g} / \text{g}$ of wet tissue. Parker (1962) in his study of Zinc in a Texas Bay found animals containing from 9 to 130 $\mu\text{g} / \text{g}$.

Chipman, Rice and Price (1968) analysed sea water and shellfish for zinc content prior to a study of the uptake of radioactive zinc. They found that oysters, taken from sea-water containing an average 0.01 p.p.m. of zinc, contained on average 5090 μg of zinc / g of dried meat. This appeared to be much higher than that of clams, containing on average 2620 μg of zinc / g of dried meat and scallops, containing only 610 μg to 1430 μg of zinc / g of dried tissue. They found that when they added radioactive zinc to the water the shellfish took it up rapidly and accumulated great amounts in their gills. They also found that marine fish quickly absorbed $\text{Zn} - 65$ into the body from the digestive tract, but that most of it was lost when the fish were returned to non-radioactive water.

The lobster (Homarus vulgaris) was found by Bryan (1964) to contain between 20 and 35 $\mu\text{g} / \text{g}$ of zinc. Experiments showed that the animal appears to be able to regulate the concentration of zinc in its tissues. Long exposure of lobsters to sea-water containing 100 μg of zinc per litre instead of the usual 5 $\mu\text{g} / \text{l}$ fails to alter the zinc concentration in the blood muscle and gonads, but increases the levels in the urine, excretory organs, hepatopancreas and gills. Probably extra zinc is absorbed then excreted. In 1968 Bryan analysed seventeen other species of decapod crustaceans and again found zinc concentrations of between 20 and 35 $\mu\text{g} / \text{g}$. This is further evidence for zinc regulation in decapod crustaceans.

It seems that certain conclusions can be drawn from this survey of the literature.

The first is that living organisms, plant or animal, have in their tissues, much higher concentrations of heavy metal ions than the concentrations found in sea water. Accumulation of these ions in an organism appears to occur whether the element is involved metabolically or not.

It would appear from the literature that marine plants are incapable of regulating the concentrations of trace elements they contain. This also applies to lower animals such as clams and oysters but higher animals such as decapod crustaceans and marine fish can, and do, effect regulation.

One further conclusion that can be drawn is that, for any of the ions, there is tremendous variation in the concentrations reported in the literature. Variations occur between species, between sites and with time.

Clearly the information that is available is, as yet, incomplete.

Materials and Methods

At each of the major sites a collection was made of individuals of the following species, when present:

Enteromorpha (intestinalis)* (L.) Link.

Fucus vesiculosus L.

Laminaria saccharina (L.) Lamour,

Laminaria digitata (Huds.) Lamour,

Laminaria hyperborea (Gunn.) Fosl.,

Rhodomenia palmata Greville

Littorina littorea (L.) Johnston,

Mytilus edulis L.

Nucella lapillus L.

and Asterias rubens L.

(* Identification of the various species of Enteromorpha is based on microscopic characteristics such as, the shape of the pyrenoids, the shape of the plastids and the arrangement of the cells and therefore some other species of Enteromorpha may have been included with the bulk of E. intestinalis).

This list was chosen to include species from the three trophic levels, - primary producers, herbivores, and carnivores, which were likely to be available in sufficient quantity to allow representative numbers of several age or size classes of each species to be collected. L. hyperborea, A. rubens, and some M. edulis were collected from the sub-littoral zone, the other species from the littoral zone.

As the collection and preparation of the samples is time consuming it was impossible to sample all the sites concurrently. The sample period was spread over about five weeks from May 14th onwards. In view of the work of Young and Langille (1958) and Black and Mitchell (1952) there is unlikely to have been seasonal variation during this period. Young and Langille (1958) found no characteristic seasonal variation in the trace elements in algae from the Atlantic coast of Canada. Black and Mitchell (1952), however, found a seasonal

variation in the concentration of trace elements around Great Britain, concentrations being higher in summer. The samples collected by the author should therefore all be representative of the more active summer metabolic state.

After collection the samples were cleaned by washing in distilled water, and sorted. This washing should not have affected the heavy metal ion concentrations. Young and Langille (1958) found that thorough washing of marine algae only lowered the content of total ash, silicon, sodium and potassium, and had no appreciable effect on the other elements. Such washing therefore removes traces of adherent sand and silt and apparently leaches out soluble salts of the alkali metals. Both Black and Mitchell (1952) and Young and Langille (1958) suggest the failure of washing to remove trace elements is due to the fact that they are fixed as insoluble salts, probably of acidic polysaccharide or protein.

Because one of the aims of this investigation was to examine the accumulation of heavy metal ions with age, sorting of the species had to be into selected age classes.

Satisfactory methods are available for the age determination of L. hyperborea (after Kain, 1963). After checking to ensure that each dark growth ring, seen in section at the base of the stipe, is associated with a hapteron level, the distinct annual growth rings can be counted. This prevents the boundary of the medulla being mistaken for a growth line and allows recognition of what are purely interference lines. John (1968) has found that plants growing off the North-East coast of England and the South-East coast of Scotland show, after the third years growth, distinct annual growth rings associated with hapteron levels.

This method cannot be used for L. saccharina. Parke (1948) suggested that the age of the plant can be determined by counting the number of distinct growth rings seen in transverse section at the base of the stipe. More than one hapteron whorl, however, may be produced in a growing season in North-East England and South-East Scotland (John, 1908) and so there is difficulty in distinguishing growth rings from supposed interference ones.

The same applies to L. digitata. John (1968) did find that he could group individuals from a sample of a population of L. digitata into classes based on the length of the stipe alone. These size classes were more than 90% correlated

with age classes later determined using only the distinct growth rings.

The age determination of M. edulis (Seed, 1969) has also been shown to be reliable for the North-East coast. The animal is aged by counting the distinct rings on the shell.

For the species for which no reliable methods of age determination are available, the organisms were grouped into size classes. L. littorea and N. lapillus were separated into size classes of 5 m.m. i.e (1) 0 - 5 m.m. (2) 5 - 10 m.m. (3) 10 - 15 m.m. etc. The measurement was made on the longest axis. This method was also tested on M. edulis and gave similar groupings to the method of separation by age determination. For A. rubens size groups based 5 cm. were used, and for L. digitata stipe lengths of (1) 0-5 cm, (2) 5-12 cm, (3) 12 - 25 cm, (4) 25-35 cm, (5) 35-45 cm, etc. were used. Fucus plants were merely separated into (1) sporelings and (2) adults. It is probable that in most cases, as with L. digitata above, the larger organisms are the older ones.

After sorting, the moisture content of the samples was determined. They were first dried at room temperature for 24-48 hours to remove excess moisture, then weighed. Each sample was then dried to constant weight in a forced draught oven at 105°C.

Sea-water samples were collected at each site, filtered and stored, both in Pyrex and Polythene containers, though Black and Mitchell (1952) found that analyses were identical for sea-water samples stored in Pyrex and Polythene bottles.

Weighed aliquots of the dried material were prepared for analysis by atomic absorption, as described by Jefferies and Willis (1964). As the concentration of the heavy metal ions in some of the samples is low, it was found, on a test run, to be necessary to use dry weights of about 5 g., accurately weighed, to increase the concentration above the lower limit of determination of the spectrophotometers. Whole specimens of the animals were taken for analysis, but only the base of the stipes, and pieces of the lamina could be used due to the large size of some of the specimens. Sampling the base of the stipe includes tissue of all ages. Taking 5 g also meant that each aliquot could be made up of the

ground material of at least ten individual animals or samples of plant and this helps to eliminate variation in the samples. Each aliquot was then 'wet ashed' by digesting it in a Kjeldahl flask to which was added 20 ml of concentrated nitric acid, 5 ml of concentrated hydrochloric acid and 5 ml. of concentrated perchloric acid. This is the same quantity of acid recommended by Jefferies and Willis (1964) for 1 g of material. On the test run, however, this quantity of acid was found to result in the release of the same concentration of ions from up to 10 g of dry material as from similar samples digested in twice the quantity of acid. It was therefore presumed to be sufficient for the complete digestion. (See Appendix I). All chemicals used were of analytical grade, and care was taken throughout the preparation, extraction and analysis to avoid any metallic contamination. The samples were heated carefully in order to minimise foaming and prevent the loss of sample. When foaming had ceased the rate of heating was increased and all excess acid was boiled off so that only a little perchlorate remained. The level of fluid in the flask was maintained by the addition of distilled water. When the digestion was complete the neck of the flask was washed down with distilled water and the contents filtered through Whatman No. 42 paper, which had been previously soaked in 10% perchloric acid to remove trace elements from the paper. The filtration removed any silica that was present.

Analysis of the samples for Iron was carried out on the HILGER and WATTS Atomic Absorption Spectrophotometer. The instrument was set up as described in the instruction manual using a wave length of 2483 \AA° , which gives a theoretical sensitivity for 1% absorption of 0.15 p.p.m.

It is international practice to quote the sensitivity (the concentration required to give 1% absorption) rather than a 'limit detection' as the latter depends very much on experimental conditions. Usually the absorbance is directly proportional to concentration, but some curvature may be found at high concentrations.

Copper, lead, mercury and zinc were determined with the EEL Atomic Absorption Spectrophotometer, following the method outlined by Evans Electro Selenium Limited. For copper a wavelength of 325 m μ was used. This gives a typical theoretical

"sensitivity for 1% absorption" of 0.1 p.p.m. As the samples included quantities of sodium which can cause troublesome light scattering effects in the determination of lead at the most absorbing wavelength of 217 nm it was found to be necessary to use the 283 nm wavelength. This gives a theoretical "sensitivity for 1% absorption", of 0.85 p.p.m. The determination of mercury was carried out at a wavelength of 254 m u which gives a typical value of 4.75 p.p.m. for the theoretical "sensitivity for 1% absorption." Finally, for zinc a wavelength of 214 m u was used, giving a typical theoretical "sensitivity for 1% absorption" of 0.05 p.p.m.

RESULTS

I have only included in this section histograms and graphs which illustrate the characteristic trends in the results. This has been done in an attempt to prevent the reader being lost in tables of figures representing the analyses for four metal ions in various age or size classes of thirteen main species from six major sites.

The complete results for each site are included in the appendix.

All results are expressed in micrograms per gram (u g / g) of dried material. Micro grams per gram are equivalent to parts per million (p.p.m.). The conversion factors for dry to wet weight are included in the appendix.

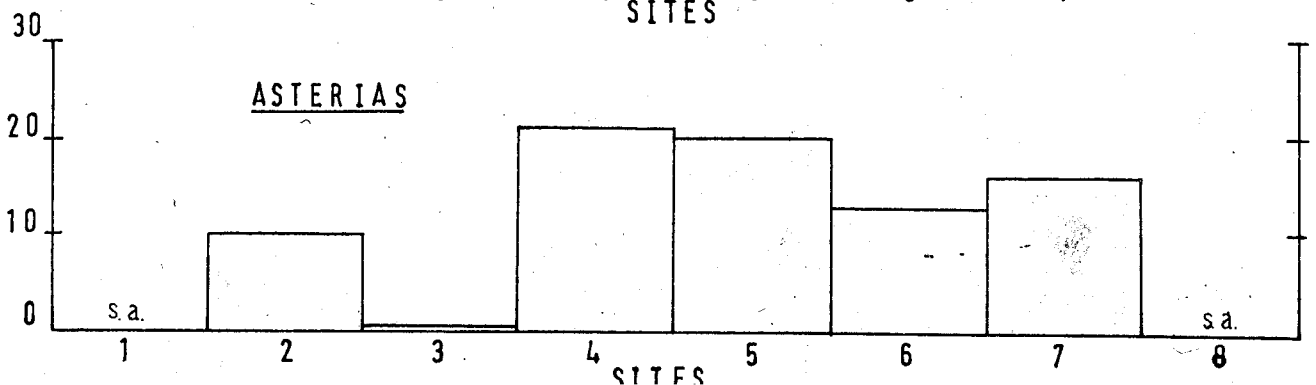
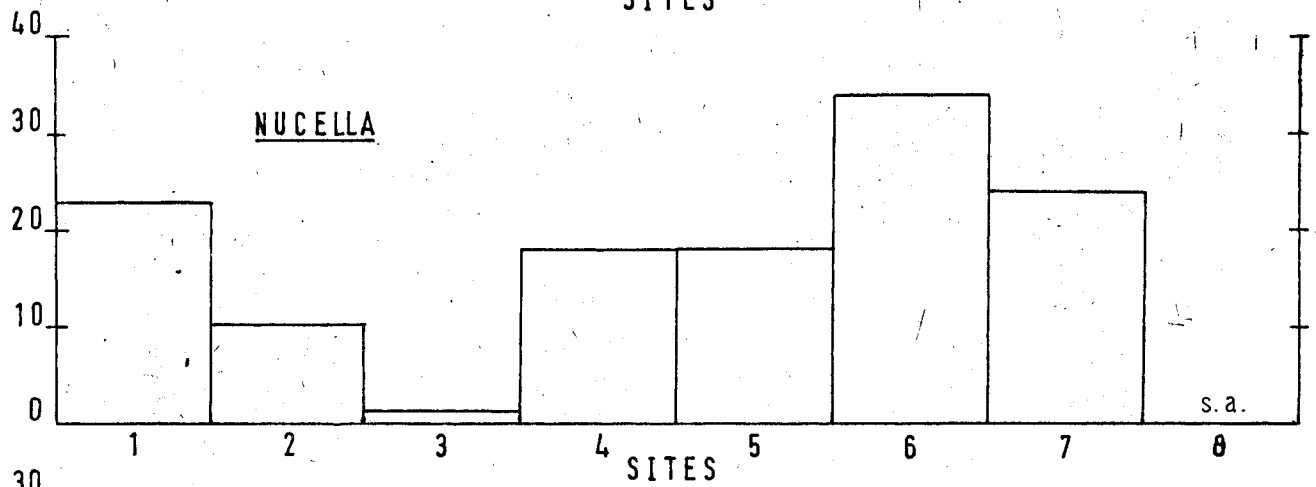
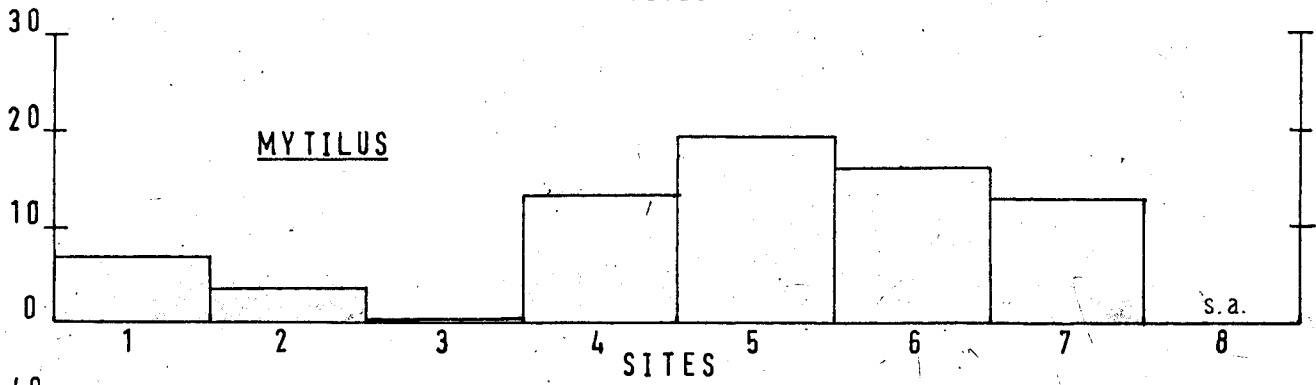
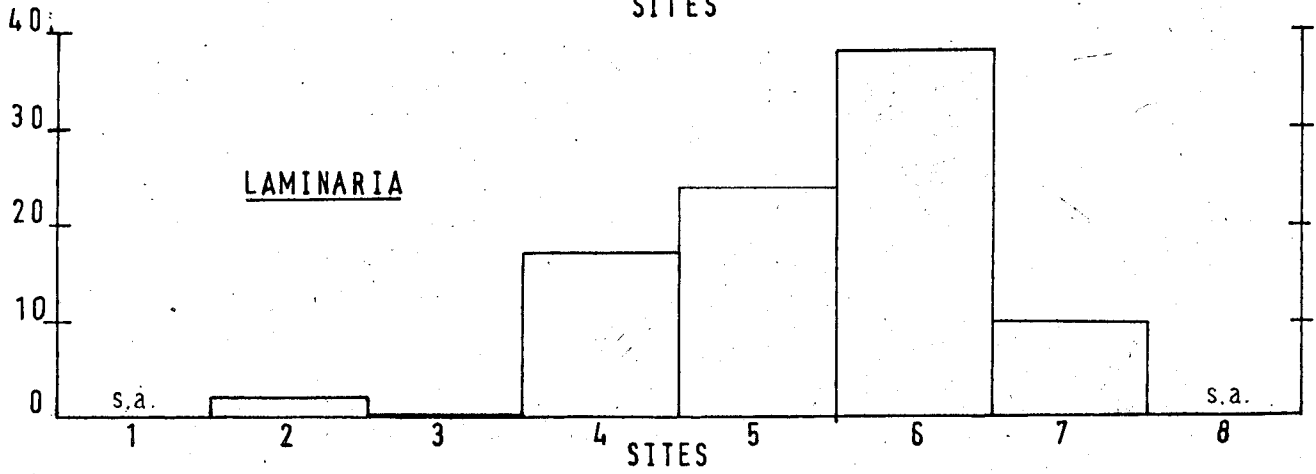
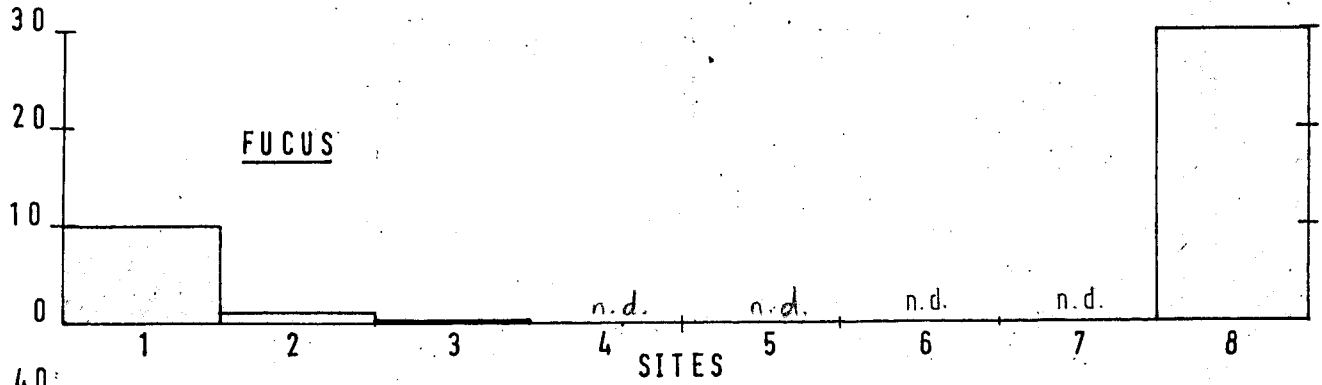
The samples were all analysed for mercury but the concentration present proved to be too low for detection with the method used. This means that the concentration in all samples was less than 250 u g / g dry weight.

HISTOGRAMS OF VARIOUS SPECIES SHOWING THE CONCENTRATION OF COPPER AT DIFFERENT SITES
 (The names and numbers of the various sites are given in Table I, opposite page 3).

Concentration of COPPER(ug/g).

s.a. = species rare or absent at the site.

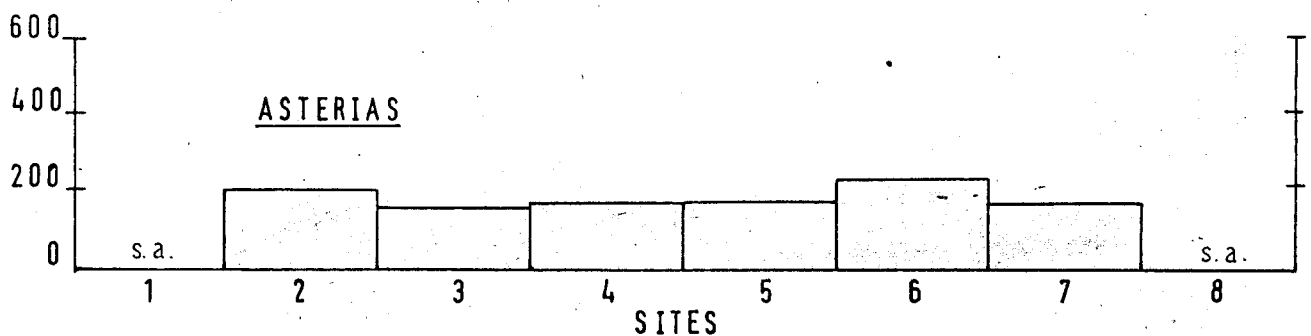
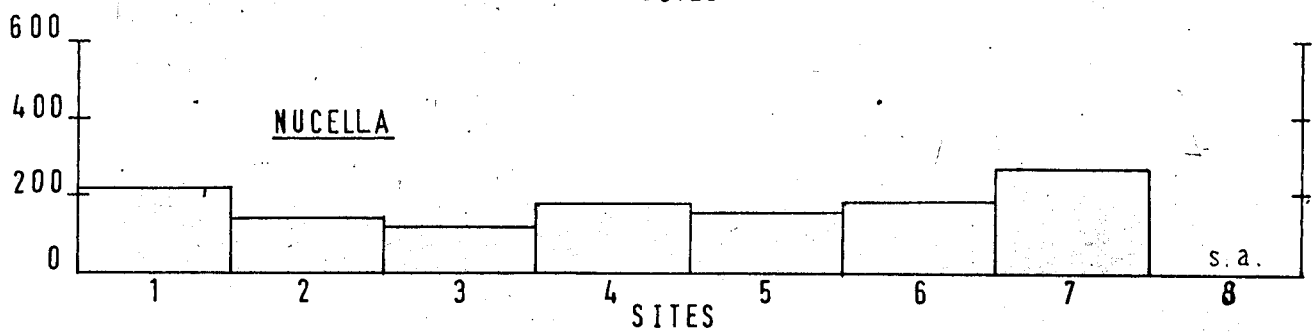
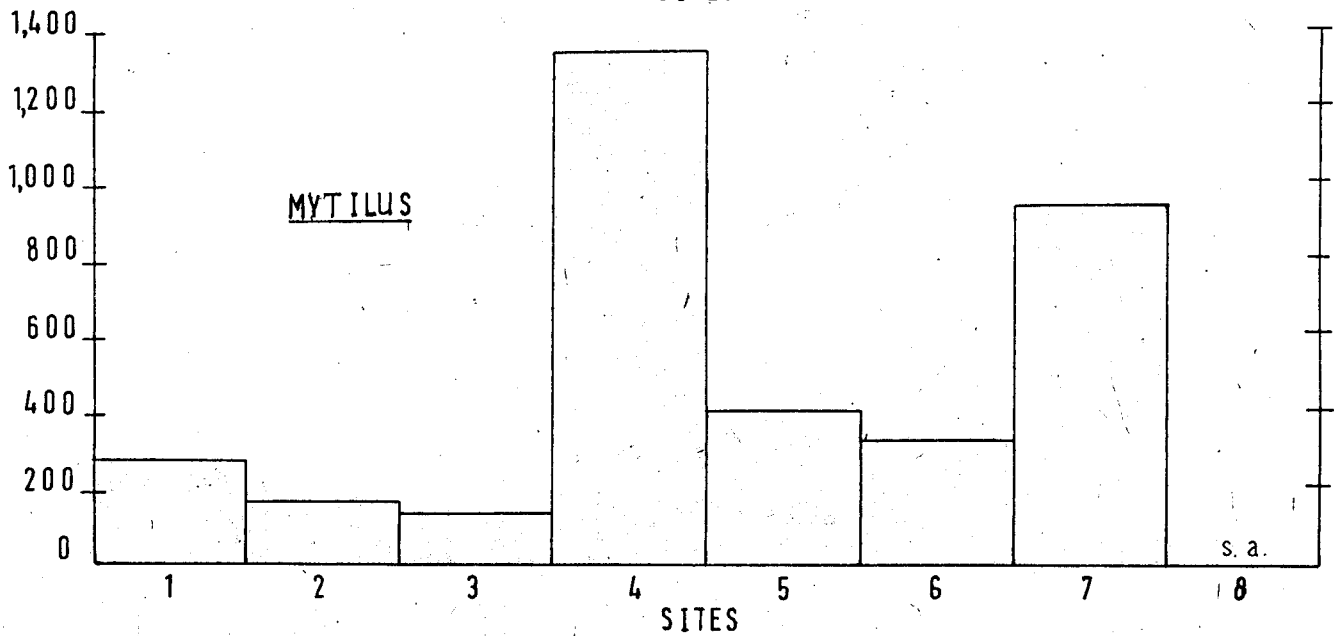
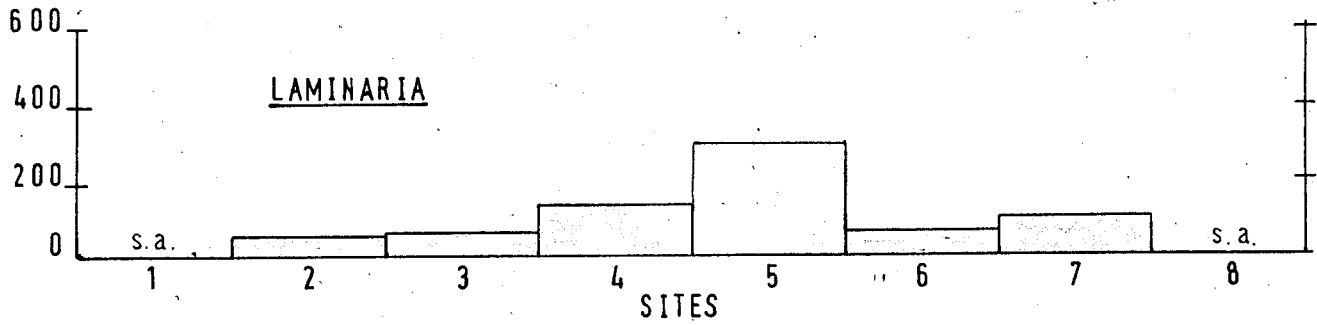
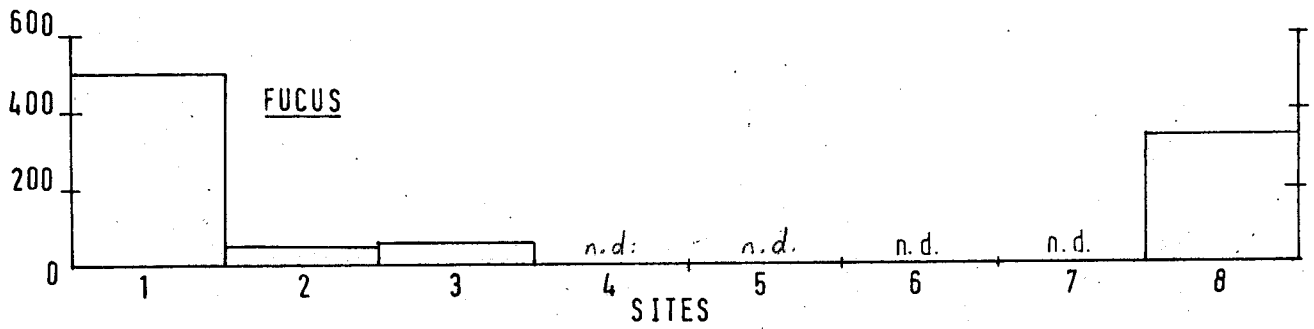
n.d. = no data



HISTOGRAMS OF VARIOUS SPECIES SHOWING THE CONCENTRATION OF IRON AT DIFFERENT SITES
 (The names and numbers of the various sites are given in Table I, opposite page 3).

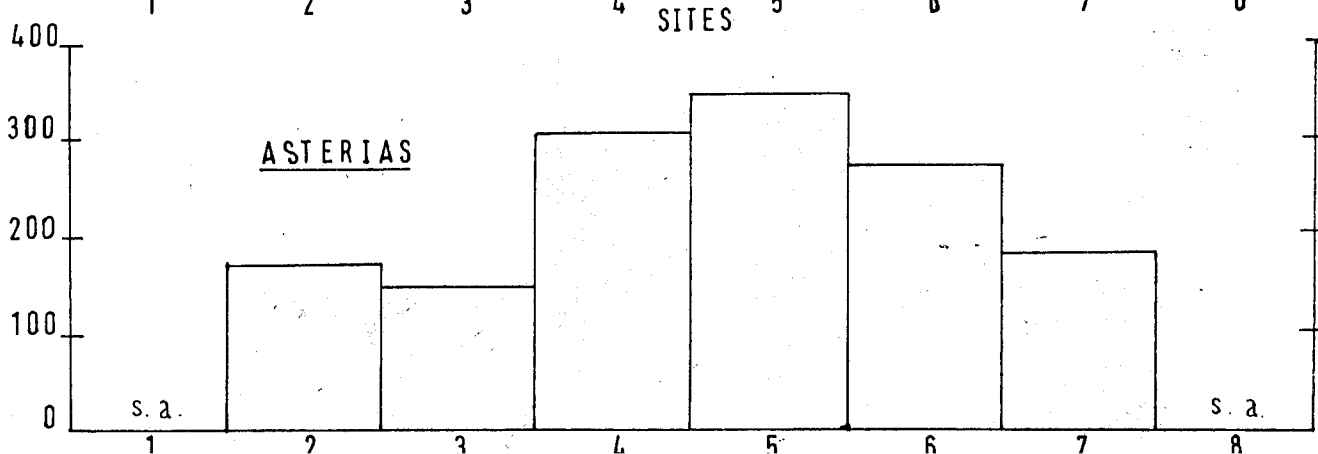
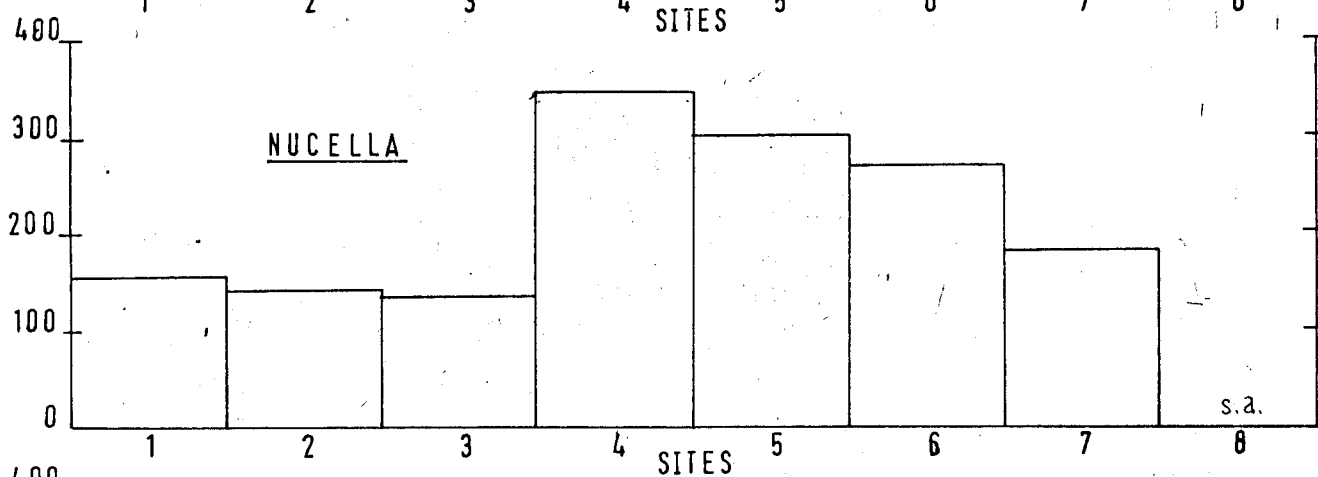
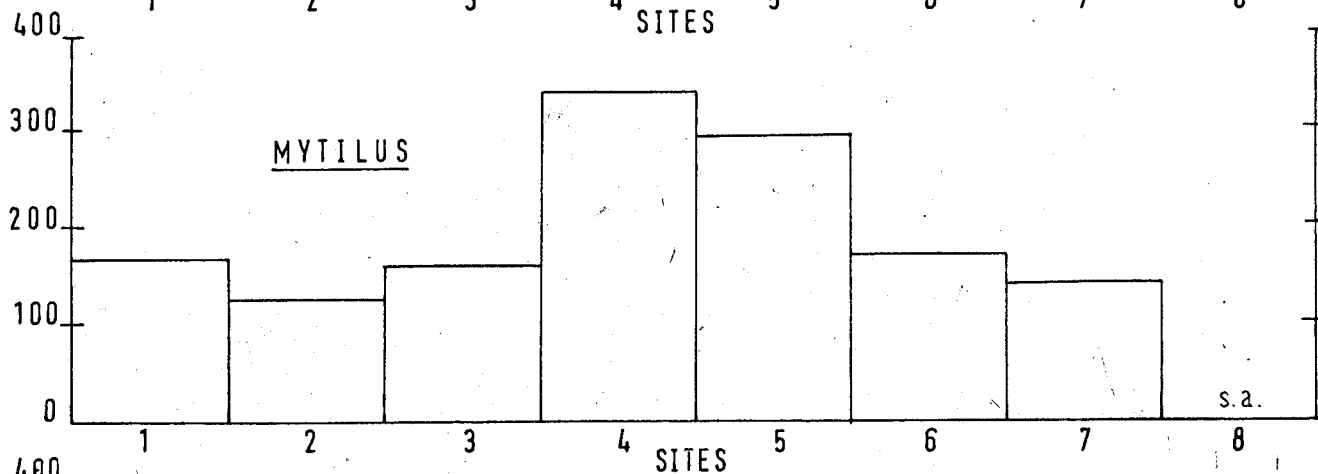
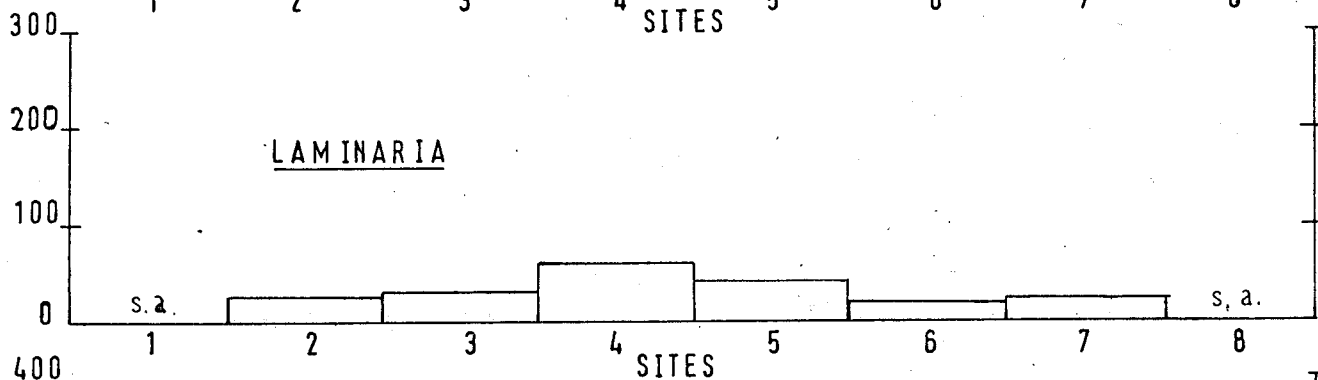
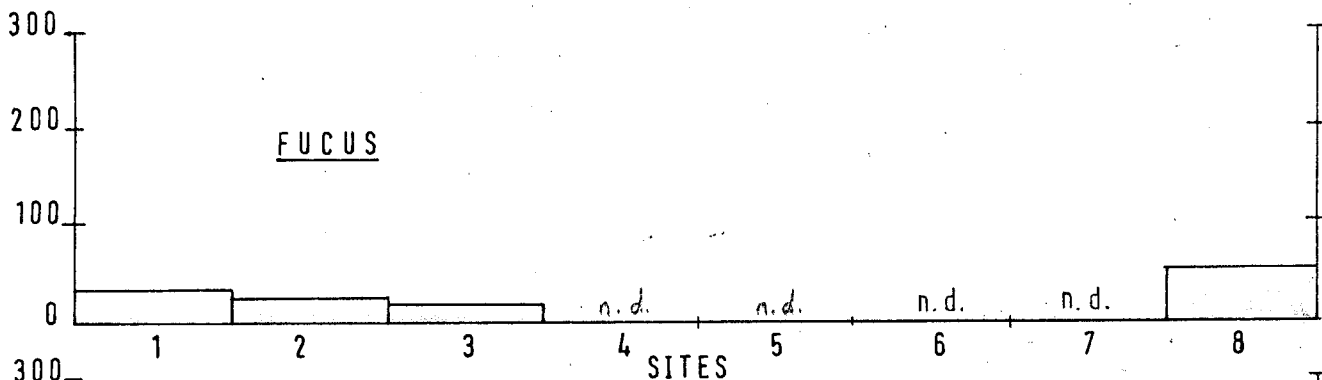
s.a. = species rare or absent at the site n.d. = no data

Concentration
 of IRON ($\mu\text{g/g}$).



HISTOGRAMS OF VARIOUS SPECIES SHOWING THE CONCENTRATION OF LEAD AT DIFFERENT SITES
 (The names and numbers of the various sites are given in Table I, opposite page 3).
 s.a. = species rare or absent at the site. n.d. = no data

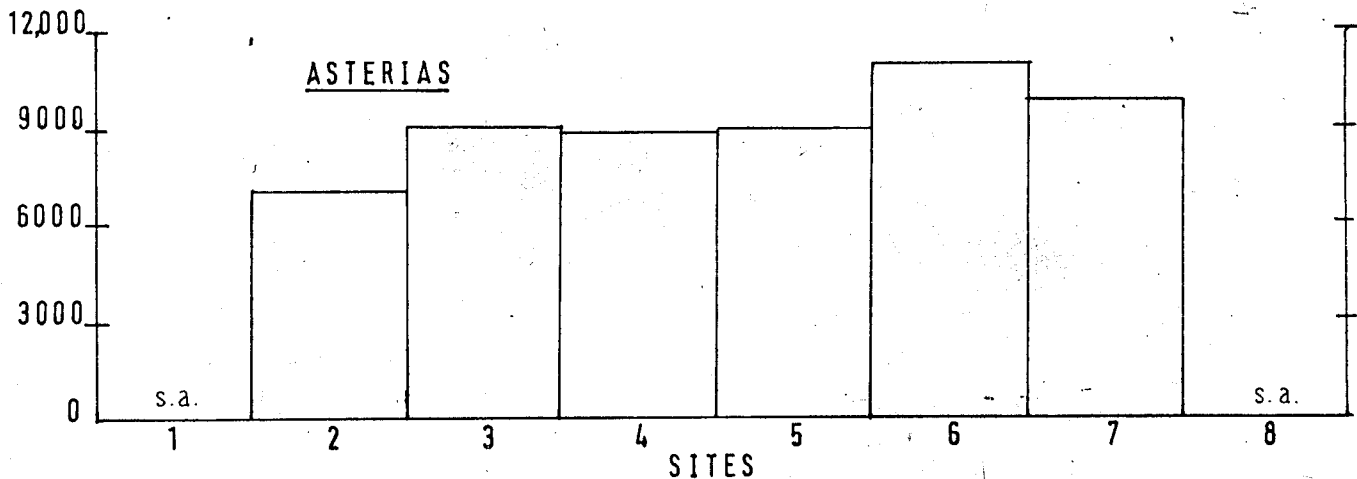
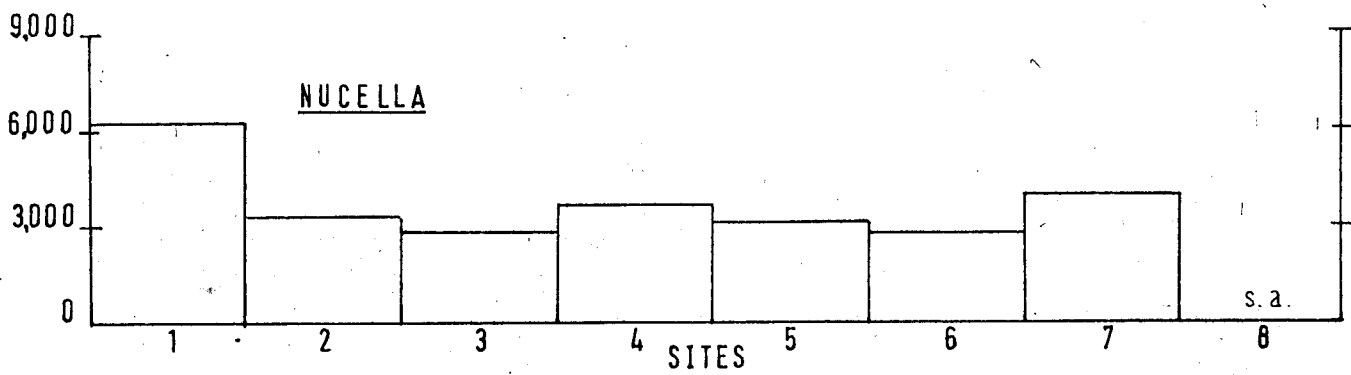
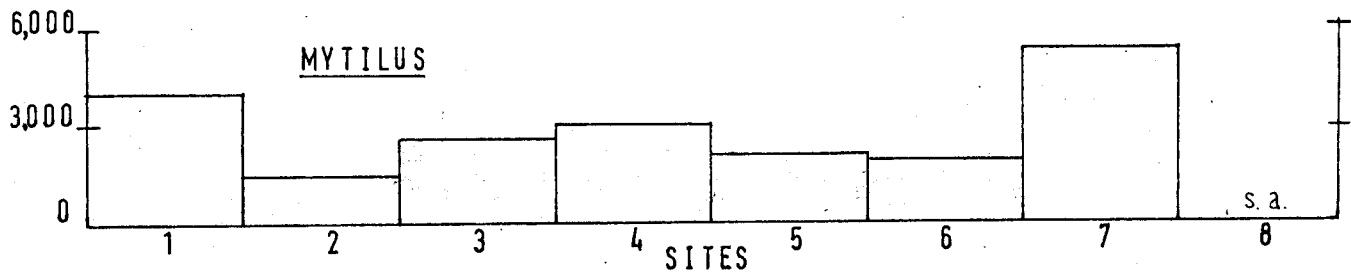
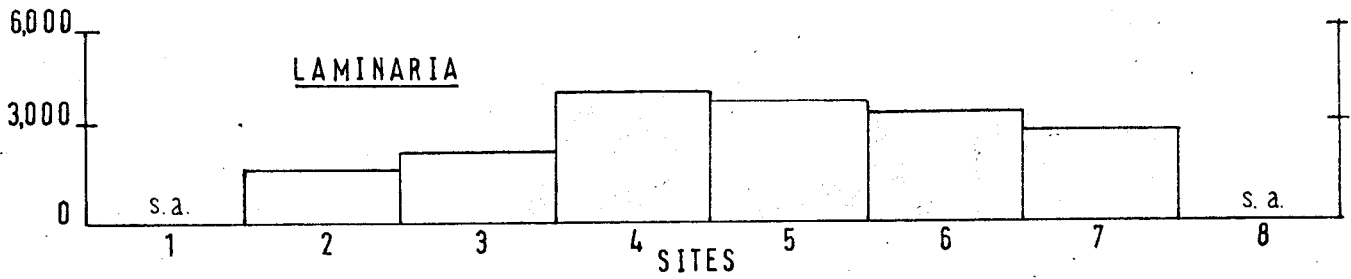
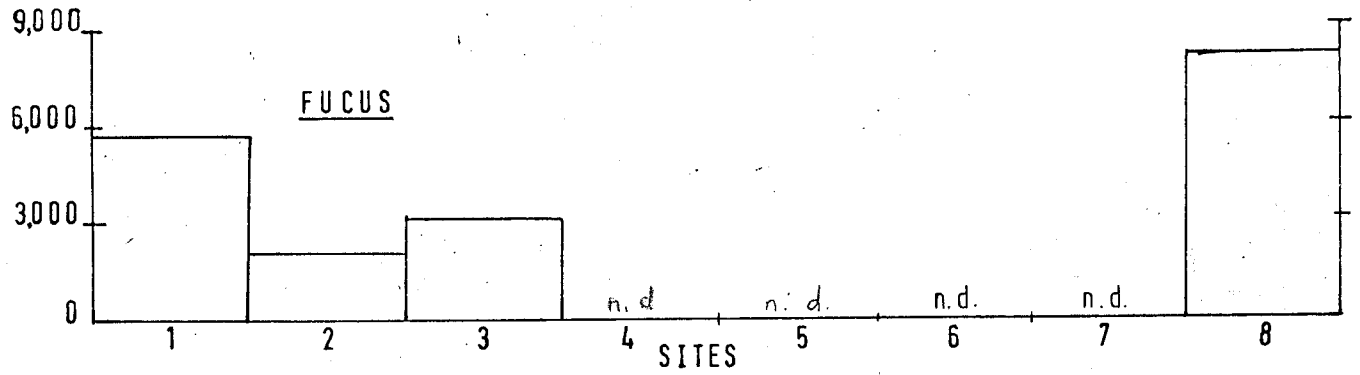
Concentration
of LEAD (ug/g).



HISTOGRAMS OF VARIOUS SPECIES SHOWING THE CONCENTRATION OF ZINC AT DIFFERENT SITES
 (The names and numbers of the various sites are given in Table I, opposite page 3).

s.a. = species rare or absent at the site n.d. = no data

Concentration
 of ZINC (ug/g).



DISCUSSION

The most striking feature of the results is the variation. This is complex but essentially of three main types:- (a) variation between sites (b) variation with age/size and, (c) variation between species. For the sake of convenience these three categories will be discussed separately.

a). Variation between sites

It is possible to arrange the sites in order of the concentration of heavy metal ions contained by a species from the sites. Beadnell and St. Abbs have the lowest concentrations, next are Redcar, Robin Hood's Bay and the Firth of Forth and finally, with the highest concentrations Hartlepool and Souter. For example the level of zinc in L. hyperborea from St. Abbs is significantly different, ($p = 0.1\%$) from that at Redcar, and at Souter. The difference between Redcar and Souter however is only significant at the 5% level. Similar figures can be quoted for other species and ions.

This ordination of sites, based on increasing concentrations of heavy metal ions, agrees very well with that based on various parameters indicative of pollution and tabulated earlier in this dissertation. Perhaps the only exception is Robin Hood's Bay appearing to be a polluted site.

Two possible explanations immediately spring to mind for the fact that Robin Hood's Bay appears to be a polluted site. The first is that polluted water is carried south from the Durham coast by water currents, (See page 4 in site selection), and this may carry pollutants to this part of the coast. This seems unlikely at least to be the only explanation as some samples from Robin Hood's Bay have higher concentrations of heavy metal ions than those taken from the Durham Coast. For example, the concentration of iron in M. edulis from Robin Hood's Bay is 699 ± 255 u g / g dry material (a mean value for all age classes over one year) whereas the comparable mean value for Hartlepool is only 395 ± 86 u g / g dry material. Both samples have a large standard error, the reason for which is explained below.

The second explanation is that the large quantities of eroded inorganic material in suspension are creating conditions at Robin Hood's Bay similar to those of an estuarine site such as Musselburgh. Iron is known to be brought to

the sea in relatively large quantities in colloidal clay particles (Sverdrup et al., 1942).

It is of course possible that the effect is due to a combination of the above two factors. Chemical analyses of the suspended material in the fresh water streams of the Robin Hood's Bay area may help to clarify the situation. It was stated in the literature review that copper, iron and zinc are metabolically involved in organisms. If a species is present in abundance at a site it is unlikely that it is suffering from nutrient deficiency. Presumably then the concentration of these ions that is vital to an organism is not more than that found at the site having the lowest concentration. Thus, it is probably true to say that an organism having an ion at a concentration above this lower limiting value for normal growth is showing the effects of the increased concentration of the ion in the water in which it is living.

The same argument applies to an element such as lead or mercury which does not appear to be metabolically involved but in this case the lower limiting value for normal growth is zero.

b). Variation with age

Variation often occurs in the heavy metal ion concentrations within a species at a given site. This variation is not random but correlated with age. As there are differences between the species each species will be considered separately.

1. M. edulis This species shows a most pronounced variation in the heavy metal ion concentration with age such as that shown in the results section for iron at four sites. The trend is constant for all sites, a rapid decrease in the concentration of the iron occurring in the first year of life. The decrease thereafter is slight. There is, however, still a marked difference, in the levels of concentration at any given age, between unpolluted and polluted sites.

The decrease of iron with age may be either a real phenomenon resulting from the animal being able to regulate the concentration of trace elements, or it may be an apparent phenomenon resulting for example from an increase in the shell to tissue weight ratio with age. In this latter case it is possible to imagine

a situation in which the concentration of iron in the tissue appears to be reduced when the whole animal, with an increased proportion of shell, is sampled intact.

In order to come to a conclusion regarding these two possibilities it will be necessary to sample the tissue and shell of all age groups of the animal separately.

The other heavy metal ions in M. edulis usually show a decrease with age, but the decrease occurs almost completely in the first year. The two exceptions are Souther and Hartlepool lead concentrations. Here the mean lead concentrations in the young animals are lower than those in the adults. For example the mean lead concentration in the spot is 180 and 200 u g / g and in the older animals is 343 and 289 u g / g at Souther and Hartlepool respectively. It is interesting to note, however, that the values for the spot are of the same order of magnitude as those of the other sites (which have a mean value of 180 ± 6.86) and are not significantly different whereas the values for the adults are significantly higher than those of the other sites ($p = 1\%$). This would seem to suggest that of the sites examined only those in the very polluted water of the Durham coast is there sufficient lead present to result in significant accumulation with age.

2. A. rubens, and

3. N. lapillus

The various size classes of these two species had few

significant differences except a tendency for the smallest

size class of individuals to have higher concentrations than the other size classes.

There were no significant differences between the dead Norfolk A. rubens and A. rubens from other sites that could be used to explain the death of the former.

4. F. vesiculosus

In this species there is some evidence of the concentration of heavy metal ions with age. Both sporelings and adult

plants were examined and some significant differences in concentrations found.

For example the difference between the concentration of zinc found in sporelings and adult plants from Musselburgh is significantly different at the 5% level,

though respective differences in the St. Abb's and Beadnell concentrations are not.

5. L. hyperborea

There was found to be no significant variation with age in

L. hyperborea after the third year. Unless skin diving

equipment is used it is difficult to collect a sufficiently large sample of the

younger plants. Unfortunately then none of the samples of *L. hyperborea* included age groups less than three years old, and it would seem from the other species examined, such as *F. vesiculosus*, that this is the age group in which significant variation can occur.

6. *L. digitata* The stipe of individual plants of this species usually had higher concentrations of heavy metal ions than the lamina. For example the mean value for the zinc concentration in the stipe of plants taken from all sites is 3170 ± 261 u g / g and in the lamina is 2172 ± 103 . This difference is significant ($p = 2\%$). The significance is, of course, greater when one compares concentrations in the stipe and lamina at one site as some of the variation in the mean is caused by variation between sites.

c). Variation between species

In addition to showing variation in heavy metal ion concentrations between sites the histograms also show a marked variation between species at some of the sites. For example, at St. Abbs the lead concentration in u g / g dry weight is:

50	in	<u><i>E. intestinalis</i></u>	}	primary producers	}	plants
25 + 3.54	in	<u><i>F. vesiculosus</i></u>				
30 + 4.95	in	<u><i>L. digitata</i></u>				
25 + 2.35	in	<u><i>L. hyperborea</i></u>				
36 + 9.82	in	<u><i>L. saccharina</i></u>				
127 + 6.87	in	<u><i>M. edulis</i></u>	}	predominantly herbivores	}	animals
153 + 25.70	in	<u><i>E. estuense</i></u>				
170 + 7.60	in	<u><i>L. littorea</i></u>				
170 + 16.0	in	<u><i>A. rubens</i></u>				
146 + 4.50	in	<u><i>N. lapillus</i></u>				
				predominantly carnivores		

The most obvious difference is that between plants and animals. It is highly significant. There are similar differences in the lead concentrations at all other sites, and this is probably indicative of the accumulation of heavy metal ions up the food chain. Copper and iron concentrations at the unpolluted sites, St. Abbs and Beadnell, show similar differences. In polluted waters, however, the concentrations of copper, iron and zinc in the plants tends to be almost as high as in

the animals.

Thus, in unpolluted water the concentration of all ions in plants is low, being high in the animals. In polluted water the concentration of ions is high in the plants but usually only slightly higher in the animals.

This requires an explanation and there are two likely possibilities. The fact that there is usually in animals in polluted water no significant accumulation of ions, other than lead, above the concentrations found in plants suggests that the animals are capable of regulating the levels of these ions in their tissues, at least to a certain extent. Secondly, it is also possible that this could be caused by the breakdown of the natural food chains in polluted waters. For example, A. rubens, when feeding directly on raw sewage in polluted waters, may have a lower intake of heavy metal ions than it would have if it was feeding on M. edulis feeding on algal suspension high in heavy metal ions.

If the animals investigated are capable of regulating these ions this would help explain the decrease with age in the concentration of heavy metal ions that was observed in many of the animals sampled. It would be feasible to postulate that this was also due to regulation, and that the regulatory mechanism in M. edulis for example became established shortly after the animal had settled and quickly reduced the high concentrations of ions present.

In conclusion then it seems that the method of comparing the heavy metal ion concentrations of a sample of individuals, of any of the species analysed in this study, seems to provide a good means of comparing the degree of pollution of the water from which they were taken.

By analysing a series of samples taken at different distances from a known source of pollution it will be possible to discover where over the range the pollutant ceases to have a significant effect on living organisms.

This study has also brought to light some problems. The answers to these problems will have to be known before a comprehensive picture of pollution involving heavy metal ions can be drawn up.

These problems include determining the reason for the apparent decrease with age of heavy metal ion concentrations that was found to occur in most of the animals investigated, especially M. edulis. This is probably tied in with the problem of determining whether or not the animals investigated in this study can regulate the concentrations of any of the heavy metal ions in their bodies or not. If regulation is found to be carried out, as it is for zinc and copper in decapod crustaceans (Bryan, 1968) it will be interesting to find out just how efficient the process is, and whether or not it is capable of coping with increased levels of pollution.

It will probably be worthwhile, from this point of view, to carry out such experiments as (1) transplanting organisms from unpolluted to polluted water and visa versa and, (2) growing organisms in sea water tanks to which could be added (a) different concentrations of heavy metal ions and (b) the radioactive forms of heavy metal ions. This should allow us to determine whether or not regulation is carried out, what concentrations of pollutants can be coped with, whether species from unpolluted and polluted sites are genetically different and/or tolerant of varying levels of pollution.

Once the critical levels of pollution and the susceptible species are known it should be possible to monitor the heavy metal ion concentrations in the organisms of polluted areas and prevent them being killed off by heavy metal ion poisoning.

Monitoring the heavy metal ion concentrations in the organisms themselves is probably a much more accurate way of determining when critical levels of heavy metal pollution are reached than a method of monitoring levels in the sea water or sediments.

Analysis of the latter may, however, be equally as good from the point of view of defining merely the extent of pollution.

ACKNOWLEDGEMENTS

I wish to thank my supervisor, Dr. D. J. Bellamy, for his assistance with this study, and Dr. J. Turner for her helpful criticism of this manuscript in his absence. My thanks are also due to Miss M. Dodd for typing this manuscript, and to my wife for her help and encouragement throughout.

This work was carried out while I was holding a studentship awarded by the Natural Environment Research Council.

B I B L I O G R A P H Y

- THE ADMIRALTY TIDE TABLES for 1970, European Waters including the Mediterranean Sea. Admiralty Hydrographic Department.
- AMERICAN PUBLIC HEALTH ASSOCIATION, 1965, Standard Methods for the examination of Water and Wastewater. 12th Edition.
- ATKINS, W. R. G., 1936. The estimation of zinc in sea water. J. Mar. Biol. Ass. U.K., Vol. 20, pp 625.
- BELLAMY, D. J., BELLAMY, R., JOHN, D.M., AND WITTICK, A., 1967 Some effects of pollution on rooted marine macrophytes on the North-east Coast of England. Br. Phycol Bull., Vol. 3, pp 409.
- BELLAMY, D. J., 1968. The effects of pollution on the marine plant life of the Tees-mouth area. Tees-side Sewerage and Sewage Disposal, Final Report. I, pp 103 - 107.
- BELLAMY, D. J., JOHN, D. M. AND WITTICK, A., 1968. The "kelp forest ecosystem" as a phytometer in the study of pollution of the inshore environment. Underwater Association Report 1968, pp 79 - 82.
- BLACK, W. A. P. and MITCHELL, R. L., 1952. Trace elements in the common brown algae and sea water. J. Mar. Biol. Ass. U.K., Vol. 30, pp 575 - 84.
- BODANSKY, M., 1920. Biochemical Studies on marine organisms II The occurrence of zinc. J. Biol. Chem. Vol. 44, pp 399 - 407
- BOURY, M., 1938. Le plomb dans le milieu marin. Rev. Trav. Off. Peches marit., Vol 11, pp 157 ff.
- BRYAN, G. W., 1964. Zinc Regulation in the lobster. Homaris vulgaris. I. Tissue zinc and copper concentrations. J. Mar. Biol. Ass. U.K., Vol. 44, pp 549 - 63
- BRYAN, G. W., 1966 The Metabolism of Zn and ⁶⁵Zn in crabs, lobsters and freshwater crayfish. Syrup Radioecological concentration Processes, Stockholm, Sweden. pp 1005 - 16, Oxford: Pergamon Press
- BRYAN, G. W., 1968. Concentrations of zinc and copper in the tissues of decapod crustaceans. J. Mar. Biol. Ass. U.K., Vol 48, pp 303 - 21.
- BRYAN, G. W., 1969. The absorption of zinc and other metals by the brown seaweed. Laminaria digitata. J. Mar. Biol. Ass. U.K., Vol. 49, pp 225 - 243

- CHILMAN, W. A., RICE, T. R., AND PRICE, T. J., 1958. Uptake and accumulation of radioactive zinc by marine plankton, fish and shellfish. Fish Bull., U.S. Vol. 58 pp 279 - 92, No. 135.
- CHOW, T. J., and THOMPSON, T. G., 1952. The determination and distribution of copper in sea water. Pt. I., J. MAR. RES. Vol. 11, p 124 ff.
- CORNEC, E., 1919. Spectrographic studies of the ash of marine plants. Comp. Rend. Acad. Sic. Paris., T.1 68, pp 513 - 514.
- DAVIS, J. J., PERKINS, R. W., PALMER, R. F., HANSON, W.C. AND CLINE, J. F., 1958 Radioactive materials in aquatic and terrestrial organisms exposed to reactor effluent water. Proc. Intern. Conf. Peaceful Uses of Atomic Energy, 2nd Conf., Geneva, vol. 18, pp 423 - 8.
- GOLDBERG, E. D., 1952. Iron disimilation by marine diatoms. Biol. Bull. Vol 102, pp 243 - 248
- GUTNECHT, J., 1963 Zinc 65 uptake by benthic marine algae. Limnol. Oceanog., Vol 8 pp 31 - 38.
- GUTNECHT, J., 1965 Uptake and retention of cesium 137 and zinc 65 by seaweeds. Limnol. Oceanog., Vol 10, pp 58 - 66.
- HAEV DLER, H.M., AND THOMPSON, T. G., 1939 Determination and occurrence of aluminium in sea water. J. Mar. Res., Vol. 2, pp 12 ff.
- HARVEY, H. W., 1937. The supply of iron to diatoms. J. Mar. Biol. Ass. U.K., Vol. 22, pp 205 - 219
- HARVEY, H. W., 1945 Recent Advances in the Chemistry and Biology of Sea Water. 164 pp Cambridge.
- HARVEY, H. W., 1955 The Chemistry and Fertility of Sea Waters. 224 pp. Cambridge Univ. Press.
- HAYWARD, J., 1969. Studies on the growth of Phaeodactylum tricornutum - V The relations of Iron, Manganese and Zinc. J. Mar. Biol. Ass. U.K., Vol. 49, pp 439 - 446.
- ISHIBASHI, M., UEDA, S. and YAMAMOTO, Y., 1959. Studies on the utilization of the shallow water deposits - on the zinc content of the shallow deposits. Rec. oceanogr. Wks. Jap. Vol. 3, pp 123 - 133.
- JEFFERIES, R. L., and WILLIS, A. J., 1964. Studies on the calcicole-calcifuge habit I Method of analysis of soil and plant tissues. J. Ecol., Vol. 52, pp 121 - 138.

- JOHN, D. M. 1968, Studies on Littoral and Sub-littoral Ecosystems.
Ph.D. Thesis, University of Durham.
- JOHNELS, A. G., WESTERMARK, T., BERG, W., PERSSON, P.I., AND SJÖSTRAND, B., 1967.
Pike (Esox lucius L.) and some other aquatic organisms in Sweden as
indicators of mercury contamination in the environment.
Oikos Vol. 18 (2) pp 323 - 333
- JONES, D. J., 1970 Ecological studies on the fauna of the kelp (Laminaria
hyperborea) holdfast. Ph.D. Thesis, University of Durham.
- KAIN, J. M., 1963 Aspects of the biology of Laminaria hyperborea II. Age,
Weight, and Length. J. Mar. Biol. Ass. U.K. Vol 43 pp 129 - 151.
- LEGENDRE, R., 1947. Les industries cliniques de la mer. Bull. Inst. Oceanograph.
Monaco. Vol. 44, No. 922, 15 pp.
- LEWIS, J. R., 1964 The Ecology of Rocky Shores. English Univ. Press : London.
- LIHNELL, D. and STENMARK, A., 1967, On the occurrence of mercury in small rodents.
With some analyses of mercury in birds and other vertebrates.
National Swedish Institute for Plant Protection, Contributions 13 : 110,
pp 361 - 379. Stockholm.
- MALMSTROM, B. G., 1956. Determination of zinc in biological materials. In
D. Glick, Methods in Biochemical Analysis. Interscience Publishers,
New York. Chapter II, pp 327 - 352.
- McFARREN, E. F., CAMPBELL, J. E., ENGLE, J. B., 1961. The occurrence of copper
and zinc in shellfish. Proc. Shellfish Sanitation Workshop, 1961. pp 229-234.
- MOORE, N. W., 1967. A synopsis of the Pesticide Problem. In Adv. in Ecol. Res.
Vol 4., pp 75 - 130.
- NODDACK, I., AND NODDACK, W., 1940 Die Häufigkeiten der Schwermetalle in
Meerstieren. Ark. Zool. Vol. 32A, No. 4.
- OLSON, T. A., AND BURGESS, F. J. (Editors) 1967 Pollution and Marine Ecology
364 pp Interscience.
- ÖY, E., 1940 Content of iron, copper, manganese and boron in seaweeds.
Lidskr. Kem. Bergr., Vol. 20, pp 570 - 2.
- PARKER, P. L., Zinc in a Texas Bay. Publ. Inst. Marine Sci. Univ. Texas.
Vol. 8, pp 75 - 79.
- PHILIPS, A. H., 1917 Analytical search for metals in Tortugas marine organisms.
Pap. Tortugas Lab., Vol. 11, pp 91 - 93.

- RAEDER, M. G., AND SNEKVIK, E., 1941. Quecksilberhalt Mariner Organismen. Kongl. Vidensk. Selsk. Forhandl. Vol. 13 (42) pp. 169 - 172.
- RYTHER, J. H. And KRAMER, D. D., 1961. Relative iron requirement of some coastal and offshore plankton algae. Ecology, Vol. 42, pp 444 - 6.
- SCHAEFFER, M. B. and BISHOP, Y. M. M., 1958. Particulate iron in the offshore waters of the Panama Bight and in the Gulf of Panama. Limnol. Oceanogr., Vol. 3, pp 137 - 149.
- SEED, R., 1969. The ecology of Mytilus edulis L. (Lamellibra nehiata) on exposed rocky shores. II Growth and Mortality. Oecologia (Berl) Vol. 3, pp 317 - 350.
- SEVERY, H. W., 1923. The occurrence of copper and zinc in certain marine animals. J. Biol. Chem., Vol. 55, pp 79 - 92.
- SIMONS, L. H., MONAGHAN, P. H., and TAGGART, M. S., 1953. Aluminium and Iron in Atlantic and Gulf of Maine waters. Analyt. Chem. Vol. 25, pp 989.
- STOCK, A., and CUCUEL, F., 1934. Die Verbreitung des Quecksilbers. Naturwiss. Vol. 22/24, pp 39 - 393.
- SVERDRUP, H. U., JOHNSON, M. W. and FLEMING, R. H., 1942. The Oceans, Their Physics, Chemistry and General Biology. 1087 pp. New York.
- "TAKEN FOR GRANTED" July, 1970. Her Majesty's Stationery Office, 10/-d.
- THOMPSON, T. G. and ROBINSON, R., 1932. Chemistry of the Sea. Bull. Nat. Res. Coun., Wash. No. 85.
- VALLEE, B. L., 1962. Zinc. pp 443 - 472. In C. L. Comar. and F. Bronner (editors) Mineral Metabolism, an advanced treatise, Vol. 2., Part B. Academic, New York.
- VERWEY, 1952. The Ecology, distribution and source of food supply of the Mussel. Arch. Neerl. Zool., Vol. 10. pp 171 - 239.
- WIESSNER, W. 1962. Inorganic micronutrients. pp 267 - 286. In R. A. Lewis (Ed.) Physiology and biochemistry of Algae. Academic, New York.
- YOUNG, E. G. and LANGILLE, W. M., 1958. The occurrence of inorganic elements in marine algae of the Atlantic provinces of Canada. Can. J. Bot., Vol. 36, pp 301 - 10.

A P P E N D I X I

Test run showing the effect of extracting various weights of sample with various quantities of acid.

- (a) Various weights of all age classes of Mytilus edulis from Hartlepool's Point extracted using 20 ml concentrated nitric acid, 5 ml. concentrated hydrochloric acid and 5 ml. concentrated perchloric acid.

Sample weight (in g.)	Concentration, in u g / g dry weight, of			
	<u>Copper</u>	<u>Iron</u>	<u>Lead</u>	<u>Zinc</u>
2	21 ± 3.8	563 ± 103	242 ± 39	2502 ± 299
5	19.4 ± 4.2	619 ± 94	229 ± 27	2721 ± 354
10	21.8 ± 4.6	597 ± 114	240 ± 42	2894 ± 317

- (b) 5 g. samples of all age classes of Mytilus edulis from Hartlepool's point extracted with either single or double quantities of concentrated acids, a single quantity being 20 ml. nitric, 5 ml. hydrochloric and 5 ml. of perchloric acid.

Quantity of Acid used	Concentration, in u g / g dry weight, of			
	<u>Copper</u>	<u>Iron</u>	<u>Lead</u>	<u>Zinc</u>
Single	19.4 ± 4.2	619 ± 94	229 ± 27	2721 ± 354
Double	21.1 ± 3.6	601 ± 63	212 ± 31	2914 ± 323

n = 8 in all cases

A P P E N D I X I I

Dry to Wet Weight Conversion Figures

Species		Wet Weight	Dry Weight	% Water per g.
<u>Fucus vesiculosus</u>		1	0.194	80.6
<u>Laminaria digitata</u>	stipe	1	0.180	82.0
	lamina	1	0.137	86.3
<u>Laminaria hyperborea</u>	stipe	1	0.174	82.6
	lamina	1	0.142	85.8
<u>Littoria littorea</u>		1	0.782	21.8
<u>Mytilus edulis</u>		1	0.4953 ± 0.0016	50.46
<u>Asterias rubens</u>		1	0.418 ± 0.036	58.2
<u>Nucella lapillus</u>		1	0.8105	18.95

APPENDIX III.

RESULTS SUMMARIES FOR THE VARIOUS SITES.

SUMMARY OF RESULTS FOR MUSSELBURGH

(Concentrations in ug / g dry matter).

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
Sea Water	0.2	14	1.75	3
<u>E. intestinalis</u> , all classes	30	6230	260.	6230
<u>F. vesiculosus</u> sporelings	10	360 ± 28	20	4405 ± 166
adults	10	510 ± 60	30	5635 ± 124
<u>L. littorea</u> less than 0.5 cm	10	560	210	7340
over 0.5 cm	15 ± 2.5	215 ± 13	192.5 ± 12.4	6120 ± 408
<u>M. edulis</u> spat	20	820	200	4360
older age groups	7 ± 1	284 ± 30	161 ± 7	4156 ± 163
<u>N. lapillus</u> less than 0.5 cm	20	400	140	7340
over 0.5 cm	22.5 ± 4.33	200 ± 5	143 ± 16	6120 ± 408

SUMMARY OF RESULTS FOR ST. ABBS, PETTICOE WICK

(Concentrations in $\mu\text{g} / \text{g}$ dry matter)

Specimen	COPPER mean Concentration	IRON mean Concentration	LEAD mean Concentration	ZINC mean Concentration
Sea Water	0.08	7.5	1.5	3
<u>E. intestinalis</u> all classes	3	370	50	1270
<u>R. palmata</u> all classes				
<u>F. vesiculosus</u>				
sporelings	2.5 \pm 0.35	45 \pm 3.54	25 \pm 3.54	1805 \pm 67
adults	1 \pm 0.71	45 \pm 10.60	25 \pm 3.54	1945 \pm 159
<u>L. digitata</u>				
stipe	3	35 \pm 3.54	30 \pm 4.95	2125 \pm 382
lamina	trace	40	20	1920
<u>L. hyperborea</u>				
stipe	1.9 \pm 0.2	50 \pm 3	25 \pm 2.35	1438 \pm 263
lamina	1 \pm 0.71	4	20	1235 \pm 32
<u>L. saccharina</u>				
stipe	3 \pm 2.94	30 \pm 8.17	36 \pm 9.82	2406 \pm 53.3
lamina	1 \pm 0.71	45 \pm 3.54	25 \pm 3.54	1465 \pm 116.5
<u>L. littorea</u> all classes	5	200	170	950
<u>Echinus estulentus</u>				
less than 5 cm	3.33 \pm 0.27	187 \pm 22.3	140 \pm 21.6	2140 \pm 9.4
over 5 cm	3.52 \pm 0.39	227 \pm 54.9	164 \pm 24.6	2195 \pm 521
<u>Ophuroids</u> all classes	trace	160	150	3650
<u>M. edulis</u> spat	20	280	150	2450
older age groups	8.6 \pm 0.8	164 \pm 7.2	125 \pm 20.6	1550 \pm 83
<u>N. lapillus</u> all classes	10 \pm 3	140 \pm 8	146 \pm 5	3560 \pm 270
<u>A. rubens</u>				
less than 5 cm	10	150	90	7330
over 5 cm	10 \pm 0.6	193 \pm 17.8	170 \pm 16	7200 \pm 285

SUMMARY OF RESULTS FOR BEADNELL

(Concentrations in ug / g dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
Sea Water	trace	13	1.5	2
<u>E. intestinalis</u> , all classes	3	430	30	2300
<u>R. palmata</u> all classes	4 ± 0.7	150 ± 90	60 ± 7	2885 ± 90
<u>F. vesiculosus</u> sporelings	trace	50	20	2885 ± 81
adults	trace	35 ± 3.54	15 ± 10.6	3270 ± 148
<u>F. serratus</u> adults	trace	40	20	3760
<u>Ascophyllum nodosum</u> all classes	trace	50	20	3700
<u>Himantalia elonga</u> all classes	trace	60	trace	3380
<u>L. digitata</u> stipe	trace	63 ± 23	40 ± 12	4480 ± 1043
lamina	trace	55 ± 3.54	10 ± 7	2480 ± 42
<u>L. saccharina</u> stipe	trace	100	50	6170
lamina	trace	10	trace	4040
<u>L. hyperborea</u> stipe	trace	59 ± 8.2	29 ± 2	2243 ± 179
lamina	trace	45 ± 3.54	trace	3375 ± 265
<u>Gibbula</u> all classes	1.5 ± 0.75	220 ± 21.6	136 ± 11.4	1890 ± 37
<u>L. littorea</u> less than 0.5 cm.	trace	160	150	1510
over 0.5 cm.	trace	158 ± 3.4	140 ± 5	2228 ± 106
<u>L. obtusata</u> all classes	trace	210	80	2720
<u>M. edulis</u> spat	trace	1470	130	3920
older age classes	trace	144 ± 6	176 ± 8	2582 ± 420
<u>A. rubens</u> less than 5 cm.	trace	170	140	8850
over 5 cm.	trace	153 ± 7	147 ± 10	9195 ± 449
<u>N. lapillus</u> less than 0.5 cm.	trace	180	130	3360
over 0.5 cm.	trace	115 ± 3.54	132.5 ± 10	2926 ± 246

SUMMARY OF RESULTS FOR SOUTER POINT

(Concentrations in ug/g dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
Sea Water	0.08	14	2	3
<u>E. intestinalis</u> all classes				
<u>R. palmata</u> , all classes	35 ± 3.54	845 ± 88.5	35 ± 3.54	3450 ± 567
<u>F. vesiculosus</u> sporelings adults				
<u>L. digitata</u> stipe lamina	12 ± 1.5 13 ± 1.8	80 ± 8 148 ± 11.4	36 ± 10.7 116 ± 20.2	3242 ± 448 2875 ± 642
<u>L. hyperborea</u> stipe lamina	17 ± 1.6 65 ± 12.2	131 ± 9.5 305 ± 42	57 ± 8 40 ± 3.8	4096 ± 325 3860 ± 247
<u>L. littorea</u> less than 0.5 cm. over 0.5 cm.				
<u>M. edulis</u> spat older age classes	20 13 ± 3	2680 1350 ± 14.1	180 343 ± 99	3570 3016 ± 333
<u>Patina pellicenda</u> all classes	40 ± 28	1025 ± 268	507 ± 104	5730 ± 542
<u>A. rubens</u> less than 5 cm. over 5 cm.	50 21 ± 2	230 168 ± 39	470 305 ± 90	8830 8812 ± 401
<u>N. lapillus</u> less than 0.5 cm. over 5 cm.	30 20 ± 5	380 173 ± 7.2	210 313 ± 124	5870 2846 ± 719

SUMMARY OF RESULTS FOR SEABURN

(Concentrations in ug / g dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
Sea Water	0.08	16	2	2.5
<u>M. edulis</u>				
Spat	20	3440	210	2970
Older Age Classes	13 ± 1.22	999 ± 24.6	146 ± 9.4	2375 ± 141
<u>N. lapillus</u>				
all Classes	13 ± 3.4	183 ± 17.3	93 ± 7.5	1316 ± 97.5

SUMMARY OF RESULTS FOR HARTLEPOOL'S POINT

(Concentrations in $\mu\text{g/g}$ dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
Sea Water				
<u>E. intestinalis</u> all classes				
<u>R. palmata</u> all classes	n.d.	5200	300	12600
<u>F. vesiculosus</u> sporelings adults				
<u>F. serratus</u> Adults				
<u>A. nodosum</u> all classes				
<u>L. digitata</u> stipe lamina				
<u>L. hyperborea</u> stipe lamina	25 22	380 1080	40 40	3420 3910
<u>L. saccharina</u> stipe lamina				
<u>M. edulis</u> spat older age classes	30 19 \pm 2.8	1400 395 \pm 86	200 289 \pm 39	3280 2183 \pm 289
<u>A. rubens</u> than ^{less} 5 cm. over 5 cm.	20 20 \pm 1.2	230 163 \pm 11.9	220 390 \pm 78	9333 8973 \pm 600
<u>N. lapillus</u> all classes	20	140	170	3290

SUMMARY OF RESULTS FOR REDCAR

(Concentrations in u g/ g dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
<u>R. palmata</u> all classes	60 ± 6.4	1255 ± 24.7	40 ± 4.3	2965 ± 38.8
<u>L. digitata</u> stipe lamina	30 20	130 70	100 40	3680 2130
<u>L. hyperborea</u> stipe lamina	48 ± 14 23 ± 2.7	60 ± 5.9 137 ± 39	18 ± 6 16 ± 5.6	3205 ± 742 3265 ± 682
<u>L. saccharina</u> stipe	5 ± 3.54	65 ± 17.7	30 ± 7.2	1520 ± 368
<u>M. edulis</u> spat older age classes	40 16.2 ± 2	13650 320 ± 66	210 162.5 ± 9	3510 2009 ± 170
<u>A. rubens</u> all classes	13 ± 2.7	490 ± 261	146 ± 36	10960 ± 377
<u>N. lapillus</u> all classes	34 ± 1.8	184 ± 26	274 ± 50	2136 ± 284

SUMMARY OF RESULTS FOR ROBIN HOOD'S BAY

(Concentrations in $\mu\text{g/g}$ dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
Sea Water				
<u>E. intestinalis</u> all classes	20 \pm 4.2	14630 \pm 850	115 \pm 11	3585 \pm 131
<u>R. palmata</u> all classes	16 \pm 4	470 \pm 12.5	30 \pm 5.7	2443 \pm 126
<u>L. digitata</u> stipe lamina	10 \pm 2.8 10 \pm 1.4	50 \pm 6.4 165 \pm 10.6	30 \pm 5.7 30 \pm 5.8	2325 \pm 98 2545 \pm 142
<u>L. hyperborea</u> stipe lamina	12 \pm 2 10 \pm 1.7	98 \pm 7.7 402 \pm 42	22 \pm 2.2 30 \pm 7.1	2736 \pm 407 3630 \pm 268
<u>L. saccharina</u> stipe lamina	10 trace	140 130	80 40	4182 2380
<u>L. littorea</u> less than 0.5 cm. over 0.5 cm.	10 14 \pm 2.6	250 441 \pm 57.5	240 259 \pm 7.7	6340 4341 \pm 326
<u>M. edulis</u> spat older age classes	20 12 \pm 1.8	5170 944 \pm 255	210 118 \pm 7.7	5850 5696 \pm 299
<u>A. rubens</u> less than 5 cm. over 5 cm.	10 16 \pm 4	120 160 \pm 2.8	100 120 \pm 18	5920 10074 \pm 343
<u>N. lapillus</u> less than 0.5 cm. over 5 cm.	10 24 \pm 5	200 274 \pm 36.8	120 180 \pm 25	4760 4830 \pm 204

SUMMARY OF RESULTS FOR PAULL

(Concentrations in $\mu\text{g/g}$ dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
<u>E. intestinalis</u>	100 \pm 7.2	11250 \pm 1420	255 \pm 10.6	6900 \pm 863
<u>F. vesiculosus</u>				
sporelings	30 \pm 4.2	1875 \pm 357	65 \pm 9.8	9085 \pm 1679
adults	30 \pm 6.1	305 \pm 10.2	51 \pm 7.8	838 \pm 1032

SUMMARY OF RESULTS FOR CLAY

(Concentrations in μ g/g dry matter)

Specimen	COPPER Mean Concentration	IRON Mean Concentration	LEAD Mean Concentration	ZINC Mean Concentration
<u>A. rubens</u>				
0 - 5 cm.	10 \pm 1.4	185 \pm 4	150 \pm 1.4	8735 \pm 1799
5 - 7.5 cm.	3.6 \pm 0.2	224 \pm 3.6	118 \pm 9.5	8140 \pm 298
7.5 - 10 c.m.	less than 3	200 \pm 7.5	84 \pm 2.2	7538 \pm 1933
10 - 12.5 cm.	3.0 \pm 0.27	166 \pm 11.5	76 \pm 3.6	7012 \pm 2239
12.5 cm. and over	5.2 \pm 0.42	136 \pm 2.2	78 \pm 1.8	8688 \pm 2287

(after Bellamy et al 1967, John 1968 and Jones 1970)

NO4 Ug / l	Turbidity	Natural Allochthonous Material	Pollution
n.d.	0	++++	++++
2.10	2	+	-
10.50	1	++	+
19.0	0	++	++++
14.0	0	++	++++
18.7	0	+++	+++
18.8	1	++++	+
n.d.	0	++++	++++
22.7	0	++	++++
n.d.	n.d.	n.d.	n.d.