Aspects of rocky shore pollution on sections of the north east coast between Redcar and Whitby

Hughes, Jane P.

ASPECTS OF ROCKY SHORE POLLUTION ON SECTIONS OF THE NORTH EAST COAST BETWEEN REDCAR AND WHITBY

Jane P. Hughes

The University of Durham.

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I N D E X

SUMMARY.

Considerable quantities of sewage are piped into the sea along the coast between Whitby and Tessside with little thought to the consequences. This sewage, although very varied in quality, contains a variety of types of material including organic matter, nutrients, conservative material like heavy metals, bacteria and inert suspended matter. Skinningrove Beck contains very high concentrations of particulate iron and this has two important effects - on the adsorption of light resulting in a reduction in photosynthesis and a smoothering effect on filter and detritus feeders. However, it was found that it was also a major factor in the distribution of other heavy metals from the outfall at Skinningrove.

This sewage outfall was considered from the view point of a heavy metal pollutional source. The biogeochemical movements of iron, lead, zinc and copper were considered by looking at seawater, silt and organisms' concentrations in the sample sites away from the outfall. For a number of different organisms, the behaviour of each heavy metal was described in terms of its absorption, storage, excretion and regulation. This description was utilised in explaining inter-site variations in heavy metal concentrations. Close to the outfall where there were higher concentrations, the sub-lethal and lethal effects were examined and a number of factors such as interaction with other heavy metals were seen to be a controlling influence over the different toxic effects.

Population studies were made for <u>Laminaria digitata</u>, <u>Ulva lacuta</u>, <u>Mytilus edulis</u>, <u>Patella vulgata</u> and <u>Nucella lapillus</u> and diversity indices calculated for each site. Variations between sites were noted and some attempt was made to understand the interaction between factors which could cause these variations. For the effects of heavy metal pollution, age and size distribution data was found to be more valuable in this assessment than mere presence or absence or total productivity.

INTRODUCTION.

This study was stimulated by the differences in the North Yorkshire rocky shore communities. Many of the variations are the result of effects of man whose waste is carried into the sea by local rivers, or piped directly into the sea. It was decided to concentrate most of the work in the Skinningrove area where large amounts of iron waste are carried to the sea by the local Beck, and where there is a sewage outfall for the Skinningrove, Loftus, and Carlin How areas. For the sake of comparison, a polluted site close up to the River Tees was selected, this was located on Coatham rocks, Redcar, and a relatively unpolluted site at Kettleness.

Five sampling sites were selected at Skinningrove, each at varying distances to the East of the sewage outfall. It was hoped that it would be possible to look in detail at the ecology of each of these sample sites, and to give some consideration to species diversity, population studies, bacterial levels and heavy metal concentrations, away from this point pollution source.

It was expected that this data would shed some light on the effects of heavy metals and other waste material on rocky shore communities, and to assess how far community variation is a product of the effects of man. Careful site selection was necessary in order to minimize inter-site variation or other factors which would influence the rocky shore communities.

The pollutional aspects of the sites would be assessed by measuring the levels of heavy metals, (iron, zinc, copper and lead), and bacteria, with some consideration of varying salinities. These measurements were compared with other ecological data to help to isolate other possible causal relationships. The analysis of these relationships it was thought, would have to rely partially on previous work wherever possible, as time would not allow a series of laboratory experiments to establish more firmly inferred toxic effects of these heavy metals. This would be an important area for further investigation.

KEY TO FIGURES.

Rocky shore sample sites.

Sk.1.	Skinningrove Area 1.
Sk.2.	Skinningrove Area 2.
Sk.3.	Skinningrove Area 3.
Sk.4.	Skinningrove Area 4.
Sk.5.	Skinningrove Area 5.
K.	Kettleness.
R.	Redcar.

Skinningrove Beck sample sites.

1.	Above coast road.
2.	Below second drainage point from disused iron mines.
3.	Below third drainage point from disused iron mines.
4.	Pool.
5.	Junction of sea and river water.

U.	Upper shore.
L.	Lower shore.
L.W.	Low water tide level.
H.W.	High water tide level.
n.d.	No available data.
g	Gram
l.	Litre
m.	Metre

FIGURE 1. MAP OF SEWAGE OUTFALLS ALONG THE NORTHERN SECTION OF THE STUDY AREA.

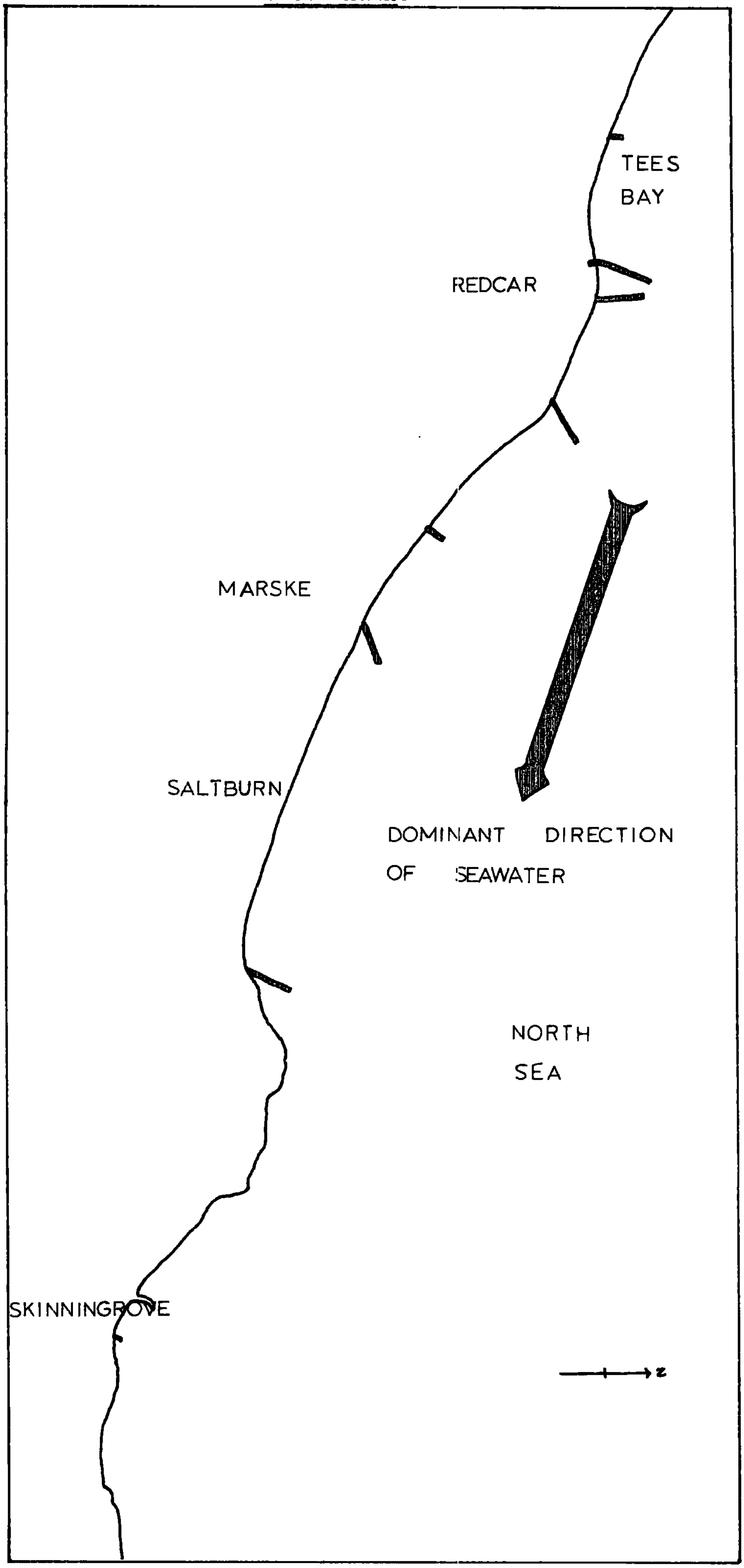


FIGURE 2 . DISTRIBUTION AND MAGNITUDE OF SEWAGE OUTFALLS IN THE SAMPLING REGION.

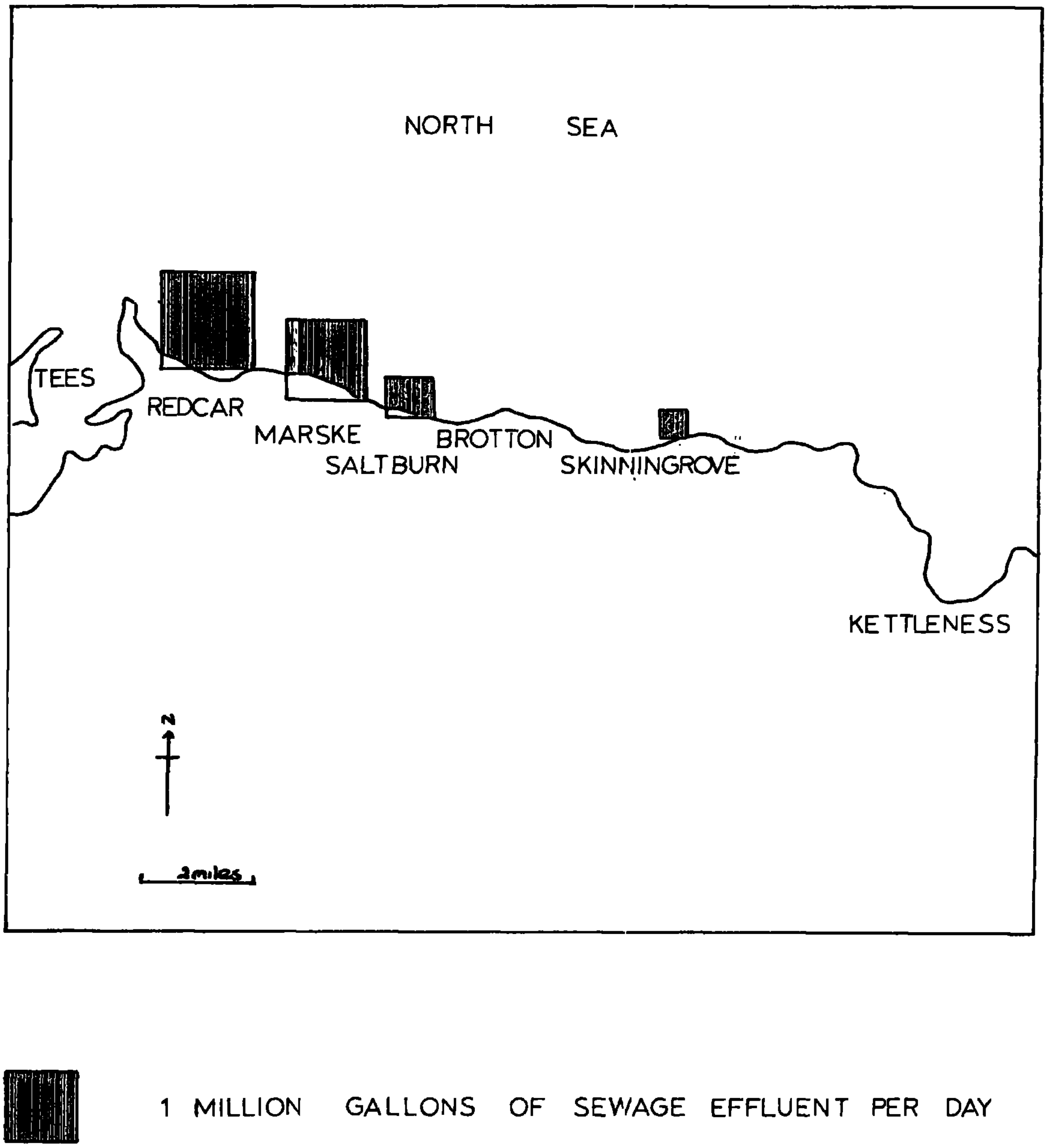
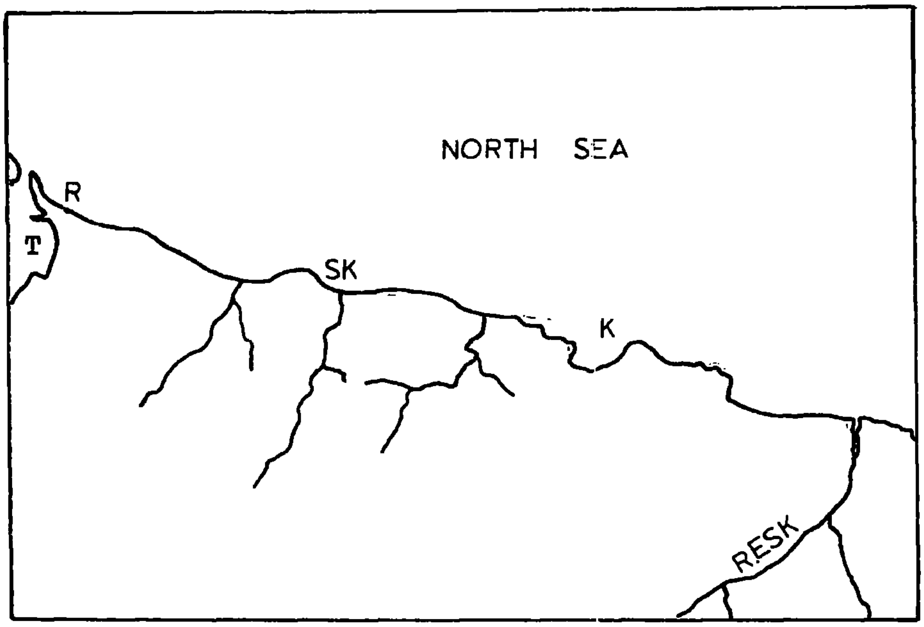


Figure 3a. <u>Map of the location of sites</u>.



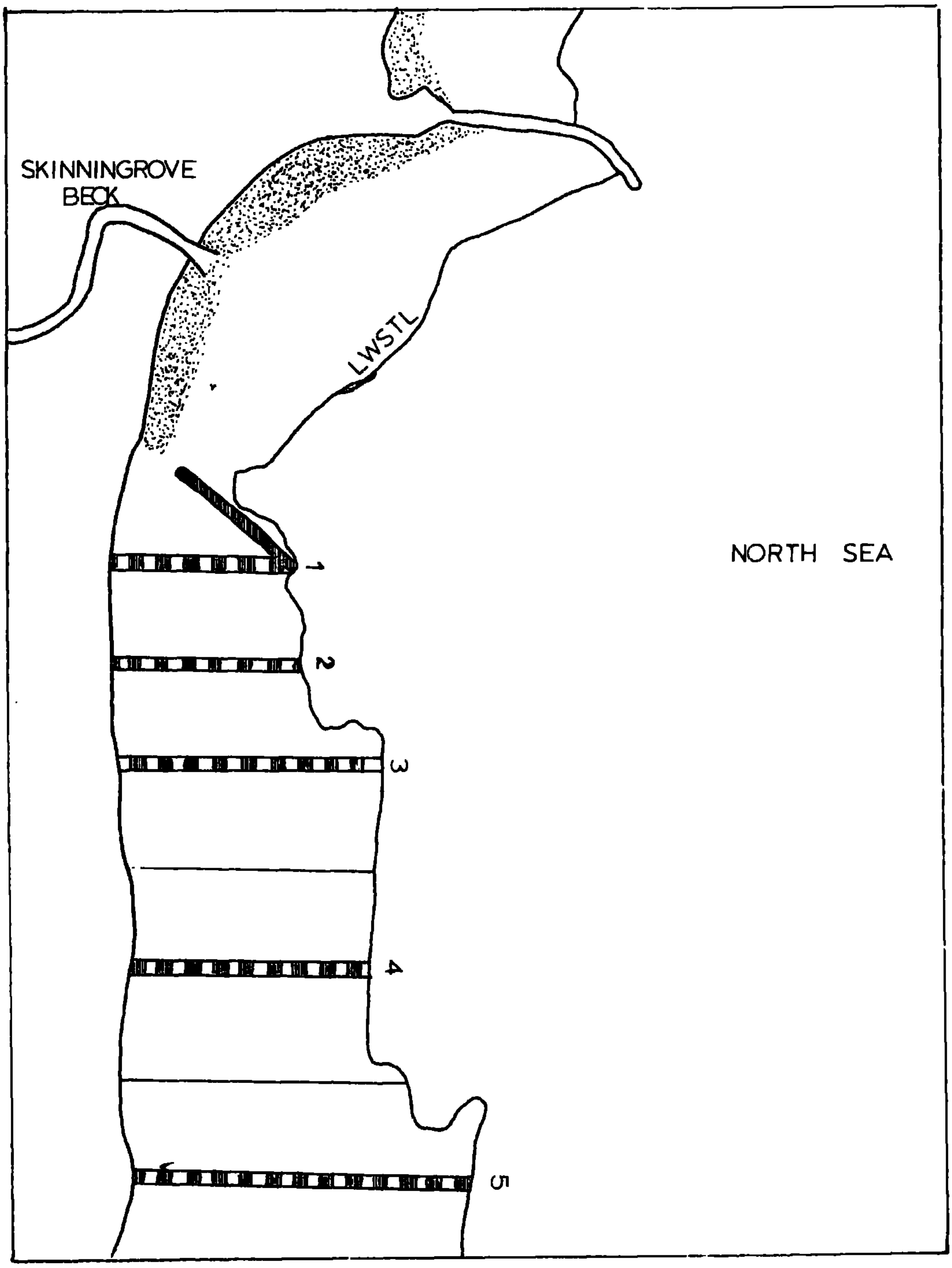
R- Redcar

SK- Skinningrove

K- Kettleness

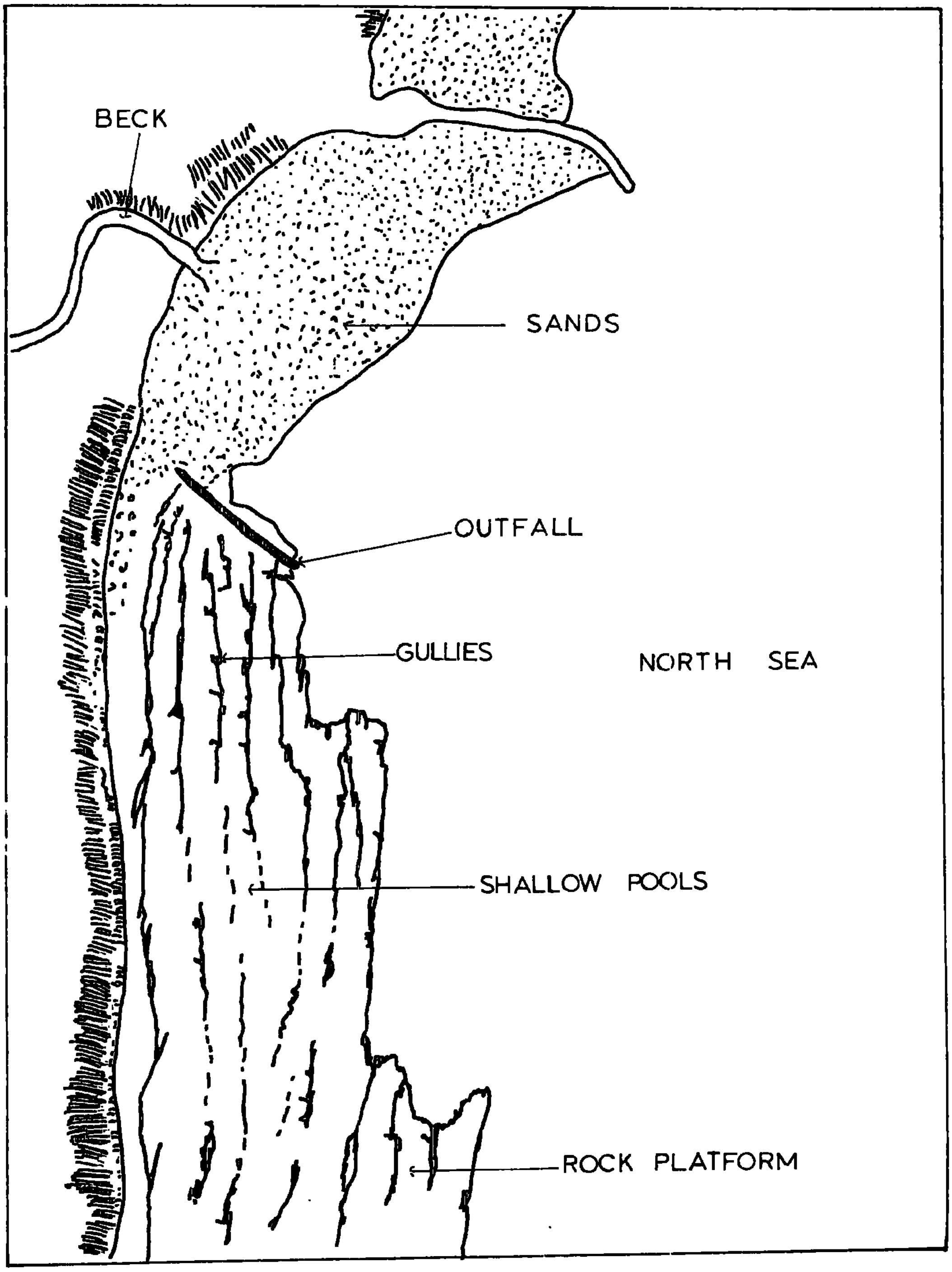
T- River Tees

Figure 3b Map of sample sites at Skinningrove.



sample sites 1,2,3,4,5.

Map of Skinningrove Rocky Shore.



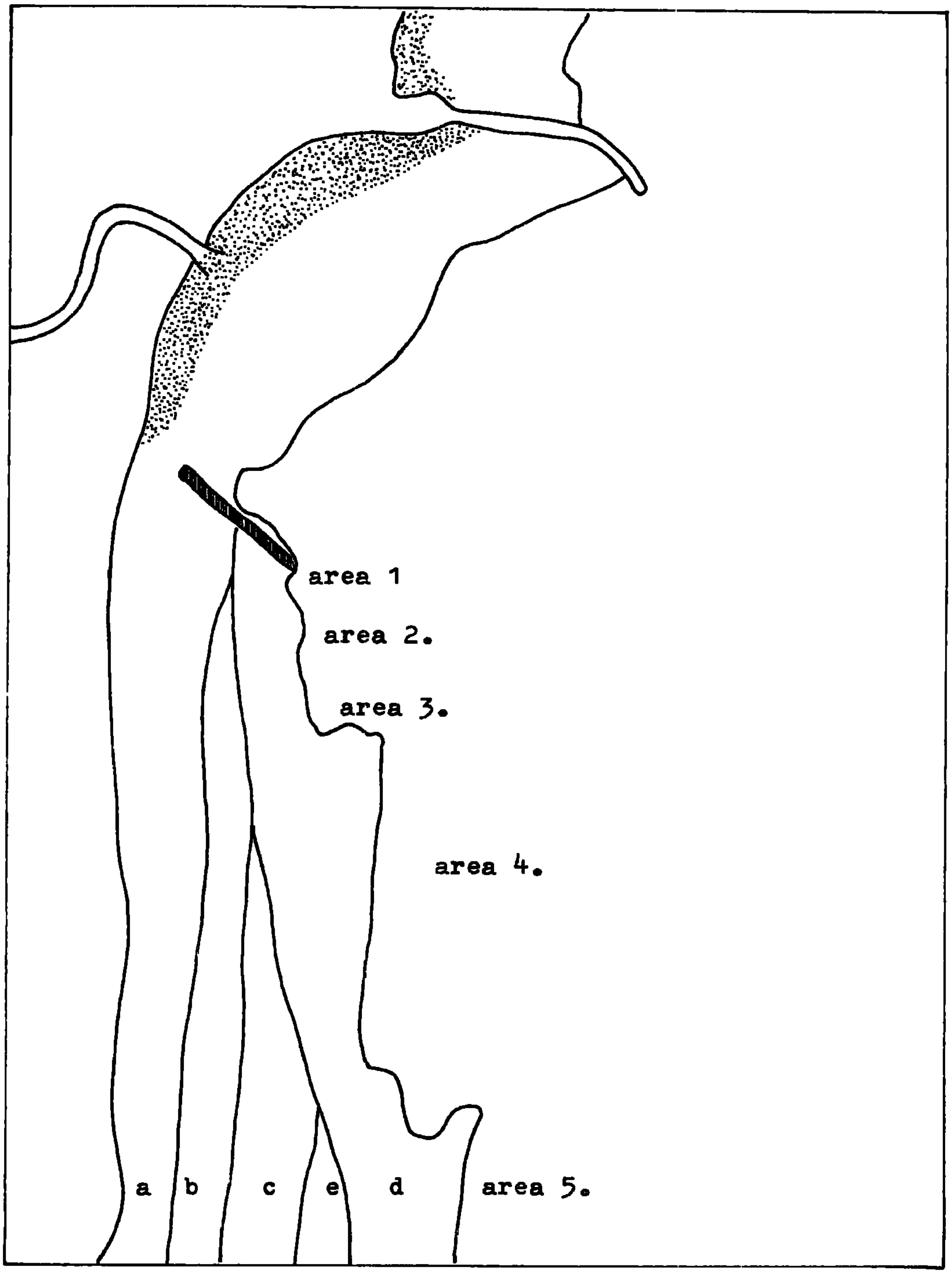
SAMPLE SITES.

Sample sites are located on the Northern section of the Yorkshire coast and are shown in Figure 3a. The movement of the seawater is in a Southerly direction due to the combination of tidal and residual current effect. The polluted water of the River Tees and all the sewage outfalls along the coast is carried in a Southerly direction and this results in a pollutional gradient in this direction. The point sources of pollution, sewage outfalls, along this section of the coast, are shown in Figure 1. The output of each sewage source is summarised in Figure 2. The Coatham Rocks have a number of sewage outfalls and it is the largest of the input sources. By comparison, the Skinningrove outfall is the smallest input source in the study area. However, the end of the outfalls at Redcar are well below the low water spring tide level, while at Skinningrove it does not extend below the low water spring tide level.

The Redcar site lies about seventeen miles from the Kettleness site, and the Skinningrove sites lie roughly inbetween. The sampling sites at Skinningrove extended from the sewage outfall Eastwards being approximately half a mile from the outfall. (See Figure 3b). The sites were chosen to minimize other variations. The nature of the substrate at each sample site was a flat rock platform. The Skinningrove sites were slightly more varied, with a number of gullies running along the shore, and, in part, boulder strewn in the upper shore zone. The upper section of the Redcar shore is a sandy beach.

The main variable between sites is wave action. No attempt is made to use a biological index of exposure as the effects of pollution have largely made this impracticable. Without longer periods of analysis of physical parameters, it is only possible to suggest a subjective but comparative assessment. The areas at the Western part of Skinningrove were moderately exposed, while all the other sites were more highly exposed, each being roughly of the same magnitude.

Figure 4. Map of vegetation zones at Skinningrove.



SPECIES DIVERSITY.

It is generally accepted that an adverse environment will result in a decrease of the number of species, although the total number of organisms of a given species may increase because of reduced competition, Abbott (1967). Thus a measure of the 'general health' of the environment may be provided by an examination of the diversity of organisms. In order to avoid subjective appraisals or measures, it is preferred to have a quantitive, mathematically defined concept of diversity. Such a definition would be reproducible and would allow comparison of diversity measures with physical, chemical, or biological characteristics of the environment. Any meaningful definition of diversity must consider the number of different types of organisms as well as the relative numbers of organisms of each type.

A number of workers have proposed indices of diversity. For instance, in 1943, Fisher, Corbet and Williams (1943) developed an index which is one parameter of a logarithmic series describing the relationship between the total number of species in a sample, and the number of species represented by only one individual. However, this index has the drawback of attempting to adjust a natural distribution to a simple mathematical expression. Information theory though, provides a way to overcome this difficulty adopting, as an index of diversity, a more exact expression of the information contained in the structure of the community.

In this study, the Shannon - Weaver diversity index is used. (Shannon and Weaver 1949). This diversity index employs the use of information theory, and was used here to assess the diversity of the algal component of the sample sites. The index is as follows :-

$$H' = -\sum_{i=1}^{s} \left(\frac{n_i}{n}\right) \log_2 \left(\frac{n_i}{n}\right)$$

The equation involves the observed proportion ($\frac{n_i}{n}$) of species in samples.

The number of individuals, n, can be replaced by the biomass. Biomass was used in this investigation rather than the number of individuals, due to the difficulty experienced in counting the number of individuals.

The diversity index will be high in communities which have a high biomass, and in which the total biomass of each species decreases relatively slowly on passing from the more abundant to the less abundant ones. On the other hand, when there is a rapid decrease in the biomass per species on passing from the dominant ones to those successively less important, or the community has only a low total biomass, the index of diversity is low. Thus high diversity indices represent diverse stable communities allowing maximal utilisation of the total energy input from any source.(Odum 1967).

Lloyd and Ghelardi (1964), indicated that there are two separate components to the Shannon Weaver index. These are species richness, and the "equitability" or "evenness" of species abundance. Species richness is equivalent to S, the number of species in the sample. The relative abundance component is measured by the following index :-

$$J' = H' / H' \max.$$

in which H' max is log S . The index represents the ratio of the observed diversity to the maximum diversity possible for the same number of species. It has a maximum value of unity when all species have equal abundance, while the minimum value is obtained when all the species, except the most abundant, are represented by only a very low biomass.

For calculation of the diversity indices, random samples were taken in each of the vegetation zones (see Map 4). The taking of each sample involved clearing 0.5 square metre of rock surface of all algae, except encrusting algae and those less than ten millimetres in length. The algae were taken back to the laboratory, sorted into species and then dried to constant weight in an oven at 105°C. Twenty random samples were taken in each of the vegetation zones at each of the sample sites.

Values of H' and J' were calculated for each sample

SPECIES DIVERSITY.

Shannon Weaver diversity index $H' = -\sum_{i=1}^{S} p_i \log_2 p_i$

where p_i is the importance probabilty of each species.

Maximum diversity for the same number of species $H'\ max = \log S$

S = number of species.

The equitability $J' = H' / H'\ max$.

KEY.

A. refers to the Redcar sample site.
B. refers to the Kettleness sample site.
C. refers to the Skinningrove Area 1 sample site.
D. refers to the Skinningrove Area 2 sample site.
E. refers to the Skinningrove Area 3 sample site.
F. refers to the Skinningrove Area 4 sample site.
G. refers to the Skinningrove Area 5 sample site.

MEAN FIGURES FOR EACH SITE :-

H' ± 2 SE.	A	B	C	D	E	F	G
Zone 1.	1.21 ± 0.14	1.62 ± 0.06	1.15 ± 0.16	1.43 ± 0.10	1.19 ± 0.06	1.20 ± 0.16	1.45 ± 0.22
Zone 2.	1.56 ± 0.12	1.73 ± 0.10	1.37 ± 0.12	1.48 ± 0.14	1.59 ± 0.04	1.73 ± 0.10	1.78 ± 0.04
Zone 3.		1.43 ± 0.08		1.25 ± 0.08	1.22 ± 0.18	1.31 ± 0.08	1.44 ± 0.08
Zone 4.		1.66 ± 0.08				1.44 ± 0.06	1.51 ± 0.06
Zone 5.							1.28 ± 0.12
Zone $\bar{x}$	1.39	1.61	1.26	1.39	1.33	1.43	1.50

S ± 2 SE.	A	B	C	D	E	F	G
Zone 1.	3.8 ± 1.0	4.2 ± 1.2	2.8 ± 0.08	3.4 ± 1.0	4.2 ± 1.2	4.0 ± 1.0	3.8 ± 1.0
Zone 2.	6.5 ± 1.4	12.2 ± 2.2	4.5 ± 1.2	4.8 ± 1.2	6.2 ± 1.4	8.2 ± 1.6	9.4 ± 1.6
Zone 3.		5.4 ± 1.2		5.2 ± 1.4	5.4 ± 1.2	5.4 ± 1.2	6.0 ± 1.2
Zone 4.		9.6 ± 1.8				5.8 ± 1.2	5.6 ± 1.4
Zone 5.							6.6 ± 1.2
Zone $\bar{x}$	5.15	7.85	3.65	4.37	5.6	5.85	6.28

FIGURE. 5.

MEAN FIGURES FOR EACH SITE :-

J' ± 2 SE.	A	B	C	D	E	F	G
Zone 1.	0.71 ± 0.05	0.80 ± 0.06	0.73 ± 0.08	0.81 ± 0.07	0.59 ± 0.03	0.60 ± 0.02	0.74 ± 0.08
Zone 2.	0.57 ± 0.03	0.48 ± 0.02	0.65 ± 0.06	0.66 ± 0.06	0.60 ± 0.03	0.57 ± 0.02	0.56 ± 0.01
Zone 3.		0.60 ± 0.03		0.52 ± 0.04	0.51 ± 0.02	0.54 ± 0.01	0.55 ± 0.02
Zone 4.		0.51 ± 0.03				0.57 ± 0.02	0.59 ± 0.03
Zone 5.							0.47 ± 0.02
$\bar{x}$	0.64	0.65	0.69	0.66	0.57	0.57	0.58

Total Biomass per 0.5 m in gm	A	B	C	D	E	F	G
Zone 1.	20.76	15.77	20.42	34.39	54.82	20.95	9.76
Zone 2.	34.40	612.2	9.72	25.76	25.2	131.30	242.9
Zone 3.		337.5		14.13	58.4	115.01	151.8
Zone 4.		74.29				123.55	102.7
Zone 5.							181.0
$\bar{x}$	27.58	269.94	15.07	23.82	46.14	100.2	113.76

FIGURE 6.

and a regression of H' against the logarithm of the number of species was then determined. Means, and two standard errors of the mean of H', S, and J' were calculated for each community.

The H', S and J' indices for the sample sites are summarised in Table 5 & 6From this table, it is evident that variations between sites are small and, considering standard errors, could not be considered significant. The reason for the small variation can be related to the low regional species diversity which has been noted by a number of writers. Bellamy (1968). The low species diversity and performance being attributed to suspended matter reducing the light available to the plants. Bellamy, Bellamy, John and Wittick (1967), Bellamy (1968), and Bellamy, John and Wittick (1968). Local variations of H', S and J' indices would therefore occur between a narrow range; small variations being locally significant.

Unfortunately other environmental factors, other than pollution, can result in low H', S and J' indices. The J' equitability index at Skinningrove illustrates this complication. The Skinningrove Areas 3, 4 and 5 have lower indices than Skinningrove Areas 1 and 2. The reason for this is related to the higher wave action at Skinningrove Areas 3, 4, and 5, as the rock platform extends further to seaward and subsequently is more exposed. As a result Fucus serratus is dominant, and so there is a subsequent reduction in J' value, and relative reduction in H' and S values. It would be reasonable to put in a minor correction for this variable which would result in higher H' and S values, perhaps making only a slight difference to make Skinningrove Area 5 similar to the Kettleness site.

Even without this correction it is possible to pick out the trend of increasing H' and S away from the sewage outfall. Between Skinningrove Areas 1 and 5, the species richness value doubles, and H' shows a marked increase also. This is the result of some limiting factor to certain organisms closer to the sewage outfall. This limiting factor would seem likely to be related to the increasing levels of toxic materials found both in seawater and silt levels as the sewage outfall is approached.

The results for Kettleness, with the highest H' and S indices, and the next highest J' value, reflect the comparatively unpolluted character of this site. In addition, the similarity of the biological indices for Kettleness and Skinningrove Area 5, is an indication of the steepness of the gradient of the pollution at Skinningrove and the possible extent of pollution. From this data the effects of the pollution has been largely nullified by Area 5 at Skinningrove.

The Redcar results indicate that it is a pollutional site, similar to Skinningrove Area 1, but that its values are intermediate, suggesting that the sample site was some short distance from the outfall itself. This was the case.

The figures for biomass in representative half metre square areas show that not only does species diversity increase away from the sewage outfalls, but there is also a substantial increase in production. The lowest levels of biomass occur at Redcar and Skinningrove Area 1, and the highest at Kettleness and Skinningrove Area 5. There are a number of possible reasons for this. Firstly, there may be an increase in the amount of suspended matter, so reducing photosynthesis. Secondly, toxic effects could reduce growth, as was found by Bryan (1971) for Laminaria digitata. A third possibility is a lethal effect resulting in a direct loss of biomass. The other interesting feature is the biomass at Kettleness being over twice the Skinningrove Area 5 figure. This indicates that there may be still a pollutional effect at Skinningrove Area 5; for example, heavy metal inhibition of growth, or increased suspended material limiting growth. This possible effect is not highlighted in any of the H', S, or J' indices.

This is an important point. Many pollution studies using indicator species or index, may not be as valuable or as sensitive as more detailed study on performance and production.

POPULATION STUDIES.

Population studies were made on four species, *Patella vulgata*, *Mytillus edulis*, *Nucella lapillus*, and *Laminaria digitata*, at each of the selected sites in order to look at age structures and other parameters of the population, for the purpose of relating differences between sites to possible lethal effects of pollutants.

In looking at morphological characters during their growth periods, it is evident that sampling must occur over a short time period for all sites in order for them to be comparable. For example, Russell (1909) observed that limpets in their first year show about a three millimetre increase in size per month during the summer, and thus, if there were time lapses between sampling at the different sites, size differences could not be attributed only to intersite variation. Subsequently, the sampling period for any one species was restricted to one particular day.

FIGURE 7 . GRAPH TO SHOW THE RELATIONSHIP BETWEEN STIPE LENGTH AND THE NUMBER OF GROWTH RINGS AT SKINNINGROVE.

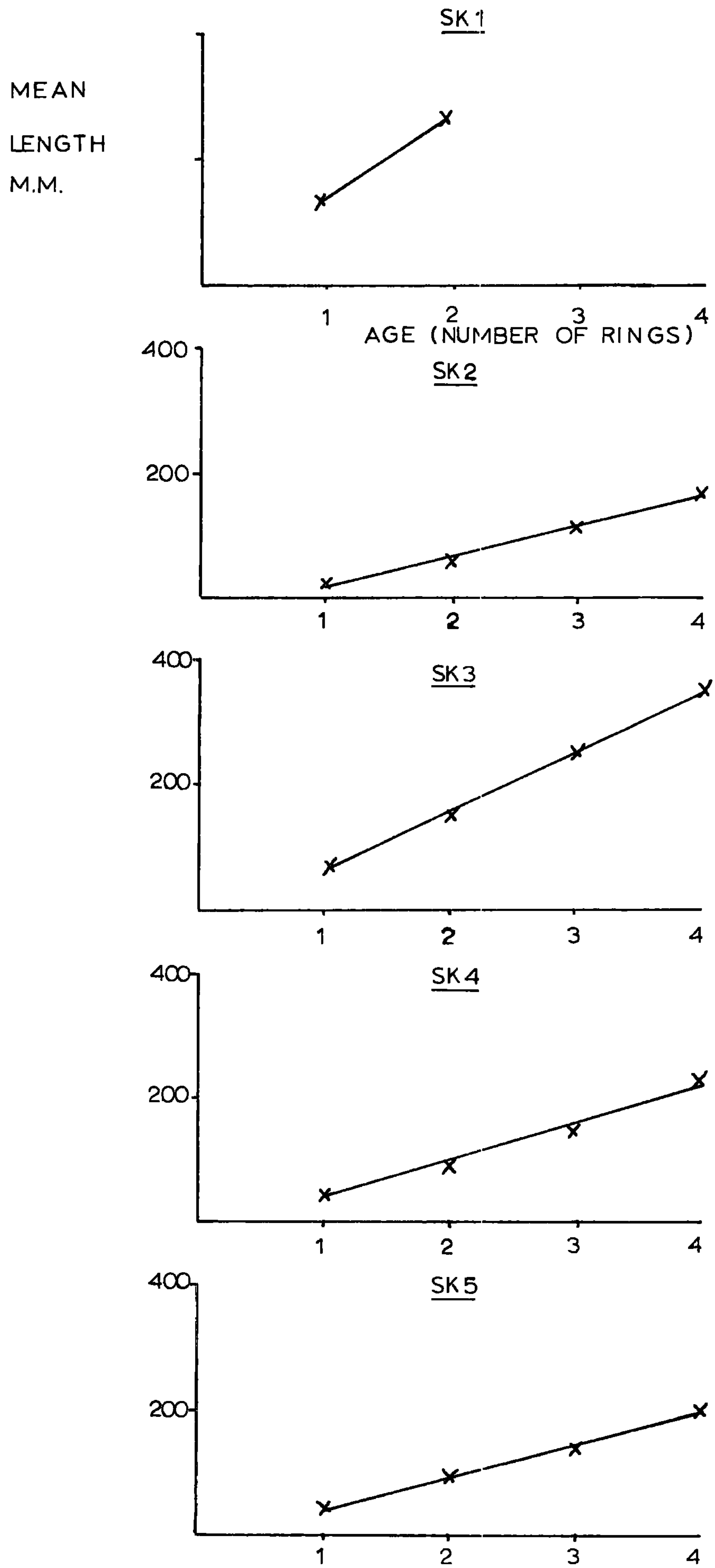
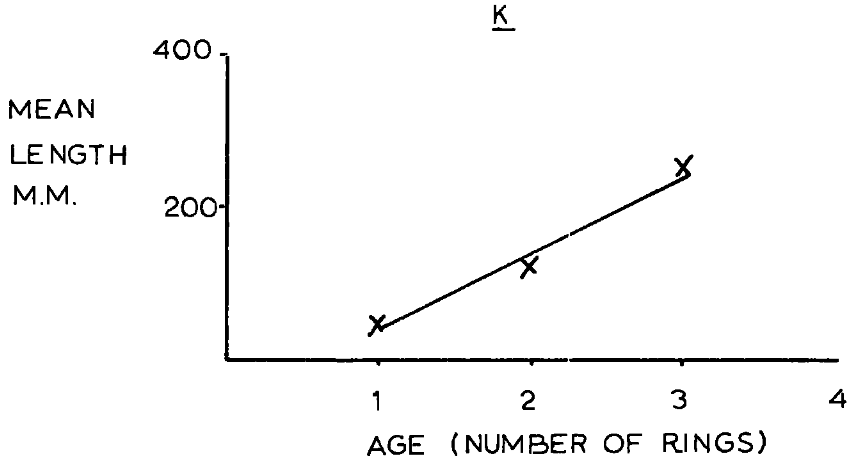


FIGURE 7 .(continued). <u>GRAPH TO SHOW THE RELATIONSHIP BETWEEN STIPE LENGTH AND THE NUMBER OF GROWTH RINGS AT KETTLENESS AND REDCAR</u>.



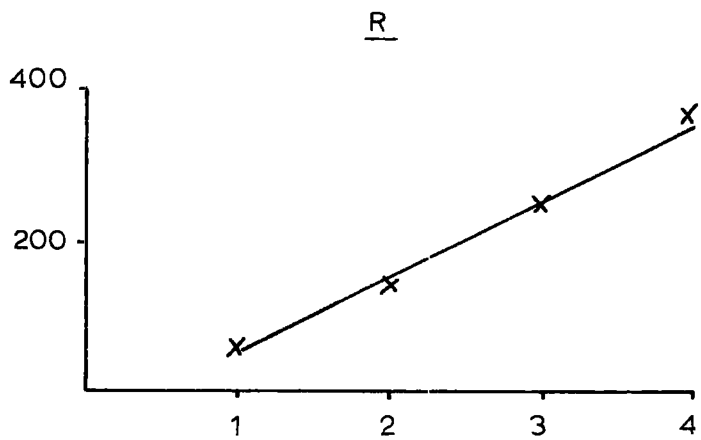


FIGURE 8. AGE STRUCTURE OF LAMINARIA DIGITATA POPULATIONS AS DETERMINED BY GROWTH RINGS

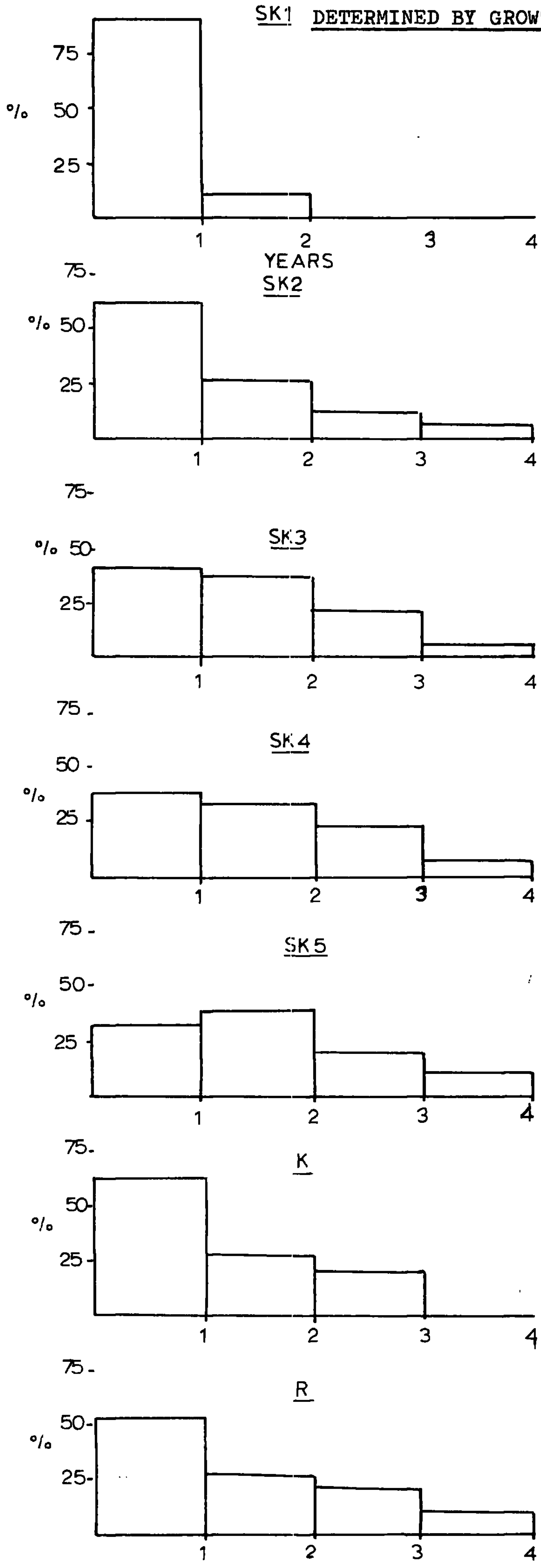
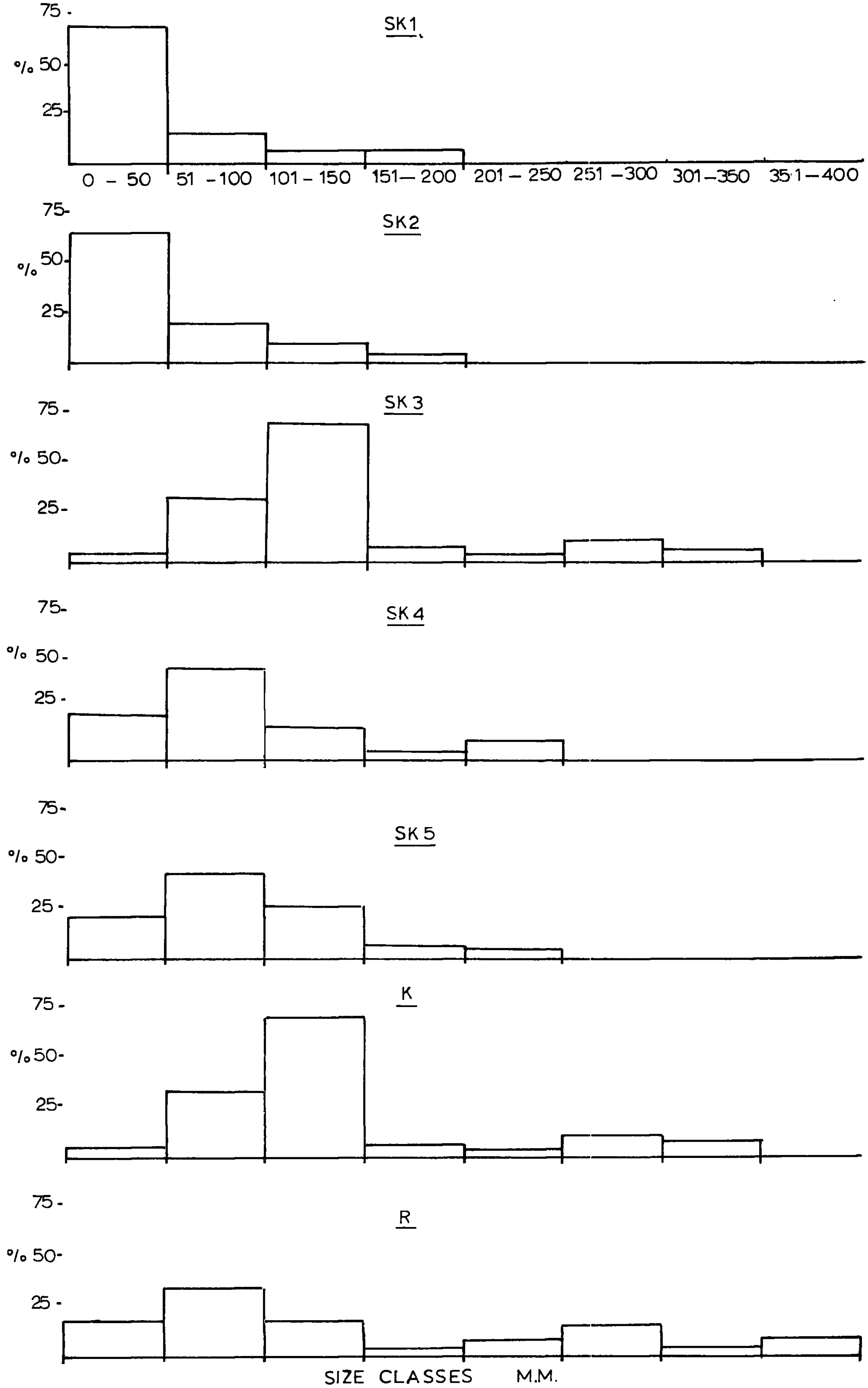


FIGURE 9. AGE STRUCTURE OF LAMINARIA DIGITATA POPULATIONS AS DETERMINED BY STIPE LENGTH.



POPULATION STUDIES ON LAMINARIA DIGITATA.

Plants of Laminaria digitata were collected from all the seven sample sites. The whole stipe was obtained by levering the holdfast from the rock surface with a knife. All plants of this species were removed from 0.5 metre square quadrats, counted, and then taken back to the laboratory for weight and length determinations.

Age can not satisfactorily be determined, as found by Kain (1963) for Laminaria hyperborea by counting the number of growth rings seen in transverse section at the base of the stipe, as John (1968) found that more than one hapteron whorl may be produced in a growing season in North East England. However, using the length of the stipe, John (1968) found that Laminaria digitata plants could be grouped into classes. These size classes were more than 90 per cent. correlated with age classes later determined using only the distinct growth rings. Graphs of the length of the stipe against the number of growth rings for Laminaria digitata at the sample sites are shown in Figure 7.

Stipe dry weight determinations were also made; the stipe only being used, as it represents the perennial part of the plant and so avoids incorporating the weight of the frond which varies so much with the season.

The age structures of the Laminaria digitata populations at each of the sample sites, as determined by the number of growth rings are shown in Figure 8 , and as determined by stipe length in Figure 9 . A completely stable population would be comprised of plants of all ages within the life span of the species with no particularly large proportion of plants which arose during a certain period but with somewhat more young plants than old. Less stable populations would be formed when some environmental factor or factors removed some of the plants. If the environmental factor or factors were fairly constant this would result in a loss of plants every year. The continual output of sewage containing its heavy metals and the addition of iron from Skinningrove Beck, may be such factors. This would explain the results obtained at Skinningrove Areas 1 and 2 which have a greater proportion of young plants than the other sample sites at Skinningrove. On the other hand, if the factor or factors acted intermittently, then this would result in an irregular age composition as was found at Skinningrove Areas 3, 4 and 5. Although the output of sewage and iron from Skinningrove Beck is continual, the heavy metal concentrations are varied with time. The resulting spatial variations are subsequently very complex. However the occurrence of possible lethal or sublethal levels of heavy metals would decrease away from the outfall. The results of the heavy metal work suggest that by Skinningrove Area 3 and subsequently Areas 4 and 5, the occurrence could be considered infrequent and subsequent effects on age structures would be of an intermittent character. This is further complicated by site variation in the exposure factor with the increasing exposure from one to five. This factor could explain the variability in age structure and lower age span in Areas 4 and 5.

FIGURE 10. THE RELATIONSHIP BETWEEN STIPE WEIGHT AND LENGTH FOR LAMINARIA DIGITATA AT SKINNINGROVE AREAS 1, 2, & 3.

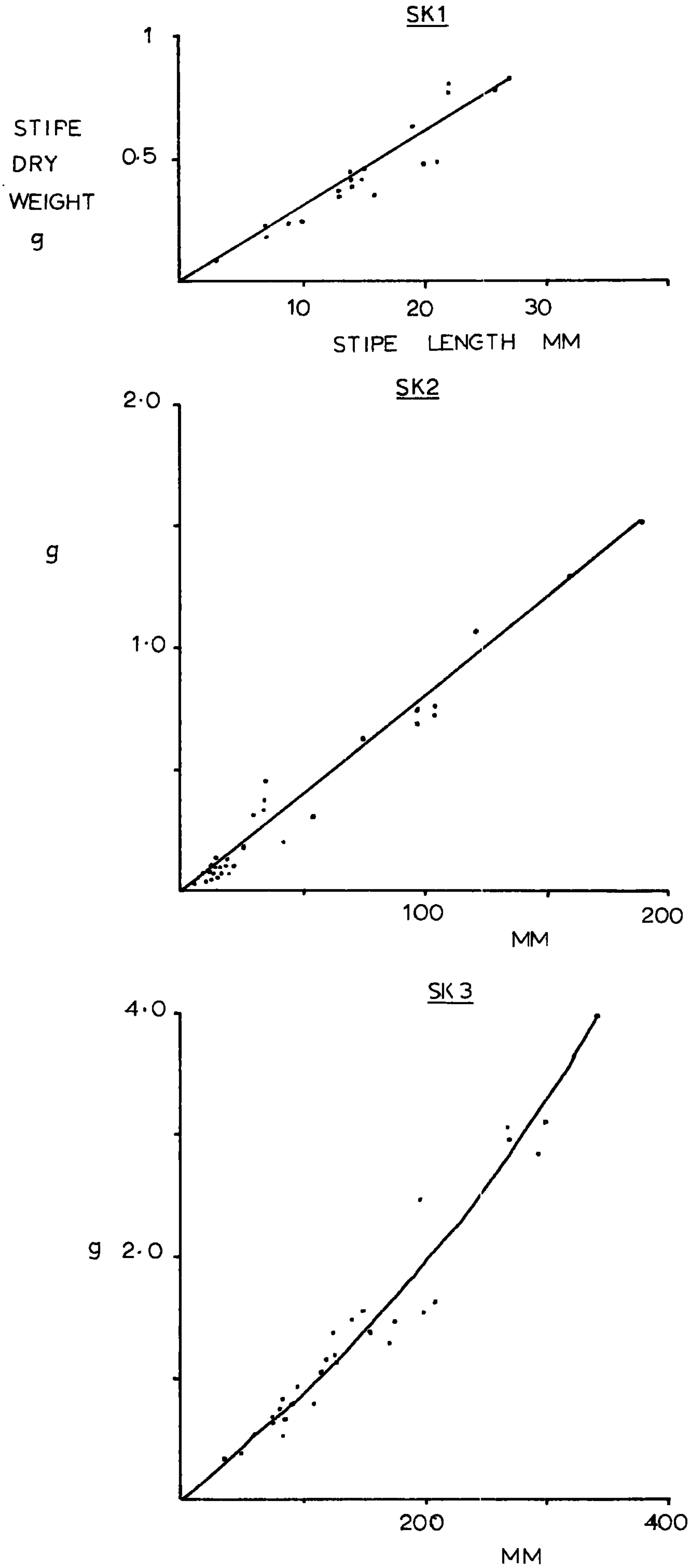
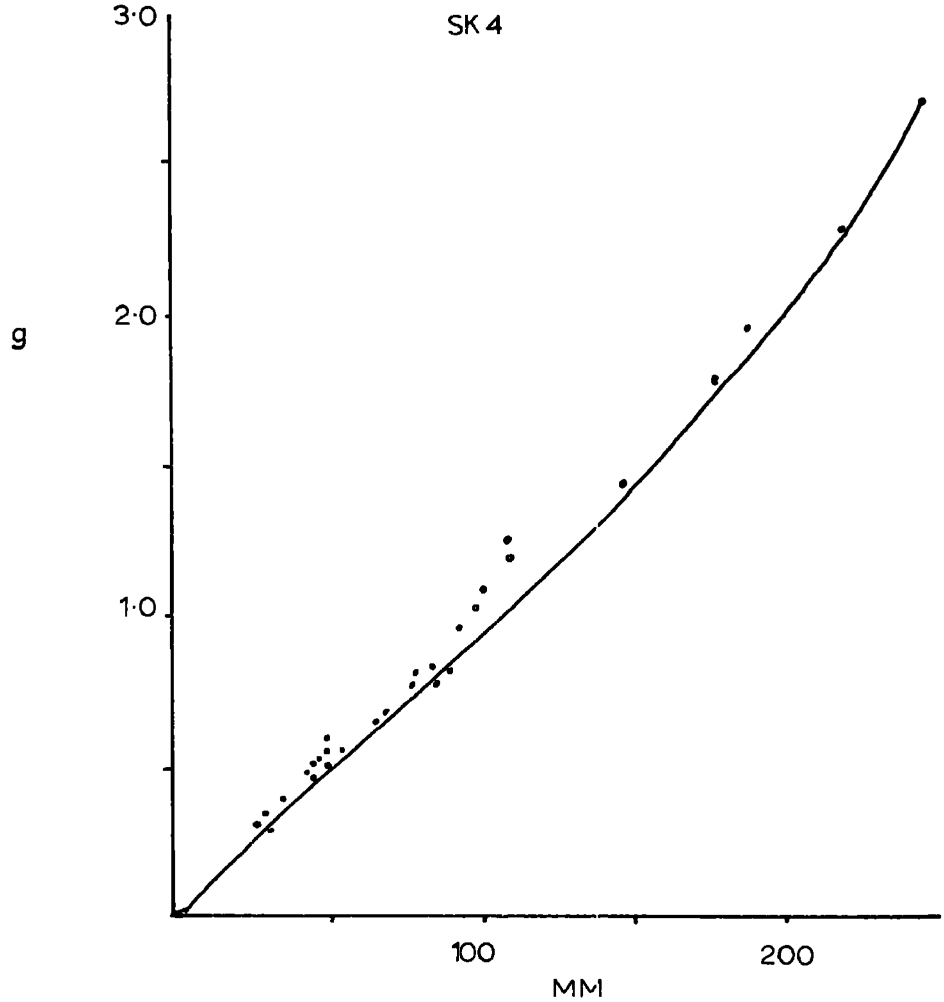


FIGURE 10(continued). THE RELATIONSHIP BETWEEN STIPE WEIGHT AND LENGTH FOR LAMINARIA DIGITATA AT SKINNINGROVE AREAS 4 and 5.



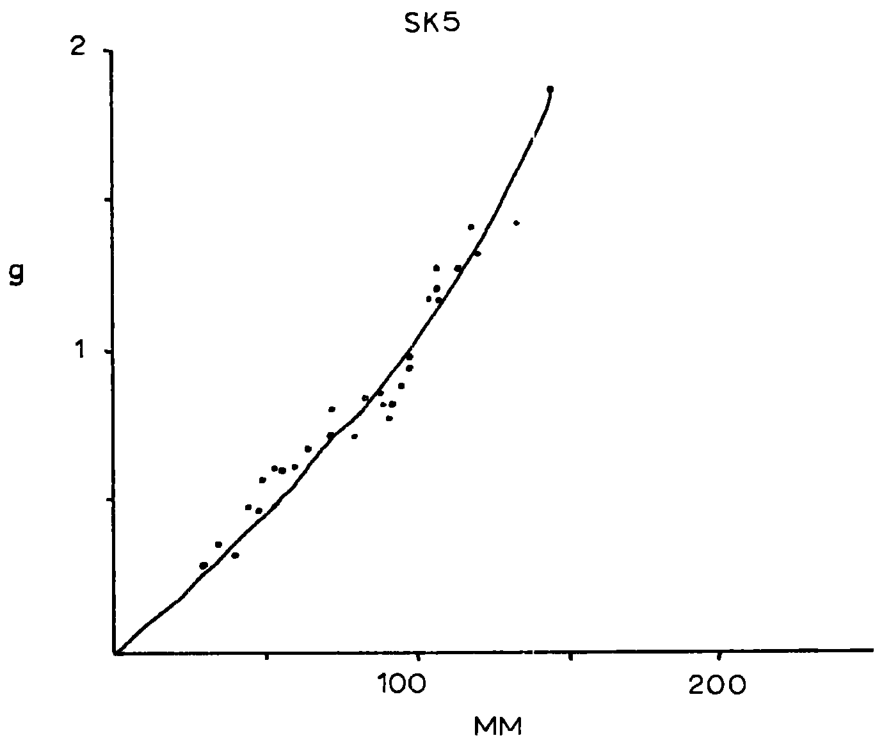
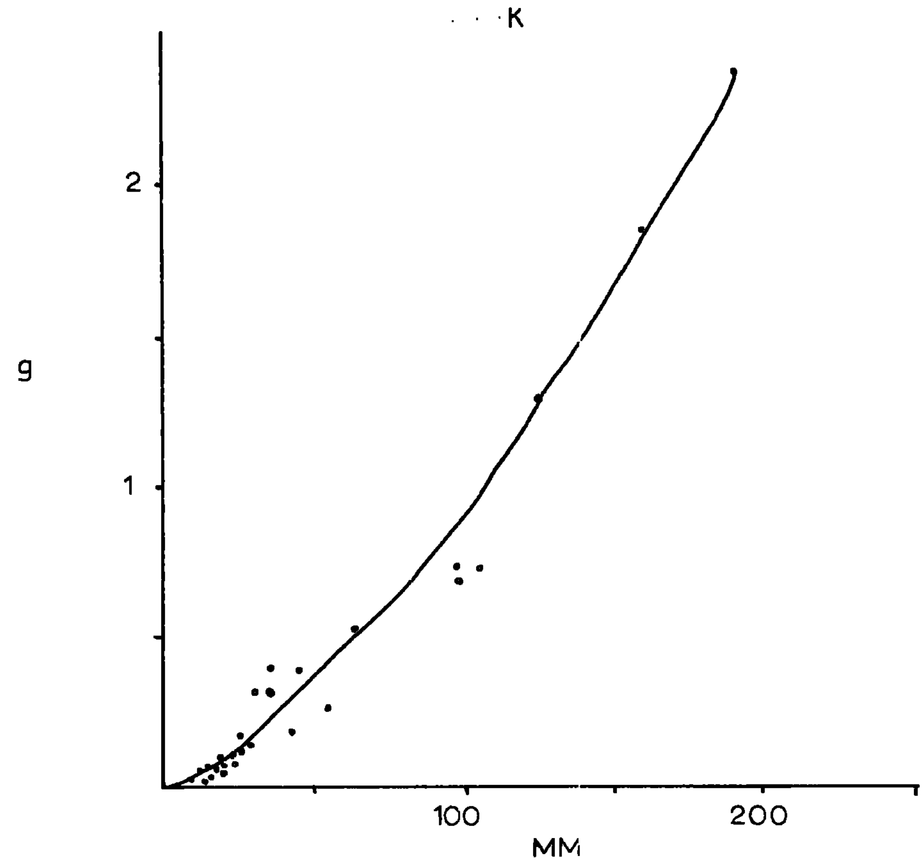
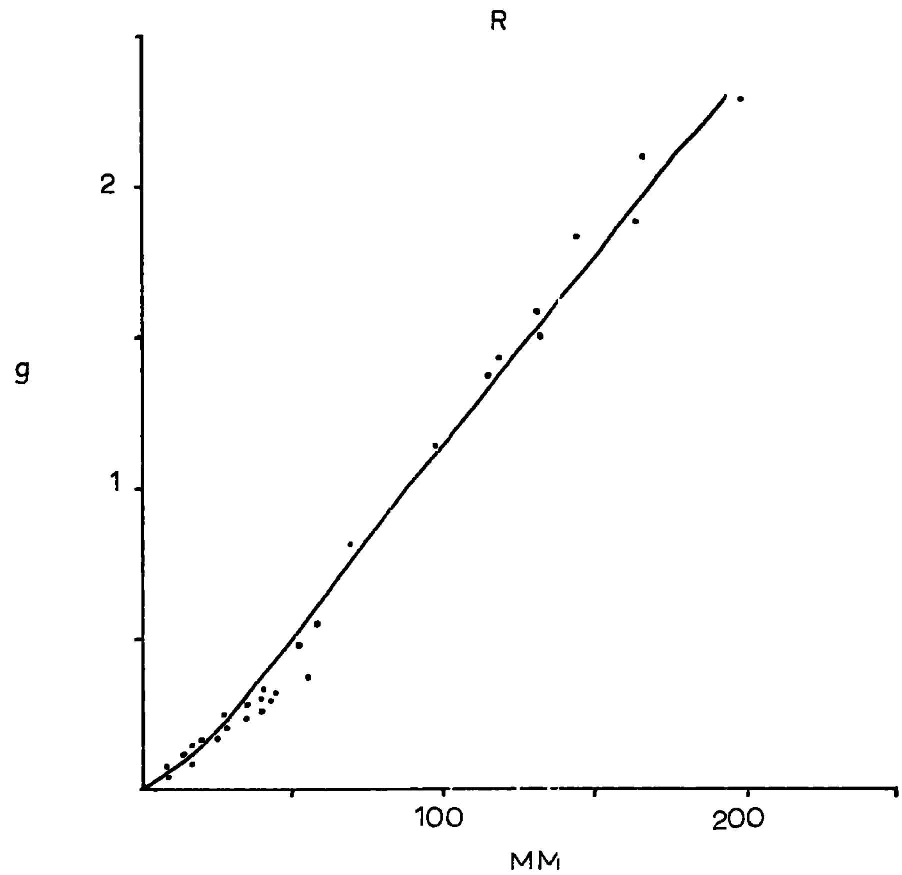


FIGURE 10 (continued). THE RELATIONSHIP BETWEEN STIPE WEIGHT AND LENGTH FOR LAMINARIA DIGITATA AT KETTLENESS AND REDCAR.



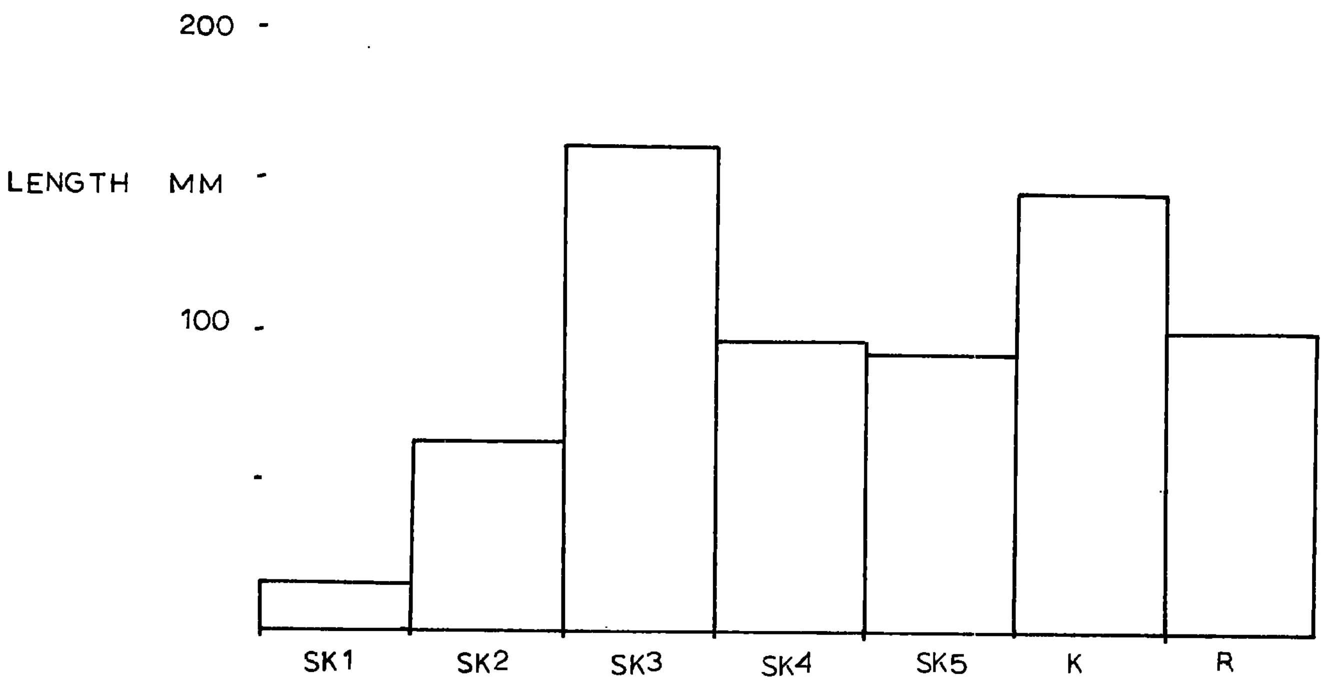


The Kettleness results are a reflection of some very abnormal wave conditions causing wholesale destruction locally of Laminaria species. There was insufficient time to sample the washed up debris at this site.

From this work on population structures of Laminaria digitata, it is possible to suggest that firstly, there is a possibility that heavy metals have a lethal effect on Laminaria digitata and this effect results in premature death of the plant. Secondly, there are possible differences in the susceptibility to high exposure in larger, older age groups on this substrate to high wave action. Thirdly, interspecific competition as seen by other workers could be an important determinant of the age structure of Laminaria populations. However, this is unlikely, and factors such as high wave action and pollution would seem to cause the irregular but dominant effects. Unfortunately the most polluted sites in this study are the sites of least exposure, and the most unpolluted,the sites of highest exposure. Subsequently the population structure data at both ends of each scale show similarities. The effects of pollutants seemingly have greater but similar effects to those of wave action. Redcar, with intermediate exposure and moderate pollution, Kettleness, with high exposure and low pollution levels, and Skinningrove Area 3, with moderate pollution and intermediate wave action, have the least unstable population characteristics.

The relationship between stipe weight and length are shown for the sample sites in Figure 10. For all but the Skinningrove Areas 1 and 2 samples, the graphs take the form of

FIGURE 11 . MEAN LENGTH OF STIPES OF LAMINARIA DIGITATA PLANTS AT EACH OF THE SAMPLE SITES.



a curve; Kain (1963) has reported that young plants of Laminaria hyperborea, below the canopy of the forest itself, are retarded in growth, presumably by the reduction in illumination. It would seem likely that these plants would be able to assume a fast rate of growth only when a mature plant within its vicinity is removed. It would then rapidly grow to the length of a mature plant after which growth in length would slow down. Any one plant would thus spend least of its time at an intermediate length, having been held up in its growth when short and slowing down with age when long. This would result in the non linear relationship between stipe length and weight as seen in Figure 10,; where the density of Laminaria plants is considerably less as at Skinningrove Areas 1 and 2 no shading effects would occur and a linear relationship between stipe length and weight would be expected.

Mean stipe lengths of Laminaria digitata samples are shown in Figure 11. The decrease in mean length from Skinningrove Areas 3 to 1 could be due to the inhibitory action of certain heavy metals, for example, zinc, as was reported by Bryan (1969), the effect of the heavy metals decreasing as you go away from the sources of pollution. Another fact which has been reported by Bellamy, Bellamy,John and Wittick (1967), Bellamy (1968), and Bellamy, John and Wittick (1968) to decrease production is an increase in the amount of suspended matter. This causes a decrease in the amount of photosynthesis carried out by a plant. At Skinningrove Area 1 there is certainly a great amount of matter in suspension, and as you go away from the sewage outfall the amount decreases quite considerably. This factor therefore is most likely to be of significance at Skinningrove.

The decrease in the mean size from Areas 3 to 5 may be explained by the higher wave action that occurs at the more distant sites.

The results at Kettleness and Redcar are more difficult to explain. The mean length of the stipes at Redcar is the highest of all the sites, so presumably the heavy metals from sewage and the increase in suspended matter are having less effect than they do at Skinningrove. This might be expected when the distance of the sample sites from the outfall is considered. The Kettleness value is only slightly higher than Skinningrove Areas 4 and 5. Higher wave action, as was the case at Skinningrove Areas 4 and 5, may also be considered a factor limiting stipe size at Kettleness.

The populations of Laminaria digitata have been seen to be influenced by environmental factors like wave action, but these effects are markedly modified by pollution factors. For instance, heavy metals are thought to have a lethal effect close to the Skinningrove outfall. The growth rates are also thought to be limited further away by heavy metals. Decreased light due to suspended material is also a possible important factor limiting growth rates closer to the outfalls.

Close to the outfalls age structure indicates the occurrence of constant limiting factors. Further away they are distinctly intermittent in character. Longevity seems to be influenced by pollution and the absence of older members close to the outfall is thought to be a lethal effect due to the non-regulative, cumulative nature of uptake where finally a threshold of tolerance is reached.

Stipe length is clearly influenced by exposure, but this factor is greatly modified by pollution factors. High levels of wave action and high levels of pollution reduce stipe length. However, the sites with highest exposure were found to be the lowest in the degree of pollution and these two factors operate in opposite directions at each site . The results reflect this interaction and suggest that the effect of pollution on this study is more significant.

POPULATION STUDIES ON MYTILUS EDULIS.

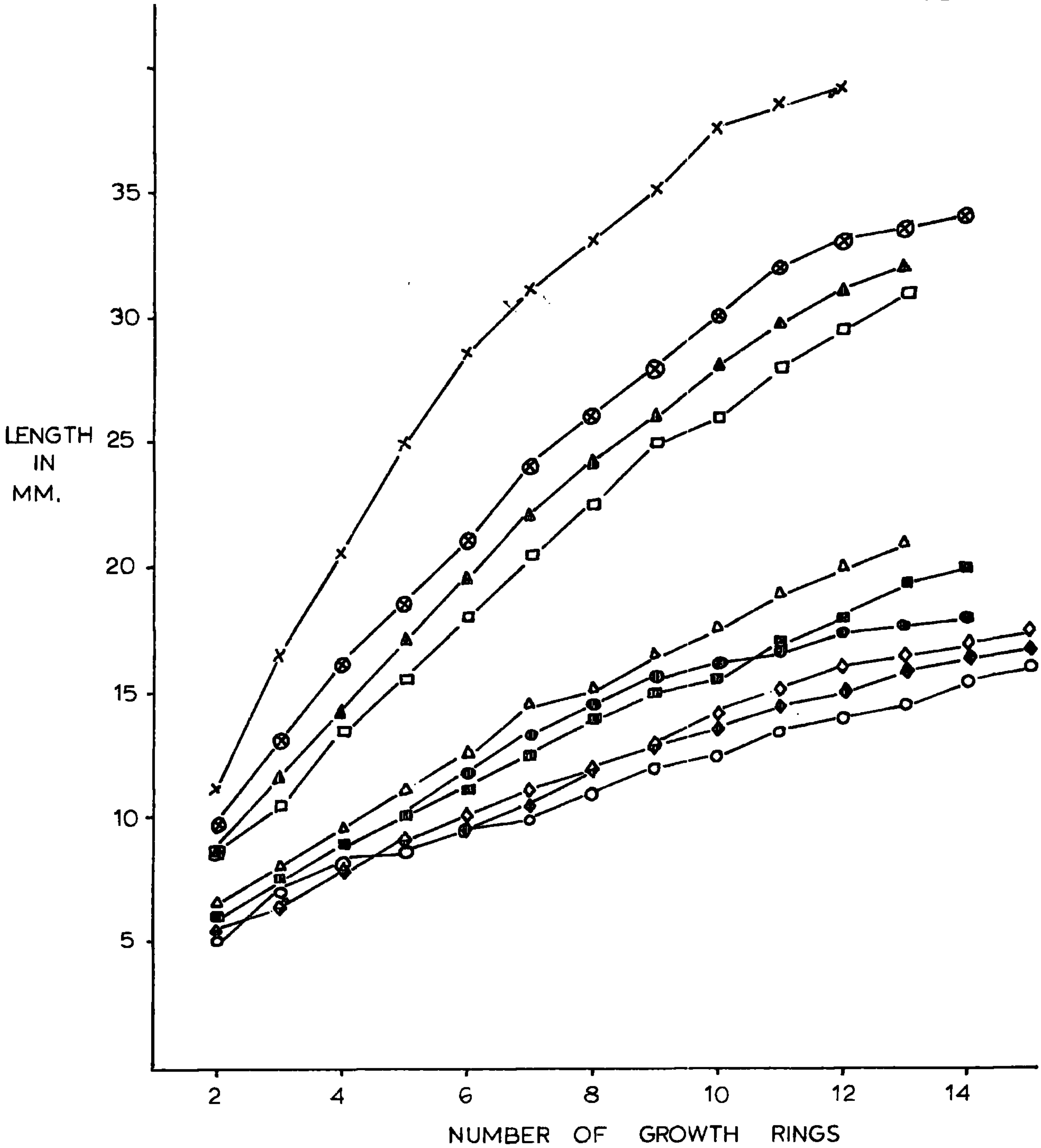
The collection method used for population studies of Mytilus edulis (L) consisted firstly of selecting two areas in each of the five sites, the first upper shore area corresponding to the mean tide level and the second lower shore area to low water spring tide level. In each of these areas random samples of Mytilus edulis were taken. In each case a 10 centimetre area was completely cleared of Mytilus. Samples of Mytilus edulis were also taken back to the laboratory where size and the number of growth rings of each individual were determined.

Several methods are known for the analysis of bivalve growth. In this study growth was assessed by counting the number of annually formed disturbance or growth rings present on the shell and by measuring shell length. Although there are conflicting opinions concerning the value of disturbance rings in aging mussels. Mossup (1922) and Mateeva (1948) have both shown that for Mytilus edulis these rings are formed annually.

In practice the use of growth rings in constructing growth curves is made more difficult by the fact that often many of the earlier rings have been obscured by erosion. When this is the case the number of growth rings has to be inferred by comparing shells of all ages from the same locality. Growth curves can thus be constructed by using a series of shells. Since only the largest occurring animals were used to construct growth curves, these curves can be regarded only as a potential and not a mean rate for each habitat. However, Seed (1968) reports that the great local variations which are found are in fact due to differences in the maximum growth rate for each locality, since individuals can be found in all habitats that show little or no signs of linear growth, especially those which are found amongst the byssus threads of larger animals where feeding rates are severely impaired.

The actual age of the mussels in years can be obtained from the ring number values by subtracting approximately six months since the first ring is often produced about six months after the animals have been settled on the shore.

FIGURE 12 . GROWTH CURVES FOR MYTILUS EDULIS AT VARIOUS SITES.



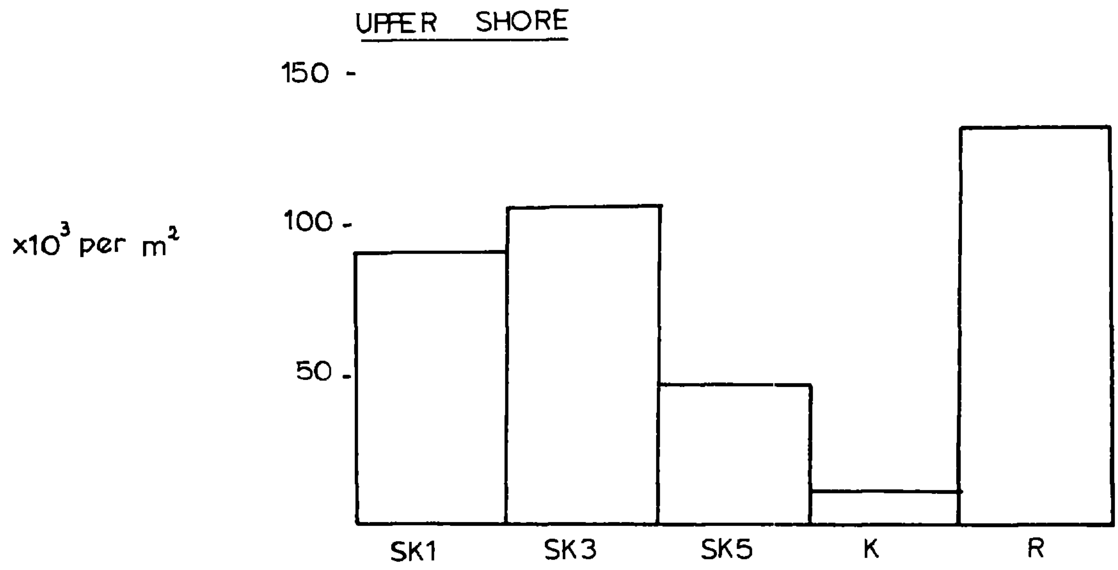
KEY.
- △ Sk.1. Upper shore
- ▲ Sk.1. Lower shore
- □ Sk.3. Upper shore
- ■ Sk.3. Lower shore
- ◇ Sk.5. Upper shore
- ◆ Sk.5. Lower shore
- ○ K. Upper shore.
- ⊗ R. Upper shore.
- ● K. Lower shore.
- × R. Lower shore.

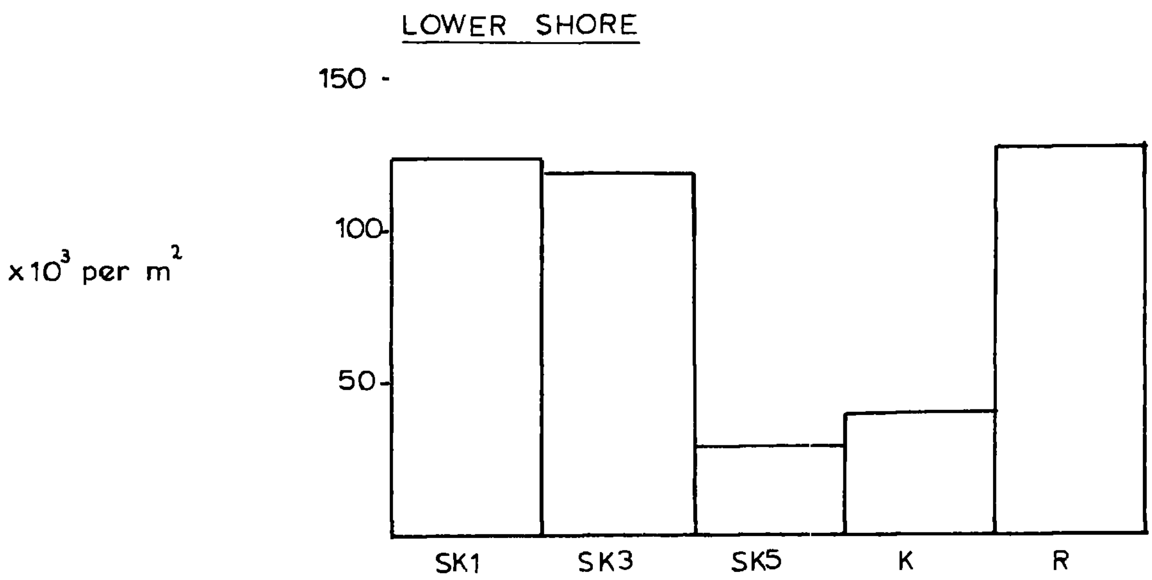
Growth curves for Mytilus edulis from the five sites are shown in Figure . All of the growth curves show that with increased age there is a slowing down in the rate of growth. However, there is considerable variation in the rates of growth of Mytilus edulis in the different areas. Fast growth rates are seen in Mytilus edulis from Redcar, both upper and lower shore, Skinningrove Area 1 lower shore, and Skinningrove Area 3 upper shore. Faster growth rates are generally associated with lower shore mussel populations, whilst slower growth rates are associated with higher shore mussels and exposed positions. At Redcar, Skinningrove Area 1, and Kettleness, it is the lower shore populations which have faster growth rates, whereas at Skinningrove Areas 3 and 5 it is the upper shore populations which have faster growth rates. MacGintie and MacGintie (1949) suggest that faster growth rates may be found in higher shore populations when, due to rougher conditions of the alongshore water, a mussel higher up may be able to feed for much longer periods with reference to the tide. This may explain the anomalies at Skinningrove Areas 3 and 5 as they have higher wave action than the other sites.

Seed (1968) reports that mussels high in the intertidal, although slow growing, can live to considerable ages in the absence of major predators. In the low shore on many exposed coasts on the other hand, an abundance of major predator species Nucella lapillus (L), Asterias rubens (L), Carcinus maenas (L), Cancer pagurus (L), may severely curtail life expectancy. At Redcar and Kettleness it is the upper shore populations which live longer, presumably due to the absence of major predators. It is the other way round with Mytilus edulis at Skinningrove Area 3, Individuals on the lower shore live longer than those higher up. At the two other sites, Skinningrove Areas 1 and 5, the longevity of individuals was the same for both upper and lower shores.

The difference in the results at Skinningrove Area 1 compared with Redcar and Kettleness can be explained in three ways. Firstly, it could be due to a decrease in the predation rate of the lower shore as a result of a toxic effect on the predators, a lower tolerance of the addition of freshwater, or lower wave action. Secondly, there may be an increase in mussel production on the lower shore as a result of a decrease

FIGURE 13. <u>MEAN DENSITIES OF MYTILUS EDULIS AT THE VARIOUS SITES</u>.





in competition for such factors as space. Thirdly, a lower value for the upper shore population may have been obtained due to the scouring effect of sand.

The results at Skinningrove Area 5 also infer that there was little difference in the predator populations between upper and lower shore.

There are two possible explanations for the results at Skinningrove Area 3. An increased longevity of the lower shore population may have arisen due to reduced predation due to the toxic effect of sewage on the predators. Secondly, lower shore mussel production relative to that of the upper shore may have increased due to a decrease in competition and enrichment factors.

Areas where the life expectancy of mussels is increased due to the absence of major predators reveal a high incidence of old individuals, whereas populations in which the mussel turnover is more rapid show a preponderance of relatively young mussels. This is shown for example, by the Redcar mussel samples where there are twice as many individuals above twelve years on the higher shore samples as there are on the lower shore, and one and a half times as many individuals under five years on the lower shore as on the upper shore.

Mean densities of Mytilus edulis at the various sites are shown in Figure 13 . The densities at Redcar and Skinningrove Areas 1 and 3 are relatively high compared with those found at Skinningrove Area 5 and Kettleness. Various researchers have carried out work into the factors influencing the density of Mytilus edulis. Seed (1968) has indicated that high densities of Mytilus frequently occur with moderate to severe wave action, lower levels of the shore and slow draining platforms, especially where surfaces are roughened or broken up. Chipperfield (1953), on the other hand, suggests that Mytilus densities are greater in areas with some degree of shelter from water currents and wave action, and much lower on clean smooth, non-toxic exposure panels. The differences in wave action between sample sites in this study are not great and all lie between moderate to severe. However the highest wave action does not have the highest density.

In same cases, for example Skinningrove Area 5, the opposite is true. The reason for this can be seen in an increase in Fucus serratus in Skinningrove Area 5 with a subsequent greater competition and thus a reduction in Mytilus edulis density. The low densities at Kettleness are related partly to the point made by Chipperfield. Areas in the Kettleness site are horizontal smooth bare rock surfaces with little localised shelter. Others have Fucus serratus cover. The shelter factor is only a relative one. In this study it is possible to suggest that the density of Mytilus can be controlled by factors other than the environmental ones. Factors influencing the growth performance of Mytilus and rival species like Fucus serratus are thought to be significant. The highest densities of Mytilus edulis are at Skinningrove Areas 1 and 3, and Redcar, areas of the highest pollution. The seawater chemical conditions seem to favour the more tolerant mussel even when wave action is only moderate. This point will be considered in more detail at a later stage in connection with the bio-chemical variation between sample sites.

In this study Mytilus edulis was found to occur from below low water spring tide level right up to the mean tide level. According to Seed (1969) the upward extension of mussel is limited by physical factors such as temperature and desiccation. Chipperfield (1953), found that settlement above low water spring tide level though was small, no surviving settlement at all persisting at mean tide level. He suggested that this could arise due to the fact that the time required for complete attachment by the byssus is of the order of four and a half to six hours, and this only occurs when the mussel is immersed, and so spat settling in positions higher in the intertidal zone would not persist unless they happen to be in a position where they are constantly wetted. The mussels in the study areas extended beyond the limit suggested by Chipperfield, and it is likely, as he suggests, that the reason for this is the increased length of submergence allowing time for complete byssus attachment. This increased submergence in all the sample sites is the result of ponding effects across the irregular flat scars and the moderate to severe wave action.

Variations in mussel populations between sample sites suggest a number of points :-

1. Growth rates are highest in areas of great input of sewage. "Eutrophication effect".
2. Variations between upper and lower shore populations which do not follow the expected pattern, generally reflect the importance of high wave action rather than any other factor.
3. Longevity of mussels is largely determined by the occurrence and size of predator populations. A number of factors are thought to be important in influencing predator population including, pollution induced mortality rates, and pollution effects on the seaweed cover.
4. Difficulties in distinguishing selective predation effects on population structures and age related toxic effects.

FIGURE 14 . HISTOGRAMS OF MEAN DENSITIES OF PATELLA VULGATA AT EACH TIDAL LEVEL.

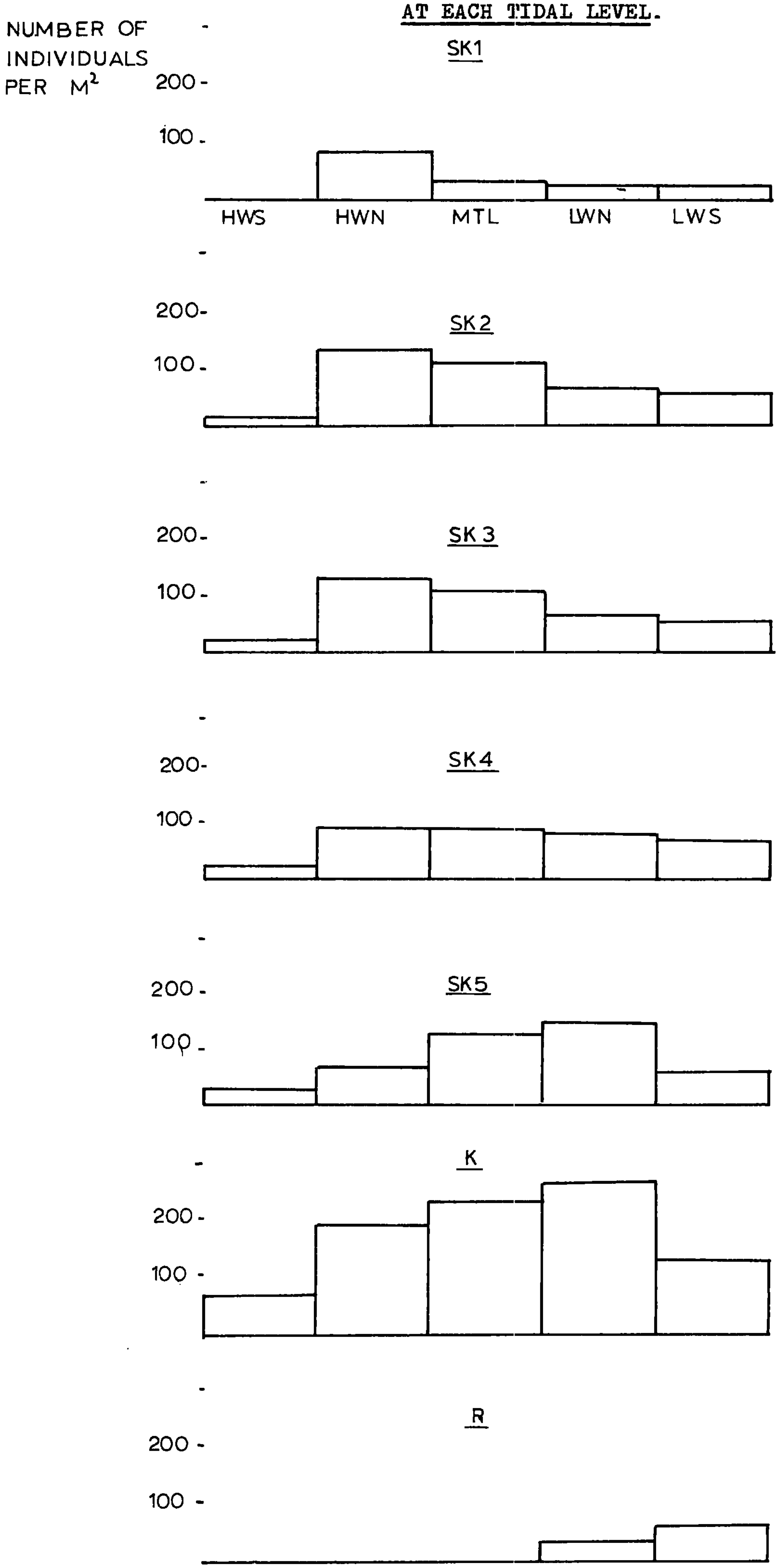
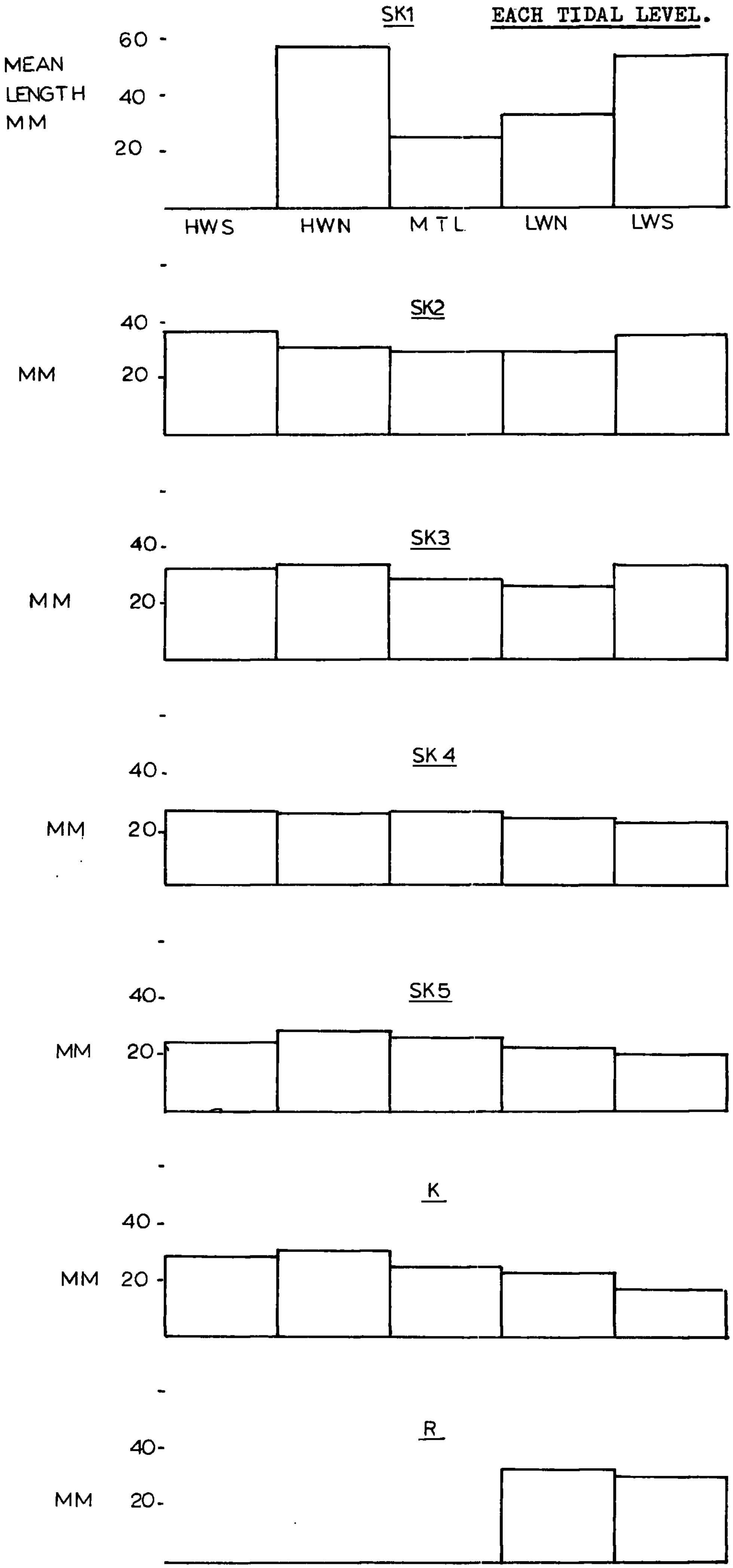


FIGURE 15 . HISTOGRAMS OF MEAN LENGTH OF PATELLA VULGATA AT EACH TIDAL LEVEL.



POPULATION STUDIES ON PATELLA VULGATA.

The patchy distribution of Patella vulgata on the rocks renders accurate population studies of this species difficult. Areas were chosen where the rock surface was as flat and even as possible, so reducing the number of cracks where smaller individuals can be lodged. The five zones, which correspond to high water spring tide level (HWS), high water neap tide level (HWN), mean tide level (MTL), low water neap tide level (LWN), and low water spring tide level (LWS), were marked off along transects at right angles to the shore line and in each zone five one metre square quadrats were taken. The number of Patella vulgata individuals in each quadrat were counted, but for one quadrat in each zone all the individuals were removed and taken back to the laboratory for size determination. Newly settled spat, i.e. Patella under six millimetres long, have not been taken into consideration.

Histograms of mean densities and mean lengths of Patella vulgata at each tidal level for the sample sites are shown on Figures 14 and 15.

In general the population densities increase from high water spring tide level to low water spring tide level, the maximum population density though occurring at low water neap tide level for the Patella vulgata populations at Skinningrove Areas 3 and 5, and Kettleness. These results are in agreement with the findings of Das and Seshappa (1947). At Redcar however, Patella vulgata was only found to occur at Low water neap tide level and low water spring tide level, and at this site the population density was greater at low water spring tide level. The absence of Patella vulgata at higher levels at Redcar may possibly be explained by the lack of food. The higher levels of the Redcar shore had a complete cover of mussels plus sand and silt deposits, and this would be limiting to the food sources of limpets, which are algal and diatom films and sometimes larger fucoids.

The distribution of Patella vulgata at Skinningrove Areas 1, 2 and 3 could also be explained similarly. At these three sites the highest densities are found at high water neap tide level, the densities then decreasing gradually towards low water spring tide level. The lower levels of these sites each have a very high cover of mussels, being about 100% at Skinningrove Area 1. This would mean a restricted number of sites where encrusting algae and diatoms could occur. Fucoid plants are also either entirely absent as in Skinningrove Area 1 or low in number as at Skinningrove Area 3. Higher up the shore, especially at Skinningrove Areas 2 and 3, there are more areas available for encrusting algae and diatoms to grow, and also a greater number of fucoid plants occur in the higher zones of Areas 2 and 3.

The lower overall densities at Redcar and Skinningrove Area 1 compared with the other sample sites could also be explained by the availability of food for Patella vulgata.

Moore (1958) describes how limpets occur on rocky shores from about extreme low water to high water of neap tides. Orton (1929) also considers this their upper limit where they are exposed to insolation, but explains that under the influence of either shade or splash, two factors which reduce desiccation, they may extend to higher levels. The limpets in the study areas extended beyond the limit suggested by Moore, and it is likely, as Orton suggests, that the reason for this is the reduction in the degree of desiccation. The study areas were on North facing shores so shade from cliffs would be available. The higher areas are boulder strewn, which also adds to the amount of shade. The moderate to severe wave action encountered by these sites would also mean considerable splash. Thus these sites offer both shade and splash.

With reference to size distribution across the shore of limpets, two major effects can be seen; a zonal effect as noted by Das and Seshappa (1947), and a pollutional effect as noted by Moore (1958). The zonal effect is one of decreasing mean size as you go from high water tide levels to low water tide levels and the results of this study at Kettleness and Skinningrove Areas 4 and 5 are in agreement with this effect. (See Figure 15). This general zonal effect is modified at Skinningrove Areas 1, 2 and 3 which lie closest to increased organic and pollutant loads from the sewage outfall. This results in an increased average size of the limpets compared with the other sites, besides a marked increase in the size of the limpets found at low water spring tide level. This confirms the point made by Moore (1958).

In conclusion a number of points can be made. Firstly, the upper limit of Patella vulgata is extended at certain sites due to a combination of shading factors and also splash factors.
Secondly, the zonal effect on Patella vulgata density is modified especially in the lower zones. Densities are limited by competition for space and availability of food.
Thirdly, overall densities for each sample site indicate a lower density in the population close to the pollutional sources. The reason for this is thought to reflect not a direct lethal effect but indirect via increased competition for space and a reduction of available food. The large amounts of suspended material, heavy metals silt deposits close to the outfalls are thought to limit the occurrence of the encrusting algae. For instance, the latter was only seen to occur by Skinningrove Area 3 and beyond.
The fourth point is that the size distribution of Patella vulgata was influenced by the zonal effect and this was then modified by a pollutional effect.

Pollution can be seen to affect not only density but also size distribution. However, it was not possible to isolate pollution as a factor limiting overall distribution.

POPULATION STUDIES ON NUCELLA LAPILLUS.

At each of the sample sites even areas of rock surface where Nucella lapillus (L) was found to be fairly uniformly distributed, were chosen. Five zones which correspond to High water spring tide level, high water neap tide level, mean tide level, low water neap tide level and low water spring tide level were selected. To estimate densities of Nucella lapillus in each zone, five, one metre square areas of rock were cleared of all Nucella lapillus individuals, care being taken that the areas of collection did not have abnormally dense patches of dog-whelk were determined. Those individuals less than five millimetres in length were not included.

The results are shown in Figures 16 and 17 below -

FIGURE 16

MEAN LENGTH OF NUCELLA LAPILLUS AT EACH TIDAL LEVEL IN MM.

	A.	B.	C.	D.	E.	F.	G.
HWS.	-	-	-	-	-	-	-
HWN.	-	29.71	-	28.73	28.80	28.64	25.36
MTL.	24.19	29.36	34.79	30.23	25.11	24.13	22.24
LWN.	23.82	21.50	29.37	24.10	26.04	16.92	17.76
LWS.	19.45	12.56	25.36	19.25	18.13	14.47	13.33

FIG.17.

MEAN DENSITY OF NUCELLA LAPILLUS AT EACH TIDAL LEVEL.NUMBER PER M

	A.	B.	C.	D.	E.	F.	G.
HWS.	-	-	-	-	-	-	-
HWN.	-	25	-	17	21	22	14
MTL.	5	99	11	52	73	64	52
LWN.	28	73	23	51	69	55	48
LWS.	24	49	15	22	38	30	27

KEY.

A. refers to the Redcar sample site.

B. refers to the Kettleness sample site.

C. refers to the Skinningrove Area 1 sample site.

D. refers to the Skinningrove Area 2 sample site.

E. refers to the Skinningrove Area 3 sample site.

F. refers to the Skinningrove Area 4 sample site.

G. refers to the Skinningrove Area 5 sample site.

With regard to the average length of Nucella lapillus two main gradients appear. Firstly, there is generally a decrease in the mean length from high water neap tide level to low water spring tide level. This decrease in mean size is due to the greater number of small individuals in the samples at low water spring tide level. Moore (1938) reports that there tends to be a separation between adults and young into two different zones. Although the eggs are laid in the tidal levels inhabited by the adults, the young, once hatched, are thought to be washed down the shore by wave action. Here they live among the tubiculous polychaete Spirorbis.borealis. When the dog-whelks begin to change their diet it is thought that they begin to move up the shore on to the barnacle covered areas.
Secondly, there is a general gradient of decreasing length at Skinningrove, the larger individuals being found at Skinningrove Area 1, the smaller at Skinningrove Area 5. This could be explained by the degree of wave action in harsher conditions as found at Skinningrove Area 5. Nucella lapillus may be driven to the shelter of crannies during periods of high wave action and this limits their feeding since they normally prey on the barnacles and mussels growing on open rock surfaces. Such Curtailment of feeding time has been found by Moore (1958) to be a serious limiting factor.

Besides these major gradients other variations can be seen. For instance, the mean length of Nucella lapillus at Skinningrove Area 1, is appreciably higher than the measurements at the other sample sites. Moore (1958) and Fischer-Piette (1931) report that both eggs and young dog-whelks have a lower tolerance to low salinities than adults. At Skinningrove Area 1 it is possible that the addition of sewage and stream water causes a sufficient decrease in salinity in the near vicinity of the outfall to kill the eggs and young.Adults present at Skinningrove Area 1 would presumably have moved to this area from other sites where young can survive. This would account for the lack of small immature individuals at Skinningrove Area 1, and also the lower densities compared with other sites. The addition of heavy metals and other pollutants from the sewage and stream may act in a similar way to salinity, in decreasing the viability of the young.

The upper limit at which Nucella lapillus occurred varied for the different sites. This upper limit in all cases corresponded to the highest level at which the food source, either barnacles or mussels, was found. This upper limit for Nucella lapillus is the same as that given by Fischer-Piette (1936).

The densities of Nucella lapillus at each site show that there is an increase in the mean density at Skinningrove Areas 2, 3, 4, and 5, and Kettleness from low water spring tide level to mean tide level. Above this height the density decreases until by high water spring tide level no Nucella lapillus could be found. At Skinningrove Area 1 and Redcar, the maximum densities were found at low water neap tide level, no individuals being found by high water neap tide level. As previously suggested this may be related to the absence of suitable food.

For studies on Nucella lapillus on the North East coast distinctive differences occur in the population papameters. These differences can partly be attributed to variations in wave action, salinity and pollutants. The latter two factors seem to be important in restricting intertidal distribution and density and in reducing viability. It is impossible to say whether this latter character is the result of reduced fertility of adults or reduced juvenile survival rates through toxic or reduced food supply effects.

SEWAGE AND BACTERIA.

Domestic sewage is a potential hazard to human health as it always contains a certain amount of foecal material which includes pathogenic bacteria, viruses and resistant stages of parasites. The amount of pollution is normally measured by counting the number of Escherictia coli present in the water. Coliforms in themselves are not a danger but serve to indicate the likelihood of disease causing bacteria and viruses present. Numbers of coliforms in the receiving water can rise to very high levels, but ZoBell (1936) reports that in fact, they do not survive very long when emptied directly into the sea unless there is appreciable organic matter present, or considerable freshwater dilution. Colon bacilli are rarely recovered from the open sea and they occur far less frequently in the vicinity of sewage effluents than can be accounted for by dilution alone. Waksman and Hotchkiss (1937) have suggested several reasons for the failure of freshwater bacteria to survive in the sea. These include :-

1. The presence in sea water of toxic substances which are destructive to bacteria under natural conditions.
2. The presence of bacteriophage in the water.
3. The adsorption of the bacteria by the sea bottom and their sedimentation.
4. The bactericidal effects of sunlight.
5. The consumption of the bacteria by protozoa and other small annual organisms.
6. The possible presence in the sea of inactive bacteria which are capable of developing only under more favourable conditions of temperature, aeration and food supply.
7. The lack of sufficient nutriment in the water.
8. The antagonistic relations of other micro-organisms.

Survival, and more especially reproduction of bacteria under most circumstances is associated with available nutrient materials. Russell (1891) found that multiplication of bacteria was quite marked in marine muds which are relatively rich in organic matter. He did not however, comment on the survival of bacteria in waters containing different concentrations of organic matter.

Burke and Baird (1931) believed that the presence of organic matter in sea water would increase the survival times of non-marine bacteria.

Waksman and Carey (1935) in their investigation of the decomposition of organic matter in the sea concluded that sea water contains enough organic substances in true solution to support an extensive population of bacteria. They did not indicate though whether they believed that enteric bacteria or fresh water bacteria could thrive in such an environment.

However, Greenberg (1956) stated that it should not be concluded that under all circumstances the chance of survival or of reproduction of the enteric bacteria is improved by the presence of organic matter. In the event that there is sufficient organic matter present to support growth a competition between enteric organisms and saprophytes indigenous to either the fresh water or marine habitat would follow. Generally the enteric organisms would be unequal to the competition. If the total number of bacteria in the sea is considered as a direct function of the concentration of organic matter, it follows that there will be more competitors of the enteric bacteria as more organic substances occur and that these other organisms either directly, or indirectly, will reduce the growth and survival of the foecal bacteria. This has been shown by de Glaxa (1889) and Korinek (1927).

An extensive literature exists on the subject of contamination of bathers by sewage derived pathogens. However as far as Redcar is concerned the sewage pollution is not thought to constitute a health hazard except on the few occasions when the beach and water were contaminated with solids, Donaldson (1972).

Contamination through eating shellfish presents a much greater hazard however. Many commonly eaten shellfish such as mussels, oysters and cockles are filter feeders and they ingest and accumulate material including pathogens from sewage. Mussels in particular, are very likely to accumulate sewage derived bacteria as they are relatively insensitive to low salinity and mild pollution. This problem of the pollution of filter feeding does not arise in the case of Redcar and Skinningrove sewage disposal as there are no commercial fisheries of shellfish in the area likely to be affected, nor are there likely to be in the future.

Estimations of the number of coliform bacilli in the sea water at the sample sites were made according to the method given by Cruickshank (1908). Varying quantities of the water, from 0.1 ml. to 10 ml. were added to MacConkey's broth (with an indicator of acidity), contained in test tubes with Durham tubes to show the formation of gas; acid and gas formation indicates the growth of coliform bacilli. This method requires examination by culture of several samples of several quantities of the water so that an average result can be stated. Five 10 ml., five 1 ml., and five 0.1 ml. volumes of water were tested and the probable number of coliform bacilli in 100 ml. were computed according to the various combinations of positive and negative results, using the tables compiled by McCrody for this purpose.

The sea water samples were taken at low tide on 26th July,1973. The wind direction at the time of collection was from the North East, approximately Force 3 to 4, and causing a moderate swell.

Waksman and Hotchkiss (1937) reported that a considerable increase may take place in the number of bacteria within two to four hours - the time taken for the samples to be taken to the laboratory. For this reason the samples were kept in ice during transport.

Each test was carried out in duplicate.

The number of bacilli per 100 ml. are shown below :-

Site.	Number of Bacilli/100 ml.
Redcar A.	900
Redcar B.	550
Kettleness A.	80
Kettleness B.	50
Skinningrove Area 1. A.	1800 +
Skinningrove Area 1. B.	1800 +
Skinningrove Area 3. A.	170
Skinningrove Area 3. B.	130
Skinningrove Area 5. A.	35
Skinningrove Area 5. B.	25

The sites differed in the amount of coliform bacteria present. The highest figures were found at Skinningrove Area 1 and Redcar, and the lowest figures at Skinningrove Area 5 and Kettleness. The figure 1 of the sewage outfalls along this coast illustrate the large inputs at point sources. The Redcar site, although close to the prime source of sewage with its number of outfalls on or close to Coatham rocks, is much further from the ends of these outfalls, and subsequently because of dilution and probably death, its coliform bacteria figures are less than Skinningrove Area 1. At Skinningrove there is a clear gradient in the number of coliform bacteria away from the source of sewage. The reduction in numbers is due to a number of factors previously considered.

In terms of coliform bacilli, Skinningrove Area 5 has less than half the number compared to Kettleness, both of which could be considered unpolluted, and it is possible that the high levels of heavy metals result in a rapid kill away from the end of the sewage pipe at Skinningrove. Jones (1967).

Little is known of the effects of bacteria on the growth and development of the marine organisms considered in this study.

MATERIALS AND METHOD.

At each site samples of the following species were collected for chemical analysis. Where possible, collections were made from both upper and lower shore area for the animal species. *Laminaria digitata* was only collected from lower shore areas and *Ulva lactuca* from upper regions of the shore:-

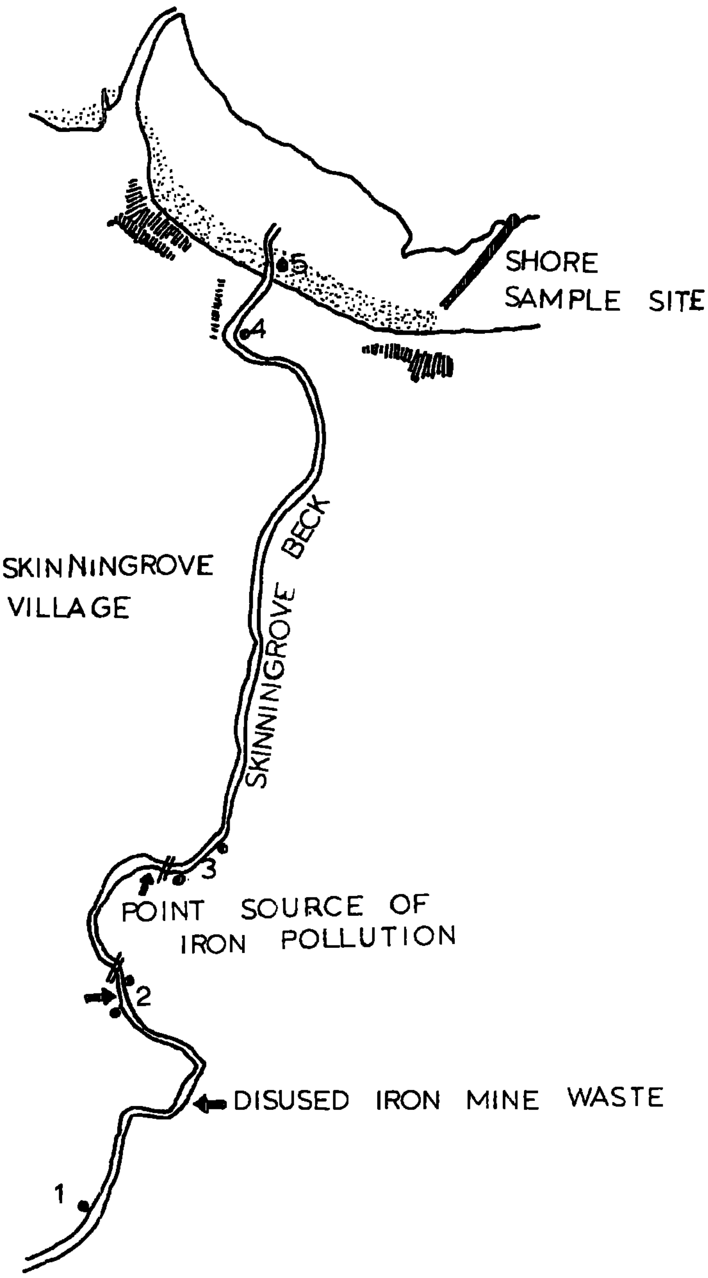
Laminaria digitata L.
Ulva lactuca.
Nucella lapilus.
Patella vulgata.
Mytilus edulis.

The species chosen included at least one species from the three trophic levels, primary producers, herbivores, and carnivores.

The fact that collection and preparation were time consuming processes, necessitated the sampling period to be spread over several weeks. However, in view of the work of Young and Langille (1958), and Black and Mitchell (1952), it seems unlikely that errors due to seasonal variations during this period would have occurred. Young and Langille (1958), found that in the trace elements in algae from the Atlantic coast of Canada there was no characteristic seasonal variation. However, around the coast of Great Britain, Black and Mitchell (1952) found a seasonal variation in the concentration of trace elements. As all the collections in this investigation were taken during a relatively short period, seasonal variation is thought to be small, and all the results will be characteristic of the more active summer metabolic rate.

The samples were washed in distilled water after collection, and the soft parts of the animals removed and dried to constant weight. The washings should not have affected the heavy metal ion concentrations in the tissue. It was found by Young and Langille (1958), that washing of marine algae only lowered the content of total ash, silicon, sodium and potassium, but there was no appreciable effect on other elements. Washing, therefore, will remove the traces of sand

Figure 18. Map of Skinningrove Beck sample sites



and silt, and can leach out soluble salts of alkali metals. It was suggested by both Young and Langille (1958), and Black and Mitchell (1952), that 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.

Sea water samples were collected at low tide for all the sample sites, in triplicate. Water samples were also collected from the various sites along Skinningrove Beck, as shown in Figure 18 . Off-shore water was also sampled at Skinningrove opposite the entrance to the Beck, and sample sites Areas 1, 3, and 5. All these samples were collected in polythene bottles and stored until analysis at 0 C. Black and Mitchell (1952) found that analyses were identical for seawater samples stored in 'Pyrex' and polythene bottles, so polythene bottles were used in this study for convenience. Before storage, a small aliquat of water was filtered through a millipore filter using a disc with a 0.45 u pore size. This water was stored separately and used for soluble iron determinations. Samples of silt were also collected from both upper and lower shore areas at each of the shore sample sites, and from the sample sites in Skinningrove Beck. The silt was dried to constant weight.

Samples were then prepared by a wet digestion technique for analysis by atomic absorption. Analytical grade chemicals were used throughout all the techniques described below. Care was taken throughout the preparation, extraction, and analysis, to avoid any metallic contamination.

100 ml. aliquats of the water samples were used for each digestion, and 10 ml. of concentrated nitric acid and 5 ml. of perchloric acid were added, and then heated on a sand bath until nearly dry. The remaining perchlorate was then dissolved in a little distilled water and filtered through Whatman No.42 filter paper which had previously been soaked in 10% perchloric acid to remove trace elements from the paper.

For the tissue samples, exactly 2 gm. of tissue were

FIGURE 19

INTERFERENCE LEVELS.

Sodium Concentration. ug / l.	Copper ug/l.	Zinc ug/l.	Iron ug/l.	Lead. ug/l.
10,000	0.052	0.048	0.175	0.20
5,000	0.030	-	-	0.07
3,000	-	0.015	0.06	-
2,000	0.010	-	-	-
1,000	0.006	-	-	0.02

Calcium Concentration. ug/l.	Copper ug/l.	Zinc ug/l.	Iron ug/l.	Lead. ug/l.
500	-	-	-	0.06
350	0.025	0.012	0.07	-
150	0.008	-	-	-
100	0.008	0.005	0.030	-
50	0.002	0.003	0.02	-

weighed out, 20 ml. of concentrated nitric acid were added, and then these were left for twenty-four hours before adding perchloric acid and hydrochloric acid, and heating on the sand bath. Distilled water was then added to the samples, and then they were filtered through Whatman No.42 filter paper. The same procedure was carried out for the silt samples.

Analysis of the samples was then carried out on a Perkin-Elmer No.403 Atomic Absorption Spectrophotometer. The instrument was set up as described in the instruction manual. The limit detection for lead was 0.02 ug/l aspirating, 0.002 ug/l for zinc aspirating, 0.002 ug/l for copper aspirating, and 0.01 ug/l for iron aspirating.

Sodium and calcium concentrations were also determined using the Atomic Absorption Spectrophotometer. These results were used to assess the degree of interference of the sodium and calcium ions from the results of simulated digests. The levels of interference found are given in Figure 19 . All the sample results were then corrected according to the degree of interference found.

FIGURE 20 . ZINC LEVELS IN SEAWATER.

Author	Year	Concentration ug/l
Atkins	1936	8
Noddack	1940	14
Wattenburg	1943	5 - 30
Buch	1944	4.5 - 23
Morita	1950	2.8 - 11.7
Black & Mitchell	1952	9 - 21
GoIdberg	1957	10
Chapman Rice et al	1958	1.2 - 19.6
Parker	1962	8
Gutnecht	1963	2 - 18
Riley & Taylor	1968	4

FIGURE 21 . ZINC CONCENTRATIONS IN WATER FROM SKINNINGROVE BECK.

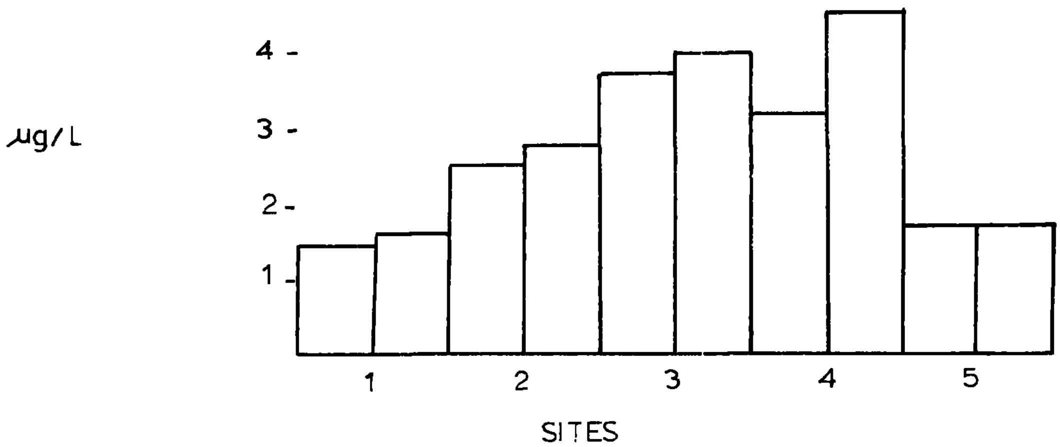


FIGURE 22 . ZINC CONCENTRATIONS IN SEAWATER AT THE SAMPLE SITES.

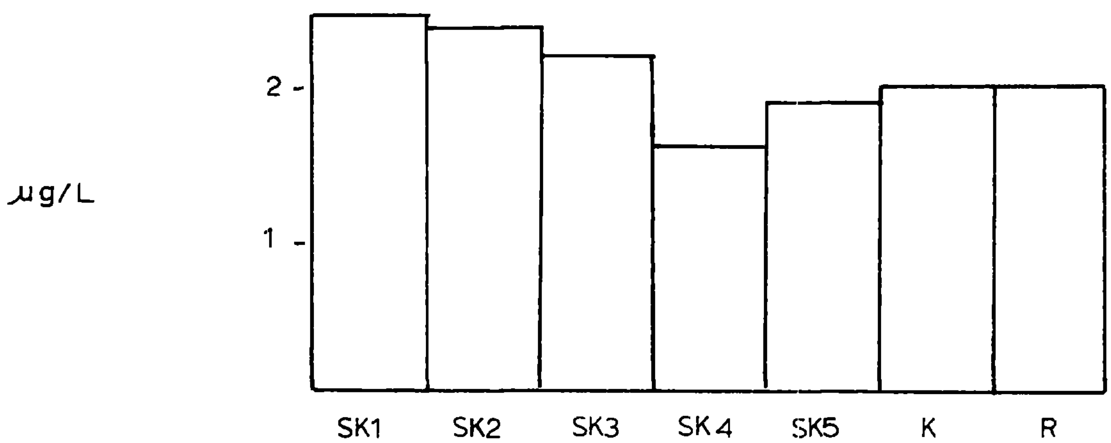


Figure 23. Map of the distribution of Zinc at Skinningrove.

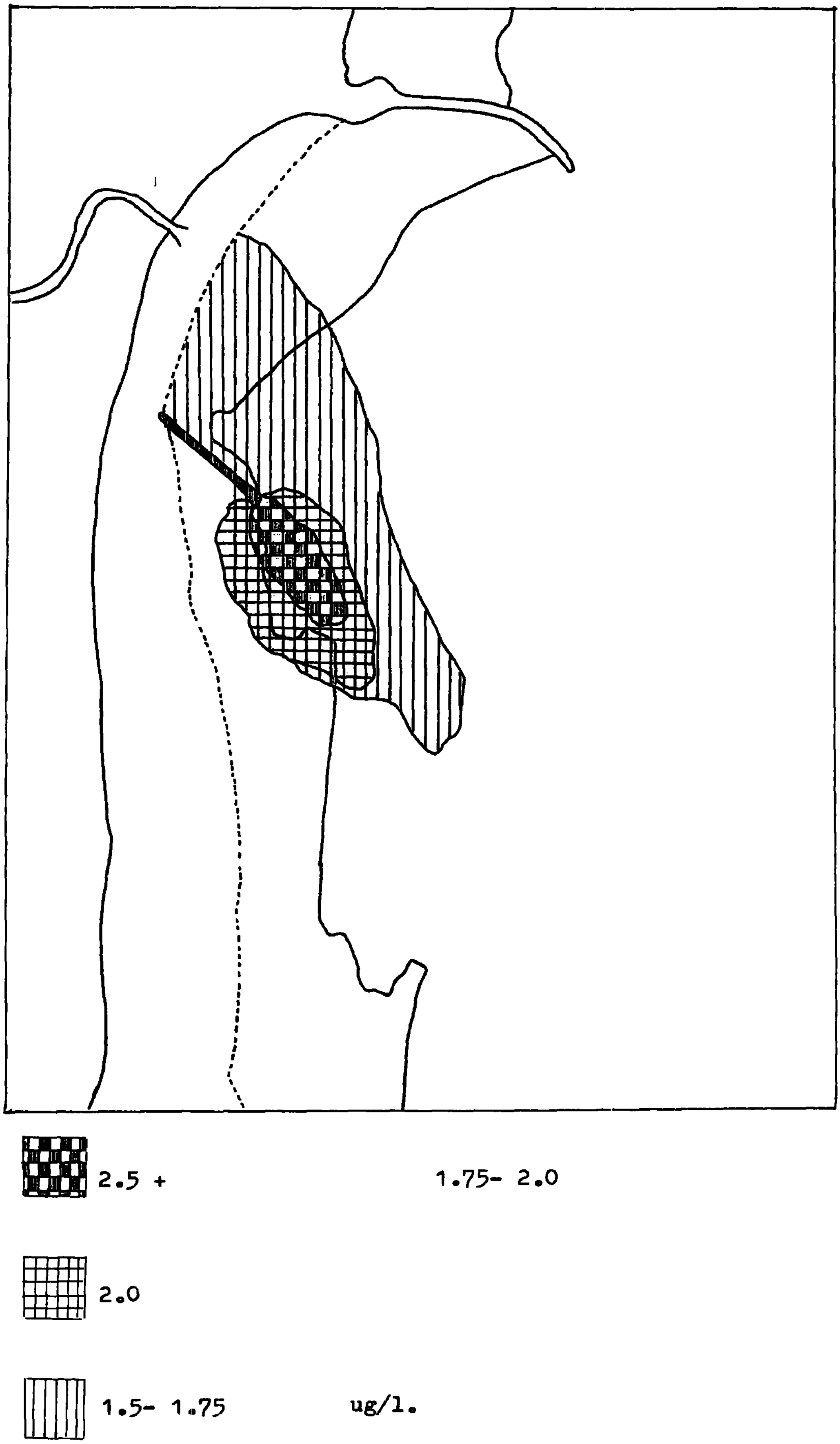
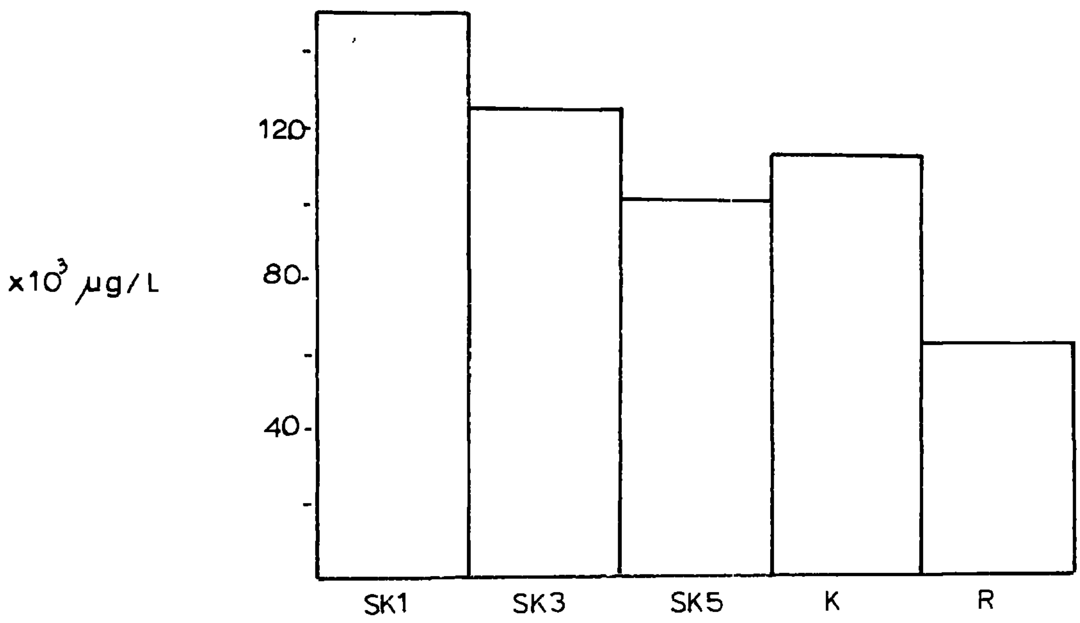
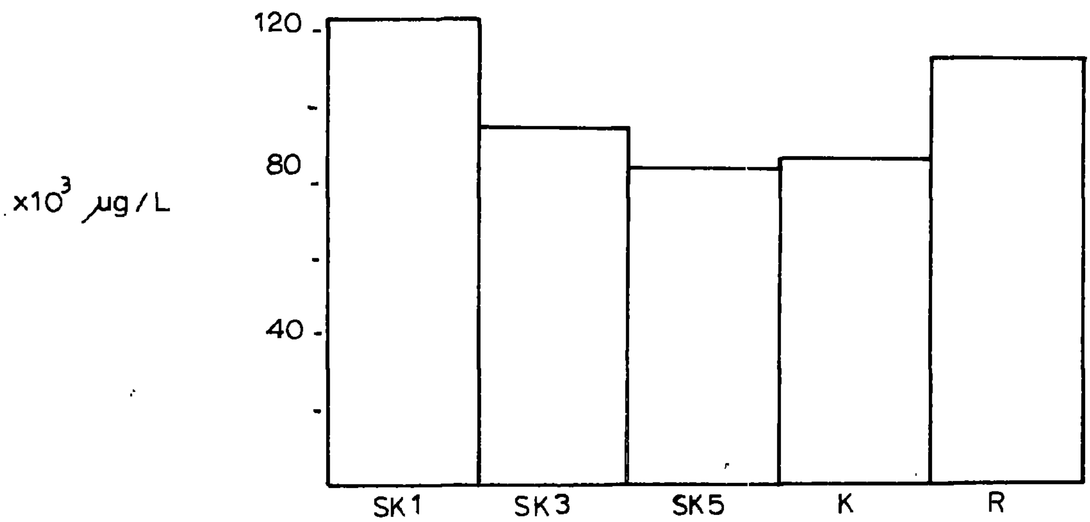


FIGURE 24 . ZINC CONCENTRATIONS IN SILT AT THE SAMPLE SITES.

UPPER SHORE



LOWER SHORE



ZINC.

Zinc concentrations in seawater have been analysed by a number of writers (illustrated in Figure 20). Krauskopf (1956) has shown that common to other heavy metals, zinc levels are well below saturation levels in seawater. The results of other writers generally lie in the 1 ug/l to 30 ug/l range for seawater zinc. The higher values are associated with inshore waters where terrestrial sources are an additional source of zinc at high concentrations. The results of this study varied between 1 ug/l and 4 ug/l, and lie at the lower end of the range of values recorded in Figure 20 . As with other heavy metals it is probable that at certain sites higher values would have been recorded if the sampling period had been much longer.

The levels of zinc in the Beck water are shown in Figure 21 and, although higher than seawater values of zinc concentration are evident, it is unlikely that the Beck acts as an important source of zinc. Much of the river zinc is precipitated within the stream itself, and particulate iron has an important role in this. The stream water with its high iron levels causes a reduction in the zinc seawater levels due to dilutional effects and increased precipitation (Figure 23). This map illustrates the importance of the sewage outfall as a source of zinc and shows the areal dispersion of this additional zinc in seawater. There is a gradient in the zinc concentration and the decrease to the East is due to mainly dilutional effects. The more rapid decrease to the North and West is due to the effects of adsorption onto the surfaces of hydrated ferric oxide and its subsequent precipitation.

These variations in zinc seawater levels at the sample sites are shown in Figure 22 . The results for Kettleness and Redcar are not very different and compare with the Skinningrove sites further away from the outfall.

The silt values at the sample sites show a similar pattern (Figure 24) as those considered above. The only difference is the Redcar silt values are more similar to the figures of Skinningrove Area 1. This suggests that the seawater

FIGURE 25 . ZINC LEVELS IN SEAWEED.

Author	Year	Concentration ug/l
Beharrell	1942	40
Black & Mitchell	1952	62 - 92
Young & Langille	1958	35 - 97
Parker	1962	60 - 100
Bryan	1969	5.4 - 7.9

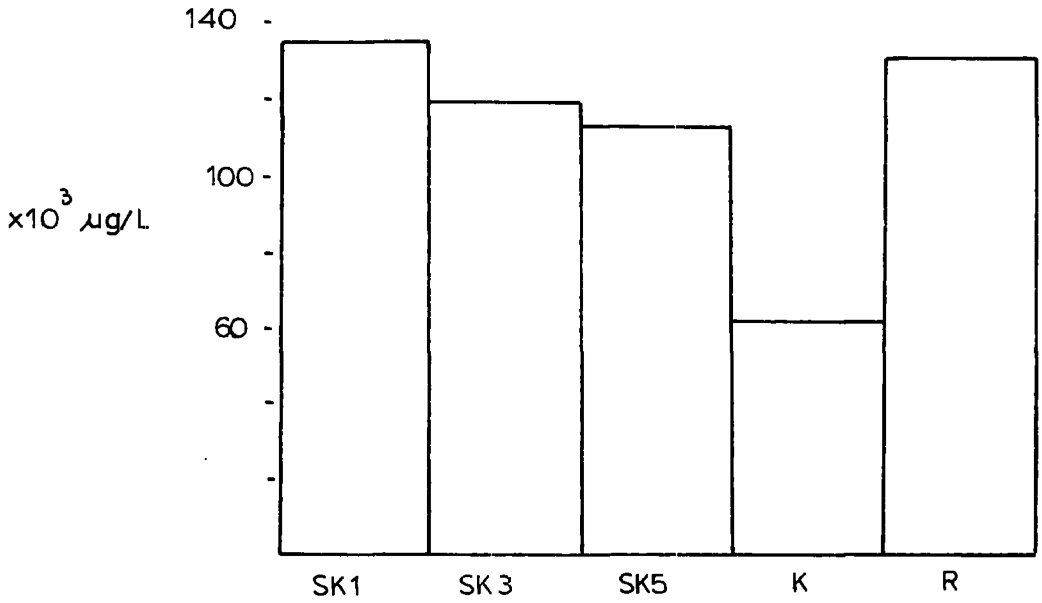
FIGURE 26 . ZINC LEVELS IN MARINE ORGANISMS.

Author	Year	Concentration ug/l x 10
1. Webb	1957	2.5
2. Parker	1962	9 - 130
3. Brooks & Rumsby	1965	50 - 180
4. Bryan	1968	28

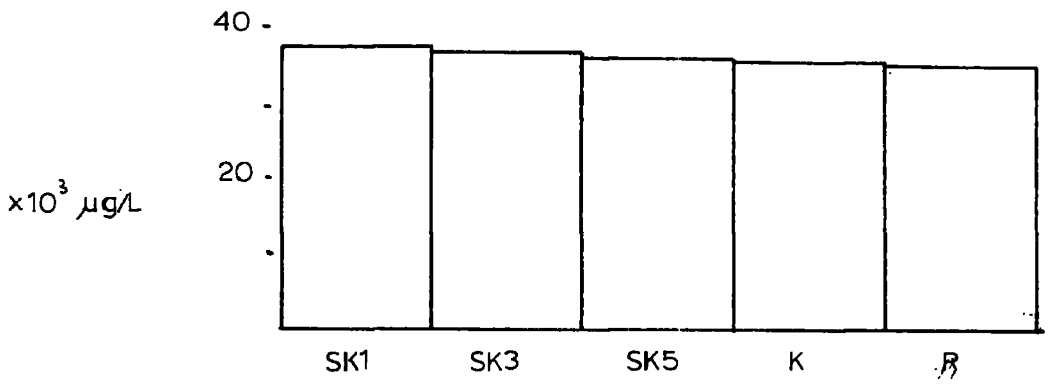
1. Dog-whelk
2. Marine animals
3. Mussels
4. Hermit crab

FIGURE 27 . ZINC CONCENTRATIONS IN SELECTED SEAWEEDS AT THE SAMPLE SITES.

LAMINARIA DIGITATA



ULVA LACUTA



value at Redcar is generally much higher. This would be reasonable considering the sewage outfalls at Coatham.

No attempt to separate particulate and soluble zinc was attempted. Bryan (1969) gives figures that indicate that total zinc in seawater had an average of 82% zinc in solution. However, the dispersion of either form of zinc is unlikely to be very different due to the controlling influence of the high concentrations of iron in the seawater. This iron limits dispersion and subsequently concentrates the precipitation closer to the outfall. As a result the effects of zinc pollution are likely to be more localised at Skinningrove.

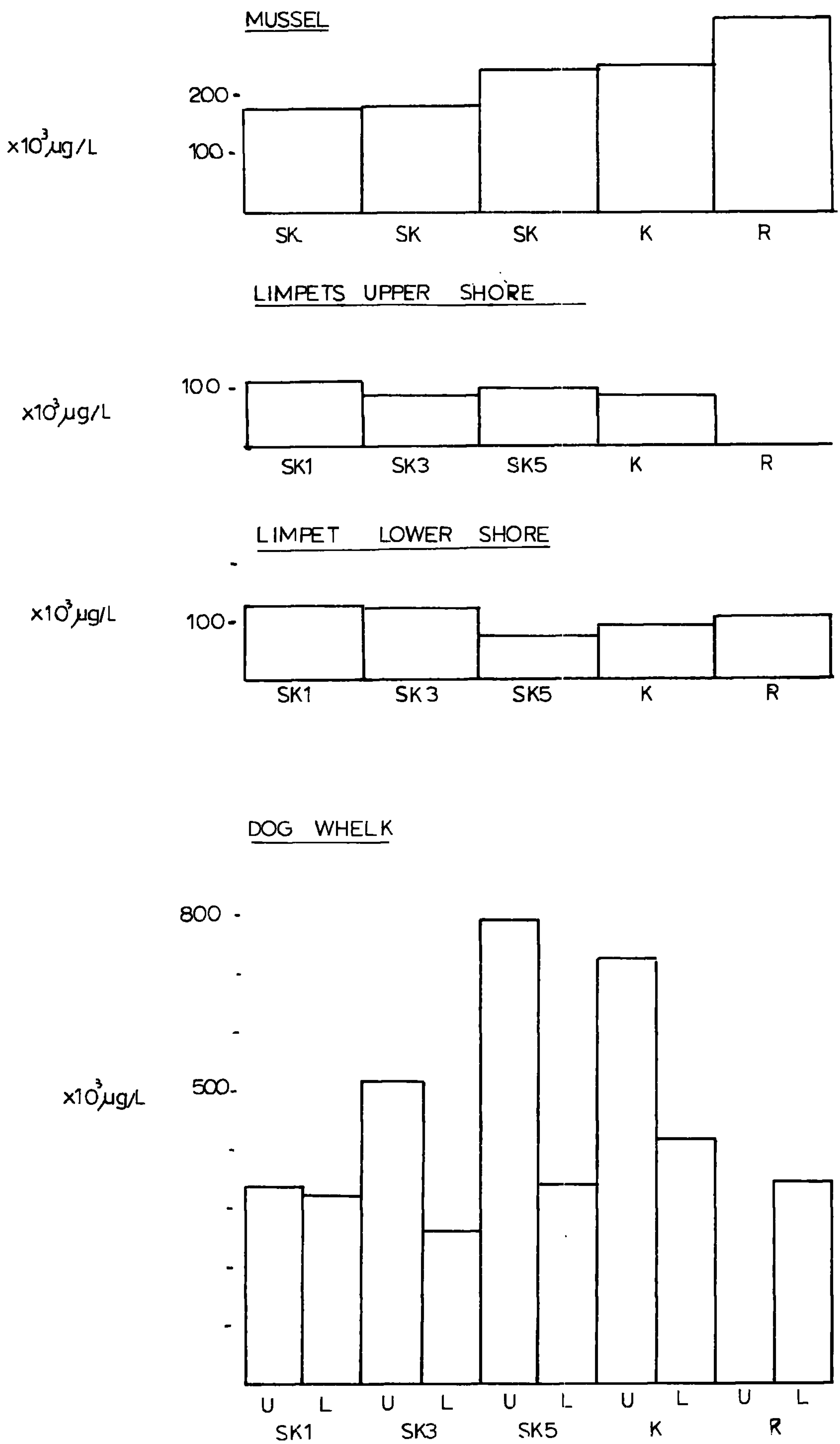
The results of the zinc levels in seaweeds have been noted for other workers in Figure 25. In comparison to the results of Black and Mitchell (1952) for Laminaria stipes, the results of this study waried between values of about 60,000 ug/l at Kettleness to 135,500 ug/l at Skinningrove Area 1. This suggests that higher environmental zinc levels are evident at one Skinningrove site than at the pollution free sites considered by Black and Mitchell (1952).

The variations of zinc levels in seaweeds between sample sites is given in Figure 27 . The highest values are recorded at Skinningrove Area 1 and Redcar, both of which could be expected to have high zinc concentrations in seawater. The lowest values are recorded at Skinningrove Area 5 and Kettleness which are furthest from the point sources of zinc pollution and have the lowest recorded seawater zinc levels. The difference between the two species of seaweed samples illustrates the length of exposure to additional zinc. The perennial Laminaria shows greater variations between sites than Ephemeral Ulva lactuca. Bryan (1971) points out that organisms, poorly equipped for excreting zinc, tend to accumulate zinc, and in this accumulative process, the length of exposure is very important. When critical internal concentrations are reached, harmful effects can, and do, occur. Age seems to be an important factor in determining the concentration of zinc in organisms, especially seaweeds. Subsequently, sample sites should be standardised in terms of age structure to avoid

FIGURE 28. RELATIONSHIP BETWEEN ZINC CONCENTRATION AND AVERAGE AGE AT THE SAMPLE SITES.

Site.	Zinc concentration ug/l	Average age. Years.
Skinningrove Area 1.	135.5	1.10
Skinningrove Area 2.	n.d.	1.60
Skinningrove Area 3.	119.8	1.87
Skinningrove Area 4.	n.d.	2.00
Skinningrove Area 5.	116.5	1.97
Redcar	130	1.87
Kettleness	60.28	1.50

FIGURE 29 . ZINC CONCENTRATIONS IN SELECTED MARINE ORGANISMS AT THE SAMPLE SITES.



distortions due to, firstly, differing absorption rates depending on the age, and secondly, differences in overall age of the populations at the different sites. (See Figure 28). The lower concentrations and lower variability of zinc concentrations in Ulva is not thought to be due to any regulative mechanism but simply the limited exposure period, and possibly the low zinc concentrations when Ulva has been able to absorb the seawater zinc.

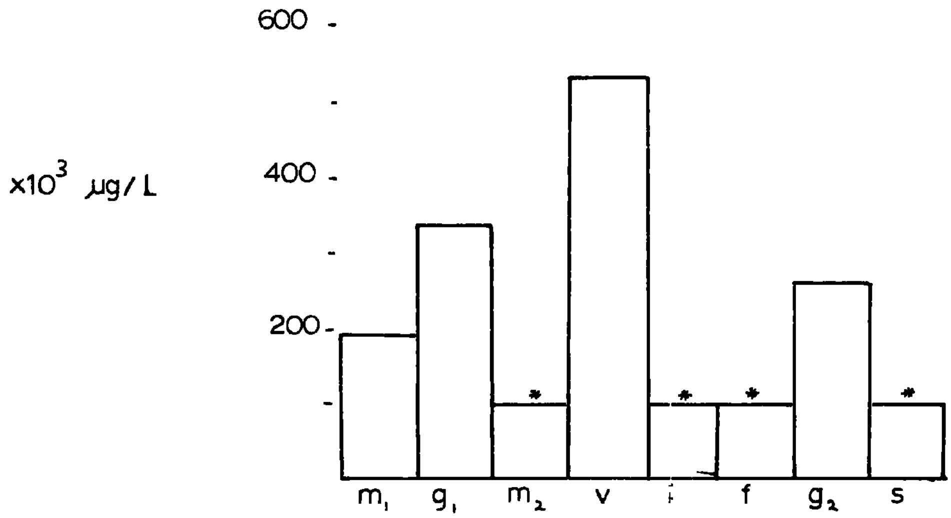
With reference to seaweeds, it is possible to state that zinc is absorbed from seawater, but its rate of absorption is influenced by a number of factors including age of seaweed, time of exposure to zinc in seawater, level of zinc concentrations in seawater, and antagonistic effects of manganese.

In Figure 26 the zinc concentrations in marine animals found by other workers are summarised. The average figures for zinc levels in this study of dog-whelks, limpets, and mussels are illustrated in Figure 29 . The dog-whelk and mussel results are generally higher in this study than found in the earlier work. There are a number of possible reasons for this as follows :-

1). Greater contamination and gut contents resulting in higher values.
2). Higher environmental levels of zinc either in solution or particulate form.
3). Difference in population structures between sites. A higher proportion of young in the mussel populations with their higher rate of uptake would result in higher zinc concentrations in the mussels.
4). For dog-whelks, the concentration may be greater due to the factor that it is higher up the food chain.

Variations between organisms are generally consistent for the sites sampled, with the order of increasing concentration of zinc being limpets to mussels to dog-whelks. Variations of each organism between sample sites do not vary in the same manner. Limpets decrease in zinc concentration at Skinningrove in a similar way to that of Laminaria digitata and seawater. Low values are recorded at Kettleness which are

FIGURE 30 . INTERNAL DISTRIBUTION OF ZINC IN MUSSELS.
(DATA FROM BROOKS AND RUMSBY 1965)



KEY

*	less than
m_1	mantle
g_1	gills
m_2	muscle
v	visceral mass
i	intestine
f	foot
g_2	gonads
s	shell

similar in magnitude to Skinningrove Area 5, and intermediate values were recorded for Redcar. In contrast, dog-whelks and mussels have a general increase in zinc levels away from the outfall at Skinningrove. The Kettleness dog-whelk results are difficult to interpret as upper shore values are more similar to Skinningrove Areas 3 and 5, and lower shore values more similar to those of Skinningrove Area 1. Also the Redcar dog-whelk results are similar to those for Skinningrove Area 1. The mussel results for Redcar and Kettleness are equally confusing, as the Redcar results are more like those of Skinningrove Area 5 than Skinningrove Area 1, and the converse is true of the Kettleness results. There is a possibility that absorption rates of zinc are adversely influenced by the presence of interfering substances closer to the outfall. Higher levels of iron, copper, or manganese may be important in this respect. For instance, manganese has been shown to influence the absorption rate of Laminaria digitata. Bryan (1967, 1969).

The movement of zinc from seawater to organisms is comparatively well documented. Two major pathways have been considered. Firstly, absorption from solution and, secondly, absorption from food and ingested particles. Much of the initial work was on the former which, until recently, was considered more important. Bryan (1971).

Workers using a variety of marine organisms, have presented evidence of the importance of absorption from food and ingested particles. Hess (1964), Preston and Jeffries (1969), Bryan (1964), and Bryan and Ward (1965). As of yet, of all the organisms considered, there is only evidence for oysters and lobsters being able to control the rate of uptake.

It is difficult to say whether the organisms studied control the rate of uptake,but it seems unlikely. They may however, be able to regulate total concentration. Of the organisms studied, the limpet is the most likely example, as its results between sample sites are less varied. (See Figure 29). However, both the other organisms may regulate their levels partially by an excretory mechanism, or by internal storage.

Brooks and Rumsby (1965), show the distribution of zinc in mussel, and this work is summarised in Figure 30 . This work suggest possible sites for internal storage or axcretion. The variation of zinc concentrations with age for mussels may be in the ability to remove high proportions of particulate matter, older members being more efficient. As of yet, no work has been carried out with the internal distribution of this element with different ages of mussels.

It is difficult to conclude whether zinc in seawater, or zinc in sedimentary material and ingested food, is the main source of environmental zinc for the organisms studied. No attempt in this study is made to examine the removal of zinc in these organisms. No work is available in the literature, although for other organisms three methods of removal have been examined as follows :-

1. Loss across the body surface or gills or in excretion. Bryan (1966), Nakatani (1966).
2. Excreting metal into the gut. Bryan (1967),
3. In urine. Bryan and Ward (1965 and 1968).

Bryan (1971) has considered the absorption, excretion, and storage mechanisms, and indicates that higher organisms should be more capable of regulating the concentration of heavy metal. The efficiency of certain organisms has been checked by exposing them to different concentrations of a metal and then analysing their tissues. For zinc in Carcinus maenas he showed that regulation was "quite good". In contrast work carried out on zinc accumulation in Mya arenaria, Pringle, Hissong, Katz and Mulawka (1968) showed a gradual uptake of zinc over a period of fifty days with a threefold increase of zinc in the tissue and little or no apparent regulation. In this study the results suggest that mussels are more like lower animals with limited or no regulation, and limpets are more like higher animals with some indication of regulation. The results for dog-whelks are more complex. Pringle, Hissong, Katz and Mulawka (1968) indicated that for molluscs there appears to be a direct relationship between uptake rate for a given metals and its depletion. Unfortenately, hidden in this relationship is the proportion being stored and illustrates the problem in understanding the results when the biochemical aspects of these possible pathways are poorly understood.

FIGURE 31 . FACTORS INFLUENCING THE TOXICITY OF ZINC IN AQUATIC ORGANISMS.

Factors.			Reference	Organism.
1. Form of metal in water	Soluble		Doudoroff (1956)	fish.
			Grande (1967)	fish.
	Particulate	precipitate	Herbert & Wakeford (1964)	fish.
		adsorbed		
2. Presence of other metals or poisons.	antagonistic effects		Lloyd & Herbert (1962)	fish
	additive effects		Brown (1968)	fish
	synergistic effects			
3. Factors influencing physiology of organism and possibly form of metal in water.	salinity		Herbert & Wakefore (1964)	fish
	temperature		Lloyd & Herbert (1962)	fish
	dissolved oxygen		Lloyd (1961)	fish
	pH		Sprague (1964a)	fish
	light		Gutnecht (1963)	seaweed
4. Condition of the organism	size of organism		Skidmore (1967)	fish
	activity of organism		Herbert & Shurben (1963)	fish
	acclimatization to metals		Edwards & Brown (1967)	fish

Although very few species have been studied, it seems fairly clear that some organisms or individual tissues will reflect the concentrations of heavy metals, like zinc, in the environment and may be suitable indicator species, whereas others will not. Even in animals where the concentration of zinc is regulated, some tissues such as gills or the hepatopancreas may accumulate high concentrations, and this raises the question of detrimental effects either of the organism, or of their use as food.

Zinc has been shown to have sub-lethal effects at high concentrations. Bryan (1969) Figure , and O'Sullivan (1971) have shown that for certain species of seaweeds growth is depressed by high concentrations. Zinc is an element essential for proper growth, but the optimum concentrations are presumable those normally found in the environment, and higher concentrations generally lead to inhibition. This has been found in all organisms from fish to crustaceans to phytoplankton and bacteria.

Clarke (1947) has shown that zinc has less toxic effects than copper but, where there is considerable zinc precipitation, according to Tobata (1969), mussels are prone to toxic effects mainly because of their feeding habits.

Much of the work on zinc toxicity has been done on fish. In Figure 31 there is an outline of this research, and it illustrates the factors which, in part, control the rate of uptake. Experiments so far have been generally carried out on relatively tough species, and effects of zinc have been recognised at levels much higher than are found in the sea. Other species, perhaps from the sublittoral zone, and especially their larvae, may be affected at still lower concentrations. Far too little information is available for any proper assessment to be made. It is not known which species or types of organisms are more sensitive to zinc. Susceptibility may depend on permeability of organisms to zinc as to its feeding habits or to the efficiency of its regulatory or detoxification system. For instance, the ability to regulate zinc may be less efficient in the larval than in the adult stage. In this instance, dog-whelks may be less sensitive than the other organisms studied in this respect.

COPPER.

The analysis of seawater levels of copper has been carried out by a number of observers, some of which are shown in the Table below. The range of values tabulated by Chow and Thompson (1952) have not been extended by more recent studies.

COPPER LEVELS IN SEAWATER.

Author	Year	Copper in ug/l fresh weight
Atkins	1932	10
Riley	1937	5 - 11
Noddack	1940	4
Webb	1937	0.1
Chow and Thompson	1952	21 - 25
Brooks and Rumsby	1965	3
Riley and Taylor	1968	5
Bryan	1969	0.4 - 5.9

Experiments carried out by Krauskopf (1956) on the concentrations of copper that can be held in solution in seawater, gave figures as great as 400 - 800 ug/l. This indicates that seawater is not saturated with copper and much higher levels are possible where there is a sufficient supply of additional copper.

The copper levels found off the North Yorkshire coast were 0.64 ug/l to 0.92 ug/l . In comparison to those found by other writers the copper concentrations are at the lower end of the range. However, it would be necessary to sample over a longer period before drawing conclusions, as it is reasonable to assume that, because of the variability of the quality of the untreated effluent, much greater variations and much higher levels would be experienced locally over short periods.

Figure 32. Map of the distribution of Copper at Skinningrove.

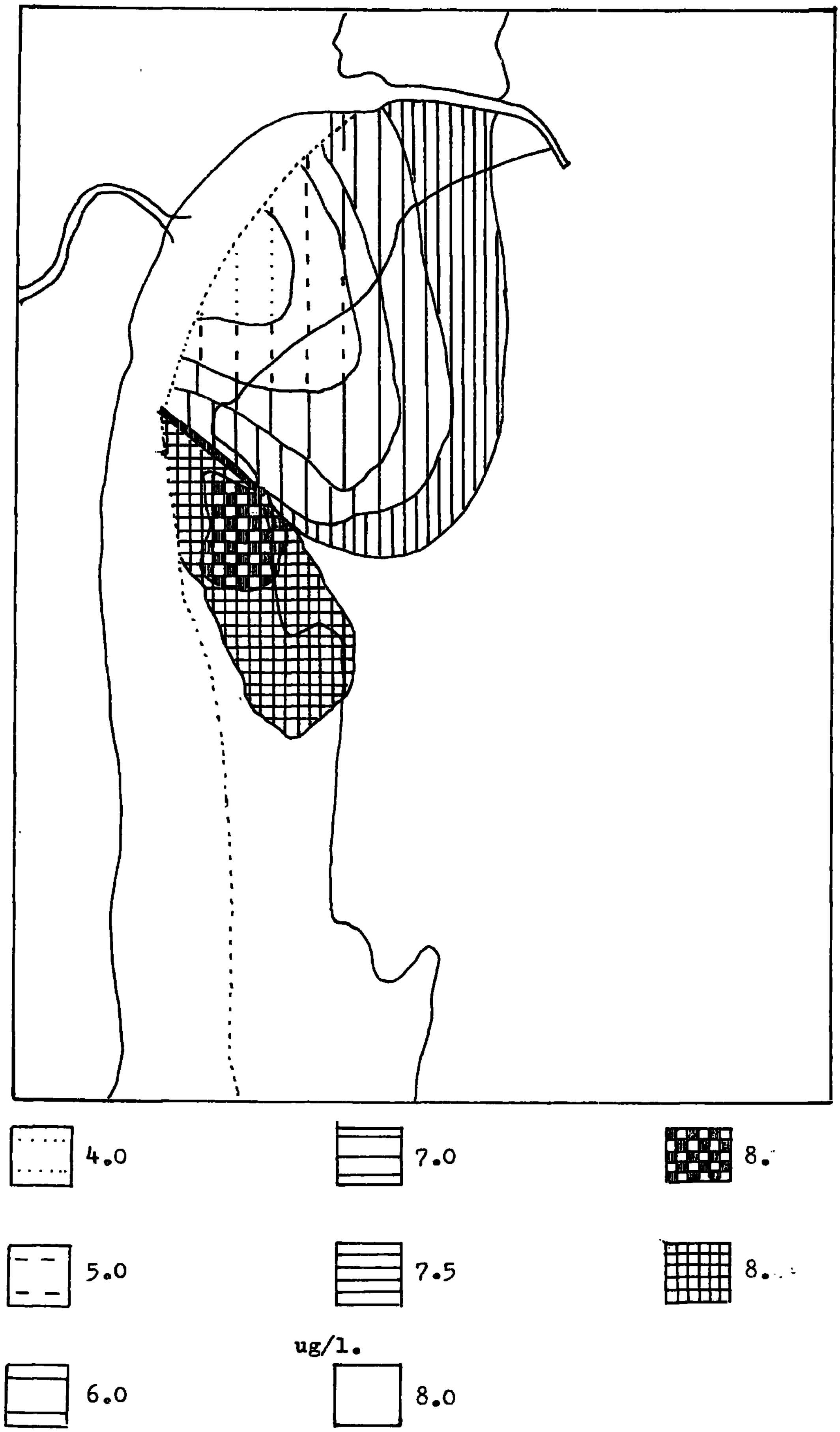


FIGURE 33 . COPPER CONCENTRATIONS IN SKINNINGROVE BECK.

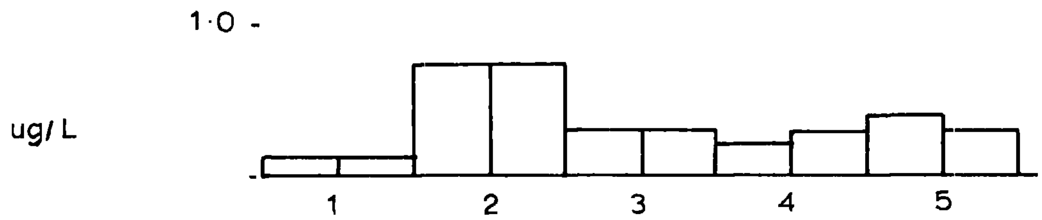


FIGURE 34 . COPPER CONCENTRATIONS IN SEAWATER.

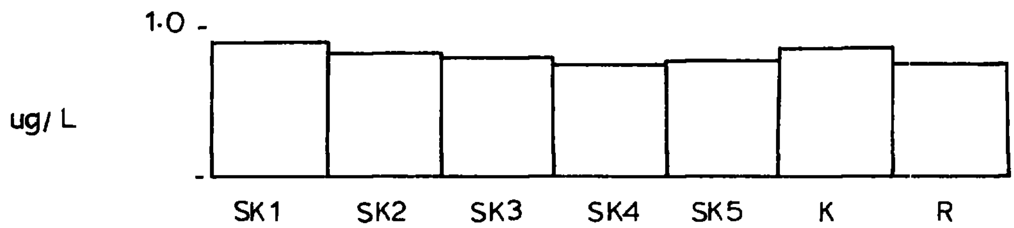
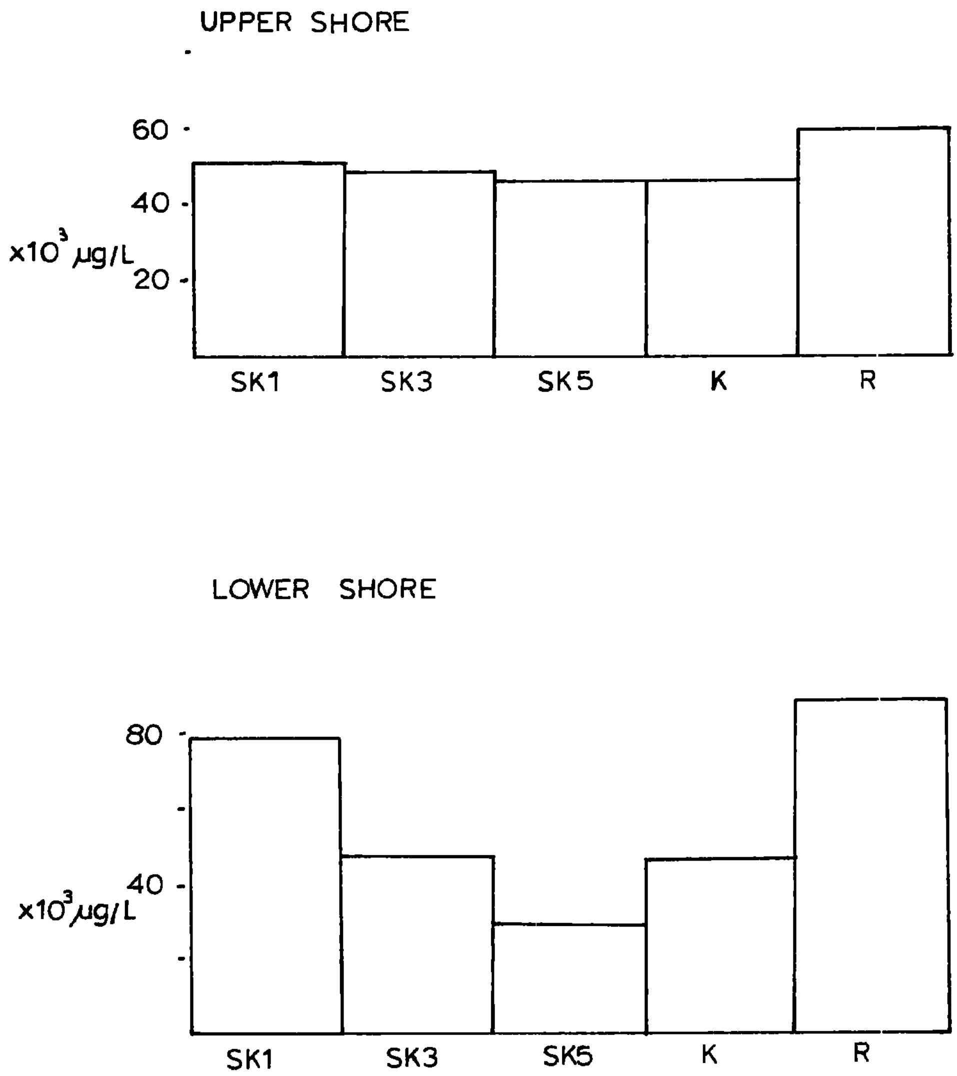


FIGURE 35. COPPER CONCENTRATIONS IN SILT.



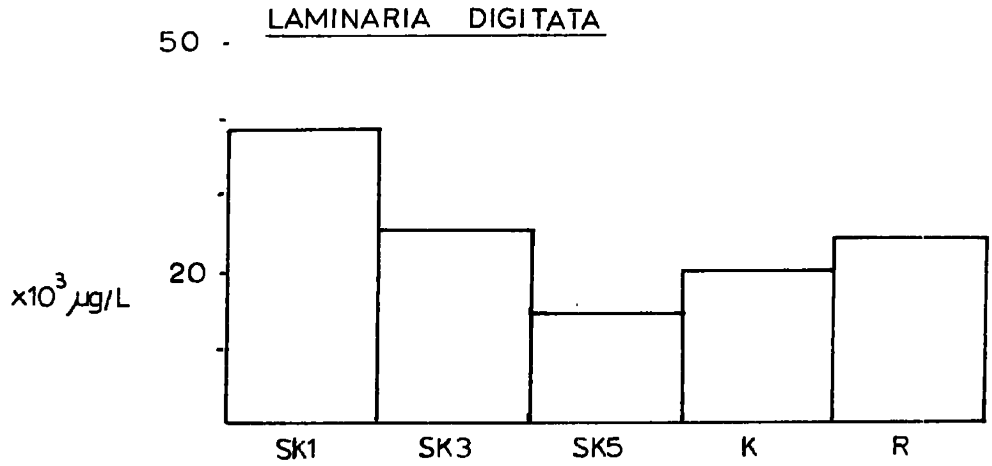
The map of the off-shore copper concentrations of seawater at Skinningrove, are shown in Figure 32 . This map brings out two major points. Firstly, Skinningrove Beck does not add to the copper concentrations of the seawater. Its main effect is one of dilution. Secondly, there is a small increase of seawater copper levels close to the sewage outfall. The outfall acts as a source of additional copper and, as the sewage copper levels are slightly higher than those of the seawater, there is a slight gradient in the copper concentrations away from this outfall. This gradient would be expected to be much steeper at times of high copper output from the sewage outfall. The areas which vary markedly from the general seawater copper concentrations are influenced by two major factors. The presence of an off-shore current which carries both the water from Skinningrove Beck, and the sewage outfall, eastwards, almost parallel to the shore. The second factor is the interference of the Beck water with its high levels of soluble and particulate iron oxide. The high levels of iron result in the precipitation of soluble copper. This is also important in explaining the low concentrations at the mouth of Skinningrove Beck and in the immediate off-shore area.

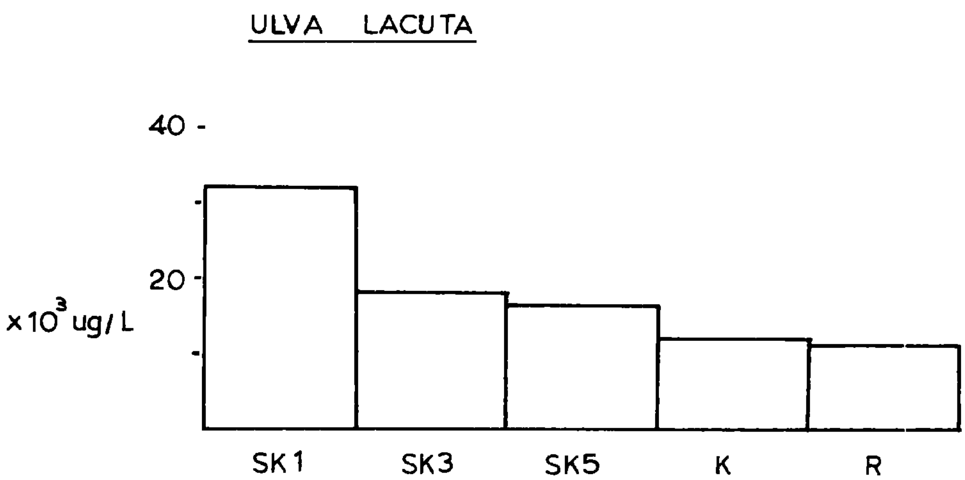
The interference of iron oxide also has an important effect on the copper levels along the last mile of the Beck itself. Low copper levels of the Beck water are associated with high levels of iron oxide. This is illustrated in Figure .

With the lack of long term recordings of copper levels from the sewage outfall, the levels of copper in the silt give a partial guide to levels in the immediate past, and they show a similar decrease away from the outfall, as is shown in the table below :-

Skinningrove Area	1	3	5
Copper concentration in ug/l	26300	15900	9600

FIGURE 36 . COPPER CONCENTRATIONS IN SEAWEEDS.





The high concentrations of copper in silt are of the order of between 10,000 to 30,000 times greater than the copper held in solution or suspension in the seawater. Much of the sewage derived copper seems to get rapidly precipitated close to the outfall and results in high silt copper levels. The copper levels in the Laminaria digitata are even higher than those for silt, but show a similar decrease in concentration away from the sewage outfall. This is summarised in Figure 36 . All this points to the outfall being an important source of copper, and over periods of time (may be days or months), much higher concentrations of copper have been evident in the seawater closest to the outfall. The order of magnitude is difficult to assess. Using an approximate of the enrichment factor found for Laminaria digitata by Bryan (1969), it is possible to estimate a concentration of 25 ug/l copper in solution. But this figure is of dubious value as it ignores the cumulative nature of uptake,and assumes absorption from solution only. However, it compares to the highest levels recorded in seawater in the first table, and may therefore have some limited value in a short term study.

The levels of copper concentrations in silt have been found by other writers. Bryan (1970) quotes concentrations for the Plym and Tamar, as 49,000 ug/l and 407,000 ug/l respectively, while Brooks and Rumsby (1965) quote for marine sediments, a value of 102 ug/l . Clearly, the results of this study are not as high as those found in the Tamar estuary, but much higher than sediments taken from further off-shore.

The levels of copper in Laminaria digitata are many times greater than the concentrations in seawater, but these copper levels being lower in the plant material than those found for lead, support the work of Haig (1961). Haig suggested that concentrations of divalent heavy metals in algae could be directly related to alginate affinity of these respective metals.

The decline in the copper concentrations of Laminaria digitata away from the outfall reflect the conclusions of Bryan (1969). He concluded that Lamimaria digitata accumulates copper in a non-regulatory way, and the levels of copper reflect the length of time that the organism is exposed to high levels of this element in seawater. From the previous discussion, higher levels of copper are periodically dispersed from the sewage outfall and these concentrations decline towards the East away from the outfall. This decline in seawater concentration of copper would reduce directly the rate of copper absorption and would influence the length of exposure to greater than average seawater levels of copper. This line of argument is supported by the available data.

The Kettleness results for copper show a greater similarity to Skinningrove Area 3 than Skinningrove Area 5. These relatively high copper concentrations in seawater and silt are difficult to explain, but may simply reflect local variations along the coast in these two parameters. However, it points to the fact that Skinningrove Area 1 has abnormally high copper levels. Similarly, the Redcar results for seawater, silt, and *Laminaria digitata* reflect the presence of inputs of higher copper concentration. Of all these parameters, seawater levels show marked variability with wind direction, wave conditions, state of the tide, as well as dilution and chemical interference from the input sources. Silt, as a parameter, seems less prone to short term fluctuations or distortions but, where ther is little protection from tidal scouring, the subsequent redistribution of sediments complicates the data. The mussel beds at Skinningrove Areas 1 and 3, and at Redcar limit the effect of this latter factor, and act as sediment traps. But this is less true of Skinningrove Area 5 and Kettleness. The third of these parameters, copper levels in *Laminaria digitata* does not seem to suffer the problems of the previous two, and is likely to be a more reliable monitor of the environmental copper levels, avoiding both short term fluctuations and redistribution.

The results of other writers working on copper levels in seaweeds are given below -

Author	Year	Laminaria digitata	Fucoids	Algae
Öy	1940	4,000 ug/l	3,400 ug/l to 8,400 ug/l	
Beharrel	1942			10,000 ug/l
Webb	1937		3,300 ug/l	Ulva 30,000 ug/l
Black and Mitchell	1952	11,000 ug/l to 21,000 ug/l	6,000 ug/l to 10,000 ug/l	
Young and Langille	1958			Ulva.100,000 ug/l Algae 6,000 to 62,000 ug/l
Bryan	1969 1970	1,600 ug/l to 4,000 ug/l		

The results in the above Table varied for Laminaria digitata from 1,600 ug/l to 21,000 ug/l compared to this study's variation of 11,200 ug/l to 49,000 ug/l. Even allowing for the results of Bryan (1969) being low as they were taken for fresh weight, the results, especially those close to the outfalls are much higher than those found by these other writers. An alternative explanation to the higher local input of copper is to explain these results by preferential uptake by seaweeds in certain localities. No evidence seems to be forthcoming in the support of this idea.

The results for Ulva lactuca show a similar pattern to Laminaria digitata, with high concentrations at Skinningrove Area 1 and Redcar, a gradient of concentration from Areas 1 to 5 at Skinningrove, and the lowest values recorded at Kettleness. Webb (1937) found values of 30,000 ug/l copper for Ulva, and in exceptional circumstances, Young and Langille (1958) recorded values of up to 100,000 ug/l. The areas closest to the outfall are nearing Young and Langille's " exceptional circumstances" values.

FIGURE 37 . COPPER CONCENTRATIONS IN SELECTED MARINE ORGANISMS AT THE SAMPLE SITES.

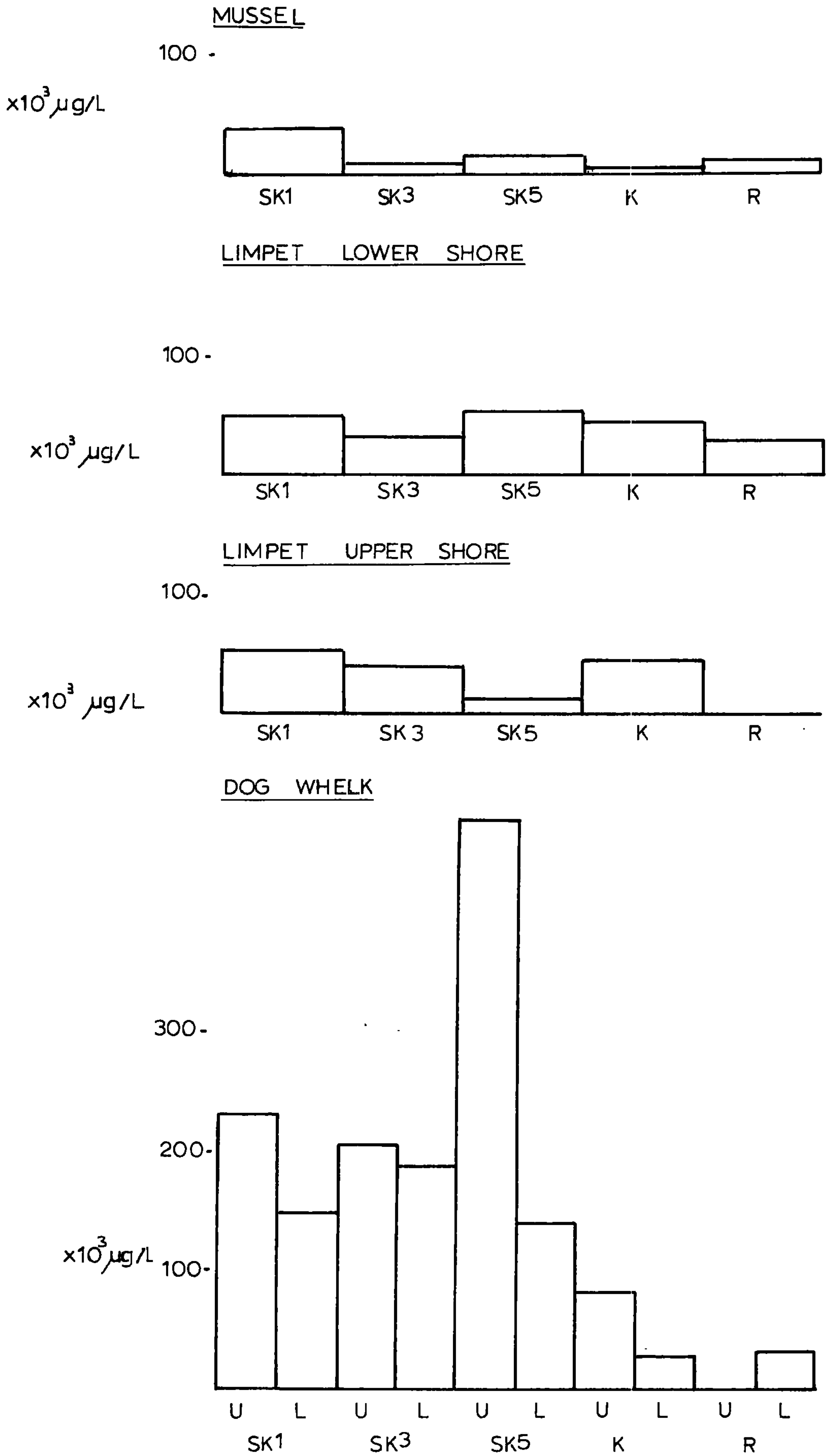
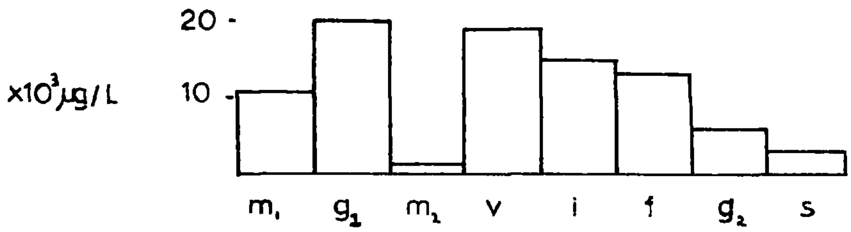


FIGURE 38 .INTERNAL DISTRIBUTION OF COPPER IN MUSSELS.

(DATA FROM BRROKS AND RUMSBY 1965).



KEY.

m_1	mantle
g_1	gills
m_2	muscles
v	visceral mass
i	intestine
g_2	gonads
s	shell
f	foot

Copper levels in marine animals examined in this study are generally much higher than those for seaweeds. Each organism showed the same trend at Skinningrove as has been illustrated for seawater, silt and seaweed. There is a general decrease in copper levels away from the outfall to the East. However, limpets and mussels show this trend better than dog-whelks. The major problem with marine animals is errors caused by including gut contents and contaminating particles, both of which proved difficult to remove. These errors are the most likely reason for the rather high results for upper shore dog-whelks and lower shore limpets in Skinningrove Area 5.

The wide variations in total copper levels for each of these organisms (Figure 37) suggest their inability to regulate their total copper levels. Limpet results are noticeably less varied and significantly grouped in the 20,000 ug/l to 23,000 ug/l range. This indicates a possible higher efficiency in its regulation of total copper levels. Each of these organisms may, in fact, regulate copper levels not by an efficient excretion mechanism, but by storage.

Storage could occur at sites where it would not interfere with the metabolism, or in a site from which it could subsequently be excreted. Not much is known though of these pathways. The work carried out by Brooks and Rumsby (1965) shows the distribution of copper within various parts of mussels. The data is summarised in Figure 38 . The high values of the intestine, gills, viscera and foot, could reflect storage, excretory sites, and possible contamination. Clarke (1947) sheds some light on the uptake and efficiency of excretion of mussels. His work brings out a number of points as follows :-

1) The rate of uptake is related to the concentration of seawater copper levels, with larger amounts of absorption with greater concentration of copper in the seawater.
2) The rate of excretion was rapid once the mussels were put back into fresh seawater.
3) This excretion rate was influenced by the mode of uptake. Slow accumulations at lower copper concentrations took longer periods to be excreted.

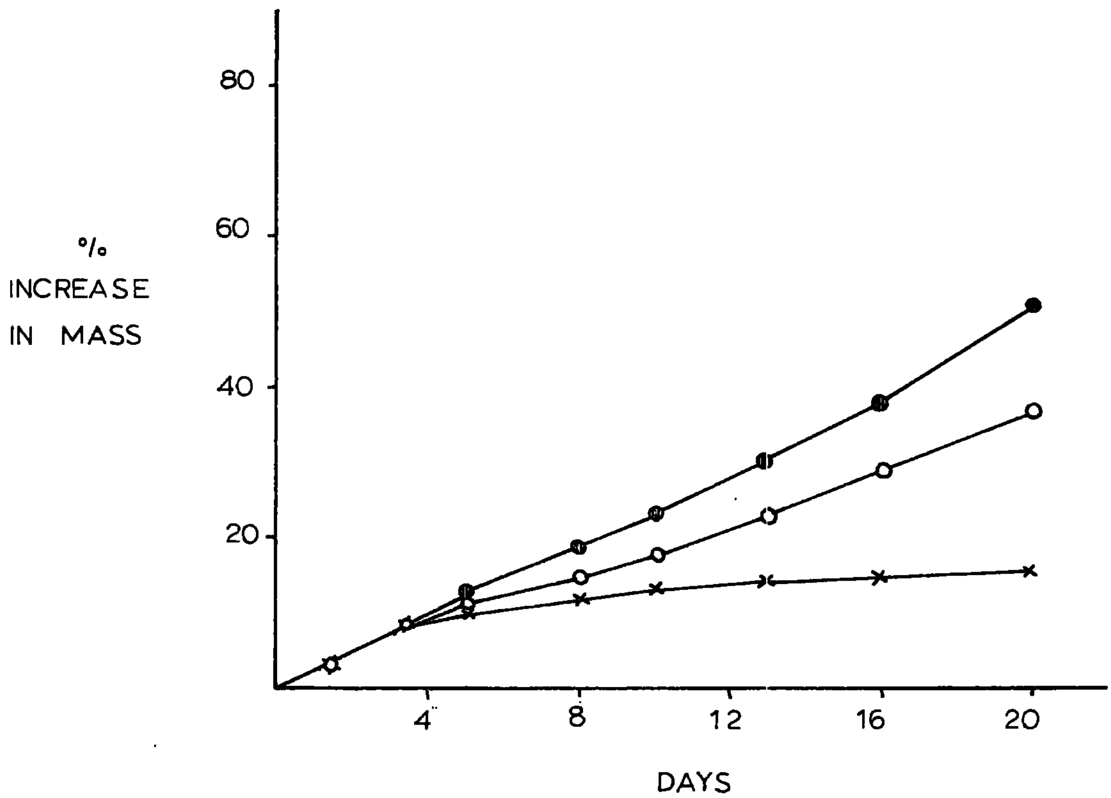
4) Excretion could occur even if the mussel subsequently died. In these cases the excretion would be rapid, and the levels when death occurred, would be substantially lower than those necessary to kill the organism.

This work indicates the problems of leaving the mussels in seawater to enable them to excrete their gut contents. Such a procedure would result in a rapid reduction in some mussels, while in others, a much slower rate of excretion would be involved. The distortion would be greater with the mussels subjected to higher levels of copper previously. Much of this excretion of copper would involve copper which was not present in the gut contents. The variations between mussel copper levels reflect sources of additional copper. However, the differences in these levels are not as varied as for the other organisms studied. This perhaps reflects a less efficient excretory mechanism.

All the results of copper concentrations in organisms indicate the importance of sewage as sources of additional copper in seawater. This explains the generally easterly decrease in animal copper levels away from the sewage outfall at Skinningrove (Figure 37), and the higher copper concentrations of these organisms at Redcar. Kettleness results also appear to be high, although it was not possible to locate the source. Kettleness would not appear to be a satisfactory copper control site in terms of its general unpolluted character. However, the copper levels reached at Kettleness are generally less than those recorded at Redcar and Skinningrove Areas 1 and 2.

Without exception, animals studied have higher copper levels than the silt levels in the same sample site. This indicates that, although the values of these organisms may be high, due to unavoidable errors of contamination and inclusion of gut contents, they still indicate a concentration over the environmental copper levels in silt or seawater. This evidence could suggest a number of points. Firstly, the rate of uptake is greater than excretion of this element. Secondly, the occurrence of a non-regulative uptake of copper by these organisms. Thirdly, the cumulative nature of uptake.

FIGURE 39 . EFFECT OF COPPER ON THE GROWTH OF LAMINARIA DIGITATA. (BRYAN 1971).



KEY

●	1.2 ug/l
o	11 ug/l
×	51 ug/l

Fourthly, internal regulation, with internal storage in sites of high concentration.

Turning to the effects of copper on organisms, it is possible to consider both lethal and sub-lethal effects. One sub-lethal effect of copper has been recorded on the oyster by Boyce and Herdman (1898). They found that at 25 ug/l copper levels, oysters had a morphological change and turned green. However, this threshold value is much higher than recorded for coastal waters. There is a remote possibility that the occurrence of a high proportion of green sea-anenome close to the outfall at Skinningrove may relate to higher copper levels found there. Copper has also been shown to exert an inhibitory effect on the growth of a number of organisms, including Polyzoa, Miller (1946), larvae of sea urchins, Soyer (1963), and Laminaria digitata, Bryan (1969). With reference to this study, it is difficult to separate the effects of a number of inhibitory factors on the growth of organisms. The reason is that they occur together and have a similar effect. For instance, production in Skinningrove Area 1, is reduced by particulate iron reducing the degree of sunlight penetration, a sub-lethal effect of heavy metals like copper and zinc, besides a range of other factors. The magnitude of each is impossible to separate out from field evidence. Clarke (1947) has indicated that sub-lethal doses of copper have stimulated development of barnacles, and also aided recovery from heavy metal poisoning.

The lethal effects of copper, and perhaps zinc, have been better documented for aquatic organisms than the other heavy metals considered in this study. Much of the work with copper toxicity has been concerned with ship fouling organisms, like mussels and limpets.

It is well known that the toxicity of different heavy metals varies considerably. Similarly, the susceptibility of different organisms varies enormously. Clarke (1947) in comparing a number of heavy metals in a variety of forms, showed that copper was generally more toxic than zinc. In the same study, in comparing the susceptibility of barnacles and mussels to copper, he showed that mussels were more susceptible to copper toxicity. This susceptibility was marked by a lower lethal

FIGURE 40 FACTORS INFLUENCING THE TOXICITY OF COPPER IN AQUATIC ORGANISMS.

Factors.			Reference	Organism.
1. Form of metal in water	soluble	ion	Clarke (1947)	crustaceans
		complex	Doudoroff (1956)	fish
		chelate	Grande (1967)	fish
		compound	Corner & Sparrow (1957); Clarke (1947)	crustaceans
2. Presence of other metals or poisons	antagonistic effects		Lloyd & Herbert (1962)	fish
	additive effects		Brown (1968)	fish
	synergistic effects		Corner & Sparrow (1956)	crustaceans
3. Factors influencing physiology of organism and possibly form of metal in water.	dissolved oxygen		Lloyd 1961	fish
4. Condition of the organism.	stage in life history		Pyefinch & Mott (1948)	crustaceans

threshold in the copper levels, and also shorter periods of exposure time, to kill.

This information is especially interesting as it may hold the answer to a distinctive zonal distribution close to the outfall at Skinningrove. The area within two metres of the outfall can be divided into three distinctive zones. The first zone, closest to the outfall, where there is only a bare flat rock surface. The second, a very narrow zone of adult barnacles of low density in cover, and the third zone is patches of young barnacles with some older barnacles. By about four metres, the increasing density of mussels has an increasing detrimental effect on the barnacle population. There is a distinct possibility that two factors are especially important in determining this pattern in copper toxicity and competition.

Harvey (1955) points to the poisonous effect of 1,000 ug/l cupric ions. Seawater levels never remotely reached this concentration in this study. Organisms only once reached a concentration of over 0.5 ug/l . It could be that, higher up the food chain, sufficient concentration of copper may result in levels reaching the threshold value found by Harvey (1955). However, much lower levels of copper have been recorded as having a lethal effect on marine organisms; for example, larvae of barnacles and copepods with lethal thresholds of 10,000 ug/l and 300 ug/l respectively.

In Figure 40, the factors influencing the toxicity of copper on aquatic organisms are summarised. Hunter (1949) showed that for the amphipod Marionogammarus marinus, toxicity of copper increased with decreasing salinity, but Pyefinch and Mott (1948) cyprid larvae of the barnacle Balanus balanoides, showed that the toxicity of copper was lower in dilute seawater. This may be an important consideration in understanding the distribution of mussels and barnacles at the end of the Skinningrove outfall. Clarke (1947) did not consider variations in toxicity due to changes in salinity. Clearly the sewage outfall also alters the salinity values in the seawater close to its point of entry.

In conclusion, the following points may be made :-

1.) The main source of additional copper at the sample sites, is sewage, as at Skinningrove and Redcar.

2.) The distribution of copper in seawater, silt, and organisms, illustrates the interaction with other heavy metals. Iron is an important controlling influence in this distribution.

3.) The sub-lethal and lethal effects of copper on marine organisms are an important factor on the rocky shore at Skinningrove. Copper is suspected to have an effect on the distribution of both mussels and barnacles, and may have a controlling influence over the presence, or absence, of other organisms in Skinningrove Area 1, besides having sub-lethal effects.

FIGURE 41. IRON LEVELS IN SEAWATER.

Author	Year.	ug/l Total particulate	ug/l Total dissolved
Lewis & Goldberg	1954	4.5	3.4
Laevestu & Thompson	1958	114	17.8
Hashitani & Yamamoto	1959	-	9 - 156
Parker et al.,	1963	200	30
Williams & Chan	1966	3 - 706	1 - 39
Ryther et al.,	1967	3.5 - 3340	12.3 - 81
Bryan	1969	7 - 668	

FIGURE 42 . IRON CONCENTRATIONS IN SEAWATER AT THE SAMPLE SITES.

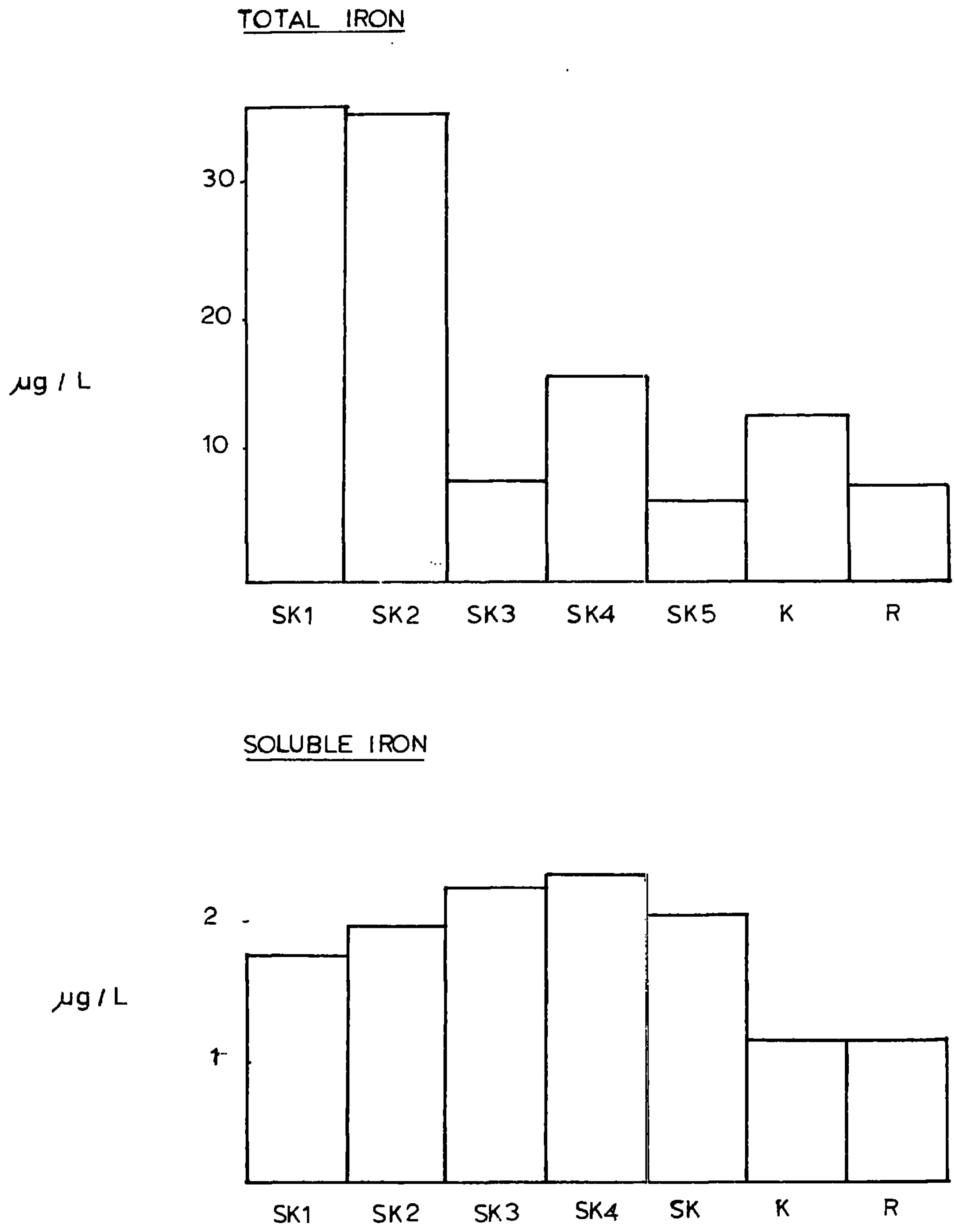
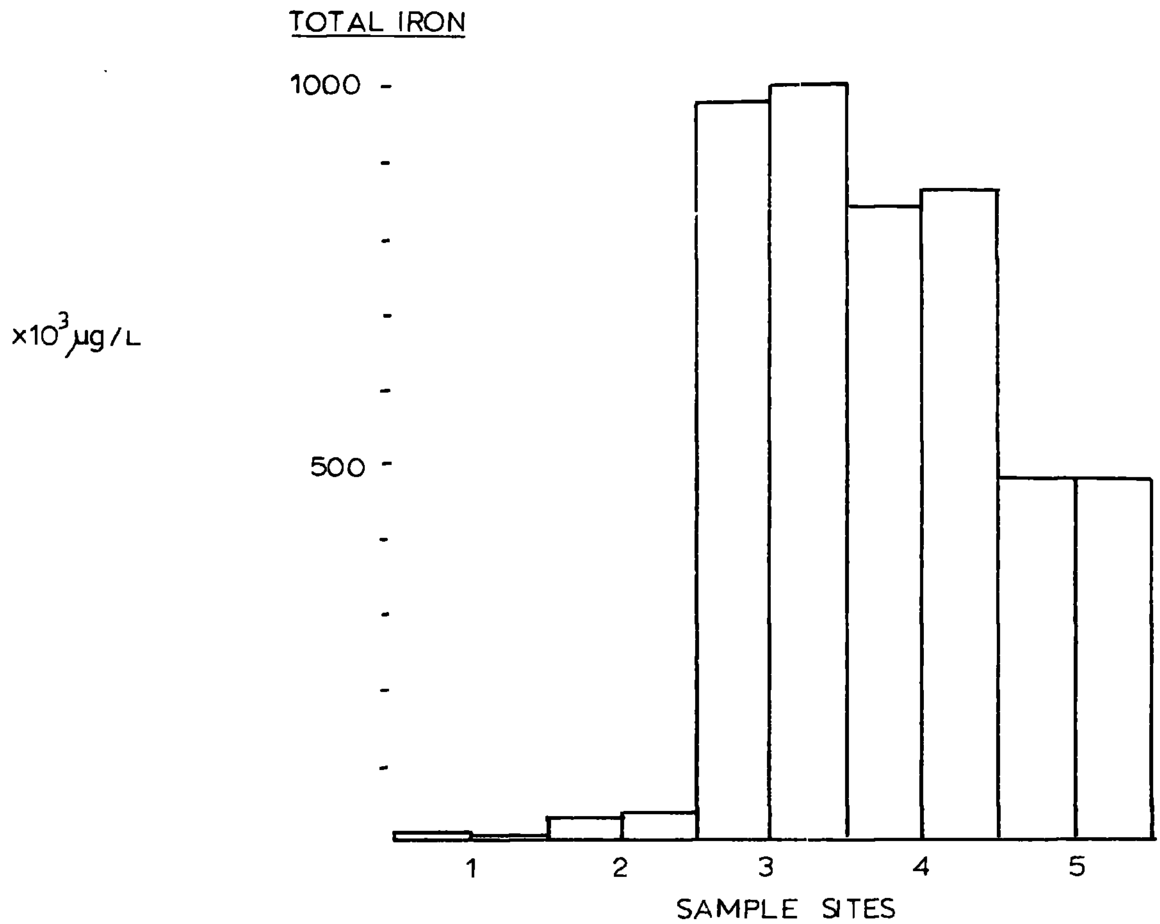


FIGURE 43 . IRON CONCENTRATIONS IN THE WATER FROM SKINNINGROVE BECK.



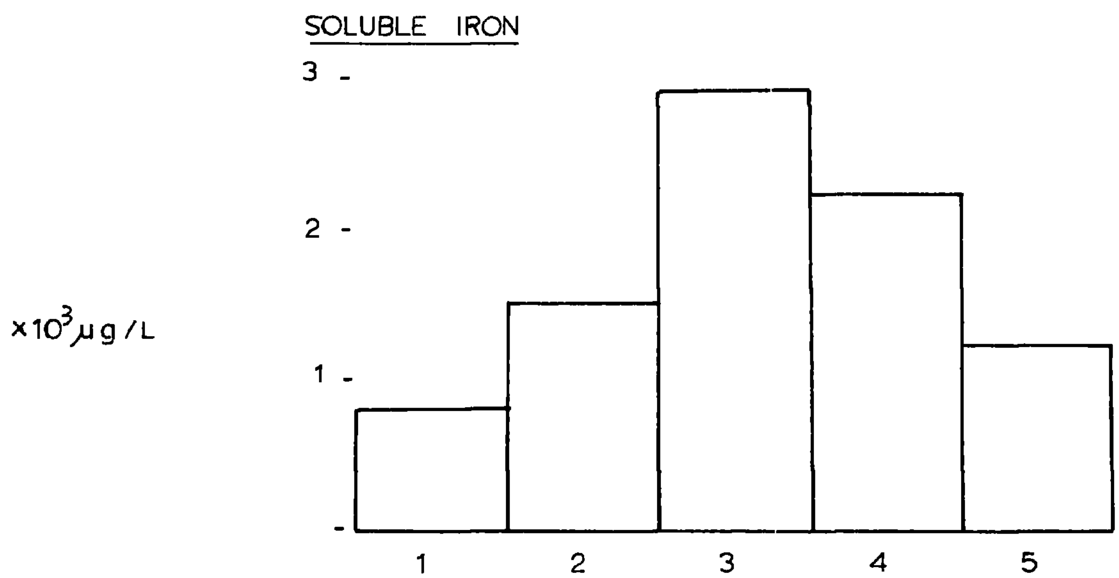


FIGURE 44 . CHLOROSITY VALUES OF WATER SAMPLE FROM SKINNINGROVE BECK.

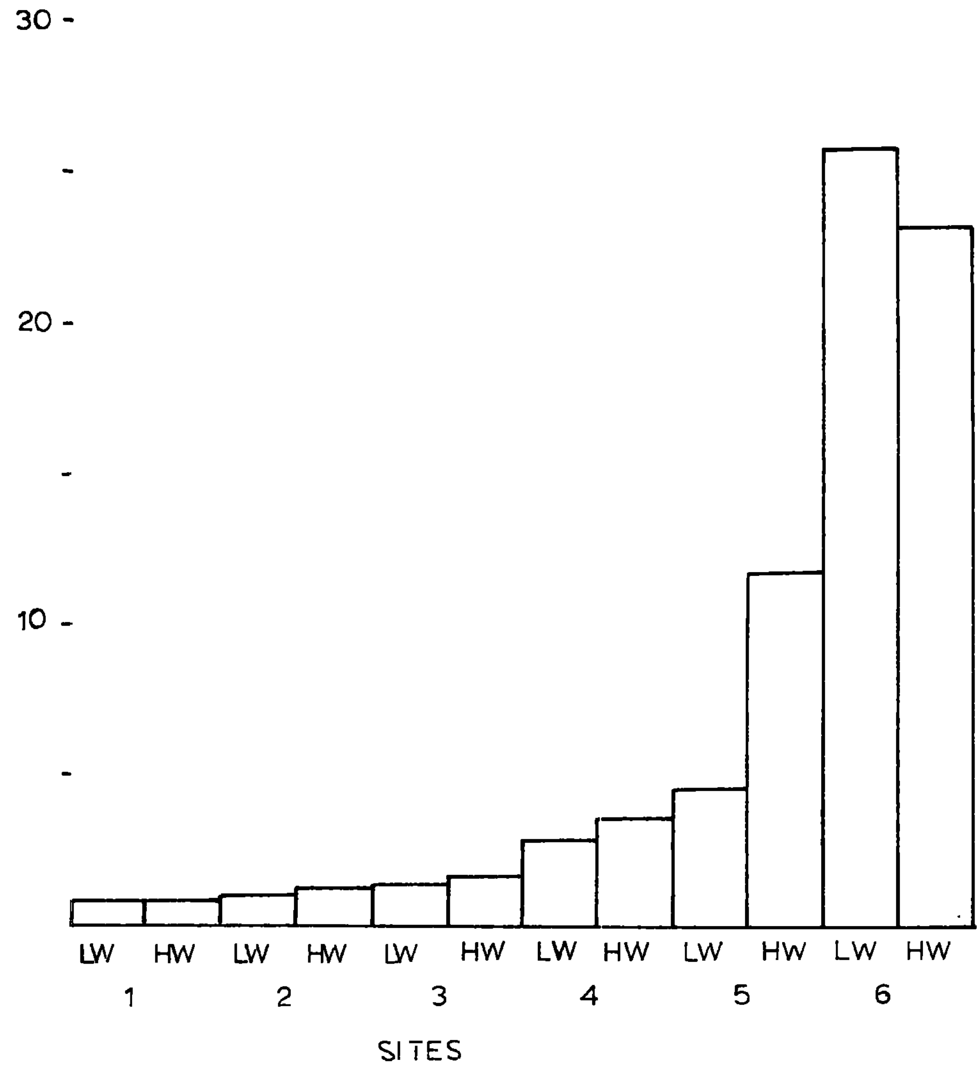
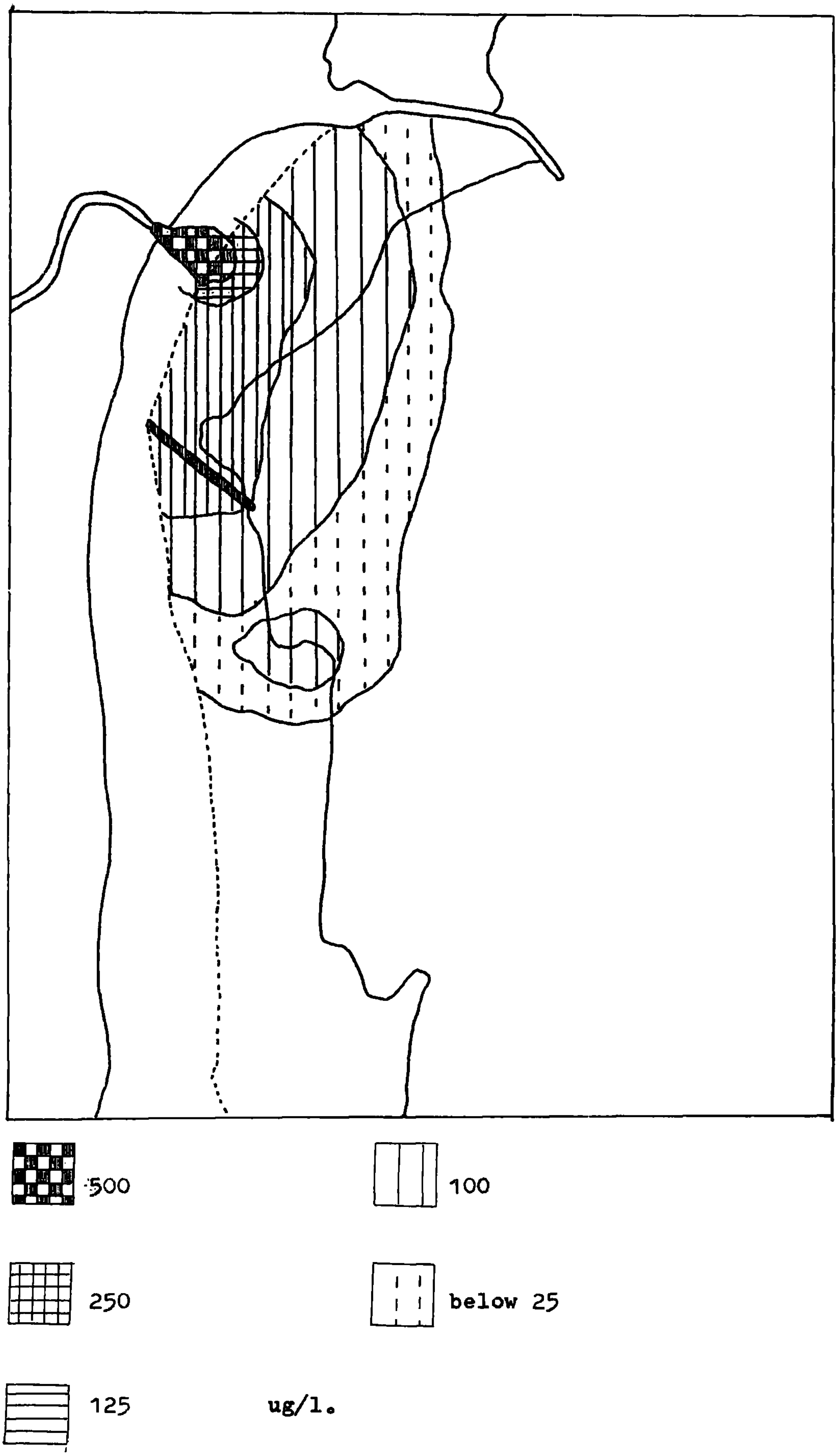


Figure 45.Map of the distribution of Iron at Skinningrove.



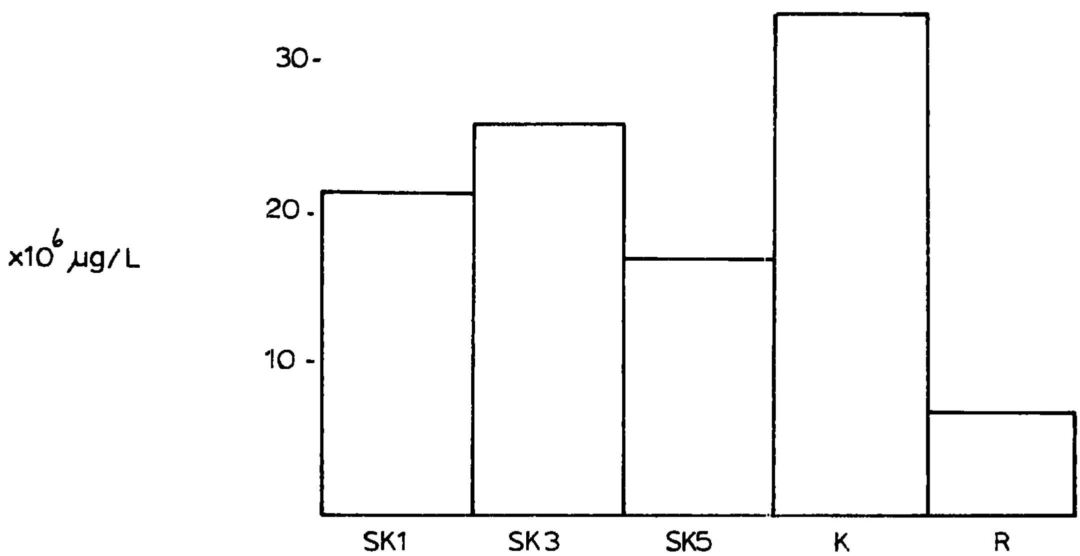
IRON.

"Natural" seawater varies in iron content and, according to Harvey (1955), varies from 1 ug/l to 60 ug/l. The results of other observers can be seen in Figure 41 . Due to the insolubility of ferricoxide in the alkaline pH range, only small quantities are found in solution in seawater. However, in coastal waters with large iron inputs from land drainage, high concentrations are found, mainly due to a large increase in particulate iron. This was found to hold true for the high concentration of iron in seawater at Skinningrove. (See Figure 42 .)

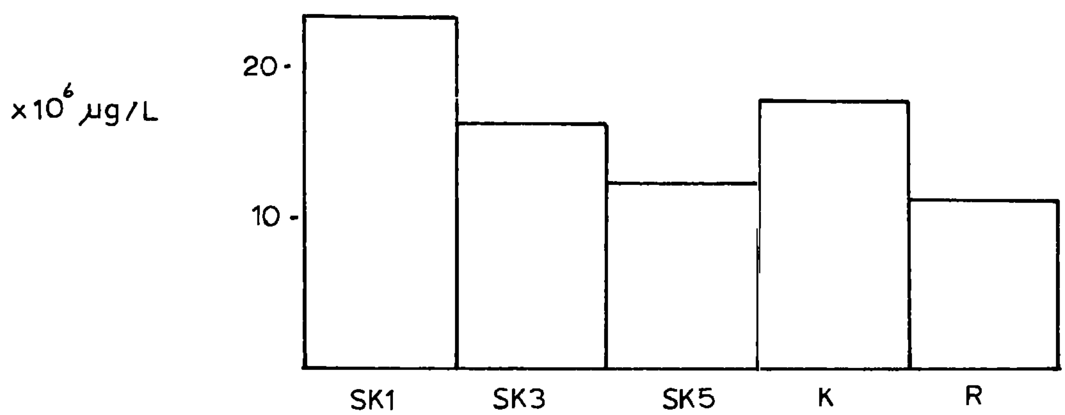
The levels of iron in the lower section of Skinningrove Beck are shown in Figure 43 . There is a number of point pollutional sources, and these are the drainage outlets from old iron mines. The iron in suspension and solution is carried down to the pool, (Figure 18), and here, the first effects of the sea are noticed with an increased precipitation of the iron. Figure 44 illustrates the tidal section of the Beck. The orange suspension in the river is carried out to sea and can be seen on a calm day to stretch as far as half a mile from the mouth of the Beck. The areal dispersion of this iron solution and suspension varies greatly according to local conditions, like state of tide, wave size, wave direction and stream discharge. Figure 45 shows the distribution of the iron in seawater under one set of conditions. The large drop in the iron levels in the river as it passes into the sea is due to both dilution and precipitation. The total iron concentration is roughly halved as the river passes into the seawater, and about equal proportions of soluble and particulate iron are involved. The river is the cause of the abnormal sea levels of iron at Skinningrove. The iron level in the sewage was found to be low, and this was not a significant source of either particulate or soluble iron. The input of the sewage does not have a great effect on the levels of iron in the sea as far as either dilution or concentration is concerned. In contrast, the high levels of iron are thought to have a significant effect on the dispersion of heavy metals from this sewage outfall.

FIGURE 46 . IRON CONCENTRATIONS IN THE SILT AT THE SAMPLE SITES.

UPPER SHORE



LOWER SHORE



As shown in Figure 41 , the total unfiltered iron values given by other observers, ranged from 1 ug/l to 424 ug/l. In this study, the range recorded varied between 18 ug/l and 433 ug/l , which is indicative of the high values recorded at Skinningrove. It would be reasonable to expect in periods of high run-off and increased stream turbulence, even higher stream water iron values. This would be largely due to the flushing out of the stream bed with its thick layer of iron rich sediments. Stored samples in the initial pilot study were taken in high run-off conditions, and had very much higher values. However, the period of storage in glass in an untreated condition before analysis was possible, makes the absolute value of these results questionable. Under these weather conditions the seawater iron levels were also correspondingly higher.

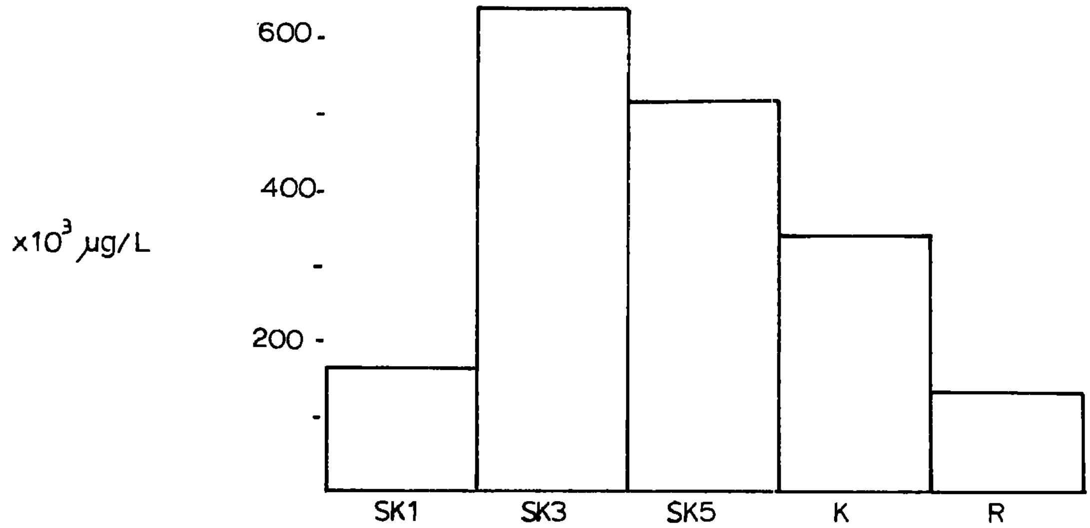
The variation of soluble iron range from 1.15 ug/l to 2.5 ug/l , and the particulate iron from 1.45 ug/l to 481 ug/l . The high sea level values are the result of large inputs of particulate iron. The soluble levels, when compared to the results of other writers, are not exceptional, being at the lower end of the range recorded.

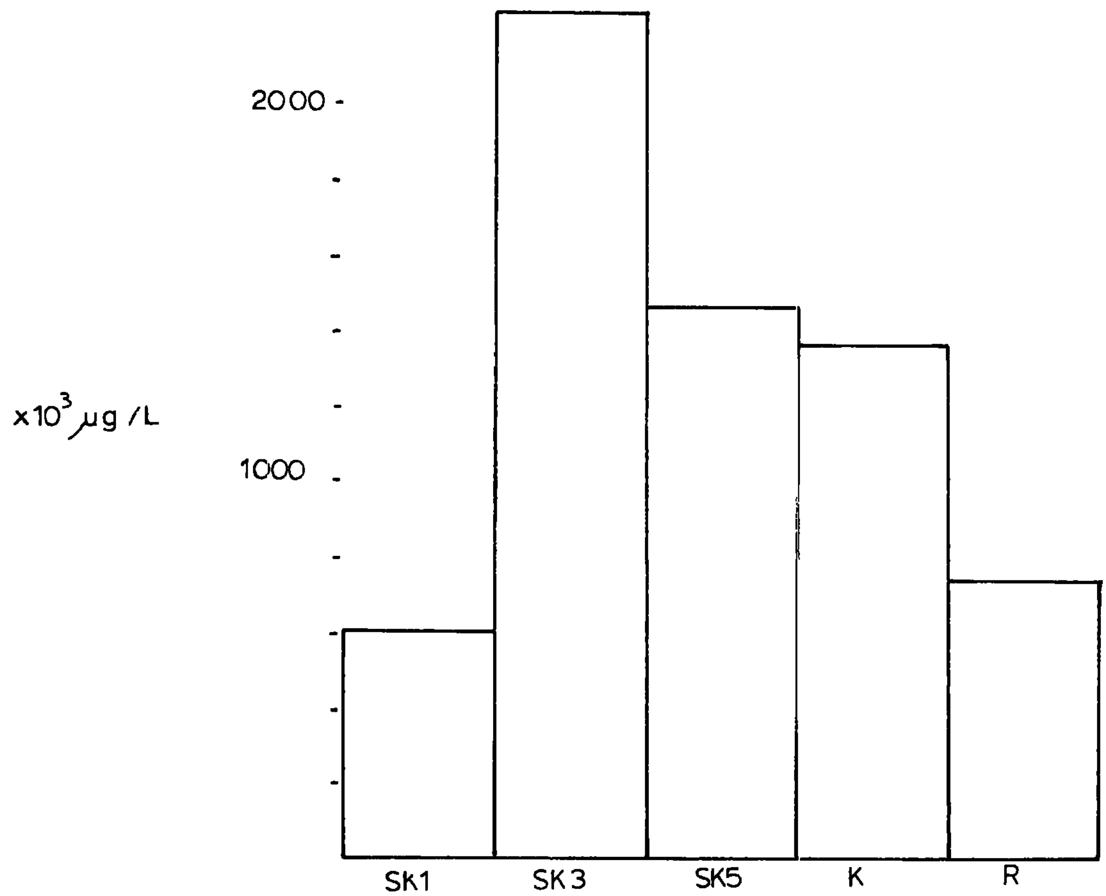
As a result of the high particulate iron, the levels in the silt are high, the highest levels being recorded closest to the mouth of the Beck. The values decrease in an easterly direction away from the Beck. This is important as it is known that zinc, lead and copper are adsorbed on to the surfaces of iron oxide particles. The sewage outfall, being a source of heavy metals, has its effect for these three metals limited by the interaction with particulate iron. Firstly, it causes an immediate reduction in the zinc, lead and copper concentrations. Secondly, it is a controlling influence on the area with levels of these heavy metals well above the surrounding seawater levels. Thirdly, it accentuates the deposition of these heavy metals close to the outfall. This increases the chance of toxic effects on organisms whose major pathway for these heavy metals is via suspended material or silt.

Harvey (1937) and Goldberg (1952), have presented evidence that algae can, and do, utilize particulate iron as

FIGURE 47 . IRON CONCENTRATIONS IN SELECTED SEAWEEDS AT THE SAMPLE SITES.

LAMINARIA DIGITATA





their major source of this element, presumably by hydrolysing particles adsorbed on their surfaces. This is probably an important source of iron for Laminaria digitata and Ulva lactuca. The study found iron levels in Laminaria digitata stipes to vary between 164 ug/l to 640 ug/l. By comparison, Black and Mitchell (1952) recorded 1260 ug/l to 1570 ug/l, and Bryan (1969) recorded 316 ug/l to 100 ug/l . Bryan's results are winter values and subsequently low, requiring a seasonal correction. Even allowing for these corrections, the results of this study lie above Bryan's results, but are much lower than those of Black and Mitchell (1952). The marked variability in iron levels in seaweeds is evident. Öy (1940) found for several species of algae values which ranged from 120 ug/l to 1330 ug/l. Others have recorded this range for Laminaria stipes alone. The variations are thought to be as much the product of the interactions of heavy metals affecting absorption and adsorbtion rates, as the variations in the concentrations of iron (particulate and, or, soluble) in seawater. For instance, uptake of zinc is affected by copper and manganese levels. Although only a little work has been carried out with other metals, it is clearly important to clarify for all metals the interaction effects,at the chemical level, in the seawater, and at the biochemical level in the seaweed. The latter is the least well understood despite some knowledge of alginate affinity for divalent metals.

The iron levels in the algae in this study show little in the way of a direct relationship to iron levels in the environment, either in particulate, soluble, or total iron in seawater or in the sediments. Variations in levels of iron for Laminaria digitata are shown in Figure 47 . This figure illustrates a number of points:-
Firstly, the expected decrease in iron concentration in Laminaria digitata from Areas 1 to 5 at Skinningrove, does not occur. The reason for this is the influence that other heavy metals have on iron uptake - an interference effect. The reduced uptake of iron at Skinningrove Area 1 is so great that in the area of high iron concentrations (actual and potential), the Laminaria digitata has the lowest concentration.

Secondly, by Skinningrove Area 3 the interference of other heavy metals is much less and the uptake is much greater, resulting in the highest iron concentrations. Despite even less interfernece from other heavy metals, the lower results at Skinningrove Area 5 reflect largely the distance from Skinningrove Beck and subsequently the limited occurrence of additional iron in the seawater.
Thirdly, unfortunately Kettleness is not a good control site with reference to the iron results. The wave-cut platform of the headland follows one of the minor iron ore seams in this geological series. This increases the iron concentrations in both the seawater and silt in this locality. Similarly, the iron values in the *Laminaria digitata* are high, although not as high as at Skinningrove Area 5. The lower values at Redcar are a reflection of the low iron levels in seawater and silt. The Ulva results show a similar pattern to those of *Laminaria digitata*. (See Figure 47).

The iron levels in marine animals are given in Figure 48 . The Redcar samples have the lowest iron concentrations for dog-whelks, mussels and limpets. These values are a reflection of the low iron values in the seawater. At Skinningrove, all, but the mussels, show a gradient in concentration away from the source of the iron. This gradient corresponds well with seawater iron levels. Mussels show a similar pattern in iron concentration to *Laminaria digitata*. More detailed consideration of the chemical and biochemical aspect is necessary, though, Goldberg (1957) has concluded that in general fractionation factors (relative enrichments) in the marine biosphere follow the stability of complexes formed with a number of organic ligands. Schubert (1954) has shown that the stability of complexes formed between divalent metal ions and ligands increase with increasing basicity of the metal ion in the order of copper $>$ lead $>$ zinc $>$ iron. For mussels, Brooks and Rumsby (1965) found that iron $>$ zinc $>$ lead $>$ copper.

Below, a table is given for comparison of the results

FIGURE. 48 . IRON CONCENTRATIONS IN SELECTED MARINE ORGANISMS AT THE SAMPLE SITES.

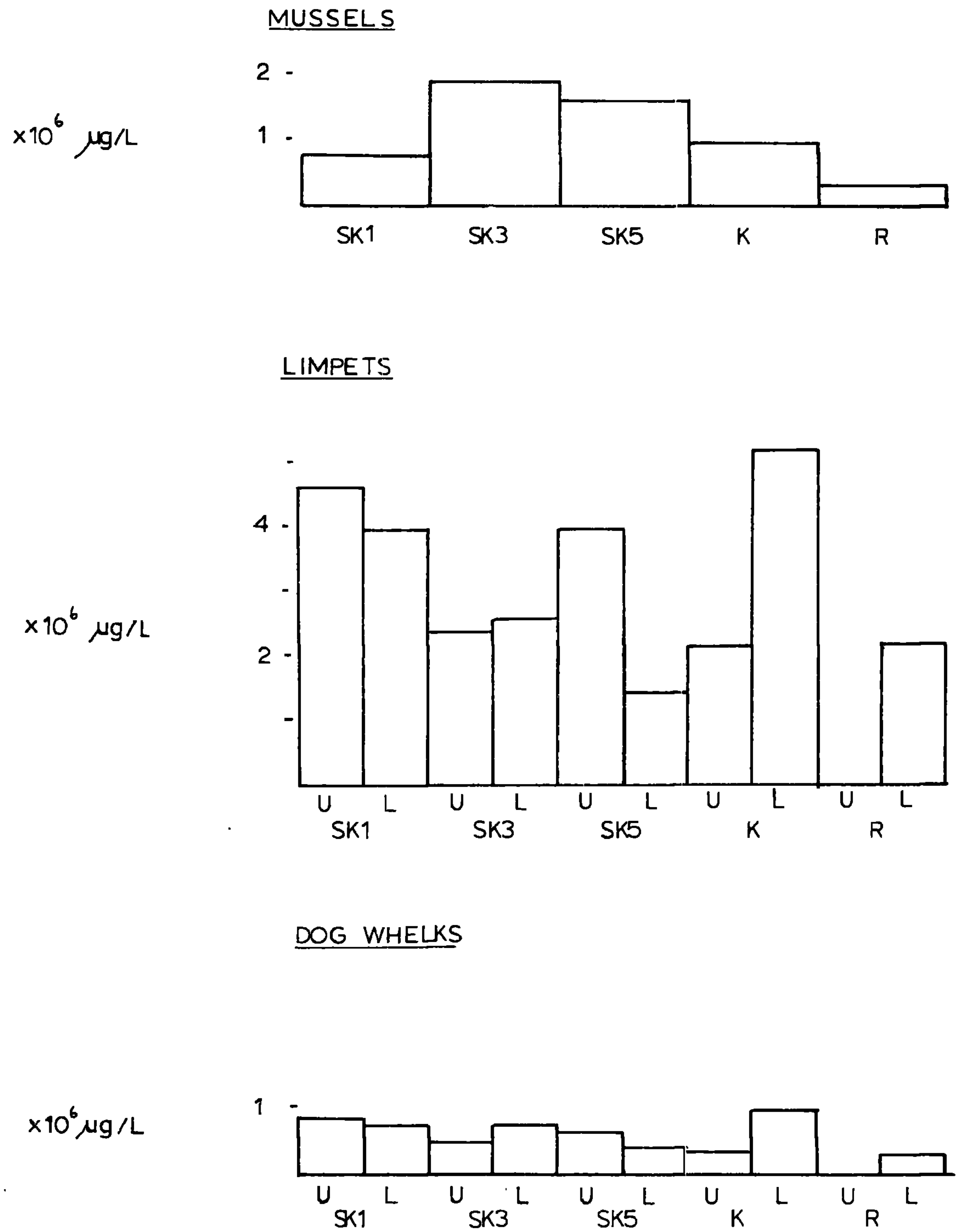
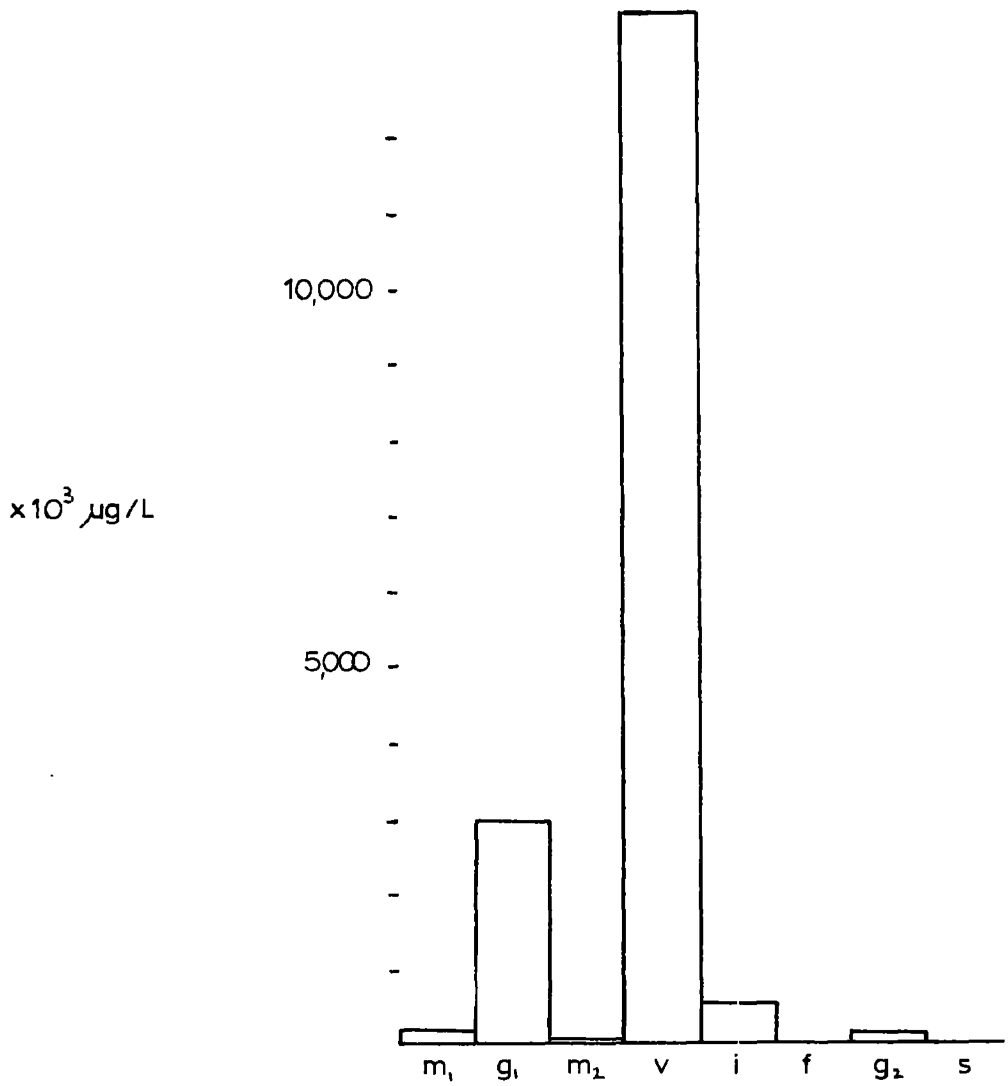


FIGURE 49 . INTERNAL DISTRIBUTION OF IRON IN MUSSELS.
(DATA FROM BROOKS AND RUMSBY 1968)



KEY

m_1	mantle
g_1	gills
m_2	muscle
v	visceral mass
i	intestine
f	foot
g_2	gonads
s	shell

FIGURE 50 . IRON LOSS BY MYTILUS EDULIS
(DATA FROM HOBDEN 1967).

Time after collection.	Mean Value (ug/l wet weight)
a) short term	
3 - 4 hours	80.2
4 days	35.3
11 - 18 days	25.0
b) long term	
3 days	26.4
5 months	27.4

of this study for each site :-

Skinningrove Area 1	iron > zinc > copper > lead
Skinningrove Area 3	iron > zinc > lead > copper
Skinningrove Area 5	iron > zinc > lead > copper
Kettleness	iron > zinc > lead > copper
Redcar	zinc > iron > lead > copper

These results are similar to those of Brooks and Rumsby (1965). The only inconsistency is the low iron value at Redcar and relatively high copper value at Skinningrove Area 1. These results are in some conflict with the copper lead zinc iron results of Schubert (1954). It does not seem that his theory will fit the observations, and the results appear to indicate that direct co-ordination of metal ions with suitable organic ligands is marked by some other factor such as contamination by, and particulate ingestion of, sedimentary material. This idea is supported by the data of the internal distribution of iron in mussels fiven in Figure 49 , and the relationship between iron concentration in silt and mussels in the sample sites.

Without more detailed work on the distribution of iron in other organisms' excretion and storage mechanisms, it is difficult to suggest that any regulation of iron occurs. There is little evidence to support the regulation of total iron in tissue but this might find some internal regulation like storage.

Hobden (1967) has studies iron metabolism in <u>Mytilus edulis</u> . He suggests that <u>Mytilus edulis</u> usually have between 20 to 40 ug iron per g wet weight after the animals have eliminated their gut contents. Higher values, sometimes in excess of 100 ug/g occurred in Spring, but he considered much higher values reported by some authors to be erroneous. He found that prolonged starvation in seawater of low iron content will not reduce the mean iron content of the animals below 20 to 25 ug/g. This, he stated, represents a permanent store. Higher values are produced by a temporary store that is fairly rapidly lost on starvation. The highest iron concentrations are usually in the digestive gland which contains the major part of the temporary store. Much of this can be regarded as particles being subjected to the digestive processes. This temporary store is in part at least, particulate. As soon as active feeding ceases the store declines (see Figure50). Its levels reflect the available iron supply of the previous few days. Time allowed for gut clearance would cause a significant decrease in the temporary store. The figures in this study include both the temporary and permanent store. Owen (1956) found that iron containing granules occurred in the digestive glands of Nucella , but unlike Hobden (1967) he suggested that these granules originated from the digestive gland. At this stage of experimental work it is difficult to conclude whether the high iron levels of digestive organs are the result of temporary uptake or digesting material, or the result of storage by the organism at a point of possible excretion.

Hobden (1969) considering the uptake and distribution of radio-active iron has shown that Mytilus edulis does absorb radio-active soluble iron from aerated seawater either directly or onto the mucus during feeding. The absorption is slow and the amount of uptake is generally low being roughly 1% of the total iron contained in the tissues. Clearly a dynamic equilibrium between the tissues and external iron concentrations was not established during his experiments. Heavy metals concentrated in animal tissue are frequently bound to tissue so that their exchange with the environment is low. The unusually high external iron concentrations allowed a certain amount of extra iron to be bound into the permanent store. This process would be limited by the availability of suitable unoccupied sites so the amount of uptake would be limited.

Contamination and the presence of gut contents must be considered a serious problem and make it difficult to comment further on variations between sites and variations between organisms.

The work of Tabata (1969) with reference to dissolved iron at the pH of seawater, has indicated that the maximum levels possible are not toxic to aquatic animals.

To be toxic high levels of soluble iron would have to be necessary in acidic water. However, this only limits the possible toxic influence of iron to a consideration of particulate iron. No work or data is readily available to shed light on this part of the problem.

The absorption of heavy metals in the form of particulate matter by organisms has been suggested by a number of workers, for example Bryan (1969). Toxic levels could be reached firstly, if there was a long enough period of non-regulative cumulative uptake from the low concentrations of soluble iron. This is considered highly unlikely. Secondly, if the major pathway was via particulate sources of high concentration, the absorption and subsequent uptake would be high. This seems more likely. In this case it is probable that uptake would occur through the gills or digestive system, and filter feeders would be more likely to accumulate higher iron levels and more likely to be prone to toxic effects. Thresholds for toxic effects are not known but do not seems to have been reached in this study.

Iron would seem to have little or no direct toxic effect. Despite this, it is likely that it is important as a controlling influence over the toxic effects of other heavy metals. By inducing greater precipitation rates in other heavy metals it reduces the concentration levels of the soluble metals, and subsequently, reduces the toxic effects. However, it increases the concentration in particulate form and in the silt as a direct result, and thus increases the likelihood of toxic effects where the pathways via an insoluble form are more significant. By increasing the precipitation of other heavy metals close to the outfall, it increases the concentration in the silt of these elements, and also reduces the areal dispersion of high concentrations of these elements.

In conclusion, the following points can be made :-

1.) High levels of iron are evident in the seawater at Skinningrove due in particular to the particulate iron inputs from Skinningrove Beck.

2) There is a decrease in levels of iron in the seawater, silt and seaweed to the East. This is the result of precipitation and dilutional effects.

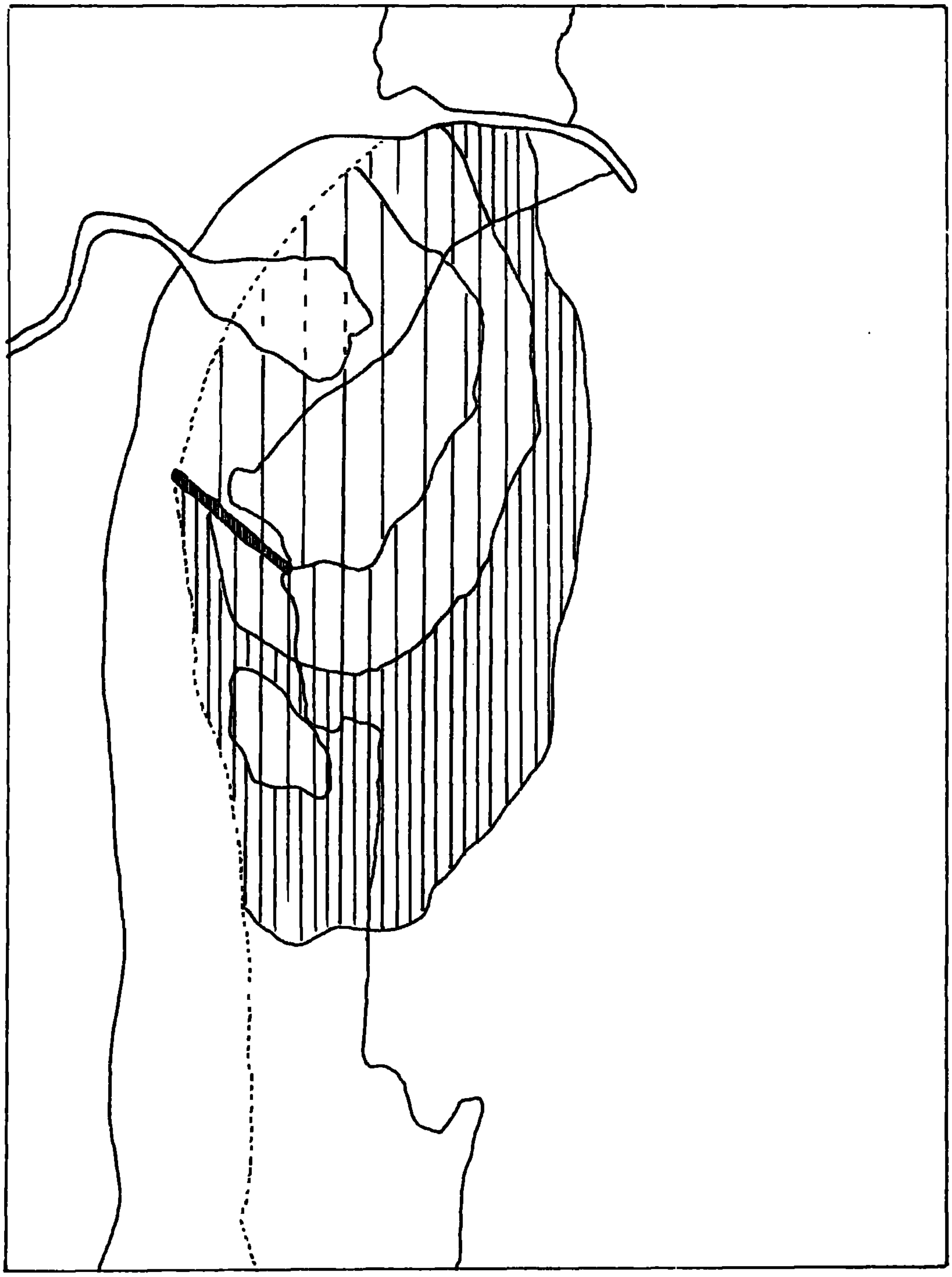
3) There is little evidence of any direct lethal or sub-lethal effect of these high seawater levels of iron on the organisms studied.

4) Iron levels in the seawater have an indirect lethal effect due to their effect on other toxic heavy metals. Also an indirect sub-lethal effect is evident. The high levels of suspended material, including particulate iron, reduces the degree of penetration of sunlight and subsequently reduces the primary productivity of the seaweeds.

FIGURE. 51 LEAD LEVELS IN SEAWATER.

Author.	Year	Concentration ug/l.
Boury	1930	4
Webb	1937	3
Noddack	1940	5
Black & Mitchell	1952	5 - 8
Loveridge et al	1960	1
Brooks & Rumsby	1965	2
Bryan	1969	1

Figure 52. Map of the distribution of Lead at Skinningrove.



2.0

3.0

2.5

3.5

3.5+ ug/l.

FIGURE 53 LEAD CONCENTRATION IN SKINNINGROVE BECK

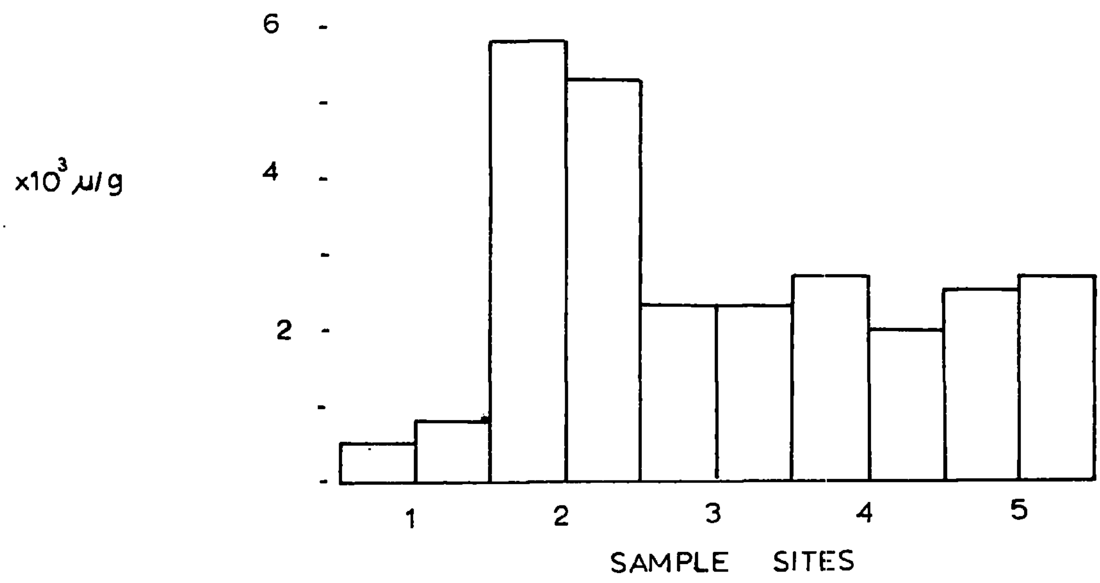
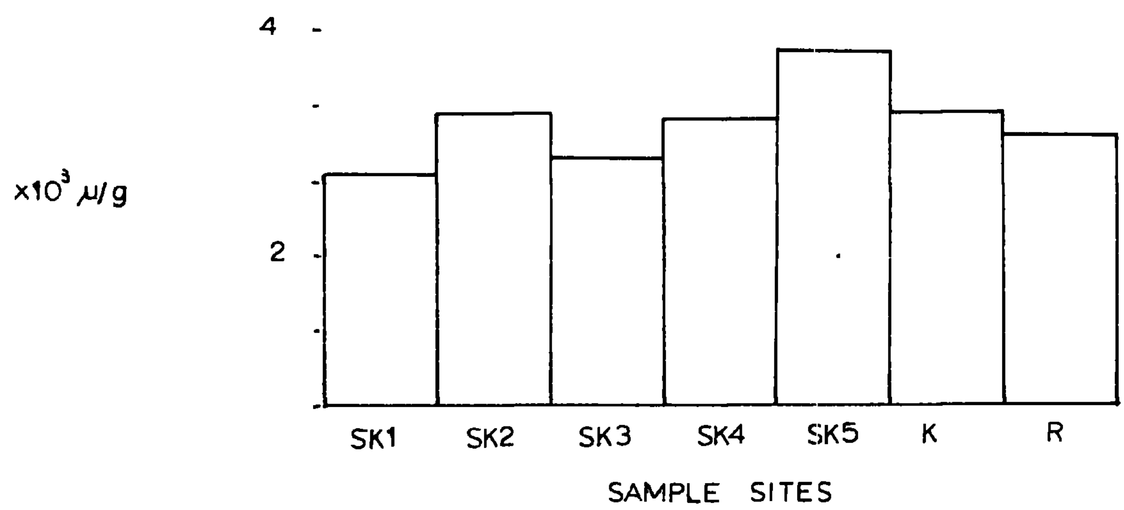


FIGURE 54 LEAD CONCENTRATION IN SEAWATER



LEAD.

The heavy metal, lead, is a normal constituent of the marine and estuarine environments, and in trace element amounts occurs as a normal constituent of marine organisms. Abnormal amounts added in sewage waste can result in a number of possible effects. A significant alteration of the biochemical cycle can result in lead having toxic, and even lethal effects.

Various writers have recorded a range of lead levels in seawater extending from 1 ug/l to 10 ug/l (see Figure 51), and this compares to the results of this study off the North Yorkshire coast, of 2.5 ug/l to 5.2 ug/l. This suggests that, at least at the time of sampling, there is not any abnormal amount of lead being added to the seawater lead concentrations. In Figure 52 both the possible input sources seem to have a dilutional effect on the lead levels in the seawater at Skinningrove at the time of sampling.

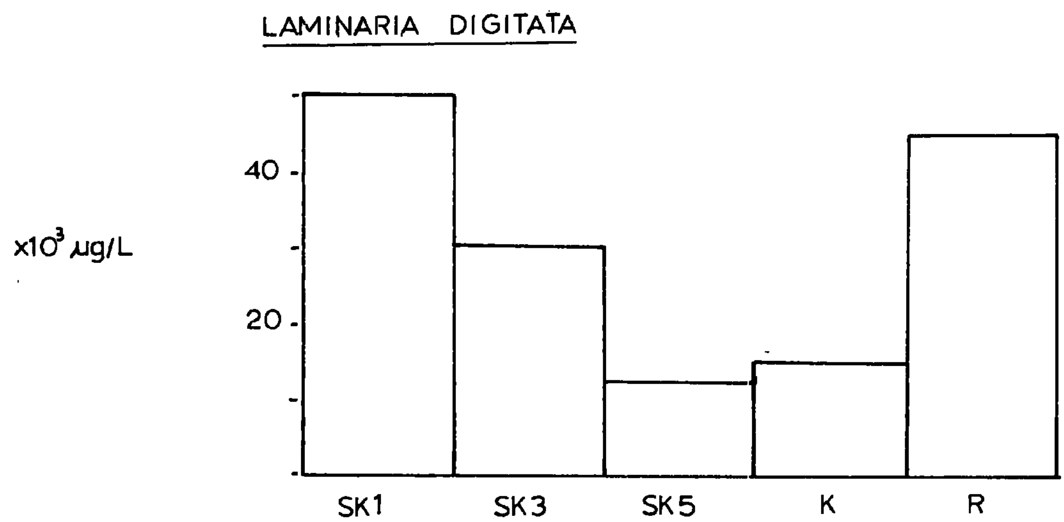
From consideration of the Beck as a possible source of additional lead, it is evident in Figure 53 , that upstream, the Beck has much higher lead levels, but these are drastically reduced where there are rapid increases in the iron oxide levels in the stream. The presence of particulate iron results in an increased precipitation of the river lead. A similar effect can be seen as the river passes into the sea. The Beck reduces the lead levels of the seawater for some distance off-shore. This is the result of direct dilution and increased precipitation due to high levels of particulate iron on to which the lead is adsorbed. Subsequently large amounts of lead are precipitated. It is likely, considering the consistently high levels of iron in the Back, that this is unimportant as a source of additional lead, and that it would probably generally have the reverse effect on seawater lead levels. From the evidence of lead levels in silt, and especially seaweed, it is reasonable to conclude that sewage waste is an important source of additional lead at Skinningrove. However, the iron concentration in the seawater of this area would limit the seawater concentration of lead and subsequently increase the silt levels by limiting the areal dispersion of the additional lead. This pattern is partly modified by the redistribution of the silt by tidal scouring. This point reflects the increased length of time since this outfall was a source of additional lead. No other heavy metal has its areal distribution of silt modified to the same extent.(See sections on copper and zinc). The lower lead levels of seawater and silt at Skinningrove Area 1, at the time of sampling, are a reflection of the fluctuation in the composition of the sewage waste, with periods of high and low concentrations of lead. Prior to sampling, the output over a considerable period of time, was of a low concentration, allowing the previously deposited silt to be partially redistributed. The seaweed results give a more accurate long term pattern. The reason for this is that seawater levels are modified by short term fluctuations in input sources, and silt levels can be modified by redistribution. Accumulations in seaweeds do not suffer from these two problems to the same extent. Perennial seaweeds, like <u>Laminaria digitata</u>, are useful monitors because of the cumulative non-regulatory nature of their uptake.

In Figure 53 ,the Beck, and the sewage outfall, both produced a dilutional effect on the seawater lead levels, and in this respect the Beck, with high concentrations of particulate iron, had a greater modificatory effect. From seaweed evidence, the sewage outfall acts over-all as a source of additional lead, and this produces the decrease in seaweed lead levels to the East at Skinningrove. (see Figure 55).

The distortions to the results considered previously, are also suggested to reduce the seawater and silt levels at Redcar. By comparison, the Kettleness lead levels in silt and seawater appear relatively high, but they cannot be considered abnormal for this section of the coast.

The relative proportions of lead, zinc, and copper in the Laminaria are Zn Pb Cu . This is different to the work carried out by Haig (1969) who studied the alginate affinity of divalent metals, and showed Pb > Cu > Zn . The problem of high zinc values has been noted also in the work of Bryan (1971), who indicated that consideration of alginate affinity did not apply to the uptake of zinc.

FIGURE 55. LEAD CONCENTRATIONS IN SEAWEEDS AT THE SAMPLE SITES.



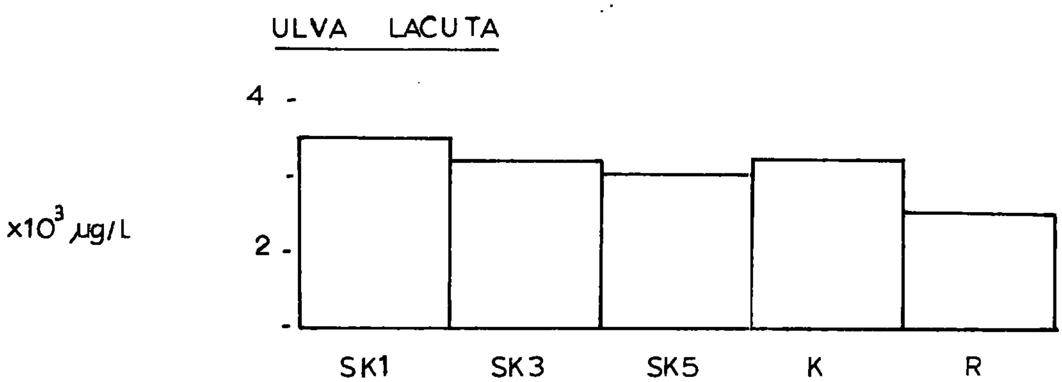
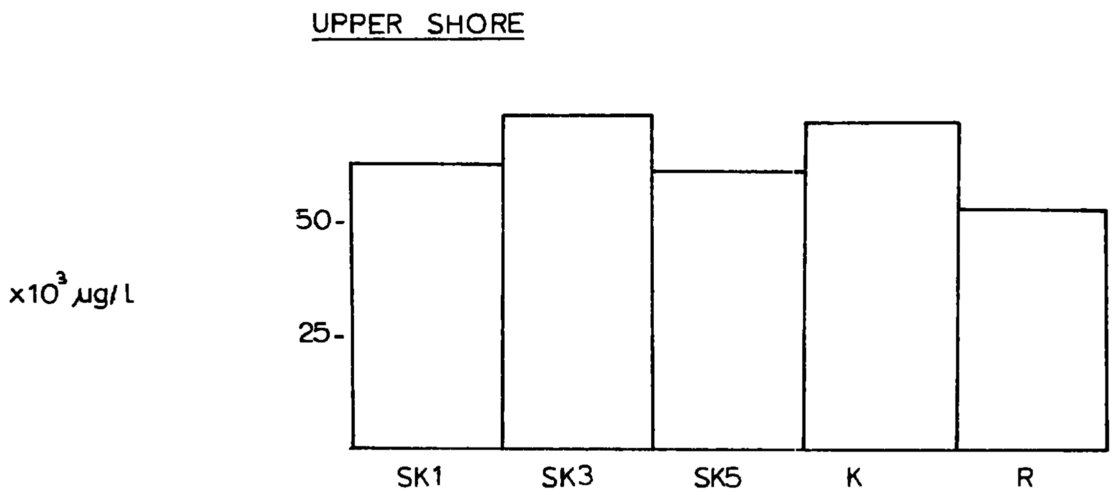


FIGURE 56. LEAD CONCENTRATIONS IN SILT AT THE SAMPLE SITES.



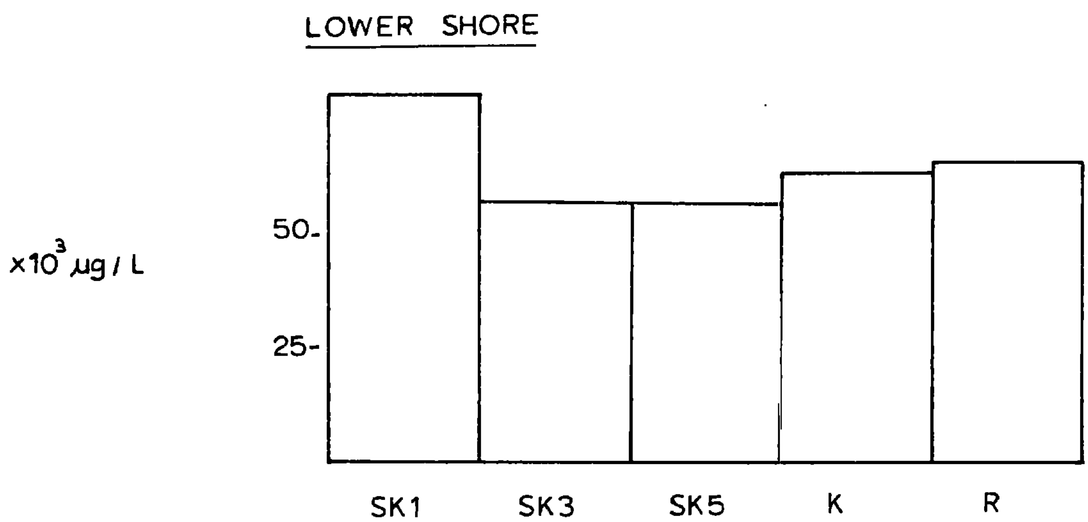
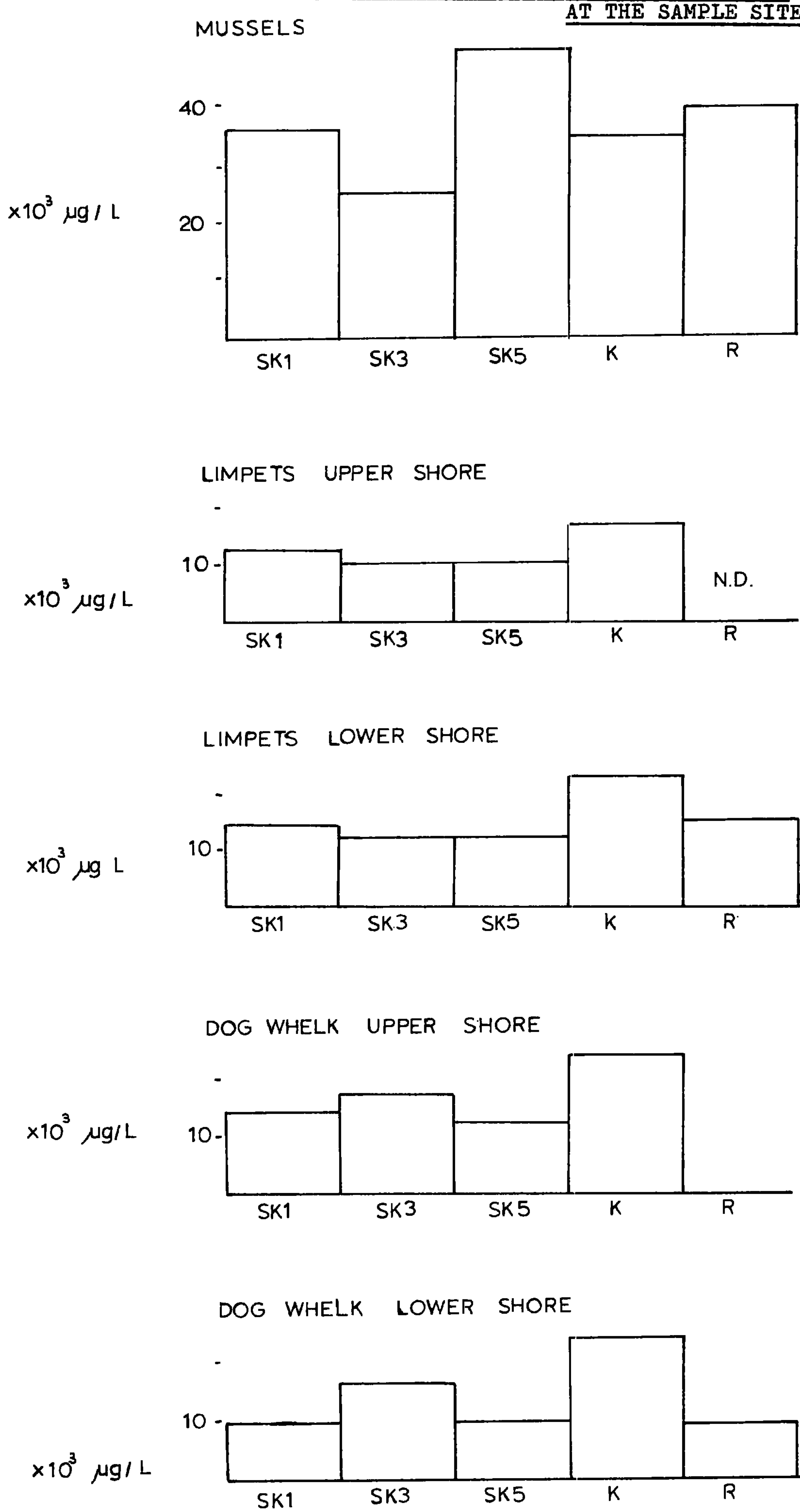


FIGURE 57. LEAD CONCENTRATION IN STIPE OF LAMINARIA DIGITATA.

Author	Lead concentration ug/l
Beharrell (1942)	1.0
Black & Mitchell (1952)	7 - 16 dry weight.

FIGURE 58. LEAD CONCENTRATIONS IN SELECTED MARINE ORGANISMS AT THE SAMPLE SITES.



The Ulva lactuca results in relation to variations in lead levels between sites, and relative proportions of these heavy metals, illustrate a similar pattern to that of Laminaria digitata, although lower concentrations are involved. This latter point may reflect the length of time in which accumulation could have taken place.

In comparison to the levels found by Black and Mitchell (1952), (see Figure 57), the Laminaria stipes in this study have generally a much higher lead concentration. Kettleness and Skinningrove Area 5 are very close to the values that they found for pollution free sites in Scotland. The higher values are consistent with the expected seaweeds cumulative, non-regulative, uptake of lead close to sewage sources.

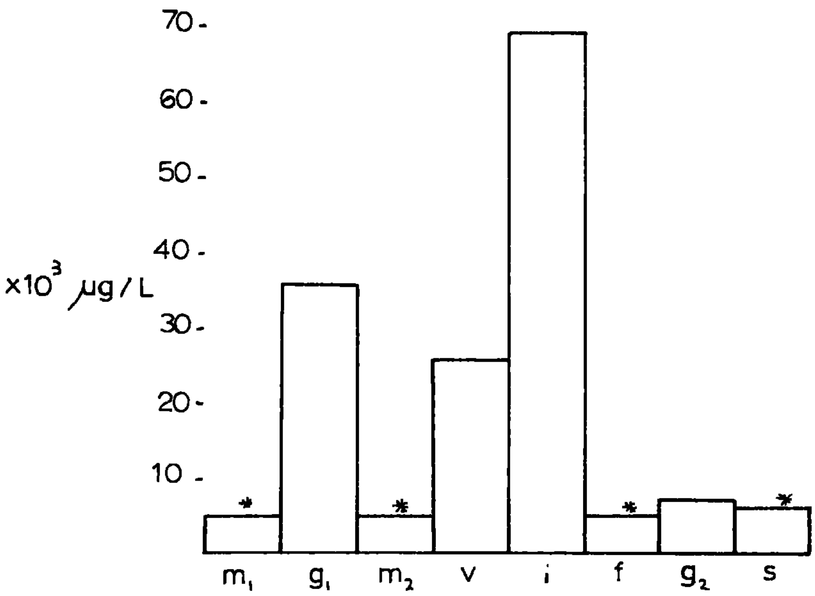
The silt levels of lead found by Bryan (1971), varied from 56,000 ug/l and 230,000 ug/l , while Brooks and Rumsby (1965), found less than 5,000 ug/l lead. For comparison the results of this study ranged from 55,000 ug/l to 82,000 ug/l lead. The variations are largely the result of the site characteristics; high values are associated with more estuarine conditions with high concentration being produced by additions from terrestrial sources, and lower values being associated with more marine conditions. In this respect, the values of this study are either unexpectedly high or low.

The levels of lead in dog-whelks and limpets are generally lower than those for seaweeds. This contrasts with the results for zinc, iron, and copper, where, with the exception of copper levels in limpets, the concentrations in these organisms is greater than those for seaweeds at the same sample site. These low lead levels in dog-whelks and limpets may either reflect their efficiency in excreting this element, or the length of time that excretion into seawater of low lead levels has been possible. Mussels, in contrast, have higher levels of lead (see Figure 58), than these two other organisms and, as has been suggested in other sections on heavy metals, may be more similar in their rate, mode of uptake, and their regulation, to the seaweeds than to the higher animals.

Variations between lead levels of the organisms at each sample site, reflect a more confused pattern than has been

FIGURE 59 . INTERNAL DISTRIBUTION OF LEAD IN MUSSELS.

(DATA FRIM BROOKS AND RUMSBY 1956)



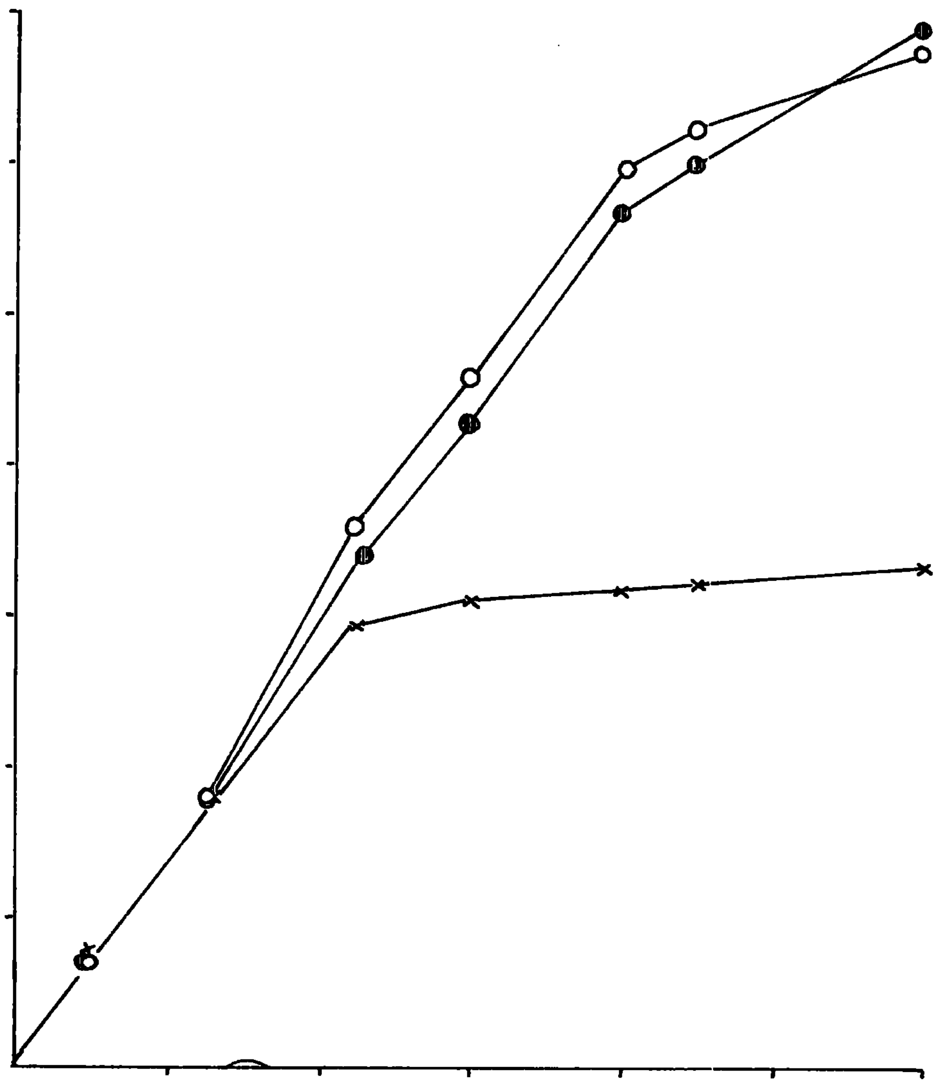
KEY

*	less than
m_1	mantle
g_1	gills
m_2	muscles
v	visceral mass
i	intestine
g_2	gonads
s	shell
f	foot

FIGURE 60 . FRACTIONAL FACTORS IN MUSSELS. (AFTER BROOKS & RUMSBY 1965)

Iron > zinc > lead > copper

FIGURE 61. EFFECT OF DIFFERENT CONCENTRATIONS OF LEAD ON PIECES OF LAMINARIA DIGITATA. (BRYAN 1971)



KEY.

● nearly 0 x 10 ug/l

○ 100 ug/l

× 500 ug/l

found for other heavy metals. The reason for this is related to the modifications that have occurred during this period of low lead discharge from the outfalls at Skinningrove and Redcar. Using the Laminaria digitata results as a base which is less subject to short term fluctuations, the other results do show varying degrees of modification of lead levels between sites. Further study is necessary to be able to understand these areal and temporal variations of lead levels, and whether or not animals of the same species have different excretion rates at different sites. The work of Clarke (1947) indicates this possibility with copper.

Brookes and Rumsby (1965) have analysed the distribution of lead in mussels, and this data is illustrated in Figure 59 . Again, a similar pattern to that of other heavy metals has been found. The high values of the visceral mass and intestine may be due to the inclusion of gut contents, and of gills, be due to contamination particles. This makes it difficult to explain the distribution unless the lead reflects high concentration at sites of uptake,-or excretion, or both. However, since lead is strongly basic it will readily co-ordinate with suitable organic ligands (see Figure 60). Lead is also toxic to the majority of enzyme systems studied so far, Brookes and Rumsby (1965). It seems unlikely that lethal levels of this element are reached, but more likely that lead has a sub-lethal effect by inhibiting growth. Copper and zinc are more likely to have significant effect in these respects, than lead.

In conclusion, the fluctuations in the lead sewage levels have caused marked modification in the pattern of lead levels at Skinningrove and Redcar. This makes it only possible to infer the pattern that would occur when there is a high lead output from the outfalls. Different rates of excretion between different species, and between animals of the same species at different sites, are difficult to quantify, and make it impossible to interpret more fully the data for lead. It is thought that lethal effects are less likely for lead than those for copper, but sub-lethal effect of lead can not be dismissed.

CONCLUSION.

The scope of this study has been purposely broad and although attempts have been made in sample site choice to minimize many of the abiotic variables, other than those related to man made waste, some variables in the field are difficult to measure and almost impossible to correct for. An increased period of observation would be necessary before it would be safe to assume that the differences in the rocky shore community were caused only by various pollution parameters. However, it is thought the major differences in these rocky shore communities are the result of the effects of the waste material.

The inter-site variation in the communities are characterised by a number of features. Firstly, the sites varied in total productivity, with the more polluted sites (close to the outfalls) having reduced productivity for *Laminaria digitata* and with increased productivity for *Mytilus edulis*. Secondly, the sites varied in species present and the diversity indices. A sub-lethal effect of heavy metals is reduction in performance, and this varies between species with resulting effects on the competitive balance in the community. At higher levels, the heavy metals would have a direct lethal effect on organisms. The thresholds vary between organisms. The local distribution of mussels and barnacles close to the outfall is thought to be controlled by copper concentrations in the seawater. Thirdly, variations in population structure indicates a number of ways that pollution parameters effect the organisms. Where uptake of heavy metals is by cumulative processes, the effects of the heavy metal would initially be sub-lethal, and then lethal in character. This is thought to be important in reducing the age span of *Laminaria* digitata population close to sewage outfalls. High concentrations of heavy metals could have a direct lethal effect on a specific age range of an organism, for example, the absence of young limpets may indicate such an effect at Skinningrove Area 1.

A breakdown of pollution into its component parts, like concentrations of individual heavy metals, has indicated that although levels of one metal may be important, the interaction between metals is critical at a number of different levels. At Skinningrove, the areal distribution of lead, zinc and copper in seawater was largely controlled by the levels of particulate iron in the water. At the organism level, the internal concentrations of lead, copper and iron were inter-related, and for some organisms followed the expected relative values, suggested by the work on alginate affinity. Further, at the toxic levels the interaction of heavy metals can have synergistic or antagonistic effects, although our knowledge is far from complete on this matter.

Except where there is other work available, it has proved difficult, using field evidence only, to be objective about the inter-relationship between biotic and abiotic components of this study. A number of inferential relationships can be deduced from the data. A longer period of study in the field and series of laboratory experiments on the biochemical aspects of uptake and toxicity of metals (singly or in multiples) would enable the writer to expand more on the causal relationships between pollutional parameters and ecological effects on the rocky shore.

Substances like heavy metals are non-biodegradable or breakdown is so slow that as a consequence there is a distinct risk of accumulation in some parts of the marine ecosystem. The frequent occurrence of sewage outfalls on rocky substrates amplifies the possibility of such risks in the rocky shore communities and considerable accumulations occur at Skinningrove and Redcar. Pollutants reduce the species diversity, simplify the ecosystems and short-circuit the energy flow through the communities. The addition of organic waste (in sewage) results in some instances in a change in the major energy source on the rocky shore. The waste provides energy in the form of chemical bonds and oxidisation of organic waste instead of photosynthesis dominates. This is certainly evident in the case of mussels close to the outfalls. The nutrient increase due to the sewage would be expected to increase productivity in areas previously limited in nutrient availability. However, in this study, the occurrance of poisons and toxic substances combined to sudden changes in salinity, oxygen content and pH, close to the outfall are thought to limit total production. Only the most tolerant species to all these environmental variations, like mussel, could be expected to show any marked increase in productivity. However, this would largely be controlled by the magnitude of each of the variables likely to cause sub-lethal effects. A wider study would be necessary to determine precisely the extent and magnitude of this widespread sub-lethal effect. The resilience of some animal populations to pollutional stress indicate the importance of consideration of the rate of turnover of individuals, and hence the age and size distribution rather than the size of the standing crop.

The introduction of toxic waste combined to other environmental stresses on the rocky shore communities have the effect of eliminating species. This effect can be due to a direct lethal effect or a reduction in competitive ability due to a reduction in performance and subsequent elimination. The loss of species could be expected to have ramifications higher up the food chain and subsequent further reduction in diversity. Limpets may be an example of this, as it is possible that they may be able to regulate uptake of possible toxic materials, but these some toxic materials could still cause their elimination, by the removal of their food sources. There are many problems still to be solved.

It is possible that inter-tidal sands act as a sewage filter bed and each of the sample sites have sand beaches to the North of them. The effect of pollution at Redcar may be lower than would be expected considering the total amount of waste dumped into the sea there. The reason could lie in the larger areas of sand evident around that sample site. This may reduce the effect despite an increase in sand scouring which has a similar effect to those of pollution. (Russel, 1971).

A possible interesting application of this point would be to require local authorities to pipe their raw effluent below low water spring tide level on sandy shores rather than on rocky shores. However, little work has been done on the relative effects of sewage on these two intertidal habitats.

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