NGU Report 95.028
Distribution of Heavy Metals in the
Brown Alga, Ascophyllum nodosum along
the fjords of the Trondheim Region,
Norway

REPORT

Report no.: 95.028		ISSN 0800-3416		Grading: Open			
Title:			14-00				
Distribution of Heavy N	Metals in the Bro	own Alga, As	cophy	llum nodosum alo	ng the fjords of the		
Trondheim Region, No							
Authors:			Client	:			
W.E. Sharp			NGU, NTNF and University of South Carolina				
County:			Commune:				
Nord-Trøndelag, Sør-T	røndelag and						
Møre og Romsdal							
Map-sheet name (M=1:250.000))		Map-sheet no. and -name (M=1:50,000)				
Trondheim, Kristiansur	nd and Ålesund						
Deposit name and grid-reference	e:		Numb	er of pages: 56	Price (NOK): 80		
			Map e	nclosures:			
Fieldwork carried out:	Date of report:	1	Projec	t no.:	Person responsible:		
1976 - 1977	03.01.1995		15	45	D. B_4		
Summary:							

A regional heavy-metal survey of the Trondheim (1:500 000) map sheet was carried out using seaweed as a sample medium. No values elevated above that explainable as regional background were observed for ash, Mo, Pb, Hg or As. Analyses were also performed for Ca, Na, and F but are not reported here. Significant variations in Zn, V, Cd, Co, Cu, Mn and Fe were observed; elevated values usually being associated with the mouths of the major river systems suggesting an excess of these elements is being supplied by fresh water. Elevated values of Ni and V show an areal distribution dependent on the rock substrate while very high values of Zn and Cu appear to be derived from mine wastes along the Orkla river. No individual element seems to be diagnostic of incoming sea water. Recommendations are made for follow-up surveys of Ag and V in Halsafjord, V in Aafjorden, and U on Hitra.

Although the initial impetus for this survey was for prospecting the region for metallic ore deposits, it would appear that, because of extensive mining in the past, the method is better suited for monitoring heavy-metal contamination, establishing regional backgrounds, and defining chemically distinct water masses within fjord systems.

Keywords: Geokjemi	Tungmetaller	Tang
		Fagrapport

AN ODE TO SEAWEED

Tang

Jeg så deg på stranden. Du var lite menneske i bikini og der du gikk ble du bare mindre og mindre i billedrammen mens jeg satt og så på tang, tang i strandkanten duvende med sine blaerer i vanntaket. duvende av de minste bølgeslag mot land, som et svaiende tre oppad begrenset til vannspeilet, et surkl-surkl liv med vann som vind i treets grener å jo, ting foregår, ting foregår hele tiden, plastikkposer og karamell papir, drivende kanner og plankebord, en uryddet strand, slik strender er, i dag, ting foregår, selv etter at du har begynt å vandre tilbake til huset, selv etter at jeg, solbrent og mutt, følger samme vei, tangen ligger i stranden og surkler (for nå bare å snakke om tangen, for nå å utelukke alt annet enn tangen), tangen ligger der stadig, ja også nå, i skrivende stund, etter at vi forlengst har flyttet ut av sommerhuset, også nå, i lyttende stund, som vi alle er i ferd med å flytte ut av tangdiktet - å ja surkl under sommer sol, surkl under vinterstjerner, surkl surkl surkl.

Jan Erik Vold

Copyright 1968, reproduced by permission Gyldendal Norsk Forlag [Oslo] from Mor Godhjertas glade versjon. Ja. also on Philips compact disk with Briskeyby blues.

Seaweed

I saw you on the strand. a little creature in bikini and as you walked onward you got smaller and smaller inside the picture frame while I sat looking at the seaweed, seaweed at the edge of the beach quivering with its bladders on the surface. quivering with the slightest shoreward wash of wave, like a swaying tree its height bounded by the water-level. a slooursh - slooursh existence with water instead of wind in the branches of the tree - oh yes, things happen, things do happen all the time, plastic bags and caramel wrappers, floating cans and boards, a cluttered beach, as beaches tend to be nowadays, things happen, even after you have started walking back to the house, even after I, sunburnt and peevish, go the same way, the seaweed lies along the shore and sloourshes (to speak now only of seaweed, to ignore everything but seaweed), the seaweed is still lying there, yes even now, as I write, long after we have left the summer house, even now as you listen, when we are leaving this seaweed-poem - oh yes slooursh under summer sun, slooursh under winter stars, slooursh slooursh slooursh.

Colleagues

PREFACE

This work was carried out while the author was on sabbatical leave from the University of South Carolina during the academic year 1976-77. The stay in Norway was generously supported by a post-doctoral fellowship from the Royal Norwegian Council for Scientific and Industrial Research (NTNF). The suggestion for the study and inspiration for undertaking it was derived from Bjørn Bølviken who acted as my sponsor during my stay with the geochemical section at the Norwegian Geological Survey (NGU). Since my stay was only for the academic year, a distinct advantage of this particular project was that the field work could readily be carried out during the winter months. The field work was generously supported and analytical facilities were provided by the Geological Survey with the endorsement of the section leader, Aslak Kvalheim. I received much advice and help with the many questions I had on seaweed from Professor Jenssen and Mr. Eide in the Institute for Marine Biochemistry at the Norwegian Technical University (NTH). I am grateful for the hard work of Gunnar Næss, Tore Volden, and Kirsti Buvarp who carried out the atomic absorption analyses for the heavy metals, Asbjørn Flårønning who performed the uranium analyses, Mr. Arnold Kuldvere who performed the analyses for arsenic, Messers Kuldvere and Andreassen who performed the mercury analyses, and Frederik Wolff who supplied the geological map for the Trondheim region. I would also like to thank Klaas Zwaan for suggesting the Norwegian ode to seaweed and to Klaas Zwaan, Tor Erik Finne, and Arthur Clayborough (UNIT) who rendered it into English.

W.E. Sharp
6 October 1978
Revised 8 March 1990
Updated 15 September 1997

CONTENTS

1. RECOMMENDATIONS	7
2. INTRODUCTION	7
3. SAMPLING	9
3.1 Sample Medium	9
3.2 Sample Design	10
3.3 Sampling Plan	12
3.4 Sample Site Variance	12
3.5 Sample Collection and Preparation	13
4. ANALYTICAL METHOD AND RESULTS	15
5. PRECISION AND BACKGROUND MEAN	21
5.1 Precision from Probability Paper	21
5.2 Background Mean from Probability Paper.	22
6. STATISTICAL AND REGIONAL DISTRIBUTIONS	23
6.1 Ash	25
6.2 Molybdenum	27
6.3 Lead	29
6.4 Mercury	31
6.5 Arsenic	33
6.6 Uranium	35
6.7 Nickel	37
6.8 Cobalt	39
6.9 Manganese	41
6.10 Silver	43
6.11 Iron	45
6.12 Copper	47
6.13 Zinc	49
6.14 Vanadium	51
6.15 Cadmium	53
7. DISCUSSION	54
8 REFERENCES	EE

TABLES

Table 1	•		nitudes of Rivers entering fjords of the Trondheim Region,	10
Table 2	,	Norway	ysis of Ascophyllum nodosum from the Trondheim Region,	12
Table 2	•			17
T-61- 2			tal analysis of Assayla Home and assays	
Table 3			tal analysis of Ascophyllum nodosum	
Table 4	-		n of the Heavy Metal Content of Ascophyllum nodosum	
Table 5	٠.	Median Heavy M	etal content of Ascophyllum nodosum	20
FIGUE	RES			
Figure	1.	Index map of I	Norway showing the Trondheim 1:500 000 map sheet	8
Figure	2.	View of Ascor	phyllum nodosum showing the typical branching pattern	
_		of the shoots		10
Figure	3.		the river and fjord magnitudes for the Trondheim region	
Figure	4.		p of the Trondheim region	
Figure	5.		the sample sites used in the Trondheim regional study	
Figure	6.1a	Ash	- Dot Map	
0	6.1b		- Probability Plot	
Figure	6.2a	Molybdenum	- Dot Map	
8	6.2b	1.101,000	- Probability Plot	
Figure	6.3a	Lead	- Dot Map	
8	6.3b	22444	- Probability Plot	
Figure	6.4a	Mercury	- Dot Map	
8	6.4b	11101041	- Probability Plot	
Figure	6.5a	Arsenic	- Dot Map	
1 15410	6.5b	1 H Seine	- Probability Plot	
Figure	6.6a	Uranium	- Dot Map	
1 15010	6.6b	Oramani	- Probability Plot	
Figure	6.7a	Nickel	- Dot Map	
riguic	6.7b	TVICKCI	- Probability Plot	
Figure	6.8a	Cobalt	Dallfan	20
riguie	6.8b	Cobait	-	
Figure	6.9a	Managanaga	- Probability Plot	
riguie	6.9b	Manganese	- Dot Map	
Eiguro		Cileron	- Probability Plot	
Figure	6.10a		- Dot Map	
Eigen	6.10b		- Probability Plot	
Figure	6.11a		- Dot Map	
Ei	6.11b		- Probability Plot	
Figure	6.12a	* *	- Dot Map	
T.	6.12b		- Probability Plot	
Figure	6.13a		- Dot Map	
r:	6.13b		- Probability Plot	
Figure	6.14a		- Dot Map	
	6.14b		- Probability Plot	
Figure	6.15a		- Dot Map	
	6.15b	ı	- Probability Plot	53

1. RECOMMENDATIONS

The seaweed survey of heavy-metals for the Trondheim region has uncovered a number of anomalous values which warrant further investigation.

- a. Overbank sediments should be collected, analysed, and special attention paid to the the following heavy metals:
 - 1. Vanadium on the Norddal and Stordals rivers in Aafjorden.
 - 2. Molybdenum on the Skaua river (Rissa) in the Trondheim fjord.
 - 3. Cobalt-vanadium on the Surna river in Surnadal fjord.
 - 4. Copper-vanadium on the Driva river in Sunndal fjord.
 - 5. Molybdenum on the Eira river at Eresfjord (Langfjord).
- b. Prospecting for silver and vanadium including soil and lithogeochemistry should be carried out on on Bølia Mountain adjacent to Halsa fjord.
- c. A gamma-ray survey for uranium on Hitra should be made by vehicle along all roads and by boat along the shore-line.

Additional studies are needed to determine the optimal distance from fresh water sources to sample in a prospecting program, the extent to which suspended particulates are adsorbed onto the seaweed, the influence of the local substrate, and if other important heavy metals are accumulated in seaweed.

2. INTRODUCTION

A regional survey of the heavy metal content of the surface waters of fjords would be valuable in determining the extent of natural regional differences and contamination caused by waste disposal. Such knowledge in recent years is of increasing importance not only to mineral resource evaluation but in settling law suits that have been brought to protect the coastal fisheries from the effects of modern industry. In the absence of specific knowledge as to actual natural and regional distribution of contamination and whether these are changing, these suits will be difficult and expensive to resolve.

A useful and direct estimate of heavy metal content of actual surface waters is difficult to obtain, but as suggested by Haug et al. (1974, p. 180), seaweed might be a useful sampling medium because a close correspondance between the metal content in seaweed and the metal content of seawater should be expected. That indeed seaweed could be utilized in this manner for heavily contaminated areas was demonstrated by Haug et al. (1974, p. 185, 188) in the Trondheim and

Hardanger fjords. From Haug's early results (1972, p. 198-206), the idea arose that analyses of seaweed might be used in the search for mineral deposits. This possibility was investigated for a number of mineral deposits by Lysholm (1972), who showed the presence of high heavy metal content in the vicinity of several known deposits and whose results suggested the feasiblity of undertaking regional surveys. A related study by Bollingberg (1975) demonstrated the utility of seaweed for prospecting in an uncontaminated area of Western Greenland.

As a result of these earlier studies, it seemed certain that differences in the heavy metal content in the surface waters of fjords will appear as differences in the heavy metal content of seaweed and that seaweed could be used as a sampling material for regional geochemical mapping. To demonstrate this, a regional survey of the heavy metal content of seaweed from fjords in the Trondheim area was undertaken (Fig. 1).

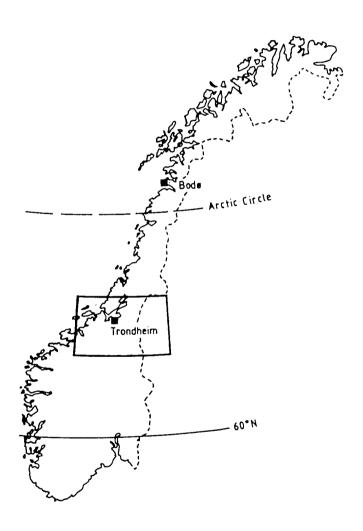


Figure 1. Index map of Norway showing the Trondheim 1:500 000 map sheet

3. SAMPLING

If accurate regional mapping of the distribution of heavy metal contents of seaweed is to be used for comparison with future studies and with other regions of Norway, careful attention must be paid to the specific species, the pattern of sample sites, the local sample site variance, the sample collection, and its preparation for analyses.

3.1 Sample Medium

If seaweed is to be used successfully in a sampling program, it must be common and dense, easy to collect and have well known growth characteristics. All of these requirements are clearly met by the common brown alga, Ascophyllum nodosum. A. nodosum (Fig. 2) is a common brown alga occurring not only in Norway but on both sides of the Atlantic from 40°N latitude to 70°N (Baardseth 1970, p. 2.2). It occurs in the littoral zone from slightly above the mid-tide level down to just above extreme low water (Baardseth 1970, p. 2.1). It is most abundant along protected gently sloping shores and requires rocky beaches or large stable stones for attachment (Baardseth 1970, p. 2.1, 2.3). It has a wide tolerance for temperature and salinity (Jorde & Klavestad 1963, p. 61), but cannot resist heavy wave action (Baardseth 1970, p. 2.3) nor strong ice scraping (Printz 1957, p. 14). Except where the water is quiet, it does not occur along vertical cliffs. It is commonly associated with the other brown alga, Fucus vesiculosus. In places of heavy growth of A. nodosum, F. vesiculosus becomes rare, but when salinities drop too low or where wave action is strong, then F. vesiculosus becomes the dominant littoral species. Higher up in the littoral zone, these two species are replaced by Fucus spiralis while below in the sublittoral zone, they are replaced by Fucus serratus (Jorde & Klavestad 1963, p. 30, 31). As all four of these species have a wide occurrence (Jorde & Klavestad 1963, p. 54), any one of them could have been chosen as a sampling medium. Because of its wider range of occurrence F. vesiculosus should be carefully considered as an alternative sample medium in future studies.

A distinct advantage of A. nodosum over F. vesiculosus is the ease with which age in the plant and any of its parts maybe determined; this lends itself well to studies of developmental or seasonal effects (Baardseth 1970, p. 1.8) and this property was used to determine the fixation of zinc (Skipnes et al., 1975). A. nodosum grows in the form of branched shoots without fronds. At regular intervals along the shoots, air bladders are formed (Fig. 2). These shoots and bladders undergo a definite seasonal development (Baardseth 1970, p. 1.7, 1.8; Printz, 1959). The air bladders begin to grow in February and March and are completed in April at which time the shoot begins to extend itself. In June, the shoot bifurcates and continues to grow into August-September. This sequence repeats itself annually and a simple count of the air bladders gives the age of each shoot. During April, fertile receptacles sprout on the sides of the shoot, ripen in May, and then are shed in June.

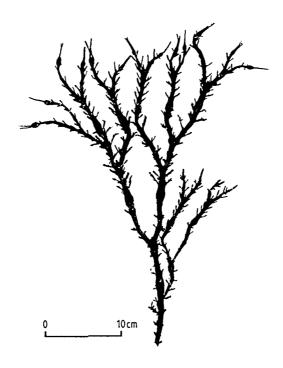


Figure 2. View of Ascophyllum nodosum showing the typical branching pattern of the shoots.

3.2 Sample Design

The most prolific growth of seaweed occurs along the shores in the intertidal zone. This is an area influenced most by the brackish surface waters formed by the mixing of river water with seawater and this floats on the denser oceanic salt water. Normally, the excess fresh water run off produces a net surface flow from the head of the fjord toward the entrance (Duxbury 1971, p. 242; Braarud 1975, p. 11). For sampling design, the fjord as a first approximation may be treated as if it is a very wide river and as an extension of the rivers feeding into the fjord in which case the concept of river "magnitude" (Scheidegger, 1965; Shreve, 1967, p. 179) can be applied not only to the rivers but to the fjords as well. The determination of the magnitude first requires that each "fingertip" or source river shown on a map of specified scale be assigned a magnitude of one. Then a magnitude can be assigned to each section of river downstream of any fork by assigning to it a magnitude equal in sum to the magnitudes of the two sections of river upstream of a fork. Where a river enters a fjord, it can be assumed to continue toward the entrance of the fjord along the center line of the fjord (Fig. 3) and side rivers can be assumed to come in and to flow straight out to the center line of the fjord. Although this is a very simplistic view of the surface circulation in a fjord, it does permit a rapid estimate of the total fresh water input inland from any point along the fjord. This magnitude can be be called the "fjord magnitude".

Once magnitudes have been assigned (Fig. 3), a sampling plan based on successive halving of the magnitude can be designed similar to that for rivers (Sharp, 1971). However, experience shows this plan to be inconvenient because of the truncation in magnitude which occurs wherever a river enters the fjord. Rivers entering fjords can be divided by counting into two groups (Table 1):

first, a group consisting of a large number of small rivers and secondly a group consisting of a small number of very large rivers. A noticeable gap separating the two groups occurs for rivers between a magnitude of 25 and 43. The initial design was prepared to ensure sampling near the mouths of all rivers having a magnitude of 32 or greater. Later this value was halved to 16 to include more of the smaller fjords. Then to ensure that the accumulative effect of small rivers and the effects of dispersion were accounted for, the selected magnitude was incremented along the fjord. Finally, to provide for the great width of fjords when compared to rivers, paired sample sites were taken on opposite sides of the fjord at each selected magnitude. Pairing the samples gave control on erratic values and on the effects of circulation.

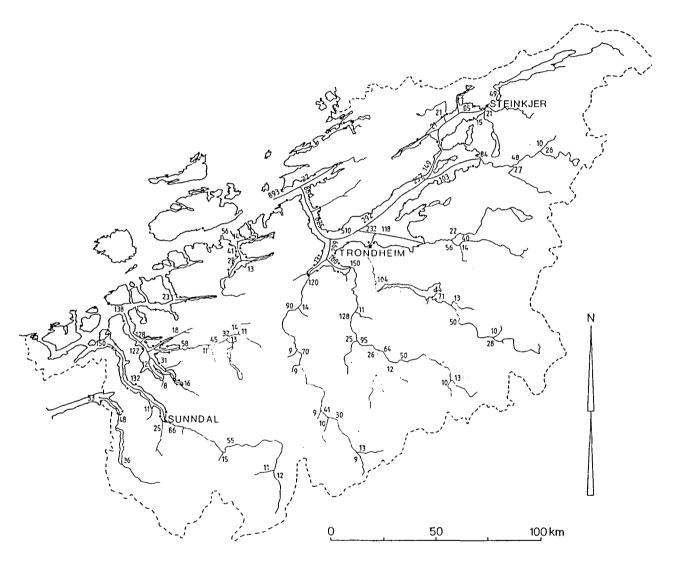


Figure 3. Map showing the river and fjord magnitudes for the Trondheim region.

3.3 Sampling Plan

The actual sampling plan for the Trondheim (1: 500 000) map sheet was obtained by assembling and then outlining on the 1:250 000 drainage maps of the Trondheim region, all of the river basins so that the river magnitudes could be obtained and then extending these as fjord magnitudes (Fig. 3). For each river having a magnitude of 16 or greater, paired sampling sites were marked on the map as close as practical to each river but beyond the actual river delta. Additional paired samples were taken along the fjord wherever the fjord magnitude had increased by a magnitude of 16 or more from the previous sample site (Fig. 3 - small dots; also Fig. 5).

Table 1. Number and Magnitudes of the Rivers entering Fjords of the Trondheim Region, Norway (map scale 1: 500 000)

Rivers	of Low	Mag	nitude
--------	--------	-----	--------

Magnitude	Number	Magnitude	Number
1	101	9	1
2	24	10	1
3	12	11	2
4	10	12	1
5	8	13	0
6	4	14	0
7	3	15	3
8	4	16	0

Magnitudes of the 13 remaining individual Rivers

18	84
21	86
22	89
25	113
43	120
58	150
70	

3.4 Sample Site Variance

In order that analytic results can be compared from one place to another, it is important to minimize the variance within the local sample site. This variance was estimated in a preliminary survey taken of 16 individual shoots (A. nodosum) spaced so that the variance associated with separations of zero, one, three, and five meters as well as combinations of these could be tested. For whole plants cut at the hold fast, it was found that for several elements, averages of 4 plants gave reproducible averages, but for other elements, an average of 8 plants was required.

Subsequently, it was pointed out (Eide, 1976) that whole plants cut at the base may have been broken and regrown from the stump, so that the basal parts might be quite old and the tops very young. To reduce any variance from this source in the actual survey, only complete, unbroken shoots having a minimum of 4 bladders were selected. To further reduce the possibility of variance all lateral shoots and receptacles were removed.

Work at the Institute of Marine Biotechnology at the Norges Tekniske Høgskole in Trondheim has shown that cut shoots of an age of three years give heavy metal values close to those obtained when whole plants are cut at the hold fast (Eide & Myklestad, 1976). In addition their figures show that averages of cut shoots consisting of the first and third internodes give heavy metal contents close to that of the second internode (Haug et al., 1974, p. 183). Thus, cut shoots consisting of the first, second, and third internodes can be used to obtain reliable estimates of the heavy metal content in these plants.

3.5 Sample Collection and Preparation

Seaweed sampling for the Trondheim region was carried out during the dormant winter months: October, November, February, and early March. As long as the fjord is not actually covered with ice, seaweed could always be collected. Only in a couple of the smaller fjords was any problem with ice encountered. The biggest restriction during the winter months was the lack of daylight. Useful collecting during the monthly tidal cycle was limited in November through February to a 6 day period around the twice monthly, noon day, low tide. Cold temperatures were not a problem but did require rubber boots with thermal socks for the feet and woolen thermal gloves inside of rubberized cotton gloves for the fingers.

As A. nodosum is a mid-littoral zone seaweed, it is well exposed during the three hours before and after low tide. This permits sampling on foot along the shore while traveling between sites can be done by car or by boat. In an area with reasonable access from the road, 4 to 8 reconnaissance samples can be collected during a 6 hour low tide period. Access to the shore when using a car was not difficult as the roads typically follow the coast line. Starting in January sufficient snow had accumulated that it was helpful and in one specific case imperative to carry along a pair of snowshoes. Skis were of no value because of the steep slopes and short distances to the shore line. Ice along the shore can be a problem, but in most cases there was sufficient snow for safe walking. However, it was always wise to carry in ones pocket a pair of 'isbrodden' which can be strapped on over a pair of boots and these allowed easy walking even on absolutely shear ice. From a boat 8 to 12 reconnaissance samples can be collected during an 8 hour period, the extra time is gained if the first and last samples are collected from a row boat.

Keeping in mind that A. nodosum prefers sloping, protected, rocky sites, favorable sample locations are readily selected from topographic maps. At the selected site, the area of most luxuriant growth was chosen and then three replica samples were taken. One for analysis of the ash, a second for analysis of volatiles such as mercury, and a third as a back up for estimation of sample variance or to confirm high or erratic results.

Samples at each site were collected using a bar bell pattern. This consisted of a total of 8 shoots taken in a fixed pattern relative to the shore line. The bar bell pattern consisted of two squares with one meter sides aligned parallel to the shore and separated by 5 meters. One shoot, having a minimum of 4 bladders, was plucked at each corner of each square. This ensured that each individual shoot came from individually separate holdfasts.

On cold days, it was necessary to knead the seaweed so as to loosen and separate the frozen shoots. The shoots are resilient and do not break as easily as one might suppose. In areas where strong waves can pound the shore, the plants may be badly broken so that it is difficult to find continuous shoots of more than 2 years duration. In the heads of the fjords where ice forms in cold winters, entrapment in the ice can tear up the seaweed as the tides rise and fall. This is particularly true in the upper portions of the growth zone. Excessive fresh water makes the A. - nodosum fragile, so that even minor ice or wave action can break the plants. In practice, only a minority of sample sites had plants so badly damaged that shoots of desired age could not be obtained.

After plucking, the shoots were placed into clear plastic sample bags, then the bag was tagged, twisted closed, and the end folded over and wrapped with a rubber band. To prevent rotting, samples not cut within 24 hours must be stored in a refrigerator. On short field trips, the samples were brought to the laboratory, but on long trips the samples were cut in the field camp. Each plant was cut with a scissors at the base of the fourth bladder and at the top just below the first bladder to obtain a single clean shoot consisting of the first, second, and third internodes (Fig. 2). Finally all of the side shoots and receptacles were trimmed off.

Generally, the shoots were quite smooth and clean looking, however, in some localities it was necessary to remove attached materials. In areas of abundant fresh water, the green algae - - Entermorpha (Jorde & Klavestad 1963, p. 31) were attached and could not be removed. Otherwise, attached growths such as Polysiphonia fastigiaba or the mollusc - Mytilus edulis were cut off. The air bladders were cut open to prevent "popping" during ashing and to ensure that no sand or mollusc were inside. After cutting, the shoots were rinsed in metal free water or sea water and allowed to dry at room temperature. Once dried the samples can be kept in clear plastic bags until ready for analysis. A total of 8 dried shoots prepared in this way yielded the necessary one gram after ashing for the analyses.

4. ANALYTICAL METHOD AND RESULTS

Dried seaweed shoots were ashed in porcelain trays overnight at 425°C. The ash was cooled in a desiccator and homogenized in an agate mortar. One gram of ash was digested in 5 ml. of 6 M. nitric acid for 3 hours at 110°C. After dilution to 20 ml. and settling, the solution was decanted through a nylon cloth with a 20 micrometer mesh. The elements V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, and Pb were determined in the supernatant liquid using standard atomic absorption spectrophotometry. Uranium was determined in the ash using fluorimetry. The analytical results were calculated back to and expressed as concentrations in unashed, air-dried samples of A. - nodosum (Table 2).

The analyses for mercury and arsenic were performed by methods specifically developed for this project by Kuldvere and Andreassen (1979). The dry seaweed samples were wet ashed by digesting 0.4 g for mercury or 0.1 g for arsenic in a 5 per cent 2:3 mixture of nitric and sulfuric acid. The wet ashing was first performed at room temperature, then on a water bath, and followed by a short period of heating at higher tempertures. Once in solution, the samples to be analysed for mercury were reduced by stannous chloride and the mercury analysed by cold vapor atomic absorption spectrophotometry (Kuldvere and Andreassen 1979). The samples to be analysed for arsenic were added to a 4 per cent hydrochloric acid solution followed by the addition of a 5 per cent sodium borohydride solution to generate arsine which was then analysed by atomic absorption spectrophotometry (Kuldvere 1980).

The chemical analyses for the trace metals in dry *Ascophyllum nodosum* from 72 locations (Fig. 5) with the corresponding geology (Fig. 4) from the Trondheim region are summarized in Table 2. Also included are analyses of seaweed from four exposed coastal locations (Table 3). To estimate sample and analytical error, replica analyses of samples from Østmarkneset adjacent to the survey's laboratory, and a bulk sample from the seaweed factory at Brønnøysund were determined (Table 3). The standard deviations of the replicas for all elements except As and Hg were computed and reported (Table 4).

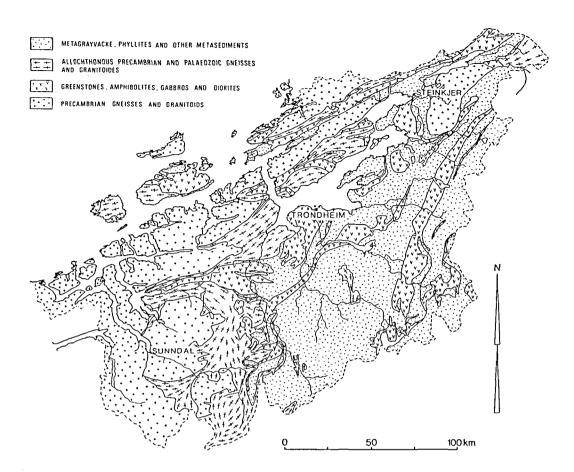


Figure 4. Geological map of the Trondheim region.

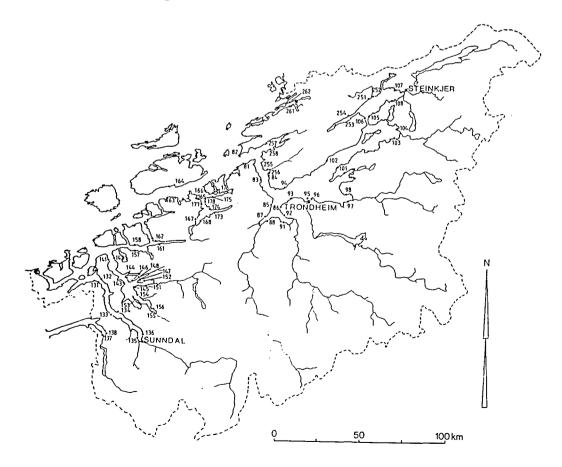


Figure 5. Map showing the sample sites used in the Trondheim regional study.

Table 2. Heavy metal analysis of Ascophyllum nodosum from the Trondheim region, Norway (ppm of dry plant tissue).

Sample	Ash (%)	V	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Hg	Pb	U
81	18.54	1.9	12.4	37.1	2.4	2.6	9.3	63.0	18.	0.6	0.26	0.43	0.023	1.9	0.28
82	17.07	2.4	12.0	34.1	2.6	3.1	12.2	76.8	24.	0.7	0.31	0.41	0.018	2.2	0.24
83	17.55	1.8	11.1	10.5	2.5	3.2	17.2	87.8	22.	0.5	0.33	0.40	0.015	1.9	0.37
84	18.41	2.2	13.1	18.2	2.6	3.5	16.2	100.3	23.	0.6	0.31	0.46	0.020	1.8	0.29
85	17.80	3.2	11.9	25.5	2.9	3.6	40.1	218.9	18.	0.4	0.27	0.46	0.014	1.8	0.28
86	19.59	3.7	18.4	34.3	3.3	3.9	42.7	242.9	18.	0.6	0.35	0.51	0.016	2.4	0.24
87	19.28	2.7	14.5	29.1	3.3	2.9	75.2	300.8	18.	0.4	0.29	0.48	0.012	2.1	0.21
88	18.74	4.3	13.7	73.1	3.4	3.0	251.0	496.6	22.	0.4	0.30	0.71	0.017	2.3	0.22
91	18.61	4.7	14.7	26.8	3.5	6.0	89.3	414.0	22.	0.4	0.28	0.56	0.015	2.6	0.28
92	19.30	4.6	15.4	73.3	2.5	4.1	41.1	270.2	21.	0.6	0.29	0.60	0.013	2.3	0.33
93	18.63	2.4	13.6	21.8	2.8	4.3	28.0	154.6	18.	0.4	0.28	0.35	0.015	2.1	0.30
94	18.19	2.2	12.7	33.8	2.4	3.5	13.6	91.0	22.	0.7	0.29	0.36	0.022	2.0	0.31
95	17.23	2.4	12.8	20.3	2.6	6.0	25.0	199.0	-	0.5	0.34	0.62	-	2.1	0.38
96	19.96	4.8	21.6	117.8	2.0	4.4	15.4	628.7	15.	0.6	0.42	0.44	0.028	3.2	0.28
97	18.34	4.8	10.1	22.7	2.4	4.4	11.6	123.8	24.	0.4	0.37	0.44	0.012	2.4	0.28
98	18.19	5.1	11.8	49.1	2.7	4.2	10.9	115.5	22.	0.4	0.31	0.51	0.013	2.7	0.27
101	18.29	2.4	13.4	13.5	2.2	4.8	9.0	83.2	25.	0.6	0.33	0.44	0.018	2.0	0.37
102	17.81	2.1	9.6	11.2	1.8	3.6	8.2	49.9	23.	0.5	0.28	0.36	0.017	2.0	0.28
103	18.37	2.4	11.4	48.7	2.8	4.2	5.1	46.8	22.	0.4	0.31	0.42	0.024	2.2	0.33
104	17.92	3.1	11.5	44.8	3.2	4.5	5.9	71.7	20.	0.5	0.30	0.52	0.028	2.3	0.39
105 106	16.95 16.74	2.0 1.8	8.3	13.8	2.2	4.4	2.9	39.8	20.	0.5	0.29 0.27	0.44	0.028 0.023	2.4	0.27 0.17
100	19.96	3.2	11.7 15.0	32.6 40.9	2.2 3.0	3.7 5.8	2.7 3.6	36.0 62.8	21. 21.	0.3 0.4	0.27	0.39 0.54	0.023	2.0 2.2	0.17
107	17.52	2.3	11.2	22.8	2.1	3.8 3.7	3.0	44.2	18.	0.4	0.30	0.34	0.030	2.2	0.28
131	16.99	4.3	9.3	22.8 14.4	2.1	2.9	3.0 2.6	51.0	36.	0.4	0.23	0.33	0.023	1.7	0.21
131	17.31	3.5	9.3	11.8	2.4	2.6	2.4	54.5	33.	0.5	0.24	0.40	0.022	2.3	0.27
132	17.12	5.5	11.0	39.0	2.4	2.7	3.3	53.1	35.	0.5	0.23	0.47	0.025	1.9	0.23
134	18.17	7.3	12.2	71.8	2.5	2.2	4.0	104.5	28.	0.6	0.17	0.47	0.023	2.2	0.21
135	19.11	10.1	19.1	46.4	3.8	3.3	8.8	127.1	42.	0.8	0.40	1.11	0.038	2.9	0.22
136	14.51	9.0	12.7	25.6	2.9	2.6	7.7	100.1	48.	0.4	0.10	0.77	0.035	2.5	
137	17.53	6.7	8.9	27.4	1.9	1.8	5.6	125.3	39.	0.9	0.25	0.44	0.036	2.5	0.28
138	19.44	12.8	11.3	26.8	2.1	2.3	3.5	62.2	44.	0.8	0.29	0.64	0.024	2.7	
141	17.31	2.8	9.0	23.0	1.9	1.7	1.7	34.6	40.	0.4	0.23	0.38	0.027	2.4	0.26
142	18.57	3.9	16.2	37.2	2.2	2.0	2.0	54.8	38.	0.7	0.22	0.37	0.026	2.4	0.26
143	18.98	5.7	8.7	10.6	1.9	2.3	1.7	37.0	35.	0.4	0.27	0.38	0.024	2.9	0.30
144	18.74	7.1	10.9	13.7	1.9	2.3	2.6	43.1	37.	0.4	0.32	0.43	0.026	2.8	0.26
145	19.07	6.5	8.2	13.4	2.3	2.5	2.7	36.2	37.	0.4	0.40	0.48	0.024	2.5	0.27
146	19.91	10.2	13.5	20.1	2.4	2.0	2.6	59.7	37.	0.4	0.52	0.40	0.024	2.8	0.24
147	17.96	5.2	7.7	15.1	2.0	2.0	1.4	35.9	33.	0.2	0.23	0.41	0.021	2.3	0.20
148	18.23	5.3	8.6	20.6	2.2	1.8	2.0	39.2	29.	0.4	0.22	0.42	0.025	2.0	0.15
151	18.64	8.0	11.0	26.7	3.2	3.2	2.4	66.2	34.	0.4	0.30	0.56	0.020	2.4	0.19
152	19.28	9.5	13.5	39.1	3.9	2.5	4.2	90.6	35.	0.4	0.29	0.62	0.027	2.5	
153	18.27	4.2	8.2	28.0	2.0	1.6	1.3	34.7	31.	0.4	0.26	0.38	0.027	2.4	0.18
154	18.77	5.6	8.8	16.5	1.9	1.9	1.3	44.1	35.	0.4	0.26	0.39	0.025	1.9	0.19
155	17.78	6.2	10.0	36.5	2.1	2.1	2.0	56.0	34.	0.4	0.23	0.52	0.027	2.1	
156	18.92	11.7	17.4	49.4	3.4	3.2	3.2	70.0	34.	0.4	0.32	0.78	0.026	2.8	
157	17.30	2.1	7.1	16.8	1.6	1.7	1.2	32.0	38.	0.5	0.26	0.35	0.025	2.1	0.26
158	17.02	1.2	9.0	13.8	1.5	2.0	1.7	37.4	39.	0.5	0.22	0.36	0.021	2.2	0.12
161	18.01	2.2	10.1	12.3	2.2	2.3	1.3	41.4	41.	0.5	0.29	0.41	0.018	2.5	0.29
162	17.52	1.4	7.4	8.8	1.9	1.9	1.4	32.4	44.	0.4	0.26	0.46	0.021	2.6	0.33
163	18.25	1.8	10.4	15.5	1.8	2.2	1.6	51.1	42.	0.6	0.27	0.47	0.018	2.6	0.42

Table 2, continued.

Sample	Ash (%)	V	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Hg	Pb	U
164	16.71	1.5	8.5	7.0	1.8	2.3	1.5	48.5	41.	0.7	0.23	0.40	0.017	2.5	0.62
165	18.04	1.4	7.8	10.1	1.6	2.0	1.6	37.0	42.	0.5	0.22	0.38	0.019	2.0	0.22
166	17.93	1.1	8.3	10.2	1.8	1.6	1.6	36.8	41.	0.7	0.23	0.39	0.018	2.3	0.39
167	18.38	2.6	8.8	12.9	1.7	2.0	2.0	47.8	40.	0.6	0.26	0.44	0.017	2.0	0.20
175	16.95	1.7	6.1	14.1	1.9	1.7	1.7	36.4	41.	0.5	0.25	0.42	0.021	2.4	0.29
176	16.75	1.7	10.4	25.6	2.0	1.8	1.3	45.2	43.	0.5	0.27	0.42	0.022	2.5	0.20
177	17.61	1.9	7.4	10.0	1.4	1.9	1.8	35.2	37.	0.5	0.23	0.42	0.017	2.1	0.25
178	17.63	1.9	9.5	11.5	1.9	2.1	2.1	40.6	39.	0.5	0.26	0.49	0.017	2.3	0.28
251	16.22	2.0	7.1	15.4	1.8	2.6	2.1	46.1	26.	0.5	0.18	0.44	0.020	1.6	0.23
252	17.95	1.8	9.3	18.9	2.3	2.7	3.1	59.4	28.	0.4	0.22	0.41	0.014	1.8	0.25
253	17.02	2.2	7.7	23.0	1.9	2.4	2.2	56.2	26.	0.5	0.26	0.44	0.021	1.5	0.27
254	17.22	1.7	5.7	15.0	1.7	2.1	2.2	40.3	21.	0.3	0.26	0.40	0.018	1.7	0.21
255	16.50	2.8	13.7	37.3	2.1	3.0	12.5	94.1	32.	0.8	0.23	0.43	0.017	2.3	0.26
256	17.49	2.6	13.8	46.2	2.5	3.3	12.4	98.8	22.	0.9	0.21	0.44	0.023	1.9	0.24
257	18.96	1.9	13.3	18.8	2.3	2.5	12.9	106.2	38.	8.0	0.27	0.46	0.026	1.9	0.36
258	16.72	1.7	10.0	19.4	2.2	2.7	12.9	81.1	31.	8.0	0.23	0.35	0.015	1.8	0.27
261	18.07	16.6	16.4	45.2	2.9	3.1	2.0	79.5	34.	0.9	0.25	0.52	0.020	1.8	0.27
262	18.02	12.3	13.5	52.3	2.7	3.1	2.0	66.7	31.	0.5	0.23	0.47	0.020	2.0	0.27
168	18.18	2.9	11.1	36.4	2.0	2.0	2.6	52.7	33.	0.4	0.24	0.51	0.021	2.2	0.18
173	18.53	1.9	9.1	16.5	1.7	2.2	2.4	61.2	40.	0.6	0.24	0.39	0.019	2.4	0.20
174	17.53	2.3	8.1	11.8	1.8	1.9	2.3	48.2	46.	0.5	0.26	0.46	0.017	2.5	0.37

Notes:

- (1) Analyses were also performed for Ca, Na and F Analytical reports 82/77 and 7/77.
- (2) Cd, V, Pb, Ag, Cu, Co, Ni, Fe, Mo, Zn, Mn were analysed by AA Analytical report 142/76.
- (3) Hg and As were wet ashed and then analysed by AA Analytical report 66/77.
- (4) U was analysed by fluorometry Analytical report 72/77.

Table 3 Replica heavy metal analysis of Ascophyllum nodosum in ppm of dry plant tissue

-ump.u	Ash (%)	V	Mn	Fe	Co	Cu	Ni	Zn	As	Mo	Ag	Cd	Hg	Pb	U
150	18.27	3.7	14	46	2.4	16.6	3.3	221	-	0.4	0.31	0.47	-	2.9	0.20
159	17.61	4.4	12	43	2.3	15.4	3.2	204	-	0.5	0.28	0.37	-	3.0	0.20
169	18.04	4.0	11	49	1.8	17.1	2.5	198	-	0.5	0.31	0.41	-	3.1	0.20
180	17.75	4.4	11	47	2.5	18.6	3.2	206	-	0.4	0.28	0.46	-	3.2	0.21
199	17.72	6.9	14	60	2.5	19.1	3.0	234	-	0.5	0.25	0.37	-	2.5	•-
210	18.14	6.2	13	53	2.7	16.9	3.6	229	-	0.5	0.29	0.40	-	2.4	*-
219	18.10	6.3	13	53	2.5	18.3	2.9	243	-	0.9	0.31	0.51	-	2.9	•
259	16.75	4.7	12	48	2.0	15.7	3.4	214	-	0.7	0.23	0.39	-	2.0	0.20
Factor	y at Brøi	nnøys	sund (Coarse	e fragi	nents)									
Sample	Ash (%)	V	Mn	Fe	Co	Cu	Ni	Zn	As	Mo	Ag	Cd	Hg	Pb	U
149	21.20	4.2	15	102	2.1	2.1	3.6	49	-	0.6	0.32	0.78	-	3.2	0.28
200	20.06	6.6	15	100	2.2	2.0	3.4	50	-	0.6	0.30	0.68	-	2.4	
209	20.20	6.1	14	107	2.2	1.8	3.0	49	-	0.8	0.24	0.69	-	2.4	
220	20.83	5.2	16	106	2.5	1.9	3.1	54	-	0.8	0.31	0.74	-	2.9	
224	21.72	4.8	13	272	2.0	4.3	3.3	50	-	0.4	0.30	0.65	-	3.7	0.33
230	20.27	4.9	15	180	1.8	2.0	3.0	47	-	0.4	0.26	0.71	-	2.8	0.39
237	20.38	5.1	17	224	2.2	2.4	3.9	52	-	0.6	0.33	0.79	-	3.7	
Factor	y at Brør	ınøys	sund (1	Fine fr	agme	nts)									
	A =1- (0/)	X 7	Mn	Fe	Co	Cu	Ni	Zn	As	Mo	Ag	Cd	Hg	Pb	U
Sample	ASII (%)	V	14111	10	Cu										_
Sample 130	20.54	v 4.7	11	17					_	0.6	0.29	0.51	-	2.2	
_					2.9 1.8	3.1 2.0	3.5 2.2	60 47	-	0.6 0.8	0.29 0.30	0.51 0.64	-	2.2 2.8	0.41 0.34
130	20.54	4.7	11	17	2.9	3.1	3.5	60						2.2 2.8 3.7	0.41
130 140	20.54 20.22	4.7 4.2	11 15	17 89	2.9 1.8	3.1 2.0	3.5 2.2	60 47	•	0.8	0.30	0.64	-	2.8	0.41 0.34
130 140 160	20.54 20.22 20.36	4.7 4.2 3.7	11 15 15	17 89 104	2.9 1.8 2.2	3.1 2.0 2.6	3.5 2.2 3.5	60 47 50	-	0.8 0.6	0.30 0.33	0.64 0.71	-	2.8 3.7	0.41 0.34 0.31
130 140 160 170	20.54 20.22 20.36 20.52	4.7 4.2 3.7 3.3	11 15 15 13	17 89 104 85	2.9 1.8 2.2 1.6	3.1 2.0 2.6 2.1	3.5 2.2 3.5 2.5	60 47 50 45	-	0.8 0.6 0.6	0.30 0.33 0.31	0.64 0.71 0.65	- - -	2.8 3.7 2.5	0.41 0.34 0.31 0.33
130 140 160 170 179	20.54 20.22 20.36 20.52 20.27	4.7 4.2 3.7 3.3 4.3	11 15 15 13 16	17 89 104 85 130	2.9 1.8 2.2 1.6 2.6	3.1 2.0 2.6 2.1 2.3	3.5 2.2 3.5 2.5 4.1	60 47 50 45 53	-	0.8 0.6 0.6 0.8	0.30 0.33 0.31 0.28	0.64 0.71 0.65 0.87	- - -	2.8 3.7 2.5 3.4	0.41 0.34 0.31 0.33 0.32
130 140 160 170 179 229 260	20.54 20.22 20.36 20.52 20.27 20.21 20.01	4.7 4.2 3.7 3.3 4.3 3.8 4.6	11 15 15 13 16 13	17 89 104 85 130 113 104	2.9 1.8 2.2 1.6 2.6 1.8 2.4	3.1 2.0 2.6 2.1 2.3 1.8 2.0	3.5 2.2 3.5 2.5 4.1 2.6 3.0	60 47 50 45 53 45 44	-	0.8 0.6 0.6 0.8 0.6	0.30 0.33 0.31 0.28 0.24	0.64 0.71 0.65 0.87 0.67	- - -	2.8 3.7 2.5 3.4 2.4	0.41 0.34 0.31 0.33 0.32 0.30
130 140 160 170 179 229 260 Expose	20.54 20.22 20.36 20.52 20.27 20.21	4.7 4.2 3.7 3.3 4.3 3.8 4.6	11 15 15 13 16 13	17 89 104 85 130 113 104	2.9 1.8 2.2 1.6 2.6 1.8 2.4	3.1 2.0 2.6 2.1 2.3 1.8 2.0	3.5 2.2 3.5 2.5 4.1 2.6 3.0	60 47 50 45 53 45 44	-	0.8 0.6 0.6 0.8 0.6	0.30 0.33 0.31 0.28 0.24 0.24	0.64 0.71 0.65 0.87 0.67		2.8 3.7 2.5 3.4 2.4	0.41 0.34 0.31 0.33 0.32 0.30
130 140 160 170 179 229 260 Expose Sample	20.54 20.22 20.36 20.52 20.27 20.21 20.01 ed Coasta Ash (%)	4.7 4.2 3.7 3.3 4.3 3.8 4.6	11 15 15 13 16 13 13 ations Mn	17 89 104 85 130 113 104 (Haug	2.9 1.8 2.2 1.6 2.6 1.8 2.4	3.1 2.0 2.6 2.1 2.3 1.8 2.0	3.5 2.2 3.5 2.5 4.1 2.6 3.0 p. 19 0 Ni	60 47 50 45 53 45 44 Zn	- - - - -	0.8 0.6 0.6 0.8 0.6 0.8	0.30 0.33 0.31 0.28 0.24 0.24	0.64 0.71 0.65 0.87 0.67 0.64	- - - - -	2.8 3.7 2.5 3.4 2.4 2.0	0.41 0.34 0.31 0.33 0.32 0.30 0.28
130 140 160 170 179 229 260 Expose Sample	20.54 20.22 20.36 20.52 20.27 20.21 20.01 ed Coasta Ash (%) 21.34	4.7 4.2 3.7 3.3 4.3 3.8 4.6 V 1.3	11 15 15 13 16 13 13 ations Mn 9.8	17 89 104 85 130 113 104 (Haug	2.9 1.8 2.2 1.6 2.6 1.8 2.4 Co 1.7	3.1 2.0 2.6 2.1 2.3 1.8 2.0 , 1974, Cu 10.9	3.5 2.2 3.5 2.5 4.1 2.6 3.0 p. 19 0 Ni	60 47 50 45 53 45 44 0) Zn	-	0.8 0.6 0.8 0.6 0.8 Mo	0.30 0.33 0.31 0.28 0.24 0.24	0.64 0.71 0.65 0.87 0.67 0.64		2.8 3.7 2.5 3.4 2.4 2.0	0.41 0.34 0.31 0.33 0.32 0.30 0.28
130 140 160 170 179 229 260 Expose Sample	20.54 20.22 20.36 20.52 20.27 20.21 20.01 ed Coasta Ash (%)	4.7 4.2 3.7 3.3 4.3 3.8 4.6	11 15 15 13 16 13 13 ations Mn	17 89 104 85 130 113 104 (Haug	2.9 1.8 2.2 1.6 2.6 1.8 2.4	3.1 2.0 2.6 2.1 2.3 1.8 2.0	3.5 2.2 3.5 2.5 4.1 2.6 3.0 p. 19 0 Ni	60 47 50 45 53 45 44 Zn	- - - - -	0.8 0.6 0.6 0.8 0.6 0.8	0.30 0.33 0.31 0.28 0.24 0.24	0.64 0.71 0.65 0.87 0.67 0.64	- - - - -	2.8 3.7 2.5 3.4 2.4 2.0	0.41 0.34 0.31 0.33 0.32 0.30 0.28

⁰ Vardø - 11/15/52 Institutt for marin biokjemi, NTH

¹ Ingøy - 02/09/52 2 Reina - 30/09/57 5 Espevaer - 01/10/52

Table 4. Standard Deviation of the Heavy Metal Content of Ascophyllum nodosum

	Slope of Proba	bility Graphs	Replica
	Trondheim Region	Tosen Fjord (2)	Analyses
V	0.80	0.80	0.8
Mn	1.3	1.3	1.3
Fe	20.0	20.0	5.3
Co	0.38	0.33	0.3
Ni	0.34	0.34	0.34
Cu	1.10	0.60	0.9
Zn	10.0	10.0	6.0
As	5.0	-	-
Mo	0.16	0.16	0.16
Ag	0.04	0.03	0.03
Cd	0.05	0.05	0.05
Hg	0.005	0.005	-
Pb	0.32	0.50	0.54
U	0.05	-	0.04

⁽²⁾ Sharp and Bølviken 1979.

Table 5. Median Heavy Metal Content of Ascophyllum nodosum in ppm of dry Plant Tissue

Element	Trondheim region (1)	Tosen Fjord (2)	Brown Algae Summary (3)
V	2.52	3.2	2
Mn	9.7	9.0	53
Fe	22.0	22.0	690
Co	2.20	2.3	0.7
Ni	2.30	2.7	3
Cu	2.80	1.3	11
Zn	50.0	50.0	150
As	24.0	=	30
Mo	0.51	0.45	0.45
Ag	0.265	0.24	0.28
Cď	0.44	0.48	0.4
Hg	0.022	0.0275	0.03
Pb	2.20	2.3	8.4
U	0.27	-	-

^{1.} This Work

^{2.} Sharp and Bølviken, 1979

^{3.} Bowen, 1966, p. 68, 69

5. PRECISION AND BACKGROUND MEAN

A direct estimate of precision can be made from the three sets of replica analyses that were randomly interspersed with the regularly analysed samples. These consisted of replicas sampled adjacent to the survey offices at Østmarkneset and samples obtained from the seaweed factory at Brønnøsund which consisted of fine or coarse fragments (Table 3). The values of the standard deviations calculated from these replicas (Table 4) represent a direct estimate of the sample-analytical precision.

5.1 Precision from Probability Paper

An indirect estimate of precision can also be made, as was discovered during this study, by the use of normal probability paper. An important feature of this graph paper is that the slopes on the graph correspond to the standard deviation of a normal distribution. However, in order to position the slope properly on the paper, the analyses were sorted in descending order and the median value (Table 5) obtained from the list and plotted. Then the expected slope for the probability graph was obtained from the standard deviation of the sample-analytical precision (Table 4) and this was plotted on the paper (not shown in the figures presented later) by recalling that one standard deviation on each side of the median (50 percentile) corresponds to the 16th and 84th percentiles. Next, the 5 per cent confidence bounds were calculated and plotted about this line. To complete the probability graph for an individual element, the values from the 72 sample sites (Table 2) that had been previously sorted in descending order were plotted on the normal probability paper according to their rank percentile. Examination of all the plots (i.e. Figs. 6.1b - 6.15b) shows that virtually all of the values less than the median when plotted on a properly prepared probability graph fall within the 5 per cent confidence bounds and furthermore, the observed slope for these values corresponds closely with the slope obtained directly from the standard deviation for the sample-analytical precision (Table 4). A similar feature is also shown in the probability plots of the heavy metals from Tosen fjord (Sharp and Bølviken, 1979, p. 353 -355). This offers in the case of seaweed, an alternate method for estimating the sample-analytical precision when direct estimation is not available from analysed replicas.

Specifically, when no direct estimate of the sample-analytical precision is available, the slope of those values less than the median when plotted on normal probability paper will give a reasonable estimate of the sample-analytical precision. For example, in this study no direct estimates for the sample-analytic precision were available for mercury or arsenic, however the slope for the right tail on normal probability graphs for these elements (Figs. 6.4b and 6.5b) yield estimates of 0.05 ppm for mercury and 5 ppm for arsenic. For comparison, similar estimates were made from the probability graphs for all the other elements both in the Trondheim and Tosen fjords. The agreement (Table 4) between the precisions estimated using slopes obtained from the probability graphs and direct estimates from replica analyses are excellent. Only the element Fe shows any significant discrepancy.

5.2 Background Mean from Probability Paper.

All values falling within the 5 per cent confidence bounds were accepted as simply the result of variation in sampling or in analysis; values falling outside these bounds would be taken as representing anomalous variations beyond sample precision. If the values which have values greater that the 5 per cent confidence bounds are considered anomalous, they cannot be used in the estimation of the average heavy-metal content of the background. It can be observed that in most of the graphs that the median lies within the confidence bounds, thus the median is a reasonable measure for estimating the mean background. The probability paper gives a way of differentiating anomalously high values from the general background. Thus the median is the proper measure for estimating the mean of the regional background and the values for each element have been tabulated in table 5. Once the background mean has been determined, it can be subtracted from the observations and the difference used in coding maps so that they clearly show the location of elevated heavy-metal concentrations (cf. Sharp and Bølviken, 1979).

Inspection of the probability plots for ash, Mo, Pb, and Hg (Figs. 6.1b, 6.2b, 6.3b, and 6.4b) suggests that the majority of samples for these elements have variation simply due to sample-analytical precision. In the case of Mo, the observed values are so close to the scale of the instrument that the values fall on the lattice of integral read-out values. Values falling beyond the confidence bounds thus should not be considered significant. Only at a few sites did the observed values fall outside the 5 per cent bound but not beyond the 1 per cent bound and such sites would need to be resampled to determine if they are indeed due to real variation. In these cases the mean and the median correspond quite closely and there is no question that the median is the proper estimator for the regional background.

In contrast, the probability plots for copper and zinc (Figs. 6.12b and 6.13b) have very anomalously high values which are known to be the result of waters rich in copper and zinc entering the Trondheim fjord from the Orkla river. To estimate the regional background, these anomalously high values must be ignored. Again the median falls within the 5 per cent confidence bounds and represents the best estimate of the mean for the regional background. The validity of this estimator is supported by the close correspondence with the median obtain from Tosen fjord (Table 5) which is in an isolated region with no mining or other industrial activity.

6. STATISTICAL AND REGIONAL DISTRIBUTIONS

To interpret the results, analyses for each element were plotted first on normal probability paper. This was done to evaluate the sample-analytical precision (Table 4) and to estimate, using the median, the regional background mean (Table 5). The probability graphs of the elements segregate themselves into two groups. Those in which the majority of the samples show variation simply due to sample-analytical precision. These are represented by ash, Mo, Pb, Hg, and probably As and U (Figs. 6.1b to 6.6b). The remaining elements Ni, Co, Mn, Ag, Fe, Cu, Zn, V, and Cd have probability graphs which show anomalously high values relative to the median and the 5 per cent confidence bounds. The only exceptional graphs are Mo and As. In the case of Mo, the observed values are so close to the scale of the instrument that the values fall on the lattice of integral read-out values and none of the values falling beyond the confidence limits can be considered significant. In the case of arsenic, the probability graph consists of two normal distributions with the same slope. This difference is the result of analysing the samples as two separate batches on two different dates. This batch effect is clearly visible as low values along the Trondheim fjord (Fig. 6.5a).

The probability graphs and the median estimated from the graphs were then used in selecting from among a series of 11 sequentially proportioned dots which could be used to show the relative heavy-metal concentrations. The value for each element was plotted using this series of proportional dots to represent the relative concentrations on a drainage basin map prepared from the Trondheim 1:500 000 map sheet. The values used for selecting the dots, starting with the smallest, were as follows: (1) 100 to 84 %, (2) 84 to 60 %, (3) 60 to 33 %, (4) below 33 %. For percentiles below 33 %, the median was multiplied by the following coefficients: (5) 2.74, (6) 3.84, (7) 5.38, (8) 7.53, (9) 10.54, (10) 14.76, and (11) 20.66. This scaling permitted even copper, with the widest range in variation, to be plotted. By this method of display, simple visual inspection allows one to quickly see the regional distribution of each element.

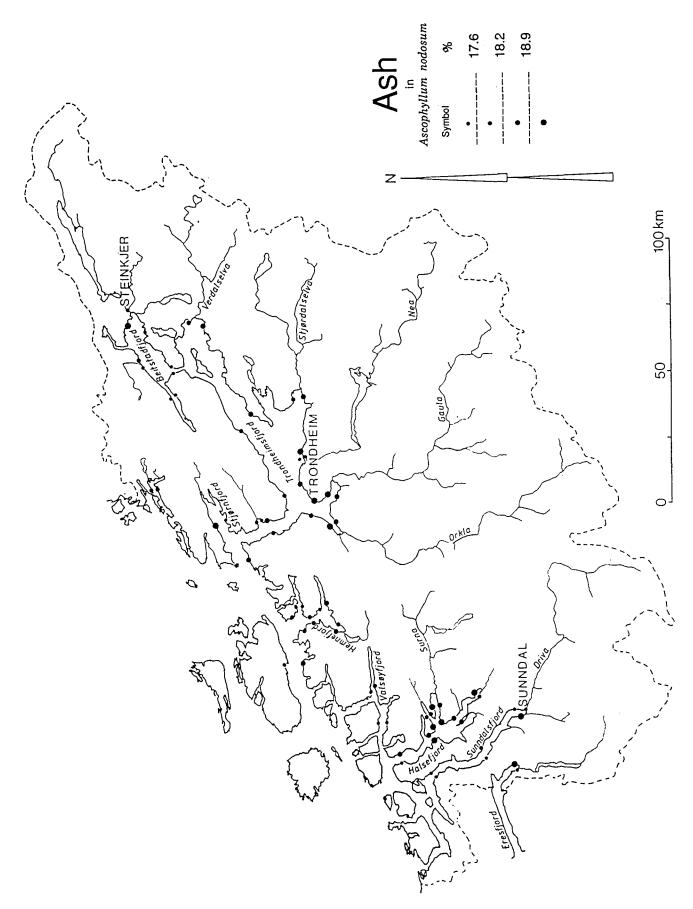


Fig. 6.1a Ash contents in samples of Ascophyllum nodosum in the Trondheim region

6.1 Ash

The accumulative distribution of ash is normally distributed with respect to the sample-analytical error with a median value of 18 per cent. Inspection of the map indicates a slight clustering of high values in Surnadal fjord and west of Trondheim. Comparison with the geological map (Fig. 4) suggests that slightly elevated ash values may be associated with gneisses and granites.

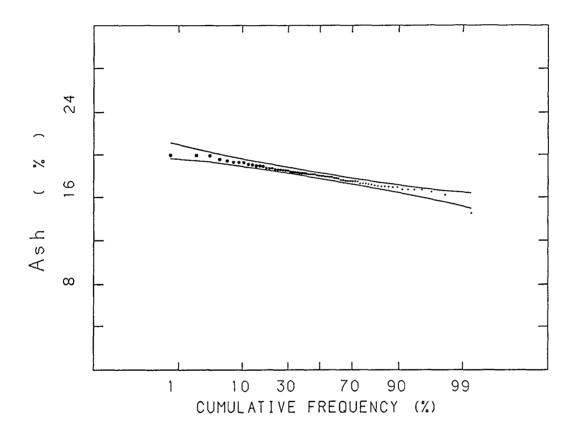


Figure 6.1b Normal Probability Plot: Ash in Ascophyllum nodosum in the Trondheim Region.

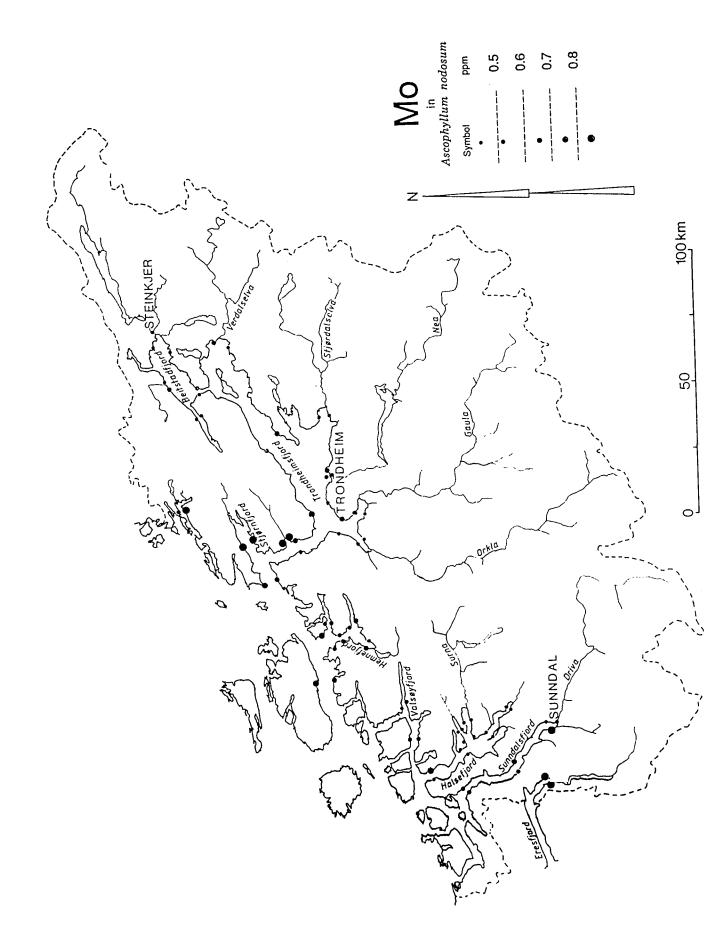


Figure 6.2a Molybdenum concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.2 Molybdenum

The observed values of molybdenum are so close to the limits of analytical detection and the measuring scale of the instrument that the values fall on the lattice of integral read-out values. This gives rise to the lattice like appearance of the normal probability plot. Values falling beyond the 5 per cent confidence should not be taken as anomalous. The median observed value was 0.5 ppm. Highest values were observed at the head of Eresfjord, Sunndalsfjord, and the outer part of the Trondheim fjord. Earlier work on Tosen fjord (Sharp and Bølviken, 1979) had suggested elevated Mo values might be associated with incoming sea water but this could not be confirmed in the present investigation.

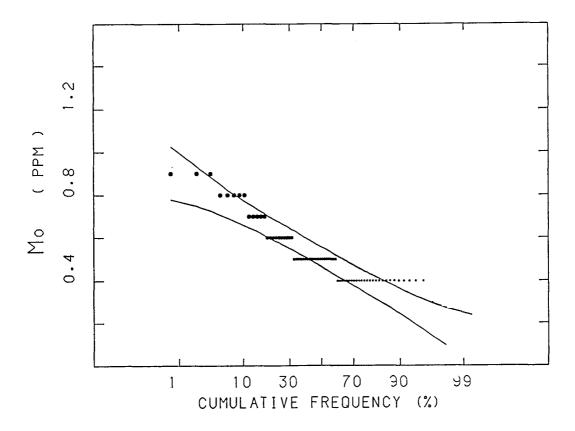


Figure 6.2b Normal Probability Plot: Mo in Ascophyllum nodosum in the Trondheim Region.

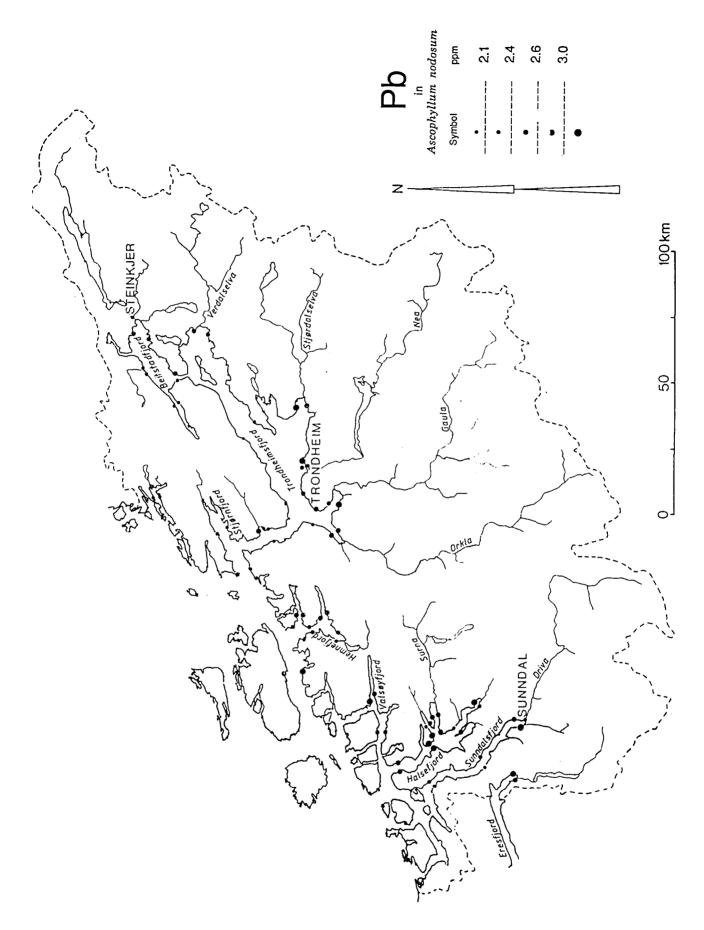


Figure 6.3a Lead concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.3 Lead

The accumulative distribution for lead is normal with a median value of 2.2 ppm and indicates no anomalous values. This is in marked contrast to the higher values and the occurrence of anomalous Pb values found in Tosen fjord (Sharp and Bølviken, 1979). Slightly elevated values of Pb do seem to be associated with the granitioids (Fig. 4) draining into Eres, Sunndal, and Surnadal fjords.

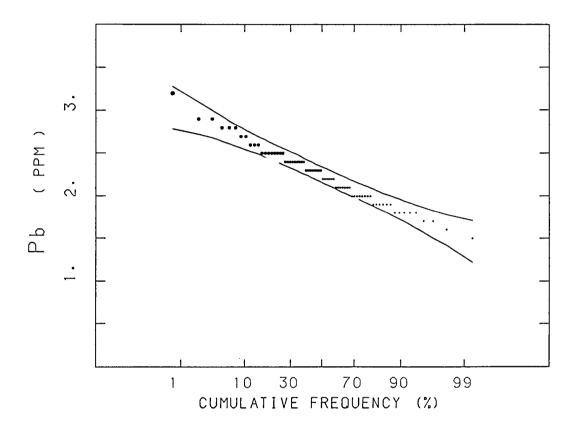


Figure 6.3b Normal Probability Plot: Pb in Ascophyllum nodosum in the Trondheim Region.

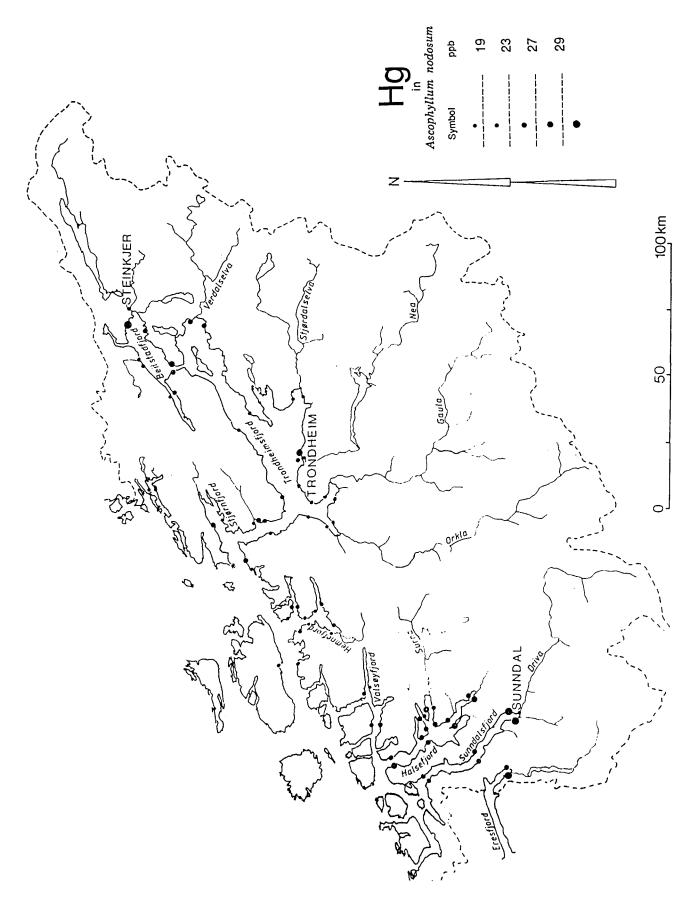


Figure 6.4a Mercury concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.4 Mercury

Except for 3 values, the accumulative distribution for Hg is normal with a median value of 21 ppb. There does seem to be some spottiness in the distribution with slightly elevated values associated with the industrial centers at Trondheim, Sunndal, and Steinkjer.

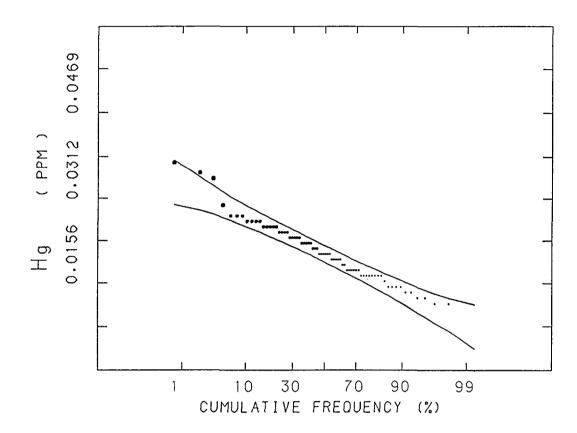


Figure 6.4b Normal Probability Plot: Hg in Ascophyllum nodosum in the Trondheim Region.

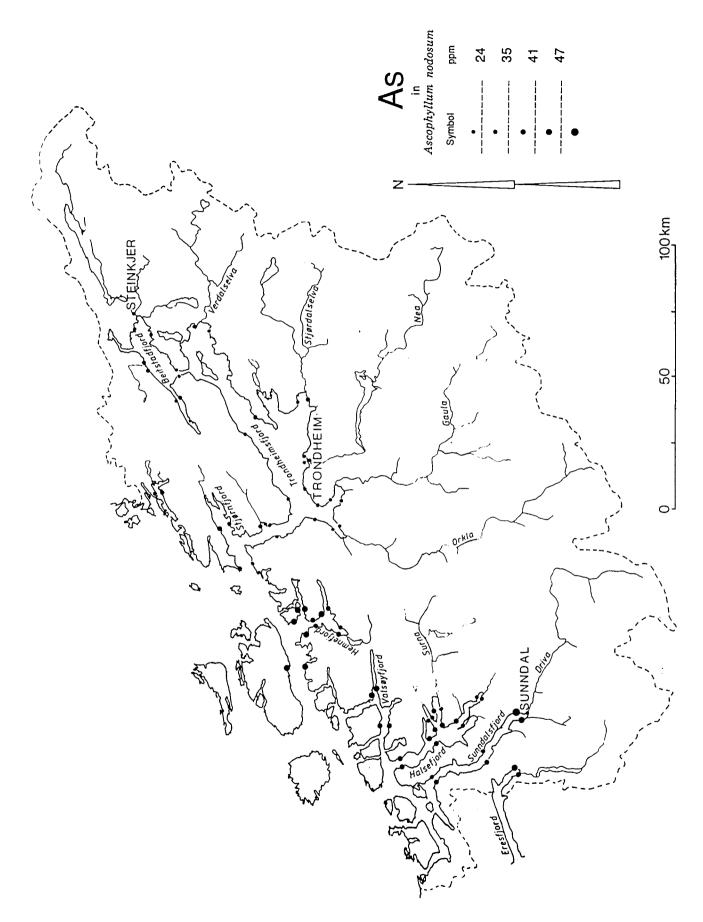


Figure 6.5a Arsenic concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.5 Arsenic

The accumulative distribution for arsenic consists of two normal distributions having the same slope. The median for the lower distribution is 22 ppm and that for the upper is 35 ppm. The two distributions are the results of two batches of samples being analysed at separate times. No obvious explanation is available to account for this discrepancy. This batch effect shows up as a set of low values along the Trondheim fjord. Otherwise there appears to be no spatial pattern to the As values.

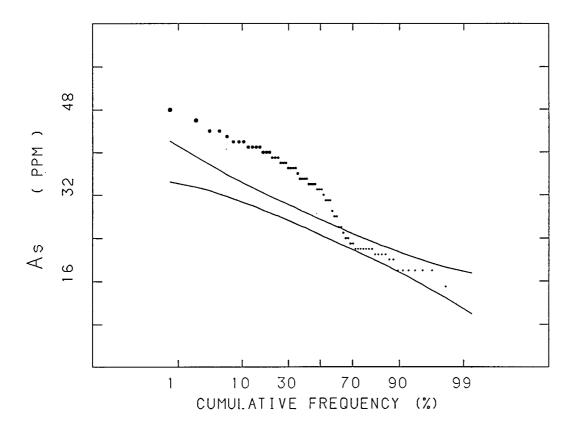


Figure 6.5b Normal Probability Plot: As in Ascophyllum nodosum in the Trondheim Region.

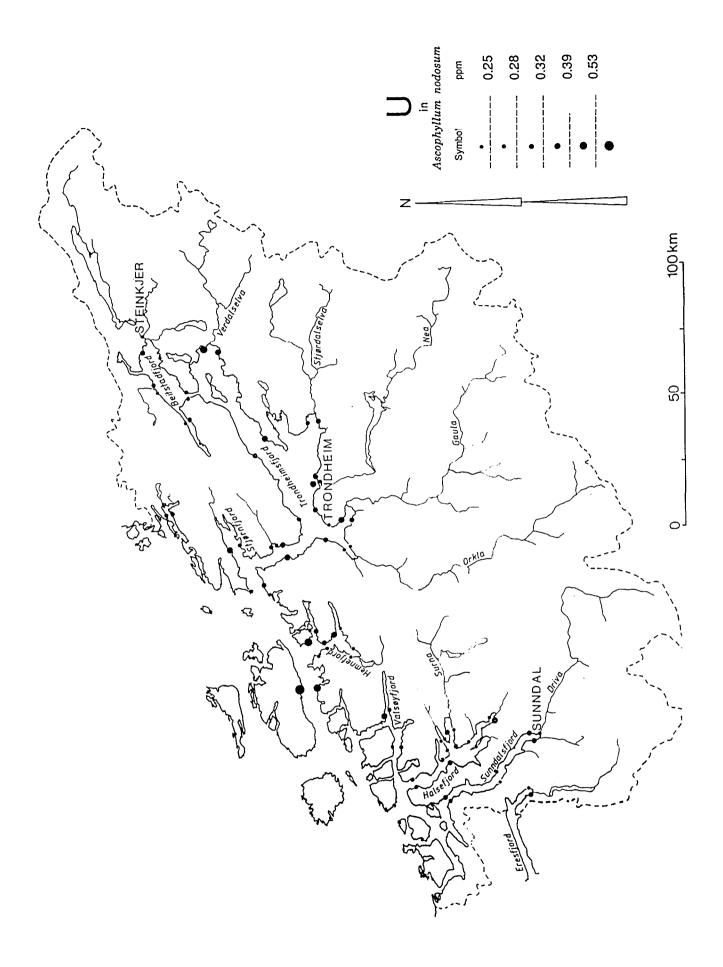


Figure 6.6a Uranium concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.6 Uranium

The raw accumulative probability plot for U suffered from distortion as a result of a number of missing values (Table 2). To compensate, the missing values were simulated by random draws from a normal distribution with a median of 0.27 ppm. After the addition of the simulated values, the uranium became essentially a normal distribution. A small cluster of high values occurs near the island of Hitra. Otherwise there were no discernable U concentrations. Preliminary results (Sharp and Bølviken, 1979) had suggested slightly elevated values of U associated with incoming sea water but this could not be substantiated.

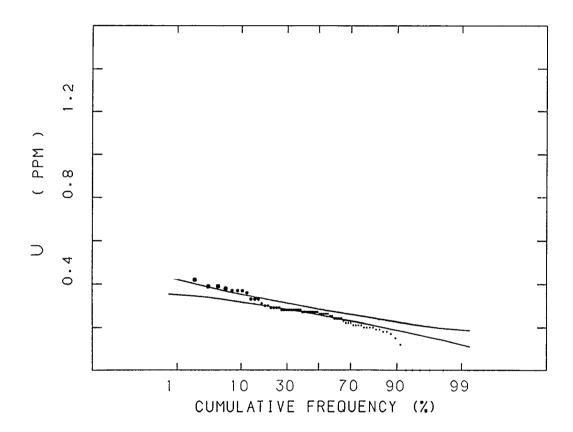


Figure 6.6b Normal Probability Plot: U in Ascophyllum nodosum in the Trondheim Region.

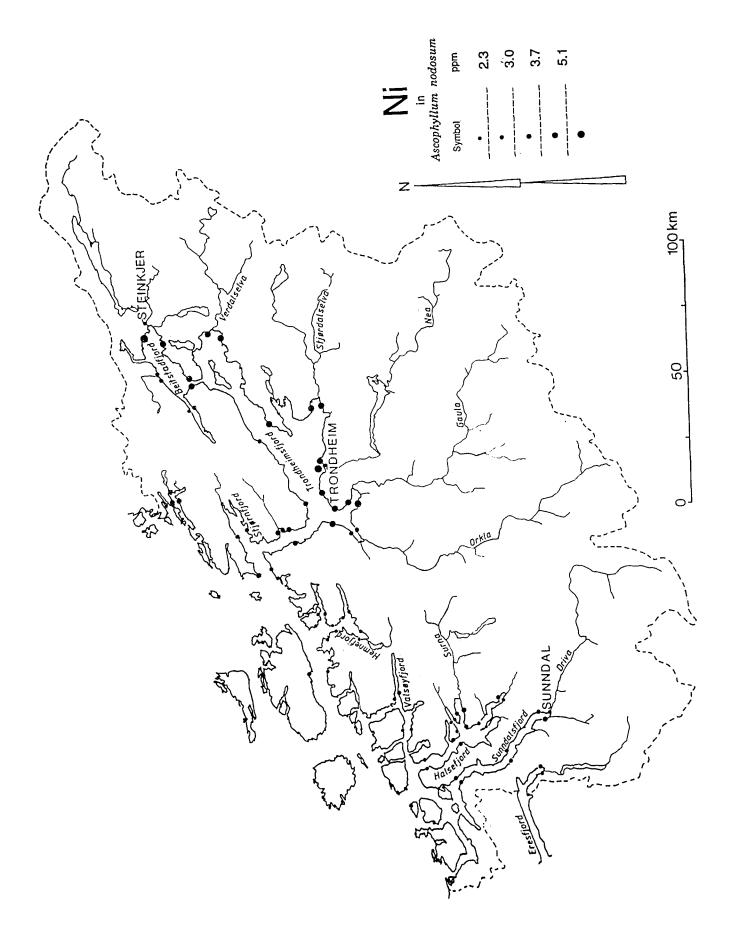


Figure 6.7a Nickel concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.7 Nickel

The accumulative distribution for nickel yields a median of 2.6 ppm with a maximum of 6 ppm which is about 2 times the median. The highest nickel values are associated with the greenstones (Fig. 4) of the Trondheim area.

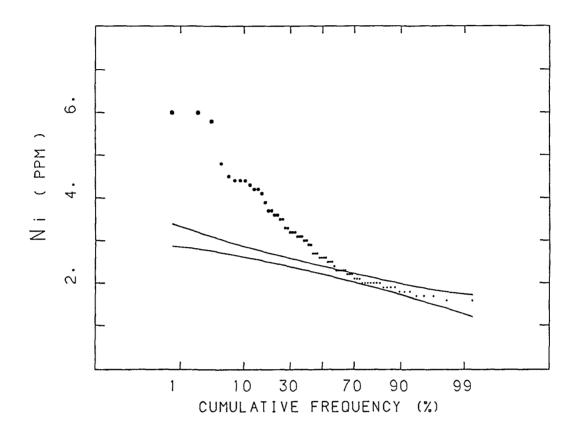


Figure 6.7b Normal Probability Plot: Ni in Ascophyllum nodosum in the Trondheim Region.

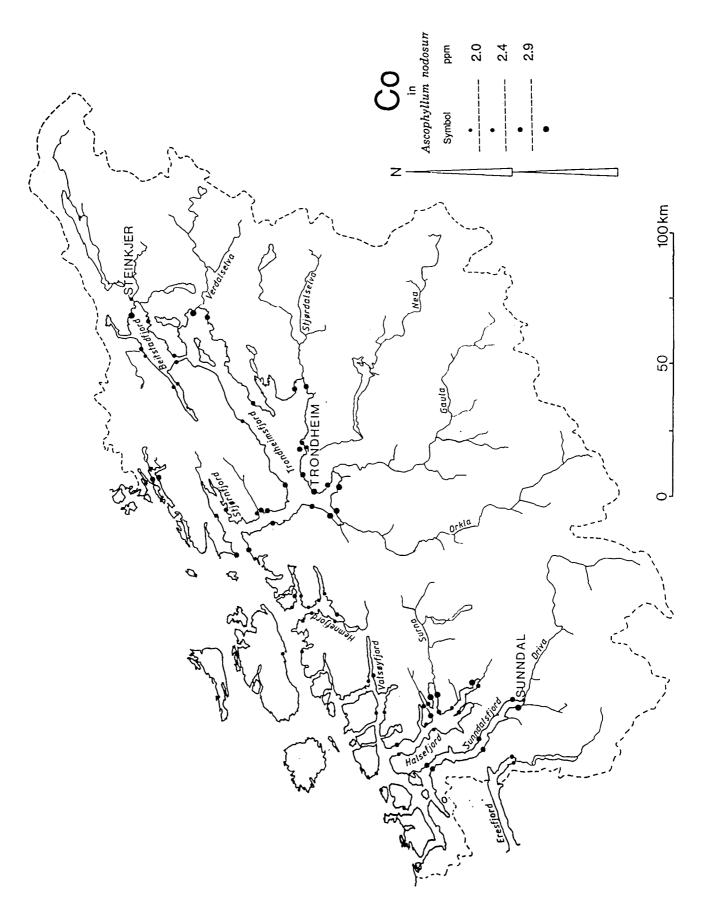


Figure 6.8a Cobalt concentrations: from samples of Ascophyllum nodosum in the Trondheim Region.

6.8 Cobalt

The accumulative distribution for Co yields a median of 2.2 ppm with a maximum of 3.9ppm, about 2 times the median. A majority of the high values are associated with the mouths of the important rivers. Notable exceptions are the Nid and the Stjørdal river.

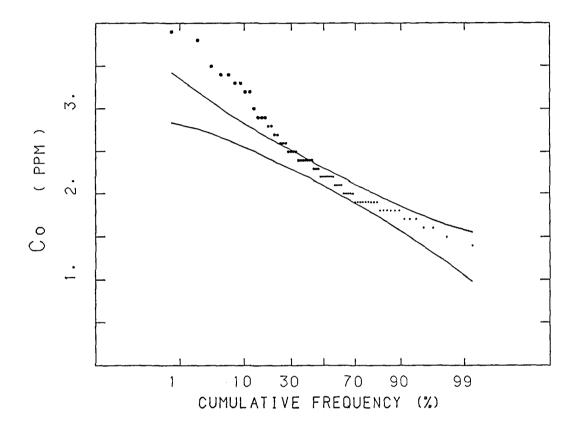


Figure 6.8b Normal Probability Plot: Co in Ascophyllum nodosum in the Trondheim Region.

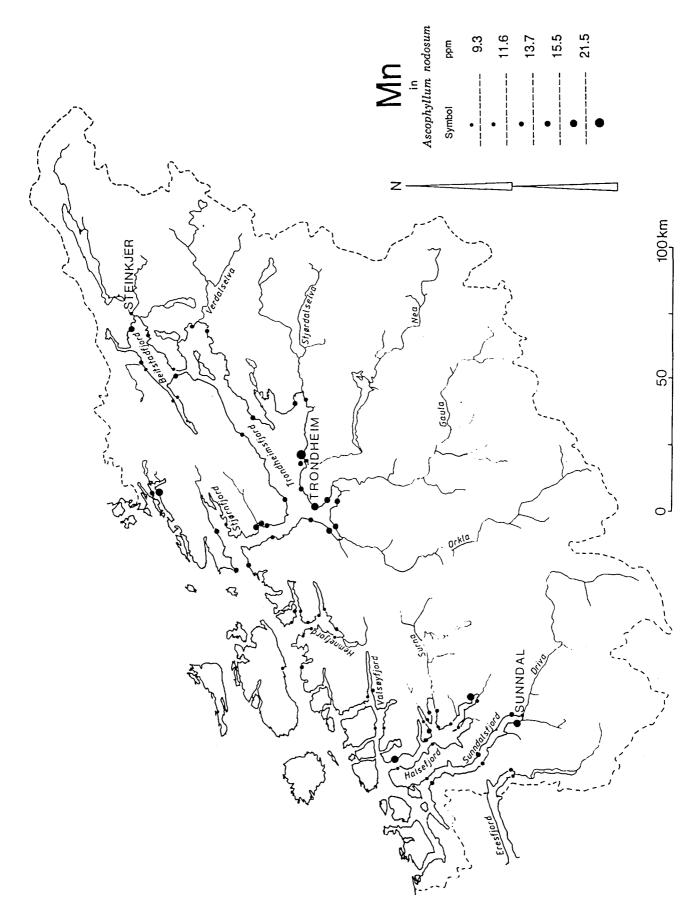


Figure 6.9a Manganese concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.9 Manganese

The accumulative distribution for Mn yields a median of 11 ppm with a maximum of 21.6 ppm about 2 times the median. As with Co, a majority of the high values are associated with the mouths of the major rivers.

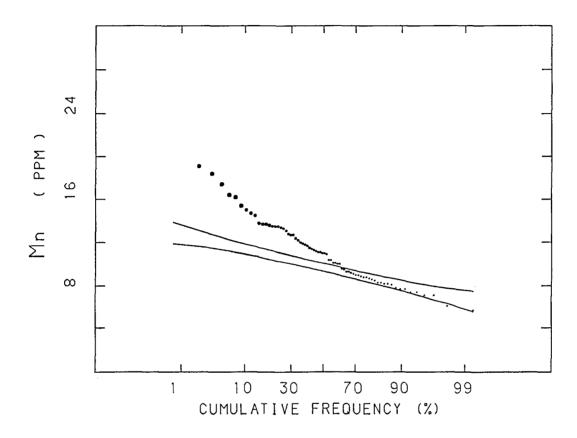


Figure 6.9b Normal Probability Plot: Mn in Ascophyllum nodosum in the Trondheim Region.

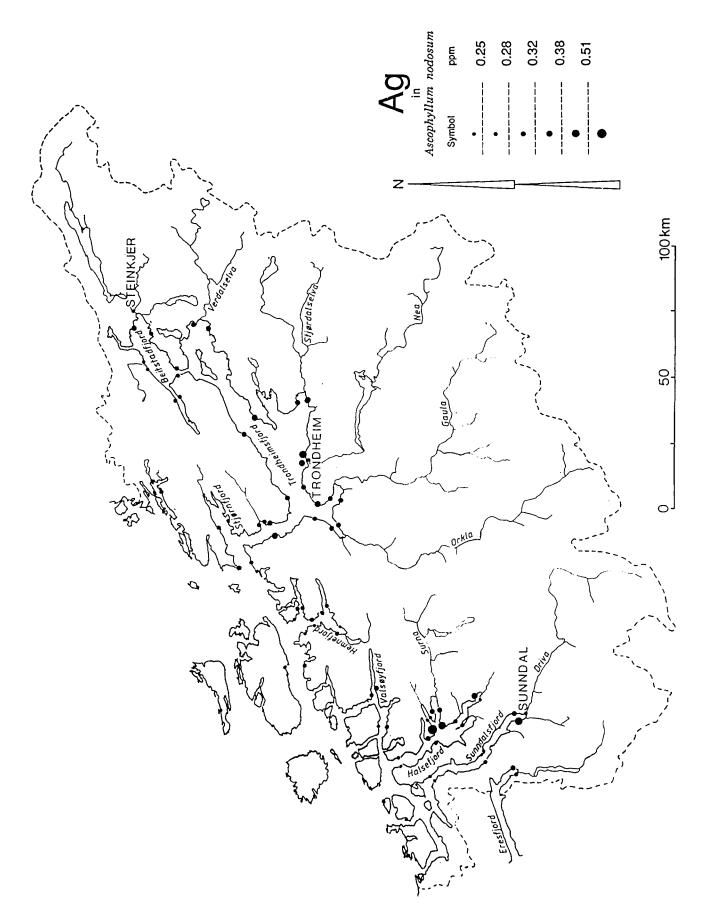


Figure 6.10a Silver concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.10 Silver

The accumulative distribution for Ag yields a median of 0.265 with a maximum of 0.52 ppm which is about 2 times the median. High values are associated with the industrial works at Sunndal and Trondheim. Of particular note are the high values on Surnadal fjord which coincides with the center of high vanadium values. These sites should be resampled to test their validity.

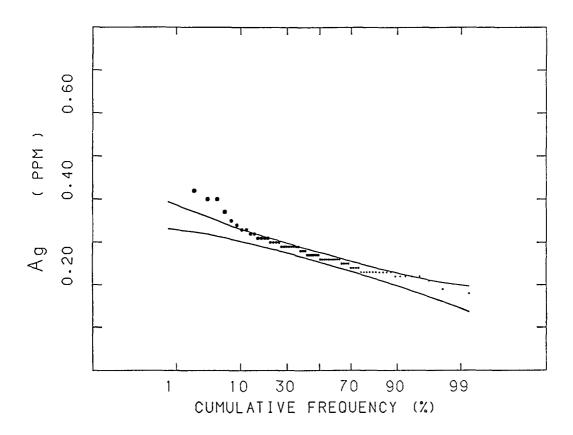


Figure 6.10b Normal Probability Plot: Ag in Ascophyllum nodosum in the Trondheim Region.

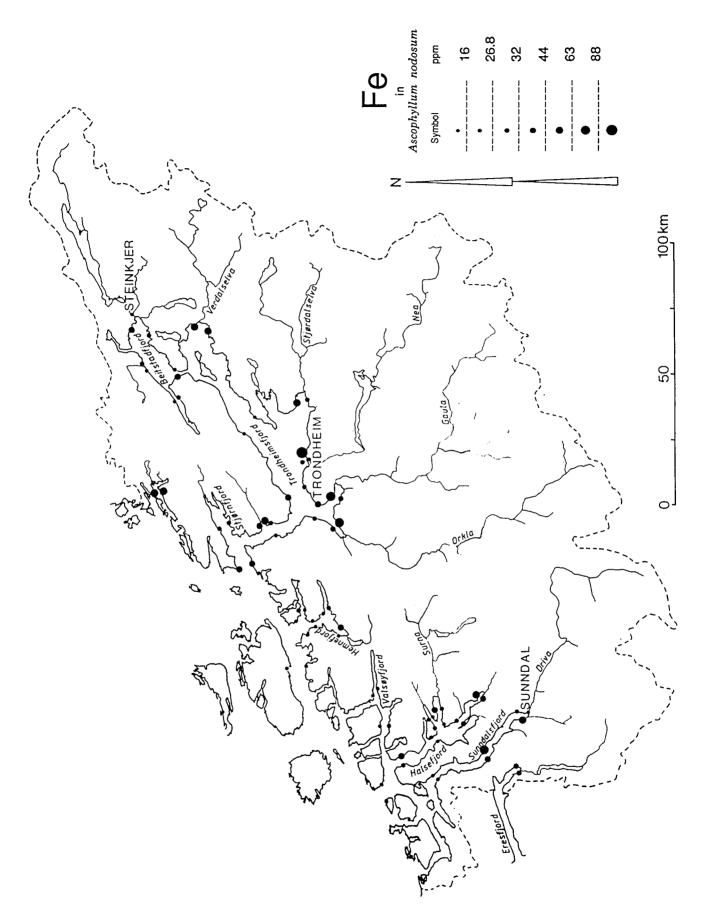


Figure 6.11a Iron concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.11 Iron

The accumulative distribution for Fe has a median of 23 ppm with a maximum of 118 ppm which is 5 times the median. For this element it is not at all clear as to what is the correct sample-analytical precision. Replica analyses from Østmarkneset (Table 3) yield a standard deviation of 5 ppm while replica analyses from Brønnøysund yield a standard deviation of 20 ppm. If the 5 ppm value is used, the Fe plot is quite similar to that of Mn (Fig. 6.9b). If 20 ppm is used only a few sample sites show anomalous values. It still is not clear which is the proper choice but for now it will be assumed that 5 ppm is the proper value. If the smaller value is selected, it appears (as with Co and Mn) that high values of Fe are associated with the mouths of the major rivers.

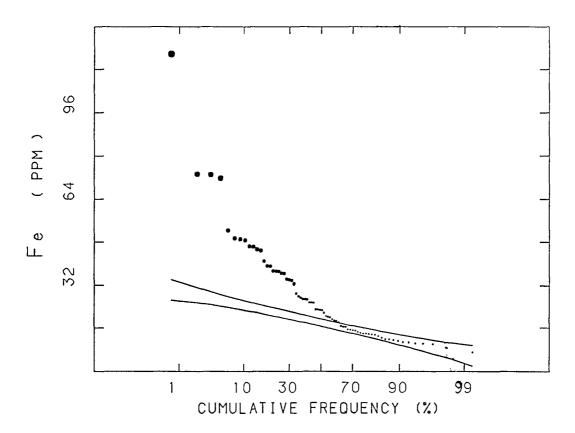


Figure 6.11b Normal Probability Plot: Fe in Ascophyllum nodosum in the Trondheim Region.

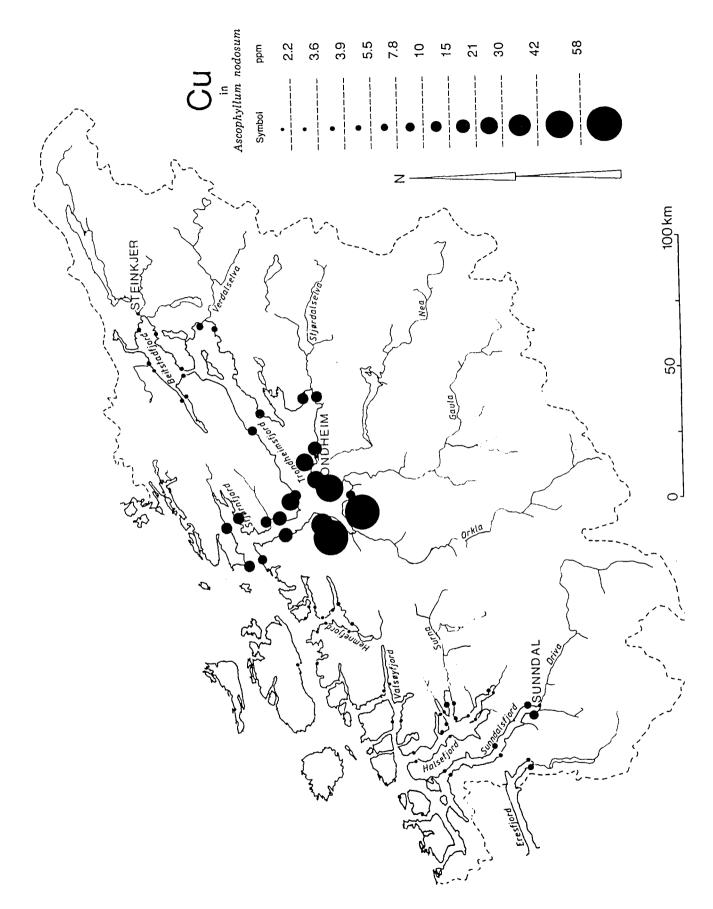


Figure 6.12a Copper concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.12 Copper

The accumulative distribution for Cu has a median of 2.8 ppm with a maximum value of 251 ppm which is 90 times the median. Copper shows the greatest range in total variation. The high values are clearly from the Orkla river system which carries leachate from mine wastes from the Løkken mine (Nilsen, 1973). The distribution of copper along the fjord clearly shows the counterclockwise circulation pattern (Jacobsen, 1976) with little copper reaching the inner parts of the Trondheim fjord. On the other hand copper values have a strong signature right at the entrance of the fjord. It would be interesting to investigate the extent to which copper is carried beyond the mouth of the fjord.

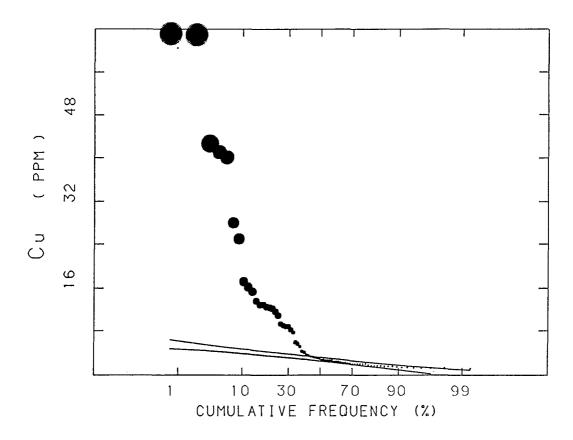


Figure 6.12b Normal Probability Plot: Cu in Ascophyllum nodosum in the Trondheim Region.

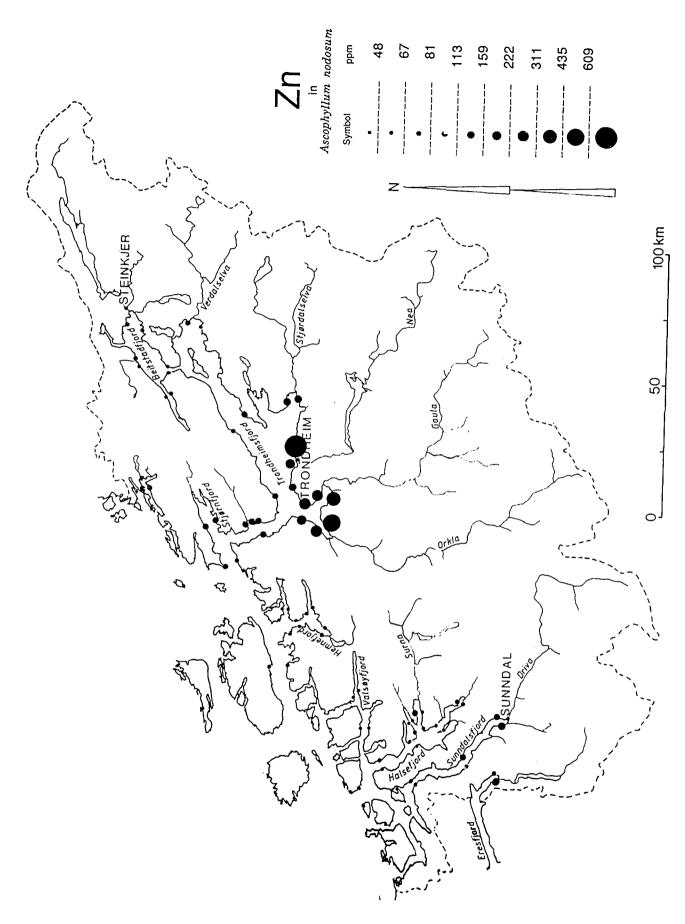


Figure 6.13a Zinc concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.13 Zinc

The accumulative distribution for Zn has a median of 58 ppm and a maximum of 629 ppm which is about 11 times the median. The pattern for Zn follows that of the high Cu values because Zn is also coming down the Orkla river from the Løkken mine wastes. Notice also the secondary high at the city of Trondheim; this high value maybe related to a galvanizing plant. Although nearly hidden by the high contamination, there do appear to be slightly elevated values of Zn associated with the mouths of major rivers. A similar results was found in the study of the Tosen fjord (Sharp and Bølviken, 1979).

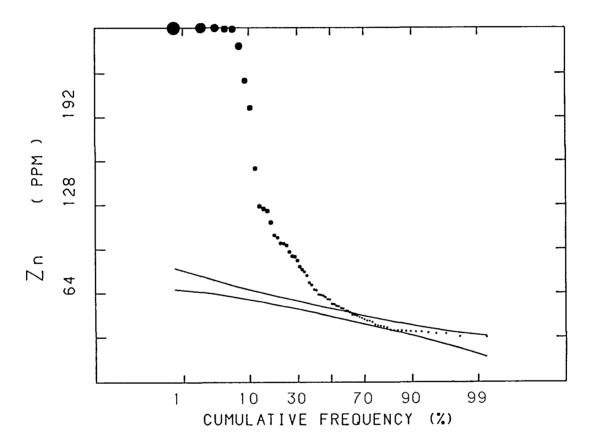


Figure 6.13b Normal Probability Plot: Zn in Ascophyllum nodosum in the Trondheim Region.

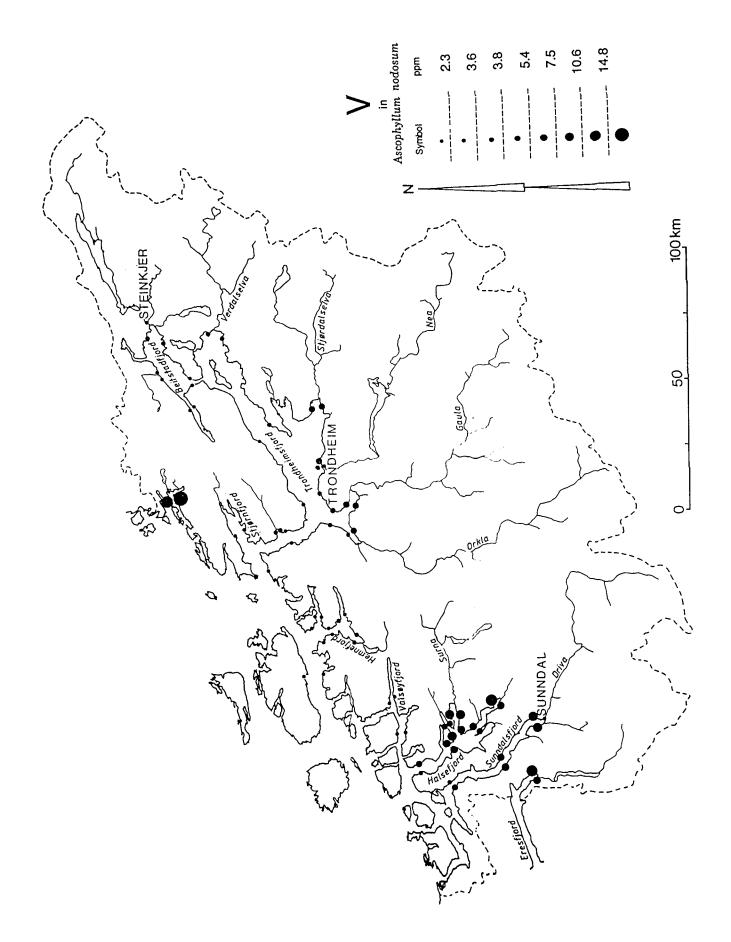


Figure 6.14a Vanadium concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.14 Vanadium

The accumulative distribution for V has a median of 2.8 ppm and a maximum of 16.6 ppm which is 6 times the median. The high V values are associated with rivers which are draining Precambrian gneisses and a granitioids (Fig. 4); however seaweed attached to such rocks as a substrate seem unaffected. Rivers draining other terranes have only slightly elevated values of vanadium.

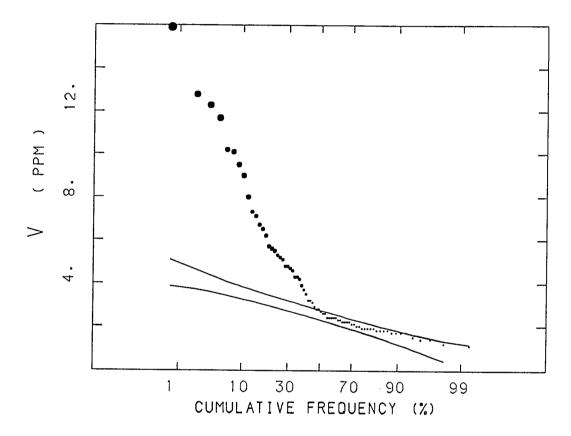


Figure 6.14b Normal Probability Plot: V in Ascophyllum nodosum in the Trondheim Region.

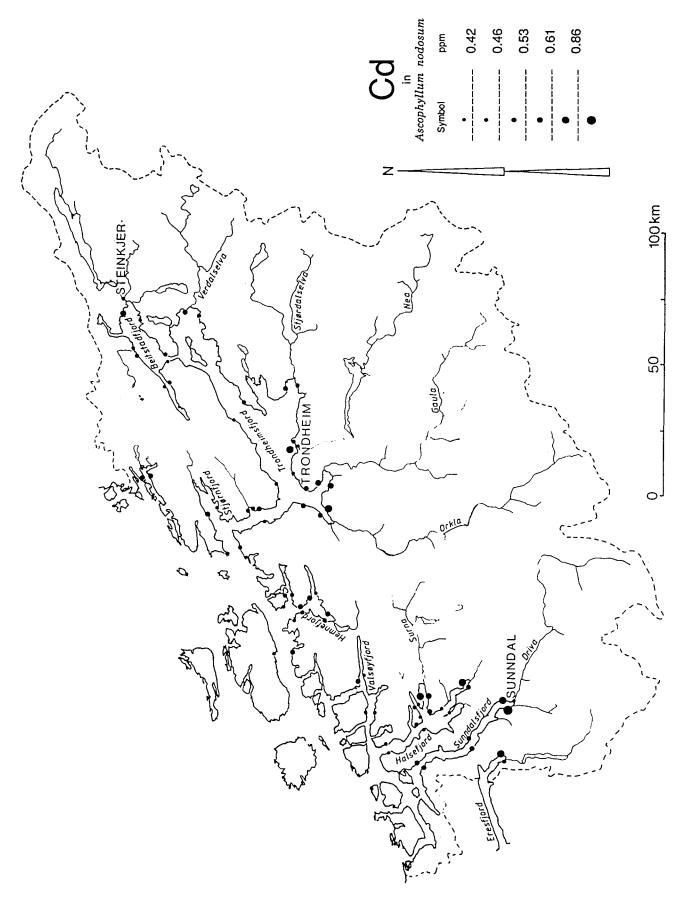


Figure 6.15a Cadmium concentrations from samples of Ascophyllum nodosum in the Trondheim Region.

6.15 Cadmium

The accumulative distribution for Cd has a median of 0.44 ppm, and a maximum of 1.11 ppm which is 2.5 times the median. As with Co, Mn, Fe, and V, elevated values of Cd are associated with the mouths of the major rivers. Unlike V, the distribution appears to be independent of rock type. Although Zn and Cd are commonly associated with each other in sulfide minerals, there is no large zone of Cd dispersion associated with the large zone of Cu and Zn from the Orkla watershed.

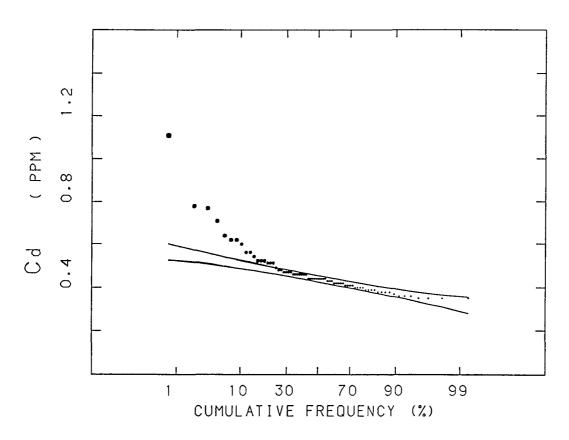


Figure 6.15b Normal Probability Plot: Cd in Ascophyllum nodosum in the Trondheim Region.

7. DISCUSSION

To interpret the results, the analyses for each element were sorted in descending order and the median value located. Concentrations were then plotted relative to the median by the use of a series of proportional dots on probability graphs. A comparison (Table 5) of the median background values of heavy metal content for *A. nodosum* with the values reported for brown algae in the literature shows excellent agreement for V, Ni, Mo, Ag, and Cd. The values reported here are much lower for Mn, Fe, Cu, Zn, and Pb but higher for Co. The lower values found here could be explained in part by the fact that brown algae reported in the literature may include other species and may have been collected near populated areas having polluted waters. The higher value found for cobalt is unexplained but could arise from interference from silica in the analyses (Slavin 1968, p. 100). «Elevated» values were distinguished from «background» by plotting standard deviations from the analysed replicas along with the 5 per cent confidence limits on normal probability paper (Figs. 6.1b - 6.15b). No elevated values were observed for Ash, Mo, Pb, Hg, or As. Samples were also analysed for Na, Ca and F but are not reported here (see notes, Table 2). Real elevated concentrations are observed for Zn, V, Cd, Co, Cu, Mn, and Fe and this demonstrates that regional heavy metal surveys in fjords can be carried out.

Concentrations, as in the probability plots, were plotted relative to the median using a set of proportional dots on a series of drainage basin maps for the Trondheim 1:500 000 map sheet (Figs. 6.1a - 6.15a). Inspection of the maps reveals several patterns. The most important pattern is the occurrence of high heavy metal values near the mouths of the major fresh water drainages. Although it has been suggested that less saline waters may enhance the uptake of certain metals into seaweed (Dahlgaard, 1984), it more likely that the increased uptake indicates an excess of these elements being carried into the fjord by the fresh water rivers. This feature is evident (with decreasing importance) for Zn, V, Cd, Co, Mn, Fe and Cu. The strongest effect and greatest dispersion is shown by Zn and V while Cd and Co are confined to areas nearest the mouth. Values for Mn, Fe and Cu are erratic but follow the pattern of Cd. Unusually high values of Fe and Mn are associated with those rivers having organic pollution.

Of considerable interest are the very high values of both Zn and Cu in the outer parts of the Trondheim fjord. As indicated earlier these are from mine pollution from the Orkla river. These high values show that the waters of the Trondheim fjord can be divided into two quite distinct water masses: (i) an innermost portion with relatively low copper values which has over many years managed to remain uncontaminated by the polluted values from the central and outer portions of the fjord, and (ii) an outer portion where the high values extend all the way to the very entrance of the fjord. Tests should be made to determine if these high values can be traced either north or south along the Norwegian coast line. It also raises the possibility of using other elements to define individual water masses within a fjord system.

The second most important map pattern is an areal one suggesting a general regional effect from the local geology (Fig. 4) either from river waters entering the fjords or from the local substrate. This is illustrated by the anomalous values of Ni and V. The elevated values for V are associated with Precambrian gneissic rocks while the elevated values for Ni are associated with greenstones.

Finally, it was hoped that a pattern could be found associated with the mouths of the fjords. Although it was initially thought (Sharp and Bølviken, 1979, p. 347) that Mo, U, and Cu might be associated with incoming sea water [as suggested by the elevated values found in exposed coastal locations (Table 3)], this could not be substantiated.

When the above regional effects have been taken into account, there remains special anomalies for Zn, Cu, V, Ag, Mo and U. The Zn and Cu anomalies occur in the main Trondheim fjord and are clearly the result of mine wastes on the Orkla river and probably also industrial pollution from the city of Trondheim. Some of the high Ag values also occur here. Clearly anomalous values of V are found west of Surnadal (sites 145 and 146) and in Aafjorden (sites 261 and 262). Both of these sites are in remote uncontaminated areas. Of particular interest is the coincidence of the highest Ag values with the center of the V anomaly. Finally, anomalies for Mo were found at the head of Eresfjord (sites 137 and 138) and for U on Hitra (site 164).

8. REFERENCES

- Baardseth, A. 1970: Synopsis of Biological Data on Knobbed Wrack. United Nations food and Agricultural Organization, FIRM/S38 Rev. 1, pp. 1:1 9:66.
- Braarud, T. 1975: The natural history of the Hardangerfjord. 12 The late summer water exchange in 1956, its effect upon phytoplankton and phosphate distribution and the introduction of an offshore population into the fjord in June, 1956. Sarsia. 58, 9-30.
- Bollingberg, H. J. 1975: Geochemical prospecting using seaweed, shellfish, and fish. Geochimica et Cosmochimica Acta. 39, 1567-1570.
- Bowen, H. J. M. 1966: Trace Elements in Biochemistry. Academic Press, London, 234 pp.
- Dahlgaard, H., 1984: Transuranics, rare earths and cobalt, zinc and cesium in Fucus vesiculosus (seaweed): Laboratory exercises and field realities, p. 347 354. In A. Cigna and C. Mytteraere, International Symposium on the behavior of long-lived radionuclides in the marine environment. Commission of the European Communities, EUR-9214-EN.
- Duxbury, A. C. 1971: The Earth and its Oceans. Addison-Wesley, Reading, Mass., 381 pp.
- Eide, I. 1976: Personal Communication, Norges Tekniske Høgskole, Trondheim.
- Eide, I. and Myklestad, S. 1976: Personal Communication, Norges Tekniske Høgskole, Trondheim.
- Haug, A. 1972: Akkumulering av tungmetaller i marine alger. In, Symposium om tungmetallforurensinger. NTNF, Oslo, pp. 198-206.
- Haug, A., Melsom, S., Omang, S. 1974: Estimation of heavy metal pollution in two Norwegian fjord areas by analysis of the brown algae Ascophyllum nodosum. Environ. Pollut. 7, 179-192.
- Jacobson, P. 1976: Resipientundersøkelse av Trondheimsfjorden. Vassdrags- og Havnelaboratoriet Rapport no. F76082, Norges Tekniske Høgskole, Trondheim, 28 pp.
- Jorde, I. and Klavestad, N., 1963. The natural history of the Hardangerfjord. 4 The benthonic algal vegetation. Sarsia. 9, 1-99.

- Kuldvere, A. 1980: Atomic absorption determination of arsenic in seaweed by arsine generation using the Perkin-Elmer MHS-1. Atomic Spectroscopy. 1 (5), 138 142.
- Kuldvere, A. & Andreassen, B. Th. 1979: Determination of mercury in seaweed by atomic absorption spectrophotometry using the Perkin Elmer MHS-1. Atomic Absorption Newsletter. 18, 106 110.
- Lysholm, C. 1972: Tungmetallinnhold i tang som en mulig geokjemisk prospekteringsmethode. (Unpublished Thesis). Norges Tekniske Høgskole, Trondheim, 78 pp.
- Nilsen, R. 1973: Transport av oppløste tungmetaller i elvene Gaula, Orkla og Orva. Industri og Miljø. 4 (4-6), 37 43.
- Printz, H. 1957: Norges forekomster av drivtang og drivtare. Norsk Institutt for tang og tareforskning, Rapport Nr. 18, Norges Tekniske Høgskole, Trondheim, 50 pp.
- Scheidegger, A. E. 1965: The algebra of stream order numbers. U. S. Geological Survey Professional Paper. 525, B187-B189.
- Sharp, W. E. 1971: A topologically optimum water sampling plan for rivers and streams. Water Resources Research. 7, 1641-1646.
- Sharp, W. E. & Bølviken, B. 1979: Brown algae: a sampling medium for prospecting fjords. In Watterson, J. L. (ed.), Geochemical Exploration 1978, Elsevier, Amsterdam, p. 347 353.
- Shreve, R. L. 1967: Infinite topologically random channel networks. Journal of Geology. 75, 178-186.
- Sinclair, A. J. 1976: Application of probability graphs in mineral exploration. Assoc. of Exploration Geochemists, Special Volume 4, Rexdale, Ontario, 95pp.
- Skipnes, O., Roald, T., & Haug, A. 1975: Uptake of zinc and strontium by brown algae. Physiol. Plant. 34, 314-320.
- Slavin, W., 1968. Atomic Absorption Spectroscopy. Interscience, New York, 307 pp.