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THE OCCURRENCE OF MAJOR AND MINOR CHEMICAL ELEMENTS IN THE MORE COMMON BALTIC SEAWEED

For many years, seaweed has been utilized in many countries as a complementary foodstuff for both humans and animals and also as a source of some minerals of inorganic (iodine and potash) and organic (agar-agar, alginates and mannitol) origin. Interest in marine algae continues to grow steadily as new substances of utility value are found to be contained in them, e.g. certain vitamins, antibiotics, sterols and other drugs. They are also used willingly in agriculture to improve the soil structure and fertilize it with easily assimilable microelements (Chapman 1970).

Simultaneous with the development of the employing of atomic energy, studies of seaweed have taken on an additional aspect. It has been confirmed that they are able to take in and retain radionuclides which are found in their environment as the result of radioactive fallout or the discharge of radioactive waste from nuclear installations. Concentration factors for certain radioactive elements in algae, can attain values as high as tens of thousands. This property can be utilized in the monitoring of radioactive contamination in the marine environment, as thanks to natural processes of concentration, it is possible to detect such small quantities of some radionuclides as would be undetectable in direct analysis of sea water. At the same time, these properties may result in the introducing into humans or animal organisms of excessive amounts of radioactive substances, if such algae are utilized as a source of food.

Literature on the chemical composition of marine algae is very extensive (Winogradow 1953; Campbell 1952—1968). Numerous publications on the subject of uptake, accumulation and excretion of various radionuclides by different marine organisms, are also available, (Polikarpow 1964). From a review of papers on the subject so far, it can be concluded that neither the amount nor the character of concentrations of chemical elements in living organisms can be attributed to their taxonomical affiliation to a given systematic group and existing physiological state only, as environmental conditions play a very important rôle. They determine the intensity of biological processes and are decisive in supplying organisms with necessary nutritive substances. Apart from this, as regards trace elements, each basin has its own individuality of distribution pattern. Although the problem has not been thoroughly studied as yet, the data available indicate the huge differences in both concentrations of various elements and in the mutual ratios. There are also various physico-chemical forms in which trace elements occur in sea water and which are not equally available to marine organisms. All these factors influence the mineral composition of seaweed more or less directly, which in consequence sometimes results in considerable differences in the distribution of chemical elements, if one compares the analytical results quoted by various authors. Thus Pillai (1956) observed a distinct seasonal dependence on the occurrence of inorganic macro- and micro-constituents in algae growing along the coast of India, simultaneously the maximum occurrence of trace elements accompanied the minimum amount of major ions (and vice versa). Variations in the total ash content were in a narrow range and did not appear to be of a seasonal character.

Black and Mitchell (1952) also suggest the occurrence of seasonal fluctuations in the amounts of certain microelements in cl. *Phaeophyceae*, altough in view of the scatter of analytical data and limited number of samples, it is difficult to speak of it being more than a tendency. It was however, possible to observe differences between species and even between different parts of plant tissue within the same species, whereas there was no correlation between the contents of trace elements and the total ash content. Algae from the east coast of Canada were analyzed by Young and Langille (1958) and Wort (1955), who stated that distinct seasonal changes in the potassium and total ash contents can be observed, but the fluctuations in the contents of trace elements did not yield any correlation. Similarly Ishibashi and others (1964) did not find any correlation between the time and place of sampling algae and the nickel and cobalt content, when the differences between the species were considerable. The differences in the absolute amounts of some inorganic microconstituents are sometimes surprisingly big, even between samples of the same species. Thus for instance, according to Black and Mitchell (1952) the iron content of *Pelvetia canaliculata* varied from 195 to 2040 mg/kg and of *Fucus sp.* from 62 to 3380 mg/kg. A characteristic feature is the concentrating of manganese in plants. Land plants usually contain from 2 to 200 mg Mn/kg in terms of dry mass (Bertrand et al. 1921), whereas in aquatic plants the most frequent concentrations are from 500 to 2000 mg/kg (Oborn 1964). According to Bertrand, fresh water algae contain up to 7700 mg Mn/kg sometimes. Marine algae show a definitely lower although somewhat changing Mn content. Young and Langille (1958) found about 50 mg Mn/kg in species of genus *Fucus* whereas Black and Mitchell (1952) give the value as from 100 to 800 mg/kg for the same species. The scatter of analytical results and lack of any regularity are characteristic for copper. Several other microelements also show fluctuations to a greater or smaller extent. All this indicates that there are frequently differences in the chemical composition of plants growing in water with differing hydrochemical characteristics and lying in different climatic regions, even among the same species. It can also be expected then, that the concentration factors of certain trace elements will fluctuate in correspondingly wide limits. It is difficult to foresee the extent and character of such changes however, and the only way to obtain information on the subject is by direct chemical studies in the given environment.

This present work was taken up with the aim of determining the extent to which the brackish Baltic water influences the mineral composition of acquatic plants living in it, what are the mutual ionic ratios and in what concentrations several trace elements occur in certain widely distributed kinds of water plants collected in various places and in various seasons. The work is of a reconnaissance character, as such studies have not so far been carried out in the region mentioned.

CHARACTERIZATION OF THE STUDY REGION

The biogeographic character of the Baltic differs considerably from most seas and oceans. It is a shallow land-locked sea lying completely within a continental platform. The average depth of the Baltic is 55 m., the maximum depth — 459 m. (the Landsort Deep). A characteristic feature of the Baltic is that it has a low salt content, this resulting from its geological history and the present hydrological conditions. The maintaining of a low salt content is assisted by the high percentage of river inflow (500 km^3/year) in relation to the total capacity of the basin (22 000 km^3), as well as the fact that communication with the open sea is hindered by the shallow Danish Straits. As the result of this, plant life develops in a brackish environment.

Kornaś (1957) divides Baltic flora into three ecological groups: 1. marine euryhalic species which tolerate low salinity, 2. extremely euryhalic, fresh water species, which still tolerate the Baltic salinity, and 3. species attached to brackish waters, both eury- and stenohalic. All three groups have relatively few representatives and this mainly explains the floristic poverty of the Baltic in all systematic groups. There are only a few species of flowering plants, of which only *Zostera marina* is a typically marine plant. The fresh water species of the family *Potamogetonaceae* are fairly widespread. Genus: *Enteromorpha, Cladophora, Chara* and *Tolypella* are the most frequently met cl. *Chlorophyceae*. Cl. *Phaeophyceae* are less frequently represented. Mention should first be made of the largest and most important filamentous algae of *Phaeophyceae: Fucus vesiculosus*. Other species occurring: *Chorda filum, Dictyosiphon foeniculaceus, Enctocarpus siliculosus, Pylaiella rupincola*, are much rarer. Cl. *Rhodophyceae,* which are the most numerous and most varied group of algae in the open seas, play a very modest role in the flora of Polish coastal waters. The most widespread is *Furcellaria fastigiata*. Other species more frequently met are: *Ceramium spp., Polysiphonia spp., Rhodomela subfusca* and *Phyllophora Brodiaei*, these being much smaller in numbers and usually accompanying larger plant associations. Due to the poor transparency of the Baltic waters, the bottom limit of plant growth does not usually exceed a depth of 25 m. It should be emphasised that several species of marine algae living in the Baltic waters show considerable morphological changes, these being manifested in stunted growth, the creating of more delicate forms, deformation etc. Such changes are frequently accompanied by the loss of some modes of reproduction, especially the sexual.

As distinguished from the rocky northern coast, the southern coast of the Baltic is formed of sandy material which is the remains of postglacial forms. Most of the Polish coast is formed of such soft unconsolidated sediments, which undergo continued movement and shifting as the result of the action of waves and currents. As the character of the substratum is especially unfavourable for the growth of macrobenthos, there is a lack of flora altogether for the most part. Flora find favourable conditions only there where the coast forms cliffs built of morainic formations. As the result of erosion, the bottom at the foot of such diluvial hillocks is covered with pebbles and gravel, forming a substratum to which plants can attach themselves. Plant life is most abundant however, in the relatively shallow lagoons sheltered from stronger waves, and here is found to grow on both sandy and muddy bottoms, often forming extensive underwater meadows. Gdańsk Bay, forming the southern part of the Central Baltic Basin, is an example of such conditions. Its western part is occupied by Puck Bay, which creates especially favourable conditions for marine plant life. It is in this region that *Furcellaria fastigiata* and *Fucus vesiculosus* are exploited on an industrial scale to obtain agar-agar, alginic acids and mannitol. The stocks of *F. fastigiata* and *Fucus vesiculosus* in that part of Puck Bay which is assigned for working, are estimated at about 20,000 tons, the annual extraction being about 1,000 tons at present. The distribution and characteristics of the bottom flora in this region has been discussed extensively by Kornaś (1959) and Kornaś and others (1960).

MATERIAL

Flora was collected in the years 1965—1968 from various regions of Puck Bay, Gdańsk Bay along the stretch between Gdańsk and Gdynia and from the open sea in the region of Rozewie. The places from which samples were taken are shown in Fig. 1 (p. 10). Most of the material was collected by a diver, a few specimens of red algae freshly washed up, were occasionally collected from the beach. Cl *Chlorophyceae* overgrowing stones in shallow water, were available from the water's edge.

The species represented in the material collected, were as follows: Chlorophyceae: *Enteromorpha sp., Cladophora sp.;* Phaeophyceae: *Fucus vesiculosus;* Family *Potamogetonaceae* and *Hydrocharitaceae; Zostera marina, Potamogeton pectinatus, Elodea canadensis;* cl. Rhodophyceae: *Furcellaria fastigiata, Polysiphonia nigrescens* and *Polysiphonia violacea, Rhodomela subfusca, Ceramium rubrum, Ceramium diaphanum, Phyllophora Brodiaei.*

In these regions, plants usually occur in phytocenotic communities. The material collected was thus usually a mixture of several species, which required the arduous work of separation. It was impossible to collect many species in sufficient amounts or good enough condition to enable the sample formed to be considered representative or suitable for analysis. Work was thus restricted to those species occurring most frequently and which could be collected in the purest possible state. Mechanical separation of red algae to obtain the required amounts of pure species, was impossible in practice. With the exception of *Furcellaria fastigiata* then, samples from this class should be treated as a mixture of the above-named species. In Table 5, the name of the predominant species in a given sample and comprising not less than 2/3rds of it, is given at the side of the analytical results.

As plant life develops here on a sandy substratum, sand frequently accompanied the specimens collected, mainly in specimens of genus *Enteromorpha* and genus *Cladophora*, to a lesser extent those of *Rhodophyceae*. A frequent „contamination" are mussels *(Mytilus edulis)*, which grow in abundance attached to thallus of *Rhodophyceae*. Young specimens of mussels (a couple of millimetres) could be overlooked among the entangled, delicate branches of algae and influence the analytical results for calcium.

Some samples of plants had a white coating, more or less consistent, sometimes mucous. This mostly occurred on the older parts of the thallus of *Fucus* and on *Potamogeton*. As Oborn (1964) states, such cases are met especially among plants growing in fresh and brackish waters. This author studied the chemical nature and the bacterial microflora of mineral incrustations on leafs of genus *Potamogeton* and states that over 90% of their mass is calcite.

Perennial plants were analyzed in entirety, the roots of f. *Potamogetonaceae* and *Hydrocharitaceae* being removed from species. In a couple of cases species *Fucus vesiculosus* was divided into old and young parts and receptacles, and analyzed separately. After mechanical cleaning, larger specimens of plants were rinsed under a small stream of distilled water to wash out the adhering sea water. More highly contaminated samples required more careful rinsing, which might have caused the loss of a certain amount of the the more loosely-bonded cellular electrolytes, but not the trace metals (Black and Mitchell 1952; Young and Langille 1958). The material was first air-dried and then vacuum dried at a temperature of about 40°C, after which it was ground in a porcelain mill.

ANALYTICAL PROCEDURE

1. Major elements an total ash content. A two-gramme sample of plant material oven-dried at 110°C was ashed in an electric furnace at 550°C for 24 hours. The remaining ash was weighed and expressed in percentage of oven-dry matter. The ash was dissolved in concentrated HCl, evaporated to dryness on a water bath and dissolved in 0.02 N HCl. After filtration, the solution was passed through a column

with cation-exchanger Dowex 50 W × 8 in the hydrogen form and washed with 0.02N HCl. In the effluent, sulphates were determined gravimetrically as barium sulphate and phosphorus — spectophotometrically with ammonium molybdate, after reduction to phosphomolybdate blue with $SnCl_2$.

Cations were washed out of the column with 3N HCl. After removing excess HCl by evaporation, the solution was diluted to a fixed volume, calcium and magnesium were determined in aliquots titrimetrically with EDTA and sodium, potassium and calcium — by the flame photometry method.

2. Trace Metals. 10 ÷ 25 g of material dried at a temperature of 110°C, was gently charred over a flame burner, to destroy the major part of the organic matter, and then ashed in an electric oven at 550°C for 24 hours. The ash was moinstened with water, dissolved in HCl and evaporated on a water bath. The salts were dissolved in concentrated HCl and filtered. The residue on the filter paper was ashed and treated with HF + $HClO_4$. (Some authors do not recommend the use of hydrofluoric acid when carrying out analyses of plant material, as any mineral particles adhering to seaweed after the silicate lattice is broken down, may release considerable amounts of some trace elements of non-biological origin. Experience indicates however, that if this stage of the analysis is omitted, serious losses of certain elements can be expected, viz. iron and zinc, especially if the silica content in the undissolved residue is high). After fuming off the perchloric acid, the residue was dissolved in HCl and joined with the main filtrate. This solution was used for all subsequent analyses.

Iron — was determined spectrophotometrically as a Fe^{2+} ortho-phenantroline complex after reducing Fe^{3+} with hydroquinone.

Manganese — An aliquot of the solution was fumed off with H_2SO_4 to remove chlorides and the manganese was determined spectrophotometrically after the oxidation of Mn^{2+} to permanganate with potassium persulphate.

Copper — A Cu-diethyl-dithiocarbamate complex was extracted from citrate solution in the presence of EDTA as a masking agent. The chloroform extract was measured spectrophotometrically.

Zinc — was determined by a single colour method, measuring the optical absorption of zinc-dithizone complex in a carbon teatrachloride solution. This complex was extracted at pH ~ 7 in the presence of diethanolamine-dithiocarbamate as a masking agent. The excess of dithizone was removed by shaking the CCl_4 extract with a phosphate buffer solution of pH = 11.

Nickel — was separated by extraction in the form of a dimethylglyoxime complex. It was determined by measuring the Ni-dimenthylglyoxime complex in an ammonium hydroxide solution after previous oxidation of the Ni with bromine.

Cobalt — was extracted with chloroform as a Co^{3+} — 1-nitroso-2-naphtol complex. After mineralization the cobalt was determined with nitroso-R salt in an acetate buffered solution.

Strontium — was coprecipitated with calcium as an oxalate from a solution buffered with acetate at pH 5.5 in the presence of EDTA as a masking agent. Oxalates were burned and weighed as carbonates, these were then dissolved in diluted HCl and made up to about 4 mg Ca/ml (2 mg/ml for samples of *Fucus* sp.) The concentration of calcium was tested by titration with an ETDA solution. Strontium was determined by a flame spectrophotometric method. The spectrophotometer was calibrated with a series of standard solutions containing various amounts of strontium and Ca concentrations fixed at 2 mg/ml and 4 mg/ml. Solutions were prepared of spectrographically pure strontium and calcium carbonates.

RESULTS

The distribution of inorganic macro- and microconstituents in individual species of seaweed studied, is given in tables 1 ÷ 7. The results of the analyses refer to plant material dried at 110°C.

When considering the ionic relation between the aquatic organism and the environment, and assessing the concentration of the individual elements in the biosphere the results expressed on fresh weight basis are often taken. At the same time, a simplified form of calculation is adopted most frequently, dividing the concentration of elements in the dry matter by five, which means assuming that the water content is 80%. The amount of water in plants can vary considerably however. Thus e.g. it amounts to 13 ÷ 14% of the weight of dry seeds, about 50% in woody tissues, 80 ÷ 90% in leaves and up to 95% in certain fruits. The non-membraned plasma of the myxophyta contain 70 ÷ 94% (Strasburger et al. 1962).

Fukai (1968a) gave data on the subject of the water content of various types of organisms, this including marine algae. It results from these that the distribution frequency is that of a normal Gaussian distribution curve, with the maximum lying between 80 ÷ 90%. Over 60% of all the species studied showed a water content of 80% or more. On analysing seaweed from the Indian Ocean, Pillai (1956) stated that the water content

Table 1

Inorganic macro- and microconstituents in *Enteromorpha sp.*

Place and date of collection	Total ash	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
	% of dry matter							mg/kg						
Puck Bay														
22 July 1965	25,1	3.17	0,89	1,47	2,52	9,57	0,072	140	530	190	45	11,3	1,3	0,19
19 October 1965	17,1	1,90	2,80	1,41	2,77	7,50	0,274	170	760	—	55	14,6	—	—
Gdańsk Bay														
4 June 1968	27,2	—	—	1,38	—	—	—	180	210	20	55	14,1	1,9	0,26
7 August 1966	27,6	4,63	0,72	1,89	1,67	7,15	0,142	165	590	90	90	7,9	1,5	0,21
7 August 1966	29,6	5,48	1,97	0,77	1,44	7,83	0,312	95	1610	90	70	12,5	2,4	0,56
3 September 1966	22,7	3,27	1,25	1,01	3,10	7,33	0,413	115	510	70	75	12,7	2,5	0,22
6 October 1966	23,6	4,70	2,67	1,17	2,17	9,36	0,162	130	520	50	35	9,4	1,9	0,29
20 October 1965	18,2	1,29	1,42	1,12	1,34	6,62	0,237	95	2740	220	75	16,6	4,8	0,73

Table 2

Inorganic macro- and microconstituents in *Cladophora sp.*

Place and date of collection	Total ash	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
	% of dry matter							mg/kg						
Puck Bay														
22 July 1965	22,3	1,71	2,45	0,85	0,78	8,37	0,092	90	2400	470	60	10,2	3,1	0,50
Gdańsk Bay														
4 June 1968	18,8	—	—	0,74	—	—	—	70	1210	80	80	13,0	4,5	0,53
5 June 1966	16,8	1,20	0,17	0,63	0,46	3,50	0,028	80	680	50	100	6,2	2,0	0,28
7 July 1965	42,4	1,39	0,21	0,65	0,40	2,52	—	65	3730	420	130	13,3	5,2	1,87
7 July 1966	24,3	5,29	0,98	0,89	1,48	5,57	0,052	—	380	150	45	6,9	1,6	0.28

Table 3

Inorganic macro- and microconstituents in *Fucus vesiculosus*

Place and date of collection	Total ash	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
	% of dry matter							mg/kg						
Puck Bay														
6 June 1966	17,2	2,21	0,83	1,95	1,11	8,02	0,156	890	720	1090	230	3,7	12,8	1,39
7 June 1966	19,3	1,86	3,23	1,84	0,72	7,56	0,138	1550	360	1270	350	4,1	13,1	1,20
17 June 1968	14,7	—	—	—	—	—	—	—	490	820	150	9,4	9,5	0,92
7 July 1966	19,0	1,77	3,13	1,94	0,67	7,54	0,134	1390	250	1380	330	4,0	13,7	0,98
7 July 1968	—	—	—	—	—	—	—	—	730	—	260	5,3	9,8	0,97
21 July 1965	18,1	0,83	3,03	1,92	0,92	7,43	0,126	850	360	1200	340	8.0	10,6	1,08
7 August 1966	18,4	1,78	3,08	1,70	0,96	7,20	0,142	1040	330	1620	330	7,0	18,0	1,12
28 August 1966	19,2	1,87	3,21	1,48	0.87	7,01	0,139	900	430	1530	390	6,3	22,4	1,04
5 October 1966	19,0	1,86	3.25	1,96	0,90	6,43	0,100	880	340	1240	260	3,6	15,5	10,2
Gdańsk Bay														
13 August 1965	15,9	1,18	1,62	1.78	0,87	9,02	0,080	930	230	1090	500	6,3	14,2	2,08
24 October 1966	—	1,48	2,32	—	—	6,93	0,119	—	—	1460	—	—	—	—
Baltic Sea at Rozewie														
17 April 1968	16,4	1,47	1,59	1,58	0,83	7,38	0,170	720	220	280	330	6,6	18,2	2,20
8 August 1968	14,8	1,60	1,52	1,42	0,90	—	—	690	290	340	270	4,3	17,0	2,49
4 December 1968	17,9	1,81	2,70	1,60	1,04	—	—	790	170	440	350	4,4	21,3	2,28

Table 4

Inorganic macro- and microconstituents in *Furcellaria fastigiata*

Place and date of collection	Total ash	Na	K	Ca	Mg	SO4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
	% of dry matter							mg/kg						
Puck Bay														
6 June 1966	19,3	1,48	3,87	0,71	0.96	10,08	0,172	—	880	3440	110	9,3	13,8	2,31
6 June 1966	12,4	1,88	—	0,58	0,68	—	0,119	145	970	2870	190	10,5	13,0	2,17
7 July 1966	18,6	1.53	3,73	0,45	0,98	9,86	0,150	70	700	3360	90	9,8	11,9	2,02
21 July 1965	15,3	0,90	2,95	0,52	1,01	8,72	0,105	75	560	1120	80	13,3	9,6	1,00
7 August 1966	18,8	1.53	3,62	0,74	0,99	9,88	0,168	135	1020	4060	80	8,4	12,4	2,22
28 August 1966	18,5	1,53	3,73	0,44	0,89	9,47	0,178	75	930	3980	120	14,0	12,5	2,29
5 October 1966	18,6	1,55	3,76	0,52	0,93	9,28	0,177	65	940	3090	150	16,3	20,2	1,93
19 October 1965	15,7	0,89	2,60	0,41	0,78	8,83	0,168	60	670	1100	60	12,4	8,4	0,83
22 November 1968	19,4	1,50	4,20	0,45	1,03	9,68	0,172	60	720	2320	140	15,2	16,7	1,58

Table 5

Inorganic macro- and microconstituents in *Rhodophyceae*

Place and date of collection and name of predominant species	Total ash	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
	% of dry matter							mg/kg						
Puck Bay														
Ceramium rubrum 7 July 1966	14,8	1,63	1,59	0,74	0,62	4,84	0,086	100	1920	3770	170	20,1	13,6	2,34
Polysiphonia sp. 7 August 1966	15,8	1,25	2,95	0,64	0,62	5,75	0,140	80	830	4200	140	14,2	9,6	2,04
Polysiphonia sp. 28 August 1966	18,5	2,23	2,61	1,35	1,01	6,69	0,142	280	2570	3780	280	13,5	13,9	2,52
Rhodomela subfusca 5 October 1966	21,4	1,36	3,24	1,06	0,69	6,31	0,145	110	1580	3440	440	36,8	14,2	2,84
Polysiphonia sp. 19 October 1965	12,9	1,01	0,98	1,52	0,43	4,17	0,116	—	2500	4330	390	19,8	12,9	3,90
Rhodomela subfusca 22 November 1968	—	1,17	2,43	0,48	0,68	—	—	70	1100	5230	170	19,3	16,8	7,01
Phyllophora Brodiaei 22 November 1968	20,1	1,81	3,11	0,73	1,00	—	—	70	1190	4720	260	19,9	—	6,30
Ceramium rubrum 22 November 1968	22,8	1,34	3,81	—	—	—	—	—	1340	3330	480	26,0	21,0	5,61
Gdańsk Bay														
Polysiphonia sp. 6 October 1966	32,8	1,95	3,10	2,24	1,31	7,00	0,105	160	3910	930	80	20,2	7,9	1,68
Polysiphonia sp. 20 October 1966	11,5	—	—	0,72	0,58	2,26	0,029	65	2780	4880	140	22,4	15,8	5,60
Rhodomela subfusca 20 October 1966	14,7	—	—	0,79	1,01	3,86	0,134	115	2800	3890	130	21,4	12,3	4,77

Table 6

Inorganic macro- and microconstituents in *Zostera marina*

Place and date of collection	Total ash	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
	% of dry matter							mg/kg						
Puck Bay														
6 June 1966	21,1	3,42	4,53	0,96	1,12	1,55	0,297	—	560	460	150	17,5	4,6	0,75
7 July 1966	24,3	3,48	5,35	1,23	1,02	1,55	0,325	195	300	610	90	16,5	4,8	5,54
7 August 1966	15,5	1,99	3,52	0,90	0,82	1,21	0.199	155	250	860	200	13,4	2,8	1,30
28 August 1966	20,2	2,83	3,93	1,15	0,93	1,40	0,267	180	180	130	80	9,4	3,2	0,27
5 October	18,7	2,38	3,62	1,52	0,98	1,28	0,251	285	120	320	80	8,0	1,3	0,28
Gdańsk Bay														
4 June 1968	16,7	2,66	3,28	0,94	0,96	1,16	0,286	—	170	420	150	16,9	3,2	0,96
5 June 1966	21,7	2,75	2,84	1,00	1,12	1.40	0,263	210	1540	630	820	22,6	3,6	1,70
7 July 1966	17,5	2,47	3,88	0,88	1,00	1,04	0,384	180	350	1240	120	11,4	4,8	1,97
7 August 1966	15,7	2,10	3,73	0,93	0,92	1,07	0,182	180	250	1070	240	11,7	4,0	1,80
13 August 1965	13,3	1,00	1,28	1,69	0,97	1,14	0,231	355	1110	940	630	33,5	6,1	1,40
3 September 1966	16,8	2,33	3,85	—	—	1,05	0,262	—	280	1010	250	9,0	3,2	2,48
6 October 1966	16,8	2,25	3,04	1,10	0,96	1,24	0,199	—	350	1250	390	11,3	4,5	2,54
27 October 1965	17,8	1,87	2,76	2,18	1,08	1,14	0,302	410	420	1970	480	15,5	6,2	4,00
22 November 1968	19,3	2,47	3,07	0,94	1,04	—	—	—	780	2270	510	16,5	11,8	6,80

Table 7

Inorganic macro- and microconstituents in *Potamogeton pectinatus.*

Place and date of collection	Total ash	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
	%/0 of dry matter							mg/kg						
Puck Bay														
6 June 1966	20,3	3,14	2,54	1,57	0,96	3,10	0,330	150	490	610	150	11,1	7,1	0,98
7 July 1966	17,8	3,22	2,97	0,88	1,81	2,88	0,289	115	160	280	150	7,6	3,2	0,17
7 August 1966	17,5	2,30	2,33	2,18	0,98	2,94	0,207	205	110	200	110	7,2	4,3	0,34
28 August 1966	16,9	2,43	2,43	1,86	0,78	3,00	0,202	180	130	240	120	6,2	4,1	0,25
5 October 1966	19,2	2,58	2,22	2,32	1,04	3,15	0,217	210	350	480	130	7,4	3,7	0,54
Gdańsk Bay														
4 June 1968	18,0	—	—	—	—	—	—	—	510	—	170	—	4,6	0,90
7 July 1966	19,3	2,83	2,75	0,91	1,20	2,94	0,280	—	370	740	140	8,2	2,6	0,78
7 August 1966	16,3	2,50	2,60	1,17	1,20	2,95	0,179	170	230	740	110	5,8	2,5	0,87
3 September 1966	16,5	2,52	2,68	0,87	1,27	2,94	0,195	—	310	700	140	6,2	2,8	1,51
6 October 1966	17,1	2,27	2,65	0,86	1,23	3,28	0,142	—	240	1170	150	7,0	3,8	1,87
27 October 1965	16,4	1,89	2,55	1,75	0,94	2,66	0,245	140	390	2100	200	15,7	4,5	2,80
Puck Bay														
Elodea canadensis														
28 August 1966	12,4	2,09	0,91	1,34	0,90	1,92	0,147	180	220	420	110	5,4	2,9	0,58

in almost all species studied was approximately the same, the fluctuations not exceeding 5%. The author attributes these not so much to seasonal climatic changes as to various development stages of plants. All the results of the natural moisture content in the plants were between 83 and 93%. No regular measurements of water content were carried out in this work. The average moisture contents given in Table 8 are not average in the sense that the remaining analytical results are, as they originate from another series of tests on the same species. They are however, undoubtedly a better approximation of the true values than the 80% mentioned which was adopted in calculations from dry matter to natural (Young and Langille, 1958).

The surface salinity of the Baltic amounts, on average, to 7 ± 0.5‰. This means that plants live and grow in an environment where the main ionic components amount to about 5 times less than in typical ocean water with a salinity of 35‰. The hydrological conditions of the Gdańsk Bay coastal waters, with reference to the seasonal changes in the amounts of nutrients, were already described by Ostrowski and Bojanowski (1964), also Bojanowski and Ostrowski (1965). Fig. 2 (p. 22), which originates from the latter paper, illustrates the course of the average monthly changes in salinity and temperature in this region in the years 1961 ÷ 1964. The changes in salinity were between 5.0 ÷ 7.0‰ in monthly averages and 2.65 ÷ 7.96‰ with regard to single measurements. The highest salinity is during the winter months, the lowest — in April/June, when the Vistula flood waters discharge into the Bay. Average monthly temperatures amount to between 0°C and 19°C, single measurements not exceeding 25°C.

The Baltic water is very similar to typical sea water as regards the mutual proportions of the main ionic components. There are certain anomalies however, especially in the region of the coastal waters and surface layers, this undoubtedly being the result of river discharge and the influence of the land. Table 9 illustrates the mutual proportions between certain macroelements and chlorides characteristic for the surface waters of Gdańsk Bay, and the concentration of these elements calculated for average salinity of water in the region from which the plant samples were taken. These values, together with the results of analyses, illustrated in Table 8, served to estimate average abundance ratios of sodium, potassium, calcium, magnesium and strontium in the seaweed studied (Tabl. 10). The accuracy of these abundance rations is restricted by both errors in chemical analyses and inaccurate estimations of the water content in plants, as well as natural fluctuations in salinity. The accuracy of determining the chemical macrocomponents was not less than ± 5%, for strontium however, it was determined as ± 17%. The difference in salinity of ± 1‰ results in an error of ± 14%, an error in the accuracy of estimating the water content depends upon the percentage content and amounts to 100% for example when the error in estimating the water content amounts to 10% at an 80% level of natural moisture, or 5% at a 90% natural moisture level in a given species of algae. It can be seen from this that errors in estimating the water content are those which have the greatest influence on the accuracy of estimating abundance ratios (expressed on wet weight bases).

As regards the estimating of the degree of concentration of microelements, the main difficulty lies in the lack of knowledge as to the contents of trace elements dissolved in sea water, from this region. This shortcoming concerns the whole of the Baltic. From the region of Gdańsk Bay, we have at our disposal only a few results of analyses for copper, zinc, manganese and nickel, and a few more for iron and cobalt contents. This enables only a tentative approximation of estimated concentration of these elements, but does not enable anything to be said about seasonal changes. This is an urgent problem for the near future. The approximate values for Zn, Fe, Mn, Cu, P, Ni and Co, in sea water, are given in Table 9, and the abundance ratios — in Table 10. If however, the problem is not considered from the point of view of correlation between chemical components of plants and the surrounding water, the results given in Tables 1—8 well characterize the Baltic plants both from the point of view of distribution of inorganic main and trace elements and also enables interesting observations to be made of the environment.

DISCUSSION

Total Ash

The mineral components of plants expressed in percentage of ash in relation to the dry mass. comprise on average, from 17.5% to 25% of their weight and do not differ much in species (17.5 ÷ 18.5%) with the exception of cl. *Chlorophyceae* (24—25%). The high ash content in specimens of genus *Enteromorpha* is related to its high natural moisture content (to 96%) and the correspondingly higher percentage of electrolytes in the cell sap. In these samples the percentage of sodium and magnesium is about twice as high as in the remaining species, and the similarity of mutual ionic ratios and concentration coefficients is evidence of a high percentage of sea water. Samples of genus *Cladophora* contain from 17% to 42% ash, but as opposed to genus *Enteromorpha* these changes are not accompanied by corresponding changes in the contents of

Table 8

Average chemical composition of various species of seaweed

Species	Number of samples	Moisture %	Total ash	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
			% of dry matter							mg/kg						
Enteromorpha sp.	8	93	23,9	3,49	1,82	1,28	2,14	7,82	0,230	135	930	100	60	12,0	2,3	0,35
Cladophora sp.	5	90	24,9	2,40	0,94	0,75	0,78	5,00	0,057	75	1680	230	80	9,9	3,3	0,53
Fucus vesiculosus	14	82	17,5	1,64	2,46	1,75	0,89	7,45	0,130	980	380	1060	310	5,6	15,1	1,44
Furcellaria fastigiata	9	82	17,4	1,42	3,57	0,53	0,92	9,48	0,157	90	820	2820	110	12,1	13,2	1,82
Other *Rhodophyceae* (mixed species)	11	85	18,5	1,53	2,65	1,03	0,80	5,11	0,112	110	2050	3860	240	21,2	13,8	4,05
Zostera marina	14	86	18,3	2,43	3,47	1,18	0,99	1,25	0,252	240	480	940	300	15,2	4,6	1,91
Potamogeton pectinatus	11	88	17,7	2,57	2,57	1,44	1,04	2,98	0,229	164	300	730	140	8,2	4,0	0,91

Table 9

Average composition of the coastal waters of Gdańsk Bay (Southern Baltic)

Ionic species	Ion to chlorinity ratio	Concentration in sea water (at a salinity of 7,25‰)	Author
Chlorinity	—	4,00 ‰	
Natrium	0,553	2210 mg/kg	Trzosińska (1967)
Potassium	0,0210	84 mg/kg	Trzosińska (1967)
Magnesium	0,0671	268 mg/kg	Trzosińska (1967)
Calcium	0,0256	103 mg/kg	Bojanowski (1968)
Strontium	0,000384	1,54 mg/kg	Bojanowski (1968)
Sulphate	0,1410	564 mg/kg	Bojanowski (unpubl.)
	Rough estimates (in µg/litre)		
Zinc		20	
Iron. Manganese		10	
Copper, Phosphorus		5	
Nickel		0,6	
Cobalt		0,1	

the main ionic components. The main ash component in samples with a high ash content, is silica, originating from diatom frustules which thickly overgrow the delicate thallus of genus *Cladophora*. The phenomenon of epiphytic populations of diatoms appearing, occurs fairly frequently. Boney observed (1966) that diatoms of genus *Grammotophora* overgrowing thallus of *Cladophora* have well expressed seasonal cycle with spring and autumn maxima resembling the growth cycle of pelagic diatoms.

There is no clear seasonal change in the ash content of any of the species studied, as far as one can conclude from the incomplete annual observation cycle. The fluctuations noted are not very great and their irregular character may indicate inhomogenity of plant material, as well as temporary environmental changes such as eg. salinity. Against these fluctuations, possible changes related to the growth cycle of plants might go unnoticed. At any rate, if such differences exist, they must be small.

There are however, certain differences in the mineral components, depending upon the origin of the sample. Plants taken from Puck Bay always contained a certain percentage more ash than specimens of the same species collected at the same time in Gdańsk Bay or the open Baltic. Bearing in mind that the sea water originating from these places

Table 10

Average abundance ratio of chemical elements in seaweeds
(expressed on wet weight basis)

Name of species	Na	K	Ca	Mg	SO_4	P	Sr	Fe	Mn	Zn	Cu	Ni	Co
Enteromorpha sp.	1,1	15	9	6	10	3300	7	7000	700	200	200	250	250
Cladophora sp.	1,1	11	7	3	9	1100	5	17000	2000	400	200	550	550
Fucus vesiculosus	1,3	53	31	6	24	4700	110	7000	19000	3000	200	4500	2600
Furcellaria fastigiata	1,2	77	9	6	30	5700	10	15000	51000	1000	400	4000	3300
Other *Rhodophyceae* (mixed species)	1,0	47	15	5	14	3400	11	30000	60000	2000	600	3500	6100
Zostera marina	1,5	58	16	5	3	7100	22	7000	13000	2000	400	1100	2700
Potamogeton pectinatus	1,4	37	17	5	6	5500	13	4000	9000	900	200	800	1100

has the same salinity, the differences can be explained by a certain difference in conditions of vegetation.

It is characteristic that both the total ash content and that of the individual mineral macrocomponent do not differ much from the analogical contents in ocean species. Having a five-fold difference in salinity, the differences in the main ionic components are not usually more than double, and such components as calcium, sulfates or phosphorus are on about the sam level. The ionic components of sea water influence the organisms living in it in two ways, namely by supplying them with ions essential to maintain the metabolic processes (specific action) and by participating in the regulation of intracellular osmotic pressure (non-specific action). Although several main ionic components of sea water fulfil functions of a specific character in the tissues of organisms, they are often present in excess of their physiological demand. Their presence in plant tissues is also related frequently primarily to the regulation of water in the cells: providing proper physico-chemical structure of the protoplasm and maintaining the cell turgor at a suitable level (Guillard 1962). Sea algae are known for their tolerance to environmental changes in salinity; e.g. those species which overgrow ships' hulls or live in estuaries, have to be capable of withstanding salinity changes of from 0 to 35‰. Several species can withstand salinity changes of from 0.1 to 3-times the normal, thanks to osmoregulation processes (Biebl 1962). Thus the concentration of electrolytes in cell sap is, to a certain extent, independent of the concentration of external solution, and the mutual ionic proportions in the internal and external solution may differ from each other considerably. This would explain the fact that the relationship between the total ash content and the salinity is not uniform and is 2 ÷ 3 times higher for Baltic seaweed than for oceanic seaweed.

Sodium and Potassium

The average sodium and potassium content varies between 1.42 ÷ 3.49% and 0.94 ÷ 3.57% respectively. The greatest amounts of sodium are met in class *Chlorophyceae* and *Potamogetonaceae*, whereas cl. *Rhodophyceae* and cl. *Phaeophyceae* have about half that amount. Those richest in potassium included species *Furcellaria fastigiata* (3.57%) and species *Zostera marina* (3.47%), followed by the other *Rhodophyceae* (2.65%), species *Potamogeton pectinatus* (2.57%) and species *Fucus vesiculosus* (2.46%); the poorest were cl. *Chlorophyceae* (0.94 ÷ 1.82%). With the exception of cl. *Chlorophyceae*, individual fluctuations within a given species are not very big and greater deviations (in minus) from the average values were only sporadic, which might have been the effect of the washing out of some electrolytes in the course of purification of the specimens. It is impossible to detect any tendencies in the fluctuations of sodium and potassium contents which could be put down to seasonal changes in vegetation conditions. The fact is worth noting that samples of species *Fucus vesiculosus* and species *Zostera marina* (but not species *Potamogeton pectinatus)* originating from Puck Bay, contained more potassium and ash than those collected during the same period of time in Gdańsk Bay or in the open Baltic. As already mentioned, the salinity in these regions does not show such important differences as to influence the mineral components of plants. The distribution of sodium, in which no such differentation was noted, is also proof of this. It is known that at least part of the potassium is „actively" transported into the cells of plant tissue and related to the metabolic cycles which supply energy to realise this transport against the concentration gradient. Where metabolic processes are especially intensive (e.g. in young plant tissues) the intake of potassium increases considerably. Environmental conditions such as temperature and availability of nutrients also influence the extent of potassium intake. These environmental factors probably play a certain role in the differences in potassium contents, but it is also possible that specific species properties are the decisive factors.

The distribution of sodium content does not differ much between species. After calculating the results of analyses for concentration in material with a natural moisture content and comparing them with the existing concentration of sodium in the Baltic waters, it appears that seaweed does not concentrate this element (concentration ratio 1 ÷ 1.5) nor does it exclude it. Algae growing in oceanic waters indicate abundance ratios less or equal to unity (Young and Langille 1958). The ionic regulation system, probably located in the plasmalemma, (the so-called sodium pump) counteracts the concentrating of excessive amounts of sodium (Scott and Hayward 1953; Eppley 1962). The abundance ratios of potassium in Baltic seaweed are somewhere between 11 and 77, and indicate a characteristic relation to species.

At the same time, the K/Na ratio which, with the exception of cl. *Chlorophyceae* (0.64 ÷ 0.68) is greater than unity (1.44 ÷ 2.65), changes. For comparison, in Baltic waters this ratio is almost 0.038 (Trzosińska 1967). Thanks to the permanency of mutual ionic proportions in sea water, the range of concentrations of main ions in algae is much less than in land plants, in which according to Bertrand and Piertzenau (1927), the mutual K/Na ratios are between 1.15 ÷ 1057.

The highest K/Na values, differing clearly from the remaining, occurred in species *Furcellaria fastigiata* and other cl. *Rhodophyceae*. Simultaneously, these same species had the lowest figure for calcium. As it is considered that calcium participates in the neutralization of acidic groups of structural material of plant tissue, it is to be supposed that in cl. *Rhodophyceae*, this function is fulfilled by potassium ions. Kylin put forward such a suggestion (1943) when studying agar-like mucilage obtained from species *Furcellaria fastigiata*. This galactan polysaccharide, partly estrified by sulphuric acid, occurred as a potassium and, in part, magnesium salt. Other cl. *Rhodophyceae* are also composed of polysaccharides, with various amounts of sulphate groups, showing a certain affinnity to potassium ions. The paragraph dealing with sulphates and their distribution also refers to this problem.

Magnesium

The distribution of magnesium in the specimens analyzed is, alongside sodium, the most uniform of all the elements tested. There is a lack of any characteristics which would indicate the existence of dependence on seasons, species or places in which samples are collected. Both the average content of this element in individual species and most of the individual results comes within the narrow range of concentrations from 0.8% to 1.0% of dry matter. An exception is genus *Enteromorpha*, which contains more than two times as much magnesium than other species, but this results, as already mentioned, from there being about twice the amount of cell sap calculated in dry weight. In effect, the abundance ratio is very similar for all species and in most cases is from 5 ÷ 6.

Magnesium is the second most common cation after sodium from the point of view of abundance in sea water. The concentrations considerably exceed the physiological requirements of plants. The amount of magnesium in land plants is generally less than 0.5%, but this varies within the same species, depending upon the nutritional conditions (Nowotny-Mieczyńska 1965). In cases of profuse fertilizing with magnesium ions, its content in the green parts of plants may reach 0.8% ÷ 1.0% of dry matter. The amount of magnesium bound with chlorophyll is 10 ÷ 20% of the total, whereas 60 ÷ 85% occurs in the dissolved form. According to Kreger (1962) and O'Colla (1962) a certain fraction of this element in marine algae is bound to the cell wall material. It can also be presumed that it plays an important role in osmoregulation processes.

Sulphates

Sulphur is one of the most important mineral components of plants, as it participates — as a component of certain aminoacids — in the synthesis of protein. Apart from this it is part of the composition of several important physiological organic compounds as enzymes, vitamins etc. The physiological demand for sulphur is not so high however, and amounts to 0.2 ÷ 1.5% of the dry matter in land plants (as a sulphate ion). The amount of sulphate ions contained in the cell sap of aquatic plants is not very great. According to Schiff (1962) species living in salt water (typically marine e.g. genus *Valonia* and genus *Halicystis)* contain lower sulphate concentrations in the cell sap than in the surrounding water (concentration ratio < 1). Fresh water algae on the other hand accumulate considerable amounts of sulphates (e.g. genus *Nitella);* those species found in brackish water adapt themselves to existing concentrations of SO_4^{-2} in the water (e.g. species *Chara ceratophylla*).

A characteristic feature of Baltic seaweed is the fact that the sulphate content is high as compared with the existing concentration of SO_4^{-2} in the water and there are also considerable differences between the species studied. The greatest amounts, coming up to 10% of dry weight (average 9.48%) occurred in samples of species *Furcellaria fastigiata;* the remaining algae contained an average of from 5.0% to 7.8% SO_4^{-2} . As compared with this the family *Potamogetonaceae* and *Hydrocharitaceae* are low in sulphate content (1.25 ÷ 2.98%). Comparing these concentrations with the amount of SO_4^{-2} in the waters of the Baltic, we note that cl. *Chlorophyceae* can concentrate these ions 9 ÷ 10 times, cl. *Phaeophyceae* — 24 times and cl. *Rhodophyceae* 14 ÷ 30 times, whereas higher aquatic plants had abundance ratios of from 3 ÷ 6 (all the abundance ratios were expressed on a wet weight basis). As regards the occurrence of sulphates, there is a distinct difference between the lower water plants and the higher aquatic and land plants. Because, as mentioned, the concentration of sulphate ions in the cell sap of algae is low, the main part of the sulphur must be bound with the insoluble material of the cell walls.

A common feature of marine algae is that they contain mucilaginous substances — polysaccharides esterified with sulphuric acid to varying degrees. Thus agorose and agaropectin which are the main components of agar-agar occur in red agar-bearing algae (e.g. *Ceramium sp., Phyllophora sp., Gelidium sp.).* These are polymers of d- and l-galactose with small amounts of 3.6-anhydro- l-galactose, containing 3 ÷ 5% of sulphate groups. Species of family *Gigartinaceae* (e.g. *Gigartina stellata, Chondrus crispus*) contain so-called carrageenin, a structural substance similar to agar, but containing more sulphates (20 ÷ 30%). The mucilage of species *Furcellaria fastigiata* (furcellarin) is the potassium magnesium salt of a galactan which contains pentoses. Sulphate groups form about 20% of this material. The furcellarin content of species *Furcellaria fastigiata* can reach 60% of the total dry matter. Similar material occurs in cl. *Clorophyceae,* with a greater percentage of pentoses and uronic acids. Here sulphates form 10—20% of the dry weight of polysaccharides. The main component of cell walls in species *Fucus vesiculosus* is, alongside alginic acid, fucoidin, a polysaccharide built of units of fucopiranose esterified with sulphuric acid. Fucoidin occurs in species *Fucus vesiculosus* in amounts of from several to up to twenty percent and contains almost 40% sulphates, mainly neutralized with calcium ions. Thus algae sulphates are immobilized in the cell walls. Their amounts depend upon the physiological state and the stage of development of plants and is not directly related to the salinity of the environment. Therefore, the relative content of sulphates in Baltic species is higher than in oceanic specimens, the absolute contents are comparable however (Winogradow 1953). Although there is a lack of experimental proof, it can be presumed that ester sulphate groups, together with the carboxyl and hydroxyl groups make algae a specific cation-exchanger of considerable capacity which plays an important role in the sorption and retention of many trace elements.

Phosphorus

Tests carried out show that phosphorus accumulates in the greatest amounts in green plants, thus in f. *Potamogetonaceae* and in genus *Enteromorpha*. Genus *Cladophora* with its low concentrations of phosphorus (0.03 ÷ 0.09%) is an exception, but in view of the small number of samples of this species, it is difficult to give any comments on the results. The remaining species have about half the concentration of phosphorus. The biggest fluctuations within a species have been observed in genus *Enteromorpha*, there is a lack of distinct correlation with seasons however. The seasonal variations in other plants studied are not very great and with a few exceptions, comes within ±30% of the average values.

Phosphorus is an essential mineral component in all plants. The amounts taken in by plants depend upon those contained in the environment. Where it is plentiful, plants can accumulate it in amounts which exceed their requirements, in situations wehere there is a shortage of phosphorus, plants develop normally until the amount stored has been exhausted, after which their rate of development becomes restricted by the external source of phosphates (e.g. released upon mineralization of organic debris). Redfield et al. (1963) describe the results of experiments in which marine phytoplankton bred in an environment rich in nutrients had a C/P weight ratio of 18, but on decreasing the phosphate content in the growth medium so that it became a restricting factor in cell growth, this ratio rose to 90. In normal conditions the C/P ratio in marine phytoplankton amounts to about 42 and does not show any considerable fluctuations. Aquatic plants studied in this research had a C/P ratio of 160—360. Such high values are characteristic for the non-assimmilating parts of plants, whereas the green parts usually show a value less than 120. To explain these differences it must be taken into account that aquatic plants grow in an environment which is especially poor in phosphorus. Whereas land plants derive phosphorus from soil solutions, with a concentration of $10^1 \div 10^3$ μg P/l, the concentration in the coastal sea water during periods of intensive vegetation, does not exceed a couple of μg of phosphorus per litre, and it is usually less than 1 μg P/l. The annual average phosphorus content in Baltic coastal waters is about 5 μg/l on the surface, but fluctuations of from $0 \div 20$ μg/l have been noted. It has also been proved that during periods of intensive blooming of phytoplankton, phosphorus became the main restricting factor in the growth of plankton in Gdańsk Bay (Ostrowski and Bojanowski 1964). In such conditions, aquatic plants can contain smaller amounts of phosphorus than land plants, even so, the concentration ratios reach as much as $3{,}000 \div 7{,}000$. It should also be mentioned that the phosphorus content of Baltic seaweed is, in practice, the same as that in plants collected in other seas and oceanic regions (Winogradow 1953, Schmid 1959).

Calcium and Strontium

The occurrence of these elements in the marine biosphere, has recently become the subject of special interest in view of the danger of radioactive contamination of the sea by strontium isotopes. From this point of view both the absolute values of these elements and their mutual relationship in various organisms and different environments are important in estimating the potential hazard from Sr 90.

The distribution of calcium in Baltic plants showed a certain differentiation depending upon the species. Basically, the only species in which calcium occurred in all samples tested, in greater amounts, was species *Fucus vesiculosus*. The concentrations found were in the narrow range of from 1.48% to 1.96% Ca. It is a characteristic feature that specimens collected from the open sea had, on average, less calcium (1.57%) than plants originating from Puck Bay (1.83%), similarly to the case with the total ash content and that of potassium (but not sodium and magnesium). Species *Furcellaria fastigiata* had the lowest calcium content: from 0.4% to 0.7% (average 0.53%). Whereas for both these species and *Chlorophyceae*, individual differences did not exceed ±30% of the average values and were of a random character, the remaining species showed several postive anomalies sometimes exceeding by 100% the average values of generally low concentrations. Thus the remaining red algae (except species *Furcellaria fastigiata)* usually contained from $0.5 \div 0.8$% calcium (similar to species *Furcellaria fastigiata)* but such high values as 1.53% and 2.24% were also found in this group.

One cannot exclude the possibility of certain species of cl. *Rhodophyceae* being especially rich in this element, as e.g. specimens with exceptionally high concentrations of calcium comprised mainly of genus *Polysiphonia*. On the other hand, small, twisted thallus of cl. *Rhodophyceae* caused considerable trouble to clean and it is possible that the reason for the high concentrations of calcium in some samples was due to the presence of small pieces of mussels *Mytilus edulis*.

Among the plant material of the species *Potamogeton pectinatus* collected from Gdańsk Bay, with an average calcium content of 0.9%, there was once sample containing 1.8% Ca; in turn, a concentration of 0.9% Ca was found in one case only in specimens collected from Puck Bay, the remaining results were from 1.6 ÷ 2.3% Ca. The same is the case, only to a lesser extent, in species *Zostera marina*. Here also most of the results are between 0.9 ÷ 1.1% Ca, but such high results as 1.7% and 2.2% also occur. The fluctuations mentioned do not show any seasonal changes, nor do they correlate to any changes in contents of other macroelements; they also occur most frequently in plant material from Puck Bay.

It has also been noticed that the calcium content in plants from Puck Bay is always higher or equal, never less than in the same species collected at the same time, in Gdańsk Bay. If it was a case of slight differences, it would be possible to explain them by a certain difference in vegetation conditions in the basins, as the water in Puck Bay becomes warmer faster, and photosynthesis as well as the intake of certain mineral elements takes place more intensively. It is more difficult, however, to explain in the same way the occurrence of greater fluctuations, especially as they are met in both regions. Attention must be paid here to the fact that certain specimens of the plants studied were covered with gelatinous mucilaginous deposits which, when dry, formed an incrustation of a rather brittle consistency. Such incrustations occurred most frequently on the stems of genus *Potamogeton*, rarely at the base of leaves in genus *Zostera*. These residues were not tested separately, it is probably however, that they are deposits of calcium carbonate agglomerated with an organic binding agent similar to those described by Oborn (1964) on plants living in both fresh and brackish inland waters. According to this author about 90% of the mineral components of this residue is calcium carbonate, the most widely distributed additions including manganese, iron, magnesium, cobalt, barium and strontium, which substitute calcium ions in the crystal lattice of calcite, in varying amounts. The weight ratio of carbonate material in dry specimens of genus *Potamogeton* can reach 12%. So far, the origin of this incrustation has not been explained univocally. It is improbable that it is related to the chemical precipitation of $CaCO_3$ after simple exceeding the ionic product of $CaCO_3$. It is a known fact that the surface waters of seas on low geographical latitudes, are, as a rule, supersaturated with $CaCO_3$. In spite of this, with the exception of certain species of algae with calcareous skeletons, seaweed living in these waters have neither incrustations nor excessive amounts of calcium inside cells. The phenomenon of supersaturation with $CaCO_3$ is not met in the Baltic. It would seem more propable that certain types of bacteria influence the appearing of carbonate deposits. Oborn (1964) was engaged in research on bacterial microflora of fresh water plants, finding numerous bacteria of species *Bacterium precipitatum Kalin* in carbonate incrustations, these being known for their ability to precipitate calcium carbonate.

Generally speaking, Baltic seaweed, from the point of view of calcium content, is very similar to the species growing in waters of a normal salinity. Young and Langille (1958) found 0.85 ÷ 2.40% Ca in the Atlantic species of cl. *Chlorophyceae*, 0.47 ÷ 2.34% in cl. *Rhodophyceae* and 0.98 ÷ 1.1% Ca in cl. *Phaeophyceae*. Bowen (1956) gives the following average calcium content for cl. *Chlorophyceae* 0.58%, cl. *Rhodophyceae* 0.34% and cl. *Phaeophyceae* 0.77 ÷ 1.63%. Mauchline and Templeton (1966) found 0.83 ÷ 1.04% Ca in cl. *Chlorophyceae,* 0.10 ÷ 1.56% Ca in cl. *Rhodophyceae* and 0.31 ÷ 2.41% Ca in cl. *Phaeophyceae;* Pillai (1956) on the other hand found the calcium content of all species studied, originating from the Indian Ocean, to be below 1% (all results expressed on a dry weight basis). In the higher land plants, the calcium content is most frequently between 1 ÷ 3% (Nowotny-Mieczyńska 1965).

Most calcium is in an immobile form, insoluble in water. It can be washed-out almost completely with dilute mineral acids, which would indicate the rather labile character of the binding. In higher plants, relatively large amount of calcium occur in pectic substances creating the main structural material around which the cell wall proper is formed. The main component of the cell walls of *cl. Chlorophyceae* on the other hand, is alginic acid, which amounts to 10 ÷ 25% of their dry matter. This most probably plays an important role in the retention of calcium in these algae.

Wassermann (1949) made experimental studies on the ability to absorb cations by various species of *cl. Phaeophyceae* algae and stated that this was of an ion exchange character. The plant material thus suggests by its behaviour, a weak cation exchange resin with an ionic capacity of 2 ÷ 3 meq/g dry weight, in which carboxyl groups of insoluble polyuronic matrix are capable of exchanging their protons for cations in the external solutions. In physiological conditions, acidic groups of cell wall material are mainly neutralized by divalent cations, in relation to which they show a greater affinity than to sodium or potassium. Basing on Wassermann's observations, the cations studied by him can be placed in the following series according to their sorption ability:

$$\mathrm{Na} < \mathrm{K} < \mathrm{Mg} = \mathrm{Ca} < \mathrm{Ag} < \mathrm{Cu}$$

If all the acid groups were occupied by calcium ions alone, then with an ion exchange capacity of algae of between 2 ÷ 3 meq/g dry weight, they should contain 4 ÷ 6% calcium. Due to competition of other ions, mainly magnesium and potassium, the true calcium content in cl. *Phaeophyceae* is less, and according to various sources is between 0.3 ÷ 2.5%.

Characteristic for Baltic species is the fact that they contain the same or even larger amounts of calcium than oceanic seeawed. The ion exchange properties of plants are more decisive as to the calcium content than the salinity dependent passive diffusion transport of the ions. With there being about four times less calcium in the Baltic coastal waters than in oceanic waters, the abundance ratio of calcium in the species studied is higher than in oceanic species and amounts to 7 ÷ 9 for cl. *Chlorophyceae* and species *Furcellaria fastigiata* and an average of 15 ÷ 17 for species with individual anomalies in Ca content. Against this background, species *Fucus vesiculosus* stands out, having a high concentration ratio of 31 on average.

The distribution of strontium in the samples studied follows the general distribution pattern of calcium. In spite of a certain scatter of results, a tendency for proportional increase in the concentration together with the calcium content, can be seen (Fig. 3, p. 36). Both elements belong to the same family of alkaline earth metals and are similar from the point of view of both chemical properties and their geochemical fate. However, due to differences in solubility of their salts and the selective processes of biological accumulation, their paths diverge in the sea, which is reflected in the differentiating of their mutual proportions in various phases of the marine environment (Thompson and Chow 1955; Bowen 1956; Odum 1957; Mauchline and Templeton 1966; Winogradow 1967). We know from research so far, that in most marine organisms, the calcium uptake is favoured as compared with strontium, the Sr/Ca relation being less than in sea water. For example: the Sr/Ca proportion in marine invertebrates is 0.0024 ÷ 0.0151, in mollusc shells 0.0028 ÷ ÷ 0.0083: in fish flesh 0.0039 ÷ 0.0070, in the skeletons of fish — 0.0033 ÷ 0.0046, whereas this is 0.0188 in sea water. It would seem from this that the abundance ratio for calcium is 1.2 ÷ 8 times higher than that of strontium.

In calcareous bottom sediments of biogenic origin, the Sr/Ca ratio is between 0.005 ÷ 0.010, which means that it is also 2 ÷ 4 times less than in sea water. It is also known that the mineralogical form of $CaCO_3$ influences the strontium content of carbonate material. For example, algae in which $CaCO_3$ is structural material of the cell wall contain varying amounts of strontium depending upon whether the carbobonate material is of an aragonite or calcite structure. In the former case, the $CaCO_3$ may contain up to 2.5% $SrCO_3$ and the Sr/Ca ratio reach 0.0340, in the latter $SrCO_3$ amounts to 0.25 ÷ 0.37% in weight of the carbonate material and Sr/Ca lies between 0.0037 ÷ 0.0055 (Lewin 1962). Thus as the result of biological processes the proportions may be reversed, i.e. to favoured accumulation of strontium. It is not known however, whether or not any physical factors play a role in this process. It is probable that the crystal nucleus of calcium carbonate grows by the accumulating on its walls of consecutive layers of carbonate material from supersaturated sea water; at the same time, thanks to the similarity of the crystallic structure of $SrCO_3$ and aragonite (the central atom in the crystal lattice unit of aragonite and $SrCO_3$ has a coordination number of 9, whereas in calcite, this number is 6), solid solutions form easier and the strontium content in aragonite can attain higher values than in calcite.

Seaweed not having carbonate skeletons contain strontium and calcium in proportions which indicate a certain discrimination against strontium. Species of the class *Phaeophyceae* are exceptions in this way; more strontium is accumulated than calcium. According to Mauchline and Templeton (1966) the concentration ratio of strontium to calcium in cl. *Phaeophyceae* from the Irish Sea is 2.5 ÷ 4.5 : 1, these ratios being reversed for cl. *Chlorophyceae* and cl. *Rhodophyceae* — 0.31 ÷ ÷ 0.66 : 1. According to Bowen's data 1956) the abundance ratio of strontium to calcium for cl. *Phaeophycea* is still higher, being 4.7 ÷ 5.9 : 1; this amounting to 1.44 : 1 and 0.57 : 1 in the species of cl. *Rhodophyceae* and cl. *Chlorophyceae* respectively.

The absolute strontium content in non-calcareous sea algae varies considerably. In literature we meet such low values as 12 mg Sr/kg dry matter and an abundance ratio of 0.2 (*Rhodymenia palmata*, according to Mauchline and Templeton 1966), and such high ones as 4400 mg Sr/kg dry matter and a ratio of 71 (*Laminaria digitata*, according to Black and Mitchell 1952). The ranges of results in the individual species are also considerable. For example *Fucus serratus* analyzed by Black and Mitchell contained $>$ 2800, $>$ 700 and 520 mg Sr/kg dry matter; Bowen (1956) gives 1045 mg Sr/kg dry matter for the same species, and Mauchline and Templeton 370 mg Sr/kg. Strontium concentrations of 240 ÷ 2600 mg Sr/kg dry matter have been found in species *Ascophyllum nodosum*. Fluctuations thus cover a whole order of magnitude. It would be interesting to learn the reasons for such wide ranges of results. Certain authors prescribe this to seasonal changes in growth conditions. There is still however, too little information to back these suggestions.

Against the background of the results, strontium distribution in Baltic seaweed does not show any important differences, but the abundance ratios $(\frac{\text{Sr in the plant}}{\text{Sr in the sea water}})$ are $2 \div 8$ times higher than in oceanic seaweed. Mention must be made of the fact, however, that the calcium abundance ratio has risen similarly, so that in effect, the mutual proportion of Sr and Ca have remained the same, in practice. Agnedal et al. (1958) studying the distribution of strontium and calcium in Baltic fish also found that the abundance ratios of these elements are about 7 times higher than in similar fish species from the Atlantic.

It can be seen from Fig. 3 that most of the analytical data are in the neighbourhood of or below the line ilustrating the Sr/Ca ratio in the Baltic surface water. The points lying on this line indicate the lack of differentiation between the accumulation of Sr and Ca in given samples in relation to sea water (Enrichment Factor = 1). Of the species studied, the closest to this character is *Furcellaria fastigiata.* The remainder, with the exception of species, *Fucus vesiculosus* and *Zostera marina*, come between the lines EF = 1 and EF = 0.5, or they indicate a certain discrimination against strontium. Species *Zostera marina* in turn indicates a somewhat greater affinity to strontium than to calcium $(1 < EF < 2)$. The deviations observed are so slight however, that it is difficult to speak of any decided leaning towards selective accumulation of any of these elements. With regard to *Fucus vesiculosus* however, the tendency towards selective sorption of strontium is very distinct. In all the specimens tested, strontium was concentrated $3 \div 5$ times more than calcium, this meaning to the same degree as in Atlantic specimens, (Bowen 1956; Mauchline and Templeton 1966). Information available from literature would appear to indicate that this property is characteristic for all algae of the *Phaeophyceae* and not found outside this class. It is to be presumed that this is related with the occurring of specific chemical compounds present only in those algae and capable of favoured strontium fixation. Alginic acid would correspond to the first of these conditions.

Trace metals

Before commencing a detailed discussion of the distribution of the individual microelements in Baltic seaweed, several general comments concerning all these elements in the plant species studied, should be given. As can be seen from the figures given in Tables $1 \div 7$, they occur in varying amounts, their concentrations often fluctuating within a whole order of magnitude. In this they differ from the macroelements, the concentrations of which are fairly uniformly distributed. A characteristic feature is that the greatest scatter is not for the elements of the smallest concentrations such as copper, nickel or cobalt, but in iron and manganese which often occurred in concentrations in the range of tenths of a percentage, in other words — typical for macroelements. This fluctuation, which is not usually accompanied by changes in other parameters, considerably hinders the detection of any general regularity ruling the occurence of individual trace elements.

Basing on observations made so far, a whole series of factors can be mentioned which probably influence the accumulating of trace elements in seaweed. The most important include the concentration of a given element and its physical and chemical forms in sea water, the individual properties of a plant resulting from it belonging to a given species, class or family, its life activity and stage of development, also environmental conditions such as temperature, salinity and light conditions.

In research on the distribution of trace elements in marine algae, it is impossible to control all parameters influencing the uptake and accumulation of chemical elements by plants. With regard to the macroelements of sea water, which are fairly stable in their mutual proportions, to check the chemical composition it is sufficient to determine the salinity and it is often possible to omit this. As regards trace elements, concentrations of these are not proportional to the salinity and show such variability that the utilizing of any constant numerical values is risky. To determine the influence the concentration of such an element in the surrounding water has on its contents in a plant organism studied, continuous studies on the changes in concentrations in the given environment should be carried out. Single analyses of water samples taken at the same time as the plant specimens (if such analyses are carried out) can only give some idea as to the order of magnitude of a given trace element and not the true abundance in the given environment. Experimental data indicate that the response of plants to changes in concentrations of many trace elements is not as rapid as to changes in concentrations of alkali metals. It is frequently weeks before balance can be established and often such stability is impossible even after longer periods of time (Ericson 1952; Ichikawa et al., 1961; Hiyama et al., 1964). It is also the rule rather than an exception, that concentration factors determined experimentally, e.g. using isotope indicators, are lower than those obtained by means of analysis of stable counterparts (Ichikawa et el, 1961; Polikarpow 1964). It results from this that a certain fraction of trace elements is irreversibly bound to plant material and is not available for isotope exchange. Proof of the strength of bonding of trace metals to plant tissue is the fact that even after soaking in fresh water for long periods, they are not leached, as opposed to most of the inorganic macroelements (Black and Mitchel 1952; Young and Langille 1959).

There is also a shortage of satisfactory information as to the physical-chemical forms of many trace elements in sea water and it is difficult to assess the proportion of the total amount of a given element which occurs in a form which is assimilable for marine organisms.

When considering the influence concentrations of trace elements in the surrounding water have on their abundance in aquatic plants, we should also take into account the huge temporary fluctuations which might occur as the result of uncontrolled pollution of the sea by domestic and industrial sewage. Such a situation is typical for coastal waters in heavily urbanized or industrialized regions.

As regards the influence of the development stage of plants on the contents of various elements, this should be reflected in the results of analyses of samples taken at different times. Owing to the variety of environmental conditions however, it is difficult, with a few exceptions, to determine such relationship clearly. The situation is further complicated by the fact that many species are perennial organisms and as the chemical composition of the young and old parts of plants differ greatly, the results of analyses depend upon their proportions in the sample.

Such environmental conditions as temperature, salinity, nutrient salts and light conditions have a direct influence on the physiological activity and thus on the balance of mineral components in plant organisms. Acording to Black (1948, a, b; 1949) the iodine content of cl. *Phaeophyceae* algae increases with the depth, which suggests a direct connection with light conditions. The same author has also indicated a connection between the abundance of the main ionic components and the total ash content, and the time at which the sample was taken. It is difficult however to speak of such relationship in respect of trace elements, although authors (Black and Mitchell 1952) try to suggest its existence, but the arguments put forward are not very convincing as they are based on a small number of analyses (three series). The works of Young and Langille (1959) and Pillai (1956) based on more extensive observations do not indicate the existence of any clearly defined seasonal relationships in the occurring of many trace metals, whereas such a relationship has been noticed in the main ionic components as well as in iron and manganese (Pillai). Ishibashi et al. (1964) basing on the results of studies on 77 samples of seaweed from 38 species, stated that there was a lack of any seasonal dependence in the occurring of nickel, cobalt and iron in every one of the species.

Authors are agreed on the fact that individual classes of algae show differences in the contents of trace metals. Although the concentrations of individual elements differ from sample to sample and also depending upon the environment from which the plants originate, there are also differences between species from other classes of plants when we consider specimens collected from the same region at the same time. It would be too simple to expect such consistency when comparing the analytical results of single samples.

The greatest difficulty occurs when interpreting results which differ considerably from the average. In such cases the analytical procedure, during which contamination or loss of an element could occur, are often suspect. The danger of contamination most frequently occurs during the collecting and preliminary preparation of the samples. Material collected from an unconsolidated substratum often contains mineral particles, some of which adhere strongly to the plant surface in spite of rinsing, and these are analyzed together with the specimen. Such a situation is typical for the southern coasts of the Baltic and its bays. The sporadic occurrence of mineral deposits on certain parts of plants is a separate problem. Carbonate incrustations have already been mentioned when discussing the occurring of calcium. Iron hydroxides may be another type of mineral deposit. The sandy bottom sediments along the coast of the Bay of Gdańsk and in the whole of Puck Bay, in contact with the interestitial water and with the participation of organic substances release certain amounts of iron which, after diffusion to the bottom water is precipitated as hydroxide on the exposed parts of plants. Quartz sand with limonitic coatings can be met in the regions mentioned. Plants from these regions were not specially studied from this angle, but occasionally brown stains were noticed on their surfaces and these could be attributed to the presence of iron hydrated oxides. Certain fresh water algae with limonitic coatings were described by Starmach (1936). Finally, epiphytic microforms of plants can also, to a certain extent, change the chemical character of a host plant.

All the circumstances mentioned mean, in effect, that it is difficult to asses the occurrence and distribution of trace elements in aquatic plants, but as the result of the numerous factors influencing the plant — water environment system, it is easy to relapse into the habit of simplified interpretation.

The greatest shortcoming of all such work is the insufficient quantative representation of plant material specimens. Authors usually work on collections of from several to tens of samples. After sorting according to species, study regions and time of collection, the number of specimens in individual sub-collections is frequently reduced to single specimens, which eliminates the possibility of any statistical description whatsoever. In such a situation, the results of analyses give only an idea as to the order of magnitude, differences between species and the mutual proportions of the elements denoted, rarely to they show the variation of concentrations in the individual plant species, and in general say little about the reasons for the changes, i.e. whether and to what extent they are connected with the changing external conditions or the life cycle of a plant.

This paper discusses, in principle, the occurring of several trace elements in Baltic seaweed to the same extent as other papers of the same character. It is, in the same way, not free of the same shortcomings. In spite of a fairly large collection, (over 70 specimens from 7 species), the relationships observed are not very clearly outlined and should rather be treated as a tendency. Even so, the results of determinations supply a considerable amount of interesting information about th species studied and the environment, as well as the range of concentrations occurring, which differs frequently from the information published so far for other regions. These first analytical data originating from the region of the southern Baltic, together with the conclusions drawn from them, can provide the basis to further, more detailed research on microelements in the Baltic biosphere.

Zinc

Of the trace elements occuring in Baltic seaweed, in respect of abundance, zinc comes next after iron and manganese. Its distribution pattern confirms the earlier findings as to the relation between the occuring of microelements and the taxonomic position of plants analyzed. Taking the average values as the basis for comparison for the individual species, we can state that the lowest concentrations of zinc are in cl. *Chlorophyceae* (genus *Enteromorpha sp.* 60 mg Zn/kg in dry matter; genus *Cladophora sp.* 80 mg Zn/kg in dry matter; and species *Zostera marina* (300 mg Zn/kg dry matter). The highest values being in species *Fucus vesiculosus* (310 mg Zn/kg dry matter). The average concentration for the remaining species is as follows: species *Furcellaria fastigiata* — 110 mg Zn/kg, species *Potamogeton pectinatus* — 140 mg Zn/kg and the remaining cl. *Rhodophyceae — 240 mg Zn/kg*. Cl. *Chlorophyceae,* although not represented in great numbers, were characteristic for their relatively small scatter of analytical results (35 ÷ 130 mg Zn/kg). This scattering does not appear to depend on either the place or the season in which the specimens were collected, but it has been noticed that the amounts of other microelements (but not major cations) increase together with the increase in the amount of zinc. The distribution of zinc is even more uniform in species *Potamogeton pectinatus,* where all the results were between 110 ÷ 200 mg/kg. The lowest concentrations were in the summer months. As in the case of cl. *Chlorophyceae* there is a certain correlation between the zinc content and that of other trace metals. Specimens of plants originating from Puck Bay did not differ from the point of view of zinc content, from specimens collected in Gdańsk Bay. Species *Zostera marina,* also belonging to the higher plants, has a greater average zinc content and a much bigger range of individual results, covering a whole order of magnitude (from 80 to 820 mg Zn/kg). When comparing samples of *Zostera* and genus *Potamogeton* collected simultaneously, in the same place, it appears that in most cases, specimens of the latter species are more abundant in zinc. The difference lies in the fact that the samples of genus *Zostera* originating from Gdańsk Bay contained more zinc than those collected at the same time in Puck Bay, nothing like this being observed for genus *Potamogeton.* It can also be seen that the results of analysis are influenced to a certain extent by the time at which samples were collected. In the autumn months the zinc content in genus *Zostera* specimens begins to rise gradually, this increase being more marked than in genus *Potamogeton,* which is reflected in the average content of this element in each species. Mention must also be made of two cases of exceptionally high zinc contents (630 and 820 mg/kg) unrelated to any special physiological state of the samples. Both originated from Gdańsk Bay and were collected during the summer. A characteristic feature was the high iron and copper content not met in the remaining specimens, whereas other elements were on the normal level. It would be difficult to explain the anomalies mentioned other than that during the time the specimens were taken, the sea water in the region contained especially large amounts of zinc (and possibly iron and copper). There is no experimental proof to this however, as these amounts of elements in sea water were not determined at that time. Intermediate proof of such a conclusion can be obtained by comparing the results of analyses of several other specimens of plants collected at the same, or almost the same time. All of them, irrespective of differences in species and even place where the specimens were collected, were conspicuous among others by the higher content of zinc, copper and iron simultaneously. Genus *Zostera* is the only showing such a high range of results. The concentrations of zinc in cl. *Rhodophyceae* (80 ÷ 480 mg Zn/kg) change to a lesser extent. Specimens originating from Gdańsk Bay have a lower concentration (80 ÷ 140 mg/kg) than those from Puck Bay (140 ÷ 480 mg/l). Of the elements studied, only copper showed a certain similarity to zinc in its occurrence. Considebrable accumulations of all the remaining trace metals have been observed in this group of seaweed in which the highest concentrations are reached (Table 5). Against their background, the zinc contents are not conspicuous amongst the species already discussed. Species *Furcellaria fastigiata*, also belonging to cl. *Rhodophyceae*, contain on average, more than two times less zinc than other species of the same class. Here also a certain correlation can be seen between the zinc and copper contents, and lack of such as compared with the remaining trace elements.

Fucus vesiculosus shows the greatest affinity to zinc, this being visible in this species having the highest average content with a relatively small range of fluctuation 150—500 mg/kg. After discarding the two extreme concentrations, the range narrows to 230 ÷ 390 mg/kg. It results from the data given in Table 3, that the zinc content is very similar to that of iron, but no correlation between these two elements has been observed. Here again, however, similar to the case with cl. *Rhodophyceae*, there is a correlation with copper, and in view of the low concentration of this element in *Fucus vesiculosus* the Zn/Cu ratio reaches the high value of 65, not met in the Baltic seaweed species studied so far. It should also be added that — as far as can be judged from the data on hand — the distribution of zinc in *Fucus vesiculosus* is not affected by seasonal changes nor does it indicate any relationship with the place in which specimens are collected.

Zinc is one of the elements essential for growth and development of both plants and animals. In living organisms it fulfils a series of important biochemical functions as a component of the enzymes: carbonate anhydrase, carboxypeptidase and dehydrogenases, as well as participating in the regulation of protein metabolism and the synthesis of plant growth factors (Nowotny-Mieczyńska 1965). It is thus a common mineral component of plants which occurs in small amounts depending upon the species of plant and type of substratum. In land plants, the amount of zinc is usually from 10 ÷ 200 mg/kg dry matter, the greatest amounts being in the green parts of the plants. There are symptoms of zinc deficiency where the concentration is less than 10 mg/kg.

According to various authors, the zinc content of marine algae is similar to that of land plants. The results put forward in this paper indicate that the upper limit of concentration can considerably exceed 200 mg/kg, this undoubtedly depending upon the environmental conditions specific to a given water region. The amount of zinc in sea water can fluctuate considerably. According to Branica (1968), who compared the analytical data published up to the present, the zinc concentrations met come between 3 ÷ 86 µg/l (most frequently between 5 ÷ 20 µg/l).

Only part of the zinc occurs as simple metal ions, the remainder comprises undefined organometallic complexes and colloidal particles.

Rona et al. (1962) found large amounts of zinc — mainly in the bound form — in coastal waters containing large amounts of organic substances. E.g. they stated that in Redfish Bay with a total zinc content equal to 32.8 µg/l, the ionic fraction extractable with diethyldithiocarbamate comprised barely 1.8 µg/l, i.e. not quite 6%. In the Baltic coastal waters 4.5 ÷ 23 µg Zn/l have been found (Buch 1944, according to Branica 1968).

In order to estimate the abundance ratio of zinc in Baltic seawed, 20 µg Zn/l has been accepted as the average concentration in the water of the region from which the specimens are taken. The coefficients are given in Table 10. These cover a range of from hundreds to thousands, the lowest value (200 ÷ 400) being for cl. *Chlorophyceae*, the highest in species *Fucus vesiculosus* (3,000). These figures should be treated as approximate values ah their accuracy is restricted by the simplifications mentioned. As however, the plant specimens were uniform to a large extent from the point of view of place and time of collecting, mutual proportions between the abundance ratios for the individual species illustrate their true properties. Thus we can say that cl. *Rhodophyceae* and flowering plants concentrate 3 ÷ 7 times more and species *Fucus vesiculosus* 10 times more zinc than cl. *Chlorophyceae*. Pillai (1956) found a similar tendency in seaweed from the Indian Ocean, only that the absolute zinc contents were 10 times lower than in Baltic plants (10 ÷ 90 mg/kg). Concentrations of zinc in algae from the Canadian Atlantic coast were somewhat higher, although also less than in the Baltic (Young and Langille 1958). The authors give the values to be between 35 ÷ 97 mg Zn/kg; they mention at the same time, that certain species originating from the Pacific coast are much richer in zinc. No differences between the individual classes of algae were noticed however. The analytical results given by Black and Mitchell (1952) are similar (40 ÷ 148 mg Zn/kg). As mentioned, species *Fucus vesiculosus* stands out from the Baltic seaweed, having the highest concentrations of zinc and a relatively low scattering of results. It is interesting to note that these tendencies were not noted in the publicacions mentioned; e.g. Langille gives 49 mg Zn/kg and Black 60 and 105 mg Zn/kg. Information is also to be found however, of exceptionally high concentrations of zinc, e.g. in specimens of *Fucus vesiculosus* collected on the Atlantic coast at Woods Hole, 472 mg Zn/kg have been found (Gutknecht 1965) and even 829 mg Zn/kg (Gutknecht 1963). An analysis of sea water sampled at the same time showed the presence of 18 µg Zn/l. The abundance ratio here reaches considerable values, up to 7.000 (reckoned in material with natural moisture content). Other authors give values between 400 ÷ 3.000, depending upon the species, in other words, similar to those given in this paper.

The high abundance ratios and the role fulfilled by zinc in the biochemical reactions taking place in living organisms, give rise to the presumption that the intake of this element is an active process, controlled by the rate of carbon assimilation. Such an opinion was put forward by Bachmann and Odum (1960) basing on the simultaneus measurement of the rate of zinc uptake and primary production for six species of marine algae. The results of later research however (Gutknecht 1961; 1963; 1965) indicate that the sorption of zinc by plants is of both biological and physical origin, the latter being the dominating. The nature of the zinc sorption is fairly accurately described by Freundlich's equation of isotherm adsorption:

$$\log\left(\frac{x}{m}\right) = \log a + b \log c,$$

where $\frac{x}{m}$ is the amount of zinc adsorbed per mass unit of adsorbent,
c — the concentration of zinc in the external solution,
a and b — constants.

It results from the character of the sorption forces that the accumulation of Zn is not a selective process. One can speak of competition between zinc and other ions to win cation binding sites. As already mentioned, polysaccharides from which algae cell walls are built, indicate ion-exchange properties thanks to the presence of such acid groupings as $-COOH$ and $-OSO_3H$. There also exists another mechanism of binding zinc ions, namely by forming reversible complexes with proteins (Johnson and Schrenck 1964). The equilibrium of this reaction depends upon the hydrogen ion activity:

$$Zn^{2+} + \text{protein} \rightleftarrows Zn - \text{protein} + 2H^+$$

and moves towards the zinc bindings as the pH rises. Both these mechanisms can, in effect, lead to the accumulating of considerable amounts of not only zinc but other metals such as copper, nickel, cobalt and manganese, in sea-weed, on condition that they are present in sea water in sufficient concentrations and assimilable forms.

Copper

The average copper contents varied between 5.6 mg/kg and 21.2 mg/kg, depending upon the species. As regards the maximum range between individual results, these covered values from 3.6 to 36.8 mg Cu/kg. The lowest concentrations of copper, both individual and average, occurred in species *Fucus vesiculosus*, the highest in cl. *Rhodophyceae* and species *Zostera marina*.

When discussing zinc, mention was made of the fact that there was a certain similarity between this distribution pattern and that of copper in the specimens studied. The latter element usually occurs in concentrations an order of magnitude lower than the Zn content, but the relationship between the average contents of zinc and copper are not the same for individual species of seaweed. As can be seen from Table 11, the differences are considerable, the numerical values on the other hand could indicate a certain affinity of these plants to zinc. To prove that this is so, these values should be normalized to the actual ratio of Zn/Cu in sea water. So far however, no systematic research on the distribution pattern of trace metals in the Baltic has been carried out, in view of which there is a lack of reliable information on this subject. From a review of papers published so far (see Winogradow 1967), it would seem that the amounts of copper most frequently met in oceanic water are between 1 ÷ 10 μg/l, althought later research mentions lower concentrations, e.g. from 0.00 to 3.86 μg/l (Fonselius 1970) and 0.00 ÷ 5.53 μg/l (Slowey and Hood 1966). A few samples of filtered sea water taken at Sopot gave values ranging from 1.8 to 9.7 μg/l with an average of almost 5 μg Cu/l. The approximate ratio of Zn/Cu would thus be roughly 4 for Baltic coastal waters, which would be similar to the typical values for sea waters which, according to Winogradow (1967) range from 3 ÷ 4. The same author noticed that marine organisms which do not indicate special tendencies to accumulate these elements, contain zinc and copper in the proportions 3 ÷ 5 : 1, which would confirm the principles accepted above.

Table 11

Mutual Proportions of *Zinc* and *Copper* in Baltic Seaweed

Class	Average Zn/Cu values in seaweed	$\frac{\text{Zn/Cu in seaweed}}{\text{Zn/Cu in seawater}}$
Chlorophyceae	5—8	1—2
Phaeophyceae	65	16
Rhodophyceae	9—11	2—3
Potamogetonaceae	17—20	4—5

Dividing the average values of Zn/Cu for the individual species of seaweed by the estimated ratio of Zn/Cu in sea water, we obtain a figure which is the index of a certain preference in favour of zinc (Table 11).

It would seem from these data that cl. *Chlorophyceae* take in both Cu and Zn in proportions approximately equal to those which occur in sea water, whereas cl. *Phaeophyceae* species *Fucus vesiculosus* exhibit a strong affinity to zinc.

The abundance ratios for Cu are relatively small and do not show such differences between species as other trace metals (Table 10). These, in most cases, amount to about 200 with the exception of cl. *Rhodophyceae* (400 ÷ 600) and *Zostera marina* (400).

It is difficult to find any simple explanation as to why copper binds to plants much weaker than e.g. zinc, nickel or cobalt, even thought that element forms complexes of a similar or even greater stability with organic compounds (Sillén et al., 1964). One could assume that the mode of occurrence of Cu in sea water, plays a certain role. Since copper ions tend to bind with organic matter, a large proportion occurs in the form of dissolved, poorly recognised complexes with humic and fulvic acids (Winogradow 1967). Assuming that processes of adsorption and ionic exchange play a greater role in the accumulation of this element than active process related to plant metabolism, organic substances dissolved in sea water could fulfil the role of competitive ligands for Cu ions, lowering their effective concentration and thus their availability to seaweed. Organical-bound copper was found by Slowey and Hood (1966) in many places in the oceans, the amounts being greater in surface and coastal waters. In highly productive areas the role of complexing agents is fulfilled by external metabolites of marine organisms and the products of their decay (Chajłow 1964). There is also evidence of correlation between organic matter and the copper content in marine sediments, this including the Baltic (Bojanowski et al., 1964). How far the processes mentioned influence the intake of copper by aquatic plants, it is difficult at present to assess, as knowledge of these natural chelators is very slight still. It is also impossible to state with any degree of certainty that the presence of complexing agents lessens the intake of one or another element, until information is obtained as to the form in which the given element is taken up by a plant (as a free ion or together with an organic ligand), also how fast the new state of equilibrium between the ion and the complex is established in the case of ionic mechanism of accumulation.

From the point of view of copper content, the Baltic seaweed does not differ from algae living in other seas and oceans. According to Pillai (1956) species growing along the coast of India contained up to 30 μg Cu/kg; most results were below 10 μg Cu/kg and samples of inteterminable concentrations (i.e. less than 1 μg Cu/kg) were not infrequent. The distribution of copper content in individual species was of a chance character however. It was also impossible to find the relationship between the development stage and the occurring of this element in species studied. Amounts of between 6 ÷ 62 mg Cu/kg were found in Atlantic seaweed (Young and Langille 1958), the greatest concentrations being in cl. *Chlorophyceae*, the lowest — in cl. *Phaeophyceae*. Similar to Baltic seaweed the average Zn/Cu value for individual classes of algae increases as follows:

Chlorophyceae < *Rhodophyceae* < *Phaeophyceae*

and the concentration ratio is several times less for copper (50 ÷ 600) than zinc (100 ÷ 3000). The average concentration of copper in land plants is between 3 ÷ 40 mg/kg. This element participates in a number of enzymatic reactions involved in electron transfer, thanks to the following reversible redox reaction:

$$\mathrm{Cu}^{+} \rightleftarrows \mathrm{Cu}^{2+} + \bar{e}.$$

The more important copper enzymes include: polyphenol oxidase, laccase and ascorbid acid exidase, as well as certain flavoproteins. It has also been confirmed that copper plays a role in the reduction of nitrates and also is part of the composition of certain cytochromes which regulate the redox reactions in plant tissue. These important functions which copper fulfils in biological systems explain its presence in living organisms. The physiological demand for this component is not very great however, and it is only when the copper content of the vegetative parts of plants is less than 1.5 ÷ 3 mg/kg that signs of its dificiency appear (Majewski 1961).

Most probably only a small fraction of this element occurs as a component of the enzymes mentioned. Very little is known as yet about other forms of its occurrence. According to some authors, copper is strongly bound to protoplasm (Erkama 1950). It is possible that certain proteins exist which can easily bind with this element. It is also considered that the main form in which copper occurs is in chelate compounds (Mengel 1961). As shown by Black and Mitchell (1952), as well as Young and Langille, copper cannot be removed by prolonged soaking in fresh water, which would indicate its relatively strong binding to the cell structure material. This appears to be typical for most trace metals.

Nickel

Nickel is present in Baltic seaweed in amounts of from 2.3 to 15.1 mg/kg (average value), depending upon the species. Extreme values for individual specimens amounted to 1.3 and 22.4 mg/kg respectively. The lowest average concentration (and individual) occurred in cl. *Chlorophyceae*. For genus *Enteromorpha* they amounted to 2.3 mg/kg and for genus *Cladophora* 3.3 mg/kg.

Family *Potamogetonaceae* contained an average of 4.0 mg Ni/kg *(Potamogeton)* and 4.6 mg Ni/kg *(Zostera)*. The remaining species studied had a nickel concentration several times higher, reaching an average of 13.2 mg/kg species *Furcellaria fastigiata*, 13.8 mg/kg — other cl. *Rhodophyceae* and 15.1 mg/kg species *Fucus vesiculosus*.

The scatter of individual results within the particular species is relatively small, the maximum deviation does not exceed twice the value of the average. There is nothing to indicate any seasonal variations however. A review of the results of analyses of samples taken from various places also fails to offer any basis for conclusions as to the influence of environment. Thus the only relationship which was clearly defined results from the taxonomical position which plants occupy. It can be seen from the data presented here, that algal species within the same class do not differ greatly in their nickel content, whereas there are substantial differences between the classes.

No much is as yet known of the biological function of nickel in plant tissue. We know of no biochemical reactions in living organisms which are specifically catalyzed or activated by nickel ions. Therefore, in the light of Arnon's criteria (1954) the question of the indispensability of nickel has not yet been solved. If it is really an essential microelement, the demand for it is many times less than the amount found in plants. It can be said then, that the biological accumulation of nickel does not result from the physiological requirement of plant organisms, but from the sorption properties of their tissue. When studying average abundance ratios (Table 10), the privileged position of brown and red algae in the accumulation of nickel can be seen clearly. As the cell wall material is composed of polysaccharides with strong ion-exchange properties, there is an automatic suggestion of participation of these compounds in the processes of sorption and retention of trace metals, including nickel.

From the point of view of chemical properties, nickel is similar to cobalt. The geochemical fate of both elements results from this similarity. This is especially clearly marked in processes of crystalization of igneous rocks. Ultrabasic and basic rocks are particularly rich in Ni and Co, their mutual ratio being close to 20. In the hypergenic zone however, partial separation of these elements takes place, this resulting in the lowering of the Ni/Co value. Marine sediments have a Ni/Co ratio of from 1.5 to 5, the lower values being met in pelagic sediments in the Pacific, iron-manganese nodules and red clay (Landergreen 1964; Goldberg and Arrhenius 1958; El Wakeel and Riley 1961), and the higher — in Atlantic bottom deposits and off-shore mud, (Landergreen 1954; Wedepohl 1960; Hirst 1962).

Own research carried out on bottom sediments from Gdańsk Bay showed that they contain nickel and cobalt in ratios of almost 4 : 1 (the average value from 38 samples), the Ni/Co ratio for sandy sediment being between 1.4 and 2.7 and that for fine-grained mud with a high organic carbon content 3.4 to 4.4. The character of the bottom substratum has a varied influence on the supply of phytobenthos with trace elements. This influence is probably greater in the case of *Potamogetonaceae* plants which can take in certain mineral components by means of roots. In the remaining cases this mainly leads to controlling the concentrations of trace metals in sea water by the regulation of reversible sorption processes on the mud-bottom water interface (Hays 1964). Here bottom sediments play the role of a high capacity ion-exchange buffer and as Parker showed (1966), are involved in the exchange of certain trace elements between sea water and marine plants.

The mutual proportions of nickel and cobalt in sea water vary. The following list contains certain data taken from literature on the subject (Table 12).

These data indicate that individual results for nickel and cobalt vary and in extreme cases, may cover two orders of magnitude. The same is the case with the mutual ratios of Ni/Co, which for single samples may have values ranging from 1.0 (Young and Langille 1958) to 130 (Schutz and Turekian 1965). Such a great variety of analytical data indicates that spatial distribution of both these elements can vary greatly in various parts of the oceans, even if allowance is made for a broad margin of uncertainty resulting from different analytical methods used.

Comparing the Ni/Co ratio in marine sediments ($2 \div 4$) with the average ratios of these elements in sea water ($5 \div 20$), it can be stated that cobalt is less stable and readily removed from the sea water on to sea bed. Nickel on the other hand shows a greater tendency to remain in a dissolved state and is thus available for marine organisms in larger amounts. These differences in behaviour of both elements causes increased disproportions in their occurring in sea water, as they recede from the land and the Ni/Co ratio — as we see from available data — is higher for the open sea than for the coastal zone. It is to be presumed that the ratio of average Ni and Co contents in oceanic waters, amounting to about 20 (basing on data by Schutz and Turekian), reflects reasonably truly the situation in regions sufficiently distant from continental influences; on the other hand a ratio of $1 \div 10$ Ni to Co is more characteristic for coastal waters where the algal population is most dense.

Table 12

The occurrence of nickel and cobalt in natural waters

Region of investigations	Nickel µg/l	Cobalt µg/l	Ni/Co	Reference
Seas				
Dannish Straits (Gullmar fiord)	0.5	0.1	5,0	Noddack and Noddack (1939
Black sea	6.0	3.5	1,7	Maluga (1945)
English Channel	5—6	0.3	17	Black and Mitchell (1952)
Pacific (Japan)	0.75	0.5	1,5	Ishibashi (1953)
Pacific (Puget Sound)	2.0	0.28	7,2	Thompson and Laevastu (1960)
Atlantic	0.5	0.5	1,0	Young and Langille (1958)
All oceans	5.4 (0.43—43)	0.27 (0.03—4.1)	20 (5.8-130)	Schutz and Turekian (1965)
Baltic	0.6a)	0.1b)		a) Dobrowolski and Ostrowski (1965)
		(0.03—0.37)b)	6	b) Bojanowski (unpubl.)
Rivers				
Ob (USSR)	1.8	1.7	1,1	Nesterowa (1960)
Ket (USSR)	1.7	1.0	1,7	
Large rivers of North America	10 (0—71)	0 (0—5.8)		Durum and Haffty (1963)
		0.20 (0.037—0.05)	50	Kharkar et. al. (1968)
Vistula (Poland)				Bojanowski (unpubl.)
dissolved		0.02—0.05		
suspended		0.17—0.35		

The Ni/Co ratio in Baltic seaweed has several interesting properties (Table 13). In species belonging to cl. *Chlorophyceae* it has the same values as in the surrounding water, from which it results that these algae do not show selectivity towards either of these elements. Simultaneously, the Ni and Co abundance ratios take on the lowest values here. Observations indicate a similar accumulation mechanism for both nickel and cobalt in the species discussed. Species *Fucus vesiculosus* differs greatly from the remaining species. It shows a strong affinity towards nickel and the amounts it can accumulate in its tissues can reach as

Table 13

Nickel to cobalt ratio in the baltic seaweeds

Species	Ni/Co			Ni/Co Puck Bay / Ni/Co Gdańsk Bay	Ni/Co in plants / Ni/Co in sea water
	For all samples	Puck Bay only	Gdańsk Bay only		
Entermorpha spp.	6.6	6.8			1.1
Cladophora spp.	6.2	6.2			1.0
Fucus vesiculosus	10.5	12.9	8.1*	1.6*	1.8
Furcellaria fastigiata	7.2	7.2			1.2
Other *Rhodophyceae*	3.4	3.6			0.6
Zostera marina	2.4	5.3	1.6	3.4	0.4
Potamogeton pectinatus	4.4	9.8	2.4	4.1	0.7

* Southern Baltic (at Rozewie).

high as 30 mg/kg dry matter (in comparison, it is worth mentioning that the the average contents of this element in other marine algae do not exceed 10 mg/kg). This is the only species where it is possible to observe differentation in the intake of cobalt and nickel, in favour of the latter (erichment factor 1.8 — the last column in Table 13).

In f. *Potamogetonaceae* and cl. *Rhodophyceae* (with the exception of species *Furcellaria fastigiata*) cobalt occupies the preferential position, in the case of species *Zostera marina* for example, the amount of cobalt is more than twice that of nickel.

Comparing the results of analyses of plant specimens collected in the region of Puck Bay and Gdańsk Bay, no essential differences in the nickel contents have been noted. There are, however, considerable differences in the mutual Ni/Co ratios, as can be seen from comparison of average values for f. *Potamogetonaceae* from both regions (Table 13), and also the list of data for individual samples from the remaining species taken from both regions at one time. The differences mentioned indicate that as compared with nickel, the amount of cobalt in plants is 3—4 times lower in Puck Bay than in Gdańsk Bay.

Fig. 4 (p. 56) illustrates the frequency distribution for nickel in Baltic seaweed. When drawing up this diagram, all specimens were treated as if they belonged to a homogenous class. The shape of the histogram obtained indicates however, that it comprises at lease two subclasses. The first, with a modal value of between 2 ÷ 4 mg Ni/kg, consists of all the samples of cl. *Chlorophyceae*, all the samples of

f. *Potamogetonaceae* (with the exception of one) and one sample of cl. *Rhodophyceae.* These have concentrations of from 0 to 8 mg Ni/kg and comprise 54% of all cases. The second part of the histogram, with a modal value of between 12 ÷ 14 mg Ni/kg, is flatter and includes concentrations of from 8.1 to 24 mg Ni/kg. This part comprised all samples of species *Fucus vesiculosus* and species *Furcellaria fastigiata,* all (except one) samples of the remaining cl. *Rhodophyceae* and one sample of species *Zostera marina.* Thus in spite of a small collection of analytical data, the statistical division into species rich and poor in nickel is clearly outlined.

Data on determination of nickel content in marine algae are relatively few. The nickel content in oceanic species is generally somewhat less than in Baltic seaweed. Ishibashi (1964) states that in algae growing in the region of the Japanese Island, nickel occurs in concentrations of from 0.44 to 10.1 mg/kg, the highest being most frequently found in cl. *Phaeophyceae* and the lowest — in cl. *Rhodophyceae.* There were exceptions however. Most of the samples had a Ni/Co ratio of between 3 ÷ 5. It was not possible to establish any seasonal variations nor those related to the place in which the samples were taken. A lack of relationship between the nickel content and the total ash content was also established. According to Black and Mitchell (1952) cl. *Phaeophyceae* on the coast of England contained 1.5 ÷ 9.3 mg Ni/kg, the mutual ratio of nickel and cobalt being between 3.4 ÷ 9.6. It results from observations of Young and Langille (1958), that algae of the cl. *Rhodophyceae* are richer in nickel than cl. *Phaeophyceae* and the Ni/Co ratio may exceed 15. Land plants most frequently contain 0.1 ÷ 5 mg Ni/kg (Mengel 1961), but in certain soils derived from basic or ultrabasic rocks (e.g. serpentinite, dunite), a concentration of a whole order of magnitude higher may be reached. In such cases the Ni/Co ratio in plants, is almost 20 (Winogradow 1957). Thus then, both the absolute concentrations of nickel and its ratio to cobalt are connected not only with individual properties of the various plant species, but also the overwhelming influence of environmental conditions.

Iron and Manganese

Of all the trace elements studied, iron and manganese are the ones which occur in the largest amounts in Baltic algae. The amounts change considerably in the individual systematic groups and also depend, to a great extent, on the locality. Differences between species are most characteristic, these including both the absolute values of both elements and their mutual ratios. Of special interest is the fact that the distribution of manganese does not follow the distribution pattern of iron.

In both genus of cl. *Chlorophyceae* algae, iron occurs in relatively large amounts. The average iron content which is 930 and 1,680 mg/kg for genus *Enteromorpha* an genus *Cladophora* respectively, can only be treated as representative with considerable approximation in view of the small number of samples and the wide scatter of results covering a whole order of magnitude. For example, half the genus *Enteromorpha* samples contained between 510 ÷ 590 mg/kg of iron, the greatest and smallest results amounting to 2740 and 210 mg/kg respectively. The specimens of genus *Cladophora* did not indicate a similar tendency; in this case the results covered a wide range of concentrations in a haphazard manner (Fig. 4), which made any statistical interpretation impossible.

In species *Fucus vesiculosus*, iron is more uniformly distributed. The average content amounted to 380 mg/kg and over 60% of the samples lay in the 200 ÷ 400 mg Fe/kg range. Specimens taken from Puck Bay are conspicuous by the higher average iron content as compared with the remaining samples (450 and 230 mg Fe/kg respectively).

Species *Furcellaria fastigiata* is characteristic for its higher average iron content (820 mg/kg) with a relatively small range of fluctuation of the individual results (560 ÷ 1020 mg/kg). All the samples originated from Puck Bay; the lack of data from other places hindered the checking of whether in this case there was any regional variation. The iron content in the remaining species of cl. *Rhodophyceae* is even higher (an average of 2050 mg/kg), and fluctuates between 830 ÷ 3910 mg/kg.

Species *Zostera marina* is characteristic for extensive fluctuations in iron content, these covering a whole order of magnitude (120 ÷ 1540 mg/kg). Of the samples analyzed, two differed considerably from the remainder from the point of view of iron content (1110 and 1540 mg/kg). This was accompanied by exceptionally large amounts of zinc and copper. The average iron content for this species amounts to 440 mg/kg. Samples taken from Gdańsk Bay appear to be on average, over twice as rich in this element than those originating from Puck Bay. This difference is only an apparent one, as after rejecting the two highest results mentioned, the average value for both regions then becomes 280 and 370 mg Fe/kg respectively. A similar situation has been observed for the second species of family *Potamogetonaceae* — *Potamogeton pectinatus* — where the average concentrations amount to 250 and 340 mg Fe/kg for the two regions. As regards seasonal fluctuations in the occurring of iron, it is difficult to speak of any correlation in respect of lower plants. Certain opposing tendencies occur in higher plants, as e.g. whereas from June to October the iron content in genus *Zostera* samples from Puck Bay dropped gradually, that in specimens from Gdańsk Bay rose.

On the basis of data so far available, it is impossible to state whether or not seasonal changes do take place. At any rate, if there are any seasonal dependent variations, they are overlapped by random variations of Fe content.

Frequency distribution of iron in Baltic seaweed is shown in Fig. 5. As can be seen, this is not of a normal character, which it would be difficult to expect for this collection of data, but it is far more uniform than for Ni, in that it does not show sings of bimodal distribution. The tailing of the diagram is formed by samples of *Chlorophyceae* and *Phaeophyceae* algae, these showing the greatest scatter of results among the species studied. After rejecting these data and arranging the samples in logarithmic order the symmetry of the histogram is greatly improved (Fig. 4).

A large number of trace elements is lognormally distributed in geological samples. This regularity was first formulated by Ahrens (1954) in the fundamental law of geochemistry. It has also been shown that the distribution of a number of elements in natural waters is lognormal (Hanya and Sawada 1956; Oleksynowa 1970). The working out of the statistical distribution of the content of trace elements in plant material causes considerable difficulty however, in view of the generally small number of analytical results in statistically uniform specifications.

Figs. 5, 6 and 7 (p. 57, 58, 59) illustrate consecutively the stages of the final histograms for iron, manganese and cobalt in Baltic algae. Numerical representation of samples in individual species is too modest for separate treatment, but for the composite diagram each species adds its individual qualities which often distort it to such an extent that it loses its uniformity. The distribution of iron contents however shows certain sings of being lognormal (with a well-expressed positive asymmetry). Zinc and to a lesser extent copper, also show a similar distribution characteristic, the remaining trace elemente such as nickel and cobalt however, are clearly divided into two or three subclasses or, as in the case of manganese, have such a large dispersion that there is not clearly defined character of distribution.

One of the most important features of Baltic algae which distinguish them from most oceanic algae, is the high content of manganese. Whereas in the latter typical concentrations are most frequently less than 100 mg/kg, certain Baltic species of the cl. *Rhodophyceae* have concentrations exceeding 0.5% of dry matter. This element, in Baltic algae, occurs in very wide ranges of concentration — from 20 to 5200 mg/kg. The average content in *Enteromorpha spp.* and species *Cladophora spp.* amounts to 100 and 230 mg/kg respectively, and individual fluctuations lie within the range of one order of magnitude, not showing any seasonal variability.

Samples of species *Cladophora* spp. with. exceedingly high iron contents also contained the greatest amounts of manganese, which is not the rule in this class of algae. It should be emphasized however, that cl. *Chlorophyceae* were the only ones of those studied in which the Mn/Fe ratio was less than 1 (Table 14). All the remaining species had ratios ten times greater.

Fig. 6 illustrates the distribution of the occurring of Baltic seaweed samples with various concentrations of manganese, and the particular stages of the forming of this histogram. As compared with the elements so far discussed, concentrations of manganese are widely distributed and do not have a distinct maximum in any range of concentration. The Mn content changes depeding upon the plant species, as can be seen on the individual fragments of the histogram mentioned. All the samples of cl. *Chlorophyceae* are in the first part, the end part comprising only cl. *Rhodophyceae*, 80% of which are within the concentration ange 2800 — — 5400 mg/kg. Samples of species *Fucus vesiculosus* appear in two concentration ranges: from 200 to 600 mg Mn/kg and are typical for specimens from the Baltic and from 800 to 1800 mg Mn/kg — characteristic for samples from Puck and Gdańsk Bays.

Samples of rooted plants indicated considerable changeability in view of which the results of Mn determination are spread across a wide range of concentrations from 0 to 2400 mg Mn/kg. An interesting fact has been observed, plants growing in Gdańsk Bay have 2 ÷ 3 times more manganese than analogical specimens originating from Puck Bay. There are thus certain differences in the supplying of plants with this element in these two regions. Hydrochemical investigations carried out in these regions have shown that the coastal water of both bays is practically the same from the point of view of the main ionic composition and inorganic nutrients.

As regards the amounts of manganese, there is as yet no information with regard to Puck Bay. Studies of the waters of Gdańsk Bay showed that in the coastal regions, the concentration of this element oscillated between 3 ÷ 20 μg/l. Somewhat higher values were met in the regions influenced by the influx of Vistula waters, where amounts of up to 50 μg Mn/l were found. 10 μg Mn/l in the dissolved state can be accepted as the average value for the coastal waters of Gdańsk Bay, although it must be realized that there may be noticeable temporary fluctuations in concentrations of this element, depending upon the existing hydrological conditions in the individual regions. In the surface waters of the open Baltic, Hartmann (1964) found an average of 5 μg Mn/l or less, but in the deeper waters the Mn concentrations reached 100 μg/l, this being the result of stagnation and the setting up of reductive conditions (as in the Black Sea).

Table 14

Mutual proportions of iron, manganese and cobalt in marine plants and bottom deposits

Material	Co/Fe ×1000	Co/Mn ×1000	Mn/Fe	Reference
1	2	3	4	5
Plants				
Enteromorpha spp.	0,38	3,5	0,11	This work
Cladophora spp.	0,32	2,3	0,14	This work
Fucus vesiculosus	3,8	1,4	2,8	This work
Furcellaria fastigiata	2,2	0,65	3,4	This work
Other Rhodophyceae	2,0	1,0	1,9	This work
Zostera marina	4,0	2,0	2,0	This work
Potamogeton pectinatus	3,0	1,3	2,4	This work
Chlorophyceae	0,4—0,8			Fukai (1968b)
Phaeophyceae	0,3—1,7			Fukai (1968b)
Rhodophyceae	0,5			Fukai (1968b)
Potamagetonaceae	0,7—4,4			Fukai (1968b)
Chlorophyceae	0,88			Ishibashi (1964)
Phaeophyceae	1,3			Ishibashi (1964)
Rhodophyceae	1,2			Ishibashi (1964)
Phaeophyceae	0,36—4,2	0,59—92	0,02—1,1	Black and Mitchel (1952)
Phaeophyceae		15		Young and Langille (1958)
All plants (average)	5	0,5	0,1	Winogradow (1953)
Bottom deposits				
Sand				
Puck Bay	0,21	79	0,026	Bojanowski (unpubl.)
Gdańsk Bay	0,23	80	0,029	Bojanowski (unpubl.)
Souther Baltic	0,18	50	0,034	Bojanowski (1964)
Mud				
Puck Bay	0.29	26	0,011	Bojanowski (unpubl.)
Gdańsk Bay	0,32	26	0,012	Bojanowski (1964)
Bornholm basin			0,025	Bojanowski (1964)
(Southern Baltic)	0,46	18		
Iron-manganese nodules				
Southern Baltic	0,50—22	0,63—3,0	0,21—2,8	Bojanowski (unpubl.)
Atlantic	18	19	0,93	Mero (1960)
Pacific	25	14	1,73	Mero (1960)

Considering the source of origin of manganese in the Baltic, attention should be paid chiefly to material from the land, carried to the sea by rivers either in the dissolved state or as suspended load, or coarse inorganic debris. In the region of Gdańsk Bay, the only larger natural stream is the Vistula with an average output of about 1.000 m^3/sec. The average amount of dissolved manganese in the Vistula water amounts to about 30 μg/l (Ostrowski 1963), but as later investigations proved, the main mass of this element occurs in a suspended form. In this form it occurs in concentrations of 20 ÷ 1000 μg/l, the most frequent concentrations being between 200 ÷ 400 μg/l.

The average amount of manganese in suspended matter equals about 0.5%, but single samples may show considerable fluctuations from 0.01 to 2%. In the coastal waters of Gdańsk Bay, both the amount of suspended manganese (0 ÷ 25 μg/l) and the average concentration in the suspension (about 0.2%) are lower. It appears from the data given that the sea water in the region of the Vistula estuary (thus in practice the whole of Gdańsk and Puck Bays), is assured a continuous and fairly abundant source of manganese ions, at the same time, a significant fraction of insoluble manganese can pass into solution upon mixing river and sea waters. The plant vegetation is therefore in conditions where there is a good supply of this element, which fact is very rare in the open ocean. This would also explain the exceptionally high manganese content in all the species studied.

As mentioned, however, both species of higher plants i.e. species *Zostera marina* and *Potamogeton pectinatus* indicate differences in the manganese content, depending upon the place of origin, and they do not clearly result from the hydrochemical difference of the Gdańsk and Puck Bay basins. The remaining species, although not so numerously represented from both these basins, do not evince such a tendency; the results are comparative and sometimes even slightly higher for samples from Puck Bay. Lower plants, with no root system, take in mineral elements directly from the water. They thus are influenced by the existing concentrations of such elements in the surrounding water. Comparing samples of species *Fucus vesiculosus* from Puck Bay and Gdańsk Bay, no noticeable difference can be stated in the manganese content, but specimens collected in the region of Rozewie (South Baltic) contained almost 4 times less.

Bearing in mind the influence of the Vistula on the waters of Gdańsk Bay, this fact can be associated with the differentiating of manganese contents in sea water in which the plants studied, lived. Such an explanation does not however, clear up the facts observed amongst flowering plants which do not respond (or do so to a very small extent) to the concentration of manganese in the surrounding environment in the dissolved form.

There is a fairly common conviction among limnologists that rooted plants, in spite of being completely submerged, obtain the major portion of mineral salts not from the surrounding water, but from the substratum (Oborn 1964). It is thus probably that most of the trace metals are taken up by plants in the same way, the rate being connected in some way with the properties of the bottom sediment.

Table 15

Chemical characterization of the bottom deposits in the near shore zone of Gdańsk Bay and Puck Bay

	Gdańsk Bay	Puck Bay
Type of sediment	Medium-grained quartz sand	Fine-grained quartz sand
Depth	2,5	4,0
pH, m	7,80	7,55
Moisture %	20,2	32,9
Loss on ignition at 500°C %	0,4	1,3
Total iron %	0,25 (100%)	0,54 (100%)
Iron soluble 0, 1N HCl, %	0,030 (12%)	0,022 (4%)
Total manganese, %	0,0076 (100%)	0,0140 (100%)
Manganese soluble in 0, 1N HCl, %	0,0021 (28%)	0,0014 (10%)
Total cobalt, % × 10^4	0,61 (100%)	1,11 (100%)
Cobalt soluble in 0,1N HCl, % × 10^4	0,10 (16%)	0,10 (9%)
Iron in interstitial water, μg/l	620 (nondialysable)	1900 (5% dialysable)
Manganese in interstitial water, μg/l	260 (100% dialysable	440 (100% dialysable)
Cobalt in interstitial water, μg/l	< 1,0	< 1.0

Table 15 gives same date about bottom sediments from the region in which the plant samples were collected.

As can be seen from this data, the differences in the character of the bottom substratum in both basins are fairly distinct, although both sediments belong to one type of sandy formation. The material occupying the Gdańsk Bay coastal zone in the neighbourhood of Orłowo, originates from recently eroded moraine formations. It is thus poorly sorted and rounded, and is of a coarse grained character, as the finer fraction is carried away from the abrasion zone to the deeper parts of the basin. Iron, manganese and cobalt occur in very small amounts and it can be concluded from the character of their solubility that a considerable fraction is located in relatively easily weathered accessory minerals, or occurs in the form of limonitic coatings on quartz sand grains. Certain amounts of iron and manganese upon interaction with interstitial water pass into solution and become available for the plants root systems. Only Mn occurs in true solution however, iron proved to be present in colloidal form, as could be inferred from its behaviour in dialysis and filtration experiments. In this form iron was relatively stable and did not tend to precipitate upon exposure to atmospheric oxygen over a period of a few days (i.e. not readily). The sand covering the bottom of Puck Bay is much finer grained and more homogeneous, as well as having a certain amount of organic matter which facilitates the mobilization of Mn from the sediments. Although the absolute amount of iron, manganese and cobalt is almost double that contained in the sand of Gdańsk Bay, the percentage of easily dissolved fractions is lower. This is most probably due to extensive exposure to the action of leaching agents, (i.e. CO_2 rich sea water with dissolved natural chelators derived from organic debris), which have already managed to decompose and wash away most of the less resistant mineral structures and the elements bound to them. Plants living on such a substratum take up mineral salts at a rate proportional not to the total amount of the given element, but to its available fraction and on this principle the differences in the chemical composition of rooted plants could be explained.

One fact which is apparantly contradictory to the facts as given above, should be explained, namely, if the take up and accumulation of manganese is directly related to its concentration in the „soil'' solution, then the plants in Puck Bay should be better supplied with this element. Assuming however, that all the manganese dissolved in diluted HCl is the reserve assimilable by plants and expressing this amount in the concentration value in interstitial water, we obtain about 100 mg Mn/l for sediments in Gdańsk Bay and about 40 mg Mn/l for Puck Bay. With these figures stated by chemical analysis, true concentrations of Mn in interestitial water, amounting to 0.26 and 0.44 mg Mn/l, cannot change the picture substantially. Apart from this it is most probable that this part of the manganese is not derived from the mineral portion of the bottom sediments, but from organic remains which, falling to the bottom, undergo decay processes and liberate mineral components into the surrouding water. By occupying the upermost part of the sea bed, this matter suplies manganese to the sea water and not to the root system of flowering plants, which reaches much deeper than the 15 cm layer of bottom deposits taken for analysis.

The physiological functions of manganese in plant organisms have been the subject of numerous studies. (Lamb et al. 1958; Wiesner 1962; Nowotny-Mieczyńska 1965). There have been many studies on the distribution of this element in marine algae, but the results given are generally much lower than those found in Baltic plants. For example, Young and Langille (1958) found 25 ÷ 50 mg Mn/kg in cl. *Phaeophyceae*, Black and Mitchell (1952) give concentrations of 9 ÷ 155 mg/kg for the same class of algae, and in one case even 800 mg/kg (species *Fucus serratus*). Öy (1940) found up to 130 mg Mn/kg in species of genus *Fucus*. In certain *Rhodophyceae* the manganese level was between 7.5 ÷ 130 mg/kg (Schmid 1959). According to Pillai (1956) the amount of this element fluctuates depending upon the species, also showing certain seasonal dependencies. The highest values were found in certain *Rhodophyceae* (in species *Gracilaria lichenoides* up to 550 mg/kg) and in *Phaeophyceae* (up to 575 mg/kg in species *Rosenarindia intricata*). The lowest concentrations for these species amounted to 20 and 76 mg Mn/kg respectively, which gives some idea as to their changeability. The author also stated that about 60% of manganese in young plants is in the soluble form, whereas in mature specimens only 30% can be extracted with water.

It thus results from the comparative data given, that specimens of plants living in the Baltic are, on average, ten times richer in manganese than other plants (including land plants), being in this, similar to certain fresh water plants (Oborn 1964). Attention should also be paid to the exceptionally high accumulation ratios which, e.g. reach an average of 50,000 ÷ 60,000 (with regards to plants with a natural moisture) in the case species of *Rhodophyceae*. Mn has thus been shown to have the highest abundance ratio as compared with other elements and the highest so far published for manganese.

The extent to which the accumulation depends upon the characteristics of plant species is shown by the example of certain cl. *Chlorophyceae* (species *Enteromorpha sp.*), for which the average ratio of concentration amounted to 700, in other words it was two orders of magnitude less than in cl. *Rhodophyceae*. Taking into account the characteristic features of the occurrence of manganese in Baltic algae mentioned in this paragraph, it can be stated that it shows several features resulting from the specifics of the environment. In view of its meaning for living organisms and the role which biological factors play in the circulating of this element in the marine environment, it would be worth while continuing studies in this field.

Cobalt

Of all the elements investigated, cobalt occurs in the lowest concentrations. The amounts are between 0.35 ÷ 4.05 mg/kg as regards average concentrations for individual species, the results from individual analyses however, fluctuate between 0.17 and 7.01 mg Co/kg. The lowest average values are found in the group of cl. *Chlorophyceae* (species *Enteromorpha sp.* 0.35 mg/kg and species *Cladophora* sp. 0.55 mg/kg), followed by species *Potamogeton pectinatus* (0.91 mg/kg), species *Fucus vesiculosus* (1.44 mg/kg), species *Furcellaria fastigiata* (1.82 mg/kg) and species *Zostera marina* (1.91 mg/kg). Samples of cl. *Rhodophyceae* differ from the species mentioned by having exceptionally large concentrations of cobalt reaching an average of 4.05 mg/kg.

The range of individual fluctuations in the amounts of this element and the frequency with which samples occur in the concentration ranges changes considerably depending upon the species investigated and the place in which they were collected as is illustrated in Fig. 7. Samples from the cl. *Chlorophyceae* are concentrated in the relatively narrow range of accumulation between 0 ÷ 0.6 mg Co/kg with the exception of two which differ at the same time by having much higher concentrations of all the other trace elements. Species *Fucus vesiculosus* differs clearly depending upon the origin of the samples. Specimens from Puck Bay are marked by a small scatter of analytical results. These are between 0.8 ÷ 1.2 mg/kg. Samples from outside this region have twice that amount of cobalt. The most frequent concentrations of this element in species *Furcellaria fastigiata* are between 2.1 ÷ 2.4 mg/kg, in the remaining cl. *Rhodophyceae* however, results are distributed between 1.5 and 7.2 mg/kg and there does not appear to be any most frequent range of concentration. Of f. *Potamogetonaceae* the species *Potamogeton pectinatus* shows slightly more consistent results. Most of these occur within 0 ÷ 1.2 mg/kg range; as regards species *Zostera marina,* cobalt seems to be evenly distributed over the whole range of concentrations recorded for all species of Baltic algae. Notice should be made of the fact however, that there are distinct differences in cobalt content in both species, depending upon the place in which the samples were collected. Specimens orginating from Gdańsk Bay (shaded areas in Fig. 7) contained greater amounts. The composite histogram for cobalt in Baltic seaweed does not reveal a uniform distribution pattern. Distribution peculiarities in individual species are clearly outlined. The first (0 ÷ 0.9 mg/kg) comprises cl. *Chlo-*

rophyceae in the main,. the next narrow zone (0.9 ÷ 1.2 mg/kg) includes almost exclusively samples of species *Fucus vesiculosus* from Puck Bay, the third part (1.2 ÷ 3.0) comprises specimens of species *Furcellaria fastigiata* and species *Fucus vesiculosus* from outside Puck Bay, and finally the tailing off from 3.6 to 7.2 mg/kg formed from single samples of cl. *Rhodophyceae* and species *Zostera marina* comprising about 10⁰/₀ of the whole collection of data. The shape of this histogram is mainly defined by algae, as higher plants have a fairly flattened frequency diagram and are almost equally distributed in each class of cobalt concentrations (Fig. 7). The evident lack of similarity precludes the possibility of reaching any conclusions as to typical, most frequent or average contents of cobalt in Baltic algae as a whole. Nor does it seem probable that the situation would have improved upon increasing the number of samples, as individual species indicate tendencies towards their own distribution patterns which differ from each other in modal value and dispersion. From this point of view the distribution pattern for cobalt differs considerably from that of iron and zinc and is more similar to that of manganese and nickel. This similarity suggests certain common mechanisms of accumulating the three elements mentioned, in marine plant organisms.

Fukai (1968 b) utilizing his own data and that published so far on the subject of amounts of cobalt in marine algae, drew up a frequency diagram (Fig. 8, p. 67). On drawing up this graph, all the velues were treated equally, irrespective of the geographical origin of the plants analyzed and their taxonomical position. The graph obtained did not resemble the Gaussian distribution pattern, but was similar to the log-normal, with a modal value rather 0.25 ÷ 0.50 mg/kg. Despite the fact that this is more uniform than that based on the results cited in this paper, there are three distinguishable subclasses, i.e. first 0 ÷ 1 mg Co/kg represented most numerously (about 75⁰/₀ of the cases), then between 1 ÷ 2 mg Co/kg (about 20⁰/₀) and finally, covering the concentrations between 2 ÷ 3.25 mg Co/kg and represented by 5⁰/₀ of the cases. The author apparently excluded samples with higher cobalt values which, althought infrequent, indicate the capabilities of certain plants to accumullate this element.

On comparing numerical values it can be seen that plants growing in the Baltic are relatively better supplied with this component than specimens from other regions. Simultaneously, the concentrations of cobalt ions in the waters of Gdańsk Bay is very low and according to own observations fluctuates between 0.02 ÷ 0.37 μg Co/l. These are fairly exceptional values for land-locked seas, which are strongly influenced by river discharge and matter washed from the land. It should be noted however, that the Vistula water is also exceptionally poor in cobalt, concentrations in dissolved form being estimated at between 0.02 ÷ 0.05 µg/l. Most of the cobalt contained in the Vistula exists in a suspended form, its concentrations amounting to 0.17 ÷ 0.35 µg/l. The cobalt content in the suspended matter equals about 8 ÷ 14 µg Co/g. According to Kharkar et al. (1968) the suspended solids contain part of the cobalt adsorbed on their surface, which is released upon mixing with sea water. Depending upon the mineral composition of the suspension, the amount of exchangeable cobalt may reach 80%.

Desorption processes also take place in the waters of Gdańsk Bay, as the suspended matter of sea water from this region has a lower Co content (2 ÷ 10 µg/lg) as compared with the suspended load carried by the Vistula. Despite this source of supply, the amount of cobalt in sea water is maintained at a low level. Sandy bottom sediments from the coastal regions of Gdańsk and Puck Bays, play a relatively small role as a source of cobalt, as they are poor both from the point of view of total content and in the loselybound (form (Table 15). The cobalt dissolved in HCl at pH ~ 1 is a bare 1 × 10^{-5}% and would produce a concentrations of 3 ÷ 5 µg Co/l if dissolved completely in the volume occupied by interstitial water. In actual fact the amount of cobalt in the interstitial water was not more than 1 µg/l. It would appear however, that the conditions existing in the substratum favour the supplying of rooted plants with cobalt, this being shown in the higher content of this element in such plants as compared with algae.

To estimate the degree to which Co can be concentrated in the algae investigated, 0.1 µg Co/l was accepted as the representative concentration for surface water in the region. The respective abundance ratios are between 200 ÷ 500 for cl. *Chlorophyceae* and form 3000 ÷ 6000 for cl. *Rhodophyceae*. From the point of view of magnitude they are most similar to the abundance ratios for zinc, with the exception of cl. *Rhodophyceae*, where they are three times higher. These figures place cobalt among the most absorbable trace metals after manganes and iron.

The comparing of the occurrence of cobalt with that of iron and manganese, supplies interesting information. These elements show certain similarities which are revealed in the course of marine sedimentation. In view of the dimensions of ionic radii of Fe^{3+} and Co^{3+} isomorphic substitution of Co for Fe in the crystal lattice of hydrated iron oxides, is possible. On the other hand, higher manganese oxides exert strong adsorption properties towards Co ions. Both these processes are effective in removing cobalt from sea water and the mutual relations of Co/Mn, Co/Fe and Mn/Fe in bottom sediments supply information as to environmental conditions of these elements in various marine basins. As can be seen from the data in Table 14 the mechanisms of biological accumulation differ markedly from those involved in inorganic sedimentation of these elements. Apart from the differences of 1 ÷ 2 orders of magnitude in absolute concentrations, low ratios of Co/Mn are characteristic for Baltic algae, as are the small range of variations of this ratio, in spite of the fact that manganese is the most variable element of all investigated. In Fig. 9, p. 69 analytical data for Co, Mn and Fe are plotted against each other, Co-Mn being to be best correlated, whereas in the remaining combinations (i.e. Co-Fe, Mn-Fe) the scatter of results is much greater. Of the species investigated, only in cl. *Chlorophyceae* is there a better correlation of Co with Fe than with Mn; the values for Co-Fe ratio fall within the limits common to marine sediments.

As in the case of other trace metals mentioned, cobalt does not indicate any distinct changes in concentrations due to seasonal variations. Only in both species of family *Potamogetonaceae* originating from the region of Gdańsk Bay can we observe — as from September — a gradual increase in the cobalt content, this being maintained to the end of the observation cycle. This increase is especially noticeable in species *Zostera marina*, where the difference between the average amount of Co in the summer months and concentrations found in specimens collected at the end of November, is more than threefold (Fig. 10, p. 71).

It is not unlikely that the remaining species also have their specific seasonal fluctuations, they must be less intensive however, then the random fluctuations of the Co content and in effect, is over shadoved by them. The example of f. *Potamogetenaceae* would also indicate that seasonal fluctuations may become apparent in the late autumn months, whereas the fluctuations of trace element concentrations are occasional during the period from June to October. Due to technical difficulties related to the collecting of plant material during the cold months, the number of samples from that period is not very high, which does not give any reason for drawing conclusions on the subject of seasonal fluctuations in the whole annual cycle.

It is worth taking note of important differences occurring between samples depending upon the place in which they were collected. Analyses indicate that the uptake of cobalt by plants in Puck Bay, is less intensive. This refers to both lower plants (e.g. species *Fucus vesiculosus*) and higher ones. It is difficult to state at the moment whether this fact results from the region being poorly supplied with cobalt, or whether it is the indirect result of changes in plant metabolism induced by changes of environmental conditions.

Fukai's publication (1968 b) summarizes the results of investigations on the subject of the distribution of cobalt in various species of marine algae. The author states that information so far is still insufficient to solve the question of the significance of cobalt for marine plants. There is no indication that the Co content in plant tissue undergoes variations resulting from periodic changes in their physiological activity.

As regards defining the „typical or average" concentration of Co in individual species of algae, such an idea is of a relative character. It is even sometimes possible to observe a reversing of ratios in individual classes of algae. For example, Ishibashi et al. (1964) gives the following order for algae growing round Japan (according to the rising ratio of cobalt):

Rhodophyceae $<$ *Phaeophyceae* $<$ *Chlorophyceae*

on the other hand, basing on results illustrated in this paper, the opposite sequence can be suggested for species growing in the Baltic. Other papers usually present results of analyses of single samples from various species and because of the wide seatter of data, do not enable a similar comparison (Maluga 1946; Black and Mitchel 1952; Smales et al. 1957; Young and Langille 1958; Fukai 1968 b).

On the whole it can be stated that the amount of cobalt in all species of Baltic algae is higher than in those originating from other seas and oceans. This does not result from differences in concentrations in the sea water, as — as already mentioned — the Baltic water has a lower average content of this element than is typical for oceanic waters and the geological structure of the drainage area does not favour the carrying by the rivers of larger amounts of cobalt to the Baltic sea. In this situation it seems possible that the main ionic composition of the water, especially the major cation content which may compete for the binding sites in plant cell material, decides on the degree of absorption of certain trace metals. Ishibashi et al. (1964) stated that fresh water plants contain more cobalt than marine algae do. On the other hand, the Co content of streams and lakes is as low or even lower than that of seas and oceans (e.g. Benoit 1957); simultaneously their total dissolved solids is lower by two orders of magnitude. The disproportions between major cations and trace metals content fall as they salinity of the water decreases.

It would, however, be hard to explain the tremendous differences between the abundance ratios of univalent and divalent cations of the main groups in the periodic table of element and the abundance ratio of the transition elements with partly filled d-electron orbitals, on the basis of simple ion-exchange absorption. For this reason it is assumed that in biological accumulation chelate structures participate, these being selective in respect of the latter group of ions.

Goldberg (1965) turns attention to the fact that the degree of accumulation of several trace metals in marine organisms is related, to a certain extent, to the magnitude of stability constants of metal complexes with organic ligands. The arranging of transition metals in order of their increasing abundance ratios in seaweed, agrees faily well with the order of increasing stability of the complexes of these metals with various complexing substances known as the Irving-Williams order:

$$Zn < Cu > Ni > Co > Fe > Mn.$$

Of the major cations, mainly calcium and to a lesser extent magnesium can be taken into account as ions competing for chelator groupings with trace metals. At the same time, the changes in the content of calcium ions when passing from fresh water to oceanic waters, are an order of magnitude less than changes in the total salt content of those waters and usually fall within the range of tens to hundreds of mg Ca/l. In plant organisms, in the presence of organic ligands, the following equilibrium between calcium ions and trace metal ions is set up (for simplicity, the signs of charged ions are omitted and the case of M : A = 1:1 complex is considered):

$$M + Ca\,A \rightleftarrows M\,A + Ca$$

the equilibrium constant being:

$$K = \frac{[MA] \cdot [Ca]}{[M] \cdot [Ca\,A]}$$

As

$$\frac{[Ca]}{[Ca\,A]} = \frac{1}{K_{Ca} \cdot [A]} \text{ and } \frac{[M\,A]}{[M]} = K_M \cdot [A]$$

then:

$$K = \frac{K_M}{K_{Ca}},$$

where K_M and K_{Ca} are stability constants of trace metal and calcium complex with ligand A respectively.

It results from these relationships that the greater the difference between stability constants K_M and K_{Ca}, the more the exchange reaction is shifted to the right and the more trace ions will be complexed.

By rearranging the relationships, the following expression is obtained:

$$\frac{[M\,A]}{[M]} = \frac{K_M}{K_{Ca}} \cdot \frac{[Ca\,A]}{[Ca]}$$

According to the assumptions that Ca is the dominating macrocation in competition for complexing sites in plant tissue and taking into account that $[Ca] \gg [M]$, further simplification can be made i.e. $[Ca\,A] = [Ao]$ where $[Ao]$ is the total complexing capacity of plant material.

Then:

$$\frac{[M\,A]}{[M]} = \frac{K_M \cdot [A_o]}{K_{Ca} \cdot [Ca]} = \frac{\text{Const.}}{[Ca]}$$

It results from this that the degree of formation of metal chelates in biological systems decreases with the rise in competing calcium ion concentrations. Differences in abundance ratios of several microelements in algae originating from waters of varying salinity can be explained on this basis. It would be more difficult however, to illustrate this relationship quantitatively. First and foremost, the nature of the chemical structures involved in the binding of trace metals and the stability of such binding of trace metals and the stability of such bindings, is unknown. Generally speaking, not much is known of the forms in which trace metals occur in biological systems. As regards cobalt, apart from a family of vitamin B_{12} compounds, attempts to find stable complexes of biological origin have not yet succeeded.

Ericson and Scott (1955) reported on the discovery in species *Rhodymenia palmata* (grown in the presence of Co^{60}) of a cobalt-containing organic compound, but they were unable to identify the nature of this substance. It is not impossible that the phenomenon observed was an artifact. Information so far leads, in practice, to the fact that cobalt is fairly strongly bound with undissolved plant cell material — a conclussion resulting from the analyses of soaked and unsoaked plant specimens (Black and Mitchell 1952; Young and Langille 1958).

A certain mobility of cobalt in plants can be assumed on the basis of analytical results of individual anatomical fragments. Black and Mitchel are of the opinion that certain amounts of cobalt and other biologically important trace metals are expended in sporogenesis, as the result of which their content in fertile parts of species *Laminaria cloustoni* is lower than in sterile parts. As regards the cobalt partition between young and old parts of plants, information on the subject is conflicting, as sometimes younger, sometimes older fragments of thallus turn out to contain more cobalt. It appears that cobalt and certain other microelements are more mobile and undergo greater variations of concentration in the younger parts than in the older ones.

Fukai (1968 b) turned attention to the fact that of the plants growing in the Mediteranean sea, the flowering plants have an exceptionally high cobalt concentration (similar to the Baltic species) and as opposed to algae — a lack of correlation between the iron and cobalt contents.

The relationships mentioned here lead to the conclusion that it is not possible to describe the accumulation of Co in all species of algae, by means of a simple mechanism and that the investigating of its distribution alone, together with the contents of other trace elements offers valuable information as to a given environment, but does not say much about the reasons why such concentrations occur.

Differentiation of the Chemical Composition of Young and Old Parts of species *Fucus vesiculosus*

Seaweed growing in the Baltic is not the best material for studying seasonal fluctuations. Macrophytes of the class *Chlorophyceae* are annual plants and their vegetation cycle lasts only a few months, the maximum being in July/August. Thus, growing in a narrow border zone with the coast line, at depths of between 0 — 0.5 m., they are especially susceptible to changes in the environment, pollution etc. It would thus be difficut in this situation, to observe changes in the chemical composition of such algae, caused by seasonal fluctuations in physiological activity. In turn, species belonging to the class *Rhodophyceae*, have very delicate habits, which made it impossible to select an adequate number of similar specimens from the point of view of age and stage of development, for analysis. Of the species met in this region of the Baltic, only species *Fucus vesiculosus* has tissues enabling easy distinction between old and young parts and also easy collecting in sufficient amounts for investigations.

The plant material was collected in three different periods of time from the same place in the open Baltic (Rozewie) at a depth of about 2 metres. The choice of place was dictated by the fact that the plants occurred attached to the stony bottom, which enabled samples of the same population to be taken each time. The nature of the bottom in Puck Bay does not favour attached forms and the algae lie loose, continually being shifted over the sea bed. After collecting specimens, they were dissected into young and old parts, the apical parts with receptacles being taken separately. The adhering sea water was removed by filtration tissue, samples being air dried and then vacuum dried in a temperature of 40°C. The dry material was then comminuted in a porcelain ball mill. Oven-dried (at 110°C) samples were analyzed according to the previously described procedure. The results of analyses are given in Table 16.

The most important observations from these data can be summarized as follows:

The mineral composition of species *Fucus vesiculosus* undergoes distinct changes depending upon the stage of development. Younger outgrowth of shoots are richer in the main cation and total ash content, as compared with older parts of the thallus. These differences are not great however, and with the exception of potassium, do not exceed 30%. It can

Table 16

Inorganic macro- and microconstituents in different parts of thallus
Fucus vesiculosus

Date of collection and kind of sample	Total ash	Na	K	Ca	Mg	Sr	Fe	Mn	Zn	Cu	Ni	Co
	% of dry matter					mg/kg of dry matter						
17 April 1968.												
Young offshoots	16,9	1,53	1,77	1,68	0,85	790	170	280	330	6,3	15,3	1,95
Old thallus	16,0	1,34	1,19	1,32	0,81	640	289	280	349	7,6	25,3	2,77
Y/O ratio	1,1	1,1	1,5	1,3	1,0	1,2	0,6	1,0	0,9	0,8	0,6	0,7
8 August 1968												
Receptacles	22,4			1,61		930	177	249			16,5	1,67
Young offshoots	13,3			1,46		740	77	274			8,1	1,24
Old thallus	12,1			1,30		650	187	471			25,1	2,51
Y/O ratio	1,1			1,1		1,1	0,4	0,6			0,3	0,5
4 December 1968												
Young offshoots	18,8	1,96	3,24	1,69	1,05	820	148	420	360	4,5	16,9	2,07
Old thallus	16,0	1,56	1,75	1,40	1,03	680	208	480	320	3,1	29,9	2,70
Y/O ratio	1,2	1,3	1,9	1,2	1,0	1,2	0,7	0,9	1,1	1,5	0,6	0,8

also be seen that the division of macroelements into younger and older parts, does not seem to depent on the season; once more, potassium is the exception, amounts of this in the younger parts increasing in time much faster than in old parts.

The most spectacular differentiation can be observed in the reproduction period in the summer months. It appears that then there is a flow of macroelements to the apical parts of outgrowths ending in receptacles. The parts contain almost twice as much ash than the rest of the *Fucus vesiculosus* thallus.

The distribution of trace metals shows a different character. The greatest amounts of these elements appear in the oldest parts of *Fucus vesiculosus*, the character of their distribution differing depending upon the element investigated. The greatest difference is in the distribution of nickel, iron and cobalt, the abundance ratio of these metals in old and young plants amounting, on average, to 0.5, 0.6 and 0.7 respectively. During the rproduction period, there is considerable differentiation of trace metal contents in young off-shoots whereas is the case with macroelements — the apical parts together with the receptacles have higher contents than the parent thallus. Whereas in the latter the absolute concentration of trace elements fall (often by half, as in the case of iron and nickel), in the old parts, nogreater change in their content is noted. Thus a characteristic feature of the *Fucus vesiculosus* at the stage of development is the extending of the existing differentiation in the partition of microelements between young and old tissues.

On the basis of the relationships described here, it can be concluded that the main mineral components are taken up in greater amount by those parts of plants which are undergoing the most active phase of growth and metabolism. These ions are thus more or less directly involved in the metabolic cycle. As regard trace metals however, these appear to play a certain role in the reproduction processes and are probably used up in the forming of gametes. The trace metal content in younger parts of the thallus decreases presumably as a result of the flow towards the apical parts. On the other hand, the mobility of metals in older parts of species *Fucus vesiculosus* appears to be negligible, this resulting in the lack of exchange (or very limited) between older and younger parts of the algae.

The intensity of metabolic processes depends on the age of plants, as well as on the environmental conditions. Seasonal variations of metabolic products content in algae, such as mannitol, laminaran, fucoidin or alginic acid, influence the mutual ratio or organic and inorganic matter within plant cells. The distribution of microelements is apparently governed by other factors, as these elements occur most abundantly in the least active parts of algal thallus and in fertile apexes which have been stated to contain smaller amounts of protein, mannitol and alginic acid than steril ones (Boney 1966).

Black and Mitchell (1952) have already mentioned the possible role of certain trace elements in sporogenesis, indicating the differences in their content in sterile and fertile fronds of species *Laminaria* cloustoni. The results of own observations (Table 16) show that for *Fucus vesiculosus* the greatest differentiation was found in the distribution of nickel, which fact is puzzling in so far as the biological significance of this element is still not clear.

In conclusion it should be noted that if the drop in the content of trace metals in the young parts of plants is really caused by them being used during the reproduction cycle, then the losses due to this are relatively quickly replenished, so that after several months, the concentrations of microelements in specimens of species *Fucus vesiculosus* are similar to those prior to the period of reproduction.

SUMMARY

In 73 samples of the most common Baltic algae, the contents of the following inorganic macro- and microelements were determined: ash, Na, K, Ca, Mg, SO_4, P, Sr, Fe, Mn, Zn, Cu, Ni and Co. The species analyzed were as follows: (the number of samples is given in brackets): genus *Enteromorpha sp.* (8), genus *Cladophora sp.* (5), species *Fucus vesiculosus* L. (14), species *Furcellaria fastigiata* (9), other *Rhodophyceae* (11), species *Zostera marina* (14), species *Potamogeton pectinatus* (11) and species *Elodea canadensis* Rich. (1).

As resultet of the low salinity of the Baltic water (about 7‰ on the surface) the sodium and potassium content is half that of algae living in oceanic waters (about 35‰ salinity), but the salinity has no important influence on the calcium and magnesium content. The amount of sulphates also does not indicate any relation with the salinity, but depends in the main on the amounts of esterified polysaccharides. All the abundance ratios for the main ions equal to or more than one and they can be placed in the following series:

$$Na < Mg < Ca < K$$

The Sr/Ca ratio is less than in sea water for most of the species investigated, with the exception of species *Fucus vesiculosus*, which concentrates strontium 4 times stronger than calcium, and species *Zostera marina* for which the Sr abundance ratio is about 1/3 higher than that for calcium.

The amounts of trace elements in Baltic plants considerably exceed the concentrations met so far in species from open seas. This greatly depends upon the type of plant and the place at which specimens were collected, seasonal fluctuations not being clearly defined. The average concentrations of individual elements vary as follows (as referred to dry matter): Fe 380 ÷ 2050 ppm., Mn 100 ÷ 3860 ppm., Zn 60 ÷ 310 ppm., Cu 5.6 ÷ 21.2 ppm., Ni 2.3 ÷ 15.1 ppm., Co 0.35 ÷ 4.05 ppm. The average abundance ratios are arranged in the following series:

$$\mathrm{Mn} > \mathrm{Fe} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn} > \mathrm{Cu}$$

This suequence changes for certain species. Generally, cl. *Rhodophyceae* had the highest abundance ratios, the lowest — cl. *Chlorophyceae; Phaeophyceae* and f. *Potamogetonaceae* and f. *Hydrocharitaceae* were in an intermediate position. The distribution of elements in the various parts of species *Fucus vesiculosus* differs considerably depending upon age, the young parts of the plant having a higher ash content and a greater (on average $10 \div 30^{0}/_{0}$) content of the main ions, whereas the older parts of plants have almost twice the content of trace elements.

During the reproduction period, the apical parts of species *Fucus vesiculosus,* with the receptacles, accumulate considerable amounts of trace elements and almost double the·amunt of the main mineral components. Especially large disproportions have been observed in the distribution of nickel, which may suggest that this elements participates in the reproduction cycle. The young parts of the plants show a greater fluctuation of trace elements, which would indicate their mobility.

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