

Concentration of elements in some seaweeds from coastal region of the southern Baltic and in the Żarnowiec Lake

OCEANOLOGIA, 25, 1988
PL ISSN 0078-3234

Seaweeds
Concentration metals
Żarnowiec Lake
Baltic Sea

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Manuscript received June 6, 1986, in final form September 8, 1987.

Abstract

Contents of the following elements: Fe, Mn, Pb, Ni, Cu, Co, Zn, Cd, Ti, Al, Ca, Mg, K, and Na were determined in samples of some seaweeds from the coastal region of the southern Baltic and in the Żarnowiec Lake. The levels of metals found in the samples were essentially similar to those reported by other authors for seaweeds from various areas of the world. The Baltic seaweeds contained significantly larger amounts of K, Al, Fe, and Zn, and similar levels of Mn compared with plants taken from the Żarnowiec Lake. Mean concentration, selectivity, and enrichment factors for analysed metals were calculated. Concentration factors are arranged in the following order: $Al > Fe > Pb > Mn > Co > Ni > Zn > Cd > Cu > K > Ca > Mg > Na$. The correlation coefficients for all pairs of metals were also calculated.

1. Introduction

World literature on the occurrence of metals in marine plants is abundant. It follows from these papers that some of the plants absorb metals from water especially actively, thus reflecting their levels in the surrounding environment. Such plants can play a role of so-called bioindicators in the evaluation of a degree of pollution of coastal regions. A content of trace metals depends not only on particular systematic groups the plants belong to and current physiologic condition; of great influence are also environmental conditions (Bojanowski, 1973). The majority of papers pertaining to this topic have dealt with the concentration of elements in brown algae which are

particularly capable of accumulation of trace metals from the surrounding water (Agadi *et al*, 1978; Bryan, 1983; Fuge, James, 1973, 1974; Haug *et al*, 1974; Lunde, 1970). Also other plants are characterized by similar ability to accumulate metals; these include red seaweeds (Preston *et al*, 1972), green algae (Seeliger, Edwards, 1977; Shiber, Washburn, 1978), and flower plants (Brix *et al*, 1983; Lyngby, Brix, 1983).

2. Materials and methods

The plants were collected at the coast of the Gulf of Gdańsk, open Baltic Sea, and in the Żarnowiec Lake (Fig. 1) in July 1978 and 1979. The plants were drawn by a scuba diver and after delivery to the laboratory were

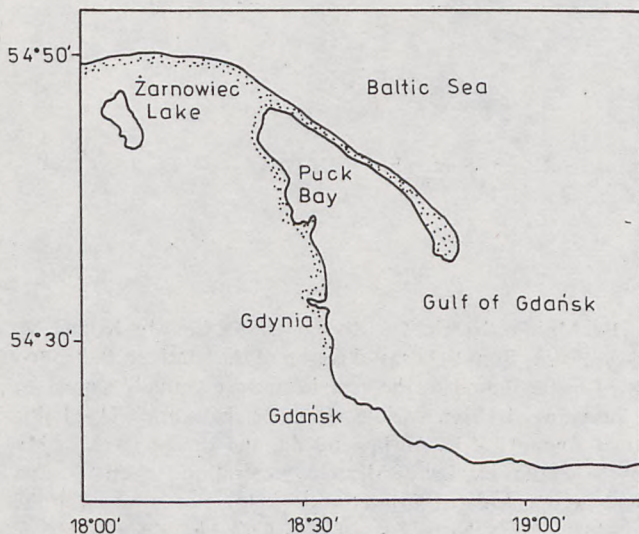


Fig. 1. Plant samplings sites

separated into individual species. The plants were cleaned of foreign matter, washed with distilled water and subsequently dried at 110°C. From twenty to one hundred grams of dry matter was taken for the analysis. Depending on the amount of plants, one or two parallel samples were prepared. The plants were combusted in a muffle furnace at 500°C for 48 hours after removal of the majority of volatile components by heating on a gas burner. The resulting ash was dissolved in concentrated HNO₃ and the solution was evaporated to moist residue which was subsequently dissolved in redistilled water and filtered. The precipitate on the filter was ignited and the ash was heated in a mixture of concentrated HF and HClO₄. After evolving white fumes of HClO₄, the residue was dissolved in 4 M solution of HNO₃ and

added to the filtrate. One fifth of this solution was taken for the determination of a content of Fe, Ti, Al, Ca, Mg, K, and Na. The remaining solution was evaporated to dryness and the residue was converted into nitrates by repeated evaporation with concentrated HNO_3 . Further ion-exchange procedure was described in the previous paper (Szefer, Falandysz, 1983).

The content of Al and Ti was determined spectrophotometrically using 8-hydroxyquinoline ($\lambda = 410$ nm) and chromotropic acid ($\lambda = 460$ nm), respectively (Skwarzec *et al.*, 1984). The content of the remaining metals was determined by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Iron and manganese

It follows from a comparison of the data listed in Tables 1 and 2 that the Baltic seaweeds contain on average much more iron and similar levels of manganese comparing to the plants from Żarnowiec Lake. The content of iron and manganese in Baltic seaweeds ranged from 0.4 to 5 and from 0.1 to 3.5 mg/g of dry weight, respectively. Similar levels of concentration were found by Bojanowski (1973) for the Baltic seaweeds (0.11–3.91 mg Fe/g of dry weight, 0.05–5.23 mg Mn/g of dry weight) and by Agadi *et al.* (1978) for seaweeds coming from the coast of India (0.128–1.796 mg Fe/g of dry weight, 0.025–3.421 mg Mn/g of dry weight). Although insufficient number of samples does not allow to treat the observed local relationships as functional dependences, still a tenfold higher content of manganese in *Cladophora rupestris* from the Puck Bay compared to the content in specimens collected at the coast of open Baltic sea is worth noticing. The occurrence of such a trend can be explained by the Vistula River run-off of suspended matter enriched in manganese to the estuarine waters of the Gulf of Gdańsk.

Larger than unity values of the selectivity coefficients (Table 3) indicate that the Baltic seaweeds are characterized by the highest ability to accumulate iron from water compared to the remaining metals.

3.2. Zinc

Large variations in the content of zinc, *viz* 17 to 256 $\mu\text{g/g}$ of dry weight (Table 1), are observed in the Baltic seaweeds, whereas fresh-water plants revealed smaller fluctuations falling within the range from 9 to 31 $\mu\text{g/g}$ of dry weight (Table 2). Similar variability for seaweeds was found by other authors (Hägerhäll, 1973; Lande, 1977; Patin *et al.*, 1980).

On the basis of data listed in Table 3 it can be thought that Baltic plants

Table 1. Contents of Na, K, Ca, Mg, Al, Fe, and Mn [mg/g of dry weight], Ti, Ni, Pb, Cu, Co, Zn and Cd [$\mu\text{g/g}$ of dry weight] as well as content of water and ash [%] in seaweeds of the southern Baltic Sea

Species	Sample collection site	Humidity	Ash	Na	K	Ca	Mg	Al	Fe	Mn	Ti	Ni	Pb	Cu	Co	Zn	Cd
Chlorophyta																	
<i>Enteromorpha</i> sp.	Puck Bay	90	27.4	5.3	8.7	0.49	10.2	2.6	3.7	0.1	65	2.5	20	5.6	0.8	256	0.33
<i>Enteromorpha</i> sp.	Puck Bay	90	18.8	10.6	9.6	0.66	10.8	1.2	2.6	0.1	26	1.2	30	15.2	0.6	140	0.45
<i>Enteromorpha intestinalis</i>	Puck Bay	90	20.7	3.5	10.2	0.78	25.8	0.4	0.8	0.6	140	2.4	0.45	2.8	0.9	35	0.36
<i>Enteromorpha crinita</i>	open Baltic	90	31.6	3.7	44.9	1.84	2.3	1.2	3.0	1.7	—	1.1	31	2.6	0.6	17	0.37
<i>Cladophora rupestris</i>	Puck Bay	90	26.7	5.7	21.0	20.3	4.8	1.6	5.0	1.8	—	7.9	18	6.6	2.0	54	0.59
<i>Cladophora rupestris</i>	open Baltic	90	35.7	7.3	5.2	—	2.2	6.1	4.5	0.2	—	7.3	16	2.4	1.2	190	0.83
Phaeophyta																	
<i>Ectocarpus siliculosus</i>	open Baltic	86	24.7	1.5	2.4	18.8	15.4	1.4	2.3	0.7	46	5.2	15	6.4	0.5	203	0.61
Spermatophyta																	
<i>Zostera marina</i>	Puck Bay	86	13.8	9.0	25.7	8.6	8.5	0.2	0.4	0.7	32	2.6	—	1.6	0.6	37	0.38
<i>Acorus calamus</i>	open Baltic	—	28.6	9.8	56.1	14.6	8.1	1.0	1.4	3.5	55	4.6	30	7.2	1.2	71	0.55
<i>Elodea canadensis</i>	open Baltic	88	27.2	9.4	29.2	9.8	3.0	1.2	1.9	1.0	22	5.3	33	1.6	0.8	24	0.63
<i>Potamogeton pectinatus</i>	open Baltic	88	17.7	5.8	13.7	11.1	4.6	0.8	1.3	1.2	60	2.9	34	1.8	0.5	21	0.68
Mixed species																	
<i>Zostera marina</i>	Puck Bay	86	17.7	12.5	22.3	25.5	8.3	1.2	0.9	0.5	—	2.5	13	3.2	0.4	166	0.34
and	Puck Bay	86	20.7	15.0	30.5	29.8	7.6	1.6	1.5	0.7	—	3.1	13	2.0	0.7	122	0.33
<i>Ectocarpus siliculosus</i>	Puck Bay	86	16.5	3.7	3.2	19.3	5.0	0.9	0.7	0.4	—	1.7	10	2.0	0.4	42	0.18
	Puck Bay	86	16.9	16.1	32.2	11.3	8.2	1.3	2.3	0.3	—	4.6	18	3.6	0.5	110	0.29
	Puck Bay	86	22.5	11.2	19.6	53.1	6.1	1.3	1.7	0.7	—	5.6	15	2.6	0.6	71	0.28

Table 2. Contents of Na, K, Ca, Mg, Al, Fe, and Mn [mg/g of dry weight], Ni, Pb, Cu, Co, Zn and Cd [$\mu\text{g/g}$ of dry weight], as well as content of water and ash [%] in plants from Żarnowiec Lake

Species	Humidity	Ash	Na	K	Ca	Mg	Al	Fe	Mn	Ni	Pb	Cu	Co	Zn	Cd
<i>Potamogeton pectinatus</i>	92	19.7	7.7	15.6	36.3	8.5	0.2	0.4	1.4	5.2	18	2.4	0.7, 22	0.35	
<i>Myriophyllum spicatum</i>	—	—	1.2	2.6	—	3.0	0.1	0.2	1.4	2.4	44	0.4	0.3	9	0.04
<i>Enteromorpha</i> sp.	93	18.7	25.6	3.4	5.4	1.8	0.5	0.7	1.5	5.3	18	5.6	0.7	31	0.10
<i>Chara vulgaris</i>	90	48.4	3.0	3.5	17.6	2.2	0.8	1.0	3.2	3.6	40	2.4	1.0	19	0.95

Table 3. Selectivity factors SF^* for individual pairs of elements in seaweeds of the southern Baltic

M_2	M_1										
	Co	Cd	Cu	Ni	Pb	Zn	Mn	Fe	Ca	Mg	Na
Co	1										
Cd	3.7	1									
Cu	9.3	2.7	1								
Ni	1.2	0.36	0.14	1							
Pb	0.05	0.01	0.006	0.04	1						
Zn	1.6	0.46	0.18	1.3	32.1	1					
Mn	0.09	0.03	0.01	0.07	18.2	0.06	1				
Fe	0.04	0.01	0.004	0.03	0.7	0.02	0.42	1			
Ca	41	11.8	4.4	33	820	25.6	460	1000	1		
Mg	250	74	27	210	5100	160	2900	10000	6.2	1	
Na	2100	610	230	1700	42200	1300	23900	57300	52	8.3	1
K	31	9	3.4	25	630	20	360	850	0.8	0.12	0.02

* SF values were calculated according to a formula:

$$\frac{(C_{M_1}/C_{M_2})_R}{(C_{M_1}/C_{M_2})_S}$$

where $(C_{M_1}/C_{M_2})_R$ and $(C_{M_1}/C_{M_2})_S$ are the ratios of mean contents of compared metals M_1 and M_2 in plants and Baltic water, respectively.

reveal lower affinity to zinc than to such metals as iron, lead, and manganese, and that they absorb zinc together with cadmium, cobalt, and nickel in proportions approximately equal to those occurring in the Baltic water.

3.3. Cadmium

Of all the analysed metals, cadmium occurs at the lowest concentrations, *viz* from 0.18 to 0.83 $\mu\text{g/g}$ of dry weight in Baltic seaweeds and from 0.04 to 0.95 $\mu\text{g/g}$ of dry weight in fresh-water plants (Tables 1 and 2). These values are comparable with those obtained for seaweeds from the coast of Townsville, Australia (0.2–1.4 $\mu\text{g/g}$ of dry weight), Japan Sea (0.04–1.18 $\mu\text{g/g}$ of dry weight), Trondheimsfjord, Norway (< 0.7 –1.0 $\mu\text{g/g}$ of dry weight) and the Adriatic (1.04 $\mu\text{g/g}$ of dry weight) (Haug *et al*, 1974; Patin *et al*, 1980; Burdon-Jones *et al*, 1982; Kosta *et al*, 1978).

It follows from Table 3 that the Baltic plants reveal lower selectivity towards cadmium than towards cobalt, nickel, manganese, lead, and iron.

3.4. Copper

The levels of copper in Baltic plants vary from 1.6 to 15.2 $\mu\text{g/g}$ of dry weight, whereas the lake plants contain from 0.2 to 2.8 $\mu\text{g Cu/g}$ of dry weight (Tables 1 and 2). A similar range of content was found for plants from the Japan Sea (0.9–7.6 $\mu\text{g/g}$ of dry weight) and from the Townsville coast (2.0–11.1 $\mu\text{g/g}$ of dry weight) (Saenko *et al*, 1976; Burdon-Jones *et al*, 1982).

Mean selectivity coefficients for copper (Table 3) are surprisingly low, similarly to the values of concentration factors. It is difficult to substantiate such a low affinity of copper towards the plant material taking into account a strong tendency of this metal to form stable complexes with organic compounds. It can be assumed that availability of copper for plants is limited by competitive processes of complexing this metal by organic substances dissolved in water which results in a decrease of the effective concentration of copper (Bojanowski, 1973).

3.5. Lead

Baltic plants contained from 8 to 34 $\mu\text{g Pb/g}$ of dry weight; such concentrations are higher than those found for seaweeds from the Japan Sea (0.76–10.7 $\mu\text{g/g}$ of dry weight), Townsville (< 0.3 –10.2 $\mu\text{g/g}$ of dry weight) and Anglesey, Wales (2.2–3.2 $\mu\text{g/g}$ of dry weight) (Foster, 1976; Patin *et al*, 1980; Burdon-Jones *et al*, 1982). Substantially higher levels of this element were found in specimens of *Zostera* sp. originating from the southern coast of Spain (1800 $\mu\text{g/g}$ of dry weight) (Stenner, Nickless, 1975).

It follows from Table 3 that seaweeds reveal higher affinity towards lead than towards the remaining metals except iron.

3.6. Nickel and cobalt

Nickel occurs in the Baltic plants in amounts ranging from 1.1 to 7.9 $\mu\text{g/g}$ of dry weight, while the content of cobalt falls within the range from 0.5 to 2.0 $\mu\text{g/g}$ of dry weight (Table 1). The results are comparable with those obtained by Burdon-Jones for the Townsville coast plants (Burdon-Jones *et al.*, 1982).

The mean ratio of Ni/Co concentration for the Baltic plants is very similar to the ratio calculated for sea water which results in the Ni/Co selectivity coefficient being ≈ 1 (Table 3). This means that the plants do not reveal a significant selectivity towards either of these metals.

3.7. Aluminium and titanium

Baltic seaweeds are characterized by much higher content of aluminium compared to the Żarnowiec Lake plants (Tables 1 and 2). Levels of titanium in the Baltic plants varied from 22 to 141 $\mu\text{g/g}$ of dry weight. According to Yamagata (1976) as well as Koriakova and Saenko (1981) the Japan Sea seaweeds contain from 0.94 to 2.95 mg Al/g of dry weight and from 0.1 to 67.0 $\mu\text{g Ti/g}$ of dry weight.

3.8. Calcium and magnesium

In contrast to magnesium the distribution of calcium in the Baltic seaweeds is characterized by large variability. Limiting levels of calcium and magnesium fell within the ranges of 0.49–29.8 and 2.2–25.8 mg/g of dry weight, respectively.

Some of the samples contained high levels of calcium which can be attributed to the presence of small fragments of mollusc shells in the analysed plant material.

The mean values of Ca/Mg ratio of concentration for the individual classes of plants ranged from 1.2 to 2.0 and were consistent with the values obtained for seaweeds from the coast of Japan (Yamagata 1977).

3.9. Sodium and potassium

Baltic seaweeds contained on average more potassium (2.4–56.1 mg/g of dry weight) than sodium (1.5–16.1 mg/g of dry weight)—Table 1. Too large negative deviations of individual levels from the mean values can be related to the loss of a certain amount of cell electrolytes during preconditioning of the investigated material.

The mean K/Na ratio of concentrations calculated for the analysed seaweeds is greater than unity, while for the fresh-water plants it does not exceed a unity. According to Bojanowski (1973) the value of this quotient for the Baltic seaweeds ranges from 1.44 to 2.65.

3.10. Concentration factors (*CF*)

In order to determine quantitative proportions in which a given element occurs in a plant and in sea water concentration factors were calculated according to the following formula:

$$CF = \frac{C_R}{C_S},$$

where C_R and C_S are the contents of a given element in a plant and in sea water, respectively. The values of *CF* (Table 4) can be arranged in the following order:

Al > Fe > Pb > Mn > Co > Ni > Zn > Cd > Cu > K > Ca > Mg > Na.

Table 4. Mean concentration factors *CF* and enrichment factors EF_{Al}^M for individual elements in southern Baltic plants

Metal	<i>CF</i> *	EF_{Al}^{M**}
Fe	21200	2
Mn	8800	75
Pb	15600	110
Ni	630	3.3
Cu	90	5.3
Co	710	1.9
Zn	490	95
Cd	230	150
Ti***	—	0.8
Al	35600	—
Ca	19	24
Mg	3	23
K	25	58
Na	0.5	—

* Calculated on a wet weight basis. The data concerning the content of metals in Baltic water were taken after Bojanowski (1973), Brüggmann (1982), and Kremling, Peterson (1984).

** Calculated on a dry weight basis.

*** Correction for a fraction of Ti of marine origin in the analysed samples was not taken into account due to lack of data on the content of this element in Baltic water

3.11. Enrichment factors (EF)

In order to determine a biological affinity of individual metals to the Baltic seaweeds the mean enrichment factors were calculated according to a formula:

$$EF = \frac{(C_M/C_{Fe})_R}{(C_M/C_{Fe})_E},$$

where $(C_M/C_{Fe})_R$ and $(C_M/C_{Fe})_E$ are the ratios of content of a metal M to the content of iron in plants and in earth's crust or in soil particles, respectively. Aluminium was used for calculations, and thorium and iron were used for comparison as standardizing elements of terrigenous origin keeping in mind Li's report (1981) that $EF_{Al}^{Fe} \approx 1$ and $EF_{Al}^{Th} \approx 1$. It means that $EF_{Al}^M \approx E_{Fe}^M \approx E_{Th}^M$. The share of components of marine origin present both in plants and in the earth's crust (a standard) was eliminated from the calculations assuming that sodium is a typical element of marine origin. In such a case the share of a metal of marine origin in a sample equals (Li, 1981):

$$C_{Na} (C_M/C_{Na})_S,$$

where C_{Na} denotes the content of sodium in a sample and $(C_M/C_{Na})_S$ is a mean ratio of concentrations of a given metal and sodium in the Baltic water.

Accordingly, EF values greater than unity mean that earth's crust, soil particles and sea salts cannot be primary sources of a given element in plants. It follows from Table 4 that Pb, Cd, Zn, Mn, K, Ca, and Mg are typical biophilic elements ($EF > 10$). Ti, Al, Fe, and Co belong to elements of low biologic affinity ($EF \approx 1$); terrigenous material or sea salts can be sources of their occurrence in plants. The remaining elements, *viz* Cu and probably Ni ($2 < EF < 10$), derive primarily from other sources than earth's crust and sea salts and their biological activity is lower than that of typical biophilic elements.

3.12. Correlations

In order to find any correlation between the individual elements, linear correlation coefficients were calculated (Table 5). Statistically significant correlations ($p < 0.01$) were found for the following metal pairs: Co-Ni, Cu-Fe, Ni-Ca, Pb-Mn, Zn-Al, Fe-Al, and Ca-Al. Weaker correlation ($p < 0.05$) was found for Co-Cd, Fe-Cd, Al-Cd, Fe-Ni, Zn-Mn, Zn-Fe, and Pb-Mg pairs.

Table 5. Linear correlation coefficients for individual metal pairs in the analysed plants calculated on a dry weight basis

	Co	Cd	Cu	Ni	Pb	Zn	Mn	Fe	Ca	Mg	Na	K
Co	1											
Cd	0.48**	1										
Cu	0.24	0.03	1									
Ni	0.67*	-0.36	-0.04	1								
Pb	-0.02	0.34	0.00	-0.13	1							
Zn	0.02	0.13	0.40	0.08	-0.36	1						
Mn	0.40	-0.02	-0.02	0.14	0.54*	0.52**	1					
Fe	0.61*	0.42**	0.36	0.45**	0.11	0.51**	0.08	1				
Ca	0.23	0.35	0.30	0.58*	-0.13	0.24	-0.22	0.25	1			
Mg	-0.02	-0.15	0.03	-0.20	-0.47**	0.19	-0.35	-0.12	-0.29	1		
Na	-0.04	0.33	0.18	0.22	-0.26	0.04	-0.09	-0.13	-0.26	-0.20	1	
K	0.16	0.01	-0.02	0.02	0.10	-0.15	0.36	0.07	0.28	-0.08	0.20	1
Al	0.36	0.44**	0.06	-0.41	-0.29	0.64*	-0.10	0.73*	0.68*	-0.10	-0.03	-0.10

* Significance level $p < 0.01$.** Significance level $p < 0.05$

4. Summary

(i). Individual variations in concentration, even among specimens of the same species, are so significant for some elements that they practically preclude detailed interpretation of data in terms of interspecies and interregional variability due to relatively small number of samples. It should be pointed out that part of the biological material (*eg Cladophora, Enteromorpha, Potamogeton*) contained mineral particles (carbonate incrustations, fragments of tiny shells of mussels, diatoms or sand grains) which were incompletely removed despite repeated washing. Due to all these facts distribution of metals in plants cannot be readily assessed; the results, however, throw some light on a degree of concentration of elements and their biological affinity to the Baltic seaweeds.

(ii). It follows from the calculated values of selectivity and concentration factors that the analysed Baltic seaweeds are characterized by the highest affinity to iron, aluminium, and lead, and the lowest affinity to copper.

(iii). Three groups of elements of different biological activity were distinguished on the basis of the values of enrichment factors, *viz*:

- biophilic metals ($EF > 10$): Pb, Cd, Zn, Mn, K, Ca, and Mg,
- metals of low biological affinity ($EF \approx 1$): Ti, Al, Co, and Fe,
- metals of medium biological affinity ($2 < EF < 10$): Cu and Ni.

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