Changes in heavy metal accumulation in *Enteromorpha* spp. from the Gulf of Gdańsk*

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Enteromorpha spp.
Heavy metals
Gulf of Gdańsk

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Abstract

The contents of Cu, Zn, Cd, and Pb were determined in samples of *Enteromorpha* spp. collected at Jurata at monthly intervals from November 1992 to October 1993, and at different stations on the coast of the Gulf of Gdańsk during one month. Of all the metals analysed, Zn occurs in the highest concentrations, followed by Cu, Pb and Cd. In the samples from Jurata all the four metals displayed considerable seasonal variations in their concentrations, the ranges for each element being Zn – 29.80–90.05 μg g^{-1} dry wt., Cu – 12.82–28.41 μg g^{-1} dry wt., Pb – 1.81–7.08 μg g^{-1} dry wt. and Cd – 0.08–0.51 μg g^{-1} dry wt. The highest concentrations of all elements except Pb were recorded in November 1992.

Different concentrations of these metals were recorded in *Enteromorpha* spp. collected at different stations on the same day; the highest concentrations of Zn, Cu, and Pb were found in samples from Jastarnia (Zn – 72.11 μg g^{-1} dry wt., Cu – 48.19 μg g^{-1} dry wt. and Pb – 9.41 μg g^{-1} dry wt.), and from Gdynia (Zn – 65.29 μg g^{-1} dry wt., Cu – 29.13 μg g^{-1} dry wt. and Pb – 5.72 μg g^{-1} dry wt.). This implies a high level of pollution at these stations in comparison with the others.

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The highest concentration of Cd was recorded in samples from Puck (0.43 μg g^{-1} dry wt.).

1. Introduction

Monitoring of metal pollution in marine environments is becoming more and more important. It has long been recognized that the release of waste into the marine environment not only affects the composition of water and sediments, but adversely affects the flora and fauna as well.

The ability of seaweeds to accumulate trace metals is well documented (Lunde, 1970; Preston *et al.*, 1972; Fuge and James, 1973; Haug *et al.*, 1974; Saenko *et al.*, 1976; Zingde *et al.*, 1976; Seeliger and Edwards, 1977; Agadi *et al.*, 1978 and Bryan, 1983). Keeping in mind the importance of seaweeds as primary producers, and their role in detritus formation and as indicators of pollution (Fuge and James, 1974), it was felt necessary to study the accumulation of some of these metals in *Enteromorpha* spp. Some of the most common algae in the Gulf of Gdańsk, they have been used in several studies, such as the mapping of pollution sources and establishing base-line data on metal contamination in Brazilian estuaries (Seeliger and Knak, 1982).

Skwarzec *et al.* (1988) stated that Pb and Cd occur mostly in suspended form whereas Cu and Zn are present mostly in the dissolved form. The mean total concentrations of Cu, Pb, Zn and Cd in southern Baltic water were: Cu – 0.58 μg dm^{-3}, Pb – 0.57 μg dm^{-3}, Zn – 13.0 μg dm^{-3} and Cd – 0.09 μg dm^{-3}; the mean contents of the same metals in the bottom sediment of the Gulf of Gdańsk were: Cu – 67 μg g^{-1} dry wt., Pb – 256 μg g^{-1} dry wt., Cd – 4.4 μg g^{-1} dry wt. and Zn – 264 μg g^{-1} dry wt.

Zn displays the highest concentration of all the heavy metals studied in Baltic water, and is readily accumulated by mesozooplankton (Szefer, 1985; Szefer *et al.*, 1985). The concentration of Cu in suspension is much higher than in the bottom sediments: this elevated Cu content is probably due to its bioaccumulation by mesozooplankton and its complexing by organic matter (Kremling *et al.*, 1981) and humic substances (Pempkowiak, 1983). The considerably higher content of Cd in suspension can probably be attributed to its accumulation by marine organisms (Skwarzec *et al.*, 1984). The Pb concentration in the bottom water layer is a little higher than that in the surface layers. This becomes clear if not only the sedimentation processes but also the possibility of Pb desorption from the bottom sediments to water are taken into consideration. Lead enters the water mostly from the air over the southern Baltic (Brzezińska and Garbalewski, 1980) and remains there in suspension.

Little information on the accumulation of heavy metals by algae in the Gulf of Gdańsk was found in the literature (Bojanowski, 1973; Szefer and Skwarzec, 1988 and Szefer and Szefer, 1991).

The aim of this work was to collect recent data on the accumulation of some heavy metals in *Enteromorpha* spp. (green algae from the family Ulvaceae, widely distributed in the Gulf of Gdańsk), close attention being paid to seasonal variations in the concentrations of these metals.

2. Materials and methods

The study was carried out in the Gulf of Gdańsk (Fig. 1). Samples of *Enteromorpha* spp. were collected at Jurata at monthly intervals from November 1992 to October 1993, and at different localities along the Gulf of Gdańsk coast during September 1993. The algae samples were hand-picked, cleaned, and washed with fresh water. They were subsequently dried at 60°C to constant weight, then powdered sieved through a piece of muslin and stored for analysis.

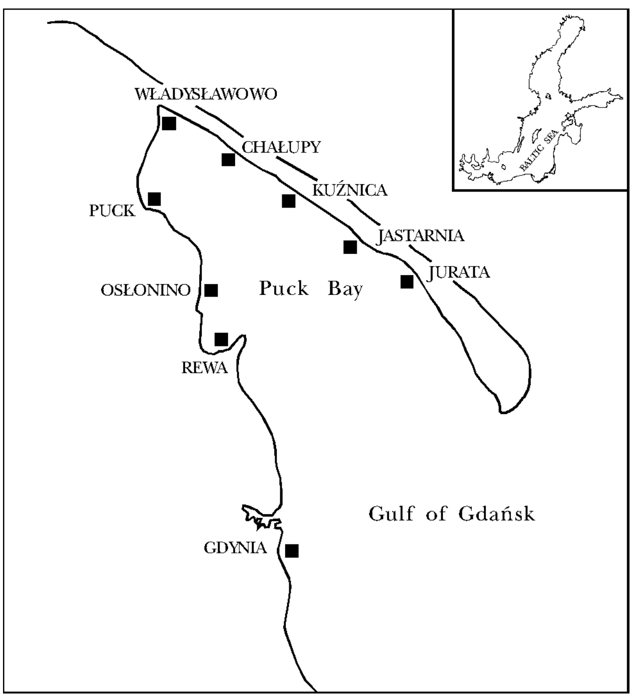

Fig. 1. Distribution of stations from which material was collected

Digestion of samples was carried out according to the method described by Soria (1988), in which 20 mg dry wt. of sample were digested in a mixture of concentrated nitric and perchloric acids (1:1 v/v) in a quartz tube with a loose Teflon stopper. The samples were fumed to near dryness in an aluminium heat block at about 190°C for 12–15 h, which was sufficient to decolorize the samples. After digestion, each sample was dissolved in analytical grade water (Milli – Q 50 system, Millipore), made up to 1 ml in an Eppendorf Polyethylene Vial and stored in a refrigerator until analysis for heavy metals.

Each digested sample was measured by graphite – furnace atomic absorption (Perkin – Elmer Zeemann 3030), the samples being introduced into the graphite tube with a platform through a small hole in the tube wall. Through a series of stepwise or ramped temperature increases, as many of the concomitants as possible were removed before the element was atomized by a final, rapid increase in temperature.

The heavy metal concentrations were calculated using the following equation:

$$C = \frac{c\ v\ df}{w}, \tag{1}$$

where

C – heavy metal concentration in the dry tissue [μg g^{-1}],
c – heavy metal concentration in the sample [μg ml^{-1}],
v – final volume of the sample diluted after digestion [ml],
df – dilution factor of the sample,
w – dry wt. of the sample [g].

The glassware used in the determination of all heavy metals was previously rinsed with dilute nitric acid, and all reagents used were of analytical reagent grade. Quality control of all analyses was ensured by routine analysis of the reference material 'Lobster Hepatopancreas' (TORT–1) obtained from the National Research Council, Canada. The percentage recoveries of analysed TORT–1 were 95% for Cu and Zn, 96% for Pb and 100% for Cd.

Dry weight was determined by drying the samples at 60°C to constant weight followed by 24 hours' drying at 105°C; the results are expressed in g (100 g)$^{-1}$ of wet algae.

3. Results and discussion

Tab. 1 presents the average values for Cu, Zn, Cd and Pb in *Enteromorpha* spp. collected at Jurata during the period from November 1992 to October 1993.

The results show that cadmium occurs in *Enteromorpha* spp. in amounts ranging from 0.08 to 0.51 μg g^{-1} dry wt. (Fig. 2), whereas the level of lead

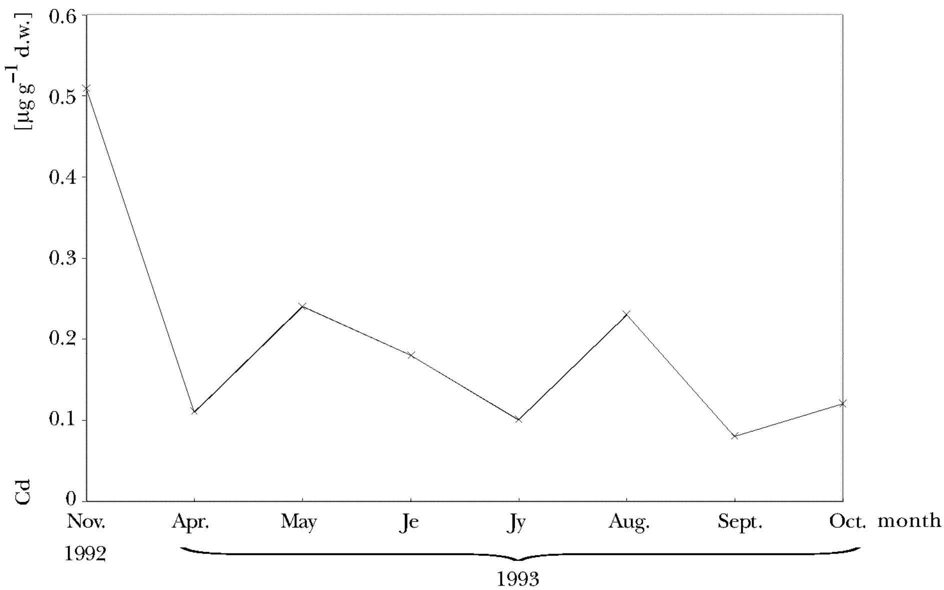

Fig. 2. Seasonal changes in cadmium content in *Enteromorpha* spp. from Jurata

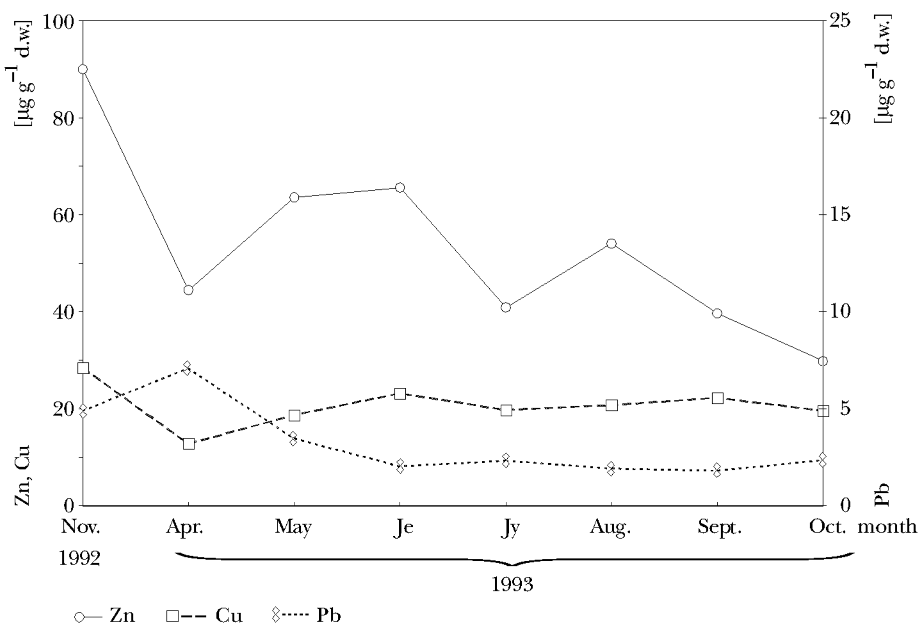

Fig. 3. Seasonal changes in lead, copper and zinc contents in *Entromorpha* spp. from Jurata

varied between 1.81 and 7.08 μg g^{-1} dry wt. Zn is present in concentrations from 29.80 to 90.05 μg g^{-1} dry wt., the highest amounts of all the metals analysed (Fig. 3). Copper also occurs at high levels varying between 12.82 and 28.41 μg g^{-1} dry wt.

The large quantities of Zn and Cu and the small quantities of Cd and Pb in *Enteromorpha* spp. from Jurata could be due to the high concentration and the dissolved form in which Zn and Cu occur in seawater; at the same time Pb and Cd occur mostly at low concentrations and in suspended form, which make its absorbtion by algae difficult.

Table 1. Content of Cd, Pb, Zn, and Cu [μg g^{-1} dry wt.] and dry weight content (g (100 g)$^{-1}$ wet wt.) in *Enteromorpha* spp. from Jurata

	[μg g^{-1} d.w.]				g (100 g)$^{-1}$ w.w.
Date	Cd	Pb	Zn	Cu	Dry wt.
1992					
Nov.	0.51	4.89	90.05	28.41	12.14
1993					
Apr.	0.11	7.08	44.47	12.82	7.53
May	0.24	3.47	63.63	18.75	6.15
June	0.18	2.04	65.64	23.15	8.08
July	0.10	2.33	40.90	19.76	13.05
Aug.	0.23	1.91	54.10	20.77	12.47
Sept.	0.08	1.81	39.67	22.26	7.85
Oct.	0.12	2.35	29.80	19.56	6.67
Mean ± SD.	0.20 ± 0.14	3.23 ± 1.87	53.53 ± 19.20	20.68 ± 4.41	9.24 ± 2.82
Minimum	0.08	1.81	29.80	12.82	6.15
Maximum	0.51	7.08	90.05	28.41	13.05

The results in Tab. 1 show that seasonal changes take place in the accumulation of Pb, Zn and Cu. The highest concentration of Pb and the lowest concentration of Zn and Cu were recorded at the beginning of the growth period (April 1993). Following this, Zn and Cu increased and Pb decreased until maturity. Finally, at the end of growth period, Zn and Cu decreased and Pb increased again. For Cd very little change was recorded.

The growth of a plant is influenced by the content of various elements; moreover, its physiological activity, and hence its mineral balance, is directly affected by environmental factors, *e.g.* temperature, salinity, nutrient concentration and light conditions. However, in *Enteromorpha* spp. these relationships are difficult to determine unequivocally, as is the principal factor affecting seasonal changes in heavy metal accumulation in these algae.

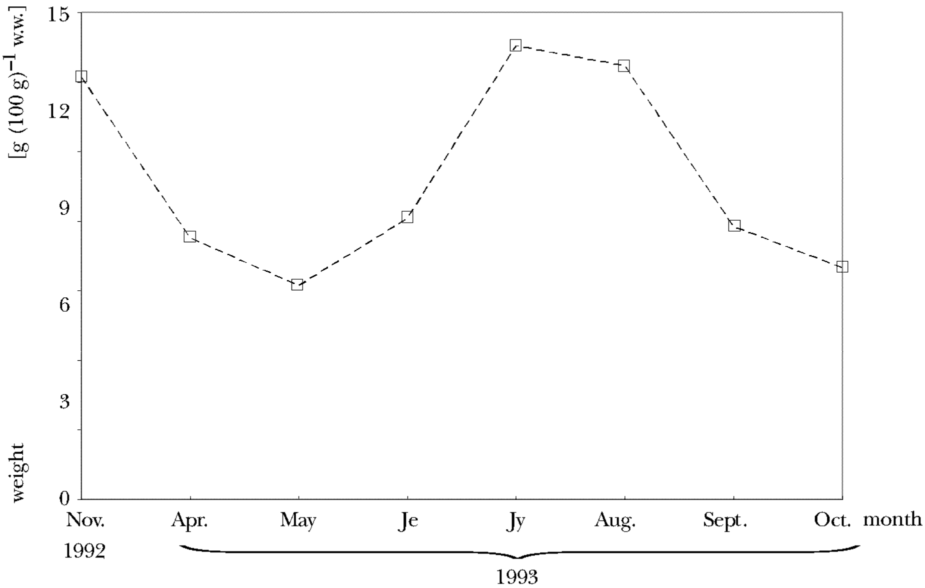

Fig. 4. Seasonal changes in dry weight of *Enteromorpha* spp. from Jurata

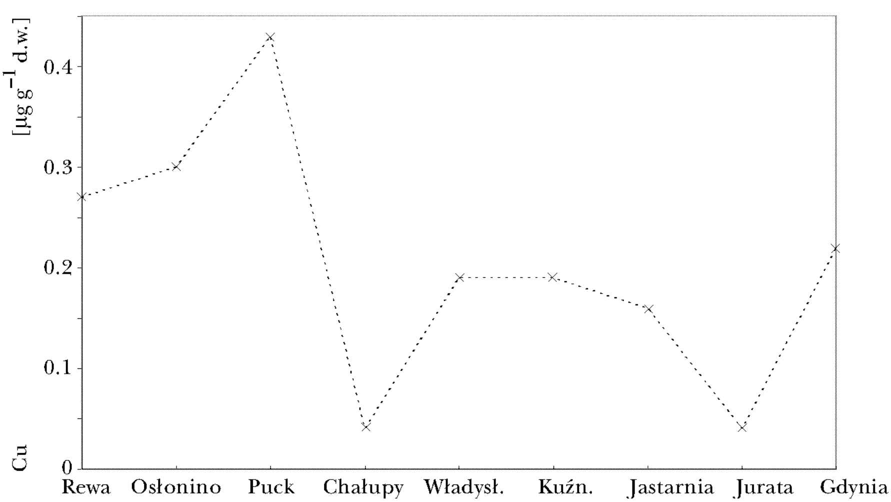

Fig. 5. Changes in cadmium content in *Enteromorpha* spp. at different stations on the Gulf of Gdańsk

Low dry weights were recorded in samples of *Enteromorpha* spp. from Jurata at the beginning and end of the growing seasons (from 6.15 to 6.67 g (100 g)$^{-1}$ wet wt.), while high values were recorded during July and August, when the alga reaches maturity (13.05 and 12.47 g (100 g)$^{-1}$ wet wt. respectively) (Fig. 4). These results are in agreement with the ones obtained by Munda and Gubensek (1976, 1986) for *Enteromorpha ahleriana* and *Enteromorpha intestinalis* L. Link from Iceland and the northern Adriatic (8.8 and 11.5 g (100 g)$^{-1}$ wet wt. respectively).

Table 2. The concentration of Cd, Pb, Zn, and Cu [μg g^{-1} dry wt.] and dry weight content (g (100 g)$^{-1}$ of wet wt.) in *Enteromorpha* spp. from different stations on the coast of the Gulf of Gdańsk

	[μg g^{-1} d.w.]				g (100 g)$^{-1}$ w.w.
Station	Cd	Pb	Zn	Cu	Dry wt.
Rewa	0.27	1.44	42.22	15.41	10.41
Osłonino	0.30	1.74	38.79	19.22	4.15
Puck	0.43	1.96	34.39	2.20	11.77
Chałupy	0.04	0.43	7.87	4.46	7.83
Władysławowo	0.19	3.80	43.39	25.00	8.98
Kuźnica	0.19	0.57	39.86	15.11	20.55
Jastarnia	0.16	9.41	72.11	48.19	4.33
Jurata	0.04	1.92	45.58	19.79	7.85
Gdynia	0.22	5.72	65.29	29.13	11.66
Mean ± SD	0.20±0.12	3.00±2.91	43.28±18.33	19.84±13.72	9.73 (4.92)
Minimum	0.04	0.43	7.87	2.20	4.15
Maximum	0.43	9.41	72.11	48.19	20.55

Tab. 2 and Figs. 5, 6 show the concentrations of heavy metals in *Enteromorpha* spp. collected on the same day from different stations along the coast of the Gulf of Gdańsk. There, the concentration of Zn is highest, and is followed by Cu, Pb and Cd. The highest levels of all these metals except Cd were recorded in the samples from Jastarnia – 72.11, 48.19 and 9.41 μg g^{-1} dry wt. for Zn, Cu and Pb respectively, followed by Gdynia, where the respective concentrations of Zn, Cu and Pb were 65.29, 29.13 and 5.72 μg g^{-1} dry wt. (Fig. 6). This high concentration of heavy metals in the samples from Jastarnia and Gdynia may be due to the high level of pollution in these areas from ports and shipyards, as well as other industrial plants such as oil refineries, nitrate fertilizer plants, a phosphoric acid factory and sulphur transshipment facilities.

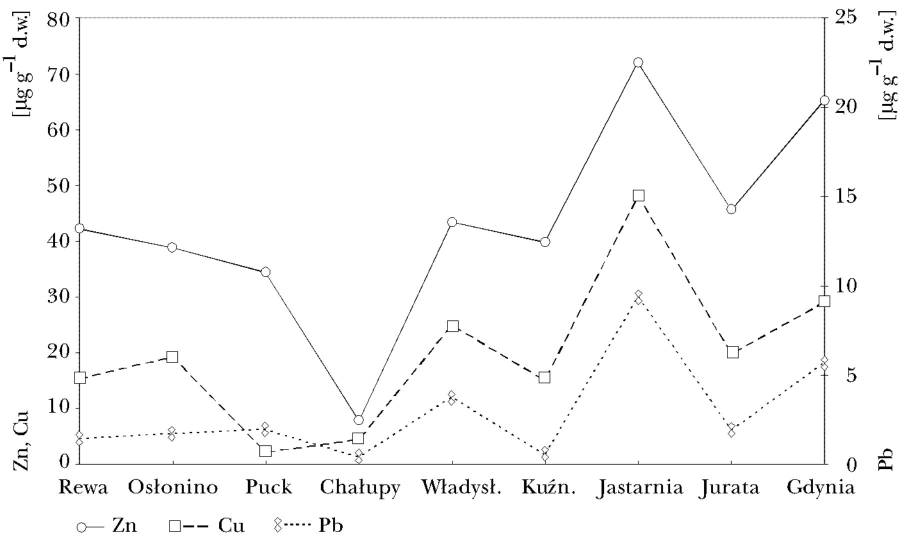

Fig. 6. Changes in lead, zinc and copper contents in *Enteromorpha* spp. at different stations on the Gulf of Gdańsk

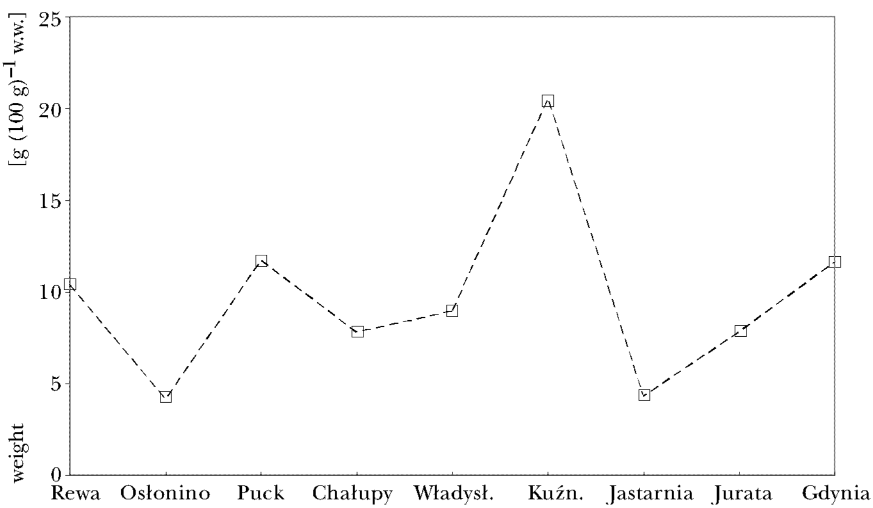

Fig. 7. Changes in dry weight of *Enteromorpha* spp. at different stations on the Gulf of Gdańsk

The lowest concentrations of these metals were recorded in samples from Chałupy: Zn – 7.87 μg g^{-1} dry wt., Cu – 4.46 μg g^{-1} dry wt., Pb – 0.43 μg g^{-1} dry wt. and Cd – 0.04 μg g^{-1} dry wt.

The fact that different concentrations of heavy metals were recorded in *Enteromorpha* spp. collected from different stations on the Gulf of Gdańsk on the same day may be due to the environments to which these algae are exposed. Another reason for this variation could be the stress to which the algae are subjected as a result of fluctuations in temperature, salinity or turbidity (Seeliger and Edwards, 1977).

However, Cd concentrations in *Enteromorpha* spp. from the Gulf of Gdańsk are in good agreement with the results obtained for *Enteromorpha* spp. from Puck Bay (Szefer and Skwarzec, 1988) and the British North Sea coast (Say *et al.*, 1990). On the other hand, Zn and Pb are low and Cu is high when compared to the values obtained by Szefer and Skwarzec (1988). At the same time a similar range of Zn was found for *Enteromorpha* spp. from Puck Bay and the Gulf of Gdańsk (Bojanowski, 1973). The difference in these concentrations may be due to several factors, like period of collection, environmental conditions, age and maturity of algae at the time of collection.

The data presented in Tab. 2 and Fig. 7 reveal differences in the dry weight values in *Enteromorpha* spp. samples from different stations on the coast of the Gulf of Gdańsk: the highest value was recorded in a sample from Kuźnica (20.55 g (100 g)$^{-1}$ wet wt.) and the lowest ones in samples from Osłonino and Jastarnia (4.15 and 4.33 g (100 g)$^{-1}$ wet wt. respectively).

4. Summary

The changes in heavy metal accumulation in *Enteromorpha* spp. from the Gulf of Gdańsk in relation to season and place were studied. On the basis of the results it can be stated that, of all the metals analysed, Zn occurs at the highest concentration, and is followed by Cu, Pb and Cd. In the samples from Jurata the seasonal changes in the accumulation of Zn, Cu and Pb are obvious: here the content of Zn ranged from 29.80 to 90.05 μg g^{-1} dry wt., Cu from 12.82 to 28.41 μg g^{-1} dry wt. and Pb from 1.81 to 7.08 μg g^{-1} dry wt. The Cd content hardly changes at all.

Different concentrations of these metals were recorded in samples of *Enteromorpha* spp. collected on the same day from different stations along the Gulf of Gdańsk coast: the highest concentrations of all the metals except Cd were recorded in the samples from Jastarnia (Zn – 72.11 μg g^{-1} dry wt., Cu – 48.19 μg g^{-1} dry wt. and Pb – 9.41 μg g^{-1} dry wt.), followed by Gdynia, where the following concentrations were recorded: Zn – 65.29 μg g^{-1} dry wt., Cu – 29.13 μg g^{-1} dry wt. and Pb – 5.72 μg g^{-1} dry wt.

Low dry weights were recorded in the samples of *Enteromorpha* spp. from Jurata at the beginning and end of the growing season, while high values were recorded during July and August. Also certain differences in the dry weights were recorded in samples of *Enteromorpha* spp. from different stations along the coast of the Gulf of Gdańsk.

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