Distribution and relationships between selected chemical elements in green alga Enteromorpha sp. from the southern Baltic

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Enteromorpha sp. can be used as efficient biomonitor for chemical elements in coastal areas of the Baltic Sea.

Abstract

The concentrations of heavy metals (Cd, Cu, Ni, Pb, Zn and Mn) and macroelements (K, Na, Ca and Mg) were determined in green alga Enteromorpha sp. from the coastal zone of the southern Baltic including Gulf of Gdańsk and Vistula Lagoon in 2000–2003. In order to estimate the degree of accumulation of each element by the green alga, concentration and discrimination factors (CFs) with respect to seawater were calculated. The results of factor analysis (FA) and ANOVA clearly indicate geographical differences between concentrations of chemical elements. Enteromorpha sp. from Vistula Lagoon and the southern Baltic exhibited higher levels of Mn and Ni, and Na and K, respectively. Anthropogenic impact of Cu, Pb and Zn, possibly originated from municipal sewage, was identified in alga samples collected in the Gulf of Gdańsk, especially in the vicinity of Gdynia. From comparison our data with those published earlier results that Pb content in Enteromorpha sp. from the Gulf of Gdańsk decreased within 1978–2003 reflecting reducing use of leaded petrol in Baltic countries in this period. The alga Enteromorpha sp. can be used for biomonitoring surveys of metal contaminants in coastal areas of the Baltic Sea.

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Keywords: Chemical elements; Enteromorpha sp.; Bioaccumulation; Southern Baltic; ANOVA; Factor analysis

1. Introduction

The Baltic Sea, with an average depth of 56 m, is much shallower than most of the world’s seas. The water exchange with North Sea through the Danish Straits is small and its residence time is 20–35 years. Due to developed shore line and drainage area which is more than four times greater than the Baltic Sea it is especially subjected to contaminants flowing from the surrounding land. Therefore, there are favourable conditions for accumulation of different dissolved pollutants in living organisms (Szefer, 2002).

Macrophytes have a high capacity to bind trace metals because cellular wall is rich in hydroxyl, sulphate and carboxyl groups of the polysaccharides which are strong ion-exchangers, and therefore they are important complexion sites for metal cations (Ragan et al., 1979; Bryan et al., 1985; Steffens, 1990; Tropin, 1995). Additionally seaweeds are the base of aquatic chain and therefore can influence the chemical elements content in higher trophic levels (Bryan et al., 1985; Sanchiz et al., 2001; Szefer, 2002; Amado Filho et al., 2004). Coastal and estuarine habitats are highly productive and support complex ecosystems, these regions in general are also exposed to the greatest degree of human impact and activity. A few studies have been done on heavy metals content in benthic plants from the coastal zone of Poland (Bojanowski, 1973; Szefer and Skwarzec, 1988; Szefer, 1991; Szefer and Szefer, 1991; Szefer et al., 1994; Haroon et al., 1995; Kruk-Dowgiello and Pempkowiak, 1995). In coastal zone of the southern Baltic especially Enteromorpha sp. is often abundantly growing and dominant benthic plant
and contributes significantly to the primary production of near-shore ecosystem. Studies have indicated that metal concentrations in Enteromorpha sp. reflect metal concentration in surrounding water (Munda, 1978, 1984; Ho, 1987; Haritonidis and Malea, 1995), so analyses of this green alga are important for the detection of metals discharged into the environment. Because metals are available to the alga only from the dissolved phase, concentrations in these organisms may reflect the bioavailable levels of a metal in the solute phase. In HELCOM MONAS 3/2001 meeting it has been suggested that Fucus vesiculosus and Zostera marina could serve as Baltic biological indicators. Unfortunately the bladderwrack disappeared in 1970s from Polish coastal zone of the southern Baltic (Kruk-Dowgiallo, 1994) and Z. marina distribution is not as widespread as Enteromorpha sp. Therefore the green alga was selected taking into account that extensive samplings are required for monitoring heavy metal pollution. There are a number of examples where species of green alga Enteromorpha have been used as indicators of metal contamination in coastal areas because of adequate tissue for analysis, simple morphology and tolerance to metals. Moreover, it is sedentary, easily collectable and also widespread along the coast all over the world (Bryan et al., 1985; Leal et al., 1997; Brown et al., 1999; Fytianos et al., 1999; Serfor-Armah et al., 1999; Sfriso et al., 1995; Wang and Dei, 1999).

The aim of this study was to obtain background data and evaluate distribution (seasonal and spatial) and relationships (inter-element correlation, concentration factors) for heavy metals (Cd, Cu, Pb, Ni, Zn, Mn) and macroelements (Ca, Mg, Na, K) content in Enteromorpha sp. from the coastal zone of the southern Baltic Sea. The heavy metal concentrations in the green alga were compared with data reported in previous study in order to provide information on the present status of heavy metal pollution in coastal zone of the southern Baltic.

2. Material and methods

2.1. Description of the study areas

The investigation was carried out in coastal zone of the southern Baltic, Gulf of Gdańsk and Vistula Lagoon in 2000–2003 (Fig. 1). Four stations, i.e. Ustka, Jarosławiec, Darlowo and Wolin are situated in coastal zone of the open southern Baltic waters. This area is free from industrial inputs except sewage effluents.

The Gulf of Gdańsk is semi-closed basin of the southern Baltic. Important source of heavy metals input to the gulf is derived from the Vistula River (Sokołowski et al., 2001), which transports pollutants from the entire drainage area, including heavy industry area of the southern Poland. Vistula River is the second longest river (after Neva) draining into the Baltic and is responsible for ca. 10% of the element input of Cd, Cr, Cu, Pb and Zn to the sea (Matschullat, 1997). Gdańsk–Gdynia metropolitan area with a total population exceeding 1 million inhabitants spreads along the southern coast of the Gulf of Gdańsk. Due to intensive local shipping, industry and urban activity, especially in Gdańsk and Gdynia, the Gulf of Gdańsk is one of the ecologically endangered areas in the Baltic and has been classified as so-called “hot spot” by Helsinki Commission (HELCOM, 2003).
Vistula Lagoon is split between Poland (west part) and Russia (east part). The lagoon is cut off from the Gulf of Gdańsk by the Vistula Spit and connected to the gulf only by the Strait of Baltyjsk. The lagoon is characterized by intensive eutrophication due to nutrient loads from urban areas, industry and agriculture. The importance of the lagoon is shown by its inclusion in the list of Baltic Sea Protected Areas (HELCOM, 1996).

2.2. Sampling and analytical methods

Green alga Enteromorpha sp. samples were collected from rocks and stones from several stations in coastal zone of the southern Baltic (Usłka, Jarosławice, Darlowo, Wolin), Gulf of Gdańsk (Hel, Jurata, Jastarnia, Chłuppy, Władysławowo, Puck, Rewa, Gdynia Bulwark, Gdynia Orłowo) and Vistula Lagoon (Frombork, Tolkmicko, Suchacz, Nowakowo, Kąty Rybackie) every month from May to October in 2000–2003 (Fig. 1). After delivering to the laboratory, the plant material was cleaned from epiphytes, organic and mineral particles and rinsed in distilled water. Next the samples were dried at 60 °C to a constant weight and homogenized manually into powder. From each sample three replicate subsamples were prepared. Then they were digested in Microwave Digestion System (MLS 1200 MEGA) using analytically ultrapure HNO₃. All the glassware was cleaned prior to use by soaking in 1 M HNO₃ for 72 h and rinsed with Milli-Q water. The levels of six heavy metals (Cd, Cu, Ni, Pb, Zn and Mn) and four macroelements (Ca, Mg, Na and K) were determined by flame atomic absorption spectroscopy (FAAS) in Shimadzu AA 6501 and Philips PU9100X spectrometers, respectively. The quality of the method was checked and confirmed by analysis of seaweed reference material (BCR 279-Ulva lactuca). The agreement between the analytical results for the reference material and their certified values was satisfactory, i.e. the recoveries and the relative standard deviations were >92% and <10%, respectively. To check for contamination, blanks were analyzed using this procedure after every five samples.

2.3. Concentration factors

In order to determine quantitative proportions in which given element occurs in a macrophyte and in the surrounding environment, concentration factors (CF) were calculated:

\[ CF = \frac{C_1}{C_2} \]

where \( C_1 \) and \( C_2 \) are average chemical element content in wet weight of macrophyte and in seawater, respectively. The mean value of the dry/wet weight ratio for Enteromorpha sp. was estimated as 0.1. Metals concentration in seawater can be very variable in sampling period so values of concentration factors on the base of single or few determinations can be misleading. Thus in this work concentration factors were calculated by dividing the mean concentration of given metal in the alga by its mean concentration in seawater. Such approach is recommended by IAEA (1985). The water concentrations of the heavy metals in the southern Baltic and Gulf of Gdansk (in parentheses) were as follows [μg/l]: Cd – 0.010 (0.014); Cu – 0.55 (0.80); Pb – 0.0095 (0.088); Ni – 0.72 (1.08); Zn – 0.48 (1.62); Mn – 16.9 (15.8) (Pempkowiak et al., 2000). Macroelements concentrations in the areas studied amounted to [mg/l]: Ca – 101, Mg – 273, Na – 2230, K – 85 (Porcelli et al., 1997). There are no available data on actual concentrations of the elements studied in Vistula Lagoon water except the following metals [μg/l]: Cd – 0.1, Cu – 4.0, Pb – 1.0, Ni – 5.0, Zn – 3.5 (WIOŚ, 2002), which were taken in calculations of CFs.

Knowledge of the concentration factor (CF) values permits recognition of the relative ability of organism to adsorb and/or take up selected metals from the medium in which they live. If CF values amount to ~1 this means that there is no enrichment of each element in the macrophyte in relation to seawater. When CF values are higher than unity, then given element is concentrated in organism with respect to the ambient seawater (Szefer, 1991; Szefer and Szefer, 1991). CFs may be estimated basing on the experimentally derived data; however, they are sometimes incomparable with the corresponding environmental data, since short-term laboratory experiments have usually insufficient duration to use laboratory derived data (IAEA, 1985; Szefer, 2002).

2.4. Statistical analysis

The concentration data were processed statistically using STATISTICA for Windows (version 6.0, Copyright© Statsoft, Inc. 2003). Multivariate techniques such as factor analysis (FA) and non-parametric statistical analysis were used, i.e. ANOVA Kruskal–Wallis to investigate influence of individual factors on variations in metal concentrations. Moreover R-Spearman rank order correlation coefficient was calculated to see if there is any relationship between concentrations of chemical elements in the investigated alga.

3. Results

3.1. Heavy metals and macroelements distribution

Mean concentrations of heavy metals such as Cd, Cu, Ni, Pb, Zn, Mn and macroelements Ca, Mg, Na, K in Enteromorpha sp. collected in 2000–2003 from the southern Baltic, Gulf of Gdansk and Vistula Lagoon are shown in Table 1. Cadmium content in Enteromorpha sp. from the southern Baltic was very low, i.e. below of the detection limit, while for the algae from the Gulf of Gdansk and Vistula Lagoon it was higher. The relative average abundance of chemical elements in the alga from the areas studied decreased in the order K > Na > Mg > Ca >> Mn > Zn >> (Cu, Pb, Ni) > Cd. Variations of heavy metals and macroelement concentrations in the benthic plant studied are illustrated in Figs. 2–4. Each element displayed a characteristic pattern of variation during the sampling period. Changes of heavy metals concentration in Enteromorpha sp. from the southern Baltic are significantly smaller than those from the Gulf of Gdansk. The concentrations of Cu, Pb and Zn, generally higher in the surrounding

<table>
<thead>
<tr>
<th>Heavy metals [μg/g d.w.]</th>
<th>Macroelements [μg/g d.w.]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
</tr>
<tr>
<td>Southern Baltic</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>not detected</td>
<td>3.78 ± 0.87</td>
</tr>
<tr>
<td>Northern Baltic</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>0.44 ± 0.24</td>
</tr>
<tr>
<td>Gulf of Gdansk</td>
<td>0.03–1.08</td>
</tr>
<tr>
<td>Vistula Lagoon</td>
<td>0.24 ± 0.18</td>
</tr>
<tr>
<td>5</td>
<td>0.07–0.55</td>
</tr>
</tbody>
</table>
Fig. 2. Concentration of Cu, Pb and Zn [mg/dw] in the green alga Enteromorpha sp. sampled from May to September from individual stations of the southern Baltic (2001-2003), Gulf of Gdansk (2000-2003) and Vistula Lagoon (2001-2003).
Fig. 3. Concentration of Cd, Ni and Mn [mg/g d.w.] in the green alga Enteromorpha sp. sampled from May to September from individual stations of the southern Baltic (2001-2003), Gulf of Gdańsk (2000-2003) and Vistula Lagoon (2001-2003).
area of Gdynia (sampling point 2) were possibly municipal sewage origin (Fig. 5). However, the green alga samples from Vistula Lagoon were characterized by higher content of Ni and Mn (Fig. 3). As regards macroelements, Enteromorpha sp. from the southern Baltic contained more Na and K than that from the Gulf of Gdańsk and Vistula Lagoon (Fig. 4). The concentrations of Ca and Mg in the alga from the southern Baltic, Gulf of Gdańsk and Vistula Lagoon were relatively constant (Fig. 4).

3.2. Statistical relationships

ANOVA Kruskal–Wallis data (p < 0.01, p < 0.05) clearly indicate spatial variations of the concentrations of Cu, Pb and Zn in Enteromorpha sp. from the Gulf of Gdańsk (Table 2). However, if we consider the whole area of the gulf, insignificant seasonally dependent variations in metal concentration, except Ni were observed. Considering long-term changes within the period of 4 years (2000–2003) statistically significant (p < 0.01, p < 0.05) diversity in concentrations of Cu, Ni and Zn in Enteromorpha sp. from the Gulf of Gdańsk was observed. There were statistically insignificant spatial and seasonal changes in concentration of all heavy metals in Enteromorpha sp. collected from the southern Baltic. In the case of Ca and Mg, their temporal and spatial concentrations in the green alga also varied insignificantly. However, differences between concentration of Na and K in Enteromorpha sp. collected from the southern Baltic, Gulf of Gdańsk and Vistula Lagoon were highly significant (p < 0.01).

ANOVA Kruskal–Wallis data for Enteromorpha sp. from the three closely located sampling points at Gdynia Bulwar indicate that effect of sampling site on metal concentration was statistically significant (p < 0.01, p < 0.05) (Table 3).

Spearman’s rank correlations were listed in Table 4. Significant positive correlations (p < 0.01; p < 0.05) between concentration of Cu and Pb, Ni and Zn were obtained for Enteromorpha sp. from the Gulf of Gdańsk. Concentrations of Cd and Ni as well as Ni and Pb were correlated significantly. Positive correlations were also observed between
Ni—Ca, Mn—Na, K—Mn and Cu—K. Regression lines for relationships ($p < 0.05$, $p < 0.01$) between heavy metals in Enteromorpha sp. from the Gulf of Gdańsk are presented in Fig. 6. The scatterplot shows that associations between metal concentrations are connected with spatial differentiation of their concentrations. Due to greater concentrations of Cu, Pb and Zn in Enteromorpha sp. from Gdynia Bulwar and Gdynia Orłowo, points corresponding to these sampling sites located in upper right part of the scatterplot are clearly separated from those corresponding to other studied areas.

3.3. Concentration factors

The variations in concentration factors (CFs), ranging within 3—4 orders of magnitude, are presented in Fig. 7. CF values for Enteromorpha sp. from the southern Baltic, Gulf of Gdańsk and Vistula Lagoon decreased in the following order: (Pb, Zn) > Cd > Mn > (Ni, Cu) > K > Ca > Mg > Na. In most cases CFs for heavy metals in Enteromorpha sp. from the southern Baltic and Gulf of Gdańsk were similar or higher than those from Vistula Lagoon.

3.4. Factor analysis (FA)

Since relatively many samples were analyzed in this study, multivariate factor analysis (FA) was employed in order to reduce the large number of variables to a smaller number of orthogonal factors. Using this approach we could also estimate quantitatively the influence of natural environmental or
Table 2
Effect of location, season and year on the variability of heavy metals and macroelements concentrations in Enteromorpha sp. from the southern Baltic, Gulf of Gdańsk and Vistula Lagoon in view of analysis of variance ANOVA Kruskal–Wallis

<table>
<thead>
<tr>
<th>Effect</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
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</thead>
<tbody>
<tr>
<td>Southern Baltic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station</td>
<td>5.58</td>
<td>2.23</td>
<td>3.69</td>
<td>7.32</td>
<td>7.76</td>
<td>3.40</td>
<td>2.96</td>
<td>3.83</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>Season</td>
<td>1.57</td>
<td>0.63</td>
<td>0.11</td>
<td>0.12</td>
<td>0.32</td>
<td>1.05</td>
<td>0.32</td>
<td>0.01</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Year</td>
<td>2.50</td>
<td>1.78</td>
<td>2.51</td>
<td>2.67</td>
<td>0.27</td>
<td>1.63</td>
<td>4.41</td>
<td>0.49</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Gulf of Gdańsk</td>
<td>8.76</td>
<td>33.36**</td>
<td>7.29</td>
<td>17.03*</td>
<td>20.60**</td>
<td>10.39</td>
<td>13.33</td>
<td>9.25</td>
<td>13.92</td>
<td>8.13</td>
</tr>
<tr>
<td>Season</td>
<td>6.38</td>
<td>3.11</td>
<td>16.95**</td>
<td>2.02</td>
<td>4.79</td>
<td>5.99</td>
<td>7.44</td>
<td>4.10</td>
<td>5.07</td>
<td>1.71</td>
</tr>
<tr>
<td>Year</td>
<td>2.67</td>
<td>9.47*</td>
<td>14.26**</td>
<td>2.33</td>
<td>40.10**</td>
<td>5.50</td>
<td>7.96*</td>
<td>4.23</td>
<td>7.52*</td>
<td>2.57</td>
</tr>
<tr>
<td>Gdynia Bulwar</td>
<td>4.37</td>
<td>6.02</td>
<td>3.04</td>
<td>3.12</td>
<td>2.73</td>
<td>3.60</td>
<td>6.17</td>
<td>1.17</td>
<td>3.31</td>
<td>1.80</td>
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<tr>
<td>Season</td>
<td>2.52</td>
<td>3.42</td>
<td>9.11*</td>
<td>0.58</td>
<td>8.19*</td>
<td>5.42</td>
<td>2.20</td>
<td>6.30</td>
<td>5.44</td>
<td>5.46</td>
</tr>
<tr>
<td>Year</td>
<td>1.03</td>
<td>1.05</td>
<td>6.12</td>
<td>0.44</td>
<td>3.03</td>
<td>1.09</td>
<td>3.00</td>
<td>3.56</td>
<td>2.77</td>
<td>4.12</td>
</tr>
<tr>
<td>Gdynia Orłowo</td>
<td>0.72</td>
<td>5.59</td>
<td>0.38</td>
<td>7.51*</td>
<td>6.65*</td>
<td>0.14</td>
<td>2.22</td>
<td>1.45</td>
<td>1.56</td>
<td>3.45</td>
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<td>Southern Baltic, Gulf of Gdańsk, Vistula Lagoon</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Region</td>
<td>1.37</td>
<td>13.02**</td>
<td>2.83</td>
<td>3.81</td>
<td>10.59**</td>
<td>0.37</td>
<td>6.25</td>
<td>8.30**</td>
<td>16.00**</td>
<td></td>
</tr>
</tbody>
</table>

*p < 0.05; **p < 0.01.

anthropogenic parameters on the elemental composition of the samples (objects). Therefore, identification of Enteromorpha sp. samples affected by contaminants with respect to their geographical location was possible. Factor analysis (FA) enables determining percentage of the total variance described by the first two or three factors. The first three factors describe 63.8% of the total variance and eigenvalues of these factors are 2.4, 2.0 and 1.4, respectively.

A plot of the samples based on their factor scores shows a clustering of the Enteromorpha sp. samples into three main areas, each corresponding to a geographically distinct zone. Thus, samples of Enteromorpha sp. taken from the Vistula Lagoon are characterized by higher values of F2 and are grouped in upper left part of the plot, however, object samples for the Gulf of Gdańsk with higher values of F1 are distributed in lower right part of the plot (Fig. 8A). Samples of Enteromorpha sp. from the southern Baltic are characterized by higher values of F3 and are situated in upper left part of the scatterplot (Fig. 9A).

In order to demonstrate which elements control the grouping of the samples, a plot of loadings is presented in Figs. 8B and 9B. Samples from the Vistula Lagoon have the highest contents of Mn and Ni described also by the highest values of F2. Points corresponding to samples from the Gulf of Gdańsk, especially from Gdynia stations (with high values of F1) are identified by Cu, Pb and Zn, possibly anthropogenic in origin. The southern Baltic samples (with higher values of F3) are attributable to loadings of Na and K (Fig. 9B). These macroelements are associated with the open-sea samples and may reflect the influence of more saline water in this region.

Table 3
Effect of sampling site and month on the variability of heavy metal concentrations in Enteromorpha sp. from three Gdynia Bulwar sampling stations (s1, s2, s3) in view of analysis of variance ANOVA Kruskal–Wallis

<table>
<thead>
<tr>
<th>Effect</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
</tr>
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<tbody>
<tr>
<td>Stations (s1, s2, s3)</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sampling month</td>
<td>6.89</td>
<td>4.46</td>
<td>6.63</td>
<td>2.91</td>
<td>3.43</td>
<td>5.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling site</td>
<td>0.32</td>
<td>7.52*</td>
<td>0.29</td>
<td>7.61*</td>
<td>9.90**</td>
<td>1.20</td>
<td></td>
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</tbody>
</table>

*p < 0.05; **p < 0.01.

4. Discussion

Concentrations of heavy metals and macroelements in macrophytes are regulated to a large extent by metabolic requirements for essential macronutrients and micronutrients. The determined mean concentration of chemical elements in Enteromorpha sp. decreased in the following sequence: K > Na > Mg > Ca > Mn > Zn > (Cu, Pb, Ni) > Cd. The presented rank with high concentrations of ions essential for metabolism and the partial exclusion of non-essential ions is comparable to literature data reported for the Gulf of Gdańsk (Szefer and Skwarzec, 1988; Pempkowiak, 1994; Bojanowski, 1973) and other areas, e.g. the coast of Argentina (Zn > Cu > Pb > Cd) (Muse et al., 1999) and Aegean Sea (Zn, Mn) > (Pb, Cu) > (Cd) (Sawidis et al., 2001).

4.1. Temporal distribution

Temporally dependent trends in variations of some heavy metals concentration in Enteromorpha were observed (Table 2) in view of analysis of variance ANOVA (p < 0.05; p < 0.01). For instance, statistically significant temporal variations were noted for Cu (Gulf of Gdańsk), Ni (Gulf of Gdańsk, Gdynia

Table 4
Statistically significant correlations (Spearman rank correlation) between selected chemical elements in Enteromorpha sp. from the Gulf of Gdańsk

<table>
<thead>
<tr>
<th>Enteromorpha sp.</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
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<tbody>
<tr>
<td>(+)Ni**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+)Pb**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(+)Zn**</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>(+)Cu**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(+)Zn*</td>
<td></td>
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<tr>
<td>(+)Cd*</td>
<td></td>
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(+): Positive correlation; (-): negative correlation; *p < 0.05; **p < 0.01.
Bulwar), Pb (Gdynia Orłowo) and Zn (Gulf of Gdańsk, Gdynia Bulwar, Gdynia Orłowo). It is interesting to note that increasing seasonal tendency in metal concentrations was identified between May and September 2000 for most sampling stations, i.e. Jastarnia, Chałupy, Puck, Rewa (Cd), Chałupy, Jastarnia, Jurata (Zn), Jurata, Jastarnia, Puck (Ni) and at Gdynia Bulwar (Cu).

Other authors also reported seasonally dependent variations in metal concentrations. Villares et al. (2002) observed highly significant ($p < 0.001$) differences in content of Al, Cr, Cu, Ni, Zn as well as insignificant variations in the case of Fe and Mn for Enteromorpha sp. from coastal waters of the Northwest Spain. Haritonidis and Malea (1995) reported statistically insignificant variations in concentration of Ni, Co and Cr in Enteromorpha linza from the Thermaikos Gulf, Greece. Chemical elements content in macrophytes may be dependent on various environmental factors, e.g. concentrations of chemical elements in water (Skipness et al., 1975; Haritonidis and Malea, 1995; Malea, 1994; Andrade et al., 2004), interactions between chemical elements (Broekaert et al., 1990), salinity (Munda, 1984), pH (Wang et al., 1996; Kratochwil and Volesky, 1998; Zhou et al., 1998), light intensity (Gutknecht, 1961; Munda, 1978) and metabolic factors such as dilution of metal contents due to algae growth (Bojanowski, 1973; Fuge and James, 1973; Brix and Lyngby, 1983; Munda and Hudnik, 1991). It is difficult to determine unequivocally the principal factors affecting seasonal changes in heavy metal accumulation in macrophytes because they may be due to interactions between them (Vasconcelos and Leal, 2001; Szefer, 2002). Seasonal variations in metal concentrations have been reported for Enteromorpha sp. from different regions all over the world (Haritonidis and Malea, 1995; Leal et al., 1997; Vasconcelos and Leal, 2001; Villares et al., 2002). Leal et al. (1997) found that the concentrations of Cd, Hg and Pb in Enteromorpha sp. from the coastal waters of Portugal were higher in spring (April–June) than in winter (November–March). However, it has been known that metals content in macrophytes are generally low in the warmer months due to high growth rates resulting in dilution of the accumulated metals, whereas in winter the heavy metals content is higher due to slowing down of metabolic processes (Brix and Lyngby, 1983; Malea, 1994; Hou and Yan, 1998; Villares et al., 2002).

4.2. Spatial distribution

The anthropogenic sources are responsible for much of the input of Cd, Cu, Pb, Zn and Mn in near-shore regions of the Gulf of Gdańsk (Szefer et al., 1995). In that case Cu and Zn are introduced mainly from the Vistula river whereas Cd and Pb, in part, by atmospheric transport (Renner et al., 1998). Enteromorpha sp. from the Gulf of Gdańsk was characterized...
by higher contents of Cu, Pb and Zn which are possibly suspected to be anthropogenic in origin. Probably, for this reason concentrations of Cu, Pb and Zn were noticeably higher in Enteromorpha sp. collected from municipal sewage at Gdynia area. The green alga samples from Vistula Lagoon were characterized by higher content of Ni and Mn. Uścinowicz and Zachowicz (1996) found concentration of Mn in surface sediment from this region amounting to 1500 μg/g d.w. which was much higher than that in Gulf of Gdańsk, i.e. 563 μg/g d.w. (Szefer et al., 1995). Probably, concentration of Mn in the Vistula Lagoon water is also higher, so Enteromorpha sp. from this area could be exposed to elevated levels of Mn. In the case of Ni its higher concentration in the green alga can be caused by local sources of contaminants like sewage treatment plants in Tolkmicko and Frombork (WIOS’, 2002). Due to salinity impact, the highest concentrations of Na and K were noted in Enteromorpha sp. from the southern Baltic while lower and the lowest ones in the algae from the Gulf of Gdańsk and Vistula Lagoon, respectively. This result is in agreement with data reported by Struck et al. (1997) where F. vesiculosus from the North Sea (salinity ~30‰) contained more Na and K than that from the southern Baltic Sea (salinity ~8‰). In the case of other essential biophilic macroelements, Ca and Mg are regulated to a large extent by biological processes and hence their contents in Enteromorpha sp. from the southern Baltic, Gulf of Gdańsk and Vistula Lagoon were relatively constant.

4.3. Interelemental relationships

The obtained CF values for Enteromorpha sp. are comparable to those compiled for macroalgae in IAEA (1985). Concentration factors show that samples of Enteromorpha sp. from the southern Baltic and the Gulf of Gdańsk were characterized by the greatest affinity for Pb and the lowest one for Cu and Ni. Estimated on the basis of CFs, discrimination factor values (CFx/CFy where x and y are compared chemical elements) for Cu to other metals, i.e. Cd, Pb, Zn and Mn are significantly lower than unity, indicating that Cu is less extensively concentrated in Enteromorpha sp than the other elements studied. It can be assumed that availability of Cu to the green algae is limited by competitive processes of complexing this metal by organic substances dissolved in water which results in decrease of the effective concentration of this metal (Bojanowski, 1973; Szefer, 2002). The result is in agreement with the data for other Baltic organisms which were also characterized by the greatest affinity for Pb and the lowest for Cu (Szefer, 1991; Szefer and Szefer, 1991; Szefer...
and Skwarzec, 1988; Szefer et al., 1994; Kruk-Dowgiało and Pempkowiak, 1995). CFs depend on environmental conditions as well as algal metabolism. In field experiments, Vasconcelos and Leal (2001) found seasonal variations of concentration factors for Cu, Pb, Cd and Hg in Enteromorpha sp. Hou and Yan (1998) reported that CFs are likely correlated with atomic radius of the chemical element. In our work CFs also increase with the atomic radius, i.e. from Na to K and Mg to Ca. In the case of Pb, with larger atomic radius than for other heavy metals studied, its concentration factors were also higher.

4.4. Comparison with literature data

The obtained results, expressed as mean values in Enteromorpha sp. are compared to the literature data indicating that heavy metal contents in the green alga from the Gulf of Gdańsk varied in similar range of values, except Pb, where decreasing tendency from 1978 to 2003 was observed (Fig. 10). Most probably, it is attributed to the decline in atmospheric Pb caused by the reduced use of leaded petrol in Baltic countries in this period. This finding is in agreement with data reported by Harms (1996) who also observed the decreasing Pb concentration during ca. a 10-year period studied in cod liver collected from the southern Baltic. Recent data indicate that the annual average riverine inputs of Pb into the Baltic Proper decreased during the period of 1994–2000 (HELCOM, 2003). The present status of metals content in Enteromorpha sp. from the southern Baltic, was compared with world-wide literature data (Fig. 11). Such comparison should not be interpreted as an absolute measure of the pollution status for each area because of different sampling regimes and specific geographical signals. This is probably a question of the relative strengths of geographic versus anthropogenic signals. If the latter is enough stronger than any natural biogeographic variability (specific for each geographic area) then assessment of the metal pollution in world-wide scale is reliable and justified. As can be seen in Fig. 11 the levels of Cd and Zn in the Enteromorpha sp. from the Gulf of Gdańsk were generally comparable to the data reported for the same taxa from coastal and estuarine areas all over the world. Wide concentration
Fig. 11. Ranges of concentration of heavy metals [µg/g d.w.] in Enteromorpha sp. from different coastal regions all over the world: 1 — Leal et al. (1997); 2 — Villares et al. (2002); 3 — Munda and Hudnik (1991); 4 — Sfriso et al. (1995); 5 — Storelli et al. (2001); 6 — Fytianos et al. (1999); 7 — Haritonidis and Malea (1995); 8 — Sawidis et al. (2001); 9 — Topcuoglu et al. (2003); 10, 11 — Biao-Olayan and Subrahmanyam (1996); 12 — Agadi et al. (1978); 13 — Rajendran et al. (1993); 14 — Sivalingam (1978); 15 — Hou and Yan (1998); 16, 17, 18 — Ho (1987); 19 — Brown et al. (1999); 20 — Serfor-Armah et al. (1999); 21 — Muse et al. (1999); 22 — Ratkevicius et al. (2003); 23 — Szefer et al. (1998); 24 — present study.
range of Mn in the algae from the gulf was noted, but its average content (173 ± 86.3 μg/g d.w.) was similar to that observed for other regions. In the case of Pb, Cu and Ni their concentrations were noticeably lower than those reported for algae inhabited highly industrialized area of the Hong Kong (Ho, 1987).

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Villas, R., Puente, X., Carballeira, A., 2002. Seasonal variation and background levels of heavy metals in two green seaweeds. Environmental Pollution 119, 79–90.

