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Harri JANKOVSKI, Henn KUKK, Yulia VOLOZH

ACCUMULATION OF HEAVY METALS IN THE BALTIC SEA ALGAE

Algae, the main components of the Baltic Sea plant associations are of economic importance and serve as the indicators of both the saprobic and toxic pollution, since among them there occur highly sensitive as well as very resistant to pollution species (Кукк, 1983; Järvkülg, Kukk, 1985).

The studies carried out show that in the past decades the concentrations of heavy metals have increased in the Baltic Sea environment due to human impact (Assessment..., 1981). According to long-term prognoses heavy metals concentrations may increase in the coastal waters of the Baltic Sea two- or threefold by the end of the century (Пыдер, 1981), and it may exert a remarkable influence on the biota (Патин, 1979). For this purpose the knowledge of the concentrations of trace metals in the Baltic Sea biota, including macrophytes, is of urgent necessity.

Materials and methods

Of marine species bladder wrack, a brown alga, is distributed throughout the whole Baltic Sea, except the northernmost part of the Gulf of Bothnia (Luther et al., 1975) and the easternmost part of the Gulf of Finland (Кукк, 1979). Its communities have the greatest biomass which may account for 99% of the total biomass of the communities in the littoral zone (Hällfors, pers. comm.). The species is characterized by high productivity. For this reason we used bladder wrack as the object while studying heavy metals concentration in macrophytes. In addition, studies were performed also on widely distributed species of *Cladophora glomerata* and *Enteromorpha intestinalis*. Besides, the accumulation of heavy metals was evaluated also in *Furcellaria lumbricalis*, *Rhodomela confervoides*, *Phyllophora truncata*, *Ceramium tenuicorne*, *C. rubrum*, *Cladophora rupestris* and *Pilayella littoralis*. From phanerogams *Zostera marina* and *Potamogeton perfoliatus* were subjected to studies.

The samples of phytobenthos were collected in 1983—1985 from different Baltic Sea areas during the cruises of research vessels the Aju-Dag and the Arnold Veimer, as well as in the course of special field works from coastal shallow waters of the Baltic Sea.

The material collected was immediately grouped by species and placed into polyethylene bags. The samples were labelled and kept in a frozen state as long as chemical analyses were performed under laboratory conditions. Atom absorption method was applied to evaluate heavy metals concentration in plants. For these purposes Perkin Elmer photospectrometer (models 460 and 5000), graphite cuvette were used.

Results and discussion

As macrophytes are not included in the Baltic Sea monitoring programme, only a few data about the concentration of toxicants in them have been published so far (Bojanowski, 1973; Jankovski, Pöder, 1981; Dieckmann, 1982; Пыдер, 1981; Хёдрейарв et al., 1983; Сейсума et al., 1983 a, b, 1984).

In addition to the above-mentioned, there are a few papers dealing with the problem indirectly, as they are devoted to species which are not distributed in the Baltic Sea itself, but in the estuaries of the rivers discharging into it, where the salinity of water is below 0.1‰ (Cajander et al., 1984), or in Limfjord (Denmark) connecting the Kattegat with the North Sea where the salinity of water ranges from 12 to 30‰ (Brix et al., 1983; Brix, Lyngby, 1984).

Table 1 shows that heavy metals concentrations in bladder wrack vary with areas. The highest Cu concentrations were registered in the environs of Seskar Island, Toolse settlement and Kaberneeme Peninsula (the Gulf of Finland), in the Gulf of Riga comparatively high Cu concentrations were found in the plants near the harbour of Ruhnu Island, however, in the specimens of bladder wrack distributed in the coastal waters of the island it was considerably lower. In bladder wrack high Cd concentrations were registered in the vicinity of the islands of Seskar, Moshchnyi and Hogland, the highest Pb concentrations were found in the vicinity of Seskar Island, in Kolga Bay and in the Baltic Proper. Our data on Vergi Bay are in good agreement with those obtained for the adjacent Käsnu Bay (Jankowski, Pöder, 1981). The concentrations obtained by us for the area of Ragaziems in the Gulf of Riga agree with the results by Z. K. Seisuma et al. (Сейсума, 1984) with respect to Cu. However, in case of Cd and Pb they are 1.5 and 14–40 times lower, respectively.

Table 1
Heavy metals concentration in *Fucus vesiculosus*
(mg/kg in dry weight)

Sampling site	Cu	Cd	Pb
Seskar Island	13.20±0.39	13.43±0.65	1.62±0.22
Moshchnyi Island	5.24±0.12	14.75±0.61	0.14±0.06
Hogland Island	5.12±0.46	9.76±1.55	0.34±0.03
Toolse	9.47±0.18	2.65±0.06	0.48±0.10
Vergi	1.93±0.06	2.18±0.07	2.18±0.02
Kaberneeme	8.11	2.40	—
Kolga Bay	4.12	5.49	1.25
Suurupi	2.09	1.94	—
Riguldi	7.84	2.53	—
Ruhnu Island	2.35±0.11	2.92±0.17	0.71±0.18
Ruhnu Island (harbour)	7.78±0.50	2.83±0.06	0.50±0.12
Ragazieme	5.42±0.28	2.40±0.16	0.40±0.11
Baltic Proper	5.83	1.05	1.33

In *Cladophora glomerata* the highest concentrations of Cu were registered in the area of Liepaja, Sosnovyi Bor and Sillamäe (Table 2). The highest concentrations of Cd were related to Liepaja and Kaberneeme, the concentrations of Pb were highest near Sosnovyi Bor and Vergi. The comparison of our data with those of H. Jankovski and T. Pöder (1981) shows that the concentrations of Cu and Cd obtained by them are about

three and six times, respectively, higher in Käsnu Bay than the corresponding values obtained by us for the adjacent Vergi Bay, the concentration of Pb was 21 times lower, respectively. With respect to the results obtained by Z. K. Seisuma et al. (Сейсума et al., 1984) our concentration of Cu was two times, and that of Cd and Pb two and five times higher, respectively.

Table 2

Heavy metals concentration in *Cladophora glomerata* (mg/kg in dry weight)

Sampling site	Cu	Cd	Pb
Bolshaya Izhora	6.00	0.42	—
Sosnovyi Bor			
24. 05. 1983	14.29	0.68	—
23. 05. 1984	20.35±1.24	0.79±0.02	6.35±0.5
Kokpolovka	2.58±0.11	0.38±0.02	3.15±0.25
Sillamäe	12.79	0.38	2.15
Toolse	3.58±0.15	0.24±0.02	1.16±0.25
Vergi	2.35±0.13	0.29±0.02	6.45±.017
Kaberneeme	3.98±0.25	0.17±0.02	2.08±0.61
Häädemeeste	5.8 ±0.25	1.92±0.59	1.68±0.38
Kaltene	7.54±0.19	0.22±0.01	2.24±0.25
Liepaya	23.09±1.60	2.75±0.35	2.82±0.27
Klaipeda	5.4 ±0.30	0.34±0.06	1.08±0.23

Enteromorpha intestinalis accumulates Cu in relatively high and stable amounts (Table 3). As an exception serves the area of Sillamäe, where the concentration of Cu in this species is a bit higher than in other areas. The same applies to Cd and Pb. If we compare our data for the area of Vergi with the results obtained by H. Jankovski and T. Põder (1981) for the adjacent bay, it becomes evident that all the concentrations are higher in Vergi Bay. According to T. Põder (Пыдер, 1981) in *Enteromorpha intestinalis* the concentration of heavy metals in the Gulf of Riga is lower than it is in the Gulf of Finland.

Table 3

Heavy metals concentration in *Enteromorpha intestinalis* (mg/kg in dry weight)

Sampling site	Cu	Cd	Pb
Sillamäe	32.17	0.54	5.87
Toolse	7.8	0.18	0.8
Vergi	9.62	0.19	1.1
Kaberneeme	7.09±0.34	0.35±0.02	4.10±0.27
Riguldi	6.53	0.23	

Table 4 shows that two close species *Ceramium rubrum* and *C. tenuicorne* reveal a great difference as regards the concentrations of Cu and Cd. In the coastal waters of Ruhnu Island (the Gulf of Riga) *C. rubrum* being coated by cortical layers accumulates these metals about a half less than *C. tenuicorne* which has no cortical layers. No difference has been observed in the concentration of Pb.

Table 4

Heavy metals concentration in *Ceramium tenuicorne* (A) and *C. rubrum* (B)
(mg/kg in dry weight)

Sampling site	Cu	Cd	Pb
Moshchnyi Island A	14.09±0.54	0.70±0.06	3.02±0.10
Ruhnu Island A	13.73±0.57	0.62±0.04	3.36±0.18
Ruhnu Island B	6.23	0.29	3.33
Ariste Bay B	8.18±0.19	1.34±0.12	16.54±1.54
Baltic Proper B	29.63	0.33	4.06

In *Furcellaria lumbricalis* the concentrations of heavy metals (Table 5) are a bit higher in the open Baltic in Ariste Bay than near Ruhnu Island in the Gulf of Riga. The value we have obtained for Cu and Cd are close to those by Z. K. Seisuma et al. (CeйcyMa et al., 1984), however, with respect to Pb they are twice lower. In *Rhodomela confervoides* all these values appeared to be higher in Ariste Bay (Table 5).

Table 5

Heavy metals concentration in *Furcellaria lumbricalis* (A),
Rhodomela confervoides (B), *Phyllophora truncata* (C)
(mg/kg in dry weight)

Sampling site	Cu	Cd	Pb
Hiiumaa Island C	7.47	0.2	2.66
Hiiumaa Island B	1.53	1.21	7.36
Ruhnu Island A	8.03	0.34	0.92
Ariste Bay A	9.34±0.06	0.65±0.02	3.08±0.22
Ariste Bay B	10.91±0.45	2.29±0.07	19.86±0.4

In bottom vegetation the heavy metals concentration fluctuate within wide limits (Table 6). The highest Cu concentrations were registered in *Cladophora rupestris* and *Ceramium tenuicorne*, Cd — in *Fucus vesiculosus* and Pb — in *C. tenuicorne*.

Table 6

Heavy metals concentration in different species of algae
in the area of Ruhnu Island 26. 10. 1984
(mg/kg in dry weight)

Species	Cu	Cd	Pb
<i>Fucus vesiculosus</i>	7.78±0.50	2.83±0.06	0.50±0.12
<i>Ceramium tenuicorne</i>	13.73±0.57	0.62±0.04	3.36±0.18
<i>Furcellaria lumbricalis</i>	8.03	0.34	0.92
<i>Cladophora rupestris</i>	17.42±1.17	0.67±0.04	0.04±0.38

Heavy metals concentrations decrease in the following order in the algae studied: Cu > Pb > Cd. If we include here Fe and Hg then the row will be as follows: Fe > Cu > Pb > Cd > Hg.

While comparing the data in the above way one has to consider the seasonal character of the dynamics of trace metal concentration in macrophytes. For example, in the coastal waters of Great Britain the concentration of Cu in bladder wrack is 30 times higher at the end of summer than it was in spring (Romeril, 1977). The results obtained by Z. K. Seisuma and others (Сейсума et al., 1984) do not reveal such an increase, however, the decrease in the concentration of some elements is still observed.

Besides, the concentration of heavy metals depends on the size of thalli, and it is also of importance which parts of the thallum were subjected to studies (Христофорова, 1979). In old parts which remain far from the growth cell heavy metals concentrations are considerably higher and they do not reveal such distinct changes as are observed in the growing parts of thallum (Table 7).

Table 7

Heavy metals concentration in different parts of thalli of *Fucus vesiculosus* in the area of Kaberneeme — K, Vergi — V, Suurupi — S and Riguldi — R (mg/kg in dry weight)

Part of thalli	Cu	Cd
apical — K	7.85	4.62
basal — K	8.37	4.17
apical — V	2.48	1.86
basal — V	2.87	4.73
apical — S	1.95	1.85
basal — S	2.23	2.03
apical — R	7.01	1.90
basal — R	8.63±0.04	3.09±0.06

One has to consider that the seasonal trace metals concentrations in algae are due to changes in metabolic activity and growth rate of the plant, besides, certain role is played by climatic conditions and hydrobiologic situation as well (Христофорова, 1979). It is especially well defined in one-year-old plants. Thus, in May in the area of Kaberneeme the concentration of Cu in *Cladophora glomerata* constituted 3.98 mg/kg in dry weight, whereas in September, at the end of the vegetational period it was 8.01 mg/kg in dry weight. In addition to the above we determined heavy metals concentrations in *Pilayella littoralis* in Kolga Bay (the Gulf of Finland). The results obtained were as follows: Cu — 1.88±0.17, Pb — 3.72±0.47, Cd — 1.67±0.10 mg/kg in dry weight. In *Potamogeton perfoliatus* distributed in the area of Bolshoi Izhory the values obtained were as follows: Cu — 7.60±0.19, Pb — 5.19±0.42 and Cd — 2.70±0.08 mg/kg in dry weight. In *Zostera marina* the concentrations of heavy metals were studied in the Baltic Proper. The concentration of Fe ranged from 13.38 to 13.64, that of Cu equalled 4.85, the concentration of Pb fluctuated from 0.67 to 2.2 and Cd from 0.66 to 0.78 mg/kg in dry weight.

In the leaves of *Zostera marina* in Limfjord (Denmark) the average Fe concentrations were somewhat higher than those obtained by us (390 mg/kg in dry weight), with respect to the other metals the results showed good agreement (Brix, Lyngby, 1984).

In recent years much attention has been paid to the studies on heavy metals concentrations in different species of macrophytobenthos, since macrophytes are stable, being attached to hard substrates or the sea floor. In macrophytes the concentration of heavy metals is not subjected to short-term fluctuations which may take place in sea water, and therefore they may be considered a smoothed average indicator,

Macrophytes are applied to the permanent observation of the level of the pollution of water with heavy metals due to the circumstance that heavy metals concentrations in the thalli of algae depend, first of all, on absolute and relative content of these metals in surrounding environment (Христофорова, 1979, 1983).

From a great variety of algae distributed in different seas the most promising for the monitoring of sea environment with heavy metals are cosmopolitan species, since the data obtained may be compared with those by other investigators. First of all it is *Fucus vesiculosus*, however, there are several other easily accessible species suitable for these purposes as well (Fuge, James, 1973, 1974; Bryan, Hummerstone, 1973, 1977; Morris, Bale, 1975; Seelinger, Edwards, 1977; Romeril, 1977; Philips, 1979; Luoma et al., 1982; Христофорова, 1979, 1983; Иванов, 1982; Бурдин et al., 1982; Хёдреярв et al., 1983; Brix et al., 1983; Brix, Lyngby, 1984).

One also has to consider the fact that the species attached to the bottom by their roots accumulate heavy metals from deposits, prevailingly, while those attached to hard substrates take them from sea water (Atri, 1983). According to the data published the concentrations of Cu, As, Pb, Zn and Ag in *Fucus vesiculosus* ($r=0.98$, $n=32$) are in good agreement with those in deposits but not in the sea water (Luoma et al., 1982). For these purposes we cannot agree with W. Kistner (1984) who suggests using artificial "mussel" instead of bioindication, since hydrobionts including macrophytes, integrate small-scale fluctuations in heavy metals concentration in sea water, and, as a result, it is possible to estimate the mean concentration of heavy metals in sea water on the basis of a few analyses only.

In addition, the method of bioindication enables one to establish the number of forms of heavy metals assimilable by organisms, which is not possible by using analytical methods.

In further studies attention should be focused on such species as *Fucus vesiculosus* and *Cladophora glomerata*, since these species have a sufficiently long life-cycle, they have the ability to accumulate heavy metals, are easily accessible and suitable for analysis, and, in addition, they are included in the feed-chain.

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Academy of Sciences of the Estonian SSR,
Institute of Thermophysics and Electrophysics

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Tallinn Department
of the Baltic Fishery Research Institute

RASKMETALLIDE AKUMULATSIOON LÄÄNEMERE VETIKATES

Vetikad on Läänemere põhjataimestikus valitsevad. Suurima massiga on põisadru kooslus. Et pruunvetikad sisaldavad algiinhapet, mis metalle sidudes moodustab vees lahustumatuid soolasid, on nad ideaalsed raskmetallide monitooringuks. Raskmetallide sisaldus põisadrus erineb piirkonniti: kõrgeim vase kontsentratsioon oli Seskari saare piirkonnas, kaadmiumi kontsentratsioon osutus kõrgeimaks Seskari ja Moštšnõi saare rannikumeres, tinal Vergi sadama ja Seskari saare piirkonnas. Rohevetikaist sisaldas vaske kõige rohkem *Cladophora glomerata* Liepāja, Sosnovõi Bori ja Sillamäe piirkonnas, ka *Enteromorpha intestinalis*'es oli vaske Sillamäe piirkonnas rohkem kui mujal. Puna-vetikaliikide *Ceramium rubrum* (kaetud koorkihiga) ja *C. tenuicorne* puhul oli vase sisaldus suurem viimases.

Raskmetallide sisaldus põisadru tipmistes osades on väiksem kui basaalosades. Eri-nevusi täheldati ka ühest ja samast piirkonnast kogutud eri vetikaliikide raskmetallide sisalduses.

Харри ЯНКОВСКИЙ, Хенн КУКК, Юлия ВОЛОЖ

НАКОПЛЕНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ В ВОДОРΟΣЛЯХ БАЛТИЙСКОГО МОРЯ

Приводятся данные о содержании тяжелых металлов (медь, кадмий, свинец) в водорослях *Fucus vesiculosus*, собранных из различных мест, а также в других видах водорослей, собранных из одного места Балтийского моря.

В дальнейших исследованиях следует обратить внимание главным образом на такие виды, как *Cladophora glomerata* и *Fucus vesiculosus*, поскольку они имеют наибольшую биомассу и встречаемость.