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TRACE METALS IN SOME ORGANISMS FROM THE SOUTHERN BALTIC

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Abstract

Plankton, mussels and fish species caught in 1979 in the Polish economic zone of the Baltic have been analyzed. The metals in plankton were determined by the flameless AAS technique (Cd, Hg, Pb, Cu, Zn) and by NAA technique (Se, Cr, Ag, Sb, Cs, Co, Fe). In mussels and fish they were determined by the ASS technique only.

Significant variations in the contents of metals between particular regions and species of the organisms from the Southern Baltic have been observed. The data obtained were compared with the concentration levels of metals observed in other marine regions. Metal bioaccumulation coefficients are of the order from 10^5 to 10^2 decreasing from phyto- and zooplankton, through zoobenthos to fish.

1. INTRODUCTION

Trace metals are natural constituents of sea water occurring at very low concentrations of the order of micrograms or nanograms per litre. Some of them, for instance iron, copper, cobalt and zinc are required in small quantities for normal functioning of the organisms. Many metals, including essential ones, can however be hazardous due to their relatively low toxic concentration levels dependent mostly on the chemical form of a metal on one hand, and low tolerance of marine organisms on the other. The most hazardous metals include cadmium, mercury and lead.

The enhanced supply of metals to the marine environment due mostly to the development of industry manifests itself distinctly in the organisms, suspended matter and bottom sediments, where this effect is potentiated by accumulation. Hence, the capability of the organisms to raise many times the metal levels in edible portions of their flesh becomes at the same time hazardous to the human health and life. The intensity of bioaccumulation of metals is not directly related to their concentrations in aquatic environment and to their level in food. Even with the same species of plants or animals this intensity depends on a variety of physical and chemical features of the environment the organisms live in [11].

During the past decade, an upsurge of interest in the metal content of the living organisms and in the mechanism of their accumulation has also had methodological grounds. From the analytical standpoint, the monitoring of the state of pollution of

the sea is still poorly precise and reliable as far as trace elements are concerned. The process of natural accumulation of metals by organisms facilitates the monitoring and at the same time affords information about the quality of sea food. In spite of numerous studies and programmes all over the world [20], we have not yet arrived at a sound theoretical basis enabling to correlate fluctuations of metal concentrations in organisms with their fluctuations in the environment. This can be explained in terms of plurality of chemical forms of metals and complexity of the chemical composition of the marine environment on one hand, and the plurality of marine species and variety of their adoptional mechanisms, on the other [10].

A great interest in trace metals occurring in the sea is reflected in sample literature on the subject. For instance, in a review of 167 species of crustaceans, finfish and molluscs in respect of trace metal levels in them, based on 224 papers published from 1896 - 1977, almost 50 per cent of them was published in the period 1960 - 1977 [9]. The contribution of papers concerned with the Baltic organisms is unsatisfactory. In a survey on trace metals in the Baltic Sea prepared in 1980 for the Helsinki Convention [5], there are data on the levels of 5 elements only (Hg, Cd, Cu, Pb and Zn) in 4 fish species and generally in mussels and sea weeds. It is expected that owing to the compulsory monitoring of the pollution of the Baltic Sea, in force since 1979, the number of data concerning the organisms will soon increase.

Organisms taken from the Southern Baltic were examined in the Department of Marine Physics and Chemistry of the Institute of Meteorology and Water Management in 1979. The investigations were the last stage of a more extended programme of the studies on the pollution of the Polish economic zone of the sea. Beside the living organisms, the programme included 3-year study of the aquatic environment (1977 - 1979) and a one year study on the suspensions and bottom sediments [6].

2. MATERIALS AND METHODS

The organisms were collected in May, August and October 1979 from the r.v. "Hydromet" (Fig. 1).

Plankton was sampled by means of a WP2 plankton net with the mesh diameter of 200 μm and the inlet diameter of 58 cm, adapted for quantitative catch of zooplankton. Plankton collected with this net constituted the main fraction of total plankton with the respect of biomass and was free of microplankton. For analysis two vertical hauls from the whole depth of a particular station were pooled and kept in tightly closed glass jars at -20°C .

The composition of the plankton according to species was determined and the count of the population and biomass of the organisms were evaluated. In the open-sea area and the coastal zone copepodas prevailed including: *Pseudocalanus elongatus*, *Acartia longiremia*, *Acartia bifilosa* and *Temora longicornis*, among *Cladocera* the following species were most abundant: *Bosmina coregoni maritima*, *Evadne normani*, *Podom intermedius* and *Podom polyphemoides*. These species constituted jointly more than 90 per cent of the plankton biomass. In samples taken in August in the coastal zone there was increased contribution of the blue-green algae (*Cyanophyta*) in parti-

cular *Nodularia spumigena*, which constituted almost the sole species in the plankton of the Gulf of Pomerania. In all samples other species of blue-green algae and diatoms occurred occasionally.

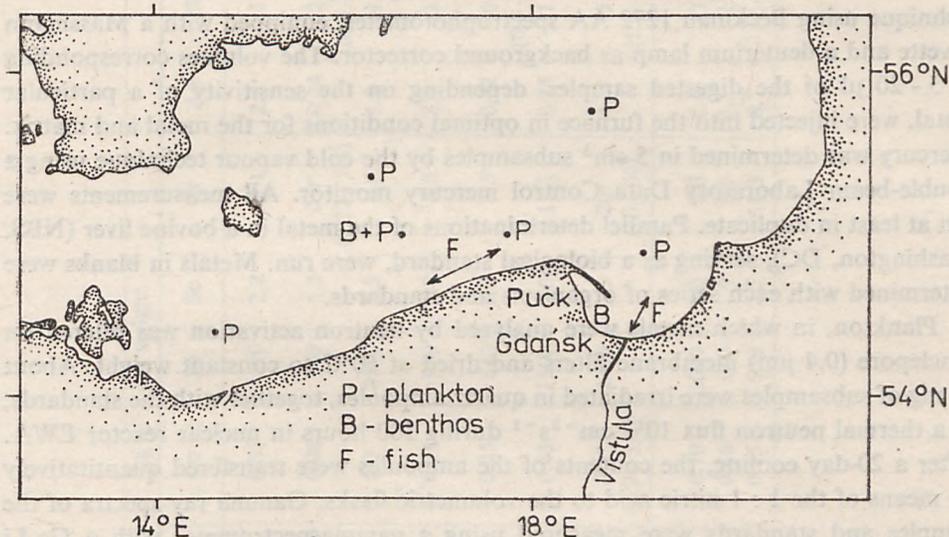


Fig. 1. Location of sampling stations for organism in the Baltic Sea.

Zoobenthos was collected by means of a bottom dredge. Two species of mussels, *Mytilus edulis* and *Macoma baltica*, were collected for analyses. The animals were rinsed with sea water, in which they resided in the sea, and then they were left for 12 hours in a fresh portion of sea water to allow them to clean off the sediments and extraneous matter. After repeated washing they were transferred to polyethylene bags and kept at -20°C .

The following fish species were caught for analyses: *Gadus morrhua* (cod), *Clupea harengus* (herring), *Sprattus sprattus* (sprat) and *Platichthys flesus* (flounder). Particular individuals were packed tightly into polyethylene bags and were kept frozen at -20°C .

The metal content in plankton was assayed by using two analytical methods: AAS — the flameless atomic absorption spectrometry (Hg, Cd, Cu, Pb, Zn) and NAA — the neutron activation analysis (Co, Cr, Cs, Se, Ag, Sb, Fe). The metal content in mussels and fish (Hg, Cd, Cu, Pb, Zn) was determined by the flameless AAS method only.

Before the AAS analysis, the thawed organisms were homogenized in a teflon homogenizer. To the analysis were taken about 5 g of the plankton homogenate, 3 - 5 g of the homogenate from the soft tissue of mussels, and 2 - 4 g of the homogenate of liver or muscle of fish cut off the dorsal portion. The samples were digested with nitric acid (MERCK suprapur, free of mercury) in closed teflon vessels, initially for several hours at the room temperature, and then for 3 hours at $120 - 130^{\circ}\text{C}$ under a pressure of about 0.2 MPa (2 atm). With the plankton and mussels, 5 cm^3

of concentrated HNO_3 was used, whilst with fish 10 cm³ of a 1 : 1 acid. In separate samples the water content was determined by drying at 105°C to constant weight. After digestion, the contents were diluted with demineralized water to a volume of 25 cm³. Cadmium, copper, lead and zinc were assayed by electrothermal atomization technique using Beckman 1272 AA spectrophotometer, equipped with a Massmann cuvette and a deuterium lamp as background corrector. The volumes corresponding to 5 - 20 µl of the digested samples, depending on the sensitivity of a particular metal, were injected into the furnace in optimal conditions for the metal and matrix. Mercury was determined in 5 cm³ subsamples by the cold vapour technique using a double-beam Laboratory Data Control mercury monitor. All measurements were run at least in duplicate. Parallel determinations of the metal in a bovine liver (NBS, Washington, DC), serving as a biological standard, were run. Metals in blanks were determined with each series of organisms and standards.

Plankton, in which metals were analyzed by neutron activation was filtered on Nuclepore (0.4 µm) membrane filters and dried at 60°C to constant weight. About 10 mg of subsamples were irradiated in quartz ampoules, together with the standards, at a thermal neutron flux 10^{13} cm⁻²s⁻¹ during 100 hours in nuclear reactor EWA. After a 20-day cooling, the contents of the ampoules were transferred quantitatively by means of the 1 : 1 nitric acid to the volumetric flasks. Gamma ray spectra of the samples and standards were measured using a gamma spectrometer with a Ge-Li detector (Ortec) of the effective volume of 55 cm³ and the resolution of 2.4 keV (for ⁶⁰Co 1332 keV line), and a Plurimat analyzer coupled with a Multi 8 minicomputer (Intertechnique). The time of measurements was 3000 and 500 s for the samples and standards respectively. The following photopeaks were used for quantization:

| | | | |
|--------------------|-------------------|-------------------|-------------------|
| ⁶⁰ Co | 1173 and 1332 keV | ¹²⁴ Sb | 603 keV |
| ⁵¹ Cr | 320 keV | ⁷⁵ Se | 246 keV |
| ¹³⁴ Cs | 796 keV | ⁵⁹ Fe | 1099 and 1292 keV |
| ^{110m} Ag | 657 and 884 keV | | |

The determinations were carried out in a duplicate or triplicate for each sample.

The AAS methods employed in this work were checked by participation in the 5th and 6th ICES intercalibration exercises concerned with biological material [21, 22]. A good agreement was obtained with mean results of interlaboratory experiments, the coefficients of variation ranging between 4 and 15 per cent depending on the metal and sample.

3. RESULTS OF INVESTIGATIONS AND DISCUSSION

Plankton collected in the Southern Baltic shows considerable regional differences in respect of the levels of such metals as Cd, Hg, Pb and Cr (Table 1). Samples taken in the coastal zone (off the shore to 20 - 30 m isobath), consisting mostly of *Copepoda* with a relatively small constitution of *Cladocera* or blue-green algae, contained on an average from 5 - 6 (Cd, Hg) through 3 (Cr, Pb) to 2 (Cu, Zn) - fold greater amounts of these metals than similar in respect of specific composition samples from

Table 1. Concentration of trace metals in plankton from the Southern Baltic

| Catching area | Dominant (+frequent) organisms | $\mu\text{g}\cdot\text{g}^{-1}$ dry weight | | | | | | | | | | | |
|---|---|--|------|-------|-----|-----|------------------|-------------------|-----|------------------|------|------------------|------|
| | | Cd | Hg | Pb | Cu | Zn | Co | Fe | Se | Cr | Ag | Sb | Cs |
| Bornholm Deep | <i>Copepoda</i> (+ <i>Cyanophyta</i>) | 0.06 | 0.23 | 43.2 | 149 | 184 | 0.31 | 1120 | 2.2 | 3.1 | 2.5 | 1.6 | 0.05 |
| Gotland Deep | <i>Copepoda</i> (+ <i>Cladocera</i>) | 0.07 | 0.11 | 38.3 | 152 | 265 | 0.08 | 160 | 1.2 | 0.9 ^a | 0.24 | 2.2 ^a | 0.03 |
| Gdańsk Deep | <i>Copepoda</i> (+ <i>Cladocera</i>) | 0.39 | 0.14 | 32.3 | 172 | 139 | 1.0 | 8500 ^c | 2.3 | (0.32-1.4) | 1.8 | 1.0 | 0.13 |
| Ślupsk Furrow | <i>Copepoda</i> (+ <i>Cyanophyta</i>) | 0.67 | 0.16 | 70.4 | 139 | 266 | 0.71 | 900 | 1.7 | 4.8 | 1.0 | 1.7 | 0.09 |
| Coastal zone | <i>Copepoda</i> (+ <i>Cladocera</i>) | 1.55 | 0.63 | 123.0 | 221 | 426 | 0.25 | 640 | 2.5 | 5.5 | 0.62 | 0.7 ^a | 0.05 |
| Gulf of Pomerania | <i>Copepoda</i> (+ <i>Cyanophyta</i>) | 2.06 | 0.89 | 142.0 | 244 | 525 | 0.45 | 1300 | 2.5 | 17.1 | 0.75 | 1.4 | 0.05 |
| | <i>Cyanophyta</i> ^b | 2.07 | 0.48 | 166.8 | 462 | 330 | 2.1 ^a | 2300 | 1.3 | 20 ^a | 4.1 | 5.5 ^a | 0.23 |
| | | 1.57 | 2.14 | 318.6 | 780 | 514 | (0.7-3.4) | | | (10-30) | | (1.5-9.4) | |
| Mean values: | | | | | | | | | | | | | |
| - whole area | | 1.04 | 0.64 | 111.1 | 286 | 330 | 0.70 | 1070 | 2.0 | 8.3 | 1.6 | 2.0 | 0.09 |
| - open sea region (mainly <i>Copepoda</i>) | | 0.39 | 0.15 | 49.0 | 155 | 221 | 0.46 | 640 | 1.9 | 3.5 | 1.5 | 1.6 | 0.07 |
| - coastal zone (mainly <i>Copepoda</i>) | | 1.93 | 0.87 | 155.3 | 349 | 420 | 0.35 | 970 | 2.5 | 11.3 | 0.7 | 1.1 | 0.05 |

^a - Median.^b - Not included into regional means.^c - Not included into means; sample probably contaminated.

Table 2. Average concentrations of trace metals in plankton and seaweeds ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight) from different sea areas

| Organisms | Area and period of sampling | Cd | Hg | Pb | Cu | Zn | Co | Fe | Ag | Reference |
|------------------------|--------------------------------|------------------------|------------------------|---------------------|-----------|-----------|-----------|------------|-----------|-----------|
| Phytoplankton | Southern Baltic, 1979 | 1.6 | 2.1 | 319 | 780 | 514 | 1.3 | 2300 | 4.1 | [4] |
| " | " " 1975 | — | — | 22 | 251 | 561 | — | — | — | [4] |
| " | Baltic Sea, 1975 | 5.4 | — | 309 | 175 | 1065 | — | — | — | [16] |
| " | Gulf of Finland, 1971 - 3 | — | 0.0 - 3.3 | — | — | — | — | — | — | [18] |
| " | Atlantic, Antarctic, 1978 - 9 | 2.7 | — | 54 | — | 249 | — | — | — | [13] |
| " | North Pacific, 1971 | — | 0.2 - 0.4 | — | — | — | — | — | — | [14] |
| " | N. Pacific, Monterey Bay, 1971 | — | — | — | — | — | — | — | — | [3, 5] |
| Seaweeds | Baltic Sea, 1965 - 77 | 1.5 - 3.9 | 0.1 - 0.6 | 1 - 47 | 1 - 45 | 3 - 703 | — | 224 - 1510 | 0.0 - 0.6 | [14] |
| Zooplankton | Southern Baltic, 1979 | 2.1 - 5.0 ^a | 0.0 - 1.8 ^a | 0 - 50 ^a | 6 - 21 | 110 - 240 | 0.0 - 0.8 | 380 - 2050 | — | [18] |
| " | Atlantic, Antarctic, 1978 - 9 | 0.4 - 1.9 | 0.1 - 0.9 | 49 - 155 | 155 - 349 | 221 - 420 | 0.3 - 0.5 | 640 - 970 | 0.7 - 1.5 | [24] |
| " | North Atlantic, 1969 - 71 | 3.6 | — | 8 | — | 130 | — | — | — | [13, 14] |
| Zoo- and mikroplankton | North Pacific, 1971 | — | 0.1 - 5.3 | — | — | — | — | — | — | [13, 14] |
| Zooplankton | N. Pacific, Monterey Bay, 1971 | 0.4 - 2.3 | 0.1 - 0.7 | 2 - 39 | 6 - 104 | 50 - 4190 | — | — | — | [13, 14] |
| | | 2.8 - 6.4 | 0.1 - 0.3 | 1 - 12 | 4 - 23 | 53 - 279 | — | 92 - 1985 | 0.0 - 0.3 | [13, 14] |

^a — Recalculated to dry weight, assuming 90% of moisture.

the open sea. The highest concentrations of Hg, Pb, Cu, Zn, Co, Fe, Cr, Ag and Sb were found in the plankton from the Gulf of Pomerania, consisting mainly from *Cyanophyta*. Blue-green algae crops are characteristic of strongly polluted waters. Hence, it seems reasonable that the observations reported here cannot be ascribed to specific differences in the plankton only. This conclusion has been supported by parallel investigations of the aquatic environment, which showed that the degree of the pollution of the coastal zone is very variable in time and much dependent on actual hydrological conditions. This was further confirmed by chemical composition of plankton collected in the region of the Słupsk Furrow, which contained much more Cd, Hg, Pb and Cu than that collected in the Bornholm Deep, very similar taxonomically.

The results listed in Table 1 show some inconvenience of nondestructive neutron activation analysis. The NAA determinations, run repeatedly with a filtered dry plankton revealed considerable inhomogeneity of certain samples. This was particularly evident in the case of Cr and Sb in zooplankton and Co, Cr and Sb in phytoplankton. This inconvenience may be largely avoided, when wet homogenized material is taken for analysis.

Owing to the scarcity of data on trace metals in the Baltic plankton, the results can be compared mainly with those of other sea regions (Table 2), e.g. the Pacific along the western coast of the USA [13, 14], Atlantic along the eastern coast of the USA [24], or the Antarctic sector of the Atlantic Ocean [18]. The comparison is more reliable with zooplankton, for which analyses of eleven samples are available, than with phytoplankton, for which only one sample taken from the Gulf of Pomerania was analyzed. Bearing in mind specific differences in the plankton taken from so diverse sea regions, good convergence of the mean metal levels has been found, in particular those of mercury, zinc and iron. The Baltic plankton contained slightly less cadmium, more silver and much more lead and copper than did the plankton taken, for instance, in the Monterey Bay, California [14]. Recently high lead and cadmium levels have also been found by Suplińska and Soszka [18] in plankton collected in the Antarctic regions, which have commonly been considered as slightly polluted. Azam *et al.* [1], who carried out biotests with bacterioplankton revealed an interesting phenomenon of immunization against copper of organisms living in medium with high mercury levels, in spite of the fact that copper was not added to the cultures. Similar effect associated with enhanced accumulation of copper is likely to occur in the Baltic plankton, particularly that from the coastal zone,

Table 3. Mean concentrations of trace metals in mussels from the Southern Baltic ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight)

| Species | Length of the organisms [cm] | Dry matter [%] | Cd | Hg | Pb | Cu | Zn |
|-----------------------|------------------------------|----------------|------|-------|------|------|-------|
| <i>Mytilus edulis</i> | 3 - 5 | 14.1 | 1.10 | 0.042 | 0.49 | 15.6 | 63.6 |
| <i>Mytilus edulis</i> | 0.5 - 3 | 10.1 | 1.65 | 0.070 | 0.80 | 23.2 | 133.1 |
| <i>Macoma baltica</i> | 0.3 - 1 | 16.5 | 0.59 | 0.036 | 0.94 | 58.6 | 325.3 |

Table 4. Average concentrations of trace metals in mussels ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight) from different sea areas

| Mussel | Area and period of sampling | Cd | Hg | Pb | Cu | Zn | Co | Fe | Mn | Reference |
|----------------------------------|------------------------------------|-----------|-----------|-----------|---------|----------|-----|-----------|-----------|-----------|
| <i>Mytilus edulis</i> | Southern Baltic, 1979 | 1,0 - 1,7 | 0,0 - 0,1 | 0,5 - 0,8 | 16 - 23 | 64 - 133 | — | — | — | [16] |
| " | Gulf of Finland, 1971-3 | — | 0,1 | — | — | — | — | — | — | [7] |
| " | Barents Sea, 1976-7 | 0,6 | — | 1,9 | 8 | 80 | 0,0 | 204 | — | [7] |
| " | White Sea, 1976-7 | 0,9 | — | 0,6 | 5 | 100 | 0,3 | 424 | — | [7] |
| " | N. Atlantic Narragansett Bay, 1976 | 1,7 - 1,5 | — | 4,1 - 5,1 | 10 | 127 | — | 81 - 370 | 0,1 - 0,6 | [20] |
| " | North Atlantic, 1976 | 2,0 | — | 3,2 | 7 | 106 | — | — | 0,0 - 0,7 | [20] |
| " | North Pacific, 1976 | 4,8 | — | 3,5 | 7 | 149 | — | 150 - 710 | 0,1 - 2,3 | [20] |
| " | Oslofjord, 1972 | 3,3 | — | 7,5 | 9 | 141 | — | — | — | [15] |
| " | Different areas, 1900-77 | 3,8 | 8,2 | 6,1 | 12 | 185 | 0,1 | 77 | — | [9] |
| <i>Mytilidae^a</i> | | | | | | | | | | |
| <i>Mytilus galloprovincialis</i> | Black Sea, 1976-7 | 6,7 | — | 6,6 | 11 | 210 | 0,4 | 160 | — | [7] |
| " | North Pacific, 1976 | 5,1 | — | 3,6 | 7 | 127 | — | 59 - 630 | 0,0 - 1,4 | [20] |
| <i>Mytilus californianus</i> | N. Pacific, Bodega Head, 1976 | 7,5 - 9,9 | — | 0,8 - 2,2 | 6 | 122 | — | 150 - 450 | 0,1 - 0,4 | [20] |
| " | Southern Baltic, 1979 | 0,6 | 0,0 | 0,9 | 59 | 326 | — | — | — | [5] |
| <i>Macoma baltica</i> | Baltic Sea, 1970-9 | 0,3 - 3,1 | 0,0 - 1,6 | 0,9 - 8,6 | 5 - 88 | 88 - 605 | — | — | — | [8] |
| " | Southern Baltic, 1979 | 0,4 | 0,2 | 3,5 | 58 | 723 | — | — | — | [8] |
| " | Gulf of Finland, 1971-73 | — | 0,1 | — | — | — | — | — | — | [16] |
| <i>Modiolus modiolus</i> | Oslofjord, 1972 | 15,6 | — | 32,4 | 72 | 1680 | — | — | — | [15] |

^a - Recalculated to dry weight, assuming 82% of moisture.

exposed to enhanced input of mercury from the land. Brüggmann [4], Bojanowski (cit. after Brüggmann) and Nuorteva *et al.* [16], who carried out their investigations during 1971 - 75, reported high accumulation levels of trace metals in the Baltic phytoplankton, too. Much lower concentrations, comparable with trace metal content in oceanic plankton, contain the Baltic seaweeds [3, 5].

The metal levels in mussels seem also to be resultant of the specific bioaccumulation capacities and regional differences of the metal concentrations. The values shown in Table 3 are averages of several determinations in a big homogenized sample consisting of several tens of specimens from a particular colony. They show that *Macoma baltica* typical deposit feeder, accumulated particularly strongly copper and zinc but less efficiently cadmium than *Mytilus edulis*, typical filter feeder. With the remaining metals (Hg, Pb) there are no distinct differences between the two species of mussels in respect of accumulation. *Mytilidae* have commonly been considered as proper pollution indicators of the seas. They are also very abundant, the fact that facilitates regional comparisons to be done. Their capacity to accumulate metals is, however, a very complex phenomenon, dependent on many environmental and physiological factors, and increases, for instance, when the salinity of water decreases [11]. *Mytilus edulis* collected in the Gulf of Gdańsk contained more of all metals than the same species taken from the off-shore waters of the Slupsk Furrow. At the same time mussels from the Gulf were much smaller than those from the Slupsk Furrow.

All Baltic mussels have had comparable metal levels (Table 4). Certain regional differences in the degree of the pollution of aquatic environment can be seen in the maximum values, which can be even by one order of magnitude higher than the minimum concentrations. However, some mussels have shown quite evident specific ability to accumulate selected metals in their soft tissues, resulting probably from their way of feeding. The accumulation of copper and zinc by *Macoma baltica* and of cadmium by *Modiolus modiolus* seems to belong to such kind of abilities [5, 8, 15]. *Mytilus edulis* from the Baltic Sea contains higher cadmium levels than *Mytilus edulis* from the White Sea and the Barents Sea, but the levels are markedly lower than those in *Mytilus galloprovincialis* from the Black Sea, mussels from Oslofjord as well as *Mytilus edulis* and *Mytilus galloprovincialis* from the Pacific Ocean along the coast of the USA [7, 15, 20]. The copper and zinc levels in *Mytilidae* mussels from various sea regions were very similar [9]. In case of lead, the concentrations were significantly lower in mussels from the Baltic Sea, the White Sea, the Barents Sea and some regions of North Pacific than in the Atlantic Ocean along the USA coast, in the Black Sea or Oslofjord. This seems to be important, because *Mytilidae* have proved to be good bioindicators of lead pollution in the marine environment [20]. No significant regional differences in the mercury levels in mussels were found in the Baltic Sea, with the exception of local increase in *Mytilus edulis* from near-shore regions of the Gulf of Gdańsk, the Gulf of Finland, the Bothnian Bay and Swedish archipelagoes [5].

It is difficult to relate directly the metal levels in fish muscles to those in water in the site of catch, with the exception of flounder living on the bottom, which had the highest cadmium levels among the studied fish species. Table 5 lists ave-

Table 5. Mean concentrations of trace metals in some species of fish ($\mu\text{g}\cdot\text{g}^{-1}$ wet weight) from the Southern Baltic (ranges are given in brackets)

| Species | Length [cm] | Cd | Hg | Pb | Cu | Zn |
|---|-------------|--------------------------|--------------------------|--------------------------|--------------------|---------------------|
| Cod (<i>Gadus morrhua</i>) | 25 - 44 | | | | | |
| - flesh | | 0.053 (0.008 - 0.124) | 0.008 (0.004 - 0.013) | 0.060 (0.041 - 0.097) | 1.3 (0.6 - 2.3) | 7.0 (3.0 - 21.3) |
| - liver | | 0.068 (0.008 - 0.202) | 0.007 (0.004 - 0.013) | 0.049 (0.038 - 0.059) | 3.0 (0.6 - 5.1) | 6.9 (1.8 - 16.2) |
| Herring (<i>Clupea harengus</i>) | 22 - 24 | 0.047 | 0.020 | 0.047 | 1.3 | 4.7 |
| Flounder (<i>Platichthys flesus</i>) | 24 - 25 | 0.14 | 0.004 | 0.06 | 0.9 | 1.6 |
| Sprat (<i>Sprattus sprattus</i>) | 10 - 12 | 0.026 | 0.007 | 0.12 | 2.5 | 4.0 |

range values and the ranges of metal concentrations in flesh and liver of 5 cods as well as the average values for the remaining fish species obtained by a repeated analysis of a large, homogenized sample formed by pooling wet fragments of the muscles of a few (5 - 6) specimens. This poor material does not allow any general conclusions to be drawn. Taking, however, into consideration the results of fish analyses reported by other authors [8, 5, 16, 17, 19], one can state that the metal levels in common Baltic species, such as cod, herring and sprat fall at the time being well below the permissible food standards. Cases of an overstepping those standards belong to the exceptional ones. Slightly elevated levels of cadmium, mercury and lead can be observed in flounder living in muddy bottom, rich in metals, but in this instance there is also no obstacle for consumption as far as trace metals are concerned. In comparison with fish caught during 1972 - 74 in clean off-shore regions of the North Sea [12], the Baltic species contain, however, more cadmium, lead, copper and zinc but less mercury (Table 6). Considering, in turn, the same fish species from different seas [9], this conclusions holds true for cadmium and copper in cod as well as for cadmium in flounder only.

The coefficients of bioaccumulation of metals in the Baltic organisms (Table 7), calculated as a ratio of the metal concentration in dry mass of tissue to the concentration in aqueous solution, tend to decrease on going from phyto- and zooplankton through zoobenthos to fish. As a rule, lower accumulation of metals has been observed in oceanic plankton [23]. With cadmium, mussels living in the Southern Baltic exhibit accumulation coefficients comparable with that of the plankton, with mercury and copper the coefficients being by an order of magnitude lower, and with lead by two orders of magnitude lower. The accumulation of zinc depends mainly on mussel

Table 6. Average concentrations of trace metals in flesh of some species of marine fish ($\mu\text{g}\cdot\text{g}^{-1}$ wet weight)

| Fish | Area and period of catching | Cd | Hg | Pb | Cu | Zn | Reference |
|----------|--------------------------------|-------------|-------------|-------------|-------------|------------|-----------|
| Cod | S. Baltic, 1980 | 0,03 - 0,12 | 0,00 - 0,08 | 0,18 - 0,29 | 0,17 - 0,22 | 3,5 - 57 | [8] |
| " | S. Baltic, 1979 | 0,05 | 0,01 | 0,06 | 1,7 | 7,0 | |
| " | Baltic Sea, 1975 | <0,01 | — | 0,46 - 0,94 | 0,02 - 0,15 | 4,2 - 4,8 | [19] |
| " | Baltic Sea, 1974 - 6 | — | 0,04 - 0,05 | — | — | — | [17] |
| " | Gulf of Finland, 1970 - 2 | — | 0,02 - 0,05 | — | — | — | [16] |
| " | Baltic Sea, 1970 - 9 | 0,00 - 0,05 | 0,02 - 0,88 | 0,03 - 1,30 | 0,08 - 2,40 | 1,2 - 9,2 | [5] |
| " | Different seas, 1896 - 1977 | <0,05 | <0,05 | 0,3 | 0,3 | — | [9] |
| " | N. Sea, German Bight, 1972 - 4 | — | — | — | — | — | [12] |
| " | — off-shore area | <0,01 | <0,14 | <0,10 | 0,4 - 0,7 | 4,0 - 5,0 | |
| " | — on-shore area | <0,02 | <0,35 | <0,10 | 0,4 - 0,7 | 4,0 - 5,0 | |
| Herring | S. Baltic, 1980 | 0,05 - 0,10 | 0,01 - 0,02 | 0,27 - 0,33 | 0,66 - 0,86 | 7,7 - 9,2 | [8] |
| " | S. Baltic, 1979 | 0,05 | 0,02 | 0,05 | 1,2 | 4,7 | |
| " | Baltic Sea, 1975 | 0,01 - 0,02 | — | 0,17 - 0,84 | 0,04 - 0,24 | 9,6 - 10,7 | [19] |
| " | Baltic Sea, 1974 - 6 | — | 0,03 - 0,05 | — | — | — | [17] |
| " | Gulf of Finland, 1970 - 2 | — | 0,12 | — | — | — | [16] |
| " | Baltic Sea, 1970 - 9 | 0,00 - 0,20 | 0,00 - 0,09 | 0,01 - 1,4 | 0,30 - 1,90 | 3,4 - 32,0 | [5] |
| " | Different seas, 1896 - 1977 | 0,1 | 0,2 | — | 1,7 | 1,7 | [9] |
| Flounder | S. Baltic, 1980 | 0,04 - 0,05 | 0,04 | 0,33 - 0,37 | 0,21 - 0,29 | 5,4 - 5,6 | [8] |
| " | S. Baltic, 1979 | 0,14 | 0,004 | 0,06 | 0,9 | 1,6 | |
| " | Baltic Sea, 1974 - 6 | — | 0,05 - 0,07 | — | — | — | [17] |
| " | Gulf of Finland, 1970 - 2 | — | 0,02 - 0,17 | — | — | — | [16] |
| " | Baltic Sea, 1970 - 9 | 0,00 - 0,10 | 0,01 - 0,45 | 0,02 - 0,26 | 0,10 - 0,89 | 3,5 - 11,3 | [5] |
| " | Different seas, 1896 - 1977 | <0,05 | 0,2 | 0,4 | 1,7 | 4,6 | [9] |
| " | N. Sea, German Bight, 1972 - 4 | — | — | — | — | — | [12] |
| " | — off-shore area | <0,01 | <0,14 | <0,10 | 0,4 - 0,7 | 4,0 - 5,0 | |
| " | — on-shore area | <0,02 | <0,35 | 0,08 - 0,15 | 0,4 - 1,0 | 4,0 - 5,0 | |
| Sprat | S. Baltic, 1979 | 0,03 | 0,01 | 0,12 | 2,3 | 4,0 | |
| " | Baltic Sea, 1974 - 6 | — | 0,02 - 0,03 | — | — | — | [17] |

Table 7. Average coefficients of enrichment of trace metals in some organisms from the Polish economic zone of the Baltic Sea and other sea regions

| Region | Organisms | Cd | Hg | Pb | Cu | Zn | Reference |
|---|----------------------------------|---------|---------|---------|---------|---------|-------------|
| | | | | | | | |
| Southern Baltic — open sea — coastal zone | Plankton | 3.3 | 5.6 | 125 | 151 | 42 | [4] [23] |
| | Zooplankton | 1.8 | 1.8 | 48 | 69 | 35 | |
| | Zoo- and phytoplankton | 4.3 | 13.6 | 184 | 254 | 49 | |
| | Phytoplankton | 2.0 | — | 35 | 2.5 | 7 | |
| Baltic Sea | Zooplankton | 9.4 | 0.2 | 15.5 | 0.4 | 1.8 | [23] |
| Ocean | | | | | | | |
| Southern Baltic " " | <i>Mytilus edulis</i> | 3.4 | 0.6 | 0.6 | 10 | 14 | [7] |
| | <i>Macoma baltica</i> | 2.5 | 0.4 | 0.9 | 29 | 458 | |
| | <i>Mytilus galloprovincialis</i> | 2-7 | — | 1-13 | 1-10 | 7-70 | |
| Black Sea | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| Southern Baltic " " " " " " " " | Fish | 0.8 | 0.4 | 0.3 | 4.2 | 3.5 | [23] |
| | — cod | 1.0 | 0.5 | 0.3 | 7.2 | 5.6 | |
| | — herring | 0.8 | 0.2 | 0.2 | 3.0 | 3.3 | |
| | — flounder | 2.0 | 0.2 | 0.3 | 4.8 | 1.0 | |
| | — sprat | 0.5 | 0.5 | 0.7 | 2.0 | 3.6 | |
| Ocean | Fish | 0.2-0.7 | 0.05-12 | <0.6-10 | 0.1-0.7 | 1.6-2.1 | |

species, with some influence of metal concentration in sea water. There is also qualitative likelihood between the rank order of accumulation coefficients in zoobenthos and fish and that in suspended matter and silts [6], as well as lower organisms, which constitute the main foodstuff for mussels and fish (Fig. 2, Table 7). Further decrease of metal accumulation in fish muscles as compared with that of soft tissue of mussels is observed mostly with cadmium and zinc and to a lesser extent with lead and copper. Contrary to expectation, the concentrations of trace metals in wet mass of liver and flesh of cod were much similar (Table 5). Owing to the low water content, coefficients of enrichment of cod liver with trace metals are 2- to 3-fold lower than for cod flesh.

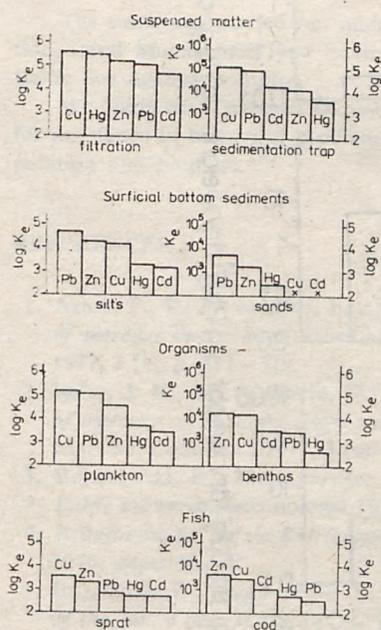


Fig. 2. Coefficients of enrichment (K_e) of trace metals in suspended matter, surficial bottom sediments and selected organisms from different trophic levels in the Southern Baltic (mean values).

The analogies and differences between accumulation of particular metals by organisms from various trophic levels in the Southern Baltic are shown in Fig. 3 together with the behaviour of these metals in the sedimentological cycle [6]. These differences are likely to be due to chemical properties of a metal and its concentration in the environment. The analogies can be ascribed to trophic interrelationships and different demand for a given trace element. In this figure a tendency can also be observed to redistribution of a particular metal in the marine environment, either by bioaccumulation and persistence at still higher trophic levels (Cu, Zn) or by sedimentation of suspended matter and deposition in the bottom sediments. As compared with lead, remarkable is extremely different behaviour of mercury and its facility to return to the aquatic environment from both the suspended matter and the organisms. In

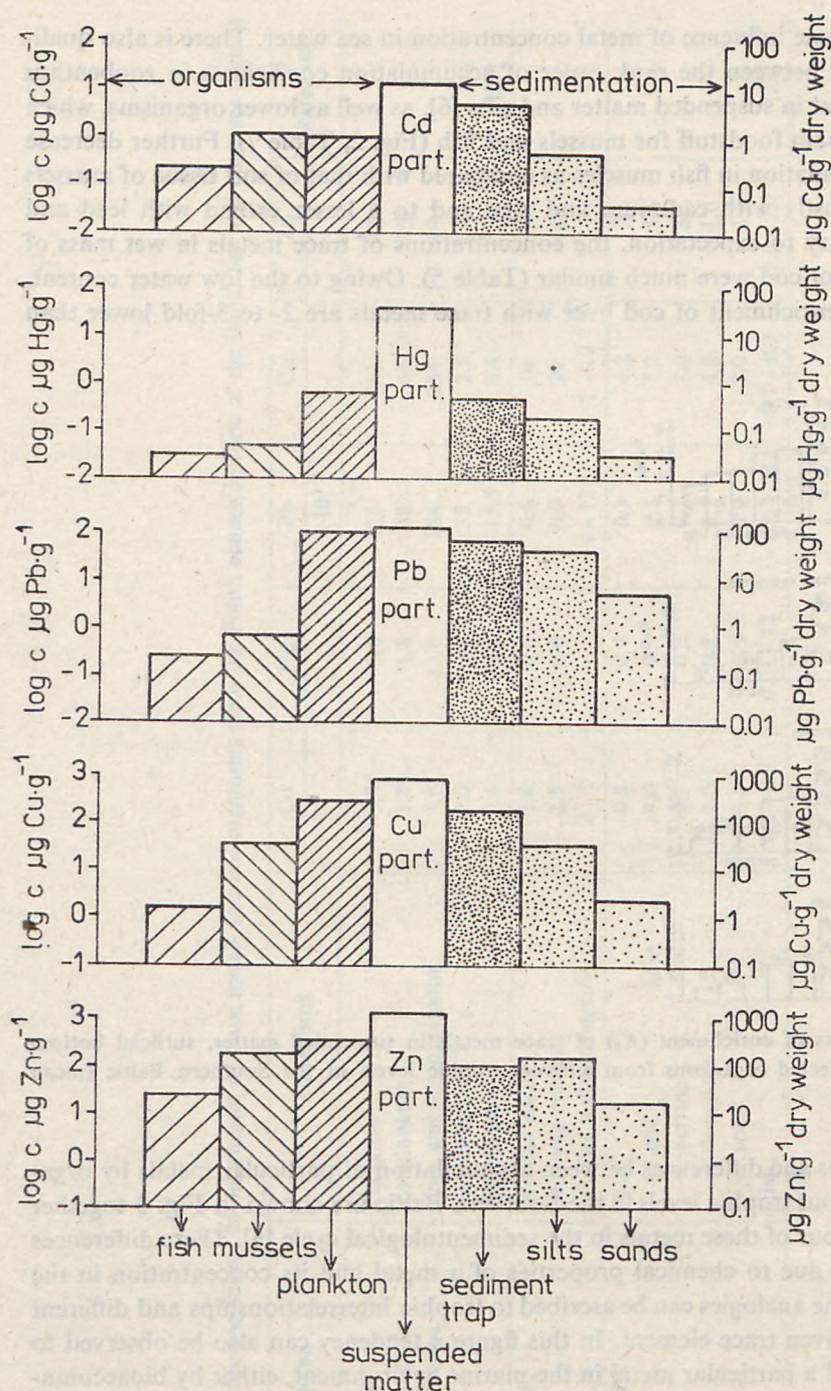


Fig. 3. Trace metal concentrations in different components of the marine environment in the Southern Baltic (mean values).

view of the growing evidence of genotoxic effects of cadmium remarkable is a considerable percentage of the metal penetrating to high trophic levels.

The results obtained in this study suggest that plankton and molluscs can be used for monitoring the pollution levels of seas with metals, at least for inter-regional comparisons. This calls, however, for extended fundamental research on the bio-accumulation process in the sea, involving not only individual animal or plant species and their various development stages, but also the influence of ecological conditions.

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