ACTA ICHTHYOLOGICA ET PISCATORIA
Vol. XXI Supplement Szczecin 1991

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THE LEVEL OF HEAVY METALS I NTHE ECOSYSTEM OF THE BALTI CSEA

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The following heavy metal levels were found in plankton of the Gulf of Riga and of the open Baltic Sea: 0.89–10.20 mg Cu/kg; 10.89–106.96 mg Zn/kg; 2.31–199.9 mg Mn/kg 0.19–0.85 mg Cd/kg; and 0.35–9.35 mg Pb/kg wet weight.

Heavy metal accumulation in the plankton was found to depend on species composition of the community and on development stage of a species.

Heavy metal contents in bottom sediments increase near densely populated coastal areas. Levels of lead, copper, and zinc depend on the season, increasing in spring in areas affected by river runoff. Maximum concentrations of the metals studied were found in 0.05–0.063 mm sediment fractions. Accumulation patterns of each metal exhibited their own respective peculiarities.

INTRODUCTION

Numerous publications concerning heavy metals in the marine environment evidence a great and growing interest in this problem in general an in the behaviour of each metal in the organism-sediment system in particular. Most publications concern basic research. However, a number of questions still remain unclear because of the complexity of natural systems and difficulty with following processes taking place in them. The Baltic Sea itself consists of various ecosystems, for which reason the data obtained in different areas are difficult to compare. The Laboratory of Marine Biology, Institute of Biology in Salaspils, Latvia has been carrying out long-term studies on heavy metals in marine organisms and bottom sediments in the Baltic (Fig. 1).

MATERIALS AND METHODS

Sampling method and treatment of organisms and sediment samples followed the description in Morozov and Petukhov (1981) and Seisuma et al. (1984). Assays were

Table 1

Metal levels in plankton of the Gulf of Riga and the Baltic Sea

Sampling time		Depth		mg/kg	wet	wt		Dominating species (percent of the total biomass)
year	month	m	Cd	Cu	Pb	Mn	Zn	
Station Ragciems								
1983	Oct.	20	0.22	0.89	1.39	17.75	12.42	*Synchaeta baltica* (41%), *Eurytemora hirundoides* (29%)
1984	July	20	0.85	1.35	0.53	9.81	10.87	*E. hirundoides* (41%), *Podon* sp. (25%), *Evadne* sp. (13%)
1986	July	20	0.38	1.50	0.35	16.05	22.40	*E. hirundoides* (73%), *Bosmina* sp. (15%)
Station Roja								
1983	Oct.	10	0.26	0.68	1.81	21.55	30.13	*Acartia* sp. (44%), *E. hirundoides* (36%)
1986	July	10	0.50	1.40	0.44	21.79	27.70	*Eurytemora* sp. (52%), *Podon* sp. (35%)
1987	June	10	0.19	1.35	1.25	18.63	28.44	*Synchaeta baltica* (81%)
1986	July	20	0.56	1.52	0.36	16.68	26.27	*Bosmina cor. maritima* (43%), *Podon* sp. (40%)
1987	June	20	0.28	2.22	5.70	23.62	106.96	*Synchaeta baltica* (74%), *S. monopus* (23%)
Station Liepāja								
1983	Oct.	10	0.69	10.20	9.35	199.90	54.42	*Acartia* sp. (78%)
1984	Sep.	10	0.36	3.40	2.64	51.07	69.01	*Acartia* sp. (97%)
1986	July	10	0.38	1.38	0.39	4.29	38.04	*Acartia* spp. (56%), *Balanus* sp. (29%)
1987	May	10	0.22	1.39	1.39	3.24	81.20	*Acartia* sp. (93%)
1984	July	30	0.26	1.09	0.72	2.31	31.92	*Acartia* sp. (56%), *Podon* sp. (22%)
1987	May	30	0.34	1.97	3.70	13.80	96.31	*Acartia* sp. (48%), *Synchaeta baltica* (27%)

Table 2

Metal levels in various plankton fractions in the Gulf of Riga and the Baltic Sea

Sampling time		Depth	Fraction	mg/kg wet wt					Dominating species (percent of the total biomass)
year	month	m		Cd	Cu	Pb	Mn	Zn	
1	2	3	4	5	6	7	8	9	10
Station Ragciems									
1986	July	20	a	0.49	1.68	0.46	17.90	27.74	*Eurytemora* sp. (67%), *Bosima* sp. (16%)
1986	Sep.	20	a	0.08	0.27	1.22	59.69	12.40	*Acartia* sp. sp. (55%), *Eurytemora* sp. (26%)
1987	July	20	a	0.34	0.62	0.41	35.05	11.66	*Podon* sp. (33%), *Synchaeta baltica* (32%), *Keratella quadrata* (25%)
1987	Sep.	20	a	0.43	0.88	0.49	17.05	17.40	*Podon* sp. (67%), *Synchaeta* sp. sp. (20%)
1987	July	20	b	0.33	0.86	0.30	32.28	10.89	*Keratella quadrata* (70%), *Synchaeta baltica* (27%)
1987	Sep.	20	b	0.27	0.97	1.00	43.40	18.45	*Acartia* sp. (57%), *Synchaeta* sp. sp. (20%), *Eurytemora* sp. (15%)
Station Roja									
1986	July	10	a	0.68	1.32	0.43	19.43	28.40	*Eurytemora* sp. (42%), *Podon* sp. (32%)
1986	Sep.	10	a	0.22	0.92	1.83	143.93	17.78	*Acartia* sp.sp. (53%), *Eurytemora* sp. (27%)
1987	July	10	a	0.29	1.02	0.44	21.41	13.82	*Synchaeta baltica* (47%), *Eurytemora* sp. (31%) *Podon* sp. (12%)

Continuation of Table 2

1	2	3	4	5	6	7	8	9	10
1987	Sep.	10	a	1.60	1.19	0.63	22.01	23.73	*Eurytemora* sp. (40%), *Acartia* sp. (32%)
1986	July	10	b	0.45	1.00	0.34	24.13	23.16	*Eurytemora* sp. (57%), *Acartia* sp. (35%)
1987	July	10	b	0.22	0.65	0.23	19.11	9.29	*Keratella quadrata* (50%), *Synchaeta baltica* (34%)
1987	Sep.	10	b	0.34	1.59	0.70	24.49	19.66	*Synchaeta* spp. (43%), *Acartia* sp. (42%)
1986	July	20	a	0.60	1.40	0.35	15.49	24.79	*Eurytemora* sp. (68%), *Podon* sp. (17%)
1986	Sep.	20	a	0.22	0.89	1.24	64.08	15.19	*Acartia* sp. (47%), *Synchaeta baltica* (41%)
1987	July	20	a	0.15	0.48	0.19	6.85	7.79	*Synchaeta baltica* (49%), *Podon* sp. (32%)
1987	Sep.	20	a	0.61	0.87	0.52	17.58	23.52	*Acartia* sp. (43%), *Eurytemora* sp. (30%), *Podon* sp. (15%)
1986	July	20	b	0.38	1.17	0.67	19.10	40.24	*Eurytemora* sp. (67%), *Acartia* sp. (29%)
1987	July	20	b	0.31	0.45	0.32	21.20	13.29	*Keratella quadrata* (68%), *Synchaeta baltica* (21%)
1987	Sep.	20	b	0.26	1.03	0.91	25.94	22.00	*Synchaeta* spp. (39%), *Eurytemora* sp. (26%), *Acartia* sp. (48%)

Continuation of Table 2

1	2	3	4	5	6	7	8	9	10
Station Liepāja									
1986	July	10	a	0.57	1.87	0.39	5.62	47.61	*Eurytemora* sp. (95%)
1987	Sep.	10	a	0.24	1.27	0.42	4.50	34.86	*Acartia* sp. (95%)
1986	July	10	b	0.31	1.29	0.45	6.86	30.28	*Acartia* spp. (51%), *Bosmina* sp. (24%)
1987	July	10	b	0.55	10.03	3.10	9.23	67.73	*Synchaeta* spp. (43%), *Acartia* sp. (31%)
1987	Sep.	10	b	0.16	1.10	0.80	5.26	21.25	*Acartia* sp. (67%), *Keratella* spp. (21%)
1986	July	30	a	0.51	1.18	0.36	2.41	40.37	*Acartia* sp. (79%), *Eurytemora* sp. (13%)
1987	July	30	a	0.45	1.28	1.01	2.70	36.04	*Acartia* spp. (57%), *Temora* sp. (15%), *Podon* sp. (14%)
1987	Sep.	30	a	0.37	1.59	0.49	4.46	43.75	*Acartia* spp. (96%)
1986	July	30	b	0.53	1.54	0.25	3.04	41.21	*Temora* sp. (46%), *Acartia* spp. (28%), *Eurytemora* sp. (24%)
1987	July	30	b	0.26	2.26	3.08	20.22	69.61	*Acartia* sp. (44%), *Temora* sp. (41%)
1987	Sep.	30	b	0.22	1.00	0.65	4.00	17.50	*Acartia* sp. (51%), *Keratella quadrata* (22%)

performed using atomic absorption spectrophotometry. The confidence interval ($t_{0.5}$ $S\bar{x}$) for all the metal contents was below 10–15% .

RESULTS AND DISCUSSION

Our investigations on concentrations of heavy metals at the stations off Ragciems and Roja (the Gulf of Riga) and Liepaja (open Baltic) revealed the following levels of the metals in plankton: 0.89–10.20 mg Cu/kg; 10.87–106.96 mg Zn/kg; 2.31–199.90 mg Mn/kg; 0.19–0.85 mg Cd/kg; and 0.35–9.35 mg Pb/kg wet weight (Table 1). During the 5-yr period, no increase in the metal levels was observed in the plankton. One can mention here that the highest levels of copper, lead, and manganese were observed in October 1983 at Liepaja (open Baltic) with *Acartia* sp. dominating (78%) in the plankton. The highest cadmium levels were observed in July 1984 at Ragciems with *Eurytemora hirundoides* (41%), *Podon* sp. (25%), and *Evadne* sp. (13%) as the dominant plankton species. The highest zinc levels in the plankton were observed in June 1987 at Roja (20 m depth) and in May 1987 at Liepaja (30 m depth). At that period, the zooplankton was dominated by *Synchaeta baltica* (74%) and *S. monopus* (23%) at Roja and by *Acartia* sp. (48%) and *Synchaeta baltica* (27%) at Liepaja. These data confirm our previous results concerning an increased concentration of copper and zinc in planktonic organisms during a certain period of the year, related to seasonal changes in biological and biochemical activities of the organisms.

To study the metal levels simultaneously in various species of the plankton, the organisms in samples were divided into two fractions: fraction "a" containing large and medium-size forms, and fraction "b" with small forms. The division was made possible by using a complicated juvenile fish-neuston trawl. As opposed to the commonly used neuston trawl, ours consisted of two parts, one within the other, differing in their mesh size. The fraction "a" plankters were trapped in the ourter part (mesh size No. 38), while those of fraction "b" were caught by the inner part (mesh size No. 71) (Table 2).

When comparing the data obtained, levels of zinc, copper and cadmium in plankton samples off Ragciems and Roja (the Gulf of Riga) and Liepaja (open Baltic) were found to be higher in fraction "a" when the latter was dominated by the copepod *Eurytemora* sp. Manganese and lead contents were higher in the samples with *Acartia* sp. dominating. Low concentrations of all the metals were observed in those plankton samples consisting of small forms: *Acartia* sp. nauplii, *Synchaeta baltica, Keratella quadrata.* Metal concentrations at all the stations were similar when various plankton fractions did not differ in terms of their dominants.

The manganese level in the Gulf of Riga plankton was higher than that of the open sea, while concentrations of zinc showed a reverse pattern. Levels of cadmium, copper, and lead in the plankton of the Gulf of Riga and of the open sea ranged within approximately the same interval. Exceptions were found in September of 1983 and 1984,

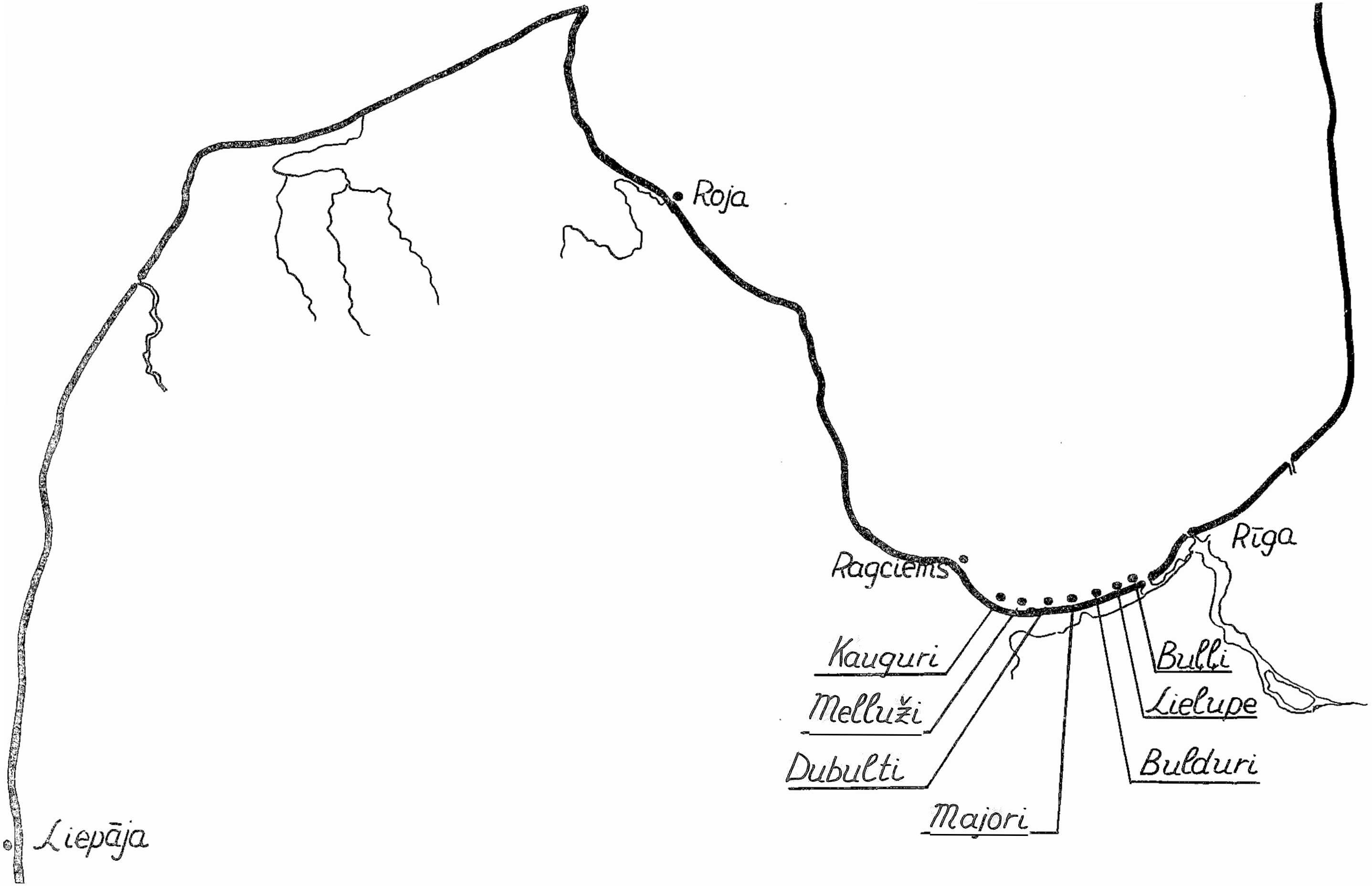

Fig. 1. Location of sampling sites in the Gulf of Riga and the open Baltic

with increased concentrations of manganese, lead, and copper being observed in the plankton (Table 1), which may point to the presence of a temporary local metal pollution source.

As shown by our data obtained previously (Seisuma et al., 1984), a synoptic study of plankton and molluscs and a comparison of the results gives a broader view of the water metal pollution as, during the growth season, the abundant plankton participates actively in assimilation and transport of metals in the marine environment.

Bottom sediments are of a considerable importance in an aquatic ecosystem, particularly the surface layers in the littoral. Depending on their activity, the sediment is called a "pump" or a "buffer". From April until November 1988, we were studying the heavy metal levels in bottom sediments of the Gulf of Riga at 7 stations (1 m depth) on a transect off Jurmala (Bulli, Lielupe, Bilduri, Majori, Dubulti, Melluži, Kauguri) (Fig. 1). The area is most affected by the anthropogenous effects, being the initial recipient of pollutants from various sources. We were estimating that part of the metal pool which is incorporated into the sediments as a result of pollution and does not enter the silicate structure. At all the stations of the Jurmala transect, the sediment granulometry is typical of sand and silt with grains differing in size.

The sediment levels of the metals studied were found to range within 0.114–0.279 mg Cd/kg; 0.23–1.61 mg Pb/kg; 0.27–8.39 mg Cu/kg; 2.49–8.04 mg Zn/kg; and 12.0–44.64 mg Mn/kg sediment dry weight (Figs 2–6). The average metal contents at 1 m depth along the transect sampled can be arranged in the following order: Cd<Pb< < Cu< Zn<Mn.

Cadmium. Non-polluted marine sediments may contain only 0.01 mg Cd/kg, while in areas affected by industrial pollution, the level may exceed 50 mg/kg (Mur and Ramamurti 1987). In the Baltic Sea, the cadmium level in bottom sediments ranges within 0.01–8.1 mg/kg dry weight (Kremling et al. 1987; Morozov and Petukhov 1981)

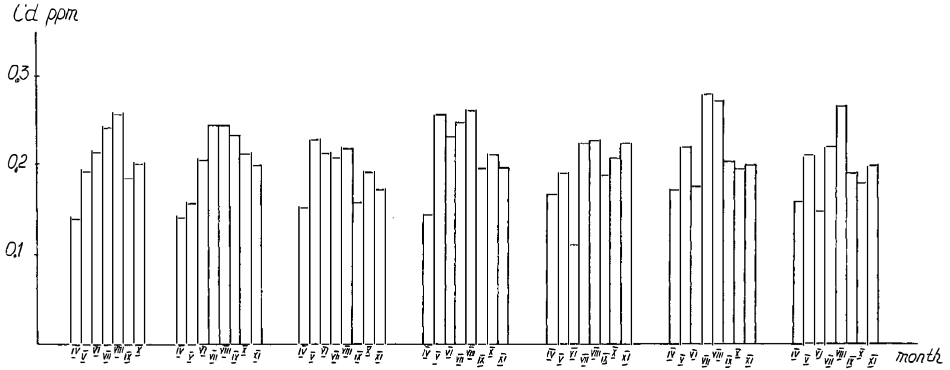

Fig. 2. The level of Cd in bottom sediments along the transect off Jurmala

The cadmium concentrations found in the sediments off Jurmala (Fig. 2) point to the presence of small pollution sources. The concentrations vary seasonally. The lowest levels at all the stations were found in spring (April) and the highest in summer (July, August). Cadmium concentrations in sediments are very similar at all the stations visited.

Lead. The levels of lead in bottom sediments of the Baltic Sea range within 2–400 mg/kg dry weight (Kremling et al. 1987; Morozov and Petukhov 1981). In non-polluted areas, the levels ranged within 2–50 mg/kg sediment, the level depending greatly on the sediment type. Data in Anonymus (1987) reveal that lead in various areas of the Baltica Sea, including the Gulf of Riga, is supplied by the river runoff.

In spring, the lead levels in the sediments off Bulli, Lielupe, and Bulduri are several times higher than those in other months and at other stations (Fig. 3), which indicates the presence of high contents in waters of the rivers Lielupe and Daugava in spring. In winter, all the snow from the streets of Riga, containing obviously high quantities of lead, is dumped into the Daugava. The lowest lead levels in the sediments were recorded in summer. In autumn, the levels were similar at all the stations.

Copper. Botom sediments of non-polluted marine and freshwater areas usually contain below 20 mg Cu/kg dry weight. In the Baltic Sea, the concentrations range within 1–283 mg/kg, rivers being the main source of copper pollution. This is the case in the Gulf of Riga, as shown by our data. The highest copper levels in the sediments along the Jurmala transect were observed in spring, particularly at Bulli, Lielupe, and Bulduri which are the primary recipients of the Lielupe and Daugava runoff. Copper

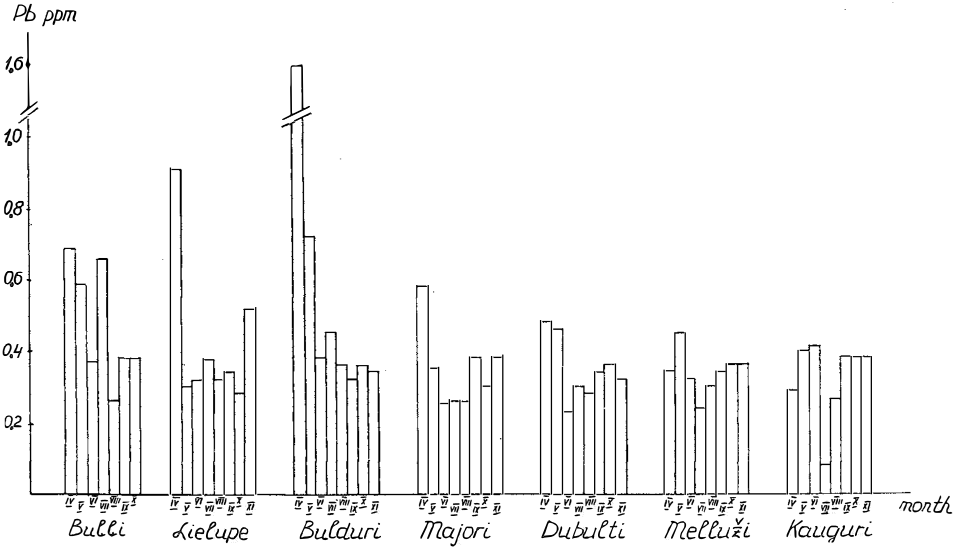

Fig. 3. The level of Pb in sediments along the transect off Jurmala

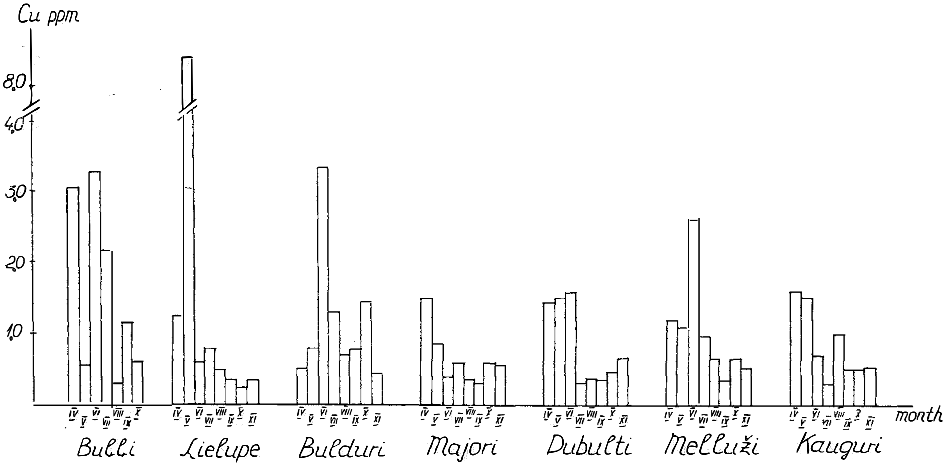

Fig. 4. The level of Cu in sediments along the transect off Jurmala

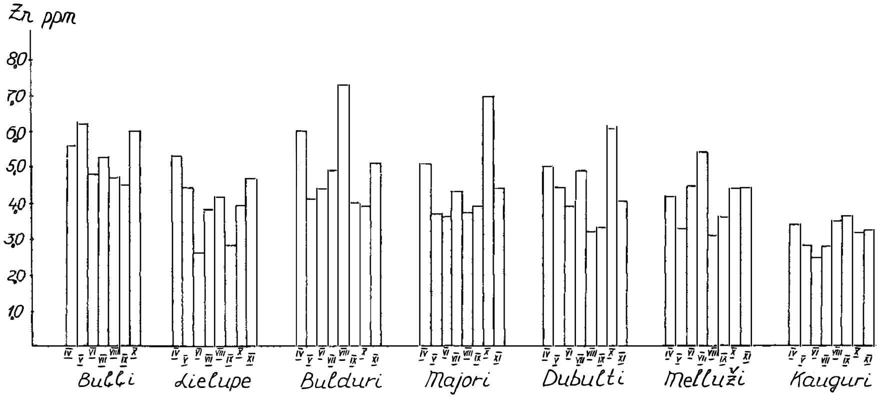

Fig. 5. The level of Zn in sediments along the transect off Jurmala

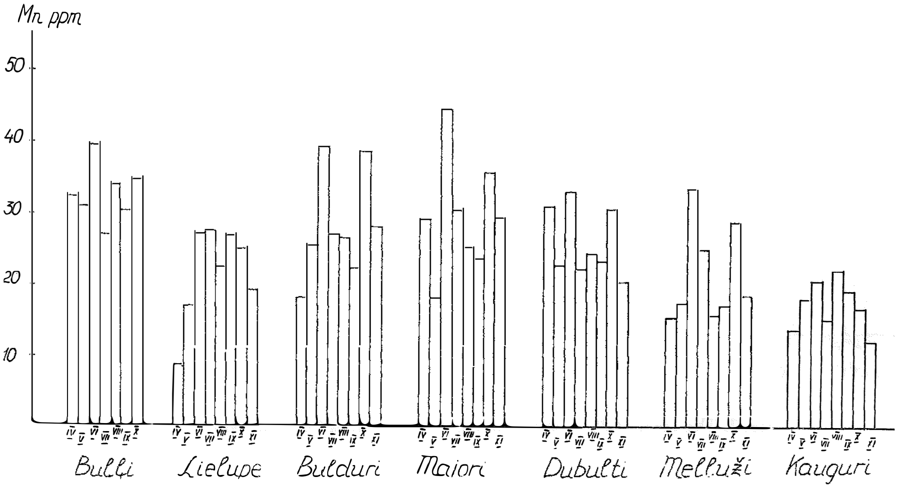

Fig. 6. The level of Mn in sediments along the transect off Jurmala

levels in the sediments at Majori, Dubulti, Melluži, and Kauguri differed slightly, except for Melluži in June (Fig. 4). That was, obviously, related to a local pollution.

Zinc. The total content of zinc in bottom sediments of nonpolluted coastal areas is below 50 mg/kg dry weight (Mur and Ramamurti 1987). Zinc contents in the bottom sediments of various Baltic areas range within 6–2090 mg/kg dry weight. Data in Anonymus (1987) demonstrate that most of zinc in the Baltic is discharged by rivers. Our research shows that zinc levels are higher on the Jurmala transect in spring and autumn (Fig. 5) when the rivers Lielupe and Daugava carry most of their water. Zinc levels in sediments at Bulli, Lielupe, Bulduri, and Majori are higher than those at the stations located farther away from the river mouths.

Manganese. In non-polluted marine areas, the sediment manganese levels range within 0–500 mg/kg dry weight (Mur and Ramamurti 1987). The Gulf of Riga sediments are rich in ferromanganese concretions. Maximum sediment concentrations of manganese on the Jurmala transect were recorded in June and October, and minimum concentrations in spring (Fig. 6). Comparison of the data from all the stations shows the lowest Mn concentrations to be typical of sediments at Kauguri, the highest levels being found at Bulli, which may be related to the effect of the manganese-rich Daugava waters.

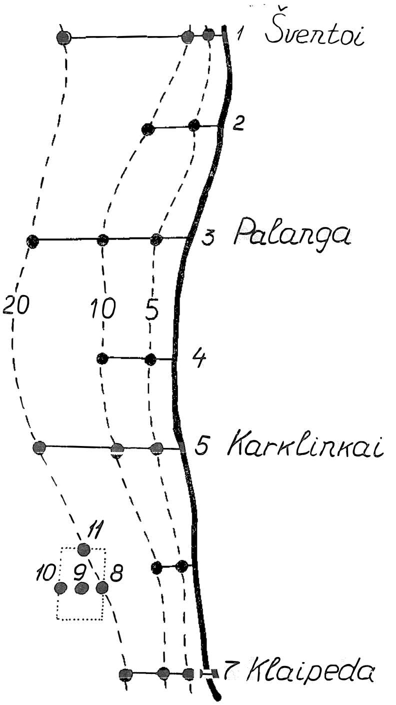

Fig. 7. Location of sampling sites in the open Baltic from Šventoi to Klaipeda

Granulometry of the bottom in the area of Šventoi – Klaipeda (Fig. 7) is typical of sand and silt with particles of various size. Only at Station 3 (10 m depth) did the sediment contain 54.19% of gravel. A comparative analysis of the heavy metal contents in all the sediment fractions revealed the 2–5 mm fraction (Station 3; 10 m) to have the highest manganese levels, medium levels of zinc, and low levels of all the remaining metals (lead, cadmium, copper) (Figs 8–12). Generally, high levels of all the heavy metals were observed in 0.05–0.063 mm fractions. At the same time, the occurrence of each element differs in various sediment fractions. Thus zinc, for instance, in contrast to all the other metals, showed its maximum concentrations in 0.16–1 mm fractions (Station 1; 5 m depth). Zinc levels at 7 sampling sites were higher in all the large grain size fractions, the stations being situated off the human settlements of Šventoi, Palanga, Karklininki, and Klaipeda. Obviously, the finding can be explained by the highest mobility of zinc, compared with other heavy metals.

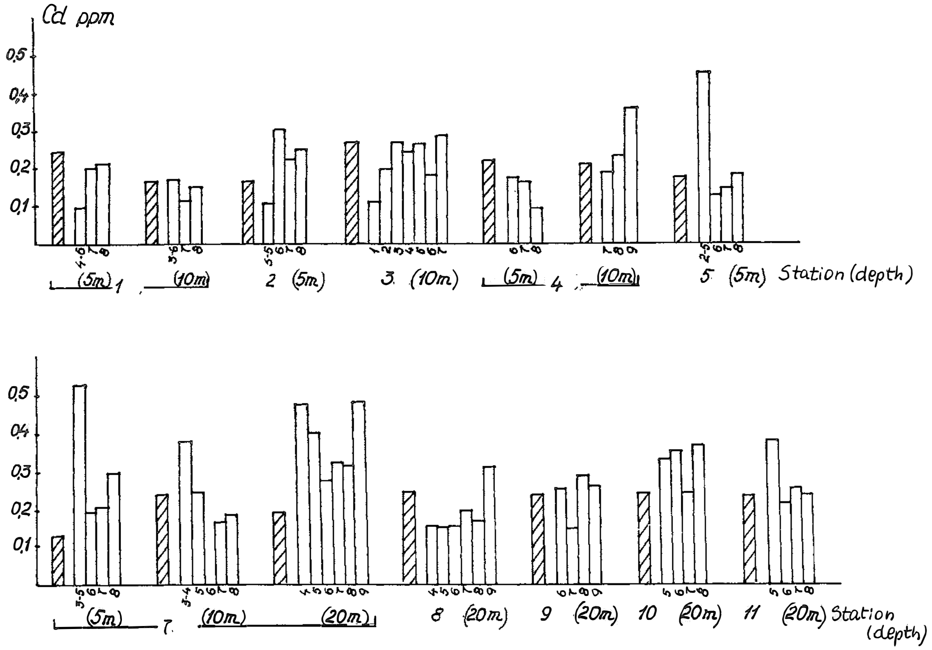

Fig. 8. The level of Cd in sediments of various fractions in June 1986 (signs in figures 8–12: ▨ – total content; ▯ – content invarious fractions; fractions of particle size, mm: 1 – 10.0–5.0; 2 – 5.0–2.0; 3 – 2.0–1.0; 4 – 1.0–0.5; 5 – 0.5–0.25; 6 – 0.25–0.15; 7 – 0.15–0.10; 8 – 0.10–0.063; 9 – 0.063–0.05).

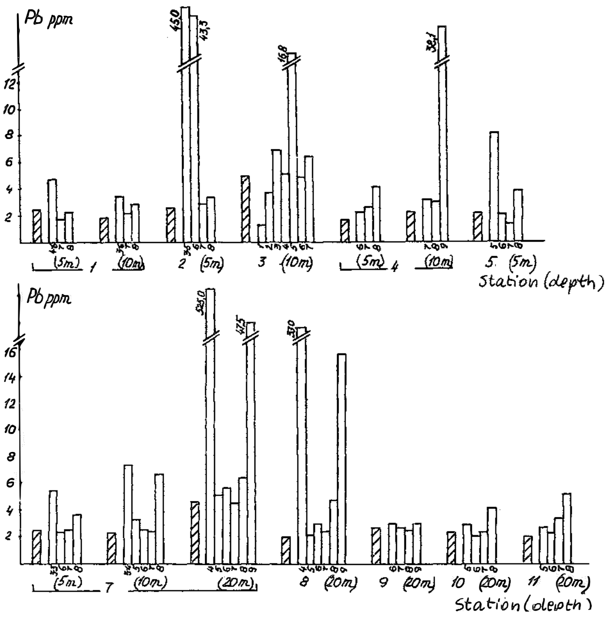

Fig. 9. The level of Pb in sediments of various fractions in June 1986

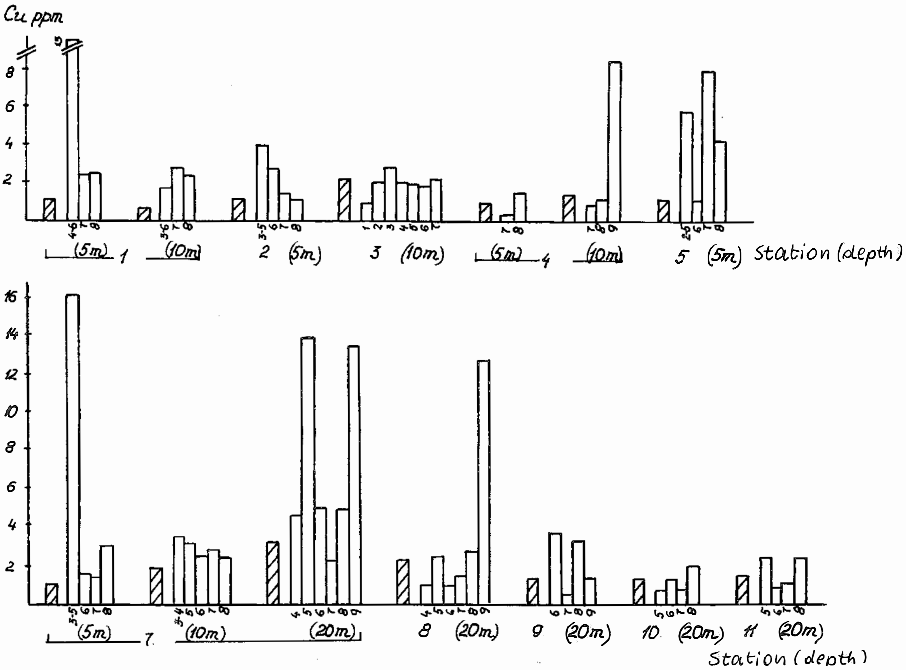

Fig. 10. The level of Cu in sediments of various fractions in June 1986

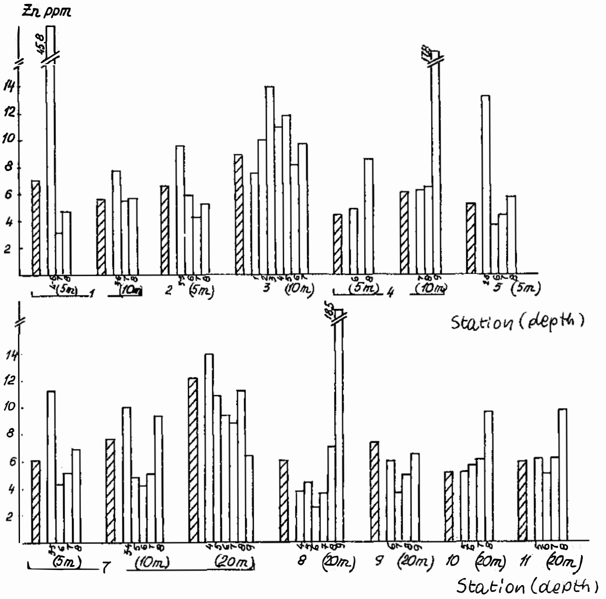

Fig. 11. The level of Zn in sediments of various fractions in June 1986

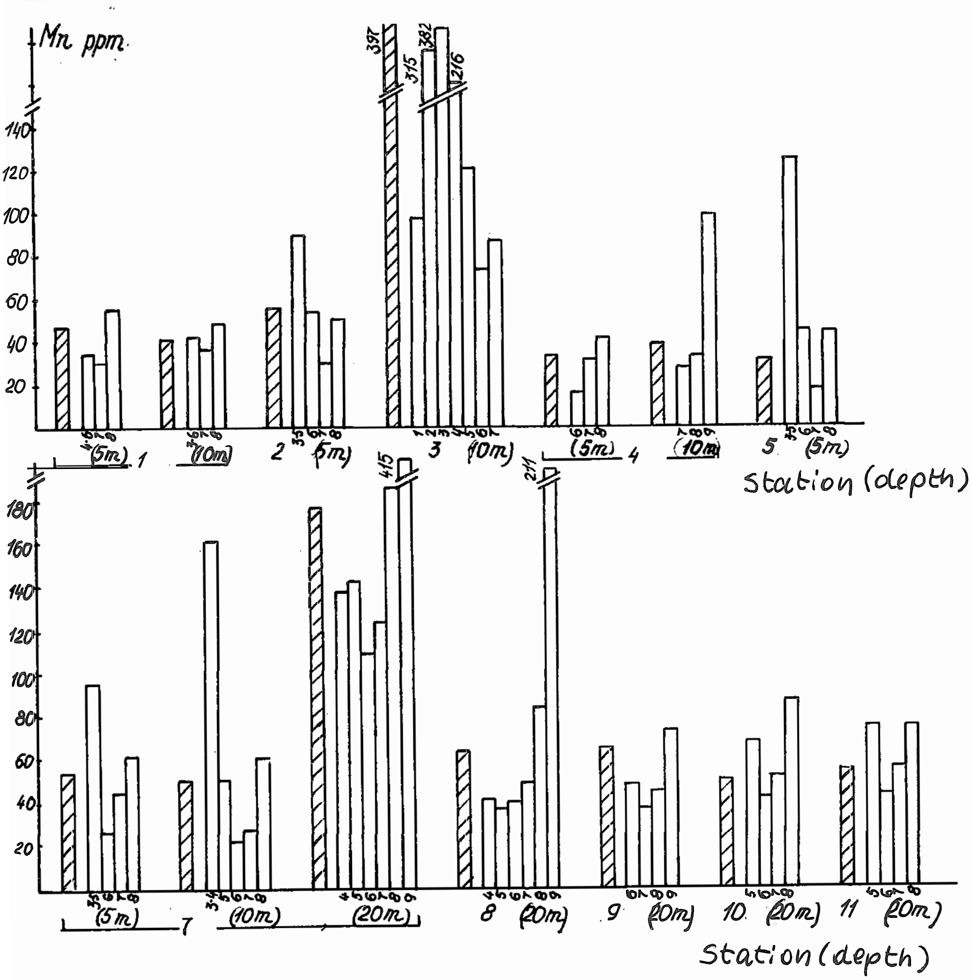

Fig. 12. The level of Mn in sediments of various fractions in June 1986

The tendency of manganese to form compounds difficult to solve in sea water during mineralization of organic substances results in a considerable concentration of the metal in the bottom sediments. In this study, manganese differed from other metals by its highest concentrations at all the stations of the area. Manganese levels were particularly high in various sediment fractions at Station 3 (10 m) and Station 7 (20 m) located off Palanga and Klaipeda, respectively.

Lead and copper levels in various sediment fractions were very different. Thus, the highest levels of the metals were observed in 5.0–0.25 to 0.063–0.05 mm fractions. The concentration of lead was high in various sediment fractions at Stations 2 (5 m), 3 (10 m), 4 (10 m), 7 (20 m), and 8 (20 m), while high copper concentrations were recorded at Station 1 (5 m), 4 (5 m), 5 (5 m), 7 (5 and 20 m), and 8 (20 m).

Among all the metals studied, cadmium showed the lowest concentrations in all the sediment fractions, compared with other metals. The highest Cd levels were observed in both the large – (Stations 5 and 7) and small-grain size fractions (Station 7). Higher Cd levels in all the fractions are typical of Station 3 (10 m) and 7 (20 m) off Palanga and Klaipeda, respectively.

Heavy metal concentrations in the sediment of the Klaipeda – Šventoi area do not exceed either the allowed levels or those in other Baltic areas. However, distribution of the metal contents in the sediment show certain patterns:

– the heavy metal level in sediments consisting of various fractions depends on the particle size as well as on the anthropogenous impact on a given locality;

– the highest levels of lead, zinc, and copper were found at the depth of 20 m, while the highest cadmium levels occurred at the depth of 10 m;

– sediment concentrations of heavy metals are higher off the more densely populated coastal areas (Palanga, Klaipeda).

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