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Behaviour of heavy metals in the Daugava plume zone (1999–2003, Gulf of Riga, the Baltic Sea)

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Seawater in the Gulf of Riga is a complicated mixture of freshwater from a large number of rivers and the inflowing saline waters of the central Baltic Sea. The Daugava River alone gives 65% of freshwater runoff. In all seasons of the year the concentrations of metals were investigated in water (surface and 1 m above sediment) and in sediment samples from the Daugava River, the mixing zone and the Gulf of Riga. Stations were chosen to cover the salinity gradient inside the freshwater plume as well as adjacent waters.

The concentrations of Cu, Zn, Ni, Mn and Fe in water of the Daugava plume zone in the surface layer and in water 1 m above sediments are different, so are the concentrations of metals distinguished in the Daugava River, the mixing zone and the Gulf of Riga. The seasonal variability of concentrations in water is significant for all metals studied. Principal component analysis (PCA) with Varimax rotation of initial factors showed differences among the Daugava River, mixing zone and the Gulf of Riga. In all seasons there was a significant correlation among the concentrations of Hg, Cd, Pb, Cu, Zn, Ni, Mn and Fe in sediments, but only in spring the concentrations of metals in sediments correlated with water salinity and oxygen. The concentrations of metals in water in different zones showed no essential correlation with the physical-chemical parameters.

Key words: the Baltic Sea, the Daugava plume zone, metals (Cd, Cu, Fe, Hg, Mn, Ni, Pb, Zn), sediment, water

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INTRODUCTION

Hydrochemical investigations of the southern part of the Gulf of Riga have shown that the main characteristic feature of its hydrochemical regime is a certain admixture of freshwater from the inflowing rivers. 82% of freshwater runoff is contributed by three biggest rivers of Latvia, Daugava, Lielupe, Gauja, falling into its southern part. The Daugava River alone gives 65% of the runoff. The plume of the Daugava River with its pollutants is expected in the south of the gulf (Пасторс, 1988). The Daugava River originates in the neighboring country Russia and transits waters from Russia and Belarus; the total catchment area of the river is 87 000 km^2. The length of the Daugava River is 1020 km (357 km in Latvia) and its catchment area in Latvia is 24,700 km^2 i. e. 38.2% of Latvia's total surface (Anonymous, 1999).

Water regime in Latvian rivers is characterized by spring floods and flow water periods in late summer, as well as periodic summer falls and winter rises in water level. During the spring floods, the rivers carry about 45–55% of the total annual water volume. The low water salinity in the Gulf of Riga can be explained by a relative isolation of the gulf from the Baltic Sea and a rather high river discharge (Berzinsh, 1995).

The salinity of the gulf water varies greatly – from 0.5–2.0‰ in spring in the surface layers of the shallow zone of the southern district to 7.5–7.7‰ in the bottom layers of the Irbe Sound in spring and summer. In spring, along with the increasing freshwater influx and the origination of stratification, salinity in the upper layers declines. The salinity is minimum from May to August. In summer and winter, stratification has been observed, related to salinity increasing with depth (Matisone, 1974). To find out the water dynamics in the southern part of the Gulf of Riga and of the admixture processes, four groups of water have been singled out, differing in salinity and in relative content of river water: group 1 – strongly refreshed sea water with salinity up to 3‰ and relative river water content >50%; group 2 – partly refreshed sea water with salinity 3.0–4.5‰ and relative river water content 50–25%; group 3 – slightly refreshed sea water with salinity 4.5–5.5‰ and relative water content 25–10%; group 4 – relatively unadmixed sea water with salinity >5.5‰ and relative river water content <10%.

In this study, our aim was to analyse the levels of Cu, Zn, Ni, Mn and Fe in water and Hg, Cd, Pb, Cu, Zn, Ni, Mn and Fe in sediments of the Daugava plume zone under different conditions of physical-chemical parameters, especially salinity in different seasons of the year.

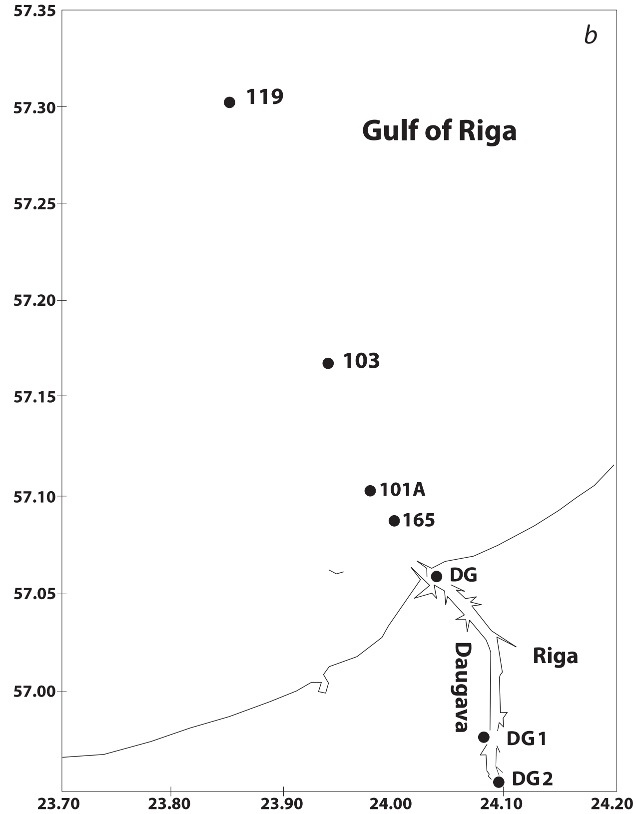


Fig. 1. The Gulf of Riga map with investigated area (*a*) and location of sampling sites in the Daugava River, mixing zone and in the Gulf of Riga (*b*)

1 pav. Rygos įlankos žemėlapis su tiriamuoju plotu (*a*) ir ėminių atrankos vietos Dauguvos upėje, mišrioje zonoje ir Rygos įlankoje (*b*)

METHODS

Five cruises were conducted in the Daugava plume zone on the RV "Antonija" during autumn (September 1999), spring (May 2000, April 2003), winter (December 2001) and summer (July 2002). Stations were chosen to cover the salinity gradient inside the freshwater plume as well as the adjacent marine waters. Water and sediment samples were collected at seven stations in the Daugava River (DG, DG1 and DG2), in the mixing zone (165, 101A) and in the Gulf of Riga (103, 119) (Fig. 1).

The mouth-bed of the Daugava River consists of gravel and inequigranular sand covered with mud. In the mixing zone, sediments consist of inequigranular sand. An intensive abrasion had a strong impact on it. The sediments of the stations of the Gulf of Riga mainly consisted of mud.

Cd, Pb, Cu, Zn, Ni, Mn and Fe in water and sediment samples were analysed using a flame Varian AA Spectrophotometer (model Spektra AA880), while Hg in sediment samples was analysed using a Flow Injection Mercury System (FIMS-Perkin Elmer). Blank and standard reference materials were analysed similarly. Internationally accepted standard samples from the National Research Council of Canada were used (for marine sediments: BEST-1, MESS-2 for mercury, HISS-1, MESS-2 for other metals; and for estuarine water: SLEW-2) for quality control. The error of analysis was estimated to be about 10–5% (Seisuma, Kulikova, 2002).

By means of Principal Component analysis (PCA) with Varimax Rotation, several plume zone processes could be identified, which determine the behaviour of the individual metals in three different zones.

RESULTS AND DISCUSSION

In different seasons of 1999–2003, the change in salinity (5.37–5.74 PSU) was the least in the water of the Gulf of Riga 1 m above sediment. In surface water, salinity (4.23–5.41 PSU) showed large fluctuations, and in spring it had the lowest value. Also, in the mixing zone, salinity changes in water 1 m above sediments (4.44–5.57 PSU) was less than in surface water (1.58–5.28 PSU), the lowest value (1.58–1.61 PSU) being found in spring.

All seasons of the year were characterized by an ele-vated level of marine flow in water of the mouth of the Daugava River 1 m above sediments (3.31–5.27 PSU). In surface water of the Daugava River there was freshwater (0.08–0.31 PSU) in spring, but in other seasons there was refreshed seawater with salinity 1.53–3.52 PSU. Spring (May 2000; April 2003) was characterized by a strongly elevated fresh water flow in the Gulf of Riga. Other seasons (September 1999; December 2001; July 2002) were characterized by an elevated level of marine flow in the Daugava River.

Sediments of the Gulf of Riga (Table) contained the highest concentrations of all metals. Sediments of the mixing zone showed the lowest metal concentrations, because an intensive abrasion in this area had a strong impact on it. Sediments of the Daugava River were characterized by an elevated level of metals in the mouth bed where gravel is covered with mud, and concentrations of metals were low in other places where sediment consist of gravel. Irrespective of the season (spring, summer, autumn, winter), the concentrations of all metals (Hg, Cd, Cu, Zn, Ni, Pb, Mn, Fe) in sediments of the Daugava River, mixing zone and the Gulf of Riga preserved typical values for each zone.

Table. **Mean concentrations of metals (mg/kg dry wt) in sediments of the Daugava plume zone (September 1999; May 2000; December 2001; July 2002 and April 2003)**

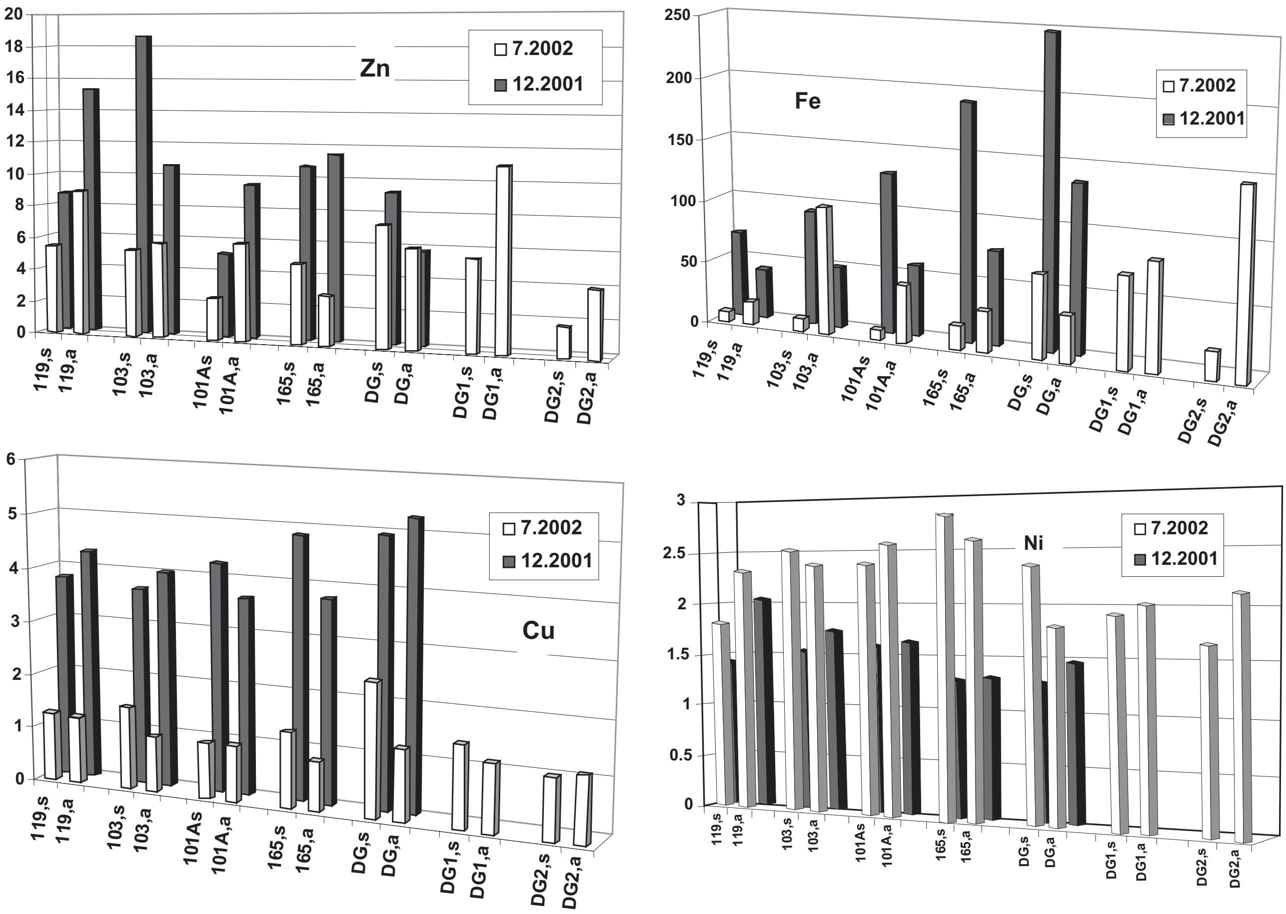
Lentelė. **Vidurkiniai metalų kiekiai (mg/kg sausos masės) Dauguvos hidrofronto zonos nuosėdose (1999 m. spalis; 2000 m. gegužė; 2001 m. gruodis; 2002 m. liepa, 2003 m/ balandis)**

Station	Hg					Cd				
	IX 1999	V 2000	XII 2001	VII 2002	IV 2003	IX 1999	V 2000	XII 2001	VII 2002	IV 2003
119	0.087	0.072	0.301	0.22	0.045	1.2	1.44	0.729	1.29	1.09
103	0.072	0.061	0.244	0.1	0.27	1.33	1.67	0.702	1.2	0.98
101A	0.067	0.02	0.082	0.05	0.02	0.94	0.33	0.179	0.35	0.304
165	0.045	0.057	0.072	0.07	0.02	0.64	0.73	0.142	0.2	0.211
DG	0.081	0.084	0.193	0.18	0.045	1.11	0.82	0.402	0.98	0.908
DG1				0.068	0.027				0.52	0.37
DG2	0.072	0.054		0.054	0.1	0.2	0.26		0.6	0.174
Station			Cu					Ni		
	IX 1999	V 2000	XII 2001	VII 2002	IV 2003	IX 1999	V 2000	XII 2001	VII 2002	IV 2003
119	22.67	25.92	33.26	21.5	25.78	18	16.7	39.33	70	31.86
103	23.33	25.33	22.91	22.4	22.17	13.33	14.13	22.12	31.9	26.77
101A	7.41	1.6	5.03	4.02	3.57	4.71	1.8	3.73	4.3	4.5
165	4.04	3.53	5.31	3.25	2.22	2.69	2.8	3.24	2.5	2.56
DG	16	4.47	19.07	18.4	30.67	5.78	3.55	9.78	16.2	15.08
DG1				15.9	22.67				5.4	5.64
DG2	1.07	0.47		6.2	4.28	1.07	1.4		8.3	2.58
Station			Pb					Zn		
	IX 1999	V 2000	XII 2001	VII 2002	IV 2003	IX 1999	V 2000	XII 2001	VII 2002	IV 2003
119	38.6	34.56	28.7	37.5	27.25	112	105.1	128.6	109.6	123.6
103	30.6	28	21.73	33.6	22.63	87.3	83.33	73.5	98	105.4
101A	8.01	2	1.91	3.9	1.97	23.2	9.8	11.9	11.2	1.5
165	5.93	5.33	2.29	2.27	1.73	14.1	11.1	10.6	8.8	0.7
DG	13.27	7.78	7.05	1.5	15.68	41	16.27	52.5	60	88
DG1				8.9	6.24				42	49.7
DG2	1.27	2		2.6	2.01	7.7	7.8		32	2.2
Station			Mn					Fe		
	IX 1999	V 2000	XII 2001	VII 2002	IV 2003	IX 1999	V 2000	XII 2001	VII 2002	IV 2003
119	1100	1368	1064	2400	1573	20400	20088	32767	33689	28554
103	427	1133	550	2756	3233	17333	16533	22962	27889	24627
101A	343	173	238	165	539	4713	2133	3623	3355	3396
165	89	153	185	113	222	3000	2867	3329	2178	2059
DG	291	173	910	815	1628	7178	4911	10204	14222	16127
DG1				127	729				5333	6658
DG2	49	65		587	288	3000	1867		10689	2959

Cu, Zn, Ni, Mn and Fe concentrations in water differed depending on zones and seasons (Seisuma, Kulikova, 2002). Autumn and spring measurements showed the highest changes (Mn 4.0–47.0 µg/l, Fe 7.8–105.1 µg/l) in water of the mixing zone. In the river, fluctuations (Mn 29–40 µg/l, Fe 45.7–150.8 µg/l) were lower, and the lowest were in the gulf (Mn 1.45–4.7µg/l, Fe 6.2–38.4 µg/l). In spring, high concentrations of Mn and Fe in water of the mixing zone were due to fresh water flow in the Gulf of Riga with a low level of salinity.

Cu, Zn, Ni, Mn, and Fe concentrations in water of the Daugava plume zone in the surface layer and in water 1 m above sediment are different; so are also the concentrations of metals distinguished in the Daugava River, the mixing zone and the Gulf of Riga (Fig. 2). In most cases the concentrations of Zn, Ni, and Mn were higher in water 1 m above sediment and of Cu in the surface layer. Fe concentration was higher in winter in the surface layer, but in summer it was higher in water 1 m above sediments. In summer, the concentrations of Cu, Zn, Fe in water were lower than in winter, because water organisms (particularly phytoplankton) utilize these metals in their development (Jurkovskis, 2004; Schoemann et al., 1998). The concentration of Mn was higher in water of the Gulf of Riga in winter, but in the Daugava River in summer. Ni concentration was higher in summer.

PCA with Varimax rotation of initial factors showed differences among the Daugava River, mixing zone and the Gulf of Riga. Both in autumn (September 1999) and spring (May 2000) (Seisuma, Kulikova, 2002) there was a very good positive correlation ($r = 0.9–1.0$) among Cu, Zn, Mn and Fe in the sediments. In spring, there was a good correlation among metals (Cu, Zn, Mn, Fe) and oxygen in water, salinity in the surface layer and in water 1 m above the sediment. This could illustrate most likely the importance of oxidation processes. In summer (July 2002) and winter (December 2001), statistical analysis with PCA showed that Cu, Zn, Cd, Ni, Pb, Mn levels (only in summer), Fe



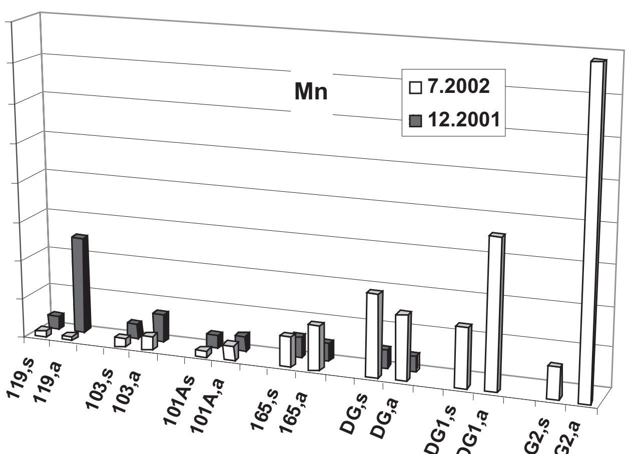


Fig. 2. Concentrations of Cu, Zn, Ni, Mn and Fe (µg/l) in water of the Daugava plume zone (December 2001 and July 2002; *s* – surface water, *a* – 1 m above sediments)
2 pav. Cu, Zn, Ni, Mn ir Fe kiekiai (µg/l) Dauguvos hidrofronto zonos vandenyje (2001 m. gruodis ir 2002 m. liepa; *s* – paviršinis vanduo, *a* – metras virš nuosėdų)

and Hg (only in winter) in sediment were positively correlated (Figs. 3, 4), while in spring, summer, autumn and winter changes in salinity, oxygen, pH in water 1 m above the sediments were insignificant, and the concentrations of metals in sediments were determined mainly by the type of sediment and the site of their occurrence.

In the surface layer of water, salinity showed essential differences in all seasons of the year. In spring (May 2000), autumn (September 1999) (Seisuma, Kulikova, 2002) and summer (July 2002) (Figs. 5, 6) metals of natural origin (Mn, Fe) showed a good correlation in water. An intensive freshwater flow from the Daugava increased Mn concentrations 4–7 times and of Fe 12 times in water of the mixing zone.

Higher concentrations of total Mn and Fe in the river water were most probably due to the resuspension of fine bottom sediment fractions, similarly to the Scheldt estuary (Baeyens et al., 1998). The bottom sediments are eroded by the spring flood tidal current.

CONCLUSIONS

Irrespective of salinity and other physical-chemical parameters in different seasons, Hg, Cd, Cu, Zn, Ni, Pb, Mn and Fe concentrations in sediments of the Daugava River, the mixing zone and the Gulf of Riga maintain amplitudes characteristic of each zone.

The concentrations of Cu, Zn, Ni, Mn and Fe in water of the Daugava plume zone in the surface layer and in water 1 m above

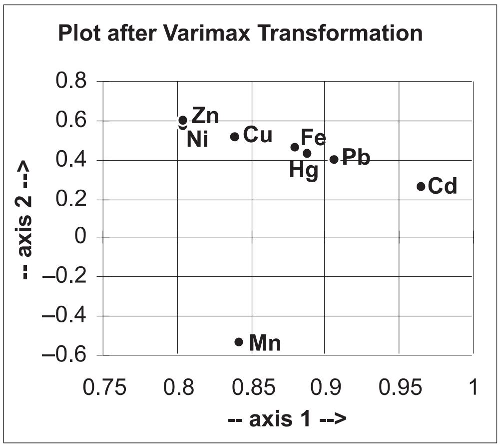


Fig. 3. Correlation for variables of metals in sediments (December 2001)
3 pav. Kintamųjų metalų kiekių nuosėdose koreliacija (2001 m. gruodis)

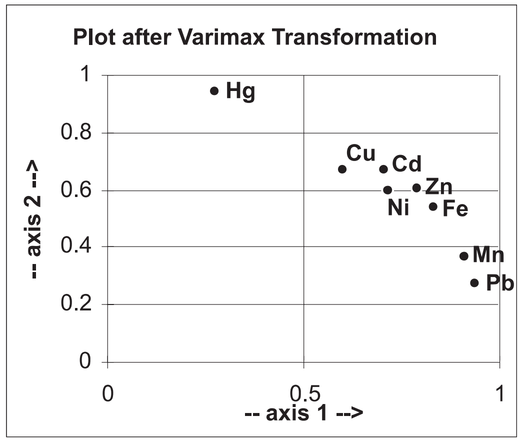


Fig. 4. Correlation for variables of metals in sediments (July 2002)
4 pav. Kintamųjų metalų kiekių nuosėdose koreliacija (2002 m. gruodis)

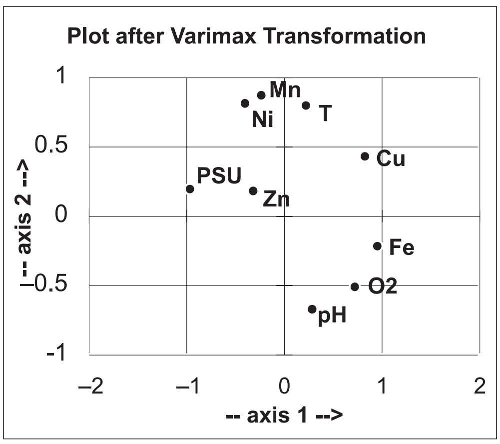


Fig. 5. Correlation for variables of metals and PSU, pH, T°, 0_2 in water (December 2001)
5 pav. Kintamųjų metalų kiekių ir PSU, pH, 0_2 vandenyje koreliacija (2001 m. gruodis)

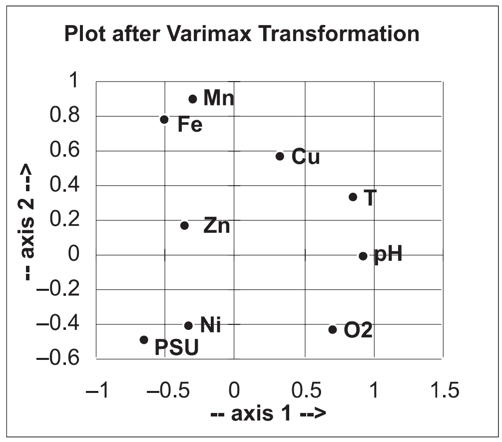


Fig. 6. Correlation for variables of metals and PSU, pH, T°, 0_2 in water (July 2002)
6 pav. Kintamųjų metalų kiekių ir PSU, pH, 0_2 vandenyje koreliacija (2002 m. liepa)

sediment are different in all seasons of the year, so are the concentrations of metals distinguished in the Daugava River, the mixing zone and the Gulf of Riga.

There were significant correlations among Hg, Cd, Pb, Cu, Zn, Ni, Mn and Fe concentrations in sediments, but only in spring the concentrations of metals in sediments correlated with salinity and oxygen in water.

Only metals of natural origin (Mn, Fe) show a good correlation in water. The concentrations of metals in water in different zones had no essential correlation with the physical-chemical parameters.

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References

1. Anonymous A. 1999. Environmental Performance Reviews, Latvia. United Nations, New York and Geneva. 175 p.
2. Baeyens W., Elskens M., Gillain G., Goeyens L. 1998. Biogeochemical behavior of Cd, Cu, Pb and Zn in the Scheldt estuary during the period 1981–1983. *Hydrobiologia*. ***366***. 15–44.
3. Berzinsh V. 1995. Hydrology. In: Ojaveer E. (ed.). *Ecosystem of the Gulf of Riga between 1920 and 1990*. Tallinn: Estonian Academy Publishers. 7–31.
4. Jurkovskis A. 2004. Dynamics of particulate major and trace elements in the lower reaches of the Daugava River and adjacent area of the Gulf of Riga (Baltic Sea). *Marine Pollution Bulletin*. ***49***. 249–263.
5. Matisone M. 1974. Seasonal changes in salinity in the southern part of the Gulf of Riga under the influence of freshwater inflow. In: Andrushaitis G. (ed.). *Biology of the Baltic Sea. Hydrochemistry and Hydrobiology of the Gulf of Riga*. ***1***. 39–61.

6. Schoemann V., de Baar H. J. W., de Jong J. T. M., Lancelot C. 1998. Effects of phytoplankton blooms on the cycling of manganese and iron in coastal waters. *Limnology and Oceanography*. ***43****(7).* 1427–1441.
7. Seisuma Z., Kulikova I. 2002. Behaviour of Hg, Cu, Zn, Mn and Fe in the Daugava plume zone (Gulf of Riga, Baltic Sea). *Fresenius Environmental Bulletin*. ***11****(2).* 67–73.
8. Пасторс А. 1988. Сток пресной воды в Рижский залив. *Режимообразующие факторы, гидрометеорологические и гидрохимические процессы в морях СССР.* Ленинград: Гидрометеоиздат. 80–94.

Zinta Seisuma, Irina Kulikova

SUNKIŲJŲ METALŲ REAKCIJA DAUGUVOS UPĖS HIDROFRONTE (1999–2003, RYGOS ĮLANKA, BALTIJOS JŪRA)

Santrauka

Aprašomi Hg, Cd, Pb, Cu, Zn, Ni, Mn ir Fe reakcijos Dauguvos upėje, maišymosi zonoje ir Rygos įlankoje tyrimai. Cu, Zn, Ni, Mn ir Fe kiekiai viršutiniame vandens sluoksnyje ir vandenyje per metrą nuo Dauguvos hidrofronto grunto, taip pat Dauguvos upės, maišymosi zonos ir Rygos įlankos vandenyje skiriasi. Visų tirtų metalų kiekių sezoniniai pokyčiai vandenyje yra reikšmingi. Pagrindinių komponenčių analizė (PCA) su varimakso posūkiu atskleidė Hg, Cd, Pb, Cu, Zn, Ni, Mn ir Fe kiekių grunte reikšmingą koreliaciją. Vandenyje gerai koreliuoja tik gamtinės kilmės metalai (Mn, Fe). Įvairių zonų vandenyje su fizikiniais ir cheminiais parametrais metalų kiekių koreliacija nereikšminga.

Hg, Cd, Pb, Cu, Zn, Ni, Mn ir Fe kiekiai Dauguvos upės, maišymosi zonos ir Rygos įlankos grunte nepriklausomai nuo druskingumo ir fizikinių bei cheminių parametrų įvairiais sezonais (pavasarį, vasarą, rudenį, žiemą) išlaiko kiekvienai zonai būdingas amplitudes.

Зинта Сейсума, Ирина Куликова

ПОВЕДЕНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ В ГИДРОФРОНТЕ РЕКИ ДАУГАВА (1999–2003 ГГ., РИЖСКИЙ ЗАЛИВ БАЛТИЙСКОГО МОРЯ)

Резюме

Исследовано поведение Hg, Cd, Pb, Cu, Zn, Ni, Mn и Fe в реке Даугава, в зоне смешивания и в Рижском заливе. Концентрации Cu, Zn, Ni, Mn и Fe различны в воде верхнего слоя и в 1 м над грунтом гидрофронта реки Даугава, а также в воде реки Даугава, в зоне смешивания и Рижского залива. Сезонные изменения концентраций в воде существенны для всех исследованных металлов. Анализ главных компонентов (PCA) с ротацией Варимакс показал существенную корреляцию между концентрациями Hg, Cd, Pb, Cu, Zn, Ni, Mn и Fe в грунтах. В воде только металлы природного происхождения (Mn, Fe) имеют хорошую корреляцию. Концентрации металлов в воде разных зон не имеют существенной корреляции с физико-химическими параметрами.

Вне зависимости от солености и физико-химических параметров в разные сезоны (весна, лето, осень, зима) концентрации Hg, Cd, Pb, Cu, Zn, Ni, Mn и Fe в грунтах реки Даугава, в зоне смешивания и Рижского залива сохраняют характерные амплитуды для каждой зоны.