Original Research

Distribution of Heavy Metals in Sediments of the Nemunas River (Lithuania)

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Abstract

The distribution of heavy metals in sediments of the Nemunas river have been investigated. The most obvious anthropogenic impact has been observed in the middle part of the river. Nevertheless, sediment metal concentrations are within the limits of global, regional and local concentration levels.

Particular attention has been paid to the Kaunas Reservoir. Although it is a part of the river, sediment characteristics, including metal distribution, have been found to follow the bottom dynamic zones, as in lakes. Metal concentrations in the Kaunas Reservoir are close to the concentrations in the upstream part of the Nemunas river, without indicating increased contamination with metals due to the lower flow velocity. An unusual Fe/Mn ratio is characteristic to the Reservoir. Fe concentrations confirm the occurrence of anoxic hypolimnion, whereas Mn concentrations indicate the possibility of Mn transport from the nearshore sediments to the deepest places.

Keywords: sediments; heavy metals; the Nemunas River, the Kaunas Reservoir

Introduction

Various media are analyzed to monitor, assess, and control metal pollution. The most obvious media are surface waters. The investigation of sediments from the water bodies is of great interest in aquatic systems research. Sediments reflect the current quality of the system as well as provide information on the impact of pollution sources.

There were hardly any heavy metal investigations in the water bodies of Lithuania until 1990s, mainly due to the lack of instrumentation. One of the very first investigation programmes of the Nemunas river basin was carried out in 1991-92, and included the overview of metal distribution in the water phase. Since then, heavy metals in waters have been monitored by the State Monitoring System (Table 1). Some analyses of heavy metals in riverine sediments and in other media by State Monitoring and by individual researchers were carried out as well [1-5]. Nevertheless, there is still very little information available to the international audience.

The objective of the present study is to analyse the distribution of heavy metals in bottom sediments of the Nemunas river, paying particular attention to a special part of the river – the Kaunas Reservoir – and to trace the impact of the heavy metal pollution sources on the sediments.

The Study Area

The Nemunas river, with a drainage area of 98,220 km^2, total length of 937 km, and mean water discharge of 674 m^3/s, is one of the biggest rivers flowing into the Baltic Sea. Its headwaters originate in Byelorussia. Some 359 km flow through Lithuania, and the remaining 116 km run along the border between Lithuania and the Kaliningrad region, Russia, until inflowing into the Baltic

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Table 1. Metal concentrations in water of the Nemunas river. Monitoring data 1996-2005 (up to 11 monitoring sites monthly) [4].

Zn, μg/l	Cu, μg/l	Pb, μg/l	Cr, μg/l	Ni, μg/l	Cd, μg/l	Mn, mg/l	Fe, mg/l
3.60 – 83.85	0.00 – 21.20	0.00 – 6.90	0.00 – 3.74	0.00 – 5.71	0.00 – 0.14	21.7 – 263.0	0.08 – 1.00

Sea. The Hydroelectric Power Station (100 MW), built on the Nemunas 223 km away from its mouth in 1959, has formed the Kaunas Reservoir. The total length of the Reservoir is 95.0 km, the length of lacustrine part is 19.0 km, the maximum width is 3.5 km, average width 0.67 km, maximum depth 24.6 m, average depth 7.3 m.

The Nemunas river is the main river in Lithuania. Since most Lithuanian territory (71.5%) belongs to the basin of the Nemunas river, both industrial and agricultural pollutants from nearly all the country reach the river directly or via tributaries.

Materials and Methods

Sampling

Surficial sediment samples were collected between the end of August and the end of September. The sediments were taken from a rubber boat using a modified Petersen grab sampler, and stored in acid-washed plastic bottles.

A total of 17 sites located with regard to the main point sources, like towns and tributaries (Fig. 1), were sampled, covering the full length of the Nemunas river in Lithuanian territory: from the Byelorussian–Lithuanian border to the branching of the Nemunas into the Atmata and the Skirvyte.

In addition, 19 samples were taken from 5 cross-sections in the lacustrine part of the Kaunas Reservoir. The length of the sampling point net was around 15 km. The samples were taken from 2–24 m depth.

Analysis

The sediment samples from the Kaunas Reservoir were split into two parts, and the sediment samples from the Nemunas river into three parts.

In the first sub-sample dry matter content was determined by drying for 24 h at 105°C. The content of organic matter as a loss on ignition (IG) was estimated by combustion at 550°C for 2h. In order to analyze metals, digestion was performed by extracting the sediments with 1:1 HNO_3. The extract was analyzed for Fe, Mn, Ca, Zn, Cu, Pb, Cr, and Ni by flame atomic absorption spectrophotometry. Cd was additionally analyzed in the samples from the Kaunas Reservoir by atomic absorption spectrophotometry with the graphite furnace.

Sediment texture was analyzed in the second sub-sample. The percentage of sand particles in the samples from the Nemunas river was determined by sieving dried (at 105°C) sediments. Granulometric analysis of the sediments from the Kaunas Reservoir was carried out by sieving and pipette analysis.

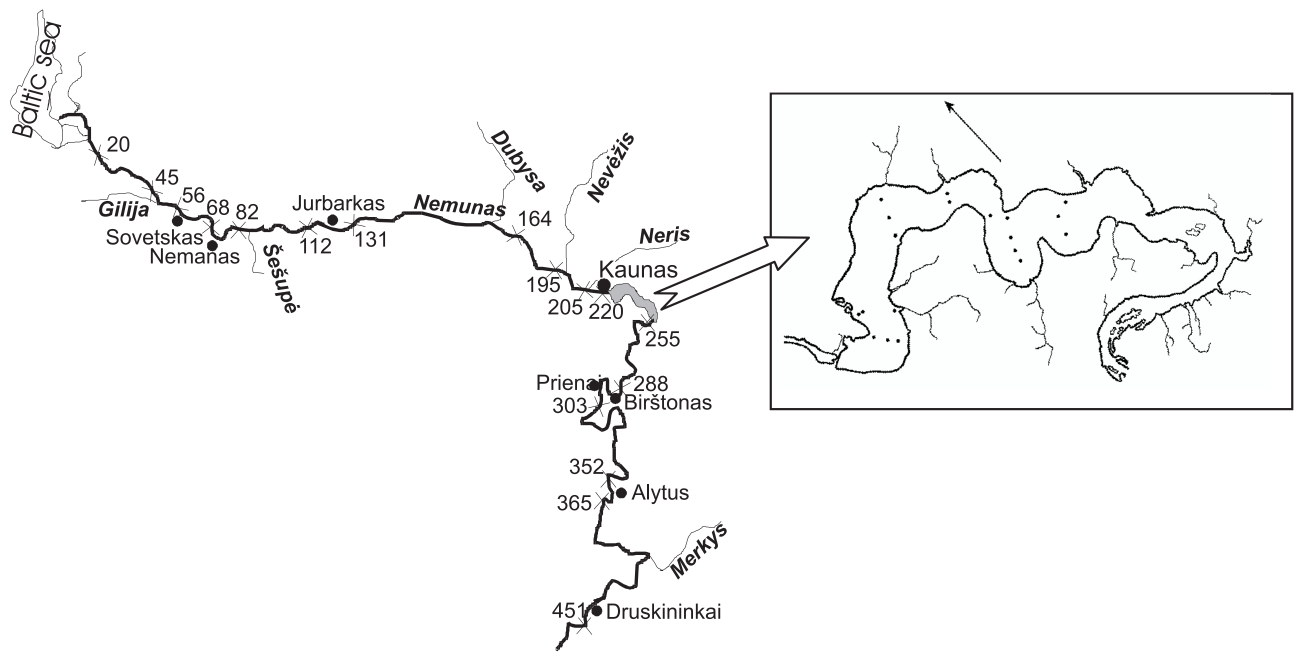

Fig. 1. Sampling sites in the Nemunas river (× 131 – sampling site and its distance from the mouth) and in the Kaunas Reservoir.

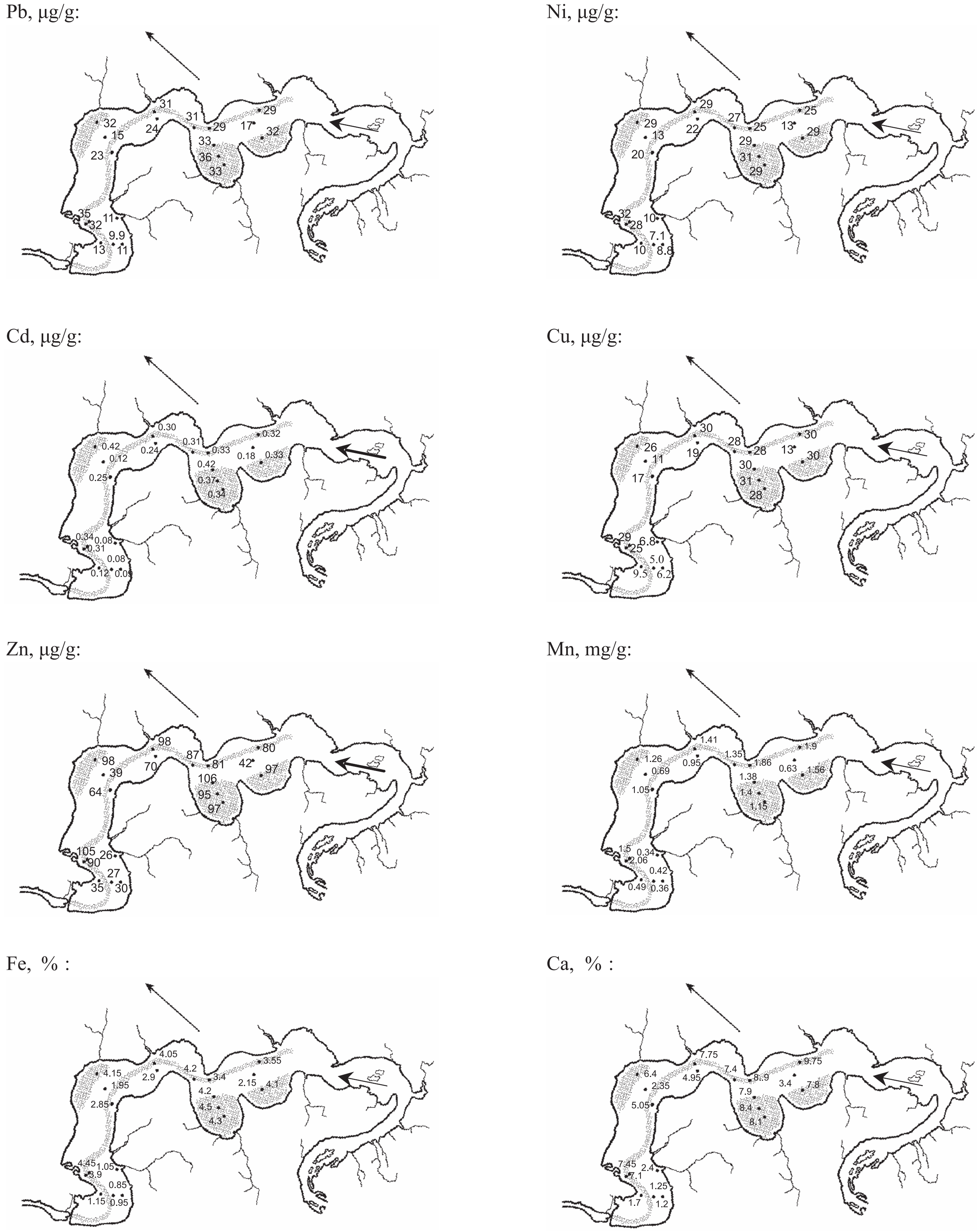

Fig. 2. Metal concentrations in bulk sediments of the Kaunas Reservoir. The accumulation zones are marked with dark colour.

The third sub-sample from the Nemunas river was used for the analysis of a grain size fraction <63 µm. The required sediment fraction was collected by means of wet-sieving through a nylon mesh. The separated <63 µm fraction was dried at 105°C, afterwards digested and analyzed for metals following the same procedures as for bulk sediment.

Duplicate analyses were carried out and recovery of the known additions was used to ensure data quality. 7%-

Table 2. Average heavy metal concentrations in the sediments of the Kaunas Reservoir (in bulk sediments and "sand corrected").

	Zn, μg/g		Cu, μg/g		Pb, μg/g		Cr, μg/g		Ni, μg/g		Cd, μg/g	
	bulk	corr.	bulk	corr.	bulk	corr.	bulk	corr.	bulk	corr.	bulk	corr.
Accumulation zones	94	95	29	29	32	33	43	45	28	29	0.34	0.35
Transportation zones	42	87	11	21	15	31	15	36	13	26	0.14	0.28

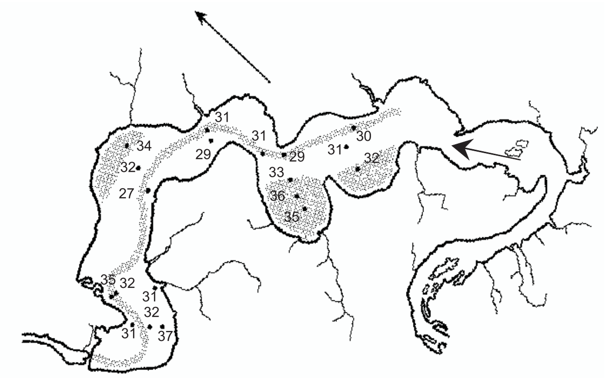

Fig. 3. Lead distribution in the Kaunas Reservoir. Sand-corrected concentrations, μg/g.

30% of samples, depending on the analysis, were analyzed in duplicate.

All the results were expressed on a dry-weight basis.

Results and Discussion

Metals in Sediments of the Kaunas Reservoir

Metal concentrations in bulk sediments of the Kaunas Reservoir are following the pattern of bottom dynamic zones of the Reservoir (Fig. 2). Although the Reservoir is a part of the river, the zones of accumulation and transportation could be distinguished on the basis of sediment water content and sediment texture (grain size) like in the lakes [6]. The accumulation was found to take place in the former riverbed, i.e. in the deepest places of the Reservoir, and in quiet bays. The organic matter as loss on ignition was estimated here to be 10.4-12.6%, water content – 75-80%. Transportation takes place in the rest of the Reservoir. The sediment water content as well as other parameters are much more varying here. Water content changes from 39-46% close to the hydropower station, up to 52-68% further in the lacustrine part. Organic matter as loss on ignition in the transportation zones was estimated to be 2.8-7.5%. The sediments are badly sorted, sand dominates.

The variation of metal concentrations in the sediments of accumulation zones is not big. Metal concentrations in the sediments of transportation zones are apparently lower and more varying. Differing sediment heavy metal contents do not necessarily indicate varying degrees of pollution, but rather reflect dissimilarities in grain size. A variety of approaches exist for normalization of concentrations allowing to distinguish anthropogenic pollution effects from natural variability [7]. Sand correction method was successfully employed in this study in order to reduce grain size effects [8]. Metals are mainly accumulated in fine-grained sediments, therefore, larger particles have a dilution effect on metal concentrations. Metal concentration can thus be calculated in the following manner by eliminating the dilution effect of sand (>0.1 mm) particles:

$$Metal_{corrected} = \frac{Metal_{measured} \times 100}{(100 - sand\%)}$$

The corrected metal concentrations in the entire Reservoir became rather uniform with almost no difference between the accumulation zones and the transportation zones (Table 2 and Fig. 3). In this way, grain size effects were reduced, and the samples from different bottom dynamic zones became comparable. The results do not indicate any effect of local pollution point sources to the Reservoir.

An unusual Fe/Mn ratio is characteristic to the Kaunas Reservoir. Figure 4 presents Fe/Mn ratios in all the sampling sites. Four of the samples were taken from a depth of over 20 m, i.e. from the former riverbed. In all these locations, except one, Fe/Mn ratio is around 18, while in other locations the ratio is around 30. Figure 5 presents Fe and Mn concentrations in the samples from the accumulation zones. Fe concentrations in the deepest sites (>20 m) are lower or similar compared to other sampling sites, whereas Mn sediment concentrations are highest in the deepest sites.

Fe and Mn are mobile metals, influenced by the changes of redox potential. Mn is mobilized from the sediments at oxygen concentrations below 2 mg/l [9, 10]. Fe becomes mobile (i.e. released or precipitated again) at lower redox potential, i.e. at lower oxygen concentrations than Mn. This suggests a greater release of Mn in the case of anoxic hypolimnion resulting in the increased Fe/Mn ratio. Similar behaviour of Fe and Mn could be expected in the Kaunas Reservoir. It is known that temporary stratification is established in the Reservoir during summer time, and oxygen is depleted in deep places during hot weather periods [4]. The decreased sedimentary Fe concentrations in the deepest places of the Kaunas Reservoir confirm the fact of oxygen depletion. However, Mn concentrations increase instead

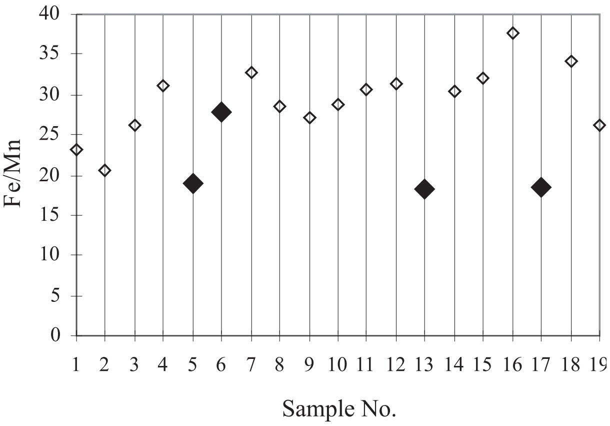

Fig. 4. Fe/Mn ratio. Dark squares show the ratios in the samples taken from places deeper than 20 m.

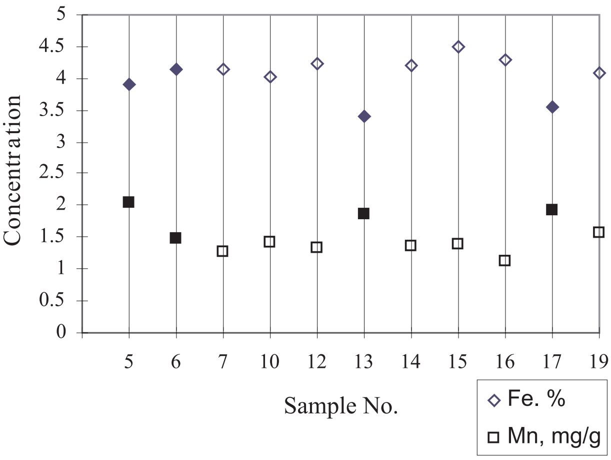

Fig. 5. Fe and Mn concentrations in the accumulation zone. Dark squares show the concentrations in the samples taken from places deeper than 20 m.

of decreasing even more than Fe concentrations. One of the possible explanations can be secondary accumulation, when Mn is transported from the nearshore sediments to the open water areas and precipitated again in the deepest zones of the Reservoir. Regarding sample No.6 – with a view to all the performed analysis, it could have been taken from the slope. That would explain why its Mn concentration has not increased compared to other samples.

Metals in the Sediments of the Nemunas River

There are several point sources, including industrial centres and inflowing rivers, which can be expected to contaminate the sediments of the Nemunas river with heavy metals. Such industrial centres are the towns of Alytus (textile and metal industries), Kaunas (metal, electronical, textile, furniture industries) in Lithuania, Neman and Sovetsk (pulp and paper industry) in Kaliningrad region. Big tributaries are the Neris, the Nevėžis, and the Šešupė rivers. On these rivers some important industrial towns are situated. The Neris river gets the effluents from Jonava (chemical industry) and from the capital Vilnius, the Nevėžis receives the effluents from Panevėžys (metal and electronical industries) and from Kėdainiai (chemical industry).

The distribution of metals in sediment fraction <63 µm shows a very clear pattern of anthropogenic impact on the Nemunas river (Fig. 6). The impact of Kaunas contributed with the impact from the Neris and Nevėžis rivers results in higher sediment metal concentrations in the middle part of the river compared to those in the upper part of the river. The sediment metal concentrations again decrease in the lower part of the river. For Zn, however, concentrations remain elevated all the way down to the mouth. The concentrations in the Kaunas Reservoir, situated just upstream from Kaunas city, are very close to those upstream in the river without indicating an increased contamination due to the lower flow velocity.

Several types of metal concentrations were used as the reference concentrations in order to evaluate the degree of anthropogenic impact (Table 3). First of all, metal concentrations in the sediments of various Lithuanian rivers were used for comparison [11]. These concentrations were measured in bulk sediments taken from river areas, where sedimentation dominates. The composition of riverine sediments is dependent on the composition of soil and bedrock in the catchment area of the river. Therefore secondly, metal concentrations in soils of Lithuania were used for comparison [11, 12]. Then concentrations were compared with concentrations in the sediments of Latvian rivers (the neighboring country) [13]. And finally, metal concentrations in the average shale were used for comparison with a world-wide background [14]. According to [15, 16] and others, there are serious flaws associated with the concept of average background. Constant background values are not supported by worldwide survey data, which indicate that the natural abundance of trace elements in many surface samples can vary even over short distances. Nevertheless, such a comparison provides a broader view on sediment quality in the water body being investigated.

Although there are cases with very high riverine sediment metal concentrations according to [11], normally metal concentrations in soils and sediments of Lithuania

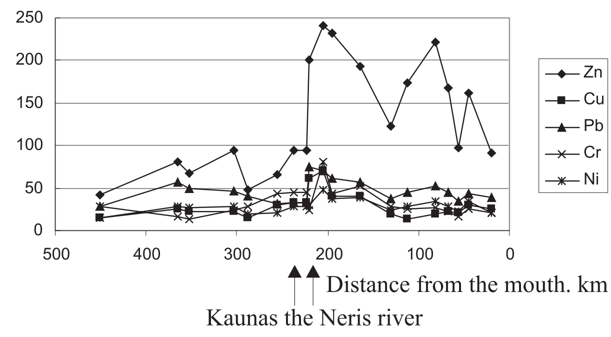

Fig. 6. The profile of sediment metal concentrations (in <63 µm fraction).

Table 3. Comparison of heavy metal concentrations in sediments of the Nemunas river with concentrations in sediments of other rivers, in soils, and in average shale.

Media	Zn, µg/g		Cu, µg/g		Pb, µg/g		Ni, µg/g		Cr, µg/g		
Nemunas, km from the mouth	in < 63 µm fraction	in bulk sediments	in < 63 µm fraction	in bulk sediments	in < 63 µm fraction	in bulk sediments	in < 63 µm fraction	in bulk sediments	in < 63 µm fraction	in bulk sediments	Organic matter,%
451	43	3.1	16	0.7	28	2.1	16	1.4	29	1.6	0.61
365	81	3.8	25	0.6	56	2.8	29	1.4	17	1.1	0.33
352	67	3.4	23	0.5	50	2.1	27	1.2	14	0.9	0.64
303	94	2.8	22	0.5	46	2.1	28	1.1	24	1.3	0.56
288	48	20	15	8.0	40	19	19	9.0	28	15	7.31
255	66	48	31	23	32	22	21	15	44	34	9.85
220	201	73	62	24	76	34	30	13	24	11	8.30
205	241	17	70	4.7	70	5.3	48	3.6	81	4.9	0.41
195	232	7.4	40	1.1	61	3.6	38	1.8	43	1.7	0.59
164	193	6.9	41	0.8	57	2.9	38	1.5	52	1.5	0.57
131	122	7.1	20	0.7	38	3.0	23	1.6	28	1.2	0.35
112	174	6.3	14	0.5	45	2.3	28	1.2	26	1.1	0.46
82	222	11	20	0.6	53	2.4	34	1.6	27	1.3	0.35
68	167	8.6	23	0.6	45	2.4	28	1.5	22	1.1	0.61
56	97	13	20	2.2	35	7.9	22	3.6	16	2.6	1.68
45	161	11	30	0.7	43	2.3	34	1.5	25	1.2	0.48
20	91	57	26	15	39	21	20	11	21	12	8.21
Lithuanian rivers, median 1)		42.4		10.4		14.9		13.2		33.3	
Lithuanian rivers, ranges 2)		1.6–3053		0.5–325		1.2–126.1		0.4–1123		1.5–5822	
Latvian rivers, ranges 3)			2.03–16.25		9.21–65.5		1.305–24.38				1.15–12.7
Topsoil 4)		7–60		2–32		2 – 36		2 – 33		5 – 44	
Topsoil, middle Nemunas basin 5)		33.1		9.4		17.4		13.4		36.7	
Topsoil, lower Nemunas basin 6)		28.9		10.3		15.5		14.1		41.1	
Average shale 7)		95		45		20		90		68	

1) Various Lithuanian rivers, median values [11]; 2) Various Lithuanian rivers, concentration ranges [11]; 3) Latvian rivers, concentration ranges [13]; 4) Topsoil of Lithuania, concentration ranges [12]; 5) Topsoil of the middle Nemunas basin, median values [11]; 6) Topsoil of the lower Nemunas basin, median values [11]; 7) Average shale [14]

and the region are lower than the estimated world averages. According to the current investigation, metal concentrations in the sediments of the Nemunas river in general are within the limits of the concentrations used for comparison. Extreme concentrations have not been detected in sediments of the Nemunas river. Nevertheless, the impact of Kaunas and the Neris river (220 – 205 km away from the mouth) results in the concentrations exceeding the background and average values. Zn levels remain high all the way down to the mouth. According to the data from the Environmental Protection Agency, in 2004, for example, 6.544 tones of Zn were discharged into the surface waters from Kaunas city, while this number for the whole of Lithuania was 9.77 tons [4].

It is important to notice, that the used digestion gives the results, which are 80-100% of the total concentrations of the measured metals, but for Cr the digestion is only approximately 50% effective. Therefore, Cr concentrations measured in this study should be used to trace the change of Cr along the river rather than estimate the degree of contamination.

Fe, Mn and Ca are among the most abundant metals in the earth's crust. The major cations Fe and Ca have high initial natural concentrations in the sediments; therefore, they are less likely to be influenced by anthropogenic activities than trace metals. Fe concentration in <63 µm fraction of the Nemunas river sediments varies from 1.21% to 3.84%. The downstream part of the river seems to be richer in iron than the upstream (Fig. 7b). The sediments are enriched with Ca (Fig. 7c). Ca concentrations, in contrast to Fe, are slightly higher in the upstream part of the river. The concentrations in fraction <63 µm vary between 7.1% and 17.4%. There are natural reasons behind this enrichment – bedrocks comparatively rich with carbonate and calcerous soils in the catchment area, high Ca concentrations in the river water (57.1 – 69.3 mg/l) [4]. Also, concentrations of Mn in fraction <63 µm are elevated (Fig. 7a). It can be explained by natural reasons and anthropogenic impact. The waters of the Nemunas river carry big amounts of Mn (0.091 – 0.187 mg/l) [4]. According to the monitoring data, the concentrations of Mn in water along the river are rather uniform and high starting already from the Belorussian–Lithuanian border. Mn concentrations in bulk sediments according to the current investigation vary from 115 µg/g to 994 µg/g, the concentrations in silt/clay (<63 µm) are 800 – 12800 µg/g. The ratio between the concentrations in silt/clay fraction and in bulk sediments for Mn is higher than for the rest of the measured metals. Mn seems to be almost exceptionally concentrated in silt/clay fraction. The correlation coefficient between Mn concentration in silt/clay fraction and the percentage of silt/clay fraction in the sample itself is -0.563. If the results from sampling points at 205 km and 195 km are eliminated from the calculations, the correlation coefficient becomes -0.710. This suggests that Mn concentration in fraction <63 µm is inversely proportional to the percentage of the fraction in samples. There is a constant amount of Mn getting into the bottom sediments all along the river, but the size of fine-grain fraction itself is different, resulting in non-uniform Mn concentrations. However, the impact of Mn concentrations downstream from Kaunas and the Nevėžis river (205 km and 195 km) on the correlation coefficient shows that the elevated concentrations in these locations are not only due to the above-mentioned effect, but also due to the anthropogenic activities.

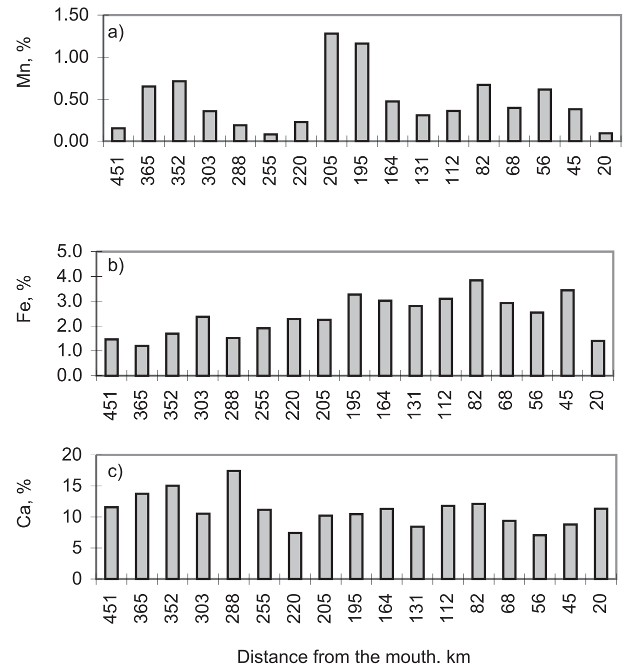

Fig. 7. Mn, Fe and Ca concentrations in sediments (<63 µm fraction) of the Nemunas river.

Conclusions

The sediment metal concentrations (in <63 µm fraction) show a clear pattern of anthropogenic impact on the Nemunas river. The effluents from the city of Kaunas contributed with the impact from the Neris and Nevėžis rivers result in the highest metal concentrations in the middle part of the Nemunas. The concentrations again decrease in the lower part, but not for Zn. In spite of obvious anthropogenic impact, metal concentrations remain within the limits of global, regional and local concentration levels.

Metal concentrations in the sediments of the Kaunas Reservoir are close to the concentrations in the upstream part of the Nemunas. Although it is a part of the river, the sediment characteristics, including metal distribution, were found to follow bottom dynamic zones like in the lakes.

An unusual Fe/Mn ratio – the lowest in the deepest places – is characteristic of the Kaunas Reservoir. Fe concentrations confirm the occurrence of anoxic hypolimnion, whereas Mn concentrations indicate the possibility of Mn transport from the nearshore sediments to the deepest places.

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