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Metals in sediments of inland waters of Latvia

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Multielement analysis (by means of instrumental neutron activation analysis — INAA) of sediments in streams and lakes in Latvia was conducted. Total element concentrations, their variability and their speciation forms in sediments (exchangeable, carbonate bound, iron-manganese oxide bound, organic matter bound and residual) were compared. Increased metal concentrations were found in the lower reaches of the largest rivers and locally around known industrial pollution sources. Metal concentrations in stations from different regions of Latvia were related to natural geochemical processes and contamination levels. Metal speciation analysis showed that the dominant metal species were residual metals and those bound to organic matter. Residual and carbonate-bound forms dominated only in rhitral regions of rivers. The concentrations of exchangeable metals increased below pollution sources. Metal concentrations were compared with their geochemical mean values.

Introduction

Trace elements, and especially so-called heavy metals, are among the most common environmental pollutants, and their occurrence in waters, sediments and biota indicates the presence of natural or anthropogenic sources (Förstner and Wittman 1979). The main natural source of trace elements is weathering of minerals. Industrial effluents, non-point pollution sources, as well as atmospheric precipitation (Salomons and Förstner 1984), can also be sources of increased concentrations of heavy metals. Air masses supplying acidic pollutants also carry significant amounts of certain metals which contaminate the terrestrial and, in particular, aquatic environments. However, concentrations of metals and their actual impacts can be greatly modified due to interaction with natural water ingredients (Pettersen *et al*. 1993). Therefore, knowledge of the concentrations of trace elements is desirable for the estimation of pollution levels of waters and the determination of background values of metal concentrations in corresponding regions. Rivers serve as conveyors for transport of dissolved and particulate matter from continents to seas and oceans (Martin and Meybeck 1979, HELCOM 1998). In case of anthropogenic pollution, substantial trace element accumulation in sediments may take place. Trace element metal concentrations in waters and aquatic ecosystems have been studied world-wide (Borg and Johan-

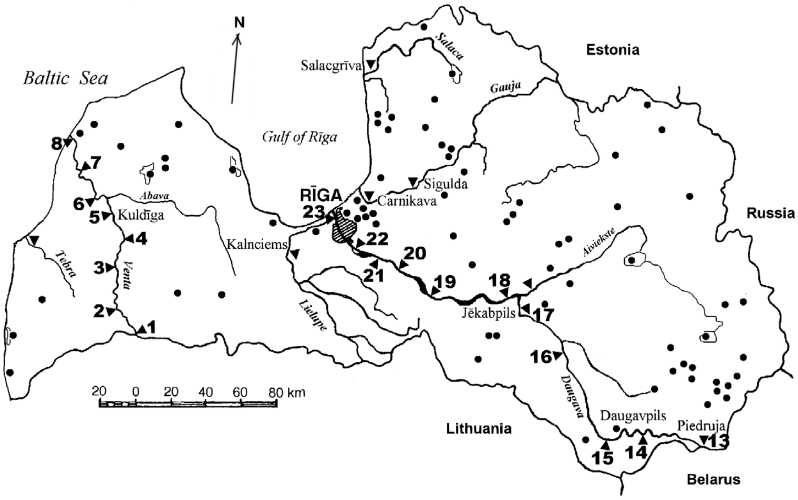

Fig. 1. Study area. Sampling stations on rivers(▲) and lakes (●).

son 1989, Gadh *et al.* 1993, Lenvik *et al.* 1978, Runnels *et al.* 1992, Turekian 1969, Dekov *et al.* 1998). Heavy metals have been studied in the Gulf of Riga (Leivuori *et al.* 2000), but there are few publications on their concentrations in the rivers of Latvia (Kļaviņš *et al.* 1995, 2000). The objectives of the present study were to determine the trace element concentrations and their speciation forms in sediments of rivers in Latvia and to evaluate the general pollution levels in inland waters of Latvia.

Material and methods

Surface sediment samples (0–2 cm for the studied sediments) were collected in the largest rivers of Latvia (Venta, Lielupe, Daugava, Gauja, Salaca) along their watercourses (29 sampling stations), in several small rivers, as well as in some lakes (Fig. 1) during 1992–1999 (June–September). Sediment columns were sampled by a core sampler and cut into 4 cm sub-sample slices. Samples were sealed in plastic bags and stored frozen until drying.

Metal concentrations were determined by flame atomic absorption spectrometry (Perkin Elmer 403). Limits of detection were (μg l^{-1} in 100 μl measuring solution): Cd — 0.003, Co — 0.02, Cu — 0.02, Mn — 0.01, Zn — 0.001, Pb — 0.05. For analytical quality control of total metal concentrations, the following SRMs were used: Marine Sediment Reference Materials (BCSS-1, MESS-1) from the National Research Council (Canada). The results from the analyses of SRM were all within the 95% confidence levels of the certified values.

The speciation of metals into exchangeable, carbonate-bound, iron–manganese oxide bound, and organic matter bound fractions was carried out using a sequential extraction procedure as outlined in Table 1 (Tessier *et al.* 1979, Kļaviņš

Table 1. Method of metal speciation analysis in sediments (Tessier *et al.* 1979).

Metal form extracted	Reagents and their concentration	Duration of treatment (hr)	T (°C)
Exchangeable	1.0 M $MgCl_2$, pH 7	2	20
Carbonate-bound	1.0 M CH_3COONa, pH 5	12	20
Fe/Mn oxide-bound	0.1 M NH_2OH +0.01 M HNO_3, pH 2	12	20
Organic/sulphide-bound	a) 30% H_2O_2, 0.01 M HNO_3, pH 2	3	25
	b) 1 M CH_3COONH_4	5	80
Residual	HNO_3:$HClO_4$ (5:1 v/v)	2	100

et al. 1995).

Instrumental neutron activation analyses were carried out using the facilities at the Research Nuclear Reactor at Salaspils, Latvia described in detail elsewhere (Vircavs *et al.* 1995). Samples and standards were wrapped in Al foil for irradiation. Short and long irradiations were made at the following fluxes of thermal and resonance neutrons: $F_{\mathrm{th}} = 1.6 \times 10^{13}$ n cm^{-2} s^{-1}; $F_{\mathrm{res}} = 8.5 \times 10^{11}$ n cm^{-2} s^{-1} (long irradiations: $F_{\mathrm{th}} = (1.2–5.2) \times 10^{13}$ n cm^{-2} s^{-1}; $F_{\mathrm{res}} = (2.1–4.2) \times 10^{11}$ n cm^{-2} s^{-1}). Gamma spectra of the irradiated samples and standards were recorded using a Ge(Li) detector coupled to a 4000 channel analyser (NTA-1024, Hungary, and Nokia LP-4900, Finland). Certified reference material SOIL-5 (International Atomic Energy Agency reference material for multielement determination in INAA) was used as a calibration standard.

Macroinvertebrates in the sediment samples were separated from mud and debris. The various communities were then identified on the basis of dominant taxa. Chironomid larvae were gathered as those retained on a 500 μm sieve. Chemical analyses of water composition were conducted as described elsewhere (Kļaviņš *et al.* 2000).

Results and discussion

The chemical composition of surface waters in Latvia is influenced by geographical, geological, geochemical and many other processes. The surface is characterised by a flat surface topography: 57% of Latvia's territory is located below 100 m above sea level, and only 2.5% of the area reaches 200 m. The surficial geology has been formed from Quaternary glacial and ancient sea sediments and by recent exogenous processes. The most widely distributed parent soil materials are moraine loam and sands which are resistant to weathering processes. More than one half of Latvian soils are humic podsols with a high content of organic matter. Latvia has a dense net of rivers. The total number of rivers is 12 500, of which 770 (6%) are longer than 10 km. Total length of rivers is ~ 37950 km and the mean density of the river network is 588 m per 1 km^2. There are 2256 lakes having an area of more than 1 ha. The mean precipitation in the studied river basins ranges from 600 to 900 mm per year. Mean annual runoff is 35 km^3, of which only 15 km^3 (43%) is formed in the territory of Latvia. The studied basins (Fig. 1) are representative of Latvia in their aquatic chemistry and land-use patterns, but also several representative small rivers and lakes were considered in study (Table 2).

The greater part of the area of the river and lake basins is covered by forests, but also bogs are important. The dominance of these natural habitats indicates a rather low level of anthropogenic impact. Concentrations of Ca^{+2}, Mg^{+2}, Cl^-, SO_4^{-2}, HCO_3^-, and NH_4^+ in the river

Table 2. Characteristics of rivers studied.

River	Basin size (km^2)	Length (km)	Water runoff (km^3 y^{-1})	Forest area (%)	Bog area (%)	Agricultural area (%)
Daugava	87900	1005	20.4	43	5	50
Dubna*	2780	120	0.5			
Aiviekste*	9160	114	1.81			
Lielupe	17600	119	3.6	22	3	71
Misa**	862	108	0.22			
Iecava**	1166	136	0.26			
Venta	11800	346	2.9	32	5	62
Gauja	8900	452	2.2	47	5	48
Tūlija***	57		0.018			
Tebra	585	69	0.18	38	6	55
Salaca	3420	95	0.95	34	15	45

* Daugava river basin, ** Lielupe river basin, *** Gauja river basin.

Table 3. Characteristics of lakes studied.

	Average	Maximal	Minimal
Area (*f*) (km^2)	7.9	80.7	0.06
Drainage area (*F*) (km^2)	233.5	2515.0	1.4
Altitude (m)	81.5	203.0	0.1
Average depth (m)	3.9	16.5	0.4
Maximal depth (m)	12.1	65.1	1.1
Lake volume × 10^6 (m^3)	52.7	405.0	3.0
Δf*	32.3	299.0	0.5
Forests in drainage area (%)	50.0	10.0	80
Cultivated lands in drainage area (%)	29.0	10.0	51
Bogs in drainage area (%)	24.0	1.0	97
pH	7.69	3.74	9.10
Conductivity (μS m^{-1})	198	22	903
Color (°APHA)	41	11	171
Ca^{+2} (mg l^{-1})	26.1	1.0	96.1
Pb^{+2} (μg l^{-1})	0.09	0.01	2.20
Ni^{+2} (μg l^{-1})	0.52	0.10	3.02
Cu^{+2} (μg l^{-1})	0.56	0.18	2.46
Zn^{+2} (μg l^{-1})	3.35	0.40	33.50
NO^{-}_{3} (mg l^{-1})	0.4	0.0	6.9
PO_4^{-3} (μg l^{-1})	14	4	290

* $\Delta f = (F - f)/f$

Table 4. Mean water chemistry of the studied rivers (1993–1997 seasonal samples).

River	HCO_3^- (mg l^{-1})	SO_4^{-2} (mg l^{-1})	Ca^{+2} (mg l^{-1})	Mg^{+2} (mg l^{-1})	Cl^- (mg l^{-1})	COD (mg l^{-1})	N-NH_4^+ (mg l^{-1})	Cu (μg l^{-1})	Pb (μg l^{-1})	Zn (μg l^{-1})	Cd (μg l^{-1})
Daugava	187.3	28.8	43.3	12.8	14.2	31.2	0.5	1.2	0.1	4.4	0.06
Lielupe	310.0	119.2	96.2	24.0	25.5	39.6	0.6	2.5	0.3	4.1	0.09
Venta	295.5	44.8	52.5	17.4	19.5	27.3	0.4	0.9	0.3	2.7	0.04
Gauja	254.1	34.0	52.6	13.6	14.5	28.5	0.3	1.9	0.7	4.8	0.03
Salaca	244.4	31.9	54.5	13.2	12.8	32.2	0.4	2.3	0.6	3.3	0.02
Ciecere	225.0	42.0	40.8	26.0	12.7	28.5	0.3	1.0	0.1	2.9	0.05
Abava	298.7	50.8	83.8	24.4	15.8	28.5	0.3	1.1	0.1	3.2	0.05

Table 5. Mean metal concentrations in surface waters of Latvia (μg l^{-1}).

Metal	Present work	Norway[1]	Background concentrations, world average[2]	Background concentrations, Sweden[3]	River Rhine[4]
Cu	0.56	–	1.00	0.70	3.4
Cd	0.02	0.17	0.02	0.03	5.3
Co	0.06	0.16	0.08	0.20	0.34
Zn	3.35	24	10	3.00	33.0
Mn	3.00	–	6	40.00	5.2
Pb	0.10	–	0.2	0.40	5.7
Ni	0.34	–	0.3	0.50	2.0

[1] Lenvik *et al*. 1978; [2] Turekian 1969; [3] Borg and Johanson 1989; [4] Anonymous 1976

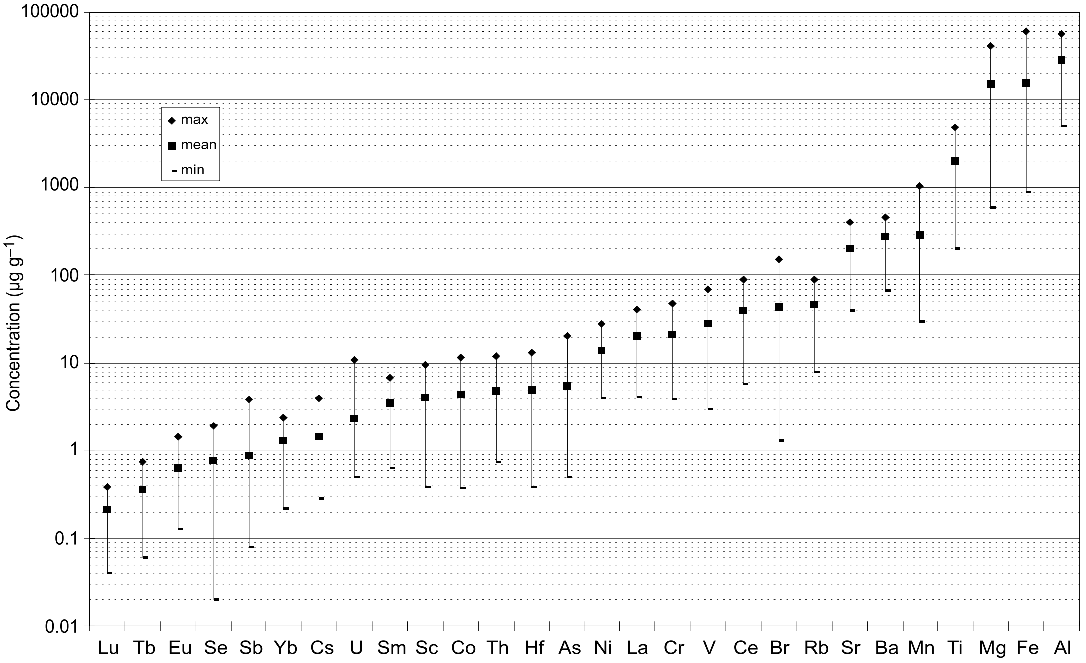

Fig. 2. Trace element concentrations in sediments of lakes and rivers in Latvia.

and lake waters, in comparison with mean values in other water bodies of Latvia, indicated that the selected samples are quite representative for Latvia (Table 3). Latvian inland waters are characterised by comparatively high concentrations of HCO_3^- and organic matter (due to eutrophication and wetland drainage), but low concentrations of total dissolved solids (Table 4). The selected water bodies have not been subjected to major anthropogenic pollution, with the exception of the lowest reaches of the rivers and selected sites on the Daugava river, below cities such as Daugavpils, Līvāni and others. Therefore, the typical water chemistry for all studied water bodies may be considered to be a fairly good average for the whole country.

Mean metal concentrations in river waters of Latvia are summarised in Table 5 and compared with concentrations in Norwegian rivers and estimates of world averages (Lenvik *et al.* 1978, Turekian 1969). The mean metal concentrations in rivers of Latvia are generally lower than the estimated world averages, metal concentrations in other regions of world and even lower than assumed metal background concentrations (Salomons and Förstner 1984, Lithner 1989) determined for industrially developed countries. None of the observed concentrations in Latvia seem to be alarmingly high from a toxicological point of view (Lithner 1989). Nearly all of the observed element concentrations may be explained by natural sources and processes. However, metal concentrations are elevated below large cities (Rīga, Daugavpils, Ventspils, Kuldīga, Jelgava), and these sources influence the metal concentrations in river waters along the watercourses.

Sediments can accumulate substantial amounts of persistent xenobiotics (Burton 1992). The accumulated substances may be released in a changing environment, thus causing environmental contamination. Sediments of rivers and lakes in Latvia are rich in organic matter, and nutrient concentrations may be quite high (Kļaviņš *et al.* 2000). The concentrations of metals in the upper layer of the studied sediments vary greatly in Latvia (Fig. 2). In total, concentrations of 28 elements were determined. The concentrations range from 60 mg g^{-1} Fe to 0.04 μg g^{-1} Lu. Variability of element concentrations (c_{max}/c_{min}) differs: the highest variability is for Br (c_{max}/c_{min} = 117), and lowest for Ba (c_{max}/c_{min} = 7). Considering their concentrations, the elements found can be divided into three groups (Danzer *et al.* 1976):

- major elements that compose of 10^4–10^5 μg g^{-1} of the sediment mass (Al, K, Ca, Fe),
- minor elements in a concentration range from 10^4–10 μg g^{-1} (Na, Mg, Ti, V, Cr, Mn, Ni, Cu, Zn, Sr, Ba, Ce), and
- trace elements with concentrations smaller than 10 μg g^{-1} (Sc, Co, As, Rb, Sb, Cs, La, Sm, Eu, Tb, Yb, Hf, Ta, Th, U).

The element concentrations (c) in sediments were compared (Table 6) with element clark (C_c) values in Earth's crust and sediments (Bowen 1979). For major and minor elements, the present concentrations in sediments are lower than their clarks in sediments and the crust: $c < C_c$ (with the exception of Mg ($c_{Mg} \approx C_{Mg}$) and Br ($c_{Br} > C_{Br}$). Concentrations of the trace elements Lu, Tb, Eu, Yb, Cs, Sm, Sc, Co, Th in the studied sediments are substantially lower ($c < C_c$) than in the Earth's crust and mean clarks in sediments worldwide, but for Sb, As, U, and Hf, there exist specific relationship patterns for each elements ($c_{As, Sb} > C_{As, Sb}$, $c_{U, Hf} \gg C_{U, Hf}$).

A measure of the relative concentration of elements in the studied environment is their concentration clark — a ratio between their

Table 6. Element concentrations (*c*) in sediments of inland water bodies in Latvia in comparison with element clarks (C_c) (Bowen 1979).

Element	*c* (μg g^{-1})	C_c (μg g^{-1})	
		Mean in Earth's crust	Mean in sediments
Major elements (10^4–10^5 μg g^{-1})			
Mg	14000	23000	14000
Al	28100	82000	72000
Fe	1240	41000	41000
Minor elements (10^4–10 μg g^{-1})			
Ni	14.0	80	52
La	22.0	32	41
Cr	17.1	100	72
V	25	160	105
Ce	37.7	68	83
Br	31.3	0.37	19
Rb	44.0	90	135
Sr	210	370	320
Ba	320	500	460
Mn	205	950	770
Ti	1900	5600	3800
Trace elements (< 10 μg g^{-1})			
Lu	0.23	0.51	0.7
Tb	0.40	1.10	1.0
Eu	0.69	2.10	1.3
Se	0.70	0.05	0.4
Sb	0.73	0.20	1.2
Yb	1.40	3.30	3.6
Cs	0.95	3.00	4.2
U	1.90	2.40	3.1
Sm	3.56	7.90	6.4
Sc	3.85	10.00	10.0
Co	3.50	20.00	14.0
Th	4.50	12.00	9.6
Hf	5.10	5.30	2.5
As	4.65	1.50	7.7

concentration in sediments and clark (c/C_c) — or the dissemination clark (C_c/c). The values of concentration clarks and dissemination clarks for elements in sediments in rivers and lakes in Latvia are summarized in Table 7.

From element clark concentration data, an element dissemination row has been developed in which elements are arranged in order of increasing dissemination clark value and decreasing concentration clark value: Ni > V > Cr >Mn > Tb > Lu > Fe > Al > Sc, Cs, Rb > Yb > Eu > Ti > Sm, La > Th > Ce > Ba > Sr > Mg > U, Sb, Se > As > Hf > Br. The element position in this row illustrates its tendency to disseminate in the environment, mobility of the element and thus possible danger in case of environmental contamination.

Metal concentrations are commonly increased in the lowest reaches of rivers below pollution sources. In river regions which are minimally polluted, regional differences in metal concentrations can be explained by natural means, for example by comparing metal concentrations in rivers in Vidzeme (Gauja, Salaca) and Kurzeme (Venta and small rivers).

Often, the determination of total metal concentrations does not allow to extrapolate the obtained results to biological consequences of metal contamination. Metal speciation analysis, proposed by Tessier *et al.* (1979), can be used to

Table 7. Concentration (*c*), concentration clarks (c/C_c) and dissemination clarks (C_c/c)for elements in sediments of inland water bodies in Latvia.

Element	c (μg g^{-1})	c/C_c*	C_c*$/c$	c/C_c**	C_c**$/c$
Major elements (10^4–10^5 μg g^{-1})					
Mg	14000	0.65	1.54	1.00	0.99
Al	28100	0.38	2.66	0.34	0.30
Fe	1240	0.34	2.90	0.39	0.35
Minor elements (10^4–10 μg g^{-1})					
Ni	14.0	0.18	5.67	0.27	3.69
La	22.0	0.64	1.57	0.50	2.00
Cr	17.1	0.21	4.76	0.29	3.48
V	25	0.18	5.65	0.27	3.71
Ce	37.7	0.59	1.70	0.48	2.08
Br	31.3	118.62	0.0008	2.31	0.43
Rb	44.0	0.52	1.94	0.34	2.90
Sr	210	0.55	1.80	0.64	1.56
Ba	320	0.56	1.78	0.61	1.64
Mn	205	0.30	3.28	0.32	3.17
Ti	1900	0.36	2.74	0.54	1.86
Trace elements (< 10 μg g^{-1})					
Lu	0.23	0.41	2.44	0.30	3.33
Tb	0.40	0.33	3.03	0.36	2.78
Eu	0.69	0.30	3.28	0.53	1.87
Se	0.70	15.40	0.06	1.90	0.52
Sb	0.73	4.40	0.23	0.58	1.71
Yb	1.40	0.40	2.48	0,36	2.77
Cs	0.95	0.47	2.11	0.33	3.00
U	1.90	0.96	1.04	0.68	1.48
Sm	3.56	0.44	2.27	0.55	1.83
Sc	3.85	0.25	4.00	0.41	2.44
Co	3.50	0.22	4.62	0.31	3.26
Th	4.50	4.04	0.25	0.50	1.98
Hf	5.10	0.92	1.09	1.96	0.51
As	4.65	3.58	0.28	0.64	1.57

* Mean C_c in Eart's crust (Bowen 1979); ** Mean C_c in sediments (Bowen 1979).

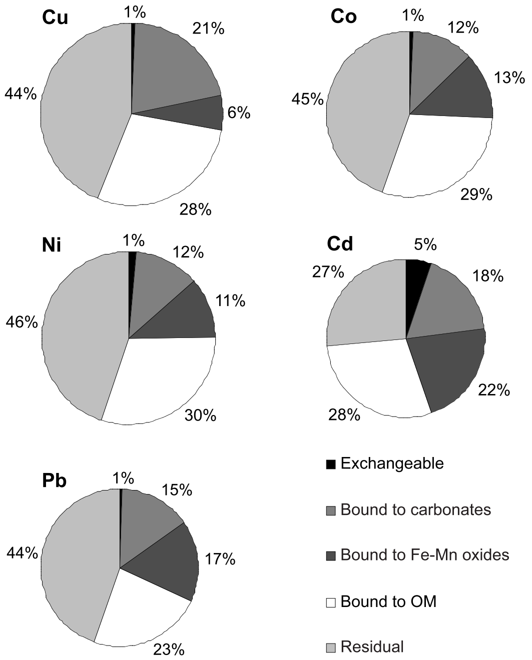

Fig. 3. Distribution of metal speciation forms in sediments of rivers in Latvia.

determine metal fractions released in controlled conditions, thus approximating metal leakage to the natural environment. It is recognized that this method allows to predict metal impact on biota in aquatic ecosystems more correctly than total metal concentrations (Morrison *et al*. 1996). The metal concentrations associated with different phases in lakes according to the Tessier *et al.* (1979) scheme are given in Fig. 3.

Metal speciation analysis of sediments in inland water bodies of Latvia indicated that only a very small portion of the total metal in sediment is easily available (found in exchangeable fraction). The proportion of metal as exchangeable increases in contaminated sites where pollution sources are evident. In more polluted sites, metal concentrations in the Fe/Mn oxide-bound and organic fractions are also higher. However, in sampling stations with background levels, the metals are mostly bound in organic, residual and carbonate fractions. Lead and copper concentrations in organic phases are relatively lower than in the case for cadmium or zinc. In all cases studied, the major portions of metals are stably bound in the residual fraction which is chemically and biologically inert. Metal speciation analysis showed also different types of metal binding. Copper, more than other metals, showed a tendency to prefer the organic phase. The relatively preferential carbonate binding of Cd and Zn can be attributed to the relatively high stability of cadmium and zinc carbonates under the pH conditions and river bed conditions common for Latvia, as well as by the characteristic precipitation of these compounds with calcium carbonate (Vaithiyanathan *et al.* 1993). The relative enrichment of cadmium in the exchangeable fraction indicated the potential of this metal to have a direct impact on biological processes in the aquatic environment.

The heavy metals accumulated in sediments may be portrayed in concentrations in benthic organisms which, thereby, can serve as bioindicators. When further bioconcentration in food webs occurs, human health may be affected. Therefore, the community composition of benthic macroinvertebrates in rivers was studied.

The macrobenthos community composition and distribution was related to the sediment chemical composition, for example, in the river Venta (Fig. 4). Molluscs dominate in biomass in polluted segments of the Venta, followed by oligochaetes, but the communities are more diverse in less polluted sites.

Pollution levels can be monitored using saprobity indexes calculated based on community composition of benthic organisms. The changes of saprobity index along a waterflow, in comparison to changes in metal concentrations (Fig. 5), suggest that saprobity is rather stable, except in lower reaches of rivers where the metal concentrations are highest. Thus, the comparatively minimal metal contamination levels directly do not influence this complex indicator of riverine ecosystems. For analysis of contamination impacts in case of minimal contamination levels, community structure analysis of benthic organisms can be a better indicator.

Conclusion

The metal concentrations in rivers of Latvia are around regional background values. This may

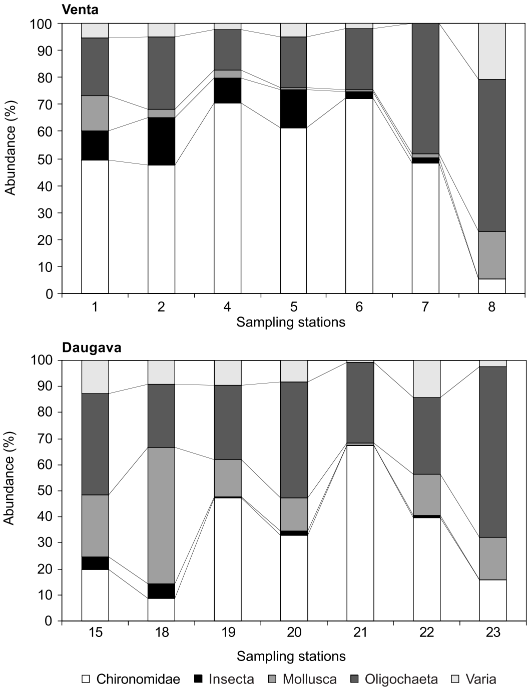

Fig. 4. Composition of benthic invertebrate communities in the Venta river in 1994 and Daugava river in 1991 (summer seasons).

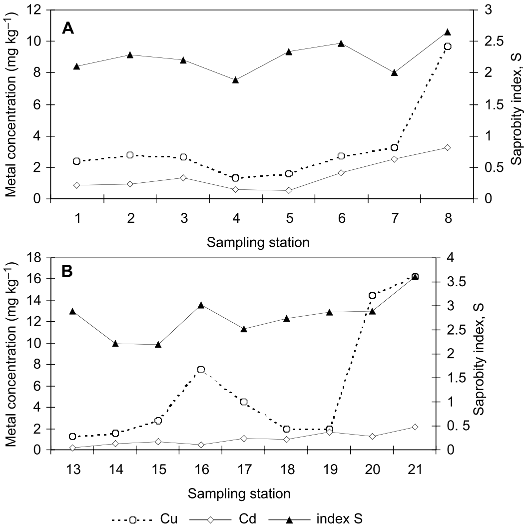

Fig. 5. Changes in copper and cadmium concentrations and saprobity index (S) in sediments along the Venta (A) and Daugava (B) rivers.

be explained by geochemical factors and the abundance of sedimentary deposits in the drainage basins of rivers in Latvia, as well as by minimal anthropogenic loads. Metal speciation in sedimentary phases shows considerable differences, both among metals and among their binding to different phases as indicated by speciation analysis. The metal accumulation processes also influence the loads of metals entering the Baltic Sea from Latvia.

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