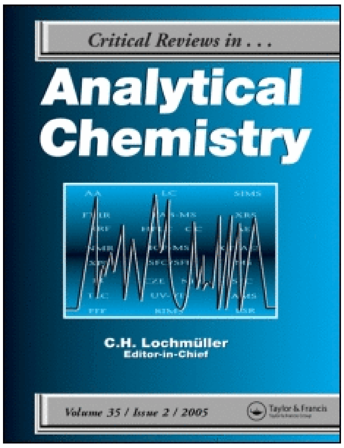

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POLLUTION OF THE SURFACE WATERS OF LATVIA WITH HEAVY METALS

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INTRODUCTION

Trace elements, and especially the so called heavy metals, are among most common environmental pollutants and their occurence in waters indicate pollution sources [1].

The main natural sources of metals in waters are weathering of minerals. In the same time different industrial effluents and non-point pollution sources, as well as atmospheric precipitation [2] can be sources of increased concentrations of heavy metals. So, air masses supplying acidic pollutants to Scandinavia also carry significant amounts of certain metals, which give rise to significant contamination of the terrestrial and aquatic environments in particular [3]. However, concentrations of metals and their actual impact can be greatly modified due to interaction with different natural water ingredients [4]. Therefore knowledge of the concentrations of heavy metals is desirable for the estimation of pollution levels of waters and the determination of background values of metal concentrations in corresponding regions. Heavy metal concentrations in river waters have been analysed worldwide [5-8], but there are no publications on their concentrations in waters of the Latvia.

The aim of this study is to determine heavy metal concentrations in the major rivers of Latvia and to compare them with metal levels in other countries.

EXPERIMENTAL

The rivers and lakes investigated and the sampling sites used are listed in Table 1, Figure. Seasonal samples (February, April, Jule, October) were taken from rivers and lakes in 1993-1995 at a depth 0.5 m (total 12 samples in each sampling site). Samples were collected in 1 liter polyethylene bottles which had previously been washed with detergent, water and 2 M high-purity concentrated nitric acid, water. Samples were acidified with 5 ml high-purity concentrated nitric acid. The acidified samples were analysed for different heavy metals within 2 weeks of collection with a Perkin Elmer 403 AAS after enrichment of metals with extraction with dithizone [9]. A more complete description of analytical procedures is given elsewhere [10]. Each of the samples were analysed in triplicate. Minimum detection limits for Cu, Cd, Co, Pb, Zn, Ni and Mn were found to be respectively (μg/l): 0.01; 0.002; 0.002; 0.05; 0.01; 0.01; 0.01. The reliability and accuracy of analytical results were checked using blank and reference (SLRSS-2 river water, CASS-2 coastal seawater; Analytical Chemistry Standards, Canada) samples and during Latvian National laboratory intercalibration program.

In the same samples water chemical composition were determined. pH, conductivity and total dissolved solids was measured immediately on arrival of samples to the laboratory (using Hach Model 44600 Conductivity/TDS Meter). Color was determined spectrophotometrically at wavelength 455 nm in the PtCo scale. Cl was determined by silver nitrate titration, sulfates by turbidimetric method and hardness by EDTA titration in presence of Eriochrome Black T. Nitrates were determined using diazotization of gentisic acid after reduction of nitrates with cadmium. Phosphorous content was determined with ammonium molibdate.

The concentrations of Ca, Mg were determined using a flame photometer Flapho 3 (Carl Zeiss). All analytical methods used were based on the standard methods for examination of water and waste water [9, 11].

RESULTS AND DISCUSSION

The selected (Fig.) surface water bodies (lakes and rivers) are a representative sample of typical waters in Latvia. The waters have a comparatively high content of hydrogencarbonates and organic matter (originating from eutrophication process and draining from wetlands), but low mineralization (Table 1). Also determination of Ca, Mg, Cl^-, SO_4^{-2}, HCO_3^-, Fe, NH_4^+, NO_2^- , NO_3^-, PO_4^{-3} in the same samples and comparison with mean values in other water bodies of Latvia indicate that the waters of selected water bodies are representative for inland waters of Latvia (Table 1). In the same time most of the selected water bodies has not been subjected to anthropogenic pollution (with exception of lakes situated in the borders of cities - Juglas, Liepājas, Ęģųezers). Therefore, the typical water chemistry for all rivers and lakes may be considered as fairly good average for the whole country.

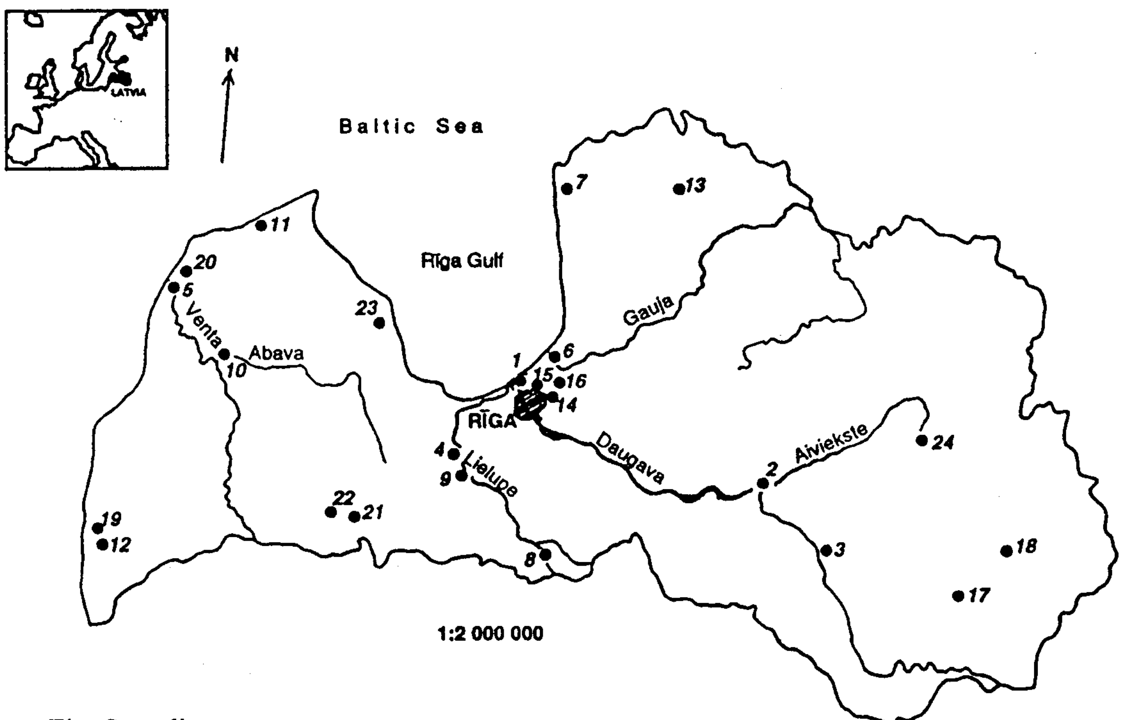

Fig. Sampling area

Sampling stations and mean (1993-1995 seasonal samples) water chemical composition

N°	Sampling site	pH	Color, °Pt/l	NO_3^-, mg/l	PO_4^{-3}, mg/l	Ca^{+2}, mg/l	Mg^{+2}, mg/l	SO_4^{-2}, mg/l	Cl^-, mg/l
Rivers									
1	Daugava	7.20	74	0.65	0.04	30.1	14.6	13.9	12.1
2	Aiviekste	7.25	45	0.37	0.06	43.9	12.6	7.4	33.6
3	Dubna	7.25	50	0.32	0.05	72.7	20.1	16.4	26.4
4	Lielupe	8.00	39	0.45	0.18	89.5	28,4	53.2	21.4
5	Venta	7.80	25	0.23	0.04	65.7	29.2	27.0	30.8
6	Gauja	7.60	98	0.58	0.02	53.3	23.8	15.5	14.9
7	Salaca	7.80	47	0.28	0.02	42.1	9.7	19.7	9.2
8	Mśsa	7.30	45	0.54	0.08	49.3	23.6	45.3	11.3
9	Svete	7.50	55	1.20	0.11	96.3	26.1	69.8	15.2
10	Abava	7.75	31	0.61	0.02	71.5	29.5	47.6	19.5
11	Irbe	7.30	58	0.42	0.05	45.1	13.4	26.9	15.2
12	Barta	7.90	22	0.30	0.01	83.0	8.9	15.8	22.3
Lakes									
13	Burtnieku	8.06	28	1.50	0.10	34.0	13.7	18.9	9.0
14	Juglas	7.40	29	1.70	0.10	70.5	18.8	57.6	14.2
15	Ęģųezers	7.70	26	2.10	0.15	59.5	34.5	62.6	134.5
16	Baltzers	8.10	43	0.70	0.02	59.0	20.0	48.0	180.0
17	Ruųons	7.40	29	0.30	0.007	42.6	13.3	11.6	9.8
18	Rāznas	7.60	18	0.15	0.002	35.5	14.0	10.1	8.0
19	Liepājas	7.60	31	0.80	0.03	52.9	17.0	19.0	143.0
20	Buųnieku	7.30	33	0.60	0.01	28.0	7.5	20.0	12.4
21	Zebrus	7.90	56	0.52	0.03	31.1	15.2	29.6	10.6
22	Cieceres	7.30	73	0.35	0.02	32.6	15.4	27.5	10.9
23	Engures	8.00	35	1.20	0.01	28.9	17.2	16.0	7.1
24	Lubāns	7.90	28	2.20	0.10	74.1	19.3	38.9	15.9

The mean metal concentrations in the major rivers and lakes of Latvia are listed in Table 2. Mean metal concentrations in river waters of Latvia are summarized in Table 3 and compared with data from rivers in Norway and estimates of world averages [5, 12].

The mean concentrations of metals in rivers and lakes of Latvia in general are substantially lower than the estimated world averages, metal concentrations in other regions of world and even assumed metal background concentrations [1, 13] determined for industrially developed countries. Observed concentrations of heavy metals seem not to be alarmingly high from a toxicological point of view [13]. Nearly all of the observed elemental concentrations may be explained by natural sources and processes. However in vicinity of biggest cities it is posible to observe increase of metal concentrations in river waters (Daugava below Riga, Daugavpils) and lakes (lakes Juglas, Liepājas, Ęģųezers). It can be proposed that the same factors influence increase of the metal concentrations in river waters along the watercourses. In all cases, when increased metal concentrations are found, presence of pollution sources (introduction of domestic or industrial wastewaters, dumping of soild wastes) is evident.

Influences of geochemical processes is evident, if analyzing differences in metal concentrations, especially in case of cadmium and lead. Cadmium values in rivers of Latvia are at the same level as background levels in Sweden (in oligotrophic-humic lakes in northernmost Sweden which hitherto have been relatively spared acidification and atmospheric deposition of metals). In relation to the geochemically associated element zinc, the cadmium values in Latvian waters seem surprisingly high. The Zn/Cd ratios of 400-600

Table 1
Concentrations (mean, minimal and maximal values in parenthses from 12 analyses) of heavy metals (µg/l) in rivers and lakes in Latvia

Nr	Sampling site	Cu	Cd	Co	Zn	Mn	Pb	Ni
Rivers								
1	Daugava	0.55 (0.24-1.46)	0.01 (0.01-0.03)	0.05 (0.02-0.13)	3.55 (2.78-3.75)	1.13 (0.95-2.36)	0.06 (0.04-0.24)	0.22 (0.10-0.56)
2	Aiviekste	0.75 (0.34- 0.88)	0.01 (0.01-0.02)	0.05 (0.04-0.09)	3.68 (2.85-6.15)	3.43 (1.65-6.20)	0.05 (0.03-0.07)	0.33 (0.23-0.47)
3	Dubna	0.43 (0.38-0.65)	0.01 (0.01-0.02)	0.06 (0.02-0.08)	3.65 (2.75-4.85)	1.88 (1.70-4.55)	0.05 (0.04-0.16)	0.38 (0.16-0.58)
4	Lielupe	0.65 (0.18-1.65)	0.02 (0.01-0.04)	0.06 (0.03-0.09)	3.67 (1.60-4.38)	4.28 (2.75-5.63)	0.07 (0.04-0.18)	0.24 (0.18-0.34)
5	Venta	0.72 (0.25-1.55)	0.02 (0.01-0.04)	0.08 (0.04-0.10)	2.75 (1.00-5.75)	1.75 (1.23-3.05)	0.04 (0.02-0.17)	0.28 (0.71-1.65)
6	Gauja	0.53 (0.29-0.76)	0.02 (0.01-0.04)	0.07 (0.05-0.10)	2.55 (1.90-4.34)	1.85 (1.34-2.76)	0.09 (0.06-0.16)	0.27 (0.15-1.80)
7	Salaca	0.53 (0.16-1.63)	0.01 (0.01-0.03)	0.06 (0.04-0.09)	2.78 (2.10-3.65)	1.15 (0.75-2.15)	0.10 (0.07-0.16)	0.28 (0.09-1.85)
8	Mūsa	0.46 (0.18-0.58)	0.03 (0.01-0.06)	0.08 (0.06-0.10)	3.20 (1.70-6.65)	1.30 (1.15-2.70)	0.11 (0.09-0.17)	0.22 (0.18-0.96)
9	Svēte	0.64 (0.55-0.93)	0.02 (0.01-0.03)	0.07 (0.06-0.07)	3.95 (1.53-3.54)	2.05 (1.45-2.20)	0.09 (0.08-0.10)	0.56 (0.19-1.93)
10	Abava	0.47 (0.34-0.75)	0.01 (0.01-0.02)	0.08 (0.07-0.10)	2.64 (2.10-4.85)	1.17 (0.70-1.75)	0.11 (0.09-0.14)	0.62 (0.14-1.05)
11	Irbe	0.40 (0.37-0.64)	0.02 (0.01-0.04)	0.06 (0.04-0.08)	2.29 (1.48-2.43)	2.15 (1.85-3.25)	0.12 (0.09-0.14)	0.26 (0.11-0.44)
12	Bārta	0.68 (0.28-1.14)	0.03 (0.02-0.07)	0.05 (0.04-0.07)	2.70 (1.45-3.55)	3.50 (0.45-3.95)	0.09 (0.07-0.15)	0.52 (0.24-1.13)
Lakess								
13	Burtnieku	0.32 (0.25-0.76)	0.01 (0.01-0.03)	0.04 (0.02-0.06)	2.85 (1.75-3.86)	1.63 (1.15-3.24)	0.06 (0.04-0.12)	0.23 (0.17-0.48)
14	Juglas	0.86(0.64-1.15)	0.04 (0.03-0.08)	0.09 (0.05-0.13)	4.34 (2.32-9.15)	2.38 (1.18-4.15)	0.17 (0.12-0.25)	0.73 (0.56-1.34)
15	Ķišezers	0.93 (0.78-1.64)	0.05 (0.03-0.11)	0.09 (0.06-0.17)	8.15 (3.15-11.75)	6.75 (2.75-9.13)	0.18 (0.08-0.29)	0.85 (0.65-1.76)
16	Baltezers	0.48 (0.38-0.65)	0.02 (0.01-0.03)	0.05 (0.02-0.08)	2.38 (2.12-3.16)	2.14 (1.85-4.14)	0.04 (0.03-0.08)	0.18 (0.12-0.45)
17	Rušons	0.35 (0.29-0.76)	0.01 (0.01-0.02)	0.06 (0.03-0.14)	2.14 (1.85-3.74)	1.85 (0.87-3.15)	0.03 (0.02-0.06)	0.24 (0.18-0.39)
18	Rāznas	0.32 (0.23-0.85)	0.01 (0.01-0.02)	0.05 (0.04-0.06)	2.25 (1.63-3.05)	1.95 (0.84-2.15)	0.03 (0.02-0.06)	0.28 (0.21-0.43)
19	Liepājas	0.79 (0.56-1.73)	0.08 (0.03-0.12)	0.09 (0.08-0.11)	14.34 (6.53-21.34)	16.15 (11.32-22.75)	0.14 (0.07-0.21)	0.85 (0.65-1.64)
20	Bušnieku	0.65 (0.64-1.14)	0.03 (0.01-0.07)	0.06 (0.04-0.13)	3.95 (3.12-6.17)	3.15 (1.32-6.75)	0.09 (0.07-0.14)	0.43 (0.28-1.12)
21	Zebrus	0.54 (0.48-0.85)	0.01 (0.01-0.02)	0.04 (0.02-0.07)	3.43 (2.85-4.73)	2.17 (1.85-4.86)	0.06 (0.04-0.12)	0.23 (0.18-0.46)
22	Cieceres	0.52 (0.45-0.76)	0.01 (0.01-0.02)	0.03 (0.01-0.06)	3.25 (2.17-3.85)	2.85 (2.12-6.75)	0.05 (0.05-0.08)	0.15 (0.12-0.39)
23	Engures	0.61 (0.34-0.95)	0.04 (0.01-0.07)	0.08 (0.04-0.17)	4.15 (2.85-6.96)	4.15 (3.17-8.19)	0.09 (0.06-0.12)	0.21 (0.17-0.46)
24	Lubāns	0.39 (0.29-0.58)	0.02 (0.01-0.03)	0.03 (0.02-0.06)	3.65 (3.12-5.14)	3.71 (2.85-4.68)	0.08 (0.04-0.10)	0.27 (0.17-0.39)

has been reported for common types of igneous and sedimentary rocks [12] while a ratio 150 was typical for rivers of Latvia. The substantial difference might indicate that processes other than the weathering of rocks, sucs as atmospheric precipitation [14] and nonpoint sources contribute to the supply of these elements to the rivers. Similarly the concentrations of lead are somewhat increased in comparison with those of other elements.

Table 3
Mean metal concentrations in surface waters of Latvia (μg/l)

Metal	Present work	Norway[5]	Background concentrations, world average [1]	Background concentrations, Sweden [13]	River Rhine [6]
Cu	0.56	-	1.00	0.70	34
Cd	0.02	0.17	0.02	0.03	5.3
Co	0.06	0.16	-	0.20	-
Zn	3.35	24	10	3.00	330
Mn	3.00	-	6	40.00	5.2
Pb	0.09	-	0.2	0.40	57
Ni	0.34	-	0.3	0.50	20

Metal atmospheric deposition can be considered to be important for Latvia [14]. Also, the dominance of quarternary sediments in Latvia and their geochemical composition [15] can principally influence metal concentrations in river waters.

CONCLUSION

The metal concentrations in rivers of Latvia are at a background levels. This may be explained with a geochemical factors and abundance of sedimentary deposits in the drainage basins of rivers in Latvia, as well as minimal anthropogenic load. In the same time in several places direct anthropogenic impacts are evident, regarding influences of point sources both transboundary transport impacts.

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