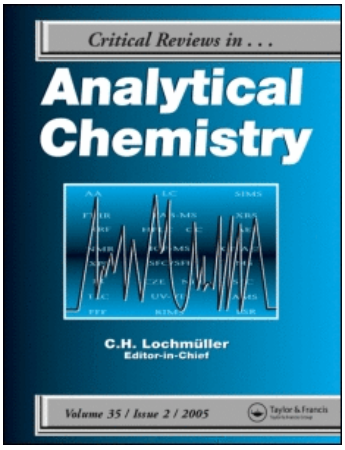

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HEAVY METALS IN THE ENVIRONMENT OF ESTONIA AND IN THE BALTIC SEA

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Introduction

Because of its high sensitivity up to 10^{-11} mol l^{-1} stripping voltammetry is a powerful tool in environmental analysis as so as it allows the direct determination of trace elements in natural waters and their speciation studies at very low concentration level. Complicated content of natural waters ("dissolved" metal, bounded with polymeric ligands, adsorbed on organic and inorganic colloidal particles, possibility of different redox states etc.) presents problems to the analyst (1). More often the "dissolved" metals from the samples are passed through 450 nm filter or "total" metals without filtering are measured. The aim of this paper is to report methods and some results of analysis of precipitations, sea- and freshwater.

Experimental and results

Seawater samples were collected during cruises on the research vessel Aranda in June- July 1994 and October 1996 using Teflon sampling system (if the depth was more than 180 m, samples were taken from bathymeter). Part of the water was filtered through 450 nm filter to determine "dissolved" metals, acidified with Suprapur nitric acid (pH< 2) and irradiated under 800 W UV- lamp during 4 hours. Another part was acidified and UV- digested for analysis on "total" metals. Precipitation samples were filtered and acidified after sampling. Freshwater samples of phreatic, lake- and river waters, collected by the Central Laboratory of Environmental Research were acidified and UV- irradiated.

Voltammetric measurements were provided with a Tacussel Polaropulse PRG5 analyser with rotating disc electrodes (RDE) and an Autolab Electrochemical System (Ecochemie) attached to a 663 VA Stand (Metrohm) with multimode mercury electrode or RDE. For determination of Hg^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} differential pulse anodic stripping voltammetry (DPASV) was used and differential pulse cathodic adsorptive stripping voltammetry (DPCAdsSV) in analyses of Ni^{2+}, Co^{2+}, Mn^{2+} and Cu^{2+}. The electrochemically activated gold RDE in acidified sample with deposition time of τ=10 min guarantees the detection limit of 2 ng l^{-1} Hg^{2+}. The same sensitivity for cadmium and lead was observed on glassy carbon "in situ" deposited thin film RDE when 2 10^{-5} M $Hg(NO_3)_2$ was added into the cell and mercury film was formed during 10 min at deposition potential E_d= -0.8 V. The analyse was provided with E_d= -1.0 V. Because of known difficulties for determination of copper in seawater using ASV, samples were analysed with both, DPASV on RDE and DPCAdsSV on hanging mercury electrode (HMDE) using 8- hydroxychinolin as the ligand at pH= 7.5- 8 (2). In most of cases the results were similar but the sensitivity of the second method occurs to be higher. Nickel and cobalt were measured on HMDE in DPCAdsSV regime with dimethylglyoxim as the ligand and addition of NO_2^- (3) to reach sufficient sensitivity for Co^{2+}. For analyse of manganese the DPCAdsSV with Eriochrom Black T was used (4).

In 1991 the deep waters of the Eastern Gotland Deep (station BY 15) were anoxix , the concentration of H_2S , determined by the cathodic srtipping voltammetry on the silver RDE, arised from 10^{-8} mol l^{-1} on 120 m up to 4.5 10^{-5} mol l^{-1} on 235 m, near the bottom. In 1993/1994, very large volume of saline waters intruded the Baltic Sea from the North Sea.

This caused a sudden redox potential turnover in the bottom waters and serious changes in metal content and speciation (5). The oxygen minimum replaced from 170 m in June to 120 m in August 1994. In 1996 conditions changed again and in October the concentration of H_2S was two times higher if to compare with June, but it was less yet than in 1991.

The results of some seawater samples analysis are presented in Table 1.

Table 1.

Heavy metals ("total") in the Baltic sea, October 1996. The "dissolved" fractions concentration is noted as D.

STATION	DEPTH,m	Cu, ng l^{-1}	Pb, ng l^{-1}	Cd, ng l^{-1}	Zn, ng l^{-1}	Zn, ng l^{-1}, D
RUHNU 1	8	820	207	11.1	493	
	28	567	151	10.2	878	
S-maa 1	10	655	155	93	1010	
	28	328	155	10.3	813	
IRBEN 1	10	580	124	22.4	520	
	20	730	77	12.3	910	
LL 23	10	945	97	15	717	
	150	662	56	11.8	1170	
	200	567	88	8.4	943	
	300	378	88	14	1020	
	400	466	97	12.3	1495	
BY 15	10	365	20.1	7.4	3670	1150
	70	277	31	12.3	2827	1170
	150	252	35	9.7	1463	940
	200	315	38	11.7	1560	1020
	225	265	37.3	7.5	1530	980
	237	277	38.3	7.8	1593	936

It must be noted differences between metal contents in Eastern Gotland Deep in anoxic waters in 1991 (5) and in 1996, especially absence of levels with the very low concentration of Cu and Zn. From the other side, similar occurs behaviour of Co with content in anoxic zone in 1996 much higher than in surface waters. In samples from June 1994 there was observed the minimum content of Pb (21 ng l^{-1}) and Cd (7 ng l^{-1}) in depth of the oxygen minimum. Except the well mixed waters of the Gulf of Riga there were differences in "total" and "dissolved" metal contents up to 3 times for Zn between surface and bottom water. In most samples from the Baltic Sea the part of particulated Cu was in the range of 10- 30 % and less for Pb and Cd.

The precipitation samples were collected by Geological Survey of Estonia from different regions of Estonia, each during 3 months and in Table 2 there are presented results of analyses for some sampling points.

Table 2. Heavy metals in precipitations , January- March 1995 and 1996 (noted with *)

STATION	Cu, ng l^{-1}	Pb, ng l^{-1}	Cd, ng l^{-1}	Zn, ng l^{-1}	Hg, ng l^{-1}	Ni, ng l^{-1}
NARVA	3150	190	130	58500	5	
SÕRVE	3490	600	40	350000	10	
KUUSIKU	3275	580	110	884000	15	
RISTNA	10050	2070	235	520000	10	
RUHNU	3400	1000	60	16800	3	
HAANJA	8820	1240	82	13000	8	
RISTNA *	10660	1770	430	7000	20	2410
TÜRI *	3130	2410	440	40800	15	1940
TOOMA *	3010	2450	130	10400	8	2130
NARVA *	3320	480	100	17900	8	2480

Relatively high concentrations on islands (Sõrve, Ristna, Ruhnu) , far from industrial objects, means that the contamination is obviously transported by the predominant here winds from South- West and West.

In Table 3 some results of heavy metals "total" content in the river waters are presented, all they run into the Lake Peipus.

Table 3. Heavy metals in eastern rivers of Estonia (April 1996).

THE RIVER	Hg, ng l^{-1}	Cu, ng l^{-1}	Pb, ng l^{-1}	Cd, ng l^{-1}
EMAJÕGI (VORBUSE)	20	115	370	34
EMAJÕGI (IHASTE)	40	270	695	134
JÕUGA	20	295	685	67
PUNGERJA	30	815	715	100

The river Emajõgi flows through the Tartu, the sampling point Vorbuse is upstream and Ihaste downstream from Tartu and a sensible change in concenrtation of metals is noticeable. Into Jõuga and Pungerja there is pumped phreatic waters from oil- shale mines.

The phreatic and lake waters from the Kurtna area were analysed to get information about trace metals in this industrial and oil- shale region. Earlier there was an information that the content of metals, especially Hg is abnormal high in lakes (micrograms per litre).

Table 4. The phreatic waters from Kurtna area (1995)

Bore No.	Cu,ng l^{-1}	Pb,ng l^{-1}	Cd,ng l^{-1}	Zn,ng l^{-1}	Hg,ng l^{-1}	Ni,ng l^{-1}	Co,ng l^{-1}
51	120	190	33	4750	28	680	20
32	290	435	55	3900	12	400	15
00632	1600	460	50	13000	30	1280	50
00699	30	130	10	2800	10	320	10
7312	145	200	20	7800	170	1000	30
00640	1660	1800	45	65000	350	3000	17
218	10600	18600	32	31200	50	760	25
215	76800	134000	<100	117000	400	14700	470

Because of extremely high concentration of lead in the sample from bore No.215 it was diluted 10 times but exact determination of cadmium was difficult. The waters are from the

Cambrian layers, part of them are in use as the drinking water in this region and their quality is very different, especially if to compare bores No. 215 and 218 with the other ones.

Table 5. Lake waters from the Kurtna area (1995)

Sample No.	Cu,ng l^{-1}	Pb,ng l^{-1}	Cd,ng l^{-1}	Zn,ng l^{-1}	Hg,ng l^{-1}	Ni,ng l^{-1}	Co,ng l^{-1}
107	780	765	120	5200	20	550	20
111	380	445	26	5000	20	600	20
123	145	345	25	4850	25	700	20
128	700	350	30	3100	30	520	8
135	375	470	35	7150	80	600	15
138	380	135	18	3950	100	1130	20
142	1070	555	55	7310	120	440	8

It seems to be not very bad situation in these lakes while the concentration of mercury is abnormally high in all samples, especially in No. 135, 138 and 142. The reason of so high level of Hg is not clear today.

Conclusions

The analyses of sea- and freshwater were provided using stripping voltammetry. There was not found good correlation between vertical concentration profiles in Eastern Gotland Deep under anoxic conditions in 1991 and 1996. The part of particulated metals is determined and noted different behaviour of metals. In inner waters of Estonia (precipitations, phreatic, lake and river waters) the situation seems to be very different depending on the region.

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