The analysis of results of heavy metals concentrations in samples of sedimentation

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SYKE

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1. Introduction

Within the framework of the Interreg project "Development and introduction of a joint system of monitoring and assessment of the state of the environment in the border area of Norway, Finland and Russia", sedimentation samples (totalling 86) (Lapland Regional Environment Centre) were collected annually using sedimentation traps in six lakes in Finnish Lapland (Table 1) during 1988 - 2005, and the heavy metal concentrations in the sediments determined (SYKE). The aim of the Interreg project is to estimate and monitor changes in the environment resulting from emissions from the Pechenganickel smelters.

Table 1. List of lakes where the sediment traps were placed. The code numbers of the lakes correspond to the numbers in Figure 1

No	Name	Depth, m	First sampling	Last sampling	Times	X, latitude	Y, longitude	Distance, km
1	Lampi 222	22	14.9.1988	19.4.2005	18	69 26.775	29 06.478	46
2	Äälisjärvi 3	21.5	22.8.1989	14.9.2005	16	69 25.935	29 03.693	48
3	Surnujärvi V4	10.7	14.7.1983	12.4.2005	19	69 23.863	29 07.479	46
4	Pitkä-Surnujärvi V6 105001	11.3	18.7.1983	01.9.2005	19	69 15.480	28 42.990	62
5	Harrijärvi H62 123001	11	26.3.1990	29.3.2006	24	69 17.737	28 37.476	65
6	Kauralampi 1	12	15.2.1989	21.9.2005	17	67 16.176	29 26.466	160

The purpose of determining heavy metal concentrations in the sedimentation samples was to answer the following questions:
1. Is it possible, on the basis of the results from sedimentation traps, to draw conclusions about changes in the environment, including changes in the level of atmospheric deposition?
2. Is there a relationship between changes in annual emissions from the Pechenganickel smelters and the concentrations of heavy metals in sedimentation samples?
3. Is there a relationship between the accumulation of heavy metals in lake sediments and sedimentation samples?
4. Is it is possible, on the basis of the collection area of the sedimentation traps, dry mass and concentration of metals in the sedimentation samples, to determine the deposition per unit lake area, and to compare the deposition values with emissions from the Pechenganickel smelters?
5. Is the sedimentation method used in the Interreg monitoring programme suitable for the future assessment of atmospheric deposition?

2. Analysis of results

Chemical analysis of the sedimentation samples and water samples was carried out by the Lapland Regional Environment Centre (LREC), the results of the chemical analyses of the sediment core from Lampi 222 were kindly provided by Dr. Jaakko Mannio, and chemical analysis of the sediment core from Kauralampi was performed in the laboratory of the Institute of the North Industrial Ecology Problems (INEP), Apatity.

The results of chemical analysis of the sedimentation samples were used to calculate the accumulation rates of heavy metals. The accumulation rate was derived from the concentration of each element in each annual sample from the sedimentation trap (µg/g), and the rate of sediment

accumulation in each year (g/cm^2) by dividing the annual sediment accumulation (dry weight, g) by the collection area of the sedimentation trap (sum of the area of the trap tubes, cm^2):
Accumulation rate in year = $(\mu g/g) \cdot (g/cm^2) = \mu g/(cm^2 \cdot yr)$

Figure 1. Location of the lakes where the sediment traps were placed. The code numbers of the lakes correspond to the numbers in Table 1.

As Lake Lampi 222 is located closer than the other lakes to the Pechenganickel smelters, the sedimentation samples have the highest concentrations of Cu, Ni and Zn (Table 3), which are all metals emitted by the smelters in elevated concentrations. The time of minimum concentrations of Cu, Ni and Zn (as well as almost all of the heavy metals investigated) in the sedimentation samples from Lampi 222 coincides with the period of minimum emissions from the Pechenganickel smelters (Figure 2) in the beginning of the 1990s (the period of economic crisis in Russia). The highest Cu, Ni, Zn and Co concentrations were found at the end of the 1990s, which corresponds to the period with increasing industrial production in Russia and, therefore, with increased emissions of pollutants into the atmosphere from the smelters (Table 2, Figure 2).

Table 2. Annual emissions of Ni, Cu (t/yr) and SO_2 (10^3 t/yr) from the Pechenganickel smelters (data were kindly provided by the Company).

Year	**Emission**			**Year**	**Emission**		
	SO_2 10^3 t	**Ni t**	**Cu t**		**SO_2 10^3 t**	**Ni t**	**Cu t**
1977	400	539	323	1993	227	282	162
1978	396	555	335	1994	198	297	163
1979	396	526	288	1995	245	299	178
1980	383	513	285	1996	236	298	177
1981	360	537	311	1997	253	321	183
1982	358	441	261	1998	189	323	188
1983	369	427	261	1999	150	329	193
1984	365	408	231	2000	151	354	206
1985	354	375	227	2001	147	348	191
1986	343	386	229	2002	124	328	168
1987	338	394	225	2003	124	329	167
1988	290	376	214	2004	110	329	168
1989	277	332	196	Min	251	279	171
1990	258	301	180	Max	400	555	335
1991	258	279	171	Average	337	418	245
1992	251	295	175	St. deviation	53	93	53

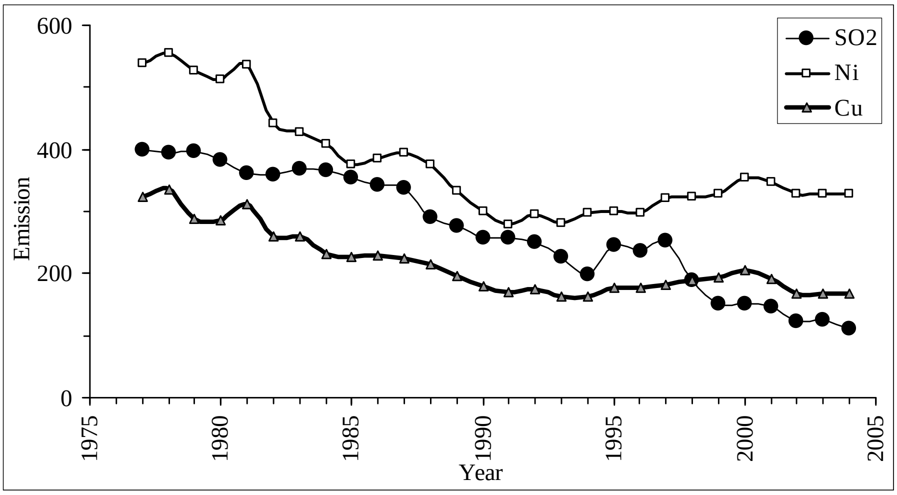

Figure 2. Annual atmospheric emissions of Ni, Cu (tonne/yr) and SO_2 (10^3 tonne/yr) from the Pechenganickel smelters (data were kindly provided by the Pechenganickel Company).

Table 3. Concentrations (µg/g dry weight) of heavy metals and arsenic in the annual sedimentation samples and in the upper layer (0-1 cm) of the sediment core from Lampi 222.

Date	As	Cd	CO + 566X	CO + 1324X	CR + 567X	CR + 755X	CU + 569X	CU + 757X	PB + 576X	PB + 756X	NI + 575X	NI + 760X	Zn
14.09.88	4.2	0.85	29	27	28	25	120	110	50	48	78	76	97
22.08.89	3.9	2.60	23	22	35	34	110	110	120	120	82	81	120
12.09.90	4.2	0.90	16	15	19	18	88	87	28	28	70	69	100
18.09.91	3.8	0.85	18	16	18	17	88	84	27	25	71	67	110
29.09.92	4.4	0.82	24	23	27	25	110	110	58	53	63	64	150
15.09.93	5.1	0.89	24	23	30	30	130	130	34	37	93	96	140
31.08.94	4.2	0.76	27	26	24	23	120	110	33	34	88	89	130
29.08.95	4.6	0.71	26	25	26	26	150	150	34	33	120	110	110
19.09.96	5.1	1.30	33	32	27	27	190	190	39	39	170	170	120
03.09.97	3.3	0.64	23	21	24	23	100	100	27	24	82	73	90
08.09.98	5.3	1.00	33	32	27	26	190	180	38	32	200	180	180
31.08.99	6.1	1.10	39	37	24	23	200	190	40	41	210	200	150
14.09.00	4.9	0.87	31	30	24	23	290	280	35	35	130	130	130
28.08.01	4.7	0.88	36	34	19	19	140	130	41	37	140	130	110
17.09.02	4.1	1.00	26	25	17	17	100	100	31	30	110	100	110
09.09.03	4.3	0.71	25	23	20	19	120	110	30	28	130	120	110
07.09.04	4.5	0.83	28	27	27	27	160	160	32	30	210	200	100
19.04.05	5.3	0.80		36		24		250	34			400	110
Min	3.3	0.64	16	15	17	17	88	84	27	24	63	64	90
Max	6.1	2.60	39	37	35	34	290	280	120	120	210	400	180
Average	4.6	0.97	27	26	24	24	142	143	41	40	120	131	120
Standard deviation	0.7	0.43	6	6	5	5	52	56	21	22	50	81	23
Sediment core 0-1 cm	2.3	0.30			27		94		40		44		51

Comparison of the average heavy metal concentrations in the sedimentation samples from Lampi 222 with the concentrations in the upper layer (0-1 cm) of the sediment core from the same lake showed that the Pb and Cr concentrations were the same, for Cu 1.5 times less, for As and Zn 2 times less, and for Cd and Ni 3 times less in the upper layer of the sediment core than in the sedimentation samples (Table 3). This may be connected to diagenesis processes in the sediment column due to changes in the physical and chemical conditions, mainly in the pH and redox potential (Eh), in the water column and in the sediments of the lake. The results of water chemistry monitoring suggest that, due to the reduction in water pH to 6.0, there may have been a decrease in the particulate forms of heavy metals and dissolution of metals into the water column. Overall, the concentrations of Ni, Pb andAs increased towards the sediment surface (Figure 4) compared with the background values. A depth of 20 cm was considered to represent the background, i.e. before the onset of anthropogenic pollution, because the average sedimentation rate for Northern lakes is, according to the studies of Norton et al. (1992, 1996), not more than 1mm/yr. However, there were some decreasing Pb, Cu, Zn, Cd and As concentrations in the upper sediment layers, which may be caused by the acidification processes reported in earlier studies on acidifying lakes in Finnish Lapland (Dauvalter, 1997).

The sedimentation rate in Lampi 222 ranged from 437 to 2142 µg/cm^{2}yr, the minimum and maximum values occurring in 1993 and 1997, respectively (Table 4). These values are in agreement with the investigations carried out on the sedimentation rate in Norwegian and Russian lakes in the vicinity of the Pechenganickel smelters, calculated using the CRS and CIC models (Norton et al., 1992, 1996). The minimum and maximum concentrations of almost all the heavy metals coincided with the minimum and maximum sedimentation rate values (Table 4). The maximum accumulation rate values (~ 0.1 µg/cm^{2}yr) for Cu, Ni and Zn (as for the concentrations of these metals in the sedimentation samples) corresponded to the increased concentrations in emissions from the smelters. Cadmium had the minimum accumulation rate (less than 0.001 µg/cm^{2}yr in average) (Table 4) due to the low Cd concentrations in the sedimentation samples. The accumulation rate for As in this lake was approximately 4 times higher than that for Cd (Table 4). The average accumulation rate for Co and for Cr was approximately the same (slightly above 0.02 µg/cm^{2}yr), and for Pb approximately 2 times higher (Table 4).

There was correlation between the accumulation rate values for Pb, Cu, Cd, Co and Ni (in descending order) and the annual emissions of the main polluting metals (Figure 3), which means that there were clear connections between changes in annual emissions from the Pechenganickel smelters and the heavy metal concentrations in the sedimentation samples. Therefore, this lake (Lampi 222) is suitable for monitoring and assessing the state of the environment in the joint Norwegian, Finnish and Russian border area in the coming years.

Lake Äälisjärvi is located at almost the same distance from the Pechenganickel smelters as Lampi 222 (48 km). As was the case in Lampi 222, the highest heavy metal concentration found in sedimentation samples from Lake Äälisjärvi were for Cu, Ni and Zn (Table 5), which are the metals emitted by the smelters in the highest concentrations. However, the concentrations of these metals were relatively higher in Lake Äälisjärvi than in Lampi 222. The time with minimum concentrations of Cu, Ni and Zn (as well as almost all the other heavy metals) in sedimentation samples from the Äälisjärvi coincided with the period of the lowest emissions from the smelters (Figure 2, Table 2) in the beginning of the 1990s (the period of economic crisis in Russia). The maximum Cu, Ni, Zn and Co concentrations occurred at the end of the 1990s and at the beginning of the 2000s at the same time as the increase in industrial production in Russia and, correspondingly, emissions from the Pechenganickel smelters. Furthermore, the average concentrations of heavy metals in sedimentation samples from Lake Äälisjärvi followed the decreasing order: Pb, Co, Cr, As and Cd.

Table 4. Dry weight of sediments annually accumulated in the sedimentation trap, sedimentation rate and accumulation rates (µg/cm^{2}yr dry weight) of heavy metals and arsenic in the sediment samples from Lampi 222.

Date	**Area, cm^2**	**Dry weight, g**	**Sedimenta-tion rate, µg/cm^{2}yr**	**ASar**	**CDar**	**CO566ar**	**CO1324ar**	**CR567ar**	**CR755ar**	**CU569ar**	**CU757ar**	**PB576ar**	**PB756ar**	**NI575ar**	**NI760ar**	**ZNar**
1988	192	0.232	1206	0.0051	0.00102	0.035	0.033	0.034	0.030	0.145	0.133	0.060	0.058	0.094	0.092	0.117
1989	192	0.153	794	0.0031	0.00207	0.018	0.017	0.028	0.027	0.087	0.087	0.095	0.095	0.065	0.064	0.095
1990	192	0.172	895	0.0038	0.00081	0.014	0.013	0.017	0.016	0.079	0.078	0.025	0.025	0.063	0.062	0.089
1991	192	0.264	1372	0.0052	0.00117	0.025	0.022	0.025	0.023	0.121	0.115	0.037	0.034	0.097	0.092	0.151
1992	192	0.237	1233	0.0054	0.00101	0.030	0.028	0.033	0.031	0.136	0.136	0.072	0.065	0.078	0.079	0.185
1993	192	0.084	437	0.0022	0.00039	0.010	0.010	0.013	0.013	0.057	0.057	0.015	0.016	0.041	0.042	0.061
1994	192	0.115	597	0.0025	0.00045	0.016	0.016	0.014	0.014	0.072	0.066	0.020	0.020	0.053	0.053	0.078
1995	192	0.172	895	0.0041	0.00064	0.023	0.022	0.023	0.023	0.134	0.134	0.030	0.030	0.107	0.098	0.098
1996	192	0.125	652	0.0033	0.00085	0.022	0.021	0.018	0.018	0.124	0.124	0.025	0.025	0.111	0.111	0.078
1997	192	0.412	2142	0.0071	0.00137	0.049	0.045	0.051	0.049	0.214	0.214	0.058	0.051	0.176	0.156	0.193
1998	192	0.146	758	0.0040	0.00076	0.025	0.024	0.020	0.020	0.144	0.136	0.029	0.024	0.152	0.136	0.136
1999	192	0.137	712	0.0043	0.00078	0.028	0.026	0.017	0.016	0.142	0.135	0.028	0.029	0.150	0.142	0.107
2000	192	0.124	643	0.0031	0.00056	0.020	0.019	0.015	0.015	0.186	0.180	0.022	0.022	0.084	0.084	0.084
2001	192	0.155	804	0.0038	0.00071	0.029	0.027	0.015	0.015	0.113	0.105	0.033	0.030	0.113	0.105	0.088
2002	192	0.236	1224	0.0050	0.00122	0.032	0.031	0.021	0.021	0.122	0.122	0.038	0.037	0.135	0.122	0.135
2003	192	0.151	786	0.0034	0.00056	0.020	0.018	0.016	0.015	0.094	0.086	0.024	0.022	0.102	0.094	0.086
2004	192	0.153	793	0.0036	0.00066	0.022	0.021	0.021	0.021	0.127	0.127	0.025	0.024	0.167	0.159	0.079
2005	154	0.157	1017	0.0054	0.00081		0.037		0.024		0.254	0.035			0.407	0.112
Min			437	0.0022	0.00039	0.0105	0.0101	0.0131	0.0131	0.0568	0.0568	0.0149	0.0162	0.0407	0.0420	0.0612
Max			2142	0.0071	0.00207	0.0493	0.0450	0.0514	0.0493	0.2142	0.2543	0.0953	0.0953	0.1756	0.4069	0.1928
Average			942	0.0041	0.00088	0.0246	0.0240	0.0225	0.0218	0.1234	0.1272	0.0373	0.0358	0.1050	0.1166	0.1096
Standard deviation			390	0.0012	0.00040	0.0090	0.0086	0.0097	0.0088	0.0396	0.0496	0.0208	0.0206	0.0400	0.0800	0.0371

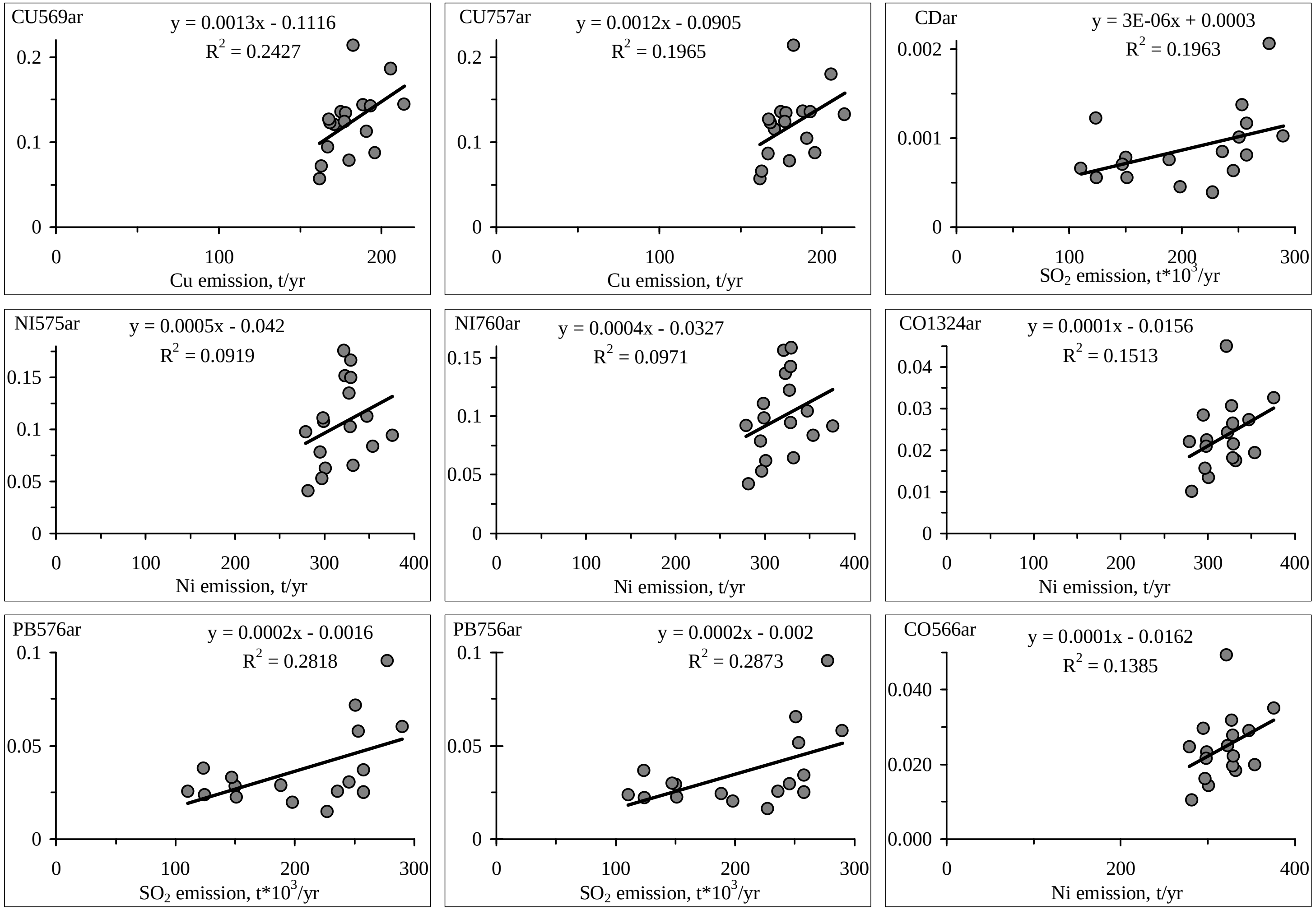

Figure 3. Dependence of the accumulation rate (μg/cm^{2}yr dry weight) of heavy metals in Lampi 222 on annual emissions from the Pechenganickel smelers.

Table 5. Concentrations (µg/g dry weight) of heavy metals and arsenic in the annual sedimentation samples from Äälisjärvi.

Date	**As**	**Cd**	**CO+566X**	**CO+1324X**	**CR+567X**	**CR+755X**	**CU+569X**	**CU+757X**	**PB+576X**	**PB+756X**	**NI+575X**	**NI+760X**	**Zn**
15.09.1988	5.6	1.68	24.1	24	27.9	28	165	170	65.4	65	139	140	120
22.08.1989	5.14	1.92	26.5	25	23.3	23	133	130	64.2	61	115	110	130
12.09.1990	3.97	1.21	22.4	21	16.1	16	119	120	41.2	40	94.6	92	120
17.09.1991	3.93	1.33	18	17	15.6	15	95	96	33.1	34	102	99	120
30.09.1992	3.89	1.67	18.8	18	18.4	18	119	120	34.4	35	79.4	79	150
15.09.1993	4.19	1.3	19	18	19.1	19	138	140	31.9	38	135	130	150
27.09.1994	4.67	0.96	27.1	25	23.9	24	131	130	41	45	134	130	130
29.08.1995	5.31	1.51	29.1	29	24	24	174	180	43.3	41	181	180	160
16.09.1996	5.1	1.02	23.5	23	26.1	25	121	120	43.2	41	121	120	95
02.09.1997	6.4	1.02	27.7	28	25.8	26	163	170	37.7	38	158	160	110
07.09.1998	6.23	1.46	32.6	32	22.6	23	247	260	42.4	44	256	260	160
30.08.1999	6.48	1.56	33.9	34	25.6	26	217	230	44.7	44	260	260	150
11.09.2000	6.55	1.26	97.5	97	29.7	30	202	210	43.9	45	218	220	120
27.08.2001	7.38	1.47	36.3	37	26.6	28	210	230	58.4	59	222	230	180
17.09.2002	6.37	1.68	29.6	30	31.8	33	138	150	97.1	99	148	150	180
08.09.2003	4.89	1.18	24.5	25	19.5	20	144	160	40.4	40	177	180	170
14.09.2005	4.4	2.5		19		18		210	28			310	120
Min	3.9	0.96	18	17	16	15	95	96	28	34	79	79	95
Max	7.4	2.50	98	97	32	33	247	260	97	99	260	310	180
Average	5.3	1.45	31	30	24	23	157	166	46	48	159	168	139
Standard deviation	1.1	0.38	19	18	5	5	42	47	17	16	56	67	25

The sedimentation rate in Lake Äälisjärvi ranged from 404 to 2175 µg/cm^{2}yr, the minimum and maximum values occurring in 1993 and 1996, respectively (Table 6). These values are in agreement (as for Lampi 222) with the results of studies on the sedimentation rate in Norwegian and Russian lakes in the vicinity of the Pechenganickel smelters, calculated using the CRS and CIC models (Norton et al., 1992, 1996). The minimum and maximum concentrations of almost all the heavy metals coincided with the minimum and maximum sedimentation rate values (Table 6). Copper, Ni and Zn had the maximum accumulation rate values (slightly more than 0.1 µg/cm^{2}yr), as was the case for the concentrations of these heavy metals in the sedimentation samples, due to elevated emissions of Cu, Ni and Zn from the Pechenganickel smelters. Cadmium showed the minimum accumulation rate (~0.001 µg/cm^{2}yr) (Table 6) due to the low concentrations in the sedimentation samples. The accumulation rate for As in this lake was approximately 4 times higher than that for Cd (Table 6). The average accumulation rate for Co and for Cr was almost the same (~0.02 µg/cm^{2}yr), and for Pb approximately 2 times higher (Table 6). The distribution of the metal concentrations in Lake Äälisjärvi it was very similar to that in Lampi 222.

There was correlation between the accumulation rates values for Co, Cu and Ni (in descending order) in Lake Äälisjärvi and the annual emissions of these metals (Figure 5), thus indicating a connection between changes in annual emissions from the Pechenganickel smelters and the concentrations of heavy metals in the sedimentation samples. However, the correlations were not as strong as those for Lake Lampi 222.

Lake Surnujärvi is located at almost the same distance from the Pechenganickel smelters as lakes Lampi 222 and Äälisjärvi (46 km). This lake was investigated only during the 10-year period 1988-1997, and therefore there is no information about the situation during the last 8 years. As was the case for the Lampi 222 and Lake Äälisjärvi, Zn, Ni and Cu had the highest heavy metal concentrations in the sedimentation samples from lake Surnujärvi: on the average more than 100 µg/g dry weight (Table 7). However, the Zn concentrations were somewhat higher than in Lake Äälisjärvi and Lampi 222. The Ni concentration was almost the same as in Lampi 222, and the Cu concentration lower than in the other two lakes. The minimum Cu and Ni concentrations (as well as almost all the other heavy metals) in sedimentation samples from Lake Surnujärvi occurred in 1988. The maximum Cu, Ni and Co concentrations occurred in 1996. The average heavy metal concentrations in sedimentation samples from Lake Surnujärvi followed the decreasing order: Pb, Cr, Co, As and Cd.

The sedimentation rate in Lake Surnujärvi ranged from 1207 to 21190 µg/cm^{2}yr, with minimum and maximum values in 1994 and 1988 respectively (Table 8). These values are also in agree
ment with the results of studies on the sedimentation rate in Norwegian and Russian lakes in the vicinity of the Pechenganickel smelters, calculated using the CRS and CIC models (Norton et al., 1992, 1996), except for the maximum value. The maximum Cu, Ni and Zn accumulation rate values (more than 0.4 µg/cm^{2}yr) were the highest of the three lakes, as was the case for the concentrations of these heavy metals in the sedimentation samples. Cadmium had the lowest accumulation rate (~0.007 µg/cm^{2}yr) of all the heavy metals determined in Lake Surnujärvi (Table 8). However, the minimum value in this lake was higher than that in the other two lakes. The accumulation rate for As in this lake was approximately 2.5 times higher than that for Cd (Table 8). The average accumulation rate for Co and for Cr was almost the same (~0.06 and 0.08 µg/cm^{2}yr, respectively), and for Pb approximately 2 times higher (Table 8). In other words, the distribution of metal concentrations in Lake Surnujärvi was very similar to that for Lampi 222 and Lake Äälisjärvi, but the average heavy metal and As concentrations in the sedimentation samples from Lake Surnujärvi were 3-7 times higher than those in Lampi 222 and Lake Äälisjärvi.

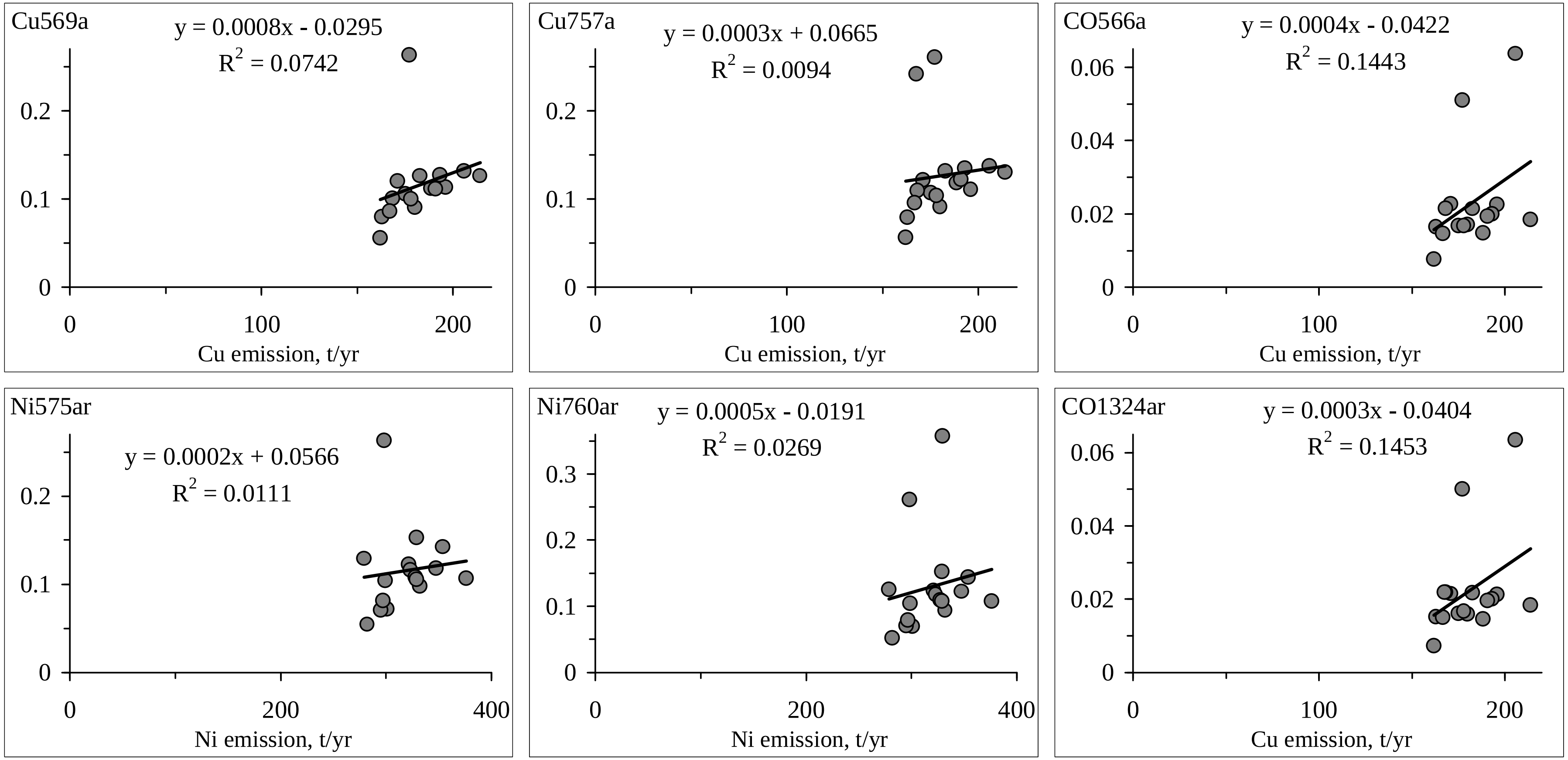

Figure 5. Dependence of the accumulation rate (µg/cm^{2}yr dry weight) of heavy metals in Äälisjärvi on annual emissions from the Pechenganickel smelters.

Table 6. Dry weight of sediments annually accumulated in the sedimentation trap, sedimentation rate and accumulation rates (µg/cm^{2}yr dry weight) of heavy metals and arsenic in the sediment samples from Äälisjärvi.

Date	**Area, cm^2**	**dry weight, g**	**Sedimen-tation rate, µg/cm^{2}yr**	**ASsr**	**CDsr**	**CO566sr**	**CO1324sr**	**CR567sr**	**CR755sr**	**CU569sr**	**CU757sr**	**PB576sr**	**PB756sr**	**NI575sr**	**NI760sr**	**ZNsr**
1988	192	0.147	766	0.0043	0.0013	0.018	0.018	0.021	0.021	0.126	0.130	0.050	0.050	0.107	0.107	0.092
1989	192	0.164	852	0.0044	0.0016	0.023	0.021	0.020	0.020	0.113	0.111	0.055	0.052	0.098	0.094	0.111
1990	192	0.147	762	0.0030	0.0009	0.017	0.016	0.012	0.012	0.091	0.091	0.031	0.030	0.072	0.070	0.091
1991	192	0.243	1266	0.0050	0.0017	0.023	0.022	0.020	0.019	0.120	0.121	0.042	0.043	0.129	0.125	0.152
1992	192	0.172	892	0.0035	0.0015	0.017	0.016	0.016	0.016	0.106	0.107	0.031	0.031	0.071	0.070	0.134
1993	192	0.078	404	0.0017	0.0005	0.008	0.007	0.008	0.008	0.056	0.057	0.013	0.015	0.055	0.053	0.061
1994	192	0.117	609	0.0028	0.0006	0.017	0.015	0.015	0.015	0.080	0.079	0.025	0.027	0.082	0.079	0.079
1995	192	0.111	577	0.0031	0.0009	0.017	0.017	0.014	0.014	0.100	0.104	0.025	0.024	0.104	0.104	0.092
1996	192	0.418	2175	0.0111	0.0022	0.051	0.050	0.057	0.054	0.263	0.261	0.094	0.089	0.263	0.261	0.207
1997	192	0.149	775	0.0050	0.0008	0.021	0.022	0.020	0.020	0.126	0.132	0.029	0.029	0.122	0.124	0.085
1998	192	0.087	454	0.0028	0.0007	0.015	0.015	0.010	0.010	0.112	0.118	0.019	0.020	0.116	0.118	0.073
1999	192	0.113	588	0.0038	0.0009	0.020	0.020	0.015	0.015	0.127	0.135	0.026	0.026	0.153	0.153	0.088
2000	192	0.126	654	0.0043	0.0008	0.064	0.063	0.019	0.020	0.132	0.137	0.029	0.029	0.143	0.144	0.078
2001	192	0.102	532	0.0039	0.0008	0.019	0.020	0.014	0.015	0.112	0.122	0.031	0.031	0.118	0.122	0.096
2002	192	0.140	729	0.0046	0.0012	0.022	0.022	0.023	0.024	0.101	0.109	0.071	0.072	0.108	0.109	0.131
2003	192	0.115	598	0.0029	0.0007	0.015	0.015	0.012	0.012	0.086	0.096	0.024	0.024	0.106	0.108	0.102
2004	192	0.444	1153	0.0051	0.0029		0.022		0.021		0.242	0.032			0.357	0.138
Min			404	0.0017	0.00053	0.0077	0.0073	0.0077	0.0077	0.0558	0.0566	0.0129	0.0154	0.0545	0.0525	0.0606
Max			2175	0.0111	0.00288	0.0638	0.0634	0.0568	0.0544	0.2632	0.2611	0.0940	0.0892	0.2632	0.3574	0.2067
Average			811	0.0042	0.00118	0.0228	0.0224	0.0185	0.0186	0.1158	0.1267	0.0369	0.0371	0.1154	0.1294	0.1065
Standard deviation			418	0.0020	0.00064	0.0142	0.0137	0.0111	0.0102	0.0443	0.0516	0.0203	0.0199	0.0473	0.0746	0.0361

Table 7. Concentrations (µg/g dry weight) of heavy metals and arsenic in the annual sedimentation samples from Surnujärvi.

Date	AS	CD	CR	CO	CU	PB	Ni	Zn
12.09.1988	3.4	2.00	18	9	83	41	84	140
23.08.1989	5.4	1.20	24	15	99	48	110	400
13.09.1990	4.3	1.40	19	17	100	36	120	160
19.09.1991	4.0	1.10	18	15	100	29	130	100
30.09.1992	4.4	0.88	19	16	92	35	110	110
15.09.1993	3.8	0.94	17	20	99	31	120	130
30.08.1994	4.1	2.40	23	19	120	28	160	130
29.08.1995	4.0	1.70	19	16	110	32	130	130
17.09.1996	5.3	1.60	22	21	190	30	230	180
02.09.1997	4.4	1.20	21	20	100	32	130	110
Min	3.4	0.9	17	9	83	28	84	100
Max	5.4	2.4	24	21	190	48	230	400
Average	4.3	1.4	20	17	109	34	132	159
Standard deviation	0.6	0.5	2	4	30	6	39	88

Table 8. Dry weight of sediments annually accumulated in the sedimentation trap, sedimentation rate and accumulation rates (µg/cm^{2}yr dry weight) of heavy metals and arsenic in the sediment samples from Surnujärvi.

Date	Area, cm^2	Dry weight, g	Sedimentation rate, µg/cm^{2}yr	ASar	CD565ar	CRar	COar	CUar	PBar	NIar	ZNar
1988	29	0.606	21190	0.0720	0.0424	0.381	0.191	1.76	0.869	1.78	2.97
1989	29	0.120	4197	0.0227	0.0050	0.101	0.063	0.42	0.201	0.46	1.68
1990	98	0.168	1713	0.0074	0.0024	0.033	0.029	0.17	0.062	0.21	0.27
1991	98	0.301	3065	0.0123	0.0034	0.055	0.046	0.31	0.089	0.40	0.31
1992	98	0.180	1829	0.0080	0.0016	0.035	0.029	0.17	0.064	0.20	0.20
1993	98	0.147	1498	0.0057	0.0014	0.025	0.030	0.15	0.046	0.18	0.19
1994	98	0.118	1207	0.0049	0.0029	0.028	0.023	0.14	0.034	0.19	0.16
1995	98	0.199	2028	0.0081	0.0034	0.039	0.032	0.22	0.065	0.26	0.26
1996	98	0.161	1644	0.0087	0.0026	0.036	0.035	0.31	0.049	0.38	0.30
1997	98	0.445	4535	0.0200	0.0054	0.095	0.091	0.45	0.145	0.59	0.50
Min			1207	0.0049	0.0014	0.025	0.023	0.14	0.03	0.18	0.16
Max			21190	0.0720	0.0424	0.381	0.191	1.76	0.87	1.78	2.97
Average			4291	0.0170	0.0071	0.083	0.057	0.41	0.16	0.47	0.68
Standard deviation			6049	0.0202	0.0125	0.108	0.051	0.49	0.25	0.48	0.92

There were high correlation coefficients between the accumulation rates of Zn, As, Cr, Co, Ni, Cd and Cu (in descending order) in Lake Surnujärvi and annual emissions from the smelters (Figure 6) and the concentrations of these metals in the sedimentation samples. Therefore, Lake Surnujärvi (in addition to Lampi 222) is recommended as a suitable site for monitoring and assessing the state of the environment in the joint Norwegian, Finnish and Russian border area in the future,.

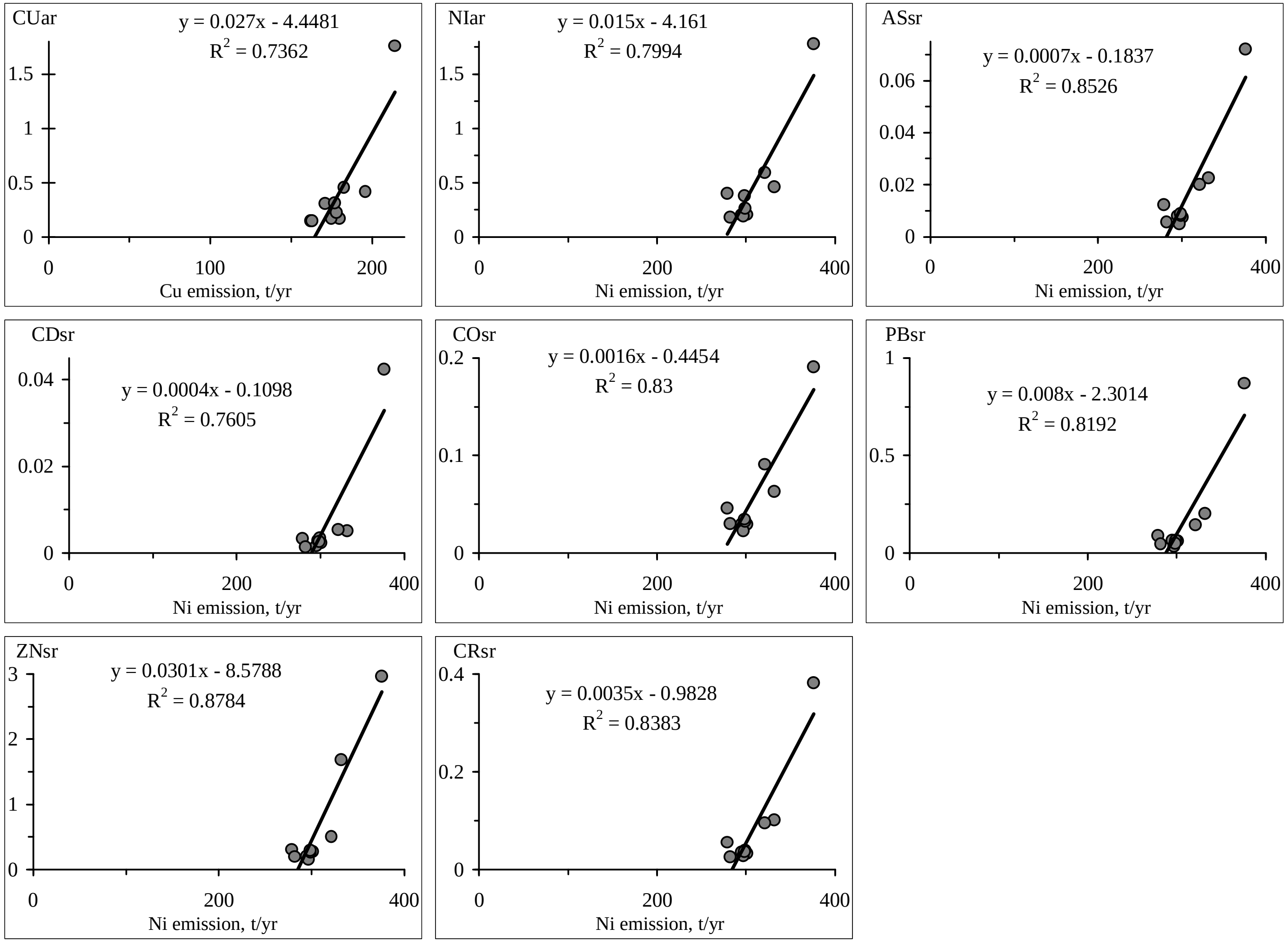

Figure 6. Dependence of the accumulation rate (µg/cm^{2}yr dry weight) of heavy metals in Surnujärvi on annual emissions from the Pechenganickel smelters.

Lake Pitkä-Surnujärvi, as well as the adjacent Lake Harriärvi, are located slightly further away (62 and 65 km, respectively)from the Pechenganickel smelters than the previous three lakes. This lake was investigated during the 15-year period 1989-2004. As was the case for the previous three lakes, the concentrations of Zn, Ni and Cu were the highest (on average less than 100 µg/g dry weight) of the heavy metal concentrations in sedimentation samples from Lake Pitkä-Surnujärvi (Table 9). However, the concentrations of Zn, Ni and Cu were lower than in the previous three lakes owing to the greater distance to the smelters. The minimum Cu and Ni concentrations (as well as of almost all the other heavy metals) in sedimentation samples from Lake Pitkä-Surnujärvi occurred in the beginning and middle of the 1990s, and the maximum Cu, Ni and Co concentrations at the end of the 1990s and beginning of the 2000s. Furthermore, the average concentrations of heavy metals in the sedimentation samples from Lake Pitkä-Surnujärvi followed the decreasing order: Pb, Co, Cr, As and Cd. The concentrations of these heavy metals and As in the sedimentation samples from Lake Pitkä-Surnujärvi were, in general, less than those in the previous three lakes.

Table 9. Concentrations (µg/g dry weight) of heavy metals and arsenic in the annual sedimentation samples from Pitkä-Surnujärvi.

Date	AS	CD	CR	CO	CU	PB	NI	ZN
27.09.1989	3.8	1.30	19	16	72	33	47	130
09.10.1990	3.9	1.00	18	19	72	27	46	84
24.09.1991	4.0	1.00	20	22	63	45	48	89
30.09.1992	3.7	0.86	17	25	80	28	45	83
08.09.1993	3.2	0.92	17	21	67	27	50	89
10.10.1995	3.0	1.30	16	10	62	19	36	120
01.10.1996	3.4	1.00	19	23	55	22	54	91
27.09.1997	3.6	0.88	19	24	73	21	80	86
29.09.1998	4.5	1.10	20	26	82	25	68	100
21.09.1999	5.1	1.10	21	31	89	26	82	93
16.09.2000	3.8	0.86	19	22	69	23	51	84
03.10.2001	4.9	0.99	21	26	150	28	71	93
02.10.2002	4.7	0.78	21	23	93	27	62	91
30.09.2003	4.4	0.85	21	26	66	24	52	86
04.10.2004	4.3	0.86	19	25	86	24	61	93
Min	3.0	0.8	16.0	10.0	55.0	19.0	36.0	83.0
Max	5.1	1.3	21.0	31.0	150.0	45.0	82.0	130.0
Average	4.0	1.0	19.1	22.6	78.6	26.6	56.9	94.1
Standard deviation	0.6	0.2	1.6	4.9	22.5	6.1	13.4	13.4

The sedimentation rate in Lake Pitkä-Surnujärvi ranged from 2506 to 46255 µg/cm^{2}yr, with minimum and maximum values in 1993 and 1989 respectively (Table 10). These values are also in agreement with the results of studies on the sedimentation rate in Norwegian and Russian lakes in the vicinity of the Pechenganickel smelters, calculated using the CRS and CIC models (Norton et al., 1992, 1996), apart from the maximum values higher than 10000 µg/cm^{2}yr. Zinc, Cu and Ni had the maximum accumulation rate values (0.95, 0.7 and 0.5 µg/cm^{2}yr, respectively), as was the case for the concentrations of these heavy metals in the sedimentation samples. Of the individual heavy metals, Cd had the lowest accumulation rate (on the average ~0.01 µg/cm^{2}yr) in the sediments from Lake Pitkä-Surnujärvi (Table 10). The accumulation rate for As in this lake was approximately 3.5 times higher than that of Cd (Table 10). The average accumulation rate for Co and Cr was almost the same (less than 0.2 µg/cm^{2}yr), and for Pb approximately 1.5 times higher (Table 10). Approximately the same distribution of heavy metal concentrations occurred in Lake Pitkä-Surnujärvi as in the previous three lakes, but the average heavy metal and As concentrations in the sedimentation samples from Lake Pitkä-Surnujärvi were 3 - 7 times higher than in Lampi 222 and Lake Äälisjärvi, and slightly higher than in Lake Surnujärvi.

Table 10. Dry weight of sediments annually accumulated in the sedimentation trap, sedimentation rate and accumulation rates (µg/cm^{2}yr dry weight) of heavy metals and arsenic in the sediments from Pitkä-Surnujärvi.

Date	Area, cm^2	Dry weight, g	Sedimentation rate, µg/cm^{2}yr	ASar	CDar	CRar	COar	CUar	PBar	NIar	ZNar
1989	29	1.324	46255	0.176	0.0601	0.879	0.740	3.330	1.53	2.17	6.01
1990	79	0.346	4413	0.017	0.0044	0.079	0.084	0.318	0.12	0.20	0.37
1991	98	0.748	7623	0.030	0.0076	0.152	0.168	0.480	0.34	0.37	0.68
1992	98	0.489	4986	0.018	0.0043	0.085	0.125	0.399	0.14	0.22	0.41
1993	98	0.246	2506	0.008	0.0023	0.043	0.053	0.168	0.07	0.13	0.22
1995	79	0.966	6153	0.018	0.0080	0.098	0.062	0.381	0.12	0.22	0.74
1996	98	1.319	13444	0.046	0.0134	0.255	0.309	0.739	0.30	0.73	1.22
1997	98	0.973	9912	0.036	0.0087	0.188	0.238	0.724	0.21	0.79	0.85
1998	98	0.573	5841	0.026	0.0064	0.117	0.152	0.479	0.15	0.40	0.58
1999	79	0.330	4204	0.021	0.0046	0.088	0.130	0.374	0.11	0.34	0.39
2000	79	0.967	12321	0.047	0.0106	0.234	0.271	0.850	0.28	0.63	1.03
2001	79	0.290	3689	0.018	0.0037	0.077	0.096	0.553	0.10	0.26	0.34
2002	98	0.357	3636	0.017	0.0028	0.076	0.084	0.338	0.10	0.23	0.33
2003	98	0.576	5874	0.026	0.0050	0.123	0.153	0.388	0.14	0.31	0.51
2004	98	0.553	5636	0.024	0.0048	0.107	0.141	0.485	0.14	0.34	0.52
Min			2506	0.008	0.0023	0.043	0.053	0.168	0.07	0.168	0.22
Max			46255	0.176	0.0601	0.879	0.740	3.330	1.53	3.330	6.01
Average			9100	0.035	0.0098	0.174	0.187	0.667	0.26	0.667	0.95
Standard deviation			10756	0.040	0.0143	0.204	0.170	0.758	0.36	0.758	1.43

There was correlation between the accumulation rate values for Cd, Zn, Pb, Cr, Ni and Cu (in descending order) in Lake Pitkä-Surnujärvi and the annual emissions from the smelters (Figure 7) and the concentrations of heavy metals in the sedimentation samples. However, the correlation were not very high and were approximately the same as those in Lake Äälisjärvi.

Lake Harriärvi was studied during the 13-year period 1992-2005. As was the case in the other lakes, the concentrations of Zn, Cu and Ni were the highest in the sedimentation samples from Lake Harriärvi, with average values of 274 µg/g (the highest concentration among all the lakes), 59 and 52 µg/g dry weight, respectively (Table 11). The minimum Cu, Ni, Co, Cr and As concentrations in the sedimentation samples from Lake Harriärvi occurred in the beginning of the 2000s (in 2004), and the maximum Cu, Ni, Co and As concentrations occurred in the middle of the 1990s. The average heavy metal concentrations in the sedimentation samples from Lake Harriärvi followed the decreasing order: Pb, Cr, Co, As and Cd, i.e. the same as for the majority of the other lakes.

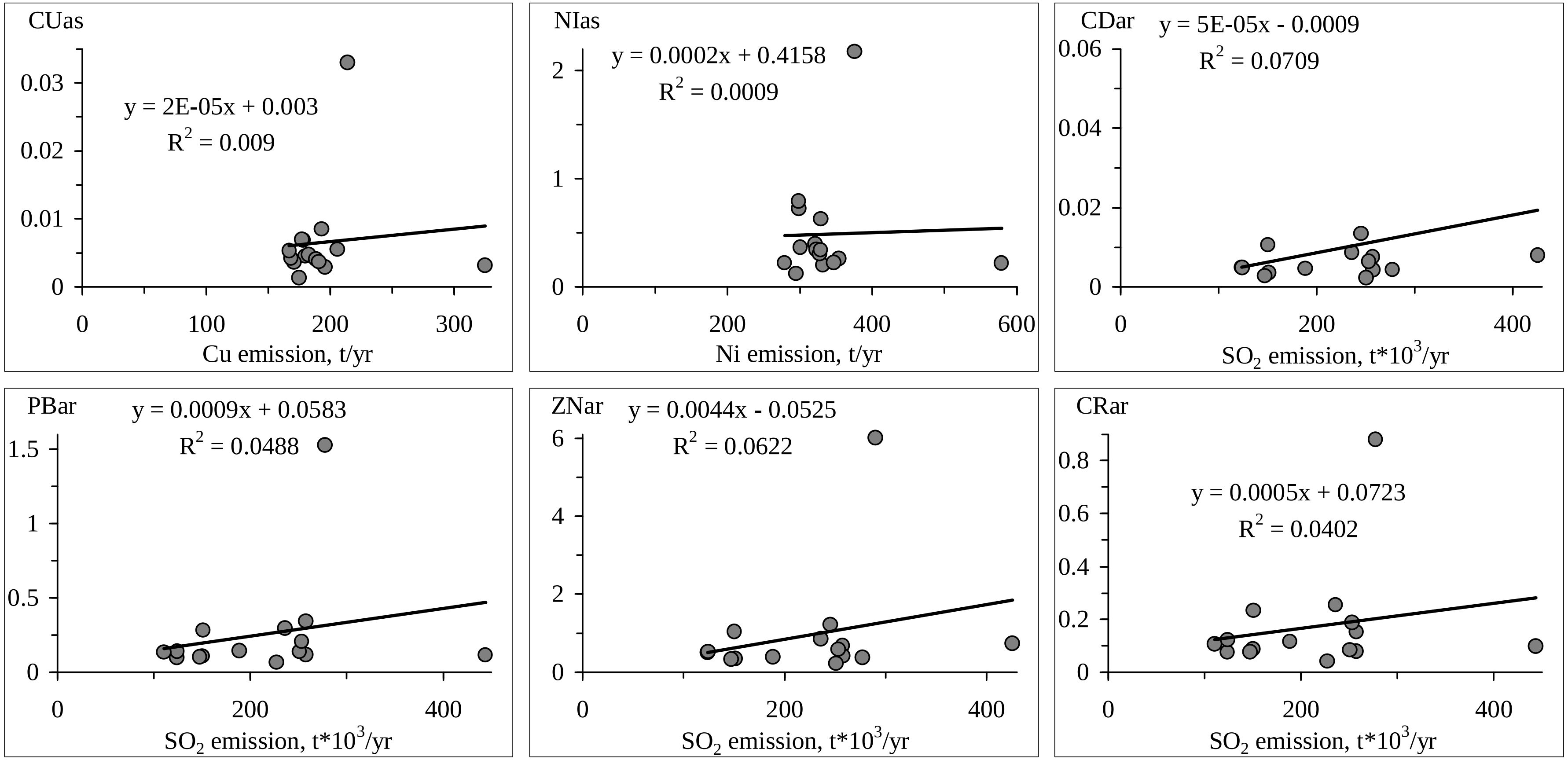

Figure 7. Dependence of the accumulation rate (μg/cm^{2}yr dry weight) of heavy metals in ?sediment samples from? Pitkä-Surnujärvi on annual emissions from the Pechenganickel smelters.

Table 11. Concentrations (µg/g dry weight) of heavy metals and arsenic in the annual sedimentation samples from Harriärvi.

Date	As	Cd	Cr	Co	Cu	Pb	Ni	Zn
17.03.1992	2.1	1.70	10	4	41	22	38	1400
05.04.1993	2.8	1.90	12	4	34	24	32	520
15.03.1994	3.0	1.90	14	5	160	31	62	190
14.03.1995	2.2	1.40	11	5	41	18	47	86
25.03.1996	3.0	1.60	10	7	67	21	53	390
17.03.1997	3.1	1.30	11	7	73	22	89	110
04.05.1998	2.7	1.20	11	3	61	22	48	140
14.03.2000	3.1	1.10	11	5	70	22	88	68
20.03.2001	2.0	0.70	9	3	47	21	42	56
12.03.2002	2.4	0.92	9	3	39	19	43	170
25.03.2003	3.0	1.10	11	5	40	19	50	67
29.03.2004	1.5	9.80	6	2	32	11	25	190
11.04.2005	2.2	5.80	10	5	56	14	55	180
Min	1.5	0.70	6	2	32	11	25	56
Max	3.1	9.80	14	7	160	31	89	1400
Average	2.5	2.34	10	4	59	20	52	274
Standard deviation	0.5	2.58	2	2	34	5	19	364

The sedimentation rate in Lake Harriärvi ranged from 1539 to 5168 µg/cm^{2}yr, with minimum and maximum values in 1996 and 2001, respectively (Table 12). These values are also in agreement with the results of studies on the sedimentation rate in Norwegian and Russian lakes in the vicinity of the Pechenganickel smelters, calculated using the CRS and CIC models (Norton et al., 1992, 1996). The maximum accumulation rates for Zn, Cu and Ni were ~0.8, 0.15 and 0.14 µg/cm^{2}yr, respectively. The minimum accumulation rate for Cd and As in Lake Harriärvi were, on the average, 0.007 and 0.008 µg/cm^{2}yr, respectively (Table 12). The average accumulation rate for Co was 0.012 µg/cm^{2}yr, for Cr ~0.03 µg/cm^{2}yr, and for Pb approximately 2 times higher (Table 12). In other words, the distribution of metal concentrations in Lake Harriärvi was approximately the same as in the other lakes, but the average heavy metal and As concentrations in the sedimentation samples from Lake Harriärvi were slightly smaller than those in Lake Pitkä-Surnujärvi.

There was correlation between the accumulation rate values for Ni and Cu (in descending order) in Lake Harriärvi and the annual emissions of heavy metals from the smelters (Figure 8) and the concentrations of heavy metals in the sedimentation samples. However, the correlations were not very high and were approximately the same as in Lake Pitkä-Surnujärvi.

Lake Kauralampi is located further away than the other lakes from the main pollution sources, the Pechenganickel and Severonickel smelters, and the distribution of heavy metal concentrations in the sedimentation samples was therefore different from those in the other investigated lakes. The Zn and Pb concentrations in sedimentation samples from the lake were the highest: approximately 60 µg/g dry weight for both metals(Table 13). The maximum Ni, Pb, Cr, Co and As concentrations in the sedimentation samples from Lake Kauralampi occurred in the beginning of the 1990s (Table 13), and of Zn, Cu and Cd (as well as a new peak in the Cr and As concentrations) in the beginning of the 2000s. The minimum concentrations of Pb (due to prohibition of the use of leaded gasoline), Ni, Zn and As in the sedimentation samples occurred in the beginning of the 2000s, of Cu, Cd and Co in the beginning of the 1990s, and of Cr at the end of the 1990s (Table 13).

Table 12. Dry weight of sediments annually accumulated in the sedimentation trap, sedimentation rate and accumulation rates (µg/cm^{2}yr dry weight) of heavy metals and arsenic in the sediment samples from Harriärvi.

Date	Area, cm^2	Dry weight, g	Sedimentation rate, µg/cm^{2}yr	ASar	CDar	CRar	COar	CUar	PBar	NIar	ZNar
1991	79	0.263	3352	0.0070	0.0057	0.0335	0.0134	0.137	0.074	0.127	4.69
1992	98	0.221	2254	0.0063	0.0043	0.0271	0.0090	0.077	0.054	0.072	1.17
1993	98	0.178	1814	0.0054	0.0034	0.0254	0.0091	0.290	0.056	0.112	0.34
1994	98	0.194	1979	0.0044	0.0028	0.0218	0.0099	0.081	0.036	0.093	0.17
1995	98	0.193	1967	0.0059	0.0031	0.0197	0.0138	0.132	0.041	0.104	0.77
1996	98	0.151	1539	0.0048	0.0020	0.0169	0.0108	0.112	0.034	0.137	0.17
1997	98	0.231	2356	0.0064	0.0028	0.0259	0.0071	0.144	0.052	0.113	0.33
1999	98	0.380	1934	0.0060	0.0021	0.0213	0.0097	0.135	0.043	0.170	0.13
2000	98	0.484	4934	0.0099	0.0035	0.0444	0.0148	0.232	0.104	0.207	0.28
2001	98	0.507	5168	0.0124	0.0048	0.0465	0.0155	0.202	0.098	0.222	0.88
2002	98	0.200	2036	0.0061	0.0022	0.0224	0.0102	0.081	0.039	0.102	0.14
2003	98	0.408	4157	0.0062	0.0407	0.0249	0.0083	0.133	0.046	0.104	0.79
2004	98	0.444	4528	0.0100	0.0263	0.0453	0.0226	0.254	0.063	0.249	0.82
Min			1539	0.0044	0.0020	0.0169	0.0071	0.077	0.034	0.072	0.13
Max			5168	0.0124	0.0407	0.0465	0.0226	0.290	0.104	0.249	4.69
Average			2924	0.0070	0.0080	0.0289	0.0119	0.155	0.057	0.140	0.82
Standard deviation			1318	0.0023	0.0118	0.0102	0.0042	0.069	0.023	0.055	1.21

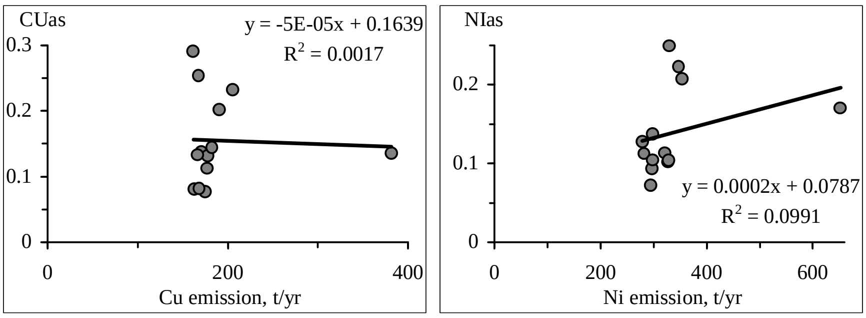

Figure 8. Dependence of the accumulation rate (µg/cm^{2}yr dry weight) of heavy metals in Harriärvi on annual emissions from the Pechenganickel smelters.

Comparison of the average heavy metal concentrations in the sedimentation samples from Lake Kauralampi with those in the upper layer (0-1 cm) of the sediment core from the lake (data from INEP, Dauvalter 1997) showed that the concentrations of Zn were almost the same, for Pb, Cu and Co approximately 2 times lower, for Cd 4 times lower, and for Ni 7 times lower in the upper layer of the sediment core than in the sedimentation samples (Table 13). This may be connected to the effect of diagenesis processes in the sediment column resulting from changes in the physical and chemical conditions (primarily pH and the redox potential) in the water column and in the lake sediments. The reduction in the water pH in Lake Kauralampi down to 5.2 may have resulted in the dissolution of particulate forms of heavy metals and their release into the water column. There was in increase in the Cu, Pb and Zn concentrations on moving towards the surface of the sediment in Lake Kauralampi compared to the background values at a depth of 20 cm (Figure 10), i.e. before the onset of anthropogenic influents, because the average sedimentation rate for Northern lakes is below 1mm/yr (Norton et al. 1992, 1996). However, there were some decreasing concentrations of Ni, Pb, Zn, Cd and Al in the upper sediment layers of Lake Kauralampi, which may have been caused by the acidification processes earlier reported in acidifying lakes in Finnish Lapland (Dauvalter, 1997) (Figure 10).

Table 13. Concentrations (µg/g dry weight) of heavy metals and arsenic in the annual sedimentation samples from Kauralampi

Date	**As**	**Cd**	**CO + 566X**	**CO + 1324X**	**CR + 567X**	**CR + 755X**	**CU + 569X**	**CU + 757X**	**PB + 576X**	**PB + 756X**	**NI + 575X**	**NI + 760X**	**Zn**
05.09.1990	9.2	0.88	2.3	2.0	10	10	24	24	59	58	12	15	82
02.10.1991	9	0.45	3.5	3.0	12	12	24	23	91	88	18	20	58
16.09.1992	10	0.65	2.9	3.0	13	13	23	23	91	88	14	16	50
21.09.1993	9.3	0.81	7.1	7.0	12	12	23	22	86	80	13	15	65
14.09.1994	9.2	0.74	6.4	6.0	11	11	17	17	62	59	13	15	48
13.09.1995	8.3	0.69	3.9	4.0	12	12	22	20	62	59	13	13	48
09.09.1996	9.1	0.69	5.2	6.0	11	10	18	16	62	57	14	14	51
22.09.1999	6.7	0.98	3.2	3.0	8.1	8	18	17	50	45	16	15	75
16.09.2000	7.1	1.6	6.1	6.0	11	11	52	50	50	46	12	12	95
27.09.2002	4.8	0.78	3.4	4.0	9.7	9	19	18	45	41	12	11	40
16.09.2003	5.1	0.76	4.2	4.0	9	9	25	25	46	44	10	9	53
27.09.2004	5.6	0.59	4.6	4.0	13	13	20	18	44	43	11	10	64
20.09.2005	11	0.79		4.0		11		44	51			12	61
Min	4.8	0.45	2.3	2.0	8	8	17	16	44	41	10	9	40
Max	11.0	1.60	7.1	7.0	13	13	52	50	91	88	18	20	95
Average	8.0	0.80	4.4	4.3	11	11	24	24	61	59	13	14	61
Standard deviation	2.0	0.27	1.5	1.5	2	2	9	11	17	17	2	3	16
Sediment core 0-1 cm		0.20	2				10		31		2		57

The sedimentation rate in Lake Kauralampi ranged from 1622 to 3685 $\mu g/cm^2yr$, with minimum and maximum values in 2004 and 1999 respectively (Table 14). These values are in agreement with the results of studies on the sedimentation rate in Norwegian and Russian lakes in the vicinity of the Pechenganickel smelters, calculated using the CRS and CIC models (Norton et al., 1992, 1996). There were maximum accumulation rate values (on average ~ 0.15 $\mu g/cm^2yr$) for Zn and Pb due to the fact that the concentrations of these heavy metals in the sedimentation samples from Lake Kauralampi were the highest. Cadmium had the minimum accumulation rate (on average ~ 0.002 $\mu g/cm^2yr$) (Table 14) due to the low concentrations in the sedimentation samples. The accumulation rate for Co in this lake was approximately 5 times higher than that for Cd, and for As and Cr one order of magnitude higher than that for Cd (Table 14). The average accumulation rates for Cu and Ni were 0.056 and 0.033 $\mu g/cm^2yr$, respectively.

There were high correlation coefficients between the accumulation rate values for Cd, Zn, Ni, As, Pb and Cu (in descending order) in the lake and the annual emissions of these metals (Figure 9) and their concentrations in the sedimentation samples. Lake Kauralampi can therefore be recommended, in addition to lakes Lampi 222 and Surnujärvi, as a suitable site for monitoring and assessing the state of the environment in the joint border area.

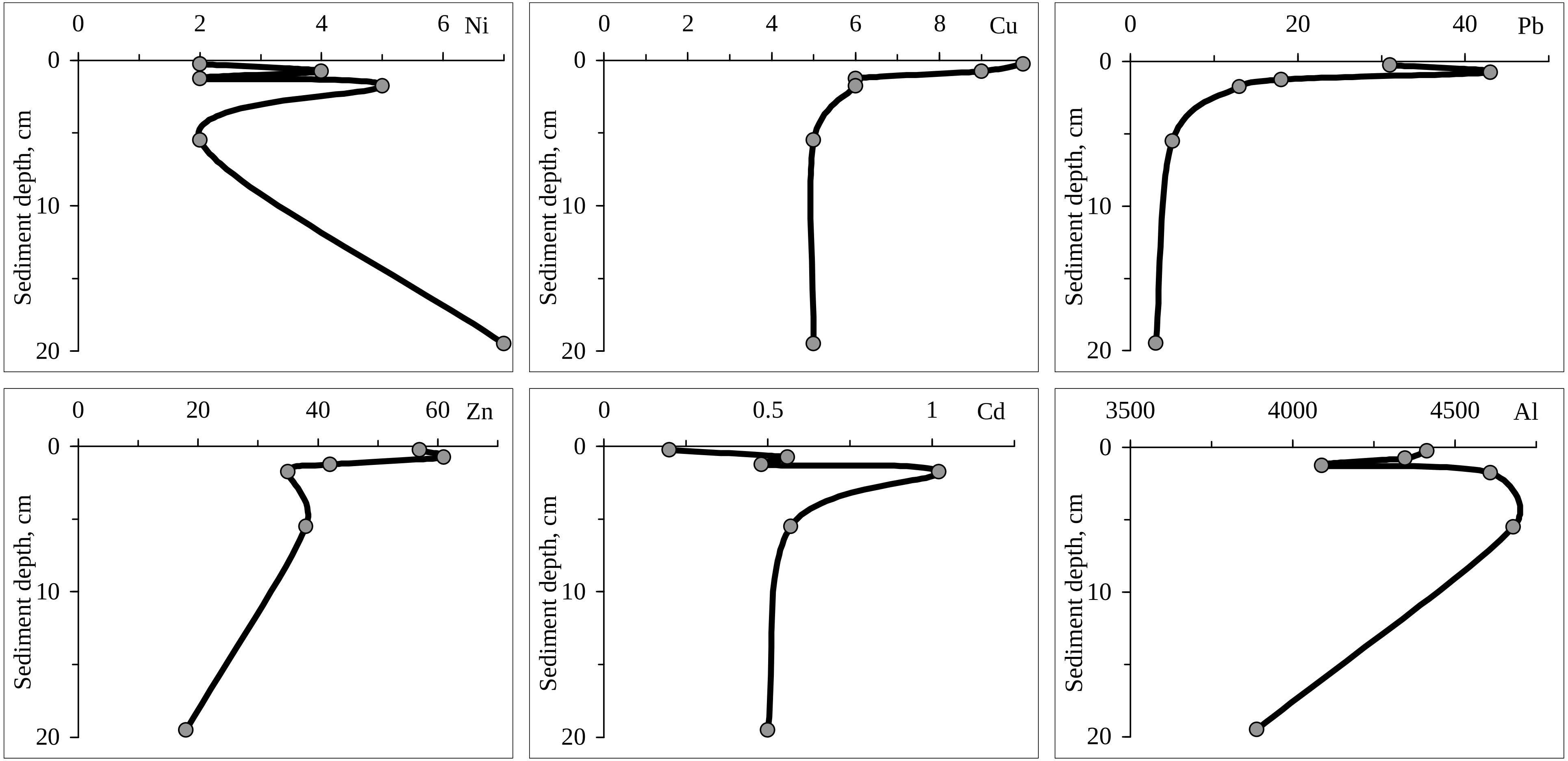

Figure 10. Concentrations (µg/g dry weight) of heavy metals and aluminium in the sediment core from Kauralampi.

Table 14. Dry weight of sediments annually accumulated in the sedimentation trap, sedimentation rate and accumulation rates (µg/cm^{2}yr dry weight) of heavy metals and arsenic in the sediment samples from Kauralampi.

Date	**Area, cm^2**	**Dry weight, g**	**Sedimen-tation rate, µg/cm^{2}yr**	**ASar**	**CDar**	**CO566ar**	**CO1324ar**	**CR567ar**	**CR755ar**	**CU569ar**	**CU757ar**	**PB576ar**	**PB756ar**	**NI575ar**	**NI760ar**	**ZNar**
1990	49	0.088	1794	0.0165	0.00158	0.0041	0.0036	0.0179	0.0179	0.0430	0.0430	0.106	0.104	0.0215	0.0269	0.147
1991	98	0.256	2604	0.0234	0.00117	0.0091	0.0078	0.0312	0.0312	0.0625	0.0599	0.237	0.229	0.0469	0.0521	0.151
1992	98	0.207	2113	0.0211	0.00137	0.0061	0.0063	0.0275	0.0275	0.0486	0.0486	0.192	0.186	0.0296	0.0338	0.106
1993	98	0.315	3214	0.0299	0.00260	0.0228	0.0225	0.0386	0.0386	0.0739	0.0707	0.276	0.257	0.0418	0.0482	0.209
1994	98	0.226	2302	0.0212	0.00170	0.0147	0.0138	0.0253	0.0253	0.0391	0.0391	0.143	0.136	0.0299	0.0345	0.111
1995	98	0.207	2109	0.0175	0.00145	0.0082	0.0084	0.0253	0.0253	0.0464	0.0422	0.131	0.124	0.0274	0.0274	0.101
1996	98	0.199	2029	0.0185	0.00140	0.0106	0.0122	0.0223	0.0203	0.0365	0.0325	0.126	0.116	0.0284	0.0284	0.103
1999	79	0.868	3685	0.0247	0.00361	0.0118	0.0111	0.0299	0.0295	0.0663	0.0627	0.184	0.166	0.0590	0.0553	0.276
2000	79	0.140	1782	0.0127	0.00285	0.0109	0.0107	0.0196	0.0196	0.0927	0.0891	0.089	0.082	0.0214	0.0214	0.169
2002	98	0.638	3249	0.0156	0.00253	0.0110	0.0130	0.0315	0.0292	0.0617	0.0585	0.146	0.133	0.0390	0.0357	0.130
2003	98	0.250	2546	0.0130	0.00193	0.0107	0.0102	0.0229	0.0229	0.0636	0.0636	0.117	0.112	0.0255	0.0229	0.135
2004	98	0.159	1622	0.0091	0.00096	0.0075	0.0065	0.0211	0.0211	0.0324	0.0292	0.071	0.070	0.0178	0.0162	0.104
2005	98	0.213	2168	0.0238	0.00171		0.0087		0.0238		0.0954	0.111			0.0260	0.132
Min			1622	0.0091	0.00096	0.0041	0.0036	0.0179	0.0179	0.0324	0.0292	0.071	0.070	0.0178	0.0162	0.101
Max			3685	0.0299	0.00361	0.0228	0.0225	0.0386	0.0386	0.0927	0.0954	0.276	0.257	0.0590	0.0553	0.276
Average			2401	0.0190	0.00191	0.0106	0.0104	0.0261	0.0256	0.0556	0.0565	0.148	0.143	0.0323	0.0330	0.144
Standard deviation			634	0.0058	0.00077	0.0047	0.0047	0.0059	0.0057	0.0177	0.0203	0.059	0.057	0.0121	0.0121	0.050

3. Conclusion

The six lakes were divided into two groups: five of the lakes are situated relatively close (46-65 km) to the main heavy metal pollution sources in the Murmansk Region (the Pechenganickel smelters), and one lake (Kauralampi) is located at a relatively long distance (>150 km) from the smelters. As a result, these lakes have a specific heavy metal distribution in the sedimentation samples and in the sediment cores.

The lakes in the first group had the following heavy metal and As distribution in the sedimentation samples (in descending order): Cu ≈ Ni ≈ Zn > Pb > Co ≈ Cr > As > Cd. The lakes are also characterised by the following features: the lakes at the greatest distances from the smelters (Surnujärvi, Pitkä-Surnujärvi and Harrijärvi) had the highest Zn concentrations in the sedimentation samples, and the closest lakes (Lampi 222 and Äälisjärvi) had the highest Cu and Ni concentrations. The minimum concentrations of Cu, Ni and Zn (as well as almost all of the other heavy metals) in sedimentation samples from the lakes in the first group coincided with the period of minimum emission from the smelters at the beginning of the 1990s (the period of economic crisis in Russia). The highest Cu, Ni, Zn and Co concentrations occurred at the end of the 1990s when there was an increase in industrial production in Russia and, consequesntly, also at the Pechenganickel smelters.

Lake Kauralampi, which was located furthest from the smelters, had a clearly different heavy metal and As distribution in the sedimentation samples: Zn ≈ Pb > Cu > Ni > Cr > As > Co > Cd. Interestingly, Pb was one of the major pollutants in this lake: the Pb concentration increased in the upper sediment layer (0-1 cm) to more than 10 times the background values at a depth of 20 cm in the lake sediment core. The maximum Ni, Pb, Cr, Co and As concentrations in the sedimentation samples occurred in the beginning of the 1990s. The highest concentrations of Zn, Cu and Cd (as well a new peak in the Cr and As concentrations) occurred at the beginning of the 2000s. The minimum concentrations of Pb (due to prohibition of the use of leaded gasoline), Ni, Zn and As in the sedimentation samples occurred at the beginning of the 2000s, of Cu, Cd and Co in the beginning of the 1990s, and of Cr at the end of the 1990s.

Comparison of the average heavy metal concentrations in the sedimentation samples from Lampi 222 with the corresponding concentrations in the upper layer (0-1 cm) of the sediment core showed that those that the Pb and Cr concentrations were the same, the Cu concentration 1.5 times lower, the As and Zn concentrations 2 times lower, and the Cd and Ni concentrations 3 times lower in the upper layer of the sediment core than in the sedimentation samples. In the sedimentation samples from Lake Kauralampi the Zn concentrations were almost the same as in the upper layer (0-1 cm), the Pb, Cu and Co concentrations approximately 2 times lower, the Cd concentrations 4 times lower, and the Ni concentrations 7 times lower in the upper layer of the sediment core. This fact may be due to the effect of the diagenesis processes in the sediment column resulting from changes in the physical and chemical conditions (primarily pH and the redox potential) in the water column and sediments of the lake. The decrease in the water pH down to 6.0 and 5.2 in Lampi 222 and Lake Kauralampi, respectively, may have resulted in dissolution of particulate forms of heavy metals their release into the water column. Overall, there was an increase in concentrations, on moving towards the sediment surface, for Ni, Pb and As in Lampi 222, and for Cu, Pb and Zn in Lake Kauralampi. However, there were some decreasing concentrations of Pb, Cu, Zn, Cd and As in the upper sediment layers, most probably due to the acidification processes reported earlier in acidifying lakes in Finnish Lapland.

The sedimentation rate of the lakes ranged from 404 to 46255 µg/cm^{2}yr. Maximum values of 46255 and 21190 µg/cm^{2}yr were found in lakes Pitkä-Surnujärvi and Surnujärvi, respectively. The average sedimentation rate values of these lakes were also the highest – 9100 and 4291 µg/cm^{2}yr, respectively. In the other lakes the values were in agreement with results of studies on the sedimentation rate in Norwegian and Russian lakes in the vicinity of the Pechenganickel smelters, calculated using the CRS and CIC models (Norton et al., 1992, 1996). The minimum and maximum concentrations of almost all the heavy metals coincided with the minimum and maximum sedimentation rate values. On the average, maximum accumulation rate values of more than 0.5 µg/cm^{2}yr were obtained for Cu, Ni and Zn in Lake Pitkä-Surnujärvi. A minimum accumulation rate value for Cd of less than 0.001 µg/cm^{2}yr Cd occurred in lakes Lampi 222 and Äälisjärvi. The distribution of the heavy metal accumulation rate was similar in the lakes. The lakes in the first group had the following distribution of heavy metal and As accumulation rate in the sedimentation samples (in descending order): Cu ≈ Ni ≈ Zn > Pb > Co ≈ Cr > As > Cd. The distribution for Lake Kauralampi, which was located furthest from the smelters, was different: Zn ≈ Pb > Cu > Ni > Cr > As > Co > Cd.

High correlation was found between the accumulation rate values in lakes Lampi 222, Surnujärvi and Kauralampi and annual emissions of heavy metals from the smelters, as well as with the concnetratiuons of heavy metals in the sedimentation samples. It is therefore recommended that these three lakes (Lampi 222, Surnujärvi and Kauralampi) be used for monitoring and assessing the state of the environment in the joint Norwegian, Finnish and Russian border area in the coming years.

4. Recommendations concerning the use of the sedimentation method

Traditional sediment core analysis has been widely used in retrospective, historical trend assessments. Determination of the age of lake sediments by radioactive isotopes (e.g. ^{210}Pb, ^{37}Cs for 10-150 yrs) is rather expensive, but can be used to estimate the accumulation rates of different elements. However, in northern lakes with an extremely small sedimentation rate (even < 1 mm/yr) and possible bioturbation problems, it is almost impossible to quantify the annual variation in a sediment core with or without dating methods. In contrast, the sedimentation measurement method provides unambiguous annual data. Therefore, the analysis of "fresh" material deposited in sedimentation traps is fully complementary with the widely used method of determining element concentrations in sediment layers.

Sedimentation measurement also permits calculation of the rate of deposition of elements per unit area, which can then be compared qualitatively with atmospheric deposition (precipitation; snow and rain). Correlation was found between the reported emissions and the measured sedimentation of metals. By combining these methods with determination of the concentration of e.g. metals in the lake outlet, it would even be possible to calculate the total budget (output - input = retention) of heavy metals on the catchment scale. This, however, is beyond the scope of the present study.

The apparent "depletion" of metals in the surface of sediment compared to the concentrations obtained in the sedimentation tubes is interesting and might be due to the effect of diagenetic processes or acidification, as well as to physical, chemical or biological changes in the sedimentation traps. It is not possible, on the basis of the material obtained in this study, to draw any final conclusions on this phenomenon. If the logistical constraints are not too limiting, it might be better to remove the traps from the lakes before the annual freeze-over.

It is recommended that the sedimentation measurements be continued in the three lakes (Lampi 222, Surnujärvi and Kauralampi). These lakes are deep enough to avoid the problems associated with turbulence caused by wave and wind activity. Analysis of base cations and those elements determined in the sedimentation samples should also be performed on water samples from the same lakes. Sediment core analysis should be repeated after a relatively long period of 10-15 years.

5. References

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