REPORT

Spatial Trends of Trace-Element Contamination in Recently Deposited Lake Sediment Around the Ni–Cu Smelter at Nikel, Kola Peninsula, Russian Arctic

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Abstract A large copper–nickel smelter complex is located at the Kola Peninsula, Russia, close to the Norwegian border. Trace-element concentrations in surface sediments (0–0.5 cm) and pre-industrial sediments from 45 lakes in the region were used to uncover spatial deposition patterns and contamination factor of sediments. Elevated concentrations were found, especially for Ni and Cu, but also for Pb, Co, Hg, As, and Cd. Highest concentrations were found up to 20 km from the smelter, but the concentrations decreased exponentially with distance from the smelter. Increasing Ni, Cu, As, and Hg concentrations from sub-surface to surface sediments were found for lakes at intermediate distances (20–60 km). This may reflect recent changes in atmospheric depositions, as shown in nearby Norwegian areas. However, we cannot rule out that this also may have been caused by diagenetic processes, especially for the most redox-sensitive elements such as As.

Keywords Metals · Smelter · Sub-arctic · Sediments · Lakes

INTRODUCTION

The contamination of aquatic ecosystems by metals, persistent organic compounds, and acidifying compounds has been of major concerns for people in the northern areas (AMAP 2002). Long-range transported metals have affected aquatic ecosystems in Arctic for decades (AMAP 2011), but this region also include large local point sources, the

Ni–Cu smelters, located in northern Siberia (Norilsk) and at the Kola Peninsula (Monchegorsk and Nikel), north-western Russia. These are among the largest Ni–Cu smelters in the world, emitting large amounts of metals and sulfur dioxide to the atmosphere severely affecting nature in wide areas (AMAP 2002).

Lakes are an important part of the landscape around these smelters (Surinin et al. 1997; Dauvalter and Rognerud 2001; Kashulin et al. 2012). Generally, lake sediments typically have metal concentrations several orders of magnitude higher than in lake waters, and appear to contain good temporal records of atmospheric deposition for several elements (Schindler et al. 1995). Thus, sediments from lakes around Ni–Cu smelters have been used to uncover the extension and degree of impact of atmospheric deposited trace elements (Gunn et al. 1995; Blais et al. 1999; All-Gill et al. 2003; Dauvalter et al. 2011; Kashulin et al. 2012), as well as temporal changes in atmospheric deposition (Norton et al. 1992).

We have studied trace-element concentrations in lake sediments around a Ni–Cu smelter complex consisting of a smelter in Nikel, and roasting and dressing plants in Zapolyarnij (Fig. 1). It is operated by the Petchenganikel Mining and Metallurgical Combine (PMMC) and reported annual emissions of Ni and Cu have decreased from about 500 and 335 metric tons in 1979 (peak), to about 350 and 180 metric tons in 2007, respectively, but no data are available after 2007 (Stebel et al. 2007). However, wet deposition of Cu and Ni more than doubled from 2004 to 2010 compared to previous 5 years at Svanvik (Berglen et al. 2011), coincident with a 50 % increase Ni and Cu concentrations in small lakes at the Jarfjord mountains (Klif 2011). This has been explained by increasing emissions of metals or changes in local meteorological factors (Stebel et al. 2007).

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Fig. 1 Map of the studied area in the border areas between Norway and Russia, close to the Barents Sea, including location of the Russian smelter complex at Nikel and Zapolyarnij

Here, we report regional variations in surface sediments (0–0.5 cm), sub-surface sediments (0.5–1 cm), and reference sediments (30 ± 5 cm), from 20 Norwegian and 25 Russian lakes, located in the region around the smelter complex in Nikel and Zapolyarnij. Our primary objectives have been to: (i) uncover spatial patterns of trace-element contamination and natural background levels, and discuss them with respect to atmospheric sources and wind direction, (ii) discuss temporal trends in trace-element concentrations by comparing concentrations in surface and sub-surface sediments.

MATERIALS AND METHODS

Lake Selection and Description of Lakes

Sediments and water from 45 lakes were sampled during September 2010. The lakes were selected based on the

following criteria: (i) covering areas on both sides of the border, but with more lakes from areas close to and at intermediate distances from the smelter complex, and along the dominating wind direction, (ii) including a few remote lakes supposed to be marginally affected by emissions from the smelters. The lakes are located from 13 to 395 m above sea level and are small- to medium-sized, 12–63 m deep with surface area from 0.05 to 19.88 km² and catchment area from 0.61 to 628 km² (Table 1). The lakes are oligotrophic, slightly acidic to circum-neutral, and have low to medium concentrations of total organic content (tot-P: 1–10 µg P l⁻¹; pH: 6.0–7.3; TOC: 0.7–9 mg C l⁻¹) (Table 1).

Sampling Procedures

Water samples were collected from 1 m depth at the center of the lake. We collected three cores from the deepest part of the lake using a modified Kajak-Brinkhurst (KB) gravity-type corer (inner diameter: 8.3 cm, Norway; 4.4 cm, Russia). Only cores with undisturbed sediment–water interfaces were used in the study. The cores were extruded and sectioned (0–0.5, 0.5–1, and ≈ 30 cm) in the field. Sections from the three cores were mixed in order to make one sample from each layer and each lake. The samples were placed in acid-washed polyethylene cups, stored dark in a cold storage bag until processed further in the laboratory. We defined the deepest layer as a reference layer likely to have been deposited in pre-industrial times, and therefore representing natural (or close to) background concentrations of metals.

Analytical Methods

Sediments were dried, homogenized, and sieved to obtain the <0.070 mm fraction, which was analyzed for loss on ignition (LOI) after combustion at 520 °C, and metals after digestion with conc. HNO₃–water 1:1 and detection using ICP-MS (Norway). LOI was included because it is an important sediment constituent and a well-known complexing agent for many heavy metals (Santschi 1988).

Table 1 Summary statistics of physical and limnological characteristics of the study lakes ($n = 45$)

Variable	Mean	SD	Min	Quantiles 25	Median	Quantiles 75	Max
m.a.s.l.	182	92.3	13	116	171	230	395
Lake surface area, km ²	2.32	4.19	0.05	0.18	0.61	2.67	19.88
Catchment area, km ²	40.5	109.2	0.6	2.5	9.9	20.3	628.4
Max. depth, m	14.6	11.0	2	7	12	20	63
pH	6.77	0.26	6.01	6.60	6.81	6.89	7.31
TOC, mg C l ⁻¹	3.47	1.95	0.74	2.2	2.8	4.6	9.0
tot-P	4	3	1	3	4	6	10

Calibrations were done by using matrix matched multi-standards and five internal standards. Quality control in the Norwegian samples was done by using NRC-INMS, MESS 3, and HISS marine sediment reference material, in addition to an internal standard developed at Norwegian Institute for Water Research (NIVA). The Norwegian sediment samples were analyzed for mercury with a Lumex RA 915 + Mercury Analysis equipped with a thermal decomposition attachment PYRO-915. Certified standards (IAEA 405 and MESS 3) were run for every tenth sample.

The Russian samples were prepared as the Norwegian. The solutions obtained were analyzed by atomic absorption spectrophotometry (AAS-30-Cr) in acetylene–air flame and in air–acetylene flame (Perkin-Elmer 360; Ni, Cu, Zn, Co, Fe, Mn). The concentrations of Cd, Pb, and As were determined by electrothermal atomization (AAN-800). Hg concentrations were determined using atomic absorption cold vapor (Perkin-Elmer FIMS 100). Quality control was carried out by analysis of certified reference materials PACS-2 (Canada) and L6M (Finland). All metal concentrations are based on dry weight calculations. Organic content was measured as LOI.

Statistical Analysis

A hierarchical clustering was applied to evaluate similarity of trace-element concentrations in surface sediments from the different lakes sampled (Wards minimum variance method, standardized data, two-way clustering). The interrelationships of elements in surface sediments, distance from the smelter and LOI, a major constituent of sediments, were also examined by a principal component analysis (PCA). All concentrations were log-transformed to improve normality in the multivariate analyses. A significance level of 0.05 was used in the significance tests (*t* tests). The computer program JMP was used for the statistical analyses (SAS Institute Inc., 2010).

RESULTS

Metal Concentrations and Organic Content

The sediments were taken from deepest part of the lake, and can be characterized as mixture of fine-grained inorganic particles and organic matter, measured as loss on ignition (LOI, %). Generally, for all three layers (0–0.5, 0.5–1, and ≈ 30 cm), sediments were slightly more organic (10 %) at the most remote lakes from the smelter. There were no significant differences between LOI in surface (0–0.5 cm) and sub-surface (0.5–1 cm) layers within groups, but slightly lower (2–5 %) in reference sediments than the upper layers for all three groups (Table 2).

There was a wide range in trace-element concentrations in surface sediments (0–0.5 cm) (Fig. 2). We define Hg and Cd as low concentration elements with median values $\leq 1 \mu\text{g g}^{-1}$; As, Pb, Co, Cr, and Zn as an intermediate group with median values of 10–100 $\mu\text{g g}^{-1}$; and Cu and Ni concentrations as high ($>200 \mu\text{g g}^{-1}$) to extremely high ($>1 \text{ mg g}^{-1}$, 6 lakes). Generally, a pronounced and statistically significant increase in concentrations from the reference layer (≈ 30 cm) to the surface layer was found for all trace elements (pairwise *t* tests: $p < 0.005$)—with exception for Cr ($p = 0.07$) and Zn ($p = 0.29$).

Fe and Mn were metals with substantially higher concentrations than the trace elements, and the mean concentrations ($\pm$ SD) in surface sediments were 47.4 (± 31.7) mg g^{-1} and 15.2 (± 28.5) mg g^{-1} , respectively.

A cluster analysis based on trace-element concentrations in surface sediments identified three groups with different distributions around the smelter complex (Fig. 3, Fig. S1 Electronic Supplementary Material). The lakes in Cluster 1 ($n = 12$) had in general the highest metal concentrations and were lying close (<20 km) to the sources in Nikel and Zapolyarnij. The lakes in Cluster 2 ($n = 24$) had intermediate metal concentrations and in general they were located at intermediate distances (≈ 20 – 60 km), whereas Cluster 3 ($n = 8$) was characterized by generally low concentrations and located more distant to the smelter (≈ 30 – 110 km), generally in south-west direction. Thus, the clusters show a spatial pattern where the concentrations in surface sediments for most trace elements show an exponential decrease with distance from the emission sources (Fig. 4). This decrease was most pronounced for Ni and Cu, to a lesser extent for Co, As, Cd, and Hg, and marginally—if any—for Zn, Cr, and Pb.

Contamination Factor (Cf) for Trace Elements

In order to give an impression of the degree of impact, contamination factors (Cf) were calculated as the ratio between concentrations of trace elements in surface and reference sediments (Table 2). Surface sediments close to the emission sources (Cluster 1) were heavily polluted by Ni and Cu (mean Cf: 63 and 50) and in decreasing order from 18.8 to 2.4 for Pb, Co, Hg, Cd, As, Cr, and Zn. This ranking changed at intermediate distances (Cluster 2) from the emission sources. Here, the Cf values were highest for Ni (8.1), and in decreasing order (6.1–1.8) for Pb, Hg, As, Cd, Cu, and Co, whereas no significant contamination ($\text{Cf} \leq 1$) was observed for Cr and Zn. At the most remote lakes (Cluster 3), mean Cf was highest for Pb and Ni (4.4 and 4.3) following in decreasing order (3.7–1.1) for Cu, Hg, Cd, As, and Co, whereas no significant contaminations ($\text{Cf} \leq 1$) were observed again for Cr and Zn.

Table 2 Mean and standard error (SE) for concentrations ($\mu\text{g g}^{-1}$) of metals in surface (A), sub-surface (B), and reference sediment layers (C) for lakes in the different cluster groups. Cf contamination factor, i.e., ratio between concentrations in surface and reference sediments

Cluster group	A, 0–0.5 cm		B, 0.5–1 cm		A–B		Cf		C, Reference	
	Mean ($\mu\text{g g}^{-1}$)	SE ($\mu\text{g g}^{-1}$)	Mean ($\mu\text{g g}^{-1}$)	SE ($\mu\text{g g}^{-1}$)	Mean ($\mu\text{g g}^{-1}$)	SE ($\mu\text{g g}^{-1}$)	Mean ($\mu\text{g g}^{-1}$)	SE ($\mu\text{g g}^{-1}$)	Mean ($\mu\text{g g}^{-1}$)	SE ($\mu\text{g g}^{-1}$)
As 1	46.83	8.91	44.97	10.34	1.86	7.46	11.2	2.0	6.79	1.99
As 2	12.85	1.48	9.17	0.89	3.68**	1.19	4.2	1.0	7.30	1.55
As 3	4.11	1.12	4.15	0.73	−0.04	0.56	1.7	0.5	4.00	1.79
Cd 1	1.528	0.236	1.219	0.205	0.308	0.127	10.2	2.1	0.186	0.033
Cd 2	0.722	0.103	0.638	0.094	0.084	0.081	2.1	0.3	0.448	0.089
Cd 3	0.324	0.046	0.371	0.067	−0.048	0.041	2.2	0.6	0.274	0.074
Co 1	144.1	29.1	155.8	36.3	−11.71	18.77	12.5	3.2	14.80	3.03
Co 2	53.07	6.40	48.59	6.09	4.48	6.85	1.8	0.2	41.81	10.86
Co 3	10.73	2.30	10.31	2.31	0.41	0.35	1.5	0.3	9.93	3.79
Cr 1	152.1	37.5	152.61	39.51	−0.53	7.12	3.5	0.9	46.01	5.24
Cr 2	56.56	5.69	54.65	5.80	1.91	1.35	0.9	0.1	64.80	4.99
Cr 3	25.74	3.16	25.25	3.13	0.49	0.32	0.9	0.1	31.58	5.13
Cu 1	1810	494	1560	478	253.1	160.2	49.7	12.2	38.3	3.9
Cu 2	218.1	23.4	166.2	21.5	51.9**	17.1	3.1	0.6	148.2	32.8
Cu 3	86.1	20.8	93.9	21.9	−7.9	10.1	3.7	1.8	84.7	40.7
Hg 1	0.499	0.069	0.596	0.232	−0.096	0.189	12.2	1.7	0.053	0.013
Hg 2	0.211	0.020	0.140	0.016	0.071***	0.015	3.4	0.7	0.092	0.010
Hg 3	0.090	0.014	0.089	0.018	0.001	0.017	2.2	0.5	0.067	0.026
Ni 1	2990	785.6	2970	811	19.1	365.8	63.1	16.2	69.3	19.5
Ni 2	286.9	50.0	196.9	37.6	90.0*	34.6	8.1	1.6	54.3	12.5
Ni 3	71.5	30.2	74.9	27.9	−3.4	7.1	4.3	1.6	18.9	2.7
Pb 1	36.0	6.4	31.5	5.0	4.6	3.1	18.8	6.1	3.1	0.7
Pb 2	37.2	2.9	33.4	2.6	3.8	1.4	6.1	0.9	11.6	3.1
Pb 3	16.3	2.3	18.7	2.8	−2.4	1.4	4.4	0.8	4.5	0.9
Zn 1	234.1	99.5	248.1	96.7	−14.0	18.4	2.4	0.7	83.3	10.0
Zn 2	111.9	7.8	108.3	8.8	3.6	4.2	1.0	0.1	128.1	12.2
Zn 3	62.9	10.8	62.0	10.2	0.9	1.7	0.8	0.1	75.7	10.7
Fe 1	20 930	18 850	20 010	18 620	922	2394	1.51	1.05	16 090	14 010
Fe 2	57 840	33 340	58 120	33 690	−277	24 910	1.20	0.75	59 620	41 380
Fe 3	43 290	25 490	44 890	32 150	−1597	20 050	2.72	1.72	22 200	18 970
Mn 1	423	477	424	484	−0.4	47.9	2.42	2.13	196	154
Mn 2	24 949	34 601	25 390	40 750	−441.4	16 180	14.83	19.09	2590	4001
Mn 3	4729	12 210	4985	13 890	−256.2	1953	5.14	6.19	392	535
LOI 1	26.9	3.8	26.5	4.0	0.4	0.6	1.3	0.1	21.2	2.3
LOI 2	25.3	1.7	24.1	1.5	1.2***	0.3	1.2	0.0	22.6	1.8
LOI 3	36.8	3.4	36.6	3.2	0.2	0.6	1.1	0.1	32.7	3.4

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

Principal Component Analysis (PCA)

Correlations between distance from the Nikel smelter, LOI, and trace-element concentrations identified a close positive relation between log-transformed concentrations of Hg and

As ($r = 0.87$), Ni and Cu ($r = 0.92$), and between Cu, Ni, Co, and As ($r = 0.78$ – 0.92), whereas Pb and Zn generally were more weakly correlated with the other elements (Table 3). The trace elements showed a similar pattern in their correlations with decreasing distance from the smelters.

Fig. 2 Box-and-whisker plots showing metal concentrations in surface (0–0.5 cm) and reference sediments (30 ± 5 cm). The median (50th percentile) is marked as a horizontal line across the interquartile box (25th and 75th percentiles), and the 10th and 90th percentiles are shown as horizontal lines outside the box ($n = 45$)

Fig. 3 Location of the study lakes ($n = 45$). The lakes are grouped according to a cluster analysis based on metal concentrations: Cluster 1 (red): high impact group, located close to the smelter complex. Cluster 2 (orange): intermediate impact group, located at more intermediate distances. Cluster 3 (blue): low impact group, lakes more remote from the smelter complex. The numbers (1–45) refer to the coding scheme used in Electronic Supplementary Material

Fig. 4 Metal concentrations in surface sediments (0–0.5 cm) in the study lakes ($n = 45$) and their distance from the Nickel smelter. The lakes are grouped according to a cluster analysis (see text)

Table 3 Correlation coefficient matrix (Pearson's r) for distance (from lake to the Nickel smelter, logarithmic transformed), LOI (loss on ignition) and concentrations of metals in surface sediments (0–0.5 cm, logarithmic transformed)

	LOI	log Dist.	log As	log Cd	log Co	log Cr	log Cu	log Ni	log Pb	log Zn	log Hg	log Fe	log Mn
LOI	1.00												
log Dist.	0.33	1.00											
log As	−0.28	−0.76	1.00										
log Cd	0.01	−0.62	0.55	1.00									
log Co	−0.28	−0.53	0.69	0.67	1.00								
log Cr	−0.33	−0.48	0.62	0.31	0.65	1.00							
log Cu	−0.13	−0.76	0.81	0.68	0.78	0.72	1.00						
log Ni	−0.20	−0.77	0.74	0.75	0.81	0.67	0.92	1.00					
log Pb	0.03	−0.17	0.36	0.53	0.43	0.20	0.35	0.26	1.00				
log Zn	−0.29	−0.29	0.43	0.52	0.70	0.57	0.49	0.55	0.21	1.00			
log Hg	−0.14	−0.65	0.87	0.57	0.64	0.62	0.75	0.69	0.49	0.39	1.00		
log Fe	−0.40	−0.16	0.45	0.31	0.60	0.35	0.29	0.37	0.37	0.62	0.40	1.00	
log Mn	−0.36	0.00	0.20	0.34	0.45	−0.02	0.04	0.18	0.34	0.47	0.10	0.72	1.00

None of the trace elements were positively correlated to LOI, and for some elements (Zn, As, Co, and Cr) we found a moderate negative correlation (−0.33 to −0.28).

We made a PCA on surface sediments to reveal the multivariate relationship between all the elements, distance from the Nickel smelter, and LOI (Table 4; Fig. S2 in

Table 4 Principal component analysis (PCA) of metal concentrations and LOI (loss on ignition) in surface sediments. Eigenvalues, percent variance explained, and eigenvectors for the first three principal components (PC 1–3) are given, $n = 45$

Statistic	Variable	PC 1	PC 2	PC 3
Eigenvalue		6.83	1.97	1.29
Percent		52.6	15.1	9.9
Cum Percent		52.6	67.7	77.7
Eigenvectors	LOI	−0.13	−0.27	0.61
	log Distance	−0.29	0.29	0.14
	log As	0.33	−0.13	−0.06
	log Cd	0.29	−0.03	0.38
	log Co	0.34	0.11	0.02
	log Cr	0.28	−0.12	−0.31
	log Cu	0.34	−0.25	0.01
	log Ni	0.35	−0.16	−0.03
	log Pb	0.18	0.14	0.57
	log Zn	0.26	0.27	−0.11
	log Hg	0.32	−0.17	0.09
	log Fe	0.23	0.48	−0.04
	log Mn	0.14	0.60	0.12

Electronic Supplementary Material). The first three principal components (PCs) described 77.7 % (cumulative) of the total variance in the dataset (Table 4). PC 1 described 52.6 %, and the eigenvectors were positively dominated by most of the trace elements (except for Pb and Zn), and negatively by distance. PC 2 described 15.1 % of the variance and was in decreasing order positively dominated by Mn and Fe and distance, and slightly negatively by LOI. PC 3 described 9.9 % of the variance and was dominated by a positive influence of mainly LOI and Pb.

Spatial Distribution of Metal Concentrations in Surface Sediments

The general decrease in surface concentrations with distance from the smelter is visualized in thematic maps (Figs. 5, 6). We have excluded Cr and Zn from the maps, as these elements were enriched only in surficial sediments close to the smelter complex (Table 2; Fig. 4). The maps show that the highest concentrations could be found in NNE direction from the smelter complex.

Lakes close to the smelter complex (Cluster 1) had substantially higher concentrations of Ni, Cu, Co, Cd, Hg, and As in surface sediments than the other clusters (Table 2; Fig. 4). The surface concentrations of Ni and Cu here were exceptionally high (mean values of 2990 and 1810 $\mu\text{g g}^{-1}$, respectively), but declined rapidly at intermediate distances to nearly an order of magnitude lower for Cluster 2, and were rather low at the most remote sites (72 and 86 $\mu\text{g g}^{-1}$).

Differences in Concentrations Between Surface and Sub-surface Sediments

For lakes in the vicinity of the smelter complex (Cluster 1) there was no general trend in the concentration differences between subsurface to surface sediments (Table 2; Figs. 5, 6). No statistical significant differences could be detected (pairwise t tests, $p > 0.05$). This applies for both trace elements and Fe and Mn. However, for the majority of lakes at intermediate distances (Cluster 2) there was a general increase in trace-element concentrations. The relative increase were 31–51 % for Cu, As, Ni, and Hg (increasing order), and 3–11 % for Zn, Cr, Co, Pb, and Cd. t tests revealed significant increases for Hg, Ni, As, and Cu ($p < 0.05$). No statistical significant changes could be found for Fe and Mn. In the most remote lakes (Cluster 3) no general trend or any statistical significant differences between surface and sub-surface could be detected.

DISCUSSION

Spatial Distribution, General Trends

We show here that lake sediments in the vicinity of the smelter complex at Nikel and Zapolyarnij are severely polluted by several trace elements originating from the metallurgical processes and related industrial activities—and that there is an exponential decrease in sediment concentrations with distance from the smelter.

Fig. 5 Concentrations of Ni, Cu, Co, and Zn in the study lakes. Concentrations in surface sediments (0–0.5 cm) are indicated by the area of the circles. Differences between surface and sub-surface sediments (0.5–1 cm) are indicated by a color gradient. Blue negative values. Red positive values. No color zero

Highest concentrations were found along the prevailing wind direction (NNE), decreasing almost exponentially with distance to 20 km from the smelter, then level off up to 40 km and only minor degrees of pollution were observed at longer distances from the source. A similar deposition pattern along the prevailing wind directions are also observed in sediments from lakes around the smelters in Monchegorsk (Kashulin et al. 2012) and Norilsk (Blais et al. 1999) (see Fig. S3 in Electronic Supplementary

Material). The lakes are circum-neutral and the reported pH-dependent decrease in sedimentation of Cd, Zn, and Ni in Norwegian lakes (Rognerud and Fjeld 2001) should not be an important factor to consider in this survey.

A cluster analysis and PCA revealed a common pattern of deposition or supply for several elements (Figs. S1 and S2 in Electronic Supplementary Material). The cluster analysis identified three groups of lakes with different trace-element concentrations in surface sediments: a high

Fig. 6 Concentrations of As, Pb, Cd, and Hg in the study lakes. Concentrations in surface sediments (0–0.5 cm) are indicated by the area of the circles. Differences between surface and sub-surface sediments (0.5–1 cm) are indicated by a color gradient. Blue negative values. Red positive values. No color zero

impact cluster, an intermediate impact cluster, and a low impact cluster (Clusters 1 to 3). The clusters showed a spatial pattern where the concentrations in general decreased with distance from the smelter complex (Fig. 4).

Cluster 1 was lakes with exceptional high concentrations of Ni and Cu (mean values: 2992 and 1812 $\mu\text{g g}^{-1}$, respectively), and to a lesser extent for As, Co, Hg, and Cd. In average, the Ni and Cu concentrations were about 63 and 50 times higher than concentrations in pre-industrial

sediments. These lakes were situated within 20 km to the emission sources at the smelter complex. Cluster 2 was lakes with moderate concentrations of all trace elements situated at intermediate (≈ 20 – 40 km) distances from the emission sources. The mean Ni and Cu concentrations in surface sediments were almost an order of magnitude lower than for Cluster 1. Cluster 3 was the most remote lakes (≈ 40 – 110 km) with low concentrations of all trace elements.

The first three principal components of the PCA counted for 77.7 % of the variation in the dataset. The first dimension (PC 1) described the main variation of sediment concentrations for several trace elements (positive loadings) and their distance from the smelter complex (negative loading). The most important elements were Ni, Cu, Co, As, Hg, and Cd (decreasing rank, ranged after their eigenvectors). This captures the central spatial trend showing decreasing trace-element concentrations with distance from the smelter complex. The second dimension (PC 2) described the main variation in Mn and Fe and distance (positive loadings) together with distance (negative loading). This indicates that there in general was a weak association between the trace-element group and Fe and Mn. PC 3 was a dimension dominated mainly by a positive influence of LOI together with residual variation of Pb and Cd. This indicates that these two elements have other significant sources or different deposition patterns than the other elements.

Spatial Distribution, Element-Specific Behavior

Trace elements emitted to the atmosphere at the smelter complex are mainly associated to mixture of geogenic or technogenic particles (Gregurek et al. 1999). The geogenic particles in the study area are primary minerals found in the local bedrock and Pechenga ore. They are exposed to the atmosphere as windblown dust when ore from the mine is transport and processed during production of Cu–Ni concentrate, whereas technogenic particles are products of different kinds of metallurgical processes emitted from smelter complex (Gregurek et al. 1999). In the following discussion, we will divide trace elements into groups based on their characteristics with respect to sources and deposition pattern.

Ni, Cu, Co, Cr, and Zn

These elements are significantly enriched in the ore (Gregurek et al. 1998) and are associated to larger particles produced at high temperatures in the smelter at Nickel (Dauvalter et al. 2011). These particles are supposed to be deposited mainly as dry deposition in the vicinity of the smelter (Steinnes et al. 2000).

The spatial pattern in surface sediments for these elements is likely caused by the prevailing north-northeast wind direction from the smelter complex. However, the ore processing, the size and the origin of the metal particles emitted, as well as the total amount emitted are also important factors for the spatial distribution (Gregurek et al. 1999).

Ni and Cu concentrations in surface sediments close to the smelter complex (Cluster 1) were about one order of magnitude higher than the other metals. These high concentrations, 5–10 mg Ni g⁻¹ and 1–5 mg Cu g⁻¹, are most

likely caused by a combination of deposition of geogenic particles (dust) originating in the open pit in Zapolyarnij, or during transportation of ore to the smelter, as well as deposition of heavy technogenic particles from smelter complex in Nickel (Gregurek et al. 1999).

Concentrations of Ni and Cu in surface sediments declined rapidly from lakes close to the emission sources to lakes at intermediate and more remote distances. This reflects the substantial emissions of these elements and that they are associated to larger particles that deposit rapidly (Steinnes et al. 2000). However, this picture is complicated by a declining trend in background concentrations of Ni from the smelter complex to more intermediate and remote distances. Also, geogenic particles may be more present in sediments from lakes close to the emission sources due to runoff from these catchments, which can be characterized as industrial deserts with barely any vegetation (Dauvalter 2003).

The declining trend was not so clear for the other elements. This may partly be due to higher natural background concentrations in lake sediments at intermediate distances from the smelter complex (Cluster 2).

Hg, Pb, As, and Cd

These elements are also emitted to the atmosphere by the smelters, but in much smaller quantities compared to the first group (Gregurek et al. 1999)—and they are also susceptible for long-range transport (Steinnes et al. 2000). Hg is known to be emitted as gaseous Hg-species (Pacyna and Pacyna 2002), whereas As and Pb are associated to small aerosol particles produced at low temperature of fusion (Steinnes et al. 2000). Cd from non-ferrous smelters is also known to be associated to small aerosols (Pacyna 1987).

The concentration gradients from the smelter complex for these elements (Fig. 4) were in general less steep (total span in concentrations: ≈ 1 –2 orders of magnitude) than for the other group associated to larger particles with a shorter atmospheric residence time (total span in concentrations: ≈ 2 –3 orders of magnitude). This was especially pronounced for Pb where the mean sediment concentrations in Clusters 1 and 2 were almost identical. For As, Hg, and Cd there was declining trend across the cluster groups, most evident for As. Such spatial patterns can be expected for elements susceptible to long-range atmospheric transport.

However, the smelter complex at Nickel and Zapolyarnij is not the sole anthropogenic source for trace-element depositions in the study area. More remote emissions can also have an impact on trace-element concentrations in lake sediments in our study area (Dauvalter 1994; Rognerud and Fjeld 2001), and it is known that long-range transported Hg and Pb have caused elevated concentrations in lake sediments from the Norwegian Arctic (Cf for Hg and Pb were

generally 2–4 and 3–5, respectively, Rognerud et al. 1998). Local atmospheric emissions from burning of fossil fuels and other anthropogenic activities in the Kirkenes-Pasvik region, as well as in the Murmansk region may also contribute to this.

It is well worth noting that As and Hg are not associated with the organic fraction of surface sediments in our study, which is contrary to many lakes in Norway (Fjeld et al. 1994; Rognerud and Fjeld 2001) and the Arctic (Rognerud et al. 1998), where the sources are dominated by long-range transported depositions. Thus, this may indicate that the fallout of Hg and As are mainly associated to small inorganic particles originating at the smelter and its roasting and dressing plants, windblown dust from tailings, transportation, and handling of ore as mentioned by Gregurek et al. (1999). Further, Pb are usually strongly associated to organic matter in lakes dominated by long-range transport (Rognerud and Fjeld, 2001) and the common loadings of LOI and Pb on principal component 3 in the PCA (Table 4) may indicate that other sources in the region, such as burning of fossil fuels, incineration, and long-range transported deposition, also may be sources for Pb.

Temporal Trends

Differences in concentrations in surface and sub-surface sediment layers can be used to reveal recent temporal trends, assuming that they are not significantly influenced by post-depositional redistribution. Such redistribution in hypolimnetic sediments may be caused by both bioturbation and diffusive migration of dissolved species in redox-related concentration gradients (Boudreau 1999; Boyle 2001). Elements having more than one oxidation state in lake sediments (such as As, Co, Cr) are known to undergo diffusive migration in response to redox gradients, whereas those with one stable oxidation state (such as Cd, Cu, Pb, and Zn) only show significant migration at extremely low sediment mass accumulation rates (Boyle 2001). Such diffusive migration of trace elements towards an oxygenated sediment surface often results in sub-surface concentration peaks together with iron hydroxide precipitates.

The study lakes are oligotrophic, slightly dystrophic, and the sub-arctic cold climate makes them less susceptible to experience long periods with anoxic conditions. When comparing the two upper 0.5 cm surface sediment layers, we could not prove any significant statistical difference in the concentration of the redox-sensitive metals Fe and Mn (Table 2). Although we have not done any speciation of these elements, we believe these conditions indicate that upper 1 cm layer most likely are oxygenated and without any strong redox gradients. This lowers the possibilities for diagenetic processes as a significant effect on trace metal

concentrations in the sediment surface layers. Further, the profundal bottom fauna in lakes from the study area are usually dominated by chironomides (Mousavi et al. 2003). Thus, bioturbation of surface sediments in the study lakes are probably of less importance compared to lakes with larger burrowing or surface living zoobenthos, but we cannot rule out the homogenizing effect caused by bioturbation.

The time period the individual layers represent can be determined by an estimation of the sedimentation rates. We have not dated the cores, but the general sedimentation rates in subalpine lakes in the region, as well as in other subalpine regions, are about 0.3–0.7 mm year⁻¹ (Norton et al. 1992; Wathne et al. 1995; Dauvalter 2003). Accordingly, our surface sediments (0–0.5 cm) are likely to represent about a decade of sedimentation (2001–2011), and subsurface (0.5–1 cm) layer will be deposited the decade before (1990–2000), whereas reference sediment layer (≈ 30 cm) are likely more than 600 years old.

For the whole group of study lakes, we have shown that there has been a statistically significant increase in concentrations for all trace elements, except Cr and Zn, in surface compared to pre-industrial sediments. The differences were greatest for Ni and Cu, and to a lesser extent for Pb, As, and Hg. This reflects an increase in the atmospheric depositions or supply from the catchments of these elements as compared to pre-industrial times.

Mean wet deposition of Ni and Cu during summer season has more than doubled from 1989–2003 to 2004–2009 at the Norwegian Meteorological station at Svanvik, about 8 km NW of Nikel (Berglen et al. 2011). These observations are also supported by a 50 % increase in Ni and Cu concentrations in lake waters at the Jarfjord area (Fig. 1), Norway, in the same time-period (Klif 2011). To investigate whether these changes in deposition of trace elements has led to corresponding changes in input to the lakes, we compared concentrations in surface sediments with the sub-surface layer.

For the most nearby and heavily impacted lakes (Cluster 1), we could not detect any statistical significant differences between the two upper 0.5 cm layers. However, the variations between the lakes in this cluster were large, giving high relative standard errors for the means. The catchment areas of these lakes are heavily disturbed, barren and prone to erosion. An increase in atmospheric deposition to these lakes is therefore likely to be masked by random (in statistical sense) disturbances in the catchments.

For the lakes at intermediate distances from the smelter complex (Cluster 2) we found statistically significant increases in concentrations of Cu, As, Ni, and Hg (31–51 %) from the sub-surface to the surface layers. This may reflect recent changes in the atmospheric depositions of these elements, as shown at Svanvik. However, we

cannot rule out that this also may have been caused by diagenetic processes, especially for the most redox-sensitive elements such as As.

CONCLUSION

Our sediment study of 45 lakes in the areas around the smelter complex at Nikel-Zapolyarni shows that sediments in the vicinity of the smelter are heavily polluted by several trace elements. When comparing surface sediments with pre-industrial sediments elevated concentrations of trace elements were found, especially for Ni and Cu, but also for Pb, Co, Hg, As, and Cd. The highest concentrations were found up to 20 km from the smelter complex, particularly in the prevailing NNE wind direction, but decreased exponentially with distance from the smelter. At intermediate distances (approximately 20–60 km) concentrations of Cu, Ni, As, and Hg in surface sediments (0–0.5 cm), probably deposited the last decade (2001–2010), were substantially higher than concentrations in subsurface sediments (0.5–1 cm) probably deposited the decade before. This may indicate an increase in emissions from the smelter the last decade, however, post-depositional redistribution due to bioturbation and diagenetic processes can interfere and obscure such interpretations. No emission data are available since 2007, but our suggestions are also supported by time trends in Cu and Ni concentrations in lake water and wet depositions on the Norwegian side of the border.

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