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Metal concentrations in sediments in acidifying lakes in Finnish Lapland

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Fifteen lakes in the Finnish Lapland were investigated to study acidification and pollution effects on metal concentrations in sediments. In four lakes the pH was lower than 6.0 and the alkalinity was lower than 50 meq l^{-1}. Contamination factor (C_f, ratio of metal concentration of the top layer to the bottom layer in a sediment core) of Pb ($C_f = 10.1$–10.4) was high in comparison to other investigated heavy metals, particularly in acidic lakes. Lake acidification results in decreasing Ni, Cu, Zn, Cd, and Al concentrations towards the sediment surface. Reduction of organic material content (loss on ignition) in upper sediments of acidic lakes was also noticed. The buffer capacity index (BCI, ratio of sum of alkaline and alkaline-earth metals (K, Na, Ca, Mg) to Al) was lower in the acidic lakes (0.12–0.36) than in the other studied lakes (0.42–1.34).

Introduction

Acidification of freshwater environment can significantly affect geochemical cycling of metals. Many metals of anthropogenic origin are found in acidic deposition. Physicochemical forms of metals in the biosphere are modified by acidification. These changes can greatly affect metal bioavailability and toxicity to many organisms (Nelson and Campbell 1991). Effects caused by anthropogenic acidification were first observed in freshwater ecosystems in northern America (Norton 1983, Norton *et al.* 1981, Campbell *et al.* 1985, etc.) and in Finland, Denmark, Norway, and Sweden, where severe acidification of freshwater occurred over large areas (Almer *et al.* 1974, 1978, SFT 1987, Forsius *et al.* 1988, Henriksen *et al.* 1988, Merilehto *et al.* 1988, Kauppi *et al.* 1990, Verta *et al.* 1990, Kämäri *et al.* 1991, Fleischer *et al.* 1993). Load of acidic compounds on freshwater ecosystems of northern Fennoscandia and the Kola Peninsula, Russia, is enormous and is caused by non-ferrous metallurgical foundries in the Kola Peninsula as well as atmospheric emissions from Central Europe. Annual emissions of sulphurous gases from the Kola Peninsula exceed 500 000 metric tons (Makarova and Ratkin 1991). Extensive surface-water acidification in the Kola Peninsula has taken place particularly in the mountain and remote tundra regions (Moiseenko 1994). In sediments of acidic lakes decreasing concentrations of heavy metals towards sediment surface are common, particularly in the case of mobile elements such as Cd, Zn, and Cu (Norton *et al.* 1992).

Metal geochemistry has been examined in a report by the Committee on Acid Deposition, TACAD (Campbell *et al.* 1985). One of the principal contributions of the TACAD report was identification of 18 metals, classified by Wood (1974) as "very toxic and relatively accessible", which are of most concern in the context of environmental acidification. These metals are by: (1) considerable anthropogenic emissions into the atmosphere, (2) high toxicity and potential of bioaccumulation, (3) geochemical mobility, and (4) sensitivity to changes in speciation in a pH range from 4.0 to 7.0. Campbell *et al.* (1985) have recommended that future acidification investigations should concentrate in Al, Cd, Cu, Pb, Hg, Mn, and Zn. We investigated all of these metals, except Hg. Laboratory and field studies were used to assess the influence of acidification on metal accumulation in freshwater sediments. Kinniburgh and Jackson (1981) have determined pH_{50} values (pH at which 50% of the initial metal concentration is adsorbed) for some metals by adsorption on $Fe(OH)_3$ gel (Table 1).

Investigations of the effects of pH on metal partitioning in sediments have mainly been performed using sequential extraction technique (Tessier *et al.* 1979). Studies of river sediments have shown that a pH decrease from 8 to 5 increases the levels of dissolved and exchangeable Cd, whereas little or no dissolved Pb is detectable at any pH (Gambrell *et al.* 1980, Khalid *et al.* 1981).

The concentration profiles of heavy metals in lake sediments are of interest because these elements are known to be emitted to the atmosphere in large quantities compared to the natural flux (Galloway *et al.* 1982, Norton *et al.* 1990). Atmospheric deposition of metals is mainly connected with acid precipitation originating from metallurgical works, metal rubbish heaps, and coal burning. Reduction of Cd, Zn, Ni, and Cu concentrations towards sediment surface of acidic lakes may be explained by desorption of metal compounds from sediments (Norton *et al.* 1981), decreasing metal sedimentation rate (Evans *et al.* 1983), or dynamic processes near the lake bottom during storms (Carignan and Tessier 1985). Profiles of heavy metal concentration versus depth in a sediment core typically exhibit subsurface maxima. This phenomenon could be explained by: (1) remobilization of metals from the sediment, (2) lower metal sedimentation rates due to decreased metal sorption to suspended particles in the water column and/or decreased availability of adsorbing surface. Decrease in adsorbing surface is caused by slower oxidation of Fe (II) to Fe (III) and, to a lesser extent, Mn (II) to Mn (IV), (3) differences in subsurface deposition of metals in the sediment, and (4) decreased atmospheric deposition of metals (Nelson and Campbell 1991). Of these mechanisms, only the first two can be directly linked to lake acidification.

Table 1. pH_{50} values (pH at which 50% of the initial metal concentration is adsorbed) for some heavy metals by adsorption on $Fe(OH)_3$ gel (Kinniburgh and Jackson 1981)

Heavy metal	Pb	<	Cu	<	Zn	<	Ni	<	Cd	=	Co
pH value	3.0		4.3		5.3		5.7		5.9		

The goal of the present paper is to study acidification and pollution effects on metal (Ni, Cu, Co, Zn, Cd, Pb, Mn, Fe, K, Na, Ca, Mg, Al) contents in sediments of lakes in the Finnish Lapland.

Materials and methods

Sediment cores were collected in June 1992 from the deeps (accumulation areas) of the studied lakes (Fig. 1) using a gravity corer as described by Skoghein (1979). Each core was split into 0.5 or 1 cm thick layers. Six layers were collected from each core: four 0.5 cm thick top layers characterizing modern situation in a lake, one layer from 5 to 6 cm depth corresponding with the inception of anthropogenic influence on a lake watershed, and one layer from 20 to 30 cm depth supplying background metal contents. The sediment samples were dried for 6 h at 105°C and the water content is expressed as the ratio of the weight of water to the wet weight of sediment (Håkanson and Jansson 1983). The samples were then ignited for 4 h at 550°C for determination of the loss on ignition as an indirect index of organic matter content (Håkanson 1977). Metal concentrations were determined by flame atomic absorption spectrophotometry (Perkin-Elmer 460 and 560) using the standard addition technique. For total metal analyses ca. 0.4 g (dry wt.) of sediment was digested in a Teflon digestion vessel for 4 h at 140°C with 4 ml concentrated nitric acid. The technique of chemical analyses has been described in more detail in Dauvalter (1994). To determine the extent of anthropogenic influence on lake ecosystems C_f values were calculated (Håkanson 1980, 1984). The BCI was determined to assess the ability of sediments to neutralize acidic compounds entering the lakes.

Fig. 1. Location of the 15 investigated lakes in Finnish Lapland. The lake numbers correspond to those on Tables 1 and 2.

Results and discussion

In four of the 15 investigated lakes the average (of the last 10 years) water pH was lower than 6.0 and alkalinity lower than 50 meq l^{-1} (Vasikkajärvi, Kenttälampi, Kauralampi and Silpalampi; Table 2). This study showed decreasing organic matter content (OMC) in top sediment of acidic lakes compared to deeper layers. Value of loss on ignition (LOI, as indication of OMC) in the sediment of Vasikkajärvi decreases to 48% in the top layer in comparison with 57% in the deepest layer. Decrease of LOI towards surface of sediment was evident in other acidic lakes as well (Fig. 2). Average LOI value of the 15 studied lakes is 40%, therefore all acidic lakes have high primordial OMC values that have decreased from 6 to 13% after onset of acidification. This has occurred probably due to reduction of biological activity in lakes and/or increasing flux of mineral particles from lakes' watersheds as a result of soil acidification. In non-acidic lakes OMC usually increases towards sediment surface owing to microbiological decomposition of organic materials (Kuznetsov 1970). A negative correlation (– 0.775) between lake pH and OMC of the sediments was also found in a study of 13 other Finnish lakes (Rekolainen *et al.* 1986). OMC also decreases in sediments of some acidic lakes in the United States towards surface of sediment (Norton *et al.* 1992). In all of the 15 studied lakes, decreasing LOI values with increasing water pH were observed (Fig. 3). Deceleration of microbiological decomposition of organic materials in sediments of acidic lakes could explain this relationship.

Vasikkajärvi and Silpalampi had very low acid leached Ca concentrations (10–22 µg g^{-1}), which are comparable with background trace metal contents. Calcium concentrations in the Vasikkajärvi sediments declined from 22 µg g^{-1} at sediment depth of 19–20 cm to 13 µg g^{-1} in the subsurface layer (0.5–1.0 cm), showing that decrease of Ca concentrations due to acidification are observed even in the case of very low Ca contents. Decreasing Ca contents with reduction of water pH were observed for all of the studied lakes ($r = 0.654$). Metals which are most easily liberated from sediment are in cation exchange position (largely Ca) or in easily dissolved hydroxide form such as $Fe(OH)_3$ (White and Gubala 1990). In lakes with pH initially between 5 and 6 watershed soil and lake sediment have low base saturation, and even a small decrease in base saturation of soil would predispose such a lake to further lake acidification (Norton *et al.* 1992). Sediment profiles from initially acidic lakes would probably not show marked declines in total Ca.

Significant decrease in Al concentration towards the surface of sediment was evident in Vasikkajärvi (1.46–0.94%), Silpalampi (2.33–1.05%), and Kenttälampi (0.88–0.37%) (Fig. 2), a trend probably connected with lake acidification. Aluminium concentrations in the sediment top layer of the investigated lakes decreased with reduction of water

Table 2. Values of water pH and alkalinity (Alk, meq l^{-1}) (upper numbers: 1 m from surface, lower numbers: 1 m from bottom), loss on ignition (LOI, %) and metal concentrations (mg g^{-1} dry substance) for surface (0–1 cm) sediments (upper numbers) and background contents (lower numbers) for 15 Finnish Lapland lakes. BCI- buffer capacity index.

Lake	pH*	Alk*	LOI	Ni	Cu	Co	Zn	Pb	Cd	Mn	Fe, %	Ca	Mg	Na	K	Al, %	BCI
Kemijärvi	7.47	358	10.48	50	18	19	71	< 10	< 0.70	4 263	4.77	219	7 342	445	1 380	1.34	0.70
	–	–	5.55	33	10	15	58	< 10	< 0.70	1 089	3.22	231	6 049	442	1 193	0.95	0.83
Sierijärvi	6.77	87	33.64	37	22	9	158	8	< 0.50	593	5.69	48	4 773	339	1 955	1.24	0.57
	6.46	224	32.04	40	18	15	107	< 7	0.50	777	5.84	63	4 706	356	1 026	1.70	0.36
Vasikkajärvi	5.56	– 6	47.95	20	19	5	50	52	< 0.40	83	6.84	16	779	128	784	0.94	0.18
	5.50	4	56.86	18	17	1	31	5	< 0.40	81	1.69	22	1 002	109	684	1.46	0.12
Kenttälampi	6.43	87	47.04	12	15	3	52	31	0.28	50	0.54	326	515	66	413	0.37	0.36
	5.85	59	53.75	6	11	2	24	< 6	0.31	58	0.43	157	397	38	252	0.88	0.10
Saukkojärvi	6.84	152	26.54	8	3	2	37	< 10	0.73	53	0.42	439	479	82	561	0.23	0.69
	6.76	221	11.81	6	3	< 2	41	< 10	0.29	81	0.74	233	2 041	98	848	0.42	0.76
Kauralampi	5.60	– 4	65.30	2	10	2	57	31	0.20	50	0.54	261	489	45	344	0.44	0.26
	5.47	– 2	78.22	7	5	< 2	18	3	0.50	58	0.43	323	460	52	345	0.39	0.30
Haltijärvi	7.05	174	45.29	11	11	2	61	17	0.21	21	0.12	767	924	147	573	0.18	1.34
	6.36	219	50.27	5	3	1	25	12	0.15	13	0.09	922	653	66	226	0.24	0.80
Silpalampi	4.97	1	61.51	15	13	1	55	71	0.11	26	0.44	12	662	78	531	1.05	0.12
	5.39	20	71.28	21	20	1	35	7	0.72	33	0.42	10	592	64	672	2.33	0.06
Inarinjärvi(1)	7.20	166	18.21	47	42	15	98	25	0.61	3 448	7.61	213	6 421	346	3 424	2.45	0.42
	–	–	13.71	46	41	16	97	9	0.64	2 074	7.05	286	5 695	368	3 311	2.30	0.42
Inarinjärvi(2)	7.16	157	20.19	45	58	11	83	54	1.10	359	2.84	140	3 762	346	2 508	1.88	0.36
	–	–	16.46	32	51	13	90	7	0.21	277	1.96	200	4 236	354	3 401	1.97	0.42
No. 066006	7.20	214	43.60	46	20	13	71	28	0.17	255	2.83	61	1 334	125	1 264	1.12	0.33
	–	–	33.83	57	20	23	68	17	0.41	178	3.05	55	1 013	95	795	1.32	0.08
No. 066004	7.20	239	41.16	14	15	2	43	17	< 0.50	39	0.48	283	738	109	472	0.48	0.33
	–	–	30.63	12	32	2	30	< 9	< 0.50	12	0.05	63	431	36	187	0.87	0.08
Sarelompolo	6.90	145	41.22	25	16	2	45	7	0.77	73	0.39	578	1 086	68	723	0.63	0.39
	–	–	35.24	25	18	2	36	< 7	0.43	72	0.45	390	979	81	483	0.69	0.28
No. 067000	6.50	–	61.25	29	23	1	56	49	1.85	27	0.43	74	817	72	654	0.68	0.24
	–	–	83.12	50	59	4	92	3	0.41	32	0.80	4	709	89	610	1.64	0.09
Nuttiolampi	7.60	601	37.62	28	31	12	195	36	3.13	11 490	7.58	1483	1 920	192	510	0.96	0.43
	6.90	887	32.32	36	29	32	131	7	1.69	18 221	17.8	271	1 929	166	324	0.90	0.30

* – data from Lapland Water and Environment District (LAVY), Rovaniemi, Finland.
(1) Vartasaara, (2) Vasikkaselkä.

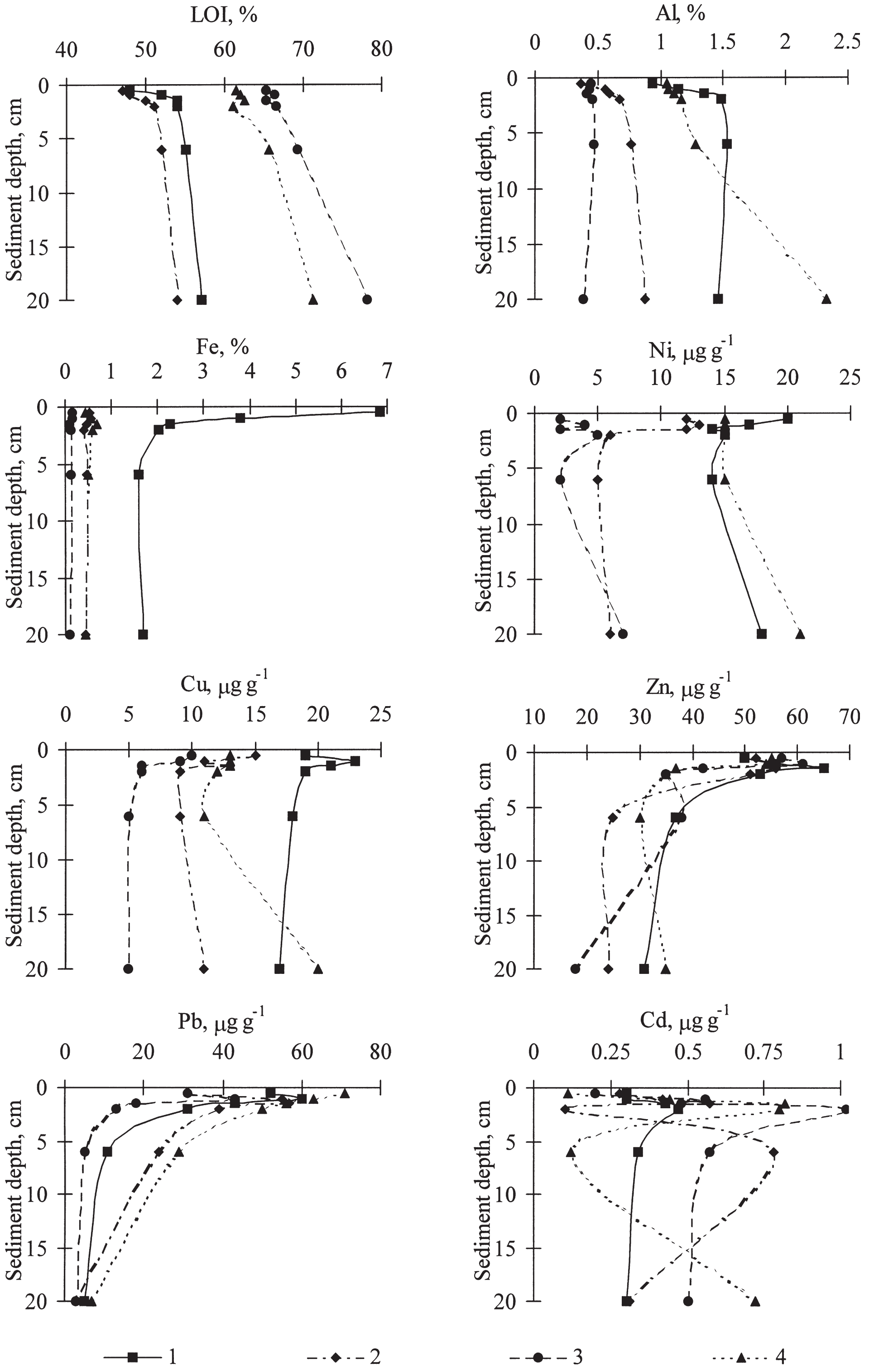

Fig. 2. Vertical distribution of organic matter contents (loss on ignition, LOI, %), Al and Fe (%), Ni, Cu, Zn, Pb and Cd (µg g^{-1} dry wt.) in the sediment cores of Vasikkajärvi (1), Kenttälampi (2), Kauralampi (3), and Silpalampi (4).

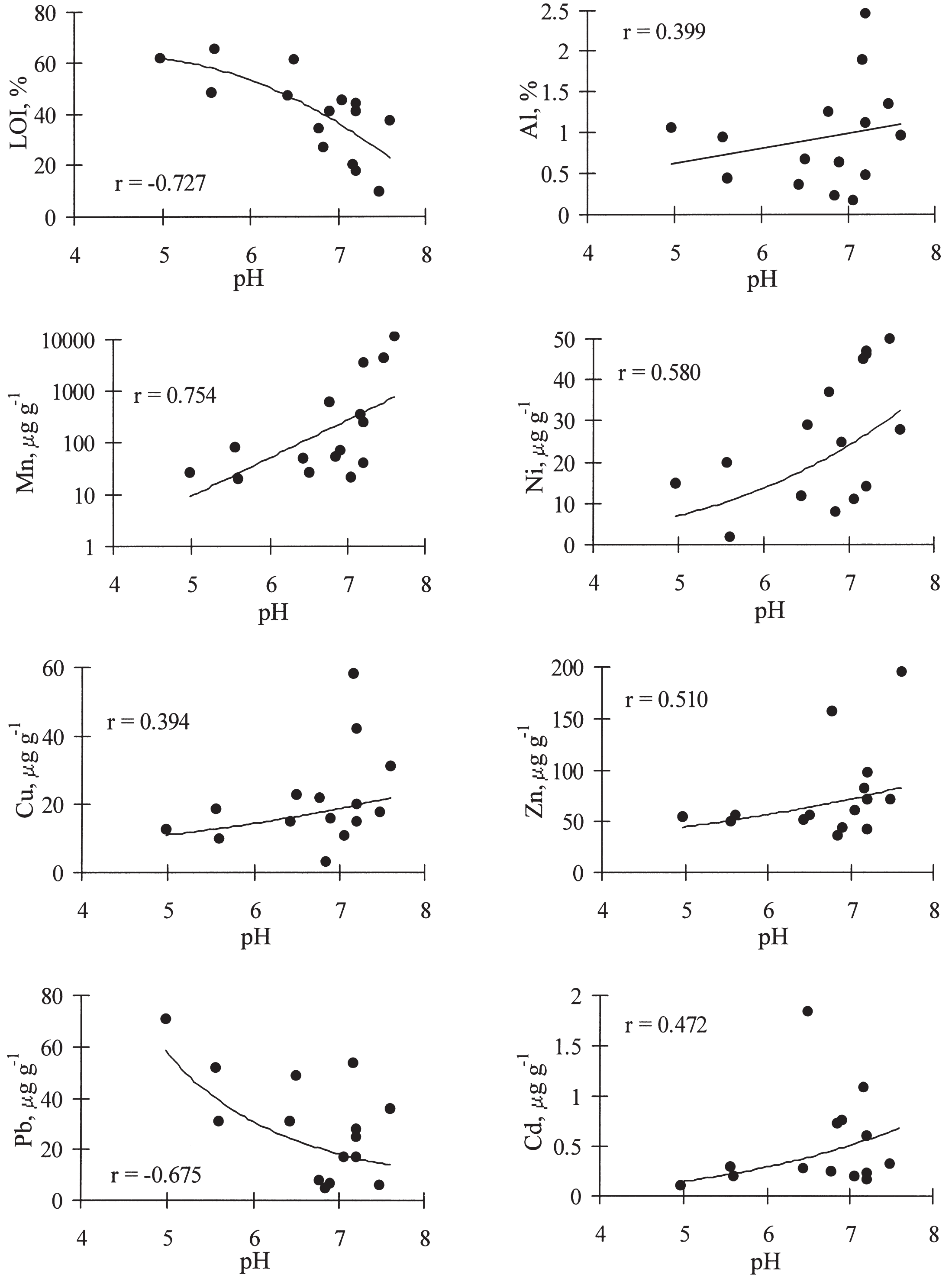

Fig. 3. Regressive trends and correlation values between lake water pH and organic matter contents (loss on ignition, LOI), Al, Mn, Ni, Cu, Zn, Pb, and Cd in the top sediment (0.0–0.5 cm) of 15 studied lakes in Finnish Lapland.

pH (Fig. 3) and correlated well with contents of Ni, Cu, Co, Mg, Na and K ($r = 0.747$–0.917). Acidification affects sediment-Al interactions (Campbell *et al.* 1985). This conclusion was based on the elevated levels of aqueous Al reported for acidic lakes (for example Moiseenko 1994 and Rodushkin *et al.* 1995) and lakes and streams subjected to artificial acidification. Aluminium concentrations in the upper sediment layers of acidified Clearwater Lake decrease slightly (Dillon and Smith 1984). However, no mechanisms affecting Al accumulation in the sediments were determined. White and Gubala (1990) suggest that increase in the amount of labile Al in recent Deep Lake sediments is consistent with pH decline (inferred from diatoms) (Charles *et al.* 1990).

Acidified lakes had lower values of buffer capacity index (BCI) (0.12–0.36), whereas other investigated lakes had higher BCI-values (0.42–1.34) (Table 2). BCI-values in the surface sediments of the investigated lakes decreased with reduction of water pH ($r = 0.680$). BCI-values for background sediments in acidic lakes were lower than in surface layers, therefore these lakes were naturally predisposed to acidification. Only small amounts of acidic compounds entering would be necessary for acidification development.

Manganese concentrations in sediments of acidic lake were very low (Table 2), particularly in Silpalampi and Kauralampi (16–33 µg g^{-1}). Manganese concentrations were comparable with Ni, Cu, and Pb contents and lower than Zn concentrations. Manganese concentrations in the surface sediments of the 15 investigated lakes decreased with reduction of water pH (Fig. 3). Manganese in sedimenting material may be largely unaffected by water column acidification if Mn is bound largely within non-labile inorganic mineral matter (White and Gubala 1990).

Surface maximum of Fe concentration was noticed in the sediments of Vasikkajärvi and Kauralampi, 6.84 and 0.16% respectively, whereas in the Silpalampi and Kenttälampi Fe demonstrated subsurface maximum, 0.70 and 0.56% in the layers of 1.0–1.5 cm and 0.5–1.0 cm, respectively (Fig. 2). Level of Fe in the upper layer of the Vasikkajärvi sediment was 4-fold greater than background level, whereas in the other acidic lakes the increase reached only some percentages. Concentrations of Fe and Mn had correlated well with contents of Ni, Cu, Co, Zn, and Cd (0.515–0.764). Oxides of Fe and Mn have long been known as excellent scavengers of trace metals from solution (Horowitz 1987). Concentration of Fe in the sediment typically increases independently at some point in the last 100 years, usually in the last 50 years (Norton *et al.* 1992). Concentration of Fe is in most cases higher in surface or near-surface sediments. Upward molecular diffusion of dissolved Fe and Mn from the reducing environment of older sediment and precipitation at or near the sediment-water interface under more oxidizing conditions is the likely cause of such enrichment (Norton 1974, Engstrom and Wright 1984). Precipitation of Fe sulphide in zones of sulphate reduction also may localize Fe enrichment (Carignan and Tessier 1988). The maximum Fe concentration for the Deep Lake, New York, USA, coincides with a maximum sulphur concentration (Mitchell *et al.* 1990) suggesting that some of the Fe exists as a sulphide mineral. The increased flux of Fe to the lake is due to mobilization of Fe from soils and stream sediment due to the increased concentration of mobile anion (excess SO_4^{-2}) and slight soil acidification (Norton *et al.* 1992). Mobilization may also occur during episodic acidic events in the early stage of watershed acidification (Borg 1986). The dissolved and particulate Fe, upon reaching the higher pH regime of the lake, would be removed by settling of allochtonous particles and precipitation and sedimentation of dissolved Fe. After a watershed has became chronically acidic, this mechanism of Fe mobilization should effectively cease operating (Norton *et al.* 1992).

Subsurface (0.5–1.0 cm) maximum of Cu concentration (23 µg g^{-1}) and decrease towards sediment surface (19 µg g^{-1}) was noticed in the Vasikkajärvi sediment core (Fig. 2). Decrease of Cu concentrations down to 13 µg g^{-1} in the upper layers from 20 µg g^{-1} in the lowest layer was found in the Silpalampi sediment core. Decreasing Ni concentrations in the upper sediments of Kauralampi, Silpalampi, and Kenttälampi were noticed (Fig. 2). Therefore, a conclusion might be done that lake acidification may decrease Ni and Cu contents in the surface lake sediments. In comparison, surface Cu maximum (10 µg g^{-1}) of twice the very low background level. Taking into account that Cu concentrations in the upper and lower sediment core layers were 24.3 and 27.7 µg g^{-1} ash weight, respectively, it is very difficult to say about influence of lake acidification on Cu geochemistry in this lake. Considering the 15 studied lakes, decreasing Cu and Ni values with reduction of water pH were observed (Fig. 3). Contamination of sediments by Ni and Cu was low and moderate (Table 3). Maxima for concentrations of Ni and Cu were most often observed in recent sediments, suggesting that these elements more faithfully track trends in atmospheric depositions than does Zn (Norton *et al.* 1992).

The Vasikkajärvi sediment had a subsurface maximum Zn concentration at 1.0–1.5 cm sediment depth (65 µg g^{-1}), which was twice the background value (Fig. 2). Concentration of Zn decreased in the uppermost layer to 50 µg g^{-1}. Kauralampi and Kenttälampi had a subsurface maximum of Zn concentration at 0.5–1.0 cm sediment depth 61 and 56 µg g^{-1}, respectively, that 3.2 and 2.2 times higher, than the background value (Fig. 2). Silpalampi had surface maximum at 55 and 54 µg g^{-1} in the layers of 0.0–0.5 and 0.5–1.0 cm, respectively, which is 1.5-fold greater than the background content. We can conclude that Zn concentration in the upper layers is considerably higher than the background concentrations (Fig. 2, Table 3) and that decreasing Zn concentrations in the upper layers may be caused by lake acidification. Concentrations of Zn in the surface sediments of the 15 investigated lakes decreased with reduction of water pH (Fig. 3). Concentrations of Zn in cores from some acidic lakes have a subsurface maxima and surface concentrations lower than background values (Norton *et al.* 1992). The subsurface maxima for anthropogenic Zn vary in age even in contiguous watersheds. For example, in lakes within 1 km^2 area Zn maxima in the sediment range from 1967 to 1982 (Norton *et al.* 1992). There are three hypotheses to explain the subsurface Zn maxima: diagenetic precipitation of downward diffusing Zn in the zone of SO_4 reduction within the sediment (Carignan and Tessier 1985), reduced adsorption of Zn onto sedimenting particles, and desorption of Zn from already sedimented material (Norton 1983).

Table 3. Values of contamination factor (C_f) for studied Finnish Lapland lakes

Lake	C_f					
	Ni	Cu	Co	Zn	Pb	C
Kemijärvi	1.5	1.8	1.3	1.2	1.0	1.0
Sierijärvi	0.9	1.2	0.6	1.5	1.0	1.0
Vasikkajärvi	1.1	1.1	5.0	1.6	10.4	1.0
Kenttälampi	2.0	1.4	1.5	2.2	10.3	0.9
Saukkojärvi	1.3	1.0	1.0	0.9	1.0	2.5
Kauralampi	0.3	2.0	1.0	3.2	10.3	0.4
Haltijärvi	2.2	3.7	2.0	2.4	1.4	1.4
Silpalampi	0.7	0.7	1.0	1.6	10.1	0.2
Inarinjärvi(1)	1.0	1.0	0.9	1.0	2.8	1.1
Inarinjärvi(2)	1.4	1.1	0.8	0.9	7.7	5.2
No. 066006	0.8	1.0	0.6	1.0	3.2	0.4
No. 066004	1.2	0.5	1.0	1.4	3.8	1.0
Sarelompolo	1.0	0.9	1.0	1.3	2.0	1.8
No. 067000	0.6	0.4	0.3	0.6	16.3	4.5
Nuttiolampi	0.8	1.1	0.4	1.5	5.1	1.9

(1) Vartasaara, (2) Vasikkaselkä.

Concentrations of Pb had subsurface maxima at 0.5–1.5 cm in the sediments of Vasikkajärvi (60 µg g^{-1}), Kauralampi (43 µg g^{-1}), and Kenttälampi (57 µg g^{-1}) (Fig. 2) and a surface maximum in Silpalampi (71 µg g^{-1}). Background Pb concentrations of these lakes were 10-fold lower (Table 3). The average upward increase in concentration of Pb in sediment profiles of 9 northern pristine Finnish headwater lakes was 14.4-fold (Verta *et al.* 1990) coinciding with our results. Other studied lakes with neutral pH had also surface or subsurface (at 0.5–1.0 cm) maxima. Atmospheric deposition of Pb has declined dramatically since the 1970's, primarily because of the decreased use of Pb in gasoline (Eisenreich *et al.* 1986). Some authors have reported of Pb decreasing towards the surface sediment (e.g. Renberg 1985). Before 1985 in lakes with relatively undisturbed watersheds Pb concentration increased continuously towards the sediment-water interface (Norton *et al.* 1981). This pattern was also noted in acidic lakes (e.g. Ouellet and Jones 1983), which suggests that the critical pH for Pb release from suspended and/or bottom sediments was below the observed water column pH. This observation has been confirmed in laboratory experiments on surface sediments: Pb release from the sediments did not occur above pH 3 (Davis *et al.* 1982). Therefore, we can conclude that reduction of Pb concentration in sediment of acidic lakes is not connected with acidification. This reduction is caused most probably by decrease in the consumption of gasoline with tetra-ethyl Pb (Norton *et al.* 1992). Concentration of Pb in the upper sediments of the 15 studied lakes increased with reduction of water pH (Fig. 3). Contents of Pb correlated positively with OMC (0.472), whereas negative correlation was noticed for other heavy metals (– 0.267– – 0.646).

Decreasing Cd concentrations down to 0.11–0.20 µg g^{-1} in the surface (0.0–0.5 cm) sediment were found in Vasikkajärvi, Silpalampi, Kauralampi, and Kenttälampi, and subsurface maximum values (0.47–1.02 µg g^{-1}) were noticed at 1.0–2.0 cm depth (Fig. 2). Contamination of sediment of the studied lakes was low to moderate (Table 2) with the exception at the deepest place of the Inarinjärvi Lake, Vasikkaselka, where considerable Cd content was expressed. Decreasing Cd concentration in the top sediment layer of 15 studied lakes with reduction of water pH were observed (Fig. 3). Based on Cd profiles in sediment cores from two acidified Norwegian lakes (mean pH 4.4 and 5.0) it may be concluded that Cd is remobilized from the sediments when the lake pH declines below 5 (Norton and Hess 1980). Concentration of Cd in sediment cores of acidified Gårdsjön Lake, Sweden, was greatest 5–7 cm below the sediment-water interface (Renberg 1985). The subsurface maxima were in sediment deposited at the onset of acidification. Once the lake water stabilized at pH 4.5, the accumulation rates of Cd returned to pre-industrial levels. Renberg (1985) concluded that Cd concentration had been reduced in recent years because water column acidification decreased the sorption of Cd on settling sediment matter. Cd was released from the sediments below pH 5 in laboratory experiments with sediment-water microcosms from the Gårdsjön Lake (Andersson and Gahnstrom 1985).

Conclusions

In acidic lakes OMC was lower in surface layer than in deeper layers of sediment. This is probably caused by reduction of biological activity in lakes and/or increased flux of mineral particles from lakes' watersheds as a result of soil acidification.

Decreased concentrations of Cd, Zn, Cu, Ni, and Al from lower to higher layers of sediment may indicate acidification. Decrease may be caused by: (1) metal sedimentation decrease due to reduced adsorption of chemical components onto sinking particles, and (2) desorption or dissolution of metals from already sedimented materials. Concentrations of Cd, Zn, Cu, Ni, and Al in the top sediment of the 15 studied lakes decreased with reduction of water pH.

The acidic lakes have lower values of buffer capacity index (BCI) than non-acidic lakes. BCI-values for background sediments in acidic lakes were lower than in surface layers, therefore these lakes were naturally predisposed to acidification.

Contamination factor (C_f) of Pb is high in comparison to other investigated heavy metals, particularly for acidic lakes ($C_f = 10.1–10.4$). Ni, Cu, Co, Zn, and Cd contents increase insignificantly towards the sediment surface in rare cases of some lakes with a neutral pH.

Thus, BCI-values, changes in Al, Cd, Pb, Cu, and Ni concentrations, as well as organic matter contents in the top layers of lake sediment are good diagnostic tools to analyze acidity status of freshwater environment.

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References

Almer B., Dickson W., Ekström C. & Hörnström E.1978. Sulfur pollution and the aquatic ecosystem. In: Nriagu J.O. (ed.), *Sulfur in the environment. Part II, Ecological impacts,* Wiley Interscience, New York, pp. 271–311.

Almer B., Dickson W., Ekström C., Hörnström E. & Miller U. 1974. Effects of acidification on Swedish lakes. *Ambio* 3: 30–36.

Andersson G. & Gahnström G. 1985. Effects of pH on the release and sorption of dissolved substances in sediment-water microcosms. *Ecol. Bull.* (Stockholm) 37: 301–318.

Borg H. 1986. Metal speciation in acidified mountain streams in central Sweden. *Wat. Air Soil Pollut.* 30: 1007–1114.

Campbell P.G.C., Stokes P.M. & Galloway J.N. 1985. *Acid deposition: Effects on geochemical cycling and biological availability of trace elements*. Subgroup on metals of the Tri-Academy Committee on Acid Deposition. National Academy Press, Washington, DC.

Carignan R. & Tessier A. 1985. Zinc deposition in acid lakes: the role of diffusion. *Science* 228: 1524–1526.

Carignan R. & Tessier A. 1988. The co-diagenesis of sulfur and iron in acid lake sediments of southwestern Quebec. *Geoch. Cosmoch. Acta* 52: 1179–1188.

Charles D.F., Binford M.W., Furlong E.T., Hites R.A., Mitchell M.J., Norton S.A., Oldfield F., Paterson M.J., Smol J.P., Uutala A.J., White J.R., Whitehead D.R. & Wise R.J. 1990. Paleolimnological investigation of recent lake acidification in the Adirondack Mountains, N.Y. *J. Paleolim.* 3: 195–242.

Dauvalter V. 1994. Heavy metals in lake sediments of the Kola Peninsula, Russia. *Sci. Tot. Envir.* 158: 51–61.

Davis A., Galloway J.N. & Nordström D.K. 1982. Lake acidification: its effects on lead in the sediment of two Adirondack lakes. *Limnol. Oceanogr.* 27: 163–167.

Dillon P.J. & Smith P.J. 1984. Trace metal and nutrient accumulation in the sediments of lakes near Sudbury, Ontario. In: J. Nriagu (ed.), *Environmental Impacts of Smelters*, John Wiley & Sons, New York, pp. 375–416.

Eisenreich S.J., Metzer N.A., Urban N.R. & Robbins J.A. 1986. Response of atmospheric lead to decreased use of lead in gasoline. *Environ. Sci. Tech.* 20: 171–174.

Engstrom D.R. & Wright H.E. 1984. Chemical startigraphy of lake sediments as a record of environmental change. In: Haworth E.Y. & Lund J.W.G. (eds.), *Lake Sediments and Environmental History. Studies in Paleolimnology and Paleoecology*, Leicester University Press, 11 pp.

Evans H.E., Smith P.J. & Dillon P.J. 1983. Anthropogenic zinc and cadmium burdens in sediments of selected southern Ontario lakes. *Can. J. Aquat. Sci.* 40: 570–579.

Fleischer S., Andersson G., Brodin Y.W., Dickson W., Herrmann I. & Muniz I.P. 1993. Acid water research in Sweden — Knowledge for tomorrow. *Ambio* 22: 258–263.

Forsius M., Kinnunen K., Kortelainen P., Kämäri I, Mannio J. & Verta M. 1988. Järvien happamoituminen etenee. (The acidification state of Finnish Lakes). *Suomen Luontc.* 47, 4: 46–51. (In Finnish with English summary).

Galloway J.N., Thornton J.A., Norton S.A., Volchok H.L. & McLean R.A.N. 1982. Trace metals in atmospheric deposition: A review and assessment. *Atmos. Envir.* 16: 1677–1700.

Gambrell W.H., Khalid R.A. & Patrick W.H. 1980. Chemical availability of mercury, lead and zinc in Mobile Bay sediment. *Environ. Sci. Technol.* 14: 431–436.

Håkanson L. 1977. An empirical model for physical parameters of recent sedimentary deposits of Lake Ekoln and Lake Vänern. *Vatten* 3: 266–289.

Håkanson L. 1980. An ecological risk index for aquatic pollution control — a sedimentological approach. *Water Res.* 14: 975–1001.

Håkanson L. 1984. Sediment sampling in different aquatic environments: Statistical aspects. *Water Resour. Res.* 20, 1: 41–46.

Håkanson L. and Jansson M. 1983. Principles of Lake Sedimentopogy. Springer-Verlag, Berlin, Heidelberg, 316 p.

Henriksen A., Lien L. & Traaen T. 1988. Lake acidification in Norway — Present and predicted chemical status. *Ambio* 17: 259–266.

Horowitz A.J. 1987. *A primer on trace metal-sediment chemistry*. United States Geological Water Supply, Paper 2277, 66 pp.

Kämäri I., Forsius M., Kortelainen P., Mannio J. & Verta M. 1991. Finnish lake survey: present status of acidification. *Ambio* 20: 23–27.

Kauppi P., Anttila R. & Kenttämies K. (eds.) 1990. *Acidificacation in Finland.* Springer-Verlag, Berlin, 1237 pp.

Khalid R.A., Gambrell R.P. & Patrick W.H. 1981. Chemical availability of cadmium in Mississippi River sediment. *J. Environ. Qual.* 10: 523–528.

Kinniburgh D.G. & Jackson M.L. 1981. Cation adsorption by hydrous metal oxides and clay. In: Anderson M.A. & Rubin A.J. (eds.), *Adsorption of inorganics at solid-liquid interfaces*, Ann Arbor Science Publishers, Ann Arbor., pp. 91–160.

Kuznetsov S.I. 1970. *Lake microflora and its geochemical activity*, Leningrad, Nauka, 440 pp. (in Russian).

Makarova T. & Ratkin N. 1991. *Complex ecologic-geographical forecast of Kola Peninsula environment condition*, Report of INEP, Kola Science Centre, Apatity, 40 pp (in Russian).

Merilehto K., Kenttämies K. & Kämäri I. (eds.), 1988. *Surface water acidification in the Ace region. Nordic Surface Water*, Miljørapport 1988, 14, 156 pp.

Mitchell M.J., Schindler S.C., Owen J.S. & Norton S.A. 1990. Factors affecting sulfur incorporation into lake sediments: paleolimnological implications. *J. Paleolim.* 4: 1–22.

Moiseenko T. 1994. Acidification and critical loads in surface waters: Kola, Northern Russia. *Ambio* 23, 7: 418–424.

Nelson W.O. & Campbell P.G.C. 1991. The effects of acidification on the geochemistry of Al, Cd, Pb and Hg in freshwater environments: A literature review. *Envir. Pollut.* 71: 91–130.

Norton S.A. 1974. Post-glacial iron-rich crusts in hemipelagic deep-sea sediment: Discussion. *Geol. Soc. Am.* 844: 159–160.

Norton S.A. 1983. The chemical role of lake sediments during lake acidification and de-acidification. In: *Proc. 11th Nordic Symp. on sediments*, University of Oslo, Norway, pp. 7–19.

Norton S.A., Bienert R.W.J., Binford M.W. & Kahl J.S. 1992. Stratigraphy of total metals in PIRLA sediment cores. *J. Paleolimn.* 7: 191–214.

Norton S.A., Davis R.B. & Brakke D.F. 1981. Responses of northern New England lakes. In: Eisenreich S.J. (ed.), *Inputs of atmospheric pollutants to natural waters*, Ann Arbor Science Publishers, pp. 402–421.

Norton S. A., Dillon P. J., Evans R. D., Mierle G. & Kahl J. S. 1990. The history of atmospheric deposition of Cd, Hg and Pb in North America: Evidence from lake and peat bog sediments. In: Lindberg S. E., Page A.L. & Norton S.A. (eds.), *Sources, Deposition and Capony Interactions. Vol. III, Acidic Precipitation*, Springer-Verlag, New York, pp. 73–101.

Norton S.A. & Hess C.T. 1980. Atmospheric deposition in Norway during the last 300 years as recorded in SNSF lake sediments: Sediment dating and chemical stratigraphy.

In: *Proc. Intern. Ecol. Impact of Acidic Precipitation*, SNSF-project, Sandefjorden, Norway, pp. 274–275.

Ouellet M. & Jones H.G. 1983. Historical changes in acid precipitation and heavy metals deposition origination from fossil fuel combustion in eastern north America as revealed by lake sediment geochemistry. *Water Air Soil Pollut., Sci Tech.*: 15: 115–130.

Rekolainen S., Verta M. & Liehu A. 1986. The effect of airborne mercury and peatland drainage on sediment mercury contents in some forest lakes. *Publ. Water Res. Inst., Nat. Board Waters, Finland* 65: 11–20.

Renberg I. 1985. Influences of acidification on the sediment chemistry of Lake Gårdsjön, SW Sweden. *Ecol. Bull.* 37: 246–250.

Rodushkin I.V., Moiseenko T.I. & Kudravsjeva L.P. 1995. Aluminium in Surface Water of Kola Peninsula. *Sci. Tot. Environ.* 163: 55–59.

SFT. 1987. The Norwegian State Pollution Control Authority. 1000 Lake Survey Norway 1986. Report 283/87. Oslo, Norway, 33 pp.

Skogheim O.K. 1979. *Rapport fra Arungenprosjektet*, Nr. 2. As- NLH, 7 pp.

Tessier A., Campbell P.G.C. & Bisson M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51, 7: 844–851.

Verta M., Mannio J., Iivonen P., Hirvi J.-P., Jarvinen O. & Piepponen S. 1990. Trace metals in Finnish headwater lakes — Effects of acidification and airborne load. In: Kauppi P., Anttila R. & Kenttamies K. (eds.), *Acidification in Finland*, Springer-Verlag, Berlin, pp. 883–920.

White J.R. & Gubala C.P. 1990. Sequentially extracted metals in Adirondack lake sediment cores. *J. Paleolim.* 3: 243–252.

Wood J.M. 1974. Biological cycles for toxic elements in the environment. *Science* 183: 1049–1052.

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