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Heavy metal concentrations in various aqueous and biotic media in Finnish Integrated Monitoring catchments

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Concentrations of Cd, Cu, Ni, Pb and Zn in various aqueous and biotic media in four small forested catchments located throughout Finland (61–70°N) are presented. The data has been collected (1989–96) as part of the UN-ECE Integrated Monitoring programme. Aqueous media included: bulk (open) precipitation, throughfall, stemflow, soil water, groundwater, and lake and stream waters. The biotic media included: moss (*Pleurozium schreberi*), needles (*Pinus sylvestris*), litterfall, humus layer, red wood ants (*Formica aquilonia* and *F. lugubris*), and common shrew (*Sorex areneus)* liver. In comparison to temperate ecosystems, the concentrations of each metal in all media were low. Levels and bioaccumulation of Cu and Zn were clearly affected by their role as micro-nutrients and, in the case of Zn at one of the catchments, by local lithological sources. Humus layer and surface water 95th percentile concentration values were below lowest effect values. Concentrations of Pb have significantly declined over the study period.

Introduction

As sulphur dioxide emissions and acidic deposition have declined over the last 1–2 decades, attention was increasingly turning towards the effects of nitrogen, and heavy metal deposition on forest and freshwater ecosystems (Tyler 1989, Adriano 1991, Alloway 1995). The environmental significance of heavy metals lies in their toxicity to organisms. Toxicity varies with heavy

metal and depends on its speciation, concentration, exposure, and interaction with other solutes. Toxicity also varies between species and position in the food chain. Some heavy metals, e.g. copper and zinc, are needed in small amounts by organisms, only becoming toxic at elevated concentrations.

Heavy metal emissions to the atmosphere in Finland for 1990 were Cd: 4 t, Cu: 37 t, Ni: 71 t, Pb: 215 t and Zn: 143 t (Berdowski *et al.* 1997). The deposition (bulk) of heavy metals in Finland has only been systematically monitored since 1990 (Leinonen and Juntto 1991). Data for throughfall are available for a limited number of stands (Hyvärinen 1990), but virtually non-existent for stemflow. However, there is considerable data on heavy metal concentrations in mosses, lichens and bark (Lippo *et al.* 1995), which are widely used as bioindicators of atmospheric deposition (Tyler 1989, Steinnes 1995, Berthelsen *et al.* 1995, Berg *et al.* 1995, Berg and Steinnes 1997). Although mosses and lichens receive most of their nutrient supply from atmospheric deposition, their use as measures of deposition depends on the sampling location in relation to canopy cover and their capacity to retain elements, which varies with heavy metal (Berg *et al.* 1995, Steinnes 1995). Calibration of heavy metal concentrations in mosses collected from canopy openings with bulk deposition collected in the open shows that mosses are reliable bioindicators of the deposition for Pb and Cd but considerably less so for Cu, Zn and Ni (Berg *et al.* 1995, Ruoho-Airola *et al.* 1995). Repeated surveys of heavy metal concentrations in mosses for Northern Europe, including Finland, have been carried out at five year intervals since 1985 (Rühling *et al.* 1987, Rühling *et al.* 1992, Rühling *et al.* 1996). Areas of relatively high heavy metal deposition in Finland reflect local emission sources which are superimposed on a general pattern of decreased concentrations northwards. Comparison of the maps from 1985–95 indicate a clear decline in the deposition of several heavy metals over this period, Pb in particular. Moss Zn concentrations, however, have remained much the same.

A comprehensive regional study into the effects of air pollution from the Kola Peninsula Cu–Ni smelters was carried out in Finnish Lapland (Tikkanen and Niemelä 1995). The results showed that deposition of Cu and Ni decreased dramatically with distance westwards from the smelters. S‡y effects in Lapland were limited to the eastern border region, where concentrations in Scots pine needles and bark were higher. There was little measurable effect on the soil and soil water concentrations beyond 30 km westward from the smelters (Lindroos *et al.* 1996, Lindroos 1998).

Average heavy metal concentrations in forest soils in southern Finland were reported by Tamminen and Starr (1990). This study and a number of case studies (e.g., Helmisaari *et al.* 1995), indicate that much of the heavy metal deposition to forest ecosystems has accumulated in the humus layer. Thus, in spite of current reductions in deposition, the accumulation of heavy metals from the past can still exert an effect in the future. The duration of this effect will depend on the size of the pool and conditions affecting the mobility of heavy metals, which are strongly related to acidity and the mobility of organic matter (Bergkvist *et al.* 1989).

Maps of heavy metal concentrations in Finnish tills show that they are strongly determined by the geochemistry of the underlying bedrock (Koljonen 1992) and to the amount of fines (< 0.06 mm) in the deposit (Lintinen 1995, Tarvainen 1995). Concentrations of heavy metals in headwater lakes, streams, and groundwater show large regional differences, reflecting differences in bedrock geochemistry and catchment characteristics in the case of Cu and Ni and also deposition in the case of Pb and Cd (Lahermo *et al.* 1990, 1996, Mannio *et al.* 1993, Mannio *et al.* 1995, Tarvainen *et al.* 1997). Nevertheless, airborne heavy metals have accumulated in lake sediments, even in background areas; the mobility of which is also dependent on acidity and humic substances (Verta *et al.* 1990, Mannio *et al.* 1993, Mannio *et al.* 1995, Tenhola 1993).

Except for mosses and lichens, which are used as indicators of deposition heavy metal, data are much less available for biota than for the abiotic media. Lounamaa (1956) reported trace element concentrations in a wide range of plants in relation to concentrations in the underlying rocks and soil in Finland. Concentrations of the trace elements Cu and Zn in Scots pine and Norway spruce needles from repeated national surveys have been

reported (Raitio 1994). There were no significant differences in concentrations between 1987, 1988 and 1989 samplings. Red wood ants (*Formica* spp.) and shrews (*Sorex* spp.) have been used as bioindicators of heavy metals in Finland because of their widespread distribution (Nuorteva 1990, Pankakoski *et al.* 1994, Heikura *et al.* 1997, Hirvi 1997). Heavy metal concentrations in aquatic plants and insects and in fish from acid and non-acid lakes were reported by Verta *et al.* (1990) and Iivonen *et al.* (1992). Concentrations, were poorly correlated to water and to sediment heavy metal concentrations, but were correlated to water acidity and dissolved humic substances, which are governed by the characteristics of the catchment rather than deposition loads.

A major problem in assessing the environmental impact of heavy metal pollution on forest ecosystems, however, is the lack of comparable and integrated data on ecosystems (Bergkvist *et al.* 1989). Most studies cover only one or two components of the ecosystem, and case studies have used different methods making comparison difficult. As a number of studies have shown, the best way of achieving integrated data is by studying the biogeochemistry of small catchments (e.g. Bergkvist 1987, Dillon *et al.* 1988, Johnson and Van Hook 1989, Lazerte *et al.* 1989, Johnson and Lindberg 1992, Kvindesland *et al.* 1994, Forsius *et al.* 1995, Aastrup *et al.* 1995 , 1997).

In this paper, we describe the levels of Cd, Cu, Ni, Pb and Zn in various aqueous and biotic media in four small forested catchments located in the southern, middle and northern (two) boreal zones in Finland. The catchments have been systematically monitored since 1989 as part of the UN-ECE International Cooperative Programme on Integrated Monitoring (IM) to monitor the effects of long-range transboundary air pollution on forest ecosystems (EDC 1993). The sampling and analytical protocols of the IM programme (EDC 1993) were followed for all media except the ant and shrew liver media. Geographic patterns, temporal changes, and bioaccumulation and toxicological implications are discussed. This is the first time such integrated data has been presented for Finland.

Material and methods

Integrated Monitoring catchments

The data were collected from the four Finnish IM catchments: Valkea-Kotinen, Hietajärvi, Pesosjärvi, and Vuoskojärvi (Table 1). The catchments are located in background areas, i.e. forested regions with little or no agriculture and no point sources of heavy metal air pollution within tens of kilometres (Fig. 1). Anthropogenic sources of heavy metals to such ecosystems are therefore considered to be due to long-range transported air pollution. For further information about nearest sources of atmospheric emissions see Ruoho-Airola *et al.* (1998). Typical of catchments in northern glaciated landscapes, the four catchments

Table 1. General characteristics of the IM study catchments.

	Valkea-Kotinen	Hietajärvi	Pesosjärvi	Vuoskojärvi
Latitude	61°14´N	63°09´N	66°17´N	69°44´N
Longitude	25°03´E	30°40´E	29°26´E	26°56´E
Catchment area, km^2	0.3	4.6	6.4	1.8
Forested area, ha	24	280	522	93
Surface water area, ha	6	124	62	19
Peatland area, ha	7	165	123	21
Elevation, m a.s.l (of lake)	156	165	256	145
Relative relief, m	40	49	44	105
Superficial deposit thickness, m	0–3	0–15	0–5	0–2
Annual mean temperature, °C	3.1	2.0	–0.5	–1.9
Annual mean precipitation, mm	618	592	571	395
Vegetation period (> 5 °C), d	112	102	82	57

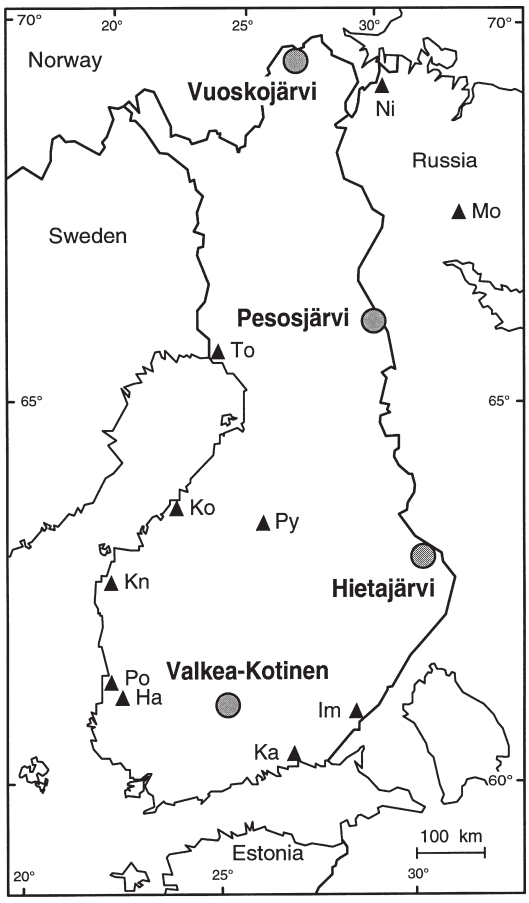

Fig. 1. Locations of IM catchments (circles) and some major point sources (triangles) for atmospheric heavy metal emissions. Ha = Harjavalta (Cu,Pb,Cd), Im = Imatra(Cr, Pb), Ka = Karhula (Cr), Kn = Korsnäs(Pb), Ko = Kokkola (Cd), Mo = Monchegorsk (Cu,Ni), Ni = Nikel (Ni), Po = Pori (Cu), Py = Pyhäsalmi mine (Zn,Cu), To = Tornio (Cr).

contain areas of forested upland, peatland and lake(s). A detailed description of the catchments is given in Bergström *et al*. (1995) but a brief description is given below.

The bedrock geology of the Valkea-Kotinen catchment is dominated by mica gneiss; that of Hietajärvi by porphyritic granodiorites; that of Pesosjärvi by arkosic and sericite quartzites contacted with greenstone bearing basaltic lavas, all bearing carbonate minerals; and that of Vuoskojärvi by gneisses (hornblende and feldspar types) and amphibolites containing sulphide bearing minerals.

The upland soils are Podzols or podzolic with a mor humus layer and developed on thin glacial or glacifluvial drift deposits. Some of the podzols of Valkea-Kotinen have transitions to Cambisols and all catchments have Leptosols and soils with lithic and rudic phases. The area of peatland (Histosols) varies from 2% (Vuoskojärvi) to 32% (Hietajärvi) of catchment area and are adjacent to or surround the lakes.

The forested parts of the catchments consist of old-growth (>100 years old) stands composed of varying proportions of Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies Karst*.), and deciduous species (mainly *Betula spp*.).

The surface water area varies from 10% (Pesosjärvi) to 27% (Hietajärvi) of catchment area. The Valkea-Kotinen catchment consists of a single small lake with a mean depth of ca. 3 m. Its waters are humic (TOC = 17 mg l^{-1}), and have exceptionally low pH (4.5) and alkalinity (– 40 mol l^{-1}). The Hietajärvi catchment comprises a large lake, Iso Hietajärvi, with a mean depth of 3.6 m, and a number smaller lakes and ponds. The waters of Iso Hietajärvi are clear (TOC = 4.5 mg l^{-1}) with a pH of 6.2 and alkalinity of 75 mol l^{-1}. The Pesosjärvi catchment also has one large lake (mean depth of 5 m) and four small lakes and ponds. Lake Pesosjärvi has clear waters (TOC = 5.2 mg l^{-1}) with a pH of 7.2 and exceptionally high alkalinity (460 mol l^{-1}). Vuoskojärvi contains a single large, clear water (TOC = 3.7 mg l^{-1}) lake with a mean depth of 3 m, pH of 7.2 and alkalinity of 170 mol l^{-1}. Chemistry values are median lake runoff values recorded during 1994–96.

Sampling

The following aqueous media were sampled: bulk precipitation (DC)[1)] throughfall (TF), stemflow (SF), soil water (SW), groundwater (GW), lake water (LC) and stream runoff (RW). The following biotic media have also been sampled: mosses (MC), needles (NC), litterfall (LF), humus layer (SC), and ants and shrew livers. The humus layer is included in the biotic media because it is derived from biomass and, like needles, litterfall, ants and shrews, is subject to biological uptake and bioaccumulation of heavy metals. Mosses were sampled as an indicator of deposition. Sam-

1) Abbreviations are those used in the UN-ECE Integrated Monitoring Manual (EDC 1993).

pling for TF, SF, NC, LF, and SC was carried out at 2–4 permanent plots located in homogeneous stands of the main habitat types in each catchment. A full description of the permanent plots is given in Bergström *et al.* (1995). Sampling procedures for all media except ants and shrews have been described in the UN–ECE Integrated Monitoring manual (EDC 1993) and Bergström *et al.* (1995), but are briefly described below.

Aqueous media

The bulk precipitation (DC) samples were collected with 2 parallel bulk (wet + dry) deposition collectors in an open area within the catchment. Throughfall (TF) was collected with bulk 12–16 collectors per plot (number depending on plot size) and stemflow (SF) with spiral collectors fitted to 2–8 pine trees per plot. The SF sampling of Scots pine at Valkea-Kotinen only started in 1992. The TF and SF samples were composited by plot for analysis. Soil water (SW) samples were collected with suction lysimeters using a vacuum of ca. 60 kPa. Only the data from lysimeters installed at 35 cm depth (i.e. below the zone of maximum illuviation and rooting) are reported in this paper. There were 3–6 lysimeters installed in each plot and the samples were analysed individually. Monthly TF (during snow-free period), SF and SW values are volume weighted values calculated from weekly values. The groundwater (GW) samples were taken from PVC tubes installed in Hietajärvi (5 locations) and in Pesosjärvi (1 location and from a spring). The other two catchments were unsuited to groundwater sampling. The GW samples were analysed individually. Lake chemistry (LC) samples were collected from the deepest parts of the lakes, at depths of 1, 3, and 5 m (mean value was used in this paper) in the case of Valkea-Kotinen and Hietajärvi, and 1 m in the case of Pesosjärvi. Runoff (RW) refers to samples taken from gauging weirs installed in the catchment outlet stream.

Biota

Only the needle chemistry (NC) data for Scots pine and for the current year's needles are presented in this paper. Each year, 2–3 shoots from the upper part of the canopy of five trees per plot were collected. The litterfall (LF) data refers to total (i.e. unfractionated) litterfall collected with six traps installed on each plot. A monthly composite sample from all the traps for each plot was analysed. The moss chemistry (MC) data refers to the heavy metal concentrations in *Pleurozium schreberi*. Samples were taken at 3–10 open (i.e. not under tree canopy) locations in each catchment and composited. Only the upper segment corresponding to the last 3 years' growth were analysed. For the humus layer (SC), four replicate samples of the Of + Oh layer were taken from each of the permanent plots. Each replicate was a composite of subsamples (one subsample from each 10×10 m subplot within each plot). The number of subsamples per replicate varied from 12 to 16, depending on plot size. The samples were taken using a stainless steel cylinder and placed in plastic bags. Specimens of red wood ants (*Formica aquilonia* and *F. lugubris*) were collected from nests located on hill tops in or near to the catchments in early May and September. Common shrew (*Sorex areneus*) specimens were trapped in May (adults) and September (juveniles) using a modified cone trap method (Pankakoski 1979).

Laboratory analysis

Analytical methods for most media were described in the UN-ECE Integrated Monitoring manual (EDC 1993) and Bergström *et al.* (1995), but are briefly presented in Table 2. Acid-washed equipment and polyethylene sample bottles were used throughout and samples acidified before analysis to promote desorption of metals from the walls of the sample storage bottles. The NC samples were not washed before analysis and therefore reported concentration values also include heavy metals absorbed to the surface of the needles. The shrews were dissected and samples of their livers taken for analysis. Concentrations of heavy and trace elements are often low, particularly in water samples, and values less than the detection limit (dl) frequently encountered. The detection limits of the different instruments used in this study are presented in Table 2. The detection limits with the ICP-ES instrument (ARL 3580) are high in

Table 2. Sampling frequency, analytical methods and detection limits used during the study (1989–1996) for aqueous media (μg l^{-1}) and biotic media (mg kg^{-1} dry matter).

Media[¤]	Institute*	Sampling frequency	Analytical method [§]	Detection limit[#]				
				Cd	Cu	Ni	Pb	Zn
Aqueous media								
DC	FMI	monthly, from 6/1990	GAAS standing sample		0.10 (90–91)	1.00 (90–91)		0.50 (90–91)
			GAAS standing sample	0.005 (90–93)	0.30 (92–93)	0.50 (92–93)	0.20 (90–93)	0.20 (92–93)
			ICP-MS standing sample	0.006 (94–95)	0.04 (94–95)	0.04 (94–95)	0.03 (94–95)	0.10 (94–95)
			ICP-MS standing sample	0.005 (96)	0.01 (96)	0.01 (96)	0.01 (96)	0.05 (96)
TF	FFRI	weekly during snow-free period, also monthly during winter from 1995	ICP-ES filtered (8 μm)	2.0 (90–96)	5.0 (90–96)	18.0 (90–96)	25.0 (90–96)	2.0 (90–96)
SF,SW	FFRI	weekly in snow-free period	ICP-ES filtered (8 μm)	2.0 (90–96)	5.0 (90–96)	18.0 (90–96)	25.0 (90–96)	2.0 (90–96)
GW[$]	GSF	6–12 times/ year from 1993	ICP-MS standing sample	0.02 (93–96)	0.04 (93–96)	0.06 (93–96)	0.03 (93–96)	0.10 (93–96)
LC,RW	FEI	monthly from 1994	ICP-MS standing sample	0.03 (94–96)	0.07 (94–96)	0.04 (94–96)	0.03 (94–96)	0.3 (94–96)
Biotic media								
MC	FEI	1991[†]	ICP-ES ($HClO_4$-HNO_3)	0.2	0.2	0.2	2.0	0.2
		1996[‡]	ICP-MS (HNO_3)	0.01 (96)	0.01 (96)	0.20 (96)	0.02 (96)	3.00** (96)
NC	FFRI	yearly	ICP-ES (HNO_3-H_20_2)	0.5 (90–96)	1.25 (90–96)	4.4 (90–96)	6.25 (90–96)	0.55 (90–96)
LF	FFRI	monthly during snow-free period	ICP-ES (HNO_3-H_20_2)	0.5 (90–96)	1.25 (90–96)	4.4 (90–96)	6.25 (90–96)	0.55 (90–96)
SC	FFRI	1988/89, 1991/92, 1995	ICP-ES (dry ash+HCl)	0.1 (90–96)	0.25 (90–96)	0.89 (90–96)	1.25 (90–96)	0.11 (90–96)
Ants	FEI	twice annually, 1993–96	ICP-MS (HNO_3)	0.001 (93–96)	0.001 (93–96)	0.001 (93–96)	0.001 (93–96)	0.004 (93–96)
Shrew liver	FEI	twice annually, 1993–94	ICP-MS (HNO_3)	0.002 (93–94)	0.004 (93–94)	0.002 (93–94)	0.002 (93–94)	0.017 (93–94)

[¤] *see* Material and methods for abbreviations

* FMI = Finnish Meteorological Institute, FFRI = Finnish Forest Research Institute, GSF = Geological Survey of Finland, FEI = Finnish Environment Institute

[§] GAAS = Graphite atomic absorbtion spectrometry, ICP-MS = Inductively coupled plasma atomic mass spectrometry, ICP-ES = Inductively coupled plasma atomic emission spectrometry

[#] Years in parentheses

[$] Only Hietajärvi and Pesosjärvi

[†] Digestions: Helsinki University; analysis: VTT, Technical Research Centre of Finland

[‡] Digestions: Helsinki University; analysis: GSF

** ICP-ES

comparison with other (newer) instruments that were used.

All the analyses were performed in laboratories that have continuous quality control programmes and which regularly participate in national and international intercalibration exercises. For example, the FMI (Finnish Meteorological Institute) laboratory found mean relative differences from test samples of: Pb 4%, Cd 11%, Cu 6%, Zn 5%, and Ni 16%. Similar intercalibration exercises by the FFRI (Finnish Forest Research Institute) laboratory found mean relative differences from water test samples of: Pb 3%, Cd 3%, Cu 4%, Zn 3%, and Ni 7%.

Results

Spatial and temporal variability

Summary statistics describing the concentrations of the aqueous media are presented in Table 3 and for biotic media in Table 4. The 50th percentile (medians) is used to describe average concentrations and the 95th percentiles to give a reliable description of maximum concentrations for toxicological purposes.

Temporal changes in Pb and Zn concentrations in DC (mean annual), MC (1991 and 1996), LF (monthly) and SC (1989, 1991–92 and 1995)

Table 3. Heavy metal concentrations (μg l^{-1}) in the studied aqueous media reported for various percentiles.

Media*	n†	Cd			Cu			Ni			Pb			Zn		
		25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th
Valkea-Kotinen																
DC	76	0.03	0.04	0.21	0.71	0.98	3.81	0.25	0.40	1.27	1.12	2.00	5.80	3.0	4.1	11.7
TF	175(91)	0.14	0.39	2.15	0.74	2.04	14.49	1.78	3.50	12.30	3.12	7.27	23.57	7.0	12.3	60.4
SF	25(17)	0.15	0.18	1.48	2.01	3.10	15.28	7.49	7.99	19.49	7.44	10.42	100.26	49.0	69.1	446.9
SW	42(17)	0.75	0.91	2.48	2.52	4.60	23.46	8.35	11.89	19.43	9.48	14.63	45.66	18.9	27.3	103.1
GW	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
LC	65	0.02	0.02	0.04	0.18	0.27	1.36	0.41	0.49	8.62	0.44	0.56	0.96	2.7	3.7	12.6
RW	35	0.02	0.02	0.05	0.16	0.20	0.84	0.40	0.46	4.26	0.48	0.60	1.04	2.2	3.8	11.0
Hietajärvi																
DC	79	0.02	0.03	0.14	0.60	1.00	4.06	0.25	0.31	0.60	0.9	1.42	3.70	2.4	3.3	9.3
TF	113(63)	0.36	0.48	1.37	1.42	1.77	32.55	2.27	2.95	11.19	5.81	7.88	22.45	4.5	6.7	23.3
SF	45(17)	0.25	0.43	1.70	1.73	2.58	22.94	9.54	9.84	19.87	5.51	8.54	81.50	27.7	42.5	99.7
SW	39(18)	0.67	0.88	2.87	1.75	4.17	25.80	6.82	8.82	11.95	10.32	13.27	44.65	7.2	13.8	35.8
GW	17	0.01	0.01	0.03	0.10	0.19	0.62	0.03	0.03	1.05	0.02	0.02	0.08	1.2	1.9	5.7
LC	73	0.02	0.02	0.02	0.08	0.11	0.34	0.09	0.11	0.19	0.05	0.07	0.97	0.4	0.6	3.5
RW	36	0.02	0.02	0.02	0.11	0.13	0.35	0.10	0.13	0.22	0.07	0.08	0.25	0.4	0.8	3.5
Pesosjärvi																
DC	77	0.02	0.03	0.09	0.82	1.20	5.52	0.25	0.35	1.41	0.60	1.00	3.32	1.5	2.3	7.6
TF	108(65)	0.12	0.66	2.72	0.21	2.75	28.15	4.09	5.37	12.91	1.98	9.75	35.50	4.5	7.0	61.3
SF	35(14)	0.01	0.03	1.27	1.26	4.89	16.06	10.57	10.90	11.69	0.99	1.83	55.35	28.0	48.3	219.0
SW	36(13)	0.35	0.54	2.52	2.75	3.72	12.42	8.14	9.18	10.19	4.46	14.91	25.49	10.0	12.1	30.9
GW	43	0.01	0.01	0.03	0.06	0.24	2.59	0.03	0.09	0.82	0.02	0.02	0.12	0.3	0.8	3.7
LC	14	0.02	0.02	0.02	0.66	0.75	1.62	0.43	0.54	0.86	0.06	0.08	1.08	0.7	1.5	3.6
RW	25	0.02	0.02	0.02	0.66	0.69	1.14	0.35	0.39	0.59	0.04	0.05	0.42	0.2	0.4	1.4
Vuoskojärvi																
DC	76	0.01	0.02	0.20	1.07	2.07	12.85	0.25	0.50	2.70	0.30	0.70	4.90	1.0	1.6	10.1
TF	103(60)	0.19	0.24	1.53	0.57	0.88	11.02	0.93	1.20	10.80	3.50	4.39	28.88	4.5	6.0	36.7
SF	32(13)	0.04	0.05	0.17	0.87	1.94	19.27	8.38	8.63	25.93	1.41	2.39	29.54	32.6	56.3	186.6
SW	35(13)	0.45	0.54	1.85	2.88	5.43	25.86	7.71	8.03	10.72	6.0	7.19	25.99	16.8	22.2	77.14
GW	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
LC	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
RW	5	0.02	0.02	0.02	0.41	0.48	2.51	0.15	0.16	0.20	0.05	0.05	0.18	0.9	1.5	34.9

* DC = bulk precipitation, TF = throughfall, SF = stemflow, SW = soil water, GW = groundwater, LC = lake water, RW = stream runoff.

† number of observations (for Ni in parentheses).

media over the study period are shown in Figs. 2 and 3. Besides representing a toxic element (Pb) and a micro-nutrient (Zn), the concentrations of these two elements were mostly above dl concentrations and therefore the percentiles are precise.

Influence of bulk precipitation

To determine whether the heavy metal concentrations in bulk precipitation had an affect on concentrations in the other aqueous media, Spearman rank correlations were computed using monthly data (Table 5). Since a delay in the response of ground and surface water concentrations to bulk precipitation concentrations maybe expected, correlations using delays of 1 and 2 months were also computed. Using this rather simplistic approach, a strong positive correlation is taken to indicate that DC exerts a determining influence. A weak or negative correlation indicates that other processes within the ecosystem, e.g. adsorption, ion exchange, nutrient cycling, weathering, and sedimentation, are determining heavy metal concentrations.

Bioaccumulation and toxicological assessment

Since most of the Pb in the ecosystem is from atmospheric deposition, biota:deposition concentration ratio should describe the degree of bioaccumulation of atmospheric Pb. We calculated such ratios using MC concentrations as an indicator of atmospheric Pb (Table 6). Median concentration values were used to calculate the ratios.

Discussion

In this paper we describe heavy metal concentrations in a range of aqueous and biotic media. We chose to present summary statistics in the form of

Table 4. Heavy metal concentrations (mg kg^{-1} dry matter) in the studied biotic media reported for various percentiles.

Media*	*n*	Cd			Cu			Ni			Pb			Zn		
		25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th	25th	50th	95th
Valkea-Kotinen																
MC	2	–	0.2	–	–	6.7	–	–	2.7	–	–	9.7	–	–	35.3	–
NC	78	0.3	0.3	0.3	2.3	2.6	4.5	n.a.†	n.a.	n.a.	3.3	3.4	3.5	34.8	40.5	64.2
LF	37	0.3	0.3	0.3	4.3	5.1	6.9	n.a.	n.a.	n.a.	4.3	6.5	9.8	55.2	65.8	107.3
SC‡	20	0.8	0.8	1.0	6.7	6.9	8.1	7.4	8.4	9.8	33.6	37.2	50.7	32.3	49.0	75.7
Ants	32	4.0	4.3	7.8	10.9	11.6	16.2	0.3	0.5	0.8	0.7	0.8	1.6	446.0	484.3	677.6
Shrew	40	1.4	2.7	6.2	18.1	19.3	22.5	0.1	0.1	0.3	0.5	0.9	1.6	64.4	67.8	79.0
Hietajärvi																
MC	2	–	0.1	–	–	5.0	–	–	1.9	–	–	5.7	–	–	23.8	–
NC	191	0.3	0.3	0.3	2.1	2.5	3.6	n.a.	n.a.	n.a.	3.3	3.4	3.4	34.4	39.8	57.0
LF	35	0.3	0.3	0.3	2.1	3.7	5.8	n.a.	n.a.	n.a.	3.3	3.4	4.7	45.9	52.5	75.0
SC‡	16	0.5	0.5	0.6	5.2	5.8	6.8	5.2	5.7	6.2	27.1	31.3	37.0	41.5	48.6	51.9
Pesosjärvi																
MC	2	–	0.1	–	–	5.2	–	–	2.2	–	–	3.7	–	–	21.6	–
NC	89	0.3	0.3	0.3	1.6	2.1	3.4	n.a.	n.a.	n.a.	3.3	3.4	3.4	29.3	33.4	44.1
LF	29	0.3	0.3	0.3	4.4	5.1	7.3	n.a.	n.a.	n.a.	3.3	3.4	5.0	60.2	66.0	105.3
SC‡	20	0.6	0.7	0.8	5.0	5.6	6.8	7.0	8.1	9.2	15.6	16.0	18.4	31.2	33.9	42.9
Ants	15	1.6	1.8	3.1	9.2	10.1	11.0	0.3	0.4	0.6	0.3	0.3	0.6	295.9	314.2	418.3
Shrew	45	0.5	0.9	3.0	17.4	18.7	26.1	0.1	0.1	0.6	0.1	0.1	0.3	60.2	63.5	72.2
Vuoskojärvi																
MC	2	–	0.1	–	–	5.9	–	–	3.5	–	–	2.6	–	–	23.7	–
NC	91	0.3	0.3	0.3	2.7	3.1	4.2	n.a	n.a	n.a.	3.3	3.4	3.4	37.7	40.8	51.5
LF	26	0.3	0.3	0.3	3.6	4.9	9.6	n.a	n.a	n.a.	3.3	3.4	4.6	55.1	77.1	147.7
SC‡	16	0.5	0.5	0.5	4.7	4.9	5.8	4.6	6.5	11.9	12.6	13.8	16.0	27.8	33.0	51.7
Ants	6	2.0	2.5	3.2	11.1	11.4	12.5	0.4	0.5	0.5	0.1	0.1	0.2	289.8	292.3	314.8

* MC = mosses, NC = needles, LF = litterfall, SC = humus layer
† n.a. data not available
‡ only 1989 data

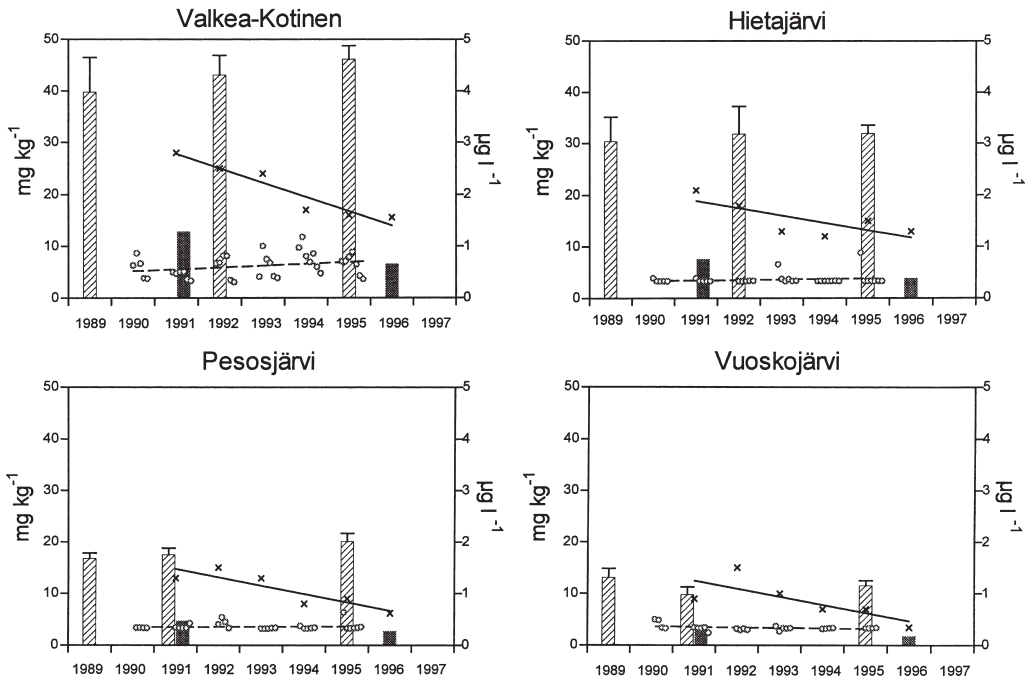

Fig. 2. Pb concentrations in bulk precipitation (mean annual DC in g l^{-1}, crosses), litterfall (monthly LF in mg kg^{-1}, open circles), moss (MC in mg kg^{-1}, solid bar) and humus layer (SC in mg kg^{-1}, hatched bar). Lines are linear regression fits for DC and LF, and SC error bars are standard deviations.

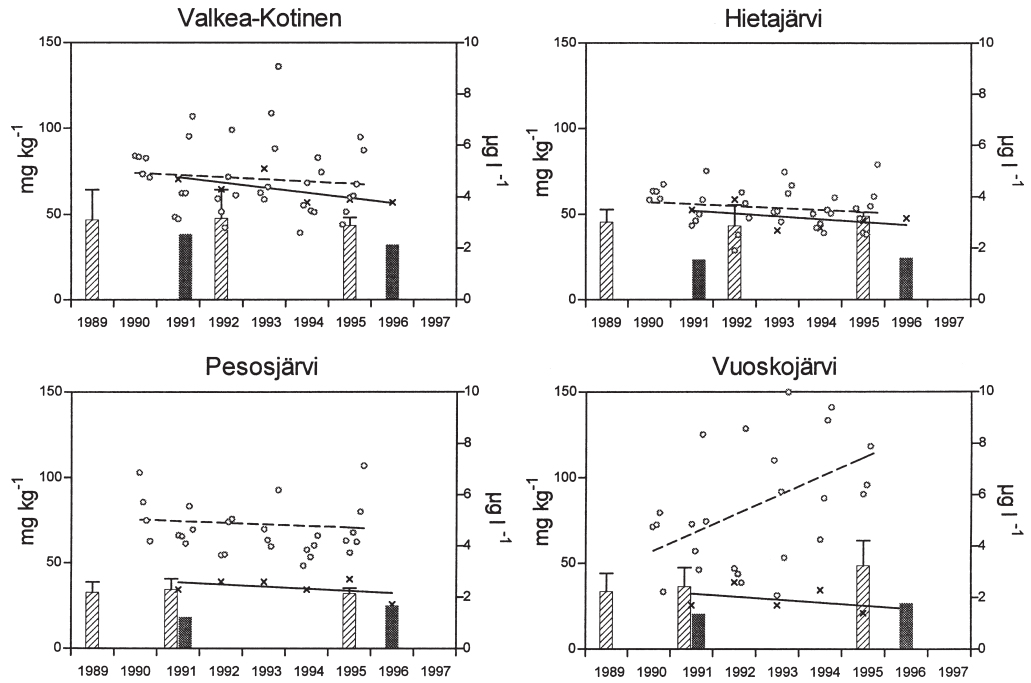

Fig. 3. Zn concentrations in bulk precipitation (mean annual DC in g l^{-1}, crosses), litterfall (monthly LF in mg kg^{-1}, open circles), moss (MC in mg kg^{-1}, solid bar) and humus layer (SC in mg kg^{-1}, hatched bar). Lines are linear regression fits for DC and LF, and SC error bars are standard deviations.

percentiles rather than means and standard deviations because of the strong positive skewed distribution showed by the data. The percentiles also describe the frequency distribution of the data.

A simple substitution protocol (one-half of the dl) for handling values less than detection limit is given in the IM manual (EDC 1993). Data containing such substituted values is referred to as censored data and enables summary statistics (mean, standard deviation, percentiles, etc.) to be calculated. Censored data with substituted values can produce considerably biased mean and standard deviation values, however (Helsel and Cohn 1988, Porter *et al.* 1988, Helsel 1990). There may also be problems with percentile summary statistics. Depending on the number of values less than dl, the same substitute value will be given for increasing percentiles. This is seen, for example, in the case of Cd for GW and LC (Table 3). Although still providing valuable information (concentrations are not higher than dl), there is a lack of precision, particularly if the dl values are high. Because of the relatively high dl values of the instrument used for TF, SF and SW, we applied a maximum likelihood method using log-normal distributions to improve the precision of the percentile values for these media (Helsel 1990). With the exception of Cd, heavy metal concentrations in the biota were not affected by concentrations less than detection limits (Table 4).

Overall, the measured concentrations in the aqueous media in our boreal ecosystems in remote locations (Table 3) are low compared to those reported for temperate forest ecosystems (Bergkvist *et al.* 1989). Concentration values in our studies are also lower than those reported for two spruce forest ecosystems in southern and western Sweden (Bergkvist 1987). Bulk precipitation concentrations were similar to those reported for six rural and remote sites in Norway in 1989–90 (Berg *et al.* 1994, Juntto *et al.* 1997). Concentrations of Pb and Zn in bulk precipitation systematically decreased northwards, reflecting decreasing long–range atmospheric transport of these metals and also decreasing population densities. The highest concentrations of Cu and Ni in DC occurred at Vuoskojärvi, reflecting the influence of emissions from the Cu-Ni smelters on the Kola Peninsula. However, the higher Cu and Ni concentrations in DC at Vuoskojärvi were not reflected in higher concentrations in TF, SF, SW and RW compared to other catchments (Table 3).

Table 5. Spearman rank correlations between Zn concentrations in bulk deposition and other aqueous media for each catchment. Significant ($p < 0.05$) coefficients are indicated in bold.

Catchment	Aqueous media†											
	TF1*	TF2*	SF	SW	GW	GW_1‡	LC**	LC_1‡	LC_2‡	RW	RW_1‡	RW_2‡
Valkea-Kotinen	**0.385**	**0.384**	–0.059	–0.154			–0.014	0.047	**0.405**	–0.145	0.034	–0.034
Hietajärvi	**0.363**	**0.245**	0.269	0.068	0.142	–0.114	0.241	0.116	**0.397**	–0.040	–0.230	**0.525**
Pesosjärvi	–0.011	0.186	–0.018	0.257	0.118	0.062	–0.214	0.037	0.046	0.118	–0.080	0.070
Vuoskojärvi	**0.310**	**0.326**	0.110	0.081						–0.100	–0.100	–0.100

† TF = throughfall, SF = stemflow, SW = soil water, GW = groundwater, LC = lake water, RW = stream runoff.
* Throughfall reported for separate throughfall plots (stands).
** LC = 1 m depth samples only.
‡ Subscripts refer to delays of 1 and 2 months.

Table 6. Biota: moss median Pb concentration ratios at each catchment.

Media	Valkea-Kotinen	Hietajärvi	Pesosjärvi	Vuoskojärvi
Needles (NC)	0.35	0.59	0.91	1.31
Litterfall (LF)	0.67	0.59	0.91	1.30
Humus layer(SC)	3.82	5.51	4.31	5.37
Ants	0.08	–	0.08	0.04
Shrew livers	0.09	–	0.04	–

The relatively high Zn concentrations in soil water and runoff at Vuoskojärvi compared to concentrations in bulk precipitation (Table 3) is probably due to the weathering of hornblende and sulphide minerals in the drift deposit.

Comparison of monthly DC (corresponding to bulk precipitation to the canopy) and TF (below canopy precipitation) concentrations showed an enrichment of heavy metals in throughfall (Table 3). The mean monthly enrichment ratios (TF:DC) for Zn, Pb, Cu, Cd and Ni averaged across catchments were: 7, 17, 11, 33 and 18, respectively. These enrichment ratios increased northwards as far as Pesosjärvi, but were lower again at Vuoskojärvi. Throughfall enrichment arises through the washing-off of dry deposition and leaching from the canopy. Coniferous forest canopies are particularly efficient in trapping aerosols (Bergkvist *et al.* 1989), the form in which heavy metals are usually present in the air (Alloway 1995). The enrichment in TF Pb is primarily due to wash-off since the internal cycling of Pb is negligible (Lindberg and Harriss 1981, Alloway 1995). Lead in precipitation is known to occur in particulate form, whereas Cd and Cu are largerly dissolved (De Boer and Fortezza 1992). The water solubility of Zn aerosols, like Pb, is relatively low compared to Cd (and Cu) (Lindberg *et al.* 1989). Therefore, much of the Zn in precipitation can also be expected to be in particulate form. The enrichment of Zn and Cu in TF is partly due also to canopy leaching since both are micro-nutrients and internally cycled. Cadmium is also readily cycled (Bergkvist 1987, Lindberg *et al.* 1989). Zinc concentrations were particularly high in SF, as has been found in other studies (Bergkvist *et al.* 1989).

Concentrations of the heavy metals, particularly Pb, sharply decreased in water passing through the soil to groundwater (Table 3). A similar pattern was also shown for spruce forest ecosystems in southern and western Sweden (Bergkvist 1987). The monthly dilution ratios (SW:GW for those months in common) for Zn, Cu, Ni, Pb, and Cd averaged across Hietajärvi and Pesosjärvi catchments were: 11, 28, 97, 552 and 83, respectively. The influence of the humus layer and organic matter in the upper soil on heavy metal concentrations, particularly on Cu and Pb, and decreasing acidity with soil depth, particularly on Zn and Cd, in reducing leachability has been documented (Bergkvist *et al.* 1989). Since most heavy metals in soil solution exist as cations, they can be retained by cation exchange adsorption (Alloway 1995). The cation exchange capacity of upland soils such as those in our study, decreases with depth and is related to the amount and distribution of organic matter and clay (Tamminen and Starr 1990). Complexation with organic matter is also important in reducing the mobility of heavy metals in soils (Fergusson 1990, Alloway 1995). The effect of acidity on heavy metal mobilisation in soil is probably mainly regulated by the formation of water soluble organic complexes (Bergkvist 1986). Organic matter storage in Finnish forest soils is strongly related to productivity, which in turn, is largely determined by temperature, and therefore shows a clear decrease northwards (Kauppi *et al.* 1997, Liski and Westman 1997). Organic matter decomposition also strongly covariates with temperature and therefore shows a strong decline northwards (Kurka and Starr 1997). Lake water concentrations of heavy metals are also strongly influenced by acidity and humic matter (Mannio *et al.* 1993). Therefore, the area of peatland in the catchment and length of shoreline contact with peatland were found to be important factors explaining surface water heavy metal concentrations (Lazerte *et al.* 1989).

Spearman correlation coefficients analyses indicated that only Zn concentrations in aqueous media were dependent on bulk precipitation concentrations (Table 5). Monthly Zn concentrations in TF were significantly ($p < 0.05$) correlated to DC concentrations in each catchment with the exception of Pesosjärvi. However, the influence of DC on Zn concentrations disappeared as the water passed on further through the ecosystem. Zinc concentrations in the lake waters of Valkea-Kotinen and Hietajärvi and RW at Hietajärvi, however, had significant positive correlations with the Zn concentration of DC from two months before.

The annual mean Pb concentrations in DC at all catchments declined over the study period (Fig. 2). Testing whether the slope of the linear regression differed from zero gave *p*-values of 0.003, 0.078, 0.020 and 0.082 for Valkea-Kotinen, Hietajärvi, Pesojärvi and Vuoskojärvi, respectively. The decline was the largest for the most southerly catchment, Valkea-Kotinen (slope = –0.023). Moss lead concentrations, which are a

reliable indicator of Pb deposition (Berg *et al.* 1995), indicate a near 50% decrease in deposition from 1991 levels to 1996 levels at all catchments (Fig. 2). However, the reduction in Pb deposition had little effect on Pb concentrations in litterfall. Needle Pb concentrations, which were similar to those in LF (Table 4), also remained unchanged. Lead concentrations in the humus layer showed significant ($p < 0.05$) differences between the sampling years at Pesosjärvi and Vuoskojärvi. However, the changes were not consistent with a decline over the study period. Annual mean Zn concentrations in DC did not significantly declined over the study period (Fig. 3). The probability of the linear slope of the relationship differing from zero varied from 0.126 (Valkea-Kotinen) to > 0.350 (others). The changes in the concentration of Zn in moss sampled in 1991 and 1996 were inconsistent among the catchments. Moss is a poor indicator of the bulk deposition of Zn because Zn is recycled as a micronutrient or leached (Berg *et al.* 1995). However, Zn concentrations in monthly litterfall at Vuoskojärvi significantly increased over the study period (slope = 0.923, $p = 0.01$). The mean Zn concentration in the humus layer at Vuoskojärvi was also significantly ($p < 0.05$) greater in 1995 than in 1989 (Fig. 3). The cause of these increases is unknown. There was no significant trend in needle Zn concentrations over the study period.

Lead concentrations in the biota tended to decrease northwards, indicating that Pb concentrations in biota are largely determined by atmospheric deposition (Table 4). Of the biotic media studied, the humus layer showed the greatest accumulation of atmospheric Pb (highest biota:moss ratios; Table 6). This can be explained by the well documented immobility of Pb in humus layers (e.g., Bergkvist 1989) and the concentrating effect of organic matter decomposition. The Pb biota:moss concentration ratio for ants and shrew livers were very low in comparison to the other biotic media, further indicating the low mobility of the atmospheric Pb deposition in the ecosystem. Copper and Ni concentrations in the biotic media at Vuoskojärvi were similar to or less than those at the other catchments (Table 4). This indicates that the Cu and Ni emissions from the Kola Peninsula had little or no effect on the biota at Vuoskojärvi.

Tyler (1992) presented heavy metal critical concentration values, so-called "lowest effective limit" (LOEL), for mor humus layers in Sweden. A LOEL value is the lowest concentration at which an effect was found, i.e. a negative influence on soil enzyme activity, soil respiration, nitrogen transformations, microflora, soil, and invertebrae. The LOEL values for Cd, Cu, Pb and Zn are: 3.5, 20, 150 and 300 mg kg^{-1} dry matter, respectively. The 95th percentile values for humus layer presented in Table 4 were less than these LOEL values, indicating that humus layer heavy metal concentrations in the IM catchments are not toxic to soil organisms.

Lithner (1989) has presented so-called "lowest known levels of effect" (LKE) concentrations for heavy metals in freshwaters at approximately neutral pH to identify toxic concentrations to aquatic organisms. The LKE values for Cd, Cu, Ni, Pb and Zn are: 0.15, 2, 25, 1.5 and 15 g l^{-1}, respectively. Overall, our surface water (LC and RW) heavy metals concentrations were below the LKE values. Only at Hietajärvi, was one Cd value greater than the LKE Cd value, and the LC 95th percentile concentration for Pb at Valkea-Kotinen is close to the LKE Pb value. Otherwise, the 95th percentile concentrations in both Hietajärvi and Valkea-Kotinen were less than 50 percent of the LKE values. At Pesosjärvi, the 95th percentile concentrations of Cu are 60-80 percent of the LKE values. At Vuoskojärvi, the low number of LC samples taken do not allow a reliable comparison to LKE values to be made, but the single observations did exceed the LKE values for Cu and Zn.

Conclusions

The concentrations of Cd, Cu, Ni, Pb and Zn in various aqueous media in boreal ecosystems were low compared to those reported for temperate ecosystems. The decline in heavy metal concentrations as the precipitation passed through the ecosystem indicate that most of the heavy metal load in deposition is retained within the catchments. The sharp decline in heavy metal concentrations, particularly in the case of Pb, as the precipitation passed through the soil indicated the central role played by the humus layer in this retention. There is ample evidence from other studies to show that lake bottom

sediments are also effective in retaining heavy metals. With the exception of Zn, heavy metal concentrations in deposition were not correlated with concentrations in the other aqueous media. This is concluded to be the result of interaction and retention as the water passes through the ecosystem. Zinc concentrations in throughfall and lake waters were correlated to bulk deposition concentrations, and this effect lagged by two months in the case of lake water. Soil water and runoff Zn concentrations at Vuoskojärvi were influenced by lithological sources of Zn.

Our results showed that the concentrations of Pb in bulk deposition have significantly declined over the study period (1989–1996). Since the IM catchments are located in background areas, this decline represents a decrease in the long-range transport of Pb. However, the reduction in Pb deposition has not yet significantly affected the levels of Pb in the ecosystem.

Current concentrations of the studied heavy metals in the humus layer and surface water were below critical levels for toxic effects. We consider that the concentration values we have presented can be used as background reference values.

Future studies will deal with the pools and fluxes of heavy metals within the IM catchments. This will enable us to quantify the amount and location of heavy metal retention in boreal ecosystems in Finland.

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