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# Multi-element, multi-medium regional geochemistry in the European Arctic: element concentration, variation and correlation

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## Abstract

A multi-medium, multi element regional geochemical survey has been carried out in an 188,000 km<sup>2</sup> area in the Central Barents Region, Finland, Norway and Russia. Four different sample materials (terrestrial moss, O-, B- and C-horizons of podzol) were collected at the same sites throughout the area at a density of 1 site/300 km<sup>2</sup>. While moss predominantly reflects the atmospheric input of elements, the O-horizon reflects the complex interplay between atmosphere, biosphere and lithosphere. The B-horizon can be used to study the influence of soil-forming processes, while the C-horizon represents the composition of the lithosphere at each sample site and thus the geogenic background. The concentration, variation and correlation between 24 elements (Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, Sr, Th, V, Zn) analysed with similar techniques in all 4 materials are compared. Some rare trace elements (Ag, As, Bi, Cd, Pb) appear to be considerably more enriched in the O-horizon of podzols than the main pollutants in the survey area (Ni, Cu, Co from the Russian nickel industry in Monchegorsk and Nikel-Zapoljarnij). Biological processes play an underestimated role in determining regional geochemistry at the earth's surface. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

“The Kola Ecogeochemistry Project” (web site <http://www.ngu.no/Kola>) gathered chemical data for up to more than 50 elements from 4 different sample materials (terrestrial moss, and the O-, B-, and C-horizon of podzols)

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within an 188,000 km<sup>2</sup> area in the European Arctic (Fig. 1). These 4 materials were collected because in combination they can reflect atmospheric input (moss), interactions of the biosphere with element cycles (moss and O-horizon), the atmosphere-biosphere-lithosphere interplay (O-horizon), the influence of soil-forming processes (B-horizon) and the regional geogenic background distribution (the lithosphere) (C-horizon) for the elements investigated. All results are documented in the form of a geochemical atlas (Reimann et al., 1998a).

Terrestrial moss (*Hylocomium splendens* and *Pleurozium schreberi*) receives most of its nutrients from the atmosphere. In Scandinavia, it has been used to monitor atmospheric deposition of heavy metals for more than 30 a (e.g. Rühling and Tyler, 1968, 1973; Tyler 1970). It was thus included in the Kola Project to reflect the input

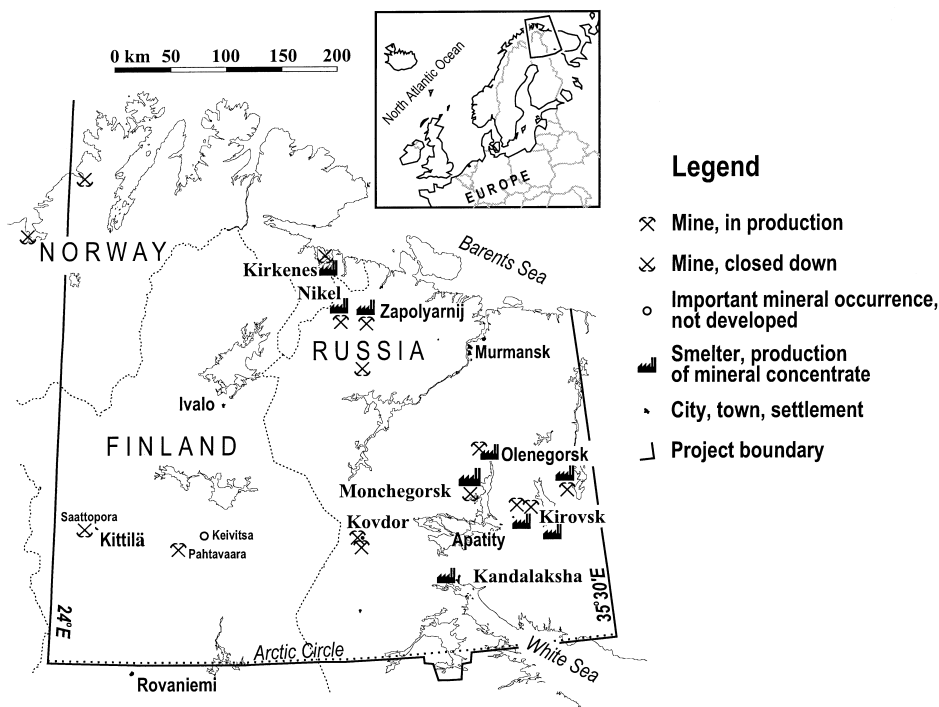


Fig. 1. Location of the survey area.

of elements from the atmosphere (wet and dry deposition, including both geogenic and anthropogenic dust) over the previous 2–3 a. At the same time the moss reflects element concentrations in an important component of the arctic ecosystem in terms of total biomass production and ecological function. It is an important supplier of litter for the formation of the organic horizon of the soils (Kashulina et al., 1997). Results of an interspecies comparison between *Hylocomium* and *Pleurozium* are presented in Halleraker et al. (1998). A review of the moss technique and a discussion of possible problems related to it as well as a comparison with the chemical composition of lichen and crowberry from this area are given in Reimann et al. (1999b). Results of regional mapping are also discussed in Äyräs et al. (1997a), Reimann et al. (1997b) and Caritat et al. (2001).

The O-horizon consists mostly of plant residues in differing stages of decay and humus, mixed with some minerogenic particles. Due to its location and genesis the organic horizon reflects the complex interplay between the lithosphere, the biosphere and the atmosphere. The O-horizon is a major sink for plant nutrients in northern ecosystems. It can accumulate and enrich many elements, e.g. via organic complexing. For many elements, both from natural and anthropogenic sources, it thus acts as a very effective “geochemical barrier” as defined first by Goldschmidt (1937). A separate interpretation of the regional distribution patterns found in the O-

horizon from the survey area is given in Äyräs and Kashulina (2000).

The B-horizon is clearly affected by soil-forming processes. Compared to the C-horizon, it is relatively enriched in clay minerals, organic matter and free and organically bound amorphous Fe- and Al-oxides and-hydroxides, which are leached from the upper soil horizons. It is less active than the O-horizon, but can still act as a second “geochemical barrier” for many elements (independent of origin) within the soil profile, e.g. via co-precipitation with the Fe-oxides/-hydroxides.

The deepest soil horizon of podzols, the C-horizon, is only slightly influenced by soil-forming processes and sometimes by anthropogenic contamination, and thus mostly reflects the natural, geogenic element pool and regional variations therein. A geological interpretation of the C-horizon results is given in Reimann and Melezhih (2001).

In addition to the sample media documented in the atlas, snow, rain water, stream water, lake water, ground water, bedrock, organic stream sediments, topsoil 0–5 cm, and overbank sediments were studied during different stages of the project (Äyräs et al., 1995, 1997a,b; Boyd et al., 1997; Caritat et al., 1996a,b, 1997a,b, 1998a,b; Cherkushin et al., 1998; Gregurek et al., 1998a,b, 1999a,b; Halleraker et al., 1998; Kashulina et al., 1997, 1998a,b; Niskavaara et al., 1996, 1997; Reimann et al., 1996, 1997 a,b,c, 1998b, 1999a,b, 2000a,b; Volden et al., 1997), often

on a spatially much more intensive scale. These data can be used to assist in the interpretation of the observed regional features.

Here the data from the 4 main sample media collected during the regional stage of the project will be used to demonstrate that multi-medium, multi-element regional geochemistry is a powerful tool for obtaining a better understanding of the sources and fate of chemical elements in the environment. Almost all other papers published on the results from the Kola project so far focus on regional distribution patterns. Here, element concentrations, variation and correlation will be compared within and between the different sample materials. Processes leading to the enrichment/depletion of elements in a sample medium will be discussed. Correlation of elements within each sample medium and between the different materials will be used to study their relationship and the most likely sources of the elements.

## 2. Material and methods

### 2.1. Survey area

The project covered the entire area north of the Arctic Circle between 24° and 35.5° East and north to the Barents Sea (Fig. 1). Relative to most of Europe the Finnish and Norwegian parts of the area are still almost pristine. Human activities are mostly limited to fishery, reindeer-herding and forestry (in the western part of the project area). Exceptions are a large iron ore mine and mill at Kirkenes, N-Norway, a small, brown coal-fired power station near Rovaniemi at the southern project border in Finland and some small mines. Population density increases gradually from north to south. In contrast, the Russian part of the project area is heavily industrialised. With the Ni refinery at Monchegorsk, the Ni smelter at Nikel and the Cu/Ni-ore roasting plant at Zapoljarnij 3 of the world's largest point-source emitters of SO<sub>2</sub> and heavy metals are located here. These 3 sources together accounted for emissions of 300,000 t SO<sub>2</sub>, 1900 t Ni and 1100 t Cu in 1994 (Reimann et al., 1997b). Apatite ore is mined and processed near Apatity, Fe ore at Olenegorsk and Kovdor, Cu/Ni-ore near Zapoljarnij. An Al smelter is located near Kandalaksha. The major towns of Murmansk and Apatity have large oil- and coal-fired thermal heating and power plants.

Topographically, large parts of the area can be characterised as highlands. In Norway, the general landscape in the coastal areas is quite rugged and the mountains reach elevations of 700 m above sea level (a.s.l.). In Russia, in the south-western part of the Kola Peninsula, there are mountains, reaching 200–500 m a.s.l. Near Monchegorsk and Apatity and near the coast of the White Sea there are some higher mountains (over 1000 m a.s.l.).

The geology of the area is rather complex and includes a multitude of different bedrock types (Fig. 2). The most unusual geochemical features are numerous alkaline intrusions that occur throughout the area. The two biggest intrusions are located in Russia (Khibiny and Lovozero), east of Apatity. The study area is part of the glaciated terrain of Northern Europe. The main Quaternary deposits are till and peat. There are also large areas without any regolith cover, dominated by outcrops and boulder fields (Niemelä et al., 1993).

The north-south extent of the survey area is about 500 km. Within this distance, 3 vegetation zones gradually replace each other (Fig. 3). The southern and central parts of the area fall into the northern boreal coniferous zone. Towards the north, this zone gradually gives way to subarctic birch forest, followed by the subarctic tundra zone close to the coast of the Barents Sea. These changes in vegetation zones can also occur with altitude. Major characteristics of the forest ecosystems in this area are the sparseness of the tree layer, a slow growth rate and the large proportion of ground vegetation in the total biomass production.

The dominant soil forming process in forested and treeless regions of northern Europe is podzolisation of mineral soils (Borggaard, 1997). Podzols are thus the most important soil type present throughout the survey area. Soils in the area are young. Their age ranges between 5 and 8 ka. A typical podzol profile consists of 5 main layers, the O, E, B, BC and C-horizons. The O-horizon of podzol is characterised by a low pH-value (median in the survey area 3.85; Reimann et al., 1998a), pH increases systematically with depth. In the C-horizon it reaches a median value of 5.8. The O-horizon varies in thickness from less than 0.5 cm to more than 20 cm, the median for the survey area being 2.5 cm. The thickness of the soil profiles can vary considerably — the depth to the top of the C-horizon varies between 10 and 123 cm, the median being 35 cm.

Major climatic differences occur within the survey area. In the NW, summers are cool and winters mild, with most precipitation between September and January (coastal climate). In the central part, warm summers and relatively cold winters are typical; the main precipitation takes the form of rain showers in July and August (continental climate). The easternmost part is similar to the central part, but with colder winters. Precipitation is in general low. The average for the whole area is < 500 mm/a. The yearly average temperature is –1°C.

### 2.2. Sampling and sample preparation

Sampling of the 188,000 km<sup>2</sup> area took place from July to September 1995. The average sample density was 1 site per 300 km<sup>2</sup>. Samples were taken at 617 sites. Depending on availability the total number of samples ranges from 598 (moss) to 617 (O-horizon). Sample site

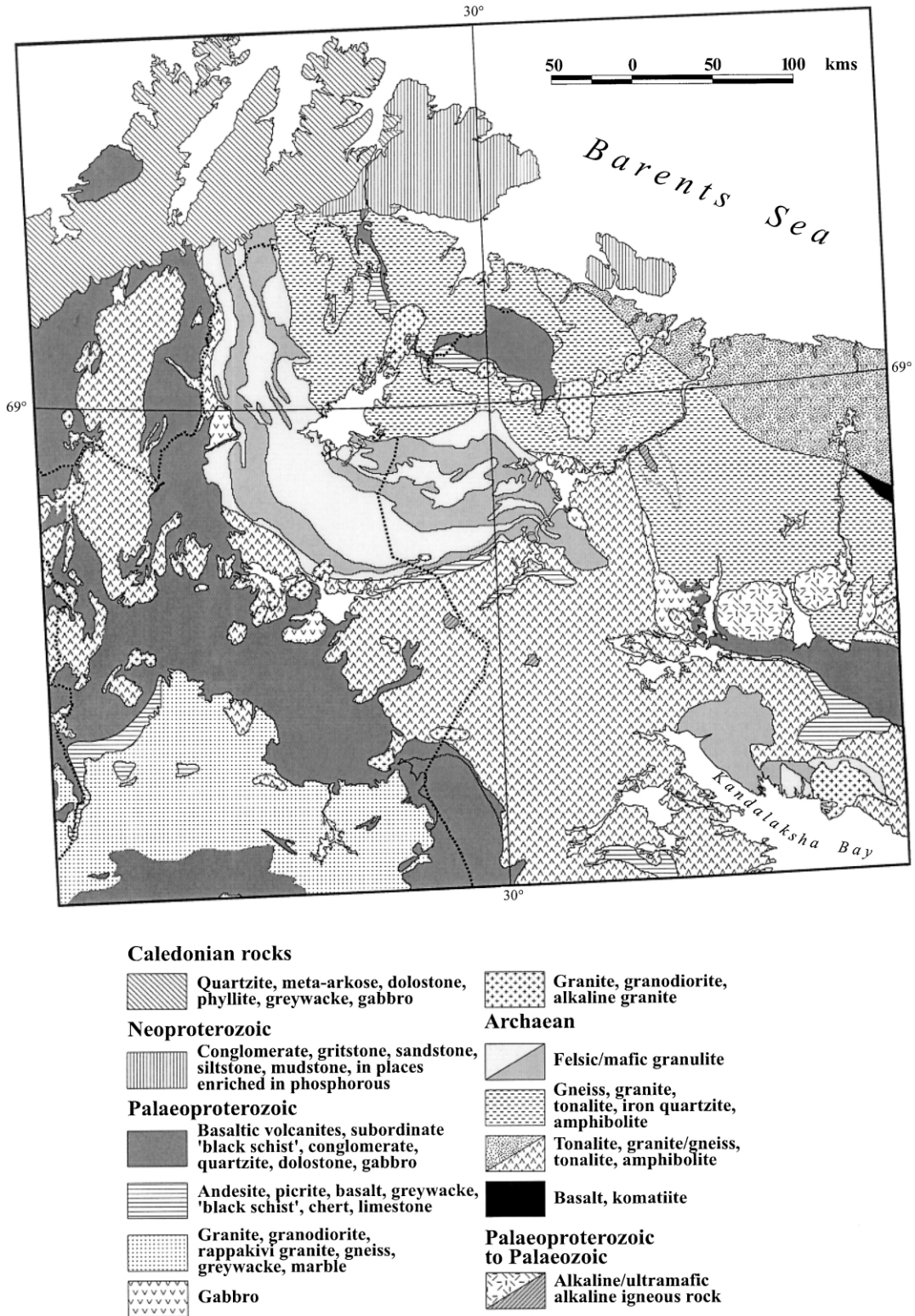


Fig. 2. Simplified geology of the survey area — for a colour version of this map see Reimann et al. (1998a) or Reimann and Melzchik (2001).

# Vegetation zones and forest composition

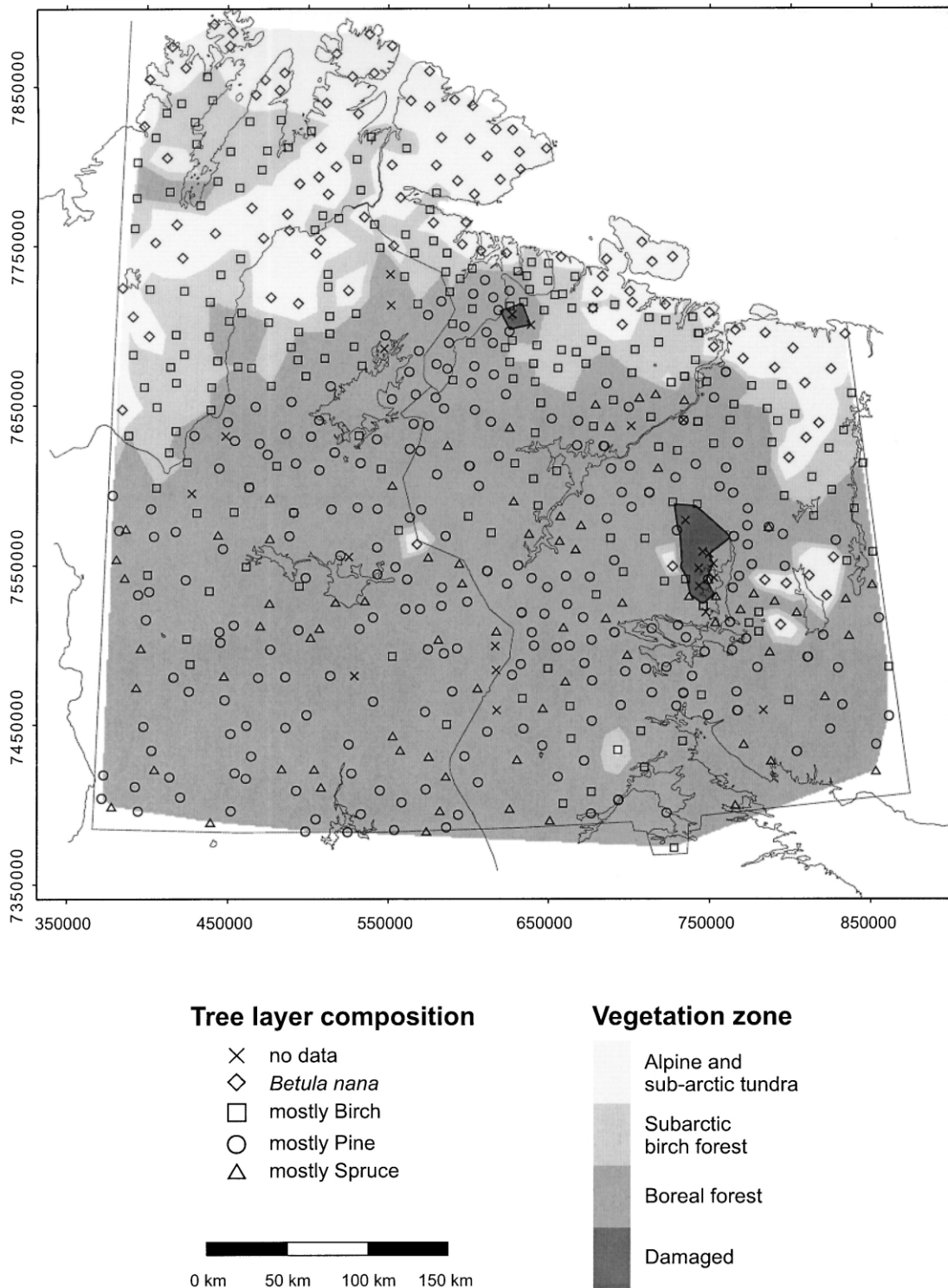


Fig. 3. Distribution of the main vegetation zones in the survey area (from Kashulina et al., 1997).

selection for the project was such that only locations where podzol developed on glacial drift is present were visited, giving genetically comparable samples over the whole area. At each site the following samples were collected [for more detailed information see Åyräs and Reimann (1995) or Reimann et al. (1998a)].

- Moss ( $N=598$ ): Terrestrial moss, preferably the species *H. splendens*, and if it was absent *P. schreberi* were collected. Only shoots representing the previous 3 years' growth were taken. Both species were collected along a gradient of decreasing pollution influence from east to west in the Norwegian part of the project area to check for the interspecies comparability of the results (Halleraker et al., 1998). All moss samples were air dried in the laboratory, fine cleaned (from other species and litter) and homogenised using a mixer equipped with non-contaminating blades.
- O-horizon ( $N=617$ ): This was collected with a custom-built tool to facilitate and systematise sampling, and to allow easy measurement of the volume of each sample (Åyräs and Reimann, 1995). For the O-horizon samples only the top 3 cm of the organic layer were taken. If the total thickness of the O-horizon was less than 3 cm, only the organic layer was sampled and the thickness was recorded on the field sheets. Between 7 and 10 sub-samples were collected at each site to give a composite sample with a minimum volume of 1 l. The field composites were air dried in the laboratory and sieved by rubbing them by hand (with talcum-free rubber gloves) through a 2-mm nylon sieve after removing large roots and/or plant fragments.
- Podzol profiles (B-horizon  $N=609$ , C-horizon  $N=605$ ): Before sampling a podzol profile, homogeneity of the soil cover was checked over an area of  $10 \times 10$  m. The exact location of the profile was chosen so that both ground vegetation and micro-topography were representative. The sampling pits were dug by spade to the C-horizon. Samples of the O, E (eluvial), B (illuvial), BC (transitional) and C (parent soil) horizons were collected, starting from the bottom to avoid contamination and mixing of the horizons. With the exception of the C-horizon, each layer was sampled over its complete thickness. If there were distinguishable layers within the B-horizon, these were collected in the same ratio as present in the profile. Each sample weighed about 1–1.5 kg, depending on grain size, mineralogy, water content, etc. All samples were air dried in the laboratory. At present only the B- and C-horizon samples have been sieved to  $<2$  mm, using nylon screening, and analysed. All other materials are stored for future reference.

For quality control purposes a complete set of duplicate samples was taken at every 15th site and put through the same sample preparation and analytical process as discussed above.

### 2.3. Chemical analysis and quality control

- Moss: a microwave-assisted concentrated  $\text{HNO}_3$  digestion was applied to dissolve the moss. The method is based on a standard released by the US Environmental Protection Agency (US EPA 3050). The digestion is efficient for most of the elements, though mineral particles (e.g. silicates) which may be caught from airborne dust are not totally dissolved. Subsequent chemical analysis was carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES with 32 fixed channels), inductively coupled plasma mass spectrometry (ICP-MS) and cold vapour atomic adsorption spectrometry (CV-AAS) for Hg. All moss analyses were carried out at GTK's laboratory. Additional details are given in Reimann et al. (1998a).
- O-horizon (0–3 cm): the same digestion and analytical procedures as described for the moss samples were used on the  $<2$  mm fraction. It should be stated, that, although this method will give total element concentrations in organic material, the O-horizon can contain mineral particles (silicates) which are not completely dissolved by this procedure (see comments below).
- B- and C-horizon samples: a 2 g subsample of the  $<2$  mm fraction was digested in aqua regia (1:3  $\text{HNO}_3$ :HCl) at  $90^\circ\text{C}$  at GTK's laboratory. The solutions were analysed by ICP-AES for 32 elements (Niskavaara, 1995) and by graphite furnace atomic absorption spectrometry (GF-AAS) for Ag, As, Cd and Pb. A second aliquot was analysed for Bi, Sb, Se and Te by GF-AAS after pre-concentration using reductive co-precipitation (Niskavaara and Kontas, 1990).

Many more chemical analyses were carried out for most materials, e.g. on an ammonium acetate leach of the humus samples, XRF (total) analysis of the B- and C-horizon samples and neutron activation analysis on the C-horizon samples. These results were not used here because the values reported would hardly be comparable to the other media, while an aqua regia dissolution and a concentrated  $\text{HNO}_3$ -leach will give comparable results. All these additional data are given in Reimann et al. (1998a).

Both the GTK and NGU chemical laboratories and the methods described above for analysing the Kola samples are accredited according to EN 45001 and ISO Guide 25. All methods have been thoroughly validated

and trueness, accuracy and precision were monitored continuously. Some of the quality control results are presented in Reimann et al. (1998a), whilst a comprehensive description of the analytical quality control data from the whole project will be given by Pakkarinen et al. (in prep.). Analytical precision is better than 5% for most elements in most media. The coefficient of variation for the field duplicates is less than 10% for B- and C-horizons for most elements and less than 20% for most elements in moss and O-horizon.

#### 2.4. Data analysis

For statistical data analysis and graphical presentation, the DAS<sup>®</sup> program (Dutter et al., 1992), based on exploratory data analysis (EDA) methods (Tukey, 1977; Velleman and Hoaglin, 1981) was used. Kürzl (1988), Reimann et al. (1988), and Rock (1988) give an introduction to the advantages of using exploratory data analysis methods when dealing with geochemical data. The construction of the box plot used in several figures follows Tukey's (1977) original definition (whiskers to last real data point up to  $1.5 \times$  hinge spread), data outliers are marked by squares ( $> 1.5 \times$  hinge spread) or plusses (far outliers -  $> 3 \times$  hinge spread). Coincidence of the median and one (or both) of the hinges is marked by a cross. The notches (square brackets), placed at  $1.58 \times (\text{hinge spread} / \sqrt{(n)})$  on either side of the median, are a test of significance of medians from different populations or boxes, comparable to a classical *t*-test (95%-significance). Values below detection were set to one half the detection limit for the purpose of graphical data analysis.

### 3. Results

To facilitate direct comparison, only those elements for which more than 90% of all analytical results were above the respective limit of detection in each of the 4 sample materials are presented here. This was the case for 24 elements. Many more elements were analysed in the different materials and readers who are interested in the behaviour of other elements are urged to extract the relevant information from the maps and tables presented in Reimann et al. (1998a). Minimum, median and maximum concentrations for these 24 elements and LOI and pH in the 4 materials are given in Table 1. Table 2 shows the spread of the data, defined as the quotient (concentration at 95th-percentile)/(concentration at 5th-percentile) and gives thus a good idea about the relative variation of the data for each element in each sample material. The well established hinge-spread (Tukey, 1977) was not used as a measure here, because data outliers caused by various sources play an important role in the data set. The chosen ratio includes the majority of data and still avoids influence from extreme

outliers. Table 3 gives the ratio of the results in the different sample materials to those from the C-horizon (and moss to those from the O-horizon) and can thus be used to study relative enrichment/depletion of elements in the different materials.

For the following discussions, it is important to note that the results for the B- and C-horizons originate from aqua regia extraction. Aqua regia digestion is the most frequently used procedure in environmental studies of heavy metals in soil samples. An aqua regia digestion will not totally dissolve all the minerals in all soils. The efficiency of digestion varies from element to element and depends on the mineralogy of the sample. Most of the sulphides, oxides, clay minerals and secondary minerals formed during soil formation processes will be totally dissolved. In addition elements bound to soil organic matter will be liberated. Most of the silicate minerals are, however, not dissolved. Thus the aqua regia extraction would be expected to reveal the differences in mineralogy and genesis of different soil layers due to altered dissolution properties, even in cases where a total dissolution would result in equal results. For the elements where the project gave results from both aqua regia digestion and total concentration (XRF or INAA) in the C-horizon ( $< 2$  mm) the following sequence (in % of total dissolved by aqua regia) of "aqua-regia-extractability" can be established:

$$\begin{aligned} P(100) &> \text{Th}(100) >> \text{Co}(54) = \text{La}(53) > \text{Fe}(43) \\ &> \text{Mg}(32) = \text{Zn}(32) > \text{Cr}(28) > \text{Mn}(24) \\ &= \text{Ti}(23) > \text{Sc}(18) > \text{Al}(13) > \text{Ca}(9) = \text{Ba}(8) \\ &= \text{K}(8) >> \text{Na}(0.6) >> \text{Si}(0.04). \end{aligned}$$

Koljonen and Malisa (1991) have established a comparable sequence of "aqua-regia-extractability" for the much finer grain size fraction  $< 0.063$  mm of Finnish tills:

$$\begin{aligned} P(89) &> \text{Cu}(88) >> \text{La}(73) > \text{Th}(67) > \text{Ni}(60) > \text{Fe}(52) \\ &> \text{Co}(46) > \text{V}(43) > \text{Mg}(42) > \text{Cr}(40) > \text{Zn}(38) \\ &> \text{Mn}(31) > \text{Ti}(28) > \text{Sc}(25) > \text{Al}(13) > \text{Ca}(9.4) \\ &> \text{Ba}(9) > \text{K}(8) > \text{Sr}(3) > \text{Na}(0.7) > \text{Si}(0.5). \end{aligned}$$

For the purposes of this paper, an aqua regia digestion as used for the B- and C-horizon soil samples will give fairly comparable results to the concentrated HNO<sub>3</sub>-extraction used for the O-horizon and moss samples. Both extractions will give a good indication of the total pool of elements that can be mobilised under a strong acid attack in the 4 sample materials.

Table 1

Minimum, median and maximum concentrations of (in mg/kg) the 24 elements and LOI and pH considered here. Moss and O-horizon (< 2 mm) concentrated HNO<sub>3</sub> extraction; B- and C-horizons (both < 2 mm) aqua regia extraction. Data are from Reimann et al. (1998a), where results for more than 50 elements are documented. LOI = loss on ignition

Element	C-horizon			B-horizon			O-horizon			Moss		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Ag	<0.001	0.008	0.119	<0.001	0.019	0.378	0.025	0.2	4.79	<0.01	0.033	0.824
Al	1840	9910	85 900	3200	18 900	83 300	372	1890	20 600	33.9	193	4850
As	<0.1	0.5	30.7	>0.1	1.1	77.8	0.36	1.16	43.5	0.04	0.173	3.4
Ba	4.7	43.5	1300	5.6	28.7	385	13.9	76.2	290	6.7	19	175
Bi	<0.005	0.026	1	<0.005	0.031	1.2	0.029	0.159	6.1	<0.004	0.018	0.69
Ca	110	1900	41 700	70	1320	7410	460	2960	25 400	1680	2620	9320
Cd	0.007	0.024	0.221	0.005	0.024	0.236	0.073	0.303	1.39	0.023	0.089	1.23
Co	1.2	7	44	0.1	5.7	21	0.21	1.57	96	0.11	0.395	13.2
Cr	2.2	28.2	471	3.8	35.2	413	0.39	2.91	109	<0.2	0.6	14.4
Cu	2.0	16.1	149	0.9	10.5	126	2.69	9.69	4080	2.63	7.2	355
Fe	3310	14 700	79 200	4980	23 500	121 000	430	1970	44 800	46	212	5140
K	<100	1100	11 000	<100	630	10 400	300	1000	5700	2260	4220	8590
Mg	370	3700	70 500	340	3030	23 800	240	750	5830	518	1090	2380
Mn	34	128	2140	24	103	1450	11.1	126	5470	28.5	433	1170
Na	20	140	19 400	20	130	4550	<10	60	2350	<10	72	918
Ni	1.2	18.6	228	1.4	16.1	179	1.5	9.18	2880	0.96	5.4	396
P	59	392	7170	64	405	3260	192	930	9280	511	1270	3800
Pb	0.3	1.6	45.3	0.81	3.05	27.7	4.1	18.8	1110	0.84	2.98	29.4
S	<5	30	531	11	162	777	400	1530	3830	543	863	2090
Si	50	140	590	70	160	464	290	530	940	25	197	983
Sr	1.6	7.7	1040	1.6	6.3	879	6.1	28.8	1430	2.47	9.4	435
Th	<3	6	66	<3	6	51	0.063	0.345	15.4	<0.004	0.023	1.14
V	4.5	30.9	183	7.8	42.1	146	1.1	4.86	49	0.28	1.6	83.8
Zn	3.7	20.9	348	3.7	25.5	209	12	46	198	11.7	32.3	81.9
LOI	0.34%	1.80%	16.40%	0.79%	7.08%	44.20%	33.50%	89.80%	98.80%			
pH	3.7	5.8	7.6	4.5	5.2	6.7	3.2	3.85	5.6			



Table 2  
Spread (defined as concentration at the 95th-%ile/5th-%ile) for the 24 elements in the 4 media discussed

Element	C-horizon	B-horizon	O-horizon	Moss
Ag	9.7	14.2	<b>16.3</b>	10.4
Al	7.8	4.9	<b>8.6</b>	8.3
As	<b>47*</b>	18	5.3	8.9
Ba	<b>12.3</b>	7.7	3.9	3.6
Bi	<b>21.3</b>	14.2	5.2	15
Ca	<b>8.5</b>	8.4	2.9	1.8
Cd	<b>6.6</b>	4.8	4	6.2
Co	6.2	5.1	19.3	<b>19.9</b>
Cr	8.1	6.8	<b>10.2</b>	9.5
Cu	12.7	10.5	<b>19.4</b>	16.5
Fe	5.8	4.4	8.6	<b>16</b>
K	<b>9</b>	8.9	2.3	1.9
Mg	<b>8.5</b>	7	3.9	2.2
Mn	8.5	7.7	<b>22</b>	6.3
Na	12.2	8.4	12.1	<b>12.6</b>
Ni	8.7	7.9	<b>68</b>	55.4
P	<b>5.4</b>	<b>5.4</b>	2.2	2.1
Pb	<b>9.9</b>	6.2	4	3.7
S	<b>9</b>	5.8	2	1.6
Si	3	2.7	1.7	<b>4.8</b>
Sr	<b>15.4</b>	11.6	5.3	10.1
Th	11.3*	9.3	<b>15.7</b>	12.5
V	5.4	4.1	7.5	<b>11.1</b>
Zn	<b>8.8</b>	8	3.3	2.8

Bold highest spread of all media.

\*5th-%ile under detection limit (DL) — value used for calculation estimated from CDF-diagram.

### 3.1. Concentrations

Fig. 4 shows the sequence of elements sorted after decreasing median value in the form of a box plot comparison for moss, O-, B- and C-horizons. In these diagrams, median concentrations and total element variation can be appreciated at one glance. The figure shows that there are big differences in concentrations and spread for the different elements. Together with Table 1, it can be used to group the 24 elements of concern here into 3 main classes for each material:

- Major elements (median concentration > 100 mg/kg) [note that this is the sequence in an aqua regia extraction (B- and C-horizons) or a concentrated HNO<sub>3</sub>-extraction (O-horizon and moss)]:

C-horizon:	Fe, Al, Mg, Ca, K, P, Si, Na, Mn
B-horizon:	Fe, Al, Mg, Ca, K, P, S, Si, Na, Mn
O-horizon:	<u>Ca</u> , Fe, Al, S, K, P, <u>Mg</u> , Si, Mn

Table 3  
Ratio of the median concentration in the C-horizon divided by the median concentration in the other sample media and ratio O-horizon/moss (values from Table 1) ranked in decreasing order

Element B-horizon/ C-horizon	Element O-horizon/ C-horizon	Element Moss/ C-horizon	Element Moss/ O-horizon
S 5.7	S 50	S 30.3	K 4
Ag 2.5	Ag 25	Ag 4.4	Mn 3.2
As 1.9	Cd 12.5	Cd 3.9	Mg 1.4
Al 1.8	<b>Pb 12.5</b>	K 3.8	P 1.3
Pb 1.7	Bi 5	P 3.2	Na 1.2
Fe 1.6	Si 3.3	Mn 3.0	Ca 0.9
V 1.34	Sr 3.3	Pb 1.64	Cu 0.7
Cr 1.26	As 2.5	Zn 1.61	Zn 0.7
Bi 1.21	P 2.5	Ca 1.42	S 0.6
Si 1.16	Zn 2	Si 1.37	Ni 0.5
Zn 1.16	Ba 1.7	Sr 1.1	Si 0.4
P 1.06	Ca 1.7	Bi 0.7	V 0.35
Cd 1	K 0.91	Cu 0.50	Co 0.33
Th 1	Mn 0.91	Na 0.45	Sr 0.32
Na 0.90	Cu 0.67	Ba 0.44	Cd 0.31
Ni 0.85	Ni 0.53	As 0.33	Ba 0.23
Mg 0.83	Na 0.37	Mg 0.29	Cr 0.23
Sr 0.83	Co 0.23	Ni 0.28	Ag 0.18
Co 0.81	Mg 0.20	Co 0.06	As 0.16
Mn 0.75	Al 0.20	V 0.05	Pb 0.14
Ca 0.71	V 0.16	Cr 0.022	Fe 0.13
Ba 0.71	Fe 0.14	Al 0.019	Bi 0.12
Cu 0.64	Cr 0.10	Fe 0.015	Al 0.11
K 0.58	Th 0.06	Th 0.004	Th 0.08

Moss: K, Ca, P, Mg, S, Mn, Fe,  
Si, Al, Na

- Minor elements (median concentration between 10 and 100 mg/kg):

C-horizon:	Ba, V, S, Cr, Zn, Ni, Cu
B-horizon:	V, Cr, Ba, Zn, Ni, Cu
O-horizon:	Ba, <b>Na</b> , Zn, <b>Sr</b> , <b>Pb</b> , Cu, Ni
Moss:	<u>Zn</u> , Ba, <b>Sr</b>

- Trace elements (median concentration < 10 mg/kg):

C-horizon:	Sr, Co, Th, Pb, As, Bi, Cd, Ag
B-horizon:	Sr, Th, Co, Pb, As, Bi, Cd, Ag
O-horizon:	<b>V</b> , <b>Cr</b> , Co, As, Th, Cd, Ag, Bi
Moss:	<b>Cu</b> , <b>Ni</b> , <u>Pb</u> , <b>V</b> , <b>Cr</b> , Co, As, Cd, Ag, <u>Th</u> , Bi

(Key: a new element in the class in relation to the C-horizon is marked in **bold**, an important shift in position within the class is underlined.)

Changes between the B- and the C-horizons are very small. Most important is the occurrence of S as a major element in the B-horizon but not in the C-horizon. This is caused by the higher amount of organic matter (see

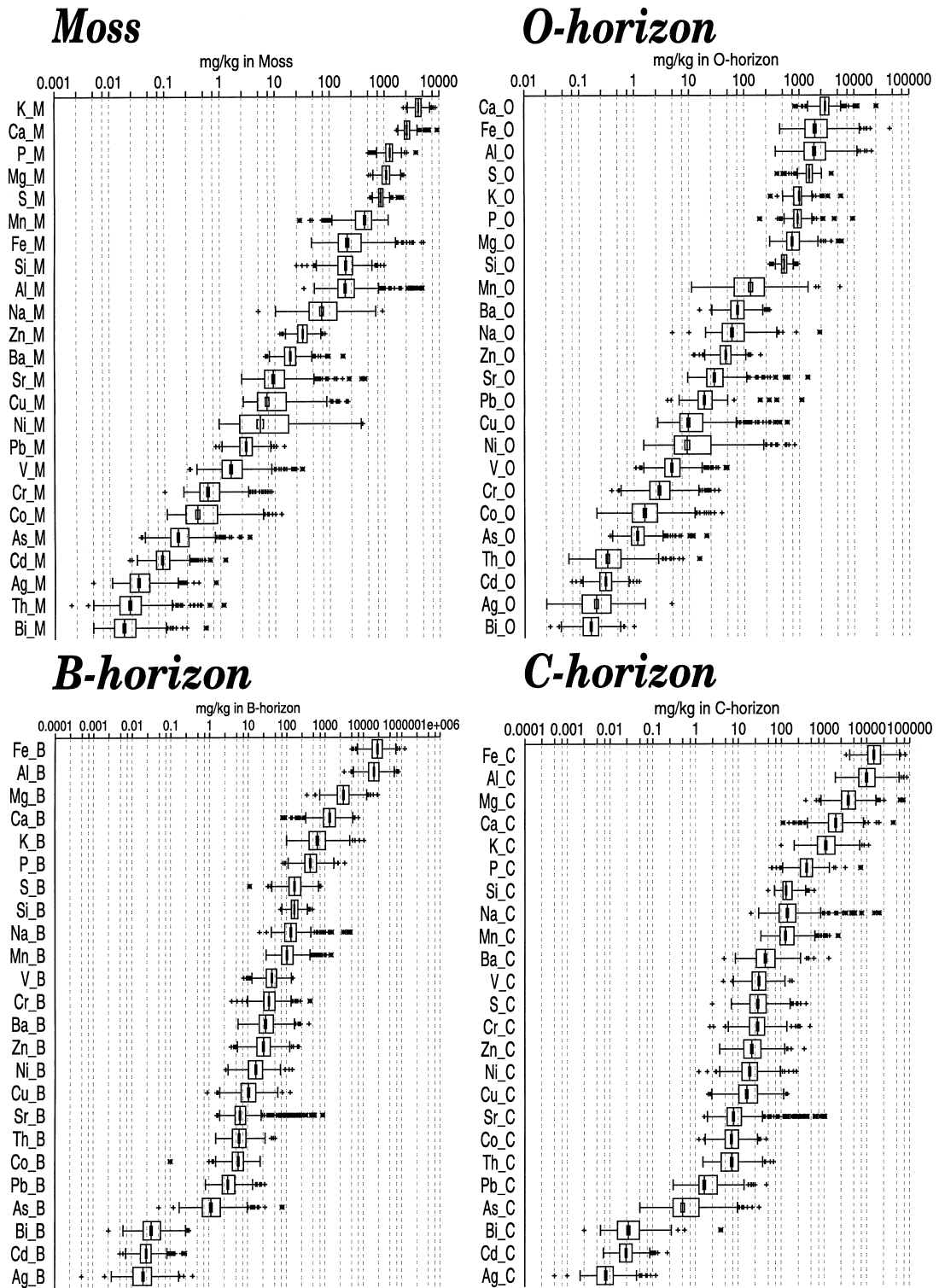


Fig. 4. Boxplot comparison of element concentration and variation in the 4 sample media. Elements sorted according to decreasing median concentration in each material.

LOI in Table 1) in the B-horizon; organic matter is highly enriched in S compared to minerogenic material.

More important changes can be observed when the O- and C-horizons are compared. Sulphur occurs in the O-horizon in position 4 of the major elements. Sodium, in contrast, is no longer a major element in the O-horizon in spite of the fact that Na is in ample supply in the survey area [high input via marine aerosols in the coastal areas (Reimann et al., 2000a) and from the alkaline rocks]. Sodium (Na) shows high values in the O-horizon samples near the coast but otherwise low values and little variation throughout the survey area. This element is very mobile in the cold arctic climate and there is no mechanism for fixing and/or enriching Na in the O-horizon. Two further important elements change position in the O-horizon: Ca and Mg. Calcium moves to the first position due to its preferred binding at ion exchange sites, while Mg moves to position 7 (from position 3) due to its higher mobility and a less preferred fixation. One of the most interesting changes is, however, the move of Pb and Sr from trace elements to minor elements in the O-horizon.

To start to understand the processes involved here the data distribution within the different materials has to be studied and compared in detail. Fig. 5 presents CDF-diagrams (CDF = cumulative distribution function) for 8 selected elements, showing the complete data distribution in every single material in just one diagram. CDF-diagrams for all elements can be found in Reimann et al. (1998a). As suggested 40 a ago by Vistelius (1960), the simple study of raw data distributions can give important geochemical insights. Different distributions can be observed in the 4 materials for the 8 elements presented in Fig. 5. The diagrams not only show the relative enrichment/depletion of element concentrations in the 4 sample materials over the whole concentration range (discussed below) but also reveal unusual sources or processes influencing the data distribution. In the C-horizon, different bedrock types can result in an uneven curve or even major breaks in the distribution — this is clearly visible in the diagram for Sr, in which the alkaline intrusions lead to a major break towards much higher concentrations at about the 95th percentile. This break is well reflected in all 4 materials but, in the O-horizon and moss, is due to pollution by dust from the big mining and processing operations of alkaline rocks in the area rather than a direct reflection of the composition of the C-horizon. It can also be seen that Sr is generally enriched in the O-horizon over the whole concentration range. This may be due to the close geochemical relationship between Ca and Sr — Ca shifted to the position of the most important major element in the O-horizon. The CDF-diagram for Al (Fig. 5) demonstrates again the influence of dust input on concentrations observed in moss and the O-horizon on the uppermost 2% of the data — but here

concentrations are generally much higher in the B- and C-horizon.

Lead appears generally highly enriched in the O-horizon (see discussion below) and shows lower and comparable concentrations in moss, B- and C-horizons. This explains the shift from trace to minor element in the O-horizon.

In moss, only S appears as a new major element when compared to the C-horizon. A relative enrichment of S from “bottom” (C-horizon) to “top” (O-horizon and moss) is very well reflected in the CDF-diagram (Fig. 5) (discussed below). Several elements show important shifts in position — compared to the C-horizon as well as to the O-horizon. Potassium is now the major element with the highest concentration in moss. Phosphorus and Mn also become more important major elements, which reflects their role in plant nutrition.

Some shifts between minor and trace element status can be observed for moss. Several of the most important pollution-related elements on Kola — Cu, Ni, V and Cr move from minor element in the C-horizon to trace element in moss. Regional maps (Reimann et al., 1998a) show the distributions of Ni and Cu in moss to be much more influenced by human activities than those of Sr and Pb. The CDF-diagram for Ni (Fig. 5) demonstrates clearly the influence of pollution on the Ni-concentrations in moss (and the O-horizon). A major break in the distribution can be seen even below the 50th percentile. Thus, although for Ni even the median is influenced by pollution, most of the concentrations observed in moss (and the O-horizon) are still below the Ni-concentrations found in the B- and C-horizons. Cobalt shows a similar distribution (Fig. 5) and is also emitted in high amounts. An important message that can be taken from the distribution of Ni and Co in moss and humus (Fig. 5) is that pollution has a more important influence on data spread than on the median.

In conclusion, based on strong acid extraction, element classes are quite comparable in the 4 sample materials. To this extent element abundance in the parent material (C-horizon, crust) finds a reflection even in moss. The median values in all materials are, in general, not (for most elements) or not seriously (Cu, Ni, Co) affected by pollution. It is not pollution that governs the observed element distributions and shifts between element classes (major, minor and trace elements) but natural sources/processes. In the case of moss and the O-horizon the most important influence on element concentrations appears to be the biological role of the different elements (e.g. S) and geochemical relationships between major and trace elements (e.g. Ca/Sr).

### 3.2. Spread

Element variation in the C-horizon is high due to the multitude of different bedrock types (Fig. 2) and several mineral deposits [for a map see Reimann et al., 1998a or

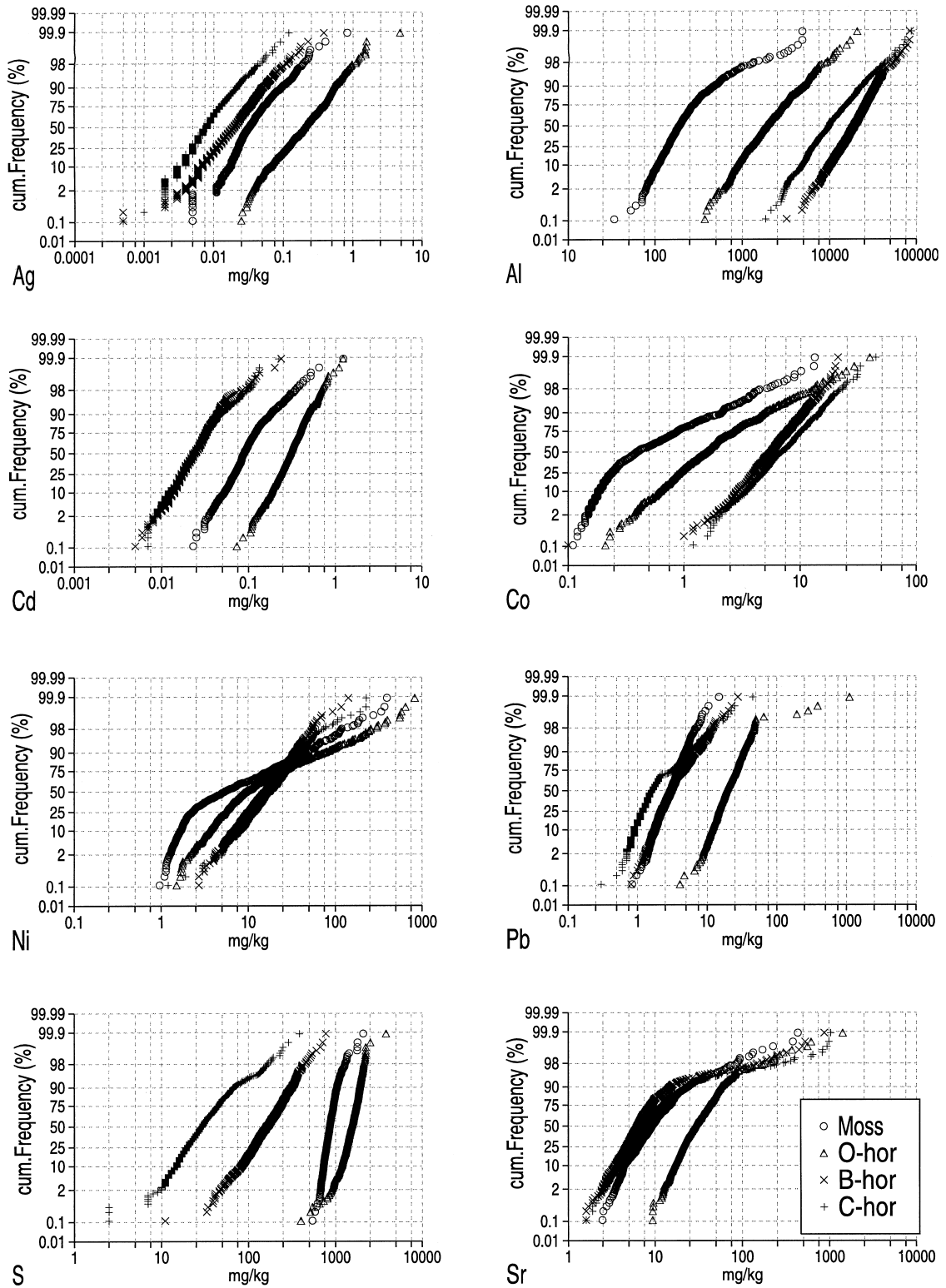


Fig. 5. CDF-diagrams showing the data distribution in the 4 sample materials for 8 selected elements. Note that for the construction of these diagrams only samples from the 581 sites at which all 4 materials were collected were used.

Reimann and Melezhik (2001)] occurring in the survey area. Anthropogenic influence on element concentrations in the C-horizon is negligible. The observed variation is due to natural processes. Arsenic and Bi show the largest spread in the C-horizon (Table 2). This is caused by the presence of mineralisation and high concentrations of these elements in some of the lithologies occurring in the survey area (e.g. the Caledonian sediments along the Norwegian coast). Strontium, Na and Th, which also show a high spread, are enriched in certain lithologies (e.g. the alkaline intrusions). Twelve out of the 24 elements discussed here show the highest spread in the C-horizon.

The soil-forming processes influencing element concentrations in the B-horizon reduce variation for quite a long list of elements (As, Ba, Bi, Cd, Co, Cu, Mg, Mn, Pb, S). The most typical elements (Al, Fe) for illuvial accumulation, a prominent feature of podzol formation, show the lowest spread in the B-horizon. Chromium and V show comparable behaviour. Silver is the only element showing a larger spread in the B- than in the C-horizon. Reasons will be discussed below. In general, it appears that natural processes tend to reduce data spread in the B-horizon.

Seven elements show the largest spread in the O-horizon, Ni, Cu and Co are prominent examples (Table 2). These are the 3 main heavy metals emitted by the Ni industry. For Mn, the reason for the large spread is not apparent at first glance. Manganese is an important plant nutrient and should thus show a low spread (see discussion below). A map of Mn in the O-horizon (Reimann et al., 1998a) shows a general increase in concentrations from north to south. The most likely reason for this north-south trend is that Mn is a very deficient plant nutrient in the survey area. Its concentration depends mostly on site fertility (intensity of biological cycling), which varies considerably with the changes in vegetation zones occurring from north to south (Fig. 3). Another interesting feature, which can be taken from a regional distribution map (Reimann et al., 1998a) is the serious depletion of Mn near major pollution sources. Silver (Ag) is another element showing a prominent north-south trend. In addition, anthropogenic emissions and a major mineralisation-related anomaly in Finland influence its distribution. These factors account for the large spread (Table 2). The large spread of elements like Th, Na, Cr, Al, Fe and V indicates differing amounts of minerogenic material in the O-horizon samples. In part it is also related to the increased input of dust near the major industrial centres.

Most of the important plant nutrients (e.g. S, P, K, Ca, Zn and Mg) show exceptionally low spreads in the O-horizon and in moss. It appears that the biological processes closely regulate the concentration of these elements in both materials. It is most surprising that S shows so little spread. One would expect that the major SO<sub>2</sub>-emissions related to the Russian Ni industry, and

the additional input of S via sea spray near the coast, would result in S showing an enormous spread in the surficial sample materials (see also Fig. 5). The massive SO<sub>2</sub>-emissions from the Russian nickel industry do not even find an expression in regional maps of the S distribution in the O-horizon (Reimann et al., 1998a). The total S-concentration observed in the O-horizon is mostly inherited from the decaying plant material. Its concentration depends on bioclimatic conditions regulating the litterfall decomposition rate (Kashulina and Reimann, submitted for publication). Sulphate originating from anthropogenic sources or from marine aerosols cannot be fixed and stored in the O-horizon and thus the high anthropogenic input does not result in high concentrations and the ensuing large spread of data.

Five elements show a large spread of concentration in moss (Table 2). All 3 main metals (Co, Cu, Ni) influenced by anthropogenic emissions in the area show a large spread, with Ni topping the list at 55.4. The effect of the anthropogenic emissions on the distribution of Co and Ni is clearly visible in the CDF-diagram (Fig. 5). The large spread observed for Fe is indicative of the uptake of dust from various industrial sources throughout the area. Iron is the one element that clearly depicts every single industrial site. The distribution of Bi in moss is, to a large extent, governed by emissions from the Russian Ni industry. Sodium and Th are indicators of dust, the processing of the alkaline rocks in Apatity being the main source here. The high spread in moss is thus mostly caused by anthropogenic activities. The input of marine aerosols near the coast is a natural process having a large influence on the concentration and thus spread of Na in moss.

In conclusion, spread can be a powerful tool to indicate pollution or other unusual element sources. All major pollutants (Ni, Cu, Co, Fe, Sr, V — note that these come from different sources) in the survey area show exceptionally high spreads in moss and the O-horizon. In contrast, many natural processes work to decrease spread (e.g. major nutrients in moss and Al, Fe, Cr, V in the B-horizon).

### 3.3. *Relative enrichment/depletion of elements*

The C-horizon samples represent the lithosphere in the survey area and can be taken as representing the chemical “background” at any point in space. The ratio of the median in all other materials to that of the C-horizon samples can be used to study relative element enrichment/depletion in the different media (Table 3 and Fig. 6). Differences can be used to better understand in which direction and manner surface processes alter the geological background.

Many elements leached from the upper soil horizons are thought to accumulate in the B-horizon of podzols. Processes leading to this accumulation include

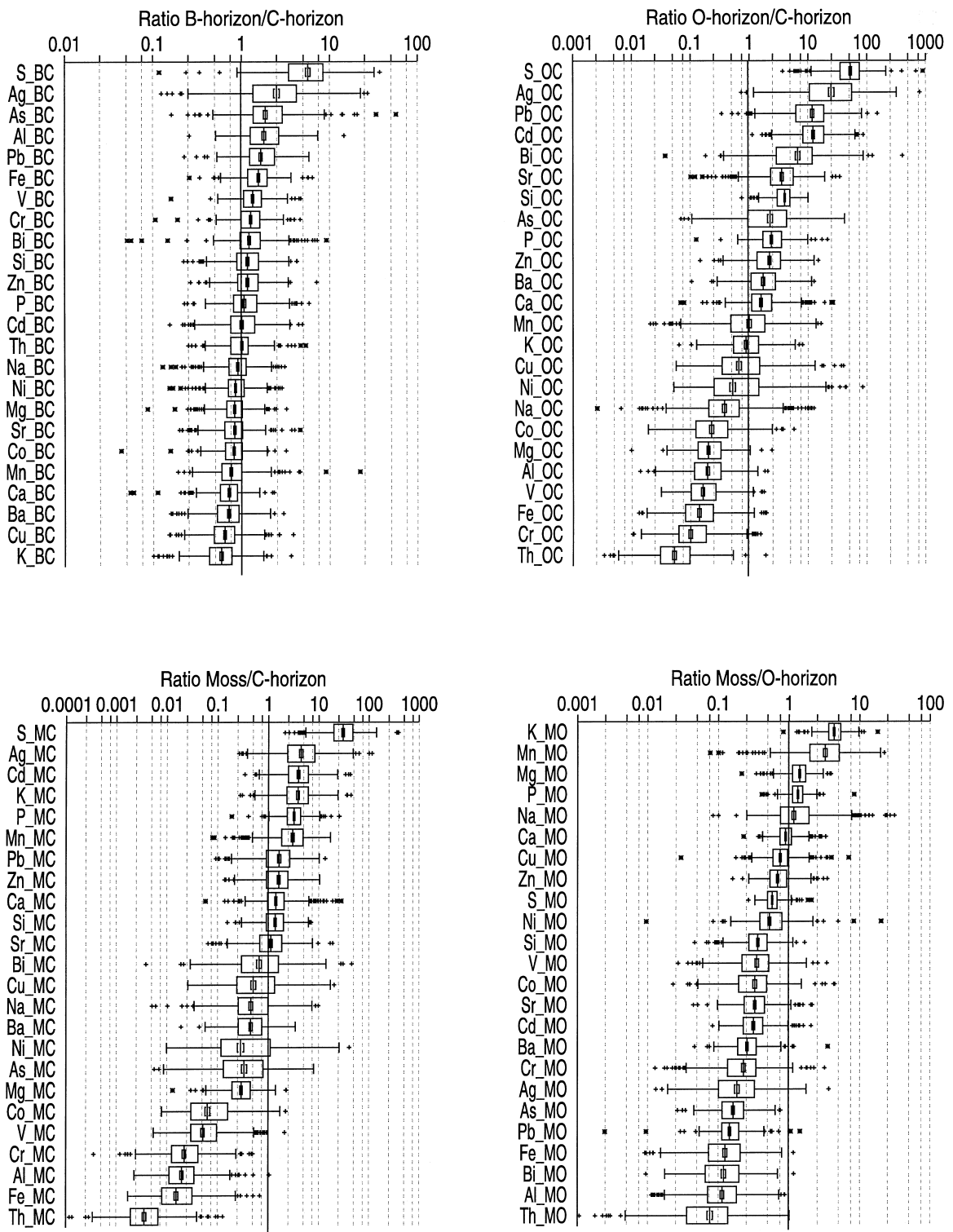


Fig. 6. Boxplot comparison of the ratio of B- and O-horizons and moss to the C-horizon and of moss to the O-horizon. The elements are sorted according to a decreasing median ratio.

co-precipitation, ion exchange, complexation and adsorption. It should not be neglected that elements can also migrate upwards in a soil profile; the B-horizon would represent a first trap for such elements as well (e.g. co-precipitation with Fe-oxide/hydroxides). From Table 3, one can take the following groups of elements that are either enriched, stable or depleted in the B-horizon relative to the C-horizon:

Enriched in the B-horizon:	S, Ag, As, Al, Pb, Fe, Bi, Cr, V, Si, Zn
Stable:	Cd, P and Th
Lower in the B-horizon:	K, Cu, Ca, Ba, Mn, Sr, Ni, Na, Mg, Co

Fig. 6 and Table 3 show that element concentrations as found in the B-horizon are still very close to those of the C-horizon. The total variation in the B/C-horizon ratio is very low when compared to ratios for all other media: from 6 (S) to 0.6 (K). Note the much higher difference in the moss/C-horizon ratio: from 30 (S) to 0.004 (Th) (Table 3). Fig. 6 demonstrates that the variation in the B/C-horizon ratio can be substantial, depending on site. Still, the boxes for the B/C-horizon ratio are tighter than for all other ratios (Fig. 6).

Sulphur, Ag, and As are the 3 elements showing the greatest enrichment in the B-horizon. The main reason for the enrichment of S in the B-horizon is the illuvial accumulation of organic matter which has much higher S-concentrations than mineral soils. The observed enrichment of S in the B-horizon is thus mostly a natural process. The existence of an anthropogenic impact is visible in the form of some outliers in Figs. 5 and 6. The enrichment of Ag, As, Pb and Bi in the B-horizon, while Co, Cu and Ni are depleted, is fascinating: are the first 4 elements co-precipitated with Fe-oxides/hydroxides, are they bound to organic material or are they hosted in sulphides? Is their relative enrichment a natural process or is it an indication of anthropogenic interference with element cycles influencing even this deep soil layer? The very high proportion of enriched samples and the fact that Co, Cu and Ni are not enriched in the B-horizon, are both arguments for natural processes causing this feature. Co-precipitation and the increase of organic matter described above, with high concentrations of these elements, appear to be the most likely processes leading to the enrichment of these elements in the B-horizon. Sodium, Mg, Mn, Ca and K are all depleted in the B-horizon. These elements cannot be fixed in the B-horizon and are removed after liberation via weathering. The most depleted element in the B-horizon is the important plant nutrient K.

Fig. 6 shows that there is a much larger fractionation of elements between the O- and C-horizons than between the B- and C-horizon. In addition, many of the boxes become much wider:

Enriched in the O-horizon:	S, Ag, Cd, Pb, Bi, Si, Sr, As, P and Zn.
Almost stable in O- and C-horizon:	Ba, Ca, K and Mn.
Clearly depleted in the O-horizon:	Th, Cr, Fe, V, Al, Mg, Co, Na, Ni, and Cu.

Sulphur, Ag, Cd, and Pb are exceptionally enriched in the O-horizon samples (Figs. 5 and 6 and Table 3). Sulphur plays an important role in the biosphere and its enrichment in the O-horizon is not related to the emissions from the Russian Ni industry or to the input via sea spray (see discussion above). The regional distribution map of S in the O-horizon (Reimann et al., 1998a) shows only a minor enrichment of S over a limited area in the surroundings of the smelters. Silver, Cd, Pb, (Bi, As, and Zn) are only minor pollutants in the survey area. Nevertheless they show a clear enrichment in the O-horizon, while the major elements emitted by industry in the survey area, namely Ni, Cu, Co and V all show O/C-ratios far below unity. Generally the influence of anthropogenic emissions in the survey area is only discernible in very wide box plots [a large spread (see discussion above); Figs. 5 and 6] and not in an enrichment in the O-horizon. Fig. 5 shows clearly the overlap of the anthropogenic emissions with the natural distributions. All regional element distribution maps in Reimann et al. (1998a) show that it is difficult to distinguish background from pollution in the O-horizon at distances exceeding 200 km from the pollution source. This observation is backed by recent results from regional-scale studies in the surroundings of the Flin-Flon smelter in Manitoba, Canada (e.g. Bonham-Carter and McMartin, 1997; Henderson et al., 1998). Here, most of the metals emitted since the start-up of the smelters were still found accumulated in the uppermost soil layer within a radius of 80 km around the source.

The observed regional-scale enrichment of Ag, Cd, Pb, Bi, As and Zn must thus be due to another source/process than anthropogenic emissions. More than 60 ago Goldschmidt (1937) noted the strong enrichment of several of these elements in the O-horizon of soil profiles without an apparent source. This observation led him to the definition of the O-horizon as an important geochemical trap for the more mobile elements. In his understanding these elements can be enriched far beyond normal “natural” concentrations in the O-horizon by biological processes (e.g. plants pumping up mobile elements from the lower soil levels where supply is virtually unlimited), and, effective complexing or exchangeable fixation of these elements with organic material. The element distributions depicted in the CDF-diagrams in Fig. 5 (only Ag, Cd and Pb shown) demonstrate that this enrichment in the O-horizon is a natural feature. Just as with Mn (discussed above), these elements also

show a north-south trend, with low values in the north (along the coast of the Barents Sea) and high values in the south (Reimann et al., 2000a). A multitude of natural processes including soil pH changes, the displacement of elements from ion exchange sites via the input of sea salts near the coast (Reimann et al., 2000a) and bioclimatic effects due to the differences in vegetation zones from north to south can all influence element concentrations. The observed north-south gradient, as well as the relative enrichment of these elements in the O-horizon, are thus both dominated by natural processes and not by atmospheric input due to human interference with global element fluxes.

Elements depleted in the O-horizon include Th, Cr, Fe and V [note that substantial amounts of Fe and V are emitted in the survey area — see regional maps in Reimann et al. (1998a)]. A high concentration of any of these elements in an O-horizon sample is often an indication of minerogenic admixtures.

Moss receives its nutrients directly from the atmosphere. One would expect to see rather low values for all elements when compared to element concentrations in minerogenic soils. This is not so:

Enriched in moss relative to C-horizon:	S, P, Ag, Cd, K, Mn and Pb
Stable concentrations in moss:	Zn, Ca, Si, Sr and Bi.
Depleted in moss:	Th, Fe, Al, Cr, V, Co, Ni, Mg, As, Na, Ba, and Cu.

While S, P, K and Mn are all known as important plant nutrients, the presence of Ag, Cd and Pb on this list of enriched elements is surprising, considering that there is no major emission source for these elements in the survey area. Nickel, Cu and Co are emitted in huge quantities but show comparatively low moss/C-horizon ratios. The fact that even these ratios are not primarily governed by the input of anthropogenic emissions is demonstrated by the fact that they do not reflect the real emission figures. While the Kola smelters emitted 2000 t of Ni and 1000 t of Cu in 1994 (Reimann et al., 1997b), the ratio moss/C-horizon is 0.5 for Cu and 0.3 for Ni. It would thus indicate just the opposite relationship, assuming that the ratio in the emissions is preserved under transport. This demonstrates that important natural processes influence the uptake/retention of the elements in biological materials. The elements that are particularly depleted in moss are Th, Fe, Al, Cr, and V — almost the same suite of elements that were depleted in the O-horizon. A high concentration of these elements in a sample can be taken as an indicator of the presence of minerogenic dust in the moss sample. A high input of Al, Fe, Cr, and V via dust was also demonstrated using snow samples (Reimann et al., 1996; Caritat et al., 1998a).

It may be more realistic to compare moss and the O-horizon, because they occur in very close connection.

Moss is, in relation to the O-horizon:

Enriched in:	K and Mn.
Unchanged for:	Mg, P, Na, Ca, Cu, Zn and S.
Depleted in:	Th, Al, Bi, Fe, Pb, As, Ag, Cr, Ba, Cd, Sr, Co, V, Si, and Ni.

Most interesting is the list of depleted elements. The presence of the “dust elements” (Th, Al, Fe, Cr, Ba, Sr, V and Si) indicates that moss has a much lower ability to accumulate minerogenic dust than the O-horizon. The presence of two of the main pollutants in the survey area (Ni and Co) in the list of depleted elements indicates that moss has a considerably larger ability (or preference) to enrich Cu than Co and Ni. It could also be related to the grain size or surface chemistry of Cu-bearing minerals as opposed to Ni-/Co-bearing minerals.

### 3.4. Correlation within each material

It has been demonstrated above that the spatial distribution of the variables in the 4 data sets is governed by a multitude of different processes, which results in multimodal populations, strong skew and many outliers. Correlation analysis of these data based purely on correlation coefficients would thus be ill advised. Any interesting element association will have to be checked graphically in *XY*-diagrams; in many cases it would be necessary to use data subsets for more detailed investigations. It is thus not surprising that correlation for most elements in the C- and B-horizons is not particularly strong. Special rock types occurring in the area (e.g. the alkaline intrusions) disturb many diagrams seriously (see Fig. 7 for examples). The very low sample density prohibits more detailed investigations in lithologically well-defined data subsets. Factor analysis is especially vulnerable to outliers, skew, and multimodal populations and should thus definitely not be used for these data. The use of factor analysis in more homogeneous data subsets is, in addition to other problems, not advisable due to the low number of samples in relation to the high number of variables.

The situation is somewhat better for the O-horizon and moss data because processes on a much larger scale govern the distribution of quite a number of elements in these media. Especially those elements originating from pollution show very high positive correlations (see Fig. 7: Cu/Ni). Nickel (Ni) and Cu are the two elements that dominate the emissions at Monchegorsk and Nikel/Zapolyarnij and the pollution by these two elements has a regional scale (see maps in Reimann et al., 1998a). It is thus not surprising that Cu and Ni show correlation coefficients of above 0.9 in both media (Table 4). Other elements showing high positive correlations with Cu



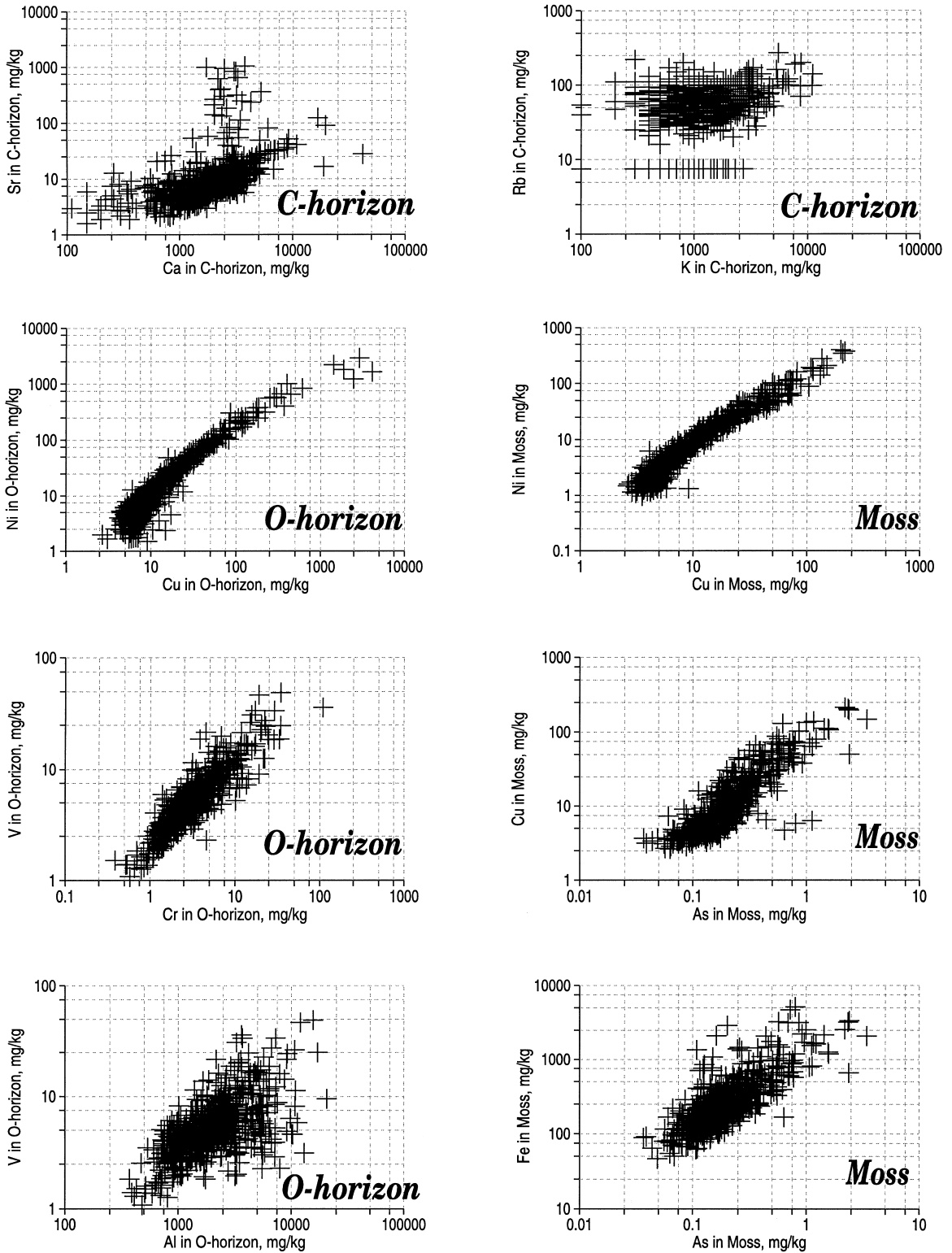


Fig. 7. XY-diagrams showing correlation between selected element pairs in C-horizon, O-horizon and moss.  $N = 598-617$ , depending on material — see Table 1).

Table 4

Correlation coefficients ( $r$ ) for the log-transformed data within each sample medium ( $N = 598$ – $617$ , for  $r = 0.13$  is  $P = 0.001$ ), sorted according to decreasing values (only  $r$ -values  $> 0.7$  were included)

$r$	C-horizon	B-horizon	O-horizon	Moss
0.9–1	–	–	Cr/V, Cu/Ni	Co/Cu, Co/Ni, Cu/Ni
0.8–0.89	Al/Zn, Co/Cr, Co/Cu, Co/Mg, Co/Ni, Cr/Ni, Fe/Mg, Fe/V, Mg/Ni, Mn/Zn	Co/Mg, Co/Ni	Co/Cu, Co/Ni, Cr/Fe	Ag/Bi, Ag/Cd, Ag/Cu, As/Co, As/Cu, As/Ni, Co/Fe, Cr/Fe,
0.7–0.79	Al/Co, Al/Fe, Al/Mn, Ba/K, Cd/Zn, Co/V, Co/Zn, Cr/Mg, Cr/V, Cu/Fe, Cu/Mg, Cu/Ni, Fe/Mn, Fe/Zn, Mg/V, Na/Sr	Al/S, Ba/Zn, Co/Cu, Co/Fe, Cr/Ni, Cr/V, Cu/Mg, Cu/Ni, Fe/V, Mg/Ni, Mn/Zn, Na/Sr	Al/Fe, Bi/Pb, Fe/V	Ag/As, Ag/Co, Ag/Ni, Ag/V, Al/Fe, Al/Sui, Al/Th, Al/V, As/Bi, As/Cd, As/Cr, As/Fe, As/S, Bi/Cd, Bi/Cu, Cd/Co, Cd/Cu, Cd/Ni, Cu/Fe, Cu/S, Fe/Ni, Fe/Si, Fe/V, Ni/S

and/or Ni include Co, Ag, Bi, Cd, Fe and S, which are all co-emitted. The fact, however, that many elements show different correlation coefficients with Cu and Ni, and the rapidly declining correlation coefficients indicate that a multitude of further processes determine the regional distribution of these elements. This leads again to conditions where it would be ill advised to use factor analysis in an attempt to understand these processes. Fig. 7 shows the very high positive correlation between Cu and Ni for moss and the O-horizon. Chromium and V are two other elements showing almost linear correlation in the O-horizon. The temptation to attribute this to an anthropogenic emission source, e.g. burning of heavy oil in the power plants in the area is high. Careful study of the regional distribution patterns in combination with further XY-diagrams (e.g. Al vs. V; Fig. 7) reveals, however, that the key process governing the regional distribution of these two elements is not pollution but varying amounts of minerogenic admixtures to the O-horizon. In the case of moss it is often the amount of dust (geogenic or anthropogenic) in the samples that governs observed high correlations (see Fig. 7, Fe vs. As).

### 3.5. Correlation between the sample materials

It is again possible to find arguments against the use of correlation analysis for comparing results between the different sample materials. The situation is easier, however, than within a single medium as long as only a one-to-one comparison is made for each element at each sample site. Nevertheless, all results had to be checked graphically in the form of XY-diagrams.

Table 5 gives the correlation coefficients ( $r$ ) between the media for the different elements. Fig. 8 shows as an example the XY-diagrams for the element Mg, which

Table 5

Correlation coefficients ( $r$ ) for all elements between the different sample media ( $N = 598$ – $617$ , for  $r = 0.13$  is  $P = 0.001$ )<sup>a</sup>

Element C/B-horizon	Element C/O-horizon	Element C-horizon/moss	Element O-horizon/moss
Sr 0.9	Sr 0.51	Sr 0.53	Ni 0.89
Na 0.89	Mg 0.32	P 0.25	Cu 0.86
Ca 0.84	Al 0.29	Na 0.17	Sr 0.72
Ni 0.84	Th 0.29	Mg 0.16	Co 0.69
Ba 0.83	Ba 0.28	Ag 0.1	As 0.63
Bi 0.83	Cr 0.28	Ba 0.1	Mg 0.61
Cu 0.82	Ca 0.24	Th 0.1	Mn 0.51
As 0.81	V 0.2	Al 0.09	Na 0.48
Cr 0.81	K 0.17	Ca 0.09	Cd 0.46
Mg 0.81	P 0.17	Cd 0.05	V 0.45
Zn 0.79	Cu 0.16	Cu 0.04	Cr 0.4
K 0.77	S 0.14	Pb 0.04	Fe 0.4
Co 0.76	Fe 0.13	K 0.03	P 0.36
Th 0.76	Si 0.13	S 0.01	Al 0.35
Pb 0.75	Co 0.12	Si -0.01	Ag 0.32
Mn 0.74	Ni 0.11	Cr -0.02	Pb 0.32
V 0.73	Na 0.1	Mn -0.03	Ca 0.31
Fe 0.71	Mn 0.09	As -0.04	Bi 0.3
P 0.63	Zn 0.08	Ni -0.05	Ba 0.29
Al 0.58	Ag 0.06	Zn -0.07	Th 0.25
Cd 0.55	As 0.06	Co -0.08	Zn 0.22
Ag 0.4	Cd 0.04	Fe -0.08	S 0.1
S 0.32	Pb -0.06	Bi -0.12	K 0.09
Si 0.07	Bi -0.13	V -0.14	Si 0.08

<sup>a</sup> All data were log-transformed before calculation of correlation coefficients.

shows very different correlation coefficients between the different media. Correlations between the results from the C- and B-horizons are generally high. They are even higher, when results from XRF-analyses are used for

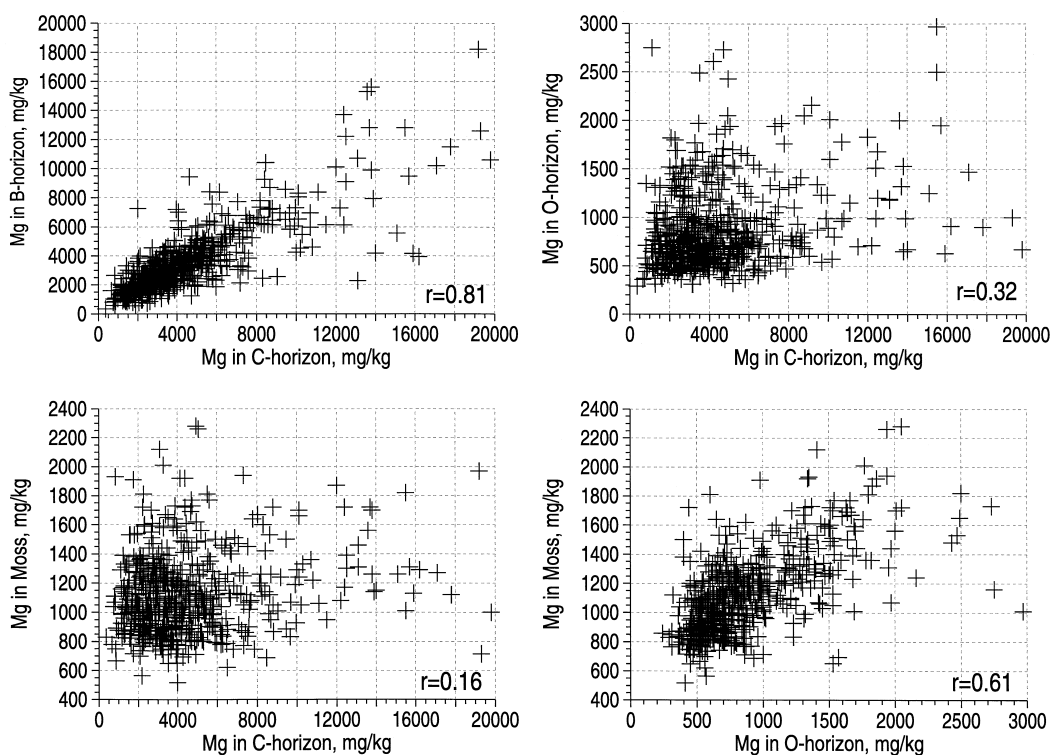


Fig. 8. *XY*-diagrams showing correlation for Mg as determined in the different sample materials.

this comparison (not shown here). In an aqua regia extraction results depend strongly on mineralogical composition and intensity of weathering at any one site. This causes additional variability in the results that can practically not be accounted for. It will be most visible for elements for which only a very small percentage of the total concentration is soluble in an aqua regia extraction. Total element values are thus better suited to investigate questions related to regional geology, while aqua regia results may be superior for studying mineralogical changes due to soil-forming processes (e.g. alteration processes). In any case, Fig. 8 demonstrates that the high correlation coefficient between Mg as analysed in the C- and B-horizons is not an artefact.

Correlation between element concentrations in the C- and O-horizons is much lower than that observed between C- and B-horizon results. Strontium is the only element with a correlation coefficient greater than 0.5 between O- and C-horizons ( $r=0.51$ ; see Table 5). An *XY*-plot for Sr (not shown) demonstrates that the high correlation is an artefact of the high Sr-values in the areas underlain by alkaline intrusions. Fig. 8 demonstrates for Mg that there is little correlation between O- and C-horizons, even with a correlation coefficient of 0.3. Not surprisingly correlation between C-horizon and moss is practically non-existent (Fig. 8), while correlation between moss and the O-horizon is much higher. One

can conclude that the chemical composition of the O-horizon is influenced surprisingly little by the composition of the substrate. Other processes play a more important role than inheritance from the lithosphere in determining the chemical composition of the O-horizon. This has far-reaching consequences. Given these results it is very questionable whether lithogenic or crustal average values can be used to represent “geochemical background” on the earth surface. It appears that the chemical composition of the O-horizon is much more dependent on surface processes (plant chemistry and atmospheric input of elements) than on the substrate.

Correlation coefficients between O-horizon and moss are generally rather high. In these sub-arctic regions the moss layer is a substantial component of the terrestrial ecosystem and plays a significant role in total biomass production. Decaying moss thus makes up a major proportion of the organic soil layer. Silicon, K and S show the lowest correlation coefficients here. The low correlation for K is again an artefact of a number of exceptional K-outliers in the O-horizon samples. Si and S are the two elements that show in reality practically no correlation between humus and moss. For Si this is most likely an extraction artefact (most silicates in the samples would not be dissolved by the conc.  $\text{HNO}_3$ -extract). For S, this is caused by the fact that moss and the O-horizon show very different uptake characteristics. Fig. 8 demonstrates that

although there is some spread in the data, there is, in general, a good correlation between moss and O-horizon. Whether this is due to decaying moss making up parts of the O-horizon or moss taking up Mg from the O-horizon, or that both are subject to the same surface processes (e.g. input via marine aerosols) is quite another question.

#### 4. Conclusion

The following conclusions can be drawn from the comparison of element concentration, variation and correlation in a concentrated HNO<sub>3</sub> (moss and O-horizon)/aqua regia (B- and C-horizon) extraction within and between 4 sample materials collected over a 188,000 km<sup>2</sup> area in the European arctic:

1. In all 4 sample materials, the major elements are practically the same (Al, Ca, Fe, K, Mg, Mn, P and Si). Sulphur is a major element in moss and in the O- and B-horizons. Sodium is only a minor element in the B-horizon but a major element in the other 3 sample media.
2. Of the 24 elements considered here, Ag, As, Bi and Cd are the rarest trace elements in all 4 materials.
3. More than a high concentration, large element variability (“spread”) provides an indication of an unusual element source or enrichment process. For example, the main “pollutant”, Ni shows the highest spread in both moss and the O-horizon.
4. A large spread of several other elements (e.g. Th, V, Sr, Fe, Cr) in moss and O-horizon is indicative of the input of minerogenic dust to the samples.
5. Most of the important nutrients (e.g. S) show an exceptionally low spread in moss and O-horizon — their uptake appears to be closely regulated by biochemical processes.
6. Soil-forming processes result in a slight enrichment of S, Ag, As, Al, Pb, Fe, Bi, Cr, V, Si, and Zn and a depletion of K, Cu, Ca, Ba, Mn, Sr, Ni, Na, Mg and Co in the B-horizon. The enrichment of Ag, As, Pb and Bi in the B-horizon, of which no substantial amounts are emitted in the survey area, must be attributed to co-precipitation with Fe-oxides/-hydroxides and the higher amount of organic material, enriched in these elements. Note that the major pollutants Ni, Cu and Co appear to be depleted in the B-horizon.
7. The major pollutants Ni, Cu and Co show considerably lower concentrations in the O-horizon than in the C-horizon. In contrast S, Ag, Cd, and Pb are exceptionally enriched in the O-horizon. This is caused by natural processes [e.g. plant pumping and organic binding (Goldschmidt (1937))] and is not related to local sources or long-range atmospheric transport of these elements into the survey area.
8. Element concentrations in all 4 materials are influenced by a multitude of different processes. This makes correlation analysis a somewhat doubtful tool for the study of inter-element relations. Even in moss and the O-horizon, where Cu and Ni display an almost linear correlation due to the regional scale of pollution a variety of other processes (input via marine aerosols, dust, minerogenic admixtures, vegetation zone and local composition) influence the correlation for most other elements. A grouping of elements according to sources should thus be based on regional distribution patterns (maps) and XY-diagrams rather than on correlation analysis.
9. For most elements good correlation exists between the results obtained for the B- and C-horizons and for the O-horizon and moss samples, not, however, between the C- and O-horizons or moss. This is an indication that surface processes dominate the chemical composition of moss and O-horizon much more than the substrate.

Multi-medium, multi-element regional geochemical mapping is a powerful tool for understanding the origin, cycling and fate of chemical elements in the terrestrial environment.

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