

# Distribution of 32 Elements in Organic Surface Soils: Contributions from Atmospheric Transport of Pollutants and Natural Sources

Tord Nygård · Eiliv Steinnes · Oddvar Røyset

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**Abstract** Data are presented for 32 elements (Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ge, As, Rb, Sr, Y, Zr, Mo, Ag, Cd, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Hf, Tl, Pb, Bi) in organic-rich surface soils in Norway, based on samples from 464 sites. By considering geographical distributions based on isopleths, results from factor analysis, and ANOVA of median values from 12 different geographical regions, the contributions from natural and anthropogenic sources are estimated for each element. Long-range atmospheric transport of pollutants from areas out of Norway is a dominant source for Cd, Sb, Pb, and Bi and also a strongly contributing factor for Zn, As, Mo, and Tl. Also V, Ni, Cu, and Ge are somewhat affected, but other factors

dominate for these elements. Local point sources of pollution provide significant contributions to soil concentrations of Ni, Cu, Zn, As, Mo, and Cd. The local bedrock is the overriding source of Li, Be, Ti, V, Cr, Mn, Rb, Zr, Cs, Ba, REE, Hf, and probably of Ge and Ag. Surface enrichment by root uptake in plants and return to the soil surface by decaying plant material is particularly evident for Mn, Zn, Rb, Cs, and Ba. These elements show no clear difference between south and north in the country, indicating that their plant uptake does not depend on latitude. In the case of B and Sr, atmospheric deposition of marine aerosols is an important source. Rb and Ag, and to a less extent Mn, Ga, and Ba, appear to be depleted in soils near the coast presumably due to cation exchange with airborne marine cations.

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## 1 Introduction

The surface soil is an important sink for metals and other air pollutants. In the boreal zone, which comprises large parts of Canada, Fennoscandia, and Russia, the surface soil is generally rich in humic substances, which have a high cation exchange capacity and may bind some metals even more strongly by complexation. The organic surface soil is therefore an efficient integrator of metals from the atmosphere and may as such be a useful supplement to other methods used to measure metal deposition on shorter time scales.

Metals in the surface soil from air pollution are not only supplied by local sources. In a review by Steinnes and Friedland (2006), scientific information regarding metal contamination of natural surface soils from long-range atmospheric transport has been summarized. For metals such as Pb, it has been understood for a long time that long-range atmospheric transport has been critical for the accumulation of Pb in the forest floor. Other elements characteristic of long-range transport of pollutants, such as Zn, Cd, As, Sb, and Se, have also been also shown to exhibit considerable surface enrichment in natural surface soils. For some of these metals, local pollution sources, too, can be of great importance, such as from metal processing industries.

In connection with the coordinated 1995 survey of atmospheric metal deposition in Europe based on moss analysis (Ruhling and Steinnes 1998) it was decided to ask the participating countries to sample and analyze humic surface soil samples in addition to moss samples (Steinnes et al. 1997b). In Norway, a full sampling program for surface soils was carried out, and in the following, the results from this survey are presented and discussed, with particular emphasis on explaining geographic patterns in the results. Corresponding papers are available from the Czech Republic (Suchara and Sucharova 2002) and Finland (Tamminen et al. 2004), in the latter case including a comparison with corresponding data for moss samples collected simultaneously.

## 2 Methods

### 2.1 Sampling

Soil samples were collected during the summer of 1995 from the O horizon of podzols or other organic-rich surface soils at 464 sites all over Norway except the arctic province of Svalbard, cf. map in Fig. 1. Sampling was carried out in small gaps in coniferous or birch forest not directly exposed to throughfall precipitation. In the far north and some coastal regions, the samples were collected on open heath or peatland. After removal of the litter layer and cutting any understorey plants at the base, humus samples of defined surface area were taken with a steel cylinder of 10 cm internal diameter. The uppermost 3 cm of the O horizon (mineral soil removed if the horizon was less than 3 cm thick)

was taken from four sub-sites within a 5×5-m plot and joined to one composite sample. Sites with an O horizon less than 2 cm were avoided.

### 2.2 Analyses

The samples were dried in paper bags at 35°C and weighed in order to determine sample density. They were subsequently crushed and sieved (nylon mesh, 2 mm). Loss on ignition was determined on separate samples after heating at 550°C for 2 h. Weighed aliquots of about 0.5 g dry matter were decomposed in Teflon bombs with 9 mL of 14 M HNO<sub>3</sub> (Merck, Suprapure) for 10 h at 180°C. After cooling to room temperature, the samples were diluted to 50 mL with demineralized water. The solution was left overnight for any undissolved material to settle, and the clear solution was decanted off before analysis.

The sample solutions were analyzed for the concentrations of 32 elements by inductively coupled plasma mass spectrometry (ICP-MS) using a Fisons PQ2+ instrument. The following elements were determined: Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ge, As, Rb, Sr, Y, Zr, Mo, Ag, Cd, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Hf, Tl, Pb, and Bi. The calibration was performed with multi-element mixtures containing 55 elements prepared from customer designed ICP-MS calibration solutions from two professional vendors (high purity primary element solutions of purity 99.99% or better). They consisted of several multi-element stock solutions at 500 and 100 µg/mL (mixed to avoid precipitation) and contained all the elements listed above. The acidity of calibration solutions was matched with that of the samples (10% vol/vol of 65% HNO<sub>3</sub>). Three internal standards containing Sc, In, and Re at a concentration of 50 µg L<sup>-1</sup> were used. The isotopes generally recommended for ICP-MS were employed. Calibration was performed at 10 µg L<sup>-1</sup> for the minor elements while additional standards at 100, 1,000, and 10,000 µg L<sup>-1</sup> were used for the major elements (Na, Mg, Al, Ca, Fe, Mn). Where molecular ion interferences were expected, several isotopes were recorded where possible and the isotope with less expected interference was selected for reporting.

### 2.3 Precision and Accuracy

The reproducibility of the analyses was tested by analysis of aliquots of real samples decomposed in

**Fig. 1** Sampling sites used in the 1995 soil survey



parallel. The following orders of magnitude were observed (RSD):

<10%: B, Mn, Co, Ni, Cu, Rb, Sr, Ba, Ce, Pr, Nd, Pb

10–15%: V, Zn, Ge, Y, Ag, Cs, La

15–20%: Li, Ti, Cr, As, Zr, Mo, Sm, Tl, Bi

20–30%: Be, Cd, Sb, Hf

Accuracy of the analyses was checked by concurrent analysis of the following certified reference materials: NIST SRM 1572 Citrus Leaves, NIST

SRM 1575 Pine Needles, and IAEA Hay V-10. Because no reference materials of humic soil matter were available at the time of analysis, plant materials were thought to be the most appropriate choice. Results from the analyses of reference materials are shown in Table 1. Among the 33 elements studied in this work, 17 were certified in one or more reference material. Ten of those (Cr, Mn, Cu, Zn, Rb, Sr, Mo, Ba, La, Pb) showed an accuracy of 15 % or better. For Cd, Sb, and Cs, the present values were 20–30% high, but the levels in the reference materials were an order of magnitude lower than in the soil samples. Arsenic was a problem at low levels, probably because of Cl interference, but again the levels in the soil samples were generally higher in the soils than in SRM 1575. Still the soil As values may be somewhat low at low arsenic concentrations in the soil. The values for Co and Ni in the reference samples were a factor of two high, probably due to interference from CaO. This interference is difficult to control in quadrupole ICP-MS in samples high in Ca, such as these reference materials. The soil samples were generally higher in these elements than the reference samples, but values

in the low end may not be very accurate. None of the reference samples had been certified for Li, Be, B, Ti, V, Ge, Y, Zr, Ag, Ce, Pr, Nd, Hf, Tl, and Bi.

In addition, three reference samples of humus-rich surface soils produced for the Joint European moss/surface soil survey and subjected to a laboratory intercomparison among laboratories in 20 countries (Steinnes 1997b) were analyzed, and the results are shown in Table 2. In this case, 14 elements (Mn, Cu, Co, Ni, Zn, As, Rb, Sr, Mo, Cd, Cs, Ba, La, Pb) agreed within 10% and additional four elements (V, Cr, Ce, Tl) within 20% of the recommended values. Among the elements for which recommended values had been issued, only the present data for Sb were more than 20% off.

### 3 Results and Discussion

#### 3.1 Presentation of Results

The primary purpose of the present work was to reveal possible contributions from air pollution to the

**Table 1** Results obtained for certified reference materials (micrograms per gram)

Element	NIST SRM 1572		NIST SRM 1575		IAEA Hay V-10		Mean deviation <sup>b</sup> (%)
	Present <i>n</i> =22	Certified	Present <i>n</i> =23	Certified	Present <i>n</i> =23	Certified	
Cr	0.98	0.8	2.72	2.6	7.54	6.5	+15
Mn	24.3	23	663	675	54.5	47	+7
Co	0.185	0.02 <sup>a</sup>	0.13	0.1 <sup>a</sup>	0.28	0.13	+115
Ni	1.74	0.6	2.61	3.5 <sup>a</sup>	5.3	4	+110
Cu	17.7	16.5	3.15	3	10.2	9.4	+7
Zn	30.4	29			24.0	24	+3
As	3.27	3.1	0.06	0.21			-34
Rb	5.03	4.84	11.7	11.7	7.64	7.6	+2
Sr	102	100	4.43	4.8	44.0	40	+2
Mo	0.14	0.17			0.94	0.9	-8
Cd	0.03	0.03			0.04	0.03	+20
Sb	0.039	0.04 <sup>a</sup>	0.185	0.2 <sup>a</sup>	0.025	0.02	+25
Cs	0.090	0.098 <sup>a</sup>			0.023	0.017	+33
Ba	20.4	21			5.7	6	-5
La	0.16	0.19 <sup>a</sup>	0.14	0.2 <sup>a</sup>	0.06	0.07	-14
Ce	0.33	0.28 <sup>a</sup>	0.26	0.4 <sup>a</sup>			-
Sm					0.011	0.02	-47
Tl			0.042	0.05 <sup>a</sup>			-
Pb	12.5	13.3	10.4	10.8	1.49	1.6	-5

<sup>a</sup> Not certified value

<sup>b</sup> From certified values only

**Table 2** Comparison of present results for soil humus reference samples with recommended values (Steinnes et al. 1997b)

Element	H1		H2		H3	
	Present	Recommended value	Present	Recommended value	Present	Recommended value
B	8.9	(6.0±2.2)	3.0	(1.8±0.9)	3.8	(2.1±0.5)
V	2.6	2.40±0.24	7.7	6.82±0.67	3.9	3.33±0.72
Cr	1.2	1.37±0.15	5.3	4.46±0.85	2.3	2.00±0.26
Mn	150	144±8	56	51.5±2.3	155	148±5
Co	1.55	1.51±0.08	8.4	7.69±0.25	0.94	0.92±0.04
Ni	4.8	4.69±0.28	93	90±6	3.3	3.00±0.25
Cu	7.2	7.18±0.47	410	401±20	7.4	6.88±0.40
Zn	51	53.9±2.6	155	149±6	43	43.7±2.5
As	0.86	0.85±0.04	6.4	6.60±0.6	1.8	1.76±0.04
Rb	11	10.5±0.3	7.2	7.37±0.34	6.1	6.18±0.28
Sr	26	25.8±1.4	28	28.6±2.0	24	24.8±1.6
Y	0.74	(0.78±0.06)	1.1	(1.09±0.13)	0.43	(0.38±0.08)
Mo	0.23	(0.18±0.03)	1.2	(1.19±0.04)	0.61	(0.59±0.04)
Cd	0.45	0.432±0.019	1.65	1.66±0.05	0.72	0.69±0.03
Sb	0.30	0.37±0.08	0.79	1.60±0.10	0.41	0.74±0.06
Cs	0.11	0.102±0.004	0.20	0.197±0.003	0.18	0.196±0.017
Ba	78	84±5	62	66±4	120	126±7
La	2.8	2.85±0.07	2.5	2.45±0.17	0.91	0.90±0.05
Ce	4.2	(4.8±0.5)	4.1	(4.9±0.7)	1.34	(1.61±0.27)
Tl	0.11	(0.085±0.005)	0.14	(0.137±0.011)	0.11	(0.099±0.011)
Pb	18	19.2±1.0	76	71.2±3.7	31	31.9±3.0

Values in parentheses are indicated values only

surface soil. Because mineral particles from the underlying mineral soil are an additional source to most of the elements in question, samples with less than 70% organic matter (loss on ignition) were removed from the material. Arithmetic mean, median, and range for the total number of samples and for those having more than 70% organic matter are presented in Table 3.

For discussion of geographical trends in the data, the country was divided into 12 regions (A–L) according to topographical and meteorological criteria, as shown in Fig. 2. Regional median values for some elements of particular emphasis in the discussion are listed in Table 4. A one-way analysis of variance was applied on the material, and the Scheffé test was used to identify significant ( $p < 0.05$ ) differences between regions. Extreme single values in the data set might influence the mean value and the variance within an area in such a way that significant regional differences

would not be shown even though they exist. Such values, e.g., in the vicinity to local air pollution sources or due to some extreme geochemical composition of the mineral soil, were excluded if they exceeded the inter-quartile range by more than a factor of 3. The results of the variance analysis are illustrated in Fig. 3 for some elements of particular interest in the discussion.

In order to help identifying different sources to the element distribution in the surface soil and explain the association of different elements to these sources, a principal component factor analysis following the procedure described by Schaugh et al. (1990) was carried out on the entire data set. Results for the first six factors, each explaining more than 5% of the variance, are shown in Table 5. The factor analysis was also run after excluding samples with >30% ash and samples in the vicinity of a Zn smelter. The result, as shown in Table 6, allows a more clear distinction

**Table 3** Concentrations of 32 trace elements in surface soils from Norway 1995 (micrograms per gram)

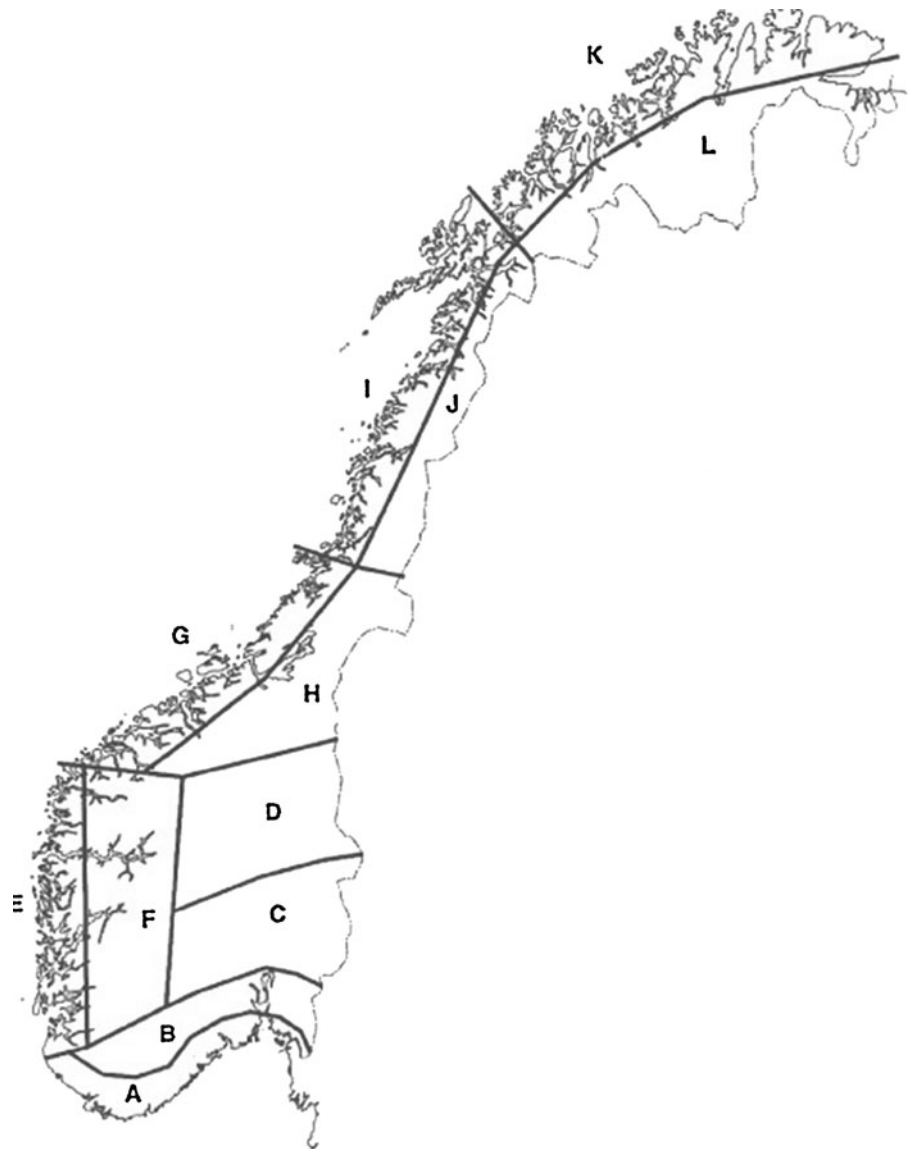
Element	All samples (464)			>70% organic matter (385)		
	Mean	Median	Range	Mean	Median	Range
Li	1.07	0.50	<0.02–18.0	0.64	0.44	0.02–9.6
Be	0.129	0.072	<0.004–1.69	0.060	0.094	<0.004–0.91
B	4.65	4.21	1.57–21.6	4.43	4.10	1.57–14.5
Ti	249	194	31–2170	194	158	31–803
V	12.3	7.99	0.90–131	8.27	6.61	0.90–56.0
Cr	7.86	14.2	<0.05–191	4.91	3.47	<0.05–46.3
Mn	330	181	15–7830	279	165	15–3980
Co	1.91	1.02	0.07–42.4	1.35	0.83	0.07–14.4
Ni	7.46	4.09	0.30–309	6.32	3.83	0.30–309
Cu	11.6	9.00	3.9–222	10.8	8.86	4.1–222
Zn	62.4	52.0	10.8–931	60.8	52.0	10.8–931
Ge	2.27	1.80	<0.01–24.3	1.94	1.26	<0.01–16.0
As	1.44	0.89	<0.03–19.2	1.12	0.97	<0.03–6.34
Rb	9.26	6.97	0.81–70.3	7.60	6.63	0.81–25.5
Sr	31.7	25.7	5.25–167	28.3	24.5	5.25–143
Y	3.01	1.60	0.11–32.2	2.95	2.17	0.11–32.2
Zr	3.24	1.92	0.32–33.8	2.21	1.60	0.32–14.1
Mo	0.671	0.395	0.009–47.8	0.532	0.395	0.04–6.28
Ag	0.44	0.34	<0.03–4.93	0.43	0.33	<0.03–4.93
Cd	0.57	0.45	0.047–6.7	0.55	0.47	0.047–6.7
Sb	0.337	0.208	<0.001–5.43	0.391	0.248	<0.001–5.43
Cs	0.53	0.33	0.03–9.43	0.41	0.30	0.03–4.71
Ba	69.4	53.0	9.1–808	64.6	49.6	9.1–808
La	5.02	2.13	0.17–136	3.54	1.65	0.17–61.9
Ce	9.77	4.30	0.31–305	6.29	3.39	0.31–68.7
Pr	1.96	1.12	0.04–25	0.78	0.40	0.04–14.4
Nd	4.22	1.96	0.21–90.8	2.96	1.52	0.21–53.4
Sm	0.77	0.37	<0.003–13.0	0.54	0.30	<0.003–10.1
Hf	0.10	0.06	<0.003–0.97	0.07	0.05	<0.003–0.37
Tl	0.184	0.154	0.020–1.40	0.171	0.146	0.020–1.40
Pb	46.4	34.5	7.05–345	43.6	32.8	8.20–288
Bi	0.167	0.122	<0.002–0.87	0.151	0.116	<0.002–0.66

between some of the potential sources. In the statistical analyses, values less than the detection limit were assigned half that value. Some elements show very clear regional trends, partly because of regional differences in geochemistry, partly because of atmospheric supply of pollutants from long-range transport and local sources. Geographical distribution maps for some selected elements, produced by a kriging procedure, are shown in Figs. 4, 5, and 6.

### 3.2 Relevant Previous Work

The regional patterns in atmospheric deposition of a large number of trace elements in Norway over the last decades are known in detail from nationwide surveys based on terrestrial moss. Such surveys were carried out in 1977 (Schaug et al. 1990; Steinnes et al. 1992), 1985 (Steinnes et al. 1994), 1990 (Berg et al. 1995), 1995 (Berg and Steinnes 1997), 2000, and

**Fig. 2** Subdivision of Norway in 12 regions for the discussion of soil data



2005 and have documented a large-scale atmospheric transport of certain trace elements to the southernmost areas in Norway from other parts of Europe, as also demonstrated independently by air trajectory analysis (Amundsen et al. 1992). Trace elements characteristic of this transport are Pb, Zn, V, As, Se, Mo, Cd, In, Sn, Sb, Tl, and Bi.

The present work is the third nationwide survey of trace elements in surface soils in Norway, but it differs from the previous ones in two ways: sampling the surface of the O horizon and including a greater number of elements. In the two previous surveys, the sample was taken deeper in the O horizon. The results

from the first survey in 1977 (Allen and Steinnes 1980; Steinnes et al. 1997a) indicated that the surface soil in the southernmost part of the country is substantially contaminated by Pb, Zn, Cd, As, and Sb from long-range transport. This conclusion was supported by the results from the second survey in 1985 (Njåstad et al. 1994; Steinnes and Njåstad 1995), which also included samples from the B and C horizons in the underlying mineral soil. Determination of stable Pb isotope ratios has shown independently that even in the far north of the country, 80–90% of the lead in the humus layer is likely to be from air pollution (Steinnes et al. 2005).

**Table 4** Median values of elements discussed in this paper in 12 different regions of Norway, cf. Fig. 2

Element	A	B	C	D	E	F	G	H	I	J	K	L
B	4.34	4.13	3.03	3.10	4.30	3.86	5.23	4.08	4.71	3.91	6.58	3.91
V	9.0	8.1	7.0	5.8	6.9	5.6	4.4	6.0	5.1	4.3	4.7	6.7
Cr	4.31	3.65	3.47	3.47	3.22	3.01	2.75	2.96	2.79	3.22	2.67	5.00
Mn	128	195	263	276	94	125	144	222	124	179	101	261
Co	0.78	0.65	0.80	0.89	0.71	0.91	0.74	0.91	0.95	0.84	1.09	1.84
Ni	5.43	3.75	3.76	3.41	3.48	3.31	2.55	5.02	2.92	2.90	4.12	6.65
Cu	10.7	8.7	7.8	6.1	10.1	8.4	7.5	8.2	9.4	8.3	9.6	10.1
Zn	68.2	68.8	62.4	44.8	57.0	56.3	32.4	40.1	37.8	50.0	37.0	47.0
Ga	2.53	2.51	4.23	4.20	2.38	3.90	1.16	3.70	1.87	2.33	2.78	3.09
Ge	1.99	2.00	1.95	1.41	1.64	2.10	1.08	1.20	1.24	1.50	1.38	1.49
As	2.35	1.42	1.16	0.52	1.52	0.69	0.48	0.46	0.53	0.53	0.39	0.51
Rb	5.7	8.2	10.8	9.1	4.0	6.6	3.0	8.7	4.8	9.1	4.0	6.7
Sr	15.2	14.3	20.8	21.9	24.3	27.0	30.3	30.2	37.3	24.1	38.8	23.2
Zr	1.52	2.15	2.09	1.73	0.93	1.34	0.86	2.03	1.33	1.95	1.43	1.92
Mo	0.79	0.53	0.51	0.27	0.56	0.47	0.25	0.18	0.38	0.26	0.32	0.26
Ag	0.45	0.41	0.56	0.54	0.27	0.26	0.13	0.40	0.14	0.31	0.11	0.25
Cd	0.86	0.69	0.53	0.37	0.58	0.53	0.22	0.19	0.48	0.32	0.29	0.29
Sb	0.74	0.56	0.37	0.21	0.54	0.25	0.13	0.10	0.22	0.24	0.15	0.16
Ba	35.6	49.9	83.3	95.3	31.2	54.9	29.2	66.4	37.3	43.1	50.3	65.1
La	1.73	1.80	2.23	1.68	1.33	2.22	1.07	1.40	1.45	1.41	1.43	2.03
Tl	0.28	0.23	0.20	0.14	0.16	0.15	0.07	0.11	0.17	0.09	0.07	0.07
Pb	77.7	65.2	52.0	29.9	50.9	30.9	15.2	15.5	26.7	24.9	14.1	14.3
Bi	0.27	0.22	0.19	0.10	0.17	0.10	0.05	0.06	0.09	0.09	0.07	0.11

In a simultaneous study in Finland (Tamminen et al. 2004), concentrations of 15 elements in humus layer samples from coniferous forests throughout Finland were compared with corresponding data from analysis of current annual growth increments of *Hylocomium splendens* moss. Except for Pb, they found that elemental concentrations in the humus layer were poorly correlated to corresponding data for moss samples, assumed to reflect levels of atmospheric deposition. They therefore concluded that for most elements, the concentration in the humus layer was a poor indicator of current atmospheric deposition levels.

As corresponding data from a simultaneous moss survey also existed in the present case (Berg and Steinnes 1997), a similar comparison of data was performed, based on data from factor analysis. Because any elements from air pollution residing in the surface soil are likely to reflect contributions over a longer period than the 3 years reflected by the moss samples, corresponding moss data from 1990 (Berg et

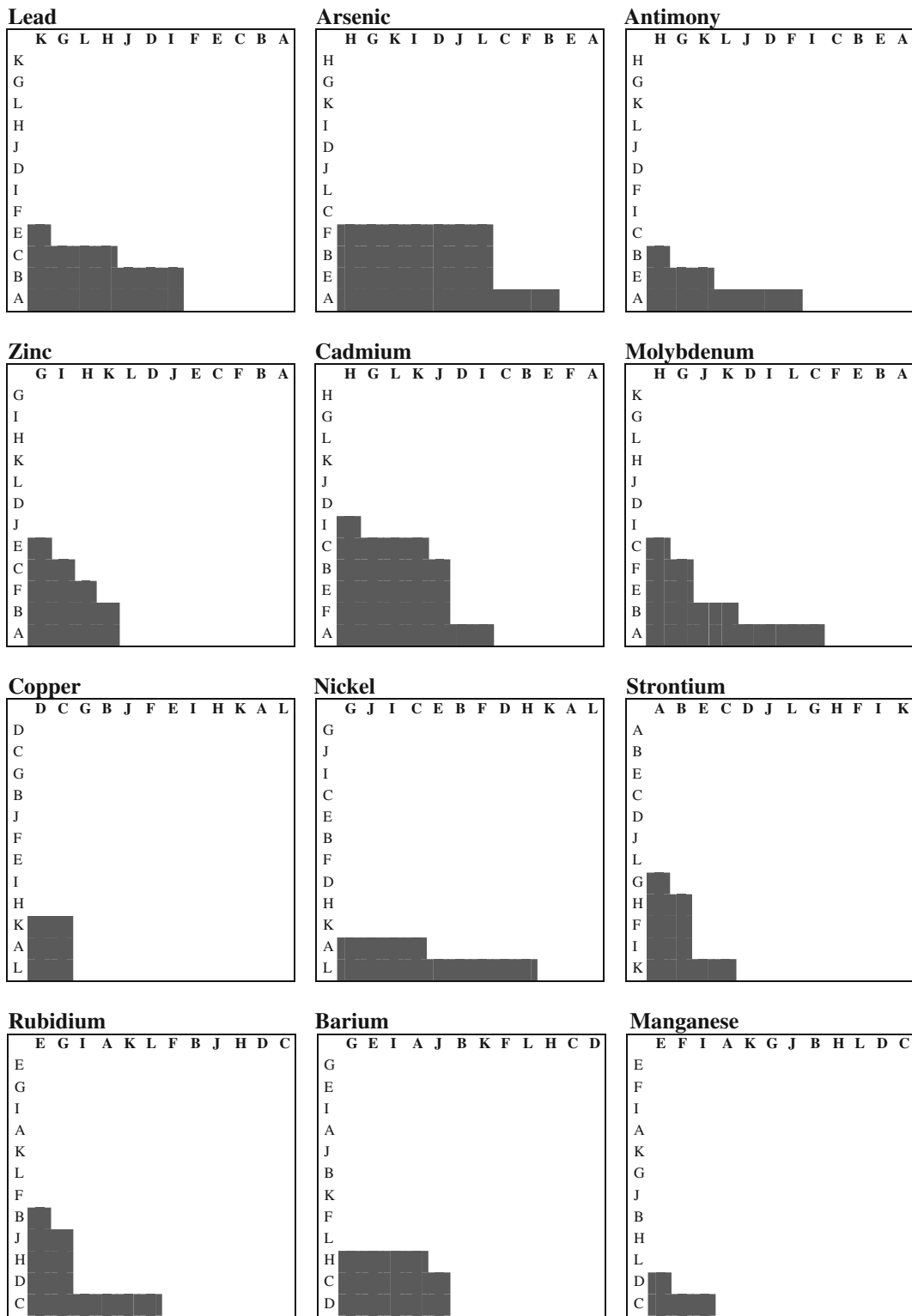
al. 1995) representing the same sampling network were also included. A comparison of the factors in the moss and surface soil assumed to be most relevant for the subsequent discussion is presented in Table 7.

### 3.3 Discussion of the Present Data

Trace elements may be supplied to the humic surface layer of the soil by the following three natural processes (Steinnes and Njåstad 1995): (a) mixing with underlying mineral soil by bioturbation or physical processes, (b) transfer from the mineral soil by root uptake in plants and return to the humus layer by leaching or by decay of plant material, and (c) atmospheric transfer from the marine environment. In addition, anthropogenic influence may modify the natural composition by atmospheric deposition of pollutants from local and distant sources.

It is difficult from the concentrations in the humus layer alone to distinguish between contributions from





**Fig. 3** Significant ( $p < 0.05$ ) differences between regions (cf. Fig. 2) as shown by one-way analysis of variance

**Table 5** Results of factor analysis: all samples

Element	F1	F2	F3	F4	F5	F6
Li		0.79				
Be	0.48	0.43				
B						
Ti		0.82				
V		0.75				
Cr		0.75				
Mn						
Co		0.64			0.45	
Ni					0.91	
Cu					0.92	
Zn						0.94
Ge	0.77					0.51
As			0.57			
Rb		0.66				
Sr						
Y	0.78	0.42				
Zr		0.54		0.71		
Mo				0.76		
Ag						
Cd			0.41		0.79	
Sb			0.61			
Cs		0.81				
Ba						
La	0.98					
Ce	0.94					
Pr	0.98					
Nd	0.97					
Sm	0.93					
Hf		0.56		0.69		
Tl			0.56			
Pb			0.76			
Bi			0.84			
Ash		0.72				
Variance explained (%)	20.8	19.1	8.4	6.4	6.4	5.9

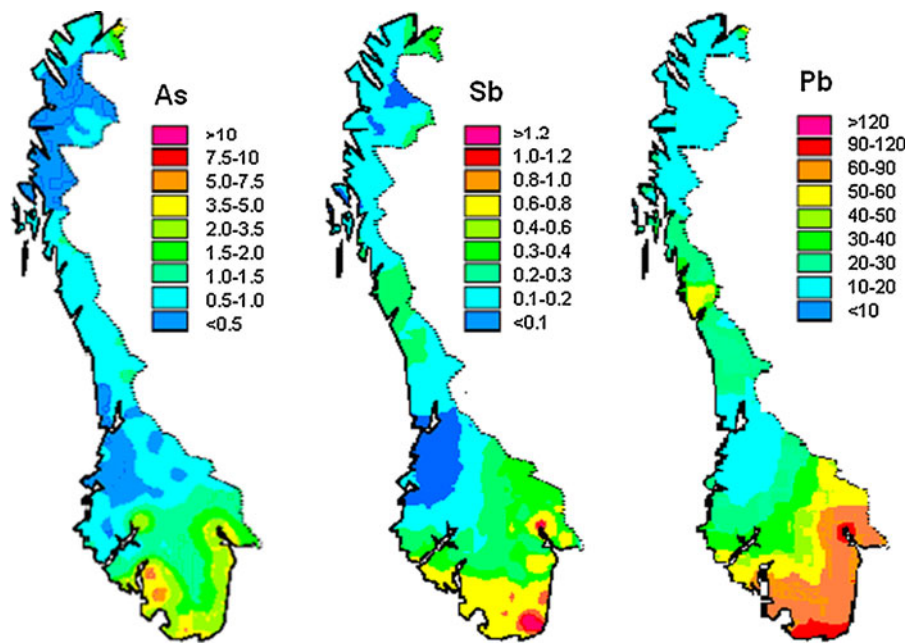
natural and anthropogenic sources. In the previous survey in 1985, however, ratios between corresponding element concentrations in the O and C horizons were useful in making this distinction (Steinnes and Njåstad 1995). Compared to elements strongly associated with the mineral soil, such as Al and Fe, a number of elements were obviously enriched in the humus layer. Some of these elements, such as Ca, Mn, and Ba, showed moderate regional variation, and the observed

regional differences did not follow known patterns of atmospheric deposition of pollutants but presumably corresponded to differences in bedrock geochemistry. The surface enrichment of these elements was probably related to plant uptake from the soil, a mechanism for surface enrichment of elements first recognized by V.

**Table 6** Factor analysis after excluding samples with >30% ash and samples near Zn smelter

Element	F1	F2	F3	F4	F5	F6
Li		0.73				
Be	0.64					
B						0.68
Ti		0.81				
V		0.79				
Cr		0.69				
Mn					0.74	
Co				0.56		
Ni				0.95		
Cu				0.94		
Zn			0.58		0.54	
Ge	0.75		0.41			
As			0.43			
Rb		0.45			0.55	-0.47
Sr	0.42					0.47
Y	0.91					
Zr		0.71				
Mo			0.52			
Ag						-0.56
Cd			0.72			
Sb			0.70			
Cs		0.47			0.46	
Ba					0.52	
La	0.98					
Ce	0.94					
Pr	0.98					
Nd	0.97					
Sm	0.94					
Hf		0.73				
Tl			0.61			
Pb			0.71			
Bi			0.84			
Ash		0.67				
Variance explained (%)	20.0	15.1	11.6	7.0	6.8	5.3

**Fig. 4** Geographical distributions of As, Sb, and Pb in natural surface soils (micrograms per gram)



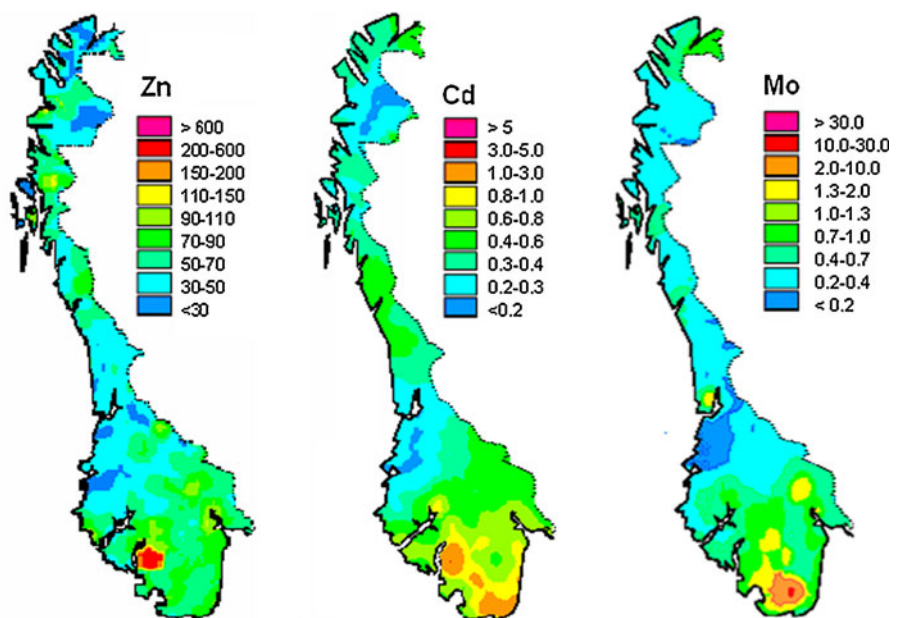
M. Goldschmidt (1937). Other elements such as Pb and Cd, and to a lesser extent V, Ni, Cu, and Zn, were clearly more surface-enriched in the far south. Hence, these elements were probably affected by air pollution from long-range transport and in the case of Ni and Cu additionally from a local Cu–Ni smelter at Kristiansand.

With these observations in mind, the present results may be interpreted as follows:

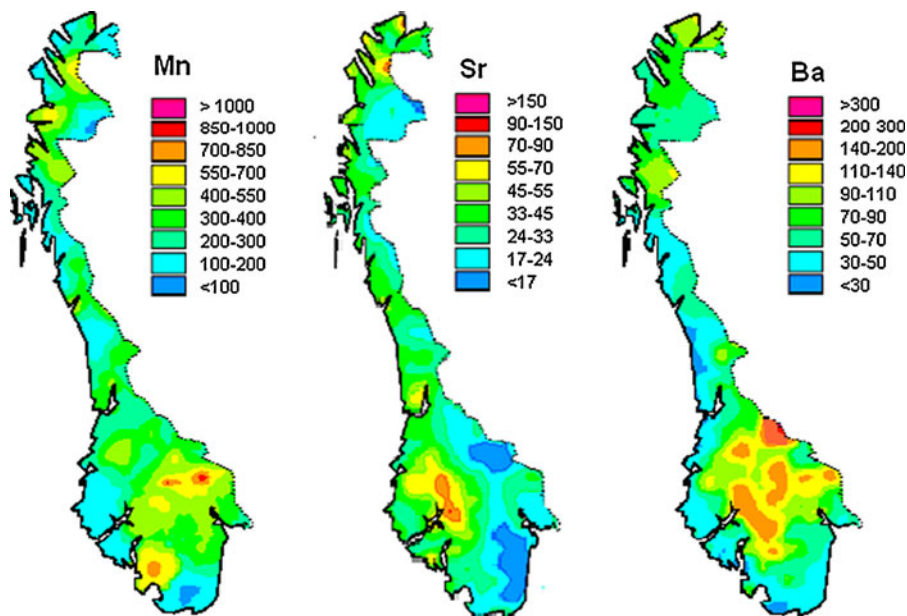
Elements associated with long-range atmospheric transport of pollutants

This group includes the elements appearing in factor 3 (Table 6): Zn, Ge, As, Mo, Cd, Sb, Tl,

**Fig. 5** Geographical distributions of Zn, Cd, and Mo in natural surface soils (micrograms per gram)



**Fig. 6** Geographical distributions of Mn, Sr, and Ba in natural surface soils (micrograms per gram)



Pb, Bi, with particularly high loadings for Bi, Cd, Pb, and Sb. With the exception of Ge, all these elements have previously been shown to be associated with long-range transport of pollutants to southern Norway in aerosol studies (Amundsen et al. 1992) and repeated nationwide deposition monitoring based on moss samples (e.g., Schaug et al. 1990; Berg and Steinnes 1997), and their concentrations in the present soils are clearly the highest in region A (Fig. 2) followed by B and E. In the case of Ge, the association with local

bedrock (factor 1) seems to be stronger than with pollution. Concerning Zn, the association with factor 5 indicates the importance of uptake by plant roots for surface enrichment of this element, an essential plant nutrient. Examples of geographical distributions related to transboundary pollution are shown in Fig. 4 for Pb, Sb, and As, respectively. In the case of As, the distribution is also affected by the Sauda ferro-alloy smelter in southwest Norway, whereas the spot a little further north appears to be natural.

**Table 7** Comparison of factor loadings related to transboundary pollution in the 1995 surface soils with corresponding data from moss surveys carried out in 1990 (Berg et al. 1995) and 1995 (Berg and Steinnes 1997) according to the same sampling network

Element	Moss samples 1990 (Berg et al. 1995)	Moss samples 1995 (Berg and Steinnes 1997)	Surface soils 1995 data from Table 6
V	0.78	0.66	— <sup>b</sup>
Co	0.93	0.92	0.56
Ni	0.98	0.97	0.95
Cu	0.97	0.97	0.94
Zn	— <sup>a</sup>	— <sup>a</sup>	0.58
As	0.64	0.45	0.56
Mo	0.87	0.79	0.43
Cd	— <sup>a</sup>	0.54	0.52
Sb	0.88	0.65	0.72
Tl	0.61	0.49	0.70
Pb	0.88	0.87	0.61
Bi	0.90	0.46	0.71
Variance explained (%)	28.8	10.3	10.7
			7.1
			11.6
			7.0

<sup>a</sup> Occurring in a separate factor related to Odda zinc smelter

<sup>b</sup> Occurring in a factor related to mineral matter

The association of the above elements with long-range atmospheric transport from other parts of Europe is further supported by the data in Table 7, showing obvious similarities in the factor analysis data between the 1995 surface soils and the 1990 and 1995 moss samples for most elements concerned.

Elements mainly reflecting the geochemistry of the mineral soil

Factors 1 (Be, REE) and 2 (Li, Ti, V, Cr, Zr, Hf) in Table 5 are most probably related to local bedrock geochemistry. It may be noted, however, that V, which is known as a component in the long-range transport of pollutants (Amundsen et al. 1992; Steinnes et al. 1992), is higher in regions A, B, and E than in the others. None of the above elements shows regional differences that clearly link them to major geological provinces in Norway.

Also factor 5 (Mn, Zn, Rb, Cs, Ba) in Table 5 likely reflects natural contributions, in this case for elements being relatively mobile in the soil and hence readily available for plant uptake. No general difference between the south and north of the country is observed for these elements, indicating that the circulation of elements between the soil and the vegetation has no clear latitudinal gradient.

Elements markedly affected by local pollution sources

The most obvious example is the impact in region L of two nearby Russian smelters polluting the surface soil with Ni, Cu, and Co, as also demonstrated in previous large-scale surface soil studies (Steinnes et al. 1997a; Reimann et al. 2001). The connection of these elements in the soil with transboundary pollution from Russia is further supported by the strong coherence with moss data demonstrated in Table 7. Higher levels of these elements also in region A may be mainly due to emissions from a copper–nickel smelter at Kristiansand rather than to transboundary pollution. Another example of a local pollution source affecting the present soil data is the emissions of Zn and Cd (Fig. 5) from the Odda zinc smelter in the southwest, cf. factor 5 in Table 5. In the case of Mo (Fig. 5), there is a “hot spot” in the south in the surroundings of a former molybdenum mine, probably related to wind erosion of tailings (factor 4 in Table 4).

Influence from the marine environment

Among the elements discussed here, B and Sr (Fig. 6) are the ones with the highest concentrations in the ocean relative to their crustal abundance. These two elements appear together in factor 6 (Table 5), with the highest median values in the northern coastal regions G, I, and K. There the intensity of winter storms, transporting marine aerosols to land, is higher than in coastal regions farther south. The contents of exchangeable Na and Mg in natural surface soils in Norway have long been known to depend strongly on the distance to the ocean (Låg 1968). Factor 6 also includes Rb (Fig. 6) and Ag with negative sign. These elements are the highest in the interior of southeastern Norway (regions C and D) and particularly low in the coastal regions (E, G, I, K). We hypothesize that exchange with marine cations (Na, Mg) leads to depletion of these elements in the surface soil. Similar geographical distributions albeit somewhat less pronounced are seen for Mn and Ba (Fig. 6) and Ga.

### 3.4 Some Concluding Remarks

A common opinion among geochemists in the past has been that the element composition of surface soils depends on the soil parent material. It has become increasingly obvious, however, that the organic-rich surface soils in boreal and montane regions are also affected by atmospheric inputs from natural and anthropogenic sources. Already over 30 years ago large-scale contamination of the forest floor with Pb from long-range atmospheric transport was shown in Scandinavia (Tyler 1972) as well as in North America (Reiners et al. 1975). More recent work (Steinnes et al. 1997a) has indicated that also other elements in the humus layer may be considerably affected by long-range atmospheric transport and that conclusion is further supported by the present work. It also seems to become increasingly evident that atmospheric deposition of ions from the marine environment can considerably affect the trace element distribution at least in coastal regions.

Systematic studies in order to examine the relative contributions of anthropogenic and natural sources to the elemental composition of organic-rich surface soils are relatively scarce in the literature. One of the few examples is from Switzerland (Blaser et al.

2000) where an enrichment factor approach was employed to distinguish contribution from pollution from the geological background in forest soils. Among the six metals studied, pollution was found to be most pronounced for Pb and Zn and somewhat less for As and Cu, whereas anthropogenic input seemed to be less important for Ni and Cr. These findings are in general agreement with the present results. In a large-scale survey carried out simultaneously with the present work in northwestern Russia and adjacent areas of Finland and Norway (Reimann et al. 2001), the authors found that Ag, Cd, Pb, Bi, As, and Zn were exceptionally enriched in the humus layer and increased in concentrations toward the south. They ascribed this enrichment to the transport from the underground soil by plant uptake, however, and explained the increase toward the south with “bioclimatic effects due to the differences in vegetation zones from north to south.” In the conclusion, they stated that the enrichment of these elements in the O horizon is due to “natural processes and is not related to local sources or long-range atmospheric transport of these elements into the survey area.” This interpretation is challenged by results from the present work and other studies in Norway. In the case of Pb, recent stable lead isotope work (Steinnes et al. 2005) shows that even in pristine areas of northern Norway more than 80% of the lead in the humus layer may be of anthropogenic origin. The same could possibly be the case with some other elements, such as Sb and Bi, not readily transferred to plants by uptake from the soil. Moreover, results from the present work with elements known to be readily available to plants (cf. Mn, Zn, Rb, Cs, Ba) do not support the idea of gradually increasing plant uptake with decreasing northern latitude.

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