

Element concentrations and variations along a 120-km transect in southern Norway – Anthropogenic vs. geogenic vs. biogenic element sources and cycles

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Abstract

Rock samples and the C-, B- and O-horizons of soils developed on these rocks were collected in forested areas along a 120-km south–north transect in southern Norway, passing through the city of Oslo. Forty samples (1 site/3 km) were analysed for 37 chemical elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, U, V, W and Zn) following an aqua regia digestion; pH (water extract) and loss on ignition were also determined. The O-horizon soils were additionally analysed for Pt. Gold is the only element that shows a clear anthropogenic peak in the O-horizon soils collected from the city of Oslo. Silver, Au, Bi, Cd, Hg, Pb, S, Sb, Se and Sr all show a strong enrichment in the O-horizon when compared to the underlying C-horizon or the bedrock along the full length of the transect. Neither geology nor anthropogenic input of elements dominate the observed patterns. The most important factors for the observed element concentrations in the O-horizon are weathering, uptake (or rejection) of elements by plants and the kinetics of decay of the organic material in the O-horizon. Climate, especially temperature and precipitation, has an important influence on the formation and decay rates of the organic soil layer. Acid precipitation will delay the decomposition of the organic layer and lead to a natural enrichment of several metals in the O-horizon. Land use change, deforestation and liming can all increase the decay kinetics of organic matter and thus result in a release of the stored element pool.

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1. Introduction

Transects have been used successfully to assess the influence of point sources on the spatial distribu-

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tion of anthropogenic influence (Wilcke et al., 1996; Reimann et al., 1997; Bonham-Carter et al., 2006), to study the spatial component of large scale natural processes (e.g., Reimann et al., 2000b), or to locate sources of diffuse PAH-contamination within cities (Wilcke et al., 1999). Here, the transect approach is used to study the behaviour of 37 (38 in the O-horizon) chemical elements, pH and loss on ignition (LOI) in four different sample materials, starting at the top with the O-horizon of forest soil profiles and ending at depth with the C-horizon and finally the rocks from which these soils have developed along a 120-km south–north transect. The area was glaciated, with the ice retreating some 10 ka ago, and the C-horizon most often represents moraine material. As long as glaciofluvial deposits are avoided, this moraine material is of such a local origin (Haldorsen and Sørensen, 1986) that the local bedrock can still be considered as the ultimate source of the elements at the scale of the transect. The transect passes through the city of Oslo, allowing a study of the impact of urbanisation on the soil profiles. At the selected sample density of 1 site/3 km it was possible to collect largely “untouched” natural soils even in the city of Oslo, by using the surrounding forests and forested parklands. Just north of the city the transect runs through a large forested area (Nordmarka), extensively used for recreation purposes by the local population. Both ends of the transect cross areas with agriculture as the dominant land use although urbanisation is spreading into the area at the southern end of the transect. The transect also lies on a number of different lithologies. Precambrian gneisses occur at both ends of the transect. Cambro–Silurian sediments, including black shales, are found in the city of Oslo and at the northern end of the transect in the Randsfjord area. Magmatic rocks of the Oslo Rift occur at the northern fringes of the city and throughout the forest to the north of Oslo.

The transect approach chosen for this study allows the investigation of the influence of a potentially important source of diffuse contamination, the city of Oslo, on the element concentrations observed in the soils. Like in any major city, a typical mix of many different emitters exist (or existed) in Oslo, e.g., chemical industry, metal industry, tanneries, power plants, garbage incinerators and, in former times, several coke factories. The inventory of possibly contaminating industrial activities in Oslo lists 1798 sites within the city borders (see: [\[mune.no/folkehelse/miljorettet-helsevern/jordforrensning_og_radon/databaser/\]\(http://www.folkehelse/miljorettet-helsevern/jordforrensning_og_radon/databaser/\)\). A high traffic density must be considered as a further major source of many metals to the urban atmosphere. At the same time, two typical lithologies for the wider Oslo area are crossed along the transect. Thus, the importance of different element concentrations in the ultimate source reservoir from which the soils have developed can also be considered. Reimann et al. \(2006\) used samples of terrestrial moss \(*Hylocomium splendens*\), collected at the same sites as the soil samples discussed here, to show that the urban environment has a demonstrable effect on the biogeochemistry of this species. They demonstrated that the elements Ag, Al, Au, Bi, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Pt, Sb, Th, Ti and Zn all show a significant peak in moss samples collected in Oslo and its surroundings as compared to moss along the rest of the transect.](http://www.helse-og-velferdsetaten.oslo.kom-</p></div><div data-bbox=)

1.1. Location and land use

The study area is located in southern Norway, in the surroundings of, and including, the city of Oslo (Fig. 1). Oslo has about 600,000 inhabitants and is Norway's largest city. Almost 2 million people, of Norway's total population of 4.5 million, live in or close to the city. Like most major European cities, Oslo has a long history of industrial development. Today most of the industry is located in the eastern parts of the city. Oslo has by far the highest traffic density in Norway and the major highway to Sweden (E6) runs through the southern part of the survey area. In general the region to the south of Oslo (towards Ås – Fig. 1) is one of the most intensely utilised and richest agricultural areas of Norway with many interspersed suburban developments. Directly north of Oslo the terrain rises abruptly to an elevation of 400–700 m above sea level (a.s.l.) and land use changes completely. This area, known as “Nordmarka”, is dominated by forests and many lakes and is extensively utilised for non-motorised recreation purposes by the Oslo population. Forestry is another important activity in the area. Further north, in the Randsfjord area (Fig. 1), agriculture is again the dominant land use. In contrast to the Ås area, animal husbandry is widespread and the area is too far inland from Oslo to feel the pressure of spreading urbanisation.

The annual precipitation in the investigated area is in the range of 700–1000 mm. The yearly average temperature varies between 4 and 6 °C. Due to the

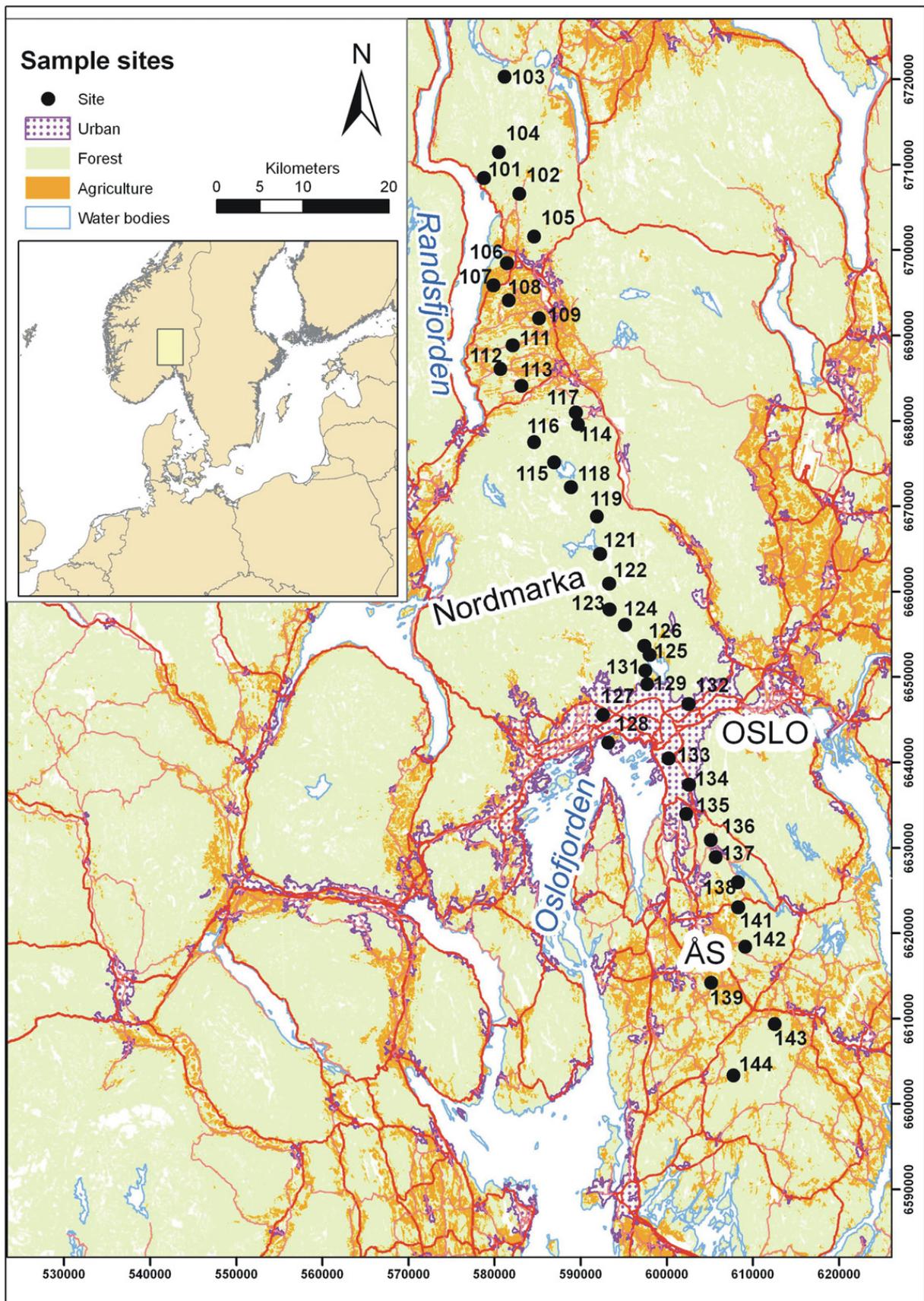


Fig. 1. Topographic map of the survey area showing the location of the south–north transect through Oslo with the sample sites identified by sample number. Different shades differentiate between forests, agricultural areas and urban developments.

higher elevation and higher precipitation, the climate in Nordmarka is markedly colder and wetter than along the rest of the transect. For detailed maps on precipitation, temperature and vegetation see Moen (1998). The dominant wind direction is towards the north, i.e. from Oslo towards Nordmarka and Randsfjord.

1.2. Geology

The transect was selected so that it crossed different lithologies, typical of the greater Oslo area. The most remarkable geological feature is the Oslo Rift. A late Carboniferous succession of shale, sandstone and conglomerate (the Asker Group) marks the onset of deposition related to the Oslo Rift (Dons and Larsen, 1978). The sedimentary sequence was deposited on a levelled surface and is overlain by basalt followed by a thick sequence of latite lava flows (rhomb porphyry) with thin beds of interlayered sand. Further evolution of this Permian rift is characterised by a number of volcanic centres with basaltic to subordinate rhyolitic lavas preserved in collapsed calderas rimmed by major ring faults and dykes. A variety of plutonic rocks cut the units described above (Dons and Larsen, 1978). Precambrian gneisses occur at the southern- and northernmost ends of the transect. Fig. 2 shows the location of the transect sampling points in relation to the geology.

For simplicity, the sampling sites can be allocated to four large lithological groups (Fig. 2). The soils in the south, the Ås area, and including the southern parts of Oslo have developed on glacial material derived from Precambrian gneisses ($N = 11$). Within the city centre of Oslo a relatively small area underlain by Cambro–Silurian shales and sandstones is encountered ($N = 4$). On leaving the city of Oslo towards the north the magmatic rocks of the Oslo Rift are encountered ($N = 13$). Along the transect these mostly have a syenitic composition. North of Nordmarka the Randsfjord area is characterised by the occurrence of the same Cambro–Silurian shales and sandstones that are encountered in Oslo ($N = 7$, total Cambro–Silurian sediments: $N = 11$). At the northern end of the transect Precambrian gneisses again form the bedrock ($N = 5$).

During the last ice age the whole study area was ice-covered. The thickness of the ice reached its maximum about 18–20 ka ago, and moraine material was deposited in the study area. Due to the melting of the ice the land rose, the previous coast-

line in the area can now be found at 150–200 m above sea level (a.s.l.) (Lundmark, 1986). Below this level, large deposits of marine clays can be found. Today most of these areas are used for agriculture and were avoided during sampling. The same applies to glaciofluvial deposits that can contain material that was transported over long distances, while most of the other moraine material is very local in origin (Haldorsen and Sørensen, 1986). Results presented here suggest that transport distance is less than 3 km – all lithological breaks can be identified via immediate changes in the geochemistry of the C-horizon material. The average transport distance of the moraine material is thus insignificant at the sample spacing used and given the length of the transect. In areas underlain by Cambro–Silurian shales, weathered material (residual soils) can be found at the surface.

The geological map of Oslo and surrounding areas (Lutro and Nordgulen, 2004) provides an excellent and more detailed geological overview of the study area.

2. Sampling and analytical methods

Sample sites were selected at an approximate spacing of 3 km along the 120 km transect. The exact location of each sample site was determined in the field based on geological and vegetation parameters. All sites were located in natural forest ecosystems with a required minimum number of typical (for the area) plant species, presence of the Norwegian spruce (*Picea abies* (L.) Karsten), birch (*Betula verrucosa* Ehrh. and *Betula pubescens* Ehrh.) and European mountain ash (*Sorbus aucuparia* L.) in the tree layer, bracken (*Pteridium aquilinum* (L.) Kuhn_[an]), cowberry (*Vaccinium vitis-idaea* L.), blueberry (*Vaccinium myrtillus* L.) and terrestrial moss (*Hylocomium splendens* (Hedw.) Br. Eur.) in the ground vegetation layer. Even in the city of Oslo there were still sufficiently “natural” forested areas to enable directly comparable sites to be sampled.

Rock samples were collected from outcrops as close as possible to all soil sample sites using a hammer. The original samples were about 3–4 kg in weight and packed in plastic bags. They were washed and air-dried at NGU’s laboratory in Trondheim to remove dust and possible contamination by soil or vegetation material. They were then passed through a steel jaw crusher. A 200-g split (Jones riffle splitter) of the crushed fraction of the rock samples was milled in an agate disk mill.

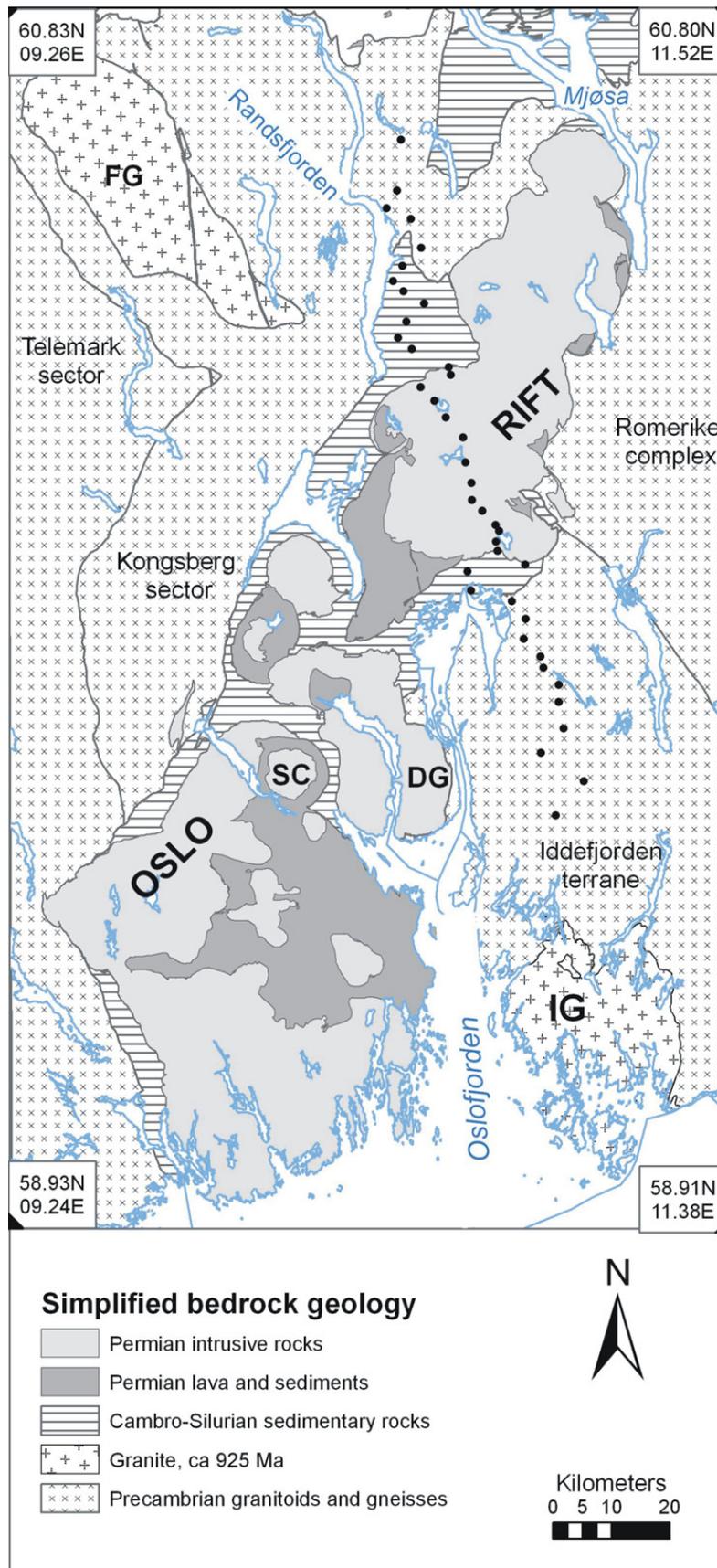


Fig. 2. Simplified bedrock geological map of the Oslo Area (from Lutro and Nordgulen, 2004), sample sites are shown, for site numbers refer to Fig. 1. Water bodies (see Fig. 1) are kept in white. FG: Flå granite; IG: Iddefjord granite; DG: Drammen granite; and SC: Sande Caldera.

O-horizon soil samples were collected as composite samples of five sub-samples taken with a special steel tool over an area of approximately 100×100 m. The steel tool was used to cut out a cylindrical sample with a diameter of 10 cm and a depth of 14 cm at each sub-site. Live plant material was removed from the top of the sample and any non-organic material was removed from the bottom so that only the uppermost 2 cm of the humus and litter layer was retained. The samples were stored in white 1 L PE-buckets with a tight lid. To collect the B- and C-horizon soil samples, a soil profile was dug at the centre of the O-horizon sample grid (100×100 m). The dominating soil type along the transect was podzol. The profile was dug down to the C-horizon (median depth to top of C-horizon: 50 cm, range 20–80 cm). A C-horizon sample was collected at the maximum depth of each profile. The B-horizon sample was collected at a depth of 15–20 cm. B- and C-horizon soil samples were also collected in white 1 L PE buckets, almost filled to the top. All soil samples were air dried upon arrival at the laboratory of the Geological Survey of Norway (NGU) in Trondheim (i.e. within less than 4 weeks). They were subsequently sieved using a <2 mm nylon mesh (lumps were disaggregated by hand) and the passing fraction was retained for analysis.

Splits of all samples were then shipped to ACME laboratories in Vancouver, Canada, by courier. The rock and mineral soil samples underwent an aqua regia digestion prior to analysis. Fifteen grams of the powdered rock samples/sieved mineral soil samples (B- and C-horizon) were digested in 90 mL aqua regia and leached for 1 h in a hot (95 °C) water bath. After cooling, the solution was made up to a final volume of 300 mL with 5% HCl. The sample weight to solution volume ratio is 1 g per 20 mL. The solutions were analysed using a Spectro Ciros Vision emission spectrometer (ICP-AES) and a Perkin–Elmer Elan 6000/9000 inductively coupled plasma mass spectrometer (ICP-MS) for 37 elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, U, V, W and Zn).

The organic O-horizon soil samples were treated somewhat differently. A 0.5 g aliquot of sample material was first leached with concentrated HNO_3 for 1 h and then digested in a hot (95 °C) water bath for an additional hour. After cooling, a modified aqua regia solution of equal parts concentrated

ACS grade HCl and HNO_3 and de-mineralised H_2O was added to each sample (6 mL/g) to leach in a hot (95 °C) water bath for 2 h. After cooling, the solution was made up to a final volume with 5% HCl and then filtered. The sample weight to solution volume ratio is 1 g per 20 mL. The solutions were analysed using a Perkin–Elmer Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS) for the same suite of 37 elements as above. In addition, 15 g of dry O-horizon material underwent controlled ignition to minimise volatilisation at 475 °C, the weight before and after ignition was used to calculate the loss on ignition (LOI) in weight%. The ash was then digested following the above procedure and analysed for Pt by ICP-MS. Results for all elements were recalculated to the dry O-horizon weight.

A water extraction of the soil samples (4 g sample and 80 mL milli-Q-water) was carried out to measure the pH of the soil samples following 1 h of shaking and 20 h resting.

2.1. Quality control

For quality control purposes CANMET lake sediment standard LKSD-4 was inserted four times with the mineral soil and rock samples and the laboratory mineral soil reference standard DS6 was analysed six times. In addition duplicates of mineral soil and rock samples were inserted at a rate of approximately 1 in 20. For the organic O-horizon samples the international reference material NIST 1575a Pine Needles (eight times) and the laboratory reference Material V13 Mountain Hemlock Needles (13 times) was used to assess quality. In addition, one sample duplicate was analysed. Table 1 shows the analytical results received for the standards in comparison to the certified or reference values. The table shows that analytical quality is excellent for the majority of elements. The observed differences for some elements (e.g., Al, Ba, Ca, K, Mg, Na) between the certified values for LKSD-4 and the results presented in Table 1 are due to the fact that the certified values for LKSD-4 relate to total concentrations, while the results presented here are for an aqua regia extraction. Rock and mineral soil duplicates show that precision (RSD) for S is in the range indicated by the results for standard DS6 (25%).

Concentrations of Sb in the O-horizon are much higher than in the plant standards used as reference material and the sample duplicate indicates that pre-

Table 1

Analytical program, detection limits (DL), mean and standard deviation (SD) for repeat analysis of reference materials compared to their certified values

	UNIT	DL	CANMET LKSD-4 (N = 4)				STANDARD DS6 (N = 6)				DL	NIST 1575a (N = 8)				V13 (N = 13)			
			CERT	MEAN	SD	CV-%	REF	MEAN	SD	CV-%		CERT	MEAN	SD	CV-%	REF	MEAN	SD	CV-%
Ag	µg/kg	2	<u>200</u>	<u>211</u>	5.37	2.5	<u>277</u>	<u>275</u>	6.21	2.3	2	<u>12.6</u>	1.19	9.4	<u>19</u>	<u>20</u>	1.19	6.0	
Al	mg/kg	100	<u>31,229</u>	<u>12,350</u>	539	4.4	<u>18,800</u>	<u>19,083</u>	354	1.9	100	<u>580</u>	<u>550</u>	53.5	9.7	<u>700</u>	<u>623</u>	44	7.0
As	mg/kg	0.1	<u>12</u>	<u>14</u>	0.769	5.6	<u>21.4</u>	<u>21.3</u>	0.412	1.9	0.1	<u>0.039</u>	<u>0.275</u>	0.14	50	<u>1.1</u>	<u>1.1</u>	0.185	17
Au	µg/kg	0.2	<u>2</u>	<u>1.53</u>	0.288	18.8	<u>46.7</u>	<u>47.2</u>	1.74	3.7	0.2	<u>0.525</u>	0.28	54	<u>0.5</u>	<u>0.68</u>	0.468	69	
B	mg/kg	1	<u>22</u>	<u>10</u>	1.41	14.1	<u>17</u>	<u>17.5</u>	1.38	7.9	1	<u>9.6</u>	<u>9.8</u>	0.89	9.1	<u>21</u>	<u>18</u>	1.76	9.5
Ba	mg/kg	0.5	<u>330</u>	<u>139</u>	7.38	5.3	<u>168</u>	<u>168</u>	3.10	1.8	0.1	<u>6.0</u>	<u>5.5</u>	0.23	4.1	<u>1</u>	<u>0.94</u>	0.0768	8.2
Bi	mg/kg	0.02		<u>0.55</u>	0.026	4.7	<u>5</u>	<u>5</u>	0.161	3.1	0.02	<u><0.02</u>			<u><0.2</u>	<u><0.02</u>			
Ca	mg/kg	100	<u>12,865</u>	<u>8533</u>	393	4.6	<u>8460</u>	<u>8583</u>	160	1.9	100	<u>2500</u>	<u>2650</u>	92.6	3.5	<u>5300</u>	<u>5431</u>	197	3.6
Cd	mg/kg	0.01	<u>1.9</u>	<u>2.09</u>	0.108	5.2	<u>6.01</u>	<u>6.25</u>	0.125	2.0	0.01	<u>0.233</u>	<u>0.253</u>	0.01	5.9	<u>0.07</u>	<u>0.07</u>	0.0087	13
Co	mg/kg	0.1	<u>11</u>	<u>10</u>	0.731	7.5	<u>10.8</u>	<u>11.0</u>	0.223	2.0	0.01	<u>0.061</u>	<u>0.08</u>	0.02	19	<u>0.6</u>	<u>0.64</u>	0.0260	4.0
Cr	mg/kg	0.5	<u>21</u>	<u>23</u>	1.27	5.4	<u>190</u>	<u>185</u>	3.83	2.1	0.1	<u>1.29</u>	0.11	8.7	<u>1.7</u>	<u>1.2</u>	0.160	14	
Cu	mg/kg	0.01	<u>30</u>	<u>32</u>	1.54	4.8	<u>123</u>	<u>123</u>	2.66	2.2	0.01	<u>2.8</u>	<u>3.4</u>	0.21	6.4	<u>2.5</u>	<u>2.4</u>	0.0993	4.2
Fe	mg/kg	100	<u>26,000</u>	<u>24,067</u>	1166	4.8	<u>28,240</u>	<u>28,350</u>	524	1.8	10	<u>46</u>	<u>44</u>	5.18	12	<u>100</u>	<u>97</u>	6.30	6.5
Ga	mg/kg	0.1		<u>3.95</u>	0.105	2.7	<u>6.2</u>	<u>6.25</u>	0.36	5.7	0.1		<u>0.075</u>	0.03	36	<u><0.1</u>	<u>0.1</u>		
Hg	µg/kg	5	<u>190</u>	<u>173</u>	11.3	6.5	<u>233</u>	<u>230</u>	4.85	2.1	1	<u>39.9</u>	<u>38</u>	2.76	7.3	<u>52</u>	<u>53</u>	3.18	5.9
K	mg/kg	100	<u>6641</u>	<u>1100</u>	89.4	8.1	<u>1520</u>	<u>1533</u>	82	5.3	100	<u>4170</u>	<u>4288</u>	181	4.2	<u>5500</u>	<u>5231</u>	189	3.6
La	mg/kg	0.5	<u>26</u>	<u>23</u>	1.12	4.9	<u>14.4</u>	<u>14.2</u>	0.308	2.2	0.01		<u>0.0375</u>	0.01	24	<u>0.02</u>	<u>0.02</u>	0.0055	34
Mg	mg/kg	100	<u>5427</u>	<u>3483</u>	214	6.1	<u>5800</u>	<u>5783</u>	117	2.0	10	<u>1060</u>	<u>1108</u>	40.3	3.6	<u>800</u>	<u>791</u>	36	4.6
Mn	mg/kg	1	<u>430</u>	<u>440</u>	19.9	4.5	<u>700</u>	<u>704</u>	13.4	1.9	1	<u>488</u>	<u>517</u>	21.5	4.2	<u>1900</u>	<u>1880</u>	62	3.3
Mo	mg/kg	0.01	<u>2</u>	<u>1.74</u>	0.116	6.7	<u>11.7</u>	<u>11.6</u>	0.256	2.2	0.01		<u>0.0163</u>	0.01	32	<u>0.07</u>	<u>0.06</u>	0.0091	15
Na	mg/kg	10	<u>5193</u>	<u>173</u>	20.7	11.9	<u>720</u>	<u>753</u>	19.7	2.6	10	<u>63</u>	<u>68</u>	4.63	6.9	<u>20</u>	<u>18</u>	4.39	25
Ni	mg/kg	0.1	<u>32</u>	<u>33</u>	1.60	4.9	<u>24.9</u>	<u>24.9</u>	0.587	2.4	0.1	<u>1.47</u>	<u>1.61</u>	0.1	6.1	<u>0.7</u>	<u>0.75</u>	0.0877	12
P	mg/kg	10	<u>1309</u>	<u>1290</u>	112	8.7	<u>780</u>	<u>825</u>	20.7	2.5	10	<u>1070</u>	<u>1261</u>	52.5	4.2	<u>1300</u>	<u>1267</u>	34	2.7
Pb	mg/kg	0.01	<u>93</u>	<u>89</u>	3.11	3.5	<u>30.3</u>	<u>29.6</u>	0.633	2.1	0.01	<u>0.167</u>	<u>0.23</u>	0.06	28	<u>1.00</u>	<u>1.01</u>	0.0658	6.5
S	mg/kg	200	<u>9900</u>	<u>10133</u>	413	4.1	<u>300</u>	<u>317</u>	75.3	23.8	100		<u>838</u>	106	13	<u>600</u>	<u>677</u>	73	11
Sb	mg/kg	0.02	<u>1.5</u>	<u>1.1</u>	0.054	4.9	<u>3.5</u>	<u>3.6</u>	0.078	2.2	0.02		<u>0.0125</u>	0	37	<u>0.02</u>	<u>0.02</u>	0.0104	50
Sc	mg/kg	0.1	<u>7</u>	<u>3.2</u>	0.234	7.2	<u>3.3</u>	<u>3.3</u>	0.089	2.7	0.1	<u>0.01</u>	<u>0.188</u>	0.04	19	<u>0.2</u>	<u>0.18</u>	0.0376	20
Se	mg/kg	0.1		<u>2.80</u>	0.190	6.8	<u>4.4</u>	<u>4.3</u>	0.089	2.1	0.1	<u>0.099</u>	<u>0.225</u>	0.07	31	<u>0.2</u>	<u>0.13</u>	0.0555	41
Sr	mg/kg	0.5	<u>110</u>	<u>40</u>	2.16	5.4	<u>39</u>	<u>40</u>	0.753	1.9	0.5		<u>7.5</u>	0.24	3.3	<u>11.8</u>	<u>12.6</u>	0.442	3.5
Te	mg/kg	0.02		<u>0.11</u>	0.010	9.1	<u>2.27</u>	<u>2.11</u>	0.056	2.6	0.02		<u><0.02</u>			<u><0.02</u>			
Th	mg/kg	0.1	<u>5.1</u>	<u>1.50</u>	0.063	4.2	<u>3.1</u>	<u>3.1</u>	0.055	1.8	0.01		<u><0.01</u>			<u><0.01</u>			
Ti	mg/kg	10	<u>2270</u>	<u>493</u>	32.66	6.6	<u>810</u>	<u>792</u>	17.2	2.2	1		<u>5.1</u>	0.35	6.9	<u>8</u>	<u>9</u>	0.494	5.4
Tl	mg/kg	0.02		<u>0.38</u>	0.021	5.6	<u>1.71</u>	<u>1.75</u>	0.040	2.3	0.02		<u>0.02</u>			<u>0.02</u>	<u>0.02</u>		
U	mg/kg	0.1	<u>31</u>	<u>30</u>	1.58	5.3	<u>6.6</u>	<u>6.7</u>	0.138	2.1	0.01		<u><0.01</u>			<u><0.01</u>	<u><0.01</u>		
V	mg/kg	2	<u>32</u>	<u>32</u>	2.16	6.7	<u>56</u>	<u>56</u>	1.17	2.1	2		<u><2</u>			<u><2</u>	<u><2</u>		
W	mg/kg	0.1	<u><4</u>	<u>0.20</u>			<u>3.44</u>	<u>3.52</u>	0.098	2.8	0.1		<u><0.1</u>			<u><0.1</u>	<u><0.1</u>		
Zn	mg/kg	0.1	<u>189</u>	<u>184</u>	5.94	3.2	<u>143</u>	<u>142</u>	2.73	1.9	0.1	<u>38</u>	<u>42</u>	1.3	3.1	<u>20</u>	<u>18</u>	0.373	2.0

CERT: certified value, REF: reference value, CV: coefficient of variation. Note the different detection limits for minerogenic and organic materials for some elements. Underlined values for standard LKSD-4 refer to total concentrations (not really comparable to an aqua regia extraction, these values do not indicate quality but rather "extractability" of these elements in aqua regia), non underlined values are for a strong acid digest, see: <http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/crmp/pricescrmp-e.htm>.

cision is in fact much better than 10%. Selenium in the soils is also 5–10 times higher than in the plant standards and again the duplicate indicates that precision is better than 5%.

3. Results

Table 2 summarises the analytical results as obtained for the four sample materials. Table 3 shows the median ratios to facilitate direct comparison of relative enrichment/depletion patterns between the sample materials. Petrologists present and study total element concentrations when discussing the geochemistry of rocks. Environmental scientists most often use comparatively weak extractions when analysing soil or sediment samples. This choice is partly due to different traditions and partly due to the fact that environmental scientists are most interested in anthropogenic additions of elements to a soil that pose an environmental risk. Elements strongly bound in the lattices of silicate minerals are considered harmless. Element concentrations for rock samples as presented in Table 2 for an aqua regia extraction will thus appear unusual to petrologists, but are the equivalent to the aqua regia analysis regularly used in environmental studies when presenting soil analysis. The differences between total and aqua regia results will be discussed in a separate publication.

Some large differences between the sample materials are apparent even from a cursory inspection of Table 2. The complex chemical reactions during weathering include dissolution, precipitation, oxidation/reduction, adsorption, ion exchange, hydration and hydrolysis. Observed element concentrations in the different soil horizons can shift substantially relative to the source in a relatively short span of geologic time. Different groups of elements will behave differently during weathering. Relative to the parent material, some are enriched in different parts of the soil profile and some are depleted. These processes start with the onset of weathering – the age of the soils in the survey area is less than 10 ka (the final retreat of the last glaciation).

Although much attention in weathering research has focussed on the major elements and the important plant nutrients, these processes affect all naturally occurring elements. This includes the “heavy metals”, discussed in studies of the impact of anthropogenic interferences with natural element cycles. Only when the natural processes of enrich-

ment and depletion of these elements during weathering are well known and documented can the anthropogenic impact on a soil be reliably judged. The chemical effects of rock and mineral weathering have been studied for more than 150 a (e.g., Rodgers and Rodgers, 1848) and a review of chemical weathering rates of silicate minerals was recently published by the Mineralogical Society of America (White and Brantley, 1995). Most of the work on chemical weathering documented in publications is, however, based on “classical” total element concentrations (e.g., Land et al., 1999) of rocks and soils and does not consider most of the elements that are of special interest for environmental studies. In environmental sciences this may have led to the misconception that these elements are unaffected by weathering and soil formation processes.

In the aqua regia extraction of the rock samples, Fe (median 25,100 mg/kg) is present at the greatest concentration (note that Si and O were not determined), followed by Al (11,600 mg/kg), Ca and Mg (both 7100 mg/kg), K (2800 mg/kg) and Ti (1160 mg/kg). All other elements show median concentrations below 1000 mg/kg. Only four elements report median concentrations between 100 and 1000 mg/kg: P (640), Mn (449), Na (320) and S (300). The median concentrations of Ba (64), Zn (59), V (34), La (28), Sr (24), Cr (12), and Ni (11) all report between 10 and 100 mg/kg. The median concentrations of Cu (9.4 mg/kg), Co (8.9), Ga (5.5), Th (4.3), Pb (3.7), Sc (3.5) and B (1) are between 10 and 1 mg/kg. All other elements show median concentrations below 1 mg/kg; for Hg, W and Te the majority of rock samples returned values below the respective limits of detection (see Table 2).

When comparing the analytical results of the four major lithologies for the rock samples in box-plots (Fig. 3) most elements show notable differences between the lithologies. Many elements show high local variability in all the lithologies (see Fig. 3 for examples). The most prominent differences between the lithologies as observed for the rock samples are

- The Cambro–Silurian sediments show especially high median values (in brackets: 2nd highest median values) of As, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Ni, Pb, S, Sb, Sc, Sr, Te and very low median values of Na and Ti when compared to the other three lithologies.

Table 2
Summary statistics for the results of analyses of rock ($N = 43$) and soil ($N = 40$) samples

Element	Unit	DL	Rocks					C-horizon					B-horizon					O-horizon				
			Median	MIN	MAX	MAD	CVR	Median	MIN	MAX	MAD	CVR	Median	MIN	MAX	MAD	CVR	Median	MIN	MAX	MAD	CVR
Ag	µg/kg	2	23	3	142	11.9	52	19	9	902	11.9	62	53.5	2	591	53.4	99.8	216	69	5350	151	70
Al	mg/kg	100	11,600	1200	55,700	9785	84	16,600	5300	42,400	6301	38	16,500	3200	34,400	5411	32.8	7600	1800	26,300	6375	84
As	mg/kg	0.1	0.5	<0.1	10.1	0.667	133	4.75	0.7	12.4	3.26	69	4.4	1	12.8	2.74	62.3	4.65	1.9	16.6	2.15	46
Au	µg/kg	0.2	0.2	<0.2	3.1	0.148	74	0.2	<0.2	1.2	0.148	74	0.35	<0.2	1.6	0.22	63.5	1.5	<0.2	58.2	2	133
B	mg/kg	1	1	<1	16	0.741	74	2	<1	5	1.48	74	2	<1	3	1.48	74.1	2	<1	5	1.48	74
Ba	mg/kg	0.5	64	2.1	397	63.3	99	58.6	15.9	380	25.1	43	54.2	8.3	438	45.2	83.4	104	42.5	517	64.3	62
Bi	mg/kg	0.02	0.06	<0.02	0.26	0.0445	74	0.1	0.03	0.48	0.045	45	0.12	0.05	0.6	0.06	49.4	0.43	0.12	16.1	0.237	55
Ca	mg/kg	100	7100	700	275,600	7116	100	1350	600	5700	519	38	750	<100	9600	519	69.2	2250	800	16,400	1483	66
Cd	mg/kg	0.01	0.04	0.01	0.61	0.0445	111	0.085	0.02	3.14	0.067	79	0.14	0.01	2.64	0.12	84.7	0.685	0.2	5.64	0.452	66
Co	mg/kg	0.1	8.9	<0.1	29.6	10.5	118	9.2	1.8	49.8	4.74	52	9.15	0.1	44.2	6.3	68.9	3.46	0.81	21	3.49	101
Cr	mg/kg	0.5	12.3	1	139	16.5	134	32.9	6.2	137	21.7	66	30.1	3	120	18.2	60.4	11.9	4	74.6	8.82	74
Cu	mg/kg	0.01	9.38	0.34	169	12.6	135	16.3	1.14	57.4	9.72	60	9.86	0.71	46.4	7.77	78.8	13.2	5.15	73.8	6.81	51
Fe	mg/kg	100	25,100	3000	68,300	17,495	70	26,200	7600	78,700	9118	35	29,750	2200	90,400	9192	30.9	13,750	2290	55,630	10,838	79
Ga	mg/kg	0.1	5.5	0.6	15.2	2.82	51	4.65	1.7	19.2	1.41	30	5.9	2.7	21.1	1.78	30.2	4.25	1.3	9.4	2.45	58
Hg	µg/kg	5	<5	<5	22			25	<5	189	15.6	62	50	7	281	24.5	48.9	211	40	661	136	65
K	mg/kg	100	2800	400	18,100	2669	95	850	200	2200	445	52	600	200	2000	297	49.4	800	400	2500	297	37
La	mg/kg	0.5	28	2	105	25.5	91	28	7.9	121	9.64	34	19.3	10.5	63.7	7.34	38	14.9	3.86	65.6	10.9	73
Mg	mg/kg	100	7100	200	25,200	5189	73	5500	1900	23,500	2372	43	3750	100	15,200	2446	65.2	1095	320	10060	801	73
Mn	mg/kg	1	449	110	2565	286	64	330	71	2337	125	38	640	96	2976	423	66.1	353	50	2666	431	122
Mo	mg/kg	0.01	0.68	0.05	5.79	0.89	131	1.96	0.27	20.4	1.62	83	2.12	0.46	10.3	1.68	79	1.66	0.77	120	0.845	51
Na	mg/kg	10	320	60	5910	237	74	60	40	190	14.8	25	50	30	220	14.8	29.7	70	30	190	29.7	42
Ni	mg/kg	0.1	11	0.5	149	15	136	27.4	4.5	182	20.8	76	15.5	0.6	93.6	12.6	81.3	8.8	2.6	92.5	6.45	73
P	mg/kg	10	640	40	5210	593	93	525	220	2390	230	44	435	130	1210	208	47.7	985	470	1450	259	26
Pb	mg/kg	0.01	3.69	0.62	21.4	2.85	77	11.7	4.23	95.3	4.9	42	14.2	5.63	141	5.75	40.6	88.5	19	2996	59.3	67
Pt	µg/kg	0.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.9	0.2	4.2	0.593	66
S	mg/kg	200	300	<200	5800	371	124	<200	<200	1300	74.1	74	300	<200	1000	148	49.4	950	<200	1900	667	70
Sb	mg/kg	0.02	0.03	<0.02	0.65	0.0297	99	0.165	0.05	0.98	0.104	63	0.18	0.03	1.27	0.07	41.2	1.23	0.19	9.49	0.919	74
Sc	mg/kg	0.1	3.5	0.4	11.1	3.56	102	2.8	1.2	10.7	1.26	45	2.25	0.1	9.2	1.11	49.4	0.9	0.4	10.2	0.593	66
Se	mg/kg	0.1	0.1	<0.1	1.2	0.0741	74	0.4	0.1	1.7	0.297	74	0.5	<0.1	4	0.3	59.3	0.95	0.3	3.4	0.519	55
Sr	mg/kg	0.5	23.6	1.7	614	27.7	117	8.05	4.2	87	3.11	39	6.35	1.2	71.8	3.85	60.7	19.1	8.6	87.3	10.1	53
Te	mg/kg	0.02	<0.02	<0.02	0.11			0.02	<0.02	0.62	0.015	74	0.02	<0.02	0.55	0.01	74.1	0.02	<0.02	13.8	0.015	74
Th	mg/kg	0.1	4.3	0.1	25.1	3.41	79	4.5	2.3	10.1	1.7	38	2.55	0.1	6.5	0.89	34.9	1.01	<0.1	3.81	1.13	112
Ti	mg/kg	10	1160	10	4290	1320	114	530	30	1640	297	56	340	10	1980	252	74.1	232	46	1270	238	103
Tl	mg/kg	0.02	0.06	<0.02	3.4	0.0593	99	0.115	0.02	1.35	0.045	39	0.115	0.02	1.49	0.05	45.1	0.195	0.1	0.56	0.052	27
U	mg/kg	0.1	0.8	0.1	7.4	0.593	74	1.35	0.5	13.7	0.667	49	1.05	0.4	3.3	0.52	49.4	0.67	0.19	5.78	0.489	73
V	mg/kg	2	34	<2	142	28.2	83	41.5	12	122	14.1	34	46.5	4	122	14.1	30.3	34.5	9	72	21.5	62
W	mg/kg	0.1	<0.1	<0.1	1.8			0.2	<0.1	1.6	0.148	74	0.1	<0.1	1.9	0.07	74.1	0.35	<0.1	64.5	0.222	64
Zn	mg/kg	0.1	59.2	15.7	185	28.2	48	56.5	14.5	946	19.9	35	65.4	17	850	35.8	54.7	99.5	19	899	45.2	45
LOI	wt%	0.1	1.03	0.16	15.2	0.96	94	6.6	1.3	37.5	3.07	47	10.1	2	41	5.23	51.8	48.8	16.2	89.9	31.8	65
pH	pH	0.1						5	4.1	6.9	0.36	7.2	4.9	4.3	6.6	0.3	6.1	4.4	3.7	6.3	0.67	15

For detection limits see Table 1, MAD: median absolute variation (robust equivalent of the standard deviation), CVR: robust coefficient of variation in %, NA: not analysed.

Table 3

Median element ratios between the different sample materials indicating relative enrichment/depletion

	Ratios						
	O/R	B/R	C/R	O/C	B/C	O/B	
Ag	9.6	2.3	0.8	12	2.8	4.1	
Al	0.7	1.4	1.4	0.5	1.0	0.5	
As	9.4	8.8	9.5	1.0	0.9	1.1	
Au	7.5	1.8	1.0	7.5	1.8	4.3	
B	2.0	2.0	2.0	1.0	1.0	1.0	
Ba	1.6	0.8	0.9	1.8	0.9	1.9	
Bi	7.2	2.0	1.7	4.3	1.2	3.6	
Ca	<u>0.3</u>	<u>0.1</u>	<u>0.2</u>	1.7	0.6	3.0	
Cd	17	3.5	2.1	8.1	1.6	4.9	
Co	<u>0.4</u>	1.0	1.0	<u>0.4</u>	1.0	<u>0.4</u>	
Cr	1.0	2.4	2.7	<u>0.4</u>	0.9	<u>0.4</u>	
Cu	1.4	1.1	1.7	0.8	0.6	1.3	
Fe	0.5	1.2	1.0	0.5	1.1	0.5	
Ga	0.8	1.1	0.8	0.9	1.3	0.7	
Hg	84	20	11	7.8	1.9	4.2	Rocks: Median < DL
K	<u>0.3</u>	<u>0.2</u>	<u>0.3</u>	0.9	0.7	1.3	
La	0.5	0.7	1.0	0.5	0.7	0.8	
Mg	<u>0.2</u>	0.5	0.8	<u>0.2</u>	0.7	<u>0.3</u>	
Mn	0.8	1.4	0.7	1.1	1.9	0.6	
Mo	2.5	3.1	2.9	0.9	1.1	0.8	
Na	<u>0.2</u>	<u>0.2</u>	<u>0.2</u>	1.2	0.8	1.4	
Ni	0.8	1.4	2.5	<u>0.3</u>	0.6	0.6	
P	1.5	0.7	0.8	1.9	0.8	2.3	
Pb	24	3.8	3.2	7.6	1.2	6.3	
S	3.2	1.0	<u>0.3</u>	9.5	3.0	3.2	C-horizon: Median < DL
Sb	41	6.0	5.5	7.5	1.1	6.8	
Sc	<u>0.3</u>	0.6	0.8	<u>0.3</u>	0.8	0.4	
Se	9.5	5.0	4.0	2.4	1.3	1.9	
Sr	0.8	<u>0.3</u>	<u>0.3</u>	2.4	0.8	3.0	
Th	<u>0.2</u>	0.6	1.0	<u>0.2</u>	0.6	<u>0.4</u>	
Ti	<u>0.2</u>	<u>0.3</u>	0.5	<u>0.4</u>	0.6	0.7	
Tl	3.3	1.9	1.9	1.7	1.0	1.7	
U	0.8	1.3	1.7	0.5	0.8	0.6	
V	1.0	1.4	1.2	0.8	1.1	0.7	
W	7.0	2.0	4.0	1.8	0.5	3.5	Rocks: Median < DL
Zn	1.7	1.1	1.0	1.8	1.2	1.5	
LOI	48	9.8	6.4	7.4	1.5	4.9	
pH				0.9	1.0	0.9	

If ratio is >2 or <0.5 it is in bold type or underlined, respectively. Note also that the medians for Hg and W in rocks, and S in the C-horizon, were all below the detection limit, half the detection limit was used for ratio calculations. R: rock samples, C, B, O: C-, B- and O-horizon soil samples.

- The magmatic rocks of the Oslo Rift (syenites) are characterised by high median values of (Cd), La, Mo, Na, P and W and low median values of Al, Co, Cr, Cu, Fe, Mg, Ni, S, Sc, Tl and V.
- The Precambrian gneisses to the south of Oslo have high median values of Ga, K, (La), Ti and Tl, and exceptionally low median values of Mn.
- The Precambrian gneisses at the northern end of the transect (Randsfjord) show exceptionally low median values for Mo compared to all other rocks.

For the elements Ag, Au, Ba, Th, U and Zn only minor differences in the median values between the main rock types are observed. When directly comparing the Precambrian gneisses at the southern and northern end of the transect a number of more subtle differences exist: the gneisses in the south show on average higher values for Cd, K, La, Mo, Ti, Tl, U, W and Zn, and lower values of Ca, Cu and Sr than the gneisses at the northern end of the transect.

The deepest soil horizon, the C-horizon, is usually considered to be only slightly influenced by soil-

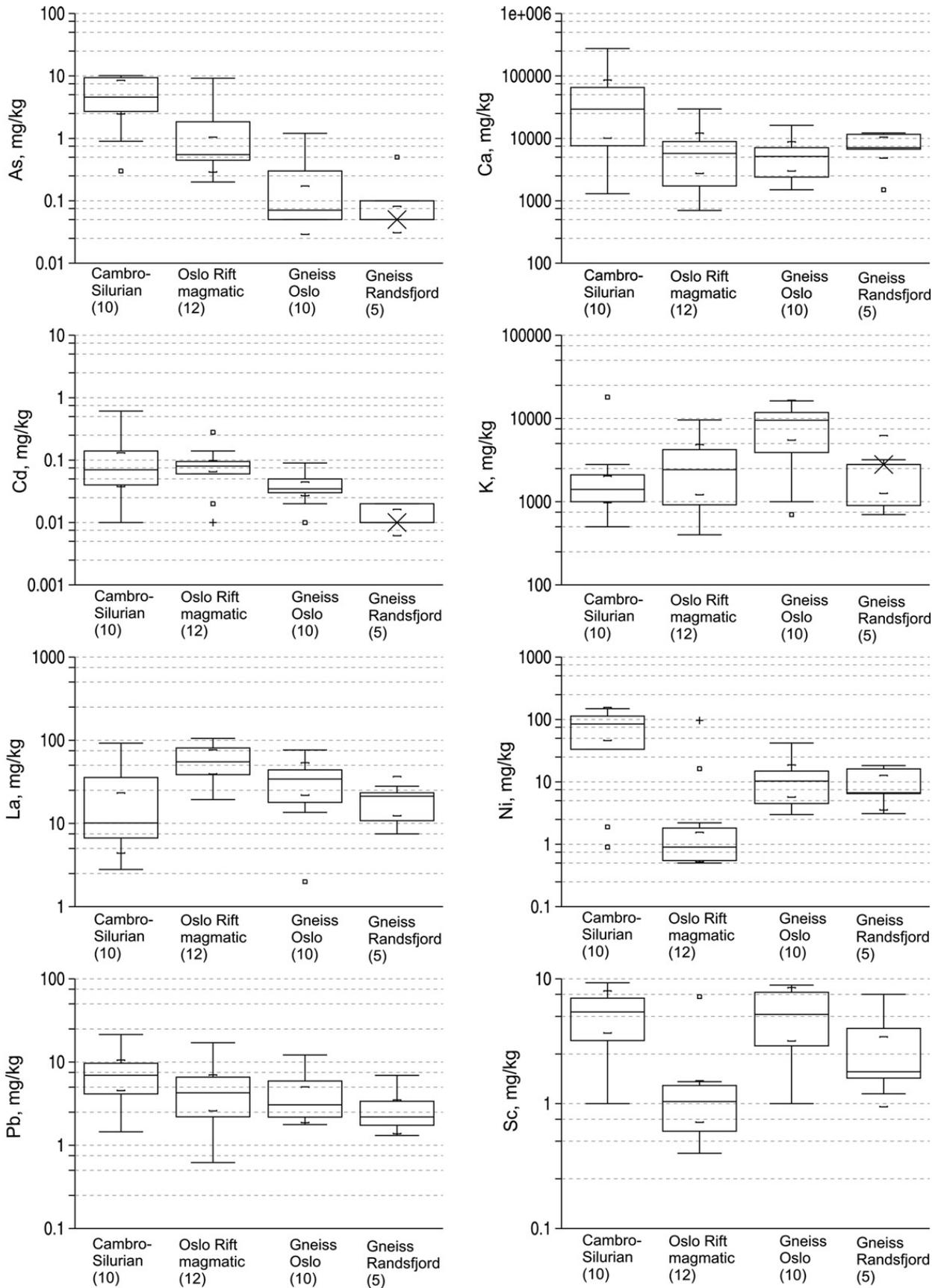


Fig. 3. Boxplots showing the variation of selected elements in bedrock samples from the four main lithologies present along the transect. The number of samples for each population is provided in brackets.

forming processes and rarely by contamination. It is thus supposed to reflect the natural, geogenic element pool and regional variations therein. The C-horizon soils along the transect represent predominantly moraine material from the last glaciation, on the Cambro–Silurian sediments residual soils can also be found. Soils developed on moraine deposits do not necessarily have a direct relation to the underlying bedrock. Transport distances are, however, very short as long as glaciofluvial material is avoided (Haldorsen and Sørensen, 1986). Thus rock and C-horizon geochemistry should be in good agreement along the transect and reflect, by and large, the same lithological differences. Shifts in observed element concentrations between bedrock and the C-horizon will be mainly due to weathering processes.

Just as for the rock samples, in the C-horizon Fe is the determined element with the greatest concentration (median 26,200 mg/kg) in the aqua regia extraction, followed by Al (16,600 mg/kg), Mg (5500 mg/kg) and Ca (1350 mg/kg). The rather strong depletion of Ca when compared to the rock samples is obvious and demonstrates the importance of weathering processes even for the composition of the C-horizon. Potassium and Ti exhibit concentrations well under 1000 mg/kg (K 850 mg/kg and Ti 530 mg/kg) and are also visibly depleted in comparison to the rock samples. Phosphorus (525 mg/kg) and Mn (330 mg/kg) are the only other two elements having concentrations above 100 mg/kg. Median concentrations for Na (60), Ba (59), Zn (57), V (42), Cr (33), La (28), Ni (27), Cu (16) and Pb (12) are between 10 and 100 mg/kg. The elements Co, Sr, As, Ga, Th, Sc, B, Mo and U fall between 10 and 1 mg/kg. All others show concentration below 1 mg/kg. Mercury, W and Te all exhibit median values above the detection limit in the C-horizon samples. Several of these elements are strongly enriched in the C-horizon when compared to the rocks: Hg (11×), As (9.5×), Sb (5.5×), Se (4×), and W (4×) are the most prominent examples (see Table 3), followed by Pb (3.2×), Mo (2.9×), Cr (2.7×), Ni (2.5×) and Cd (2.1×). This effect must be attributed to mineral weathering, the release of these elements from the lattice of silicate minerals and subsequent scavenging at the surface of newly formed clay minerals. They are then easily released by a weak aqua regia extraction.

Compared to the C-horizon the B-horizon 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 “geochemical barrier” (Goldschmidt, 1937) for many elements (independent of origin) within the soil profile, e.g., via coprecipitation with the Fe-oxides/-hydroxides. In the B-horizon, again Fe (median 29,750 mg/kg) and Al (median 16,500 mg/kg) are the two elements determined at major element levels by the aqua regia extraction. Concentrations of Fe and Al in the B-horizon are surprisingly close to those observed in the C-horizon and in the rocks. The only further element showing a median concentration above 1000 mg/kg in the B-horizon is Mg (3750 mg/kg), which displays a steady decrease from rocks through C-horizon to the B-horizon. Elements showing median concentrations between 1000 and 100 mg/kg are Ca (750), Mn (640), K (600), P (435), Ti (340) and S (300). Thus most (note that N was not analysed) of the plant macronutrients (P, K, Ca, Mg and S) are depleted in the B-horizon compared to the C-horizon. The exception is S, which is strongly enriched in the B-horizon. Of the micronutrients (B, Cu, Fe, Cl, Mn, Mo and Zn) Mn, Mo and Zn are also slightly enriched in the B-horizon. The reasons are the presence of Mn as oxyhydroxides and the strong affinity of S to organic material (indicated by the strong increase in median LOI from C-horizon (6.6 wt%) to B-horizon (10.1 wt%)). Median concentrations between 100 and 10 mg/kg are exhibited by Zn (65), Ba (54), Na (50), V (47), Cr (30), La (19), Ni (16) and Pb (14). The median levels of Cu, Co, Sr, Ga, As, Th, Sc, Mo, B and U fall between 10 and 1 mg/kg. All other elements display median concentrations below 1 mg/kg in the B-horizon. In terms of enrichment/depletion patterns in comparison to the rock samples the B-horizon follows closely the patterns described above for the C-horizon. Most elements enriched in the C-horizon are about equally or even more strongly enriched in the B-horizon (e.g., Hg where the factor changes from 11 to 20 – see Table 3). The most notable additional element is Ag, which is enriched almost three times in the B-horizon compared to the C-horizon. This provides an argument that most of these enrichments are still due to the natural processes of soil formation and not caused by anthropogenic additions.

“Critical concentrations” (for soil and plant health) of some “heavy metals” in the mineral soil layers of forest soils are compiled in the EC, and by UN/ECE and the Ministry of the Flemish Com-

munity (1997), based on values provided by Kabata-Pendias and Pendias (1984) and Witter (1992). Values suggested are Cr: 75 – 100 mg/kg, Ni: 95 mg/kg, Mn: 1500–3000 mg/kg, Zn: 170 mg/kg, Cu: 60 mg/kg, Pb: 100–400 mg/kg and Cd: 3–8 mg/kg. Above these critical concentrations the growth of many plants will be impeded. The median values reported here (Table 2) are all well below these “critical concentrations”, there exist only single samples where some of these values are occasionally exceeded (see MAX values in C- and B-horizon in Table 2). Interestingly, these “single samples” are all related to the occurrence of black shales along the transect and the observed high concentrations have thus all a natural cause. None of the samples exceeds the “critical concentrations” due to anthropogenic additions.

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 (e.g., Kashulina et al., 1997). It can accumulate and enrich many elements, e.g., via organic complexing and adsorption. For many elements, both from natural and anthropogenic sources, the O-horizon thus acts as a very effective “geochemical barrier” as first defined by Goldschmidt (1937). At the same time, the O-horizon will respond strongly to the anthropogenic input of elements via the atmosphere. In the O-horizon, again Fe (median 13,750 mg/kg) and Al (median 7600 mg/kg) are the two major elements present in the aqua regia extraction, followed by Ca (2250 mg/kg) and Mg (1095 mg/kg). Elements showing median concentrations between 1000 and 100 mg/kg are P (985), S (950), K (800), Mn (353), Ti (232), Ba (104) and Zn (100). Median concentrations between 100 and 10 mg/kg are present for Pb (89), Na (70), V (35), Sr (19), La (15), Cu (13) and Cr (12). Median levels of Ni, As, Ga, Co, B, Mo, Sb and Th fall between 10 and 1 mg/kg, all other elements exhibit median concentrations below 1 mg/kg.

Some major shifts are apparent when the O-horizon is compared to the deeper soil layers (see Table 3). Of the plant macronutrients the anionic elements S (9.5×), and P (about 2×) are enriched in the O-horizon when compared to the C-horizon. Of the cationic elements Ca (2×) is enriched and Mg is strongly depleted (about 5×). Of the cationic

micronutrients Fe is depleted and Zn is enriched in the O-horizon. Barium concentrations in the O-horizon are also about double those found in the C-horizon. In general enrichment/depletion in the O-horizon depends strongly on the function of the element in the plants: some are shed with the litter (e.g., Ca) others are recycled within the plant (e.g., Mg). A remarkable enrichment of several further elements in the O-horizon relative to the C-horizon is observed (compare median ratios in Table 3): Ag (12×), S (9.5×), Cd (8.1×), Hg (7.8×), Pb (7.6×), Au (7.5×), Sb (7.5×), Bi (4.3×), Se (2.4×) and Sr (2.4×). One source of these elements could be natural biogeochemical processes (Goldschmidt, 1937; Reimann et al., 2001, 2003; Reimann and de Caritat, 2005). Trees and other vegetation adsorb elements through dust and precipitation deposited directly to their foliage. They can actually quite effectively “comb” the atmosphere. It is thus also possible that an enrichment of these elements in the O-horizon of forest soils is due to contamination of the atmosphere via leaf-litter and biomass decomposition.

Tyler (1992) provides “critical concentrations” (for plant and animal health) of heavy metals in the mor (organic) horizon of forest soils: 30 mg/kg for Cr, 300 mg/kg for Zn, 20 mg/kg for Cu, 500 mg/kg for Pb and 3.5 mg/kg for Cd. All the median values reported here are clearly below these critical concentration (Table 2); there exist, however, single samples where each of the elements clearly exceeds these “critical concentrations” (see MAX values in the O-horizon in Table 2). For the O-horizon a few of the samples showing values above the critical concentrations are from Oslo and have a possible anthropogenic source. However, again most occurrences are related to the presence of black shales and thus have a natural origin.

In the following, the transects will be used to study the impact of different sources (Oslo vs. lithology) and thus discern the relative importance of anthropogenic vs. the natural element pool vs. climatic factors for the build-up of these elements in the O-horizon.

3.1. Gold and platinum in the O-horizon samples

Gold and Pt gave the strongest “urban signal” in the moss samples collected along this transect (Reimann et al., 2006). Plotting the analytical results for Au in the O-horizon along the transect reveals a strong peak in Oslo (Fig. 4). In Fig. 4, the boundaries between the main bedrock types encountered

along the transect are shown, O-horizon and C-horizon trendlines (loess regression) are indicated by different line types. The plot demonstrates that the Au peak in O-horizon soils collected in Oslo is probably not related to the underlying lithology. Samples collected over three different lithologies all show the highest concentrations in the city of Oslo. It is also clearly visible that levels characteristic of background variation (here taken as the variation at the northern and southern end of the transect: 0.2–2 $\mu\text{g}/\text{kg}$ Au) are reached at a distance of less than 20 km from the city centre in both directions. The difference between geogenic background variation and the values observed in Oslo (10–50 $\mu\text{g}/\text{kg}$ Au) is about one order of magnitude. However, although a clear anthropogenic Au-peak marking Oslo exists, the other message that can be

drawn from this diagram is that Au is generally enriched in the O-horizon, all along the transect and independent of any obvious anthropogenic or geogenic source. Thus there must be a natural process enriching Au in the O-horizon. Note that only at those sample locations where LOI is especially low (on top of the Cambro–Silurian sediments) are Au values in the O-horizon lower than in the C-horizon (Fig. 4).

A plot of Pt values, only determined in the O-horizon samples, looks quite different. Two peaks are observed, one in the city of Oslo and one far to the north in the Randsfjord area (Fig. 4). The latter is clearly related to the presence of Cambro–Silurian shales. The same rock types occur in the city of Oslo and the soils collected on top of these also show high values (Fig. 4). It is thus likely that these

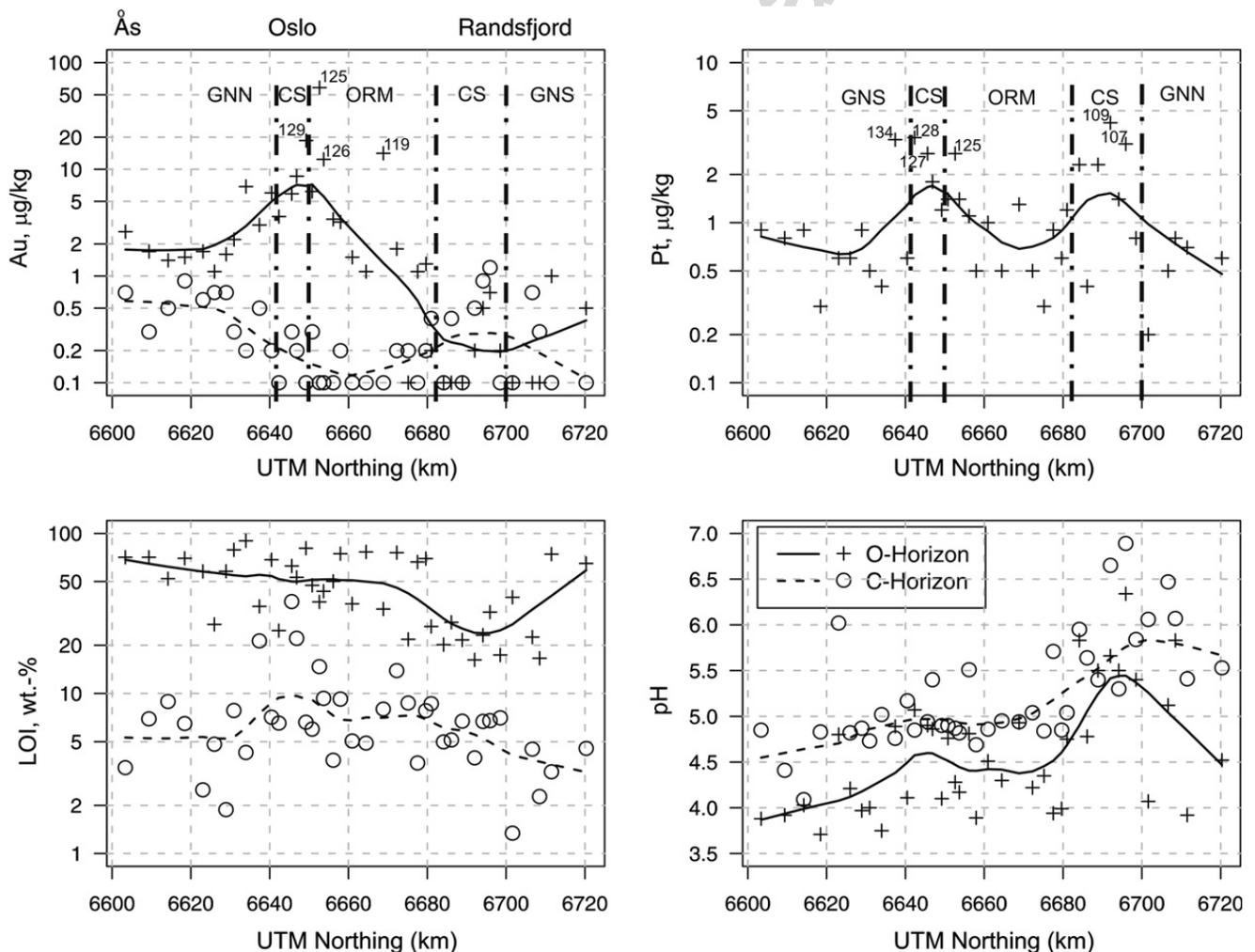


Fig. 4. Concentrations of Au and Pt, and values of LOI and pH in O- and C-horizon samples along the Oslo transect. Note that all Pt values were below the limit of detection (2 $\mu\text{g}/\text{kg}$) in the C-horizon. The boundaries between the four main lithologies encountered along the transect are shown in the upper two diagrams (Au and Pt): GNS: Gneisses at the southern end of the transect, CS: Cambro Silurian sediments, ORM: Oslo Rift magmatic rocks, GNN: Gneisses at the northern end of the transect.

high values have a natural source and are not related to anthropogenic activities. Only two samples have unusual Pt-concentrations in the city of Oslo: sample 134, that is clearly anomalous in relation to all other samples collected from locations underlain by the same Precambrian gneisses; and sample 125, that shows a somewhat higher Pt-concentration than all other soil samples collected over the magmatic rocks of the Oslo Rift (Fig. 4). Sample 134 is the only sample that was collected close to a major highway, E6, leading out of Oslo towards the Swedish border. The high Pt-value observed there is thus most likely due to Pt-emissions from car exhaust catalytic converters. The value of 3.3 $\mu\text{g}/\text{kg}$ Pt in sample 134 compares well with values from other studies where the uppermost 2 cm of soils were collected close to major highways (e.g., Parry and Jarvis, 2006). Parry and Jarvis (2006) also demonstrated that the Pt-concentrations in soil samples adjacent to the M40 motorway in the UK decrease by a full order of magnitude over a distance of just 10 m. Sample 125 was collected at the northern outskirts of Oslo and could thus be affected by both anthropogenic and geogenic processes. Thus for the transect shown here, the city of Oslo is marked by a single (and maybe two) high anthropogenic Pt-value(s) at the sample density chosen (Fig. 4). This demonstrates that anthropogenic activities may have a very local impact on the observed element concentrations in the O-horizon.

3.2. Loss on ignition and pH in the O-horizon-samples

Loss on ignition (480 °C) and pH are two important soil properties that will have strong influence on metal values observed in the soils (EC, UN/ECE and the Ministry of the Flemish Community, 1997). Organic matter content in the soil is strongly linked with soil pH, biological activity, cation exchange capacity (CEC) and hydrological conditions. The decomposition of organic matter is faster where pH is higher, conditions are neither too wet nor too dry, and soil biological activity is high. If the soil is wet and the pH is low the decomposition of organic matter is much slower. Fig. 4 shows the observed values for LOI and pH along the transect. The borders between the underlying lithologies are shown in the diagram. It is clear that the Randsfjord area is unusual in terms of LOI (very low) and pH (high) compared to the rest of the transect. Cambro–Silurian sediments that occur in this area con-

tain considerable amounts of calcite (CaCO_3), and thus raise the pH and all soil samples show unusually high Ca-concentrations. These, in turn, cause a faster decay of the organic matter in the soils in this area, thus resulting in a low LOI (EC, UN/ECE and the Ministry of the Flemish Community, 1997). Comparison of the transects for LOI and Au suggests that the low organic content of these soils may be the reason for the low Au-concentrations. Soils developed on the same rocks in the Oslo area show a higher organic content (LOI) and a lower pH, both are most likely due to the wetter climate near the sea. The low pH will result in a slower decay of organic material in these soils. A part of the observed Au-peak in Oslo may thus be due to climatic differences rather than contamination. In any case, the plots provide a strong indication that Au has a special affinity for organic matter.

3.3. Elements generally enriched in the O-horizon

The same general enrichment of the elements Ag, Au, Bi, Cd, Hg, Pb, S, Sb, Se and Sr in the O-horizon of forest soils or in the A_p -horizon of agricultural soils as described above has been observed previously on a much larger (up to continental) scale (e.g., Reimann et al., 2001, 2003). The enrichment of these elements at the Earth's surface is often interpreted as an indication of the major influence of anthropogenic activities on environmental quality at the earth surface (e.g., O'Neill, 1985; Steinnes and Njåstad, 1995; Blaser et al., 2000). Rasmussen (1998), Reimann et al. (2001, 2003), Reimann and de Caritat (2005) and Reimann and Garrett (2005) caution that this enrichment may be due to natural biogeochemical cycling and the function of the O-horizon of soils as a natural geochemical barrier for these elements. Goldschmidt (1937) described this phenomenon for the element Bi. According to Goldschmidt (1937) the enrichment of elements like Bi in the O-horizon is due to plants “pumping” these elements up from the deeper soil layers. Then following the return of dead plant material to the soil and its decomposition, the strong binding of these elements with organic material results in these elements being retained and enriched over time in the O-horizon. The enrichment relative to the underlying mineral soil horizons will in turn depend on the rate of decay of the O-horizon and on the local composition of the plant community in any one area and may thus be quite different under different natural conditions.

Fig. 5 shows plots for the elements Ag, Bi, Hg and Pb along the transect (for Au see Fig. 4) in 3 of the 4 sample materials (O- and C-horizon and rocks). The B-horizon soil chemistry generally follows that of the C-horizon; thus the B-horizon results are not shown here to improve readability of the diagrams. The plots show a general enrichment of these elements in the O-horizon along the whole length of the transect. Sample 127 shows a single high value for many elements (Ag, As, Bi, Cd, Cu, Fe, Mo, Pb, S, Sb, Se, Te, Tl, W and Zn) in the city of Oslo. It represents a geogenic anomaly, due to mineralisation in the Cambro–Silurian sediments that was detected by chance. It is currently being followed up (values up to 53,900 mg/kg Pb, 3180 mg/kg Zn, 2550 mg/kg Cu, 554 mg/kg Mo, 30 mg/kg Cd, 14 mg/kg Te and 5 mg/kg Ag have been found so far in the O-horizon at this location).

Several elements show a very typical decline in relative enrichment in the Randsfjord area, here the element concentrations in all three sample materials become quite comparable (e.g., Bi, see Fig. 5). Surprisingly there is no peak (other than sample 127) marking Oslo for any of these elements (with the exception of Au, see above). Reimann et al. (2006) have demonstrated that in terrestrial moss samples (*Hylocomium splendens*) all these elements (Ag, Al, Au, Bi, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Pt, Sb, Th, Ti, Zn), with the notable exception of Hg, show a typical contamination peak in the city of Oslo, and up to 20 km downwind (to the south) and 40 km upwind (to the north) of the city. These distances most likely mark the area of influence of fine “urban” dust. In the O-horizon, however, the city of Oslo hardly stands out at all (Fig. 5). The results from the transect thus suggests that it is unli-

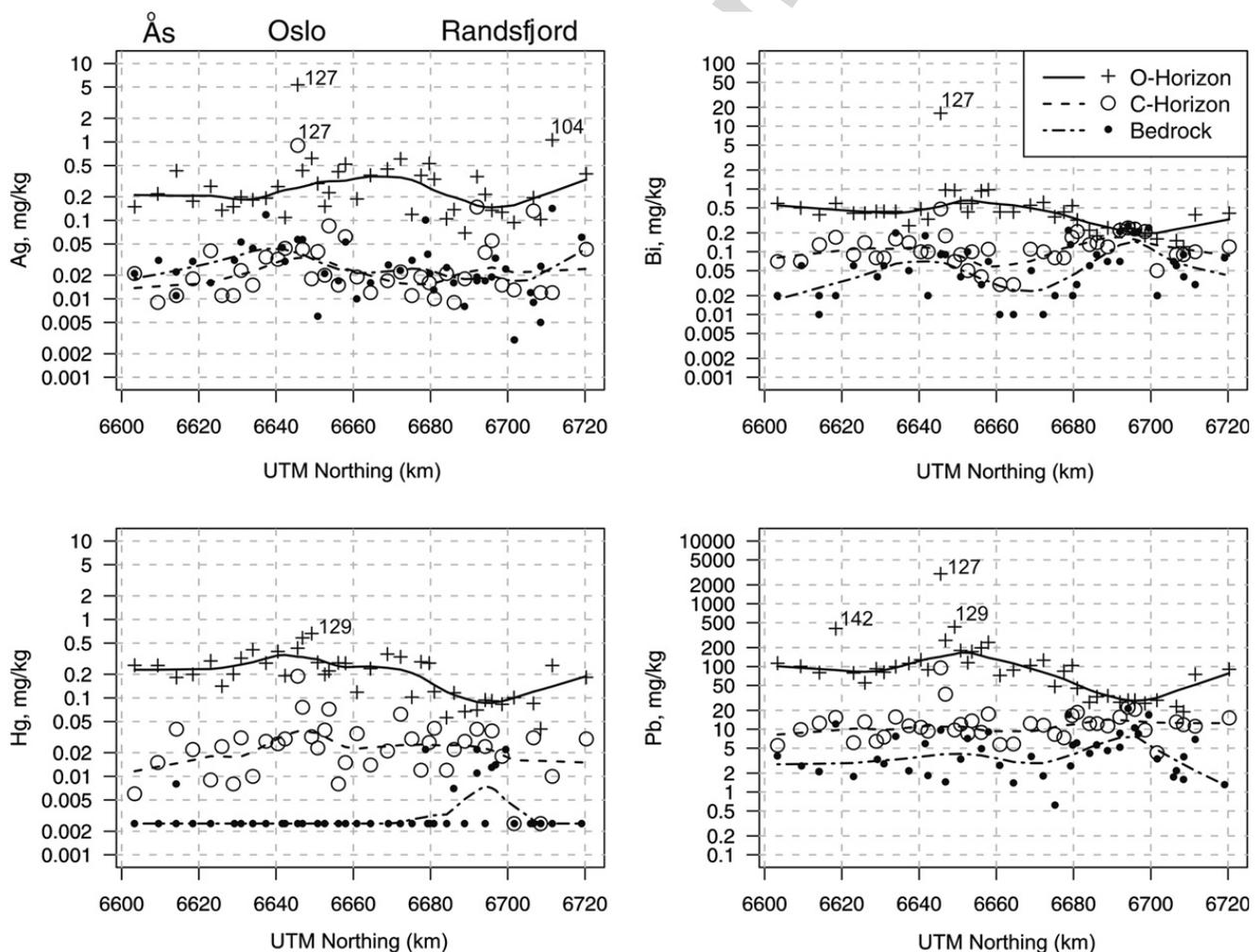


Fig. 5. Concentrations of Ag, Bi, Hg and Pb in Rock, C- and O-horizon samples along the Oslo transect. For exact location of site numbers see Fig. 1, for location of lithological breaks consult Fig. 4.

kely that the enrichment of all these elements in the O-horizon is due to anthropogenic activities.

It could be argued that the enrichment of these elements in the O-horizon is due to long-range atmospheric transport of elements from central European sources (e.g., Nord, 1992, see also the discussion of “long range transport” in Reimann et al., 1997) and that Oslo is such a comparatively clean city that its additional impact is unimportant. However, the results of Reimann et al. (2006) using terrestrial moss as a sample material prove the impact of Oslo on the metal budget in the area. If Oslo is not visible in the soil samples, which accumulate elements over much longer time spans than moss, it must be concluded that serious soil contamination usually happens at a different and much more local scale than can be detected with a 3 km sample spacing. Geochemical investigations of urban areas usually define clusters of locally high metal values that disappear at very short distance in the local background variation (e.g., Birke and Rauch, 1997). Tjehus et al. (2002) have published results of a more detailed geochemical survey of topsoil in Oslo. Although they find a general enrichment of Pb towards the city center and along the major traffic lines, local variation is still very high.

The enrichment is also not directly related to the deeper soil horizons or the soil parent material (bedrock). The plot for Hg shows that the Hg-concentrations in the O-horizon can even be lowest in the location where the observed concentration in the rocks is highest (Fig. 5). Thus, as predicted by Goldschmidt (1937), the enrichment of these elements is driven by the natural biogeochemical cycles. Differences in enrichment depend on the kinetics of elemental accumulation in soil organic matter and the different retention potential of different elements vs. the speed of decay of organic matter.

During the last 20 a, strong regulatory measures have been taken to reduce emissions from traffic and industry. Due to the age of the O-horizon, these past emissions should, however, still be clearly visible. Areas with a high degree of anthropogenic activity and much traffic, like a town or city should result in a detectable peak in a transect if the enrichment of metals in the O-horizon were due to anthropogenic input. Reimann et al. (2006) demonstrated the presence of a clear anthropogenic Oslo-peak in moss samples, which reflect a much shorter time of input, for the majority of elements discussed here. The fact that this peak is not visible in the

O-horizon samples (with the exception of Au and Pt) but that the metals are rather enriched in the O-horizon (relative to all other sample materials discussed here) all along the transect independent of distance to likely sources provides strong evidence for a natural origin of the observed element enrichment.

3.4. Elements showing different patterns along the transect

Tables 2 and 3 demonstrate that elements may not only be enriched in the O-horizon, but can show almost similar or much lower values than in the other media. Fig. 6 shows the distribution of two of these elements along the transect. Sodium is an example of an element that shows by far the highest levels in the bedrock in comparison to the sampled soil horizons. Other than that the lowest values being observed on top of the Cambro–Silurian sediments of the Randsfjord area, there is no clear relation to the underlying bedrock (compare Figs. 4 and 6). In the Randsfjord area, element concentrations in all 3 materials are again very comparable. The O-horizon samples show a clear south-north trend of decreasing concentrations. The same observation was made for the moss samples (Reimann et al., 2006). The reason for this gradient is the steady input of marine aerosols, rich in elements like Na, near the coast. This effect was observed on a much larger scale on the Kola Peninsula (Reimann et al., 2000b). This process has a clear effect on the concentrations of several elements in the soil, and will also influence the pH of the soils and receiving waters (Reimann et al., 2000a).

The Ni concentrations observed in the O-horizon transect samples are clearly dominated by geogenic sources. Nickel shows a peak in Oslo, but the peak observed on top of the Cambro–Silurian sediments in the Randsfjord area is higher (Fig. 6). The elements Ba, Co, Cr, Fe, Mg, Sc, Sr, Ti and V show similar trends.

3.5. Relation of the elements with pH and LOI in the O-horizon samples, principal component analysis

Results displayed in Figs. 4 and 5 strongly suggest that the amount of organic material in the samples as reflected by their LOI (and the pH) will have a much stronger influence on the relative enrichment/depletion of these elements along the transect than geogenic source material and/or anthropogenic input. Fig. 7 shows the relationship between LOI,

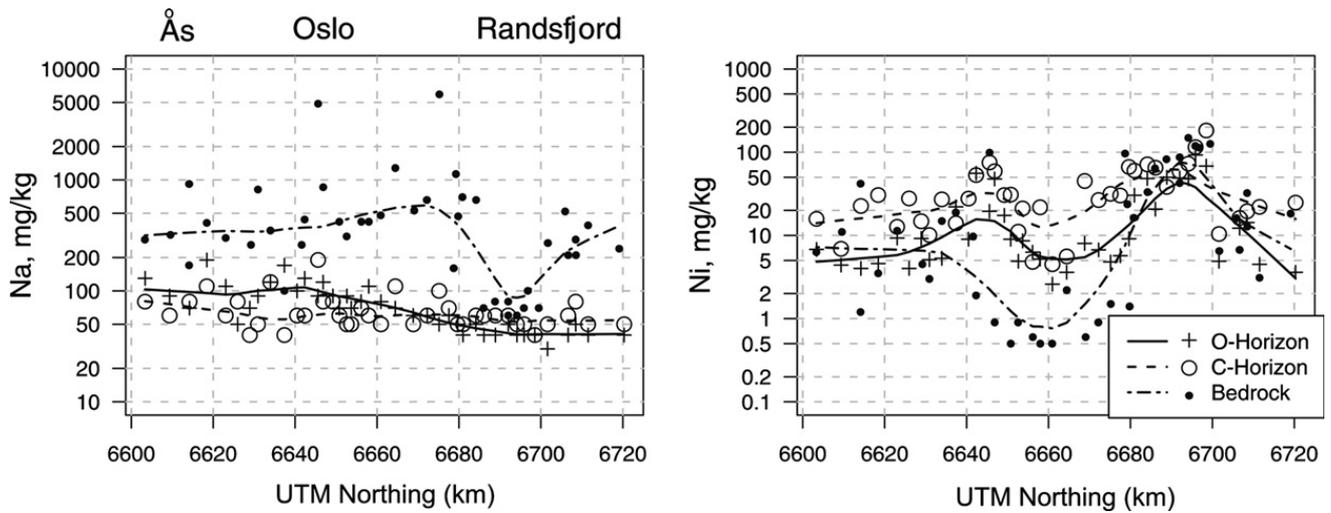


Fig. 6. Concentrations of Na and Ni in Rock, C- and O-horizon samples along the Oslo transect.

pH and two elements with opposite behaviour. Iron, just as Cr, Ni, Co, V and several other elements, increases with pH and decreases with LOI, and in strong contrast, Pb (and Ag, Bi, Cd, Hg, Sb, Se and others) decreases with increasing pH and increases with increasing LOI. These correlations are not caused by mixing of material from the four

different lithologies along the transect, they can be detected within each of the lithologies (Fig. 7).

To better understand the inter-element relations, a principal component analysis (PCA) was carried out. The data set is not ideally suited for PCA, it contains too many variables for the few samples (Reimann et al., 2002) and thus only the first two

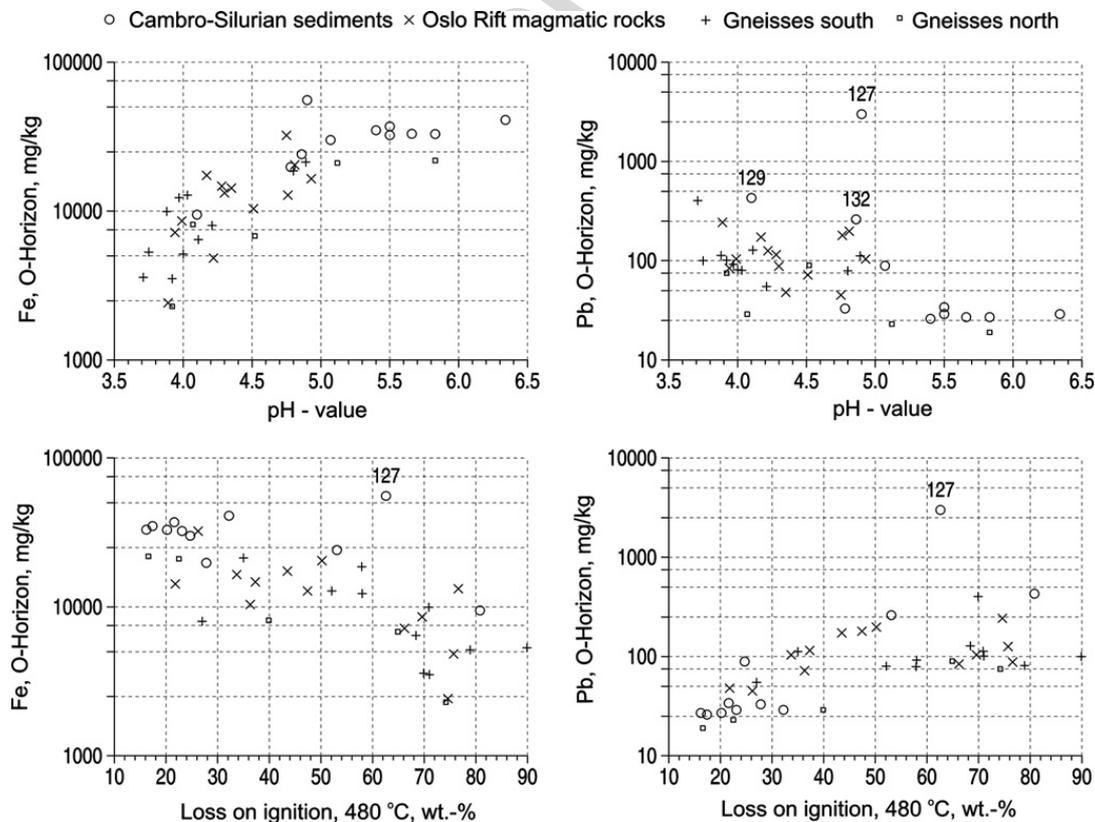


Fig. 7. Scatter plots of Fe and Pb vs. LOI and pH. The main lithologies encountered along the Oslo transect are represented by the plot symbols.

PCA loadings will be discussed. In addition, LOI (which can reach values of up to 90 wt% of the total in the O-horizon – Table 2) and the major elements (esp. Fe and Al) will cause closure effects to play an important role for this data set (Aitchison, 1982). To remove the effects of closure the data (with the exception of pH, which is already given in log-units) were log-centred prior to carrying out the PCA. Furthermore one extreme outlier (sample 127) was removed from the dataset prior to carrying out PCA.

The resulting first three components of PCA account for 72% of the total variability (53.7 + 10.8 + 7.1%). The loadings for PC-1 and PC-2 are displayed in the form of a biplot in Fig. 8.

Elements with positive loadings (cut-off: 0.666) on PC-1 are in decreasing order: Mg, Sc, Cr, Al, Fe, pH, Co, Ni, V, Th and Mn. Elements with negative loadings (cut-off: –0.666) on PC-1 are in ascending order: Hg, Sb, Pb, Bi, Se, W, LOI, Cd, S, Au, Na, P and Ag. The positive loadings reflect a geogenic association which includes the role of carbonate rocks high in Mg that are also often reflected in high soil pHs. It is noteworthy that Ga, K, Ba, Ca, U and As have loadings of 0.651, 0.633, 0.581, 0.562, 0.545 and 0.536, respectively, on PC-1. Carbonate rock influence is supported by the Ca–Mg–pH association, and the general geogenic control by the Th–U and Al–Ga associations

and the presence of K, Ba and As. Arsenic occurs bound to sulphides in the black shales.

The negative loadings reflect a biogenic association of elements connected with biological processes and the sequestration of trace elements during the biogeochemical cycle in the “geochemical barrier”, the O-horizon, as described by Goldschmidt (1937). The presence of P and the S–Se association are important indicators of biological processes. Unlike the geogenic elements there are no auxiliary elements with loadings between –0.666 and –0.5. The high negative loading of W is unexpected, rather a positive loading as a geogenic element would have been the expected result. The association of the transition elements and precious metals Hg, Sb, Pb, Bi, Cd, Au and Ag does not reflect anthropogenic contamination but rather their ability to form stable metallo-organic complexes that exhibit long residence times in the organic rich O-horizon of the soil. In Fig. 8 the biogenic elements plot to the left, and geogenic elements plot to the right of the biplot.

The observed correlations may not highlight the direct influence of organic matter and/or pH but rather reflect the status of the organic soils: high LOI and low pH are the soils that are most organic, while samples with a high pH and/or a low LOI are fast decaying organic soils. It is thus most likely that the observed element patterns reflect the kinetics of decomposition of the O-horizon in counteracting the “plant pump”. Where LOI is high and/or pH is low many (but not all) metals will accumulate in the O-horizon.

In this connection, it is a noteworthy observation that in the past the high S-load in precipitation in S-Norway had a strongly acidifying influence on forest soils. This resulted in lower soil pH and thus a slower rate of decay of organic material causing in turn a higher content of organic matter. The higher organic matter content had a higher storage capacity for the transition elements, independent of anthropogenic or natural origin. Today the load of S in precipitation has been reduced considerably, which will result in a faster decay of organic material, the release of the metals to soil and ground water and a reduced total element load in the O-horizon. The real anthropogenic impact is thus not an important input of metals to the soils via long range atmospheric transport but rather a change in the kinetics of the natural biogeochemical cycles. Climate change will have a similar impact on the metal

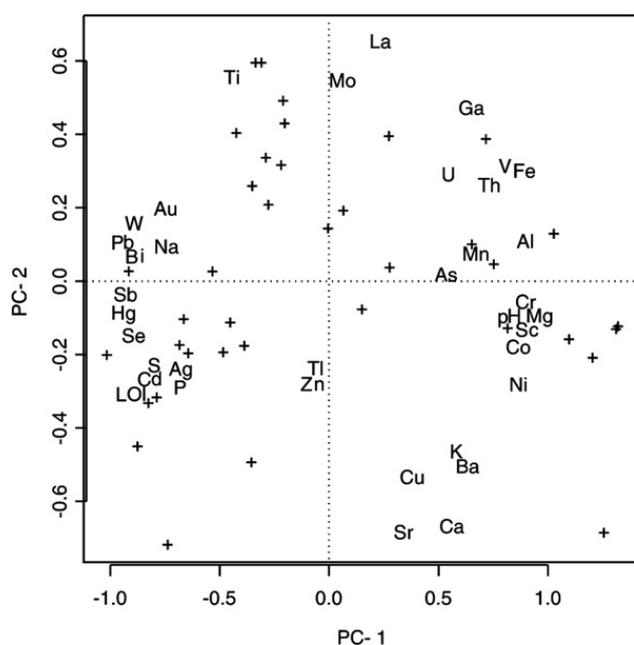


Fig. 8. Biplot of the results of PCA, O-horizon samples.

budgets in forest soils: a wetter and colder climate will result in the build-up of certain elements, while a drier and warmer climate will release stored elements at a faster rate than previously.

4. Conclusions

Along the Oslo transect Au in the O-horizon is the only element that shows a peak throughout the city that is probably related to urbanisation. For Pt only one sample, taken close to a major highway, displays a peak that is most likely caused by traffic emissions (automotive exhaust catalytic converters). All other high Pt-values observed in Oslo are related to Cambro–Silurian sediments and thus have a geogenic source. Soil samples collected above the same rocks in the Randsfjord area at the northern end of the transect also show some elevated Pt values.

Reimann et al. (2006) have demonstrated that a long list of elements (Ag, Al, Au, Bi, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Pt, Sb, Ti, Th and Zn) show a characteristic Oslo peak in samples of terrestrial moss. With the exception of Au, this peak could not be found in the O-horizon, although the O-horizon accumulates any element input, anthropogenic as well as natural, over a much longer time than terrestrial moss (tens of years vs. 2–3 years). This suggests that contamination of these surface soils happens at a very local scale, more local than the 3 km sample spacing along the transect could detect, and that otherwise the element concentrations observed in the O-horizon are still predominantly natural. Not even Pb demonstrates a clear peak related to the city characterised with a high level of traffic. The one exceptionally high Pb-value (3000 mg/kg) found in Oslo is a geogenic anomaly.

Many elements (Ag, Au, Bi, Cd, Hg, Pb, S, Sb, Se and Sr) show a strong enrichment in the O-horizon when compared to the underlying C-horizon along the whole transect and without any clear relation to bedrock, underlying C-horizon or anthropogenic sources. They are taken up by plants and then returned to the O-horizon, where they are strongly bound for varying lengths of time. The plants get rid of toxic or otherwise undesirable or no longer needed elements via litter fall, one could say that they use the O-horizon as their “garbage bin” for unwanted elements. Relative enrichment will depend on the degree of humification and on the speed of decay of organic material, which is governed by climate, geology, topography and local

conditions. LOI and pH can be used as proxies for differences in these factors.

A large number of elements are not preferentially taken up by plants and/nor bound in the organic layer. Among these are Mg, Th, Ni, Sc, Cr, Co, Ti, Al, Fe and La. They all appear depleted in the O-horizon when compared to the C-horizon along the entire transect.

Overall, it appears that climate is an important factor behind the enrichment of quite a number of metals often attributed to human activities in the organic soils of Scandinavia. Climate change will have important consequences on the metal budget. A cold and wet climate will result in a further build-up of many of these elements in the O-horizon, a dryer and warmer climate will result in their release. Acid rain will lead to a natural build-up of these elements in the O-horizon due to slower mineralisation. Once acid rain is reduced, the accumulated metals will be released over time to be removed in surface or ground water, and the concentrations of these elements in the O-horizon must decrease. Deforestation and the following decay of organic matter will also release the metals stored in the organic layer. The driving forces of mineralisation/storage are a combination of climate and geology, and acidity that can be anthropogenically modified.

The observations along the Oslo transect demonstrate that for all elements the biogeochemical cycle dominates the geochemistry of O-horizon soils over any anthropogenic or geogenic effect. Anthropogenic metal input, which may play a dominating role at a local, site-related, scale is insignificant at a regional scale when compared with the natural enrichment due to the biogeochemical cycling of these elements.

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