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Applied Geochemistry 22 (2007) 1095–1104
Applied Geochemistry
www.elsevier.com/locate/apgeochem

Sulphur behaviour in forest soils near the largest SO_2 emitter in northern Europe

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Available online 30 March 2007

Abstract

The impact of 60 a of SO_2 emissions from a Ni–Cu plant in the Kola Peninsula (Russia) on soil S contents was assessed in podzols under pine forests. Sulphate desorption and the possible delay of acidification reversal was investigated, because the plant will be reconstructed in 2006 with an expected emission reduction of 90%. Sites were sampled along a pollution gradient in the prevailing wind direction from 1 to 66 km. The investigated podzols stored S mostly in the organic form. The concentrations of total and organic S in soil organic horizons tended to be higher near the smelter but were only weakly correlated with S deposition. No relationship between distance to smelter and S contents was found for the mineral horizons. Sulphate content and desorption behavior were highly variable due to natural variations of texture and extractable Al and Fe contents of the soils. The lack of a clear strong trend with distance from the smelter except in the organic layer indicated that long range transport and diffuse input of SO_4 played a major role rather than point source impact. It was concluded that biological turnover is most likely the regulating process in these soils and thus low to medium release of SO_4 is expected under decreasing deposition scenarios because organic S was the dominant fraction of total S in all soils.

1. Introduction

The Kola Peninsula, NW Russia, has been affected by SO_2 emissions from the Ni-processing industry for several decades. The Ni–Cu plant Pechenganikel, including the Ni smelter at Nikel and Cu–Ni-ore roasting plant at Zapolyarnyy, is the largest emitter of SO_2 in northern Europe (Barrett and Protheroe, 1995). Despite decreasing SO_2 emissions, down to 40% compared to 1980 levels, most of the peninsula is still severely polluted. The long-term effect of SO_2 and heavy metal aerosols has caused severe environmental damage in the area (Reimann et al., 1998; Koptsik et al., 1999a,b). The prevailing soils in the region, thin sandy podzols, are sensitive to acid deposition due to low weathering rates, ranging from 0.05 to 0.28 $kmol_c/ha/a$ in the 0–50 cm soil layer (Koptsik et al., 1999b). SMART model simulations suggest that soils and surface waters will acidify severely within the next 20–30 a unless there are drastic reductions of the SO_2 emissions from the Pechenganikel smelter (Kämäri et al., 1995; Koptsik and Koptsik, 2001).

The amount and solubility of the soil S pools are crucial parameters for the assessment of the

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0883-2927/$ - see front matter
doi:10.1016/j.apgeochem.2007.03.044

reversibility of soil and water acidification after reduction of SO_2 inputs. Even though S in the soils of northern Fennoscandia has been investigated in a few studies (e.g. Gustafsson, 1996; Räisänen et al., 1997; Kashulina and Reimann, 2001, 2002), neither phosphate-extractable SO_4 content nor SO_4 adsorption capacity has been evaluated for Kola soils. Sulphate adsorption in soils was found to be fairly low in Finland and Norway close to present study sites at the Russian border (Gustafsson, 1996). Therefore, the storage of inorganic SO_4 in soils at Kola might be low, but organic S could be a major contributor to the SO_4^{2-} in soil solutions and waters. The objectives of this study were to quantify the S contents of forest soils along a pollution gradient in the Kola Peninsula (Russia), to describe the SO_4 desorption behavior, and to evaluate the potential effects of inorganic and organic S pools on the prediction of long-term soil and water quality.

2. Materials and methods

The study area is located around the Ni smelters in the north-western part of the Kola Peninsula, Russia (Fig. 1). It is a hilly arctic glaciated terrain covered by tills and glaciofluvial deposits with coarse texture; open bedrock is less common. The thin podzols stocked with scarce pine forests have low pH, a low pool of exchangeable base cations and low cation exchange capacity (Koptsik et al., 1999a).

The main source of air pollution in the area is the Pechenganikel smelter, which was founded in 1933. Up to 1973 the smelter used local ore with low S content (6.5%). In that time, the annual SO_2 emissions did not exceed 100,000 tons and caused insignificant local damage to the vegetation. In 1974, the smelter began processing highly sulphurous (up to 30% of bulk content) Noril'sk ore, and the volume of emissions increased. According to the data of the smelter administration, SO_2 emissions reached their maximum in 1979 (up to 400,000 tons), decreased slightly in 1980 (383,000 tons) and dropped to 266,000 tons in 1990. At present the Pechenganikel smelter emits about 152,000 tons of SO_2 annually. An overwhelming amount of SO_2 comes from high (140–160 m) chimneys and contributes to long range transport (Blatov et al.,

Fig. 1. Plot locations.

2001). Total annual S deposition significantly exceeds 2 g/m^2 within an area of 20–40 km^2 nearest to the Ni smelter, compared to about 0.1–0.2 g/m^2 in background areas (modelled data, Sivertsen et al., 1994). A reconstruction of the plant with a 90% emission reduction is planned for 2006 (Blatov et al., 2001).

Thirteen plots were selected, which are comparable in vegetation (pine forests), soils (podzols) and exposure. The plots are situated in the prevailing wind direction at distances between 1 and 66 km from the smelter (Fig. 1). At these plots, 75 soil samples were collected from the organic (O) and mineral (E, B_{sh}, BC and C) horizons. At least 9–12 sub-samples of 3 different pits were taken from each plot and horizon. The sub-samples were mixed into one sample for analysis. The samples were air dried and sieved with a 2-mm sieve. Carbon and N contents were determined after combustion using a CHN-analyzer. Total S in soil samples was determined with ICP-AES after digestion in 65% HNO_3. Total SO_4 was extracted by 2 sequential batch extractions with 0.02 M NaH_2PO_4 using a soil:solution ratio (SSR) of 1:5. Water-soluble SO_4^{2-} was extracted by distilled water in two extractions with the same SSR. Sulphate in the extracts was determined by ion chromatography (IC Dionex DX-100). Desorption isotherms were determined by extracting 20 g of soil with water in 6 sequential steps. Equilibration time in each step was 18 h, and the SSR was 1:3 for the first two extraction steps, 1:4 for steps 3–4 and 1:5 for steps 5–6. Samples were centrifuged and the supernatant solution was membrane filtered (0.45 μm). The amount of desorbed SO_4 was calculated from the SO_4 in solution at each step. The data were fitted to the Langmuir desorption isotherm:

$$S = S_o * c/(c + k), \quad k > 0 \qquad (1)$$

where S is desorbed SO_4^{2-}, c is SO_4^{2-} concentration in the equilibrium soil solution, S_o is sorption maximum, k is half maximum saturation point.

Aluminum, Fe and Si contents were determined with dithionite–citrate (Al_d, Fe_d and Si_d), oxalate (Al_o, Fe_o and Si_o) and pyrophosphate (Al_p, Fe_p and Si_p) solutions (Murashkina et al., 2005). Since geochemical properties are generally not normally distributed, non-parametric statistical description was used when appropriate in order to compare with the literature data. Correlation coefficients significant at the 0.05, 0.01 and 0.001 levels of probability are indicated in the text by *, ** and ***, respectively.

3. Results and discussion

3.1. Total concentrations of sulphur in soils

The total S in the O horizon of investigated soils ranged from 23 to 93 mmol/kg, with a median of 53 mmol/kg (Table 1). This is within the range reported by Reimann et al. (1998) for the central Barents region (12.5–120 mmol/kg, with a median of 48 mmol/kg). Organic horizons accumulated the highest total content of S within profiles (Table 1). The lowest S content was determined in the E horizon (median 1.6 mmol/kg) and the highest in the underlying B_{sh} horizons (4.1 mmol/kg) with decreasing concentration in the C layer (2.0 mmol/kg). Even though mineral horizons had low S contents, they usually represented the dominant S storage at all sites (74–98% of the total S storage in the 0.5 m layer). The O horizons contributed from 2 to 26% of the total soil S pool, with the exception of the most polluted site, the barren land, which had 52–66% of the total S in O horizons.

The soils developed on glacial till accumulated higher amounts of S (29–35 kmol/ha in the top 0.5 m layer) than those derived from glaciofluvial deposits (16–23 kmol/ha). Total S was positively correlated to the content of clay ($r = 0.90^{***}$, $n = 62$) and amorphous Al and Fe oxides ($r = 0.77^{***}$), as well as to total C ($r = 0.65^{***}$) and N ($r = 0.67^{***}$).

Spatial distribution of total S in Kola soils seems to be depended both on pollution and natural factors. Total concentrations of S in the organic horizons tended to be higher near the smelter (correlation with distance $r = -0.67^*$; Fig. 2). Total concentrations of S in the organic horizons was also weakly correlated with S deposition, however the differences between total concentrations of S in heavily polluted and background plots was not as high as those for S deposition. Even though the correlation was significant over the whole range of distance, there is a stronger correlation for up to 16 km distance, with S contents appearing to be rather unaffected for distances >20 km (Fig. 2). The total S concentrations of the mineral soil horizons did not correlate with distance from the pollution source. The latter is most likely due to the low storage capacity in the mineral soils of the acid sandy podzols. Previous studies from the surroundings of Nikel and Zapolyarnyy, did not find any relationship between distribution of total soil S and atmospheric S load (Niskavaara et al., 1996; Räisänen

Table 1
Total, organic, phosphate-extractable and water-soluble S in podzols of the Kola Peninsula

Horizon	Parameter	C (%)	N (%)	C/N (mol/mol)	C/S (mol/mol)	N/S (mol/mol)	C/N/S (mol/mol)	S_{tot} (mmol/kg)	S_{org} (mmol/kg)	S_{phos} (mmol/kg)	S_{H_2O} (mmol/kg)	S_{phos}/S_{tot} (%)	S_{H_2O}/S_{tot} (%)	S_{H_2O}/S_{phos} (%)
O ($n = 13$)	Mean	37.7	1.1	42	700	16	425/10/0.64	52.9	51.2	1.8	4.5	4	8	300
	Median	42.1	0.96	42	790	17	423/10/0.57	46.9	46.2	1.7	3.4	3	8	235
	Std	11.5	0.36	12	320	5	117/10/1.96	20.2	20.0	0.84	3.1	2	3	200
	Min	11.7	0.58	21	105	4	212/10/2.24	22.7	22.0	0.69	0.77	1	3	100
	Max	48.0	1.8	62	1140	21	622/10/0.47	92.7	90.2	3.4	12.9	8	14	600
E ($n = 13$)	Mean	0.95	0.04	29	415	14	286/10/0.72	2.2	2.1	0.14	0.17	5	8	150
	Median	0.68	0.03	26	360	14	257/10/0.74	1.6	1.6	0.07	0.10	5	7	150
	Std	0.68	0.03	13	280	5	126/10/1.83	2.3	2.0	0.23	0.19	3	3	50
	Min	0.33	0.01	13	140	5	128/10/1.83	0	0	0.04	0.06	2	3	44
	Max	2.5	0.13	55	1070	26	551/10/0.39	9.4	8.6	0.88	0.73	11	17	220
B_{sh} ($n = 22$)	Mean	1.2	0.05	31	170	6	313/10/1.7	5.9	3.2	2.7	0.48	40	10	58
	Median	0.90	0.04	31	160	5	313/10/1.9	4.1	3.0	2.0	0.42	37	7	20
	Std	1.1	0.04	8	80	3	79/10/2.99	3.4	1.8	2.6	0.32	26	7	92
	Min	0.29	0.01	18	64	2	184/10/5.79	1.8	0.18	0.12	0.06	4	1	1
	Max	4.8	0.18	44	325	15	443/10/0.68	12.4	8.9	8.7	1.3	95	27	410
BC ($n = 13$)	Mean	0.41	0.02	29	120	4	285/10/2.3	3.2	1.8	1.4	0.28	33	10	84
	Median	0.37	0.02	26	110	4	263/10/2.3	2.8	1.9	0.72	0.24	30	9	33
	Std	0.23	0.01	8	59	2	79/10/4.02	1.8	0.54	1.6	0.22	21	9	145
	Min	0.12	0	19	49	0	–	1.2	0.93	0.03	0.03	2	1	2
	Max	0.95	0.04	43	280	8	432/10/1.32	7.6	2.7	6.0	0.75	78	28	540
C ($n = 14$)	Mean	0.23	0.01	26	93	4	262/10/2.8	2.0	1.4	0.61	0.12	26	6	66
	Median	0.19	0.01	23	76	4	230/10/2.6	2.0	1.5	0.49	0.11	20	7	28
	Std	0.16	0.01	10	47	3	100/10/3.96	0.83	0.66	0.58	0.08	27	4	71
	Min	0.08	0	15	43	0	–	0	0	0.03	0.02	1	1	4
	Max	0.64	0.03	53	200	9	525/10/1.12	3.5	2.3	1.7	0.31	110	11	220

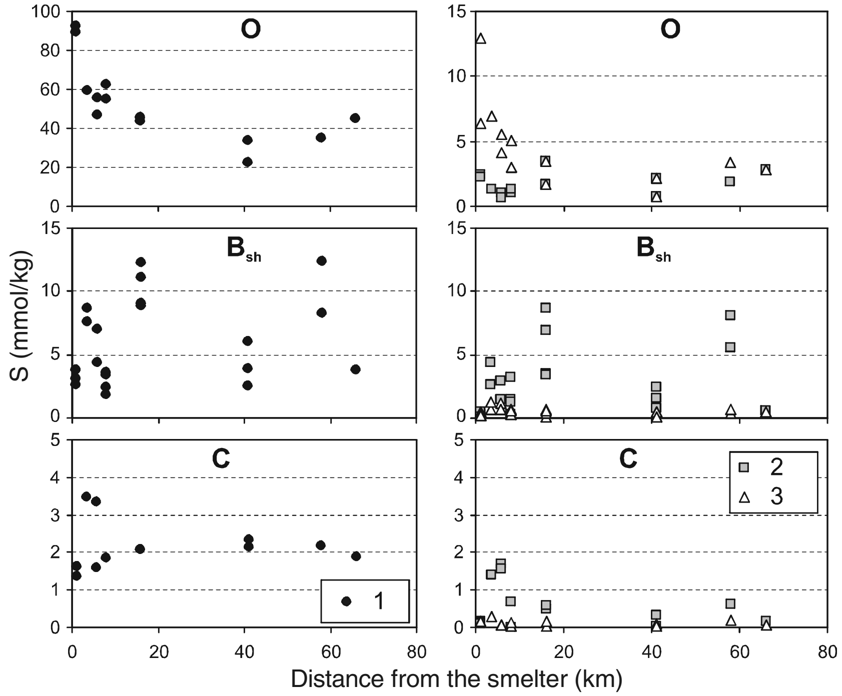

Fig. 2. Total (1), phosphate-extractable (2) water-soluble (3) S in organic (O), illuvial (B_{sh}) and C-horizons of podzols along the pollution gradient.

et al., 1997). The results of geochemical mapping of the Central Barents region did not reveal the anthropogenic enrichment of the organic horizon of the podzols with S despite the S input from the Kola smelters (Kashulina and Reimann, 2002). The B-horizon contained elevated median concentrations of total S in polluted Russian territories (5.7 mmol/kg) compared with Finnish (4.8 mmol/kg) and Norwegian (4.2 mmol/kg) territories (Reimann et al., 1998). However, S concentrations were highly variable and reflected mainly geogenic sources. The relatively weak relationship between atmospheric S deposition and soil S content in the Kola Peninsula may be due to 3 causes: (i) the relatively low S load compared with e.g. Central Europe, (ii) the low storage capacity of the acid sandy soils and (iii) most of the SO_2 is emitted via high chimneys thus contributing rather to long range transport than to local deposition. Novák et al. (1996; for Central Europe) and Novák et al. (2001; for a NW-SE European transect) reported statistically significant straight-line positive relationships between the atmospheric S input and total S concentration in the topsoil. A significant correlation was also found between total S content in the soil organic and mineral layers and the input of S from atmosphere in forest ecosystems of the USA (Mitchell and Lindberg, 1992). The impact of 40 a of S emissions from a sour gas processing plant in Alberta (Canada) has also lead to the increase in soil S pools caused by accumulation of organic S in the forest floor and accumulation of inorganic SO_4 in the mineral soil (Prietzel et al., 2004).

3.2. Concentrations of organic sulphur in soils

Sulphur in O horizons was mainly present as organic S. Organic S, calculated from total S by subtracting inorganic S (phosphate-extractable sulphates), varied between 22 and 90 mmol/kg in the organic horizons, with a median of 46 mmol/kg, which represented 99% of the median of total S content (Table 1). Mineral horizons contained significantly lower amounts or organic S. The latter is due to the combined effects of catabolism and chemical precipitation of dissolved organic S in the mineral soil (Mitchell and Lindberg, 1992). Nevertheless, the dominant form of S in most mineral soils was also organic. Organic S varied from 0.2 to 8.9 mmol/kg, with a median of 3.0 mmol/kg in illuvial horizons representing 63% of the total S content. The organic S fraction varied greatly depending on soil texture and parent material decreasing in illuvial horizons from 60 to 96% for coarse sandy podzols on glaciofluvial deposits to 22–35% for podzols derived from till.

Organic S was highly significantly correlated with organic C (0.77^{***}) and with total N (0.86^{***}) in the mineral soils. The correlation was even higher for illuvial horizons (0.92^{***} and 0.90^{***}, respectively). Stable relationships between C, N and S for different groups of soils have been reported earlier in spite of great variations in climate and parent material (Freney and Stevenson, 1966). In the present study, the median molar C:N:S ratio was 420:10:0.57 for O-, 310:10:1.9 for B_{sh}- and 230:10:2.6 for C-horizons in the soils studied. Both C:N and N:S ratios decreased towards the smelter and the highest S_{org} was observed at the lowest C:N ratio in the O-horizon. The close correlation between total and organic S, total N and organic C indicated that organic S forms a stable fraction of soil organic matter, while changes in the ratios may be the result of either net incorporation of S into organic forms or just independent transformation.

Concentrations of organic S in the soil O-horizon increased towards the smelter ($r = -0.68^{**}$) while $C{:}S_{org}$ ratios decreased ($r = 0.72^{**}$) which might be due to direct SO_2 uptake or to SO_4 immobilisation by plants and/or microorganisms (Mitchell and Lindberg, 1992; Likens and Bormann, 1995). Elevated concentrations of S in pine needles occurred over the entire area studied (e.g. 26–37 mmol/kg), and concentrations were markedly increased (30–60 mmol/kg) at sites situated within 30 km of the smelter (Koptsik et al., 2001). The sites are located within the area defined by the isocurve of the annual mean atmospheric SO_2 concentration exceeding 10 μg/m^3 as given by Sivertsen et al. (1994). Sulphur concentrations in plants at severely polluted sites have been shown to be 2–4 times higher than those at control sites (Raitio et al., 1995; Steinnes et al., 2000). Furthermore, statistically significant correlations have been found between the annual mean SO_2 concentration and needle SO_4 concentration and S:N ratios at sites close to a pollution source (Manninen et al., 1998). Calculations based on the N concentrations of the needles and a background regional S:N ratio of 0.028 gave mean values of 5–14 mmol/kg of "excess" S in the needles of polluted sites compared with remote sites (Koptsik et al., 2001). In contrast to the Kola Peninsula region, Reimann et al. (2001) found that the very high levels of SO_2 emissions are generally not reflected by increases in plant total S-content at 9 catchments within a 1,500,000 km^2 area in northern Europe. Contribution of microbial transformations to accumulation of S in organic forms is poorly known (Mitchell and Lindberg, 1992). Houle et al. (2001) showed that despite significant $^{35}SO_4$ microbial immobilisation such a contribution is not likely to exceed 1% of the total organic S in podzol under a coniferous forest in Quebec, Canada.

Gustafsson and Jacks (1993) showed that organic S retention does not seem to be an important mechanism at two sites in SW (a 400-kV powerline area, 30 kg S/ha/a) and central (an experimental plot in 15 a after a yearly application of 49 kg S/ha during 5 a) Sweden. However, those sites received considerably higher S deposition than the Kola sites (up to twice as much) and sites were characterized by higher SO_4 adsorption capacities. There is evidence from isotope studies that deposited inorganic SO_4^{2-} cycles through an organic soil pool both at high (>70 kg/ha/a) and low atmospheric deposition in the Czech Republic (Novák et al., 1996). Based on the dominance of organic S levels relative to adsorbed SO_4 in coarse grained podzols in the current study, organic S formation may represent a key S retention mechanism. According to Mitchell and Lindberg (1992) and Alewell (2001) organic S formation can be an important long-term S retention mechanism. The recent discussion about reversibility of acidification comes to the conclusion that adsorbed inorganic SO_4 is the dominant fraction as long as soils have a high S content and/or receive high deposition rates (Alewell, 2001). With low storage in inorganic SO_4 and decreasing SO_4 deposition, organic S storage and the biological turnover of S becomes increasingly important (Alewell et al., 2000; Alewell, 2001). This conclusion is supported by the results of stable S isotope analysis in the roofed catchment experiment at Gårdsjön, Sweden: while in the initial years of clean precipitation treatment the desorption of SO_4 from the mineral soil appeared to control the runoff SO_4 concentration, net mineralization of soil organic S in the humus layer was an additional source of SO_4 in runoff during the later years of the experiment (Moldan et al., 2004). The recent results of S retention/release studies in 13 Central European forested catchments using S isotopes indicated that organic S cycling plays an important role over a wide range of atmospheric S inputs from 13 to 130 kg S/ha/a (Novák et al., 2000, 2005).

3.3. Concentrations of phosphate-extractable sulphates in soils

Highest contents of Na_2HPO_4-extractable sulphates can be expected in soil B_{sh} horizons which are enriched in Fe and Al sequioxides. Phosphate-extractable sulphate ranged from 0.12 to 8.7 mmol/kg with a median of 2.0 mmol/kg, which represents 37% of the total S (Table 1). The fraction of phosphate-extractable SO_4 did not exceed 20–40% of the total S in mineral horizons of podzols on glaciofluvial deposits and reached 80% of the total S for podzols derived from till. Similar amounts of phosphate-extractable sulphates (1–9 $mmol_c$/kg) were found in spodic B horizons in the northernmost Fennoscandia (Gustafsson, 1996). The low values of phosphate-extractable sulphates is explained by the low adsorption capacity of acid sandy podzols.

A close relationship between phosphate-extractable sulphates and clay ($r = 0.90^{***}$) was found. Phosphate-extractable SO_4 was also well correlated with Al_o ($r = 0.76^{***}$) and Al_o–Al_p ($r = 0.81^{***}$) reflecting the fact that SO_4 can be bound specifically or unspecifically to Al oxides. However, the best linear fit was achieved between extractable sulphates and Al_o–Al_d ($r = 0.88^{***}$) and Si_o–Si_d ($r = 0.85^{***}$) values. These data support the results of Gustafsson et al. (1995) who showed that SO_4^{2-} adsorption occurred mainly at the Al–OH sites of imogolite-type materials.

3.4. Concentrations of water-extractable sulphates in soils

The water-extractable sulphates ranged between 0.77 and 13 (median 3.1) mmol/kg in organic horizons, and between 0.06 and 1.25 (median 0.42) mmol/kg in illuvial horizons (Table 1). The water-extractable sulphates accounted for a median of 7% of total S content in both horizons. The water-soluble fraction did not exceed 30% of the phosphate-extractable SO_4 fraction in mineral horizons of podzols derived from till. However, the greater part of phosphate-extractable SO_4 in podzols on glaciofluvial deposits was found in water-soluble form.

The water-extractable sulphates were significantly correlated with total ($r = 0.92^{***}$) and organic S ($r = 0.92^{***}$), organic C ($r = 0.65^{***}$) and total N ($r = 0.75^{***}$). The correlation with organic S was highest for the organic ($r = 0.84^{***}$), absent for illuvial and minimal for mineral ($r = 0.53^{***}$) horizons. In the latter case, a significant correlation ($r = 0.43^{***}$) between water- and phosphate-extractable sulphates was observed. These relationships might indicate that organic S is in some kind of equilibrium with water-extractable sulphates in the investigated podzols. Moldan (1999) determined a net release of S from organic matter in the soil at Gårdsjön, Sweden. This coincides with the results of stable S isotope investigations indicating that a considerable proportion of the atmospherically deposited SO_4 is cycled through the organic S pool before being released to soil solution and stream water (Alewell and Gehre, 1999; Alewell, 2001).

The water-extractable SO_4 concentrations of O-horizons were higher in soils near the pollution source (Figs. 2 and 3). The S_{H2O}/S_{tot} ratio significantly increased with decreasing distance from the smelter not only in the illuvial ($r = -0.52^{*}$) but also in all mineral horizons ($r = -0.38^{***}$). Thus, soils nearer to the smelter contained more water-soluble S compared to phosphate-extractable S, emphasising the increased mobility of S near the pollution source. Elevated concentrations of water-extractable sulphates were observed in B-horizons of Norwegian and Finnish soils situated close to the smelter (Gustafsson, 1996). In a catchment-based study in the Kola Peninsula, increased concentrations and a higher proportion of water-extractable S were found in the most polluted catchments both in the B- and C-horizons (Kashulina and Reimann, 2001). Due to increased mobility of sulphates, soil solutions close to the smelter can be expected to be acidified. Near the Cu–Ni smelter "Severonikel"

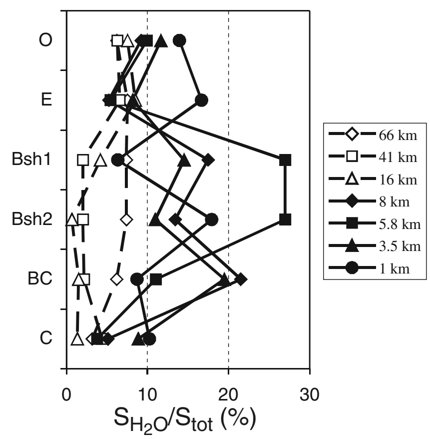

Fig. 3. Mobility of sulphates in podzols at different distances from the smelter.

in the central part of the Kola Peninsula, enlarged concentrations of sulphates and decreased pH values have been found in soil waters (Gorbacheva, 2001). Besides sulphate desorption, net S mineralisation may contribute to the S flux as has been shown for the forested catchment at Lake Gårdsjön (Mörth and Torssander, 1998; Moldan et al., 2004).

3.5. Sulphate adsorption in soils

The SO_4^{2-} desorption isotherms from the B_{sh} and BC horizons have a high degree of spatial variation (Fig. 4). By fitting the data from the polluted soils to Eq. (1) parameters of the Langmuir isotherms were determined. The median isotherm for B_{sh} horizons was significantly higher than the median isotherm for BC horizons (Fig. 4). The slope of the isotherms for the B_{sh} and BC horizons down to SO_4^{2-} concentrations of 0.04 mmol/L was generally low indicating low adsorption capacity in this concentration range. Thus, sorption processes in the frequently occurring concentration range from 0.04 to 0.1 mmol/L poorly buffer the SO_4^{2-} in solution. The maximum sorption capacity (S_o) increased while the half saturation point (k) decreased from BC to B_{sh} horizons. The high spatial variation of the parameters of the isotherm can largely be explained by soil properties influencing SO_4^{2-} sorption. The correlation of the sorption maximum S_o with pH, C_{org}, Al_o and Fe_o was statistically significant. For the half maximum saturation concentration k no significant correlation was found. Manderscheid et al. (2000) found significant relationships between SO_4 sorption isotherm parameters and soil chemical properties for each soil studied; however, they varied for different soils.

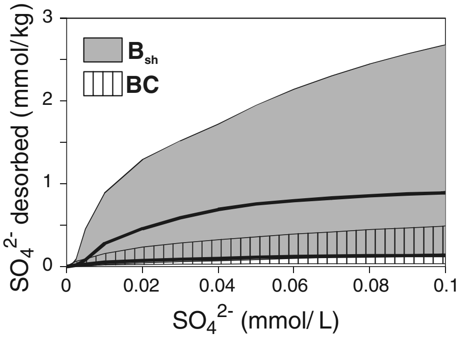

Fig. 4. Median SO_4 desorption isotherms (med) and their 10- and 90-percentiles for B_{sh} and BC horizons of podzols.

4. Conclusions

The thin sandy podzols of the Kola Peninsula developed on till and glaciofluvial deposits under scarce pine forests were characterised by low S content and storage (16–35 kmol/ha in the top 0.5 m layer). O-horizons accumulated the highest total amount of S within the profiles (22–93 mmol/kg). In the mineral soil, the highest S content occured in the B_{sh} horizons (2–12 mmol/kg).

Organic S was the predominant form of S in organic horizons of all soils and in mineral horizons of coarse podzols derived from glaciofluvial deposits. Organic S formation represents an important S retention mechanism, especially in coarse podzols with low SO_4 adsorption capacity, and may control reversibility of acidification. Because organic S is relatively stable in soils, low SO_4 release is expected from this S fraction and thus a relatively fast recovery of soil solution and waters under decreasing deposition scenarios. However, the major part of phosphate-extractable SO_4 in podzols (20–40% of total S) on glaciofluvial deposits was water-soluble. In mineral horizons of podzols derived from till the water-soluble fraction did not exceed 30% of phosphate-extractable SO_4 but the latter comprised 80% of the total S. Thus, some smaller amounts of SO_4 might be released and minor delay in recovery should be expected at all sites.

The concentrations of total and organic S in the organic horizon tended to be higher near the smelter and a clear relationship was determined for a maximum of 16 km distance. Computed for the total range of distance (up to 66 km) correlation of soil S concentrations with distance of smelter was medium and only a weak correlation was found with the modelled S deposition. Neither the total S nor the phosphate-extractable SO_4 concentrations of the mineral soil horizons correlated with the distance from the pollution source. It is concluded that long range transport due to the high chimneys of the smelter and diffuse input of SO_4 rather than point source dynamics plays an important role on the Kola Peninsula.

Acknowledgements

We are grateful to Dr. M. Novák, Dr. A. Golab and an anonymous reviewer for important comments and suggestions. The work was supported by the German Ministry for Education, Science, Research and Technology (Grants No. PT BEO 51–0

339476) and Russian Foundation for Basic Research (05-04-48460-a).

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