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pH buffering in acidic soils developed under *Picea abies* and *Quercus robur* – effects of soil organic matter, adsorbed cations and soil solution ionic strength

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Soil solution chemistry, soil acidity and composition of adsorbed cations were determined in two soil profiles developed under a mixed spruce (*Picea abies* and *Picea sitchensis*) stand and in one soil profile developed under an oak (*Quercus robur*) stand. Soils under spruce were classified as Spodosols and soils under oak were classified as Inceptisols. All profiles were developed in the same parent material; a Saahlian sandy till containing less than 2% clay. In the mineral soil, the contribution from mineral surfaces to the total cation-exchange capacity (CEC_t) was estimated to be less than 3%. Soil solution pH and the percent base saturation of CEC_t [%BS = 100 (2Ca + 2Mg + Na + K) CEC_t^{-1}] were substantially lower in the upper 35–40 cm of the two Spodosols, as compared to the Inceptisol. The total amount of soil adsorbed base cations (BC) did not differ among the three profiles on an area basis down to 1 m soil depth. Thus, soil acidification of CEC_t due to net losses of BC could not explain differences in soil pH and %BS among the soil profiles. A weak acid analogue, taking the pH-effect of metal complexation into consideration, combined with soil solution ionic strength as a covariate, could describe both the pH variation by depth within soil profiles and pH differences between the Inceptisol and the two Spodosol profiles. Our results confirm and extend earlier findings from O and E horizons of Spodosols that the extent to which organic acid groups react with Al minerals to form Al-SOM complexes is a major pH-buffering process in acidic forest soils. We suggest that an increasing Al-saturation of SOM is the major reason for the widely observed pH increase by depth in acidic forest soils with a pH less than approximately 4.5. Our results strongly imply that changes in mass of SOM, the ionic strength in soil solution and the relative composition of soil adsorbed Al and H need to be considered when the causality behind changes in pH and base saturation is investigated.

Introduction

Based on their interpretation of results from studies conducted in Scandinavian soils, Nilsson and Tyler (1995) concluded that there is strong evidence that atmospheric deposition of acidifying S and N compounds is the major cause behind decreasing soil pH and base saturation of cation-exchange sites in acid forest soils of southern Sweden. In contrast, Binkley and Högberg (1997), in a critical review of studies which have been frequently referred to as evidence for a recent soil acidification by acid deposition, argue that changes in the mass of soil organic matter (SOM), its inherent acid-base properties, the composition of adsorbed major cations and the soil solution ionic strength, rather than atmospheric deposition of S and N, in many cases may explain changes in soil pH over time.

Many different factors may influence the pH value in acidic forest soils. One factor which we believe has not received proper attention is the organic complexation of Al and how it may regulate pH in soils. After Bloom et al. (1979) proposed exchange processes between H^+ and Al-cations to be an important regulator of dissolved inorganic Al in acidic tropical soils, many studies have verified the effect of SOM on Al-solubility in other acidic soils (e.g. Walker et al. 1990; Wesselink et al. 1996; Simonsson & Berggren 1998). Most of these studies have been performed as laboratory experiments in which pH has been manipulated and viewed as a master variable for Al-solubility. Although it is correct that pH affects the solubility of Al, the organic complexation of Al itself may act as a very important pH-regulator in acidic soil (Mulder et al. 1989; Skyllberg 1994).

As pointed out by Skyllberg (1999), chemical models based on a pH-dependent Al-mineral solubility combined with cation-exchange reactions between dissolved Al-ions (mainly Al^{3+}) and base cations (e.g. Reuss et al. 1990) are restricted to a situation when soil chemical processes give rise to a positive relationship between pH and the base saturation (c.f. Reuss 1983). A typical case is the response of a soil sample to additions of strong acid or base, e.g. effects of acid rain or liming. In contrast, acid-base processes naturally active in organic rich acidic soils often give rise to a non-consistent, or even negative, relation between pH and the base saturation (Skyllberg 1994, 1999; Ross et al. 1997). The main reason for this is that pH-effects due to cation-exchange reactions between acid cations (H^+ or Al^{3+}) and base cations are overruled by pH-effects caused by reactions between Al-minerals and organic acid functional groups. The latter reaction gives rise to a variation in the ratio between organically adsorbed Al and H. An increase in the Al/H ratio results in an increased pH value, which can be explained by a weaker acidity of the organic Al-complex, as compared to the protonated form of the same organic acid site (Hargrove & Thomas 1982).

Skyllberg and Borggaard (1998) showed that acid-base titration data for the O, E, Bh and Bs horizons of the Spodosol profile used in this study could be described by a simple weak organic acid analogue, when the effect on pH caused by organically complexed Al was taken into consideration. This might suggest that weak acidic groups of SOM are the main pH buffers throughout acid Spodosol profiles and that pH effects caused by changes in the quality of SOM play a relatively minor role as compared to the composition of organically adsorbed major cations (especially Al and H).

In this study we test the hypothesis that the composition and binding strength of organically adsorbed major cations (Ca, Mg, K, Na, Al and H) and the ionic strength of soil solution are the major pH determining factors in acidic forest soils lacking significant contents of secondary clay minerals and with pH values below approximately 4.5. We used soil chemical data from three soil profiles (two Spodosols and one Inceptisol) developed in the same geological parent material but under different vegetation types.

Material and methods

Soil and site description

For the purpose of this study, soils developed under a coniferous and an oak stand located in south-west Denmark (Lovrup Skov, Ribe, 55°14′N 8°89′E), were utilised. At the time of soil sampling in March 1995, the coniferous stand was dominated by 53-years-old Norway spruce (*Picea abies*) mixed with a few Sitka spruces (*Picea sitchensis*). Field layer vegetation was absent and feather mosses covered a well-developed O horizon (humihemimor according to classification by Klinka et al. 1981). The oak stand (*Quercus robur*) was regrown after cut to root in the 1860s and had a well-developed field layer of grasses and herbs, but no feather mosses. Two soil profiles in the mixed spruce stand and one profile in the oak stand were sampled within 200 meter from each other. The parent material was similar in all profiles and consisted of a sandy glacial till deposited during the Saahlian glaciation. The two profiles in the coniferous stand were classified as Spodosols (Haplorthods) and the profile in the oak stand was an Inceptisol (Dystrocrept), Soil Survey Staff (1997). X-ray diffraction data for the mineralogy of the Spodosol II profile are given in Skyllberg and Borggaard (1998). Within a transition zone of approximately 10–15 meters, coinciding with the boundary between the coniferous and hardwood stands, the Spodosol was gradually changed into the Inceptisol, and *vice versa*. The Spodosols can be supposed to have been developed under coniferous forests and possibly under heather (*Calluna vulgaris*), which most probably covered at least parts of the area prior to plantation of Norway spruce. The Inceptisol is known to have been covered by oak for at least 300 years. A detailed morphological description of the three soil profiles is given in Appendix.

The three profiles (Spodosol I, II and Inceptisol) were sampled by horizons. Composite samples consisting of five single samples with a known volume were taken by use of steel cylinders, with a diameter of 7 cm and a depth of 5 cm. In addition, the O (O/A in the Inceptisol) and A horizons of both Spodosols and the Inceptisol were sampled systematically at 18 sites approximately 15–25 m apart along a line, nine within the spruce stand and nine within the oak stand. Samples were kept in cooling bags when brought to the laboratory where they were stored in darkness at 4 °C. Three additional cylinder volumes were taken at each sampling depth for the determination of bulk density of the soil fraction less than 2 mm.

Chemical analyses

The moist composite samples were centrifuged at 4000 g for 30 min within 2 days after sampling with a RC-5B Sorvall centrifuge (Norwalk, Connecticut, USA) and the centrifugate was collected in one homogenised sample. The centrifugate was immediately analysed for pH (691 pH-Meter, Metrohm, Switzerland), dissolved ions (Ca, Mg, K, Na, Mn, Al, Fe, Si, NH_4, Cl, SO_4, NO_3) and unfiltered dissolved organic carbon (TOC). Cations were analysed by flame atomic absorption spectroscopy (AAS, Perkin Elmer 5000, Norwalk, Connecticut, USA), the anions by ion chromatography on a Spectra 100 (Spectra-Physics, San Jose, California, USA), ammonium by the Berthelot-reaction and TOC as CO_2 by IR spectroscopy following oxidation in a 600 °C oven (Shimadzu TOC 500, Kyoto, Japan). Aluminium was determined as reactive Al (free Al^{3+} and inorganic complexes) by a slight modification of the method of Driscoll (1984). Concentration of Al^{3+} was calculated by the speciation programme MINTEQA2 (Allison & Brown 1995), taking dissolved inorganic fluoride, sulphate and hydroxide complexes into consideration. Duplicates of centrifuged soil, homogenised through a 2 mm screen, were extracted for adsorbed cations. Duplicates of organic soil samples corresponding to 0.5 grams of dry soil, or mineral soil samples corresponding to 2.0 grams of dry soil, were suspended in 20 ml of 0.5 *M* $CuCl_2$ and were shaken for 3.5 hours. After centrifugation for 10 minutes at 12 100 g, Ca, Mg, K, Na, Al and Fe were determined by AAS. Total acidity was determined in m-nitrophenol at pH 8.1 following the method of Piper (1944). Total soil N was analysed by the Kjeldahl method and total soil C on a Leco Carbon analyser (Tabatabai & Bremmer 1970). Aluminium extracted by 0.5 *M* $CuCl_2$ was taken as trivalent and organically bound. Organically bound hydrogen ions were calculated as the difference between total acidity and charges of organically bound Al (trivalent).

Soil pH modelling

Three semi-empirical models were used to interpret the pH-buffering processes in the soils. Model (1) relates pH to the degree of protonation of SOM sites (represented by the cation-exchange capacity at pH 8.1):

$$\mathrm{pH} = a - b \log \mathrm{I} - c \log \left(100\,[\mathrm{H}]\,\mathrm{CEC}_{\mathrm{pH}\ 8.1}^{-1}\right) \tag{1}$$

Model (1) is a simplified version of an acid analogue, lumping together SOM sites binding other cations than H^+ as non-protonated. The term [H] denotes soil adsorbed hydrogen ions, determined as total acidity at pH 8.1 subtracted by $CuCl_2$ extracted Al (assumed trivalent). The units of [H] and $\mathrm{CEC}_{\mathrm{pH}\ 8.1}$ are $\mathrm{mol_c\ kg^{-1}}$ (note that they will cancel in equation 1). The ionic strength (log I, mM) in soil solution is included as a covariate in the model. Parameters a, b and c are empirically fitted constants.

Model (2) is an extension of model (1) by considering pH-effects caused by differences in bonding strength of monovalent (Na^+ and K^+), divalent (Mg^{2+} and Ca^{2+}) and trivalent (Al^{3+}) metal cations to SOM sites. The binding strength is expressed as degree of specific adsorption. A specifically adsorbed cation is considered to form a surface complex with SOM sites whereas a non-specifically adsorbed cation contributes to the electroneutrality in the diffuse layer. Skyllberg et al. (2001) used the Hendersson-Hasselbalch equation;

$$\mathrm{pH} = a + b \log \left([\equiv \mathrm{RO}^-]/[\equiv \mathrm{ROH}]\right) \tag{2a}$$

a widely used weak-acid analogue, to determine the degree of specific bonding of Ca^{2+} and Al^{3+} in organic soils. In this model dissociated acid sites, $\equiv RO^-$, represent SOM surface charges balanced by non-specifically adsorbed metal cations. The term $\equiv ROH$ represents protonated sites determined as the total acidity at pH 8.1 subtracted by charges attributed to adsorbed Al. Based on the assumption that Na^+ and K^+ do not bind specifically to SOM sites, Skyllberg et al. (2001) calculated 45–61% (pH 3–6) of adsorbed Ca^{2+} and 80–92% (pH 3–4) of adsorbed Al^{3+} to be specifically adsorbed in five organic horizons.

In equation (2a) surface concentrations [ ], have the unit $\mathrm{mol_c\ kg^{-1}}$. The terms a and b are constants obtained by fitting the equation to data. The constant a traditionally has been interpreted as a conditional constant reflecting the average apparent acid strength of surface sites ($\mathrm{pKa^{app}}$, e.g.

Stevenson, 1994) and *b* the electrostatic effects at the charged surface. When applying equation (2a) to our soil data we assume that Na^+ and K^+ adsorb to negative surface sites in the diffuse layer ($\equiv RO^- - Me^+$). Divalent and trivalent cations (Ca^{2+} and $Mg^{2+} = Me^{2+}$ and $Al^{3+} = Me^{3+}$) are assumed to associate with SOM either as surface complexes ($\equiv ROMe_{1/2}$ and $\equiv ROMe_{1/3}$) or as adsorbed ions in the diffuse layer ($\equiv RO^- - 1/2\ Me^{2+}$ and $\equiv RO^- - 1/3\ Me^{3+}$). For the pH-range of our soils (3.5–4.5), Skyllberg et al. (2001) found an average specific bonding of 45% for Ca^{2+} and Mg^{2+} and 80% for Al^{3+}. Thus, 55% (100 – 45%) of $CuCl_2$ extracted Ca and Mg and 20% (100 – 80%) of $CuCl_2$ extracted Al can be assumed to neutralise SOM sites in the diffuse layer, i.e. as counter-ions to $\equiv RO^-$. A substitution of $[\equiv RO^-]$ for adsorbed cations in the diffuse layer and $[\equiv ROH]$ for organically adsorbed H, and inclusion of the soil solution ionic strength as a covariate in equation (2a), yields the final form of model (2):

$$\begin{aligned} \mathrm{pH} = \; & a - b \log \mathrm{I} + c \log (([\mathrm{K}] + [\mathrm{Na}] + 0.55 \\ & ([\mathrm{Ca}] + [\mathrm{Mg}]) + 0.20\,[\mathrm{Al}])\,[\mathrm{H}]^{-1}) \end{aligned} \tag{2b}$$

Note that [ ] designates concentrations of surface charges ($mol_c\ kg^{-1}$) and that the unit of I is mM.

Model (3) is a semi-empirical Al-H cation-exchange model which was found to give a fair fit to soil data in Spodosol O and E horizons (Skyllberg 1999):

$$\log (\{\mathrm{Al}^{3+}\}/\{\mathrm{H}^+\}^3) = a + b \log ([\mathrm{Al}]/[\mathrm{H}]) \tag{3a}$$

The model builds on the Gapon equation for cation-exchange and relates the ratio of soil solution activities of Al^{3+} and H^+ to the ratio of fractions of soil surface sites adsorbing Al and H. The brackets [] denote units in $mol_c\ kg^{-1}$. The equation was written in the following form when applied to our data:

$$\log\{\mathrm{Al}\} + 3\mathrm{pH} = a + b \log ([\mathrm{Al}]/[\mathrm{H}]) \tag{3b}$$

The model is tested by plotting log ([Al]/[H]) against log {Al} + 3pH. The fitted intercept *a* may be interpreted as a conditional Al-H exchange constant (log $K_{Al/H}$, Skyllberg 1999), whereas the slope *b* may partly account for electrostatic effects at soil surfaces.

Results and discussion

Mass of elements on an area basis and quality differences in SOM

On an area basis down to 1 m depth, the two Spodosol profiles had larger masses of accumulated carbon than the Inceptisol (Table 1). The mass of

Table 1. Total mass of carbon (C) and nitrogen (N), sum of charges pertaining to adsorbed alkali and alkaline earth cations ('base cations' BC = 2Ca + 2Mg + K + Na), total acidity and sum of Al charges (assuming trivalent Al^{3+}) calculated per hectare and one meter soil depth

Profile	C[1]	N[2]	BC	Total acidity[3]	Al[4]
	$Mg\ ha^{-1}\ m^{-1}$		$kmol_c\ ha^{-1}\ m^{-1}$		
Spodosol I	154	4.7	25.6	1300	544
Spodosol II	160	4.4	25.1	1520	598
Inceptisol	105	4.5	24.5	1330	577

[1] Determined by dry combustion (LECO analyser, Tabatabai and Bremmer, 1970).

[2] Determined by the Kjeldahl method.

[3] Determined by titration to pH 8.1 (Piper, 1944).

[4] Determined by AAS after one equilibrium extraction in 0.5 *M* $CuCl_2$.

nitrogen was on the other hand similar for all three profiles, resulting in integrated C/N ratios of 33 and 36 in the two Spodosols profiles down to 1 m, as compared to 23 in the Inceptisol. It should be noted that there was no obvious trend in C/N ratio with depth in any of the three profiles and that the Inceptisol showed lower values throughout the profiles. Considering that SOM in the Inceptisol originates from litter of oak, herbs and grasses and SOM in the Spodosols originates from litter of spruce and possibly *Calluna* heath, the difference in C/N ratio is what we may expect. Thus, as a C and N substrate for microorganisms, SOM quality differences may be greater among the soil profiles than with depth within a profile.

The absolute amount of soil adsorbed base cations on an area basis was similar for all three profiles (Table 1), but the total acidity (adsorbed H + Al) was substantially higher in Spodosol II. The soils in this study are very low in clay content and easily soluble basic minerals. Therefore, CEC sites binding major non-acidic cations (Ca, Mg, K and Na) are the main contributors to the acid neutralisation capacity (ANC) available in a short-term perspective (i.e. much shorter than silicate weathering would require). Thus, it can be concluded that the ANC available in a short-term perspective was quite similar for the three soil profiles in this study.

In general terms, the soil bulk density (BD) increased by depth in all three profiles (Table 2) and the variation with soil depth and site was a linear function of the concentration of organic C, irrespective of profile (BD [$Mg\ m^{-3}$] = 1.5 – 0.0053 org-C [$g\ kg^{-1}$], $n = 21$, r = 0.91). Enhanced concentrations of organic C in the Bs1 horizon of Spodosol I, in the Bh and Bhs horizons of Spodosol II and in the Inceptisol Bw1 horizon, coincided with a drop in the bulk density. In the lower B and in the C horizons, the concentration of organic C and the bulk densities were similar for the three soil profiles.

The total cation-exchange capacity ($CEC_{pH\ 8.1}$), calculated as the sum of the total acidity and 0.5 M $CuCl_2$ extracted BC, was 1326, 1545 and 1354 $kmol_c\ ha^{-1}\ m^{-1}$ in Spodosol I, Spodosol II and in the Inceptisol, respectively. The contribution from permanent charge sites of secondary clay minerals was approximately 42 $kmol_c\ ha^{-1}\ m^{-1}$ for Spodosol II, if the permanent charge of the Bs horizon (reported by Skyllberg and Borggaard 1998) of 3.5 $mmol_c\ kg^{-1}$ can be taken as a representative for mineral surface charges in B and C horizons (which likely results in an overestimation of mineral surface charges). Thus, mineral cation-exchange sites should contribute with less than 3% of $CEC_{pH\ 8.1}$ in the Spodosol profiles as a whole with a maximum of 5–6% in B and C horizons. We have no reason to believe these figures being significantly different in the Inceptisol.

Based on the fact that 95–97% of $CEC_{pH\ 8.1}$ was represented by SOM sites throughout the soil profiles, we can calculate the site density of SOM by a normalisation of $CEC_{pH\ 8.1}$ to the mass of organic C. The site density of SOM increased in a similar way by depth in all three profiles (Table 2). The increase by a factor of 5 from the O horizon to the lower part of the B horizon may reflect an age-gradient with older, more decomposed and highly, negatively charged SOM at greater depth. Thus, from a surface charge perspective, larger differences in SOM quality were found with depth within a profile than among profiles. It can be noted that in the mineral soil horizons calculated site densities of SOM fall within the interval given by Buffle (1973) for humified soil organic substances: 6.0–16.0 $mol_c\ kg^{-1}$ [C].

pH, base saturation and soil solution ionic strength

Soil solution pH was lower in all horizons of the Spodosols, as compared to the Inceptisol (Table 2). The difference was most pronounced at approximately 20 cm depth into the mineral soil, in the upper part of the B horizons, where Spodosols commonly accumulate SOM. It can be noted that all three profiles showed a pH minimum in the A horizon.

The percent base saturation [$\%BS = 100\ BC\ (CEC_{pH\ 8.1})^{-1}$] decreased by depth in all profiles and was fairly similar in all three B horizons (Table 2). In the lower B and C horizons, %BS increased with depth in all three profiles. Also the %H saturation of cation-exchange sites [$100\ [H]\ (CEC_{pH\ 8.1})^{-1}$] in general decreased by depth in all three profiles, reaching 35–38% of $CEC_{pH\ 8.1}$ in all three C horizons. The %Al saturation increased by depth and reached 61–62% of $CEC_{pH\ 8.1}$ sites in the C horizon of all profiles. It is interesting to note that the %Al saturation did not correlate significantly with the content of SOM in the mineral soil horizons (Table 2).

Table 2. Bulk density and selected chemical data for Spodosol I, II and the Inceptisol

	depth cm	bulk density $Mg\ m^{-3}$	OC[1] $g\ kg^{-1}$	pH[2]	I[3]	I[4]	CEC[5] $mol_c\ kg^{-1}\ C$	BC[6]	Al	H
								% of $CEC_{pH\ 8.1}$		
Spodosol I										
O	–12–0	0.11	296	3.56	2.6	2.4	3.1	9.1	4.9	86
A	0–2	1.15	55	3.49	3.1	2.4	4.6	6.1	8.2	86
E	2–10	1.44	17	3.50	3.2	2.4	4.7	3.5	14	83
BE	10–20	1.44	12	3.54	2.9	2.4	6.9	2.1	22	76
Bs1	20–40	1.34	15	4.09	2.5	1.6	11.2	0.4	48	51
Bs2	40–60	1.42	5.6	4.22	2.2	1.5	13.1	0.6	58	41
C	60–100	1.63	1.6	4.18	2.2	1.6		1.1	61	38
Spodosol II										
O	–17–0	0.18	252	3.60	3.0	2.8	3.3	11.0	7.7	81
A	0–8	1.44	18	3.34	2.8	2.5	4.8	2.4	13	85
E	8–18	1.51	4.3	3.45	2.4	2.0	6.5	1.6	12	86
Bh	18–22	1.10	42	3.60	2.5	2.0	12.0	0.6	30	70
Bhs	22–35	1.40	15	3.99	2.8	2.1	12.0	0.3	48	52
Bs	35–55	1.46	6	4.28	2.6	2.0	14.7	0.3	49	50
C	55–100	1.70	1.7	4.17	3.3	2.4		0.9	62	37
Inceptisol										
O/A	–2–0	0.28	130	4.00	2.9	2.5	3.2	19.0	6.7	74
A	0–4	0.91	33	3.93	2.2	1.4	3.5	8.8	14	77
E	4–10	1.22	14	4.05	2.0	1.0	5.1	4.4	23	73
EB	10–19	1.30	8	4.53	1.1	0.8	7.4	1.9	46	52
Bw1	19–40	1.19	10	4.42	0.9	0.8	10.3	0.6	46	53
Bw2	40–72	1.58	6.0	4.41	0.8	0.7	16.9	0.3	33	66
C	72–100	1.80	1.8	4.37	1.4	1.2		2.5	62	35

[1] Organic carbon was determined by dry combustion (Tabatabai and Bremmer, 1970).

[2] pH was measured in the centrifugate.

[3] Ionic strength was calculated by the equation $I = 1/2 \sum c_i z_i^2$ where c_i is the concentration and z_i the charge of an ion i in the centrifugate. Ions included are: Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Al^{3+}, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}.

[4] Aluminium not included.

[5] Values for the C horizon are not included since small errors in CEC and total C measurements may show up as greater errors in the quotient [6] $CuCl_2$ extracted 'base cations' (BC = Na + K + 2Mg + 2Ca), Al (3Al) and H expressed as percentage charge of total-cation exchange capacity.

Except for the O (Spodosols) and O/A (Inceptisol) horizons, the ionic strength of soil centrifugate was substantially higher in the Spodosols than in the Inceptisol. This was true irrespective of whether the ionic strength was based on all ions (except H^+) or if H, Al and Fe were excluded (Table 2). The contribution from NaCl to the ionic strength was 47–64% (excluding H, Al and Fe), reflecting a strong influence from sea salts. An exclusion of Al-cations can be justified based on the findings reported by Göttlein (1998) that the method of Driscoll (1984) may largely underestimate organically complexed Al, thus overestimating the concentration of dissolved, inorganic Al-ions. The concentration of free Fe^{3+} was no determined in solution. Considering the pH range and the presence of strong organic ligands, the concentration of free inorganic Fe-cations should be very low with no practical influence on the ionic strength.

A likely explanation for the observed soil solution ionic strength differences among the soil profiles is a more effective capture of airborne salts and dry deposited S and N compounds by conifers than by deciduous tree stands. Bergkvist and Folkeson (1995) reported the total deposition of S and N to spruce canopy of two stands in southern Sweden to be 1.5 to 3 times higher than to the canopies of two birch (*Betula pendula* Roth) and beech (*Fagus sylvatica* L.) stands in the same area. The annual leaching of Cl at 40 to 50 cm depth (the lower part of the B horizon) was 2.2 to 2.8 times higher under spruce, as compared to birch and beech (Bergkvist & Folkeson 1995), whereas the leaching of Na was 1.2 to 1.9 times higher under spruce. In rough agreement with these observations, concentrations of NaCl was 2–2.5 times higher in the Spodosols B than in the Inceptisol B horizon of our study. Interesting to note is the increase in ionic strength, as well as in %BS, in the C horizon in all profiles. This may be a combined effect of few nutrient up-taking roots at this depth (see Appendix) and an effect of a more active weathering in the C horizon, as compared to the upper part of the profiles.

Semi-empirical models for soil pH and aluminium solubility

As noted in Table 2, soil pH increased and %BS decreased with depth in all soil profiles. Thus, by depth, pH is negatively related to %BS, which is a general finding in the upper 0.5 to 1.0 m of northern acidic forest soils (e.g. Eriksson et al. 1992). Skyllberg (1994, 1999) and Ross et al. (1997) have shown that pH can be negatively related to %BS also within O and E horizons of Spodosols. As pointed out by Skyllberg (1999), this means that pH variations in these soils can not be described by chemical models based on a pH dependent dissolution of $Al(OH)_3$ (s), combined with cation-exchange reactions between Al^{3+} and Ca^{2+} (or other BC), as the major pH-buffering process (cf. Reuss et al. 1990). Instead, Skyllberg suggested chemical reac-

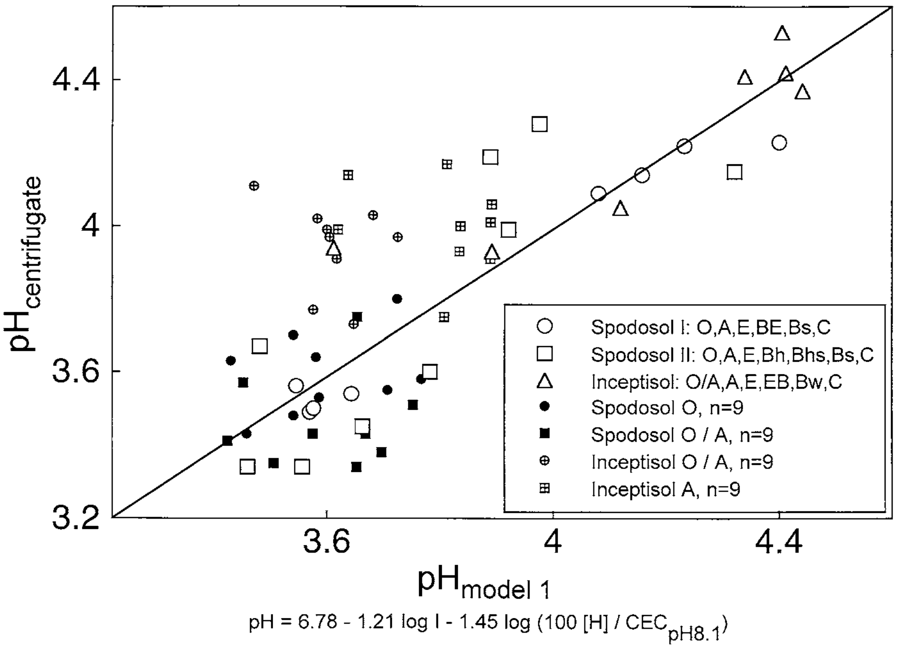

Figure 1a. Model (1); illustrating the pH effects of soil solution ionic strength (mM, excluding H^+ and Al-ions) and hydrogen ion saturation of the total cation-exchange capacity (no unit). The equation given is the least-square fit to data for the three complete soil profiles (n = 24).

tions involving SOM acidic functional groups and Al-minerals, resulting in varying ratios of organically adsorbed H and Al, to be the main pH and pAl (–log $\{Al^{3+}\}$) determining processes in O and E horizons. In order to test whether these findings apply also to complete soil profiles, we used our data to test three different types of semi-empirical models.

Figure 1(a) shows the fit of model (1) to our soil data. The model is a weak acid analogue, relating pH to % protonation of CEC [log (100 [H] $CEC^{-1}_{pH\ 8.1}$)]. It is assumed that $CEC_{pH\ 8.1}$ can be taken to represent the concentration of weak acidic functional groups of SOM. Least-square multiple regression analyses, based on data from the two Spodosols and the Inceptisol profile (n = 24) resulted in the equation pH = 6.78 – 1.21 log I – 1.45 log (100 [H] $CEC^{-1}_{pH\ 8.1}$). The multiple coefficient of determination (R^2) was 0.82. If also the separately sampled 36 O, O/A and A horizons were included (n = 60), the coefficient of determination decreased to 0.58 (Table 3). An examination of Figure 1(a) shows that model (1) fairly well describes the depth-pattern in all three profiles, whereas pH-variations within O, O/A and A horizons of both Spodosols and Inceptisols are poorly simulated.

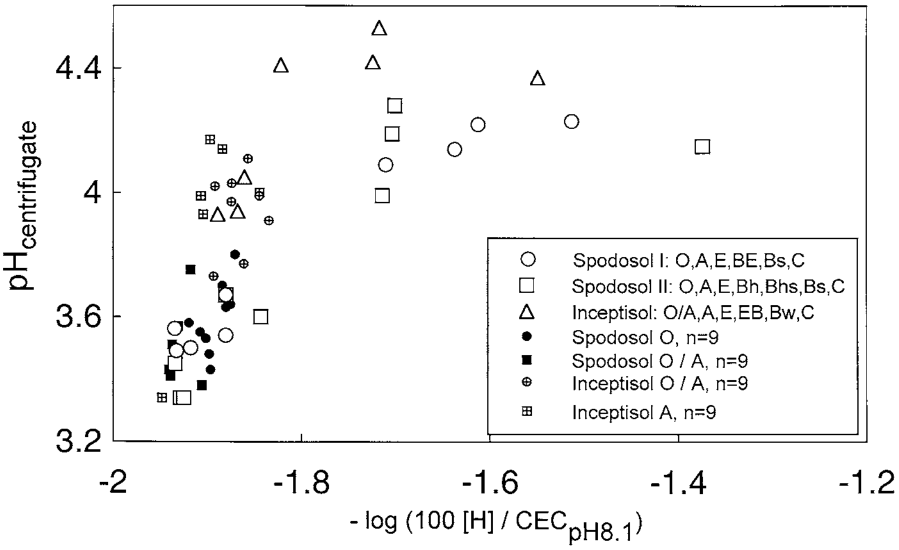

Figure 1b. Relation between pH and H^+ saturation of the total cation-exchange capacity.

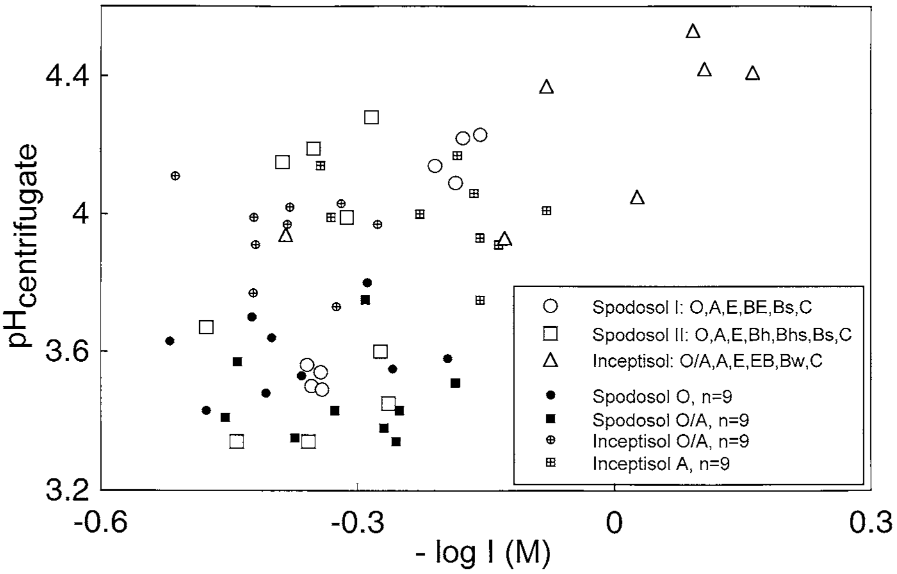

Figure 1c. Relation between pH and ionic strength in soil solution. The ionic strength is calculated as $I = 0.5 \sum c_i z_i^2$ where c_i and z_i are the mM concentration of ion i and the charge of ion i, respectively. Ions considered are Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, $NH_4{}^+$, NO_3^-, Cl^-, and SO_4^{2-}.

Table 3. Least-square fit of model (1) and model (2) when applied to data from the three soil profiles (n = 24) and to the complete data set including 36 O, O/A and A horizons from Spososols and Inceptisol

	Soil profiles n = 24	R^2	Soil profiles + O/A horizons n = 60	R^2	R^2_{simple}
Model 1	pH = 6.78 – 1.21 log I – 1.45 log (100 [H] $\text{CEC}^{-1}_{\text{pH 8.1}}$)	0.82	pH = 6.94 – 0.85 log I – 1.56 log (100 [H] $\text{CEC}^{-1}_{\text{pH 8.1}}$)	0.58	log I = 0.29 log (100 [H] $\text{CEC}^{-1}_{\text{pH 8.1}}$) = 0.44
Model 2	pH = 4.86 – 1.17 I + 0.77 log (([K] + [Na] + 0.55 ([Ca] + [Mg]) + 0.20 [Al]) $[\text{H}]^{-1}$)	0.91	pH = 4.90 – 1.08 I + 0.82 log (([K] + [Na] + 0.55 ([Ca] + [Mg]) + 0.20 [Al]) $[\text{H}]^{-1}$)	0.76	log I = 0.29 log (([K] + [Na] + 0.55 ([Ca] + [Mg]) + 0.20 [Al]) $[\text{H}]^{-1}$) = 0.52

The simple regression of each of the two independent variables log (100 [H] $\mathrm{CEC}_{\mathrm{pH}\ 8.1}^{-1}$) and log I are illustrated in Figure 1(b) and 1(c). The simple I R^2 was 0.44 for log (100 [H] $\mathrm{CEC}_{\mathrm{pH}\ 8.1}^{-1}$) and 0.29 for log I (Table 3). Thus, the contribution of log I to R^2 for model (1) is 0.14 (0.58–0.44) and the contribution from log (100 [H] $\mathrm{CEC}_{\mathrm{pH}\ 8.1}^{-1}$) to R^2 for model (1) is 0.29 (0.58–0.29). An examination of Figure 1(b) shows that at similar % protonation, the Inceptisol shows a shift to higher pH than the Spodosol both in the topsoil and in the subsoil. Figure 1(c) reveals that the higher pH in the Inceptisol subsoil can be explained by a lower ionic strength, whereas the pH differences between Spodosol and Inceptisol O, O/A and A horizons can not be explained by the soil solution ionic strength. This is also emphasized by the drop in the partial regression coefficient for –log I from 1.21 to 0.85 when the 36 O, O/A and A horizons were included (Table 3), indicating that the ionic strength has less influence on pH in these horizons.

The ionic strength effect on soil pH is a well-known phenomenon, exemplified by e.g. Richter et al. (1988) and Ross and Bartlett (1992) for acidic forest soils. Binkley and Sollins (1990) highlighted the role of ionic strength in lowering pH in soils under alders relative to conifers. The negative relation between the hydrogen ion saturation of CEC_t and pH was demonstrated in O and E horizons of Spodosols (Skyllberg 1999).

As can be seen in Figure 2, model (2) describes the pH-variation among the three soil profiles, and the pH-variation with depth within the profiles, fairly well. For this data set ($n = 24$) the equation pH = 4.86 – 1.17 log I + 0.77 log (([K] + [Na] + 0.55 ([Ca] + [Mg]) + 0.20 [Al]) $[\mathrm{H}]^{-1}$) had a multiple R^2 of 0.91. For the larger data set, including 36 O, O/A and A horizons, the multiple R^2 decreased to 0.76, but the regression coefficients remained fairly similar (Table 3). A partial regression coefficient of 1.1 for log I and 0.8 for log (([K] + [Na] + 0.55 ([Ca] + [Mg]) + 0.20 [Al]) $[\mathrm{H}]^{-1}$) show that a unit change in each of these variables (the other held constant) results in approximately a unit change in pH. A comparison of the simple R^2 for each of the two factors (Table 3) shows that the term log (([K] + [Na] + 0.55 ([Ca] + [Mg]) + 0.20 [Al]) $[\mathrm{H}]^{-1}$) contributed more to the multiple R^2 ($R^2_{\mathrm{add}} = 0.57 = 0.76\text{-}0.29$) than log I ($R^2_{\mathrm{add}} = 0.16 = 0.76\text{-}0.52$).

The residual mean square (RMS) of model (2), 0.025, was lower than for model (1), 0.045. Thus, model (2) showed a considerably better fit to data than model (1). The difference between the models was most pronounced in the O, A, E and Bh horizons (data points with a pH in centrifugate below 3.7) from the two Spodosol profiles, as well as in the 18 separate Spodosol O and O/A horizon samples. pH values in the Inceptisol O/A and A horizons were, however, still underestimated and only slightly better described by model (2) as by model (1). For the mineral horizons Bs, Bw and C (data points with

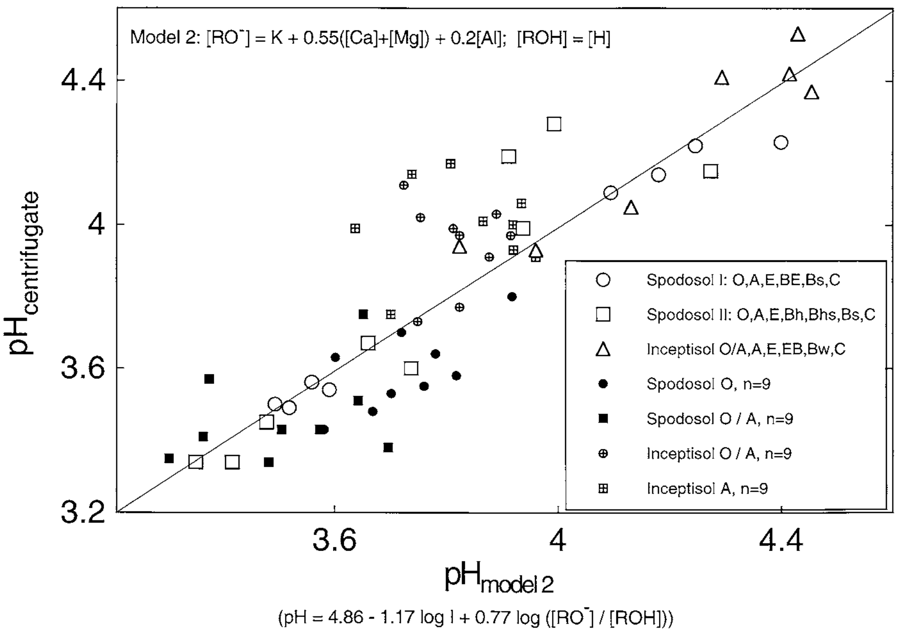

Figure 2. Model (2); illustrating the pH effects of the ionic strength (excluding H^+ and Al-ions, mM) and the degree of dissociation of acid functional groups pertaining to SOM (unit less). The equation given is the best least-square fit to data for the three complete soil profiles (n = 24).

a pH above 4), there were only minor differences between the two models. As is seen in Table 2, concentrations of adsorbed divalent cations (Ca and Mg) and Al show a similar magnitude in the surface horizons (O, O/A, A, E, EB, Bh) and therefore differences in bonding strength of divalent cations and Al will markedly affect soil pH. This is probably the major reason why model (2) gives a better description of soil pH in these horizons as compared to model (1). In the mineral soil horizons, concentrations of adsorbed divalent cations are very low and the ratio of adsorbed Al to H will be of outermost importance (Table 2).

Considering the narrow pH-range of the soil data in this study (as compared to most other evaluations of soil pH models) and that the parameters in model (2) were determined in independent titration experiments (no adjustment of parameters to the data material) strong indications are given that the theory behind model (2) is valid for both organic rich surface soils and mineral soils. Very few soil pH models have been evaluated using soil samples covering natural gradients. One exception is the study by Valentine and Binkley (1990), covering a topographic sequence in an arctic landscape. Often chemical equilibrium models of soils are parameterised and used to

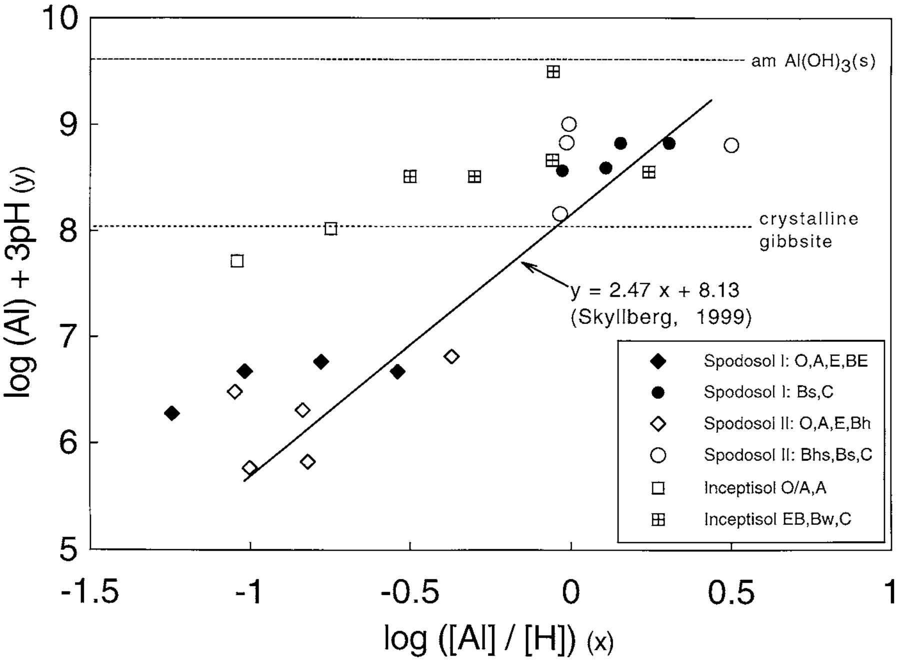

Figure 3. Model (3); illustrating the relation between the ratio of Al^{3+} and H^+ in solution, log (Al) + 3pH, and adsorbed to the soil, log [Al]/[H]. The solid line and the equation represents the fit to data from O and E horizons of Spodosols from Skyllberg (1999). The ( ) denotes activity in solution and [ ] concentrations of surface charge (molc kg^{-1}).

simulate acid-base titration data of single soil samples (e.g. Tipping et al. 1995).

The very low concentration of adsorbed divalent cations in the mineral soil in practice will simplify model (1) to: pH = $a - b$ log I – c log 100 ([H] ([Al] + $[H])^{-1}$) and model (2) to: pH = $a - b$ log I + c log (0.2 [Al] $[H]^{-1}$). The terms 100 [H] ([Al] + $[H])^{-1}$ and 0.2 [Al] $[H]^{-1}$ are strongly related to each other and can describe the pH variability caused by a variation in the ratio of adsorbed Al and H equally well. This is the main reason for only small differences between model (1) and (2) in the Bs, Bw and C horizons.

To further examine the importance of the ratio of adsorbed Al to H for the soil solution chemistry we apply model (3) to the data from the two Spodosols and the Inceptisol (Figure 3). In the figure the equation from Skyllberg (1999) fitted to O and E horizons of Spodosols from two sites in northern and southern Sweden is given. It should be noted that pH and log $\{Al^{3+}\}$ were determined in 1.0 M KCl extracts in the study by Skyllberg. Despite these differences it can be noted that data from all horizons of the two Spodosol profiles in this study falls fairly close to the line for the empirical equation derived from the O and E horizons from two sites in northern and southern Sweden. This suggests that the ratio of organically adsorbed Al to H controls pH and pAl (–log $\{Al^{3+}\}$) throughout Spodosol profiles with pH lower than 4.5. This is in agreement with recent studies demonstrating the importance of organic complexation as a regulator of pAl in Bh and Bs horizons of Spodosols (e.g. Simonsson & Berggren 1998). In the Bs and C horizons, organic Al-complexes possibly equilibrate with mineral phases such as allophane and amorphous $Al(OH)_3$, Farmer (1999). The poor fit of model (3) to the Inceptisol data may, however, indicate that mineral phases play a more important role behind Al solubility in the Inceptisol than in the Spodosols.

The success of the three models applied in this study is dependent on properly determined concentrations of organically adsorbed H and Al. We used 0.5 M $CuCl_2$ to extract organically adsorbed Al. It has conclusively been shown that organically adsorbed Al can be quantified in organic soils using 0.5 M $CuCl_2$ as an extractant (Hargrove & Thomas 1984; Walker et al. 1990). We argue that 0.5 M $CuCl_2$ is the best available extractant for organically adsorbed Al also in mineral soils. Skyllberg and Borggaard (1998) reported a good reproducibility when extracting Al by 0.5 M $CuCl_2$ from Bh and Bs horizons. Copper chloride consistently extracts lower amounts of Al than pyrophosphate, traditionally the most common extractant for organically bound Al in mineral soils. It has recently been shown that pyrophosphate in addition to organically bound Al dissolves hydroxy-interlayered Al and amorphous Al hydroxides (Kaiser & Zech 1996). Thus, by choosing 0.5 M $CuCl_2$ and using one single equilibrium extraction, we are not likely to overestimate organically bound Al.

The content of 0.5 M $CuCl_2$ extracted Fe was less than 1% of Al in B and C horizons, 13% in E horizons and 23–36% in A and O horizons. Possibly this 'fraction' of Fe represents organically complexed Fe^{3+} / Fe^{2+}, but that has not been verified. Because of the uncertainty of what 0.5 M $CuCl_2$ extracted Fe represents, and the well-known very strong complexation of Fe to SOM, extracted Fe was not considered in the models.

Implications for studies of soil acidification

From a soil acidification point of view it is interesting to note that although soil pH and %BS generally is lower in the two Spodosol profiles (under the spruce stand) than in the Inceptisol (under the oak), the absolute amount of adsorbed BC (Ca^{2+}, Mg^{2+}, K^+ and Na^+) does not differ among the three soil profiles on an area basis (Table 1). In non-calcareous soils BC adsorbed to CEC sites represents the 'short-term' available ANC. Thus, it can be concluded that the lower pH and %BS in the Spodosols, as compared to the Inceptisol, cannot be explained by soil acidification of CEC caused by net losses of base cations. The absolute losses (due to leaching and plant uptake) may differ among the profiles (and stands), but in that case weathering compensates for those differences. The fair fit of model (1) and (2) to data from both the Inceptisol (except O/A and A horizons) and the Spodosol profiles in addition suggests that differences in SOM quality among the profiles do not seem to play any major role for the pH differences.

Based on the fair fit of model (2) to most of the soil samples, irrespective of site, we suggest that the variation of pH with depth in a single profile and variations between the Spodosols and the Inceptisol profiles may be explained by the same factors. These factors are: (1) the ionic strength of soil solution and, (2) the composition of organically adsorbed metal cations, in mineral horizons mainly Al and H. Overall, the observed pH-increase by depth in most acidic forest soil may be explained by an increasing Al-saturation of SOM.

A substantial increase in forest cover and biomass production in south Sweden, and other parts of Europe, due to improved forest management and fertilisation by atmospherically deposited nitrogen, the last decades (Kauppi et al. 1992; Elfving & Tenghammar 1996) most likely have resulted in increased storage of SOM. Since the composition of H, Al and BC adsorbed to SOM is dependent on various processes like; plant nutrient uptake and litter quality, microbial decomposition and humification of SOM, physical incorporation of SOM in the mineral soil and chemical reactions between SOM and mineral matter, one question arises: How many studies giving rise to conclusions about the effects of acid rain on soil have taken changes in quality and contents of SOM, and subsequent changes in the relative composition of H, Al and BC adsorbed to SOM into consideration? Only a few studies reviewed by Nilsson and Tyler (1995) considered changes in SOM contents and soil solution ionic strength and none of the studies considered changes in the ratio of organically adsorbed Al to H. This limits their inference about the effects of atmospherically deposited strong mineral acids on soils in southern Sweden.

Organically adsorbed Al in soil has been suggested to be a product of below ground chemical reactions between Al-minerals and SOM acidic groups (Vogt et al. 1987; Skyllberg 1994). These reactions may be very slow, especially in O and E-horizons where the availability of reactive Al-minerals is low. This is also the main reason for the Al-saturation of SOM to increase with depth: increasing contact time (older SOM) and decreasing ratio of SOM to mineral matter. Given that the base saturation of SOM transported from the O and A horizons to the mineral soil is very low (i.e. this SOM is highly protonated), it is likely that an increasing storage of SOM in acidic forest soils of Europe, caused by a recent increased biomass production, has resulted in a decrease in the Al-saturation of SOM in mineral soil horizons. If so, it is likely that also pH has decreased in these soils, due to a decrease in the ratio of adsorbed Al to H.

Based on an annual removal rates of 1–2% of organically adsorbed Al from sandy Dutch Spodosols, Mulder et al. (1989) suggested that acid deposition should lead to a decrease in the Al saturation of SOM and in soil pH (especially in Bh horizons). This hypothesis was later supported by Mulder and Stein (1994) who claimed that a decrease in organically bound Al was the likely explanation for a combined decrease in pH and Al solubility over a six-year period in a Dutch acidic forest soil highly affected by acid deposition. Wesselink et al. (1996) extended the observation period to ten years and suggested that a pH decrease of 0.1 to 0.3 pH units in the pH range 3.2 to 3.6 could be explained by a decreasing Al saturation of SOM in the same Dutch acidic soil.

Reported variations in the slope between pH and%BS for different soil horizons (Stuanes et al. 1992) and for similar soils re-sampled in 1949 and 1984 (Falkengren-Grerup et al. 1987), noted by Binkley and Högberg (1997), might be explained by variations in the ratio of adsorbed Al to H. Similarly, the weak linear relationship between pH and %BS, used by Hallbäcken (1992) to estimate possible losses of base cations in a forest soil in southern Sweden between the years 1927 and 1985, may have biased the estimate owing to changes in the relative composition of adsorbed Al to H over the 60-year period.

Conclusions

Simple weak acid analogues, considering the composition of adsorbed H and metal cations and the soil solution ionic strength, could successfully describe pH-differences by depth in soils and among soils developed under spruce and oak forest stands. The ratio of Al and H adsorbed to SOM was a most important factor in the mineral soil horizons, whereas the low concentration of ‘base cations’ in the mineral soil limited their influence to the organic rich top-soil. In O and O/A horizons, sites binding base cations contributed significantly to the pH-buffering. A consideration of differences in bonding strength between mono-, di- and trivalent cations significantly improved the pH-buffering model in O, A, E and Bh horizons.

The increase in pH from the A horizon into the C horizon could be explained by an increasing ratio of adsorbed Al to H in both Spodosol and Inceptisol profiles. Our results strongly imply that changes in mass of SOM, the ionic strength in soil solution and the relative composition of soil adsorbed

Al and H need to be considered when the causality behind changes in pH and base saturation is investigated.

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Appendix

Description of soil profiles.

Spodosol I

Remarks: The layer (60–100 cm) is considered a fragipan because it is compacted but not cemented. Unless otherwise stated, mineral soil horizons had very few, fine and medium, subrounded, weathered gravel (flint, granite etc.) and a clear, wavy boundary.

Oe (–12–8): Very dark brown (10YR 2/2, m) medium decomposed needles and mosses.

Oa (–8–0): Black (N 2/–, m) well decomposed organic materials.

A (0–2): Very dark greyish brown (10YR 3/2, m) sand; massive; non sticky, non plastic, very friable; interstitial voids; common, very fine and fine and very few, medium and coarse roots.

E/A (2–10): Brown to dark brown (10YR 4/3, m) matrix with common, fine to medium, distinct, clear, very dark greyish brown (10YR 3/2, m) mottles; sand; massive; non sticky, non plastic, very friable; interstitial voids; common, very fine and fine and very few, medium and coarse roots.

BE (10–20): Dark yellowish brown (10YR 4/4, m) sand; massive; non sticky, non plastic, very friable; interstitial voids; common, faint, humus coatings on mineral grains; common, very fine and fine and very few, medium and coarse roots.

Bs1 (20–40): Strong brown (7.5YR 4/6, m) sand; massive; non sticky, non plastic, friable; interstitial voids; abundant, distinct, sesquioxide coatings on mineral grains; few, fine and very few, medium and coarse roots; gradual, smooth boundary.

Bs2 (40–60): Strong brown (7.5YR 5/8, m) sand; massive; non sticky, non plastic, friable; interstitial voids; abundant, distinct, sesquioxide coatings on mineral grains; few, fine and very few, medium roots.

Cx (60–100): Yellowish brown (10YR 5/6, m) sand; massive; non sticky, non plastic, friable to firm; interstitial voids; common, faint, sesquioxide coatings on mineral grains; no roots; gradual, smooth boundary.

C (100+): Yellow (10YR 7/6, m) sand; massive; non sticky, non plastic, very friable; interstitial voids; common, faint, sesquioxide coatings on mineral grains.

Spodosol II

Remarks: The Bh, Bhs and Bs horizons do not appear cemented. The layer (55–85 cm) is considered a fragipan because it is compacted but not cemented. Bleached, almost white sand below 85 cm. Although rock fragments are described as gravel, single stones were found. Unless otherwise stated, mineral soil horizons had few or very few, fine and medium, subrounded, weathered gravel (flint, granite etc.) and a gradual, wavy boundary.

Oe (–17–8): Very dark brown (10YR 2/2, m) medium decomposed needles and moss.

Oa (–8–0): Black (N 2/–, m) well decomposed organic materials.

A (0–8): Very dark grey (10YR 3/1, m) sand; massive; non sticky, non plastic, very friable; interstitial voids; common, very fine and fine and very few, medium and coarse roots.

E (8–18): Greyish brown (10YR 5/2, m) sand; massive; non sticky, non plastic, loose; interstitial voids; common, very fine and fine and very few, medium and coarse roots; abrupt, wavy boundary.

Bh (18–22): Black (N 2/–, m) sand; massive; slightly sticky, slightly plastic, friable; interstitial voids; dominant, prominent, humus coatings on mineral grains; few, very fine and fine and very few, medium and coarse roots.

Bhs (22–35): Yellowish red (5YR 4/6, m) sand; massive; non sticky, slightly plastic, friable; interstitial voids; abundant, distinct, humus and sesquioxide coatings on mineral grains; few, very fine and fine and very few, medium and coarse roots.

Bs (35–55): Yellowish brown (10YR 5/6, m) sand; massive; non sticky, non plastic, very friable; interstitial voids; abundant, distinct, sesquioxide coatings on mineral grains; few, very fine and fine and very few, medium and coarse roots.

Cx (55–85): Yellowish brown (10YR 5/4, m) sand; massive; non sticky, non plastic, friable to firm; interstitial voids; common, faint, sesquioxide coatings on mineral grains; no roots.

C (85+): Light grey (10YR 7/2, m) sand; massive; non sticky, non plastic, loose; interstitial voids; no rock fragments.

Inceptisol

Remarks: The layer (72–110 cm) is considered a fragipan because it is compacted but not cemented. Few earthworms and earthworm channels found. Although rock fragments are described as gravel, single stones were found. Unless otherwise stated, mineral soil horizons had few or very few, fine and medium, subrounded, weathered gravel (flint, granite etc.) and a clear, wavy boundary.

Oe (–2–0): Very dark brown (10YR 2/2, m) medium decomposed leaves and herbs.

A (0–4): Black (10YR 2/1, m) sand; very weak, very fine and fine granular structure; slightly sticky, slightly plastic, very friable; interstitial voids; common, very fine and fine and very few, medium and coarse roots; very few earthworm channels.

E (4–10): Very dark greyish brown (10YR 3/2, m) sand; massive; non sticky, non plastic, loose; interstitial voids; common, very fine and fine and very few, medium and coarse roots; very few earthworm channels.

EB (10–19): Brown to dark brown (7.5YR 4/4, m) sand; massive; non sticky, non plastic, very friable; interstitial voids; common, faint, sesquioxide coatings on mineral grains; common, very fine and fine and very few, medium and coarse roots; very few earthworm channels; gradual, smooth boundary.

Bw1 (19–40): Strong brown (7.5YR 4/6, m) sand; massive; slightly sticky, slightly plastic, friable; interstitial voids; dominant, distinct, sesquioxide coatings on mineral grains; common, very fine and fine and few, medium and coarse roots; very few earthworm channels; diffuse, smooth boundary.

Bw2 (40–72): Strong brown (7.5YR 5/7, m) sand; very weak, very fine and fine subangular blocky structure; slightly sticky, slightly plastic, friable; interstitial voids; dominant, distinct, sesquioxide coatings on mineral grains; few, very fine and fine and very few, medium and coarse roots; very few earthworm channels.

Cx (72+): Reddish yellow (7.5YR 6/6, m) sand; massive; non sticky, non plastic, friable to firm; interstitial voids; common, faint, sesquioxide coatings on mineral grains; very few, fine roots.

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