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Some chemical parameter relations in a population of German forest soils

J. Prenzel[a] and H. Schulte–Bisping[a]

[a] *Institute for Soil Science and Forest Nutrition, University of Göttingen, Germany*

Abstract: Existing pools of soil chemical data may be used in the investigation of conceptual models about soil chemical processes. Data from more than 2000 soil samples from German forests were pooled and interpreted to establish parameter relations that are related to soil acidification. A saturated water extract and an extraction of exchangeable cations by ammonium chloride were used. Activities in the soil solution were calculated by a complexation model. The change in exchangeable cation composition with decreasing pH is shown, the main process being the displacement of Ca by Al. Cation exchange selectivity coefficients do vary less than 1 log unit between most cases. For some cation pairs and regions in Ca–saturation the coefficients are much more constant. Ion activity products for gibbsite, alunite, and jurbanite indicate that one or more of these precipitates may contribute to solution composition control between pH 3.5 and 5 at least.

1. INTRODUCTION

Soil chemical parameters may be defined as concentrations, usually obtained by extracting a soil sample by an aquaeous solution. We use data on extractions by $1\,\mathrm{mol}\,(NH_4Cl)\,L^{-1}$ (exchangeable cations) and on 1–d saturation extracts by water.

The identification of relations between such concentrations may save analytical efforts. But, more important, it can also be used in the development of

[1] *Correspondence to:* J. Prenzel, Institute for Soil Science & Forest Nutrition, Büsgenweg 2, 37077 Göttingen, Germany

models that explain and predict changes in soil chemical parameters. An example of such a relation is an adsorption isotherm, which is a mathematical mapping of a concentration of a solute in the soil solution (water extract) to the concentration of the same solute in some fraction of the soil matrix (some electrolyte extract).

Forest soils in Germany are affected by acid depositions for more than 50 years (Ulrich, 1991). Soil acidification leads to changes in the composition of the soil solution and the cation–exchange complex. We are investigating parameter relations related to these changes, especially to the appearance of Al in solution and as exchangeable cation.

Three types of relations are studied: Relations between pH and exchangeable cations, relations derived from cation–exchange selectivity equations, and relations derived from solubility product equations for $Al(OH)_3$, $AlOHSO_4$, and $KAl_3(OH)_6(SO_4)_2$.

A data pool is used that has been accumulated in this institute over 25 yr. All data are from forests in North–, Central– or West–Germany. Soils influenced by fertilization, liming, or similar treatments have been excluded. The parent materials vary from limestone to loess and sand.

The data are grouped in three soil depth classes but are pooled together otherwise. The number of samples in each class is ≈ 700. A central hypothesis is that parameter relations exist within these classes. This implies that the selectivities of cation–exchange complexes and the solubilities of aluminous hydroxides are similar between soils. The results will show how far such an assumption is justified.

The concepts used here in the interpretation of soil chemical data are not new. This study uses them on a fairly broad population of soil samples. The results may help to decide whether those concepts can be used in the interpretation and modeling of soil chemical processes in this region without testing their applicability in each case.

Ulrich (1966) studied similar soil chemical parameter relations in ≈ 150 soil samples from North–West–Germany. He introduced a scheme for the acidification of soils (Ulrich, 1981)(Ulrich, 1991, p. 51) that predicts the appearance of Al–ions if certain pH thresholds are passed. A relation between exchangeable Al and pH is widely acknowledged (Schachtschabel *et al.*, 1989, p. 114) (Bolt *et al.*, 1976, p. 63).

Cation–exchange selectivity coefficients have been studied for a long time. Bruggenwert and Kamphorst (1979) summarized several hundred papers from $\approx 1959-1979$. Most researchers manipulated the composition of the exchange complex experimentally. Here, only one data point from each soil sample is presented. Results from different soils are pooled together to establish how well a spectrum of soils can be described by single selectivity constants.

The sorption of SO_4 is an important modifying process in soils that are acidified by H_2SO_4 deposition (Prenzel, 1983; Reuss & Johnson, 1986). It has been discussed whether basic aluminum sulfates may control this sorption (Nordstrom, 1982; Khanna *et al.*, 1987; Courchesne & Hendershot, 1990; Matzner & Prenzel, 1992; Prenzel, 1994). Ion activity products show how far such a control is possible.

The results presented here have been printed in different form in a more comprehensive technical report (Prenzel & Schulte-Bisping, 1991).

2. MATERIALS AND METHODS

2.1. Soil extracts

The methods have been described in detail by Meiwes et al. (1984). The extractions were done at ambient room temperature.

The soil solution was analyzed by preparing a suspension at $\approx 1\,\mathrm{kg\,soil\,L^{-1}}$ water, which stood overnight and was seperated by vacuum filtration or centrifugation. Ions were analyzed by glass electrode (pH), atomic absorption spectroscopy (Na, K, Ca, Mg, Fe, Mn, Al), or colorimetry (SO_4).

Exchangeable cations were extracted from the same sample from which the soil solution had been prepared and removed by filtration or centrifugation. 2.5 g of soil were extracted in a column–like way slowly by 100 mL of 1 mol (NH_4Cl) L^{-1} solution. pH was analyzed by a glass electrode and Na, K, Ca, Mg, Fe, Mn, and Al by atomic absorption spectroscopy in the extract.

2.2. Calculation of chemical parameters

The oxidation state of Fe was not determined. Therefore, two cases were calculated assuming Fe, both, in solution and exchangeable, to be either Fe(II) or Fe(III). Most results were uninfluenced by this distinction.

The concentrations in the soil solution were used to calculate activities of H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}or Fe^{3+}, Mn^{2+}, Al^{3+}, SO_4^{2-}, and OH^-. For this calculation the program WAKO (Prenzel, 1990) was used with complex definitions and stability constants as given by Prenzel (1990). Complexes of Fe(II) were neglected. Since no information was available about organic ligands, organic complexes were also ignored. This is a systematic error that shows up especially for the 0–10 cm depth class.

In the NH_4Cl solution the pH is usually lowered on extracting an acid soil. This drop in pH is interpreted as the extraction of exchangeable H^+. But a correction was made for exchangeable Al^{3+} that may also lower the pH by hydrolysis (Meiwes *et al.*, 1984). The amounts of cations extracted by NH_4Cl were interpreted as exchangeable H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}or Fe^{3+}, Mn^{2+}, and Al^{3+}. The (effective) cation–exchange capacity, CEC, and the equivalent fraction, x^s, are defined as

$$\mathrm{CEC} = \sum_{i \in I} c_i$$

$$x^s{}_i = c_i/\mathrm{CEC}$$

where c_i is the concentration of an exchangeable cation i in $\mathrm{mmol_c\,kg^{-1}}$, and $I = \{\mathrm{H, Na, K, Ca, Mg, Fe, Mn, Al}\}$.

2.3. Data presentation

Most data are presented in logarithmic form indicated by 'p'.

$$\mathrm{pA} = -\log_{10}(\mathrm{A^a})$$

where A is a single ion in solution with charge a and $(\mathrm{A^a})$ is its activity in $\mathrm{mol\,L^{-1}}$.

$$\mathrm{pxB} = -\log_{10} x^s_B$$

where B is an exchangeable cation. In analogy we define

$$\mathrm{pK} = -\log_{10} \mathrm{K}$$

for any equilibrium expression K.

Data are grouped in equidistant classes according to either pH or pxCa. Table 1 and 2 show typical observation frequencies in these classes. Frequencies vary between presentations because sometimes observations had to be omitted if the chemical analysis had a 'zero' or 'trace' result and no logarithm could be calculated. This occurred frequently for pxH and pxFe where frequencies were 20 to 70% lower.

Only those classes that comprise > 4 observations are shown. The results are presented as 25, 50, and 75% percentile of the different classes. The median (50% percentile) is marked by a larger symbol and the quartiles are marked

Table 1
Observation frequencies in pH–classes. pH_c = centre of class

pH_c	depth class (cm)		
	0–10	10–30	30–100
3.2	88	29	6
3.6	332	189	65
4.0	138	318	460
4.4	54	80	115
4.8	17	25	21
5.2	6	6	9
5.6	9	8	11
6.0	1	7	5
6.4	6	1	2
6.8	6	1	2
7.2	3	5	1
7.6	7	2	4
8.0	6	7	1
	673	678	702

by smaller ones. Bullets ($\bullet$) indicate 0–10, crosses ($\times$) indicate 10–30, and diamonds ($\diamond$) indicate 30–100 cm depth classes.

The depth is measured from the top of the mineral soil downwards. Organic top layers are not included. A sample was included in a depth class if it had been taken from anywhere within the range of that class.

If empirical ion activity products are displayed graphically, often a more or less hidden mathematical relation is present between x– and y–variables. For example, if the ion activity product of $Al(OH)_3$ is investigated, one may display $1/3\,pAl - pH$ across pH. Let pH vary between 3 and 8, and let for some reason pAl only vary between 4 and 5. The appearance of the graph will then indicate a strong linear relation between x– and y–variable, though pAl may, in this case, be quite independent from pH.

Table 2
Observation frequencies in pxCa–classes. $pxCa_c$ = centre of class

$pxCa_c$	depth class (cm)		
	0–10	10–30	30–100
0.1	44	36	18
0.3	26	11	23
0.5	15	18	3
0.7	48	17	10
0.9	67	43	19
1.1	109	41	34
1.3	118	64	69
1.5	92	145	141
1.7	83	155	183
1.9	63	102	107
2.1	10	35	56
2.3	3	7	11
	678	674	674

In general, if observations are displayed as

$$y = f(y) + \epsilon$$

where f is a mathematical function and the empirical information is contained in the term ϵ, it may well be that a false impression arises because f dominates the graphical appearance.

This fallacy has been criticized by Neal (Neal *et al.*, 1987; Neal, 1988). We try to circumvent these difficulties. If logarithmic activities are used, ion activity products are expressed by linear equations. The same holds for cation–exchange selectivity coefficient equations. In general, if

$$y = \sum_i a_i\, x_i \ \ ,$$

we do not display y across any variable that contains one of the x_i (the term pOH is replaced by 14 − pH in this consideration) but rather single out one

x_k as x–variable. We define

$$z = -\sum_{i \neq k} \frac{a_i}{a_k} x_i \tag{1}$$

and display z across x_k. If the discussion of the original term, y, involved the question whether $y = \mathrm{pK}$, we now have to ask whether $z = x_k - \mathrm{pK/a_k}$. Three straight lines of this type with $\mathrm{p}K$ as parameter have been included in the graphs where appropriate.

2.4. Data selection

Only those data have been included that had been approved within an identified research project. Most of the data are published, mainly in dissertations, theses, and research reports. Some of these are cited in (Prenzel & Schulte-Bisping, 1991).

Only samples from forest soils in Germany have been included. Fertilization and other experimental treatments have been excluded. Geograhically the soils are mainly from the Bundesländer Niedersachsen, Rheinland–Pfalz, and Nordrhein–Westfalen.

Among the parent materials of soil formation are limestones (4%); dark, basaltic rocks (4%); sediments with medium content of weatherable silicates like loess or schist (22%); and sediments low in silicates like drift sand or sandstone (16%) (Prenzel & Schulte-Bisping, 1991).

3. RESULTS

For most graphs the results of the Fe(II) and Fe(III) cases are apparently identical. If so, the Fe(III) case is presented. For Fig. 4, 12, and 13 the difference between both cases is discussed.

3.1. Composition of the cation–exchange complex

At pH > 6 the exchangeable cations are dominated by Ca (Fig. 1). This is in accordance with Ulrich's (1981; 1991) scheme of buffer ranges. Under present day conditions of acidic deposition such pH can only be maintained if very effective buffering of H^+ takes place, which is the case if carbonates are present.

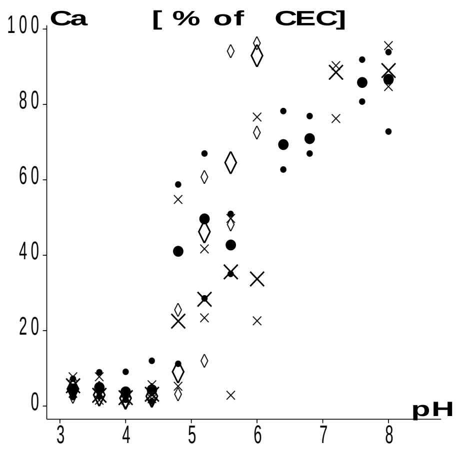

Fig. 1. Exchangeable Ca^{2+} as function of pH in saturation extract. Medians (larger symbols) and quartiles (smaller symbols) in pH–classes. Bullets ($\bullet$) = 0–10, crosses ($\times$) = 10–30, diamonds ($\Diamond$) = 30–100 cm.

The CEC saturation by Mg (Fig. 2) increases with pH above 5 but remains below 10% in most cases and seems even to drop again between pH 7 and 8. The dominance of Ca over Mg may reflect the Ca/Mg ratio in the carbonate materials that are present in the respective soil samples. It may also be due to a preferrence of the exchangers for Ca over Mg (Fig. 9).

The CEC saturation by Al (Fig. 3) increases from pH 6 to 5, reaches $> 90\%$ between pH 5 and 4 and drops to 50% at pH 3. This is again in agreement with Ulrich's scheme: In the cation–exchange buffer range and Al buffer range between pH 5 and 3.8 Al becomes dominant.

In the Al/Fe buffer range and Fe buffer range below pH 3.8 it is replaced by Fe and H (Fig. 4 and 5). Only in top soils Fe appears as exchangeable cation already between pH 6 and 4. This may be due to specific complex formation with the organic exchanger. The assumption of Fe(II) instead of Fe(III) results in apparently the same graph as Fig. 4 but the y–axis is transformed by the factor 2/3.

The Mn–saturation (Fig. 6) is higher in topsoils (0–10 cm). In subsoils it reaches a maximum at pH ≈ 5 in agreement with the findings of Ulrich (1991, p. 53).

K and Na (Fig. 7 and 8) account for less than 5% of the CEC. A clear relation to pH is not apparent.

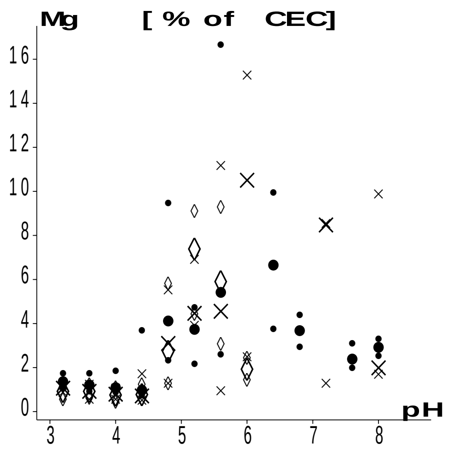

Fig. 2. Exchangeable Mg^{2+} as function of pH in saturation extract. Same symbols as in Fig. 1.

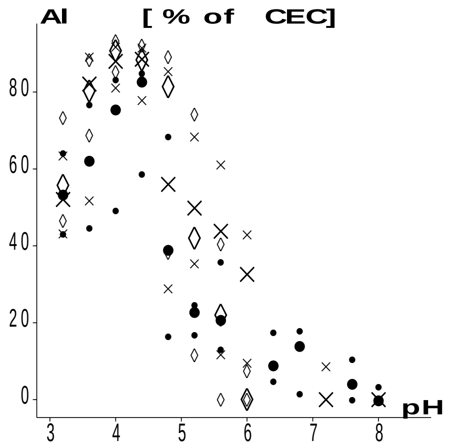

Fig. 3. Exchangeable Al^{3+} as function of pH in saturation extract. Same symbols as in Fig. 1.

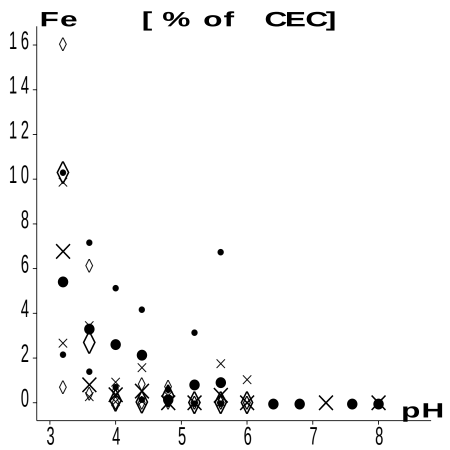

Fig. 4. Exchangeable Fe as Fe^{3+} as function of pH in saturation extract. Same symbols as in Fig. 1.

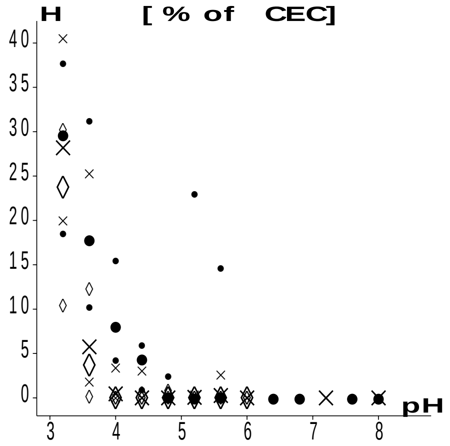

Fig. 5. Exchangeable H^+ as function of pH in saturation extract. Same Symbols as in Fig. 1.

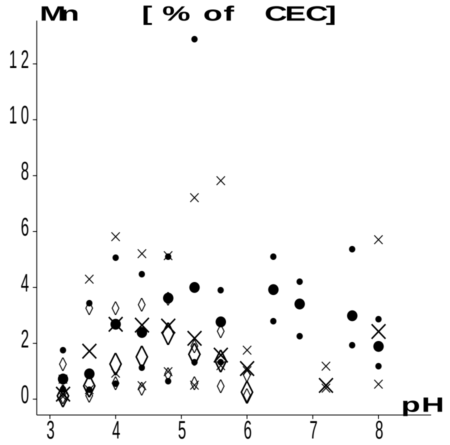

Fig. 6. Exchangeable Mn^{2+} as function of pH in saturation extract. Same symbols as in Fig. 1.

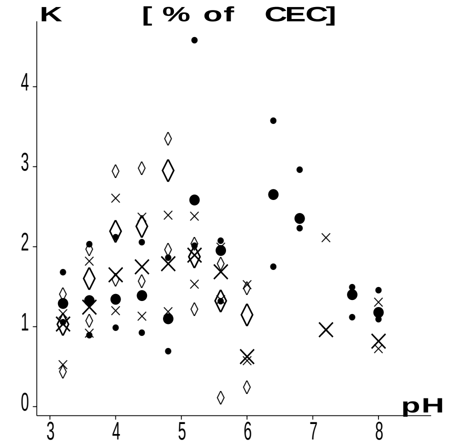

Fig. 7. Exchangeable K^+ as function of pH in saturation extract. Same symbols as in Fig. 1.

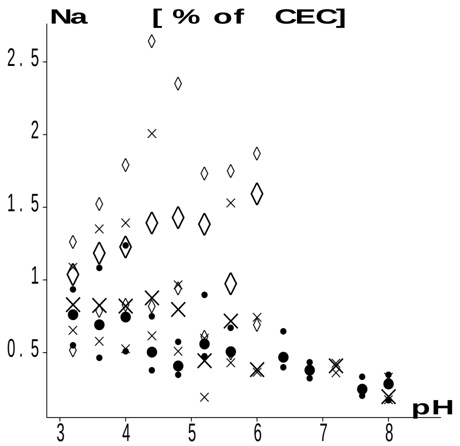

Fig. 8. Exchangeable Na^+ as function of pH in saturation extract. Same symbols as in Fig. 1.

3.2. Cation–exchange selectivity

Let A^{a+} and B^{b+} be cations and X denote one unit of charge of the cation exchanger. An exchange reaction may then be written as

$$\frac{1}{a}\mathrm{X_aA} + \frac{1}{\mathrm{b}}\mathrm{B^{b+}} \rightleftharpoons \frac{1}{\mathrm{b}}\mathrm{X_bB} + \frac{1}{\mathrm{a}}\mathrm{A^{a+}} \tag{2}$$

In analogy to the law of mass action one defines the selectivity coefficient for Eq. (2) (Bolt, 1979b) as

$$\frac{\mathrm{x_B^s}^{1/b}\,(\mathrm{A^{a+}})^{1/a}}{\mathrm{x_A^s}^{1/a}\,(\mathrm{B^{b+}})^{1/b}} = K^{\mathrm{sel}}_{\mathrm{A/B}} \tag{3}$$

or in logarithmic form

$$\frac{1}{b}\,\mathrm{pxB} + \frac{1}{\mathrm{a}}\,\mathrm{pA} - \frac{1}{\mathrm{a}}\,\mathrm{pxA} - \frac{1}{\mathrm{b}}\,\mathrm{pB} = \mathrm{pK^{sel}_{A/B}} \tag{4}$$

In modeling soil chemical processes it would be very helpful if the selectivity coefficients could be treated as constants. In that case computer programs exist that calculate the composition of the cation–exchange complex from the total amounts of cations present in the system (Prenzel, 1991).

In thermodynamic terms (cf. (Bolt, 1979b)) constant selectivity coefficients would result if the following model for the chemical potential of a cation A at the exchanger phase would hold:

$$\mu_{\bar{\mathrm{A}}} = \mu^0_{\bar{\mathrm{A}}} + RT\,\ln \mathrm{x^s_A}\ . \tag{5}$$

In this equation $\mu^0_{\bar{\mathrm{A}}}$ is a measure of specific preferrence of the exchanger for A, and the last term describes the dependence of the chemical potential on the concentration of A at the exchange complex.

In a system with n cations there are only $n-1$ independent selectivity coefficients because

$$K^{\mathrm{sel}}_{\mathrm{A/C}} = K^{\mathrm{sel}}_{\mathrm{A/B}}\,K^{\mathrm{sel}}_{\mathrm{B/C}} \tag{6}$$

for any three cations A, B, and C. It is sufficient to choose one reference cation X and to specify selectivity coefficients for all pairs $\mathrm{A_i/X}$ with $i = 1, \ldots, n; \mathrm{A_i} \neq \mathrm{X}$. Other combinations can be calculated from Eq. (6). We choose Ca as reference cation X.

We do not display selectivity coefficients directly but transform Eq. (4) according to Eq. (1) with $x_k = \mathrm{pxCa}$. Straight lines in the plots define a scale in $\mathrm{p}K^{\mathrm{sel}}_{\mathrm{A/Ca}}$, where A is an other cation.

In empirical data there is always a deviation from Eq. (5), in other words, selectivity coefficients will not be constant. It is not obvious how those deviations can be interpreted in a straightforward manner. A proper interpretation could be a parameter sensitivity analysis with a model that is based on cation selectivity constants. As a step in that direction, plots are presented that give an impression of the variance of cation–exchange selectivity coefficients in the population of soil samples under study. However any judgement on the constancy of observed cation selectivity coefficients can only describe differences among subsets of the observations as long as the context of using the cation selectivity coefficients is not defined.

The different observations in this study are not experiments with one exchange material or samples from one soil profile. But it facilitates the description of the results if we suppose so. Let it be a question under discussion how far the population of soil samples in one depth class appear as one exchanger material in different composition states.

The model Eq. (5), seems to fit best in divalent–divalent exchange. The data for both, $K^{\rm sel}_{\rm Mg/Ca}$, and $K^{\rm sel}_{\rm Mn/Ca}$ (Fig. 9 and 10) adhere relatively close to a $\mathrm{p}K^{\rm sel}$ = const line. The data points follow the slope of such a line if Eq. 5 decribes the dependence of the chemical potential of the exchangeable cations on the composition of the exchanger. The intercept then indicates the preferrence of the exchanger for the cation in question over Ca. The exchangers seem to prefer Mn to Ca and Ca to Mg.

There is no systematic difference between topsoils and subsoils for these exchange reactions. Bruggenwert and Kamphorst (1979, p. 172) report values of (recalculated) $\mathrm{p}K^{\rm sel}_{\rm Mg/Ca}$ from -0.1 to 0.4.

For the Ca–Al exchange the variability of $K^{\rm sel}_{\rm Al/Ca}$ is larger (Fig. 11). But in the range of pxCa > 1 (Ca–saturation $< 10\%$) the fit to a constancy line is similar to the divalent–divalent cases. In this range there is no difference between topsoils and subsoils. Most median points are between values of -0.3 and 0.3. Bruggenwert and Kamphorst (1979, p. 174) report values of (recalculated) $\mathrm{p}K^{\rm sel}_{\rm Al/Ca}$ from -0.2 to 0.6.

Fe is seldom considered as exchangeable cation in soils. But in acid forest soils the amounts extracted by NH_4Cl reach 15% of the CEC (Fig. 4). If Fe is assumed to be Fe(III) the Ca–Fe exchange can be described by constant $\mathrm{p}K^{\rm sel}_{\rm Fe/Ca}$ values at least at lower Ca–saturations and for topsoils (Fig. 12). The variability is larger than in the Al case. There is a clear difference between topsoils and subsoils. The exchangers prefer Fe to Al. If Fe(II) is assumed, the graph (Fig. 13) indicates a more random distribution of empirical cation selectivity coefficients.

In the determination of exchangeable H^+ the drop in pH on the addition of electrolyte is measured and a correction is made for the possible acidic effect of exchanged Al^{3+}. This correction is based on a thermodynamic complexation model (Meiwes *et al.*, 1984). Therefore the majority of exchange sites determined in this way should be strong acidic groups, comparable to a sulfonic exchange resin (Bolt *et al.*, 1976). The exchangeable H^+ thus determined is important in acid forest soils where it can amount to 40% of the CEC (Fig. 5).

The assumption of constant $pK^{sel}_{H/Ca}$ seems to be good for topsoils. The series of medians is contained between 1.4 and 1.7 (Fig. 14). The overall slope does fit rather well to that of the constancy lines, although there is a change at about 10% Ca–saturation. For subsoils the scatter is much greater.

Also Ca–Na exchange is not too badly described by constant $pK^{sel}_{Na/Ca}$, at least at Ca–saturations below 10% (Fig. 15). In that range the overall slope between the median points fits that of the constancy lines. There is a difference between topsoils and subsoils, but a range from 0.3 to 0.7 seems to cover all median values if $pxCa > 1$. Bruggenwert and Kamphorst (1979, p. 167) report values of (recalculated) $pK^{sel}_{Na/Ca}$ from 0.3 to 0.9.

The worst case for the description of observations by constant selectivity coefficients seems to be the Ca–K exchange (Fig. 16). The slope of the series of medians for different depth classes seems not at all to fit the slope of the constancy lines and the variability is greater than in all other cases. Bruggenwert and Kamphorst (1979, p. 168) report rather variable values too. But the majority of (recalculated) $pK^{sel}_{K/Ca}$ is between 0.5 and 1.5, as here in Fig. 16.

The exchangers seem to prefer H to K and K to Na, if the differences in ranges of pK^{sel} values in Fig. 14, 16, and 15 are considered.

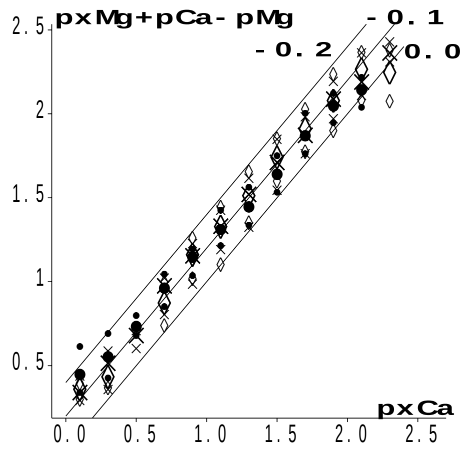

Fig. 9. Components of the empirical selectivity coefficient $\mathrm{p}K^{\mathrm{sel}}_{\mathrm{Mg/Ca}}$. Straight lines indicate $\mathrm{p}K^{\mathrm{sel}} = v$ with v noted in the graph. Medians (larger symbols) and quartiles (smaller symbols) in pH–classes. Bullets ($\bullet$) = 0–10, crosses ($\times$) = 10–30, diamonds ($\diamond$) = 30–100 cm.

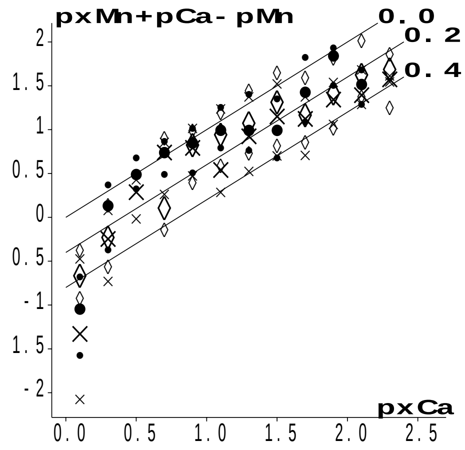

Fig. 10. Components of the empirical selectivity coefficient $\mathrm{p}K^{\mathrm{sel}}_{\mathrm{Mn/Ca}}$. Same symbols as in Fig. 9.

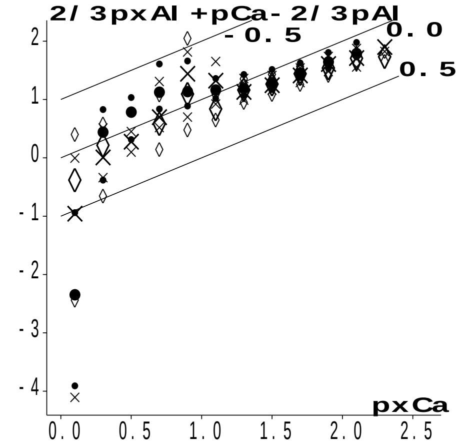

Fig. 11. Components of the empirical selectivity coefficient $pK^{sel}_{Al/Ca}$. Same symbols as in Fig. 9.

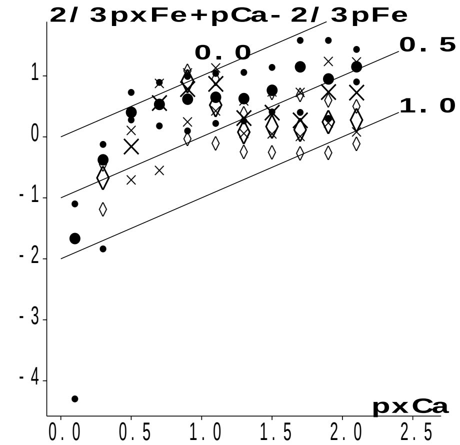

Fig. 12. Components of the empirical selectivity coefficient $pK^{sel}_{Fe/Ca}$. Fe assumed to be Fe(III). Same symbols as in Fig. 9.

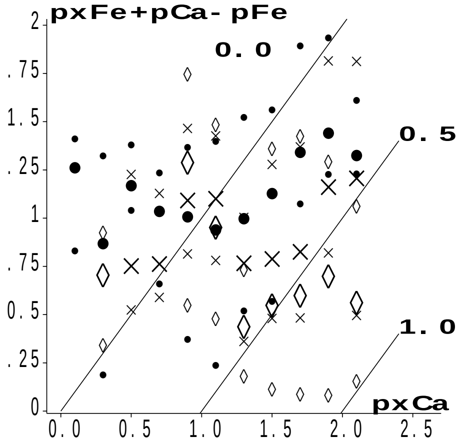

Fig. 13. Components of the empirical selectivity coefficient $pK^{sel}_{Fe/Ca}$. Fe assumed to be Fe(II). Same symbols as in Fig. 9.

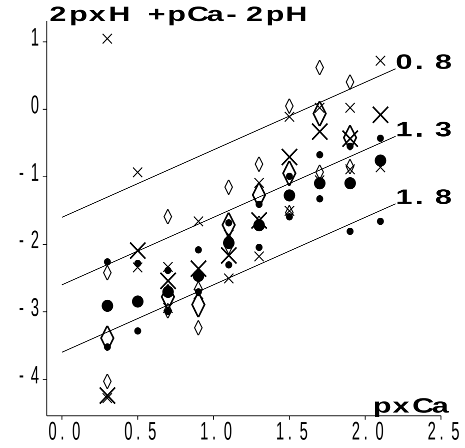

Fig. 14. Components of the empirical selectivity coefficient $pK^{sel}_{H/Ca}$. Same symbols as in Fig. 9.

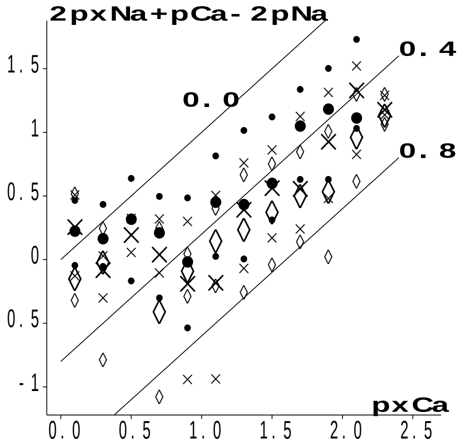

Fig. 15. Components of the empirical selectivity coefficient $pK^{sel}_{Na/Ca}$. Same symbols as in Fig. 9.

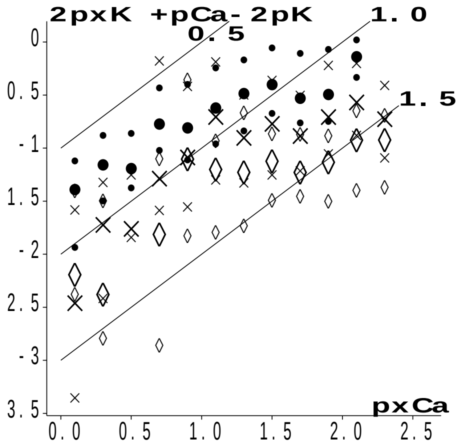

Fig. 16. Components of the empirical selectivity coefficient $pK^{sel}_{K/Ca}$. Same symbols as in Fig. 9.

3.3. Ion activity products

Let a salt be composed of n different ions $A_1, \ldots, A_n$. Let there be a_i ions of A_i in the salt formula.

If there is an aquaeous solution in equilibirum with this salt it is often found that

$$(A_1)^{a_1} \cdot (A_2)^{a_2} \cdot \ \ldots \ \cdot (A_n)^{a_n} = K_{sp} \tag{7}$$

where parentheses () indicate ionic activities in solution and K_{sp} is the solubility product of the salt.

Eq. (7) is derived from the following model for the chemical potential of an ion A in the salt phase:

$$\mu_{\bar{A}} = \mu^0_{\bar{A}} \ . \tag{8}$$

That means, the chemical potential of the ionic components of the salt is constant, it is not dependent on any concentration changes, as e. g. in Eq. (5). This implies that the salt is of constant internal composition, that no solid solutions are formed, and that the salt is homogenous.

The left hand side of Eq. (7) can be observed in aqueous solutions, regardless whether a solubility equilibirum with the salt exists. It is then called an ion activity product, IAP. In logarithmic form,

$$\mathrm{pIAP} = \sum_{i=1}^{n} a_i \, pA_i \tag{9}$$

The solubility equilibrium is then indicated by $\mathrm{pIAP} = \mathrm{pK_{sp}}$. Undersaturation would be indicated by $\mathrm{pIAP} > \mathrm{pK_{sp}}$ and oversaturation by $\mathrm{pIAP} < \mathrm{pK_{sp}}$.

We investigate ion activity products of $Al(OH)_3$, $KAl_3(OH)_6(SO_4)_2$, and $AlOHSO_4$. In the expressions resulting from Eq. (9) we first replace pOH by $14 - \mathrm{pH}$ and then, following the discussion of Eq. (1), choose pH as x–variable, x_k. The graphs display z accross x_k and contain straight lines indicating $\mathrm{pIAP} = \mathrm{pK_{sp}}$ conditions.

Amorphous precipitates are metastable phases that form quicker than the crystalline forms of the same stoichiometry. If the data points in Fig. 17 – 19 follow a line with lower pIAP parameter than that of crystalline minerals it may be that the solution composition is controlled by such amorphous precipitates. If the data points are on the undersaturated side (above) the $\mathrm{p}K_{sp}$ line of a mineral it may be that either the mineral is not present or is dissolving too slowly to attain equilibrium. The lines in Fig. 17 – 19 do not represent specific mineral modifications but are rather scales in pIAP. Reference $\mathrm{pK_{sp}}$ values for minerals are (Nordstrom, 1982) 33.9 for gibbsite, $Al(OH)_3$, 85.6 for alunite, $KAl_3(OH)_6(SO_4)_2$, and 17.8 for jurbanite, $AlOHSO_4$.

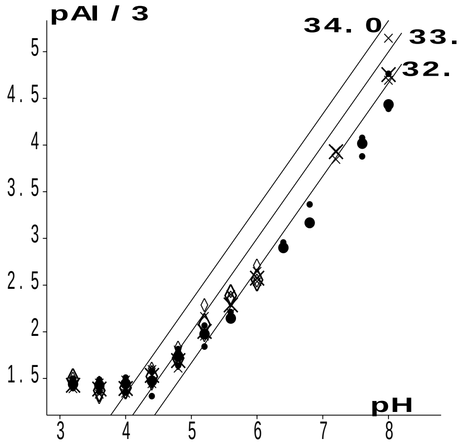

Fig. 17. Components of the empirical ion activity product for gibbsite, $Al(OH)_3$. Straight lines indicate pIAP = v with v noted in the graph. Medians (larger symbols) and quartiles (smaller symbols) in pH–classes. Bullets (•) = 0–10, crosses (×) = 10–30, diamonds (◇) = 30–100 cm.

The solutions are undersaturated with respect to gibbsite below pH 4 (Fig. 17). With increasing pH there seems to be an equilibrium with more and more soluble $Al(OH)_3$. The slope of the data points follows rather well the lines of constant pIAP. But data at pH > 6 must be interpreted with some caution because total Al concentration is low, complexed forms become dominant, and organic complexes have not been taken into account. If we take 32.3 (Novozamsky & Beek, 1976) as lower value for the pK_{sp} of an amorphous $Al(OH)_3$, we can say that equilibria with precipitates of this composition may exist between pH 4 and 5 in the soil saturation extracts under investigation.

Equilibria with alunite may exist down to pH ≈ 3.8 (Fig. 18). At higher pH values the data points follow the lines of constant pIAP till pH 7. But the solutions seem rather oversaturated at pH > 4.8. Nordstrom (1982) mentions the kinetic inhibition of alunite formation at low temperatures, which is compatible with oversaturation.

The conditions for jurbanite solubility equilibria seem to exist only between pH 3.5 and 4.8 (Fig. 19). This is compatible with the amphoteric nature of $AlOHSO_4$, which dissolves to ionic forms at lower pH and gives way to solid phases with less sulfate under more alkaline conditions (Prenzel, 1983).

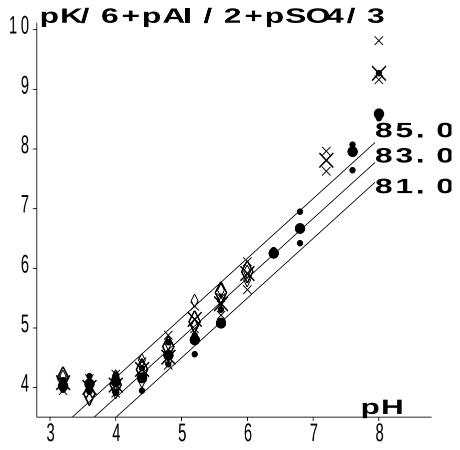

Fig. 18. Components of the empirical ion activity product for alunite, $KAl_3(OH)_6(SO_4)_2$. Same symbols as in Fig. 16.

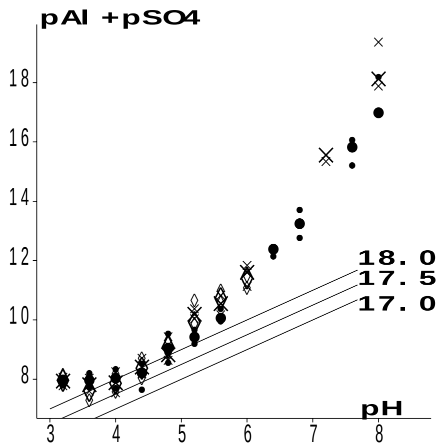

Fig. 19. Components of the empirical ion activity product for jurbanite, $AlOHSO_4$. Same symbols as in Fig. 16.

4. CONCLUSIONS

Soil chemical data from a spectrum of German forest soils have been reviewed. Despite varying geological conditions some rather close relations can be identified within this data pool.

The composition of the cation–exchange complex is related to pH in accordance with Ulrich's model (Ulrich, 1981; Ulrich, 1991). In the *carbonate buffer range* Ca (+ Mg) dominate. They are replaced by Al in the *cation–exchange and Al buffer ranges*, which is replaced by H and Fe in the *Al/Fe and Fe buffer range*.

Empirical cation selectivity coefficients vary less than 1 pK^{sel} unit in general, but in some cases and regions the variance is less than 0.3 units. Rather constant values are found for Ca/Mg and Ca/Mn exchange. For Ca/Al and Ca/Na they are more or less constant at lower Ca–saturations. For Ca/Fe (Fe assumed as Fe(III)) and Ca/H this holds only for topsoils. The preferrence of the exchangers follows Fe > Al and Mn > Ca > Mg and H > K > Na. If Fe(II) is assumed a model of constant selectivity coefficients seems to be not applicable at all.

Solubility equilibria with $Al(OH)_3$ may exist at pH > 4, with $KAl_3(OH)_6(SO_4)_2$ at pH > 3.8, and with $AlOHSO_4$ at 3.5 < pH < 4.8 in the soil samples under study as judged from median values.

No objection has been found to the use of these relations in the conceptual interpretation of soil chemical data as well as in computer–aided models, as long as the variance that shows up in the graphs is also considered.

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