Derivation of cation exchange constants for sand loess, clay and peat soils on the basis of field measurements in the Netherlands

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W. de Vries [1]
M. Posch [2]

[1] Alterra
[2] RIVM/CCE

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ABSTRACT

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This report presents extensive Tables of cation exchange constants (selectivity coefficients) for sand, loess, clay and peat soils at different depths derived from simultaneous field measurements of adsorbed in dissolved concentrations of H, Al, Ca, Mg, K and Na in several hundreds of non-agricultural soils in the Netherlands. Data are provided for the two most widely used cation exchange models (Gaines-Thomas and Gapon) and for all possible combinations of cations, including protons. Results show a wide range in exchange constants, especially when using the Gaines-Thomas exchange description. It appears that Gapon exchange constants are stronger correlated than the corresponding Gaines-Thomas exchange constants, especially for sandy soils. A strong positive correlation means that the *ratio* between two exchange constants is more characteristic, and less variable, of a certain soil (type) than their absolute numbers, which often vary by several orders of magnitude.
In deriving exchange constants, the Al constants were related to free Al^{3+}, the CEC was normalised to a buffered soil pH of 6.5 and the dissolved ion concentrations have all been derived while using a centrifugation method to extract the soil solution. Because of these methodological aspects, they cannot always be used directly in a particular model application. Nevertheless, they provide insight into the numerical ranges of and correlations between exchange constants, and are thus useful for constraining model parameters, e.g. in model calibrations.

Keywords: Cation exchange, Dynamic soil model, Gaines-Thomas, Gapon, Soil acidification

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Preface

Cation exchange, i.e. the interaction between dissolved and adsorbed cations, is a key soil chemical process. Therefore, a description of cation exchange is part of every dynamic model simulating the acidification and recovery of soils and surface waters. Depending on the model, there are one or more constants (selectivity coefficients) which are characteristic for the system (site) and determine the relative speed and magnitude of de/adsorption of the cations.

This report presents extensive Tables of cation exchange constants (selectivity coefficients) for sand, loess, clay and peat soils at different depths derived from simultaneous field measurements of adsorbed in dissolved cations in several hundreds of non-agricultural soils in the Netherlands. Data are provided for the two most widely used cation exchange models (Gaines-Thomas and Gapon) and for all possible combinations of cations, including protons.

In addition to the insight this provides into the range and variability of the different selectivity coefficients, the data presented in this Report can also assist in the selection of appropriate inputs for dynamic model applications or – if selectivity coefficients are calibrated – can provide ranges and correlations between them. Especially in regional dynamic model applications, exchange constants (and other input parameters) are unlikely to be available from on-site measurements. Thus other sources of data, which relate the exchange constants to more readily available soil properties, become indispensable. It is the hope of the authors that this Report will provide insight into cation exchange constants and their interrelations and be of help in dynamic model applications in general and the ongoing dynamic modelling work under the Convention on Long-range Transboundary Air Pollution (LRTAP) in particular.

We are grateful to Sabine Braun (Institute for Applied Plant Biology, Switzerland) for providing the data used to calculate the exchange constants presented in Tables 58 and 59. We would also like to acknowledge Cees Voogd for processing the data.

Summary

Dynamic soil acidification models are an important tool to assist in the evaluation of effects-based strategies to control sulphur and nitrogen emissions. Crucial data in such models are cation exchange constants, describing the interactions between dissolved and adsorbed cations, including protons, in soils.

This report presents the calculation of exchange constants between all combinations of H, Al, Ca, Mg, K and Na at different depths for sand loess, clay and peat soils on the basis of simultaneous field measurements of adsorbed in dissolved cations in several hundreds of Dutch non-agricultural soils. The exchange constants are calculated according to both the Gaines-Thomas and the Gapon cation exchange descriptions. The report also includes exchange constants for (a) H^+, Al^{3+} and B^+ against B^{2+} with $B^+ = K+Na$ and $B^{2+} = Ca+Mg$, (b) H^+, Al^{3+} and Na^+ against Bc^{2+} with $Bc^{2+} = Ca+Mg+K$ and (c) H^+ and Al^{3+} against BC^{2+} with $BC^{2+} = Ca+Mg+K+Na$. These aggregated exchange constants are included since such simplifications are used in some dynamic soil acidification models. Furthermore, the mathematical connections and correlations between the different exchange constants are derived and discussed.

Data sets that were used to calculate the exchange constants were:

- 12 forest stands on non-calcareous sandy soils sampled in 1992: the humus layer and the depths of 0-10 cm, 10-30cm, 30-60 cm and 60-100 cm.
- 48 stands on non-calcareous sandy soils in the Dutch dune area sampled in 1991: the depths of 0-10 cm, 10-30 cm, 30-60 cm and 60-100 cm.
- 150 forest stands on non-calcareous sandy soils sampled in 1990: the depth of 0-30 cm.
- 200 forest stands on non-calcareous sandy soils sampled in 1995: the humus layer and the depths of 0-10 cm.
- 100 forest stands sampled between 1992 and 1993 in approximately 40 loess soils, 30 clay soils and 30 peat soils: the depths of 0-10 cm, 10-30 cm, 30-60 cm and 60-100 cm.
- 63 forest stands in an area called Drentse Aa, sampled in 1994: 44 sandy soils, 4 clay soils and 15 peat soils; the mineral topsoil with depths varying from 0-10 cm and 0-30 cm.

Cation exchange constants were not only calculated for the depths 0-10 cm, 10-30 cm, 30-60 cm and 60-100 cm, but also for the layers 0-30 cm and 0-60 cm by depth weighted averaging of the adsorbed fractions and dissolved concentrations in sub-layers. The latter layers were included because of their relevance for one-layer dynamic soil models.

Results show a wide range in exchange constants, especially when using the Gaines-Thomas exchange description. It appears that Gapon exchange constants are stronger correlated than the corresponding Gaines-Thomas exchange constants,

especially for sandy soils. A strong positive correlation means that the *ratio* between two exchange constants is more characteristic, and less variable, of a certain soil (type) than their absolute numbers, which often vary by several orders of magnitude.

In deriving exchange constants, the Al constants were related to free Al^{3+}, the CEC was normalised to a buffered soil pH of 6.5 and the dissolved ion concentrations have all been derived while using a centrifugation method to extract the soil solution. This affects the results as described below.

Free Al: Free Al^{3+} concentrations were calculated from the total concentration of Al and DOC using a triprotic acid analogue model. In several dynamic soil models, however, no complexation of Al with DOC is included and the exchange constants used thus relate to total Al concentrations. To give insight in the impact of neglecting complexation, exchange constants were also calculated using total Al concentrations in solution. Results show that the impact on Gaines Thomas constants appears to be larger than on Gapon constants.

Buffered soil pH: The exchange constants derived in this report for Dutch soils, with a CEC buffered at a pH of 6.5, were compared with exchange constants derived from an independent data set of Swiss sandy to loamy soils. The results shows that both the Gaines Thomas and Gapon exchange constants in the Dutch sandy soils tend to be higher for H against total Al and lower for Al against Ca+Mg+K compared to the Swiss sandy to loamy soils. Similarly, the preference of protons against base cations is clearly higher for the Dutch soils. This is most likely due to the fact that the Dutch exchange constants have been related to a pH buffered at 6.5, whereas the CEC of the Swiss soils is the actual soil CEC.

Extraction method: Insight in the difference in ion concentrations by centrifugation and suction cup lysimeters has been derived from literature information. Comparative study of both methods at two forested plots in the Netherlands showed that ion concentrations are generally significantly higher in the centrifugates than in the suction cup lysimeters with the exception of pH, Al and NH_4. On average, Al concentrations were even higher in lysimeters compared to centrifugates. This implies that exchange constant of Al against base cations will be consistently higher when using lysimeters compared to centrifugation, a conclusion also recently drawn in the literature based on research in two Finnish plots.

In summary, the exchange constants presented are influenced by the methodology used and in certain cases they cannot be used directly in a particular model application. Nevertheless, they provide insight into the numerical ranges of and correlations between exchange constants, and are thus useful for constraining model parameters, e.g. in model calibrations.

1 Introduction

Background

During the past 20 years scientists have been developing, testing and applying dynamic models to simulate the acidification of soils or surface waters. Nevertheless, dynamic modelling is a relatively new topic for the effects-oriented work under the 1979 Convention on Long-range Transboundary Air Pollution (LRTAP). Earlier work has applied dynamic models mostly at sites for which a sufficient amount of input data was available. The new challenge is to develop and apply dynamic model(s) on a European scale and to integrate them as much as possible with the integrated assessment work under the LRTAP Convention in support of the review and potential revision of the 1999 Gothenburg Protocol.

Cation exchange, i.e. the interaction between dissolved and adsorbed cations, is a key soil chemical process, thus being part of every dynamic model simulating the acidification and recovery of soils and surface waters. Depending on the model, it includes one or more constants (selectivity coefficients) which are characteristic for the system (site) and determine the relative speed and magnitude of de/adsorption of the cations. For large-scale regional dynamic model applications, input data in general and exchange constants in particular will not be available from measurements at each 'site' (mapping unit) and they will have to be derived from available information via (pedo-)transfer functions or other inference techniques. In order to facilitate this process, a large amount of data available in the Netherlands have been collected and used to compute exchange coefficients and to explore the relationships between them. It is the hope of the authors that these data, even if they cannot be used directly in a particular model application, provide insight into the numerical ranges of and correlations between exchange constants, and are thus useful for constraining model parameters, e.g. in model calibrations.

Aim of this report

The aim of this Report is to present computations of mean values and ranges of cation exchange constants (selectivity coefficients) for different depths for sand, loess, clay and peat soils utilising data from simultaneous field measurements of adsorbed and dissolved cations in several hundreds non-agricultural soils in the Netherlands. Exchange coefficients are computed for the two most widely used cation exchange models (Gaines-Thomas and Gapon) and for all possible combinations of cations, including protons. Furthermore the mathematical relationships between the exchange coefficients are derived and examples of their correlations given. Some of the information presented in this Report is also included in the so-called "Dynamic Modelling Manual" (Posch et al., 2003). This manual provides information for the National Focal Centres of the ICP on Modelling and Mapping and their collaborating institutes on the concepts and data requirements to carry out dynamic modelling for the effects-oriented work under the LRTAP Convention.

2 Methods and data

2.1 Derivation of exchange constants: theoretical considerations and practical approach

Description of cation exchange

In general the solid phase particles of a soil carry an excess of cations at their surface layer. Since electro-neutrality has to be maintained, these cations cannot be removed from the soil, but they can be exchanged against other cations, e.g. those in the soil solution. This process is known as cation exchange; and every soil (layer) is characterised by the total amount of exchangeable cations per unit mass (weight), the so-called cation exchange capacity (CEC, measured in meq.kg^{-1}).

Equations describing cation exchange are derived using basic principles of thermodynamics. Depending on the assumptions employed, different mathematical formulations of cation exchange are obtained. Although cation exchange has been studied for a long time (e.g., Rothmund and Kornfeld, 1918; 1919), it is still the subject of many (theoretical) investigations. It is beyond the scope of this report to review the (simplifying) assumptions and considerations of the various formulations of cation exchange, and the reader is referred to textbooks (e.g. Bolt and Bruggenwert, 1978) or review articles (e.g., Bolt, 1967). In view of their (almost) exclusive use in (simple) dynamic soil models, we restrict ourselves to formulations of cation exchange by Gaines-Thomas (Gaines and Thomas, 1953) and Gapon (Gapon, 1933).

If X and Y are two cations with charges m and n, then the general form of the equations used to describe the exchange between the liquid-phase concentrations (or activities) [X] and [Y] and the equivalent fractions E_X and E_Y at the exchange complex is

$$\frac{E_X^i}{E_Y^j} = K_{XY} \cdot \frac{[X^{m+}]^n}{[Y^{n+}]^m} \tag{1}$$

where K_{XY} is the so-called exchange (or selectivity) constant, a soil-dependent quantity. Depending on the powers i and j different models of cation exchange can be distinguished: For i=n and j=m one obtains the Gaines-Thomas exchange equations, whereas for i=j=mn, after taking the mn-th root, the Gapon exchange equations are obtained. The Vanselow equations (Vanselow, 1932) of cation exchange (not considered here) are of the same type as the Gapon equations, but using mole fractions instead of equivalent fractions at the exchange complex; see Sposito (1977) and Reuss (1983) for comparisons. Although from a theoretical standpoint activities would be more appropriate, we only consider exchange equations involving concentrations, since they are mostly used in simple models.

If the exchange between N cations is considered, N^2 exchange equations (and constants) are conceivable. N equations are trivial, they involve the exchange of an ion with itself, which immediately leads to

$$K_{XX} = 1 \quad \text{for all } X \tag{2}$$

Furthermore, if the exchange between ions X and Y is given by Eq.1, the exchange between Y and X is given by the inverse of Eq.1, from which follows:

$$K_{YX} = \frac{1}{K_{XY}} \quad \text{for all } X, Y \tag{3}$$

This leaves $N(N-1)/2$ equations to consider. However, the exchange between three ions X, Y and Z can be completely described by two equations, since the third one can always be obtained by division or multiplication of the other two. Let Z be a third ion with charge k, then the three Gaines-Thomas exchange equations read (see Eq.1):

$$\frac{E_X^n}{E_Y^m} = K_{XY} \cdot \frac{[X^{m+}]^n}{[Y^{n+}]^m}\,, \quad \frac{E_Y^k}{E_Z^n} = K_{YZ} \cdot \frac{[Y^{n+}]^k}{[Z^{k+}]^n}\,, \quad \frac{E_X^k}{E_Z^m} = K_{XZ} \cdot \frac{[X^{m+}]^k}{[Z^{k+}]^m} \tag{4}$$

Taking the k-th power in the first and the m-th power of the second equation, multiplying them, taking the n-th root and comparing the result to the third equation shows that:

$$K_{XZ} = K_{XY}^p \cdot K_{YZ}^q \quad \text{for all} \quad X, Y, Z \tag{5}$$

where $p=k/n$, $q=m/n$ for the Gaines-Thomas model. For the Gapon exchange model the result is even simpler: just set $p=q=1$ in Eq.5. Thus, $N-1$ exchange constants are sufficient to describe all possible exchange reactions between N cations, since the remaining relationships and constants can be derived from them with the aid of Eqs.2-5.

If $X_1, \ldots, X_N$ are all the N ions for which cation exchange is considered, then charge balance requires that the sum of the exchangeable fractions equals one:

$$E_{X_1} + E_{X_2} + \ldots + E_{X_N} = 1 \tag{6}$$

In this report we consider as exchangeable ions only H^+, Al^{3+} and the base cations Ca^{2+}, Mg^{2+}, K^+ and Na^+; other ions (e.g. heavy metals) are subsumed under the proton fraction. The sum of the fractions of exchangeable base cations is called the *base saturation* of the soil; and it is mostly the time development of the base saturation, which is of interest in dynamic modelling.

In several models also lumped ions are considered, such as divalent base cations, $BC^{2+}=Ca^{2+}+Mg^{2+}$. Since exchange equations for such sums, even if they involve only ions of identical charge, cannot be derived by any mathematical operations from the exchange equations for the single ions, separate exchange coefficients have to be defined for them, e.g.:

$$\frac{E_H^2}{E_{BC}} = K_{HBC} \cdot \frac{[H^+]^2}{[BC^{2+}]} \tag{7}$$

where $E_{BC} = E_{Ca} + E_{Mg}$ and $[BC^{2+}]=[Ca^{2+}]+[Mg^{2+}]$.
Next we discuss the procedures for estimating exchange constants from observations and the relationships between their statistical properties.

Deriving exchange constants from data: theoretical considerations

In this report exchange constants are derived from simultaneous measurements of concentrations and exchangeable fractions of the protons, aluminium and the four base cations at different sites and soil layers. The computations are carried out for logarithms of the quantities involved. Taking the decadic logarithm in Eq.1, one obtains:

$$L_{XY} = a \cdot \log_{10} E_X - b \cdot \log_{10} E_Y + c \cdot \log_{10}[Y^{n+}] - d \cdot \log_{10}[X^{m+}] \tag{8}$$

where

$$L_{XY} = \log_{10} K_{XY} \tag{9}$$

In Eq.8 a=d=n and b=c=m for the Gaines-Thomas model and a=b=1, c=1/n, d=1/m for the Gapon model (see Eq.1); and the concentrations are to be inserted in mol/l. Eqs.2,3 and 5 can be re-written for the logarithms of the exchange constants; e.g., from Eq.5 we find:

$$L_{XZ} = p \cdot L_{XY} + q \cdot L_{YZ} \tag{10}$$

Eq.8 is applied to every measurement, resulting in a set of data $L_{XY,i}$, i=1,...,N, where N is the number of measurements. In the following we consider L_{XY} as a random variable with outcomes $L_{XY,i}$. Its expected value (mean) $\mathbf{E}(L_{XY})$ and variance $\mathbf{Var}(L_{XY})$ can be calculated according to the formulae summarised in Appendix A. From Eq.3 we find immediately:

$$\mathbf{E}(L_{YX}) = -\mathbf{E}(L_{XY}) \tag{11}$$

And since Eq.10 is linear, the mean of L_{XZ} is a linear combination of those of L_{XY} and L_{YZ}:

$$\mathbf{E}(L_{XZ}) = p \cdot \mathbf{E}(L_{XY}) + q \cdot \mathbf{E}(L_{YZ}) \tag{12}$$

The variances of inverse exchange constants are identical (see Eq.A8 in Appendix A):

$$\mathbf{Var}(L_{YX}) = \mathbf{Var}(L_{XY}) \tag{13}$$

Since the exchange constants are correlated, the variances can not be calculated from each other without the knowledge of their covariances (see Eq.A11). However, if the variances of all exchange constants of three ions are known, their covariances and correlation coefficients can be computed from them (see Eqs.A12-14).

Deriving exchange constants from data: practical approach

An overview of the computed cation exchange constants is given in Table 1. In addition to the exchange constants between the individual ions, also constants between H, Al and different combinations of base cations have been calculated, since they are used in various models.

For example, in the SMART model, the divalent base cations Ca and Mg are lumped as B^{2+}. We thus calculated the exchange constants for H^+, Al^{3+} against B^{2+}. In acidification research, use is often made of the Al/(Ca+Mg+K) ratio as an indicator for impacts on roots. Therefore, we also calculated the exchange constants K_{AlBc} and K_{HBc}, with Bc= Ca+Mg+K, assuming that Bc is divalent. Finally, on a European scale, data are often only available for the CEC and the base saturation, being the sum of the base cations Ca, Mg, K and Na. To allow model calculations in this case, we also calculated the exchange constants K_{AlBC} and K_{HBC} with BC=Ca+Mg+K+Na, again assuming that BC is divalent. Finally, for completeness, we also calculated the exchange with the sum of monovalent base cations, B^+=K+Na.

Table 1 Cation exchange constants calculated: An **X**’ *indicates that the respective constant* K_{XY} *is calculated; an ‘x’ indicates the inverse exchange constant, which is not calculated since* $K_{YX}=1/K_{XY}$*; a dash indicates ‘impossible’ exchange constants, i.e. one (or more) of the ions appear in X* ***and*** *Y.*

X	Y									
	H	Al	Ca	Mg	K	Na	B^{2+}	B^+	Bc^{2+}	BC^{2+}
H	1	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
Al	x	1	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
Ca	x	x	1	**X**	**X**	**X**	-	-	-	-
Mg	x	x	x	1	**X**	**X**	-	-	-	-
K	x	x	x	x	1	**X**	-	-	-	-
Na	x	x	x	x	x	1	-	-	**X**	-
B^{2+}	x	x	-	-	-	-	1	**X**	-	-
B^+	x	x	-	-	-	-	x	1	-	-
Bc^{2+}	x	x	-	-	-	x	-	-	1	-
BC^{2+}	x	x	-	-	-	-	-	-	-	1

2.2 Data used

Available data sets

Data for both the adsorbed and dissolved concentrations of H, Al, Fe, Mg, K, Na or NH_4, needed to calculate cation exchange constants, were available for hundreds of natural ecosystems in the Netherlands, in nearly all cases forest stands. Data sets used to calculate exchange constants were:

- 12 forest stands on non-calcareous sandy soils sampled in 1992: the humus layer and the depths of 0-10, 10-30cm, 30-60 cm and 60-100cm (De Vries et al., 1994).
- 48 stands on non-calcareous sandy soils in the Dutch dune area sampled in 1991: the depths of 0-10 cm, 10-30cm, 30-60 cm and 60-100cm (De Vries, 1993; de Vries, unpublished data).
- 150 forest stands on non-calcareous sandy soils sampled in 1990: the depths of 0-30 cm (De Vries and Leeters, 2001).
- 200 forest stands on non-calcareous sandy soils sampled in 1995: the humus layer and the depths of 0-10 cm (Leeters and De Vries, 2001).
- 100 forest stands sampled between 1992 and 1993 in approximately 40 loess soils, 30 clay soils and 30 peat soils: the depths of 0-10 cm, 10-30 cm, 30-60 cm and 60-100 cm (Klap et al., 1999).
- 63 forest stands in an area called Drentse Aa, sampled in 1994: 44 sandy soils, 4 clay soils and 15 peat soils; the mineral topsoil with depths varying from 0-10 cm and 0-30 cm (Klap et al., 1997).

In all studies, the soil solution was extracted by centrifugation and the dissolved cation concentrations were measured with ICP and AAS. The exchangeable cation fractions were always measured in an unbuffered silverthioureum solution, which is comparable to an unbuffered bariumchloride solution. More information on data assessment methods is given in the publications mentioned above.

Data used for different soil types and soil depths

An overview of the minimum available number of data points for each combination of soil type and soil depth is given in Table 2. The actually used number for certain combinations of cations could be higher, but this aspect is further discussed in Section 3. The numbers for the layers 0-10 cm, 10-30 cm, 30-60 cm and 60-100 cm were based on the numbers of measurements for those layers. The numbers for the layer 0-30 cm were based on a combination of measurements (150 sandy soils in 1990; De Vries and Leeters, 2001) and calculations by depth weighted averaging of adsorbed fractions and dissolved concentrations for the layers 0-10 cm and 10-30 cm. The numbers for the layer 0-60 cm were only based on calculations by depth weighted averaging of adsorbed fractions and dissolved concentrations for the layers 0-10 cm, 10- 30 cm (or 0-30 cm) and 30-60 cm. The latter layers were included because of their relevance for one-layer models, such as SMART, in which the considered soil depth generally equals the rootzone or the part where most of the water and nutrient uptake takes place.

The number of data points were by far largest for the layers 0-10 cm and 0-30 cm for the non-calcareous sandy soils mainly because of measurements in 200 and 150 forest stands in 1995 and 1990, respectively (De Vries and Leeters, 2001; Leeters and de Vries, 2001). The number of data points used for each combination of soil type and soil depth is however less than the number of forest stands mentioned before in the section on data sets. This is partly because we only used data in which all involved cations were measured both in solution and on the exchange complex.

Furthermore, the calculation of exchange constants is extremely sensitive (becomes unstable) in situations where the adsorbed fractions or concentrations of the involved cations is extremely low.

Table 2 Number of minimum available data points that were used to calculate cation exchange constants for each combination of soil type and soil depth.

Soil depth (cm)	Sand	Loess	Clay	Peat	All
0-10	166	37	27	34	264
10-30	48	37	5	25	115
30-60	31	0	2	21	54
60-100	11	30	1	12	54
0-30 [a)]	200	36	20	32	288
0-60 [b)]	45	0	11	25	81
All	501	140	66	149	856

[a)] There are additional measurements for the layer 0-30 cm after inclusion of the quality checks.

[b)] There are additional measurements for the layer 0-60 cm after inclusion of the quality checks.

To avoid the calculation of such outliers, the following requirements were set:

- The minimum values for adsorbed fractions are 0.001 (0.1%) for Na and K, 0.002 for Mg and Al and 0.003 for Ca and H. These rather arbitrary values avoided specifically outliers in the exchange with monovalent cations.
- The minimum value for dissolved concentrations is 0.01 meq.l^{-1} for Na, K, Ca and Mg and the pH is less than 6.5 (non-calcareous soils).

Apart from screening the data on outliers, a further reduction was due to the calculation of free Al^{3+} concentrations from total concentration and DOC, since DOC was not always available. This aspect is further discussed in the following section.

2.3 Data preparation

Calculation of the free aluminium concentration

The field measurements that were used to calculate cation exchange constants include only total Al concentrations (both free Al and Al complexed with dissolved organic carbon and other complexes). Free Al^{3+} concentrations were thus calculated from the total concentration of Al and dissolved organic carbon (DOC) using the speciation programme MINEQL+ (Schecher and McAvoy, 1994), combined with a triprotic organic acid model, in which complexation of Al by DOC is taken into account (Santore et al., 1995). In the latter model, the total concentration of organic acids is first calculated as a function of DOC according to:

$$A_T = M_D \cdot DOC \qquad (14)$$

where A_T is the total concentration of organic functional groups (mol.l^{-1}), M_D is the site density of organic solutes (mol.$molC^{-1}$) and DOC is the Dissolved Organic Carbon concentration (molC.l^{-1}). Santore et al. (1995) reported values for M_D between 0.014 for topsoil samples and 0.044 mol.$molC^{-1}$ for a B-horizon in the

Hubbard Brook experimental forest in New Hampshire. In this study we used a value of 5.5 $mol.kgC^{-1}$, or 0.066 $mol.molC^{-1}$, based on De Vries and Bakker (1998).

In the triprotic organic acid model, the various organic functional groups are represented as a triprotic organic acid. Al in solution can thus be complexed to A^{3-}, HA^{2-} and H_2A^-. The relevant reactions that were incorporated in the speciation model MINEQL+, including the associated equilibrium constants that were used to calculate complexation of Al with DOC, are given below, following Santore et al. (1995).

$A^{3-} + H^+ \rightarrow HA^{2-} \qquad \log_{10}K = 6.48$
$A^{3-} + 2H^+ \rightarrow H_2A^- \qquad \log_{10}K = 11.69$
$A^{3-} + 3H^+ \rightarrow H_3A \qquad \log_{10}K = 13.71$

$Al^{3+} + A^{3-} \rightarrow AlA \qquad \log_{10}K = 7.89$
$Al^{3+} + A^{3-} + H^+ \rightarrow AlHA^+ \qquad \log_{10}K = 12.86$

A test for soil solutions from a number of column experiments on Dutch sandy soils showed that the calculated concentrations of organically complexed Al were comparable (difference<10%) to measured concentrations (Van der Salm, 1999). The relations between pAl ($=-\log_{10}[Al]$) and pH of the soil solution were calculated for both activities and concentrations, since several models calculate H concentrations as a function of Al concentrations instead of Al activities.

Obtaining the cation exchange capacity at pH 6.5

In all the data sets that were used the CEC value was measured at the actual (unbuffered) pH. Especially in acid soils (non-calcareous sandy soils, most loess and peat soils) this implies that the cation exchange constants are only applicable in the limited pH range of the soils considered (mainly between pH 3 and 5). The CEC depends on the clay and organic matter content and increases also with an increase in pH. This is mainly due to release of protons from carboxyl groups of organic matter. These protons are irreversibly adsorbed at lower pH but can be released at higher pH and exchanged by base cations. To allow model simulations up to higher pH values, it is important to use the exchangeable cation contents related to a buffered CEC. Examples are a CEC buffered at pH 6.5 (NH_4 acetate buffered CEC) or 8.2 (barium chloride tri-ethanol amine buffered CEC). Using those extractants, the exchangeable proton fraction increases, whereas the exchangeable fraction of all other cations decreases. Since a pH of 6.5 is a reasonable upper value for non-calcareous soils, we used this CEC and the exchange constants related to those exchangeable fractions in the model (also used as input in the model SMART; De Vries et al., 1989)

One way to estimate the CEC at pH 6.5 is to derive the CEC as a function of the clay and organic carbon content, accounting for the impact of pH according to (Helling et al., 1964):

$$\mathrm{CEC} = (0.44 \cdot \mathrm{pH} + 3.0) \cdot \mathrm{clay} + (5.1 \cdot \mathrm{pH} - 5.9) \cdot \mathrm{C}_{\mathrm{org}} \tag{15}$$

where clay and C_{org} stand for the clay and organic carbon content, respectively (both in %) and the pH in this equation should be as close as possible to the soil solution pH. Eq.15 is consistent with Breeuwsma et al. (1986), who found a relationship between the CEC buffered at pH 6.5 (NH_4 acetate buffered CEC) and the clay and organic matter content, with a regression coefficient of 5.0 for clay and 30 for organic carbon.

Eq.15 was evaluated with our data set of measured CEC values for the pH in the field situation, in combination with data on clay and organic carbon. Results sometimes showed relatively large differences. Therefore, instead if directly using Eq.15, we updated the CEC calculation at pH 6.5 (with Eq.15) according to:

$$\mathrm{CEC}_{\mathrm{updated(pH6.5)}} = \mathrm{CEC}_{\mathrm{calculated(pH6.5)}} \cdot (\mathrm{CEC}_{\mathrm{measured}} / \mathrm{CEC}_{\mathrm{calculated(measuredpH)}}) \qquad (16)$$

3 Results

In this chapter we present tables with the exchange constants calculated from the data described in the previous chapter. Cations considered are H^+, Al^{3+} and the four base cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ (and combinations thereof). The results for the Gaines-Thomas model are presented in the following section, whereas results for the Gapon model are given in Section 3.2. Although all 'meaningful' exchange constants are provided (see Table 1), special reference is made to those used in the four models VSD, SMART, MAGIC and SAFE.

The tables include both the mean and the standard deviation for every combination of soil type and soil depth (if data permitted). In Section 2.2 the minimum number per soil type and soil depth has been presented (Table 2). This minimum numbers were calculated by removing a set of data on adsorbed and dissolved cations, if one or more data were:

(a) missing, i.e. not measured, or
(b) below the prerequisites for the minimum values for adsorbed fractions and/or dissolved concentrations, or
(c) DOC was missing, not allowing the calculation of free Al^{3+}.

Thus, for certain combinations of cations, the number was higher. E.g., if Al was not involved in the calculations of the exchange constant, the number of data sets was generally above the minimum value given in Table 2. In calculating the cation exchange constants given below all data sets fulfilling above criteria were used.

3.1 Gaines-Thomas exchange constants

The equation for Gaines-Thomas exchange between two cations X^{m+} and Y^{n+} is given by (see Eq.1):

$$\frac{E_X^n}{E_Y^m} = K_{XY} \cdot \frac{[X^{m+}]^n}{[Y^{n+}]^m} \tag{17}$$

Taking decadic logarithms one obtains:

$$L_{XY} = n \cdot \log_{10} E_X - m \cdot \log_{10} E_Y + m \cdot \log_{10}[Y^{n+}] - n \cdot \log_{10}[X^{m+}] \tag{18}$$

where

$$L_{XY} = \log_{10} K_{XY} \tag{19}$$

Models differ in the cations considered in the model formulation. In the Very Simple Dynamic (VSD) model (Posch and Reinds, 2003) the exchange between protons, aluminium and “divalent” base cations, i.e. Bc=Ca+Mg+K, is considered, using the following Gaines-Thomas equations:

$$\frac{E_{Al}^2}{E_{Bc}^3} = K_{AlBc} \cdot \frac{[Al^{3+}]^2}{[Bc^{2+}]^3} \quad \text{and} \quad \frac{E_H^2}{E_{Bc}} = K_{HBc} \cdot \frac{[H^+]^2}{[Bc^{2+}]} \tag{20}$$

The same equations are used in the SMART (De Vries et al., 1989; Posch et al., 1993) model, but with Ca+Mg instead of Bc, the exchange of K and Na being ignored in the current version.

In the MAGIC model (Cosby et al., 2001) the exchange of Al with all four base cations is modelled separately with Gaines-Thomas equations, without explicitly considering H-exchange, i.e.:

$$\frac{E_{Al}^2}{E_X^3} = K_{AlX} \cdot \frac{[Al^{3+}]^2}{[X^{2+}]^3}, \quad X = Ca, Mg \quad \text{and} \quad \frac{E_{Al}}{E_Y^3} = K_{AlY} \cdot \frac{[Al^{3+}]}{[Y^+]^3}, \quad Y = K, Na \tag{21}$$

It should be noted, however, that in the MAGIC model activities are used instead of concentrations. Thus the exchange constants presented here would have to be corrected with the proper activity coefficients. Note also that in an earlier version of MAGIC (Cosby et al., 1985) another, but equivalent, set of exchange equations had been used.

If the cations X, Y and Z have charge m, n, and k, respectively, then the logarithms of their exchange constants fulfil the following linear relationship (see Eq.10):

$$L_{XZ} = \frac{k}{n} \cdot L_{XY} + \frac{m}{n} \cdot L_{YZ} \tag{22}$$

and the same holds for their mean values.

Note: In the following tables, the phrase ‘X against Y’ refers to the exchange constant K_{XY}, as defined above. Mean and standard deviation (‘stddev’) refer to the expected value $\mathbf{E}(L_{XY})$ and the square root of the variance $\mathbf{Var}(L_{XY})$, respectively. A dash means that not enough data were available to estimate the respective value. If ion X has the charge m and Y the charge n, the unit of the exchange constant K_{XY} is $(mol/l)^{m-n}$. In Appendix B formulae are given to ease the conversion to other units, e.g. to powers of eq/m^3.

H against other cations

Results of exchange constants of protons against other cations are presented in the Tables 3-11.

Table 3 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***Al*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	6.872	0.774	7.473	1.386	9.470	2.376	6.713	0.812
10-30	7.133	0.741	7.523	1.215	9.350	1.442	6.677	0.621
30-60	7.358	0.702	-	-	11.666	0.367	7.677	1.502
60-100	7.812	0.350	7.486	0.982	12.208	-	7.594	1.679
0-30	6.701	0.729	7.640	1.345	9.897	2.211	6.434	0.482
0-60	7.366	0.724	-	-	10.817	1.738	6.644	0.568
All	6.924	0.781	7.532	1.241	9.923	2.168	6.842	1.010

Table 4 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***Ca*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	5.125	0.787	5.292	0.718	6.673	1.508	4.499	0.561
10-30	5.851	0.741	5.480	0.595	5.963	0.735	4.517	0.570
30-60	6.124	0.746	-	-	6.693	0.389	5.169	1.041
60-100	6.390	0.293	5.549	0.545	7.029	-	5.250	1.624
0-30	5.040	0.609	5.380	0.593	6.667	1.409	4.420	0.469
0-60	5.581	0.575	-	-	6.836	1.447	4.501	0.587
All	5.291	0.781	5.420	0.620	6.651	1.375	4.640	0.811

Table 5 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	5.363	0.813	5.354	0.687	6.806	1.511	4.744	0.586
10-30	6.087	0.752	5.473	0.628	6.103	0.761	4.763	0.666
30-60	6.365	0.661	-	-	6.830	0.252	5.454	1.135
60-100	6.403	0.238	5.494	0.597	7.517	-	5.510	1.699
0-30	5.319	0.598	5.434	0.624	6.859	1.375	4.666	0.542
0-60	5.958	0.507	-	-	7.013	1.399	4.770	0.674
All	5.553	0.772	5.436	0.632	6.815	1.363	4.897	0.877

Table 6 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	1.936	0.452	1.612	0.439	2.180	0.710	1.828	0.300
10-30	2.245	0.482	1.675	0.562	1.687	0.365	1.911	0.293
30-60	2.227	0.487	-	-	2.168	0.229	2.263	0.536
60-100	1.714	0.293	1.924	0.477	2.518	-	2.318	0.949
0-30	1.942	0.373	1.654	0.505	2.119	0.632	1.849	0.236
0-60	2.176	0.328	-	-	2.130	0.683	1.911	0.307
All	2.002	0.432	1.706	0.507	2.121	0.646	1.961	0.445

Table 7 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	2.713	0.510	3.085	0.465	3.603	0.859	2.512	0.320
10-30	3.210	0.541	2.620	0.464	3.152	0.547	2.504	0.330
30-60	3.223	0.497	-	-	3.709	0.140	2.866	0.606
60-100	2.959	0.158	2.230	0.475	4.077	-	2.825	0.875
0-30	2.893	0.383	2.879	0.408	3.720	0.716	2.507	0.282
0-60	3.182	0.326	-	-	3.850	0.686	2.529	0.351
All	2.912	0.480	2.726	0.545	3.656	0.753	2.588	0.451

Table 8 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***Ca+Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	5.200	0.779	5.306	0.704	6.703	1.500	4.573	0.549
10-30	5.968	0.715	5.474	0.587	5.999	0.740	4.579	0.576
30-60	6.249	0.660	-	-	6.734	0.344	5.243	1.042
60-100	6.393	0.249	5.519	0.553	7.155	-	5.343	1.627
0-30	5.136	0.607	5.391	0.590	6.709	1.391	4.487	0.468
0-60	5.739	0.513	-	-	6.876	1.430	4.575	0.583
All	5.387	0.771	5.418	0.613	6.688	1.365	4.712	0.812

Table 9 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	2.314	0.509	2.181	0.350	2.940	0.848	2.235	0.279
10-30	2.851	0.555	2.029	0.369	2.595	0.605	2.348	0.306
30-60	2.908	0.491	-	-	3.346	0.015	2.756	0.591
60-100	2.592	0.233	2.019	0.378	3.800	-	2.751	0.894
0-30	2.482	0.399	2.129	0.348	3.106	0.750	2.289	0.244
0-60	2.822	0.338	-	-	3.246	0.714	2.391	0.336
All	2.521	0.496	2.093	0.363	3.040	0.770	2.407	0.455

Table 10 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	5.338	0.759	5.322	0.692	6.740	1.464	4.754	0.502
10-30	6.060	0.729	5.434	0.620	6.007	0.740	4.685	0.573
30-60	6.297	0.656	-	-	6.754	0.344	5.307	1.051
60-100	6.204	0.242	5.541	0.579	7.185	-	5.386	1.636
0-30	5.236	0.614	5.386	0.606	6.728	1.373	4.615	0.439
0-60	5.863	0.495	-	-	6.887	1.423	4.651	0.562
All	5.492	0.753	5.415	0.626	6.712	1.343	4.824	0.792

Table 11 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***Ca+Mg+K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	5.595	0.790	5.558	0.654	6.914	1.447	5.064	0.507
10-30	6.485	0.777	5.580	0.567	6.245	0.829	5.048	0.626
30-60	6.759	0.678	-	-	7.175	0.146	5.676	1.117
60-100	6.575	0.229	5.582	0.552	7.804	-	5.712	1.717
0-30	5.596	0.654	5.581	0.555	6.968	1.334	4.936	0.459
0-60	6.322	0.478	-	-	7.146	1.361	4.974	0.583
All	5.840	0.807	5.575	0.579	6.940	1.321	5.157	0.832

Al against other cations

No separate calculations of the mean values would be needed, they can be calculated from linear relationships (see Eq.22). For example, $\mathbf{E}(\mathrm{L}_{\mathrm{AlBc}})$ can be calculated from:

$$\mathbf{E}(\mathrm{L}_{\mathrm{AlBc}}) = -2\cdot\mathbf{E}(\mathrm{L}_{\mathrm{HAl}}) + 3\cdot\mathbf{E}(\mathrm{L}_{\mathrm{HBc}}) \tag{23}$$

where we used $\mathbf{E}(\mathrm{L}_{\mathrm{HAl}}) = -\mathbf{E}(\mathrm{L}_{\mathrm{AlH}})$. We provide them nevertheless, since (a) it obviates numerical manipulations and (b) standard deviations cannot be obtained otherwise due to correlations between exchange constants.

The exchange constant against H can be obtained from Table 3: The mean has to be multiplied by –1 and the standard deviation is the same. For the other Al exchange constants see the following tables 12-19.

Table 12 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Al*** *against* ***Ca*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	1.630	1.581	0.931	1.194	1.080	1.814	0.072	1.242
10-30	3.287	1.542	1.395	1.122	-0.812	1.216	0.197	0.998
30-60	3.654	2.100	-	-	-3.253	0.432	0.154	1.527
60-100	3.545	1.084	1.677	1.179	-3.329	-	0.560	1.742
0-30	1.719	1.058	0.860	1.193	0.206	1.515	0.392	0.840
0-60	2.010	1.094	-	-	-1.125	1.292	0.216	0.886
All	2.026	1.531	1.195	1.205	0.106	1.893	0.237	1.159

Table 13 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Al*** *against* ***Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	2.346	1.637	1.116	1.071	1.478	1.727	0.805	1.403
10-30	3.995	1.588	1.373	0.965	-0.391	1.116	0.935	1.249
30-60	4.378	1.791	-	-	-2.841	0.022	1.010	1.742
60-100	3.583	0.670	1.509	1.032	-1.866	-	1.340	1.976
0-30	2.554	1.008	1.022	1.091	0.783	1.573	1.131	1.070
0-60	3.142	1.031	-	-	-0.594	1.195	1.024	1.154
All	2.811	1.493	1.244	1.047	0.599	1.821	1.006	1.368

Table 14 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* ***Al*** *against* ***K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-1.065	1.086	-2.637	1.032	-2.931	1.664	-1.228	0.977
10-30	-0.398	1.144	-2.498	0.972	-4.288	0.749	-0.944	0.578
30-60	-0.676	1.494	-	-	-5.162	0.319	-0.887	0.940
60-100	-2.670	0.880	-1.715	0.912	-4.653	-	-0.639	1.349
0-30	-0.876	0.816	-2.678	0.848	-3.539	1.548	-0.888	0.505
0-60	-0.838	0.868	-	-	-4.426	0.706	-0.910	0.522
All	-0.917	1.048	-2.413	1.007	-3.561	1.533	-0.958	0.804

Table 15 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* ***Al*** *against* ***Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	1.268	1.170	1.783	1.016	1.338	0.925	0.822	0.958
10-30	2.496	1.313	0.335	1.568	0.107	0.633	0.836	0.604
30-60	2.310	1.500	-	-	-0.538	0.053	0.922	0.891
60-100	1.064	0.374	-0.796	1.301	0.024	-	0.879	1.060
0-30	1.977	0.827	0.996	1.287	1.264	0.942	1.089	0.592
0-60	2.181	0.819	-	-	0.732	0.787	0.944	0.569
All	1.811	1.130	0.646	1.589	1.045	0.974	0.921	0.768

Table 16 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* ***Al*** *against* ***Ca+Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	1.856	1.557	0.974	1.154	1.170	1.781	0.294	1.230
10-30	3.639	1.517	1.376	1.045	-0.703	1.182	0.385	1.016
30-60	4.029	1.853	-	-	-3.128	0.298	0.376	1.542
60-100	3.553	0.899	1.586	1.100	-2.951	-	0.840	1.761
0-30	2.004	1.057	0.892	1.158	0.334	1.521	0.592	0.859
0-60	2.486	1.008	-	-	-1.005	1.252	0.437	0.902
All	2.314	1.506	1.190	1.139	0.219	1.863	0.453	1.169

Table 17 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* ***Al*** *against* ***K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	0.069	1.155	-0.928	0.620	-0.650	0.939	-0.007	0.821
10-30	1.420	1.354	-1.437	0.535	-1.566	0.391	0.366	0.604
30-60	1.366	1.469	-	-	-1.627	0.323	0.592	0.962
60-100	-0.037	0.560	-1.430	0.592	-0.808	-	0.658	1.127
0-30	0.744	0.899	-1.255	0.582	-0.580	0.864	0.433	0.479
0-60	1.101	0.903	-	-	-1.080	0.693	0.530	0.548
All	0.639	1.172	-1.254	0.613	-0.802	0.872	0.378	0.760

Table 18 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Al*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	2.269	1.493	1.021	1.147	1.280	1.845	0.835	1.204
10-30	3.914	1.607	1.257	0.939	-0.680	1.152	0.703	0.968
30-60	4.175	1.969	-	-	-3.070	0.298	0.567	1.474
60-100	2.988	0.763	1.652	1.082	-2.860	-	0.969	1.777
0-30	2.306	1.082	0.878	1.079	0.391	1.555	0.978	0.805
0-60	2.858	1.121	-	-	-0.973	1.230	0.666	0.846
All	2.628	1.483	1.182	1.089	0.292	1.907	0.788	1.130

Table 19 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Al*** *against* ***Ca+Mg+K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	3.041	1.591	1.729	1.241	1.802	1.762	1.765	1.200
10-30	5.191	1.811	1.692	1.053	0.033	0.735	1.790	1.177
30-60	5.559	2.104	-	-	-1.808	0.294	1.675	1.611
60-100	4.102	0.671	1.773	1.056	-1.005	-	1.946	2.022
0-30	3.387	1.274	1.463	1.246	1.111	1.505	1.940	0.944
0-60	4.234	1.289	-	-	-0.195	1.071	1.636	0.950
All	3.671	1.688	1.660	1.151	0.974	1.733	1.787	1.243

Base cations against each other

The exchange constants against H and Al can be obtained from the tables above: The mean has to be multiplied by –1 and the standard deviation is the same. For exchange constants among base cations see the following tables (see also Table 1).

Table 20 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Ca*** *against* ***Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.477	0.346	0.123	0.428	0.265	0.230	0.489	0.190
10-30	0.472	0.466	-0.014	0.453	0.280	0.117	0.492	0.239
30-60	0.483	0.536	-	-	0.275	0.274	0.571	0.237
60-100	0.025	0.459	-0.112	0.303	0.975	-	0.520	0.250
0-30	0.557	0.366	0.108	0.402	0.385	0.172	0.493	0.207
0-60	0.754	0.581	-	-	0.354	0.148	0.539	0.227
All	0.524	0.420	0.033	0.411	0.328	0.211	0.513	0.219

Table 21 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Ca*** *against* ***K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-1.253	0.669	-2.069	0.641	-2.314	0.787	-0.842	0.517
10-30	-1.361	0.519	-2.130	0.722	-2.588	0.356	-0.695	0.233
30-60	-1.669	0.793	-	-	-2.357	0.069	-0.643	0.255
60-100	-2.962	0.643	-1.702	0.582	-1.992	-	-0.613	0.535
0-30	-1.157	0.474	-2.072	0.648	-2.428	0.720	-0.723	0.346
0-60	-1.229	0.544	-	-	-2.576	0.387	-0.679	0.255
All	-1.286	0.643	-2.007	0.666	-2.409	0.666	-0.718	0.374

Table 22 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* **Ca** *against* **Na** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.302	0.545	0.878	0.632	0.532	0.573	0.524	0.342
10-30	0.568	0.607	-0.241	0.948	0.342	0.360	0.491	0.152
30-60	0.322	0.723	-	-	0.726	0.109	0.563	0.201
60-100	-0.472	0.404	-1.090	0.966	1.126	-	0.399	0.194
0-30	0.745	0.451	0.378	0.702	0.774	0.495	0.595	0.203
0-60	0.784	0.531	-	-	0.863	0.485	0.557	0.162
All	0.532	0.583	0.032	1.081	0.661	0.525	0.535	0.232

Table 23 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* **Mg** *against* **K** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-1.492	0.611	-2.130	0.622	-2.447	0.794	-1.087	0.516
10-30	-1.597	0.360	-2.123	0.773	-2.728	0.388	-0.941	0.291
30-60	-1.910	0.620	-	-	-2.494	0.206	-0.928	0.263
60-100	-2.974	0.485	-1.646	0.507	-2.480	-	-0.873	0.494
0-30	-1.436	0.392	-2.126	0.673	-2.620	0.701	-0.969	0.389
0-60	-1.606	0.379	-	-	-2.753	0.416	-0.948	0.301
All	-1.548	0.545	-2.024	0.679	-2.574	0.669	-0.974	0.389

Table 24 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* **Mg** *against* **Na** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.064	0.497	0.817	0.609	0.400	0.567	0.280	0.310
10-30	0.332	0.484	-0.234	0.928	0.201	0.336	0.246	0.133
30-60	0.080	0.583	-	-	0.589	0.028	0.278	0.137
60-100	-0.485	0.252	-1.034	0.926	0.638	-	0.139	0.117
0-30	0.466	0.375	0.323	0.681	0.581	0.458	0.349	0.170
0-60	0.407	0.362	-	-	0.686	0.444	0.288	0.126
All	0.270	0.489	0.016	1.032	0.497	0.496	0.279	0.198

Table 25 Mean and standard deviation of logarithmic **Gaines-Thomas** *exchange constants of* **K** *against* **Na** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.778	0.380	1.474	0.565	1.423	0.619	0.683	0.253
10-30	0.965	0.187	0.944	0.749	1.465	0.282	0.593	0.134
30-60	0.995	0.273	-	-	1.541	0.089	0.603	0.143
60-100	1.245	0.271	0.306	0.623	1.559	-	0.506	0.245
0-30	0.951	0.231	1.225	0.607	1.601	0.485	0.659	0.195
0-60	1.007	0.159	-	-	1.720	0.380	0.618	0.146
All	0.909	0.301	1.020	0.761	1.535	0.512	0.626	0.195

Table 26 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Na*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-0.089	0.512	-0.849	0.681	-0.466	0.622	-0.270	0.372
10-30	-0.359	0.514	0.195	0.997	-0.298	0.355	-0.323	0.182
30-60	-0.148	0.554	-	-	-0.665	0.064	-0.425	0.216
60-100	0.286	0.284	1.081	0.980	-0.969	-	-0.263	0.180
0-30	-0.549	0.405	-0.371	0.748	-0.712	0.482	-0.400	0.230
0-60	-0.502	0.393	-	-	-0.813	0.479	-0.407	0.196
All	-0.331	0.512	-0.036	1.099	-0.599	0.542	-0.351	0.258

Table 27 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***Ca+Mg*** *against* ***K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	-0.572	0.555	-0.944	0.279	-0.823	0.380	-0.103	0.313
10-30	-0.266	0.603	-1.417	0.335	-0.810	0.562	0.116	0.133
30-60	-0.432	0.654	-	-	-0.042	0.314	0.270	0.200
60-100	-1.209	0.529	-1.482	0.363	0.445	-	0.158	0.222
0-30	-0.172	0.455	-1.134	0.310	-0.498	0.381	0.091	0.162
0-60	-0.094	0.508	-	-	-0.385	0.295	0.208	0.184
All	-0.346	0.570	-1.233	0.385	-0.608	0.443	0.101	0.246

3.2 Gapon exchange constants

The equation for Gapon exchange between two cations X^{m+} and Y^{n+} is given by (see Eq.1):

$$\frac{E_X}{E_Y} = k_{XY} \cdot \frac{[X^{m+}]^{1/m}}{[Y^{n+}]^{1/n}} \tag{24}$$

where we use the lower-case k_{XY}, if we refer specifically to a Gapon exchange constant. Taking decadic logarithms one obtains:

$$l_{XY} = \log_{10}E_X - \log_{10}E_Y + \frac{1}{n} \cdot \log_{10}[Y^{n+}] - \frac{1}{m} \cdot \log_{10}[X^{m+}] \tag{25}$$

where

$$l_{XY} = \log_{10}k_{XY} \tag{26}$$

The user of the VSD model (Posch and Reinds, 2003) can choose between the Gaines-Thomas and the Gapon Bc-Al-H exchange model. The Gapon exchange equations read (compare Eq.18):

$$\frac{E_{Al}}{E_{Bc}} = k_{AlBc} \cdot \frac{[Al^{3+}]^{1/3}}{[Bc^{2+}]^{1/2}} \quad \text{and} \quad \frac{E_H}{E_{Bc}} = k_{HBc} \cdot \frac{[H^+]}{[Bc^{2+}]^{1/2}} \tag{27}$$

In the SAFE model (Warfvinge et al., 1993; Alveteg and Sverdrup, 2002) the exchange between the same cations is modelled, but the Gapon equations used are:

$$\frac{E_H}{E_{Al}} = \frac{1}{k_{H/Al}} \cdot \frac{[H^+]}{[Al^{3+}]^{1/3}} \quad \text{and} \quad \frac{E_H}{E_{Bc}} = \frac{1}{k_{H/Bc}} \cdot \frac{[H^+]}{[Bc^{2+}]^{1/2}} \tag{28}$$

i.e. the exchange constants used in SAFE, $k_{X/Y}$, are related the constants used here via

$$k_{X/Y} = \frac{1}{k_{XY}} \tag{29}$$

Independent of their charges, the logarithms of Gapon exchange constants between three cations X, Y and Z obey (see Eq.10):

$$l_{XZ} = l_{XY} + l_{YZ} \tag{30}$$

and the same holds for their mean values.

Note: In the following tables, the phrase 'X against Y' refers to the exchange constant k_{XY} as defined above. Mean and standard deviation ('stddev') refer to the expected value $\mathbf{E}(l_{XY})$ and the square root of the variance $\mathbf{Var}(l_{XY})$. A dash means that not enough data were available to estimate the respective value. If X has the charge m and Y the charge n, the unit of the exchange constant k_{XY} is $(mol/l)^{1/n-1/m}$. The formulae in Appendix B can be used to convert to other units.

H against other cations

Results of exchange constants of protons against cations are presented in the Tables 28-36 (compare Tables 3-11).

Table 28 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***Al*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	2.872	0.463	2.948	0.710	3.996	1.156	3.191	0.359
10-30	2.834	0.534	2.858	0.753	3.750	0.632	3.183	0.289
30-60	2.843	0.439	-	-	4.997	0.304	3.683	0.549
60-100	2.752	0.118	2.841	0.627	5.471	-	3.894	0.654
0-30	2.647	0.436	2.949	0.754	4.229	1.178	3.021	0.322
0-60	3.090	0.517	-	-	4.658	0.955	3.245	0.255
All	2.794	0.477	2.902	0.711	4.211	1.104	3.288	0.468

Table 29 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***Ca*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	3.194	0.334	3.238	0.290	3.728	0.557	2.778	0.225
10-30	3.593	0.320	3.424	0.277	3.333	0.273	2.724	0.152
30-60	3.769	0.424	-	-	3.556	0.230	2.947	0.342
60-100	4.199	0.172	3.404	0.331	3.640	-	3.069	0.631
0-30	3.288	0.353	3.293	0.230	3.647	0.528	2.754	0.190
0-60	3.273	0.416	-	-	3.630	0.659	2.692	0.161
All	3.334	0.406	3.337	0.290	3.651	0.537	2.797	0.291

Table 30 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	3.552	0.362	3.567	0.261	4.095	0.620	3.134	0.309
10-30	3.824	0.307	3.688	0.238	3.678	0.313	3.126	0.320
30-60	3.977	0.391	-	-	3.868	0.178	3.367	0.539
60-100	4.342	0.154	3.559	0.262	4.241	-	3.354	0.782
0-30	3.646	0.281	3.623	0.228	4.091	0.556	3.147	0.303
0-60	3.658	0.326	-	-	4.044	0.666	3.092	0.341
All	3.669	0.354	3.612	0.250	4.049	0.577	3.179	0.413

Table 31 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	1.936	0.452	1.612	0.439	2.180	0.710	1.828	0.300
10-30	2.245	0.482	1.675	0.562	1.687	0.365	1.911	0.293
30-60	2.227	0.487	-	-	2.168	0.229	2.263	0.536
60-100	1.714	0.293	1.924	0.477	2.518	-	2.318	0.949
0-30	1.942	0.373	1.654	0.505	2.119	0.632	1.849	0.236
0-60	2.176	0.328	-	-	2.130	0.683	1.911	0.307
All	2.002	0.432	1.706	0.507	2.121	0.646	1.961	0.445

Table 32 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	2.713	0.510	3.085	0.465	3.603	0.859	2.512	0.320
10-30	3.210	0.541	2.620	0.464	3.152	0.547	2.504	0.330
30-60	3.223	0.497	-	-	3.709	0.140	2.866	0.606
60-100	2.959	0.158	2.230	0.475	4.077	-	2.825	0.875
0-30	2.893	0.383	2.879	0.408	3.720	0.716	2.507	0.282
0-60	3.182	0.326	-	-	3.850	0.686	2.529	0.351
All	2.912	0.480	2.726	0.545	3.656	0.753	2.588	0.451

Table 33 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***Ca+Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	3.162	0.321	3.192	0.273	3.691	0.565	2.744	0.225
10-30	3.540	0.294	3.356	0.232	3.297	0.281	2.694	0.173
30-60	3.711	0.385	-	-	3.516	0.212	2.915	0.376
60-100	4.102	0.136	3.298	0.285	3.665	-	3.009	0.666
0-30	3.259	0.328	3.245	0.210	3.627	0.527	2.724	0.202
0-60	3.268	0.374	-	-	3.606	0.656	2.661	0.178
All	3.301	0.379	3.272	0.255	3.621	0.540	2.763	0.305

Table 34 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	2.314	0.509	2.181	0.350	2.940	0.848	2.235	0.279
10-30	2.851	0.555	2.029	0.369	2.595	0.605	2.348	0.306
30-60	2.908	0.491	-	-	3.346	0.015	2.756	0.591
60-100	2.592	0.233	2.019	0.378	3.800	-	2.751	0.894
0-30	2.482	0.399	2.129	0.348	3.106	0.750	2.289	0.244
0-60	2.822	0.338	-	-	3.246	0.714	2.391	0.336
All	2.521	0.496	2.093	0.363	3.040	0.770	2.407	0.455

Table 35 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	3.178	0.309	3.138	0.268	3.684	0.568	2.818	0.199
10-30	3.527	0.271	3.240	0.221	3.287	0.282	2.739	0.175
30-60	3.662	0.334	-	-	3.521	0.212	2.944	0.382
60-100	3.866	0.125	3.232	0.251	3.676	-	3.027	0.672
0-30	3.253	0.311	3.170	0.206	3.620	0.530	2.773	0.190
0-60	3.289	0.340	-	-	3.604	0.654	2.694	0.170
All	3.296	0.346	3.193	0.239	3.616	0.541	2.809	0.298

Table 36 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***Ca+Mg+K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	3.292	0.310	3.250	0.259	3.766	0.560	2.961	0.198
10-30	3.712	0.267	3.299	0.203	3.402	0.323	2.907	0.205
30-60	3.851	0.323	-	-	3.728	0.115	3.118	0.417
60-100	3.992	0.141	3.237	0.230	3.981	-	3.180	0.716
0-30	3.412	0.323	3.260	0.197	3.736	0.515	2.920	0.198
0-60	3.498	0.322	-	-	3.732	0.622	2.846	0.179
All	3.448	0.358	3.263	0.222	3.726	0.528	2.964	0.318

Al against other cations

The exchange constant against H can be obtained from Table 28: The mean has to be multiplied by –1 and the standard deviation is the same. For the other Al exchange constants see the following Tables 37-44 (compare Tables 12-19).

Table 37 Mean and standard deviation of logarithmic **Gapon** *exchange constants of* **Al** *against* **Ca** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.322	0.487	0.290	0.593	-0.268	0.750	-0.413	0.368
10-30	0.759	0.600	0.566	0.768	-0.417	0.452	-0.459	0.256
30-60	0.926	0.645	-	-	-1.441	0.074	-0.736	0.347
60-100	1.447	0.227	0.562	0.717	-1.831	-	-0.825	0.400
0-30	0.641	0.524	0.344	0.716	-0.582	0.733	-0.267	0.404
0-60	0.183	0.699	-	-	-1.028	0.359	-0.553	0.212
All	0.541	0.595	0.435	0.704	-0.560	0.733	-0.492	0.376

Table 38 Mean and standard deviation of logarithmic **Gapon** *exchange constants of* **Al** *against* **Mg** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.679	0.442	0.619	0.507	0.100	0.684	-0.058	0.450
10-30	0.990	0.480	0.830	0.622	-0.072	0.423	-0.057	0.322
30-60	1.134	0.511	-	-	-1.130	0.126	-0.316	0.353
60-100	1.591	0.110	0.718	0.528	-1.230	-	-0.540	0.434
0-30	1.000	0.450	0.674	0.600	-0.138	0.710	0.126	0.443
0-60	0.568	0.544	-	-	-0.614	0.357	-0.153	0.263
All	0.875	0.503	0.710	0.568	-0.162	0.689	-0.109	0.424

Table 39 Mean and standard deviation of logarithmic **Gapon** *exchange constants of* **Al** *against* **K** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-0.936	0.400	-1.337	0.478	-1.816	0.797	-1.363	0.401
10-30	-0.590	0.334	-1.183	0.411	-2.063	0.376	-1.272	0.265
30-60	-0.616	0.463	-	-	-2.829	0.075	-1.420	0.364
60-100	-1.038	0.285	-0.918	0.329	-2.952	-	-1.575	0.519
0-30	-0.705	0.317	-1.295	0.422	-2.110	0.824	-1.172	0.320
0-60	-0.914	0.394	-	-	-2.528	0.399	-1.334	0.255
All	-0.791	0.387	-1.196	0.442	-2.090	0.761	-1.327	0.360

Table 40 Mean and standard deviation of logarithmic **Gapon** *exchange constants of* **Al** *against* **Na** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-0.159	0.374	0.137	0.505	-0.393	0.538	-0.680	0.442
10-30	0.375	0.356	-0.239	0.765	-0.598	0.217	-0.679	0.302
30-60	0.380	0.488	-	-	-1.288	0.164	-0.817	0.358
60-100	0.207	0.128	-0.612	0.579	-1.393	-	-1.069	0.464
0-30	0.246	0.323	-0.070	0.663	-0.509	0.605	-0.513	0.387
0-60	0.092	0.367	-	-	-0.808	0.413	-0.716	0.272
All	0.118	0.411	-0.176	0.685	-0.555	0.550	-0.701	0.395

Table 41 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Al*** *against* ***Ca+Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	0.290	0.465	0.244	0.574	-0.305	0.735	-0.447	0.377
10-30	0.705	0.558	0.497	0.730	-0.453	0.445	-0.489	0.262
30-60	0.868	0.584	-	-	-1.482	0.093	-0.768	0.341
60-100	1.350	0.172	0.457	0.657	-1.806	-	-0.885	0.401
0-30	0.613	0.500	0.296	0.693	-0.603	0.734	-0.297	0.414
0-60	0.178	0.660	-	-	-1.052	0.361	-0.584	0.213
All	0.508	0.563	0.370	0.668	-0.589	0.724	-0.525	0.382

Table 42 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Al*** *against* ***K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	-0.558	0.355	-0.767	0.409	-1.056	0.528	-0.956	0.381
10-30	0.016	0.351	-0.830	0.436	-1.155	0.053	-0.836	0.320
30-60	0.065	0.463	-	-	-1.651	0.289	-0.927	0.393
60-100	-0.160	0.193	-0.823	0.304	-1.671	-	-1.143	0.486
0-30	-0.165	0.321	-0.821	0.453	-1.124	0.558	-0.732	0.351
0-60	-0.268	0.381	-	-	-1.412	0.345	-0.854	0.289
All	-0.273	0.409	-0.809	0.405	-1.171	0.499	-0.881	0.373

Table 43 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Al*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.306	0.440	0.190	0.546	-0.312	0.738	-0.373	0.350
10-30	0.693	0.517	0.382	0.663	-0.463	0.431	-0.444	0.255
30-60	0.819	0.527	-	-	-1.476	0.093	-0.740	0.336
60-100	1.114	0.121	0.390	0.591	-1.795	-	-0.867	0.401
0-30	0.607	0.472	0.221	0.647	-0.609	0.731	-0.247	0.404
0-60	0.199	0.633	-	-	-1.054	0.362	-0.551	0.210
All	0.503	0.523	0.292	0.614	-0.595	0.722	-0.479	0.379

Table 44 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Al*** *against* ***Ca+Mg+K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.419	0.420	0.302	0.570	-0.229	0.737	-0.231	0.322
10-30	0.878	0.489	0.441	0.682	-0.348	0.376	-0.276	0.288
30-60	1.008	0.506	-	-	-1.269	0.190	-0.565	0.371
60-100	1.240	0.136	0.396	0.585	-1.490	-	-0.714	0.426
0-30	0.765	0.471	0.311	0.675	-0.493	0.746	-0.100	0.416
0-60	0.408	0.631	-	-	-0.926	0.383	-0.399	0.235
All	0.655	0.518	0.361	0.628	-0.485	0.713	-0.325	0.385

Base cations against each other

The exchange constants against H and Al can be obtained from the tables above: The mean has to be multiplied by –1 and the standard deviation is the same. For exchange constants among base cations see the following tables (see also Table 1).

Table 45 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Ca*** *against* ***Mg*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.358	0.190	0.329	0.177	0.368	0.134	0.355	0.171
10-30	0.231	0.182	0.264	0.220	0.345	0.047	0.403	0.205
30-60	0.208	0.202	-	-	0.311	0.052	0.420	0.255
60-100	0.144	0.203	0.156	0.232	0.600	-	0.285	0.269
0-30	0.359	0.199	0.330	0.181	0.444	0.087	0.393	0.190
0-60	0.385	0.233	-	-	0.414	0.062	0.400	0.225
All	0.334	0.206	0.275	0.212	0.398	0.111	0.382	0.211

Table 46 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Ca*** *against* ***K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-1.258	0.440	-1.626	0.393	-1.548	0.342	-0.950	0.267
10-30	-1.349	0.507	-1.749	0.567	-1.646	0.225	-0.813	0.180
30-60	-1.542	0.612	-	-	-1.388	0.001	-0.684	0.247
60-100	-2.484	0.342	-1.480	0.553	-1.122	-	-0.751	0.424
0-30	-1.346	0.392	-1.639	0.485	-1.528	0.315	-0.905	0.214
0-60	-1.097	0.485	-	-	-1.500	0.174	-0.781	0.204
All	-1.332	0.483	-1.630	0.505	-1.530	0.297	-0.835	0.260

Table 47 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Ca*** *against* ***Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-0.481	0.435	-0.153	0.415	-0.125	0.433	-0.266	0.230
10-30	-0.384	0.567	-0.804	0.558	-0.181	0.308	-0.220	0.211
30-60	-0.547	0.597	-	-	0.153	0.090	-0.081	0.296
60-100	-1.240	0.221	-1.174	0.660	0.437	-	-0.245	0.315
0-30	-0.395	0.390	-0.414	0.432	0.073	0.313	-0.246	0.218
0-60	-0.090	0.495	-	-	0.219	0.244	-0.163	0.238
All	-0.423	0.474	-0.611	0.638	0.005	0.376	-0.209	0.248

Table 48 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Mg*** *against* ***K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-1.616	0.377	-1.956	0.329	-1.916	0.344	-1.305	0.274
10-30	-1.580	0.414	-2.013	0.477	-1.991	0.232	-1.215	0.144
30-60	-1.750	0.532	-	-	-1.700	0.051	-1.104	0.111
60-100	-2.628	0.275	-1.636	0.383	-1.722	-	-1.035	0.284
0-30	-1.705	0.304	-1.969	0.405	-1.972	0.310	-1.298	0.230
0-60	-1.482	0.363	-	-	-1.914	0.208	-1.180	0.161
All	-1.666	0.395	-1.906	0.424	-1.929	0.298	-1.218	0.226

Table 49 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Mg*** *against* ***Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-0.838	0.388	-0.482	0.343	-0.493	0.377	-0.622	0.143
10-30	-0.615	0.481	-1.069	0.484	-0.526	0.269	-0.622	0.066
30-60	-0.755	0.526	-	-	-0.158	0.038	-0.501	0.120
60-100	-1.384	0.078	-1.329	0.525	-0.163	-	-0.529	0.143
0-30	-0.754	0.313	-0.744	0.371	-0.371	0.277	-0.639	0.101
0-60	-0.475	0.362	-	-	-0.194	0.222	-0.562	0.083
All	-0.757	0.398	-0.886	0.532	-0.393	0.326	-0.591	0.120

Table 50 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***K*** *against* ***Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.778	0.380	1.474	0.565	1.423	0.619	0.683	0.253
10-30	0.965	0.187	0.944	0.749	1.465	0.282	0.593	0.134
30-60	0.995	0.273	-	-	1.541	0.089	0.603	0.143
60-100	1.245	0.271	0.306	0.623	1.559	-	0.506	0.245
0-30	0.951	0.231	1.225	0.607	1.601	0.485	0.659	0.195
0-60	1.007	0.159	-	-	1.720	0.380	0.618	0.146
All	0.909	0.301	1.020	0.761	1.535	0.512	0.626	0.195

Table 51 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Na*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	0.464	0.395	0.053	0.412	0.081	0.434	0.306	0.220
10-30	0.318	0.478	0.620	0.533	0.135	0.289	0.235	0.188
30-60	0.439	0.462	-	-	-0.188	0.072	0.078	0.251
60-100	0.907	0.093	1.002	0.581	-0.402	-	0.203	0.253
0-30	0.361	0.330	0.292	0.419	-0.100	0.306	0.266	0.209
0-60	0.107	0.395	-	-	-0.245	0.242	0.165	0.215
All	0.385	0.398	0.468	0.595	-0.040	0.369	0.221	0.228

Table 52 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***Ca+Mg*** *against* ***K+Na*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	-0.848	0.439	-1.011	0.251	-0.751	0.344	-0.509	0.183
10-30	-0.689	0.557	-1.327	0.381	-0.702	0.413	-0.346	0.162
30-60	-0.803	0.556	-	-	-0.169	0.197	-0.159	0.239
60-100	-1.510	0.271	-1.280	0.434	0.135	-	-0.258	0.272
0-30	-0.777	0.375	-1.116	0.326	-0.521	0.297	-0.435	0.199
0-60	-0.446	0.465	-	-	-0.360	0.163	-0.270	0.206
All	-0.780	0.460	-1.179	0.369	-0.581	0.352	-0.356	0.233

3.3 Correlations between exchange constants

Exchange constants, when considered as random variables, are not independent from each other (see section 2.1). The information in the above tables is sufficient to compute any desired covariance and correlation coefficient. For the logarithms of the X-Z, X-Y and Z-Y Gaines-Thomas exchange constants we have (interchanging Y and Z in Eq.22):

$$L_{XZ} = \frac{k}{n} \cdot L_{XY} - \frac{m}{n} \cdot L_{ZY} \tag{31}$$

where m, n and k are the charges of X, Y and Z, respectively. Thus we get from Eq.A12 in Appendix A:

$$2 \cdot \mathbf{Cov}(L_{XY}, L_{ZY}) = \frac{k}{m} \cdot \mathbf{Var}(L_{XY}) + \frac{m}{k} \cdot \mathbf{Var}(L_{ZY}) - \frac{n^2}{mk} \cdot \mathbf{Var}(L_{XZ}) \tag{32}$$

And from Eq.30 (again interchanging Y and Z) we get for the covariance of the respective Gapon exchange constants:

$$2 \cdot \mathbf{Cov}(l_{XY}, l_{ZY}) = \mathbf{Var}(l_{XY}) + \mathbf{Var}(l_{ZY}) - \mathbf{Var}(l_{XZ}) \tag{33}$$

Correlation coefficients are then obtained by dividing by the respective standard deviations (see Eq.A9). Table 53 shows correlation coefficients for all triples of ions in sand, loess and clay soils for soils depths 0-30 cm for Gaines-Thomas and Gapon exchange, using the data in the tables above.

Most of the exchange constants given in Table 53 are positively correlated; however, this should not lead to wrong conclusions, since the sign of the correlation depends on the order of the ions involved: Since $L_{YZ}=-L_{ZY}$ (see Eqs.3,9,11), it follows that $\rho(L_{XY},L_{YZ})=-\rho(L_{XY},L_{ZY})$ (see Eq.A8), etc. It appears that Gapon exchange constants are stronger correlated than the corresponding Gaines-Thomas exchange constants, especially for sandy soils. A strong positive correlation means that the *ratio* between two exchange constants is more characteristic, and less variable, of a certain soil (type) than their absolute numbers, which often vary by several orders of magnitude.

The correlation between exchange constants is important when they are drawn randomly (e.g., in Monte Carlo simulations for model calibration or uncertainty analyses) in order to obtain meaningful combinations. See, e.g., Iman and Conover (1982) on how to sample correlated random variables.

Table 53 Correlation coefficients for Gaines-Thomas and Gapon exchange constants, respectively, for all triples of ions in sand, loess and clay soils, using the data for soil depth 0-30. Correlation coefficients with $\rho^2>0.5$ *are marked in grey.*

Ions			$\rho(L_{XY},L_{ZY})$ (Gaines-Thomas)			$\rho(l_{XY},l_{ZY})$ (Gapon)		
X	Y	Z	sand	loess	clay	sand	loess	clay
H	Al	Ca	-0.030	0.856	0.297	0.744	0.952	0.953
H	Al	Mg	-0.026	0.839	0.360	0.799	0.969	0.946
H	Al	K	-0.046	0.102	0.539	0.548	0.772	0.859
H	Al	Na	-0.087	0.568	0.279	0.525	0.842	0.871
H	Al	B^{2+}	-0.024	0.874	0.331	0.763	0.961	0.953
H	Al	B^{+}	-0.071	0.676	0.150	0.478	0.955	0.865
H	Al	Bc^{2+}	-0.031	0.878	0.364	0.768	0.968	0.953
H	Al	BC^{2+}	-0.027	0.898	0.436	0.749	0.968	0.955
H	Ca	Mg	0.210	0.011	0.421	0.607	0.404	-0.248
H	Ca	K	0.068	-0.323	0.447	0.503	0.148	-0.064
H	Ca	Na	-0.023	0.215	0.129	0.472	0.368	-0.411
H	Mg	K	-0.097	-0.212	0.407	0.189	-0.211	0.017
H	Mg	Na	-0.197	0.220	0.040	0.172	0.137	-0.412
H	K	Na	0.266	0.745	0.199	0.266	0.745	0.199
H	Na	Bc^{2+}	0.602	0.703	0.288	0.628	0.876	0.743
H	B^{2+}	B^{+}	-0.111	-0.110	-0.160	0.362	0.214	-0.628
Al	Ca	Mg	0.348	0.415	-0.144	0.535	0.715	0.320
Al	Ca	K	0.159	0.501	-0.401	0.798	0.820	-0.092
Al	Ca	Na	0.075	-0.153	0.211	0.789	0.420	0.587
Al	Mg	K	-0.112	0.543	-0.406	0.711	0.712	-0.179
Al	Mg	Na	-0.200	-0.283	0.188	0.696	0.130	0.546
Al	K	Na	0.409	0.770	0.805	0.338	0.209	0.686
Al	Na	Bc^{2+}	0.757	0.909	0.591	-0.045	0.354	-0.202
Al	B^{2+}	B^{+}	-0.087	0.395	0.182	0.767	0.844	0.724
Ca	Mg	K	-0.262	0.271	-0.163	-0.179	-0.262	0.082
Ca	Mg	Na	-0.213	0.041	-0.354	-0.117	-0.121	-0.284
Ca	K	Na	0.536	0.890	0.869	0.303	0.708	0.774
Mg	K	Na	0.625	0.895	0.899	0.340	0.803	0.847

4 Discussion and conclusions

Influence of the use of free and total Al on Al-related exchange constants

The field measurements that were used to calculate cation exchange constants include only total Al concentrations (both free Al and Al complexed with dissolved organic carbon and other complexes). Free Al^{3+} concentrations were calculated from the total concentration of Al as described in Section 2.3 to derive exchange constants between Al^{3+} and protons or base cations. In the VSD and SAFE model, however, no complexation of Al with DOC is included, and the exchange constants used thus relate to total Al concentrations. This is not an adequate use of cation exchange constants, but a mere empirical description to calculate total Al concentrations while including the exchange of cations on the adsorption complex. To give insight in the impact of neglecting complexation, exchange constants were also calculated using total Al concentrations in solution. Results of major cation exchange constants involving Al are shown in Tables 54-57.

Table 54 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***H*** *against* ***total Al*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	Stddev
0-10	8.030	1.482	7.950	1.605	10.816	2.859	7.615	0.913
10-30	8.903	1.759	7.910	1.526	9.729	1.785	7.723	0.918
30-60	9.281	1.411	-	-	12.701	0.376	8.868	1.643
60-100	8.739	0.344	7.920	1.289	14.129	-	9.225	2.731
0-30	7.510	1.222	8.015	1.553	11.131	2.875	7.360	0.759
0-60	9.092	1.276	-	-	11.911	2.470	7.684	0.834
All	8.094	1.504	7.950	1.494	11.119	2.708	7.896	1.358

Table 55 Mean and standard deviation of logarithmic ***Gaines-Thomas*** *exchange constants of* ***total Al*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	Stddev
0-10	-0.046	1.118	0.066	1.331	-1.412	1.634	-0.968	0.938
10-30	0.373	1.711	0.484	1.361	-1.437	1.728	-1.390	0.718
30-60	0.330	1.431	-	-	-5.140	0.280	-1.816	0.676
60-100	1.134	0.619	0.713	1.061	-6.702	-	-2.291	0.932
0-30	0.689	1.115	0.130	1.420	-2.077	1.901	-0.875	1.022
0-60	-0.594	1.654	-	-	-3.161	1.136	-1.415	0.689
All	0.288	1.320	0.329	1.323	-2.100	1.881	-1.320	0.942

Comparison of logarithmic Gaines-Thomas exchange constants with those computed with free Al (Tables 3 and 18) shows that those of: (i) H against total Al are generally larger by about one unit compared to free Al (see Table 3 and 54) and (ii) total Al against Ca+Mg+K are generally smaller by two units compared to free Al (see Tables 18 and 55).

Table 56 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***H*** *against* ***total Al*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	3.258	0.709	3.107	0.795	4.444	1.334	3.492	0.420
10-30	3.425	0.916	2.987	0.864	3.876	0.745	3.532	0.397
30-60	3.484	0.734	-	-	5.342	0.307	4.081	0.589
60-100	3.061	0.118	2.970	0.748	6.111	-	4.437	0.973
0-30	2.916	0.637	3.074	0.826	4.641	1.411	3.330	0.419
0-60	3.665	0.767	-	-	5.022	1.207	3.592	0.334
All	3.184	0.744	3.038	0.806	4.610	1.299	3.640	0.587

Table 57 Mean and standard deviation of logarithmic ***Gapon*** *exchange constants of* ***total Al*** *against* ***Ca+Mg+K*** *as a function of soil depth for sand, loess, clay and peat soils.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-0.080	0.609	0.031	0.616	-0.761	0.872	-0.674	0.389
10-30	0.103	0.868	0.253	0.770	-0.589	0.537	-0.793	0.320
30-60	0.178	0.772	-	-	-1.821	0.096	-1.137	0.311
60-100	0.805	0.108	0.262	0.694	-2.435	-	-1.410	0.454
0-30	0.337	0.646	0.097	0.718	-1.021	0.943	-0.556	0.489
0-60	-0.376	0.875	-	-	-1.418	0.599	-0.898	0.256
All	0.113	0.726	0.155	0.701	-0.994	0.870	-0.831	0.451

Comparison of logarithmic Gapon exchange constants with those including free Al (Tables 28 and 43) show that both those of H against total Al and total Al against Ca+Mg+K are generally smaller by 0.1 (loess soils) to 0.4 (other soils) compared to free Al (see Tables 28 & 56 and Tables 43 & 57). The impact of using total instead of free Al on Gaines-Thomas constants thus appears to be larger than on Gapon constants.

Comparison with data from other countries

The exchange constants derived in this report all refer to Dutch soils. An independent data set of Swiss sandy to loamy soils (Braunerde, divided into Braunerde-Parabraunerde, Braunerde-Rendzina, mixed Braunerde, mixed Parabraunerde, mixed Regosol-Braunerde, Parabraunerde, Parabraunerde-Pseudogley, Podsol-Braunerde, pseudovergleyte Braunerde) was used to check the comparability of the exchange constants of that data set with those derived for Dutch sandy soils. The data set consisted of exchangeable and dissolved cations in three layers of 0-30cm, 30-60 cm and 60-120 cm in 13 soil profiles (39 data points in total, Sabine Braun, pers. comm.). The results thus derived for the major exchange constants are presented in Tables 58 and 59. Since DOC data were not available, the exchange constants for Al refer to total Al and should thus best be compared with those presented in Tables 54-57 given above.

The results shows that the exchange constants with Al involved are quite comparable with those presented for sandy soils and loess soils, specifically when considering the large standard deviation of the exchange constants. In general both the Gaines-Thomas and Gapon exchange constants in the Dutch sandy soils tend to be (slightly) higher for H against total Al and lower for Al against Ca+Mg+K compared to the

Swiss sandy to loamy soils (compare Tables 58 and 59 with Tables 54-57). The higher values of H against Al are most likely due to the fact that the Dutch exchange constants have been related to a pH buffered at 6.5, whereas the CEC of the Swiss soils is the actual soil CEC.

Table 58 Mean and standard deviation of major logarithmic ***Gaines-Thomas*** *exchange constants as a function of soil depth for Swiss sandy to loamy soils.*

Layer	H *vs.* Al		H *vs.* Ca+Mg+K		Al *vs.* Ca+Mg+K		Ca *vs.* Mg	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-30	7.209	0.506	4.555	0.590	0.054	2.266	0.253	0.380
30-60	7.162	0.340	4.584	0.232	0.766	1.767	0.141	0.705
60-120	7.653	1.142	5.104	0.611	0.085	2.426	0.097	0.725
All	7.353	0.731	4.765	0.520	0.302	2.139	0.164	0.608

Table 59 Mean and standard deviation of major logarithmic ***Gapon*** *exchange constants as a function of soil depth for Swiss sandy to loamy soils.*

Layer	H *vs.* Al		H *vs.* Ca+Mg+K		Al *vs.* Ca+Mg+K		Ca *vs.* Mg	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-30	2.616	0.042	2.581	0.504	0.179	1.049	0.423	0.257
30-60	2.580	0.113	2.556	0.237	0.454	0.537	0.296	0.300
60-120	2.782	0.517	2.811	0.231	-0.050	1.113	0.271	0.328
All	2.663	0.306	2.656	0.314	0.194	0.935	0.330	0.295

The preference of protons against base cations is clearly higher for the Dutch soils. Again, this is most likely due to the fact that the Dutch exchange constants have been related to a pH buffered at 6.5. The Gaines-Thomas constant for H against Ca+Mg+K for Dutch soils is approximately 0.7 unit higher for both sandy soils and loess soils (compare Tables 10 and 58) while the same Gapon constant is approximately 0.5 units higher (compare Tables 35 and 59). The Gaines-Thomas constant for Ca against Mg for the Swiss sandy to loamy soils is between the Dutch sandy soils which are higher and loess soils which are lower (compare Tables 20 and 58) whereas the same Gapon exchange constants are very similar (compare Tables 45 and 59).

In summary, it is important to note that the exchange constants presented in this report are normalised to a pH of 6.5 and can thus deviate from those obtained in other countries using the actual (measured) CEC and cation fractions at the adsorption complex.

Impact of extraction method on calculated exchange constants

The exchange constants derived for the Dutch soils have all been derived with a centrifugation method to extract the soil solution. The most common approach to extract soil solution is, however, the use of lysimeters. Unlike the use of lysimeters, centrifugation is a destructive method that is not specifically suited for regular (e.g. weekly or monthly) monitoring. Instead it has been used in the Netherlands at an annual interval. The main advantage over lysimeters is that an average value for a plot at a given period can more easily be obtained by using a pooled sample.

There are clear differences in dissolved ion concentrations in soil solution extracted by lysimeters and centrifugation. In general, the equivalent suction that can be applied by centrifugation is much higher than by vacuum extraction using suction cups. This implies that the centrifugation of fresh soil samples results in the collection of soil solution that is more strongly bound to the soil matrix than suction cups. In coarse sandy soils, this may not cause much difference, but in more loamy soils there is a clear difference in the concentration in pores within soil particles than between soil particles. Insight in the difference in ion concentrations by centrifugation and suction cup lysimeters has been derived from a comparative study of both methods at two forested plots (Speuld and Ysselstein) in the Netherlands. In this study, suction cup lysimeters were installed at fifteen spots that were situated two meters apart at two depths (10 or 20 cm and 40 or 60 cm). Soil samples for centrifugation were taken as close as possible to the lysimeters to minimise impacts of spatial variability. Results of the study showed that ion concentrations are generally significantly higher in the centrifugates than in the suction cup lysimeters with the exception of pH, Al and NH_4 (De Vries et al., 1999). On average, Al concentrations were even higher in lysimeters compared to centrifugates. Similar results were found by Zabowski and Ugolini (1990).

The impact of using lysimeters or centrifugation in deriving exchange constants of Al against base cations has recently been investigated by Nissinen et al. (2000). These authors concluded that the exchange constant of Al against base cations was consistently higher when using lysimeters while there was no systematic difference for the exchange of Ca against Mg. This conclusion is fully in line with the conclusion made by De Vries et al. (1999) that Al concentrations were higher whereas base cation concentrations were lower in lysimeters compared to centrifugates. Use of exchange constants should thus be done cautiously, keeping in mind these methodological aspects.

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Appendix A Basic statistics

Here we summarise definitions and properties of such basic statistical quantities as mean, variance and covariance for random variables defined by a finite number of outcomes.

Let X be a random variable with n outcomes x_i and weights w_i. We assume that the weights are normalised, i.e.

(A1) $$\sum_{i=1}^{n} w_i = 1$$

Then the **expected value**, **(weighted) average** or **(weighted) mean** of X is defined as:

(A2) $$\mathbf{E}(X) = m_X = \sum_{i=1}^{n} w_i x_i$$

which for identical weights, $w_i = 1/n$, is the familiar formula for the (arithmetic) mean. From eq.A2 properties of the expected value can be easily derived. For example, let $X = a$, i.e. $x_i = a$ for all i; then from eq.A2 (using eq.A1) follows:

(A3) $$\mathbf{E}(a) = \sum_{i=1}^{n} w_i a = a \sum_{i=1}^{n} w_i = a$$

Furthermore, let Y be another random variable with outcomes y_i and the same weights, and a and b two arbitrary numbers; then we get:

(A4) $$\mathbf{E}(aX + bY) = a\mathbf{E}(X) + b\mathbf{E}(Y)$$

i.e. the expected value **E**(.) is a linear function.

The **variance** of the variable X is defines as:

(A5) $$\mathbf{Var}(X) = \mathbf{E}\left((X - \mathbf{E}(x))^2\right) = \sum_{i=1}^{n} w_i (x_i - m_X)^2 = \sum_{i=1}^{n} w_i x_i^2 - m_X^2$$

The square root of the variance is known as **standard deviation**. Using eq.A3, it follows from eq.A5 that for every constant a

(A6) $$\mathbf{Var}(a) = 0$$

Similarly, the **covariance** of two variables X and Y is defined as:

(A7)
$$\begin{aligned}\mathbf{Cov}(X,Y) &= \mathbf{E}\big((X-\mathbf{E}(X))(Y-\mathbf{E}(Y))\big)\\ &= \sum_{i=1}^{n} w_i(x_i-m_X)(y_i-m_Y) = \sum_{i=1}^{n} w_i x_i y_i - m_X m_Y\end{aligned}$$

Obviously, $\mathbf{Cov}(Y,X)=\mathbf{Cov}(X,Y)$ and $\mathbf{Cov}(X,X)=\mathbf{Var}(X)$. The covariance is linear in both arguments, e.g.:

(A8) $$\mathbf{Cov}(aX+bY,Z) = a\,\mathbf{Cov}(X,Z) + b\,\mathbf{Cov}(Y,Z)$$

Finally, the **correlation coefficient** is defined as:

(A9) $$r(X,Y) = \frac{\mathbf{Cov}(X,Y)}{\sqrt{\mathbf{Var}(X)\mathbf{Var}(Y)}}$$

which can be shown to lie in the interval [-1,1].

We can now also compute the variance of a linear combination of two variables by applying Eq.A8 repeatedly:

(A10) $$\mathbf{Var}(aX+bY) = a^2\mathbf{Var}(X) + b^2\mathbf{Var}(Y) + 2ab\,\mathbf{Cov}(X,Y)$$

Setting $b=0$, one obtains in particular:

(A11) $$\mathbf{Var}(aX) = a^2\mathbf{Var}(X)$$

Eq.A10 can be used to compute the covariances (and correlation coefficients), if the variances of X, Y and $Z=aX+bY$ are known:

(A12) $$\mathbf{Cov}(X,Y) = \frac{1}{2ab}\left(\mathbf{Var}(Z) - a^2\mathbf{Var}(X) - b^2\mathbf{Var}(Y)\right)$$

If $\mathbf{Cov}(X,Y)$ is known, the other covariances can be computed by applying Eq.A8:

(A13) $$\mathbf{Cov}(X,Z) = a\mathbf{Var}(X) + b\mathbf{Cov}(X,Y)$$

and

(A14) $$\mathbf{Cov}(Y,Z) = a\mathbf{Cov}(X,Y) + b\mathbf{Var}(Y)$$

Multiplying Eq.A13 with a, Eq.A14 with b and adding Eqs.A12-14 gives the following relationship for $Z=aX+bY$:

(A15) $$a\mathbf{Cov}(X,Z) + b\mathbf{Cov}(Y,Z) = \mathbf{Var}(Z)$$

which, of course, is also obtained via $\mathbf{Var}(Z)=\mathbf{Cov}(Z,Z)=\mathbf{Cov}(aX+bY,Z)=$ $a\mathbf{Cov}(X,Z)+b\mathbf{Cov}(Y,Z)$.

Appendix B Unit conversions

For convenience we use the term “equivalents” (eq) instead of the SI-unit “moles of charge” (mol_c). If X is an ion with molecular weight M and charge z, then one has:

(B1) $$1\,\text{g X} = \frac{1}{M}\,\text{mol X} = \frac{z}{M}\,\text{eq X}$$

Obviously, moles and equivalents are the same for $z=1$.

When dealing with equations of chemical equilibria, the unpleasant task of converting the equilibrium constants to the required units often arises. In the following we give a formula which should cover most of the cases encountered: Let A and B be two chemical compounds in the following equilibrium equation:

(B2) $$[\text{A}^{m\pm}]^x = K[\text{B}^{n\pm}]^y$$

where the square brackets [...] denote concentrations in mol/L (L stands for litre), implying for the equilibrium constant K the units $(\text{mol/L})^{x\text{-}y}$. If the concentrations are to be expressed in eq/V, where V is an arbitrary volume unit with $1\text{L}=10^c\text{V}$, then the equilibrium constant in the new units is given by

(B3) $$K' = K \cdot 10^{c(y-x)}\frac{m^x}{n^y}\ (\text{eq/V})^{x-y}$$

Note: To convert to mol/V, set $m=n=1$ in the above equation; and to covert to g/V set $m=1/M_\text{A}$ and $n=1/M_\text{B}$, where M_A and M_B are the molecular weights of A and B, resp.

Example 1: The gibbsite equilibrium is given by $[\text{Al}^{3+}]=K[\text{H}^+]^3$, i.e. $m=3$, $x=1$, $n=1$, $y=3$ and (e.g.) $K=10^8(\text{mol/L})^{-2}$. To convert to eq/m^3, one has $c=-3$ and thus $K' = 10^8 \cdot 10^{-3\cdot(3-1)} \cdot 3 = 300\ (\text{eq/m}^3)^{-2}$.

The above reasoning can also be used for converting exchange constants. For example, the Gapon equation for Al-Bc exchange can be written as

(B4) $$\frac{E_{Al}}{E_{Bc}}[Bc^{2+}]^{1/2} = k_{AlBc}[Al^{3+}]^{1/3}$$

and since exchangeable fractions are dimensionless, eq.B3 can be used.

Example 2: Let $\log_{10}k_{AlBc}$=0; then $k_{AlBc}=10^0=1$ (mol/L)$^{1/6}$ (x=1/2, y=1/3). Since m=2 and n=3, one gets when converting to eq/m^3, i.e. c=–3, $k_{AlBc}=1\cdot10^{-3\cdot(1/3-1/2)}\cdot(2^{1/2}/3^{1/3})$ = 3.100806 (eq/m^3)$^{1/6}$.
And for k_{HBc} the multiplier to obtain (eq/m^3)$^{-1/2}$ is $0.002^{1/2}$=0.0447213.