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The heterogeneous distribution of mobile ions in the  
rhizosphere of acid forest soils

Facts, causes and consequences

# The Heterogeneous Distribution of Mobile Ions in the Rhizosphere of Acid Forest Soils: Facts, Causes and Consequences

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## Abstract

The structure of forest soils contains chemical information relevant to the growth of the forest. Therefore, operational analysis procedures have been developed to preserve this chemical information by not homogenizing the soil sample. Under slight suction a quasi-equilibrium is established between a circulating soil solution and the surfaces of naturally structured and homogenized soil samples. A soil structure dependent, heterogeneous distribution of water soluble basic cations is normally found in the rhizosphere of acid forest soils. Maintaining the soil structure causes a decrease in the equilibrium concentration of basic cations, especially potassium. In both naturally structured and homogenized soil samples, the exchangeable ions were determined fraction by fraction in an open percolation system. When the exchange solution is percolated under slight suction, the spontaneous exchange on both natural and artificial aggregate surfaces controls exchange with the interior of the aggregates. Aggregate surfaces in the rhizosphere of acid forest soils also have low concentrations of exchangeable nutrients. With potassium, large selectivity gradients within aggregates limit diffusion. Therefore, the soil structure causes a heavy delay of nutrient release in the soil macropores, which for many forest trees represents the effective rhizosphere.

## Introduction and Hypothesis

In most cases, analyzing forest soils for their chemical properties destroys the natural structure of the soil. When analyzing homogenized fine earth it is assumed either:

- that the soil's structure does not provide soil-chemical information, that is, that the properties to be studied are distributed independently of the structure, or
- that if an unknown microcompartmentalization of the chemical properties in the rhizosphere exists, it is not a required parameter in an evaluation of the soil's nutritional or stress situation.

The data presented here suggest that both conclusions are incorrect. Pools of ions, important to forest nutrition (e.g., water soluble and effectively exchangeable ions), show a nonhomogeneous distribution in the rhizosphere of acid forest soils which is clearly dependent on the soil's structure. To demonstrate this dependency we have developed operational analysis procedures involving naturally structured soil, "tissue aliquots" [1].

## Methods and Materials

### Materials and Sampling

The samples were taken from a soil profile in the forest district Ochsenhausen, located in the "Alpenvorland" in southwestern Germany. The parent materials for soil formation are glacial deposits of Riss. The soil type is a Gleyic Luvisol. The forest stand consists of 80-year-old spruce with a potassium deficiency documented by needle analysis. The spatial variability of chemical properties of naturally structured 100 cm<sup>3</sup> soil samples within a 0.5 m<sup>2</sup> area was documented in 10 (A and AB horizons) and in 8 to 6 (B, BC, and C horizons) repetitions. In addition, soil was taken from the area between the sampling points and homogenized for use as reference material. All samples, including the homogenized samples, were immediately analyzed in field fresh condition.

### Structure-Dependent Distribution of Water Soluble Ions

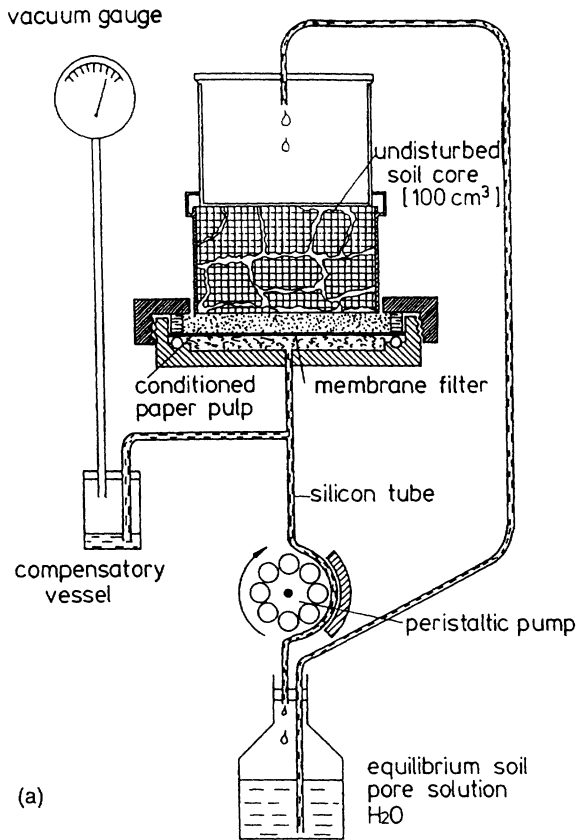
This method of determining the structure-dependent distribution of water soluble ions is based on the comparison of soil solutions in a state of quasi-

equilibrium with water films under low suction ( $4 \text{ hPa} < \psi_m < 60 \text{ hPa}$ ) in naturally structured, and sieved ( $\phi < 2 \text{ mm}$ ) soil samples with comparable soil-physical parameters (e.g., total pore volume and rock content). The device constructed for this purpose, is shown in Figure 1. A more detailed presentation of the method used is given in Hildebrand [1, 2]. The closed circulation of the soil solution (as demonstrated in Figure 1) meets the following criteria:

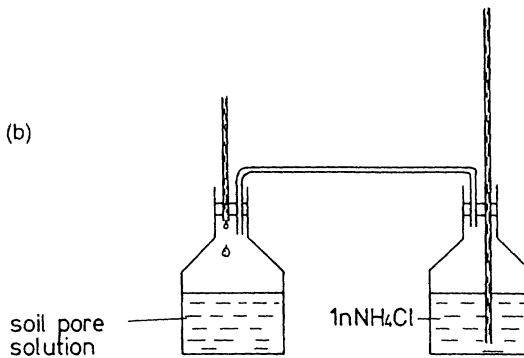
1. In order to avoid reductive mobilizations, circulation takes place by maintaining an air filled pore volume [i.e., under low suction ( $4 \text{ hPa} < \psi_m < 60 \text{ hPa}$ ) at the membrane filter].
2. The filter materials used for transferring suction do not interfere with the chemical properties of the soil.
3. A reproducible quasi-equilibrium is achieved quickly; that is, after a few circulations no chemical drift of the solution can be detected. It can be concluded, therefore, that in a quasi-equilibrium the dissolved components of the solution are almost entirely controlled by water films that were exchanged frequently during percolation. Thus, by comparing the quasi-equilibria of solutions from both the undisturbed and the sieved soil samples, it is possible to detect the structure dependent chemical concentration disequilibria.
4. Flow resistances in the disturbed and homogenized soil samples vary only slightly due to comparable bulk densities and total pore volumes. Therefore, in both cases, the intensities of interactions between the soil solution and solid soil are similar. In order to prevent an atypical increase in the activity of microorganisms, the equilibrium soil pore solutions are obtained at a controlled temperature of  $15^\circ\text{C}$ .

### **Structure-Dependent Distribution of Effectively Exchangeable Ions**

The following procedure was used to study the structure-dependent distribution of effectively exchangeable ions. Modifying the device shown in Figure 1 by separating the sampling from the storing vessel permits an exchange solution to be percolated through the undisturbed and the homogenized (100 mL) soil samples [2, 3]. This exchange solution (1 N  $\text{NH}_4\text{Cl}$ ) was percolated through samples as described above under low suction ( $4 \text{ hPa} < \psi_m < 60 \text{ hPa}$ ) and then divided into fractions of 250 mL. The procedure was stopped when the rate of exchange in the last fraction dropped below  $\pm 5\%$  of the for-



(a)



(b)

Figure 1: Device for producing equilibrium soil pore solutions (above) and fractionated soil pore solutions (below) from undisturbed and homogenized 100 cm<sup>3</sup> soil cores.

merly accumulated amounts of exchanged ions. Usually five fractions were required.

In order to distinguish between spontaneous exchange at aggregate surfaces and the subsequent supplement from the interior of the aggregates, we interrupted the percolation of a random group of five soil samples between the third and fourth fraction. At a suction of 750–800 hPa, diffusion of ions could occur in the intra-aggregate pore space. By this procedure the following information is obtained.

1. The ion pool which is spontaneously exchangeable on the aggregate surface decreases. This is seen by the threshold-like decrease of the exchange rates in Fractions 1–3 in Figure 5.
2. The ion pool, which is supplemented from the interior of the aggregates, is detected by the increases in the spontaneous exchange rates over time in Fraction 4 in Figure 5.

### Ion Equilibria

We used the GAPON equation to calculate the distribution coefficients for the ion pairs Ca/Al, Mg/Al and K/Mg.

$$K_G = \left[ \frac{Az_B}{Bz_A} \right]_{adsorbed} \left[ \frac{a^{z_B} \sqrt{B}}{a^{z_A} \sqrt{A}} \right]_{dissolved} \quad (1)$$

where

- $K_G$  GAPON coefficient
- $A, B$  ions
- $z_A, z_B$  charge of  $A$  and  $B$ , respectively
- $a$  activity

All parameters (i.e., the equivalent ratio of the adsorbed ions and the activity ratio of the dissolved ions) were determined separately for the naturally structured and homogenized soil samples. Soil material from 12 profiles with K deficient spruce stands in Southwest Germany was included [2].

In the case of K selectivity, Mg was used as reference ion because of its lower affinity to complexation. For the calculation of Ca/Al and Mg/Al coefficients, we used only those mineral soil horizons in which a low degree of complexation could be assumed, based on cation/anion-budgets.

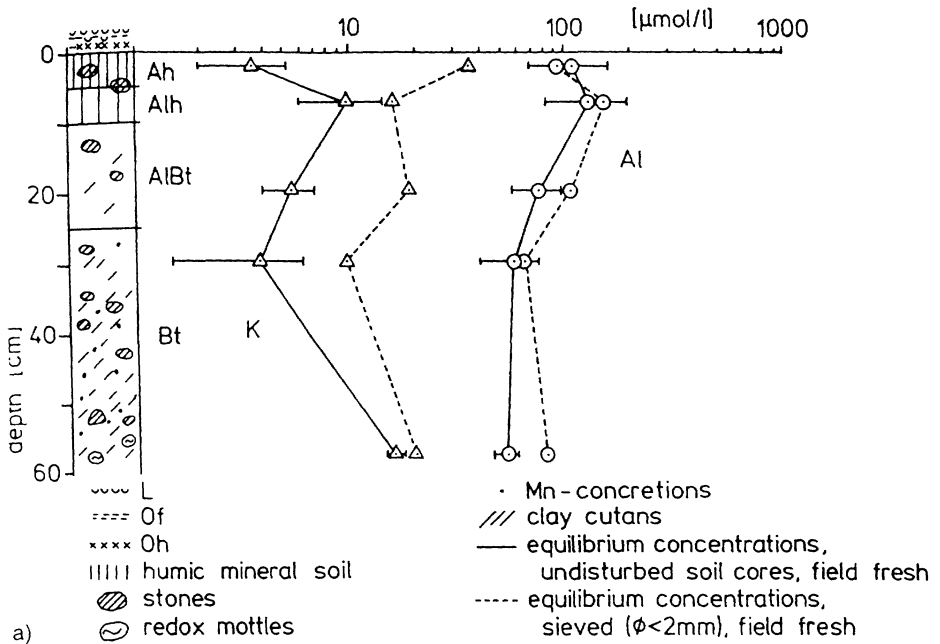


Figure 2: Depth functions of potassium, aluminum and ammonium equilibrium concentrations of naturally structured and homogenized soil samples, as well as the molar K/Al and the Ca/Al ratios.

We analyzed all aqueous solutions and exchange solutions by referring to the standard German work guide, *Bundesweite Bodenzustandserhebung im Wald* [4].

## Results

### Structure-Dependent Distribution of Water Soluble Ions

Figure 2 shows the depth functions of K, Al, and NH<sub>4</sub> equilibrium concentrations of undisturbed and homogenized soil samples. The release of K and

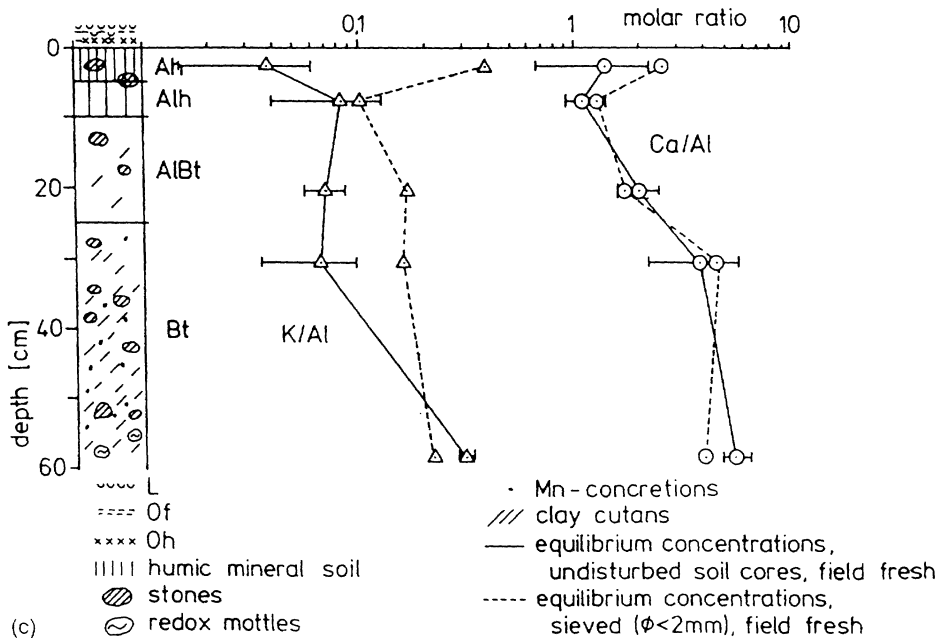
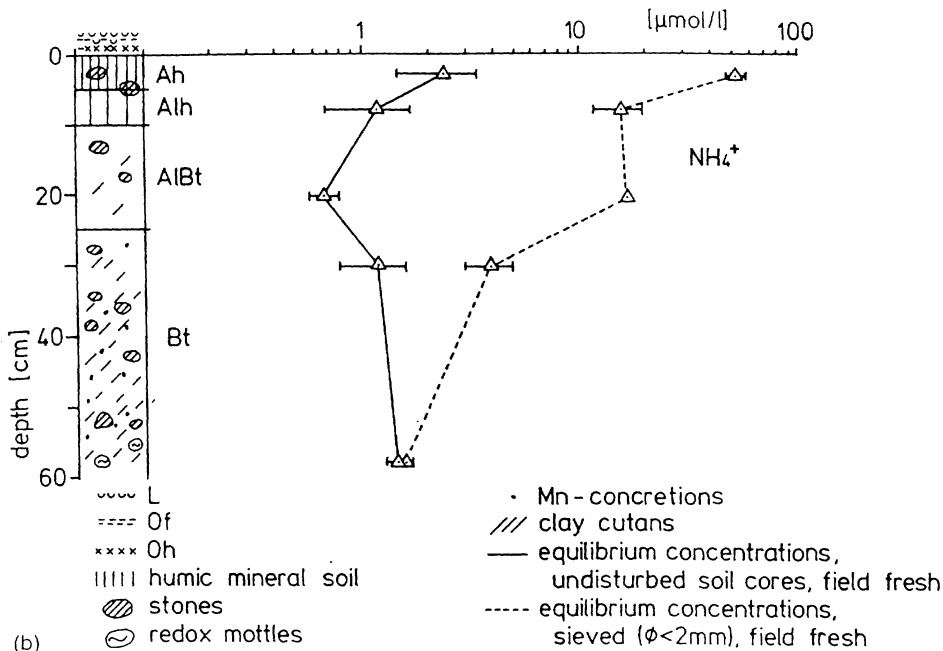


Figure 2: Continued



$\text{NH}_4$  strongly depends on the structure of the soil. However Al equilibrium concentrations proved to be nearly independent of the soil structure. Calcium and Mg take an intermediate position; the depth function of the molar Ca/Al ratio shows a clear inhomogeneous Ca distribution only in the intensively rooted Ah horizon. These results were found in most of the noncarbonate forest sites in southwestern Germany [2].

Figure 2 clearly shows that the equilibrium soil pore solution can deviate greatly from the equilibrium solution of the bulk soil. Moreover, a high variation of chemical properties in the pore solution of the undisturbed soil cores reveals a distinct microcompartmentalization of solubility conditions.

## Structure-Dependent Distribution of Exchangeable Ions

### Spontaneous Exchange on Aggregate Surfaces

Figures 3 and 4 give the rates and cumulative amounts of exchanged Ca, Mg, Mn, and Al (only Ah horizon) and of K (all horizons) when the undisturbed and homogenized  $100 \text{ cm}^3$  samples are percolated with  $5 \times 250 \text{ mL } 1 \text{ N } \text{NH}_4\text{Cl}$ . The abrupt threshold-like decrease in the exchange rate indicates the completion of spontaneous exchange on the natural and artificial aggregate surfaces. The release of K and Mn by exchange is distinctly lowered if the natural structure of the soil is not destroyed. In the case of Al, the exchange rate, as well as cumulated exchange are nearly independent of the structure. As before, Ca and Mg show an intermediary behavior. Thus, the structure dependent chemical heterogeneities within the exchangeable ion fractions are, in principle, comparable to the heterogeneities characterized by aqueous equilibrium solutions. They are, however, less distinct, especially in the case of K.

### Diffusive Supplement from the Interior of Aggregates

Figure 5 shows that increasing the time intervals between the third and fourth fraction with a suction equilibrium of 800 hPa results in the restoration of spontaneously exchangeable ions. Figure 6 shows the cumulation of spontaneously exchangeable ions ( $\Sigma \text{K}$ ,  $\Sigma \text{Ca}$ ,  $\Sigma \text{Al}$ ) as a function of  $1/t^{1/2}$ . If the restoration of the aggregate surfaces follows a linear function, then it can be assumed that the driving force of this process is constant diffusion from the interior of the aggregates. This process in its one-dimensional case is described

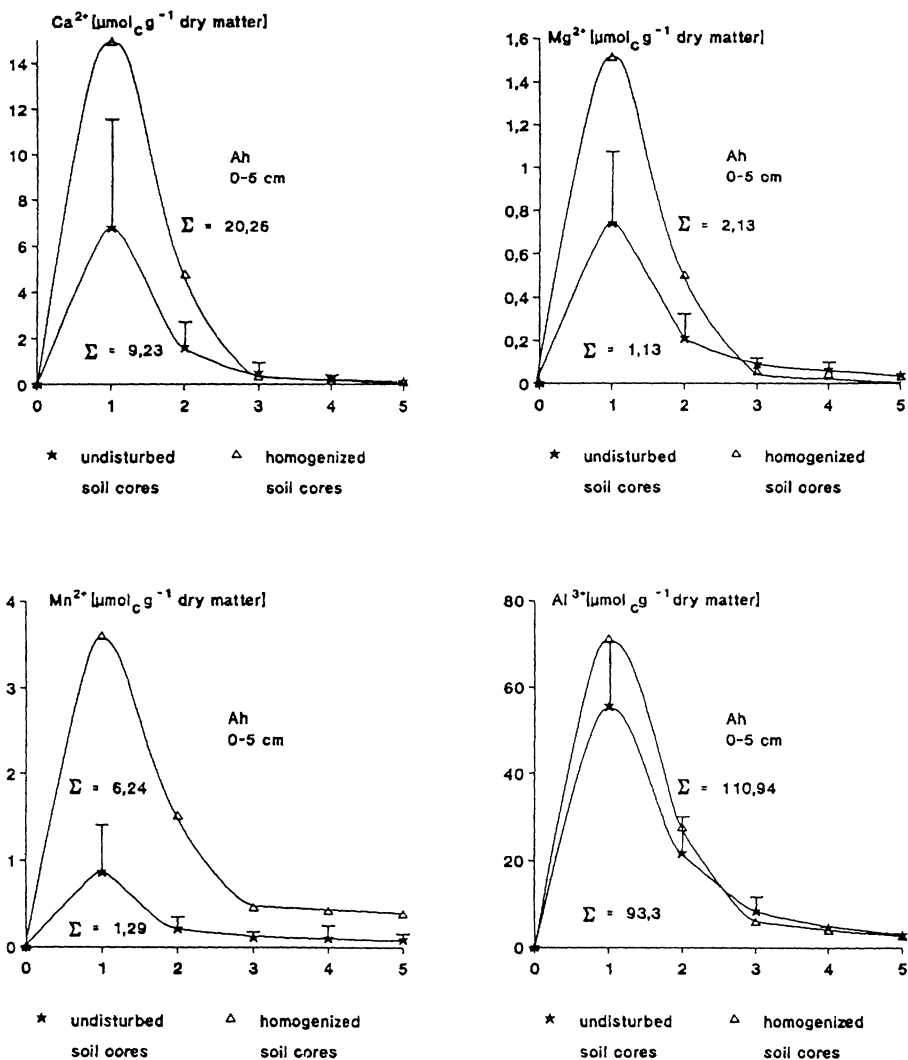
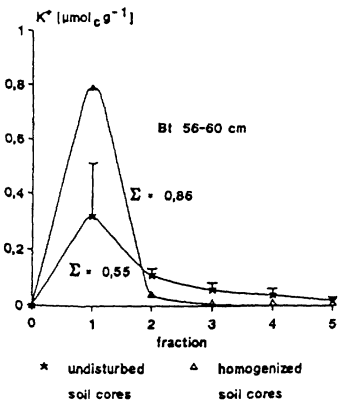
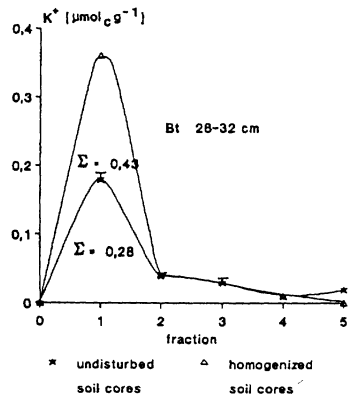
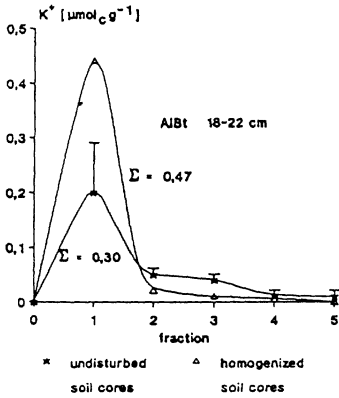
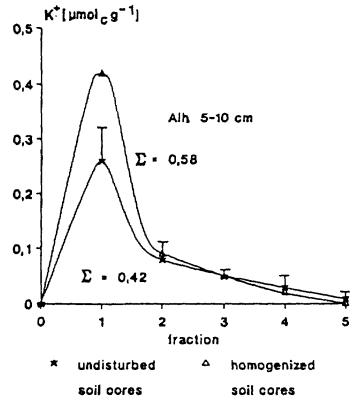
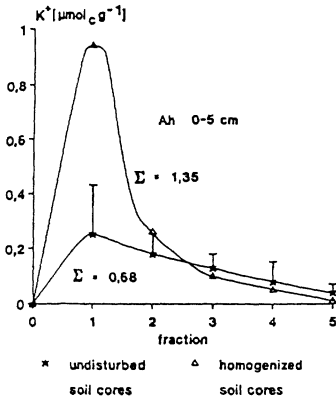


Figure 3: Rates and cumulated amounts of spontaneous Ca, Mg, Mn, and Al exchange (Ah horizon) with  $5 \times 250$  mL 1 N  $\text{NH}_4\text{Cl}$  on undisturbed and homogenized  $100 \text{ cm}^3$  soil cores from a Gleyic Luvisol. Curves are drawn by eye fit.



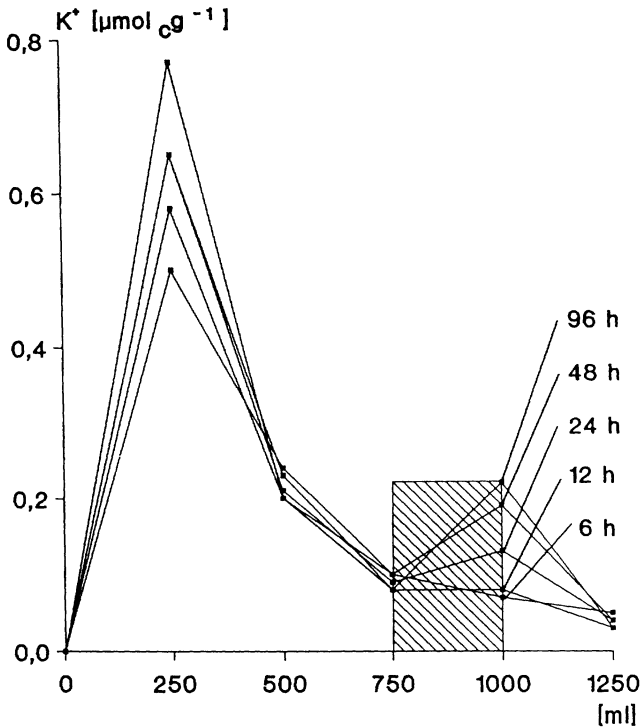


Figure 5: Rates of spontaneous K exchange with 5 × 250 mL 1 N NH<sub>4</sub>Cl on undisturbed and homogenized 100 cm<sup>3</sup> soil cores (Ah horizon). Different waiting periods between fraction 750 mL and 1000 mL function as an independent variable. Each curve represents five repetitions.

in the second Fick's Law (for example in Kemper [5]):

$$\frac{\partial C}{\partial t} = \left[ \frac{D_0}{\theta + b} \right] \frac{\partial^2 C}{\partial x^2} \tag{2}$$

Figure 4: Rates and cumulated amounts of spontaneous K exchange (all soil horizons) with 5 × 250 mL 1 N NH<sub>4</sub>Cl on undisturbed and homogenized 100 cm<sup>3</sup> soil cores from a Gleyic Luvisol. Curves are drawn by eye fit.

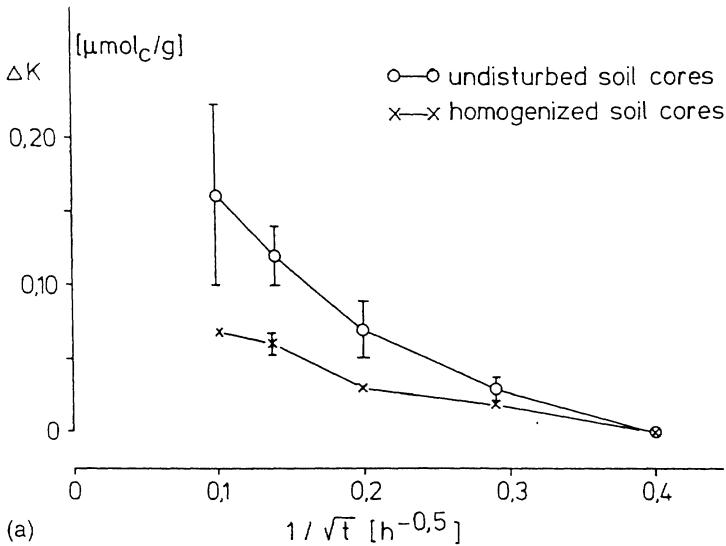


Figure 6: Cumulative restoration of spontaneously exchangeable K, Ca, and Al in naturally structured and homogenized soil samples as a function of the waiting period ( $1/t^{1/2}$ ) at a suction equilibrium of 750–800 hPa.

where

$C$  concentration

$t$  time

$D_0$  diffusion coefficient

$\theta$  volumetric water content

$b$  slope factor of the isotherm which describes the dissolution equilibrium.

The curves for Ca and Al do not conflict with this theory. Potassium, however, clearly does not show a linear function in the case of undisturbed soil cores. The shorter the time interval ( $\frac{1}{\sqrt{t}} = 0.4-0.2$ ), the lower is the replenishing rate. This behavior can be explained by the great variances in selectiv-

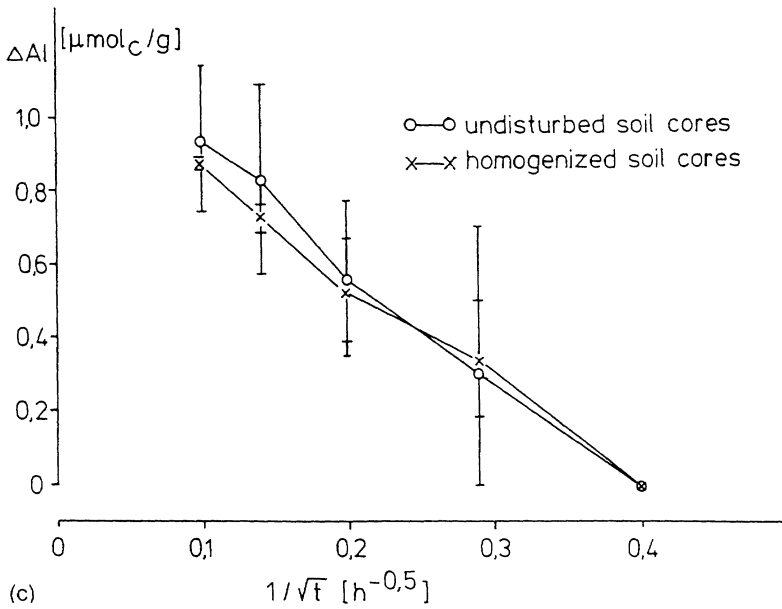
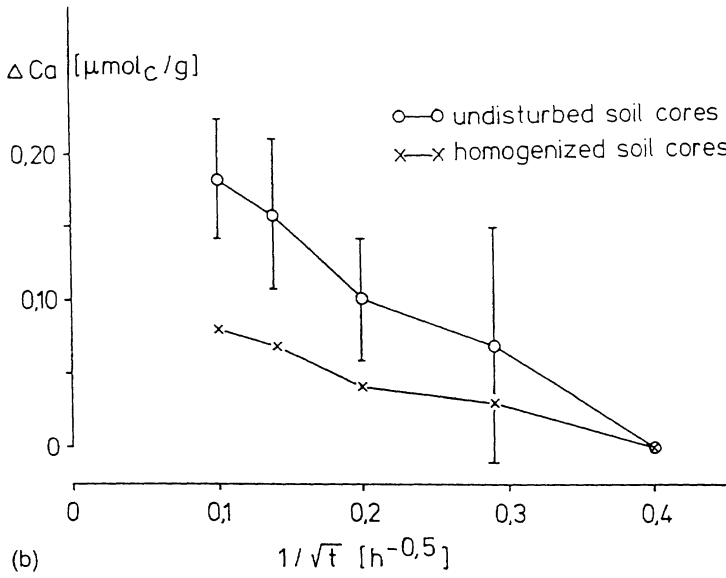


Figure 6: Continued

ity of K adsorption which can appear along small gradients of K saturation (Figure 7). Thus, the factor  $b$  in eq 2 may not be taken as being constant. Before aggregate surfaces can be replenished with spontaneously exchangeable K, it is necessary that sites with high K selectivity are saturated. In naturally structured samples, the ratio of spontaneously exchangeable K to diffusively supplemented K is lower than in homogenized samples. The great variance in the replenishment of the aggregate surfaces shows that on aggregate surfaces of naturally structured soil a distinct microcompartmentalization of the chemical soil property "spontaneously exchangeable potassium" occurs, if K saturation on aggregate surfaces was depleted by a counter ion.

### Ion Distribution Coefficient

Using the GAPON equation Figure 7 shows the relative K selectivity calculated in relation to Mg, as a function of the amount of exchangeable potassium. Selectivity greatly increases at a K level which is less than  $3 \mu\text{mol}_c/\text{g}$ . In structured soils, a combination of low levels of K and high selectivity on surfaces which can be reached by the roots directly, is common for sites with K deficiency. Figure 8 shows, in contrast to this, that in the case of Ca and Mg the selectivity decreases with an increase in saturation of trivalent cation acids (Al, Fe). A diminishing supply of exchangeable Ca and Mg on natural aggregate surfaces leads, in contrast to potassium, foremost to an increase in Ca and Mg availability in the pore solution. Thus, it is understandable that the nonhomogeneous distribution of water soluble Ca and Mg is not as extreme as in the case of K, because the drift on the aggregate surfaces can progress faster into the interior of the aggregate. In addition, Figure 8 shows that the ion equilibria of structured and homogenized soil samples follow more or less the same GAPON equation.

### Conclusions

Structure dependent chemical disequilibria are common in the rhizosphere of noncarbonate forest sites [2, 6, 7]. The fine roots of spruce and beech are predominantly found in the macropores [8, 9]. Thus, the nonhomogeneous distribution of mobile ions offers ecologically important soil chemical information, which is lost by conventional soil analysis. The macropore space can be called the "real" rhizosphere. In southwestern Germany, for example, wide-scale inventories revealed that K deficiency in spruce stands

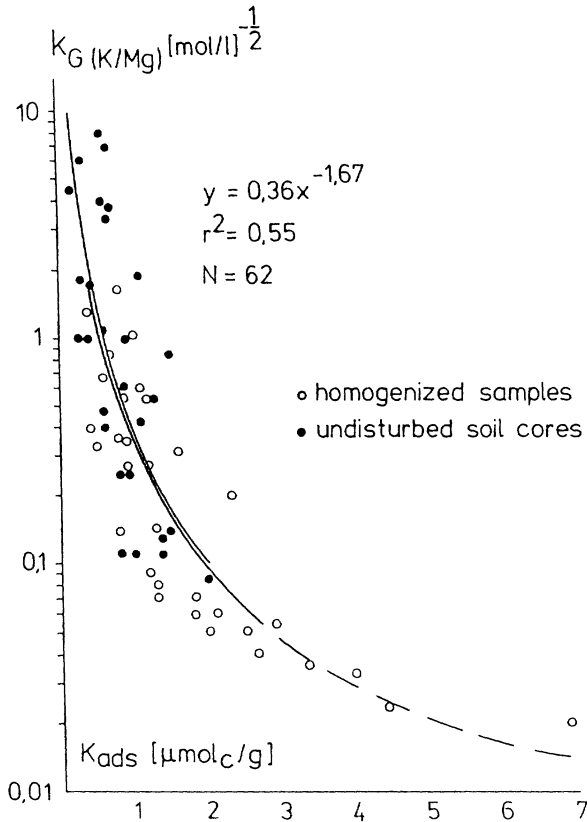


Figure 7: Relative selectivities of K binding compared to Mg calculated according to the GAPON equation plotted against the amount of exchangeable K. Independent variable: condition of soil structure (i.e., natural or disturbed).

appears commonly on loamy sites which, through conventional soil analysis, were evaluated as K rich. The study of numerous similar K deficient sites shows that the K supply in soils with distinct aggregation is determined much less from the total supply of exchangeable K in the rooted soil space than by the spontaneously exchangeable or water soluble potassium pool on the root-soil interface (i.e., the aggregate surfaces [2, 3]).



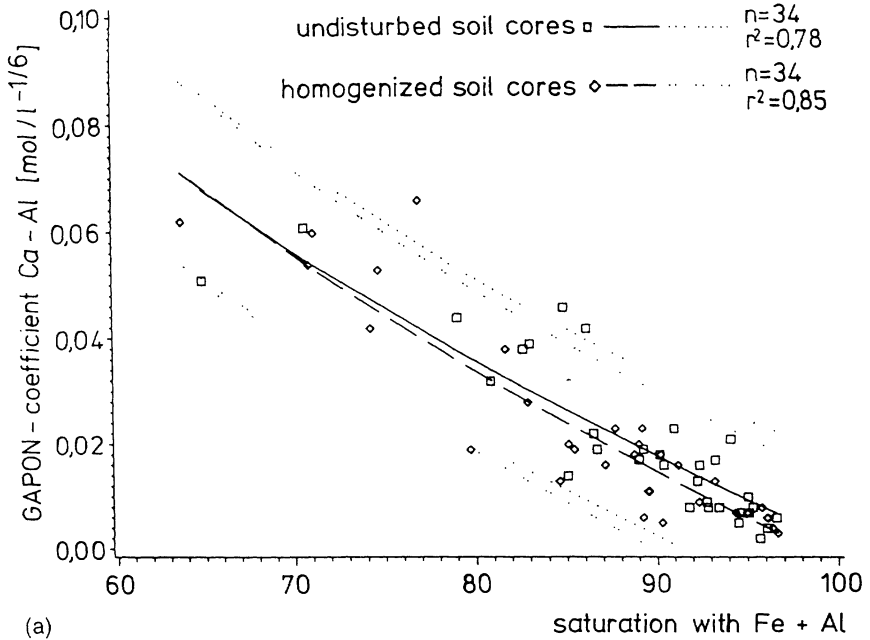


Figure 8: Relative selectivities of Ca and Mg binding compared to Al plotted against the saturation with exchangeable Al+Fe. Independent variable: condition of soil structure (i.e., natural or disturbed).

Processes which are first effective directly on the aggregate surfaces are, for example, short-term buffer reactions with the acidity of that part of the throughfall precipitation which flows as macropore water [10]. Watson and Luxmoore [11], as well as Wilson and Luxmoore [12], determined that in forested water sheds 75–85% of the water flow takes place in pores larger than 0.75 mm. This represents a suction of 20 hPa and with it the approximate mean water tension through pore solution extraction.

Also, the cation assimilation of forest trees occurs due to the “cluster formation” of the tree roots in macropores, mostly on aggregate surfaces, so that the assimilation of a cation excess also presents a nonhomogeneous source of

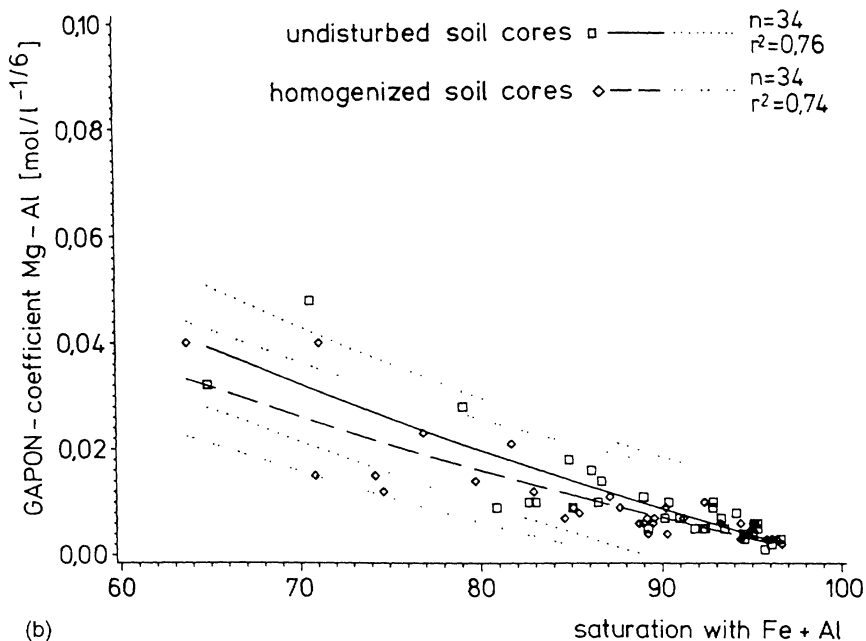


Figure 8: Continued

acidification [13]. For the restoration of a homogeneous ion distribution, two counter reactions are conceivable:

- convective and/or diffusive ion transport from the interior of the aggregates, and
- formation of new aggregates by soil fauna or by abiotic processes.

To (a): The soil solution of the intra-aggregate pore system is mainly stationary [14, 15]. Horn [16, 17] measured single aggregates, to show that the diffusion coefficients are low due to minimal pore continuity. With K a non-linear rise of the selectivity along the concentration gradient can function as additional diffusion resistance (see Figure 6 top).

To (b): The rate in which new aggregates are formed depends essentially on the biotic energy transfer in the mineral soil. The importance of biogenic aggregate formation for the restoration of a homogeneous ion distribution is indicated by sites with former liming: Despite high acid deposition, there are no structure-dependent disequilibria, because due to high densities of Lumbricidae the high rate of aggregate formation prevents the "chemical aging" of the surfaces [2]. In (a) the restoration of homogeneous ion distributions is limited by internal, physicochemical properties of the aggregates. The formation rate of new aggregates (b) would thus be the ecological key factor determining the type of ion distribution. One can assume that in most non-carbonate forest soils in southwestern Germany the aggregate formation rate lags behind the selective acidification of the aggregate surfaces.

Such a state in an open system where effect and counter effect do not neutralize themselves is called a disequilibrium. Disequilibria can only be maintained, over a longer period of time, through external driving forces. Thus, they are indicators of a drift. It is therefore possible to recognize a drift of the compartment "soil" by taking simultaneous measurements from undisturbed and homogenized soil aliquots. In that way the chemical state of the aggregate surfaces characterizes the direction of the drift and the slope of the medium gradient between bulk soil and the aggregate surfaces is a measure of the drift velocity.

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