SOIL ACIDITY AND ITS RELATIONS TO ACID DEPOSITION

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ABSTRACT

The nature of soil acidity as well as measures of the capacity and the intensity terms are discussed. According to the proton buffer reactions occuring in soils, buffer ranges are distinguished. They are defined by pH values. Forest soils on limestones which should be in the calcium carbonate buffer range, acidify under the influence of acid deposition as soon as the fine earth is free of calcium carbonate. The same may be true for soils staying in the silicate buffer range if the rate of acid load exceeds the rate of acid buffering by base cation release during silicate weathering. From existing data on the rate of acid deposition in Central Europe, it is concluded that soils staying in the cation exchange buffer range should have lost considerable amounts of exchangeable Ca due to acid deposition since beginning of industrialization. The resilience of the ecosystem becomes very limited if the soil stays with all major horizons in the aluminium or even in the iron buffer range. The iron buffer range is characterized by podzolization.

NATURE OF SOIL ACIDITY

Soil acidity has a quantitative (capacity) and a qualitative (intensity) aspect. The capacity can be defined as the equivalent sum of acids which can be neutralized by addition of a strong base to pH 7 or 8. The intensity is expressed as the thermodynamic activity of the protons and is measured as pH value, it is determined by the strength of the acids controlling the proton activity in the soil solution.

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In soils, two different kinds of Brønsted acids can be distinguished, R-OH and M^{x+}, with the following proton transfer reactions:

$$\underset{\text{acid}}{R\text{-}OH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{R\text{-}O^-}$$

$$\underset{\text{acid}}{M^{x+}} + \underset{\text{base}}{2\ H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{MOH^{(x-1)+}}$$

Strong mineral acids like H_2SO_4, HNO_3 and HCl play an increasing role at pH $<$ 4 and a dominant role at pH $<$ 3.
It is a very important feature of soil chemistry that $MOH^{(x-1)+}$ is not only a base but can react also as acid:

$$\underset{\text{acid}}{MOH^{(x-1)+}} + \underset{\text{base}}{2\ H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{M(OH)_2{}^{(x-2)+}}$$

R symbolyses carbon (mainly phenolic hydroxyl groups and carboxy groups), Si (pH dependent charge of clay minerals, dissolved silicic acid at pH above 7) and CO (carbonic acid). M symbolyzes cation acids, that is NH_4^+ (van BREEMEN, this volume) and metal cations like Al (PRENZEL, NILSSON, this volume), Mn, Fe, and heavy metals including their anionic complexes. The accumulation of positively charged ions of these metals in soil corresponds to the accumulation of acids.

MEASURES OF SOIL ACIDITY

The <u>amount of acid (capacity term)</u> can be determined by the reaction of a base in solution with the acids in solution and accumulated in the solid phase. This can be done by a continuous or discontinuous titration procedure with a strong base. The amount of base consumed to pH 8 corresponds to the base neutralization capacity (BNC). A differentiation according to acid strength can be made by recording the buffer curve (amount of base consumed versus pH).
The acids reacting include ionic species of Al, Mn, Fe and heavy metals (which may exist in different binding forms at outer and inner particle surfaces), soluble metal salts like $AlOHSO_4$ (which releases cation acids by dissolution), "exchangeable" protons at particle surfaces (including soil organic matter), and NH_4 ions (at pH above 7). The binding forms of cation acids and "exchangeable" protons are not fully understood. There is no doubt that the reactions occuring after addition of a base to an acid soil sample are complex and kinetically limited. This means that the buffer curve is a function of reaction time and of the change of pH achieved after the addition of a base increment. The reaction time is limited not only for practical reasons, but also by unwanted microbial

and chemical reactions which release acids or bases and may thus adulterate the buffer curve (e.g. ammonification, nitrification, denitrification, sulfate reduction). The buffer curve and BNC are therefore conventional measures. To approach reality best it is suggested to limit the reaction time to 24 hrs., to exceed never pH 7 to 8, and to use closed bottles (to avoid NH_3 losses if pH exceeds intermittently the value of 7).

Another way is to determine separately the different acids and acid forming substances present. This may be done by determining total and effective cation exchange capacity and the different cations balancing the negative charge of the soil exchangers (including H, NH_4, Al, Mn, Fe). Difficulties exist especially with the determination of acid forming metal salts like $AlOHSO_4$.

The buffer curve and BNC are recommended as standard procedure, with data about CEC exchangeable cations as additional information about the kind of acids.

Also the pH value as intensity parameter is subjected to systematic errors. Only in very rare cases the soil solution can be sampled directly and used for pH measurement. In most cases water or a solution has to be added to the soil in order to get a solution or suspension in which the measurement can be made. Strictly spoken, the soil itself has no pH, only the soil solution, and their pH depends upon the kind how the solution (suspension) has been prepared.

The best approach to reality are the pH of the equilibrium soil solution (pH(ESS)) and the pH of a soil/water suspension (pH(H_2O)). These values can be expected to represent the activity (mean free energy) of protons in the natural soil solution at the time of measurement. Since the acids existing in the solid phase and determining pH need not to be of constant composition, these pH values can vary as a function of time. The variation between seasons may exceed one pH unit (19). These variations reflect real changes in soil chemistry and may be of ecological significance.

To avoid the variation characteristic to pH(H_2O), pH is often measured after addition of salt solutions. Due to the reactions taking place between the added cations and cation acids present in the solid phase, the pH of such a soil solution depends upon the kind of the cation (K or Ca) and the salt concentration used. In soils with illitic clay minerals, K^+ has a specific strong exchange power for cation acids and decreases pH therefore more than Ca^{2+}. Such differences can be used to estimate the kind and binding form of cation acids present in soil, on the basis of existing knowledge and experimental correlations.

Since pH(salt) is determined by more strongly bound acids than pH(H_2O), it is changing less in time. Changes in acid composition of the solid phase during acidification pushes and deacidification phases may also be reflected in pH(salt).

In a number of investigations it has been shown (1,2,3,4) that the pH(salt) values of forest soils in West Germany have decreased during the last 5 to 30 years. A decrease in the mean pH(salt) of a group of soils indicates that an accumulation of stronger acids in soil has occured. For soils being in a steady state, that means not subjected to acidification, the natural variation in pH(salt) should not result in a decrease of the mean value.
Whereas pH(H_2O) is an approximation to the activity of protons in the true soil solution at the time of measurement, pH(salt) is an approximation to the activity of protons in the soil solution in case of acid or salt load. Both values together give in fact a good insight into the actual and potential ecochemical conditions in the soil environment of microorganisms and plant roots. In the following buffer ranges are defined as a framework for interpretation of pH values.

BUFFER RANGES IN SOILS

Considering the stability of minerals and oxides, and the possible buffering reactions involving protons, the following buffer ranges can be distinguished (5):

- calcium carbonate buffer range (pH >8 to 6.2)
- silicate buffer range (silicates being the only buffer between pH 6.2 and 5.0)
- cation exchange buffer range (pH 5.0 to 4.2)
- aluminium buffer range (pH 4.2 to 2.8)
- iron buffer range (pH 3.8 to 2.4)

In the following, buffer capacities are calculated with a bulk density of 1.5 and for a soil layer of 1 dm thickness and 1 ha area.

CALCIUM CARBONATE BUFFER RANGE

Only soil horizons containing $CaCO_3$ in their fine earth fraction stay exclusively in this buffer range. In these horizons the dissolution rate of $CaCO_3$ is high enough to keep the system close to the equilibrium described in equation 4:

$$CaCO_3 + H_2O + CO_{2(g)} \rightleftharpoons Ca^{2+} + 2\ HCO_3^-$$

The dominating acid is carbonic acid which is produced in large quantities by root and decomposer respiration. The buffer capacity amounts to 150 kmole H^+ per 1 % $CaCO_3$. The buffer rate is high, as long as it is determined by the rate of dissolution of $CaCO_3$. If $CaCO_3$ is distributed unevenly and diffusion becomes the rate limiting step, the buffer rate can be considerably lowered. Depending upon the rate of CO_2 production and of pH, the concentration of Ca^{2+} and HCO_3^- in the soil solution may be very high. Due to this high concentration the soil fabric is very stable. Ca is the dominating cation in the soil solution and at the exchanger surface. The main form of inorganic phosphates are calcium phosphates. Toxins like Al ions and water soluble phenols are missing. The organic acids formed in soil are highly polymerized, water insoluble, and possess weak acidic phenolic groups (humic acids).

There is therefore no soil-borne limitation due to toxicity to bacterial activity and growth of plant roots. The humusform is mull, indicating a high activity of soil burrowing animals like earth worms and a rapid bacterial degradation of root and leaf litter if humidity is high enough. The high bacterial activity is a precondition for the formation of stable humic substances. The soil organic matter formed has a high N content and a low C/N ratio (around 10). The level of soil organic matter accumulated is increasing with increasing rate of litter production and decreasing mean annual temperature.

Limiting factors for phytomass production may be:

- unfavourable cation ratios due to the dominance of Ca^{2+} (e.g. K/Ca, relative K deficiency)
- unbalanced NH_4^+/NO_3^- ratio in ion uptake. There may be a large nitrate surplus in ion uptake due to strong nitrification and uptake of nitrate
- limited solubility of metal trace elements may result in Mn, Fe, Cu, Zn deficiency

The role of these limitations is the smaller, the larger the internal turnover in soil. The turnover within the mineral soil can be regarded as being proportional to the rate of decomposition of phytomass. Forest ecosystems which maintain a closed herb layer including legumes, provide a source of food for decomposers at high quantity with high quality. Higher turnover rates of soil organic matter may narrow the NH_4^+/NO_3^- ratio in ion uptake by allowing the plants to take up some N as NH_4, and can also improve the uptake of metal trace elements as organic chelates.

Forests growing on calcareous soils buffer the acidity of the incoming rain during the vegetation period very efficiently at the leaf surface. The pH in the canopy drip can be higher than in the incoming rain (e.g. 4.82 compared to 4.39, from the input amounting to 0.6 kmol H^+ $ha^{-1}yr^{-1}$ 0.24 kmol H^+ have been buffered (7)). This buffering is finally taken over by the soil close to the root surface (ULRICH , this volume). The most common tree species on calcareous soils in Central Europe is the beech (Fagus silvatica). For this species the stem flow may amount to 15 % of the precipitation. The stem flow shows no buffering, it may be more acid than the incoming rain, indicating interception deposition. Also the stem flow can be assumed to reach preferably the soil close to the root surface. From this it follows that in beech ecosystems on calcareous soils the larger fraction of the deposited acidity acidifies not the soil surface, but the soil close to the root surface even in greater soil depth. Thus the most susceptible soil part in respect to tree roots is directly affected. Only the acidity carried by the throughfall in the leafless period reaches the soil surface and acidifies the top soil.

In fig. 1 two examples are given for the chemical conditions of the soil below the stem base of beech trees of age about 110 years growing on soils developed on limestone (unterer Muschelkalk) in the Göttinger Wald. Tree No. 3 grows in a Terra fusca (texture: silty clay), tree No. 6 in a loess layer covering weathered limestone. The values given represent pH(H_2O), in brackets pH(KCl). The data indicate great variation in chemical soil state. No soil volume has been found staying in the carbonate buffer range, even close to limestones. According to the pH(H_2O) values, the actual chemical soil state varies between the silicate and the iron buffer range, the most acid conditions prevailing close to large roots where the soil is influenced by the acid stem flow. The pH(KCl) lies in any case below 4.2, in most cases below 3.8. This means that with an acid input of pH below 3.8, which is quite common for stem flow in the leafless period, the soil will shift to the aluminum or iron buffer range. Soil acidification comparable to podzols can thus be found below the stem base of beech trees on limestone soils. This acidification is due to acid deposition. This soil acidification may play a role in the development of bark necrosis which is often found at the stems of the trees.

But also the densely rooted upper part of rendzina soils is acidified. Table 1 gives some data on chemical soil state and Ca/Al ratio in fine roots of ground vegetation in a beech forest on rendzina, developed on Unterer Muschelkalk in the Göttinger Wald. The samples are taken from the Ah horizon (0-10 cm) in June 1980, the soil showed mainly a polyedric fabric.

In rendzina soils being continuously in the calcium carbonate buffer range there should be no exchangeable Al and no polymeric Al masking the clay mineral surfaces available. In any of the samples polymeric Al is present in considerable amounts. This becomes clear by looking at the ratio CEC_e/CEC_t (effective to total cation exchange capacity) and to the reduction of total CEC_t (see last column) with increasing acidification.

The most acid conditions exist close to the stem base of beech trees.

Typical plants of the soil flora of a rendzina soil under beech do already reflect the acidification by poorer growth and closer Ca/Al-ratios in the roots.

Acid rain influences also rendzina soils and their vegetation. As soon as the fine earth is free of $CaCO_3$, acid rain in combination with internal proton production by nitrification may shift the buffer system acting to the Al buffer or even the iron

Fig. 1: pH(H_2O) and pH(KCl) (in brackets) below the stem of beech trees on lime stone soil

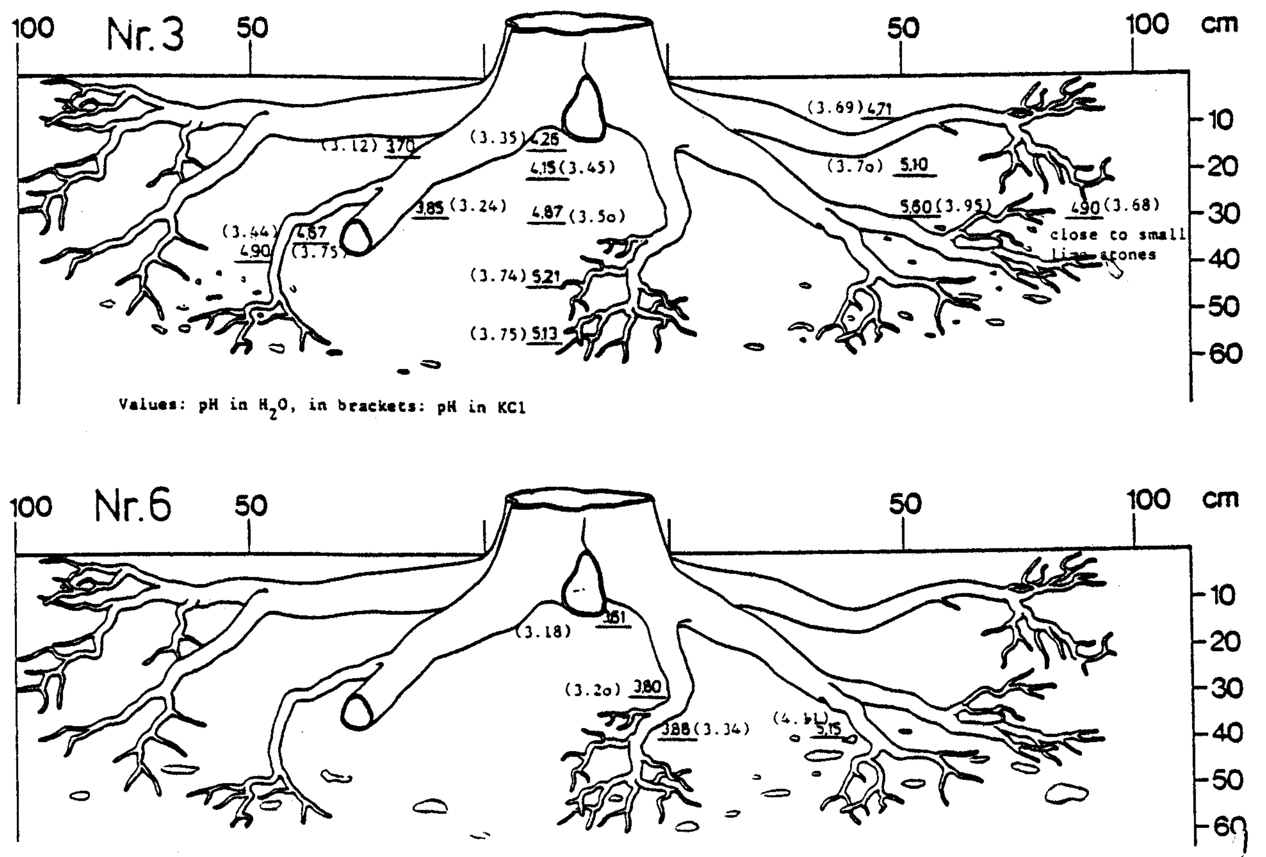

Table 1: Chemical soil state of rendzina soils and plant vitality

	pH GBL	pH $CaCL_2$	CEC_e ueq/g	$\frac{CEC_e}{CEC_t}$	Ca	Fe	Mn	Al	Ca	Al	N_{org}	$\frac{\text{mol Ca}}{\text{mol Al}}$ in ESS	$\frac{\text{mol Ca}}{\text{mol Al}}$ in roots	CEC_t μeq/g
					-% on exchanger--				-mg/l in ESS--					
Ah-horizon 0-10 cm, polyedric fabric	6.00	5.10	221	.41	82	0	2	11	16	1.5	1.3	7.0	3.1	541
0-10 cm, close to a beech stem	3.88	3.00	173	.47	7	1	1	72	2	.8	.7	1.6	no roots	370
0-10 cm, close to an esh stem	6.82	5.49	353	.57	84	0	.5	.8	22	.9	1.9	16	1.8	616
0-10 cm, adhering to roots of a vital Asarum plant	7.2	6.05	410	.66	95	0	0	0	47	.2	1.3	212	15	619
0-10 cm, adhering to roots of a less vital Asarum	7.10	4.40	210	.48	81	0	1.5	10	20	1.8	2.1	7.3	2.6	438
0-10 cm, adhering to roots of a vital Mercuria-lis perennis	7.70	6.07	454	.72	95	0	0	0	57	.1	1.5	320	13	634
0-10 cm, adhering to roots of a Mercurialis less vital	7.48	4.49	314	73	92	0	1	.3	22	1.4	1.6	11	9.4	427

buffer range at least for short time periods. As long as small limestone particles are well distributed within the A-horizon, the system may swing back to the carbonate buffer range, but the polymeric Al formed during the acidification push remains. Thus the soil has a memory for previous acidification pushes which have not been buffered in the carbonate buffer range.
From these data it must be concluded that even forest ecosystems developed on limestone are threatened by acid deposition through soil acidification. Only the homogeneous incorporation of lime ($CaCO_3$) into the fine earth of the whole rooting zone would be a countermeasure. This countermeasure can only be used for agricultural crops with short rotation periods on arable land, but not for deep rooting forests with rotation periods exceeding 100 years.

SILICATE BUFFER RANGE

pH(H_2O) values in soils approaching 6 indicate that $CaCO_3$ does not play any role in buffering, and is absent at least from the fine earth fraction of these soils. As long as carbonic acid is the only acid being produced in the soil, mass action considerations show that pH(H_2O) will stay at values > 5 (cf.6). In this range the only buffer acting in soils is through the weathering of silicates. The process involved may be described as the release of alcali and earth alcali cations from the silicate lattice under proton consumption. Equation 5 may serve as an example of the principle involved, describing the weathering of Ca feldspar to kaolinite (for other examples see 20).

$$CaAl_2Si_2O_8 + 2\ H_2CO_3 + H_2O \rightarrow Ca^{2+} + 2\ HCO_3^- + Al_2Si_2O_5(OH)_4$$

In reality this reaction is not a straightforward process, but passes through many stages. The cations liberated during silicate weathering can be bound as exchangeable cations in the clay minerals formed from the weathered silicate lattices. The protons consumed during this process are converted to undissociated silicic acid which is finally transformed to SiO_2 and H_2O. Any leaching loss of silicic acid below pH 7 is therefore not accompanied by cations. For ecosystems in the quasi-steady state there is by definition almost no nitrate loss by leaching in these soils, because the rate of nitrification does in the temporal mean not exceed the rate of nitrate uptake (closed nitrogen cycle). There is some movement of NaCl through the system, which has its origin in the sea spray being deposited from air. The only soluble anion being formed in the soil is HCO_3^-; its concentration in the soil solution reaches a minimum as pH approaches 5.0. Under these conditions the ecosystem exhibits minimal leaching losses from the soil, irrespective of the amount of precipitation: chemically the soil is tight due to the low solubility of carbonic acid. It is often said that rate of natural soil leaching and acidification increases with increasing precipitation. The fact that forest soils in medium altitudes are acidified cannot however be explained this way.

The buffer capacity as well as the buffer rate depend upon the silicate content and the kind of silicate present. The content of base cations in silicates varies between 3 (muscovite) and 20 (olivine) meq/g silicate. For sedimentary rocks a mean value of 5 may be used. This gives a buffer capacity of 75 kmol H^+ per 1 % silicate in a soil layer of 10 cm thickness, bulk density 1.5 and an area of 1 ha. The buffer rate due to base cation release with proton transfer to silicic acid may vary between 0.2 and 2 kmol $ha^{-1}yr^{-1}$ in the rooted soil layer of 1 m depth (5,8,20). For soils on sedimentary rocks values below 1 can be assumed (5, MAZZARINO, this volume). Data based on cation output from watersheds (8,20) may overestimate the actual rate of silicate weathering in the rooted soil zone due to three reasons. Usually the cation input from air is underestimated (neglection of interception deposition or of total deposition). A further assumption inherent in this concept is the constancy of exchangeable base cation storage in the soil. Soils subjected to acid deposition and/or internal proton production may loose exchangeable base cations to the seepage water and accumulate cation acids. These base cations do'nt originate from actual silicate weathering and lead thus to its overestimation. In addition, a spatial discoupling within the unsaturated zone has to be taken into account. From the viewpoint of the forest ecosystem one is interested to judge the processes in the root and decomposer environment. Acids can be leached from the top soil and neutralized by silicate weathering during their passage through the subsoil and underlying (soft) rock. In such a case the watershed balance method may indicate silicate weathering rates of 2 keq ha^{-1} yr^{-1}, whereas the silicate weathering rate in the rooted soil zone may be much less, and the soil acidifies at the same time.
The rate of protonization of silicates should increase with increasing proton activity (decreasing pH). Since the weathering of silicates is not a simple dissolution process but includes reactions on internal mineral surfaces, the rate limiting step may be the counterdiffusion of the ions involved. This can result in only limited increasing rates of protonization with decreasing pH. The variability due to pH lies probably within a factor of two, but does'nt exceed substantially 2 keq ha^{-1} yr^{-1}.

The possible buffer rate of 0.2 to 2 keq H^+ ha^{-1} m^{-1} yr^{-1} can be directly compared with the acid load. In Central Europe, the acid deposition may vary between 0.8 keq (in sheltered positions) and more than 6 keq (in positions exposed to high interception deposition, especially by capture of fog and cloud droplets). The internal proton production may vary between zero and 4 keq ha^{-1} yr^{-1}. The total acid load may thus vary between 0.8 and more than 10 keq. This comparison shows that, with the possible exception of sheltered positions, almost all forest soils will acidify under the present load, that is pass over into the buffer ranges where cation acids are produced.

If the rate of proton load exceeds the rate of silicate protonization, the chemical soil state passes over into the cation exchange buffer range. This is reversible, as soon as the rate of proton load becomes less than the rate of silicate weathering. From this it follows that the ratio of both rates determines the chemical soil state.

As with calcareous soils, soils in the silicate buffer range and not subjected to acid deposition exhibit no gradients in their chemical properties with depth. Chemical composition of the soil is characterized by the absence of polymeric hydroxo Al in the interlayers of the clay minerals, and by the absence of exchangeable Al ions. Their presence indicates that the chemical soil state has temporarily been in the cation exchange buffer range, i.e. that the soil has passed through one or more periods of higher proton load.

As in calcareous soils, soil-borne toxins are missing. In virgin forest ecosystems producing easily decomposable phytomass at a high rate, earthworms or other soil burrowing animals work over the whole rooting zone of 1-2 m depth, resulting in a crumb-like structure and a organic matter content of low C/N ratio in the rooting zone. The amount of organic matter accumulated in the soil depends upon climatic conditions (temperature and humidity). The humusform is mull which may in cool climates carry an organic top layer comparable to moder. This organic top layer may show lower pH values: the biological gradient creates a chemical gradient.

Soils remaining continuously in the silicate buffer range guarantee a high nutrient storage of cations as well as N, S and P in the deep rooting zone and a high turnover of nutrients in the soil. They thus guarantee a well balanced and always sufficient nutrient supply to plants, provided that the parent material shows no extreme mineralogical composition.

CATION EXCHANGE BUFFER RANGE

The exchangeable base cations, mainly Ca^{2+}, play a deciding role in buffering acidification pushes which are caused by the temporal discoupling of the ion cycle (ULRICH ,this volume). If a net production of a strong acid (HNO_3) occurs in the soil, the pH is buffered by proton exchange with Ca^{2+} at exchange sites in a reversible and rapid reaction:

$$\left.\begin{array}{l}\text{clay mineral}\\ \text{soil organic matter}\end{array}\right] \begin{array}{l}-\\-\end{array}\!\!\text{Ca}+2\text{H}^+ \rightleftharpoons \left.\begin{array}{l}\text{clay mineral}\\ \text{soil organic matter}\end{array}\right] \begin{array}{l}-\text{H}\\-\text{H}\end{array} + \text{Ca}^{2+}$$

If the pH drops below around 5, the solubility of the oxides of Mn and many heavy metals reaches a level where concentrations of the metal ions in the soil solution become of ecological significance (toxicity). All these metal ions including Al are cation acids, they can exist in different ion species. The kind of the ion species plays a deciding role in its physiological effect.

The release of Al ions is bound to the lasting presence of exchangeable protons at the clay mineral surface. If within days or weeks a net consumption of protons occurs within the ion cycle, the reaction can go from left to right and the soil returns into its initial state. As long as the percentage of exchangeable Ca is above 5 to 10 % of the CEC, an acid load in soil will mainly be buffered by this reaction. As long as this is true, there will be no lasting physiological strain to microorganisms and plant roots by an acid load.

If, however, protons stay long enough (weeks or months) on the surface of clay minerals, it is known that they are consumed with the release of Al ions (9). In the pH range between 5.0 and 4.2 most of these Al ions form polymeric hydroxo cations with a charge of around +0.5 per Al atom. These polymeric hydroxo Al cations accumulate in the interlayers of the swelling clay minerals. Their exchangeability is very limited, even at higher pH values. In soil horizons swinging back and forth between silicate and exchange buffer ranges, the Al hydroxo polymers remain more or less unchanged during the period with low proton load. They are like a memory, indicating that the soil has passed through periods of high proton load. The more the exchange sites are occupied by Al, the less are available for K, Mg and Ca. This is a consequence of their leaching. The anion accompaning the leached cations is no longer HCO_3^-. It may be nitrate (indicating humus disintegration and discoupling of the nitrogen cycle), or organic anions (indicating podzolization), or sulfate (indicating acid precipitation).

The buffer capacity is equal to the cation exchange capacity (CEC), in respect to clay a mean value may be 7 kmol H^+ per % clay. In addition, the CEC of soil organic matter has to be taken into account. The buffer rate is large enough to prevent soils from swinging into the aluminium buffer range (pH < 4.2) as long as the exchangeable Ca saturation is not too low (> 10 %).

As already stated, the acid load of forest soils in Central Europe may in many cases be around 7 keq acid ha^{-1} yr^{-1}. In these cases, the annual loss of exchangeable Ca may approach the CEC due to 1 % clay in a soil layer of 10 cm depth. Within 50 years, the exchangeable Ca may be completely leached from a soil containing 10 % clay to a depth of 50 cm. This indicates

that a considerable soil acidification must have occured due to acid deposition during the last century and especially since 1950 in Central Europe. This is in agreement with observed pH decreases in forest soils (1,2,3,4).
With Al appearing at the clay surface in ionic form, Al toxicity comes into play, thereby limiting the growth and regeneration of most intolerant (calcicole) species. In addition bacteria suffer from Al toxicity. These conditions and the reduced activity of earthworms initiate the accumulation of litter on the forest floor. Absence of faunal activities can easily be recognised by examining the soil structure which is no more crumb-like but polyedric or coherent. The accumulation of an organic top layer is usually connected with a substantial proton production in the mineral soil (ULRICH, this volume).

Many acid forest soils stay in this buffer range. Usually the soil exhibits chemical gradients with depth. In the case of humus disintegration (ULRICH, this volume) the lower horizons may be more acid than the upper ones. Much more common is the reverse: soil acidity is decreasing with increasing depth, and the lowest horizon may still be in the silicate buffer range. Such pH gradients in the soil profile indicate missing bioturbation. They indicate further that the soil processes operate relatively far from chemical equilibrium and that the ecosystem may be in a transition state. As a consequence of the leaching of cations and the opening of the nitrogen cycle, growth is often limited by deficiency of nutrients, mostly N, sometimes Mg, K or P in addition. Phosphates exist in binding to Fe and Al with a lower solubility compared to silicate buffer range. As long as the percentage of exchangeable Ca is not too low (exceeding 10 to 15 %), fertilizer salts can be applied to the soils without doing harm to the plants or decomposers.

ALUMINIUM BUFFER RANGE

At pH 4.2, Al^{3+} is reaching a concentration in the soil solution which makes it the most important factor in determining plant growth. Tolerance of Al toxicity becomes the deciding factor in plant competition, which in turn determines the composition of the vegetation and the rate of phytomass production. The chemical status of soils is characterized by the dominance of Al ions among the exchangeable cations. The sum of exchangeable H, Mn, Al and Fe, which represents potential acidity, will exceed 90 % of the effective cation exchange capacity of the soil. Exchangeable Ca and Mg are reduced to values below 5 to 10 %. Bacterial and soil animal activity as well as growth of roots can be restricted by Al toxicity in the mineral soil.

The Al stems from the weathering products of the primary silicates, mainly from clay minerals. The release of Al may be described by the following equation

$$AlOOH + 3\ H^+ \longrightarrow Al^{3+} + 2\ H_2O$$

For calculation of the buffer capacity one can start with the fact that the total clay content of the soil is available for buffering, the buffer capacity will be exhausted only after total clay destruction. Assuming a mean composition of clay minerals, the buffer capacity amounts to 100 to 150 kmol H^+ per % clay. The process goes not directly according to the equation given, in between new solid phases of Al compounds are formed with a positive charge between zero and 3. Examples are the polymeric Al hydroxo cations and Al hydroxo sulfates (PRENZEL, this volume). The buffer rate depends upon the dissolution rate of the solid phases, being high (several kmol H^+ per ha and year) for most of the intermediates, and being low for Al bound in silicate lattices (some tenth of kmol H^+). As a consequence, a soil horizon stays at the aluminium buffer range as long as Al hydroxo compounds of high dissolution rate are available. If they are used up, the buffer rate drops down and the horizon may switch over to the iron buffer range if the proton load is high enough. Bleached horizons have therefore lost most of their interlayer aluminium and do also not contain Al hydroxo sulfates (10).

Al toxicity is a well known phenomon since long (11,12,13) and was demonstrated for pine seedlings (14) and beech seedlings (15). For being toxic, cation acids like Al must come in contact with cell membranes of roots or mycorrhiza. This depends upon:

- the nature of the ion species present in solution. The monomeric trivalent species Al^{3+} possesses the highest potential toxicity, polymeric Al species and organic chelated Al the lowest one. At pH $>$ 4.2, the ratio of monomeric to polymeric Al species is shifted in favour of the polymeric species; at pH $<$ 4.2 in favour of monomeric species (16).
- the ability of the root or mycorrhiza to change the ionic species of Al in the free space before reaching cell membranes. This can be achieved by change in pH (see above), or by transforming Al^{3+} into phosphat, silicate or organic complexes. The formation of Al phosphate complexes may lead to phosphorus deficiency.

There are therefore soil conditions (pH value and presence of organic ligands in the soil solution) as well as plant conditions (buffering and complexing of cation acids in the free space of the root) deciding upon the toxicity of Al. The role of formation of organic complexes in the soil solution is demonstrated by the data in table 2. The data are taken from a lysimeter study performed in a mixed coniferous stand dominated by spruce on the Swedish westcoast (NILSSON, personal communication).

Table 2: Ca/Al-ratio in soil solution at Gårdsjön (NILSSON, personal communication)

Soil depth	Ca/Al	Ca + Mg	Organic aluminium complexes as a percentage of total aluminium 1)
0 - 5 cm	8.6	16.5	94
0 - 15 cm	0.7	1.5	90
0 - 35 cm	0.3	0.9	36
0 - 55 cm	0.4	1.2	14

1) determination according to DRISCOLL (17)

The data (average values for 12 months) show that in the top soil 90 % or more of the observed Al is tied to organic compounds. Even in the mineral soil a substantial part of the Al can occur in organic complexes. Since soil acidification is a natural process, species growing on acid soils (e.g. Picea abies, Pinus silvestris, Fagus silvatica) have developed tolerance mechanisms against toxic cation acids during evolution.
The formation of a mycorrhiza could be one important protection mechanism for the roots. It has been shown that mycorrhizal fungi produce substantial amounts of oxalic acid which could (by complexation) to a large extent detoxify any inorganic species present. If the mycorrhiza formation is hampered, root damages caused by aluminium might become more important. One of the factors that is of importance for the mycorrhiza is the supply of carbohydrates from the roots which in turn are translocated from the leaves. If direct leaf or needle damage (caused by any outside physical or chemical factor) results in a decrease of photosynthesis, this may in turn result in a lower production of carbohydrates and a decreased carbohydrate transport to the roots. Thereby the nutrient supply to the mycorrhizal fungi may be decreased and their development hampered. This in turn results in a lower production of oxalic acid and an increased possibility for inorganic aluminium forms to penetrate the roots and cause damage.
There are no reasons to assume that mycorrhiza fungi are not themselves subjected to Al toxicity, even if they have developed more efficient avoidance mechanisms as the roots they are protecting. It seems that the mycorrhiza does'nt prevent the entrance of cation acids into the free space of roots (which would be a bad strategy since some cation acids are needed as micronutrients). This is indicated by the data in table 3. In this table the Ca/Al ratios in the equilibrium soil solution as well as in the fine roots of trees are given for soils of different exchangeable Ca percentage, varying between > 50 % and < 5 %. Values are also given for roots developing only in the organic top layer of moder and raw humus (last line). With increasing acidity (decreasing Ca saturation) the Ca content of

Table 3: Content of Ca and Al in fine roots in soils of different Ca saturation x_{Ca}^{S}

n	x_{Ca}^{S}	$\frac{\text{mol Ca}}{\text{mol Al}}$ in ESS	ash %	fine roots SiO_2 %	Ca mg/g dm	Al mg/g dm	$\frac{\text{mol Ca}}{\text{mol Al}}$
19	> 0,5	75 ±49	6,71 ±2,75	3,00 ±2,46	8,80 ±2,41	3,06 ±1,56	2,30 ±1,47
9	0,5 to 0,1	15 ±14	7,25 ±2,25	4,24 ±2,38	5,24 ±2,95	2,25 ±0,56	1,56 ±0,89
18	0,1 to 0,05	3,5 ±6,2	8,16 ±3,54	5,25 ±3,53	2,07 ±1,40	4,06 ±1,83	0,41 ±0,32
46	< 0,05	0,96 ±0,52	8,83 ±4,90	5,79 ±3,98	1,60 ±0,81	4,82 ±2,15	0,28 ±0,19
11	OH-horizons	-	3,46 ±0,45	1,04 ±0,54	5,77 ±3,99	2,12 ±0,62	1,75 ±0,97

the roots is lowered (in the mean to 1/6), whereas the Al content increases only little. The effect is best seen at the Ca/Al mol ratio in the root, which changes from 2.3 at Ca saturation >50 % to 0.3 at Ca saturation < 5 %.
BAUCH (this volume) shows that in diseased trees Ca and Mg is lost from the cell wall of root cortex cells of fir, whereas both elements are present in the roots of healthy trees. From a physico-chemical point of view, a low Ca content in the cell wall indicates a pH in the water phase being 1 to 2 units below the pK_{diss} value of the acidic group. Therefore the low Ca content indicates the acidification of the free space. The data of table 3 show that this acidification process goes parallel with soil acidification, reaching critical values at Ca saturation degrees below 10 and especially below 5 % of the effective CEC. It is not known how this acidification causes cell injury, whether by inducing Ca and Mg loss from membranes and cells, or by allowing cation acids to come in contact with membranes and entering cells. Since it seems common that roots have now accumulated a wide variety of heavy metals (18), cell injury may be due to heavy metals more easily soluble than Al polymers.

In the organic top layer with its low primary Al content and high Al complexing capacity the Ca/Al ratio lies in the mean on the safe side. Field data show, however, that the OH horizons are accumulating Al and Fe as part of the podzolization process; both ions seem to be transported in organic compounds from the Ae to the OH. Thus the equivalent ratio of Ca to Ca+Al+Fe shows a decreasing tendency with continuing acid deposition. Field observations indicate that at Ca/(Ca+Al+Fe) ratios below 0.05

always show up in a pH decrease. If, however, the acid accumulates as a solid like $AlOHSO_4$, its accumulation may not be connected with a change in pH. In Central Europe, this approach failed to falsify the above mentioned hypothesis (1,2,3,4).

With both approaches, the depth gradient of soil chemical state has to be taken into account. If the top horizons are already staying in the Al or Fe buffer range, an increase in soil acidification may only show up in changes of the chemical state of deeper soil horizons (loss of bases, accumulation of cation acids, decrease in pH). In these cases, measurements limited to the top soil horizons are meaningless.
From the point of view of rates, the rates of deposition and of buffering of acids can be compared. This is the only approach which does'nt need baseline values from the past. The most simple approach is to compare both rates directly, assuming that acid deposition enters the soil at its surface. Calculations of this kind assume that chemical equilibrium is achieved between the acids transported downward with the soil solution and the soil matrix. In this case, an acid input by addition to the soil surface results in the development of strong depth gradients of the chemical soil state: the upper soil layer acidifies before the acid breaks through to the lower layer. Soils then behave like chromatographic columns. Depending upon the rate of water movement, the breakthrough of the acid at the bottom (pH decrease) can be retarded till the buffer capacity of the total soil column (soil depth) is exhausted, or till the rate of acid buffering becomes less than the rate of acid input. Depending upon acid load and acid buffering, the release of acid into drainage waters (in case of column experiments: the breakthrough of acid at the soil bottom) may occur only after years or even decades of continuous acid input. That the leachate of a soil is not acid does therefore not exclude ongoing soil acidification.
The higher the rate of water input (e.g. heavy rain, snow melt), and the coarser the soil texture (e.g. sandy soils with high gravel or stone content), the less favourable are the conditions to reach chemical equilibrium between the solutes and the soil matrix. In such cases substantial fractions of the soil solution may be rapidly transported through macropores and leached from the rooted soil layer already after days. In such cases acidity may be leached with drainage waters already at exchangeable Ca percentages exceeding 5 to 10 %. But in principle, there exists no exception from the physico-chemical rule that a cation exchanger, saturated with base cations, will loose base cations and accumulate acids if an acid solution percolates through. Therefore it need not to be proofed, it is proofed that the store of exchangeable base cations in a soil is diminished by an acid input. If the deposition rate of acids is known, the open problem is only at which place (soil horizon, layer) in the

between pH measured in soil/water suspension and in $CaCl_2$ or KCl suspension: on addition of soluble salts to acid soils the pH drops considerably. In most cases this is due to the exchange of Al ions by Ca and K ions; the Al ions hydrolyze in the solution to produce protons. The application of water soluble fertilizers increases Al toxicity under these circumstances, and may thus have a detrimental effect on the vegetation. Detrimental effects of fertilization have been found in fertilizer trials, but they usually have not been traced back to this cause.

IRON BUFFER RANGE

At pH values below 3.2, in horizons influenced by infiltrating organic matter already below 3.8, the solubility of iron oxides becomes high enough to reach Fe concentrations in the soil solution of ecological significance. The transport of iron leads to visible (colour) symptoms in the soil profile, which is not the case for aluminium. Due to an increase in the number of toxic elements and their concentrations in the soil solution, the effects of toxicity and nutrient deficiency become stronger at such low pH values. They are usually bound to a considerable proton production within the soil. Such phases are of only limited duration, whereas the visible symptoms, e.g. the bleached eluvial horizon, remain the same. The existence of a eluvial horizon does therefore not tell whether podzolization, the process characteristic for the iron buffer range, does actually take place.

The actual podzolization which is now widespread in beech and older spruce forests in Central Europe can only be explained as triggered by acid deposition (ULRICH, this volume).

RECOGNITION OF SOIL ACIDIFICATION BY ACID DEPOSITION

The fact that acid deposition occurs calls for the hypothesis that thereby soil acidity is increased. This hypothesis has to be falsified. There are three approaches which can be used for this purpose.

From the capacity point of view, an increase in acidity can be measured as the difference in inventories of the sum of soluble and exchangeable bases and acids in soil. Acidification is indicated by a decrease in the sum of bases and/or by an increase in the sum of acids with time. The use of this approach is very limited since there exist no data on base and acid storage of soils in the past.

From the intensity point of view, an increase in acidity may show up as a decrease in pH with time. Since pH is related to base and acid capacities only indirectly, this approach is much more limited. If pH(salt) is taken, a loss of bases should always show up in a pH decrease. If, however, the acid accumulates as a solid like $AlOHSO_4$, its accumulation may not be connected with a change in pH. In Central Europe, this approach failed to falsify the above mentioned hypothesis (1,2,3,4).

With both approaches, the depth gradient of soil chemical state has to be taken into account. If the top horizons are already staying in the Al or Fe buffer range, an increase in soil acidification may only show up in changes of the chemical state of deeper soil horizons (loss of bases, accumulation of cation acids, decrease in pH). In these cases, measurements limited to the top soil horizons are meaningless.
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unsaturated zone (soil and seepage conductor) the loss of bases and the accumulation of acids occurs. This can be estimated if the chemical state of the horizons and layers is known (including buffering rates and buffering capacities), and if the water flow characteristic in the soil is known. The objective of further soil chemical investigations in this field should be directed towards the development of a mathematical model describing solute transport and buffer reactions.

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