concentration increases strongly[12]. Normally, measurements of the aluminum concentration in the soil solution show values well below the maximum values as calculated from the solubility product of aluminum hydroxide. This shows that the soil solution is not saturated with respect to aluminum hydroxide.

The aluminum content of the soil solution depends on the aluminum saturation percentage of the cation exchange complex and the total salt concentration of the soil solution. The latter is to a large extent influenced by the amounts of anions originating from pollutants. The aluminum saturation percentage of the cation exchange complex is small at pH values above 5 but increases strongly as the pH declines below 5. The aluminum content of the soil solution, therefore, also increases strongly with declining soil pH. Hence, the more acid the soil is, the more severe are the problems caused by aluminum ions in the soil solution. The actual aluminum content in the soil solution is not likely to depend to any large extent on the absolute amount of adsorbed aluminum in the soil, since the aluminum ions removed from the adsorption complex will be rapidly replaced by mineral-bound aluminum. The only exception to this are the soils mentioned above which are low in minerals containing aluminum.

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Anthropogenic and natural acidification in terrestrial ecosystems

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Key words. Soil acidification; acid deposition; terrestrial ecosystems; H^+ budget; silicate weathering.

Acids and bases in terrestrial ecosystems

Before discussing acidification, the nature of acids and bases has to be defined. The most appropriate approach is that of Brønsted. According to Brønsted, an acid is a substance that can donate a proton, and a base is a substance that can accept a proton. In ecosystems, the acids and bases can exist as dissolved components in solution or as solid components, and they can be separated in different compartments (e.g. in soil or in plant).

The acid/base reactions can thus be grouped according to the following partial systems being involved: biota/atmosphere, biota/solution, solution, solution/atmosphere, solids/solution. They comprise formation of plant substances, including uptake of ions, decomposition of organic matter including release of ions, dissociation reactions, complexation of metal ions, redox reactions, weathering of soil minerals, formation of solid phases (e.g. hydroxides of Mn, Al, and Fe, 'reverse weathering'). A detailed overview has been presented by van Breemen et al.[3].

Magmatic rocks contain the silicate minerals as bases and only SiO_2 as acid anhydride. Due to the insolubility of the weak silicic acid, the weathering products of rocks, the soils, cannot acidify by themselves. Acidification depends therefore upon the interaction of the biota with the atmospheric constituents CO_2 and N_2. An exception is rock containing sulfides which can be oxidized to sulfuric acid, but sulfides are not common minerals. Sedimentary rocks may contain in addition carbonates as bases. The transformation of primary silicate minerals to secondary silicates is kinetically controlled and occurs relatively independently of the chemical conditions. Acid soils can therefore still contain large amounts of undissolved bases (silicate minerals). Within the pH range of soils (pH 2–9), cations forming soluble hydroxides react usually as bases (Na, K, Mg, Ca), whereas cations forming insoluble hydroxides may react as acids (Mn, Al, Fe ions). To express this briefly, the former are called cation bases, the latter cation acids.

The neutral point of terrestrial ecosystems

Pure water is neutral at pH 7. Due to the very low solubility of the silicate minerals, the solution phase of the system (the soil solution) is therefore under humid conditions primarily governed by the main acid, and this is carbonic acid. The neutral point of ecosystems is therefore close to the pH value in the system H_2O/CO_2 at the CO_2 pressure of the atmosphere (pH 5.6 on the soil solution). Systems with higher pH contain soluble bases (mainly bicarbonates and carbonates), systems with lower pH soluble acids. In the soil, the CO_2 partial pressure usually exceeds that of the atmosphere, resulting in pH values approaching 5.0.

Weak and strong acids

The sources of weak acids are CO_2 in the atmosphere and SiO_2 in silicate minerals. For both acid anhydrides their solubility is decreasing with decreasing pH. At pH values below 5, CO_2 is practically completely expelled to the atmosphere, and SiO_2 slowly precipitated as an almost insoluble solid. This implies that the acids with the highest turnover rates in the ecosystem cannot be responsible for an acidification leading to pH values well below 5.

Strong acids can be produced in all partial systems where one component is the biota. The strong acids with the highest turnover rates are organic acids and nitric acid. HNO_3 is the final product in the decomposition of organic nitrogen compounds. Other strong acids with much lower turnover rates between biota and soil solution are H_2SO_4 and H_3PO_4. By reacting with soil components, these strong acids can produce cation acids like Mn, Al and Fe ions.

A cation acid with highly variable acid strength is NH_4^+. This ion is formed in the nitrogen turnover as an intermediate product, and may, under acid conditions, be the final product. If NH_4^+ is taken up by plants, a proton is produced and transfered to the anions present in the soil solution, e.g. Cl^-, or SO_4^{2-}, or organic anions. The corresponding acid is produced.

The minimum pH which can be reached in the soil solution is given by the concentration of strong mineral acids (HNO_3, H_2SO_4, HCl, carbonic acids). Their concentration may exceed 1 mmole equivalents per liter, allowing a pH value somewhat below 3.

Ecosystem internal cycling of dissolved acids and bases

By defining the ecosystem in a proper way, all processes included in ion turnover can be reduced to four fluxes: input (e.g. from atmosphere, or by weathering of soil minerals), output (e.g. leaching, denitrification), uptake from soil solution into biomass (by plants and microorganisms), and release of ions during decomposition (mineralization). We consider an ecosystem in which input and output are equal for each element. For such an ecosystem, a quasi-steady state can be achieved: in the temporal and spatial mean all stores in the system are constant. This covers phytomass, total biomass, soil organic matter, the various chemical elements and their various binding forms. In such an ecosystem the rate of assimilation must be equal to the rate of respiration, or, if one includes also the turnover of elements other than C, H and O, the rate of phytomass production must be equal to the rate of mineralization[17]:

→photosynthesis with NO_3^- assimilation
←aerobic mineralization (decomposer respiration) with nitrification:

$$\begin{aligned}&\mathrm{a\,CO_2 + b\,NO_3^- + c\,HPO_4^{2-} + d\,SO_4^{2-} + \ldots +}\\&\mathrm{+\,g\,Ca^{2+} + h\,Mg^{2+} + i\,K^+ + f\,Na^+ + x\,H_2O\,+}\\&\mathrm{+\,(b + 2c + 2d - 2g - 2h - i - f)\,H^+}\\&\rightleftarrows \{\mathrm{2\,C_aN_bP_cS_d\ldots Ca_gMg_hK_iNa_fH_2O_x}\}\ \mathrm{biomass}\,+\\&\mathrm{+\,(a + 2b)\,O_2}\end{aligned} \quad ,$$

The cations and anions as well as the protons are taken up from the soil solution and return during mineralization into the soil solution.

With the exception of N_2 assimilation and of denitrification, the input and output of all nutrients occurs in ionic form. The precursor of assimilated N is uncharged N_2, the reaction products of denitrification are also uncharged compounds (N_2, N_2O).

As demonstrated by the above equation, the ion cycle within the ecosystem can be reduced to two processes: ion uptake and ion mineralization. The disappearance of cations from the soil solution by ion uptake or the release of anions into the soil solution by mineralization is connected with an equivalent proton production. On the other hand, the disappearance of anions from the soil solution or the release of cations into it is connected with an equivalent proton consumption. In most ecosystems, the final product of nitrogen mineralization is HNO_3. In such systems, the anion release in mineralization exceeds the cation release leading to a net proton production. In quasi-steady state, however, there is an equivalent anion excess in ion uptake, resulting in a net proton consumption. Despite a high proton turnover, there would therefore be no net production of strong acids. There can be a spatial de-coupling of both processes, leading to acidification in some compartments and alkalinization in others. This can be overcome by the activity of soil burrowing animals (bioturbation) and changing spatial pattern in the formation of new rootlets.

The net proton production (or proton consumption) within a compartment of an ecosystem (e.g. vegetation biomass or soil) can be calculated as the difference between the input and output of cations (uncharged molecules: hydroxides) and anions (uncharged molecules: acids). This principle is demonstrated in the above mentioned equation describing photosynthesis and mineralization. The net proton production cannot be estimated by looking at the gross amount of proton production of single processes. The neglect of the balance principle in arriving at net rates has caused some confusion in the past.

Characterization of the acid/base status of soils

The acid/base status of soils can be characterized by intensity and capacity parameters. Intensity parameters describe the acid/base status of the soil solution; examples are the pH value, the lime potential (pH-0.5 p Ca), and the Ca^{2+}/Al^{3+} ratio. The capacity parameters are represented by the amount of acids and bases in a distinct soil volume or soil mass. In order to judge actual and potential soil acidification and alkalinization, it is necessary to determine the titratable and the non-titratable basicity and acidity. The non-titratable basicity is located mainly in the silicate minerals and represents the potential of a soil to neutralize titratable acidity if no further acid load occurs. Due to the kinetically limited rate of reaction, the time span involved in such neutralization reactions may be centuries to milleniums. The non-titratable acidity is given by the organic bound carbon, nitrogen, sulfur and phosphorus. It represents the potential of a soil for producing weak and strong acids if the soil organic matter is decomposed.

The non-titratable acidity and basicity due to redox reactions plays a role only in soils which are periodically water saturated, leading to oxygen deficiency and reduction processes. In soils free of carbonates, the titratable basicity is governed by the exchangeable cation bases (alkali and alkali earth cations). The titratable acidity is governed by the exchangeable protons and cation acids (ion species of Mn, Al and Fe). The composition of the exchangeable cations is therefore the most informative way to characterize the actual acid/base status of a soil. It also gives information about the acid strength which increases in the sequence

$$Al(OH)_{2.5}^{0.5+} < Mn^{2+} < Al^{3+} < Fe^{3+}.$$

pH values allow the identification of the buffer system which is actually operating[21], but give no direct evidence about the capacity of the buffers involved.

If a soil acidifies, the increase in titratable acidity is the proper measure. At the inflection point of the buffer curve, a relatively large change in basicity consumed and acidity accumulated leads only to a small decrease in the pH of the soil solution. Temporal changes in soil pH may therefore be very insensitive parameters for judging soil acidification. This is the more the case the lower the pH values are at the beginning.

Assessment of net internal strong acid production

There is general agreement that the mean pH value of pre-industrial rain is around 5[5]. This means that acidification of soils to pH value below 5 under pre-industrial conditions cannot be caused by rain. Carbonic acid, which is produced within the ecosystem in large amounts, need not be considered either, since it is expelled at pH values below 5.

As stated above the titratable acidity is represented mainly by the exchangeable cation acids which have replaced the exchangeable cation bases at their binding sites. Soil acidification is thus characterized by the loss of cation bases from soil and an equivalent accumulation of cation acids or reduction in cation exchange capacity. The cation bases can be either accumulated in the biomass (with a limited capacity for accumulation), or leached with the seepage water. The capacity for leaching is limited by the presence of anions. Since organic anions are leached from mineral soils only under special conditions, inorganic anions are needed. At pH values below 5, the only anion which can be created continuously in the ecosystem in large amounts is nitrate: the N_2 in the atmosphere can be transferred to proteins by microorganisms, and during decomposition of this protein HNO_3 can be formed. The anion needed for leaching of cation bases appears in the soil solution as proton acid and is thus driving the acidification.

The internal net strong acid production can thus be assessed by measuring or estimating:

1) The increase of exchangeable acids (H, Mn, Al, Fe ions) in soil within a given time span.

2) The loss of cation bases balanced by organic anions or by nitrate within a given time span. In order to exclude the contribution of weak acids, the pH in soil solution should be below 5 throughout the whole time span.

The first approach cannot be used because there exist almost no data about stores of exchangeable acids in soils from earlier investigations. Thus only the total strong acid production can be estimated, assuming the store of exchangeable acids at the beginning to be zero (Ulrich et al.[20], pp. 206–215). Since the duration of soil development under the regime of strong acids (pH below 5) is usually not known, it is hardly possible to calculate reliable rates of strong acid production.

The second approach is more easily applicable. As already mentioned, leaching of organic anions from a forested soil is restricted to special ecosystems (rain forests on very poor sandy soils). There may be leaching of organic anions through the top mineral soil horizons and accumulation of the organic matter in a lower soil horizon. This is part of the compartment formation taking place within forest ecosystems; the cation bases are accumulated in the forest biomass and in the forest floor, leading to an equivalent accumulation of cation acids in the top mineral soil horizons. The rate of this process can therefore be estimated by the rate of cation base accumulation in biomass and in the organic matter forming the forest floor. These data are easily accessible, at least for constructing model ecosystems. An example is given in table 1. The cation excess gives the cations bound to organic anions. They have been accumulated in the biomass releasing an equivalent amount of protons to the soil. The data show that the accumulation of biomass in the growing stand produces 0.67 kmoles H$^+$ per ha and year. If the litter is accumulating on the forest floor, the total annual proton production in the mineral soil can amount to 1.85 kmoles H$^+$ per ha. If the bole is exported from the ecosystem, the annual proton production will not be balanced in a later stage of ecosystem development.

The next problem is to estimate the leaching loss of nitrate from soil. A method for collecting soil solutions for chemical analysis below the rooting zone of natural forests has been available since 1958; a method for calculating the rate of seepage water with enough accuracy since the beginning of the 1970s. The first sets of data on rates of nitrate leaching are just as old. Data from stream analysis in watersheds go back to the mid 1960s[9]. Again, there is only a short term record on a very limited number of ecosystems. The principle has been demonstrated in a deforestated watershed at the Hubbard Brook Experimental Forest in New Hampshire, where a herbicide was applied for 3 years to prevent vegetation regrowth in the deforestated area while decomposition processes continued. As a consequence of this complete decoupling of the internal ion cycle, nitrate was leached yielding a mean annual proton production of somewhat above 10 kmoles H$^+$/ha[2,4]. This is the order of magnitude of nitrogen turnover in forest ecosystems, the figure is thus in agreement with the theoretical expectation. Less drastic decouplings of the internal nitrogen cycle can be expected with any deforestation, especially if the second growth is suppressed. This may be the case as a result of forestry practices or a change in land use. Shifting agriculture therefore has a high potential for a soil acidification, especially if leguminous plants, capable of N$_2$ assimilation, are involved; they may restore the lost soil organic nitrogen, thus rebuilding the potential for the next acidification phase. Forests containing nitrogen fixing species also show nitrate leaching[8] and soil acidification[14] phases. A less significant de-coupling of the internal nitrogen cycle has been postulated[22] and demonstrated[10,11] as a consequence of climatic variation. Estimations have shown that in Central Europe the acidification potential of such decouplings increases with increasing altitude. In higher altitude it is large enough to strip a considerable fraction of the exchangeable cation bases during postglacial ecosystem development[23]. Kreutzer[8] states that in the first spruce generation following deciduous forests, the nitrate leaching from decomposing soil organic matter may continue throughout the life of the stand, that is for a century. As a consequence it can be stated that the utilization of the forest biomass (which includes wood, leaves and litter) by man, and the utilization of forests for grazing, which started 5000 years ago, has contributed to a considerable soil acidification in many areas of Central Europe. In higher altitudes the climate becomes of greater importance in triggering soil acidification. Modern forestry, which limits the export of biomass from the ecosystem to the bole, contributes 0.5–1 kmole ha^{-1} a^{-1} to soil acidification. In phases of the ecosystem development where litter is accumulating on the forest floor there will be an additional contribution to the acidification of the mineral soil of the same order of magnitude.

Table 1. Annual rates of ion uptake and cation excess in various tree compartments of a beech stand (*Fagus sylvatica*, 125 years old, Solling)

	Bole	Bole + branches	Bole + branches + leaves	Total overstorey + understorey
		(keq per ha and year)		
Sum inorganic cations	0.69	0.83	2.44	4.34
Sum inorganic anions	0.11	0.16	0.59	0.83
Cation excess*	0.58	0.67	1.85	3.51

*The cation excess may be determined directly by titrating the plant ash with a strong acid like HCl.

The role of silicate weathering in maintaining the chemical soil state

During the weathering of primary silicates two borderline cases are possible:

- The clay mineral formed possesses the same amount of negative charges as the weathered feldspar, pyroxene or mica. In this case all cation bases released during weathering are bound again as exchangeable cation bases.
- The negative charge of the silicic acid is balanced by protons. In this case the clay mineral formed (kaolinite) possesses a very low negative charge and an equivalent amount of cation bases is leached with the anion of the proton acid (e.g. as bicarbonate or nitrate).

In the first case the titratable basicity of the soil is increasing at the expense of the non-titratable basicity. In the second case the chemical state of the soil is maintained at the expense of the non-titratable basicity.

It is evident that the rate of cation base release during silicate weathering is the key parameter for an assessment of the long term acid load which a soil can withstand without undergoing changes in its chemical state. There are two approaches to estimating this rate: weathering budgets and input/output budgets of sealed catchments and soil columns. Both have their drawbacks. For medium textured soils, weathering budgets yield rates of cation losses between 0.4 and 2.0 keq ha^{-1} a^{-1}. From mineralogical studies one can calculate rates of cation release by silicate weathering of the order of 0.2–0.6 keq ha^{-1} a^{-1}. Input/output budgets of catchments give somewhat higher values of 0.2–2.3 keq; for all data see compilation in Fölster[6]. In this approach it is normally assumed that the store of exchangeable cation bases in the soil remains constant. This cannot be expected in watersheds subjected to acid deposition. The values therefore include the effect of exchange reactions in acidifying soils. One may conclude that the actual weathering rates do not exceed the range calculated from weathering budgets. The weathering rate seems to be not much influenced by pH. In experiments with artificially acidified rain, a distinct

Table 2. Deposition of acidity in Northwest Germany (values in kmoles ha^{-1} a^{-1})

Wet deposition	Rural areas, vicinity of cities 0.2–0.8		Large closed forest areas 0.6–1.1	
Dry deposition SO_2	Deciduous forests Neutral soil 0.6–1.3	Acid soil 0.3–1.0	Coniferous forests Acid soil 0.1–3.0	
	Deciduous forests Rural areas, vicinity of cities, sheltered areas	Exposed mountains	Coniferous forests Rural areas, vicinity of cities, sheltered areas	Exposed mountains
Total H^+ deposition	0.8–1.0	1.1–2.4	1.2–2.0	3.9–5.5
NH_4^+ deposition	0.4–1.0	0.9–1.3	0.8–1.0	1.0–1.6
Total deposition of acidity	1.2–2.6	2.0–3.5	2.0–2.7	2.9–6.4

step-up of weathering intensity was observed only when the pH of rain was lowered from 3 to 2[19].

With values below 1 keq ha^{-1} a^{-1} the proton consumption due to cation base release during silicate weathering is of the same order of magnitude as the proton production due to timber utilization in modern forestry. Any additional acid load therefore leads to soil acidification.

The acid load by acid deposition

Wet deposition is independent of the receiving surface. The dry deposition of gaseous SO_2 depends upon tree species (coniferous trees have a greater absorbing surface in winter), the roughness of the canopy, and the vitality of the tree (the extent to which the acidity formed after absorption of SO_2 can be buffered and the absorbing water film can act as an infinite sink for SO_2). The deposition of particles, where fog and cloud droplets are of great importance, depends upon the exposure and inclination of the site, the tree species, the tree height, and the compactness of the canopy (stand closure, leaf area index).

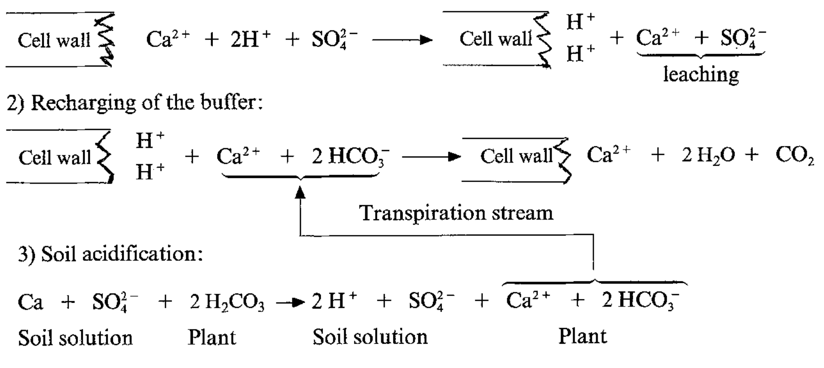
In table 2 data from 24 sites in Northwest Germany concerning the rate of deposition of acidity are compiled (Ulrich[26]). As shown elsewhere[12] the rates show a considerable variation from year to year. As far as it is known this variation has been taken into account. The wet deposition can be quite low in dry/warm years, especially in rural areas and in the vicinity of cities supplying neutralizing dust. In large closed forest areas the wet deposition amounts to around 0.8 kmoles H^+ $ha^{-1} a^{-1}$, a rate which already exceeds the rate of neutralization in most soils. The following data are calculated from the flux balance of the canopy. The acidity due to dry deposition of SO_2 can reach high values (up to 3 kmoles H^+ $ha^{-1} a^{-1}$).

The long term data available from the forest ecosystems investigated in the Solling mountain show that the variation of SO_2 dry deposition from year to year can be very great, approaching zero values in some years. This variation is probably due to changes in the vitality of the stand, limiting the buffering ability in the canopy so strongly that SO_2 absorption in the water films ceases owing to low pH. Damaged stands of low vitality can therefore show lower rates of acid deposition than before they were damaged. On neutral soils, where the uptake of basicity may not be limiting acid buffering in the canopy, dry deposition of SO_2 is always of significance.

Particle deposition reaches high values in exposed mountain areas, higher in coniferous than in deciduous forests. It also reaches quite low values in some years, probably mainly depending upon weather conditions. In sheltered positions, e.g. also in young stands of low height sheltered by higher stands, particle deposition approaches zero. In exposed mountains, however, particle deposition may be of the greatest significance. This explains the missing conformity in remote mountain areas between air quality (low concentrations of SO_2 and NO_x in air) and acid deposition (high rates of deposition).

The rates of total H^+ deposition clearly indicate the difference between sheltered and exposed sites on the one hand and deciduous and coniferous forests on the other. NH_4^+ must also be considered as an acid, since it is completely retained in the forest ecosystem, most probably being converted to organic nitrogen. This process is connected with an equivalent release of protons. The values for total deposition of acidity therefore include the deposition of NH_4^+. They vary between 1.2 and 6.4, indicating that almost all forest soils in the region investigated are being acidified owing to acid deposition.

Part of the proton load is buffered in the canopy. According to Ulrich[24] this process may be described by three steps:



1) Buffering of protons by ion exchange in the leaves:

$$\text{Cell wall}\ Ca^{2+} + 2H^+ + SO_4^{2-} \longrightarrow \text{Cell wall}\begin{matrix}H^+\\H^+\end{matrix} + \underbrace{Ca^{2+} + SO_4^{2-}}_{\text{leaching}}$$

2) Recharging of the buffer:

$$\text{Cell wall}\begin{matrix}H^+\\H^+\end{matrix} + \underbrace{Ca^{2+} + 2\,HCO_3^-}_{} \longrightarrow \text{Cell wall}\ Ca^{2+} + 2\,H_2O + CO_2$$

Transpiration stream

3) Soil acidification:

$$\underset{\text{Soil solution}}{Ca + SO_4^{2-}} + \underset{\text{Plant}}{2\,H_2CO_3} \longrightarrow \underset{\text{Soil solution}}{2\,H^+ + SO_4^{2-}} + \underset{\text{Plant}}{\overbrace{Ca^{2+} + 2\,HCO_3^-}}$$

Ca may be the dominating cation since Ca is mostly found in the cell walls of plant tissues. During the first reaction Ca^{2+} is removed from the cell wall by exchange with H^+ and reaches the soil together with SO_4^{2-}. The protonated exchange sites of the cell wall are then recharged by $Ca^{2+} + 2\ HCO_3^-$. The third reaction clearly shows the consequences of proton buffering in the canopy: During the uptake of Ca from the soil solution an equivalent amount of protons is released. That is why the buffering in the canopy does not reduce the acid load resulting from deposition. But the amount of protons buffered in the canopy causes a stress to the buffer systems of the parts of the soil surrounding the roots.

The rate of this process may be influenced by the atmospheric load of protons and by the soil conditions. In well-buffered soils without reduction of Ca-uptake by Al-ions in the soil solution, a large part of the acid load may be buffered on the leaves resulting in a strong acidification of the rhizosphere in such stands. On sites that are already strongly acidified the reduced uptake of Ca may become limiting for the buffering process in the canopy.

Increased cation leaching caused by ion exchange in the leaves and needles may contribute to nutrient deficiency as is often reported in connection with the decline of spruce and fir[27,28]. As mentioned above, the reduction of the cation uptake due to high amounts of Al-ions which was found by Rost-Siebert[16] and Hüttermann[7] will enhance this effect.

Quantifying the total acid load of forest soils: H^+-budget

At present, there is much controversy about the origin and consequences of the soil acidification which has been demonstrated over wide forest areas of Central Europe. Calculations of the soil internal rate of proton production in forest ecosystems were carried out by Likens et al.[9], Andersson et al.[1], Sollins et al.[18] and by Nilsson[15].

From the flux balance of a Douglas-Fir ecosystem in Western Oregon Sollins et al.[18] concluded that the effect of acid deposition on the proton budget is negligible. Also Nilsson pointed out that under North European conditions rain water acidity is more likely to lead to stream water acidification whereas root uptake will primarily acidify the soil.

Any evaluation of the origin of soil acidification has to quantify the rates of protons from both natural and anthropogenic sources.

As an example the H^+-ion budget of two stands in the German Solling region (beech 135, spruce 100 years, 500 m above sea level) is given here.

The mean annual rates of proton deposition in the Solling stands are given in table 3.

Owing to different rates of interception-deposition the rates of total deposition under spruce are two times higher than those of the beech stand. This is caused by the higher filtering area of the spruce stand and by the fact that hard-woods are leafless during winter when the rates of interception-deposition reach their maximum[20].

Table 3. Annual rates of proton deposition (keq ha^{-1}) (1969–1981)

	Beech	Spruce
Precipitation-deposition	0.8	0.8
Interception-deposition	1.2	3.2
Total deposition	2.0	4.0

Coming back to the rates of proton production within the soil the proton producing (and consuming) processes and their rates are demonstrated in table 4.

The processes listed in table 4 contribute to different extents to the rates of proton production. The biggest part is represented in both stands by the accumulation of 'excess cations' by increment. The term 'increment' includes the increment of timber, bark, twigs and roots (> 5 mm)[12]. The accumulation of 'excess cations' within the humus layer did not play a significant role.

The strong increase of organic matter and nitrogen storage of the humus layer during the time period from 1966 to 1979 reported by Ulrich et al.[25] and Matzner and Ulrich[13] under these stands was not connected with an equivalent accumulation of 'excess cations'. Because of low binding intensity the basic cations are released in the long run despite accumulation of organic matter. Furthermore, a slight retention of SO_4 within the humus layer was followed that counteracts the increase of the storage of 'excess cations'.

When biomass is removed from forest ecosystems, which is usually the case in managed forests, the proton consumption that would follow the mineralization of the harvested biomass is prevented, with the consequence of net production of protons within the soil. The rate of proton production caused by the removal of biomass depends on the amount of biomass and on the concentrations of 'excess cations' within that biomass[15]. If only the bole is removed, the mean annual proton production would amount to 0.5 (beech) and to 0.3 keq ha^{-1} (spruce). The additional removal of branches would account for 0.1 and 0.3 while the harvesting of the root biomass results in the production of another 0.1 and 0.9 keq $ha^{-1}\,a^{-1}$ for beech and spruce, respectively. The high value for spruce in the roots is due to high cation concentrations in lignified roots.

The very different behavior of beech and spruce becomes obvious when looking at the uptake of NO_3^- from deposition. While the beech stand is able to take up nearly the total amount of incoming nitrate, nitrate is almost completely lost from the spruce stand by the output with seepage water. As the deposited NH_4^+ is totally taken up by both stands, the net proton production caused by the uptake of N from deposition increases up to 1.0 keq $ha^{-1}\,a^{-1}$ under spruce but only to 0.2 under beech.

The production and leaching of organic acids is negligible under beech, amounting to 0.1 keq $ha^{-1}\,a^{-1}$, whereas this process took place at a rate of about 0.5 keq $ha^{-1}\,a^{-1}$ in the spruce stand.

Table 4. Proton production within the soil (keq $ha^{-1}\,a^{-1}$) (1971–1981)

	Beech	Spruce
Accumulation of 'excess cations' (increment)	0.7	1.5
Accumulation of 'excess cations' (humus layer)	0.1	0.0
Uptake of NH_4 from deposition	0.9	1.1
Uptake of NO_3 from deposition	−0.7	−0.1
Production and leaching of organic acids	0.1	0.5
H^+ buffering on the leaves	0.6	0.9
Sum	1.7	3.9

The rates of proton buffering in the crowns are calculated to be 0.6 for the beech and 0.9 keq ha^{-1} a^{-1} for the spruce stand. Owing to the load of acidity being higher under spruce and to the fact that proton buffering on the spruce needles takes place over the whole year, this difference could be expected.

The element balance of the soil used the fluxes of protons with canopy drip and stem flow as input instead of the rates of total deposition. Therefore the rates of proton buffering on the leaves occur as proton production in the soil.

Since the rates of proton buffering were also considered when calculating the rates of proton deposition they have to be subtracted from the internal production if the sum of internal and external proton load is calculated. The total proton load then increases to 3.1 and 7.0 keq ha^{-1} a^{-1} for the beech and the spruce stand.

Assuming no deposition of N and protons, the internal proton production in the soils of these ecosystems would only account for 0.9 and 2.0 keq ha^{-1} a^{-1} for beech and spruce, respectively. These rates represent the real contribution of ecosystem internal processes to the total proton load of the soil.

More than 70% of the total proton load is directly covered by the deposition of air pollutants.

If the accumulation of organic matter within the humus layer and the production and leaching of organic acids are considered as being indirectly caused by acid deposition, this proportion would be even higher.

Conclusions

The total proton load found in these ecosystems exceeds by far the known rates of buffering in soils by silicate weathering and release of basic cations (see above).

Under the present proton load most forest soils will therefore acidify and besides losses of nutrients the occurrence of possible toxic ions in the soil is unavoidable (Al-buffer range)[20,21].

The proportion of the total proton load of the soil that is represented by the internal production emphasizes the importance of acid deposition as main cause of soil acidification and destabilization of forest ecosystems under Central European conditions.

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