

EFFECTS OF ACIDIC DEPOSITION ON SOIL AND GROUNDWATER

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ABSTRACT

Acidic atmospheric deposition will result in soil acidification, which may cause serious harm to forest production. Soil acidification involves the change of several soil properties. The decrease of the acid neutralizing capacity is a suitable parameter to quantify soil acidification. A decreased pH and increased concentrations of aluminum and ammonium as compared to concentrations of cationic plant nutrients affect biological functions. The magnitudes and time scales of changes in soil chemistry depend on cation exchange properties and the nature and rate of silicate weathering. Knowledge about these two processes is also essential to evaluate strategies to abate acid conditions in soils.

INTRODUCTION

Soil acidification is a natural process which can be strongly enhanced by atmospheric deposition of SO_2 , NO_x and NH_3 . Enhanced soil acidification due to acid deposition is an important example of soil degradation because the land area involved is very large and effects on biology develop very gradually and are often difficult to distinguish from natural phenomena and effects from other changes in the environment. Evidence grows that degradation of soil conditions due to acid deposition seriously harms forest production and the functioning of valuable ecosystems in north and central Europe and the north-east of the North American continent.

In the absence of a clearcut definition of soil acidification several scientific controversies arose about the true nature of this process and about the relative importance of man-induced soil acidification versus natural soil acidification. Soil acidification can exert itself in various ways; by a decrease of pH or base saturation, by an increase in soil acidity, by an unbalanced availability of nutrients in the root environment or by a decrease of the acid neutralizing capacity (ANC) of the soil. From which angle one wishes to approach the soil acidification process depends on the question to be answered. Relevant questions are:

- To what extent is acid deposition deteriorating soil conditions now, and will it do in the future, and what are the effects on ecosystems in general and forest growth in particular?
- Which situations need amelioration and how should this amelioration of soil

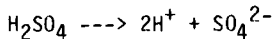
conditions be brought about?

To answer these questions we need a thorough understanding of chemical interactions in the soil related to the acidification process. Forest soils in general have a great capability to delay effects of acidic deposition due to the presence of a large, mainly bio-organic, exchange complex. However the ultimate process for acid neutralization and supply of plant nutrients in (un-fertilized) soils is dissolution of silicate minerals. Compared to current deposition rates the capacity of silicate minerals to neutralize acid is nearly infinite. However the rates of dissolution are far more important as they seem to be similar to current deposition rates. Exchange reactions and mineral dissolution need to be understood to evaluate present and future effects of acid deposition on soil and to develop abatement strategies.

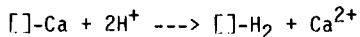
SOIL ACIDIFICATION; THE CONCEPT OF ACID NEUTRALIZING CAPACITY

The soil matrix generally consists of a large bulk of inert quartz in which various amounts of clay minerals, amorphous (hydr)oxides of aluminum and iron, primary minerals and organic matter are present. Clay minerals and organic matter have predominantly negatively charged surfaces (partly) neutralized by cations. If strong acid enters the soil it can react with the soil matrix in various ways:

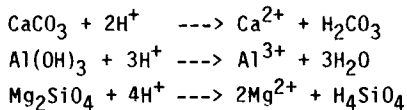
- 1) If the protons do not react with soil constituents a pH decrease will take place.



- 2) The positively charged protons can exchange against base cations (Na, K, Ca and Mg) bound to clay minerals or organic matter. The pH decrease will be less than in case (1) and will be insignificant when the proton input is negligible compared to the total amount of base cations bound to clay minerals and organic matter.



- 3) The protons can react with primary minerals or (hydr)oxides. Protons will be bound in carbonic acid, water or silicic acid and cations will be brought into solution. This can be exemplified by the following reactions:



The pH decrease will be less than in (1). If the mineral is relatively

reactive, as in the case of CaCO_3 the pH will remain approximately constant, as long as the mineral is present. If the mineral is very unreactive, the increase in pH will be noticeable only if the residence time of the percolating soil solution is long.

The above reactions illustrate the complexity of the soil acidification problem. Definition of soil acidification as a decrease of soil pH is obviously too narrow, although from an ecological point of view it might suffice because an unchanged pH generally indicates unchanged conditions for plant growth. Recently the definition of soil acidification as a decrease of the acid neutralizing capacity (ANC) was introduced (ref. 1 and 2). The ANC of a soil is defined as the sum of cations minus the sum of strong acid anions, expressed as their potential to consume or produce protons above a pH of 3:

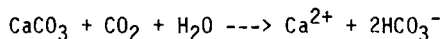
$$\text{ANC} = 6(\text{Al}_2\text{O}_3) + 2(\text{CaO}) + 2(\text{MgO}) + 2(\text{K}_2\text{O}) + 2(\text{Na}_2\text{O}) + 2(\text{MnO}) + 2(\text{FeO}) - 2(\text{SO}_3) - 2(\text{P}_2\text{O}_5) - \text{HCl} - \text{oxalate}$$

The terms correspond to the total amounts of the respective elements in an inorganic bulk soil sample, expressed eg. as capacity to consume moles of protons per kg of a bulk soil. Some consequences of the above definition are that any introduction of strong acid, eg. H_2SO_4 , will decrease the ANC. However when the strong acid would pass the soil unneutralized the ANC would remain unchanged. If a weak acid would be introduced to the soil, eg. H_2CO_3 or organic acids, the ANC would not be changed unless these acids mobilize cations which are subsequently leached from the soil system for which the ANC was defined. As in most areas in north and central Europe and the north-east of North America precipitation exceeds evapotranspiration, leaching of cations from the soil, and consequently soil acidification according to the above mechanism, is very common.

Changes of ANC can be expressed in $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$.

NATURAL AND ENHANCED SOIL ACIDIFICATION

In a clean pre-industrial situation there are two sources of protons input to soil, carbonic acid (H_2CO_3) and organic acids. Carbonic acid will only dissociate protons at pH values above 5. Soil acidification due to carbonic acid therefore is of particular interest in soils with near neutral pH, including those rich in carbonate minerals. The overall reaction in calcareous soils is:



The net effect will be leaching of Ca from the soil profile and thus a decrease of ANC. Resulting soil acidification rates can be as high as 10-20 $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$, as compared to 4 $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ due to acid deposition in the more exposed areas in the Netherlands, FRG and CSSR.

If a soil is decalcified and is covered by a vegetation, biological activity will produce organic acids, which can dissociate and cause pH values less than 4. Furthermore the organic anions can mobilize cations which are subsequently leached from the soil. This may result in a decrease of ANC in the order of 0.1 to 0.5 $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ (ref. 3).

Vegetation under unfertilized conditions tends to take up more cations than anions. For charge balance purposes this difference is compensated by an excretion of protons from the roots. Resulting soil acidification is of similar magnitude as that due to organic acids.

Regular removal of vegetation or litter by man will increase soil acidification, due to the concurrent net removal of cations from the inorganic soil system. Removal of forest litter for use in agriculture, which was common on poor soils until the beginning of this century, can increase soil acidification with 0.1 to 1, modern agriculture (fertilizer use, high harvests) with 2 to 3 $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ (ref. 4).

Wet and dry deposition of acidic or potentially acidic substances can increase soil acidification by 1 to 2 $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ in Scandinavia and the north-west of North America and by 2 to 8 $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ in west and central Europe.

CHEMICAL CHARACTERISTICS OF ACIDIFIED SOILS

Definition of soil acidification as a decrease of the ANC is unambiguous, but does not provide ecologically useful information. In this chapter we will describe some typical chemical features of naturally and antropogenically acidifying soils.

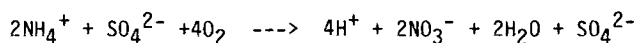
Interesting parameters are concentrations of a number of solutes in the soil solution especially of H, commonly expressed as pH ($-\log(\text{H}^+)$), Ca+Mg, hereafter adressed as M, and Al. Apart from the concentrations the fluxes of these components from the soil to the groundwater are of interest too.

In a carbonate holding soil the dominant anion will be HCO_3^- , the dominating cation will be M, the pH will be about 7, Al will be insignificant. The equivalent leachate flux ($\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) of Ca (and HCO_3^-) will equal the acidification rate. Concentrations also depend on the

difference between precipitation and evapotranspiration. The smaller the difference, the higher concentrations tend to be. The difference between precipitation and evapotranspiration increases going from coniferous forest to deciduous forest to ground vegetation (eg. heath land) to bare soil. In the same range acid atmospheric deposition tends to decrease. Discussion from here on will deal with acid soils ($\text{pH} < 6$) which are not used for agriculture. Although soil acidification is a relevant process in agricultural soils, it poses no problem as adequate liming is common practice. In fact in agriculture the ANC of the soil may remain constant or even increase due to application of lime and some fertilizers as ANC contributors.

In naturally acid soils the anions in the leachate are mainly organic, while concentrations of Al can range between 30 and 100 $\text{mmol} \cdot \text{m}^{-3}$. Concentrations within the rootzone are the overall result of a complex series of processes. Soils covered by a vegetation are involved in a cycle of nutrients (eg. NH_4 , NO_3 , M and K) which are mobilized at the surface by biodegradation of organic material, mineralization, and gradually taken up again by the roots from the percolating soil solution. The effects of atmospheric deposition on the soil solution composition is superimposed on the effects of the biocycle.

Atmospheric deposition of acidic or potentially acidic substances will increase the total amount of solutes in the soil. Generally concentrations of SO_4 and NO_3 will increase. The latter depends on whether deposited NO_3 or NH_4 is taken up by the vegetation. In the east of the Netherlands and the north-west of FRG deposition of NH_4 , up to $2 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ is common in woodlands, next to a deposition of $1 \text{ kmol} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ of NO_3 . The NH_4 in many cases is, at least partly, nitrified in the soil, leading to increased soil acidification.



If all deposited NH_3 is taken up there will be no acidifying effect, if all deposited NH_3 is nitrified and not taken up soil acidification will be 1 mole per 1 mole of deposited NH_3 . In an early stage of soil acidification the generated acid will be neutralized by dissolution of Ca, K, Na and Mg. With progressing soil acidification, especially when at high rates, acid deposition will be neutralized by dissolution of Al. The capacity of the soil to produce Al is nearly infinite: compared to base cations Al is an abundant constituent of the soil matrix. Aluminum can be toxic, especially when the concentration is high compared to M. The same is true for NH_4 , when the concentration is high compared to that of K and Mg. Toxic effect of Al and

NH_4 is diminished in the surface soil by mineralization of base cations. Absolute concentrations of Al, SO_4 , NO_3 and NH_4 depend on vegetation type and deposition rate. For Dutch forests with deposition rates of 2 (deciduous) to 3 (coniferous) $\text{kmol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$, ionic equivalent concentrations of Al can amount to 2 and 4, of SO_4 1 and 2 and of NO_3 1 and 2 $\text{mmol}\cdot\text{m}^{-3}$, for deciduous and coniferous forests respectively. Concentrations of NH_4 in solutions of forest soils are generally low. Under heath land ionic equivalent concentrations of NH_4 can be as high as $0.5 \text{ mmol}\cdot\text{m}^{-3}$ due to less nitrification, which is still comparably low compared to concentrations of, for example, NO_3 in forest soils. This difference results from low evapotranspiration and deposition. Absolute concentrations in, generally coniferous, forests in Scandinavia will be up to ten times lower due to lower deposition rates and higher precipitation surpluses.

EFFECTS ON GROUNDWATER AND DRINKING WATER

Soil leachates rich in NO_3 , SO_4 , Al and possibly NH_4 , will eventually reach deeper groundwater. For example concentrations of NO_3 in soil water and shallow groundwater under Dutch woodland soils range between 50 and 200 $\text{mg}\cdot\text{l}^{-1}$ (ref. 5). These concentrations are alarming as they exceed the current drinking water standards of 50 $\text{mg}\cdot\text{l}^{-1}$ and are comparable to concentrations under heavily manured farmland. However the velocity of the nitrate front under forest (about $0.5 \text{ m}\cdot\text{yr}^{-1}$) is lower than under farmland ($1 \text{ m}\cdot\text{yr}^{-1}$), due to a lower precipitation surplus. Current drinking water standards for NO_3 likely will be aggravated in the near future. Drinking water stations in the Netherlands are commonly located on sandy sediments under forest in areas with high ammonia deposition.

Due to denitrification the NO_3 concentration in groundwater may further decrease when moving down. However, low organic C contents and low pH may limit denitrification rates. High NO_3 concentrations in groundwater may also cause oxidation of sulfide containing sediments and explain occasionally reported low pH values at greater depths ($\sim 10 \text{ m}$) (ref. 5).

Recently one drinking water pumping station has been closed already in an area in the Netherlands with high NO_3 concentrations due to excessive manure application. Groundwater quality near pumping stations is threatened and will be threatened, also under forest areas. Sulphate concentrations in soil water under woodlands due to acid deposition, $50\text{-}100 \text{ mg}\cdot\text{l}^{-1}$, also gradually approach the Dutch drinking water standard of $100 \text{ mg}\cdot\text{l}^{-1}$ (EC $250 \text{ mg}\cdot\text{l}^{-1}$). A special problem is posed by drinking water from private wells, either for use by cattle or by man. Problems with NO_3 for cattle have been reported in the Netherlands. Recently a relation was suggested between the increasing

occurrence of senile dementia and increased Al levels in drinking water from private wells in the UK.

KEY PROCESSES AND CRITICAL PARAMETERS

In order to obtain more insight in the present and future effects of acidic deposition on the soil chemistry some key soil chemical processes will be discussed briefly.

Surface soils of forest generally have a large organic exchange complex, with equivalent capacities (CEC) up to 100 mmol.kg^{-1} . Cation equivalent exchange capacity for the rooted soil profile (0.3-1 m), converted to areal units, ranges from 200 to 500 kmol.ha^{-1} , which is considerable compared to deposition rates of 2 to $8 \text{ kmol.ha}^{-1}\text{.yr}^{-1}$. Such a large exchange capacity strongly buffers concentrations of all cations in the soil solution. In an early stage of acidic deposition a considerable portion of the exchange complex will be occupied by base cations. This fraction is generally indicated as base saturation value (BS). Protons will at first be exchanged against these base cations. As a result the pH in the soil solution remains relatively constant, while concentrations of base cations are increased and are leached from the soil. In order to lower an initial BS of 30% to 10% in a soil with an equivalent CEC of 400 kmol.ha^{-1} , 27 years of acid deposition deposition at a rate of $3 \text{ kmol.ha}^{-1}\text{.yr}^{-1}$ would be necessary, assuming no resupply of bases from additional processes. In advanced stages of soil acidification the BS often lies below 10%, while the remainder of the CEC is occupied by H and Al. In order to restore the initial BS forest soils could be limed or deposition rates could be lowered. In the latter case natural resupply of bases (to balance net loss) would occur by mineral weathering, which will be discussed later in this chapter. To bring the BS from 10 to 30% 400 kg CaCO_3 per ha would be needed. Natural resupply by mineral weathering at a common rate of $0.5 \text{ kmol.ha}^{-1}\text{.yr}^{-1}$ would take at least 160 years. These examples clearly illustrate the delaying effect of the cation exchange complex on adverse effects of acidic deposition and beneficial effects of lowering the deposition rate.

In all cases the exchange complex will prevent the occurrence of temporarily, extremely low pH values and associated high concentrations of Al. Such low pH conditions can prevail after dry periods in summer, when accumulated dry deposition is washed, all at once, from the forest canopy and infiltrates in the soil. Also acid pulses may occur at the start of snowmelt or right after a dry period.

A second crucial process is mineral weathering, which is the dissolution of primary and secondary soil minerals. The driving force for weathering is the attack of the mineral surfaces by protons. Primary minerals are generally aluminosilicates, that contain small amounts of base cations in their crystals, like eg. microcline (Na), albite and muscovite (K), anorthite and plagioclase (Ca), biotite (Ca and Mg) etc. Secondary minerals are residues of incomplete dissolution of primary minerals, or minerals newly formed from the

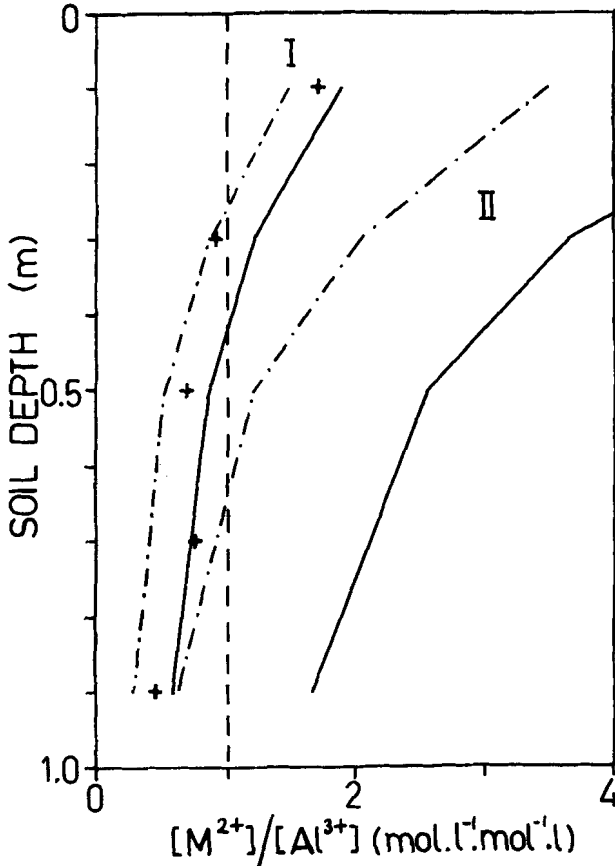


Fig. 1. Theoretical relationship between the ratio of concentrations of base cations (M^{2+}) and aluminum (Al^{3+}) in soil solution as a function of depth. The effect of increasing the dissolution rate of base cations from the mineral phase from 0.5 (---) to 1.0 (—) $kmol.ha^{-1}.yr^{-1}$ is demonstrated for soil acidification rates of 4 (I) and 2 (II) $kmol.ha^{-1}.yr^{-1}$. It is assumed that mineral weathering is the only acid neutralizing process, and that, besides the base cations, aluminum is the only dissolving ion. The present ratios between concentrations of M^{2+} and Al^{3+} in the field (+) are close to the presumably critical value of 1 (----).

reaction products of dissolution of primary minerals. The two main groups of secondary minerals are clay minerals, which in fact are a special group of aluminosilicates, and oxides and hydroxides of aluminum and iron. Secondary minerals generally have large surface areas and exchange capacities. Mineral dissolution is the primary source of base cations and plant nutrients in natural systems. The proportion of secondary minerals in the soil strongly varies and can amount to several tens of percentages, depending on rock type and geological history. Mineral weathering can be characterized by (1) the capacity to consume protons and to produce base cations and Al and (2) the dissolution rate, (3) the stoichiometry, which gives the nature and the relative occurrence of the dissolved ions.

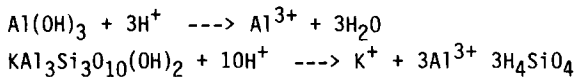
The capacity of weathering to consume protons is very large. For an average soil with 20% silicate minerals, and a rootzone of 0.5 m, the buffering capacity approximately is $20,000 \text{ kmol} \cdot \text{ha}^{-1}$. Capacities to produce base cations are also very large. Typical ionic equivalent pools for podzolic soils are 200 to 400 kmol Ca or Mg, 1000 kmol Na or K and 10,000 to 20,000 kmol Al per ha.

The dissolution rate is a far more important parameter than the capacity for mineral weathering. In the field, weathering rates of 0.5 to 5 $\text{kmol} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ (base cations + Al) are measured in chemical balance studies (ref. 2 and 6). High weathering rates correspond to situations with high acidification rates and, for acid soils, with high fractions of aluminum in the dissolved ions. In general the larger part of proton production due to acid deposition is consumed in soil, suggesting that proton consumption rates are sufficiently high to meet present deposition rates. However, of more concern are the rates of base cation weathering; these determine whether the BS, which is the readily available pool of cationic plant nutrients will decrease, increase or remain constant. If the rate of exchange and subsequent leaching of base cations is larger than the rate of resupply by mineral weathering the pool will become smaller, if it is smaller the pool will increase if they are equal the pool will remain constant. Dissolution kinetics of primary minerals are still not sufficiently understood to predict weathering rates in field situations. It is generally accepted that weathering rates increase with decreasing pH and reactive surface area, and decrease with increasing accumulation of dissolved ions in the soil solution. Theoretically, weathering rates under different field conditions may vary by a factor of 10 to 100. High weathering rates can occur during short-lasting pH drops (<3!) or excessive flushing of the soil solution (dilution).

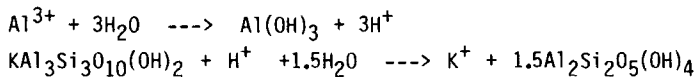
The amount of dissolved base cations and aluminum from the overall

weathering reaction (the reaction stoichiometry) is important as it determines the absolute concentration of Al and its ratio to the concentration of M, which are both important parameters with respect to damage to the vegetation. The fraction of aluminum, which dissolves from silicate minerals, tends to be high at low pH and for high acid loadings, but will gradually decrease with increasing residence times of soil solutions. The underlying mechanism is not yet clear. If the fraction of dissolving aluminum decreases with decreased acid loading, the ratio between concentrations of Al and M will eventually improve when deposition rates would be lowered (figure 1).

Soils generally contain several percents of amorphous aluminum-(hydr)oxides, which could dissolve relatively fast after a high input of protons. High initial aluminum concentrations could also result from complete (congruent) dissolution of mineral crystals.



In the course of time Al could slowly reprecipitate as a hydroxide, gradually releasing protons in solution again, which will now be consumed by base cation weathering from primary minerals.



The net result of the weathering reaction is an incomplete (incongruent) dissolution of a primary mineral. By dissolution of aluminum-hydroxide or temporarily congruent dissolution of primary minerals the soil has a mechanism to quickly consume high loads of protons.

A third process which can be critical is nitrification. Nitrification is important in situations with high deposition of NH_3 , which occur in areas with intensive animal husbandry (bioindustry), for example in the eastern part of the Netherlands and the north-west of the FRG. In contradiction with general experience nitrification in forest soils also takes place at pH values below 4, as indicated by high leachate fluxes of NO_3 when nitrogen is deposited mainly as NH_3 . A fair availability of base cations seems a prerequisite for nitrification.

SOME CONCLUSIVE REMARKS

Soil acidification is a complex process which will affect various soil parameters. Definition of soil acidification as a decrease of the acid neutralizing capacity, gives us a tool to compare rates of acidification in various soil types in various stages of natural and anthropogenic acidification. In order to evaluate ecological consequences of changes in soil chemistry due to atmospheric deposition, pH and concentrations of aluminum as compared to base cations need to be assessed. For understanding the changes of these soil chemical properties cation exchange and mineral weathering are key processes. Critical parameters are cation exchange capacity, base saturation, and the rate and the stoichiometry of mineral dissolution reactions. Soils with a low CEC and low base saturation and low base weathering rates are most susceptible to adverse effects of acidic deposition. Soils with a high CEC and high amount of exchangeable H and Al will be most difficult to ameliorate by liming. If, additionally, the dissolution rates of base cations from silicate minerals are low, natural recovery of the soil after deposition rates are lowered will be very slow. Experimental studies to obtain critical parameters in combination with the use of simulation models will be important to predict future changes in soil chemistry for different emission/deposition scenarios and to preevaluate mitigation strategies for forest soils.

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