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# The Impact of Acid Deposition on Groundwater: A Review

**Holmberg, M.**

**IIASA Working Paper**

**WP-86-031**

**July 1986**



Holmberg, M. (1986) The Impact of Acid Deposition on Groundwater: A Review. IIASA Working Paper. WP-86-031  
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# ***WORKING PAPER***

THE IMPACT OF ACID DEPOSITION  
ON GROUNDWATER: A REVIEW

Maria Holmberg

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**THE IMPACT OF ACID DEPOSITION  
ON GROUNDWATER: A REVIEW**

Maria Holmberg

July 1986

WP-86-31

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## **PREFACE**

IIASA's Acid Rain project is developing a set of computer models linking energy pathways, sulfur emissions, long range transport and deposition of sulfur compounds with environmental effects on forest soils, lake water and forests. The main purpose of the project is that this model, known as RAINS, can be used in international deliberations on reducing emissions of  $\text{SO}_2$ .

During the 1985 Young Scientists Summer Program (YSSP), Maria Holmberg worked on modeling the impact of acid deposition on groundwater. She not only succeeded in producing an excellent overview of these effects (the results of which are described in the Working Paper) but also started the development of an additional submodel of RAINS. Due to her excellent job, Maria Holmberg was awarded IIASA's Peccei Scholarship which enabled her to continue her work on groundwater modeling in 1986. The results of the modeling will be presented in a separate working paper.

Leen Hordijk  
Leader, Acid Rain Project

## **ACKNOWLEDGEMENTS**

A first draft of this report was read and commented upon by Stefan Kaden, Juha Kämäri and Michael Starr. Pertti Hari, Lena Maxe and Annikki Mäkelä reviewed the final version. The author wishes to thank the reviewers for valuable comments and fruitful discussions on the subject of the study.

## **ABSTRACT**

Theoretical mechanisms and empirical evidence of the potential acidification of groundwater under forested soils in Europe have been reviewed in order to provide a starting point for an assessment of the acidification of groundwater in the scope of the Acid Rain study carried out at IIASA. Basic characteristics of forested soil-water systems are presented as a background to a discussion of the transport and the release and retention of elements. The report relates the impact of acid deposition of groundwater to the pedology, the climatic regime and the geohydrology of the region. Some approaches of modeling the problem are reviewed, including dynamic models and sensitivity analysis. A procedure for assessing the impact of various energy pathways on the potential for acidification of groundwater is outlined. The method proposed combines a regional ranking of the static sensitivity with a dynamic simulation of the impact of acid deposition on the chemistry of top soil.

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# **THE IMPACT OF ACID DEPOSITION ON GROUNDWATER: A REVIEW**

Maria Holmberg

## **1. INTRODUCTION**

Groundwater under forested soils in Europe may be affected by the deposition of sulfuric and nitric acids on vegetation and soil. There is now increasing evidence that acid deposition causes leaching of base cations, aluminum, sulfate and hydrogen ions to groundwater. Recent changes in the chemical properties of soils and surface waters in small watersheds in Northern Europe and in the Northeastern United States have been reported (e.g. Likens et al., 1977; Overrein et al., 1980; Wright et al., 1980; Matzner, 1983; Goldstein et al., 1985; Nihlgard et al., 1985). Nutrient cycling in soil appears to be disturbed and mobilization of metals from mineral structure seems to accelerate in certain areas due to acidic precipitation (e.g. Norton et al., 1980; Hanson et al., 1982; Ulrich, 1983). The chemical composition of groundwater which is recharged by infiltration

through top soil, is likely to change as a result of changes in the properties of the overlying soil strata. The observed recent trends in the concentrations of surface waters that are fed partly by groundwater, indicates increased concentrations of aluminum and hydrogen ions in groundwater.

The term acidification will in this context be used to denote increasing trends of hydrogen ion concentrations in soil solution, in the pool of exchangeable cations on soil particles, or in groundwater. The increase in the fraction of exchangeable hydrogen ions causes an increased mobilization of aluminum, iron, calcium, magnesium, potassium etc. from the minerals. Thus the acidification of soil may not necessarily be reflected as a decrease of the pH of groundwater, but may also lead to an increase in the alkalinity.

The consequences of acidification of soils and groundwater are three-fold. Firstly, hydrogen ions originating from precipitation replace calcium, magnesium, potassium and sodium ions on the exchange sites on soil particles. Under certain hydrologic conditions these ions are leached out of the rooting zone of the plants. If they reach groundwater, they contribute to the hardness of groundwater. Secondly, high concentrations of hydrogen ions, aluminum and iron affect soil micro-organisms (e.g. Bååth et al., 1980; Bewley and Parkinson, 1986). Surface waters recharged through soil and groundwater are likely to reflect increasing concentrations of hydrogen and aluminum (e.g., Hultberg and Johansson, 1981). Thirdly, acid groundwater may corrode supply pipes (Levlin, 1978). Drinking water extracted from private wells, contaminated by aluminum, iron, copper, zinc and asbestos fibres originating from supply pipes may violate human health standards (McDonald, 1985).

Groundwater is an important source for the water supply in Europe. In Denmark all drinking water is groundwater, in Austria, Belgium, the Federal Republic of Germany, Finland, France, Great Britain, Italy, the Netherlands and Switzerland, 30-70% of the drinking water is extracted from groundwater. Norway is an exception, where almost only surface water is used (IWSA, 1985). In the United States, 50% of the population are served by groundwater (Russell, 1978). Problems related to the quantity and quality of groundwater have been largely studied.

Groundwater pollution has so far been a cause of concern mainly in connection with local pollutants and point sources (Young, 1981). Reported pollutant sources are agriculture (Csaki and Endredi, 1981; Oakes et al., 1981; Vasak et al., 1981), mining activities (Henton, 1981; Luckner et al., 1985), urbanization and industrial activities (Kondrates, 1981). The pollution of groundwater due to long range transport of atmospheric pollutants have not been extensively discussed or reported.

Groundwater in regions with granitic bedrock, shallow soils and humid climate may show comparatively high concentrations of hydrogen ions, independently of the deposition of anthropogenically derived acidic substances. In the 1970's, Swedish groundwater was reported to acidify (e.g. Hultberg and Johansson, 1981). Later, Aastrup and Persson (1984) argued that the observed acidification of superficial groundwater in Sweden probably was due to climatically induced extremely low groundwater levels, which led to the oxidation of sulfur-containing minerals to form sulfate. No increasing trends of groundwater acidity have been observed in the Nordic countries, although changes in bicarbonate, calcium, magnesium and sulfate concentrations have been noticed, according to a report

edited by Soveri (1982).

In agricultural regions in Europe, intensive fertilization contributes probably more to groundwater acidification than long range transport of atmospheric pollutants originating from energy production. The acidifying impact on soils and groundwater caused by the application of nitrogen-based fertilizers is discussed by Appelo (1982), Hoeijmakers (1985) and Paces (1985).

This report is a review of the potential impact of long range transport of sulfuric and nitric compounds on groundwater quality. It is based on literature concerning observed and assumed influence of acid deposition on soil-water systems. In the Acid Rain Project of IIASA, soil and lake acidification following the deposition of sulfur have previously been modeled by Kauppi et al. (1985) and Kämäri et al. (1985). The focus of this study is on forested ecosystems, since agricultural soils are primarily influenced by intensive management. The hypotheses and evidence presented in the literature are compiled to provide a starting point for an attempt to assess the risk of groundwater acidification on a regional scale in Europe. Future emission scenarios resulting in various sulfur deposition patterns are discussed by Alcamo et al. (1985). The question to which extent any potential change in groundwater quality may affect water supply and require new technology for adjusting the quality to human health standards, is beyond the scope of this study.

The report is divided into four chapters. Chapter 2 summarizes briefly the physical structure of the soil-water system and discusses the properties relevant for the transport, retention and release of elements. The potential impact of acid deposition on groundwater is discussed in

Chapter 3, after a presentation of the dynamics of the transport of elements in the soil-water system and the production and consumption of hydrogen ions in the soil. Chapter 4 gives examples of two different approaches on modeling the acidification processes, dynamic models and sensitivity analysis.

## **2. STRUCTURE OF THE SOIL-WATER SYSTEM**

### **2.1. Physical Structure**

The uppermost layer of the earth's crust is a multiphase system with abiotic and biotic components. The dead fraction of the solid phase consists of rocks and other aggregates of the minerals as well as organic material in various stages of decay. The liquid phase is a solution of water and elements entering with infiltration or mobilized from the solid phase or trapped from the gaseous phase. The gaseous phase consists of air, with partial pressures different from those of the ambient air. The term soil will sometimes be used to denote the entire system of solid, liquid and gaseous phase, while the term soil solution will be used for the liquid phase in the upper, unsaturated zone and the term groundwater for the liquid phase in the deeper, saturated zone. With the objective of studying the impact of acid deposition on soil and groundwater, the environment of the soil system may be defined as the atmosphere, the vegetation and the surface waters. The primary objects of interest in connection with acidification are the temporal developments of the base saturation and the concentrations of elements in the groundwater.

The long-term development of the concentration of elements in the different phases is determined by the transport of elements in the liquid and the gaseous phase as well as by the transfer of elements between the solid, liquid and gaseous phase. The dynamics of the transport processes and the mass transfers between the phases connected with the impact of acid deposition will be discussed in Chapter 3, particularly those involving the liquid and the solid phase. As a background to this, the physical structure of the soil-water system is presented here. Generalizing slightly, a picture of the vertical profile of forest soil can be drawn as in Figure 1.

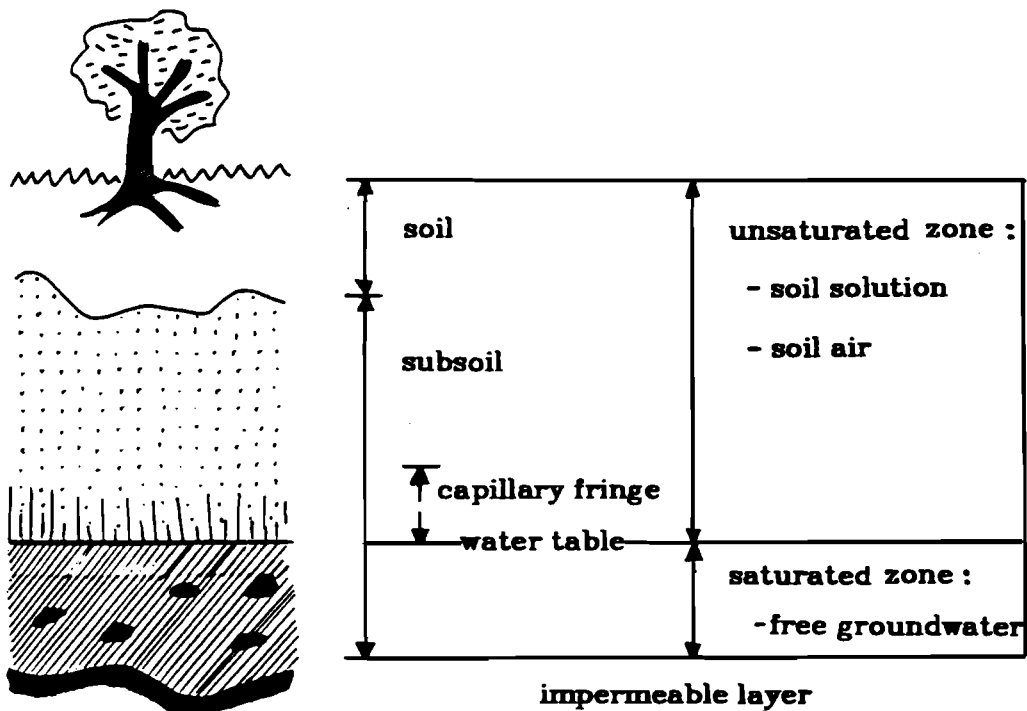


Figure 1. The coarse structure of a soil-water system (after Lee, 1980)

Beneath the forest floor vegetation there is a layer of top soil with a high content of organic matter. The top soil, or the rooting zone, is

followed by the subsoil, a layer of predominantly mineral soil which contains less or no organic matter. The subsoil may end with a layer of hard rock, impermeable clay or some other formation which prevents the transport of water. Soil and subsoil form a system of particles and pores showing diameters of varying dimensions. Colloidal particles have diameters of the dimension of  $< 1$  nm, whereas gravel and stones are much larger. Root channels and macropores with diameters of the dimension  $> 1$  cm contribute substantially to the heterogeneity of soil and subsoil.

Typically the pores in the deeper layers of the subsoil are saturated with water. This water is referred to as free groundwater (as opposed to confined groundwater, which may be found beneath an impermeable layer of rock or clay). Above the groundwater table capillary forces cause the water to move upwards, producing a diffusive boundary, called the capillary fringe, between the saturated and the unsaturated zone.

## **2.2. Properties of the Phases and the Interface**

The solid, liquid and gaseous phases of the soil-water system are characterized by very different volumetric densities. The densities of the solid phase are 100 to 1000 times larger than those of the liquid phase and the gaseous phases (see Table 1). Consequently the volumetric concentrations of elements in the solid phase are much larger than those in the other phases. The concentrations of elements in the different phases, as well as the interfacial area and the electrochemical properties of the particle surfaces, determine the rates at which the elements migrate from one phase to another.

The area of the contact surface between the solid soil matrix and the soil solution depends on the geometry of the crystal lattice and the organic matter content. The size of the soil particles varies, giving rise to interfacial areas of dimensions in the range of  $10^3$  to  $10^9 \text{ m}^2 \text{ m}^{-3}$  (see Table 2).

Table 1. Densities of the phases in the soil-water system.

Phase	Specific density $\text{g m}^{-3}$	Volumetric fraction $\text{m}^3 \text{m}^{-3}$	Volumetric density $\text{g m}^{-3}$
Solid	$0.1-1.8 \times 10^6$	0.4 - 0.7	$4.0 \times 10^4 - 1.3 \times 10^6$
Liquid	$1.0 \times 10^6$	0.03 - 0.54	$3.0 - 54.0 \times 10^4$
Gaseous	$1.0 \times 10^3$	0.06 - 0.27	$0.6 - 2.7 \times 10^2$
Sources: Kuntze et al. 1983, Westman et al. 1985			

Table 2. Properties of the solid - solution interface

Solid component	Surface area $\text{m}^2 \text{m}^{-3}$	Surface charge $\text{meq m}^3$
Sand	$6.0 \times 10^3$	$4.5 \times 10^7$
2-layer clay	$5.0 \times 10^7$	$5-30 \times 10^4$
3-layer clay	$3.0 \times 10^9$	$2-5 \times 10^6$
Organic matter	$1.0 \times 10^9$	$3.0 \times 10^4$
Sources : Talibudeen, 1981; Kuntze et al.,1983.		

The net charge of the solid soil components is negative or positive, depending on the concentration of hydrogen ions in soil solution. The dissociation of hydroxyls at the surfaces of the minerals, the dissociation of carboxyl groups and phenolic hydroxyls in soil organic matter, cause a negative charge which increases with a decreasing concentration of hydrogen ions in soil solution (Talibudeen, 1981). The permanent negative



charge is a result of isomorphous substitution of elements of smaller positive charge ( $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ) for those of higher charge ( $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ) in the crystal lattice. Polymeric aluminosilicate anions also give rise to constant negative charge. The permanent negative charge of the surface of the soil components is of dimensions in the range of  $10^4$  to  $10^6 \text{ meq m}^{-3}$  (see Table 2).

### **2.3. Cation Exchange Capacity and Base Saturation**

The negative charge of the soil particles causes them to attract cations from soil solution, generating a charge distribution in the liquid film surrounding the colloids, i.e. the diffusive layer. The charge distribution is such that the concentration of cations in the diffusive layer is greatest next to the colloid surface and drops away exponentially to that in the bulk solution. The electric double layer model (see e.g. Talibudeen, 1981), defines the cation exchange capacity as the excess of cations in the diffusive layer over that in bulk solution. These cations are readily exchangeable to others in bulk solution. The mechanism of attracting cations from soil solution gives the soil solid phase the property of a dynamic reservoir of cations. The size of this reservoir, or the cation exchange capacity, is to a certain degree a function of the concentration of hydrogen ions in soil solution. This dependency is stronger when the content of organic matter in the soil is higher. The fraction of the cation exchange capacity which is occupied by base cations (potassium, sodium, calcium, magnesium) is referred to as the base saturation. The base saturation varies with the concentrations of ions in soil solution.

### 3. TRANSPORT AND TRANSFORMATION IN THE SOIL-WATER SYSTEM

The temporal development of the concentrations of elements in the solid, liquid and gaseous phases of the soil is determined by the interaction with the environment, by the rates of the transport processes in the liquid and the gaseous phase, by chemical reactions within the phases and by the rates of the transition processes between the three phases. The long term changes in the base saturation of the soil and the concentrations of hydrogen, aluminum, bicarbonate and base cations in the groundwater are results of the interaction of the various processes occurring in the soil, in combination with the influence of the environment on the soil system. Figure 2 is a schematic picture of the interaction of the soil system with its environment and of the routes of element flux within the system.

Input of elements from the atmosphere occurs through wet and dry deposition on soil surface and vegetation (1a,c,d). The soil system acquires elements also from decaying organic matter (2a,b). Removal of elements from the soil system occurs through the uptake of nutrients and water by the vegetation (2b) and through the leaching of elements to surface water (6d,c). The transport processes within the soil system are diffusive and convective flow of solutes (6a,b) and diffusive flow of gas (7). The major phase transition processes within the soil system are the exchange of ions between the soil solution and the solid phase (4a,b,c), the weathering of mineral surfaces (5) and reduction and oxidation processes (3).

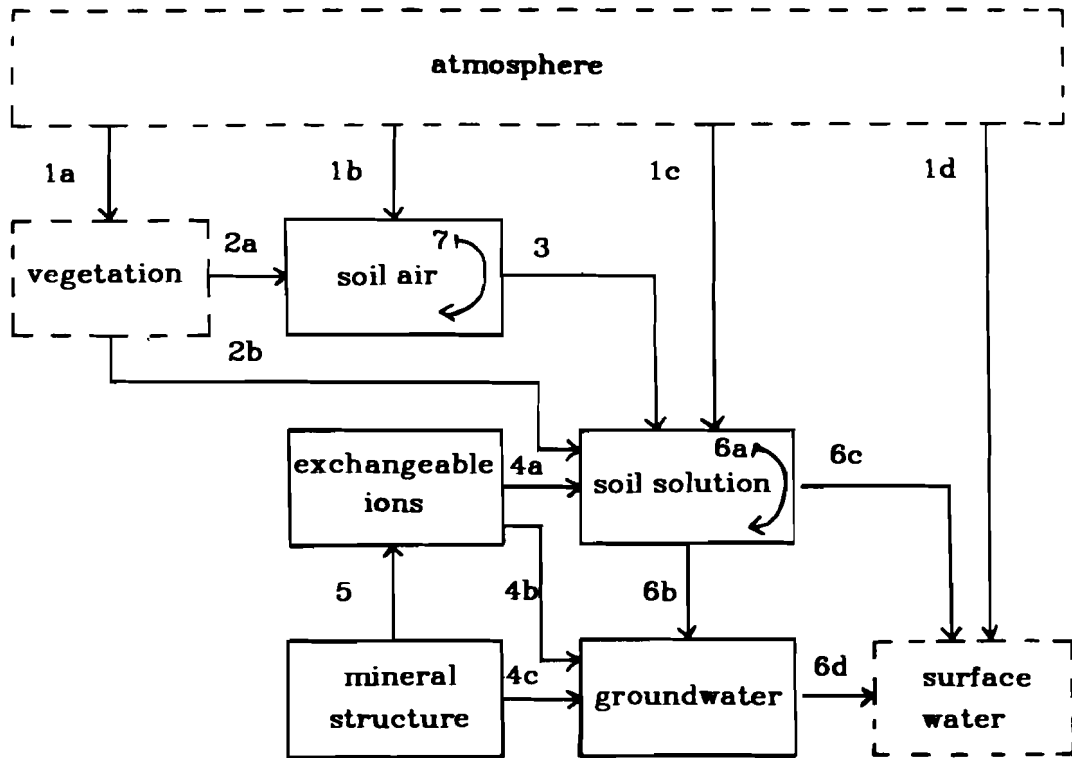


Figure 2. Major fluxes in the soil system and its environment. The boxes represent element reservoirs of the system. The environment is marked by broken contours. The arrows represent element fluxes : deposition 1a,c,d; gaseous exchange 1b; organic cycling 2a,b; reduction/oxidation 3; ion exchange 4a,b,c; weathering 5; solute transport 6a,b,c,d; gaseous transport 7. The fluxes may be either in the direction of the arrows or in the opposite direction.

### 3.1. Transport

Transport of elements within the soil system occurs in the liquid and the gaseous phase. Soil is not a homogenous medium. The pore size and hence the permeability varies with depth and the content of organic matter. Adhesive forces between soil particles and water cause small pores to be waterfilled before the larger pores. In dry soil, therefore, water flows predominantly in the small pores, whereas a higher water content may induce macropore flow. Pure transport never occurs alone under field conditions, but transfer of elements between the phases, i.e. cation exchange,

nutrient uptake, reduction and oxidation, always take place simultaneously to diffusion and mass flow.

The maximum flow rates are determined by the values of the diffusivity parameters and the hydraulic conductivity which reflects the permeability of the soil. Theoretical values of diffusion coefficients are of dimensions in the range of  $10^{-1}cm^2s^{-1}$  in air and  $10^{-5}cm^2s^{-1}$  in solution (see Table 1A in Appendix). The theoretical values of flow rate are not observed under field conditions, since the solutes are affected by various adsorption mechanisms as they move in the soil. The contribution of the diffusion in the liquid phase is usually small in comparison to gravitational mass flow.

The rate of percolation, or the rate of transport of the precipitation through the unsaturated zone to the saturated groundwater zone, depends on the rates of precipitation, evapotranspiration and the soil texture. The slower the transport, the longer the time available for the chemical reactions between the mobile phases and the solid phase and for the migration of elements from one phase to another. The higher the rate of downward transport of water, the larger the fraction of elements in the recharge which originate directly from the precipitation. This fraction decreases with the depth of the unsaturated zone and with the increase of the rates of the transformation processes in the unsaturated zone. A slow percolation rate allows for a long reaction time with the soil and the bedrock, which may cause changes in the base saturation of the soil and a recharge of low acidity but high concentrations of other elements. A fast percolation rate, on the other hand, may cause acid recharge with low concentrations of other ions.

### **3.2. Proton Production and Consumption**

The transformation processes occur along the way as elements are transported in solute or gaseous form in the soil and subsoil horizons. They include mineralization and assimilation of elements, ion exchange between solution and the solid phase, weathering of the mineral structure, reduction/oxidation processes and complexation processes.

The rates of these processes depend to a certain extent on the concentrations of cations and anions in the soil solution, which in turn are determined by the rates of the transformation processes. This feedback system is influenced by the environment through the input of atmospheric deposition of various concentration and through the uptake of solutes by the vegetation. The evapotranspiration of water from the soil causes an increase in the solute concentrations.

The potential impact of the deposition of hydrogen ions originating from anthropogenically derived sulfuric and nitric compounds on the rates of soil processes has been discussed by Abrahamsen et al. (1975), Reuss (1975), Malmer (1976), Tamm (1976), Likens et al. (1977), Mayer and Ulrich (1977), Norton (1977), Wiklander (1979), Abrahamsen (1980), Cowling (1980), Overrein et al (1980), McFee (1980), van Breemen et al. (1982), van Breemen et al. (1984), Matzner (1983), Ulrich (1983), Paces (1985) among others.

With the objective of studying the acidification of soil and water, the soil processes may be divided into proton producing and proton consuming processes. The following presentation is based on the thorough discussion of the proton balance in soil published by van Breemen et al.

(1984). They compare the internal and external sources of protons in ecosystems. The result of the quantitative analysis is that significant amounts of hydrogen ion and aluminum are leached from acidic soils with low internal rates of proton mobilization due to an external input of anthropogenically derived acidic substances.

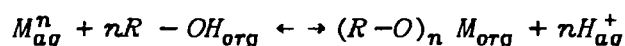
Following van Breemen et al. (1984) the proton producing and consuming processes in soil-water systems have been compiled into Table 4.

Table 4. Proton production and consumption in soil-water systems (van Breemen et al. 1984)

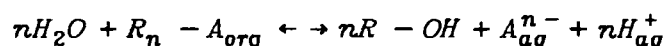
Production	Consumption
Atmospheric input	Drainage
Assimilation of cations	Mineralization of cations
Mineralization of anions	Assimilation of anions
Dissociation of acids	Protonation of acids
Oxidations	Reductions
Cation adsorption	Cation weathering
Anion weathering	Anion adsorption

These processes are in the following formulated as reaction equations, using a notation where the subscript *s* stands for the solid phase, *aq* for soil solution and *org* for organic matter. In root cation uptake, i.e. assimilation of cations by vegetation organic acids dissociate and organic salts are formed in the plant, whereby equivalent amounts of hydrogen ions are produced corresponding to the amounts of calcium, magnesium, potassium, sodium and ammonium ions assimilated. In mineralization of cations from

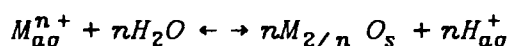
decomposing organic matter, organic acids are formed whereby hydrogen ions are consumed and cations are mobilized. van Breemen et al. (1984) give the following reaction equation:



where  $M^{n+}$  comprises  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$  and  $NH_4^+$ . In the mineralization of anions from decomposing organic matter, anions are released from organic salts, whereby organic acids are formed. Equivalent amounts of hydrogen ions are released, corresponding to the amounts of phosphate, nitrate and sulfate mobilized. In assimilation of anions, organic salts are formed and hydrogen ions are consumed. Mineralization and assimilation of sulfate and nitrate involves oxidation and reduction processes, but the net reactions are equivalent to equation given below, according to van Breemen et al. (1984).



where  $A^{n-}$  comprises  $H_2PO_4^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ . Weathering of cationic components from mineral structure can partly be seen as cation exchange between soil solution and soil particles in which equivalent amounts of hydrogen ions are bound when sodium, potassium, calcium, magnesium and aluminum ions are released from the particle surfaces and mineral structure. In adsorption of cations on mineral surfaces, hydrogen ions are mobilized and cations are immobilized:



where  $M^{n+}$  comprises  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$  and  $Al^{3+}$ .

The interaction of these processes is complex because of the large variations in the rates of the reactions and because of the coupling with the transport of solutes. The reaction rates depend on the concentrations of cations and anions and consequently also on the water content. The concentrations are in their turn influenced by the transport, which contributes to the dilution or distillation of the solutes.

In order to analyze quantitatively the interactions of the processes above, the reaction equations would be written in the form of differential equations. To formulate the differential equations giving a quantitative approximation of the change per unit time in the volumetric concentrations of cations and anions, detailed knowledge of the reaction rates is required. For the time being, approximations of the rate of ion exchange, weathering and the cycling of elements in biomass are available for certain specific minerals and soil types (e.g. Likens et al. 1977; Matzner 1983). Given approximations of the rates of the soil processes and weathering in the saturated zone, dynamic models combining the transformation processes with the transport may be written. Some attempts in this direction are referred to in chapter 4.1.

### **3.3. Impact of Acid Deposition on Groundwater**

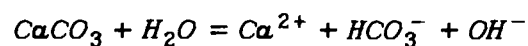
The concentrations of elements in groundwater depend on the chemical composition of the recharge from the unsaturated zone, on the mineral composition and the weathering rate in the saturated zone, and on the residence time of groundwater.



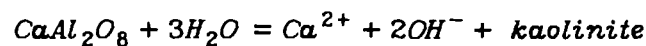
The *composition of the recharge* to groundwater is influenced by the residence time of the water in the unsaturated zone. The ion exchange equations are almost instantaneous, but the longer the time available for contact between the soil solution and the mineral surfaces, the higher the content of weathered cations in the recharge to groundwater. The residence time in the unsaturated zone increases with the depth and decreases with the permeability of the soil. Furthermore, the mineral composition of the soil and the organic matter content influence the recharge composition, through their impact on the rates of ion exchange and weathering.

The *weathering rate* and the mineral composition of the bedrock in the saturated zone determine the alkalinity production rate in the groundwater. Calcareous bedrock is easily weathered, whereas silicate bedrock weathers slowly. Examples of typical weathering reactions, as given by Stumm and Morgan (1981), show the weathering products of some minerals.

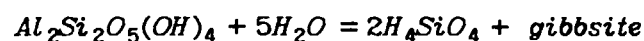
Calcite :



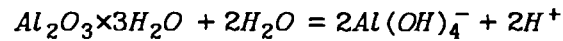
Anorthite :



Kaolinite :



Gibbsite :



Thus the weathering of calcite and anorthite produces calcium and hydroxyls. If kaolinite weathers further to form gibbsite, the production of protons cancel the production of hydroxyls connected with the weathering of anorthite. The dissolution of  $2Al(OH)_4^-$  further consumes protons and produces  $Al^{3+}$  and water under specific values of pH.

The *residence* time of the groundwater reservoirs determine the time available for the weathering reactions. The residence time of groundwater is determined by the rates of recharge, discharge and extraction, as well as by the size of the aquifer. The climatic regime influences the rate of recharge through the variables temperature and vegetation, which together affect the rates of precipitation and evapotranspiration. If there is no surface runoff, the rate of recharge may be calculated as the difference between the rates of precipitation and evapotranspiration. The rate of recharge increases with the hydraulic conductivity of the soil, which depends on soil texture and water content. The rates of recharge and discharge depends on the relief of the region, on the physical location of the aquifer, and on whether it is confined or unconfined.

The residence time of groundwater is also a measure of the reversibility of changes that occur in the chemical composition. The shorter the residence time, the faster the chemistry of groundwater reacts to the composition of the recharge and the more reversible are the changes in the chemical composition of groundwater.

On the basis of the discussion above concerning the transport and the transformation processes, it may be concluded that the deposition of acidifying substances originating from sulfuric and nitric compounds may contribute significantly to changes in the concentrations in groundwater, if the external load is high in comparison to the internal production of protons. Furthermore, the most probable impact on the concentrations in groundwater may be classified as follows.

1. *Surficial* groundwater table, *highly* permeable overburden, *slowly* weatherable bedrock and *short* residence time of groundwater may imply increasing trends of *hydrogen* ion concentration.
2. *Surficial* groundwater table, *highly* permeable overburden, *highly* weatherable bedrock and *short* residence time of groundwater may imply increasing trends of cations originating from the mineral structure (*calcium, magnesium, sodium, potassium*).
3. *Surficial* groundwater table and *granitic* bedrock may imply increasing trends of *aluminum*.
4. *Deep* groundwater table and *long* residence times of groundwater may imply that the deposition of acidic substances will have *no impact* of the concentrations in groundwater.
5. *Short* residence times of groundwater may imply that changes that occur in the chemical composition of groundwater are well *reversible*.

#### **4. MODELING THE IMPACT OF ACID DEPOSITION ON SOIL-WATER SYSTEMS**

The need for predicting the development of groundwater and soil under the influence of acidic deposition has initiated a number of modeling efforts. Structural models, based on physical and geochemical principles, have been developed for locally defined soil sites and catchments (Reuss, 1980; Arp, 1983; Booty and Kramer, 1984, Christophersen et al., 1984; Bergström et al., 1985; Cosby et al., 1985a,b; Gherini et al., 1985; Holmberg et al., 1985). Few models of regional acidification exist, exceptions being those developed by Kauppi *et al.* (1985) and Kämäri *et al.* (1985).

Another approach to assessing the impact of acid deposition on soil-water systems, besides simulating actual concentrations of elements in the soil and water, is to evaluate the regional potential for acidification on the basis of a sensitivity analysis. Work on mapping the sensitivity of soils and groundwater to acidification has been reported by several authors (Bache, 1980; McFee, 1980; Norton, 1980; Peterson, 1980; Jacks and Knutsson, 1982; Axelson and Karlqvist, 1984).

##### **4.1. Structural Models**

Structural simulation models of acidification describe geochemical and physical processes which cause some crucial variables to change with time. The mechanisms of soil processes are often well known and the main problem related to modeling lies in the quantification of the rates of the processes. The structural models are expressed as differential equations, describing the change per unit time in the state variables or as algebraic equations, describing equilibrium reactions. Their mathematical representations show various degrees of synthesizing, or lumping, depending on the need to

differentiate the dynamics of separate processes and variables within the system.

With the objective of keeping a low level of lumping, i.e. obtaining a high level of differentiating, one may argue that information on the three-dimensional distributions of the following variables is needed in order to simulate the impact of acid deposition on groundwater : 1) cation exchange capacity, 2) weathering rate 3) permeability and 4) depth of groundwater table. This data is presently not available on a regional scale.

A conceivable synthesizing strategy would be to lump the vertical distributions of the cation exchange capacity and the weathering rate. In analogy with Kauppi *et al.* (1985), these parameter values could be considered static in certain compartments of the vertical soil and subsoil profile. The problem of simulating the mixing and horizontal flow in the saturated zone might be approached through a system of linked reservoirs, in analogy with Christophersen and Wright (1981) and Gherini *et al.* (1985). Such detailed calculations on the European scale would, however, require considerable computer resources.

In the following, references are made to work on modeling the impact of acid deposition on specific soil sites and small catchments. Reuss (1980) developed a model for predicting the most likely effect of acid precipitation on the leaching of cations from noncalcareous soils. The model is based on equilibrium between solution ions and sorbed ions and describes sulfate adsorption and reactions involving hydrogen and calcium, bicarbonate and aluminum.

Christophersen and Wright (1981) developed a model for analyzing the sulfate budget of the Birkenes-catchment in southern Norway. The hydrological part of the model is a lumped two-reservoir approach, which simulates infiltration to top soil, subsurface flow to deeper layers of soil and discharge to the stream. Later, this model was extended to include the dynamics of hydrogen ions, calcium, magnesium and aluminum in the catchment (Christophersen et al. 1982). These models, as well as a further extended model, which includes sulfate chemistry in snowpack and soil, applied to the catchment of Storgama (Christophersen et al. 1984), appear very well suited for simulating subsurface flow in a small catchment and for interpreting the extensive data associated with the catchment budgets.

Arp (1983) modeled the losses of hydrogen, aluminum, iron, sodium, potassium, magnesium and calcium from soils under a constant inflow of hydrogen ions. The calculations are based on the assumption that cations are retained in the soil following an adsorption isotherm. The simulations were verified to agree rather well with experimental results (Arp and Ramnarina, 1983).

Booy and Kramer (1984) developed a model for the simulation of water and hydrogen ion flow through a forested catchment. They used a linear diffusion equation to describe groundwater flow and included evaporation, percolation, cation exchange and mineral weathering in the soil. They concluded that the key parameters that control the rate of acidification of a catchment, besides the actual acid loading rates, are the ratio of infiltration to percolation, soil depth and the acid neutralizing capacity of the soil horizons (Booy and Kramer, 1984).

A mathematical model describing quantitatively anion retention, cation exchange, primary mineral weathering, aluminum dissolution and  $CO_2$  solubility has been developed by Cosby et al. (1985a, 1985b). Equilibrium equations are used to account for the cation exchange reactions and the inorganic aluminum and carbon reactions. These equations are linked to dynamic equations based on input-output mass balances of the major ions in deposition, to provide for the long-term temporal development of the response of the catchment to changes in atmospheric deposition. Cosby et al. (1985b) have applied the model to a small forested catchment in Virginia, reconstructing historical changes in surface water quality for the last 140 years, and forecasting future water quality under three different deposition scenarios.

Bergström et al. (1985) developed models for the simulation of natural short-term variations in alkalinity and pH in running waters. The hydrochemical processes are modeled in a semiempirical way without the assumption of a complete hydrochemical mass balance. The dynamics of the models are governed by simple hydrochemical subroutines with a few coefficients which are found by calibration for a given basin. The hydrological part uses daily totals of precipitation and daily mean temperature for the calculation of the groundwater level. The models can be used to detect long term changes in the acid status of surface waters from short term natural variations, but they are not intended to simulate the impact of changes in deposition.

A structural model of transport and local processes in forest soil that influence the temporal development of the vertical distribution of water and solutes in the soil, has been developed by the author (Holmberg et al.,

1985). The model uses experimentally determined values for the vertical distribution of the cation exchange capacity at different soil sites. A lumped version of this model has been used in estimating the impact of acid deposition on the productivity of Finnish forests up to the year 2040 (Hari and Raunemaa, 1985). The simulation results have not yet been checked against historical records.

In the scope of the Integrated Lake-Watershed Acidification Study, Gherini et al. (1985) developed a model to predict changes in surface water acidity as a response to changes in the deposition. The model was applied to two geologically different basins in the Adirondack Mountains. The model calculated flow through canopy, soil, streams and lakes on the basis of hydraulic gradients. Physical and chemical processes were simulated by dynamic and equilibrium expressions accounting for the mass transfers between gaseous, liquid and solid phases.

Few dynamic models exist on a regional scale. Exceptions are the soil acidification model by Kauppi et al. (1985) and the lake acidification model by Kämäri et al. (1985). The soil acidification model by Kauppi et al. (1985) is based on the assumption that the incoming acid flow diminishes the base saturation and affects the aluminum solubility.

Kämäri et al. (1985) have developed a dynamic model for the simulation of regional acidification of surface waters. The model is a submodule in the IIASA Acid Rain Model. The IIASA soil acidity model (Kauppi et al., 1985) takes account of soil solution chemistry. The convective flows of ions from top soil to deeper zones of soil and to surface waters are estimated with a four-reservoir lumped hydrological submodule, based on the Birkenes model by Christophersen and Wright (1981). The freshwater acidification model



has been applied to individual catchments in southern Finland (Kämäri et al. 1985). It appears well suited for the description of regional changes in surface water chemistry.

#### **4.2. Sensitivity Analysis**

The sensitivity of an ecological system to variations in certain driving functions is a measure of the system's response to those variations. The response of an ecological system is the change in the values of the state variables, incited by changes in the driving functions. Apart from the driving functions, certain physical system characteristics, or sensitivity indicators, determine the amplitude of the response and the response time of the system. The sensitivity of an ecological system may be defined to increase with the amplitude of the response. If the sensitivity indicators are chosen such that they are independent of time and of the driving functions, it is possible to differentiate between the impact of physical characteristics on the one hand and the temporal development of the driving functions on the other hand.

The response time of a system with respect to a certain process is an indicator of the reversibility of that process. If a system reacts very slowly to the driving functions, i.e. if the system is highly inert, changes that occur in the state variables are hardly reversible. In assessing the anthropogenic impact on ecological systems, both the sensitivity and the inertia of the systems are taken into account. In the long run, a highly sensitive system is worse off if it is also very inert, whereas a quickly reacting system may represent the worst case in the short run. The best case with respect to environmental damage, is an inert system with low sensitivity to changes

in the driving functions. An assessment on the basis of sensitivity and inertia, is necessarily qualitative in nature. This is partly an advantage, as the inherent uncertainties are not concealed in quantitative calculations.

With the objective of assessing the impact of acid deposition on groundwater on a regional scale, an alternative to simulating actual chemical concentrations in the groundwater would be to evaluate the sensitivity to acidification and the reversibility of the acidification of groundwater. A set of regional indicators may include the type of bedrock (mineral composition, weathering rate), the type of overburden (depth, permeability, cation exchange capacity), the type of aquifer (residence time, activity) and climatic conditions (precipitation, evapotranspiration). A temporal evaluation of the impact of acid deposition may then be performed by combining the static sensitivity map with simulations of the dynamics of top soil.

In the following, some work on the sensitivity of soils and groundwater is cited from the literature. In most cases, no distinction has been made between the static sensitivity and the properties which change with time due to acid deposition. This is quite appropriate, if the objective is to provide an analysis of the situation at a certain fixed time, and not to assess the impact of various future deposition patterns.

The sensitivity of soils to acidification has been studied by several authors (Bache, 1980; McFee, 1980; Peterson, 1980). Indicators of sensitivity in these studies include the total cation exchange capacity of the soil, the base saturation, the carbonate content of the mineral fraction and the hydrological conditions of the soil.

The sensitivity of groundwater has been studied both in the case of local pollutants (Aust, 1983; Haertle 1983; Schenk, 1983; Suais-Parascandola and Albinet, 1983) and in the case of long range transport of acidifying substances (Norton, 1980; Axelsson and Karlqvist, 1984).

Aust (1983) has developed sensitivity maps for the groundwater resources of the Federal Republic of Germany. The sensitivity is classified on the basis of the aquifer type, the kind of mineral structure the percolating water is in contact with and the depth of the overburden. Schenk (1983) discusses the problems of relating the German hydrochemical maps to time and points out the importance of complementing knowledge of the anthropogenical and geological impact on groundwater quality with knowledge of the actual development of the quality with time. The French approach of the mapping of groundwater sensitivity is commented by Suais-Parascandola and Albinet (1983). It is a qualitative evaluation of the risk of groundwater pollution in different areas, based on the aptitude of local pollutants to be transported to the aquifers, coupled with assessments of the consequences of polluted groundwater.

Norton (1980) identified meteorology, pedology and geology as the major characteristics of the landscape which render an area susceptible to the impact of acid precipitation. He classified the geology of the bedrock in four categories on the basis of the buffering capacity and produced maps of some states in Eastern U.S., showing geologic boundaries according to this classification. In some instances, areas of bedrocks in the two classes with low buffering capacity have been found to show acidification of surface waters (Norton, 1980).

Axelsson and Karlqvist (1984) developed models for analyzing the sensitivity of superficial groundwater to acidification. The sensitivity indicators used were weathering ability of the bedrock, soil texture, soil type, lime content of the soil, the amount of runoff and the type of relief of the area. The total sensitivity of an area was calculated as the weighted sum of the values of the indicators. The weighting coefficients were chosen to reflect the observed acidification in different sites.

Their work was part of an extensive study of the sensitivity of Swedish groundwater to acidification, carried out at the Royal Institute of Technology, as reported by Jacks and Knutsson (1982). Large data bases of groundwater composition in Sweden were compiled.

## **5. SUMMARY**

A brief survey of the literature concerning mechanisms and observations of the acidification of soil-water systems indicates that increasing trends of deposition of nitric and sulfuric compounds would have an impact on the concentrations of elements in groundwater in regions characterized by surficial groundwater tables and short residence times. If the overburden is highly permeable and the bedrock slowly weatherable, the groundwater is likely to show increasing trends of hydrogen ions. If, on the other hand, the overburden is poorly permeable or the bedrock easily weathered, the groundwater is more likely to show increasing trends of cations originating from the mineral structure (calcium, magnesium, potassium, aluminum). Areas with long groundwater residence times react more slowly to changes in the deposition. Damage, once occurred is also not so easily reversible in such areas.

The probability of future energy pathways and corresponding patterns of deposition of acidifying substances is not addressed in this report. Several models of the impact of acid deposition on soil are documented in the literature; some of which are referred to in this report. Such models could be extended to simulate weathering and transport in the saturated zone as well. In order to predict quantitatively the impact on groundwater quality on a regional scale, very detailed spatial distributions of geological, pedological and hydrological characteristics are required. These are to date not available. Furthermore, a simulation of the three dimensional flows in the saturated zone is not feasible on a regional scale. An approach, based on the sensitivity of groundwater aquifers, is proposed as an alternative to dynamic modeling. The regional sensitivity of groundwater to acidification could be combined with a regional simulation of the impact of acid deposition on the leaching of elements from top soil.

## APPENDIX: MATHEMATICAL FORMULATION OF TRANSPORT

Assuming that the solid soil matrix is a physically homogenous system of pores and particles, diffusion equations based on Fick's law and mass conservation can be used to describe diffusive flow of elements in the soil. The equations have been compiled and modified to a uniform notation from Hillel (1971) and Greenland and Hayes (1981).

The following notation is used :  $x, y, z$  for the spatial coordinates,  $t$  for time,  $\theta(x, y, z, t)$  ( $m^3 m^{-3}$ ) for the volumetric water content,  $\theta_a(x, y, z, t)$  ( $m^3 m^{-3}$ ) for the volumetric air content,  $M(x, y, z, t)$  ( $mol m^{-3}$ ) for the volumetric element content in the liquid phase,  $M_g(x, y, z, t)$  ( $mol m^{-3}$ ) for the volumetric element content in the gaseous phase,  $q(x, y, z, t)$  ( $m^3 m^{-2} s^{-1}$ ) for the water flow,  $q_s(x, y, z, t)$  ( $mol m^{-2} s^{-1}$ ) for the flow of solutes,  $q_a(x, y, z, t)$  ( $m^3 m^{-2} s^{-1}$ ) for the air flow,  $q_g(x, y, z, t)$  ( $mol m^{-2} s^{-1}$ ) for the flow of gas,  $D(\theta)$  ( $m^2 s^{-1}$ ) for the hydraulic diffusivity,  $D_s(M, \theta)$  ( $m^2 s^{-1}$ )

for the solute diffusivity,  $D_g(M_g, \Theta_a, T, P)$  ( $m^2s^{-1}$ ) for the gas diffusivity and  $K(\Theta)$  ( $ms^{-1}$ ) for the hydraulic conductivity. The notation  $\nabla f(\cdot)$  stands for the total spatial derivative or the gradient of the function in question,  $\nabla f(\cdot) = \delta f(\cdot) / \delta x + \delta f(\cdot) / \delta y + \delta f(\cdot) / \delta z$ .

In the equations the functions  $f(\Theta)$ ,  $s(M)$ ,  $g(\Theta_a)$ ,  $h(M_g)$  are sources and sinks that represent the phase transition processes and the exchange of solute and gas between the system and its environment - atmosphere, vegetation. The flow of elements in the liquid phase depends on the flow of water and the equations take the following form:

Water flow :

$$\begin{aligned}\delta \Theta / \delta t &= -\nabla q + f(\Theta) \\ q &= -D \nabla \Theta + K\end{aligned}$$

Solute flow :

$$\begin{aligned}\delta M / \delta t &= -\nabla q_s + s(M) \\ q_s &= -D_s \nabla M + q M / \Theta\end{aligned}$$

The flow of elements in the gaseous phase depends on the flow of air as follows:

Air flow :

$$\begin{aligned}\delta \Theta_a / \delta t &= -\nabla q_a + g(\Theta_a) \\ q_a &= -D_a \nabla \Theta_a\end{aligned}$$

Gas flow :

$$\begin{aligned}\delta M_g / \delta t &= -\nabla q_g + h(M_g) \\ q_g &= -D_g \nabla M_g + q_a M_g / \Theta_a\end{aligned}$$

In the following table theoretical and measured values of the diffusion coefficients are compiled.

Table 1A. Values of transport coefficients

Diffusion	$cm^2s^{-1}$
In air ( $0^{\circ}C$ ):	
$O_2$	0.18
$CO_2$	0.13
In water:	
$O_2, CO_2$	$0.1 \times 10^{-4}$
$K^+$	$1.35 \times 10^{-5}$
$Ca^{2+}$	$0.78 \times 10^{-5}$
$NO_3^-$	$1.92 \times 10^{-5}$
$SO_4^{2-}$	$1.08 \times 10^{-5}$
In soil solution	
$K^+$	$1.71-3.68 \times 10^{-7}$
$Ca^{2+}$	$3.28 \times 10^{-7}$
Sources : Wild (1981) and Kuntze et al. (1983)	



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