5   Soil and Soil Solution Chemistry

JAN MULDER AND MALCOLM S. CRESSER

5.1   SOIL CHEMICAL REACTIONS

5.1.1   INTRODUCTION

Biogeochemical processes in the terrestrial environment dominate the hydrochemical response of small catchments, because streamwater is largely made up of drainage water from soils. Biogeochemical processes can be categorized into three major groups (Table 5.1.; cf. van Breemen et al., 1983):

1. Biochemical processes, including interactions between biota and the atmosphere (e.g. photosynthesis, respiration, N_2 fixation), and interactions between biota and soil solution (e.g. assimilation and mineralization).
2. Geochemical and soil chemical processes, including interactions between solution and the soil solid phase (e.g. cation exchange, adsorption, chemical weathering).
3. Chemical reactions in solution (e.g. hydrolysis, complexation reactions) or between solution and atmosphere (e.g. degassing of CO_2).

Processes from all three categories modify the chemical composition of infiltration water. For all major solutes the quantitative importance of individual biogeochemical processes has been estimated from input–output budgets and net assimilation rates (e.g. Driscoll and Likens, 1982; van Breemen et al., 1984; Nilsson, 1985; Binkley and Richter, 1987; Lelong et al., 1988).

In this chapter we will focus on soil chemical reactions (i.e. categories 2 and 3), and how they may affect concentrations of macro-solutes in streamwater. Besides a brief presentation of the theory of the dominant soil chemical processes and the spatial and temporal patterns of soil chemical reactions and parameters, some examples of anthropogenic impacts on soil chemistry and subsequent recovery of the soils will be discussed. This chapter will conclude with a method section, dealing with sampling and analysis of soils and soil solutions. Aspects of the chemistry of trace metals in soils will be discussed in Chapter 13.

As indicated in Table 5.1, several biogeochemical processes involve the transfer of H^+ ions, thus affecting the acid–base chemistry of soils and soil water. Net H^+ (proton) transfer may be calculated from quantitative estimates of individual chemical processes. By accounting for all proton sources and sinks a proton bud-

Table 5.1 Reaction equations of H^+ transfer processes and related processes involving biota (after van Breemen et al., 1983)

Processes from left to right	Reaction equation		Processes from right to left
	H^+ – indifferent processes		
	Biota/atmosphere		
Photosynthesis	$CO_2 + H_2O$	$= CH_2O + O_2$	Respiration
N_2-fixation	$N_2 + H_2O + 2R.OH$	$= 2R . NH_2^+ + \frac{1}{2} O_2$	
NH_3-uptake	$NH_3 + R.OH$	$= R.NH_2 + H_2O$	Volatilization of NH_3
H_2S-uptake	$H_2S + R.OH$	$= R.SH + H_2O$	Volatilization of H_2S
SO_2-uptake	$SO_2 + R.OH$	$= R.SH + \frac{3}{2} O_2$	
H^+ - source	*H^+ – transfer*		*H^+ – sink*
	Biota/solution		
Uptake of cations	$M^+ + ROOH$	$= ROOM + H^+$	Mineralization of M^+
Uptake of NH_4^+	$NH_4 + R.OH$	$= R.NH^2 + H_2O + H^+$	Mineralization of org. N
Mineralization + nitrification of organic N	$R.NH_2 + 2O_2$	$= 2.OH + NO3- + H^+$	Uptake of NO_3^-
Mineralization + oxidation of organic S	$R.SH + \frac{1}{2}H_2O + \frac{1}{4} O_2$	$= R.OH + SO_4^{2-} + 2H^+$	Uptake of SO_4^{2-}
Mineralization of P	$R.H_2PO_4 + H_2O$	$= R.OH + H_2PO_4^- + H^+$	Uptake of P
	Solution or solution/atmosphere		
Dissociation of H_2O	$2H_2O$	$= OH^- + H^+$	Protonation of OH^-
Dissociation of CO_2	$CO_2 + H_2O$	$= HCO_3^- + H^+$	Protonation of HCO_3^-

Table 5.1 (*continued*)

Processes from left to right	Reaction equation		Processesfrom t right to lef
	Solution or solution/atmosphere (continued)		
Dissociation of organic acids	$ROOH$	$= ROO^- + H^+$	Protonation of organic anions
Complexation of metal ions L = organic ligand or OH⁻	$HL + M^+$	$= ML + H^+$	Decomplexation of metal ions
Oxidation of H_2S	$H_2S + 2O_2$	$= SO_4^{2-} + 2H^+$	Sulphate reduction
Oxidation of SO_2	$SO_2 + \tfrac{1}{2}O_2 + H_2O$	$= SO_4^{2-} + 2H^+$	
Nitrification of NH_4^+	$NH_4^+ + 2O_2$	$= NO_3^- + H_2O + 2H^+$	
Nitrification of NO_x	$NO_x + \tfrac{1}{4}(5 - 2x)O_2 + \tfrac{1}{2} H_2O$	$= NO_3^- + H^+$	Denitrification
Nitrification of N_2	$N_2 + \tfrac{5}{2}O_2 + H_2O$	$= 2NO_3^- + 2H^+$	Denitrification
	Solids/solution		
Reverse weathering	$M^{n+} + n/2 \, H_2O$	$= n_{/2} M_{2/n}O + nH^+$	Weathering
M^{n+}/H^+ exchange	$M^{n+} + n\text{H.exch}$	$= \text{M.exch} + nH^+$	H^+/M^{n+} exchange
Oxidation of Fe2	$Fe^{2+} + \tfrac{1}{4}O_2 + \tfrac{5}{2}H_2O$	$= Fe(OH)_3 + 2H^+$	Reduction of $Fe(OH)_3$
Oxidation of FeS	$FeS + \tfrac{9}{2}O_2 + \tfrac{5}{2}H_2O$	$= Fe(OH)_3 + SO_4^{2-} + 2H^+$	Reduction of $Fe(OH)_3$ and SO_4^{2-}
Desorption of SO_4^{2-}	$\text{exch } SO_4^{2-} + 2H_2O$	$= \text{exch } (OH)_2 + SO_4^{2-} + 2H^+$	Adsorption of SO_4^{2-}

get may be constructed. Proton budgets, which express the relative importance of all major sources and sinks of acidity, have been used extensively in acidification research (Driscoll and Likens, 1982; van Breemen *et al.*, 1983). Major sources of protons include CO_2 dissolution in water, cation assimilation, nitrification and atmospheric acid deposition, while major sinks are cation exchange and chemical weathering.

5.1.2   REACTIONS INVOLVING INORGANIC CARBON

In soil solutions dissolved inorganic carbon (DIC) is abundant, and consists of $H_2CO_3^*$ ($CO_2(aq) + H_2CO_3$), HCO_3^- and CO_3^{2-}. The distribution of DIC species in water can be described by equilibrium relationships, where the $H_2CO_3^*$ activity is controlled by the partial pressure of CO_2 in the atmosphere (pCO_2):

$$-\text{Log}(H_2CO_3^*) = 1.46 - \text{Log}(pCO_2) \qquad (5.1)$$

where brackets indicate activity (mol l^{-1}), and pCO_2 is in atm.
    Dissociation of carbonic acid depends on pH and can be described as (Bolt and Bruggenwert, 1976):

$$-\text{Log}(HCO_3^-) = 7.81 - \text{Log}(pCO_2) - \text{pH} \qquad (5.2)$$

$$-\text{Log}(CO_3^{2-}) = 18.14 - \text{Log}(pCO_2) - 2\text{pH} \qquad (5.3)$$

    For systems open to the atmosphere, pCO_2 is *c.* 3×10^{-4} atm. However, in soils pCO_2 (ranging from 10^{-2} to 10^{-1} atm; Bolt and Bruggenwert, 1976) is generally higher, due to respiration and oxidation of below-ground organic matter. Consequently, DIC concentrations tend to be higher in soil solutions than in surface water. Degassing of CO_2 is common when soil water emerges (Reuss and Johnson, 1986).
    Carbon dioxide, dissolved in soil water, may react with minerals (including feldspars and calcite) according to:

$$n/2M_{2/n}O + nCO_2 + n/2H_2O \longleftrightarrow M^{n+} + nHCO_3^- \qquad (5.4)$$

generally resulting in soil solution pH values well above 6. Most natural freshwaters are in this carbonic acid buffer range (Stumm and Morgan, 1981).
    The presence of dissociated carbonic acid in water gives rise to alkalinity (Alk), where Alk is the equivalent sum of bases that are titratable with strong acid:

$$[\text{Alk}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (5.5)$$

with brackets indicating concentrations in mol l^{-1}. Alkalinity is also known as the acid neutralizing capacity (ANC). The equivalence point of the acidimetric titration (around pH 4.5) represents an approximate threshold below which most life

processes in natural waters are seriously impaired. Thus alkalinity is a convenient measure for estimating the maximum capacity of a natural water to neutralize acidity without permitting extreme disturbance of biological activities in the water (Stumm and Morgan, 1981).

In very dilute natural solutions (e.g. in acidic soils) DIC and therefore [Alk] in Equation (5.5) are low. In such systems additional protolytic systems (of which hydrolysed Al compounds and natural weak organic acids are the most prominent), may contribute to alkalinity. Assuming that at the equivalence point of the alkalinity titration Al is present as $Al(OH)^{2+}$ (Sullivan *et al.*, 1989) the definition of alkalinity becomes:

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$
$$+ [RCOO^-] + 2[Al(OH)_2^+] + 4[Al(OH)_4^-] - [H^+] \qquad (5.6)$$

with $[RCOO^-]$ representing the concentration of organic anions.

Alkalinity is a conservative parameter, i.e. it is pressure and temperature independent. For example, degassing of CO_2 results in the removal of equivalent amounts of H^+ and HCO_3^- from solution, thus causing no change in [Alk] in Equations (5.5) and (5.6). By contrast, degassing of CO_2 may result in a significant increase in solution pH, particularly in solutions with positive alkalinity (Reuss and Johnson, 1986; Suarez, 1987). Degassing in solutions with a negative alkalinity (i.e. solutions where strong mineral acids dominate) will have little or no effect on pH, however.

5.1.3   REACTIONS INVOLVING ORGANIC CARBON

Soil organic matter (SOM) can be subdivided into non-humified and humified material. Non-humified substances are not or are only slightly altered after decay of tissue from living organisms and include, e.g. carbohydrates, amino acids, protein, lignin, hormones and low molecular weight organic acids (Tan, 1986). Humified substances are decomposition products of non-humified constituents and include complex compounds such as humin, fulvic acid (FA), hymatomelanic acid, humic acid (HA) and their hydroxybenzoic acid derivatives (Tan, 1986).

The concentrations of non-humified organic acids are generally low and many of these acids can only be detected by thin layer or gas chromatography. Nevertheless, with their rapid turnover, low molecular weight organic acids may play a significant role in mineral weathering. In most soils the contents of HA and FA are considerably higher than those of the non-humified organic acids. The major reason for the importance of FA and HA in soil chemistry is the presence and position of functional groups (particularly carboxyl and phenolic hydroxyl groups), which make FA and HA effective in cation exchange and complexation reactions (Tan, 1986). Charge characteristics of humic substances depend upon the extent of dissociation of the functional groups. At pH < 3 HA and FA behave as

uncharged polymers, whereas at pH > 3 they behave as negatively charged poly-
electrolytes, due to dissociation of carboxyl groups (3 < pH < 9) and phenolic
hydroxyl groups (pH > 9) (Tate and Theng, 1980).

Fulvic and humic acids may form metal complexes of high stability through
chelation, where metal ions are bound as bidentate e.g. by carboxyl and phenolic
hydroxyl groups. Chelation promotes the dissolution of metals from soil minerals.
For example, in podzols chelation of Al and Fe in the surface mineral soil and sub-
sequent leaching eventually result in Al and Fe depleted eluvial (E) horizons. The
solubility of chelates decreases with increasing sesquioxide content, however, thus
resulting in precipitation in the illuvial (podzol B) horizon.

In soils, DOC concentrations decrease sharply from several tens of mg l^{-1} in the
O and E horizons to only a few mg l^{-1} in the mineral soil (e.g. McDowell and
Wood, 1984; Cronan and Aiken, 1985). Besides physicochemical sorption and pre-
cipitation, this decrease in DOC is likely due to mineralization.

As indicated in Section 5.1.2, DOC may contribute to the alkalinity of soil solu-
tions and surface waters. On the average, organic acids in natural water contribute
5 to 10 µeq of anionic charge per mg DOC. To estimate the anionic charge associ-
ated with DOC in individual samples the empirical model by Oliver et al. (1983)
has frequently been used (e.g. Driscoll et al., 1989a). Alternatively, Cronan and
Aiken (1985) and Schecher and Driscoll (1987) used analogues of monoprotic,
diprotic and triprotic acids with optimized dissociation constants. Recently,
Tipping et al. (1988) proposed a deterministic model which treats organic acids as
macroions, where interactions are modelled in terms of discrete binding sites. This
model accounts for electrostatic (macroionic) effects which depend upon molecu-
lar charge (determined by the bound cations) and ionic strength.

Because soil organic matter is a major source of negative charge in many soils it
acts as an important cation exchanger, which may represent a significant chemical
buffer (e.g. the forest floor; James and Riha, 1986). In addition, soil organic matter
may complex trace metals (e.g. Al), thus reducing phytotoxic effects (e.g. Bloom
et al., 1979). Soil organic matter is also important as a store for N and S, which
may be liberated slowly upon decay.

5.1.4   CATION EXCHANGE REACTIONS

In many soils the solid phase carries a net negative surface charge. For clay miner-
als this charge is a result of isomorphous substitution, where structural cations of
higher valence are replaced by cations of lower valence (e.g. Si^{4+} is replaced by
Al^{3+}). As a result, clay minerals have a permanent negative surface charge.

Oxides and SOM also have charged surfaces: With increasing pH (i.e. increas-
ing activity of OH^{-} ions) H^{+} is dissociated from oxide surfaces or from organic
functional groups, thus resulting in a negative charge. Because dissociation
increases with pH and ionic strength, such charge is termed variable charge.

At low pH values oxides may bind H^{+}, which results in a positive surface
charge. The pH values at which positively charged groups quantitatively equal

negatively charged groups (i.e. the net surface charge is zero) are called zero point of charge (ZPC).

In soils the overall electroneutrality is maintained by an excess of electrostatically attracted counterions in proximity to the charged surface. In the case of negatively charged surfaces a diffuse double layer will result where cations are in excess of anions. The excess ions, termed exchangeable cations (anions) may, by definition, be exchanged with neutral salts. The quantity of exchangeable cations (in meq kg^{-1} dry soil) is defined as the cation exchange capacity (CEC). Similarly the total amount of exchangeable anions is defined as the anion exchange capacity (AEC). In most soils the AEC is quantitatively far less important than the CEC.

Exchangeable cations are available to plants, for example through exchange with H^+ liberated by the roots. Exchange reactions are also responsible for the retention of freshly introduced cations into the soil solution. In this way the CEC gives the soil a buffering capacity, which may slow down the leaching of nutrient cations and positively charged pollutants.

Since cation exchange is a relatively fast process it modifies the chemical composition of infiltration water. The exchange reaction of cations M and N, with a charge of m^+ and n^+, respectively, may be represented as:

$$\text{Ads-N}_m + n\text{M}^{m+} \rightleftharpoons \text{Ads-M}_n + m\text{N}^{n+} \tag{5.7}$$

Mathematically this reaction has been described by the Gapon equation:

$$\{\text{Ads(M)}/\text{Ads(N)}\} = K_{NM}g \times \{(M^{m+})^{1/m}/(N^{n+})^{1/n}\} \tag{5.8}$$

with the left-hand side being the ratio of adsorbed M over N (both in meq per mass unit exchanger). The right-hand side contains the reduced activity ratio, where the cation activities are raised to a power equal to the reciprocal of their valence. $K_{NM}g$ in this equation represents the (Gapon) selectivity constant, which should be constant over a wide range of conditions. The selectivity constant differs from one, because small size (hydrated) ions are generally preferred over large ones (high K_{NM}), due to their smaller distance of approach of the charged surface. Also the surface structure of the exchanger may affect the selectivity constant (e.g. in case of a porous exchanger, where the binding may be determined by the "naked" cation; Bolt and Bruggenwert, 1976).

Alternative mathematical descriptions of cation exchange reactions have been proposed (e.g. the Vanselow equation), but most frequently used in hydrochemical models for small catchments is the Gaines-Thomas equation:

$$\{\text{Ads(M)}^n/\text{Ads(N)}^m\} = K_{NM}gt \times \{(M^{m+})^n/(N^{n+})^m\} \tag{5.9}$$

Also here Ads(M) and Ads(N) are adsorbed amounts of M^{m+} and N^{n+} in meq per mass unit exchanger. The three different formulations have been compared by Reuss (1983).

Note that all three exchange equations were developed for a constant capacity (permanent charge) exchanger. This implies that if the change in cation exchange complex composition is small compared to the total store of exchangeable cations (which is generally the case, particularly in the short run) the adsorbed ion ratio $\text{Ads}(N)^m/\text{Ads}(M)^n$ remains constant and hence the solution ratio $(N^{n+})^m/(M^{m+})^n$ also remains constant. For Al^{3+}-Na^+ exchange this would suggest a cubic relationship in solution, whereas for Ca^{2+}-Na^+ exchange this relationship is expected to be squared (Reuss and Johnson, 1986; Neal et al., 1990).

However, in situ soil solution data from a great number of sites in Wales, Scotland and Norway show that cation concentrations are poorly predicted by the cation exchange equations given above (Neal et al., 1990). Possibly, application of a variable-charge instead of a permanent-charge exchanger model improves the quality of the predictions. A variable-charge cation exchange model (similar to the one already discussed for DOC) was recently proposed by Tipping and Hurley (1988).

5.1.5   SULPHATE TRANSPORT AND ADSORPTION

Oxidation of reduced S (e.g. pyrite), and atmospheric deposition of S compounds are the predominant sources of sulphate in most natural soils. Atmospheric S may be of anthropogenic (e.g. SO_2 due to burning of fossil fuels), and of natural origin (e.g. SO_2 due to volcanic activity, SO_4^{2-} in sea spray aerosol, gaseous biogenic S). Most S inputs are eventually transformed into H_2SO_4, and may acidify soil and water. Only S in seaspray is accompanied by base cations and is not acidifying. In coastal areas the acidifying potential of the atmospherically derived sulphate (often termed excess SO_4^{2-}) is estimated by subtracting seaspray S from the total S deposition.

The acidifying potential of H_2SO_4 in soils is largely determined by sulphate adsorption. Particularly, Al and Fe oxide surfaces have been reported to be major adsorption sites for soil solution SO_4 (Fuller et al., 1987; Mitchell et al., 1989). Adsorption of sulphate results in displacement of -OH° ligands from oxides:

$$\text{Oxide-OH}^{\circ} + SO_4^{2-} \rightleftharpoons \text{Oxide-SO}_4^- + OH^- \qquad (5.10)$$

where OH^- is released and a cation exchange site is created (Rajan, 1978; Parfitt and Smart, 1978). Alternatively SO_4 adsorption may result in the displacement of an -OH_2^+ ligand from the oxide:

$$\text{Oxide-OH}_2^+ + SO_4^{2-} \rightleftharpoons \text{Oxide-SO}_4^- + H_2O \qquad (5.11)$$

where water is released and the site changes from positively to negatively charged. Both mechanisms result in an increased cation exchange capacity, so that adsorption of sulphate and cations occurs simultaneously (Mitchell et al., 1992). At low pH a simple ligand exchange has been shown where two adjacent -OH ligands are

replaced by one SO_4^{2-} (Rajan, 1978). Most studies indicate that SO_4 binds more weakly to oxide surfaces than PO_4, but much more strongly than NO_3 and Cl (Marsh *et al.*, 1987).

Sulphate adsorption increases with decreasing pH (Chao *et al.*, 1962; Nodvin *et al.*, 1986b; Fuller *et al.*, 1987). This pH-dependent adsorption probably results from the amphoteric character of the adsorption sites on oxide surfaces, which become negatively charged upon deprotonation, thus causing anion repulsion. The adsorption of sulphate is negatively affected by the presence of organic matter, even in soils where the contents of Al and Fe oxides are high (e.g. podzol B horizons; Johnson and Todd, 1983). This reduction in sulphate adsorption has been hypothesized to be the result of blocking of the sites by organic matter.

Sulphate adsorption is generally considered a reversible process and is frequently described by a Langmuir isotherm (e.g. Cosby *et al.*, 1985):

$$E_s = E_{mx} \times 2(SO_4^{2-})/\{C + 2(SO_4^{2-})\} \qquad (5.12)$$

where E_s is adsorbed SO_4 (eq kg^{-1}), E_{mx} maximum SO_4 adsorption capacity (eq kg^{-1}), and C the half saturation constant of the adsorption process (eq m^{-3}). Brackets indicate concentration (mol m^{-3}). Note that SO_4 adsorption in Equation (5.12) is not pH dependent. To what extent the assumption of reversibility of SO_4 adsorption is realistic will be discussed in Section 5.3.2.

Recently Nodvin *et al.* (1986a) developed the initial mass isotherm to describe adsorption reactions of anions in soils. This isotherm essentially is a simple model partitioning the anion between solid phase and solution.

In some acidic forest soils of northwestern Europe jurbanite ($AlOHSO_4.5H_2O$) has been reported to control the activity of SO_4 and Al (Nilsson and Bergkvist, 1983; Khanna *et al.*, 1987), according to:

$$(Al^{3+}) \times (OH^-) \times (SO_4^{2-}) = K_{SO} \qquad (5.13)$$

where K_{SO} is the solubility product of jurbanite ($10^{-17.8}$; Nordstrom, 1982), and brackets indicate activity (mol l^{-1}).

Microbiological transformations may play a crucial role in S cycling, as illustrated by the general dominance of organic S forms in soils (carbon-bonded S and ester-bonded S; e.g. Mitchell *et al.*, 1992). Particularly in catchments with significant amounts of wetlands, reduction of SO_4 to H_2S and FeS may be an additional important sink for SO_4 (Urban *et al.*, 1987). Biologically mediated transformation processes of S will be discussed in more detail in Chapters 6 and 11.

5.1.6   PHOSPHATE TRANSPORT AND ADSORPTION

Phosphorus, often one of the growth-limiting nutrients, is generally tightly conserved in natural ecosystems (e.g. Wood *et al.*, 1984). Living organisms contribute

significantly to P retention through close coupling of decomposition of organic matter and assimilation. These biological controls on phosphate are dominant in the O horizon and the upper mineral soil layers.

Inorganic P is adsorbed on clay minerals and on Fe and Al oxides as an inner-sphere complex through ligand exchange with -OH surface groups (Goldberg and Sposito, 1985). Adsorption processes largely control soil solution P in horizons high in sesquioxides (e.g. B horizons). The bioavailability of P in such horizons depends on the stability of the oxide–P surface complexes and the presence of ligands that can replace P. Fox et al. (1990) found that the release of both inorganic P and Al from a spodic horizon increased in the presence of simple organic acids that form stable complexes with Al. Overall the Al and P release was found to increase exponentially with increasing Al stability constant (log K_{Al}).

5.1.7   REACTIONS INVOLVING ALUMINIUM

Although Al is one of the most abundant elements in soils, it is not very mobile at the pH values encountered in most soils (i.e. between 6 and 8). The solubility of Al increases in acidic soils (pH <6) and in the presence of complexing ligands (e.g. F^-, SO_4^{2-}, DOC; Driscoll, 1989). In naturally acidic soils dissolved Al is predominantly in an organically complexed form (David and Driscoll, 1984; Driscoll et al., 1985). Introduction of high loads of mineral acidity results in a significant mobilization of inorganic Al, so that it may become the dominant cation in solution (Mulder et al., 1989b). Dissolved Al is potentially toxic to terrestrial biota and has been hypothesized to be one of the major causes of the occurrence of widespread forest decline in central Europe (e.g. Ulrich et al., 1980).

Major sources of dissolved Al include a number of operationally defined pools, such as exchangeable Al, organically bound Al, amorphous Al oxide and crystalline Al oxide (e.g. gibbsite). Unfortunately, fluxes between these (physicochemically poorly defined) pools and solution are unknown. Consequently, our understanding of Al solubility controls in soils is limited and largely based on equilibrium assumptions with respect to a few Al-containing minerals, e.g. gibbsite ($Al(OH)_3$). Gibbsite equilibria may be formulated as:

$$(Al^{3+})/(H^+)^3 = K_{SO} \qquad\qquad (5.14)$$
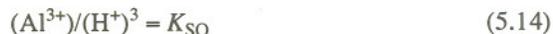
where brackets represent activities. At 25°C the equilibrium constant (K_{SO}) for gibbsite ranges from $10^{8.11}$ (synthetic gibbsite) to $10^{10.80}$ (amorphous $Al(OH)_3$). However, several studies suggest that dissolved Al does not follow gibbsite equilibrium, often not even where gibbsite is present (McMahon and Neal, 1990). Recently, Dahlgren et al. (1989) concluded from column experiments that interlayer Al may control the solubility of this metal in mineral soils. Soil solutions in organic-rich horizons are often undersaturated with respect to gibbsite, and dissolved Al may be controlled by cation exchange (e.g. Bloom et al., 1979; Cronan

et al., 1986), or complexation reactions (Tipping *et al.*, 1988; Mulder *et al.*, 1989a). Some studies in European forest soils suggest an Al solubility control by jurbanite (Equation 5.13).

5.1.8   CHEMICAL WEATHERING

Together with atmospheric input, chemical (and physical) weathering of minerals constitutes the major source of base cations in catchments (Figure 5.1). Liberation of base cations through chemical weathering increases the alkalinity of percolating water (see also Section 5.1.2). The base cation weathering rate and thus the rate of alkalinity production determines the long-term resistance of a soil to acidification (defined as a decrease in pH and base saturation) and is often taken as a measure for the critical load of strong mineral acid to a soil. The critical load is defined here as the maximum strong acid input that can be neutralized without depleting the stores of exchangeable base cations (Nilsson and Grennfelt, 1988). Rates of chemical weathering have been estimated from a combination of input–output budgets and laboratory experiments (see also Chapters 4 and 14).
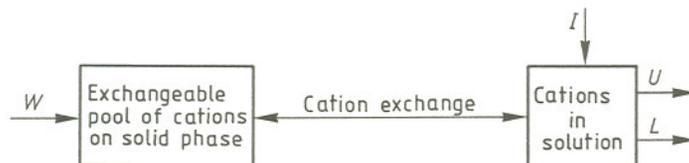
Figure 5.1   Schematic diagram of major base cation fluxes in catchments: W = supply rate of base cations through weathering; I = input rate of base cations from precipitation, dry deposition and mineralization of organic matter; U = biological uptake rate of base cations; L = leaching rate of base cations with drainage water (from Christophersen *et al.*, 1990b; reproduced by permission of Elsevier Science Publishers BV).

5.1.9   NITROGEN TRANSPORT

Biochemical transformations of N in terrestrial ecosystems generally result in a rapid decrease of dissolved NH_4^+ with depth (due to cation exchange, assimilation and nitrification). Nitrogen leaching, if occurring at all, is mostly in the form of NO_3^-. Biochemical aspects of N transformation processes will be further discussed in Chapters 6 and 11.

Nitrogen transformations also affect the acid–base chemistry of soils and soil solutions (see Table 5.1). Enhanced nitrification and leaching of NO_3^- (associated with a cation) results in progressive soil acidification and consequently in a gradual decline of soil pH. As indicated earlier, soil pH is a master variable for many soil chemical reactions.

5.2 SPATIAL AND TEMPORAL VARIABILITY OF THE SOIL

As discussed above, the chemical composition of soil solutions is affected by numerous chemical reactions. Thermodynamic and kinetic constraints involved may vary between soil types and even between soil horizons (layers), because of differences in chemical properties. Therefore, the distribution of soil types is an important factor in the hydrochemical response of catchments. In discussions of soil types we will use the FAO–UNESCO soil classification system (FAO–UNESCO, 1988). In addition to variations in space, soil chemical reactions may also vary temporarily, due to changes in temperature, moisture, biological activity, etc.

5.2.1 HORIZONS: VERTICAL VARIABILITY IN CHEMISTRY

Soil horizons (i.e. layers in the soil, matching a given set of criteria, e.g. FAO–UNESCO, 1988; Soil Survey Staff, 1975) develop as a result of long-term physical, chemical and biological processes. How a soil develops at a specific site depends on the relative importance of various soil-forming factors (i.e. climate, parent material, vegetation and fauna including man, topography, time).

Soil formation often involves transport of specific compounds resulting in depletion in some parts of the profile and enrichment in others. For example, due to the chelating power of percolating fulvic acids, Podzols have a strongly acidified, bleached Al- and Fe-depleted E horizon at the surface. At depth Fe- and Al-chelates precipitate, thus forming a spodic B, enriched in Fe, Al and organic C. At the surface, Podzols often develop a layer of acidic, slowly decomposing raw humus (O horizon). Clearly, the different chemical properties of horizons in Podzols (i.e. pH, CEC, and contents of Fe and Al oxides and soil organic matter) may lead to differences in chemical reactivity.

Other examples of soil formation, resulting in a vertical differentiation of chemical properties include the following:

1. Transport of clay minerals, giving rise to a clay-depleted horizon on top of a clay-enriched (argic B) horizon, as in Luvisols, Acrisols and Alisols.
2. Upward transport (capillary rise) of water and dissolved salts in areas with a high groundwater table and a precipitation deficit may lead to accumulation of salts at or near the surface (calcic, gypsic, natric-B horizon), as in Solonchaks and Solonetzes.
3. Intensive weathering and leaching of Si in the humid tropics may lead to a ferralic horizon, high in residual Fe- and Al-oxides and kaolinite (Ferralsols).
4. Peatlands (Histosols) may form as a result of accumulation (of organic matter, due to incomplete decomposition of plant debris), rather than leaching.

Clearly, thermodynamic equilibria and kinetics of soil chemical reactions may differ per soil horizon. Particularly in catchments with shallow soils and a strongly

fluctuating groundwater table, vertical gradients in soil solution composition may be reflected directly in the chemistry of streamwater, due to variable contributions of soil horizons to lateral transport (Mulder *et al.*, 1990; Easthouse *et al.*, 1992).

Some examples of differences in chemical constraints between various soil horizons are discussed below:

1. Adsorption of SO_4 and PO_4 in Podzols increases in the order Raw humus < E horizon < spodic B, because of the increase in oxide content.
2. Adsorption of SO_4 and PO_4 is generally higher in an argic B (of, e.g. Acrisols) than in a spodic B, due to the lower oxide and higher SOM content of the latter. In ferralic horizons (Ferralsols) the adsorption of SO_4 and PO_4 is even higher. In these variable charge horizons AEC is often even higher than CEC, so that NH_4^+ and K^+ are more mobile than, e.g. SO_4^{2-} and NO_3^- (Sollins *et al.*, 1988).
3. In sandy Podzols the CEC, largely due to SOM, is generally highest in O horizons, where it represents a significant buffer capacity, and decreases sharply in the mineral soil (with a minor peak in the spodic B).
4. In the presence of strong acid the Al mobility in Podzols increases in the order O < E < B horizon.
5. In Podzols of pristine (i.e. unpolluted) areas the alkalinity contributed by the organic and carbonic acid systems changes with depth (Ugolini and Dahlgren, 1987). While organic acids dominate alkalinity in the surface horizons (B horizon and above), this gradually changes with depth into DIC dominated alkalinity (Ugolini and Dahlgren, 1987; Ugolini *et al.*, 1988). This is due to the removal of DOC from solution (due to mineralization and sorption; see Section 5.1.3) and a simultaneous increase in the partial pressure of CO_2 (Bouten *et al.*, 1984).

5.2.2   SOIL TYPES: LATERAL PATTERNS (CATENA)

In many catchments sequences of different soil types (catena) have developed in uniform parent material, due to variation in relief, drainage and vegetation. For example, soils with eluvial (leached) horizons generally develop on hillslopes and summits (e.g. Podzols, Luvisols, Acrisols, Ferralsols), while soils in depressions (e.g. adjacent to the stream) may exhibit gleyic properties or accumulate organic matter (Histosols). Consequently, water infiltrating in hillslopes may have intimate contact with several horizons of different soil types, before emerging into the stream.

In most current hydrochemical models the complexity of soil distribution patterns in catchments is simplified by representing soils by one or more vertically related "boxes" (e.g. surface soil and subsoil). Each of these boxes has "average" soil chemical properties. Catchments having Podzols, for example, on the hillslopes are generally represented by an upper O horizon and a lower B horizon box. Implicitly, chemical modification of laterally moving drainage water from these two horizons in the wetter soils adjacent to the stream is not considered.

However, field evidence suggests that chemical modification of solutions during transport in the terrestrial environment does occur and may be significant (Bishop *et al.*, 1990; Billett and Cresser, 1992; Mulder *et al.*, 1991). Simultaneously, soils in these wet zones may become chemically modified (e.g. increased stores of exchangeable Al, due to Al transport from upslope; Mulder *et al.*, 1991). Ignoring the chemical potential of these wet zones at lower elevations seriously limits the predictive power of hydrochemical models.

Besides physical evidence, additional support for the modification of laterally transported water by gleysoils and Histosols has been obtained from mixing models. For example, Christophersen *et al.* (1990a) found that streamwater at Birkenes (Norway) could largely be explained as a mixture of solutions from upslope O and B horizons and gleysoils in the valley bottom.

5.2.3   TEMPORAL PATTERNS IN SOIL CHEMISTRY

5.2.3.1   Soil solution

The soil solution composition of a given soil horizon may vary considerably through the year, due to (i) a variable composition of infiltration water, (ii) variability in climatic conditions, and (iii) variability in biological activity.

In a recent study conducted over a six year period van Breemen *et al.* (1988) observed strong seasonal changes in the soil solution chemistry of an oak–birch woodland in The Netherlands. Particularly in the growing season nitrification of extreme loadings of atmospheric NH_3 were found to significantly increase the leaching of Al, Ca and Mg. Further increases in concentration were due to evapotranspiration throughout summer, as is evident from Cl (van Breemen *et al.*, 1988). In ecosystems which receive relatively little atmospheric N, mineralization and subsequent nitrification of soil organic N through summer may also cause a significant increase in soil solution NO_3 and Ca (e.g. Foster *et al.*, 1989).

Due to prolonged leaching, long-term natural changes in soil solution composition may occur. However, these changes are often too slow to be recorded by most monitoring programmes, which were nearly all established quite recently. Relatively fast changes in soil solution composition (e.g. decreases in base cations) have been reported in connection with anthropogenic impacts on soils (including forest production, acid rain, etc.) and will be discussed in more detail in Section 5.3.

5.2.3.2   Soil solid phase

The contents of chemical compounds in the soil solid phase are generally high relative to the rates of leaching and accumulation. Therefore, natural changes in the chemical composition of soils are generally slow. Anthropogenic impacts may speed up leaching and accumulation of chemical compounds considerably, thus causing measurable changes in soil chemical properties over relatively short time spans (Section 5.3).

5.3 ANTHROPOGENIC IMPACT ON SOILS AND SUBSEQUENT RECOVERY

5.3.1 ANTHROPOGENIC IMPACT AND RESULTING CHANGES

The impacts of humans on soils are manifold, and are generally associated with economic activities. They may be intentional, aimed at improving the economic value of a soil (e.g. for crop production through fertilization, liming, irrigation, artificial drainage), or they may be unintentional and often undesirable (e.g. salinization of irrigated land, pollution by pesticides used for crop protection, pollution by heavy metals from applied sewage sludge). Increased soil acidification is also an undesirable side effect, caused mostly by atmospheric deposition of SO_x and NO_x (from burning of fossil fuels), by oxidation of reduced S compounds in mine spoils or in artificially drained acid sulphate soils, by forest clearcutting and by plantation of coniferous forest.

Strong mineral acids (e.g. from acid deposition, pyrite oxidation, nitrification after deforestation) may cause increased leaching of base cations and depletion of exchangeable pools (Christophersen *et al.*, 1990b; Johnson and Todd, 1990). Consequently pH gradually decreases and mobilization of inorganic Al increases (van Breemen, 1976; Driscoll *et al.*, 1989c; Mulder *et al.*, 1989b). At prolonged high rates of acidification (e.g. acid atmospheric inputs of several kmol ha^{-1} year^{-1}) even the soil Al buffer in the surface horizons may be depleted, thus resulting in decreased pH buffering and consequently in a further decline of soil pH (Mulder *et al.*, 1989a; de Vries *et al.*, 1989).

Evidence for a decrease in soil pH attributed to acid atmospheric deposition has been found in a number of countries, including Germany (Ulrich *et al.*, 1980; Butzke, 1981), Sweden (Hallbäcken and Tamm, 1986; Berdén *et al.*, 1987), Norway (Dahl, 1988), and the United Kingdom (Billett *et al.*, 1990). In some studies forest growth has also been found to result in a detectable decrease in base saturation and acidification of forest soils within decades, due to net uptake of base cations (Hallbäcken and Tamm, 1986; Johnson and Todd, 1990).

A decrease in soil solution pH may also cause increased protonation of organic and bicarbonate anions (decreased alkalinity). Krug and Frink (1983) hypothesized that acidic deposition changed the source of streamwater acidity (from organic acid to mineral acid) but not the extent. However, a full neutralization of mineral acidity is unlikely as it would imply that all H$^+$ from strong acids are consumed in the alkalinity titration. Some studies suggest a decreased solubility of organic acids, due to increased acidic deposition (Marmorek *et al.*, 1987; Driscoll *et al.*, 1989a). By contrast, Wright (1989) concludes from an acid exclusion experiment in Norway that the observed decrease in streamwater SO_4 is not associated with a change in DOC. Nevertheless the dissociation of organic acids was found to increase considerably.

Soil acidification (reduced pH) may also result in increased sorption of anions in solution (e.g. sulphate and organic anions). Since anion adsorption is an acid-

consuming process, this may decrease the acidification potential for H_2SO_4. By contrast, desorption in periods of falling anion concentrations (decreased acid inputs) may significantly delay the de-acidification of soil drainage water.

5.3.2   RECOVERY FROM SOIL DISTURBANCE

Recovery of acidified soils largely depends on the rate at which exchangeable acidity can be removed (i.e. the rate at which exchangeable base cations can be replenished). In a natural situation this depends on the rate of release of base cations through chemical weathering, the deposition rate of base cations from the atmosphere and redistribution of base cations in the profile by biological processes (Figure 5.1). Liming and fertilization may speed up the recovery considerably, but unintentional side effects may occur (e.g. changing rooting structure, changing soil microbiological community) having both additional chemical and hydrological consequences.

The rate of (chemical) recovery of soils also depends on the reversibility of SO_4 adsorption. This partly depends on whether SO_4 is held electrostatically or by a stronger molecular bond at oxide surfaces (Mitchell *et al.*, 1992). Irreversibly adsorbed SO_4 will not redissolve when $SO4$ concentrations decrease. By contrast, large pools of reversibly adsorbed SO_4 could considerably delay the response of surface waters to changes in S input. Field observations suggesting that SO_4 adsorption is largely irreversible include those from the Sudbury area in Canada (Keller and Pitblado, 1986), New Hampshire, USA (Driscoll *et al.*, 1989b), New Jersey, USA (Morgan, 1990) and Norway (Christophersen *et al.*, 1990b). At all these sites a rapid decline in stream SO_4 at decreasing SO_4 deposition rates is evident. Similar results were obtained for field manipulation studies (Wright *et al.*, 1988) and soil column experiments in the laboratory (Dahlgren *et al.*, 1990).

5.4   METHODS IN THE STUDY OF SOIL AND SOIL WATER

5.4.1   SOIL SURVEY, SAMPLING AND ANALYSIS

5.4.1.1   Soil survey

In a soil survey information about the spatial distribution of soil types within a catchment is obtained. First an appropriate soil legend has to be determined in the field. At the highest level this legend should have soil properties, which are believed to be most relevant for the hydrochemical response in catchments (e.g. acidic vs. neutral soils, and well-drained vs. poorly-drained soils).

Soil sampling

After mapping, dominant soil types should be sampled with respect to both solid phase and solution. If possible, soils should be sampled according to horizon.

However, if boundaries between horizons are diffuse or if soils are only weakly developed, sampling may be done according to depth. In the latter case the thickness of the sampled layers may increase with depth (e.g. from a few cm at the surface to a few dm at depth). Since the variability in chemistry within one horizon may be significant, samples should be taken from several soil pits, randomly distributed within a soil type. The number of samples needed depends on the confidence limit for the standard error of the chemical parameter to be estimated (e.g. Johnson *et al.*, 1990).

Soil samples are generally air-dried (sometimes freeze-dried) upon return in the laboratory, sieved (< 2 mm or fine earth fraction), homogenized (sample splitter), and stored in plastic containers until analysis. Although some soil chemical characteristics may change in the drying process (e.g. mineralization of organic N and S), drying is generally preferred over working with field-moist samples. The latter has severe drawbacks: (i) samples must be analysed directly (storage may cause significant mineralization, and nitrification); and (ii) samples are difficult to sieve and homogenize.

Physical parameters

Soil physical parameters that are routinely measured include texture and hydraulic conductivity (both saturated and non-saturated). For textural analysis air-dried and homogenized soil samples are pretreated to enhance dispersion. Pretreatment includes removal of cementing particles like $CaCO_3$ (by acidification with 1 M NaOAc), Fe-oxides (by reducing and complexing free Fe, using bicarbonate-buffered, Na-dithionite-citrate) and organic matter (by oxidation with H_2O_2). After dispersion (e.g. in Na-hexametaphosphate) various sand fractions (>50µm) are determined by sieving, while clay and silt fractions are obtained from sedimentation analysis (Gee and Bauder, 1986). The hydraulic conductivity is determined in undisturbed soil columns.

Chemical parameters

Here we will briefly discuss the most common soil chemical parameters determined in catchment studies. For details concerning methods and computational procedures reference is made to the extensive reviews in Klute (1986) and Page *et al.* (1986).

Routine chemical analyses include measurement of pH, CEC and exchangeable cations. Generally pH is determined in 1 : 5 (weight to volume) ratios in both water and neutral salt solutions (often 1N KCl). In acidic soils, high in organic matter (and thus CEC), pH(KCl) is lowest, due to the contribution of some exchangeable acidity. Note that the pH of the soil extract is generally not directly comparable to the *in situ* pH of the soil solution. In the most recent years measurement of the CEC with neutral salts (often with Ba, NH_4 or both; e.g.

Hendershot and Duquette, 1986; Amacher *et al.*, 1990) has become common practice. With the same technique exchangeable cations may be determined. Further routine soil chemical analyses include the contents of $CaCO_3$, organic C, total N, total S, and free Fe and Al.

For specific purposes additional analyses may be needed, including contents of inorganic N (i.e. NH_4 and NO_3) as well as fractionation of free Al and Fe into exchangeable, organically complexed, amorphous and crystalline forms (e.g. Driscoll *et al.*, 1985; Parfitt and Childs, 1988). Total S and P are often fractionated in various forms (Page *et al.*, 1986). In particular cases adsorption characteristics of soils are determined with respect to PO_4 (van der Zee, 1988) and SO_4 (Nodvin *et al.*, 1986b; Singh *et al.*, 1980).

5.4.2   Soil water and groundwater collection

Sampling soil solutions and groundwater remains a problem area. Different techniques may each sample a specific "type" of soil water (with a unique composition). In comparative studies, solutions collected at zero tension showed fewer signs of chemical interaction with the soil or were less concentrated by evapotranspiration than solutions collected with tension lysimeters (Cozzarelli *et al.*, 1987; Joslin *et al.*, 1987; Swistock *et al.*, 1990). The difference between the zero tension and the tension lysimeter solutions decreased with increasing depth in the soil. These results suggest that preferential flow is most important in the surface layers, where the macro-pore density (related to biological activity) is highest.

More recently Zabowski and Ugolini (1990) found significant (seasonal) differences between the chemical composition of lysimeter samples (extracted at 10 kPa) and centrifugates from the same horizon (extracted at 30 kPa and 300 kPa, respectively). These authors concluded that the lysimeter solutions were more representative for moving water, whereas centrifugation would be more appropriate for forest nutrition studies.

In addition to the poorly defined "type" of soil water that is being sampled, sampling procedure and equipment may induce a chemical change in the collected solution. For example, Suarez (1987) found that vacuum extractors could result in a significant increase in soil solution pH, due to degassing of CO_2. This effect may be corrected for (Suarez, 1987). Alternatively, Takkar *et al.* (1987) proposed the use of a closed tension lysimeter system, without exposure to the atmosphere, to sample soil solutions and preserve the dissolved inorganic carbon.

Although numerous types of suction lysimeters have been proposed, the material used for the construction of the collection device (alundum, ceramic, teflon, acrylic copolymer with internal nylon support) may have a pronounced influence on the composition of the sample (Litaor, 1988). From his review Litaor concluded that there is no single and simple solution to the collection of soil water. The design and properties of a soil solution sampler should be evaluated critically for each specific problem under study.

5.4.3   CHEMICAL ANALYSIS OF SOLUTIONS

A common analysis of soil solutions includes pH, and total concentrations of DOC, DIC, Si, K, Na, Ca, Mg, Al, NH_4, F, Cl, NO_3, SO_4, and PO_4. In addition, alkalinity may be estimated from titration experiments. Often solutions are also analysed for a whole suite of trace elements, including Fe, Mn, Pb, Zn and Cu. To minimize changes in sample composition it is common practice to analyse right after sampling. Particularly sensitive parameters in this respect are pH, DOC, DIC, Al, F, NH_4, NO_3 and PO_4.

Analysed solutes generally consist of a number of species, which often differ in their bioavailability. Therefore speciation of several solutes has become common practice in catchment research. Often speciation also allows for the estimation of solute activities, necessary for the study of element solubility controls in soils.

Speciation of Al is probably most common, and involves a separation in inorganic and organic monomeric Al (generally using an acidic cation exchanger) plus polymeric Al (Barnes, 1975; Driscoll, 1984). The Al^{3+} activity may be estimated from inorganic monomeric Al (including Al^{3+}, as well as monomeric hydrolysed Al and complexes with Si, F and SO_4) using thermodynamics (e.g. Schecher and Driscoll, 1987). Dissolved F is often separated into total F and free F (after addition of TISAB buffer, which decomplexes F in solution). The difference between total and free F may be taken as an estimate of Al-bound F, and may be used as an alternative procedure to estimate the Al activity (from thermodynamics).

Since DOC consists of a wide range of organic substances with highly variable physicochemical characteristics (Pohlman and McColl, 1988), an analytical fractionation scheme was proposed by Leenheer and Huffman (1979) and Leenheer (1981). By using macro reticular resins DOC is fractionated into six classes: hydrophobic and hydrophilic acids, neutrals and bases.

5.5   SUMMARY

Streamwater runoff is dominated by drainage water from the terrestrial environment. Therefore biogeochemical processes in the terrestrial environment are of paramount importance for the chemistry of streamwater.

This chapter discusses abiotic chemical reactions in solution, gas and solid phases of the soil, with special reference to reactions involving inorganic C, organic C, SO_4, PO_4, Al, N and cation exchange. Reaction equilibria and kinetics are largely determined by soil chemical properties, which result from geological processes and subsequent soil formation.

Soil formation is the long-term vertical differentiation of physical, biological and chemical properties of rocks and sediments under the influence of soil formation factors, including parent material, climate, biota, topography and time. As soil-forming factors generally differ within one catchment, various soil types may result.

The importance of specific soil types for streamwater quality depends on the water pathways in the terrestrial system. These pathways may vary as a function of precipitation intensity. Therefore the contribution of various soils (or soil horizons) to the stream varies dynamically with runoff.

Routines for sampling and pretreatment of samples from soils and soil solutions are numerous and arbitrary. Researchers need to critically evaluate their procedures in the light of their specific aim.

5.6 FURTHER READING

There are several excellent textbooks on soils in general, such as these of Brady (1974) and Scheffer and Schachtschabel (1982). Soil classification which is widely used is based on Soil Survey Staff (1975) and FAO–UNESCO (1988). Sampling and analysis of soils are covered in authoritative volumes of Klute (1986) and Page *et al*. (1986). Sampling of soil solutions is discussed by Litaor (1988).

General discussion of abiotic chemical reactions in soils appears in Bolt and Bruggenwert (1976), Stumm and Morgan (1981) and Greenland and Hayes (1981). More detailed topics of chemistry of humic substances in soils are given in Aiken *et al*. (1985) and Huang and Schnitzer (1986); aluminium chemistry of soils is discussed in depth by Sposito (1989).

Modelling soil solution chemistry and the underlying chemical concepts are explained in Reuss and Johnson (1986). Anthropogenically induced changes in forest soils are summarized and discussed by Johnson *et al*. (1991).

Wright and Hauhs (1991) discuss the question of the reversibility of acidification.

5.7 REFERENCES

Aiken, G.R., McKnight, D.M., Wershaw, R.L. and MacCarthy, P. (1985) *Humic Substances in Soil, Sediment and Water*. John Wiley, New York, 692 pp.

Amacher, M.C., Henderson, R.E., Breithaupt, M.D., Seale, C.L. and LaBauve, J.M. (1990) Unbuffered and buffered salt methods for exchangeable cations and effective cation exchange capacity. *Soil Sci. Soc. Am. J.* **54**: 1036–1042.

Barnes, R.B. (1975) The determination of specific forms of aluminum in natural water. *Chem. Geol.* **15**: 177–191.

Berdén, M., Nilsson, S.I., Rosen, K. and Tyler, G. (1987) Soil acidification, extent, causes and consequences. Report 3292, SNV, Solna, Sweden.

Billett, M.F. and Cresser, M.S. (1992) Predicting stream-water quality using catchment and soil chemical characteristics. *Environmental Pollution* **77**: 263–268.

Billett, M.F., Parker-Jervis, F., FitzPatrick, E.A. and Cresser, M.S. (1990) Forest soil chemical changes between 1949/50 and 1987. *J. Soil Sci.* **41**: 133–145.

Binkley, D. and Richter, D. (1987) Nutrient cycles and H+ budgets of forest ecosystems. *Advances in Ecological Research* **16**: 1–51.

Bishop, K.H., Grip, H. and O'Neill, A. (1990) The origins of acid runoff in a hillslope during storm events. *J. Hydrol.* **116**: 35–61.

Bloom, P.R., McBride, M.B. and Weaver, R.M. (1979) Aluminum organic matter in acid soils: buffering and solution aluminum activity. *Soil Sci. Soc. Am. J.* **43**: 488–493.

Bolt, G.H. and Bruggenwert, M.G.M. (Eds) (1976) *Soil Chemistry. Part A. Basic Elements.* Elsevier, Amsterdam, The Netherlands, 281 pp.

Bouten, W., De Vre, F.M., Verstraten, J.M. and Duysings, J.J.H.M. (1984) Carbon dioxide in the soil atmosphere: simulation model parameter estimation from field measurements. In Eriksson, E. (Ed.): *Hydrochemical Balances of Freshwater Systems.* IAHS-AISH Publ., 150, Uppsala, pp. 23–30.

Brady, N.C. (1974) *The Nature and Properties of Soils.* Macmillan, New York.

Breemen, N. van (1976) *Genesis and Solution Chemistry of Acid Sulfate Soils in Thailand.* Agric. Res. Rep. 848, PUDOC Wageningen, The Netherlands, 263pp.

Breemen, N. van, Mulder, J. and Driscoll, C.T. (1983) Acidification and alkalinization of soils. *Plant and Soil* **75**: 283–308.

Breemen, N. van, Driscoll, C.T. and Mulder, J. (1984) Acidic deposition and internal proton sources in acidification of soils and waters. *Nature* **307**: 599–604.

Breemen, N. van, Visser, W.F.J. and Pape, Th. (1988) *Biogeochemistry of an Oak-Woodland Ecosystem in The Netherlands Affected by Acid Atmospheric Deposition.* Agric. Res. Rep. 930, PUDOC, Wageningen, The Netherlands, 197 pp.

Butzke, H. (1981) Versauern unsere Waelder? Erste Ergebnisse der Ueberpruefung 20-Jahre alter pH-Wert-Messungen in Waldboeden Nordrhein-Westfalens. *Forst u. Holzw.* **21**: 542–548.

Chao, T.T., Harward, M.E. and Fang, S.C. (1962) Soil constituents and properties in adsorption of sulfate ions. *Soil Sci.* **94**: 276–283.

Christophersen, N., Neal, C., Hooper, R.P., Vogt, R.D. and Andersen, S. (1990a) Modelling streamwater chemistry as a mixture of soil-water end members—A step towards second generation acidification models. *J. Hydrol.* **116**: 307–320.

Christophersen, N., Robson, A., Neal, C., Whitehead, P.G., Vigerust, B. and Henriksen, A. (1990b) Evidence for a long- term deterioration of streamwater chemistry and soil acidification at the Birkenes catchment, southern Norway. *J. Hydrol.* **116**: 63–76.

Cosby, B.J., Hornberger, G.M., Galloway, J.N. and Wright, R.F. (1985) Modeling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* **21**: 51–63.

Cozzarelli, I.M., Herman, J.S. and Parnell, R.A. (1987) The mobilization of aluminum in a natural soil system: Effects of hydrologic pathways. *Water Resour. Res.* **23**: 859–874.

Cronan, C.S. and Aiken, G.R. (1985) Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. *Geochim. Cosmochim. Acta* **49**: 1697–1705.

Cronan, C.S., Walker, W.J. and Bloom, P.R. (1986) Predicting aqueous aluminium in natural waters. *Nature* **324**: 140–143.

Dahl, E. (1988) *Acidification of Soils in the Rondane Mountains, South Norway, Due to Acid Precipitation.* Oekoforsk Rapport 1988:1, Aas, Norway, 53pp.

Dahlgren, R.A., Driscoll, C.T. and McAvoy, D.C. (1989) Aluminum precipitation and dissolution rates in Spodosol Bs horizons in the Northeastern USA. *Soil Sci. Soc. Am. J.* **53**: 1045–1052.

Dahlgren, R.A., McAvoy, D.C. and Driscoll, C.T. (1990) Acidification and recovery of a Spodosol Bs horizon from acidic deposition. *Environ. Sci. Technol.* **24**: 531–537.

David, M.B. and Driscoll, C.T. (1984) Aluminum speciation and equilibria in soil solutions of a Haplorthod in the Adirondack mountains (New York, USA). *Geoderma* **33**: 297–318.

Driscoll, C.T. (1984) A procedure for the speciation of aqueous aluminum in dilute acidic waters. *Int. J. Environ. Anal. Chem.* **16**: 267–283.

Driscoll, C.T. (1989) The chemistry of aluminum in surface waters. In Sposito, G. (Ed.): *The Environmental Chemistry of Aluminum*, CRC Press, Boca Raton, Forida pp. 241–277.

Driscoll, C.T. and Likens, G.E. (1982) Hydrogen ion budget of an aggrading forested ecosystem. *Tellus* **34**: 283–292.

Driscoll, C.T., Breemen, N. van and Mulder, J. (1985) Aluminum chemistry in a forested Spodosol. *Soil Sci. Soc. Am. J.* **49**: 437–444.

Driscoll, C.T., Fuller, R.D. and Schecher, W.D. (1989a) The role of organic acids in the acidification of surface waters in the eastern US. *Wat. Air Soil Poll.* **43**: 21–40.

Driscoll, C.T., Likens, G.E., Hedin, L.O., Eaton, J.S. and Bormann, F.H. (1989b) Changes in the chemistry of surface waters. *Environ. Sci. Technol.* **23**: 137–143.

Driscoll, C.T., Wyskowski, B.J., DeStaffan, P. and Newton, R.M. (1989c) Chemistry and transfer of aluminum in the Adirondack region of New York, USA. In Lewis, T.E. (Ed.): *Environmental Chemistry and Toxicology of Aluminum*. Lewis Publ. Chelsea, MI, pp. 83–106.

Easthouse, K.B., Mulder, J., Christophersen, N. and Seip, H.M. (1992) Dissolved organic carbon fractions in soil and streamwater during variable hydrological conditions at Birkenes, southern Norway. *Water Resour. Res.* **28**: 1585–1596.

FAO–UNESCO (1988) *Soil Map of the World. Revised Legend.* World Soil Resources Rep. 60, FAO Rome, 119 pp.

Foster, N.W., Nicholsen, J.A. and Hazlett, P.W. (1989) Temporal variation in nitrate and nutrient cations in drainage waters from a deciduous forest. *J. Environ. Qual.* **18**: 238–244.

Fox, T.R., Comerford, N.B. and McFee, W.W. (1990) Phosphorus and aluminum release from a Spodic horizon mediated by organic acids. *Soil Sci. Soc. Am. J.* **54**: 1763–1767.

Fuller, R.D., Driscoll, C.T., Lawrence, G.B. and Nodvin, S.C. (1987) Processes regulating sulphate flux after whole-tree harvesting. *Nature* **325**: 707–709.

Gee, G.W. and Bauder, J.W. (1986) Particle size analysis. In Klute, A. (Ed.): *Methods of Soil Analysis Part I, Agronomy 9.* ASA, Madison, WI, pp. 383–411.

Goldberg, S. and Sposito, G. (1985) On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces: A review. *Commun. Soil Sci. Plant Anal.* **16**: 801–821.

Greenland, D.J. and Hayes, M.H.B. (1981) *The Chemistry of Soil Processes.* John Wiley & Sons, New York, 714pp.

Hallbäcken, L. and Tamm, C.O. (1986) Changes in soil acidity from 1927 to 1982–1984 in a forest area of southwest Sweden. *Scand. J. Forest Res.* **1**: 219–232.

Hendershot, W.H. and Duquette, M. (1986) A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* **50**: 605–608.

Huang, P.M. and Schnitzer, M. (1986) *Interactions of Soil Minerals with Natural Organics and Microbes.* SSSA special publ. 17. Soil Sci. Soc. Am. Inc., Madison, WI, 606pp.

James, B.R. and Riha, S.J. (1986) pH buffering in forest soil organic horizons: relevance to acid precipitation. *J. Environ. Qual.* **15**: 229–233.

Johnson, C.E., Johnson, A.H. and Huntington, T.G. (1990) Sample size requirements for the determination of changes in soil nutrient pools. *Soil Sci.* **150**: 637–644.

Johnson, D.W. and Todd, D.E. (1983) Relationship among iron, aluminum, carbon and sulfate in a variety of forest soils. *Soil Sci. Soc. Am. J.* **47**: 792–800.

Johnson, D.W. and Todd, D.E. (1990) Nutrient cycling in forests of Walker Branch watershed, Tennessee: Roles of uptake and leaching in causing soil changes. *J. Environ. Qual.* **19**: 97–104.

Johnson, D.W., Cresser, C.S., Nilsson, S.I., Turner, J., Ulrich, B., Binkley, D. and Cole, D.W. (1991) Soil changes in forest ecosystems: evidence for and probable causes. In Last, F.T. and Watling, R. (Eds): *Acidic Deposition: Its Nature and Impacts.* Proceedings of the Royal Society Edinburgh, Section B (Biol. Sciences) Vol. 97, pp. 81–116.

Joslin, J.D., Mays, P.A., Wolfe, M.H., Kelly, J.M., Garber, R.W. and Brewer, P.F. (1987) Chemistry of tension lysimeter water and lateral flow in spruce and hardwood stands. *J. Environ. Qual.* **16**: 152–160.

Keller, W. and Pitblado, J.R. (1986) Water quality changes in Sudbury area lakes: a comparison of synoptic surveys in 1974–1976 and 1981–1983. *Wat. Air Soil Poll.* **29**: 285–296.

Khanna, P.K., Prenzel, J., Meiwes, K.J., Ulrich, B. and Matzner, E. (1987) Dynamics of sulfate retention by acid forest soils in an acidic deposition environment. *Soil Sci. Soc. Am. J.* **51**: 446–452.

Klute, A. (Ed.) (1986) *Methods of Soil Analysis. Part 1—Physical and Mineralogical Methods.* 2nd edition. *Agronomy 9.* ASA, Madison, WI. 1188 pp.

Krug, E.C. and Frink, C.R. (1983) Acid rain on acid soil: a new perspective. *Science* **221**: 520–525.

Leenheer, J.A. (1981) Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environ. Sci. Technol.* **15**: 578–587.

Leenheer, J.A. and Huffman, E.W.D. (1979) Analytical method for dissolved organic carbon fractionation. US Geol Survey, Water Resour. Invest., 79–4.

Lelong, F., Durand, P. and Didon, J.F. (1988) Comparaison des bilans hydrochimiques, des taux d'alteration et d'acidification dans trois petits bassins versants granitiques similaires a vegetation contrastee (Mont Lozere, France). *Sci. Geol. Bull. (Strasbourg)*, **41**: 263–278.

Litaor, M.I. (1988) Review of soil solution samplers. *Water Resour. Res.* **24**: 727–733.

Marmorek, D.R., Bernard, D.P., Jones, M.L., Rattie, L.P. and Sullivan, T.J. (1987) The effects of mineral acid deposition on concentrations of dissolved organic acids in surface waters. USEPA, Corvallis, OR., 96 pp.

Marsh, K.B., Tillman, R.W. and Syers, J.K. (1987) Charge relationships of sulfate sorption by soils. *Soil Sci. Soc. Am. J.* **51**: 318–323.

McDowell, W.H. and Wood, T. (1984) Podzolization: soil processes control dissolved organic carbon concentrations in stream water. *Soil Sci.* **137**: 23–32.

McMahon, R. and Neal, C. (1990) Aluminium dis-equilibrium solubility controls in Scottish acidic catchments. *Hydr. Sci. J.* **35**: 21–28.

Mitchell, M.J., Driscoll, C.T., Fuller, R.D., David, M.B. and Likens, G.E. (1989) Effect of whole tree harvesting on the sulfur dynamics of a forest soil. *Soil Sci. Soc. Am. J.* **53**: 933–940.

Mitchell, M.J., David, M.B. and Harrison, R. (1992) Sulphur dynamics of forest ecosystems. In Howarth, R.W., Stewart, J.W.B. and Ivanov, M.V. (Eds): *Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems and Associated Water Bodies.* SCOPE 48, John Wiley & Sons, Chichester, pp. 215–254.

Morgan, M.D. (1990) Streams in the New Jersey pinelands directly reflect changes in atmospheric deposition chemistry. *J. Environ. Qual.* **19**: 296–302.

Mulder, J., Breemen, N. van, Rasmussen, L. and Driscoll, C.T. (1989a) Aluminum chemistry of acidic sandy soils with various inputs of acidic deposition in the Netherlands and in Denmark. In Lewis, T.E. (Ed.): *Environmental Chemistry and Toxicology of Aluminum.* Lewis Publ. Inc., Chelsea, MI, pp. 171–194.

Mulder, J., Breemen, N. van and Eijck, H.C. (1989b) Depletion of soil aluminium by acid deposition and implications for acid neutralization. *Nature* **337**: 247–249.

Mulder, J., Christophersen, N., Hauhs, M., Vogt, R.D., Andersen, S. and Andersen, D.O. (1990) Water flow paths and hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in seasalts. *Water Resour. Res.* **26**: 611–622.

Mulder, J., Pijpers, M. and Christophersen, N. (1991) Water flow paths and the spatial distribution of soils and exchangeable cations in an acid rain impacted and a pristine catchment in Norway. *Water Resour. Res.* **28**: 1585–1596.

Neal, C., Mulder, J., Christophersen, N., Neal, M., Waters, D., Ferrier, R.C., Harriman, R. and McMahon, R. (1990) Limitations in the understanding of ion exchange and solubility controls for acidic Welsh, Scottish and Norwegian sites. *J. Hydrol.* **116**: 11–23.

Nilsson, J. and Grennfelt, P. (1988) *Critical Loads for Sulphur and Nitrogen*. NORD 1988:15 Nordic Council of Ministers, Copenhagen. Miljörapport 15, 418 pp.

Nilsson, S.I. (1985) Why is Lake Gårdsjön acid? An evaluation of processes contributing to soil and water acidification. *Ecol. Bull. (Stockholm)* **37**: 311–318.

Nilsson, S.I. and Bergkvist, B. (1983) Aluminium chemistry and acidification processes in a shallow podzol on the Swedish westcoast. *Wat. Air Soil Poll.* **20**: 311–329.

Nodvin, S.C., Driscoll, C.T. and Likens, G.E. (1986a) Simple partitioning of anions and dissolved organic carbon in a forest soil. *Soil Sci.* **142**: 27–35.

Nodvin, S.C., Driscoll, C.T. and Likens, G.E. (1986b) The effect of pH on sulfate adsorption by a forest soil. *Soil Sci.* **142**: 69–75.

Nordstrom, D.K. (1982) The effect of sulfate on aluminum concentrations in natural waters: some stability relations in the system Al_2O_3-SO_3-H_2O at 298 K. *Geochim. Cosmochim. Acta* **46**: 681–692.

Oliver, B.G., Thurman, E.M. and Malcolm, R.L. (1983) The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim. Acta* **47**: 2031–2035.

Page, A.L., Miller, R.H. and Keeney, D.R. (Eds) (1986) *Methods of Soil Analysis. Part 2— Chemical and Microbiological Properties*. 2nd edition, *Agronomy 9*. ASA, Madison, WI. 1159 pp.

Parfitt, R.L. and Childs, C.W. (1988) Estimation of forms of Fe and Al: a review, and analysis of contrasting soils by dissolution and Moessbauer methods. *Aust. J. Soil Res.* **26**: 121–144.

Parfitt, R.L. and Smart, R.S.C. (1978) The mechanism of sulfate adsorption on iron oxides. *Soil Sci. Soc. Am. J.* **42**: 48–50.

Pohlman, A.A. and McColl, J.G. (1988) Soluble organics from forest litter and their role in metal dissolution. *Soil Sci. Soc. Am. J.* **52**: 265–271.

Rajan, S.S.S. (1978) Sulfate adsorbed on hydrous alumina, ligands displaced and changes in surface charge. *Soil Sci. Soc. Am. J.* **42**: 39–44.

Reuss, J.O. (1983) Implications of the Ca–Al exchange system for the effect of acid precipitation on soils. *J. Environ. Qual.* **12**: 591–595.

Reuss, J.O. and Johnson, D.W. (1986) *Acid Deposition and the Acidification of Soils and Waters*. Ecological Studies 59, Springer, New York., 119 pp.

Schecher, W.D. and Driscoll, C.T. (1987) An evaluation of the uncertainty associated with aluminum equilibrium calculations. *Water Resour. Res.* **23**: 525–534.

Scheffer, F. and Schachtschabel, P. (1982) *Lehrbuch der Bodenkunde*. Enke Verlag, Stuttgart, FRG, 442 pp.

Singh, B.R., Abrahamsen, G. and Stuanes, A. (1980) Effect of simulated acid rain on sulfate movement in acid forest soils. *Soil Sci. Soc. Am. J.* **44**: 75–80.

Soil Survey Staff (1975) *Soil Taxonomy*. Agric. Handbook 436, Washington DC, 754 pp.

Sollins, P., Robertson, G.P. and Uehara, G. (1988) Nutrient mobility in variable- and permanent-charge soils. *Biogeochemistry* **6**: 181–199.

Sposito, G. (Ed.) (1989) *The Environmental Chemistry of Aluminum*. CRC Press, Boca Raton, Florida.

Stumm, W. and Morgan, J.J. (1981) *Aquatic Chemistry*. John Wiley & Sons, New York, 780 pp.

Suarez, D.L. (1987) Prediction of pH errors in soil water extractors due to degassing. *Soil Sci. Soc. Am. J.* **51**: 64–68.

Sullivan, T.J., Driscoll, C.T., Gherini, S.A., Munson, R.K., Cook, R.B., Charles, D.F. and Yatsko, C.P. (1989) Influence of aqueous aluminium and organic acids on measurements of acid neutralizing capacity in surface waters. *Nature* **338**: 408–410.

Swistock, B.R., Yamona, J.J., DeWalle, D.R. and Sharpe, W.E. (1990) Comparison of soil water chemistry and sample size requirements for pan vs. tension lysimeters. *Wat. Air Soil Poll.* **50**: 387–396.

Takkar, P.N., Ulrich, B. and Meiwes, K.J. (1987) Method for estimation of $CO_2(aq)$ plus H_2CO_3, HCO_3^- and pH in soil solutions collected under field conditions. *Z. Pflanzenernaehr. Bodenk.* **150**: 319–326.

Tan, K.H. (1986) Degradation of soil minerals by organic acids. In Huang, P.M. and M. Schnitzer (Eds): *Interactions of Soil Minerals with Natural Organics and Microbes.* SSSA Special Publication 17, Soil Sci. Soc. Am. Inc., Madison, WI, pp. 1–27.

Tate, K.R. and Theng, B.K.G. (1980) Organic matter and its interaction with inorganic soil constituents. In Theng B.K.G. (Ed.): *Soils with Variable Charge*, New Zealand Soc. Soil Sci., Soils Bureau, Lower Hutt, pp. 225–249.

Tipping, E. and Hurley, M.A. (1988) A model of solid–solution interactions in acid organic soils, based on the complexation properties of humic substances. *J. Soil Sci.* **39**: 505–519.

Tipping, E., Backes, C.A. and Hurley, M.A. (1988) The complexation of protons, aluminium and calcium by aquatic humic substances: a model incorporating binding-site heterogeneity and macroionic effects. *Water Res.* **22**: 597–611.

Ugolini, F.C. and Dahlgren, R. (1987) The mechanism of podzolization as revealed by soil solution studies. In Righi, D. and Chauvel A. (Eds): *Podzols et Podzolisation*, Association Francaise pour l'Etude du Sol et Institut National de la Recherche Agronomique, France, pp. 195–203.

Ugolini, F.C., Dahlgren, R., Shoji, S. and Ito, T. (1988) An example of andosolization and podzolization as revealed by soil solution studies, southern Hokkoda, northeastern Japan. *Soil Sci.* **145**: 111–125.

Ulrich, B., Mayer, R. and Khanna, P.K. (1980) Chemical changes due to acid precipitation in a loess derived soil in central Europe. *Soil Sci.* **130**: 193–199.

Urban, N.R., Eisenreich, S.J. and Gorham, E. (1987) Proton cycling in bogs: geographic variation in northeastern North America. In Hutchinson, T.C. and Meema, K.M. (Eds): *Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems*, Springer Verlag, Berlin, pp. 577–598.

Vries, de, W., Posch. M. and Kämäri, J. (1989) Simulation of the long-term response to acid deposition in various buffer ranges. *Wat. Air Soil Poll.* **48**: 349–390.

Wood, T., Bormann, F.H. and Voigt, G.K. (1984) Phosphorus cycling in a northern hardwood forest: biological and chemical control. *Science* **223**: 391–393.

Wright, R.F. (1989) RAIN Project: Role of organic acids in moderating pH change following reduction in acid deposition. *Wat. Air Soil Poll.* **46**: 251–259.

Wright, R.F. and Hauhs, M. (1991) Reversibility of acidification: soils and surface waters. In Last, F.T. and Watling, R. (Eds): *Acidic Deposition: Its Nature and Impacts.* Proceedings of the Royal Society of Edinburgh, Section B (Biol. Sciences), Vol.97, Edinburgh, pp.169–191.

Wright, R.F., Lotse, E. and Semb, A. (1988) Reversibility of acidification shown by whole-catchment experiments. *Nature* **334**: 670–675.

Zabowski, D. and Ugolini, F.C. (1990) Lysimeter and centrifuge soil solutions: seasonal differences between methods. *Soil Sci. Soc. Am. J.* **54**: 1130–1135.

Zee van der, S.E.A.T.M. (1988) *Transport of reactive contaminants in heterogeneous soil systems*. Ph.D. Thesis, Agric. Univ. Wageningen, The Netherlands, 283pp.