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Acid Neutralization and Sulphur retention in S-impacted Andosols

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Chapter 2

General Overview

2.1 Acid pollution and soil acidification

The formation of secondary pollutants from the oxidation of nitrogen oxides (NO_x) and/or sulphur oxides (SO_x) from metal smelters or natural sources that are released into the atmosphere are the main sources of acid pollution. It is well established that this acid loading has increased sulphate and proton fluxes through soils in affected areas, eventually enhancing soil acidification (Ulrich, 1991).

Recognition that sulphur releases from metal smelters and coalpower plants are a major contributor to atmospheric acid deposition is long standing. Natural analogues of these anthropogenic emitters are certain volcanoes, which persistently eject sulphur gases, mainly in the form of SO_2 into the atmosphere (Andres & Kasgnoc, 1998). Recent studies indicate that this natural source may create local and distant air pollution (Graf *et al.*, 1998; Delmelle *et al.*, 2002). Beside SO_2, volcanoes also emit considerable amounts of HCl and HF into the atmosphere (Symonds *et al.*, 1988). This and the low emission rate of NO_x (Mather *et al.*, 2004) make volcanogenic acid emissions distinct from anthropogenic pollution.

Soil acidification remains a major environmental issue, both in industrial and in less developed countries (Alewell *et al.*, 2000), because it alters soil and water properties, thus potentially modifying current processes in whole ecosystems (Ulrich, 1991). It is a natural process (especially in high rainfall areas) and is the result of irreversible reactions that produce H^+ (van Breemen *et al.*, 1983). However, anthropic or natural acid deposition can dramatically accelerate soil acidification. Under these conditions, acidity creates harmful chemical and biological conditions in soils to many plants. It reduces nutrient supply and

increases the solubility of toxic species such as Al^{3+} and Mn^{2+}, thus leading to a decrease in soil fertility (Sparks, 1995).

The sensitivity of soils towards acidification depends on their mineralogical and physico-chemical properties. Indeed, reactions of the solid-phase components control soil pH, and consequently, buffer soil pH against rapid changes when acid inputs are added. In the short term, acid buffering mechanisms include carbonate dissolution, cation exchange involving H^+ and Al^{3+} at mineral surfaces, specific anionic adsorption (PO_4^{3-}, F^- and SO_4^{2-}) on minerals and protonation of surface hydroxyl groups (short-range ordered minerals, oxide surfaces and organic matter). In the long term, the weathering of primary silicate minerals contributes to neutralise the acid inputs (Bloom, 2000).

The capacity of the soil to neutralise acid inputs is closely linked to the release of alkaline and alkaline-earth cations and other metals incorporated in silicates or oxides by mineral weathering. van Breemen *et al.* (1983) defined soil acidification as a decrease in the soil acid neutralising capacity (ANC_s). These authors defined ANC_s [$cmol_c\ kg^{-1}$] as follows :

$$ANC_{s\ (pH\ 3)} = 2\ (CaO) + 2\ (K_2O) + 2\ (Na_2O) + 2\ (MnO) + 6\ (Al_2O_3) + 6\ (Fe_2O_3) - 2\ (SO_3) - 2\ (P_2O_5) - (HCl)$$

Of course ANC_s must be defined with respect to a reference pH value (usually 3), and is thus measured as the proton input required to lower soil pH down to the reference pH value.

2.1.1 Detrimental effects of soil acidification

Soil acidification can have significant detrimental effects on both vegetation and soils. Acidification increases the leaching of nutrient cations such as Ca^{2+}, Mg^{2+} and K^+ from the soil, and the solubilisation of toxic metals such as Al^{3+} and Mn^{2+}. This may reduce soil biological activity as well as biological fixation of atmospheric N_2. It can also alter nutrient cycling (Sampson & Brezonik, 2003). Over time, the productivity of the vegetation is decreased due to fewer nutrients and higher levels of toxic metals (Sparks, 1995). Extreme acidification can result in poorly structured topsoils that do not support enough vegetation to prevent soil erosion.

Possible effects of acid precipitation on forests have been the topic of intensive research primarily in Europe (Matzner & Murach, 1995) and the United States (Ulrich, 1991; Driscoll *et al.*, 2003), and recently also in China. In spite of this effort, quantitative relationships between pollu-

tion factors and forest damage have been difficult to obtain. Vegetation damages may be caused by direct exposure to gaseous or particulate air pollutants or indirectly through soil acidification. Indirect effects of elevated levels of toxic aluminium in soil water, leaching of plant nutrients (particularly Mg) from soils, or reduced availability of phosphorus may also be responsible for reduced forest vitality (Johnson, 1981).

2.1.2 Environmental impacts of volcanic acid emissions*

Natural pollution caused by volcanoes may originate from various activities such as the discharge of volcanic acid crater lakes, or from F-rich volcanic ash deposits. For instance, the acid crater lake of Kawah Ijen (Indonesia) has contaminated the downstream irrigating rivers with acid, Al, F and heavy metals, leading to yield decline of crops and increase in people affected by dental fluorosis (Lohr *et al.*, 2005). Similarly, the 11 October 1995 eruption of Ruapehu volcano (New Zealand) generated thin (<2mm) but widespread (25 000 km^2) F-rich tephra deposits that resulted in the death from fluorosis of at least 2000 grazing animals (Cronin *et al.*, 2003).

Detrimental impacts on soils have also been associated with volcanogenic acid deposition. Parnell (1986) studied the acidification of Andosols downwind from Masaya volcano (Nicaragua) in the 80's. He observed a significant soil pH decrease in response to acid deposition associated with a concomitant loss of exchangeable base cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}), and an increase in soil inorganic SO_4^{2-} content. Similar effects have been observed for volcanic Regosols, in the Osorezan volcanic region (Japan), exposed to acid loading from a fumarolic source (Takamatsu *et al.*, 1992) and for alpine Andosols of Nevado del Ruiz volcano (Colombia) exposed to volcanogenic acid rainfall in mid 80's (Parnell & Burke, 1990). Investigations of the effects of volcanic fumes from Mt. Oyama (Japan) by Hayashi & Okazaki (2002; 2003) revealed negligible influence on the soil properties. However, the composition of the soil solution was affected by the volcanic degassing: an increase in SO_4^{2-} concentration in atmospheric deposition immediately followed the degassing event, while the SO_4^{2-} concentration increase in soil solution at 10-cm depth was delayed by about 2 months.

Temporary or continuous detrimental effects on natural and cultivated vegetation have been observed in relation to passive volcanic degassing (Parnell & Burke, 1990; Sandoval *et al.*, 1996; Delmelle *et al.*, 2002; Delmelle, 2003 and references therein). Damages to crops and

*Adapted from Delmelle (2003)

trees in many parts of Europe during the summer 1783 were attributed to acidic clouds generated by the Laki (Iceland) fissure Eruption (Grattan & Pyatt, 1994). In Hawaii, from 1969 to 1973, severe yield decline and quality reduction occurred on field grown tomatoes. This was related to the gas emission of Kilauea volcano 45 km distant (Kratky *et al.*, 1974). In Costa Rica, exposition to acid emission from Poás volcano affected vegetation and livestock in the 90's (Nicholson *et al.*, 1996). However, during the wet season, plant damages were reduced, probably because rainfall effectively scoured the main acid components of the plume close to their source (Nicholson *et al.*, 1996). A well-documented case of vegetative deterioration by volcanic gases is found at Masaya (Nicaragua), where a 150-year history of gas release episodes has created strong perturbations in the ecosystems downwind (McBirney, 1956; Johnson & Parnell, 1986; Delmelle *et al.*, 2002). Within 15 km of the active crater, 22 km^2 of forest and coffee plantations were destroyed by the low-altitude gas plume. Cultivation here is rendered difficult or impossible.

2.2 The sulphur cycle

2.2.1 Global sulphur cycle*

Sulphur is the tenth most abundant element in the universe (Stevenson, 1986) and ranks thirteen in the abundance in the Earth's crust. The largest global reservoir of sulphur is located in the lithosphere, which contains about 10 500 billion tons of S and is followed by the ocean, the second largest reserve (2210 billions tons S; Figure 2.1). Sulphate is, indeed the most abundant anion in seawater, second after chloride. In the atmosphere, the last of the reserves, sulphur concentration is three orders of magnitude lower, despite the large S flows into it (Figure 2.1).

The primary S components in the atmosphere are H_2S, SO_2, SO_4^{2-} and dimethyl sulphide. Residence times of sulphur compounds in the atmosphere have been estimated to range between several hours and several weeks; short enough to keep atmospheric levels low, but long enough to allow sulphur compounds to be carried long distances away from the sources.

Although more than 100 tons of H_2S are biogenically volatilised to the atmosphere annually, H_2S is oxidised to SO_2 very rapidly (Kennedy, 1986). The ultimate fate of sulphur in the atmosphere is the oxidisation into sulphate ion, usually as sulphuric acid (H_2SO_4) or as am-

*Adapted from Smil (1985) and Greyson (1990)

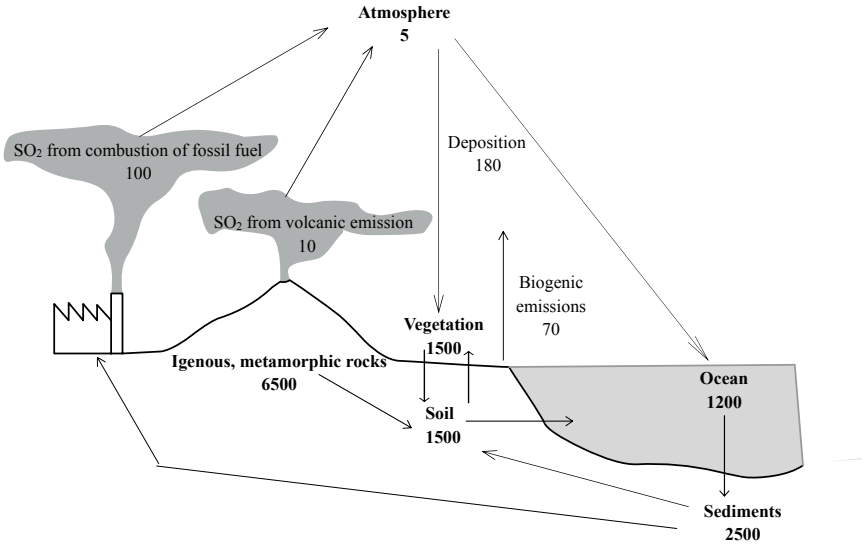

Figure 2.1: Global S cycle, values are in billions of tons of sulphur. Adapted from Smil (1985).

monium bisulphate (NH_4HSO_4) and ammonium sulphate ($(NH_4)_2SO_4$). Sulphuric acid, ammonium bisulphate and ammonium sulphate are all hydroscopic substances, readily dissolving in water. They wash out of the atmosphere during precipitation events.

The modern global sulphur cycle differs noticeably from the 'pre-industrial' sulphur cycle since a large portion of anthropogenic sulphur has been added to the atmosphere each year. Historically, anthropogenic S emissions in both Europe and North America increased gradually from the early part of the last century to a maximum in the 1970's, and since then have been decreasing due to the adoption of pollution control measures. In Western Europe, SO_2 emissions have decreased from 26 Tg S yr^{-1} in 1979 to 21 Tg S yr^{-1} in 1988 (Whelpdale, 1992). The decreases in emissions led to considerable decrease in S deposition from the atmosphere. This has reduced acid deposition but also resulted in a greater frequency of S deficiency in crops (Zhao *et al.*, 1996). In contrast, S emissions have increased substantially in developing countries during the past decades. In East Asia, SO_2 emissions have increased from 1.6 Tg S yr^{-1} in 1975 to 14.6 Tg S yr^{-1} in 1987 (Kato & Akimoto, 1992).

The largest natural source of sulphur in the atmosphere is the anaerobic bacterial decomposition of organic sulphur, which produces H_2S and dimethyl sulphide. Other major natural atmospheric sources include volcanic activity and sea spray that leads to the emission of SO_4^{2-}

and SO_2. Nowadays, the contribution of anthropogenic emission to the global atmospheric emission of SO_2 and NO_x is larger than that of natural sources. However, recent studies indicate that in some regions of the world and particularly in Asia, volcanic sources contribute significantly to total sulphur emission and deposition (Arndt *et al.*, 1997). For example, the continuous release of SO_2 from Mt. Etna (Italy) is comparable with the total industrial S emission from France on an annual basis. Furthermore, volcanoes may account for ∼30 % of the total S deposition in Japan and ∼50 % in Indonesia (Arndt *et al.*, 1997).

2.2.2 Sulphur cycling, retention and mobility in soils*

Sulphur is an essential element for all living organisms, and is often referred as the fourth major nutrient for agricultural crops, following N, P and K (Syers *et al.*, 1987). Sulphur is a structural constituent of organic compounds, some of which are uniquely synthesised by plants, providing animals with essential amino acids (methionine and cysteine).

Sulphur inputs to soils originate from three major sources: mineral weathering, atmospheric deposition, and organic matter decomposition (Edwards, 1998). In unpolluted natural situations, the primary source of S in soils is parent material weathering (Hutchinson, 1979). However, anthropogenic or volcanogenic pollutants may add considerable S to soils. Atmospheric S inputs are thus the major source of S for terrestrial ecosystems. In agricultural soils, however, S-fertiliser may become the main source of S.

Plant removal and leaching are two major outputs of S. Leaching of SO_4^{2-} is potentially the largest component of S losses (Syers *et al.*, 1987). It is generally thought that in both agricultural and forest soils, the amount of SO_4^{2-} in drainage water is similar to the amount deposited from the atmosphere. Sulphur can also be lost from both soil and vegetation as gaseous compounds such as H_2S and dimethyl sulphide. However, volatile S fluxes are very small relative to those via leaching. For example, Andrea & Jaeschke (1992) estimated that in the wet tropics, average biogenic emission ranged from 0.16 to 0.52 kg S ha^{-1}. In contrast, SO_4^{2-} leaching rates in forest ecosystems are generally greater by up to two orders of magnitude, typically ranging from 5 to 60 kg S ha^{-1} (Mitchell *et al.*, 1992).

Soil sulphur can be split into two broad pools: organic and inorganic forms. Most of the total S pool in soils is composed of organic fractions (Williams, 1967; Freney & Williams, 1983), primarily due to leaf litter

*Adapted from Edwards (1998)

inputs. Organic S in microorganisms constitutes less than 5 percent of total soil S, even in the microbially active zones (Mitchell & Fuller, 1988). Transformations between major compartments of the S cycle (Figure 2.2) result in a dynamic flux among organic and inorganic forms. One interesting feature of soil S cycle is that a significant proportion of total S can be cycled and accumulated as SO_4^{2-}, within both vegetation and soils.

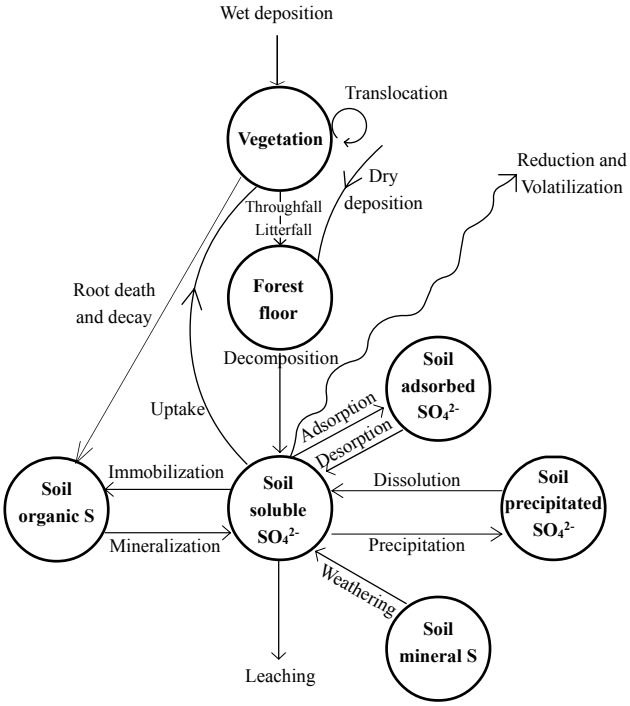

Figure 2.2: Soil S cycle, adapted from Johnson (1984).

In most forest soils, organic S is the dominant pool of S (>90%; Johnson & Mitchell, 1998) and may contribute up to 98% of the total soil sulphur (Freney, 1961). However, in soils exhibiting high sulphate retention capacity and/or high levels of S deposition, SO_4^{2-} concentrations may approach or exceed that of organic S (Mayer *et al.*, 2001). Yet, current methods for determining inorganic S content in aerated mineral soils often result in underestimates (Prietzel & Hirsch, 1998).

Soil organic sulphur

Organic S in soil organic matter occurs in two primary forms: ester sulphates, the main form of organic S, which have C-O-SO_3 linkages;

and carbon-bonded S, which has direct C-S linkages. A few other organic forms also exist, but they are of comparatively minor importance. Ester sulphates include compounds such as choline sulphate, phenolic sulphates, and sulphated polysaccharides. Carbon-bonded S is associated principally with amino acids such as methionine and cysteine, and sulpholipids (Neptune *et al.* 1975; Tabatabai & Bremner, 1972).

Classification of organic S into these two broad groups partly originated as a result of laboratory fractionation techniques described by Freney *et al.* (1970). Hydriodic (HI) acid-reducible S is believed to be composed mainly of ester sulphate S, whereas carbon-bonded S is calculated through the difference between total organic S and HI acid-reducible S. Ester sulphates originate predominantly from microbial biomass material (McLaren *et al.*, 1985) and microbially formed materials (Fitzgerald, 1978). Ester sulphate acts as readily available S pool when needed for plant and microbial nutrition (Strickland *et al.*, 1987), because it is mineralised faster than C-bonded S (Schindler *et al.*, 1986). Soil microorganisms and plant roots can hydrolyse ester sulphates when S is needed to satisfy immediate nutritional demands (McGill & Cole, 1981). In contrast, most C-bonded S in soils is derived from litter and dead root inputs, though some is present in microbial biomass. Carbon-bonded S is broken down less easily and, therefore, is less labile and available to plants and microorganisms (Fitzgerald *et al.*, 1982).

Soil inorganic sulphur

Within well-drained, well-aerated soils, most inorganic S occurs as SO_4^{2-}, and the amount of reduced S compounds are generally <1% (Freney, 1961). In contrast, under anaerobic conditions, the main form of inorganic S in soils is sulphide and often elemental S (Johnson & Mitchell, 1998). Elemental S and sulphides are uncommon in well-drained soils because they are oxidised rapidly to SO_4^{2-}. Sulphate is the most mobile form of S in forest soils (Johnson & Mitchell, 1998). In solution, SO_4^{2-} is associated with calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), ammonium (NH_4^+), hydrogen (H^+), or aluminium (Al^{3+}), depending upon the buffering character of the system. In soils, inorganic SO_4^{2-} may be retained through various processes including adsorption, precipitation, immobilisation and occlusion as detailed in section 2.2.3.

Immobilisation, mobilisation, and mineralisation

Soil sulphur is continuously cycled between inorganic and organic S forms. This cycle includes immobilisation, mobilisation and mineralisation.

Immobilisation, or the assimilation of S into microbial cells (Edwards, 1998), depends completely on microbial metabolism (Fitzgerald *et al.*, 1983). Immobilisation occurs in organic and mineral soil layers, and immobilised S usually is incorporated into organic matter by covalent bonding (Strickland *et al.*, 1987).

Mobilisation, the process by which large organic S molecules are reduced microbially to smaller S molecules (Edwards, 1998), is an important process since it controls S mineralisation rates after soluble organic S is exhausted.

Sulphur mineralisation goes beyond mobilisation in that organic S forms are transformed to inorganic forms. Mineralisation has been described as microbially driven decomposition. However, mineralisation of ester sulphates does not require direct microbial activity (McGill & Cole, 1981). Ester sulphates are mineralised more easily than C-bonded S because they are less bonded covalently to humic compounds (McGill & Cole, 1981). While microorganisms may not be necessary for S transformations, they are responsible for the majority of the activity.

Mobilisation, immobilisation and mineralisation are mainly microbially mediated. Therefore, factors that affect microbial population also affect these processes. Net S mineralisation depends upon the S supply and microbial demand. Consequently, in systems where S is limiting, a larger percentage of total S is found in microbial biomass than in systems where S is not limiting (Strick & Nakas, 1984).

2.2.3 Inorganic sulphate retention in soils

Sulphate may accumulate in soils through various processes, including (i) immobilisation as organic S, (ii) adsorption on the mineral surface, and (iii) precipitation in mineral phases (e.g. Adams & Rawajfih, 1977; Prietzel & Hirsch, 2000).

Anion adsorption can be non-specific or specific. Non-specific adsorption involves only electrostatic (Coulombic) attraction, while specific adsorption occurs by ligand exchange (Parfitt & Smart, 1978). Specific adsorption is generally believed to be the predominant mechanism of SO_4^{2-} sorption in soils (Neary *et al.*, 1987).

In non-specific adsorption, SO_4^{2-} is held within the double diffuse layer as a counter ion to positively charged surfaces on organic matter,

layer silicates, or oxide- and hydrous oxide-dominated surfaces (Figure 2.3). Because only electrostatic attraction is involved in non-specific adsorption, desorption easily occurs, either by increasing solution pH (Nodvin *et al.*, 1986) or by exchange with other anions that have a greater or equal affinity for adsorption (Parfitt, 1978).

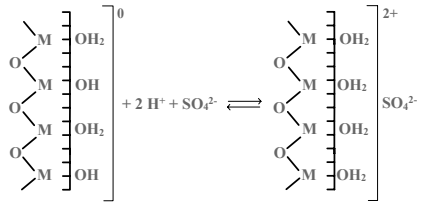

Figure 2.3: Non-specific adsorption of SO_4^{2-}.

Specifically adsorbed anions are held more tightly (Figure 2.4) than non-specifically adsorbed. Most specific adsorption occurs in soils with high levels of free iron and aluminium oxides and hydroxides (Rajan, 1978). Ligand exchange can occur when a net negative, positive, or zero charge exists. Rajan (1978) suggested two possible mechanisms for specific retention of SO_4^{2-}: a bidentate and a monodentate coordination.

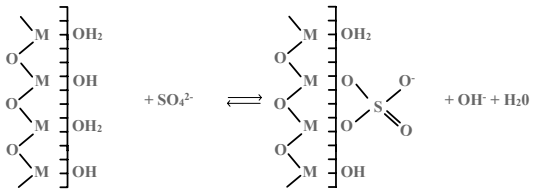

Figure 2.4: Bidentate specific adsorption of SO_4^{2-}.

The concentration dependency of SO_4^{2-} adsorption has been described mathematically in terms of several types of linear and nonlinear equations or isotherms. The Freundlich and Langmuir are the two most commonly used adsorption isotherms. The Langmuir equation probably describes SO_4^{2-} adsorption better over large concentration ranges used in the laboratory or over long periods of SO_4^{2-} accumulation in the field, because a maximum adsorption capacity is expected for most if not all soils.

Factors affecting sulphate adsorption and desorption

Anion adsorption is controlled predominantly by pH, anion concentration, the presence of other ions in solution, and the properties of the

colloidal surfaces. However, because adsorption is not a simple exchange process, it is affected by many other physical, chemical, and biological factors (Parfitt, 1978).

Laboratory studies show that adsorption typically increases with decreasing pH induced by additions of acidic compounds (Rajan, 1978; Couto *et al.*, 1979; Singh, 1984c). In general, older, highly weathered soils are thought to have greater adsorptive capacities than younger, less weathered soils. The difference is attributed to a greater development of mineral surfaces (Johnson & Henderson, 1979) or short-range ordered minerals (Camps Arbestain *et al.*, 1999) in older soils. Because adsorption is physically and chemically controlled and not microbially mediated (Edwards, 1998), in the laboratory, soil temperature and moisture have been found to affect SO_4^{2-} adsorption only minimally.

Many studies have shown that organic matter can influence adsorption. Chao *et al.* (1962) and Haque & Walmsley (1973) reported that SO_4^{2-} adsorption was positively correlated to organic matter content. Yet, Johnson *et al.* and (1979) Singh & Johnson (1986) reported a negative correlation. In soils where a negative effect was observed, a number of mechanisms have been suggested. Organic coatings may block adsorption sites (Johnson *et al.*, 1979; Singh, 1984b), or organic anions may compete with SO_4^{2-} for adsorption sites (Parfitt, 1978; Marcano-Martinez & McBride, 1989). Organic matter also may retard iron and aluminium crystallisation (Neary *et al.*, 1987), which in turn reduces the amount of available adsorption sites.

Sulphate adsorption may be significantly affected by the length of contact time between solid and liquid phases (Singh, 1984c). Many studies have shown that an increase in contact time results in an increase in SO_4^{2-} adsorption and/or of the irreversible character of the sorption process (Sanders & Tinker, 1975; Barrow & Shaw, 1977; Johnson *et al.*, 1979). The increased adsorption with contact time under field conditions has been termed 'ageing' (Johnson *et al.* 1979). In this respect, the adsorption of SO_4^{2-} is similar to the behaviour of PO_4^{3-}, which adsorption in soil is first rapid, but subsequently followed by a rate-limiting slow reaction (Rajan & Fox, 1972). The slow reaction of PO_4^{3-} has been attributed to (i) diffusion through coating of precipitated metal phosphate surrounding metal oxide particles (van Riemsdijk *et al.*, 1984) and (ii) diffusion into or between aggregates of oxide minerals (Barrow, 1983).

Sulphate precipitation

Investigations on sulphate retention in soils have frequently considered the role of precipitation in controlling solid-solution phase S distribution

(van Breemen, 1973; Adams & Rawajfih, 1977; Nordstrom, 1982; Hue *et al.*, 1985; Courchesne & Hendershot, 1990; Hue *et al.*, 1990; Wolt *et al.*, 1992; Prietzel & Hirsch, 2000; Mayer *et al.*, 2001; Agbenin, 2003).

In soils, SO_4^{2-}-bearing minerals are generally present as compounds of Ca, Ba, Na, Mg and Fe, e.g. gypsum [$CaSO_4.2H_2O$] in gypsisols, barite [$BaSO_4$] in acid sulphate soils (Hanor, 2000), Na_2SO_4 and $MgSO_4$ salts in evaporites (Keller *et al.*, 1986), and schwertmannite [$Fe_8O_8(OH)_6SO_4$] and jarosite [$KFe_3(SO_4)_2(OH)_6$] in acid sulphate soils or in soils affected by acid mine drainage (e.g. van Breemen & Harmsen, 1975; Bigham *et al.*, 1996; Sùcha *et al.*, 2002). As suggested by Adams & Rawajfih (1977), the formation of basic aluminium sulphate (BAS) minerals [$(K,Na)_nAl_x(OH)_y(SO_4)_z$], also named hydroxy aluminium sulphate, may also contribute to sulphate retention in soils.

The presence of BAS minerals in soils has been generally inferred from studies involving geochemical modelling (e.g. Courchesne & Hendershot, 1990; Wolt *et al.*, 1992; Agbenin, 2003). Alunite [$KAl_3(SO_4)_2(OH)_6$], jurbanite [$AlSO_4OH.5(H_2O)$] and basaluminite [$Al_4SO_4(OH)_{10}.5(H_2O)$] were predicted to form according to calculations based on soil solution composition from a large variety of soil environments: acid sulphate soils (van Breemen, 1973), forest soils (e.g. Courchesne & Hendershot, 1990; Prietzel & Hirsch, 2000; Mayer *et al.*, 2001, Barton *et al.*, 2002), soils fertilised with S (Hue *et al.*, 1985), and ones exposed to marine aerosols (Hue *et al.*, 1990). Despite numerous attempts to identify BAS in soils, these minerals have not yet been detected in them.

Several BAS minerals of poor crystallinity and low solubility are known to form in acid sulphate environments (Bigham & Nordstrom, 2000). These minerals occur as fine-grained materials with small particle size and poor crystallinity. Bigham & Nordstrom (2000) defined four distinct compositional sets of BAS minerals, characterised by their Al:SO_4 ratio: Hydrobasaluminite [$Al_4SO_4(OH)_{10}.15(H_2O)$] and basaluminite have the highest ratio (4:1), followed by zaherite [$Al_{12}(SO_4)_5(OH)_{26}.20(H_2O)$] (2.4:1), then meta–aluminite [$Al_2SO_4(OH)_4.5(H_2O)$] and aluminite [$Al_2SO_4(OH)_4.7(H_2O)$] (2:1), and finally jurbanite (1:1). In acid sulphate waters, most aluminous precipitates have the composition of basaluminite (Bigham & Nordstrom, 2000) but are very poorly crystalline so that structural details are lacking.

The most frequently cited BAS minerals in soils are basaluminite, alunite and jurbanite. Basaluminite was first identified by Hollingworth & Bannister in 1950 as a naturally occurring mineral in Northamptonshire, England. Since then, the natural occurrence of basaluminite has been reported by many workers; e.g. in sandstones (Frondel, 1968), in volcanic waters (Delmelle & Bernard, 2000), and even recently in Bel-

gium (Goemare, 2004). Alunite has been observed in sedimentary environments (Long *et al.*, 1992), in caves (Polyak & Güven, 1996), and it is commonly found in volcanic regions where hydrothermal alteration has occurred (Bigham & Nordstrom, 2000). Jurbanite was first discovered in underground Cu mine in Arizona by Anthony & McLean (1976) and is likely the unknown mineral that van Breemen postulated as a control on dissolved aluminium in acid mine waters and acid sulphate soils. Their formation may follow these reactions:

$$4Al(OH)_3 + 2H^+ + SO_4^{2-} + 3H_2O \rightarrow Al_4(OH)_{10}(SO_4).5H_2O \quad \text{(basaluminite)} \quad (2.1)$$

$$3Al(OH)_3 + 3H^+ + K^+ + 2SO_4^{2-} \rightarrow KAl_3(OH)_6(SO_4)_2 + 3H_2O \quad \text{(alunite)} \quad (2.2)$$

$$Al(OH)_3 + SO_4^{2-} + 2H^+ + 3H_2O \rightarrow AlOH(SO_4).5H_2O \quad \text{(jurbanite)} \quad (2.3)$$

The formation of alunite and basaluminite is (i) thermodynamically favourable in sulphate-containing acid environments at 25 °C and 1 atm, (ii) may occur at relatively low solution SO_4^{2-} concentration (Adams & Rawajfih, 1977; Adams & Hajek, 1978).

According to Nordstrom (1982; Figure 2.5), at 10^{-4} M and 10^{-2} M SO_4^{2-}, jurbanite is stable over a wide range of acid pH values from less than 0 to 3.3. Alunite is stable in the pH range 3.3-5.7. At higher pH value, gibbsite is the most stable mineral. Basaluminite shows a solubility pattern comparable to gibbsite and alunite, but it is metastable over the whole pH range (Nordstrom, 1982). Alunite may form from the transformation of less stable basaluminite in the presence of K^+ and SO_4^{2-} (Wolt, 1980).

In the laboratory, synthesis of BAS minerals resulted in amorphous product at 25 °C (Bassett & Goodwin, 1949), increasing the temperature (50 °C) or adding minerals (such as montmorrillonite) favoured the formation of more crystalline products (Singh & Brydon, 1967). This process may involve $Al(OH)_x$ precipitates initially present in the interlamellar space of the montmorillonite lattice that is progressively transformed in contact with a SO_4^{2-} rich solution to a crystalline BAS minerals (Singh & Brydon, 1967). It is conceivable that the presence of minerals like montmorrillonite may favour the formation of BAS minerals in natural conditions also (Singh & Brydon, 1969).

In pyrite-containing soils, BAS minerals and Fe-bearing sulphate minerals formation may result from pseudomorphic replacement of pyrite under an oxidising environment (Shamshuddin *et al.* 1995). In

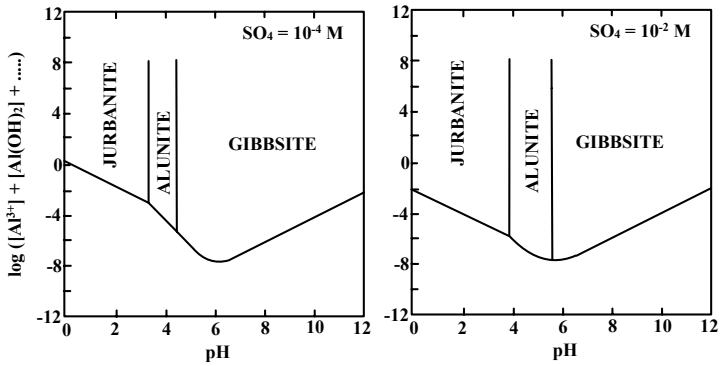

Figure 2.5: Stability diagrams showing the pH range for the most stable minerals. Adapted from Nordstrom (1982).

German forest soils, Khanna *et al.* (1987) explained the retention and release of SO_4^{2-} in acidic forest soils by the successive precipitation and dissolution of jurbanite. They suggested that jurbanite formed from the dissolution of gibbsite. This hypothesis was supported by Gundersen & Beier (1988) in Danish forest soils. The formation of BAS minerals in soils has therefore an obvious influence on Al speciation. According to Bi *et al.* (2001), increasing SO_4^{2-} concentration decreases the total Al concentration, and thus reduces Al toxicity. Overall, the formation of BAS minerals may involve direct precipitation in solution and formation of a pure mineral, or surface precipitation (Li & Stanforth, 2000).

During formation of BAS minerals, Prietzel & Mayer (2005) generally observed small but significant isotopic fractionation of +0.84‰ for alunite, and +1.2‰ for natroalunite, with the heavier isotope ^{34}S being enriched in the minerals. Adsorption and desorption of SO_4^{2-} do not involve significant S isotopic fractionation (Van Stempvoort *et al.*, 1990), and in most biological transformation processes under aerated conditions isotopic fractionation is about +5‰ (Schoenau & Bettany, 1989). It is thus likely that S isotope fractionation during the formation of BAS minerals is not confounded with other processes (Prietzel & Mayer, 2005).

The contribution of BAS mineral formation to sulphate retention in soils is thus widely accepted. Indirect proofs based on soil solution data support this hypothesis. However, Sposito (1984) emphasised that the saturation with respect to a given mineral is not sufficient proof of a precipitation mechanism. Moreover, direct evidence of the occurrence of BAS minerals in soils is still lacking.

Distinguishing between adsorption and precipitation

When a sulphate solution is added to a soil, the sulphate concentration generally decreases. The disappearance of sulphate from solution may originate from physico-chemical adsorption or precipitation (Nordstrom, 1982; Wolt *et al.*, 1992). Mechanistically, these two phenomena are different but on a macroscopic level they may be indistinguishable (Nordstrom, 1982). For instance, precipitation of alunite and basaluminite may be mistaken for specific adsorption, because OH^- is released during their formation causing solution pH to rise (Adams & Rawajfih, 1977; Marcano-Martinez & McBride, 1989). Precipitation probably only becomes important in soils at low pH since metals such as aluminium must be in solution before precipitation can occur (Rajan, 1979; Wolt, 1980).

So far, few studies have focused on SO_4^{2-} precipitation. In contrast PO_4^{3-} precipitation has been widely examined. For instance, precipitates of PO_4^{3-} have been observed in solution when sufficient PO_4^{3-} was added, however the transition point between adsorption and precipitation was not clearly defined (van Riemsdijk & Lyklema, 1980). Only recently, Li & Stanforth (2000) have clearly observed the transition between the two processes by studying zeta potential changes during PO_4^{3-} sorption on goethite. Adsorption of PO_4^{3-} indeed increased the negative charge of the hydrous metal oxide, whereas precipitation, which increased the thickness of the surface precipitate, had little effect on the surface charge.

2.3 Environmental setting

2.3.1 Masaya volcano

Masaya volcano is a basaltic shield volcano forming a large volcanic complex located at 11.984 °N 86.161 °W in south-western Nicaragua, 20 km south of the capital, Managua (Figures 2.7 and 2.6). It is composed of a nested set of calderas and craters, the largest of which is Las Sierras shield. The Masaya caldera is thought to have formed between ∼2250 and 6500 BP by a series of large ignimbrite eruptions, which ejected 8 km^3 of material (Williams, 1983). The currently active pit crater, Santiago, has been nearly continuously active since its formation in 1853, and is characterised by episodes of degassing and lava lake formation. Explosive activity at Santiago has typically been restricted to small strombolian explosions and ash emission with sporadic ejection of blocks and bombs, vesiculated scoria and juvenile ash. One of the most characteristic phenomena at Masaya are cycles of prolonged pas-

sive degassing. There have been at least five such cycles of activity at Masaya since the formation of Santiago crater in 1853 (Stoiber *et al.*, 1986; Rymer *et al.*, 1998).

Figure 2.6: Map of Nicaragua showing the location of the study area.

The most recent cycle began in May 1993 and continues to date (Rymer *et al.*, 1998; Delmelle *et al.*, 2001). The monitoring of this activity in 1999 revealed that the volcano is emitting approximately 19 kg s^{-1} of SO_2, 7 kg s^{-1} of HCl, and 1 kg s^{-1} of HF into the atmosphere (Delmelle *et al.*, 1999). The estimated cumulative SO_2 emission during the period 1993-2001 in Masaya is at least 3.0 x 10^9 kg. Masaya Volcano is currently one of the world's strongest natural sources of SO_2 and also contributes substantial amounts of halogens to the atmosphere.

For local effects, an important feature is that the volcanic plume is typically emitted at a low altitude (∼560 m a.s.l.), and is consistently transported in a NE-SW direction by the trade winds over an area with complex topography. Transport of the Masaya emissions downwind gives large ambient concentrations of SO_2, leading to enhanced SO_2 deposition within a 1250 km^2 area (Delmelle *et al.*, 2001). The degassing crater (560 m above sea level) inside the caldera is actually below the western caldera ridge (at 580 m). Approximately 15 km west, the Llano Pacaya ridge (700-920 m) is another prominent topographic feature (Figure 2.9). Reported values of SO_2 dry-deposition range between 200 and 700 mg SO_2 m^{-2} day^{-1}, with clear maxima at high altitude. The combined deposition of SO_2 and halogenated acids is equivalent to H^+ fluxes of 1-30 mg m^{-2} day^{-1}, up to 10 times larger than observed deposition worldwide (Delmelle *et al.*, 2001).

There is strong evidence that chronic and acute exposures to the volcanic acids have resulted in destruction of the natural forest stands and coffee plantations in a 22-km^2 area downwind from the volcano (Delmelle *et al.*, 2002). The Nicaraguan Union of Coffee Planters (UNI-

CAFE) concluded recently that about 57% of the total coffee-growing area (∼5180 ha) in the Las Sierras highlands are suffering from the deleterious influence of the volcanic fumes and coffee production for the period 1998-1999 dropped by almost 40% compared with the 1995-1996 period (Delmelle *et al.*, 2002 and references therein). This decrease in coffee productivity may be a consequence of higher air pollutant levels associated with substantially stronger gas emissions in 1998-1999 (1800 t SO_2 d^{-1}) than in 1995-1996 (600 t SO_2 d^{-1}). Besides coffee, other types of cultivation (e.g. citrus, mango, papaya and banana) are also affected to various degrees by the gas plume (Delmelle *et al.*, 2002).

Figure 2.7: Masaya volcano and its acid plume.

The considerable impact of Masaya's gas plume on vegetation is illustrated in Figures 2.9 and 2.10. Those are Landsat 7 satellite images collected in May 2001. Figure 2.9 is a 'true-color' composite image, whereas Figure 2.10 ('near-infrared' composite image) denotes vegetation in red. On both images, one can clearly see the area most affected by Masaya's gas plume. The transition between the affected and less-affected area is sharp as illustrated in Figure 2.8. In the affected area, vegetation consists of a gas tolerant weedy grass composite (*Malanthora* and *Lantana spp.*; Johnson & Parnell, 1986).

Parnell (1986) analysed some Andosol profiles at sites directly exposed to the gas emission from Masaya volcano in 1979-1984. This study revealed that these soils were significantly depleted in exchangeable base cations relative to unaffected sites. The Masaya Andosols also showed a striking response to acid loading, consisting of a decrease of the soil solution pH and an increase in SO_4^{2-} retention. However, contact

of volcanogenic acid rain with vegetation produces at least a 100-fold decrease in acidity between bulk deposition and throughfall (Johnson & Parnell, 1986). Plants (*Malanthora* and *Lantana spp.*) neutralise acidity by releasing K^+ at the leaf surface, while H^+ enters the plant. The source of K^+ being the soil, roots extract K^+ from soil exchange sites by releasing H^+ into the soil. Therefore, plants are acting as a short-term acid sink for incident acid rain, the final acid sink being probably the pool of exchangeable cations (Johnson & Parnell, 1986).

Figure 2.8: Areas affected by the gas plume of Masaya volcano. The dotted line represents the boundary between the most affected areas and the transition zone, where damages to vegetation mostly consist of leaf injurries and reduced growth of plants.

2.3.2 Description of the area

The area surveyed is covered with a thick succession of Holocene basaltic ash deposits from the Masaya volcano (Parnell, 1986; Walker *et al.*, 1993). The ash falls were all erupted from Masaya and overlie, to a depth of several meters, a 22 000 year old ash fall from Apoyo caldera (Sussman, 1985). A noteworthy feature of Masaya is the lack of temporal (>30 000 years) and spatial variations in the chemistry of its tephra (Walker *et al.*, 1993).

The climate is tropical, with a mean annual rainfall of 1379 mm and a mean annual air temperature of 26.3 °C (UNA & ISRIC, 1994). The rainfall pattern is strongly seasonal: the rainy season lasts from May to October and accounts for 90% of the annual precipitation; the dry season (November-March) has a water deficit (P-ETP) ranging between 72 and 239 mm (Figure 2.11; UNA & ISRIC, 1994). The soil moisture regime is ustic (Soil Survey Staff, 1999).

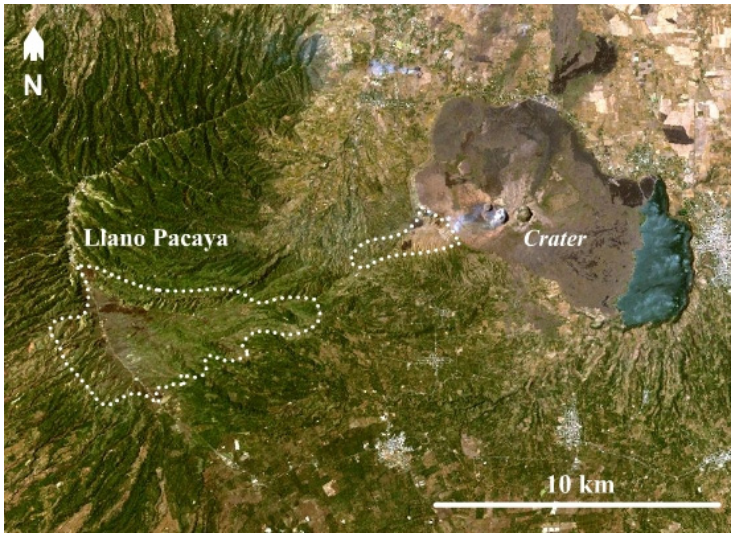

Figure 2.9: Color composite of Landsat-7 imagery created from bands 3, 2, and 1 as red-green-blue channels, respectively. The 'true-color' composite image offers a detailed view of the Masaya volcano area, the dotted lines indicate the zone most affected by the volcanic plume.

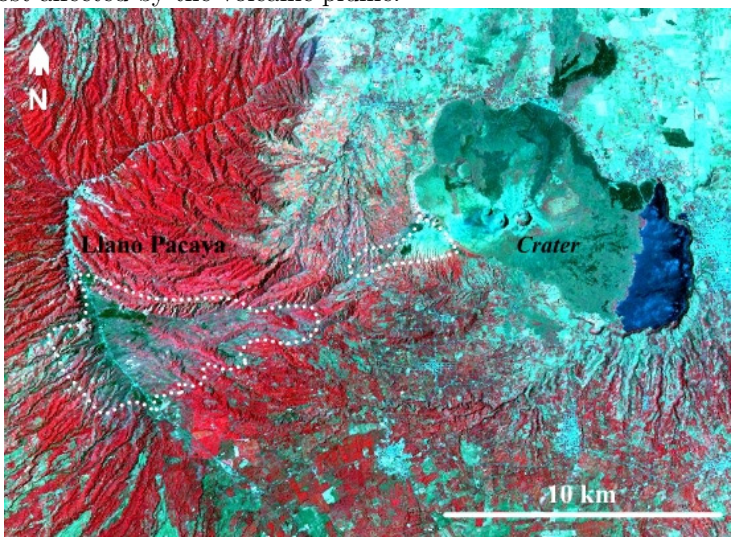

Figure 2.10: Color composite of Landsat-7 imagery created from bands 4, 3, and 2 as red-green-blue channels, respectively. The 'near-infrared' composite image offers a detailed view of the Masaya volcano area, where vegetation appears in red color.

The soil distribution pattern downwind of the volcano reflects both the age of the parent rock and distance from the source of the ash. According to a previous soil survey (Ministerio de Agricultura y Gonderia, 1971), the soils pertain to a Vitrand-Ustand-Ustoll sequence in the Soil Taxonomy (Figure 3.1; Soil Survey Staff, 1999), i.e. Vitric Andosol-Eutric Andosol-Chernozem in the WRB system (ISSS, 1998).

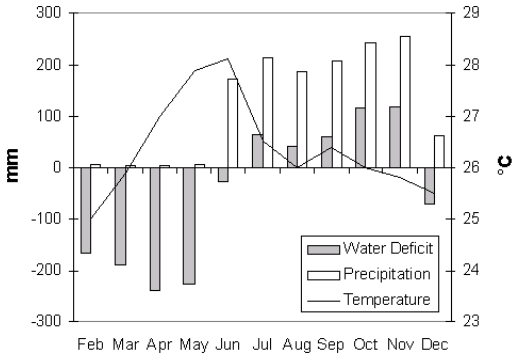

Figure 2.11: Climate diagrams of the Masaya area. Adapted from UNA & ISRIC (1994).