

This chapter is part of a Ph.D. Thesis  
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# **Acid Neutralization and Sulphur retention in S-impacted Andosols**

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# Chapter 1

## General Introduction, Objectives and Thesis Outline

### 1.1 General introduction

Sulphur releases from metal smelters and coal-power plants largely contributes to regional atmospheric acid deposition (Mylona, 1996). It is well established that this anthropogenic acid loading has increased sulphate and proton fluxes through soils in affected areas, eventually enhancing soil acidification. Today, soil acidification remains an 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).

Natural analogues of these anthropogenic emitters are certain volcanoes that can represent major sources of tropospheric S and halogen compounds (HCl and HF). In contrast to anthropogenic sources of atmospheric acidity, the environmental effects of airborne volcanic acids have been poorly studied. Yet, there is increasing evidence that these volcanic emissions enhance acid deposition significantly, both locally and regionally (Parnell, 1986; Arndt *et al.*, 1997; Delmelle *et al.*, 2001). Recent studies have also demonstrated that the dispersion and deposition of the volcanogenic pollutants can have profound impacts on the ecosystems downwind, sometimes disrupting the social and economic activities of populations (Delmelle *et al.*, 2002).

Areas exposed to prolonged addition of airborne volcanic acid compounds are typically endowed with tephra-derived Andosols presenting a range of weathering stages. Being well supplied with nutrients,

these soils support a wide variety of production systems and are usually densely settled, especially in wet intertropical areas. While Andosols have a proven capacity to buffer acid inputs, their long-term chemical response to elevated acid deposition remains poorly known (Baba *et al.*, 1995; Shindo & Fumoto, 1998; Fumoto & Sverdrup, 2000). In this respect, the high anion retention capacity of Andosols constitutes a key parameter, because it effectively increases the negative charge on the adsorbing soil constituents, thereby enhancing proton and cation adsorption (Yoshida & Kawahata, 1988; Fumoto *et al.*, 1996).

Since  $\text{SO}_4^{2-}$  concentrations are generally significant in the volcanogenic wet depositions (Delmelle *et al.*, 2001), its retention plays a key role in soils affected by acid deposition of volcanic origin (Johnson *et al.*, 1981; Fumoto *et al.*, 1996). It is also regarded as an important process in acid-buffering of Andosols (Fumoto *et al.*, 1996). In fact, all inorganic  $\text{SO}_4^{2-}$  retention processes, including adsorption and precipitation, are expected to diminish, or at least delay net acidification of soils, because (i) sulphate adsorption reduces cation leaching (Strickland & Fitzgerald, 1984; Camps Arbestain *et al.*, 1999) and (ii) both formation of  $(\text{K},\text{Na})_n\text{Al}_x(\text{OH})_y(\text{SO}_4)_z$  and  $\text{SO}_4^{2-}$  adsorption onto poorly crystalline minerals involve  $\text{OH}^-$  release or  $\text{H}^+$  consumption (Figure 2.4 and Equation 2.1; Adams & Hajek, 1978; Rajan, 1978).

There is no definitive agreement among the scientific community about the predominant  $\text{SO}_4^{2-}$  retention mechanisms, and their dependence on S deposition rates, in soils exposed to high S inputs (Mayer *et al.*, 2001). Fumoto *et al.* (1996) suggested that the amount of natively retained sulphate in Japanese Andosols is sufficient to preclude incorporation of additional atmospheric inputs. In contrast, Takamatsu *et al.* (1992) observed increased S content in soils affected by S-rich fumaroles. These have obvious implications for evaluating the long-term acid buffering capacity of these soils.

One of the most controversial issues related to  $\text{SO}_4^{2-}$  retention in soils is the hypothetical presence of  $(\text{K},\text{Na})_n\text{Al}_x(\text{OH})_y(\text{SO}_4)_z$  minerals in S-impacted soils, which has been suspected for a long time (Adams & Rawajfih, 1977; Prietzel & Hirsch, 2000). Despite numerous attempts, these minerals have not yet been detected in the soil environment (Prietzel & Hirsch, 1998) and so far, its presence has been inferred mostly from thermodynamic considerations (e.g. Nordstrom, 1982; Wolt *et al.*, 1992).

It appears that areas around degassing volcanoes may constitute well suited natural laboratories to gain insights into the sulphate retention mechanisms and acidification of Andosols exposed to prolonged deposition of acid and S compounds (Parnell, 1986; Parnell & Burke, 1990).

This is relevant to better assess and mitigate the environmental impacts of persistently degassing volcanoes. It also should be viewed in the broad context of the rapid increase of industrial  $\text{SO}_x$  and  $\text{NO}_x$  emissions in East Asia and some Latin America countries (Arndt *et al.*, 1997; Shindo & Fumoto, 1998), where volcanic sources are more important and Andosols are more common than in Europe and North America.

The present study was carried out in the vicinity of an active volcano of Nicaragua to investigate the effects of strong acid and sulphur depositions on sulphate retention and acidification in Andosols.

## 1.2 General objectives

By applying both laboratory and field-study approaches in an outstanding natural laboratory: the area of persistently degassing Masaya Volcano (Nicaragua), the general objectives of this PhD thesis are (i) to identify the major sinks of protons and (ii) characterise the retention mechanisms and the fate of sulphate anion, in Andosols exposed to strong atmospheric deposition of volcanic acid and  $\text{SO}_2$ .

These objectives were framed within several working hypotheses (Y):

- Y.1 Combined with a high CEC, the large content of weatherable minerals in Andosols should make them relatively insensitive to acidification (van Breemen *et al.*, 1983).
- Y.2 The large capacity of Andosols to retain various anions, including sulphate, also may delay net acidification (Rajan, 1978).
- Y.3 Sulphur deposition rates influence sulphate retention pattern in soils (Mayer *et al.*, 2001).
- Y.4 The nature of the soil constituents mainly governs retention of  $\text{SO}_4^{2-}$  (Camps Arbestain *et al.*, 1999).
- Y.5 The adsorption of  $\text{SO}_4^{2-}$  is influenced by the presence of  $\text{F}^-$  in soil solution (Parfitt, 1978).
- Y.6 Since various anions may be retained in soils in a way similar to  $\text{PO}_4^{3-}$  (Barrow, 1983),  $\text{SO}_4^{2-}$  retention may similarly involve various mechanisms, including occlusion.
- Y.7 Although direct evidence is still lacking, the formation of basic aluminium sulphate (BAS) minerals  $(\text{K},\text{Na})_n\text{Al}_x(\text{OH})_y(\text{SO}_4)_z$ , also named hydroxy aluminium sulphate, contributes to sulphate retention in soils (Adams & Rawajfeh, 1977).

### 1.3 Thesis outline

Figure 1.1 gives a schematic overview of the thesis outline. The thesis is structured in three parts. **Part I** is devoted to the identification and relative importance of the mechanisms involved in the regulation of volcanogenic acid flux, it also reports on the fate and distribution of the volcanogenic anions ( $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  in soils. **Part II** focuses on the sulphate retention mechanisms and the distribution of the various inorganic S pools. Finally, **Part III** discusses some potential environmental and agronomical issues related to strong volcanic acid loading. In the introductory chapter, I provide a review of the current knowledge on soil acidification and S retention in soils (**Chapter 2**).

**Chapter 3** presents the results of a field investigation aimed at characterising the physico-chemical and mineralogical properties of the soils downwind of Masaya volcano, and their response to acid and sulphur inputs. This study focuses on (i) the contrasting effect of  $\text{SO}_2$  and  $\text{H}^+$  on acidification of Andosols and (ii) the identification of the major sinks of protons in these soils.

The continuous emissions of  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{HF}$  by Masaya volcano represent a substantial source of atmospheric S-, Cl- and F-containing acid inputs for local ecosystems. In **Chapter 4**, I report on the effects of such acid depositions on the sulphate, chloride and fluoride contents and status in soils located downwind from the volcano. I also briefly discuss some potential environmental issues related to anion accumulation in the acid-impacted soils.

The dynamic of both acid neutralisation processes and retention of the volcanogenic anions in soils is described in **Chapter 5**. It reports on an acid leaching experiment on undisturbed soil columns collected around the volcano. This chapter specifically aims at gaining insights into the factors that govern (i) the dynamic of acid neutralisation processes, (ii) the conditions favouring BAS minerals formation, and (iii) the mobility of added anions ( $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$ ).

Since  $\text{SO}_4^{2-}$  retention plays a key role in soils affected by acid deposition involving S input, and is regarded as an important process in acid-buffering of Andosols, the correct assessment of the content of inorganic S is essential in the estimation of the soil susceptibility to acidification. In **Chapter 6**, I present the results of a study aimed at (i) assessing the  $\text{SO}_4^{2-}$  mobilisation by different extraction solutions ( $\text{KH}_2\text{PO}_4$ , oxalate and  $\text{NH}_4\text{F}$ ) and (ii) identifying the various pools that they extract.

The formation of basic aluminium sulphate (BAS) minerals  $(\text{K,Na})_n\text{-Al}_x(\text{OH})_y(\text{SO}_4)_z$  has often been invoked to explain sulphate retention in soils. However, these minerals have not yet been directly observed in soils. In **Chapter 7**, I report on the result of an investigation aimed at identifying BAS minerals in the clay fraction of Masaya Andosols using transmission electron microscopy coupled with energy-dispersive analysis.

The adsorption, precipitation and occlusion of  $\text{SO}_4^{2-}$  may all contribute to S retention in soils, adsorption being generally the dominant process. However, in soils where strong S deposition prevails, equilibrium may be modified and  $\text{SO}_4^{2-}$  occlusion and precipitation may become significant. **Chapter 8** focuses on the sorption of  $\text{SO}_4^{2-}$  over large concentration range with the aim to provide a better understanding and quantification of  $\text{SO}_4^{2-}$  sorption in soils affected by large S inputs.

Some environmental and agronomical issues may be addressed in light of the preceding results. In **Chapter 9**, I discuss some measures to lessen the impacts of fumigation on crops and some improvements of the models aimed at calculating critical loads. I also present several issues related to the potential impact on the surrounding environment of (i) a Laki-type eruption (Iceland) in Europe and in developing countries, and (ii) the recent eruptions of Nyamuragira and Nyiragongo volcanoes in the Virunga National Park (Democratic Republic of Congo).

Finally, conclusions and perspective are drawn in **Chapter 10**.

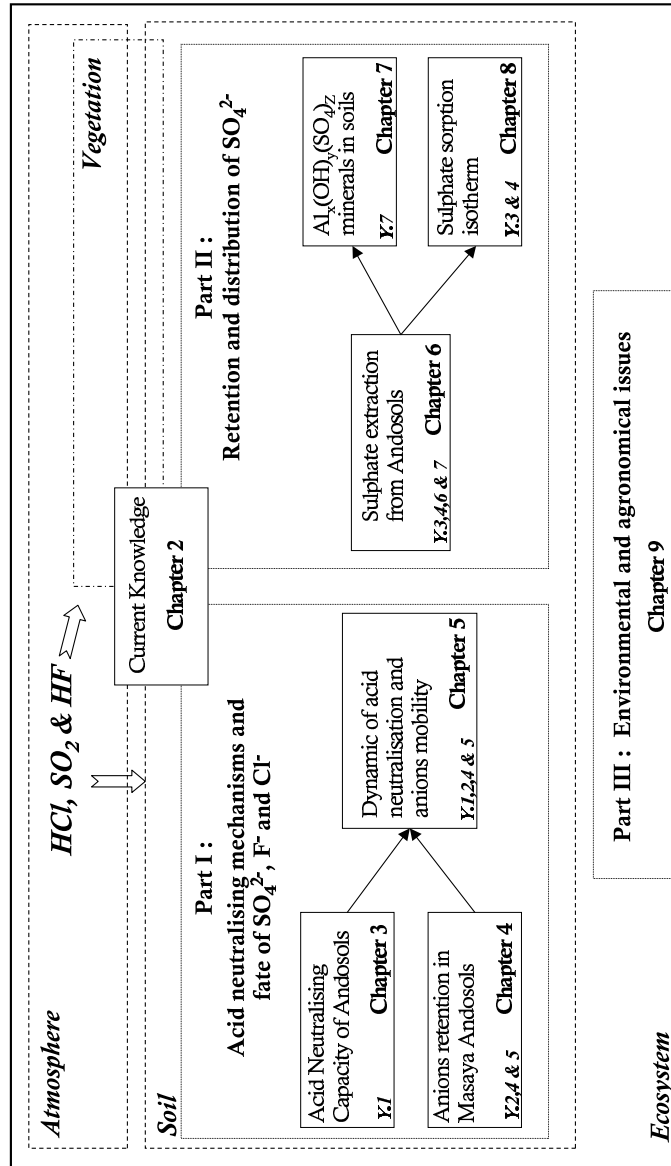


Figure 1.1: Schematic representation of the thesis outline.