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Acid Neutralization and Sulphur retention in S-impacted Andosols

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Chapter 10

General Conclusions and Perspectives

In this thesis, I investigated (i) the mechanisms involved in the regulation of acid flux and (ii) the processes involved in S retention, in Andosols downwind from Masaya volcano (Nicaragua), one of the world's largest natural source of SO₂. The following main conclusions were drawn.

10.1 Regulation of volcanic acid depositions (Y 1, 2 & 5)

The Masaya area is endowed with Vitric and Eutric Andosols developed in similar basaltic ash, but with contrasting mineral and physico-chemical properties. These soils constitute a weathering sequence, from the young, undifferentiated Vitric Andosols rich in volcanic glass to the well-developed Eutric Andosols rich in secondary alumino-silicates (allophanic substances) and iron oxide (ferrihydrite), both being short-range ordered minerals.

The long-term emission of SO₂, HCl and HF by Masaya volcano has led to important changes in the chemistry of the Andosols downwind. Continuous acid inputs have decreased pH, CEC and the content of exchangeable cations in both soils series. However, continuous inputs of volcanogenic acid have been shown to have a negligible effect on the acid neutralising capacity of the solid phase (ANC_s).

Eutric Andosols have a much larger specific surface than Vitric Andosols, linked to their large content of short-range ordered minerals. These constituents play a key role in regulating acid inputs through both cation and anion exchange. This results in (i) H⁺ removal from soil solution and (ii) reduced cation leaching in the Eutric Andosols. In

contrast, the presence of readily weatherable volcanic glass in the Vitric soil series leads to preferential lixiviation of Si and Al and slow release of alkaline and alkaline-earth cations.

Two major H^+ consumption processes were identified in the Masaya Andosols: mineral weathering in the Vitric series, and ion exchange and sorption in the Eutric series. In contrast to mineral weathering, ion exchange and sorption significantly contribute to acid-buffering in the short-term because they are rapid reactions. Soil pH was therefore lower in the Vitric than in the Eutric Andosols despite the larger ANC_s of the Vitric Andosols.

The large accumulation of inorganic SO_4^{2-} in Eutric Andosols make SO_4^{2-} retention a key process in buffering acid inputs. Indeed, sulphate adsorption, immobilisation in organic matter, or precipitation as basic aluminium sulphate (BAS; $(K,Na)_nAl_x(OH)_y(SO_4)_z$) minerals contribute to neutralise acid inputs. These processes, however, conduce to store acidity as SO_3 within the solid phase, thereby depleting ANC_s .

Immobilisation of volcanic F-containing inputs is highly efficient in the Andosols studied, although F is present in significantly less amounts than S in the volcanogenic depositions. Apparently, reaction of fluoride with Al and Fe oxyhydroxides and allophanes is an important sink for deposited volcanic F. Despite specific retention of fluoride in soils, F was transported throughout the soil profile mainly as $Al-F_x$ complexes, especially in the Vitric Andosols where volcanic glass constitutes efficient source of Al and little fluoride sorption occurred.

In contrast to sulphate and fluoride, chloride appears to exhibit an almost conservative behaviour, since accumulation of this anion is not detected in soils. Thus, deposition of volcanic HCl may be the principal acidification agent in the Masaya Andosols.

Based on these findings, it is believed that acid neutralising processes are still operative in the Masaya Andosols. Therefore, detrimental effects of acid deposition may be temporary, and the soil horizons may well recover from acidic deposition after reduction/cessation in volcanic emissions. From an agronomical point of view, weathered Eutric Andosols present better potentiality than the Vitric ones since they play a major filter role. Their buffering capacity maintain the pH, exchangeable cations and Al content at appreciable level for plant growth. It also reduces risk of fluoride pollution through specific retention. In contrast, Vitric Andosols present poorer conditions, in these soils Al toxicity and F pollution could occur.

Overall, vegetation damages in the Masaya area appear to be a consequence of persistent volcanogenic acid fumigation rather than being due to changes in soil chemistry.

10.2 Sulphate retention (Y 3, 4, 6 & 7)

Prolonged addition of volcanogenic S has modified the soil S distribution. It has noticeably increased the total S content of the Vitric and Eutric Andosols up to 5470 mg S kg⁻¹. Selective extraction data (NH₄F, KH₂PO₄ and oxalate) distinguish three major pools of inorganic SO₄²⁻: i) SO₄²⁻ adsorbed onto the surface of soil constituents, ii) SO₄²⁻ occluded into short-range ordered minerals, especially ferrihydrite, and iii) SO₄²⁻ precipitated as (K,Na)_nAl_x(OH)_y(SO₄)_z minerals. Precipitation of BAS minerals is the most effective inorganic S retention mechanism and contributes to 9-51% of the total S content. Depending on soil weathering stage and S depositions rates, sulphate occlusion and adsorption also constitute effective inorganic S retention processes, with contributions to the total S content ranging from 0 to 22% and from 1 to 36%, respectively. Acid ammonium oxalate is able to extract all these inorganic SO₄²⁻ pools and therefore is recommended as an efficient inorganic SO₄²⁻ extraction solution.

In the Vitric and Eutric Andosols, adsorption of SO₄²⁻ is mainly dictated by the content of short-range ordered minerals and thus, by surface properties. Adsorption of SO₄²⁻ dominates at low SO₄²⁻ concentration in the soil solution (< 5-7 mM), whereas precipitation of SO₄²⁻ was significant in the higher concentration range. In fact, SO₄²⁻ retention in soils is viewed as a continuum between these two processes, which explained the biphasic nature of the SO₄²⁻ retention isotherms.

Although occurrence of BAS minerals in soils has long been considered as hypothetical, sulphate precipitation appears as an efficient SO₄²⁻ retention process in Masaya Andosols. Using transmission electron microscopy coupled with energy-dispersive analysis I provide here the first direct evidence of BAS minerals in soils. It is likely that BAS minerals can form in these Andosols, since large inputs of acid and sulphur dioxide are intercepted by soils, which contain huge reserves of weatherable volcanic glass acting as an effective source of Al. Surface precipitation, i.e. two-dimensional chemisorption followed by three-dimensional nucleation and precipitation, rather than direct precipitation from solution, is the preferred formation pathway of BAS in these soils.

BAS precipitation may be more effective in the Vitric than in the Eutric Andosols. Combined with a low pH, the comparatively larger volcanic glass contents of the Vitric allow rapid release of Al, which may be readily incorporated into BAS. In contrast, the higher pH and larger SO₄²⁻ retention in Eutric Andosols, together with the presence of dissolved Al mainly as thermodynamically stable Al-F_x complexes probably impeded BAS minerals formation in the Eutric Andosols.

10.3 Further perspectives

The impacts of prolonged S and acid deposition from Masaya volcano on the chemistry of soils downwind has been clearly identified in this Ph.D thesis. However, potential impacts of worldwide volcanic emissions on surrounding ecosystems, both at a local and global scale, still remain poorly known in many volcanic areas (e.g. Virunga volcanic chain (Democratic Republic of Congo), Yasur volcano (Vanuatu) and Sakura-Jima volcano (Japan)), although several reports indicate profound impacts on soils, water, fauna and flora downwind of certain volcanoes. Therefore, detailed studies should be engaged to further assess the environmental, agronomical and economical effects of this natural pollution.

Besides SO_2 , HCl and HF , volcanoes also emit considerable amount of heavy metals in the atmosphere (Nriagu, 1989). Such emissions may thus also affect the surrounding ecosystems. Therefore, a better knowledge of the fate of these compounds in the environment is relevant to better assess and mitigate the environmental impacts of persistently degassing volcanoes. In this respect, the Masaya area may constitute a well-suited natural laboratory since Moune *et al.* (2005) reported significant heavy metal emissions (e.g., As, Zn, Cu) from this volcano.

Because they are densely settled, major concerns in areas strongly affected by persistent acid volcanic fumigation, are related to optimal agricultural practices. I suggest some measures to counteract acid fumigation in the Masaya area, but further research and especially field trials are needed to provide local farmers with useful tools and strategies for cultivating in these low-productive environment.

I show that sulphur distribution in soils is strongly influenced by prolonged deposition of atmospheric S. However, details are lacking on its effects on the S cycle. In this respect, S isotope chemistry offers promising perspectives (Mayer *et al.*, 1995). It would allow to trace the fate of added sulphur in agro-ecosystems, and identify the S pools predominantly affected by S inputs and the subsequent reallocation of S in the various pools. This would be particularly relevant in areas affected by volcanic emissions, but also by industrial S compounds, such as soils in the vicinity of large industrial complex in northern Europe (e.g. 'Pechenganikel', Russia) (Koptsik & Alewell, 2004) or in Asia (Streets & Waldhoff, 2000).

The high retention of F in the Vitric and Eutric Andosols also affects SO_4^{2-} retention, but its extent is still poorly constrained. Besides, the unexpected mobility of this toxic anion may create direct environmental threat. A better characterisation of the fate of F input, and especially its

transfer to plant and water in these ecosystems would thus be of interest.

I provide the first direct evidence of BAS minerals in soils using a combination of a well-adapted clay separation with TEM and EDS. This discovery opens new ways to identify other hypothetical mineral phases in soils (e.g. arsenate-bearing phases), to enhance the quantification of BAS minerals in soils, to confirm the occurrence of BAS minerals in other kinds of soils, and to help better elucidate the mechanisms by which BAS forms in soils. Indeed these mechanisms are still poorly known. In particular, to further distinguish between adsorbed and precipitated sulphate minerals in soils, the use of direct non-invasive technique using spectromicroscopy (synchrotron-based S K edge XANES, Solomon *et al.* (2003)) or zeta potential (Li & Stanforth, 2000) could be efficient. Moreover, BAS synthesis in the laboratory in the presence of various Al source (e.g. volcanic glass, allophane), competing anions and/or minerals onto which SO_4^{2-} sorption may occur (e.g. allophane, ferrihydrite) would probably permit to gain insights into the factors that govern BAS formation.

