Acid Neutralization and Sulphur retention in S-impacted Andosols

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Chapter 4

Sulphate, Chloride and Fluoride Retention in Masaya Andosols*

Summary

The continuous emissions of SO_2, HCl and HF by Masaya volcano, Nicaragua, represent a substantial source of atmospheric S-, Cl- and F-containing acid inputs for local ecosystems. We report on the effects of such acid depositions on the sulphate, chloride and fluoride contents in both Vitric and Eutric Andosols of the Masaya area. These soils are exposed to various rates of volcanogenic acid addition, with the Vitric sites being generally more affected.

The concentrations of 0.5 M NH_4F and 0.016 M KH_2PO_4 extractable sulphate (NH_4F-S and KH_2PO_4-S, respectively) indicate that volcanic S addition has increased the inorganic sulphate content of the Vitric and Eutric soils at all depths. In this process, the rate of sulphate accumulation is also dependent on soil allophane contents. For all soils, NH_4F extracted systematically more (up to 40 times) sulphate than KH_2PO_4. This difference suggests sulphate incorporation into an aluminium hydroxy sulphate phase, whose contribution to total inorganic sulphate in the Vitric and Eutric Andosols is estimated to ∼34-95% and ∼65-98%, respectively.

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The distribution of KH_2PO_4-extractable chloride in the Vitric and Eutric Andosols exposed to volcanic Cl inputs reveals that added chloride readily migrates through the soil profiles. In contrast, reaction of fluoride with Al and Fe oxyhydroxides and allophanes is an important sink mechanism in the Masaya Andosols exposed to airborne volcanic F. Fluoride actually dominates the anion distribution in all soil horizons, although F is the least concentrated element in the volcanic emissions and depositions. The soil anion distribution reflects preferential retention of fluoride over sulphate and chloride, and of sulphate over chloride. The primary acidifying agent of the Andosols subject to the volcanic acid inputs is HCl.

4.1 Introduction

Individual non-erupting volcanoes can represent major sources of tropospheric S and halogen compounds. For example, the continuous release of SO_2 from Mt. Etna, Italy, is comparable to the total industrial S emission from France. In contrast to anthropogenic sources of atmospheric acidity, the environmental effects of airborne volcanic acids have been poorly studied. Yet, there is growing evidence that persistent degassing of SO_2, HCl and HF by volcanoes may create local and distant air pollution (Graf *et al.*, 1998; Delmelle *et al.*, 2002). 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 S, Cl and F 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 inter-tropical areas. While Andosols have a proven capacity to buffer acid inputs, their long-term chemical response is not well 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).

Sites around degassing volcanoes may constitute well-suited natural laboratories to gain insights into the anion retention capacity and acidification of Andosols exposed to prolonged deposition of acid 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 SO_x and 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 S-, Cl- and F-containing atmospheric acid depositions on soil sulphate, chloride and fluoride contents and status. We also briefly discuss some potential environmental issues related to anion accumulation in the acid-impacted soils.

4.2 Material and methods

4.2.1 Study area

The study was conducted downwind from Masaya volcano, a basaltic caldera located about 20 km south of Managua, the capital of Nicaragua (Figure 3.2). Through recurrent crises, this volcano has been emitting acidic gases in the atmosphere for at least 150 years. Masaya volcano is currently one of the world's strongest sources of SO_2 and also contributes substantial amounts of halogens to the atmosphere. The ongoing unrest started in mid-1993, with reported emissions of SO_2, HCl and HF in the ranges 4.5-21.7 kg s^{-1}, 3.0-7.6 kg s^{-1} and 0.26-0.9 kg s^{-1}, respectively (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.

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. This consists of hills and deep valleys with an elevation range from ∼350 to 920 m a.s.l. (Figure 3.2). Atmospheric dispersion of the acid emissions generates elevated SO_2, HCl and HF concentrations in air. Within the most polluted zone (0-15 km from the volcano), the dry inputs of S averaged about 2-800 mg m^{-2} day^{-1} in 1999 (Delmelle *et al.*, 2001). These values largely exceed those measured or estimated in areas affected by anthropogenic sources (e.g., Ek *et al.* 2001). Similarly, dry deposition processes led to substantial inputs of HCl (∼1-300 mg m^{-2} day^{-1}) to the land. Equivalent proton flux is estimated to range from <1 to 30 mg m^{-2} day^{-1} (Delmelle *et al.*, 2001). The chemistry of the wet depositions is also affected by the volcanic emissions as low pH (<3) rainwater containing significant sul-

Table 4.1: pH† and anionic composition‡ of rainwater collected downwind of Masaya volcano from July the 27 to July the 31 2002. See also Annexe 2 for complete data set.

Location	pH	F	Cl	SO_4
		———	mmol l^{-1}	———
Vitric transect	3.54	0.051	0.354	0.090
Vitric transect	3.71	0.035	0.272	0.086
Eutric transect	3.76	0.019	0.270	0.058
Eutric transect	4.16	0.013	0.249	0.051

† pH measured in the field

‡ anion concentrations determined by IC on 0.45 µm filtered aliquots

phate, chloride and fluoride concentrations have been reported several km from Masaya (Johnson & Parnell, 1986; Table 4.1). 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). In this area, vegetation consists of a gas tolerant weedy grass composite (*Malanthora* and *Lantana spp.*, Johnson & Parnell, 1986).

4.2.2 Soil survey

The area surveyed has a dry tropical climate with annual mean total precipitation of 1100 mm, of which approximately 85% fall between May and December. The study was carried out in the dry season (January 2001) in a 17 x 10-km zone SW from the volcano. Soils are developed on Quaternary ash and pyroclastic deposits erupted by Masaya volcano. These materials are tholeitic basalts, which have been shown to be remarkably constant in composition, either areally (within a single unit) or temporally between eruption units (Walker *et al.*, 1993). Ten soil profiles were selected on two distinct transects located at distances of 5 and 15 km southwest of the volcano and roughly perpendicular to the prevailing wind direction (Figure 3.2).

Bulk soil samples of the various horizons were collected from a depth of ∼0 to 40 cm and were described and classified according to the WRB criteria (ISSS, 1998). The weathering of the Vitric soils is slightly advanced and the soil profile is rather undifferentiated, although several layers of ash and lapilli are often superimposed. In contrast, the Eutric profiles are fairly well differentiated. As shown in Table 3.6, these soils also have higher dark oxalate (o)-extractable Si, Al, Fe and allophane

contents than the Vitric soils. Within the Vitric soil profiles, horizons 3A and 3AB appear to be more evolved, as they display comparatively high Si_o, Al_o, Fe_o and allophane contents (Table 3.6).

4.2.3 Soil analyses

Extractable sulphate was obtained by shaking with (i) 0.016 M KH_2PO_4 (Curtin & Syers, 1990) and (ii) 0.5 M NH_4F (Prietzel & Hirsch, 1998), at a soil:solution ratio of 1:5. Five successive extractions of each 1 h were performed and sulphate concentration in the combined extracts was measured by ion chromatography (IC) after centrifugation and filtration through a 0.45-µm polycarbonate membrane (these procedures are detailed in Chapter 6). Sulphate extracted with KH_2PO_4 and NH_4F are reported as KH_2PO_4-S and NH_4F-S, respectively.

The solutions obtained after extractions of the soil samples with 0.016 M KH_2PO_4 were also analysed by IC for chloride, and the results were converted to extractable chloride (KH_2PO_4-Cl) contents. Similarly, extractable fluoride was determined after shaking the soil with 0.005 M $Ca(NO_3)_2$. In addition, the fluoride concentration of the solution obtained after shaking the soil with 0.2 M acid ammonium oxalate was analysed for fluoride (noted oxalate-F). After adding Total Ionic Strength Adjustment Buffer (TISAB) for decomplexation of fluoride, the concentration was measured by the standard addition method with a combination fluoride electrode. TISAB solution contained ∼12 mol HCl l^{-1}, 242 g l^{-1} hydroxymethyl aminomethane and 230 g l^{-1} sodium tartrate and was prepared according to the electrode manufacturer (Orion, 2001). This TISAB formulation permits measurement of ∼5.3 mmol l^{-1} of fluoride in the presence of 1.8 mmol Fe l^{-1} or 3.7 mmol Al l^{-1}. An error of 5% on fluoride determination is expected if the Al or Fe concentration is doubled.

4.3 Results and discussion

4.3.1 Sulphate retention

Extractable sulphate concentrations in the Andosols from Masaya are shown in Table 4.2. Sulphate extracted with NH_4F has recently been shown to be a good proxy for estimating total inorganic sulphate in soils (Prietzel & Hirsch, 2000). Sulphate extracted by NH_4F varies by about one order of magnitude on both the Vitric (4.1-34.0 µmol NH_4F-S g^{-1}) and Eutric (10.0-100.9 µmol NH_4F-S g^{-1}) series. On each transect, the acid-impacted sites tend to exhibit higher NH_4F-S contents at all

depths than less impacted sites (Figure 4.1). This result indicates that long-term exposure to volcanic S has increased the inorganic sulphate content of the soils located downwind from the volcano. However, the relationship of increasing NH_4F-S with increasing exposure to S emissions is confounded when comparisons are made across the Vitric and Eutric profiles. In this case, the Vitric Andosols showed generally lower NH_4F-S contents (Table 4.2), despite higher rates of volcanic S inputs. Similarly, EU-2 does not receive more S deposition than the other acid-impacted sites of the Eutric series, but it exhibits significantly higher NH_4F-S concentrations (Table 4.2, Figure 4.1). As discussed later, these results probably point to the influence of weathering stage (i.e., soil mineralogy and composition) on the sulphate retention capacity of the soils.

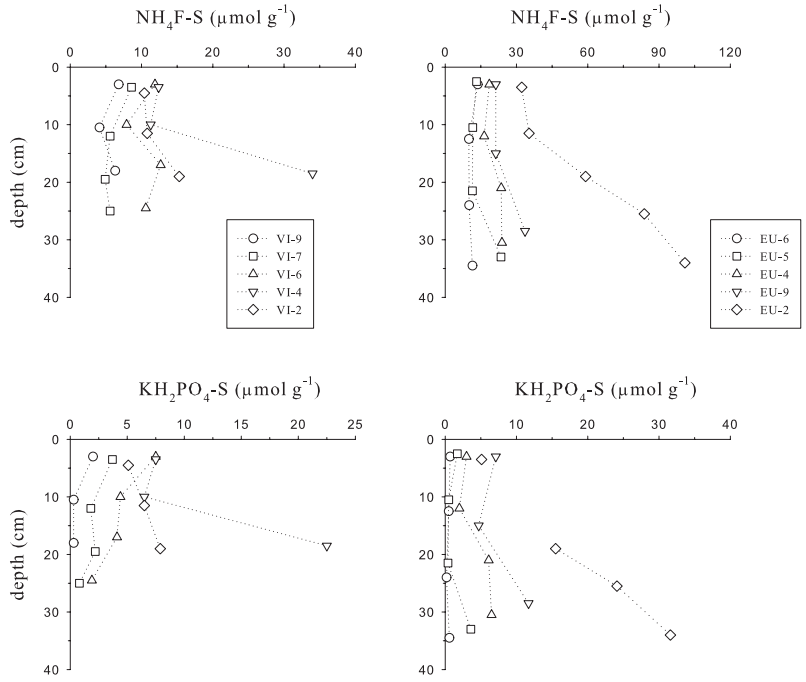

Figure 4.1: Graph of NH_4F- and KH_2PO_4-extractable sulphate (NH_4F-S and KH_2PO_4-S, respectively) versus depth in the Vitric and Eutric Andosol profiles.

The Vitric and Eutric Andosols contain KH_2PO_4-extractable sulphate in the ranges 0.3-22.5 µmol g^{-1} and 0.2-31.6 µmol g^{-1}, respectively (Table 4.2). Higher values are found at sites along a transect receiving more volcanogenic S depositions (Table 4.2, Figure 4.1), again suggesting the impact of volcanic S addition on the soil sulphate content. Noticeably, KH_2PO_4-S concentrations are about 1.5 to 40 times lower

Table 4.2: NH_4F- and KH_2PO_4-extractable sulphate concentrations in the Vitric and Eutric soils. $\Delta_{NH_4F-KH_2PO_4}$ is the difference between NH_4F-S and KH_2PO_4-S.

Profile	Horizon	NH_4F-S	KH_2PO_4-S	$\Delta_{NH_4F-KH_2PO_4}$
		/µmol g^{-1}		
VI-9	A	6.8	2.0	4.8
	2BC	4.1	0.3	3.8
	3A	6.3	0.3	6.0
VI-7	A	8.6	3.7	4.9
	AB	5.6	1.8	3.8
	2BC	4.9	2.2	2.7
	3AB	5.6	0.8	4.8
VI-6	A	11.9	7.5	4.4
	2BC	7.9	4.4	3.5
	3A	12.7	4.1	8.6
	3AB	10.6	1.9	8.7
VI-4	A	12.4	7.5	4.9
	2BC	11.3	6.5	4.8
	3A	34.0	22.5	11.5
VI-2	A	10.4	5.1	5.3
	2BC	10.8	6.5	4.4
	3A	15.3	7.9	7.3
EU-6	A1	13.7	0.7	13
	A2	10.0	0.5	9.5
	AB	10.1	0.2	9.8
	BA	11.5	0.6	10.9
EU-5	A1	13.2	1.7	11.6
	A2	11.6	0.5	11.1
	AB	11.5	0.4	11.1
	Bw1	23.5	3.6	20.0
EU-4	A1	18.6	3.0	15.5
	A2	16.4	2.0	14.5
	AB	23.6	6.1	17.5
	BA	23.9	6.5	17.4
EU-9	A1	21.3	7.1	14.1
	A2	21.3	4.7	16.6
	AB	33.6	11.7	21.9
EU-2	A1	32.2	5.1	27.1
	A2	35.3	-	-
	AB	59.1	15.5	43.6
	BA	83.8	24.1	59.7
	Bw	100.9	31.6	69.3

than those determined from the NH_4F extracts (Table 4.2). Apparently, the phosphate solution failed to mobilise a pool of inorganic sulphate present in the soils. According to Prietzel & Hirsch (2000) and Mayer *et al.* (2001), KH_2PO_4 solution displaces mainly sulphate adsorbed at mineral surfaces, while NH_4F mobilises both adsorbed sulphate and sulphate present in aluminium hydroxy sulphate precipitates such as basaluminite [$Al_4(SO_4)(OH)_{10}.5H_2O$] and alunite [$KAl_3(SO_4)_2(OH)_6$] (Prietzel & Hirsch, 1998; 2000). Thus, we strongly suspect that the acidified Andosols from Masaya contain a fraction of inorganic sulphate precipitated in an aluminium hydroxy sulphate phase.

Subtraction of KH_2PO_4-S from NH_4F-S concentrations indicates that the amount of aluminium hydroxy sulphate in the Vitric and Eutric soils may be in the ranges ∼2.7-11.5 and ∼9.5-69.3 µmol g^{-1}, respectively (Table 4.2). For all the Eutric horizons, and in 10 of the 17 Vitric horizons analysed, these concentrations are higher than the KH_2PO_4-S ones. Our data suggest that precipitated sulphate accounts for ∼34-95% and ∼65-98% of the total inorganic sulphate content in the Vitric and Eutric soils, respectively. Thus, the aluminium hydroxy sulphate phase appears to constitute a major sulphate sink in the Andosols located downwind from Masaya volcano.

Direct observations of aluminium hydroxy sulphate occurrence in soils are lacking, but conclusive evidence have been obtained from thermodynamical considerations for acidic soils subject to intense S deposition (e.g., Gebhard & Coleman, 1974b; Adams & Rawajfih, 1977; Nordstrom, 1982; Wolt *et al.*, 1992). Similarly, we tentatively tested the saturation of the acid-impacted Eutric sites with respect to alunite, basaluminite and jurbanite by applying the PHREEQC chemical equilibria code (Parkhurst & Appelo, 1999) to existing soil solution compositions (Table 4.3). These data correspond to samples collected by Parnell (1986) in the Eutric area, close to our EU-9 site, during the 1979-1984 gas activity of Masaya. The calculations indicate that alunite and basaluminite were saturated, or sursaturated in the soil solutions of the acid-impacted profiles (Table 4.3). Both phases were predicted to form until the Al concentration in the soil solution was decreased by a factor of at least 10. These results support the hypothesis that aluminium hydroxy sulphate precipitation is a plausible mechanism for sulphate retention in the acidified Andosols. The elevated proton and S inputs and the weatherable nature of the volcanic ash soils certainly provide favourable conditions for this sulphate retention pathway.

The relatively high concentrations of the aluminium hydroxy sulphate phase that may be present in the Masaya Andosols should allow for its detection using techniques such as X-ray diffraction (XRD) and cou-

Table 4.3: Soil solution compositions and saturation indices (SI) for alunite (Alun), basaluminite (Basa) and jurbanite (Jurb) for a surface horizon of an acid-impacted Eutric profile sampled by Parnell (1986) in August 1981.

pH	——Soil solution composition /mmol l^{-1}——							——†SI——		
	Ca	Mg	K	Al	Si	SO_4	Cl	Alun	Basa	Jurb
5.48	3.89	0.97	1.61	0.005	0.96	0.33	3.55	3.03	0.60	-2.03
5.99	1.17	0.35	1.20	0.003	0.85	0.12	1.85	3.23	2.55	-2.54

pled scanning electron microscopy (SEM)-energy dispersive spectrometry (EDS) techniques. However, XRD analyses performed on soil grains (sieved to < 50 µm) from the A1 horizon of EU-4 and the AB horizon of EU-2 were not successful, suggesting a poor degree of crystallinity of the aluminium hydroxy sulphate precipitate (Nordstrom, 1982). In addition, no S was observed in the EDS spectra collected for the bulk sample or for individual soil grains. This indicates that, if present, precipitated sulphate occurs as thin deposits with thickness less than a few µm (the depth from which X-rays are collected by EDS; Wells, 1974). To further test this hypothesis, we performed an analysis of the same soil samples using X-ray photoelectron spectroscopy (XPS), a technique which probes the chemical composition of the uppermost 2-10 nm thick surface layer of a solid (Hochella, 1988). Interestingly, XPS measured about 1 atomic % S (in the form of sulphate) in these soils, corroborating the idea that an extremely thin layer at the surface of the soil particles contains sulphate, a part of which is precipitated. This mode of occurrence is in agreement with a formation mechanism by which sulphate first adsorbs onto aluminous substrates and then reacts at the surface to form a sulphate precipitate (Nordstrom, 1982). The close association between aluminium hydroxy sulphate and Al-containing particles in the Masaya Andosols can be further evaluated by plotting the difference

$$\Delta_{NH_4F-KH_2PO_4} = NH_4F{-}S - KH_2PO_4{-}S \qquad (4.1)$$

against Al_o-Al_p across all soils (Figure 4.2). This plot shows that $\Delta_{NH_4F-KH_2PO_4}$ increases with Al_o-Al_p contents. Since a similar trend is also observed between $\Delta_{NH_4F-KH_2PO_4}$ and Si_o, we believe that the surfaces of allophanes constitute privileged substrates for aluminium hydroxy sulphate formation. Therefore, the higher inorganic sulphate accumulation measured at the Eutric sites is best accounted for by a higher rate of sulphate precipitation in these allophane-rich soils, because phosphate-extractable sulphate is not significantly enriched on the Eutric sites relative to the Vitric sites. Allophane-rich soils also benefit

from a high water retention capacity (Shoji *et al.*, 1993), and this property may well favour adsorption and subsequent mineral precipitation by increasing the time of contact between the solid and solution phases (Barrow & Shaw, 1977; Johnson *et al.*, 1979; Nordstrom, 1982).

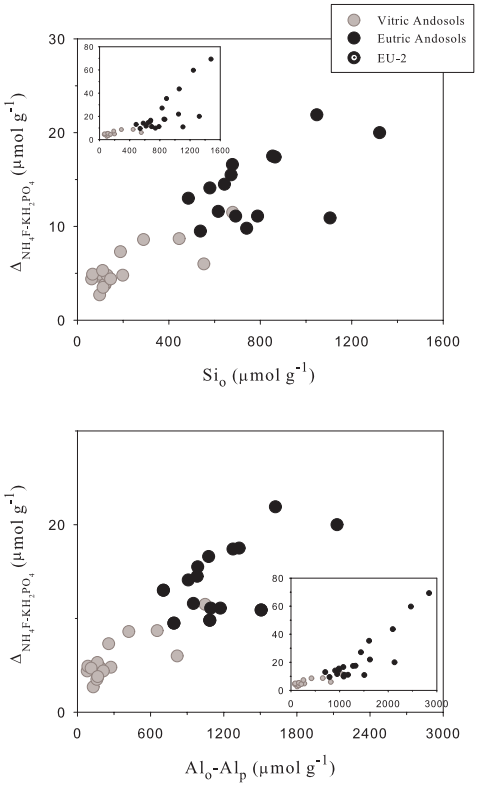

Figure 4.2: Graph of $\Delta_{NH_4F-KH_2PO_4}$ (where $\Delta_{NH_4F-KH_2PO_4}$ is obtained by substracting KH_2PO_4-extractable sulphate from NH_4F-extractable sulphate) concentration versus (A) Al_o-Al_p content and (B) Si_o content in the Vitric and Eutric Andosols. The graph shown as insets include data points for the soil profile EU-2.

Figure 4.2 also shows that the rise in $\Delta_{NH_4F-KH_2PO_4}$ associated with higher Si_o or Al_o-Al_p is much steeper for EU-2 horizons than in the other soil profiles. This behavior cannot be attributed to higher rates of atmospheric S input. Based on molar Al/Si ratio values (calculated as Al_o-Al_p/Si_o) of allophanes, we noted that allophanes in EU-2 are slightly more Al-rich (Al/Si = 1.7-1.9) than in the other profiles (Al/Si = 1.2-1.5). Wada (1989; and references therein) showed that allophane with a Al/Si ratio close to 2 develops more variable negative and posi-

tive charges than Si-rich allophane. Thus, Al-rich allophanes with more positive charges might have allowed for larger sulphate adsorption at the mineral surface, and subsequently for greater amount of sulphate precipitation. Further work is needed to confirm this hypothesis.

4.3.2 Chloride retention

Similar to the influence of volcanic airborne S on soil sulphate contents, exposure of the Andosols to the HCl-containing plume emitted from Masaya has resulted in enhanced retention of chloride. In contrast to the pattern found for NH_4F-S and KH_2PO_4-S, the concentration of KH_2PO_4-Cl in the surface soil is higher in areas close to the volcano (KH_2PO_4-Cl $\sim$ 1.9-16.5 µmol g^{-1}) than at sites located at distances of $\sim$15 km from the source (KH_2PO_4-Cl $\sim$ 0.8-8.4 µmol g^{-1}) (Table 4.4). More chloride also is extracted from the surface horizon of the Eutric sites of the devastated zone than from the site located on the plume margin (Table 4.4). All together, this implies an atmospheric source impact on soil chloride distribution within few kilometers downwind from the degassing crater.

Noticeably, both Vitric and Eutric profiles accumulated significantly lower chloride concentrations in the deeper layers (Cl $\sim$0.8 $\pm$ 0.4 µmol g^{-1} and $\sim$0.5 $\pm$ 0.2 µmol g^{-1}, respectively) compared to topsoils. This distribution is interpreted in terms of a poor affinity of chloride for the soil constituents (Gebhardt & Coleman, 1974b). Chloride is highly mobile and is known to be one of the most weakly held anions commonly found in soils (Thomas, 1960; Black & Waring, 1979). During the rainy season, any adsorbed chloride is probably readily leached through the soil layers by infiltrating water. Consequently, the chloride contents measured in the surface horizon (A) along the Vitric and Eutric series reflect mostly the impact of airborne volcanic HCl, which has been dryly deposited over the land during summer.

4.3.3 Fluoride retention

Because nitrate is unable to displace fluoride specifically adsorbed onto the soil constituents (Hingston *et al.*, 1967), fluoride extracted with $Ca(NO_3)_2$ is thought to represent the soil water-soluble fluoride fraction. Concentrations of $Ca(NO_3)_2$-F in the Vitric and Eutric soils are $\sim$0.03-0.1 µmol g^{-1} and $\sim$0.005-0.1 µmol g^{-1}, respectively (Table 4.4). These values are 1-3 orders of magnitude lower than those reported in contaminated soils in the vicinity of anthropogenic F sources (e.g., Polomski *et al.*, 1982). In these environments, water-extractable fluoride con-

Table 4.4: KH_2PO_4- and $Ca(NO_3)_2$-extractable chloride and oxalate-extractable fluoride concentrations in the Vitric and Eutric soils.

Profile	Horizon	KH_2PO_4-Cl	$Ca(NO_3)_2$-F	Oxalate-F
		/µmol g^{-1}		
VI-9	A	6.5	0.13	41.3
	2BC	1.6	0.09	140.7
	3A	0.5	0.06	117.8
VI-7	A	1.9	0.05	22.5
	AB	0.4	0.12	31.0
	2BC	1.2	0.08	23.8
	3AB	1.7	0.13	48.1
VI-6	A	16.5	0.08	19.0
	2BC	0.6	0.04	21.2
	3A	0.5	0.19	64.6
	3AB	0.5	0.22	189.3
VI-4	A	9.5	0.07	24.1
	2BC	0.6	0.06	21.4
	3A	0.6	0.18	17.1
VI-2	A	1.9	0.03	24.8
	2BC	0.5	0.04	18.3
	3A	0.6	0.11	30.7
EU-6	A1	0.8	0.02	76.7
	A2	0.4	0.02	38.8
	AB	0.3	0.02	102.1
	BA	0.3	0.01	68.9
EU-5	A1	3.4	0.01	79.4
	A2	0.8	0.01	85.8
	AB	0.5	0.01	67.6
	Bw1	0.4	<0.01	167.8
EU-4	A1	4.0	0.10	152.6
	A2	0.5	0.04	105.4
	AB	0.4	0.02	104.6
	BA	0.3	0.02	90.4
EU-9	A1	8.4	0.03	144.3
	A2	1.1	0.10	170.6
	AB	0.6	0.01	132.4
EU-2	A1	3.6	0.03	148.4
	A2	-	0.06	192.5
	AB	0.8	0.05	165.4
	BA	0.6	0.04	181.7
	Bw	0.5	0.02	262.3

centrations generally reflect the gradient of airborne F exposure (e.g., Polomski *et al.*, 1982; Arnesen *et al.*, 1995). They also have been shown to be depth-dependent, although opposite patterns within soil profiles have been reported. At Masaya, the distance to the volcano does not seem to influence $Ca(NO_3)_2$-F concentrations in the soil horizons. Variations in $Ca(NO_3)_2$-F also appear to be independent from soil depth. These results suggest that the water-extractable fluoride concentration in our Andosols is a poor indicator of fluoride contamination.

In contrast, treatment of the Vitric and Eutric Andosols with oxalate resulted in exceptionally high soil fluoride concentrations at all depths ranging about from 17.1 to 189.3 and from 38.8 to 262.3 µmol g^{-1}, respectively. Aluminium and Fe oxyhydroxides and allophanes are dissolved by oxalate. They are also the most active agents in causing adsorption of fluoride by soils (Omueti & Jones, 1977; Peek & Volk, 1985) and therefore, reaction of fluoride with these compounds is believed to constitute an important sink mechanism in the Masaya Andosols exposed to airborne volcanic F. We also noticed that the highest oxalate-F concentrations occurred in the allophane-rich Eutric series, although these soils are likely to receive less F-rich inputs than the Vitric profiles.

Profile VI-9 has a marginal location in the acid-impacted area and supports a moderately damaged vegetation (Figure 3.2). Yet, this site shows a surprisingly high oxalate-F content at all depths (up to 141 µmol g^{-1}, Table 4.4). Continuous decomposition of F-rich plant residues could provide an additional input of volcanic F to the soil profile, thereby enhancing its fluoride content. Interestingly, Garrec *et al.* (1984) measured fluoride concentrations of 20-30 µmol g^{-1} in various leaf samples collected 5 km downwind from Masaya, reflecting the capacity of plant leaves to act as a sink for airborne F (Hill, 1971).

4.3.4 Sulphate, chloride and fluoride distribution

The distribution of the three anions (as determined from oxalate-F, NH_4F-S and KH_2PO_4-Cl concentrations) in the acid-impacted Andosols of Masaya reveals that fluoride is the major anion in all soil horizons (Tables 4.2 and 4.4). This striking feature is best shown when the relative sulphate, chloride and fluoride concentrations are plotted in a ternary diagram (Figure 4.3). In this plot, fluoride concentrations are divided by 5 in order to avoid clustering of the data points near the fluoride corner. Noticeably, the observed distribution does not match the relative abundances of S, Cl and F in the volcanic emissions. Indeed, the source strength for HF is in average about 20 and 10 times lower than for SO_2 and HCl, respectively.

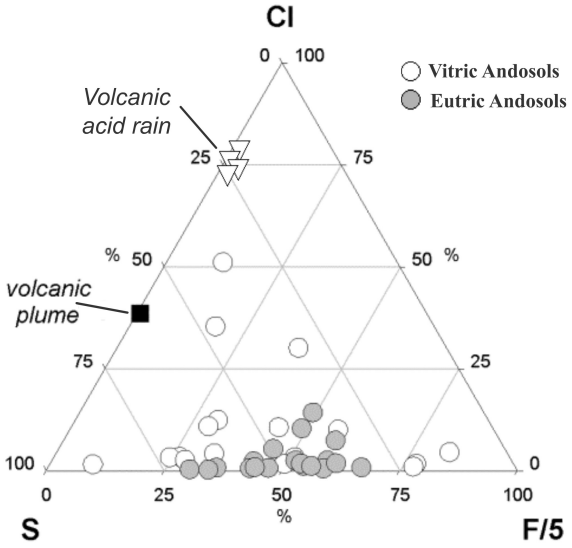

Figure 4.3: Ternary diagram showing the relative molar concentrations of sulphur-sulphate, chloride and fluoride (as determined from NH_4F-extractable sulphate, KH_2PO_4-extractable chloride and oxalate-extractable fluoride, respectively) in the Vitric and Eutric Andosols. The label F/5 indicates that the oxalate-extractable fluoride concentration in each sample has been divided by 5.

Dry deposition is one way by which airborne acid contaminants are returned to the ground. The strong partitioning of fluoride in the soil could be linked to faster removal of HF from the volcanic plume. Gaseous HF is a highly reactive molecule characterised by high dry deposition velocity values ranging from ∼1.6 to 3.7 cm s^{-1} (Sehmel, 1980). However, comparable values of dry deposition velocity are reported for SO_2 (0.1-2.8 cm s^{-1}) and HCl (0.4-17.0 cm s^{-1}) (Sehmel, 1980; Harrison *et al.*, 1989). Considering the initial gas ratios in the plume, it is unlikely that the dryly deposited amounts of HF over the land exceed substantially those of SO_2 or HCl. Fluorine inputs to the soil also occur through wet deposition processes. While rainwater affected by the acidic emissions does contain fluoride, this species is in much lower concentrations than sulphate and chloride (Table 4.1). In fact, chloride dominates the chemistry of rainwater in the vicinity of Masaya (Johnson & Parnell, 1986; Table 4.1).

The levels of sulphate, chloride and fluoride accumulation in soils depend not only on the atmospheric input but obviously also on their rates of translocation within the soil profile. The anion distribution in

the Vitric and Eutric soils best accounts for preferential retention of fluoride over sulphate and chloride, and of sulphate over chloride. This is in complete agreement with previous studies on anion adsorption by various soils (e.g., Thomas, 1960; Chao, 1964; Gebhardt & Coleman, 1974a; 1974b). According to Gebhardt & Coleman (1974a), the capacity of allophanic soils to retain chloride ion results from electrostatic adsorption on positively charged surfaces. In this case, the mechanism is largely reversible and chloride should not accumulate in the soils, as shown by our data.

Similar to chloride, sulphate retention by acid, highly weathered soils involves electrostatic interaction. However, an exchange reaction with hydroxyl ion constitutes an additional adsorption mechanism, which greatly reduces sulphate mobility (e.g., Chao *et al.*, 1965; Gebhardt & Coleman, 1974b). Precipitation of a sparingly soluble aluminium hydroxy sulphate phase also should favour accumulation of sulphate relative to chloride in the soil. However, sulphate retention can be depressed by the simultaneous presence of fluoride in the soil solution (Chao, 1964). The reducing effects on sulphate adsorption may result from (i) competition for anion exchange site or anion replacement and/or (ii) the ability of fluoride anions to form stable complexes with Al and/or Fe, resulting in occupation of the active sites on Al and Fe compounds. Besides, fluoride adsorption may become irreversible in soils rich in amorphous Al compounds (Peek & Volk, 1985). Overall, fluoride may prove to be immobile relative to sulphate, and may accumulate at comparatively high rates in the soil horizons.

4.3.5 Environmental issues

Differences in anion accumulation in the Andosols of Masaya in response to volcanogenic S, Cl and F deposition raises several environmental issues. We anticipate that acidification with volcanic SO_2 (H_2SO_4) and HF of the Andosols of Masaya is partly buffered by anion adsorption, leaving HCl as the primary acidifying agent. Leaching of chloride through the soil profile may displace cations from cation-exchange sites. While there is no doubt that sulphate and fluoride have accumulated in the soil horizons in response to prolonged acid deposition, the question remains whether current additions of S and F are being effectively retained by the soils. Recently, Fumoto *et al.* (1996) suggested that the amount of natively retained sulphate in Japanese Andosols is sufficient to preclude the incorporation of additional atmospheric inputs. This has obvious implications for evaluating the long-term acid buffering capacity of the soils.

The release of retained sulphate and fluoride in the Vitric and Eutric soils also will influence the processes of soil acidification. Parnell (1986) showed that the concentration of sulphate in deep soil solutions (>40 cm) collected from acid-impacted Eutric sites fluctuates over more than an order of magnitude, depending on the level of acidity of the rain event. This behavior was attributed to pH-induced changes in the amount of positive charges at the adsorbing soil surfaces. The situation is likely to be complicated by the presence of an aluminium hydroxy sulphate pool in the Masaya Andosols. In this case, an increase in soil solution pH may trigger partial dissolution of the precipitate, and concomitant release of sulphate (Wolt & Adams, 1979; Nordstrom, 1982). Regarding fluoride, occurrence of significant oxalate-F at all depths in the profiles suggests transport of dissolved fluoride throughout the soil profile. Yet, we suggested earlier that fluoride is highly immobile in the Vitric and Eutric soils studied. Retention and movement of a highly reactive substance such as fluoride in soils has been poorly constrained. The presence of fluoride in all soil horizons could be the result of an inadequate time period for contact between a moving stream of fluoride solution and the reactive sites of the soil. In this case, some of the fluoride may not be retained, and instead remains dissolved in the liquid phase which drains through the profile. Alternatively, desorption reactions induced by changes in the soil solution composition and pH may be operative in the soil system.

Since fluoride is regarded as a highly reactive species that can be toxic to plants and animals, the elevated oxalate-F concentrations measured in the Andosols may create a direct environmental threat. However, most of the fluoride in the Vitric and Eutric profiles studied is firmly bound to amorphous soil constituents, and its uptake by plants and soil organisms is likely to be limited, if not impeded. A different scenario may occur during and after rainfall and under a regime of high volcanic F deposition. In such case, the dissolved fluoride concentration may increase throughout the root zone for a limited period of time, a result of slow fluoride exchange between the soil solution and the solid phase (Flühler *et al.*, 1982). If ingested, soil with high concentrations of fluoride also may increase the dietary fluoride intake of grazing cattle, hence posing a health hazard (Stevens & McLaughlin, 1999). Finally, increased addition of fluoride to soil samples may enhance the solubility of organic matter, Al and Fe (Polomski *et al.*, 1982; Wenzel & Blum, 1992; Arnesen, 1998). Recently, Egli *et al.* (2001) inferred that clay mineral transformations in soils affected by anthropogenic F pollution resulted from F-induced decomposition of organic matter.

4.4 Conclusions

The results of this study and those of chapter 3 demonstrate that the long-term emission of SO_2, HCl and HF by Masaya volcano has led to important changes in the chemistry of the Andosols located downwind. Prolonged addition of volcanogenic S has noticeably increased the inorganic sulphate content of the Vitric and Eutric Andosols. Precipitation of aluminium hydroxy sulphate minerals is identified as one of the efficient sulphate retention mechanisms, but this process is probably preceded by sulphate adsorption at the surface of allophanes. Because of their higher allophane contents, the capacity of the Eutric Andosols to buffer elevated S inputs is expected to be higher than that of the Vitric Andosols.

Immobilisation of the volcanic F-containing inputs is highly efficient in the Andosols studied. While F is present in significantly less amounts than S in the dry and wet depositions, concentrations of oxalate extractable fluoride are generally higher than total inorganic sulphate contents. Apparently, reaction of fluoride with Al and Fe oxyhydroxides and allophanes is an important sink for deposited volcanic F. In contrast to sulphate and fluoride, chloride appears to exhibit an almost conservative behavior as accumulation of this anion is not detected in the soils. Thus, deposition of volcanic HCl may be the principal acidification agent in the Masaya Andosols.