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Acid Neutralization and Sulphur retention in S-impacted Andosols

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Chapter 5

Dynamic Response of Andosols to Elevated S-, Cl- and F- Acid Inputs

5.1 Summary

Acid neutralisation processes in Andosols may involve mineral dissolution and ion exchange. However, the dynamic of these processes remains poorly documented. We conducted an acid leaching experiment (solution pH 3.6 and 5.6) in undisturbed soil columns and inserted ion exchange resins and test-minerals *in situ*, from two Andosol series, namely Vitric Andosols rich in volcanic glass and Eutric Andosols rich in allophanic constituents. Acid deposition led rapidly to preferential Al and Si lixiviation in Vitric Andosols, and large cation release and net anion retention in Eutric Andosols. Overall, these results illustrate the dominance of glass hydrolysis and ion exchange as an efficient H^+ consumption process in Vitric and Eutric Andosols, respectively. *In situ*, the use of ion exchange resins and test-minerals indicated that mechanisms that govern acid neutralisation are those revealed by the column leaching experiment.

The larger volcanic glass content combined with a low pH in Vitric Andosols likely permitted the release of Al thus favouring the formation of $(K,Na)_nAl_x(OH)_y(SO_4)_z$ minerals, whereas higher pH and the dominance of Al as Al-F_x complexes probably impeded BAS minerals formation in Eutric Andosols. The formation of Al-F_x complexes resulted in high mobility of F in the Vitric Andosols.

5.2 Introduction

It is well known that the high CEC and acid neutralizing capacity of Andosols confer to these soils a remarkable potential to regulate proton inputs. However, there are evidences that Andosols may be affected by acid deposition under certain circumstances (Parnell, 1986; Chapters 3 and 4). For instance, in areas exposed to strong emissions of volcanic acidic gas (SO_2, HCl and HF), Andosols can undergo measurable pH and CEC decreases (Parnell, 1986; Chapter 3), suggesting net acidification process.

The area around Masaya volcano, Nicaragua, has proved to be a particularly interesting site for studying acidification and anion retention processes in Andosols with different weathering degrees (Chapters 3 and 4). The SO_2, HCl and HF-rich plume of the volcano fumigates a 22 km^2-area downwind, which is mantled with Vitric and Eutric Andosols. The response of these soils to the heavy acid deposition originating from dispersion of Masaya's plume into the boundary layer was shown to differ between the Vitric and Eutric Andosols (Chapter 3). Mineral weathering is the main H^+ consumption process in the young Vitric Andosols, whereas ion exchange regulated by variable-charge constituents and secondary minerals neutralises acid inputs in the more weathered Eutric Andosols (Chapter 3). These findings were based on intensive soil surveys, but did not consider the dynamics of the processes or interpretation at process level. The issues that need to be addressed in more details relate to (i) the relative importance of both these processes in neutralising acid inputs, (ii) the depletion rate of the acid neutralisation capacity in the sense of van Breemen *et al.* (1983), and (iii) the capacity of these soils to support vegetation after cessation of volcanic emission.

Previous chapters have revealed significant accumulation of F and S in the Andosols directly exposed to the volcanic emissions. In Chapter 4 we measured important oxalate-extractable F contents, ranging from 324 to 4983 mg kg^{-1}, at all depths suggesting transport of dissolved fluoride throughout the soil profile. Chapter 3 reports on 5470 mg S kg^{-1} soil, more than typical contents reported in the literature. Yet, since both F^- and SO_4^{2-} retention are believed to play a significant role in acid neutralisation, question arises whether current additions of SO_4^{2-} and F^- are being effectively retained. These considerations have obvious implications for evaluating the long-term acid neutralising capacity of these soils.

Prolonged acid and S depositions in the Masaya area have also favoured the formation of basic aluminium sulphate minerals (BAS; $Al_x(OH)_y(SO_4)_z$) providing the first direct evidence of the occurrence

of such minerals in soils (see Chapter 7). The formation of BAS is likely favoured by large SO_4^{2-} flux and Al releases from mineral weathering.

A detailed knowledge of the soil solution composition in function of time and acid input solution composition may help to gain insights into the factors that govern (i) the dynamic of acid neutralisation processes, (ii) the conditions favouring $Al_x(OH)_y(SO_4)_z$ mineral formation, and (iii) the mobility of added anions. Towards this aim, we conducted undisturbed soil column leaching experiments with acid solution in the laboratory. In parallel, we also studied ion mobility in the field, using ion exchange resins and test-minerals left in-situ for different periods of time. Ion exchange resins and test-minerals constitute useful probe to characterise ion mobility and soil-forming processes (Skogley & Dobermann, 1996; Brahy *et al.*, 2001). We report our findings below.

5.3 Materials and methods

We collected undisturbed soil columns and studied the behaviour of resins and test-minerals in the area affected by the plume of Masaya volcano. This volcano is one of the world's strongest natural sources of SO_2 and has been degassing for at least 150 years. Soils in the area are exposed to dry S deposition from about 200 to 700 mg SO_2 m^{-2} day^{-1} and equivalent H^+ fluxes of 1-30 mg m^{-2} day^{-1} (Delmelle *et al.*, 2001). Rain affected by the plume was collected in July 2002. This water had pH values ranging from 3.5 to 4.2, and was particularly enriched in Na^+, SO_4^{2-}, Cl^- and F^- relative to rainwater unaffected by the volcanic plume (Table 5.1).

Based on Chapter 3, we selected five profiles differing in soil weathering stage and SO_4^{2-}content: two young Vitric Andosols (VI2 and VI9) and three Eutric Andosols profiles (EU3, EU5 and EU9). The major properties are given in Table 5.2.A. The Vitric Andosols located about 5 km from the crater are weakly developed and have large amounts of volcanic glass, whereas the more weathered Eutric Andosols, about 15 km distant from the emission source contained allophanic constituents and ferrihydrite up to 29% and 11%, respectively (Chapter 3).

5.3.1 Collection and leaching of undisturbed columns

Undisturbed columns were collected on VI2, VI9, EU3 and EU5 sites with a soil column sampler filled with PVC tube. Columns were sealed until the beginning of the leaching experiment. Soil columns were 27 cm high and had a diameter of 7.6 cm.

Table 5.1: pH† and ionic composition‡ of rainwater collected downwind and upwind from Masaya volcano. See also Annexe 2.

Location	pH	Ca^{2+}	K^+	Mg^{2+}	Na^+	F^-	Cl^-	SO_4^{2-}
		/mmol l^{-1}						
Unaffected rain	6.2	0.014	0.011	0.003	0.033	0.001	0.041	0.006
Affected rain								
Vitric area	3.5	0.009	0.012	0.008	0.067	0.051	0.354	0.090
Vitric area	3.7	0.018	0.018	0.011	0.101	0.035	0.272	0.086
Vitric area	3.7	0.016	0.020	0.008	0.114	0.044	0.302	0.060
Vitric area	3.5	0.007	0.007	0.005	0.047	0.062	0.420	0.052
Eutric area	3.8	0.018	0.020	0.012	0.118	0.019	0.270	0.058
Eutric area	4.2	0.020	0.035	0.012	0.159	0.013	0.249	0.051
Eutric area	4.1	0.017	0.026	0.010	0.116	0.013	0.210	0.042
Eutric area	3.7	0.012	0.019	0.007	0.086	0.018	0.229	0.072

†pH measured in the field in July 2002;
‡Ion concentrations determined on 0.45 µm filtered aliquots

The leaching experiment was carried out at 20 °C. Two leaching solutions were prepared: an acid solution (AS) and a near-neutral solution (NS). The AS solution (pH = 3.6) had a composition similar to that of the volcanic acid rainwater (Table 5.1), but SO_4^{2-}, Ca^{2+} and K^+ were added to take into account enrichment by throughflow observed by Johnson & Parnell (1986). The NS solution (pH = 5.6) had a composition similar to the rainwater collected upwind from Masaya volcano in an area non affected by the volcanic plume (Table 5.1). The chemical compositions of AS and NS solution are reported in Table 5.3.

The natural spatial heterogeneity of soil cover in the Masaya area implies that soil properties might differ between the columns collected on a same site (Chapter 3). Due to field and practical constrains, it was impossible to carry a large number of columns through the custom and laboratory. Therefore, experiments were carried out on a limited number of columns, but we related the observations that we made strictly to the specific properties of each column, separately. The columns collected on a given site are thus not considered as real replicates but rather as individual columns with similar properties. In each Eutric site we collected four columns, two were leached with AS and two with NS solution, whereas two columns of each Vitric site was used, one leached with AS and one with NS solution.

Table 5.2: Major properties of the various soil horizons in the undisturbed soil columns before the leaching experiment (A) and in columns leached with neutral (NS) or acid (AS) solution at the end of the leaching experiment (B). pH, CEC and sum of exchangeable cations (Σ), oxalate (o) and KH_2PO_4 (p) extractable element content.

	Profile	Horiz.		pH H_20	CEC /cmol$_c$ kg^{-1}	Σ	Si$_o$	Al$_o$ /g kg^{-1}	Fe$_o$	SO_4^{2-}p /mg kg^{-1}
A	VI2	A		4.4	4.9	0.4	3.1	6.2	8.3	486
		2BC		4.5	4.4	0.3	4.1	7.5	7.6	620
		3A		4.9	7.8	0.9	5.3	9.6	8.5	763
	VI9	A		5.3	11.5	7.0	2.6	4.7	9.6	196
		2BC		6.1	9.8	6.4	3.4	6.2	10.1	31
		3A		6.6	11.4	22.6	15.5	24.7	25.5	29
	EU3	A1		5.4	28.1	16.6	28.3	51.4	31.6	476
		A2		5.4	24.2	19.0	16.6	35.1	26.3	533
		AB		5.8	18.6	10.5	21.2	43.1	28.1	1479
	EU5	A1		6.7	41.4	38.7	17.3	29.0	23.7	159
		A2		6.9	36.9	33.4	19.4	33.4	27.1	44
		A3		7.0	36.8	32.8	22.1	35.3	27.8	42
		Bw		6.9	25.5	15.0	37.1	61.0	45.2	344
	EU9	A1		5.9	33.3	29.5	16.3	28.9	25.9	682
		A2		5.7	21.5	11.6	19.0	34.5	29.2	452
		AB		5.5	21.0	9.2	29.4	48.4	36.9	1120
B			solution							
	VI-2	A	NS	4.8	12.5	3.1	1.9	3.9	6.9	201
		2BC	NS	4.6	12.5	2.1	2.2	4.5	5.9	335
		3A	NS	4.6	11.6	6.4	2.4	4.7	6.9	318
	VI-9	A	NS	4.6	14.6	7.3	4.6	8.7	10.0	639
		2BC	NS	4.6	13.2	2.5	3.0	6.0	6.2	408
		3A	NS	4.8	11.6	3.5	3.8	7.8	6.0	360
	EU-3	A1	NS	5.5	56.1	22.5	21.6	47.9	36.0	562
		A2	NS	5.6	62.7	21.4	61.0	133.8	100.6	854
		AB	NS	5.4	67.9	12.4	30.2	66.7	53.3	3108
	EU-5	A1	NS	6.6	27.5	21.0	29.6	44.6	42.2	292
		A2	NS	6.5	42.0	36.7	20.4	33.2	29.9	100
		A3	NS	6.5	27.4	36.8	20.8	34.1	29.3	86
	VI-2	A	AS	4.5	5.9	3.6	1.2	2.7	6.2	252
		2BC	AS	4.5	6.1	4.8	2.4	5.0	6.5	505
		3A	AS	4.6	5.0	2.6	1.6	3.1	5.5	278
	VI-9	A	AS	5.3	11.8	10.5	2.6	4.9	7.4	69
		2BC	AS	5.7	10.9	10.1	2.5	4.6	6.9	42
		3A	AS	6.0	10.6	32.3	9.4	16.1	13.1	60
	EU-3	A1	AS	5.6	21.1	23.5	20.3	45.9	35.6	874
		A2	AS	5.7	30.5	24.5	22.7	49.2	35.8	808
		AB	AS	5.7	29.9	21.9	31.8	68.9	52.8	1859
	EU-5	A1	AS	5.8	40.9	40.2	18.4	31.7	26.0	266
		A2	AS	6.2	43.4	43.3	19.6	33.0	29.5	127
		A3	AS	6.4	34.6	36.6	23.1	38.5	33.4	169

Table 5.3: Average composition of input solutions.

solution	pH	Ca^{2+}	K^+	Mg^{2+}	Na^+	F^-	Cl^-	SO_4^{2-}
		/mmol l^{-1}						
NS	5.6	0.005	0.010	0.005	0.015	0.000	0.035	0.007
AS	3.6	0.050	0.125	0.040	0.040	0.030	0.350	0.150

Prior to the experiment itself, the undisturbed soil columns were rinsed with deionised water to reach field capacity and then, repeatedly (15 minutes every two hours) eluted with AS or NS solutions at a rate of $\sim$30 ml h^{-1}. The elution was interrupted for 12 hours every two days. The experiment lasted for 19 weeks and the total amount of artificial precipitation was about 3000 mm, which corresponds to more than two years of precipitation. However, one should note that some limitations apply when trying to relate laboratory experiments to field processes, contact time between soil and the moving solution being generally lower in columns (partly because of preferential flows). For instance, weathering rates obtained with column experiments are often one or two orders of magnitude larger than field weathering rates based on input-ouptut budgets (Schnoor, 1990).

The leachates were collected three times a week (volume between 200 and 225 ml) and kept for analysis. The volume, pH and contents of Ca, Mg, K, Na, Al, Si, Fe, Mn, F^-, SO_4^{2-}, Cl^- and NO_3^- of the collected leachates were systematically determined. Concentrations of cations and anions were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and ion chromatography, respectively.

After the leaching experiment, soil columns were opened and each horizon was sampled, air-dried, sieved at 2 mm and then analysed for pH, cation exchange capacity (CEC), content of exchangeable cations, KH_2PO_4- and oxalate- extractable elements contents as described in Chapters 3 and 6.

5.3.2 Cation and anion exchange resins, and test-minerals

We used Amberlite IR-120 as cation exchange resin, Amberlite IRA-420 as anion exchange resins and synthetic ferrihydrite as test-minerals. The cation resins were saturated with Na^+ ions by using 2 M NaOH and 1 M NaCl, whereas the anion exchange resins were saturated with 1 M CH_3COOH and 1 M $NaCH_3COO$. Both resins were stored in deionised water. The ferrihydrite was synthesised according to Schwertmann &

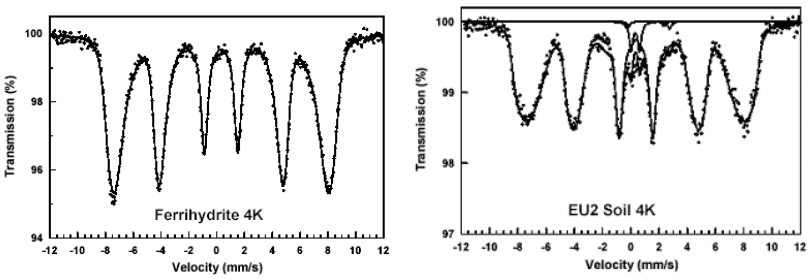

Figure 5.1: Mössbauer spectra measured at 4K of synthetic ferrihydrite and EU2-Bw sample (By the courtesy of Profs. Vandenberghe and Van Ranst).

Cornell (1991). Mössbauer analysis (Figure 5.1) indicates that the synthetic ferrihydrite consists of pure ferrihydrite of the so-called four-line type. This ferrihydrite may be somewhat more crystallised than the natural ferrihydrite in the Masaya Andosols since the measured magnetic hyperfine field values were a little higher in the former (Vandenberghe & Van Ranst, personnal communication). The resins and test-minerals (6 g fresh mass and 10 g freeze-dried mass, respectively) were then enclosed in bags consisting of 50 cm^2 of undyed polyamide-stocking material (NYTREL TI, 20 µm mesh, PROSEP S.A.), closely sealed with hot glue. The bags were previously soaked with 1 M HCl and deionised water.

In each horizon, the resin and test-mineral bags were inserted in three replicates, 20 cm away from each other, in April 2002. In VI2 and VI9, they were placed under the 2BC horizon (at about 15 cm depth). In EU3, EU5 and EU9, they were inserted under the A2 (at about 20 cm depth), and the AB or Bw (∼35 cm). The trench was then filled back by restoring the original horizon distribution. The resins and test-minerals were left in situ for 1 and 2 years, as they were collected in March 2003 and May 2004, respectively.

The elements sorbed on the cation resins (Ca, Mg, K, Al and Fe) were extracted with 1 M HCl and 0.1 M NaOH. Their contents were determined by ICP-AES. The elements retained on anion exchange resins (SO_4^{2-}, Cl^-, F^- and Si) were extracted with 0.1 M NaOH and 0.1 M KBr and were measured by IC or ICP-AES. Oxalate-, $BaCl_2$-, KH_2PO_4- and NH_4F-extractable element contents from test-ferrihydrite were determined as described in Chapters 3 and 6.

5.4 Results

5.4.1 Column leaching experiment

The major properties of the column horizons analysed after the experiment are listed in Table 5.2.B. Short-range ordered mineral contents were estimated based on the amounts of oxalate-extractable Si and Fe (Parfitt & Wilson, 1985; Mizota & van Reeuwijk, 1989). They were much larger in the VI9-3A horizon eluted with AS (Si_o=9.4 g kg^{-1}; Fe_o= 13.1 g kg^{-1}) than in that eluted with NS (Si_o=3.8 g kg^{-1}; Fe_o=6.0 g kg^{-1}).

Evolution of the cationic and anionic compositions and the pH of the column leachates are illustrated in Figures 5.2 to 5.4. For the Eutric columns, the leachate pH (∼7) were larger than that measured in both the AS and NS input solutions (3.6 and 5.6, respectively; Table 5.3). The lowest pH values were generally observed in the Vitric soil columns (∼5), whereas the leachates pH of the Eutric and AS-leached VI9 columns were higher (∼7).

The largest output Si concentrations were found in the Vitric leachates (∼0.6-1.0 mmol l^{-1}), whereas output Si concentrations in the Eutric leachates ranged from 0.2 to 0.5 mmol l^{-1}. However, output Si concentrations in two EU5 columns were larger than in the two other EU5 columns. Aluminium was almost never detected in the leachates of Eutric columns and was just above detection limit in the leachates of AS-leached VI9 column. In the other Vitric columns, the output Al concentrations were ∼0.2 mmol l^{-1}. In the Eutric columns, output Ca concentration decreased with increasing leaching volume. At the end of the leaching experiment, output Ca concentration was the largest in EU5 columns leachates (∼0.3-0.5 mmol l^{-1}) and decreased in the order EU5 > EU3 (∼0.15-0.25 mmol l^{-1}) > VI (∼0.05-0.1 mmol l^{-1}). Larger output Ca concentrations were generally observed in AS compared to NS treatment.

In EU5 columns, at the end of the experiment, output SO_4^{2-} concentration was similar to input SO_4^{2-} concentration. In contrast, in the VI and EU3 columns both the NS and AS treatment led to similar output SO_4^{2-} concentrations, which corresponded to that of AS input solutions. Output F^- concentrations from the Vitric columns (0.1-0.5 mmol l^{-1}) were larger than F^- concentration in input AS solution (∼0.03 mmol l^{-1}). In contrast, output F^- concentrations of acidified Eutric columns (0.005-0.030 mmol l^{-1}) were generally lower than F^- concentration in AS solution. Output Cl^- concentrations were rapidly equal to input Cl^- concentrations in each column.

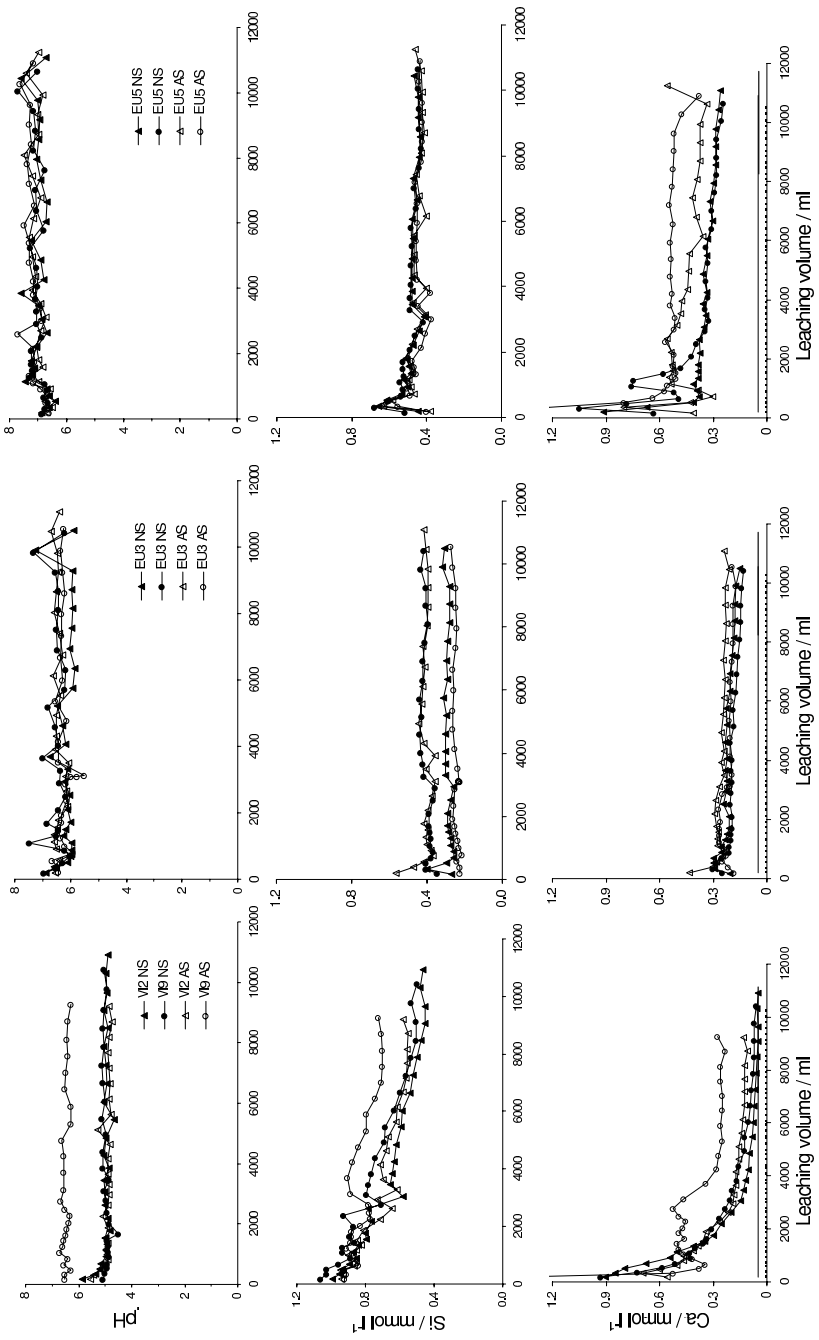

Figure 5.2: pH and concentrations of Si and Ca in column leachates as a function of leaching volume. Straight lines indicate concentration in AS input solution.

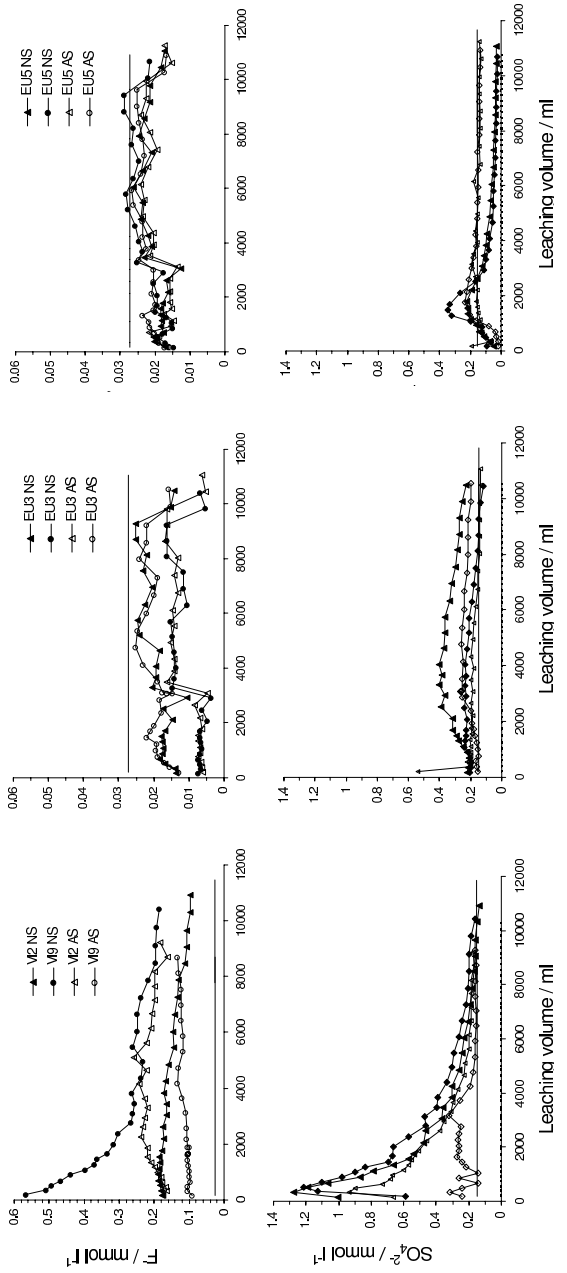

Figure 5.3: Concentrations of SO_4^{2-} and F^- in the column leachates vs leaching volume. Straight lines indicate concentration in AS input solution and dotted lines indicate concentration in NS input solution.

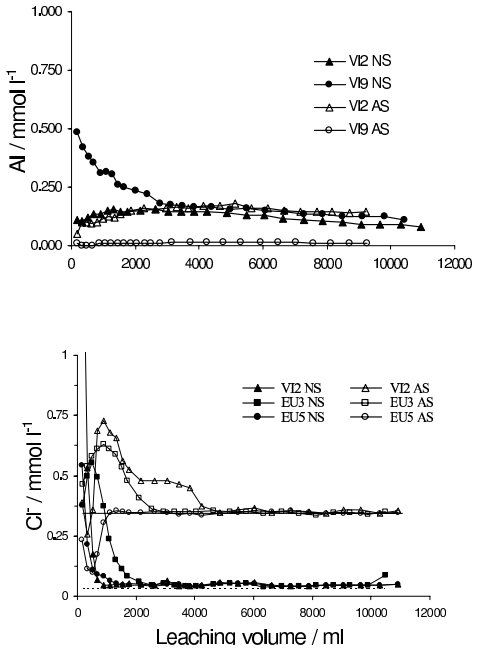

Figure 5.4: Concentrations of Cl^- and Al in the column leachates vs leaching volume. Straight line indicates concentration in AS input solution and dotted line indicates concentration in NS input solution.

For each element, we calculated the difference between the cumulative amount of this element in the output and the input solution. A positive value denotes excess release of the element, whereas a negative value indicates net retention. The excess release or net retention of each element are presented in Table 5.4. The excess release of Al and Si leached from the Vitric columns (17.5-276.2 μmol_c Al kg^{-1} and 0.282-0.410 mmol Si kg^{-1}) was larger than that leached from Eutric (0.00-1.93 μmol_c Al kg^{-1} and 0.098 and 0.263 mmol Si kg^{-1}. In contrast, the excess release of Ca leached from Eutric column was generally larger than that from Vitric columns. The excess release of SO_4^{2-} leached from both Vitric and Eutric columns, was larger in the NS than in the AS leachates. The largest excess release of F^- leached was observed in Vitric columns (46-135 μmol_c kg^{-1}) and decreased in the order Vitric > NS leached Eutric (7-12.8 μmol_c kg^{-1}) > AS-leached Eutric (-9.7 – -2.6 μmol_c kg^{-1}).

Table 5.4: Excess release (+) or retention (-) of cations and anions in the soil columns.

solution	profile	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	SO_4^{2-}	NO_3^-	F^-	Al^{3+}	Fe^{3+}	Mn^{4+}	Si
		——————/$cmol_c\ kg^{-1}$——————							——————/$\mu mol_c\ kg^{-1}$——————				/$mmol\ kg^{-1}$
NS	VI-2	0.150	0.109	0.026	0.018	0.092	0.309	0.027	66.656	167.60	0.45	1.31	0.282
	VI-9	0.185	0.051	0.033	0.017	0.027	0.390	0.024	135.509	276.21	0.05	1.99	0.350
	EU-3	0.246	0.080	0.095	0.017	0.033	0.365	0.036	11.745	1.93	0.00	0.32	0.175
	EU-3	0.227	0.039	0.066	0.023	0.020	0.240	0.003	7.043	0.35	0.00	0.01	0.263
	EU-5	0.367	0.103	0.094	0.015	0.013	0.084	0.084	11.403	0.17	0.00	0.01	0.257
	EU-5	0.392	0.142	0.130	0.017	0.034	0.084	0.163	12.809	0.09	0.01	0.01	0.256
AS	VI-2	0.177	0.060	0.023	0.022	0.043	0.182	0.044	95.320	232.28	2.79	1.71	0.354
	VI-9	0.303	0.015	0.139	0.027	0.030	0.045	0.124	46.130	17.50	0.52	0.02	0.410
	EU-3	0.249	0.013	0.046	0.012	-0.008	0.030	0.051	-9.691	1.03	0.00	0.08	0.250
	EU-3	0.128	0.027	0.041	0.010	0.020	0.053	0.001	-2.586	0.00	0.00	0.15	0.098
	EU-5	0.409	0.124	0.099	0.008	0.016	-0.004	0.065	-4.439	0.38	0.09	0.01	0.235
	EU-5	0.558	0.089	0.100	0.006	-0.006	-0.001	0.160	-2.658	0.00	0.02	0.00	0.245

5.4.2 Cation and anion exchange resins, and test-minerals

The results from the resins and test-minerals recovered after one year and two years were similar, we present only the results from the test materials recovered after one year. Table 5.5 presents the contents of Ba^{2+}exchangeable cations and elements extractable by oxalate, KH_2PO_4 and NH_4F on ferrihydrite, whereas Table 5.6 shows the content of elements sorbed on anion and cation exchange resins.

Table 5.5: Ba^{2+}-, oxalate-, KH_2PO_4- and NH_4F- extractable elements contents from the test-ferrihydrite inserted in the Andosols of the Masaya area.

	$BaCl_2$ extraction					oxalate extraction			KH_2PO_4 extraction			NH_4F extraction			
Horizon	Ca	K	Mg	Na	Σ	Al	SO_4^{2-}	Si	F^-	Cl^-	SO_4^{2-}	Al	Fe	SO_4^{2-}	Si
	———/$cmol_c$ kg^{-1}———					——/mg kg^{-1}——			——/mg kg^{-1}——			———/mg kg^{-1}———			
EU3 A2	0.76	0.04	0.04	0.22	1.06	97	4030	1095	28	137	2174	50	85	3791	80
EU3 Bw	0.95	0.05	0.04	0.23	1.28	26	5414	1193	23	73	3641	31	104	4178	50
EU5 Bw	4.82	0.04	0.34	0.46	5.66	30	2722	1634	24	72	1847	8	71	2223	-
EU9 A2	1.46	0.02	0.05	0.39	1.93	207	8780	2572	80	94	5049	102	126	7308	87
EU9 AB	2.42	0.04	0.10	0.59	3.15	32	9238	1859	16	78	5555	30	86	7890	-
VI 2	0.77	0.05	0.02	0.10	0.94	807	12094	3706	139	254	7624	492	98	9804	346
VI 9	0.56	0.03	0.06	0.05	0.69	519	11701	3245	158	458	5979	260	99	7526	161

Table 5.6: Exchangeable elements content of the resins inserted after one year in the Andosols of the Masaya area.

	Cation exchange resins					Anion exchange resins			
Horizon	Al^{3+}	Ca^{2+}	Fe^{3+}	K^+	Mg^{2+}	Cl^-	F^-	SO_4^{2-}	Si
	——/$cmol_c$ kg^{-1}——					—/$cmol_c$ kg^{-1}—			/cmol kg^{-1}
EU3 A2	4.1	95.8	0.2	22.9	11.7	92	16	170	15
EU3 Bw	2.7	85.9	0.2	11.7	29.9	36	12	114	4
EU5 Bw	0.8	68.5	0.1	23.1	9.3	24	11	120	-
EU9 A2	2.2	70.9	0.1	12.6	15.8	83	27	277	5
EU9 AB	2.1	69.4	0.2	18.0	19.3	43	9	300	-
VI 2	13.4	63.9	0.2	31.8	18.9	172	36	415	28
VI 9	21.7	34.6	0.6	20.3	7.2	263	22	359	19

In Eutric Andosols, cation exchange resins sorbed lower amounts of Al (0.8-4.1 $cmol_c$ kg^{-1}) compared to the Vitric Andosols (13.4 and 21.7 $cmol_c$ kg^{-1}). The contents of Cl^-, F^- and SO_4^{2-} sorbed on anion exchange resins were larger in the Vitric than in the Eutric, and generally decreased with depth in Eutric Andosols. The ferrihydrites inserted in the Vitric Andosols sorbed the largest contents of Al, Si, SO_4^{2-}, F^-, Cl^- and cations, whatever the extraction solution. In Eutric, the content of KH_2PO_4 extractable F^- and Cl^- content decreased with depth.

5.5 Discussion

5.5.1 Column variability and experimental quality

The charge balances in both leaching solutions and leachates were satisfactory. The ratios (Σcations – Σanions)/(Σcations + Σanions) were always less than 0.03 (data not shown), reflecting the quality of the analytical results. Output Cl^- concentrations rapidly equal input Cl^- concentrations for all columns and treatments (Figure 5.4). This behaviour was expected for this conservative element, and illustrates the well-known poor affinity of soil constituents for Cl^- sorption (Gebhart & Coleman, 1974a).

The natural heterogeneity of the soil properties accounts for the mineralogical differences observed between the columns collected at a same site. In particular, in the Vitric series, the AS-treated VI-9 column presented a 3A horizon particularly enriched in short-range ordered minerals (Table 5.2). Therefore, this column is likely to behave differently from the other Vitric columns upon solution addition.

5.5.2 Soil properties and ion mobility

Silica concentration in soil solution is controlled by soilminerals (Karathanasis, 2002). Large Si release can be associated with the presence of weatherable minerals, whereas lower release tends to indicate the dominance of more stable minerals. This is consistent with larger Si concentrations in the leachates of the young Vitric Andosols rich in weatherable minerals, as compared to more weathered Eutric Andosols rich in secondary alumino-silicates (Figure 5.2).

In contrast to Cl^-, output SO_4^{2-} concentrations are generally larger than input concentrations, especially with NS treatment. This reflects the occurrence of a large exchangeable SO_4^{2-} pool in the Masaya Andosols (Chapter 7; Table 5.2), which is progressively released during the experiment. However, output SO_4^{2-} concentrations of EU5 columns tend to be lower than AS input SO_4^{2-} concentrations, indicating net retention (Table 5.4). This can be related to the lower initial KH_2PO_4-extractable SO_4^{2-} content in EU5 compared to EU3 columns (Table 5.2).

Aluminium concentration in the soil solution is largely controlled by pH (Sposito, 1996). Therefore, the high pH values measured in the Eutric leachates (>6, Figure 5.2) prevent Al mobility. This is in contrast to the comparatively more acid Vitric leachates, where significant Al content was measured (Figure 5.4). Despite leachate pH around 6.5, measurable amounts of Al were also observed for the VI9-A column. In this column, Al is probably mobilised in the acid surface horizons in the form of Al-F_x complexes (Totsche *et al.*, 2000). This is supported by the concomitant variations in Al and F^- concentrations with leaching volume (Figures 5.3 and 5.4). In addition, speciation calculations using PHREEQC (Parkhust & Appelo, 1999) predicted that more than 90% of Al in the leachates was incorporated into Al-F_x complexes.

Similarly, F^- mobility in Vitric columns is dictated by Al-F_x complexes. Modeling results indicated that Al-F_x complexes accounted for ∼60 to ∼70 % of total F^- in the Vitric leachates. In contrast, only ∼10 to ∼20 % of F^- was in an Al-F_x complex form in the Eutric and AS-treated VI9 leachates. This is due to the lower Al concentrations in these samples. Combined with lower Al concentrations, the larger contents of short-range ordered minerals in the Eutric than in the Vitric Andosols (Table 5.2) resulted in more effective F^- retention in the Eutric soils (Figure 5.3). However, despite specific retention of F, there was still significant F^- leaching, especially in the NS treatment (Table 5.4). The AS treatment increased F^- retention in soil (Table 5.4), probably because sorption increased with a decrease in pH (Harrington *et al.*, 2003; Omueti & Jones, 1977).

The larger output Si concentration in two of the EU3 columns compared to the other columns from the same site was associated with lower output F^- concentration (Figures 5.2 and 5.4). This may reflect the ability of F^- to exchange with silicate anions (Saeki & Matsumoto, 1993). It also suggests that output Si originates from both mineral dissolution and anion exchange involving silicate.

Overall, these results are in agreement with those of Chapter 4 and reflect the preferential retention (or low mobility) of F^- over SO_4^{2-} and Cl^-, and SO_4^{2-} over Cl^-. Our results also highlight the importance of Al-F_x complexes in both Al and F mobility.

Aluminium and Si release in soil and subsequent formation of allophanic constituents are the key processes of Andosol genesis (Shoji *et al.*, 1993). However, the large Al and Si mobility in the Vitric Andosols shows that, Al may be leached through the soil profile at the early stage of Andosol genesis. In turn, this contributes to the 'anti-allophanic effect' as defined by Shoji *et al.* (1993).

5.5.3 Stability of basic aluminium sulphate minerals

We tested the saturation of various $Al_x(OH)_y(SO_4)_z$ minerals by applying the PHREEQC chemical equilibria code (Parkhust & Appelo, 1999) on the Vitric and few Eutric output solutions with measurable amounts of Al. The Eutric and AS-leached VI9 output solutions were generally undersaturated with respect to alunite, jurbanite and basaluminite, whereas the Vitric output solutions were generally oversaturated with respect to these minerals (Figure 5.5). These results may explain why $Al_x(OH)_y(SO_4)_z$ minerals could not be detected in the Eutric soils in Chapter 7. Besides, these results are in contradiction with Chapter 4 where we reported oversaturation with respect to BAS minerals in the Eutric soil solutions collected by Parnell (1986). We note that F^- concentrations were not analysed in these solution samples.

It appears that Al concentration is the limiting factor for $Al_x(OH)_y(SO_4)_z$ formation. The low pH and abundance of volcanic glass permitted sufficient Al release allowing $Al_x(OH)_y(SO_4)_z$ formation in the Vitric Andosols, whereas higher pH and competition with Al-F_x complex probably reduced $Al_x(OH)_y(SO_4)_z$ formation in the Eutric soils.

5.5.4 Acid neutralisation in Andosols

Although net acidification is taking place in the Masaya Andosols (Chapters 3 and 4), neutralisation processes remain effective. This is revealed by the fact that the column leachates showed higher pH values than the

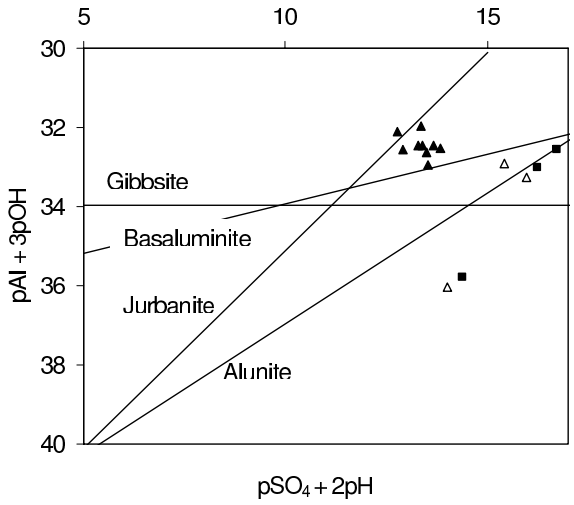

Figure 5.5: Soil solution ion activities relative to stability diagram for $Al_x(OH)_y(SO_4)_z$ minerals and gibbsite for EU3 (■), VI9-AS (△) and other VI (▲) leachates.

AS input. Such pH increase from input to output solutions may result from physico-chemical and mineralogical reactions or, from biological activity. However, at the pH of input solution (pH = 3.6), biological activity does not alter solution pH (Rufyikiri *et al.*, 1999).

Our data support the idea that acid neutralization involves mineral dissolution and ion exchange in the Vitric and Eutric Andosols, respectively (Chapter 3). Indeed, the large Al and Si concentrations in the Vitric leachates plead for large mineral hydrolysis. In contrast, the large Ca concentration in the Eutric leachates, together with net retention of SO_4^{2-} and F^- (Table 5.4), highlight the importance of ion exchange process in the Eutric Andosols.

The parabolic release rate of K observed for the Vitric columns (Figure 5.6) is also consistent with glass/mineral hydrolysis. It is attributed to solid state diffusion in silicates, whereas linear release represents chemical reactions at the aqueous/solid interface (White, 1983). Therefore, linear release rate of K in the Eutric Andosols suggests ion exchange processes.

The excess release of SO_4^{2-} content in the AS leachates is systematically lower than in the NS leachates (Table 5.4), despite larger SO_4^{2-} inputs in the former. This reflects enhanced SO_4^{2-} storage under acidic conditions, a process that contributes to acid neutralisation, as observed

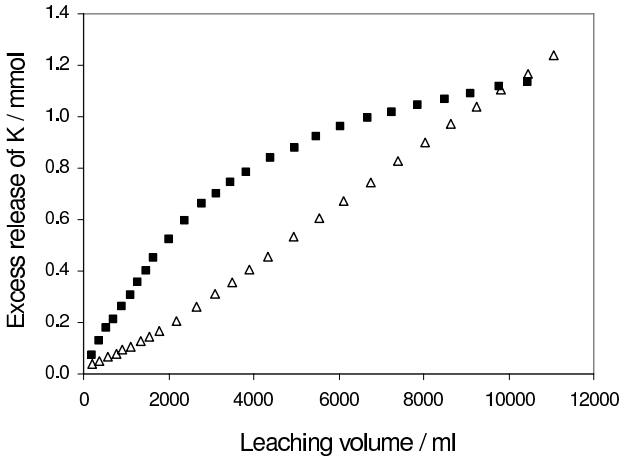

Figure 5.6: Accumulated release of K in leachates from the Vitric (■) and Eutric (△) Andosols as a function of leaching volume.

in other studies (e.g. Stumpe & Vlek, 1991; Xu & Ji, 2001; Grieve, 1999). Neutralization of the acid inputs may operate in two steps : a decrease in soil pH, with concomitant development of positive charge followed by SO_4^{2-} adsorption and releases of OH^-.

The observation that pH in the leachates does not vary with leachate volume in all columns suggests that the active 'neutralisation reserve' of the Vitric and Eutric Andosols is not exhausted. This contrasts with poorly buffered soils, which show a decrease in pH under similar conditions (e.g. Stumpe & Vlek, 1991; Grieve, 1999). However, for the Vitric Andosols, the acid neutralising reserve of exchangeable cations may be rapidly exhausted, favouring mineral hydrolysis as the main active neutralising mechanism. This is illustrated by a decrease in output Ca concentration with increasing leaching volume (Figure 5.2). Other alkaline and alkaline-earth cations behaved similarly (data not shown). The excess release of Ca, K, Na and Mg (Table 5.4) represents 14.7 to 22.0 % of the sum of exchangeable cations in the Vitric Andosol columns (Table 5.2), indicating a significant decrease in the reserve of 'exchangeable cations content'. In contrast, the excess release of cations represents only 1.4 to 3.8 % of the sum of exchangeable cations in the Eutric Andosol columns. Ion exchange thus remains an efficient process in neutralising acid inputs in Eutric Andosols.

Due to their low exchangeable cation content and anion exchange capacity, Vitric Andosols neutralise acid inputs mainly through min-

eral hydrolysis. Since mineral hydrolysis is less efficient in neutralising acid-inputs, in the short-term, than ion exchange (Bloom, 2000). This explains the comparatively low leachate pH values measured for the Vitric soils.

5.5.5 Ion exchange and weathering in situ

In situ, conditions may largely differ from laboratory conditions. However, processes governing ion mobility and acid neutralisation *in situ* are similar to those described in the column experiment.

The larger content of exchangeable cations sorbed onto ferrihydrite in the Eutric also illustrate the importance of cation exchange in these Andosols. Besides, the larger contents of SO_4^{2-}, Cl^- and F^- sorbed onto anion exchange resins and ferrihydrite in the Vitric than in the Eutric Andosols reflect mostly the lower anion retention capacity of the Vitric Andosols.

Similar to the observations made for the column experiment, larger F^- lixiviation generated larger Al content sorbed onto both resins and test-minerals in Vitric Andosols. Weathering of minerals also likely contributes to Al release, since Si contents sorbed on resins and ferrihydrite were the largest in the Vitric Andosols (Tables 5.5 and 5.6). However, in contrast to the leaching experiment, measurable amount of Al were extracted from resins and ferrihydrite indicating effective release but low mobility of Al in the Eutric soils.

The decrease in F^-content sorbed on ferrihydrite and resins with depth generally observed may be related to the rapid sorption of F^- in surface horizon. In contrast, SO_4^{2-} sorption in surface horizon may be impeded by the occurrence of organic matter (Johnson & Todd, 1983), thus enhancing its mobility. This could explain why similar contents of SO_4^{2-} in resins and ferrihydrite are found both in surface and subsurface horizons. However, we have no simple explanation for the observed decrease in Cl^- with depth.

The anion selectivity of anion exchange resins follows the order $F^- < Cl^- < SO_4^{2-}$, which largely differ from the one of soil constituents and synthetic ferrihydrite: $Cl^- < SO_4^{2-} < F^-$. This similarity between ferrihydrite and soil constituents makes it a more useful probe to study soil processes. Ferrihydrite may also sorb both cations and anions and thus accounts for both ion exchange processes simultaneously. Moreover, standard deviation was the lowest for ferrihydrite (<5%) compared to cation (∼20%) and anion (∼10%) exchange resins. All this pleads for the preferential use of test-minerals such as ferrihydrite to study soil weathering and ion exchange in situ.

5.5.6 Environmental issues

Acid inputs equivalent to two years of precipitation did not result in significant acidification of Vitric and Eutric Andosols, suggesting occurrence of acid neutralisation mechanisms. Thus, detrimental effects of soil acidification in this area may be temporary, and the soil horizons may well recover from detrimental effects of acidic deposition after reduction/cessation in volcanic emissions.

The large buffering capacity of the Eutric Andosols maintain soil pH, exchangeable cations and Al content at appreciable level for plant growth. It reduces risk of fluoride toxicity through specific retention. In contrast, the Vitric Andosols have poorer conditions and Al toxicity and F^- pollution may occur in these soils. However, this might not affect plants, because roots usually grow in the nutrient-rich and allophanic horizons. This suggests that the main cause of vegetation damage downwind of Masaya volcano is primarily due to the high atmospheric concentrations of volcanic pollutants, rather than to irreversible physicochemical changes in the soils.

5.6 Conclusion

The results of this study demonstrate that, despite a long history of acid deposition, acid neutralising processes are still active in the Andosols downwind from Masaya volcano. These operate mainly through net anion retention and exchange of cations in the weathered Eutric Andosols, and through the weathering of minerals in the young Vitric Andosols, with ion exchange being more efficient.

Although F is generally specifically retained in soils, formation of Al-F_x complexes increased its mobility, especially in the Vitric soils This process probably hinders the formation of $Al_x(OH)_y(SO_4)_z$ minerals.

Part II

Retention and Distribution of SO_4^{2-}