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Acid Neutralization and Sulphur retention in S-impacted Andosols

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Chapter 8

Sulphate Sorption at Elevated Equilibrium Concentration in Andosols*

Summary

It is well known that inorganic SO_4^{2-} inputs can be stored in soils by adsorption. At elevated SO_4^{2-} concentration in soil solution, precipitation of $Al_x(OH)_y(SO_4)_z$ minerals may also contribute significantly to SO_4^{2-} storage in soils. However, chemisorption and precipitation can rarely be distinguished experimentally. Direct evidence of $Al_x(OH)_y(SO_4)_z$ in soils was provided only recently, and calls for a comprehensive understanding of SO_4^{2-} sorption. So far, SO_4^{2-} retention studies have typically involved relatively low solution SO_4^{2-} concentrations (i.e., 0-5 mM). However, for SO_4^{2-} precipitation to occur, higher concentration may be needed. To investigate this process, we carried out SO_4^{2-} sorption experiments on Andosols using low pH (4) equilibrium solution with SO_4^{2-} concentrations ranging from 0.05 to 15 mM SO_4^{2-}. The isotherms obtained showed a distinct biphasic shape. In the low solution concentration range (<5-7 mM), the sorption of SO_4^{2-} obeyed a L-type isotherm, whereas in the higher SO_4^{2-} solution concentration (>5-7 mM) SO_4^{2-} sorption was described by a C-type isotherm. Our results argue for a SO_4^{2-} precipitation mechanism at high SO_4^{2-} concentrations, which is preceded by chemisorption at low SO_4^{2-} concentration. In addition to the SO_4^{2-} isotherm study, the capacity of the Andosols to sorb SO_4^{2-}

*Adapted from Delfosse T., Delmelle P. & Delvaux B. Sulphate sorption at elevated equilibrium concentration in Andosols. Submitted to *Geoderma*

(sulphate retention index) was mostly dictated by specific surface (r = 0.85).

8.1 Introduction

Sulphate may accumulate in soils exposed to high S input through various processes, including (i) immobilisation as organic S, (ii) chemisorption on the mineral surface, (iii) precipitation in a $Al_x(OH)_y(SO_4)_z$ mineral phase (Adams & Rawajfih, 1977; Prietzel & Hirsch, 2000) and (iv) irreversible migration of ions into short range-ordered minerals, i.e. occlusion (Chapter 6). Although most of the inorganic SO_4^{2-} in these soils tends to be retained by a sorption mechanism, precipitation processes may contribute to SO_4^{2-} storage significantly (Chapters 6 and 7).

The presence of $Al_x(OH)_y(SO_4)_z$ mineral in S-impacted soils has been suspected for a long time (Adams & Rawajfih, 1977; Prietzel & Hirsch, 2000). However, direct observation of a $Al_x(OH)_y(SO_4)_z$ phase in soil has proven to be difficult, and it is only recently that it was identified on clay soil particles of Andosols (Chapter 7). The lack of previous evidence probably originates from inappropriate methodology (Chapter 7) but also because chemisorption and precipitation mechanisms can rarely be distinguished experimentally (McBride, 2000). The major difference between the two processes being that adsorption is two-dimensional, whereas precipitation is three-dimensional. In fact, the uptake of adsorbate ions by soil, which is termed sorption, can be viewed as a continuous process that ranges from chemisorption at low adsorbate concentration, to precipitation at higher adsorbate concentration (McBride, 2000).

In general, SO_4^{2-} sorption in soils is investigated by performing sorption isotherm experiments, where the equilibrium solution concentration of SO_4^{2-} typically ranges from 0 to ~5 mM SO_4^{2-}. These conditions have led to sorption maxima of ~1100 mg S kg^{-1} (e.g. Haque & Walmsley, 1973; Singh, 1984a; Curtin & Syers, 1990) and chemisorption was inferred to dominate SO_4^{2-} sorption. However, in areas affected by strong S inputs, such as those originating from deposition of marine or volcanic aerosols, comparatively higher SO_4^{2-} concentrations in soil solution may be found. This is reflected by soil total SO_4^{2-} contents, which may exceed 5000 mg S kg^{-1} (Hasan *et al.*, 1970; Hue *et al.*, 1990; Takamatsu *et al.*, 1992; Chapter 3). Several studies have highlighted that S storage in these environments may be drawn by SO_4^{2-} precipitation (Hue *et al.*, 1990; Takamatsu *et al.*, 1992; Chapter 6). In particular, it may represent up to 50% of total soil sulphate content in Andosols affected by large

volcanogenic S deposition (Chapter 6). These considerations call for a comprehensive understanding of SO_4^{2-} sorption at large concentrations in soils.

In order to obtain further insights into SO_4^{2-} precipitation in S-impacted soils, sorption isotherms at elevated SO_4^{2-} equilibrium concentrations (i.e., > 5 mM SO_4^{2-}) are needed, since these conditions should favour the formation of an $Al_x(OH)_y(SO_4)_z$ mineral phase (Adams & Rawajfih, 1977; Nordstrom, 1982). Toward this aim, we examined SO_4^{2-} sorption in Andosols over wide range of equilibrium solution concentration.

8.2 Materials and methods

8.2.1 Sulphate sorption equilibria

Sulphate sorption isotherms were performed on four Andosol horizons (labelled EU2-Bw, EU5-A2, EU9-A2 and VI2-3A) pertaining to the Eutric and Vitric soil profiles from the Masaya area. We selected these samples because of their contrasting short-range ordered mineral and KH_2PO_4-extractable SO_4^{2-} contents. The undifferentiated VI2-3A and the well-developed EU2-Bw samples contrast in term of short-range ordered minerals, whereas having similar mineralogical properties the EU5-A2 and EU9-A2 samples differ by their KH_2PO_4-extractable SO_4^{2-} content. The soil major properties are summarised in Table 8.1. We carried out SO_4^{2-} sorption isotherms in acidic conditions at 20 °C, by shaking 3 g of soil with 50 ml Na_2SO_4 solution with concentrations 0.05, 0.1, 0.5, 1, 2, 3, 5, 7.5, 10 and 15 mM SO_4^{2-}. Solutions were initially acidified to pH 4 and contained 0.1 M KNO_3 as supporting electrolyte to keep the ionic strength constant. The initial pH condition roughly corresponds to that observed in the Masaya rainwater (Table 4.1). Reaction between SO_4^{2-} solution and soil sample was allowed to proceed for 1 hour with continuous stirring. The soil-solution mixture pH was kept constant at pH 4 by adding 0.4 M HNO_3 with an automatic titrator. The suspension was then centrifuged, filtered and analysed for SO_4^{2-} by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). For these experimental conditions, biological immobilisation is considered as negligible. Sorption experiments were done in duplicate. Sorbed SO_4^{2-} was calculated from the difference between initial and equilibrium concentration, after correction for entrapped solution. The amount of OH^- released was determined from the amount of HNO_3 consumed to maintain a constant pH value of 4.

Table 8.1: pH and CEC values, carbon contents (Org. C), oxalate (o) extractable contents, Total Reserve in Bases (TRB), specific surface (S_m), KH_2PO_4 (p) extractable SO_4^{2-} of the four Andosols samples studied in the sorption isotherm.

Profile	Horiz.	pH	Org.C	CEC	TRB	Si_o	Fe_o	S_m	SO_4^{2-} p
		H_20	%	/$cmol_c$ kg^{-1}		/g kg^{-1}		/m^2 g^{-1}	/g kg^{-1}
EU2	Bw	5.3	5.8	21.8	199	41.5	65.4	308	3.03
EU5	A2	6.9	5.1	36.9	396	19.4	27.1	170	0.04
EU9	A2	5.7	4.7	21.5	400	19	29.2	163	0.45
VI2	3A	4.9	2.0	7.8	530	5.3	8.5	83	0.76

In addition to the sorption isotherm experiments, a soil SO_4^{2-} retention index (SRI) was estimated for 37 soil samples from the same area. These samples have been characterised in Chapter 3. The SRI is assumed to be a good proxy of the soil capacity to sorb SO_4^{2-} (MacDonald *et al.*, 1994; Camps Arbestain *et al.*, 1999). SRI were obtained by performing SO_4^{2-} sorption in 5 mM Na_2SO_4 at pH 4. A solution concentration of 5 mM Na_2SO_4 roughly corresponds to the first sorption maximum of the sorption isotherm. The SRI is defined as the sum of native KH_2PO_4-extractable SO_4^{2-} content and additional SO_4^{2-} sorbed from 5 mM solution.

8.3 Results

8.3.1 Sulphate sorption isotherms

The sulphate sorption isotherms obtained for the EU2-Bw, EU5-A2, EU9-A2 and VI2-3A Andosol horizons are shown in Figure 8.1. The amount of SO_4^{2-} adsorbed and OH^- released are presented in Table 8.2. Sulphate sorption was systematically higher for EU2-Bw, and decreased in the order EU2-Bw > EU9-A2 = EU5-A2 > VI2-3A. All the isotherms exhibited a biphasic shape: characterised by a L-type shape (McBride, 2000) at low SO_4^{2-} equilibrium solution concentration range (<5-7 mM), and a C-type shape at higher concentrations (>5-7 mM).

The release of OH^- increased linearly with the sorption of SO_4^{2-} (Figure 8.2). The largest amount of OH^- released (168-210 $mmol_c$ kg^{-1}) was observed for EU5-A2. It decreased in the order: EU5-A2 > EU2-Bw (90-165 $mmol_c$ kg^{-1}) > EU9-A2 (76-117 $mmol_c$ kg^{-1}) > VI2-3A (16-39 $mmol_c$ kg^{-1}).

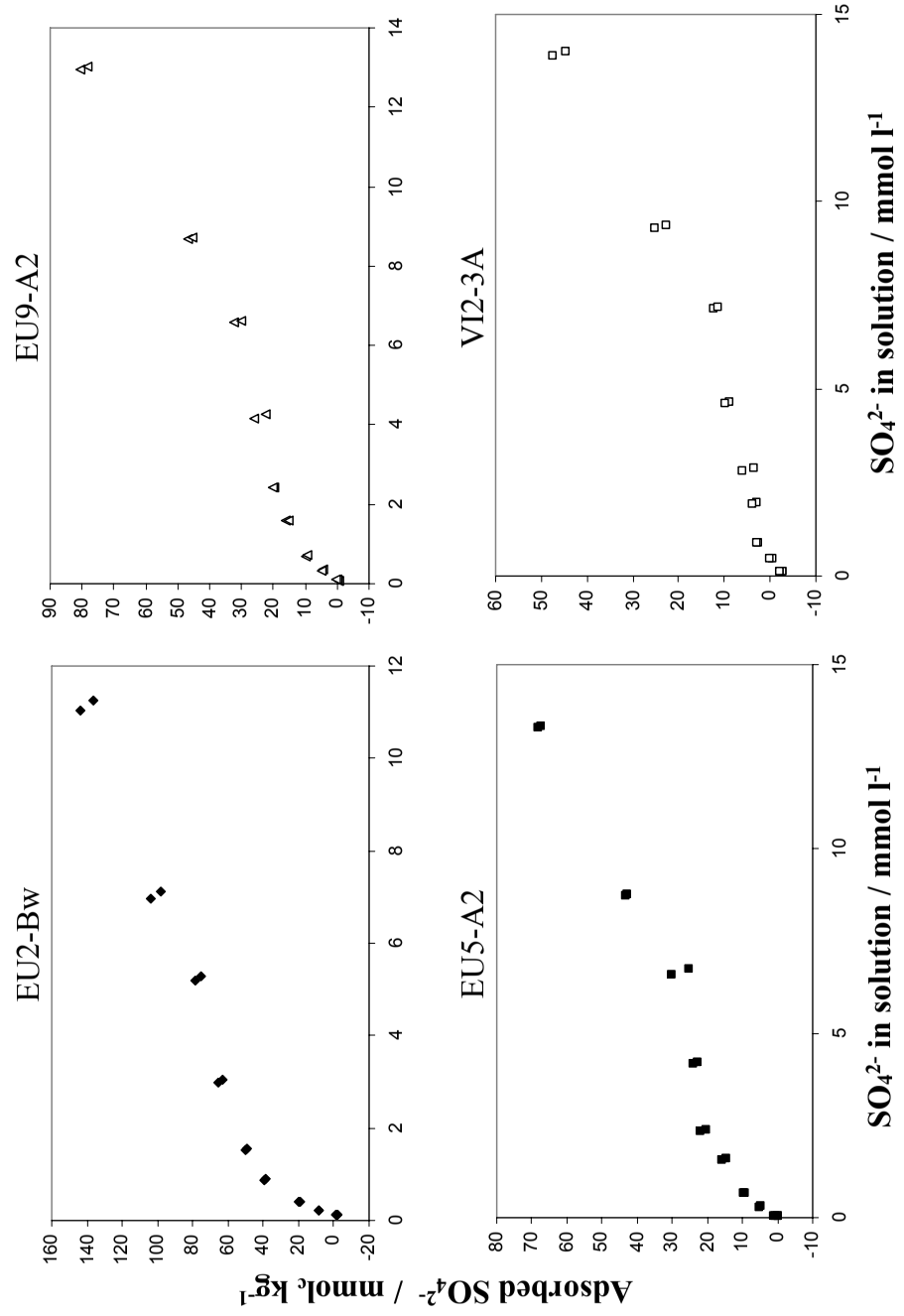

Figure 8.1: Sorption isotherms of sulphate by four Andosol samples of the Masaya area.

Table 8.2: Content of SO_4^{2-} sorbed, OH released, and Al concentrations in the equilibrium solution as a function of SO_4^{2-} added.

SO_4 added	SO_4 sorbed	OH released	Al in solution	SO_4 added	SO_4 sorbed	OH released	Al in solution
/mmol$_c$ kg^{-1}			/mmol$_c$ l^{-1}	/mmol$_c$ kg^{-1}			/mmol$_c$ l^{-1}
EU2-Bw				**EU9-A2**			
1.9	-2.2	97.2	1.05	1.9	-0.7	79.2	0.79
1.9	-2.3	95.9	1.01	1.9	-0.7	78.5	0.78
3.3	-1.1	90.4	1.00	3.3	0.1	76.8	0.73
3.3	-1.0	92.4	1.03	3.3	0.3	76.0	0.69
16.0	8.5	103.9	1.10	16.0	4.5	84.4	0.88
16.0	8.3	105.6	1.10	16.0	4.9	82.1	0.81
33.0	19.7	106.3	1.01	33.0	9.8	84.3	0.79
33.0	19.5	108.0	1.10	33.0	9.3	81.2	0.79
68.8	39.5	118.5	1.08	68.8	16.3	98.9	0.81
68.8	38.5	115.3	1.07	68.8	15.4	90.4	0.82
101.0	50.1	118.7	1.00	101.0	19.7	92.8	0.84
101.0	49.4	114.0	0.94	101.0	20.1	93.6	0.83
164.6	63.5	114.8	0.86	164.6	26.1	90.4	0.87
164.6	65.1	118.5	0.86	164.6	22.4	87.1	0.76
251.3	78.4	134.0	1.06	251.3	32.3	98.4	0.87
251.3	75.1	135.9	1.11	251.3	30.3	95.7	0.82
335.8	98.3	141.9	1.09	335.8	46.9	99.3	0.92
335.8	103.4	138.9	1.06	335.8	45.4	101.5	0.90
512.2	136.7	165.3	1.26	512.2	80.6	113.9	0.95
512.2	143.9	152.1	1.20	512.2	78.3	117.2	0.98
EU5-A2				**VI2-3A**			
1.9	-0.2	174.8	0.22	1.9	-2.6	18.5	0.57
1.9	-0.2	177.3	0.20	1.9	-2.8	17.3	0.57
3.3	0.7	173.2	0.20	3.3	-2.1	26.8	0.75
3.3	0.9	181.3	0.18	3.3	-2.2	18.8	0.64
16.0	5.0	174.1	0.24	16.0	-0.5	20.5	0.61
16.0	4.9	174.3	0.23	16.0	-0.1	17.3	0.50
33.0	9.5	177.6	0.23	33.0	2.6	16.3	0.55
33.0	9.1	180.3	0.23	33.0	2.7	20.0	0.58
68.8	14.4	168.5	0.20	68.8	2.9	24.5	0.64
68.8	15.9	187.9	0.24	68.8	4.0	21.3	0.61
101.0	22.0	190.3	0.24	101.0	3.6	19.5	0.56
101.0	20.3	189.9	0.25	101.0	6.1	20.9	0.59
164.6	23.9	181.6	0.22	164.6	8.8	26.8	0.65
164.6	22.9	196.8	0.25	164.6	9.9	24.7	0.58
251.3	25.4	188.1	0.27	251.3	12.4	31.3	0.76
251.3	30.3	178.0	0.25	251.3	11.4	29.6	0.67
335.8	42.8	199.6	0.31	335.8	25.2	30.1	0.71
335.8	43.1	187.9	0.25	335.8	22.6	29.6	0.68
512.2	68.1	204.3	0.34	512.2	44.7	39.1	0.76
512.2	67.1	209.6	0.34	512.2	47.5	35.9	0.66

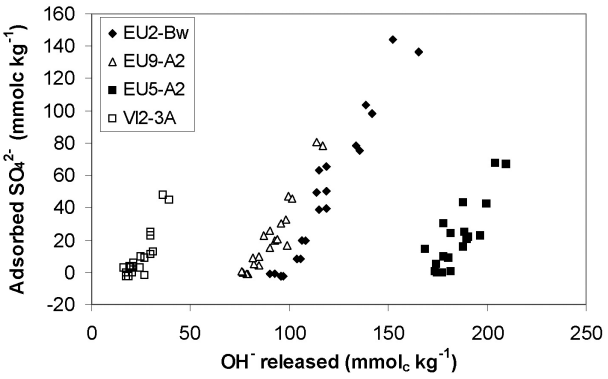

Figure 8.2: Relationship between OH^- released and sorbed SO_4^{2-} for the four sorption isotherms under study.

8.3.2 Sulphate retention index

Results of the SRI determinations are presented in Table 8.3. In general, the Vitric Andosols had lower SRI values than the Eutric Andosols (0.24-3.09 and 0.58-9.21 g kg^{-1}, respectively). However, the contribution of KH_2PO_4-extractable SO_4^{2-} to the SRI was generally larger in the Vitric (4-100%) than in the Eutric soils (1-48%).

8.4 Discussion

The biphasic shape of the SO_4^{2-} sorption isotherms obtained for the Andosols studied (Figure 8.1) suggests that two SO_4^{2-} sorption mechanisms are involved: one over a limited range of SO_4^{2-} concentrations in equilibrium solution (<5-7 mM) and one over a larger concentration range. We will discuss them separately.

8.4.1 Sulphate sorption and soil constituents

In the low concentration range, the L-type sorption isotherms of the Masaya Andosols correspond to those reported for other soil types (e.g. Rajan, 1979; Curtin & Syers, 1990). The L-type shape indicates a maximum in SO_4^{2-} sorption related to the saturation of available sorption sites in the soil. The shape of the isotherm and the fact that SO_4^{2-} sorption was accompanied by concomitant release of OH^- suggest that chemisorption was the main soil retention process occurring at low SO_4^{2-} solution concentrations (<5-7 mM).

Table 8.3: Contents of KH_2PO_4 extractable sulphate (SO_4^{2-}p) and sulphate sorbed with Na_2SO_4 5mM ($SO_4^{2-}{}_{5mM}$), Sulphate retention index (SRI) and contribution of SO_4^{2-}p to the SRI (CS-SRI), oxalate (o) extractable contents, specific surface (S_m) and organic C content.

Prof.	Horz.	SO_4^{2-}p	$SO_4^{2-}{}_{5mM}$	SRI	CS-SRI	Si_o	Al_o	Fe_o	S_m	Org. C
		——/g kg^{-1}——			/%	—/g kg^{-1}—			/m^2 g^{-1}	/%
VI2	A	0.49	0.18	0.67	72	3.1	6.2	8.3	29	2.1
	2BC	0.62	0.19	0.81	76	4.1	7.5	7.6	77	1.0
	3A	0.76	0.52	1.28	60	5.3	9.6	8.5	83	2.0
VI4	A	0.72	0.01	0.73	98	1.8	3.9	6.4	29	2.4
	2BC	0.62	-0.01	0.61	100	3.6	7.0	7.1	30	1.2
	3A	2.16	0.93	3.09	70	19.1	32.6	21.6	118	3.2
VI6	A	0.72	0.05	0.76	94	1.8	3.9	8.2	34	2.3
	2BC	0.43	0.32	0.74	57	3.1	6.0	5.8	20	0.9
	3A	0.40	0.73	1.12	35	8.1	15.2	15.1	84	3.1
	3AB	0.19	0.96	1.15	16	12.5	21.3	19.6	95	3.5
VI7	A	0.36	0.16	0.52	69	2.8	5.8	8.4	29	2.0
	AB	0.17	0.09	0.27	65	3.3	6.4	7.7	32	1.2
	2BC	0.21	0.22	0.44	48	2.7	4.9	5.6	26	0.8
	3AB	0.08	0.47	0.55	14	5.6	9.7	8.5	50	2.3
VI9	A	0.20	0.06	0.26	77	2.6	4.8	9.6	64	2.8
	2BC	0.03	0.20	0.24	13	3.4	6.2	10.1	44	1.6
	3A	0.03	0.63	0.66	4	15.5	24.7	25.5	119	3.5
EU2	A1	0.49	2.34	2.82	17	23.3	49.9	37.0	194	8.9
	A2	-	2.52	-	-	25.0	55.2	41.8	215	8.1
	A3	1.49	4.56	6.05	25	29.7	68.4	52.4	223	9.1
	AB	2.32	5.52	7.84	30	34.9	76.6	57.5	235	8.8
	Bw	3.03	6.18	9.21	33	41.5	83.6	65.4	308	5.8
EU9	A1	0.68	0.74	1.42	48	16.3	28.9	25.9	144	5.9
	A2	0.45	1.77	2.22	20	19.0	34.5	29.2	163	4.7
	AB	1.12	2.28	3.40	33	29.4	48.4	36.9	231	4.5
EU4	A1	0.29	1.30	1.59	18	18.9	31.5	28.1	146	5.4
	A2	0.19	1.43	1.61	12	18.1	32.3	26.7	155	5.2
	AB	0.58	2.51	3.10	19	24.0	40.6	33.5	176	3.8
	BA	0.62	2.04	2.67	23	24.3	38.8	31.5	193	3.7
EU5	A1	0.16	0.74	0.90	18	17.3	29.0	23.7	161	6.7
	A2	0.04	1.09	1.14	4	19.4	33.4	27.1	170	5.1
	A3	0.04	1.56	1.60	3	22.1	35.3	27.8	155	5.2
	Bw1	0.34	3.86	4.21	8	37.1	61.0	45.2	246	4.0
EU6	A1	0.07	0.51	0.58	12	13.6	21.0	19.9	147	6.7
	A2	0.05	1.25	1.30	4	15.1	23.8	21.9	166	5.2
	AB	0.02	1.74	1.76	1	20.8	31.9	31.0	186	4.3
	BA	0.06	2.84	2.89	2	31.0	43.2	37.5	222	3.3

Table 8.4: Parameters of Langmuir isotherm.

	Adsorption maximum, b / $mmol_c\ kg^{-1}$	Binding constant, K / $l\ mmol^{-1}$
EU2-Bw	70.6	1.95
EU5-A2	27.5	1.10
EU9-A2	26.9	1.26
VI2-3A	13.1	0.48

Since in the four soil samples the slope of OH^- released against SO_4^{2-} adsorbed was similar (0.4-0.45; Figure 8.2), SO_4^{2-} sorption occur through the same processes in these soils. However, Figure 8.2 indicates that the soils differ by both the amounts of OH^- released and SO_4^{2-} adsorbed. The amount of OH^- that is released to maintain the soil-solution mixture pH at constant value is dictated by (i) the soil buffering capacity, which is mainly governed by surface properties (Chapter 3), and (ii) the initial soil pH. Indeed, few H^+ were needed to decrease the pH of the VI2-3A sample (pH= 4.9; Table 8.1), whereas higher quantities were necessary for EU5-A2 (pH= 6.9). Moreover, despite the lower pH of EU2-Bw horizon (pH= 5.3) as compared to that of EU9-A2 (pH= 5.7), OH^- release was larger in the former because of its larger buffering capacity revealed by its larger specific surface (Table 8.1).

Sulphate adsorption data fitted well to the Langmuir equation in the low concentration range. The K parameter of the Langmuir equation, generally considered as a measure of the affinity of the adsorbate for the surface, was in the order VI2-3A < EU9-A2 = EU5-A2 < EU2-Bw (Table 8.4). This may indicate a higher affinity for SO_4^{2-} in soils with large short-range ordered mineral content. Besides, adsorption maximum values, estimated with the Langmuir equation, was the largest for the EU2-Bw soil sample (Table 8.4). This sample also sorbed the largest SO_4^{2-} content over the entire concentration range (Figure 8.1). This can be related to the larger short-range ordered mineral contents in this soil compared to the other Eutric and Vitric (Table 8.1). For all 37 samples, we found that SRI was significantly and positively correlated with Al_o, Fe_o, $Al_o+\frac{1}{2}\ Fe_o$ and specific surface (r = 0.85-0.87; Table 8.5). This is in good agreement with the findings of Camps Arbestain *et al.* (1999), who studied nonvolcanic Andosols and Andosols from Galicia. Our results reflect the important role of specific surface in SO_4^{2-} sorption. This property is governed by the presence of short-range ordered minerals. Positive correlations are also calculated within the Eutric and Vitric series and indicate that, independently from weathering stage, surface

Table 8.5: Values of correlation coefficients between SRI and soil properties.

	S_m	Org. C	pH	CEC	Al_o	Fe_o	n
Eutric series	0.93**	0.34	-0.55	-0.46	0.93**	0.95**	20
Vitric series	0.64	0.42	-0.18	0.25	0.77*	0.53	17
EU 4, 5, 6 & 9	0.82*	-0.76*	-0.4	-0.7	0.92*	0.92*	15
All samples	0.85**	0.55**	-0.05	0.13	0.87**	0.86**	37
	TRB	Si_o	Alp	Fe_d	$Al_o+\frac{1}{2}$ Fe_o		n
Eutric series	-0.77*	0.84*	0.54	0.93**	0.94**		20
Vitric series	-0.77*	0.74*	0.79*	0.31	0.71*		17
EU 4, 5, 6 & 9	-0.37	0.89*	0.29	0.85*	0.92*		15
All samples	-0.75**	0.79**	0.67**	0.83**	0.87**		37

*Significant at the 0.05 probability level.

**Significant at the 0.01 probability level.

properties dictate most of the SRI.

Stepwise regressions were performed on the 37 sample data set in order to find additional variables that may account for the SRI. The results indicated that, $Al_o+\frac{1}{2}$ Fe_o was the main independent variable affecting SRI ($R^2 = 0.76$) significantly. In the case of the Eutric series considered Alone (excluding EU2 samples, since they should be considered as a distinct series due to their more advanced weathering stage), the analysis predicted the same dependence on $Al_o+\frac{1}{2}$ Fe_o ($R^2 = 0.85$). In addition, organic C content was also shown to be an independent variable ($R^2 = 0.94$), but its effect was negative. The negative impact of organic carbon on SO_4^{2-} sorption was not observed in the Vitric series. These findings tend to indicate that organic C impedes SO_4^{2-} sorption in weathered soils with high short-range ordered mineral contents, in good agreements with previous studies (e.g. Johnson & Todd, 1983).

As shown in Table 8.3, the contribution of the initially adsorbed SO_4^{2-} pool to SRI was highly variable (from 1 to 100%). This is best related to a long history of S deposition over the area downwind from Masaya volcano. In Chapter 3, we showed that the amount of S deposition varied across the area, depending on the level of exposure to the airborne volcanic plume. Hence, soils located within the area of maximum deposition had the highest SO_4^{2-} content. For these soils, the contribution of native SO_4^{2-} to SRI was also the highest (up to 48% for the Eutric series). In contrast, native adsorbed SO_4^{2-} represents less than 18% of the SRI for soil profiles outside the main deposition area (EU5 and EU6). These results show that Eutric Andosols exposed to intense S loading still have the potential for retaining significant amounts of S. In the

Vitric series, native adsorbed SO_4^{2-} generally represents more than 50% of the SRI, except for the soil profile outside the main deposition area (VI9). In this soil series, the largest contributions of native adsorbed SO_4^{2-} to the SRI systematically relate to the less weathered BC horizons and to the soil profiles exposed to the highest rates of S deposition (VI2-VI4). These results highlight the outstanding capacity of Eutric Andosols to store additional SO_4^{2-} compared to Vitric Andosols. Since SO_4^{2-} retention processes are expected to diminish or delay net acidification of soils, this denotes the relative efficiency of Eutric compared to Vitric Andosols in neutralising volcanogenic acid inputs through anion adsorption.

8.4.2 Sorption-precipitation continuum

Some authors have observed that SO_4^{2-} sorption isotherms are biphasic (Wolt *et al.*, 1992; Aylmore *et al.*, 1967; Barrow, 1967). This is also the case for phosphate (PO_4^{3-}) sorption in soils (e.g. Bache, 1964; Farley *et al.*, 1985; Li & Stanforth, 2000). For such types of isotherm, the second part of the curve which corresponds to high anion concentration in solution has been interpreted in term of (i) occurrence of additional binding sites on the soil constituents for sorption (Aylmore et al., 1967); (ii) occlusion of anion within amorphous or semi-crystalline minerals (Muljadi et al., 1966); and (iii) surface-catalysed precipitation (Bache, 1964; Farley *et al.*, 1985; Li & Stanforth, 2000).

Physico-chemical sorption of SO_4^{2-} on another pool of binding sites should result in a L-, H- or F-type isotherm (McBride, 2000), since the binding site will be progressively saturated at high SO_4^{2-} concentration in solution. This process does not fit with the linear isotherm that we observed.

Occlusion of SO_4^{2-} within amorphous or semi-crystalline minerals also can be discarded. The amount of occluded material into a particle is a function of time, and is linearly dependent on the volumetric concentration of the ion at the particle surface (C_{is}) (Crank, 1975). In the equilibration experiments, time is a constant factor and C_{is} is the only variable. Therefore, there should be a linear relationship between the volumetric concentration of SO_4^{2-} and the amount of SO_4^{2-} potentially sorbed by occlusion over all the concentration range. Additional SO_4^{2-} sorbed by chemisorption should lead to an isotherm slope equal or superior to that displayed by the linear portion of the isotherm. In our experiments, the slope of the transition between L- and C-type isotherm was almost zero, indicating that SO_4^{2-} occlusion does not account for such sorption process.

The best explanation for the biphasic nature of the SO_4^{2-} sorption isotherm is precipitation of SO_4^{2-} in a mineral phase. This mechanism has been recently investigated by Li & Stanforth (2000) to explain the biphasic nature of isotherms obtained for PO_4^{3-} sorption on goethite. Occurrence of SO_4^{2-} precipitation at high SO_4^{2-} concentration is also consistent with the presence of basic aluminium sulphate minerals in the S-rich Vitric Andosols of the Masaya area (Chapter 7).

The occurrence of SO_4^{2-} precipitation during sorption experiment is also supported by thermodynamic calculations. PHREEQC code was used to predict saturation of the experimental equilibrium solution with respect to mineral phases (Parkhurst & Appelo, 1999). Calculation results indicated oversaturation with respect to jurbanite [$AlSO_4(OH).5(H_2O)$] at SO_4^{2-} concentration in equilibrium solution above 1-3 mM (Table 8.6), and undersaturation with respect to this mineral at lower concentrations. The concentration at which oversaturation was detected corresponded approximately to the transition between the L- and C-type isotherms. PHREEQC also predicted oversaturation with respect to alunite [$KAl_3(SO_4)_2(OH)_6$] and undersaturation with respect to basaluminite [$Al_4SO_4(OH)_{10}.5(H_2O)$] over all SO_4^{2-} concentration ranges. Nordstrom (1982) argued that in S-rich acidic environments, jurbanite would be favoured over alunite because at low temperature (25 °C) slow nucleation and precipitation kinetics impedes alunite formation. However, the only $Al_x(OH)_y(SO_4)_z$ minerals detected in the Masaya Andosols were aluminite-like minerals [$Al_2(SO_4)(OH)_4.7(H_2O)$], for which no thermodynamic data are available (Chapter 7). Further study is needed to determine the exact composition of the precipitated SO_4^{2-} mineral in these soils.

The progressive, rather than sudden, removal of SO_4^{2-} from solution, i.e. the small rather than infinite slope of the isotherm (Figure 8.1), at high SO_4^{2-} concentration supports the idea that chemisorption followed by surface precipitation, rather than direct precipitation from solution, is likely the formation pathway of $Al_x(OH)_y(SO_4)_z$ minerals in the S-impacted Andosols (Chapter 7). Indeed, in case of unlimited supply of the accompanying ion, as it is the case for Al at pH 4, the slope of the isotherm above critical SO_4^{2-} concentration for precipitation is infinite.

Since two mechanisms seem to be involved in SO_4^{2-} sorption, one may expect a change in the ratio of OH^- released to SO_4^{2-} sorbed from adsorption to precipitation. However, no significant change was observed (Figure 8.2), suggesting that adsorption of SO_4^{2-} and precipitation of SO_4^{2-} minerals contribute equally to acid neutralisation through the release of OH^- in solution.

Some authors consider that precipitation of a SO_4^{2-} mineral phase

Table 8.6: Saturation indices for alunite, basaluminite and jurbanite in function of added SO_4^{2-}.

	SO_4^{2-} added /mmolc kg^{-1}	Saturation Indices alunite	basaluminite	jurbanite
EU5-A2	1.7	2.99	-2.86	-0.81
	16.7	3.17	-3.88	-0.51
	33.3	3.48	-3.74	-0.15
	50.0	3.97	-3.61	-0.07
	83.3	4.29	-3.05	0.13
	166.7	4.57	-3.80	0.30
	250.0	4.66	-4.44	0.53
EU2-Bw	1.7	3.73	-1.85	-0.57
	16.7	4.76	-1.30	-0.06
	33.3	5.44	-1.24	0.13
	50.0	5.58	-1.18	0.21
	83.3	5.84	-1.35	0.60
	166.7	6.33	-1.32	0.84
	250.0	6.47	-1.45	1.00
EU9-A2	1.7	3.11	-2.51	-0.81
	16.7	4.81	-1.65	-0.04
	33.3	5.45	-1.85	0.34
	50.0	5.60	-1.50	0.49
	83.3	5.90	-1.52	0.65
	166.7	6.01	-1.86	0.81
	250.0	6.16	-1.98	0.96
VI2-3A	1.7	3.40	-2.64	-0.61
	16.7	4.62	-2.16	-0.03
	33.3	5.29	-2.06	0.23
	50.0	5.36	-2.01	0.44
	83.3	5.56	-2.09	0.58
	166.7	5.66	-2.47	0.72
	250.0	5.81	-2.57	0.84

would be accompanied by a decrease in Al concentration in the solution (e.g. Rajan, 1979). This was also proposed in the surface precipitation model to describe cation sorption (Farley *et al.*, 1985). In these models, the maximum of sorption through precipitation mechanism is dictated by the limited supply of the accompanying ion (Al in this case). In the present study, the low pH value (4), which was maintained during the experiment through a continuous H^+ input, allowed Al to be present in sufficient amounts.

In the Masaya area, SO_4^{2-} concentration in soil solution may well be in the range needed for precipitation. Johnson & Parnell (1986) observed a 100-fold increase between SO_4^{2-} concentration in Masaya rain-

water (4-9 µmol SO_4^{2-} l^{-1}) and in soil solution (0.6 mmol SO_4^{2-} l^{-1}). In Chapter 4, we measured 51-90 µmol SO_4^{2-} l^{-1} in samples of rainwater collected downwind of the volcano. These concentrations are likely to generate high SO_4^{2-} concentrations in soil solution.

8.5 Conclusion

Our results revealed the biphasic nature of SO_4^{2-} sorption isotherms obtained for the Vitric and Eutric Andosols from the Masaya region. Sorption of SO_4^{2-} corresponded to L-type and C-type isotherms at low and large SO_4^{2-} solution concentrations, respectively. The transition between the two curves occurred between 5 to 7 mM SO_4^{2-} in solution. Our results indicated that the biphasic shape of the isotherm reflects a continuum between two processes : chemisorption in the low concentration range, and surface precipitation in the higher concentrations range. The latter process is understood in terms of the formation pathway of $Al_x(OH)_y(SO_4)_z$ minerals in soils.

The importance of short-range ordered minerals, and thus of surface properties in SO_4^{2-} sorption was highlighted by calculating SRI for 37 Andosol samples. Compared to Vitric Andosols, the Eutric Andosols have a higher capacity to sorb additional SO_4^{2-}. Since SO_4^{2-} retention plays a key role in acid neutralisation, this denotes the relative efficiency of weathered Eutric compared to young Vitric Andosols in neutralising acid inputs.