Acid Neutralization and Sulphur retention in S-impacted Andosols

THOMAS DELFOSSE

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Université catholique de Louvain
Faculté d'ingénierie biologique, agronomique et environnementale
Département des sciences du milieu et de l'aménagement du territoire
Unité des sciences du sol

Croix du Sud, 2/10, 1348 Louvain-la-Neuve, Belgium
Tél. 32 (0) 10 47 36 33 – Fax 32 (0) 10 47 45 25
E-mail : delvaux@sols.ucl.ac.be - delfosse@sols.ucl.ac.be
http://www.sols.ucl.ac.be

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Part II

Retention and Distribution of SO_4^{2-}

Chapter 6

Inorganic Sulphate Extraction from SO_2-Impacted Andosols*

Summary

Sulphate sorption on to the surface of short-range ordered minerals and precipitation of Al-hydroxy sulphate contribute to the acid neutralising capacity of soils. The correct measurement of total inorganic sulphate is thus essential in soils that are accumulating SO_4^{2-} anions. We extracted SO_4^{2-} by various solutions, namely 0.005 M $Ca(NO_3)_2$, 0.016 M KH_2PO_4, 0.5 M NH_4F and 0.2 M acidic NH_4-oxalate (pH 3), from Vitric and Eutric Andosols exposed to prolonged deposition of acid and SO_2 from an active volcano (Masaya, Nicaragua). We attributed sulphate extractable by KH_2PO_4 (20-3030 mg kg^{-1}) to anion-exchangeable SO_4^{2-}, which was much smaller than NH_4F- and oxalate- extractable SO_4^{2-} (400-9680 and 410-10 480 mg kg^{-1}, respectively). Our results suggest the occurrence of a sparingly-soluble Al-hydroxy-mineral phase extractable by both NH_4F and oxalate. The formation of Al-hydroxy minerals would result from the combination of enhanced weathering caused by strong acid loading and simultaneous occurrence of elevated SO_4^{2-} concentrations in soil solution. Oxalate extracted slightly more inorganic SO_4^{2-} than did NH_4F, this additional amount of SO_4^{2-} correlating strongly with oxalate-extractable Si and Fe contents. Preferential occlusion of SO_4^{2-} by short-range ordered minerals, especially ferrihydrite, explains this behaviour.

*Adapted from Delfosse T., Delmelle P., Givron C. & Delvaux B. 2005. Inorganic sulphate extraction from SO_2-impacted Andosols. *European Journal of Soil Science*, **56**, 127-133.

If we exclude the contribution of occluded sulphate then oxalate and NH_4F mobilise similar amounts of SO_4^{2-} and are believed to mobilise all of the inorganic SO_4^{2-} pool.

6.1 Introduction

Sulphate adsorption in soils is mostly governed by poorly-crystallised Al and Fe oxy-hydroxides and short-range ordered alumino-silicates (Camps Arbestain *et al.*, 1999). Owing to their mineralogical characteristics, Andosols are amongst soils with the largest SO_4^{2-} retention capacity. These soils can contain large SO_4^{2-} concentrations caused by the deposition of sulphur either from marine aerosols (e.g. ∼7400 mg SO_4^{2-} kg^{-1}: Hasan *et al.*, 1970) or from a volcanic source (e.g. ∼4500 mg SO_4^{2-} kg^{-1}: Takamatsu *et al.*, 1992).

Deposited SO_4^{2-} may be involved in the immobilisation of organic S, sorption of inorganic SO_4^{2-} and precipitation as aluminium-hydroxy sulphate mineral $[Al_x(OH)_y(SO_4)_z]$. All these processes are expected to diminish or delay net acidification of soils. Immobilisation of S in organic matter and SO_4^{2-} adsorption indeed reduce cation leaching (Strickland & Fitzgerald, 1984; Camps Arbestain *et al.*, 1999). Both formation of $Al_x(OH)_y(SO_4)_z$ and SO_4^{2-} adsorption on to poorly-crystalline minerals involve OH^- release or H^+ consumption (Figure 2.4 and Equation 2.1; Rajan, 1978; Adams & Hajek, 1978).

Therefore, inorganic SO_4^{2-} retention plays a key role in soils affected by acid deposition involving S input (Johnson *et al.*, 1981; Fumoto *et al.*, 1996) and is regarded as an important process in acid-buffering of Andosols (Fumoto *et al.*, 1996). Yet this process stores acidity as SO_3, which might eventually produce sulphuric acid, once released (van Breemen *et al.*, 1983).

The correct assessment of the content of inorganic S is thus essential in the estimation of the soil's susceptibility to acidification. Furthermore, since one usually determines the content of organic S in soil indirectly by subtracting inorganic S from total S, accurate evaluation of the inorganic S would quantify adequately the organic S content of the soil.

Many methods have been used for the determination of diverse pools of inorganic SO_4^{2-} in soil, e.g. water-, NaCl-, $CaCl_2$-extraction displacing soluble SO_4^{2-} (Curtin & Syers, 1990; Alewell & Matzner, 1996), and $NaHCO_3$, K\NaH_2PO_4 or $Ca(H_2PO_4)_2$ extracting SO_4^{2-} adsorbed on to minerals (Curtin & Syers, 1990; Wada *et al.*, 1994; Alewell & Matzner, 1996). However, these conventional methods underestimate the pool of

inorganic SO_4^{2-} (Prietzel & Hirsch, 2000), since they fail to extract SO_4^{2-} involved in $Al_x(OH)_y(SO_4)_z$ mineral phases (Prietzel & Hirsch, 1998). Instead, Prietzel & Hirsch (2000) have recommended the use of 0.5 M NH_4F to extract inorganic SO_4^{2-} in acid forest soils because of its ability to extract both SO_4^{2-} adsorbed on to mineral surfaces and precipitated as $Al_x(OH)_y(SO_4)_z$.

Ammonium fluoride solution might therefore be a suitable solution to extract inorganic SO_4^{2-} for many soils exposed to intense deposition of S where $Al_x(OH)_y(SO_4)_z$ minerals are likely to form (e.g. Adams & Rawajfih, 1977; Nordstrom, 1982). However, the efficacy of 0.5 M NH_4F has been investigated only in acid forest soils with small contents of S (130-2000 mg SO_4^{2-} kg^{-1}; Prietzel & Hirsch, 2000). Other potential extraction solutions for inorganic SO_4^{2-} deserve to be studied. Among them, acid ammonium oxalate has, so far, never been properly considered, but it can dissolve significant amounts of $Al_x(OH)_y(SO_4)_z$ minerals (Prieztel & Hirsch, 1998) as well as short-range ordered minerals (Parfitt & Childs, 1988) on which quantitative SO_4^{2-} retention occurs.

We have studied the extraction of SO_4^{2-} by $Ca(NO_3)_2$, KH_2PO_4, NH_4F and acidic ammonium oxalate in Eutric and Vitric Andosols subject to strong deposition of S in the vicinity of Masaya volcano (Nicaragua). We assessed SO_4^{2-} mobilisation by these extractants in highly S-retentive Andosols and then identified the SO_4^{2-} pools extracted by KH_2PO_4, NH_4F and acidic ammonium oxalate solutions. We report our findings below.

6.2 Materials and methods

6.2.1 The soils

We extracted SO_4^{2-} from ten Andosol profiles downwind from Masaya volcano (Nicaragua), one of the world's strongest natural source of SO_2 (Delmelle *et al.*, 2001), the geology and climate of which are described in chapters 2 and 3. Depending on their location with respect to the volcanic source, the soils in the study area have received amounts of atmospheric S from about 200 to 700 mg SO_2 m^{-2} day^{-1} (Delmelle *et al.*, 2001; see also chapter 3, for their locations, and for their major properties).

The Vitric Andosols about 5 km from the crater are much less weathered than the Eutric ones about 15 km distant. The allophane content ranges between 1 and 13 % in Vitric Andosols and between 10 and 29 % in the Eutric ones, whilst the range of ferrihydrite content is 1-4 % in the former and 3-11 % in the latter (Chapter 3).

The content of short-range ordered minerals contributes substantially to the SO_4^{2-} retention capacity (Camps Arbestain *et al.*, 1999). Our soil samples cover a wide range of SO_4^{2-} retention capacity and sulphur deposition, and they should therefore enable us to test the efficacy of various solutions for extracting SO_4^{2-}.

6.2.2 Sulphate extractions

We determined four different 'pools' of extractable SO_4^{2-} by shaking soil samples with 0.005 M $Ca(NO_3)_2$ (10 g:50 ml), 0.016 M KH_2PO_4 (10 g:50 ml), 0.5 M NH_4F (10 g:50 ml), and 0.2 M acidic ammonium oxalate (pH 3) (1 g:100 ml), the latter for 4 hours in darkness (Blakemore *et al.*, 1987).

Wada *et al.* (1994) showed that five successive extractions with $Ca(H_2PO_4)_2$ were more effective than one single extraction, and so we compared the efficacy of successive extractions (up to 12) for 1 hour each with the single shaking for 18 hours proposed by Prietzel & Hirsch (2000) for extraction of inorganic SO_4^{2-}. Twelve successive extractions with NH_4F or KH_2PO_4 solutions extracted generally 1.6 times more SO_4^{2-} than the single 18 hours extraction, and we concluded that successive extractions were the most effective. Moreover, five sequential extractions were sufficient to extract more than 90% of SO_4^{2-} mobilised after 12 successive extractions. Consequently, we adapted the procedure of Prietzel & Hirsch (2000) as follows. This involved five centrifuge-washing steps in batch made with 50-ml aliquots of 0.005 M $Ca(NO_3)_2$, 0.5 M NH_4F or 0.016 M KH_2PO_4 on 10 g soil samples during 1 hour of shaking at 20 °C. After filtration (Whatman 41 or 0.45-µm membrane filter), SO_4^{2-} concentration in the NH_4F extracts was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), whereas SO_4^{2-} concentration in the KH_2PO_4 and $Ca(NO_3)_2$ extracts was measured with a HPLC-Dionex ion chromatograph.

6.3 Results

Table 6.1 presents the $Ca(NO_3)_2$-, KH_2PO_4-, NH_4F- and oxalate- extractable contents of SO_4^{2-}, Al content of the KH_2PO_4, NH_4F and oxalate extracts, as well as the Si and Fe contents of the oxalate extracts. In the Vitric Andosols, Al concentrations were smallest in the KH_2PO_4 solutions (20-70 mg kg^{-1}) and increased in the order $KH_2PO_4 < NH_4F$ (960-3170 mg kg^{-1}) < oxalate (3900-32 600 mg kg^{-1}). Likewise, in the Eutric Andosols, Al concentrations were smallest in the KH_2PO_4 solutions (30-280 mg kg^{-1}) and increased in the order $KH_2PO_4 < NH_4F$

(2210-5820 mg kg^{-1}) < oxalate (20 970-83 610 mg kg^{-1}). In the Vitric Andosols, SO_4^{2-} concentrations were smallest in $Ca(NO_3)_2$ solution (20-630 mg kg^{-1}), and then increased in the order $Ca(NO_3)_2$ < KH_2PO_4 (30-2160 mg kg^{-1}) < NH_4F (400-3270 mg kg^{-1}) ≤ oxalate (410-3490 mg kg^{-1}). Similarly, in the Eutric Andosols, SO_4^{2-} concentrations were smallest in $Ca(NO_3)_2$ solution (20-490 kg^{-1}) and then increased in the order $Ca(NO_3)_2$ < KH_2PO_4 (20-3030 mg kg^{-1}) < NH_4F (960-9860 mg kg^{-1}) ≤ oxalate (1180-10 480 mg kg^{-1}).

6.4 Discussion

In both Vitric and Eutric Andosols, SO_4^{2-} concentrations differed largely according to the type of extractant (Table 6.1). The largest SO_4^{2-} concentrations were obtained by oxalate, followed by NH_4F and then KH_2PO_4 and $Ca(NO_3)_2$. Mineral dissolution was limited in the two latter solutions, but appeared to be significant in the two former ones, especially oxalate, as revealed by Al, Si and Fe concentrations. The various solutions thus extracted different pools of SO_4^{2-}. The pool of adsorbed SO_4^{2-} would definitely dominate in $Ca(NO_3)_2$ and KH_2PO_4 extracts. Obviously, NH_4F and oxalate extracted additional sources of SO_4^{2-}, either precipitated in sulphate-bearing minerals or occluded into secondary short-range ordered constituents or both. Sulphate sorption on this component may not be totally reversible, as occurs for phosphate sorption (Parfitt, 1989).

6.4.1 Pool of adsorbed SO_4^{2-}

The mechanisms of SO_4^{2-} adsorption on soil are not fully understood, but non-specific adsorption (electrostatic attraction) and specific adsorption (ligand exchange) both contribute to its retention. Specific adsorption is generally believed to be the predominant mechanism. There is a general consensus that $H_2PO_4^-$ is selectively sorbed against SO_4^{2-} by the mineral constituents of soil (Wada *et al.*, 1994), whereas nitrate sorption is considered as non-specific (e.g. Kowalenko & Yu, 1996). Solution of $Ca(NO_3)_2$ is thus believed to extract aqueous and non-specifically sorbed SO_4^{2-} anions, whereas KH_2PO_4 is considered to extract these forms as well as specifically sorbed SO_4^{2-}. Our results support these assessments since extracted sulphate was systematically smaller in $Ca(NO_3)_2$ than in KH_2PO_4 solution.

Table 6.1: $Ca(NO_3)_2$-, KH_2PO_4-, NH_4F- and oxalate extractable element contents in the Vitric and Eutric Andosols.

		$Ca(NO_3)_2$	KH_2PO_4		NH_4F		Oxalate			
Prof.	Horiz.	SO_4^{2-}	SO_4^{2-}	Al	SO_4^{2-}	Al	SO_4^{2-}	Al	Si	Fe
		/g kg^{-1}								
VI2	A	0.20	0.49	0.03	1.00	1.38	1.05	6.17	3.09	8.27
	2BC	0.25	0.62	0.02	1.04	1.30	1.13	7.48	4.07	7.61
	3A	0.23	0.76	0.04	1.46	1.29	1.11	9.62	5.29	8.53
VI4	A	0.47	0.72	0.02	1.19	0.96	1.08	3.90	1.84	6.45
	2BC	0.30	0.62	0.02	1.09	1.00	1.01	7.02	3.64	7.09
	3A	0.63	2.16	0.05	3.27	2.52	3.49	32.60	19.06	21.59
VI6	A	0.47	0.72	0.03	1.14	1.07	1.08	3.92	1.75	8.24
	2BC	0.22	0.43	0.02	0.76	0.99	0.78	5.98	3.13	5.80
	3A	0.19	0.40	0.06	1.22	1.61	1.19	15.17	8.11	15.11
	3AB	0.08	0.19	0.07	1.02	2.12	1.07	21.33	12.49	19.56
VI7	A	0.17	0.36	0.03	0.83	1.98	0.88	5.83	2.76	8.43
	AB	0.11	0.17	0.03	0.53	1.06	0.68	6.37	3.33	7.71
	2BC	0.15	0.21	0.02	0.47	1.34	0.51	4.91	2.72	5.62
	3AB	0.06	0.08	0.05	0.54	2.15	0.48	9.73	5.57	8.54
VI9	A	0.21	0.20	0.05	0.65	1.48	0.63	4.75	2.55	9.57
	2BC	0.03	0.03	0.04	0.40	2.35	0.41	6.19	3.41	10.06
	3A	0.02	0.03	0.04	0.60	3.17	0.76	24.74	15.52	25.48
EU2	A1	0.10	0.49	0.13	3.09	3.26	3.27	49.89	23.26	36.96
	A2	0.08	-	0.28	3.39	3.05	3.80	55.16	24.95	41.83
	A3	0.21	1.49	0.10	5.67	5.82	6.34	68.36	29.67	52.40
	AB	0.35	2.32	0.08	8.04	4.82	8.83	76.57	34.92	57.52
	Bw	0.44	3.03	0.09	9.68	3.76	10.48	83.61	41.47	65.37
EU9	A1	0.49	0.68	0.03	2.04	2.21	1.97	28.90	16.26	25.85
	A2	0.18	0.45	0.07	2.04	2.71	2.18	34.49	19.03	29.19
	AB	0.43	1.12	0.10	3.22	2.61	3.70	48.44	29.40	36.91
EU4	A1	0.09	0.29	0.04	1.78	2.83	1.84	31.46	18.88	28.13
	A2	0.07	0.19	0.10	1.58	2.85	1.68	32.25	18.07	26.67
	AB	0.16	0.58	0.08	2.26	2.54	2.64	40.56	24.00	33.48
	BA	0.21	0.62	0.08	2.30	2.38	2.57	38.76	24.29	31.46
EU5	A1	0.12	0.16	0.05	1.27	3.07	1.34	29.03	17.31	23.68
	A2	0.02	0.04	-	1.11	3.81	1.28	33.36	19.44	27.09
	A3	0.02	0.04	0.05	1.11	3.47	1.43	35.33	22.13	27.84
	Bw1	0.07	0.34	0.10	2.26	2.66	3.09	60.97	37.13	45.24
EU6	A1	0.16	0.07	0.05	1.32	3.13	1.29	20.97	13.63	19.90
	A2	0.04	0.05	0.06	0.96	2.97	1.18	23.85	15.12	21.93
	AB	0.02	0.02	0.08	0.97	3.20	1.38	31.89	20.79	30.98
	BA	0.04	0.06	0.08	1.10	2.26	1.76	43.20	31.05	37.52

6.4.2 Dissolution of Al-hydroxy-sulphate minerals

Our results show that KH_2PO_4 solution is a less efficacious extractant for SO_4^{2-} than are NH_4F and oxalate (Table 6.1). Both oxalate and NH_4F extracted 1.5 to 40 times more SO_4^{2-} than KH_2PO_4. This suggests the occurrence of a substantial SO_4^{2-} pool non-extractable by KH_2PO_4, which might involve organic sulphur or a SO_4^{2-}-bearing mineral. However, neither NH_4F nor oxalate seem able to convert organic S into inorganic SO_4^{2-}. The equilibrium pH of NH_4F and oxalate extracts never exceeded 9 in our samples, hence impeding quantitative ester sulphate hydrolysis (Freney *et al.*, 1969; Prietzel & Hirsch, 2000). Moreover, NH_4F and oxalate can both extract appreciable amounts of SO_4^{2-} included in $Al_x(OH)_y(SO_4)_z$, whereas KH_2PO_4 extracts only part of the SO_4^{2-} from these minerals (Violante *et al.*, 1996; Prietzel & Hirsch, 1998). The larger amount of SO_4^{2-} extracted by NH_4F (and oxalate) compared with KH_2PO_4 could thus be attributed to the occurrence of an $Al_x(OH)_y(SO_4)_z$ mineral phase in the Andosols of the Masaya area.

The precipitation of an $Al_x(OH)_y(SO_4)_z$ mineral has been considered effective for retaining SO_4^{2-} in soils exposed to S deposition (e.g. Adams & Rawajfih, 1977; Wolt *et al.*, 1992). This mineral has rarely been directly identified in soils, however. So far, its presence has been inferred mostly from thermodynamic considerations (e.g. Nordstrom, 1982; Wolt *et al.*, 1992). We think $Al_x(OH)_y(SO_4)_z$ minerals are present in our samples because of the rapid deposition of SO_2 and acid and the large content of weatherable minerals (TRB between 200 and 600 $cmol_c\ kg^{-1}$; Chapter 3). The minerals could indeed result from the combination of Al solubilisation from enhanced weathering caused by strong acid loading and simultaneous occurrence of a soil solution rich in SO_4^{2-}. Moreover, basaluminite and alunite were found to be stable minerals in Eutric and Vitric Andosols according to thermodynamic calculations based on soil solution chemical composition (Chapter 4).

Additional evidence of dissolution of an $Al_x(OH)_y(SO_4)_z$ mineral by NH_4F was supported by the difference of S:Al atomic ratio between KH_2PO_4, NH_4F and oxalate extracts. As illustrated in Figure 6.1, the S:Al atomic ratio differed between these extracts by three orders of magnitude, and decreased in the order KH_2PO_4 (4.36; 1.33) > NH_4F (0.19; 0.16) > oxalate (0.03; 0.01) in the Vitric and Eutric Andosols, respectively. Obviously, this decrease is consistent with the selective extraction of adsorbed SO_4^{2-} in KH_2PO_4, and with the specific dissolution of Al-bearing allophanic constituents in oxalate. As far as NH_4F extraction is concerned, we assumed that extracted Al (Al_f) originates mainly from $Al_x(OH)_y(SO_4)_z$ mineral and that the difference (S_f-S_{ph}), as defined in

Figure 6.1, estimates the amount of sulphur precipitated in this mineral. The average values of (S_f-S_{ph}):(Al_f) ratio was 0.19 in the Vitric Andosols, and 0.16 in the Eutric Andosols. These values are close to the S:Al atomic ratio of basaluminite (0.25), and might be further evidence of dissolution of $Al_x(OH)_y(SO_4)_z$ mineral in NH_4F. The ability of NH_4F to extract Al from humus-Al (He *et al.*, 1998) might explain the difference between our computed ratios and the ideal S:Al ratio.

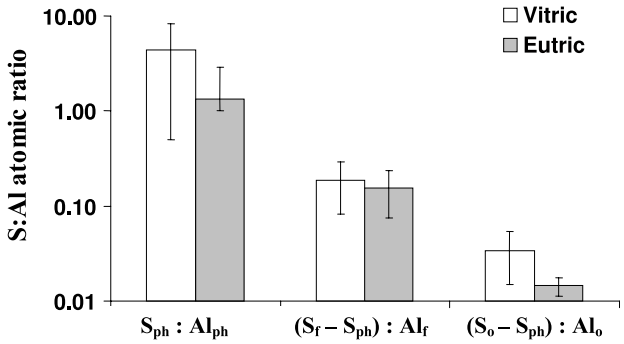

Figure 6.1: Average values of S:Al atomic ratio, as computed from SO_4^{2-} and Al concentrations in KH_2PO_4 (ph), NH_4F (f) and oxalate (o) extracts, i.e. S_{ph}:Al_{ph}, (S_f-S_{ph}):Al_{ph} and (S_o-S_{ph}):Al_o atomic ratios. Error bars denote standard errors.

6.4.3 Oxalate and NH_4F as reliable inorganic SO_4^{2-} extraction solutions

Although the mechanisms of SO_4^{2-} extraction of oxalate and NH_4F differ, these solutions extracted similar amounts of SO_4^{2-}, both in Eutric and Vitric Andosols and at all ranges of SO_4^{2-} concentration (Table 6.1; Figure 6.2). These results suggest that both extraction solutions mobilised similar pools of SO_4^{2-}.

Oxalate, a strong complexing agent, dissolves short-range ordered minerals and therefore extracts SO_4^{2-} adsorbed on to these minerals, whereas NH_4F, a weaker complexing agent, extracts adsorbed SO_4^{2-} owing to its remarkable anion desorbing capacity. Furthermore, NH_4F and oxalate can both extract appreciable amounts of SO_4^{2-} included in $Al_x(OH)_y(SO_4)_z$ minerals.

The pool of SO_4^{2-} extracted by NH_4F and oxalate is thus considered to be very close to the inorganic SO_4^{2-} soil content, given that practically all the adsorbed, dissolved and precipitated SO_4^{2-} pools in the Masaya

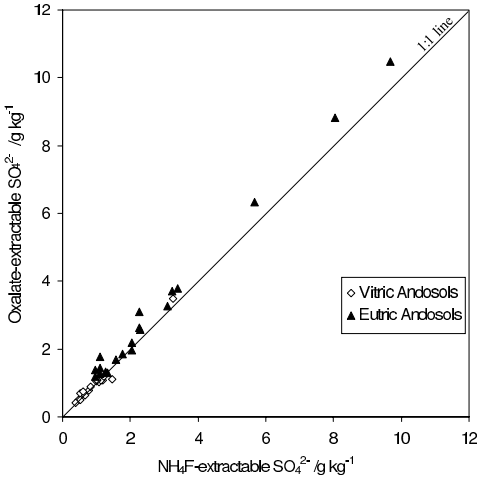

Figure 6.2: Relationship between NH_4F-extractable SO_4^{2-} and oxalate-extractable SO_4^{2-} contents in the Andosols studied.

Andosols are extracted by both solutions and since no significant contamination from organic S can be expected.

6.4.4 Sulphate occlusion as a mechanism of inorganic SO_4^{2-} retention

In spite of the similar abilities of NH_4F and oxalate to extract SO_4^{2-}, oxalate always extracted more inorganic SO_4^{2-} than did NH_4F (average difference : 2.2 % and 15.7 % for Vitric and Eutric Andosols, respectively; Figure 6.2, Table 6.1). This difference cannot be attributed to a greater efficiency of oxalate to dissolve $Al_x(OH)_y(SO_4)_z$ minerals (Prietzel & Hirsch, 1998). Moreover, the efficiency of F^- to desorb anions from mineral surfaces is well established. Thus, the effectiveness of oxalate in extracting SO_4^{2-} cannot be attributed to a better desorption of SO_4^{2-}. However, owing to its ability to dissolve short-range ordered minerals, oxalate could extract SO_4^{2-} inaccessible to NH_4F, i.e. a pool of SO_4^{2-} occluded in minerals. The process of SO_4^{2-} occlusion might be similar to that observed following phosphate (PO_4^{3-}) adsorption on to amorphous minerals.

Rájan & Fox (1972) showed that PO_4^{3-} adsorption in soil is first rapid, but subsequently followed by a rate-limiting slow reaction. The slow reaction has been attributed to (i) diffusion through coating of precipitated metal phosphate surrounding metal oxide particles (van Riems-

dijk *et al.*, 1984) and (ii) diffusion into or between aggregates of oxide minerals (Barrow, 1983). Barrow (1983) called ions that have penetrated in this way into the minerals 'diffused', 'penetrated' or 'occluded'. We prefer the term 'occluded'.

The slow reaction observed with PO_4^{3-} may occur with other anions (Barrow, 1983). Thus, if SO_4^{2-} behaves similarly then (i) SO_4^{2-} included in coatings surrounding the oxide particles would be extractable by both oxalate and NH_4F since they can dissolve $Al_x(OH)_y(SO_4)_z$ minerals (similar to precipitated metal sulphate), whereas (ii) SO_4^{2-} occluded by amorphous minerals would be extracted only by oxalate.

Furthermore, the difference between oxalate- and NH_4F- extractable SO_4^{2-}, which represents the fraction of occluded SO_4^{2-}, is strongly correlated with both Si_o and Fe_o contents (r = 0.87 for both), generally used to estimate, respectively, allophane and ferrihydrite contents in soils (Figure 6.3a and 6.3b). This correlation between the pool of occluded SO_4^{2-} and the short-range ordered minerals content supports our assumption.

Occluded SO_4^{2-} represents up to 37 % of total inorganic SO_4^{2-} in the Masaya Andosols. The pool of occluded SO_4^{2-}, poorly considered until now, is thus of significant importance in the retention of S.

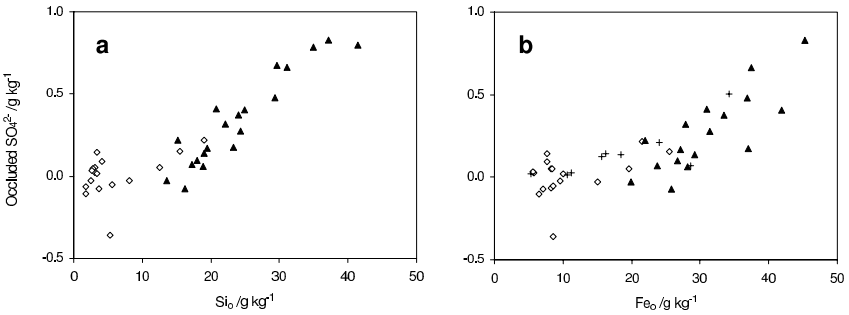

Figure 6.3: Relationship between occluded SO_4^{2-} (assessed through the difference between oxalate-extractable SO_4^{2-} and NH_4F- extractable SO_4^{2-}) and (**a**) Si_o content, (**b**) Fe_o content for the Eutric (▲) and Vitric (◇) Andosols. The data of Takamatsu *et al.* (1992) (+) are plotted in Figure 6.3b.

6.4.5 Minerals involved in SO_4^{2-} occlusion

A relationship similar to the one observed in Masaya soil samples between the oxalate-extractable Fe content and the difference between

NH_4F- and oxalate- extractable SO_4^{2-} content can be obtained from the data of Takamatsu *et al.* (1992) (Figure 6.3b). Takamatsu *et al.* (1992) made comparable extractions of SO_4^{2-} with NH_4F and oxalate of andic soils rich in Al-humus and ferrihydrite (Onishii, Japan), but devoid of allophane. These soils were exposed to volcanic fumaroles rich in H_2S and show similar ferrihydrite contents (1-6 %) to the Masaya Andosols.

We compared the regressions between occluded SO_4^{2-} (assessed by the difference between oxalate- and NH_4F- extractable SO_4^{2-}) and Fe_o. We found that there was no significant difference between our data and those of Takamatsu *et al.* (1992) (Figure 6.3b).

The absence of difference between the two approaches suggests that anion occlusion into allophane would not occur. Indeed, the Onishii soils studied by Takamatsu *et al.* (1992) contained ferrihydrite, but were devoid of allophane, whereas both ferrihydrite and allophane are present in Masaya Andosols. If both allophane and ferrihydrite could occlude SO_4^{2-}, more SO_4^{2-} per Fe_o would have been observed in the Masaya Andosols than in the Onishii soils (Figure 6.3b). Comparison of SO_4^{2-} with PO_4^{3-} occlusion supports our hypothesis. Indeed, while PO_4^{3-} occlusion into ferrihydrite is widely accepted, Parfitt (1989) suggested that a diffusive penetration reaction of PO_4^{3-} could not occur with allophane because its structure, being only three atoms thick, could be disrupted.

6.4.6 The influence of S deposition on SO_4^{2-} retention pattern

Long-term exposure to volcanic S has resulted in considerable accumulation of sulphur in the Andosols located downwind from Masaya volcano, primarily due to an increase in inorganic, occluded and precipitated SO_4^{2-}. In Eutric soils with high short-range ordered minerals content, typically ∼40–60 % of S was retained inorganically, whereas in less weathered Vitric Andosols inorganic S content was about 20–30% of total S (Table 6.2). These results are in good agreements with those of Mayer *et al.* (2001) who found a larger inorganic S retention in forest soils with high sesquioxide contents. Based on selective extractions, precipitation of aluminium hydroxy sulphate minerals was identified as the most effective inorganic S retention mechanism, but sulphate adsorption and occlusion constituted additional effective inorganic S retention processes.

Mayer *et al.* (2001) suggested that in areas where S deposition rates are less than 10 kg S ha^{-1} yr^{-1} (i.e 5.5 mg SO_2 m^{-2} d^{-1}), most of the atmospheric S input would cycle through the organic S pool in the biosphere and pedosphere of forest soils. Our results support this hy-

Table 6.2: Distribution of the various S pools: Organic S (Org. S), Exchangeable SO_4^{2-} (Exch. S), occluded SO_4^{2-} (Occl. S) and SO_4^{2-} involved in $Al_x(OH)_y(SO_4)_z$ minerals (Min. S).

Profile	Horiz.	Depth /cm	Org. S	Exch. S	Occl. S	Min. S
			/%			
VI2	A	0-9	71	13	1	14
	2BC	9-14	77	13	2	9
	3A	14-24	79	11	0	10
VI4	A	0-7	76	15	0	10
	2BC	7-13	67	19	0	14
	3A	13-24	42	36	4	18
VI6	A	0-6	71	18	0	11
	2BC	6-14	78	12	1	10
	3A	14-20	81	6	0	13
	3AB	20-29	82	3	1	14
VI7	A	0-7	71	12	2	15
	AB	7-17	84	4	4	9
	2BC	17-22	80	8	1	10
	3AB	22-28	80	3	0	17
VI9	A	0-6	74	8	0	18
	2BC	6-15	80	2	1	18
	3A	15-21	77	1	5	17
EU2	A1	0-7	57	6	2	34
	A2	7-16	-	-	-	-
	A3	16-22	61	9	4	25
	AB	22-29	41	16	5	39
	Bw	29-39	20	23	6	51
EU9	A1	0-6	56	15	0	29
	A2	6-24	53	10	3	34
	AB	24-33	30	21	9	40
EU4	A1	0-6	55	7	1	36
	A2	6-18	61	4	2	32
	AB	18-24	53	10	7	30
	BA	24-37	53	11	5	31
EU5	A1	0-5	65	4	2	29
	A2	5-16	63	1	5	31
	A3	16-27	54	1	10	35
	Bw1	27-39	57	5	12	27
EU6	A1	0-6	78	1	0	20
	A2	6-19	66	1	6	26
	AB	19-29	48	1	16	36
	BA	29-40	42	2	22	34

pothesis since, in the surface horizons of EU6-control profile (deposition of S $\simeq$ 0–50 mg SO_2 m^{-2} d^{-1}; Delmelle *et al.*, 2001) most of S was organic (66-78 %; Table 6.2).

Since SO_4^{2-} retention increased with increasing S deposition rates, this process essentially buffers elevated SO_4^{2-} inputs, depending on the short-range ordered mineral content of the soils. Under the column leaching experimental conditions (Chapter 5), large S inputs were fully retained in soils with high short-range ordered mineral contents (Eutric). This was, however, not the case in soils with lower short-range ordered mineral contents (Vitric), where elevated S deposition rates resulted in increased SO_4^{2-} export with the leachates. The ability to inorganically retain deposited S in the mineral soil horizons controlled the export of irrigation SO_4^{2-} with the seepage water, and thus, appears to be the crucial factor regulating the S export from many natural ecosystems to adjacent aquatic ecosystems (Mayer *et al.*, 2001).

Vegetative S uptake is part of the S cycle in soils, and biomass may constitute a significant reservoir for S, indeed values for S bound to plant biomass vary between $\sim$ 1 and 103 Tg S, whereas the S reservoir of soils is about 120 Tg S (Haneklaus *et al.*, 2003). Since the turnover of S is lower in forest than in agricultural ecosystems, vegetative uptake is generally higher in agricultural (10-100 kg S ha^{-1} yr^{-1}) than in forest (4-8 kg S ha^{-1} yr^{-1}) lands (Haneklaus *et al.*, 2003). Because of the acid conditions that probably lessen microbial activity, it is thus not surprising that vegetative S uptake in the Masaya area (1-9 kg S ha^{-1} yr^{-1}, Table 6.3) is rather low and similar to that of forest ecosystems despite the huge S deposition. This low vegetative uptake has a minor influence on the soil S cycle in the Masaya area since S in plants represents only 0.02 to 0.3 % of total inorganic S in soil (Table 6.3).

Table 6.3: Total S content in plants of the Masaya area (measured on a dry weight basis of plants collected on a 1 m^2 area).

Site	SO_4 bound biomass		SO_4 uptake[a]	
	/mg kg^{-1} plant	/mg m^{-2}	/mg kg^{-1} soil	/kg ha^{-1} yr^{-1}
EU3	3144	327	1	1
EU5	7387	1003	4	3
EU6	9013	2296	10	8
EU9	3907	2799	12	9
VI2	6657	374	2	1
VI9	5962	566	2	2

[a]If we assume that plants are annual

Overall, intense S deposition has considerably modified the soil S

distribution pattern. It has increased the proportion of inorganic S and concomitantly decreased that of organic S. Sulphate precipitation as BAS minerals constituted the most effective retention process, followed by S adsorption and S occlusion. The pools of S precipitated and occluded increased with S deposition but their relative distribution were apparently not affected.

6.4.7 Sulphate retention, weathering and net acidification

These data and those reported in chapter 3 give rise to following comments. All processes of SO_4^{2-} retention envisaged (specific sorption on to amorphous minerals, precipitation in $Al_x(OH)_y(SO_4)_z$ minerals and occlusion in ferrihydrite) diminish soil acidity and retard net acidification of soil because they produce alkalinity, but in the short term. Indeed, sorption of SO_4^{2-} and mineral precipitation are rapid and occur over a few seconds to a few weeks. Though they retard net acidification, these processes store acidity as SO_3, and hence deplete the acid neutralising capacity of the solid phase (ANC_s) of the soil (chapter 3). This reserve of acidity might be released, but over longer time, because SO_4^{2-}-retentive minerals, acting as current SO_4^{2-} sinks, might be unstable. The contribution of SO_4^{2-} retention to soil acidification must therefore be envisaged at the appropriate time scale, since this process diminishes soil acidification only as long as sulphate-retentive constituents are stable.

6.5 Conclusion

The SO_4^{2-} extraction efficacy of various solutions in SO_2-impacted Andosols was in the order $Ca(NO_3)_2 < KH_2PO_4 < NH_4F \leq$ oxalate, with oxalate and NH_4F being by far the most effective extractants. The different inorganic SO_4^{2-} pools are illustrated in Figure 6.4 and the efficiency of each extraction solution is illustrated in Table 6.4. In agreement with literature, KH_2PO_4 solution extracted soluble and adsorbed SO_4^{2-}, whereas acid ammonium oxalate extracted the pool of inorganic SO_4^{2-} involving soluble, adsorbed, precipitated and occluded SO_4^{2-}. However, despite similar efficiency of NH_4F compared to oxalate, NH_4F does not mobilise the occluded SO_4^{2-} pool.

Sulphate occlusion was important in the retention of S in the Andosols of the Masaya area, and was probably governed by ferrihydrite.

Finally, we recommend the use of acid ammonium oxalate to extract inorganic SO_4^{2-} from soils containing short-range ordered minerals. However, the use of NH_4F might be appropriate if the occlusion of SO_4^{2-} is thought to be limited.

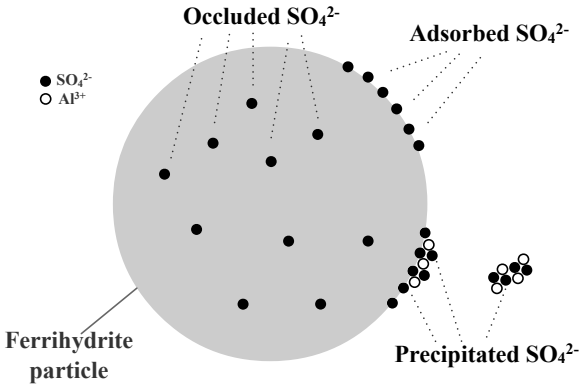

Figure 6.4: Schematic sketch of the various inorganic SO_4^{2-} pools in ferrihydrite.

Table 6.4: Schematic view of the inorganic SO_4^{2-} pools mobilized by various extraction solutions.

	Inorganic SO_4^{2-}		
	Adsorbed SO_4^{2-}	Precipitated SO_4^{2-}	Occluded SO_4^{2-}
0.016 M KH_2PO_4	← – – – – – – →		
0.5 M NH_4F	← – – – – – – – – – – – – – – – – – →		
Oxalate (pH 3)	← – →		