Biogeochemistry **16**: 167–180, 1992

Geochemical aspects of aluminium in forest soils in Galicia (N.W. Spain)

E. ALVAREZ, A. MARTINEZ & R. CALVO
Dpto. Edafología, Fac. de Biología, Univ. Santiago de Compostela, Spain

Received 16 October 1991; accepted 30 March 1992

Key words: Al speciation, soil solution

Abstract. The aqueous speciation of Al was studied in acid forest soils in N.W. Spain. Aluminum concentrations were 10–70 μmol L^{-1}, with variable proportions of *labile, non-labile*, and *acid-soluble* Al. Almost all the *labile Al* was found complexed with F^-, Al^{3+} concentrations being low. The importance of organic matter was seen in the formation of Al-organic complexes in the solid soil fraction and the presence of aqueous alumino-organic complexes in superficial horizons (umbric epipedons) rich in organic matter.

Introduction

During rock weathering and consequent soil formation in climatic areas where precipitation exceeds evapotranspiration there is a relative increase of Al and Fe as well as a gradual loss of alkaline and alkaline earth elements. Increased soil acidity results in the mobilization of Al, which competes with basic cations for sites on the soil cation exchange complex. In highly developed soils Al is one of the main components of clay fraction and may represent more than 80% of the exchange complex. Its abundance is related to fertility constraints in a large variety of soils. Aluminium can be toxic for plant growth, possibly blocks exchange sites, and facilitates the immobilization of anions due to direct precipitation or adsorption reactions.

Soils from Galicia, N.W. Spain, have been largely depleted of basic cations and the exchange complex is strongly saturated with Al. Moreover, other reactive soil minerals are also present, such as 2:1 minerals with aluminic-interlayer sheets, Al-hydroxides and aluminosilicates with a low degree of crystallinity, and various organoaluminic complexes (García-Rodeja et al. 1984, 87; Urrutia et al. 1988; Romero et al. 1991). Analysis of soil solutions reveal Al concentrations varying from <0.01 to 1.80 mg

L^{-1}, depending on geological material but being always higher in superficial horizons (Calvo et al. 1987).

The objective of this study was to establish the speciation of Al in forest soil solutions in order to determine the concentrations of its more toxic forms (Al^{3+}, $Al\text{-}OH^{2+}$, etc) and to elucidate the role of organic matter in controlling soluble Al in these soils, at least in their superficial horizons. As much of the previous work on aluminium speciation in literature was performed in temperate and cold areas in eastern and central North America and northern Europe, the study of Galician soil solutions establishes some climatic relationships, because this region is located in a transition zone to tropical regimes (*Sub-tropic with winter rainfall,* in FAO-UNESCO climatic classification) (Martinez 1987).

Material and methods

The study area was in N.W. Spain. The soil moisture regime is *udic,* with more than 1500 mm annual precipitation, and the soil temperature regime is *mesic* (Soil Survey Staff 1990), with an annual mean temperature of 12 °C. Geological materials are mostly plutonic in origin (e.g., granites, gabbros and diorites) or metamorphic (schists, amphibolites and gneisses of different compositions).

A total of fifty-six surface horizons (O/A & A) of forest soils developed over granites containing muscovite and biotite and biotite-rich schists were sampled in spring 1988. The vegetative cover was oak (*Quercus robur*), pine (*Pinus pinaster*) or eucalyptus (*Eucalyptus globulus*).

Soils, *Entic* or *Typic Haplumbrpet,* (Soil Survey Staff 1990) have a *umbric* epipedon overlying a cambic B horizon or a C horizon. In granites the clay fraction of epipedons is formed by hydroxyaluminium vermiculites and halloysites; in the lower horizons kaolinite and gibbsite are the dominant minerals. In biotite schists, the surface horizons usually exhibited *andic properties* and have a high content of Al-organic forms and amorphic or weakly crystalline aluminosilicates (halloysites) and Al-vermiculites. In B horizons kaolinite and goethites are the dominant minerals.

The soil solution was extracted by displacement in a column after Adams (1974). The extracted solution was filtered through a 0.45-μm filter (Millipore) and determinations were made of pH, electric conductivity, Ca^{2+}, Mg^{2+}, K^+, Na^+ (by atomic absorption or emission spectrophotometry), Si (by colorimetry, Corey & Jackson 1953), Cl^- and NO_3^- (by ion selective electrodes INGOLD), SO_4^{2-} (by turbidimetry, as per Bardseley & Lancaster 1990), and free and total F^- (by ion selective electrodes, and using TISAB II-ORION decomplexing solution for determining total F^-). Free and total F^- measurements were performed with a high sensitivity Solartrom 7061 apparatus. Organic matter was determined indirectly by back titration after oxidation with $KMnO_4$, by assuming that organic matter represents almost all of the oxidizable components in soil solution.

The speciation of Al was determined using acid digestion to evaluate the *total reactive Al* (*AlT*) and by titration from an aliquot, without digestion, to obtain the *reactive Al* (*Alr*). The difference between *AlT* and *Alr* is the *acid-soluble* fraction (*Alsa*), which includes colloids and/or very strong alumino-organic complexes (Driscoll 1985). *Reactive Al* is speciated using the procedures proposed by Driscoll (1984) involving a cation exchange column (Amberlite IR-120) to separate monomeric forms of *labile* and *non-labile Al*. The *labile* fraction (*AlL*) includes Al^{+3} and inorganic F^-, $SO_4^=$ and OH^- complexes of monomeric aluminium; the *non-labile* fraction (*AlnL*) includes organic complexes of monomeric Al. To evaluate Al, colorimetry with violet catechol was used as per Dougan & Wilson (1974). Driscoll's nomenclature has been slightly modified. We refrain from using the term monomeric for the *AlL* and *AlnL* forms because an inorganic synthetic polymer, prepared from $AlCl_3$ by hydrolysis with NaOH, exhibited similar behaviour to *AlL* on passing through the column and reacted in the colorimetric analysis employed (Bourrié & Alvarez, pers. comm.). Determination of *AlL* species was achieved using the values of pH and concentrations of *AlL*, total F and SO_4^{2-} in the chemical equilibrium model Solmineq.88 (Kharaka et al. 1989).

Analysis of the solid fraction included soil pH in H_2O (1:2.5), organic matter by oxidation with $K_2Cr_2O_7$, basic cations extractable with ammonium acetate at pH 7 (Soil Conservation Service 1972), and Al extractions with 1M KCl (Prat & Bair 1961); 0.33M $LaCl_3$ (Hargrove & Thomas 1981); $CuCl_2$ (Juo & Kamprath 1979); $Na_4P_2O_7$ (Bascomb 1968) and $(NH_4)_2C_2O_4$ (Blakemore 1978). Graphite furnace AA spectrophotometry was used for these determinations. In the discussion of the results, the KCl-extracted fraction (Al_k) is taken to represent exchangeable Al; the difference between the extractions with $LaCl_3$ and KCl (Al_{La}-Al_k) represents labile Al-organic forms; the difference between the extractions with $CuCl_2$ and $LaCl_3$ (Al_{Cu}-Al_{La}) depicts moderately stable Al-organic forms (Urrutia et al. 1988); the difference between the extractions with Na-pyrophosphate and $CuCl_2$ (Al_{pyr}-Al_{Cu}) is thought to include more stable organic forms; the extraction with ammonium oxalate is representative of Al in the form of low crystallinity colloids.

Results and discussion

Analysis of the soil solution

Soil solution pH values ranged from 4.0 to 6.2. The values were generally 0.4 pH units greater than bulk soil pH (Tables 1 and 2). The range is partly explained by the nature of the geological substrate from which the soil has evolved, granites being more acid than biotitic schists, and partly by the type of vegetative cover, pine resulting in less acidic soil solutions than oak and eucalyptus (Table 1).

The amount of organic matter in the soil solution was unrelated to solid organic matter ($r = 0.08$). The highest values were evident in oak stands (Table 1). Since the analyzed soils are well drained there is little doubt that the oxidizable substances correspond to anything but organic compounds.

Compared to Si values reported for similar soils from the same area (mean concentrations were about 20 μmol L^{-1}, Calvo et al. 1987), our values were considerably greater (Table 1). Normally soil solutions from granitic sites exhibited higher values than schists, and concentrations under oak were particularly high. In analysis of lysimeter waters, Calvo et al. (1979a) found high Si concentrations in oak stands during spring and autumn. The increase in biological activity in spring (coinciding with the sampling period) and elevated concentrations of Si in oak leaf litter (Calvo et al. 1979a), may explain these results. The presence of phytoliths is perhaps the reason why Si concentration in A horizons is greater than that in B horizons.

Sulphate concentration is both conditioned by coast proximity and geological parent material. The sampling area was located at 300 m altitude and 30—40 km from the coast, without any significant topographic barrier protecting it from the main wind direction (SW) and cyclonic rainfalls. Contributions of marine sulphates are relatively important, representing between 20 to 50% of the total amount in rainfall waters, which is 0—3 g of S m^{-2} year $^{-1}$ (Macias, pers. comm.). Local effects due to pollution can not be dismissed, though they have a lesser importance than in areas affected by the emissions of a coal-fired power station located to the north of Galicia (where the concentration of rain waters is 5—6 g de S m^{-2} year^{-1}).

Differences in SO_4^{2-} concentrations among various geological materials (Table 1) could be attributed to the possible presence of sulfides (pyrite) in some deeply fracturated schist areas (Merino et al. 1989). These sulfides are oxidized and incorporated as sulphates to biogeochemical cicles.

Table 1. Soil solution composition: Concentrations of aqueous Al forms (*AlT*: total reactive Al; *Alsa*: acid-soluble Al; *AlnL*: non-labile Al; *AlL*: labile Al), fluorine (total and free), SO_4^{2-}, NO_3^-, Si, organic compounds (O.C), Conductance (C) and activities of species of labile Al (Al^{3+}, *Al-F*, *Al-OH* and $Al\text{-}SO_4$) (data of 56 samples).

	PINE				OAK				EUCALYPTE			
	Granite		Schist		Granite		Schist		Granite		Schist	
	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval
pH	5.4	5.8—4.7	5.6	6.1—4.8	5.0	6.1—4.5	5.2	6.2—4.2	4.8	5.4—4.0	5.4	6.4—4.7
AlT	27.3	65.8—7.4	15.2	25.3—6.4	45.4	74.8—13.7	29.4	60.4—10.8	33.9	67.4—15.1	13.2	31.8—1.8
Alsa	7.0	13.1—2.5	0.9	2.6—0.0	15.9	24.7—3.5	3.4	10.3—0.1	9.2	18.4—0.9	1.7	5.5—0.6
AlnL	6.6	21.1—0.0	7.0	13.2—1.3	16.0	27.2—7.3	12.4	23.9—5.5	6.0	11.4—0.9	2.8	7.8—0.0
AlL	13.8	38.8—1.0	7.2	12.1—1.7	13.5	24.1—0.3	13.5	29.1—0.6	18.7	52.3—3.1	8.7	23.1—0.9
(*Al-F*)	12.3	37.8—1.0	6.3	9.8—1.6	13.1	23.1—0.3	10.3	23.4—0.5	16.1	37.1—3.0	7.5	20.8—0.9
(Al^{3+}) (× 10^{-2})	0.8	7.2—0.0	1.2	6.1—0.0	0.6	1.8—0.0	128.3	70.0—0.0	2.6	15.1—0.0	1.5	4.6—0.0
(*Al-OH*) (× 10^{-2})	1.0	6.1—0.0	38.9	151.0—1.8	0.7	2.3—0.0	80.0	187.2—1.0	2.0	9.2—0.0	61.2	426.1—1.0
($Al\text{-}SO_4$) (× 10^{-2})	0.01	0.1—0.0	0.2	0.3—0.0	0.01	0.1—0.0	19.5	337.1—0.0	25.2	176.1—0.0	0.8	7.6—0.0
F_T	135.9	259—46	30.4	44—17	143.6	788—13	24.5	39—12	60.1	91—38	31.7	59—19
F^-	41.6	81—2	23.9	34—8	26.2	79—2	9.8	25—0.8	13.1	30—2	19.2	38—1
SO_4^{2-}	53.0	92—24	139.0	263—15	59.2	122—7	221.0	427—52	94.0	144—73	103.5	279—0.1
NO_3^-	42.0	106—11	29.2	110—0.0	141.6	266—21	103.0	258—0.0	22.6	50—11	47.3	134—0.0
Si	133.0	252—62	150.1	275—75	340.0	580—102	245.0	377—93	285.9	716—133	133.5	183—73
O.C (mmol L^{-1})	1.7	4.9—0.6	2.4	4.0—0.8	3.3	5.7—1.5	3.6	6.5—1.7	1.5	2.6—0.6	1.2	2.2—0.6
C ($\mu S\ cm^{-1}$)	162.4	244—98	411.4	616—311	150.3	195—99	391.6	465—331	162.0	194—124	334.1	359—285

concentrations (or activities) of Al, F, SO_4^{2-}, NO_3^- and Si in μmol L^{-1}

The concentration of F^- in the soil solution is also related to geological material (rainfall usually has values lower than 1 mg L^{-1}). In granitic rocks that have been fracturated and affected by hydrothermal processes, minerals rich in F^-, like fluorapatite and turmaline are common. The high concentrations obtained in superficial horizons of forest soils (Table 1) show the highest degree of weathering of F^- rich minerals in these horizons and also possible biogenic accumulation processes, together with an increasing retention of F^- as solutions pass through the soil layers. Thus, F concentration decreased markedly in B & C horizons solutions and in river waters, being often lower than 0.2 mg L^{-1} (Calvo & Alvarez unpublished).

Contributions of nitrate in rainfall waters are quite variable, normally between 0.1 and 3.0 mg L^{-1} but occasionally > 16.0 mg L^{-1}.

A charge balance for the soil solution shows the importance of the marine influence, as can be seen (Fig. 1) from the dominance of Na^+ and Cl^-. The other ions are present in lower quantities, except for sulphates in schists. The charge balance also indicates the dependence of the solution composition on geological material (SO_4^{2-}, Ca^{+2}, Mg^{+2} levels are higher in schist and F^- in granites). A vegetation effect (or management system) is obvious upon Ca^{+2}, Mg^{+2}, K^+ and NO_3^- levels, which always reach their higher values on systems with lower net production, oak stands, and lower values in productive eucalyptus stands from low fertility environments (granites). The importance of mobile organic acids, fulvic acids, calculated as the difference between cations and anions (Ugolini & Dahlgren 1987), is low compared with the common levels for forest soils in temperate areas. Highest values were found in oak and pine stands over schists, without any relationship to soil total organic matter content. Charge due to aluminic ions can be considered negligible (< 0.001 mmol (+) L^{-1}).

Speciation of Al

Concentrations of *total reactive Al* varied from 10 to 70 μmol L^{-1}, being in most cases lower than 30 μmol L^{-1}. These values are in the range 10–50 μmol L^{-1} that Binkley et al. (1989) consider as critical for sensitive species. Nevertheless, this feature is uncertain in our case because of high Ca/Al and Mg/Al ratios, and the relative importance of some non-toxic Al species.

The *acid-soluble* fraction (*Alsa*) was small in soils developed over schists (generally below 6 μmol L^{-1}), and it was independent of the type of vegetation (Table 1). Variations in *Alsa* were correlated with the pH ($r = -0.51$) and the amount of organic matter in solution ($r = 0.62$), so the highest concentrations correspond to the most acidic solutions with the

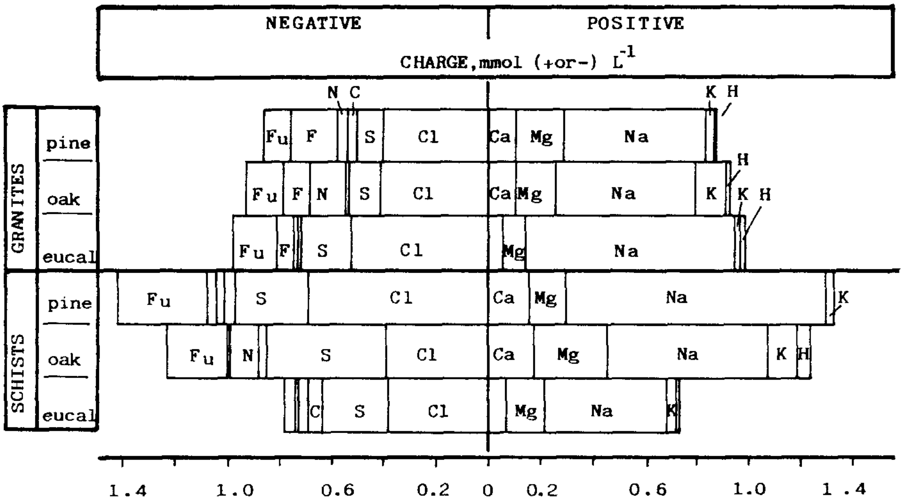

Fig. 1. Soil solution charge balance in forest soils of Galicia (Fu: fulvate anion; F: fluoride; N: NO_3^-; C: HCO_3^-; S: SO_4^{2-}; Al contribution was <0.001 mmol(+) L^{-1}).

greatest amounts of organic compounds (e.g. oak stands on granite) where *Alsa* represented more than 30% of solution Al.

In most samples, *reactive Al* exceeded the *acid-soluble* fraction. The concentration of *non-labile Al* represents between 20% and 40% of *total reactive Al,* which is less than that in podsolized soils in other areas, where this fraction can be over 80% (Ugolini & Dahlgren 1987). The *non-labile Al* correlated very well with total solubilized organic matter ($r = 0.92$), having *C/AlnL* ratios of 110—273 (Table 2). These values are similar in magnitude to the stable organic-metal complexes found in the solid fraction of epipedons (O & A) from podszolic soils, where C/metal ratios vary between 90 and 1000 (Buurman 1987). The highest values of *AlnL* can be found in soils under oak vegetation, a result that differs from that observed by David & Driscoll (1984) who found that conifers elevated concentrations of mobile organic acids and facilitated the mobilization of elements such as Fe and Al, characteristic of podzolizing environments. In contrast, both the *Alsa* and *AlnL* fractions, presumably bound to mobile organic compounds, showed higher concentrations in the surface horizons of soils beneath oak rather than pine and eucalyptus. It is possible, however, that these results are not applicable to all times of the year; samples collected in spring could exhibit particularly high concentrations of *Alsa* and *AlnL* due to leaf-litter decomposition (Calvo et al. 1979b).

Concentrations of *labile Al* were generally higher than non-labile

Table 2. % *non-labile* Al respect *reactive Al* and *total reactive Al* and ratios C/Al in soil solutions and in solid soil fractions.

	Soil solution				Solid fraction
	%AlnL/Alr	%AlnL/AlT	C/AlT	C/AlnL	C/Al + Fe (1)
Granite					
pine	39	24	43	273	5.4
oak	58	37	45	110	7.1
eucal.	26	20	29	134	6.5
Schist					
pine	47	43	93	263	4.2
oak	54	42	74	185	6.5
eucal.	21	18	70	238	3.5

(1): DCB extractable Al & Fe

species. Values were less than 15 μmol L^{-1} in solutions with pH greater than 5.0, and increased as the pH decreased ($r = -0.58$). Almost all *labile Al* was complexed with fluorine (Fig. 2a), the concentration of *Al-F* complexes was not limited by fluorine concentrations, because there is usually an excess of free F. Free F increased with increasing pH and decreasing *AlL* (Fig. 2b). Small amounts of *Al-OH* complexes were found, confined to soils over schists. The OH^- ions compete favourably with F^- when the pH is greater than 5.0; hence, these solutions contain *Al-OH* complexes as well as excess free fluorine. At lower pH, *Al-OH* complexes only appear when the fluorine has been totally consumed. The Al^{3+} and $Al\text{-}SO_4$ forms were present in very small amounts in some oak and schist samples with a high proportion of *AlL* to F total (molar ratio > 0.6).

Al in the solid fraction

Generally, more than 60% of the Al extracted from the solid fraction occured as stable organic forms (Al_{pyr}-Al_{Cu}) and overall concentrations varied from 10 to 400 mmol Kg^{-1}. Much less aluminium was found as moderately stable (Al_{Cu}-Al_{La}), labile (Al_{La}-Al_k), or exchangeable forms Al(Al_k) (Table 3).

There was no significant relationship between the amount of Al bound to organic-matter and the type of geological material, the pH, or the total amount of soil organic material. Nevertheless, there does appear to be a dependency on the nature of the organic material. The greatest values

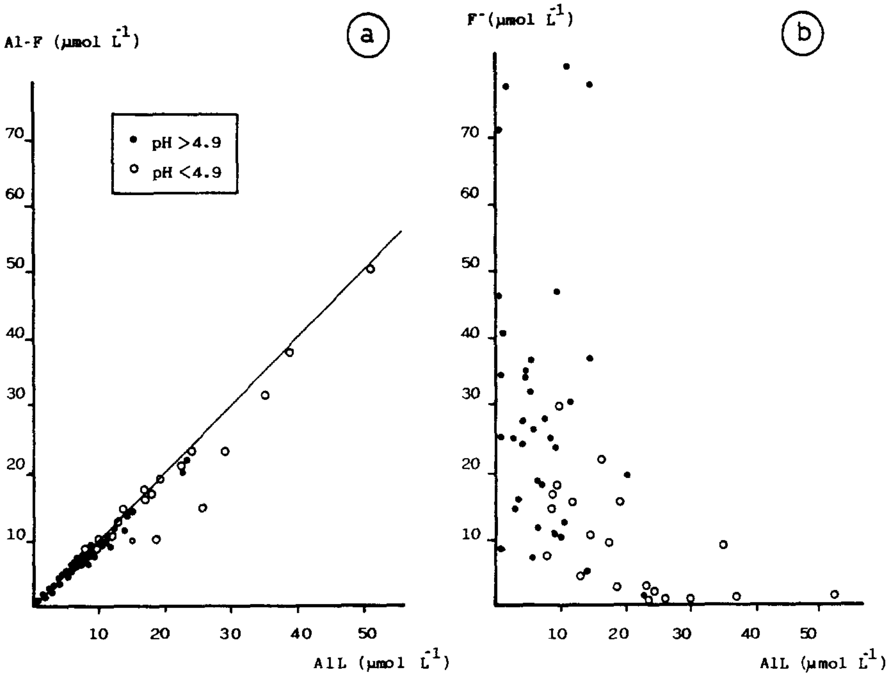

Fig. 2. Relation between concentrations of labile Al and *Al-F* complexes (a) and ditto for labile Al and free F in solution (b).

were found in pine stands (mean value = 230 mmol Kg^{-1}), then eucalyptus (200 mmol Kg^{-1}) and oak (146 mmol Kg^{-1}), perhaps because in the latter there was a greater proportion of recently incorporated material.

Exchangeable Al (Al_k) concentrations were 5—14 mmol Kg^{-1} (1.5—4.3 cmol(+)Kg^{-1}). The correlation between exchangeable (Al_k) and solution Al concentrations is lower ($r = 0.50$) when, for the latter, values of *AlL* are taken rather than grouping together the fractions *Alsa* + *AlnL* + *AlL* ($r = 0.66$) (Fig. 3). For the remaining forms of extractable aluminium, even the most labile, relations with soluble Al were very poor. Organic matter was more involved in fixing and removing Al from solution, forming moderate and highly stable forms of soil Al, relative to exchangeable Al. C/Al + Fe rations are below than 10 (Table 2), similar to the lowest C/Al + Fe (4—40) ratios found by Buurman (1987) in spodic horizons with floculated organic matter in soils of Holland and Denmark. This suggests that almost all the organic matter is floculated and that *AlnL* forms may be restricted to low, and perhaps short-lived, concentrations in the uppermost layers in contact with fresh plant material.

Table 3. Data from solid soil fractions and Al extraction with KCl (Al_K), LaCL$_3$ (Al_{La}), CuCl$_2$ (Al_{Cu}), Na-pyrophosphate (Al_{pyr}) and ammonium oxalate (Al_{ox}) in mmol Kg^{-1} (data of 56 samples).

	PINE				OAK				EUCALYPTE			
	Granite		Schist		Granite		Schist		Granite		Schist	
	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval	$\bar{x}$	interval
pH (H_2O)	4.8	5.2—4.4	4.7	5.0—4.2	4.5	5.3—4.1	4.5	4.7—4.2	4.5	4.7—4.3	4.6	4.9—4.2
% C	8.7	12—6	11.2	13—9	9.5	12—6	12.1	14—7	12.2	17—6	8.5	13—3
% B. Ech.	20.1	29—14	26.8	45—14	20.8	29—14	23.1	34—15	12.3	17—10	23.8	39—10
% Al Ech.	79.9	86—70	73.2	86—55	79.2	86—70	76.9	84—65	87.7	90—82	76.2	90—60
Al_K	9.8	15—5	10.2	14—7	12.6	20—5	12.9	16—10	13.6	18—8	7.7	12—5
Al_{La}	26.5	35—19	23.5	39—28	28.5	36—18	35.0	29—23	37.9	53—19	24.6	35—11
Al_{Cu}	84.8	119—42	95.3	125—79	76.5	107—44	92.8	132—44	103.0	141—49	66.1	88—25
Al_{pyr}	294.4	423—139	348.3	468—228	202.5	274—66	278.0	425—97	281.5	380—164	281.3	491—74
Al_{ox}	330.9	444—167	377.0	496—246	228.9	342—112	301.0	422—120	301.5	387—174	325.6	731—78

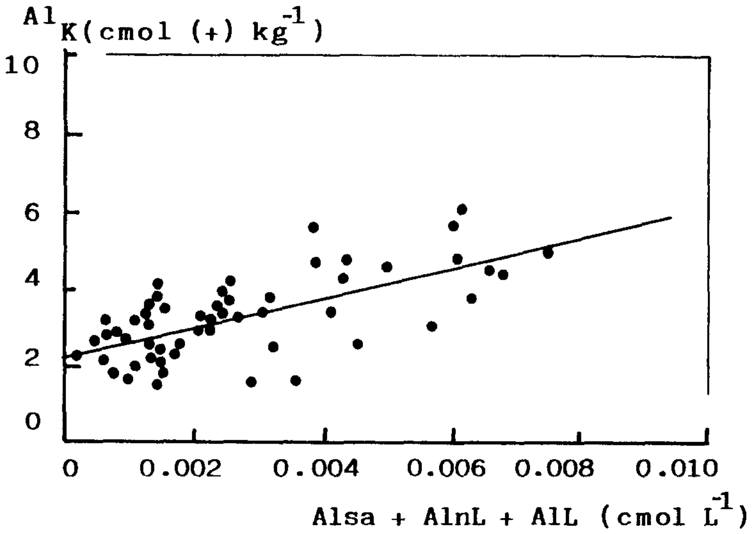

Fig. 3. Relation between Al in the aqueous phase (*Alsa* + *AlnL* + *AlL*) and that extracted with KCl from the solid fraction.

In the face of *AlL* in solution, the organic compounds could be thought of as somewhat inefficient in removing mobilized Al, particularly when the pH is less than 5.0 (concurrently reducing the active groups of the organic matter).

Most of the *AlL* is associated to fluoride (as *Al-F* complexes), with the result that the activity of Al^{3+} is very low (normally less than 0.03 μmol L^{-1}), and many samples are unsaturated with respect to gibbsite and kaolinite (Fig. 4). This is particularly common in soils developed over granites. Even though *AlL* concentrations were greater on granites, there was more fluoride in this soil.

Conclusions

The forest soils of Galicia are characterized by their high acidity and an exchange complex largely saturated with Al, generally greater than 80%. However, the high organic matter content of these soils, which is frequently 10% or more, leads to fixation of Al in the form of moderate and strongly stable complexes. A part of the mobilized Al is in *acid-soluble* and *non-labile* forms, probably bound to the organic material and precursors of precipitated complexes. Given the high acidity of the soils, Al is

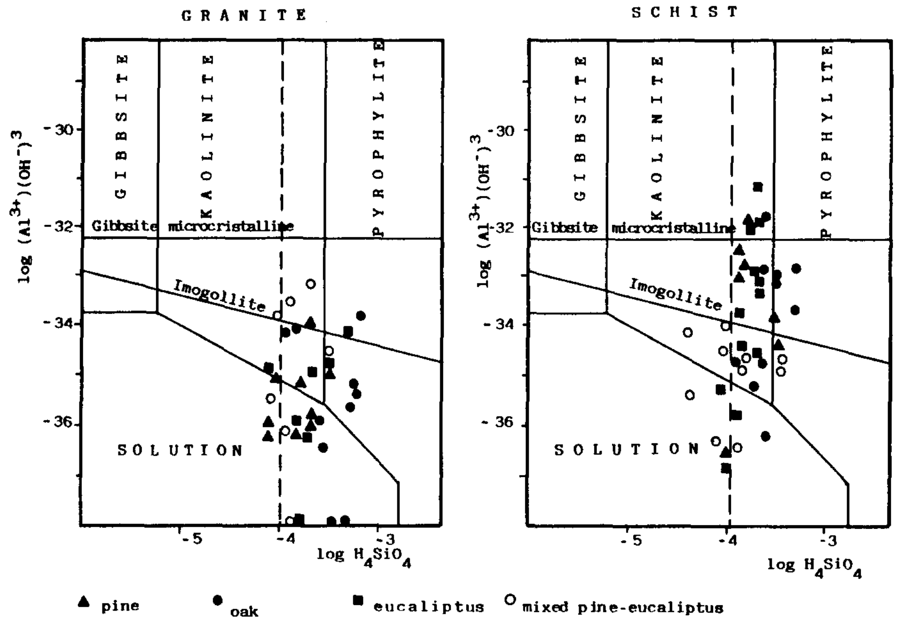

Fig. 4. Mineral stability in solutions of forest soils in Galicia (thermodynamic data by Robie et al. 1978; Hem & Robertson 1967; Farmer & Fraser 1982) (other samples from soils under mixed pine-eucalyptus are included).

solubilized in inorganic forms (particularly at pH below 5), mostly bound to fluoride. The activity of Al^{3+} is extremely low, leading to frequent unsaturation with respect to gibbsite and kaolinite, and hence conditions of instability for all the minerals, particularly in granitic areas.

References

Adams F (1974) Soil solution. In: Carson EV (Ed) The Plant Root and its Environment (pp 441—481). Univ. Virginia Press, Charlottesville, Va

Alvarez E & Calvo R (1991) Aplicacion de un metodo de fraccionamiento de especies aluminicas a soluciones de suelos de Galicia. Suelo y Planta (in press)

Bache BW (1986) Aluminium mobilization in soils and waters. J. of the Geological Society 143: 699—706

Bardseley CE & Landcaster JD (1960) Determination of reserve sulfur and soluble sulfates in soils. Soil Soc. Am. Proc. 24: 265—268

Bascomb CL (1986) Distribution of pyrophosphate extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19: 251—256

Binkley D, Driscoll CT, Allen HL, Schoeneberger P & McAvoy D (1989) Acidic deposition and forest soils. Context and case studies of the Southeastern United States. Springer-Verlag, New York

Blakemore LC (1978) Exchange complex dominated by amorphous material (ECDAM). In: Smith GD (Ed) The Andisol proposal (pp 21—22). Soil Bureau, DSIR, New Zealand

Buurman P (1988) pH-Dependent character of complexation in podzols. In: Righi D & Chauvel A (Eds) Podzols et Podzolisation (pp 181—186). INRA, Paris

Calvo R, Paz A & Diaz-Fierros F (1979a) Nuevos datos sobre la influencia de la vegetaión en la formación del suelo en Galicia. III. Aportes por hojarasca, pérdidas por drenaje y escorrentía. An. Edaf. Agrobiol. 38: 1983—2000

Calvo R, Paz A & Diaz-Fierros F (1979b) Contribución al estudio de los sistemas forestales: actividad biológica en suelos desarrollados bajo *Q. robur y P. radiata.* Trab. Comp. de Biología. 8: 145—154

Calvo R, Fernandez ML & Veiga A (1987) Composición de la solución del suelo en medios naturales de Galicia. An. Edaf. Agrobiol. 46: 621—641

Calvo R & Alvarez E (1987) Problemas de caracterización del complejo de cambio en suelos de Galicia. An. Edaf. Agrobiol. 46: 1221—1237

Corey RB & Jackson MC (1953) Silicate analysis by rapid semichromochemical system. Anal. Chem. 25: 1233—1238

David MB & Driscoll CT (1984) Aluminum speciation and equilibria in soil solutions of a Haplorthod in the Adirondack Mountains (New York, USA). Geoderma. 33: 297—318

Dougan WK & Wilson AL (1974) The absorptiometric determination of aluminium in water. A comparison of some chromogenic reagents and development of an improved method. Analyst. 99: 413—430

Driscoll CT (1984) A procedure for the fractionation of aqueous aluminum in dilute acidic waters. Int. J. Environ. Ana. Chem. 16: 267—283

Driscoll CT (1985) Aluminum in acidic surface waters: Chemistry, Transport and Effects. Environmental Health Perspective, 63: 93—104

Farmer VC & Fraser AR (1982) Chemical and colloidal stability of soils in the Al_2O_3-Fe_2O_3-SiO_2-H_2O system: Their role in podzolisation. J. Soil Sci. 33: 737—742

Garcia-Rodeja E & Macias F (1984) Caracterización de suelos ácidos (Podzoles, Andosoles-Suelos alumínicos) de Galicia. Relación con los procesos edafogeoquímicos. Actas 1° Congr. Nac. Ciencia del Suelo. Madrid: 589—602

Garcia-Rodeja E, Silva B & Macias F (1987) Andosols developed from non-volcanic materials in Galicia, N.W. Spain. Journal of Soil Science. 38: 573—591

Hargrove W & Thomas GW (1981). Extraction of aluminum from aluminum-organic matter complexes. Soil Sci. Soc. Am. J. 45: 151—153

Hem JD & Roberson CE (1967) Form and stability of aluminum hydroxide complexes in dilute solutions. U.S. Geol. Surv. Water Suppl. Pap. 1827-A

Juo AS & Kamprath EJ (1979) Copper chloride as an extract for estimating the potentially reactive aluminum pool in acid soils. Soil Sci. Soc. Am. J. 43: 35—38

Kharaka Y, Gunter W, Aggarwal P, Perkins E & Debraal J (1989) Solmineq.88: A Computer Program for Geochemical Modelling of water-Rock interactions. U.S. Geological Survey. Menlo Park, California

Martinez A (1987) Zonas agroecológicas de Galicia. Zonas climáticas FAO. An. Edaf. Agrobiol. 46: 521—538

Merino A, Monterroso C & Garcia-Rodeja E (1989) Contenido de azufre total en muestras superficiales de suelos de la provincia de La Coruña. An. Edaf. Agrob. 48: 615—626

Pratt PF & Bair FL (1961) A comparison of three reagents for the extraction of aluminum from soils. Soil Sci. 9: 357—359

Robie RA, Hemingway BS & Fisher JR (1978) Thermodynamic properties of minerals and related substances at 298. 15K and 1 bar. U.S. Geol. Surv. Bull. 1452

Romero R, García C & Macías F (1991) Utilización del test de la formamida en la identificación de los filosilicatos 1:1 de suelos de la provincia de La Coruña. Suelo y Planta 1: 33—48

Soil Conservation Service (1972) Soil Survey laboratory methods and procedures for collecting soil samples. USDA, Washington DC

Soil Survey Staff (1990) Keys to Soil Taxonomy, fourth edition. SMSS technical monograph.6. Blacksburg, Virginia

Ugolini FC & Dahlgren R (1987) The mechanism of podzolization as revealed by soil solution studies. In: Righi D & Chauvel A (Eds) Podzols et Podzolization (pp 195—203). INRA

Urrutia M, Garcia-Rodeja E & Macias F (1988) Aplicación de disoluciones no tamponadas para la extracción de Al "activo" ligado a la materia orgánica en suelos de Galicia. An. Edaf. Agrobiol. 47: 1289—1301