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Allophane, aluminum, and organic matter accumulation across a bioclimatic sequence of volcanic ash soils of Argentina

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Abstract

An investigation was conducted to study Al fractions, organic matter accumulation, and their effects on physicochemical properties in soils derived from volcanic ash at the Andinopatagonian region in SW Neuquén, Argentina. Five sites were selected in a climatic biosequence, ranging from *Nothofagus* forest with a udic soil moisture regime at the footslope of the Andes mountain range to grass-shrub steppe with a xeric soil moisture regime in the hills and plains. The morphological characteristics showed young pedons, containing andic, mollic, and cambic horizons. A change from low bulk density from <0.82 Mg m^{-3} in Andisols under a udic regime to medium density values of ~1.1 Mg m^{-3} in Xerands and Xerolls was observed. This was related to a lower rate of weathering probably coinciding with a lower content of allophane and higher clay crystallization and to a decrease in total soil organic carbon (C_{org}). The rate of soil weathering was estimated from acid oxalate extractable Al, which together with C_{org} significantly explained the bulk density variation (R^2=0.7091, p<0.00002). Soil acidity varied from moderately and strongly acidic in Andisols with a udic soil moisture regime to slightly acid and almost neutral in Xerands and Xerolls. The higher base concentration and low soil acidity in Xerolls were attributed to less leaching, due to lower mean annual precipitation. However, pH_{NaF} and C_{org} were the variables which significantly explained the pH_{water} variation (R^2=0.7806, p<0.0000). This showed that soil acidity was closely related to Al activity and organic matter content, rather than to base content. The lower C/N ratios, in the surface horizons of the Xerands and Xerolls versus the Andisols with a udic soil moisture regime, suggested that the rate of mineralization was faster under warmer conditions with xeric moisture regime than with udic moisture regime. There was also a remarkable difference in the humic C/fulvic C ratio in A-horizons, which may reflect the input of vegetation residues indicating a sensible contribution of the cover of grass-shrub steppe to the formation of humic substances. The acid oxalate extractable Si and Al values reflected a low rate of weathering, which decreased when mean annual precipitation decreased and a xeric soil moisture developed being also higher under *Nothofagus* forest than under grass-shrub steppe, which reflects the possible effect of the mean annual precipitation gradient (2000–700 mm) and vegetation types on soil weathering. The differences in type and quantity of organic matter input, with a higher organic matter content and lower humic C/fulvic C ratio under *Nothofagus*, indicate a more reactive organic matter which may be somewhat responsible for the weathering degree. No significant relationship between acid extractable Al and C_{org} was found suggesting that organically

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bound Al is not dominant. The detection of higher allophane estimations in soils with the highest C_{org} levels, may indicate that the anti-allophanic hypothesis probably does not apply to these soils.

Keywords: Volcanic ash soils; Aluminum; Organic matter; Andinopatagonia

1. Introduction

Volcanic ash soils are found under a variety of environmental conditions, and have been studied in various regions of the world. A considerable amount of information has been published, in Japan (Shoji et al., 1982, 1988; Saigusa et al., 1991; Adjadeh and Inoue, 1999), Indonesia (Tan, 1965), New Zealand (Parfitt and Wilson, 1985), Rwanda (Nizeyimana et al., 1997), Spain (Jahn, 1991), United States of America (Baham and Simonson, 1985 in Mizota and van Reeuwijk, 1989), Italy (Quantin et al., 1985), France (Aran et al., 1998), Mexico (Campos Cascaredo et al., 2001), and China (Zhao et al., 1993). Volcanic ash soils are also found in great extensions in the Andinopatagonian region, and in particular in the province of Neuquén, Argentina. These soils have attracted a limited amount of research attention, and the information available is related to some geomorphic aspects of the region and not specifically to the nature of the soils. Whatever information is available has also been published in regional reports and in Spanish. Some of the references included a chronology of postglacial volcanism in Fuegopatagonia (Auer, 1949), and a study on pedogenesis of paleosols in Neuquén (Laya, 1977). Other data that dealt briefly with the properties of volcanic ash soils in northern Patagonia were the local reports under the auspices of INTA-ORSTOM (Colmet Daage et al., 1988). Geographical factors affecting the properties of the soils in Neuquén were published as a regional report by Ferrer et al. (1990). These soils were generally classified as Andisols in the U.S. Soil Taxonomy, and their high organic matter content and the presence of allophane and imogolite are considered the cause of their very specific physical and chemical properties i.e. for the variable charges, a high water-holding capacity, and a low bulk density (Tan, 1985; Shoji et al., 1993). The soils also contain high levels of “active” Al, causing their high P-fixation capacity (Wada, 1970), although most of the free Al and Fe was assumed to be chelated by humic matter (Tan, 1985). Al- and Fe-humates were believed to inhibit the synthesis of allophane, and the mechanism was called, therefore, an anti-allophanic process (Shoji et al., 1993; Huang and Huang, 1995). Not much information is currently available about the properties of Andisols in Argentina and this research was conducted to study the Al fractions and organic matter and their effect on physicochemical properties in a Andisol–Mollisol pedosequence at the Andinopatagonian region, SW Neuquén, Argentina.

2. Materials and methods

2.1. Area description

An 80-km cross-section in SW Neuquén was studied, from the footslope of the Andes mountain range (Cordillera de los Andes) through to the hills and plains, ranging in mean annual precipitation (MAP) from 2000 mm to 500 mm and in mean annual temperature from <8 °C to 12 °C, were the vegetative cover changes from forest to grass-shrub steppe. This region was carved by glaciers and later it was covered by ash composed of superimposed tephras, from volcanoes located on the Chilean side of the Andes. The most recent tephras were the Lago Totoral and El Rincón deposits from the 1960 and 1921 ejects of acidic ash, whereas the oldest was a more basic deposit of Lago Mascardi, which was estimated to be 9000 to 10,000 years old (Auer, 1949; Laya, 1977). Volcanic ash covers 1,500,000 ha of Neuquén’s territory, representing 17% of the area, which in the udic soil moisture regime in the west has developed into Andisols, and toward the east Mollisols were formed under the influence of a xeric moisture regime (Colmet Daage et al., 1988; Ferrer et al., 1990).

2.2. Selection of sites and soils

Five sites were selected on the basis of (i) west–east spatial variation, (ii) types of dominant native vegetation, (iii) degree of the transition from Andisols to Mollisols (Colmet Daage et al., 1988; Broquen et al., 2000; Broquen, 2002). The sites, labeled as S1, S2, S3, S4, and S5 (Fig. 1 and Table 1) were located as follows. S1, S2, and S3 were located in the very humid to humid region. S1, at the footslope of the Andes mountains, has a 2000-mm MAP and a forest cover of *Nothofagus alpina* and *Nothofagus dombeyii*, with an underbrush dominated by *Chusquea culeou*. S2, away from the Andes, in the Taylor's Crossing Hill (Loma Atravesada de Taylor), has a 1200-mm MAP, and a forest cover of *Nothofagus antarctica* with an underbrush dominated by shrub and grass. S3, near S2 has a 1200-mm MAP, and a cover of grass-shrub steppe of *Stipa speciosa*, with shrubs of *Mulinum spinosum* and *Acaena splendens*. S4 and S5 were located in semihumid transitional region to the steppe at the hills and plains. S4 was characterized by a 900-mm MAP and S5 by a 700 mm MAP, both with a vegetation cover composition similar to that in S3 (Table 1). According to Laya (1977) and to Colmet Daage et al. (1988) it can be reasonably assumed that the upper horizons in all five pedons were formed in the same tephra, which becomes thinner in thickness and composition toward the east. The mineralogy of the volcanic ash is dominated by light minerals, within which coloured volcanic glass is the most abundant. Heavy minerals comprise only a small fraction and are dominated by hypersthene, hornblende, opaque minerals, augite, and others (Apcarián and Irisarri, 1993).

The soils were described in a pit and classified according to the US methods (Soil Survey Staff, 1993, 1999). Due to the structure's stability, the texture could not be determined by common methods and the term "apparent" (Soil Survey Staff, 1993) was used in naming field textures (Wada, 1977, 1985; Shoji et al., 1993). Three samples per horizon were taken, over a distance of ~80 cm along the pit wall, and combined. They were air-dried and sieved to pass a 2-mm mesh. Undisturbed core samples were taken for bulk density measurement.

2.3. Soil analysis

Bulk density (δa) was determined after SAMLA (1996) and expressed in terms of oven-dry weight soil. Moisture retention at 1.5 MPa was determined with the pressure plate method in triplicate. Volcanic glass was determined in a 0.02–2.0 mm fraction,

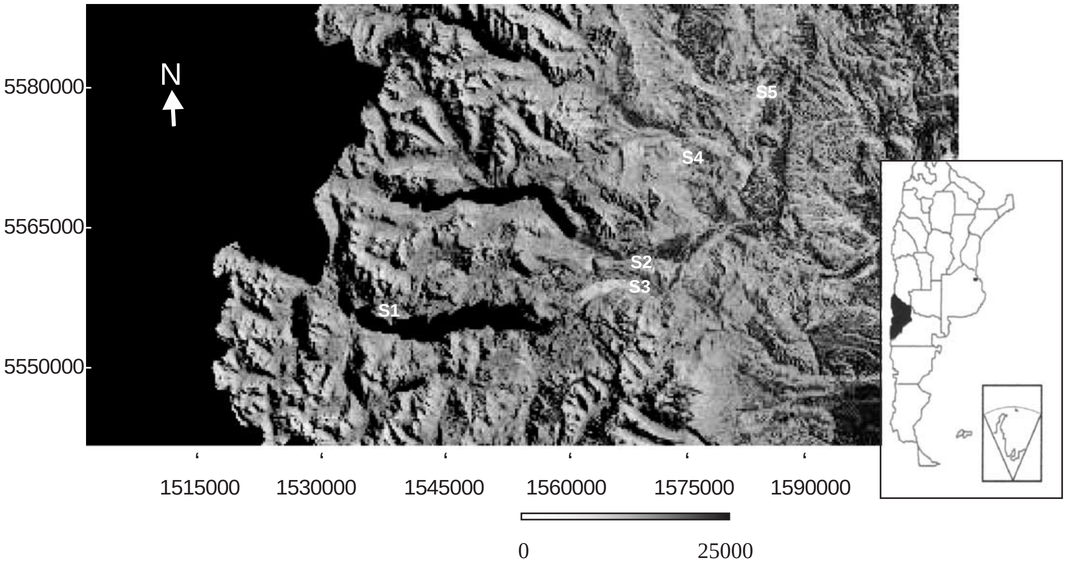

Fig. 1. Study area and location of study sites (S1, S2, S3, S4, and S5).

Table 1

Major environmental and soil morphological characteristics

Biosequence	Mean annual temperature (°C)	Mean annual precipitation (mm)	Study site	Land form	Profile position	Altitude (m)	Soil classification (Soil Survey Staff)	Vegetation type	Surface cover (%)	Drainage class	Horizons	Depth (cm)	Boundary[a]	Moist colour 10 YR (Munsell notation)	Field texture[b]	Structure[c]	Consistence[d]	Field Fieldes Test[e]	Redoximorphic features
Very wet forest	<8–10	2000	S1	Mountain slope	Foot slope	650	Thaptic Udivitrand	*Nothofagus alpina*/ *Nothofagus dombeyii*/ *Chusquea culeau*	100	well drained	O	12–0	AS						
											C?	0–3	VB	4/1	si	m/sg	NS	–	–
											2A1	3–13	CS	2/2	a si s	gr	SM	++	–
											2A2	13–35	CS	2/2	a si s	m/sg	SM	++	–
											2Bw1	35–54	CS	3/3	a si s	m/sg	WS	+++	–
											2Bw2	54–70	CS	3/2	a si s	m/sbk/sg	WS	+++	–
											2Bw3	70–90	CS	3/6	a si s	m/sbk/sg	MS	+++	–
											3Ab	90–110		3/2	a si	m/sg	SM	+++	–
Wet forest		1200	S2	Mountain slope	Foot slope	860	Typic Hapludand	*Nothofagus antarctica*/ *Lomatia hirsuta*	100	moderately well drained	O	3–0	CW						
											A1	0–30	AS	2/1	a si	gr	SM	++	–
											A2	30–43	AW	2/1	a si	sbk/gr	SM	++	–
											AB	43–55	AS	2/1	a si	m/sbk	MS	++	–
											Bw1	55–85	AS	3/3	a si s f	m/sbk	MS	+++	F3Mf[f]
											Bw2	85–110+		3/6	a si s f	m/sbk	SM	+++	F3Mc[g]
		1200	S3	Mountain slope	Foot slope	850	Typic Hapludand	*Stipa speciosa*/ *Mulinum spinosum*	70	moderately well drained	A1	0–30	CS	2/1	a si s f	gr	SM	++	–
											A2	30–70	GS	3/2	a si s f	m/sbk	MS	++	–
											Bw	70–110		3/3	a si s f	m/sbk	SM	+++	F3Mc
Steppe transition	10–12	900	S4	Hill slope	Side slope	910	Humic Vitrixerand	*Stipa speciosa*/ *Mulinum spinosum*	60	well drained	A	0–13	CS	2/1	a s f	gr	NS	++	–
											Bw1	13–35	CS	3/2	a si s co	gr/sg	WS	++	–
											Bw2	35–72	AS	3/4	a s	sbk/sg	WS	+	–
											2C	72–105		3/3	scl	sbk/sg	(w) so (w) ps	–	–
		700	S5	Hill slope	Side slope	890	Vitrandic Haploxeroll	*Stipa speciosa*/ *Mulinum spinosum*	70	well drained	A1	0–5	CS	3/1	sl f	gr	NS	–	–
											A2	5–30	CS	2/2	sl co	m/sg	NS	–	–
											Bw1	30–90	CS	2/2	sl co	m/sbk	NS	–	–
											Bw2	90–134	AS	3/2	sl co	m/sbk	NS	–	–
											2C	134+		4/2	scl f	m/sbk	(w) ss (w) ps	–	–

[a] A: abrupt; S: smooth; V: very abrupt; B: broken; C: clear; W: wavy; G: gradual.

[b] a: apparent (modifier for soil texture when not completely dispersed in the standard analysis, Soil Survey Staff, 1993); si: silt; s: sand; f: fine; co: coarse; scl: sandy clay loam; sl: sandy loam. (Soil Survey Staff, 1999).

[c] m: massive; sg: single grain; sbk: subangular blocky; gr: granular.

[d] NS: non smeary; WS: weakly smeary; MS: moderately smeary; SM: strongly smeary; (w) so: non sticky; (w) ss: slightly sticky; (w) ps: slightly plastic.

[e] –: negative; +: weakly positive; ++: moderately positive; +++: strongly positive.

[f] F3Mf: few, fine, prominent, 7.5YR 4/6 non cemented iron (Fe^{3+}) masses.

[g] F3Mc: common, fine, prominent, 7.5YR 4/6 non cemented iron (Fe^{3+}) masses.

treated with dithionite citrate after Holmgren (1967), and the amount was counted with a stereoscopic and polarizing microscope. pH was measured with the glass electrode in H_2O (1:1 w/w), 1 N KCl (1:2.5 w/v), and in 1 N NaF (1:50 w/v) according to SAMLA (1996). Total soil organic carbon (C_{org}) was determined by the Walkley–Black wet digestion method. Humic and fulvic acids were extracted with 0.1 N NaOH (Tan, 1996) and their C content estimated by dry combustion with a Carbon Analyzer LECO (Swift, 1996). The effective cation exchange capacity (ECEC) was taken as total exchangeable bases plus exchange acidity (Tan, 1998). Exchangeable bases extracted with the neutral 1 M NH_4-acetate and the bases determined by atomic absorption spectroscopy (Sumner and Miller, 1996; Tan, 1996) and exchange acidity (H^++Al^{3+}) measured by leaching a soil sample with 1 M KCl and titrating the lecheate with 0.1 M NaOH. P-retention was measured according to Blakemore et al. (1987). Acid ammonium oxalate extractable Al, Fe, and Si (Al_o, Fe_o, and Si_o) and pyrophosphate extractable Al and Fe (Al_p and Fe_p) were determined by atomic absorption spectroscopy. Si content in allophane and the percentage (%) of allophane in the fine earth fraction were estimated according to Parfitt and Henmi (1982) and Parfitt and Wilson (1985), and by applying Mizota and van Reeuwijk (1989) equation where the compositional Al/Si molar ratio is estimated by $(Al_o - Al_p)/Si_o$, and the limits to use Si_o for allophane estimation were set in the Al/Si ratio between 1 and 2.5.

3. Results and discussion

The morphological characteristics given in Table 1 showed young pedons with moderately deep profiles, with andic properties, containing mollic, and cambic horizons (Table 2). The change from an udic to a xeric soil moisture regime resulted in a change from low bulk density from <0.82 Mg m^{-3} in Andisols under udic regime into medium density values 1.1 Mg m^{-3} in the Xerand and Xeroll (Table 2). The soil consistency also became less smeary and slightly more sticky and plastic (Table 1) and the andic properties appeared to be less expressed (Table 2). Bulk density in volcanic ash soils decreases with the advance of weathering, which proceeds with a rapid development of porous soil structure to which non crystalline materials and organic matter contribute to a large extent (Shoji et al., 1993). Weathering may be estimated from Al_o figures (Shoji et al., 1993), which decreased as MAP decreases and a xeric soil moisture develops (Table 2). A clay polymerization increase may also occur, due to decreasing rainfall and to the contrasting dry season (Parfitt and Wilson, 1985; Colmet Daage et al., 1988). Parfitt and Wilson (1985) studied climosequences in New Zealand and they found that under the relatively weak leaching conditions, due to decreasing rainfall and the occurrence of a moisture deficit in summer, Si concentration was higher, leading to the preferential formation of halloysite. On the other hand, leaching of Si became more intense with increasing precipitation, leading to the formation of allophane when soluble Si concentrations are lower. On different climosequences in the Andinopatagonian region, Colmet Daage et al. (1988) found that allophane was predominant when precipitation was higher and crystalline clays were formed when precipitation decreased and there was a summer moisture deficit, whereas halloysite formed when the dehydration was moderate and smectites when it was pronounced.

We also found a decrease of about a 66% of C_{org} in the Xerands and Xerolls with respect to the Udands and Vitrands (Table 3). This may also contribute to the differences in bulk density according to the statement of Shoji et al. (1993), that bulk density values of Andisols show a tendency to decrease with increasing organic carbon content; this tendency being more marked when allophane content is lower. The possible influence of organic matter content and weathering on bulk density was shown by a multiple regression analysis, where C_{org} and Al_o were the variables included which explained a 71% of bulk density variation (R^2=0.7091, p<0.00002). Being C_{org} an integrative variable somewhat related with the differences in bulk density, it is necessary to consider other variables that may influence bulk density such as the amount and arrangement of biological pore space, which should be studied in further investigations.

3.1. Chemical properties

The data in Table 3 indicated that soil acidity varied from moderately and strongly acidic in the

Table 2
Selected andic soil properties

Study site	Soil classification (Soil Survey Staff, 1999)	Horizons	Depth (cm)	Bulk density (Mg m^{-3})	Water retention 1.5 MPa (%)	pH (NaF) 60′	P-retention (%)	Al_o[a]	Al_p[b]	Fe_o[c]	Fe_p[d]	Si_o[e]	Al_o–Al_p[f]	(Al_o–Al_p)/Si_o	Al_p/Al_o[g]	Al_o+½Fe_o	Glass[h]	Estimated allophane	Melanic Index
								(g kg^{-1})								(%)			
S1	Thaptic	O	12–0																
	Udivitrand	C?	0–3	0.78	nd[i]	8.7	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	–
		2A1	3–13	0.64	13.0	8.9	80	7.6	4.8	8.0	2.6	3.2	2.8	0.9	0.6	1.2	18	2	–
		2A2	13–35	0.72	13.0	10.2	87	10.8	5.0	8.8	2.8	3.3	5.8	1.7	0.5	1.5	26	2	–
		2Bw1	35–54	0.77	9.0	10.3	92	13.0	4.7	10.0	1.4	5.3	8.4	1.6	0.4	1.8	44	3	–
		2Bw2	54–70	0.82	9.9	10.2	97	15.7	3.1	13.1	0.6	7.4	12.6	1.7	0.2	2.2	33	5	–
		2Bw3	70–90	0.63	9.3	10.3	96	18.8	2.2	15.0	0.0	9.9	16.6	1.7	0.1	2.6	33	7	–
		3Ab	90–110	0.74	23.0	10.3	98	21.9	2.5	15.4	0.1	10.8	19.4	1.8	0.1	3.0	22	8	–
S2	Typic	O	3–0																
	Hapludand	A1	0–30	0.75	33.6	9.3	74	7.2	3.8	9.3	3.6	3.8	3.3	0.9	0.5	1.2	25	2	1.76
		A2	30–43	0.67	25.0	9.7	76	12.1	4.3	11.5	2.8	5.3	7.9	1.5	0.4	1.8	30	3	1.63
		AB	43–55	0.66	22.9	10.2	91	23.9	5.7	16.9	3.2	nd	18.1	nd	0.2	3.2	15	nd	–
		Bw1	55–85	0.67	21.2	10.3	96	26.7	6.0	26.2	2.6	10.4	20.7	2.0	0.2	4.0	30	8	–
		Bw2	85–110+	0.74	17.7	10.2	90	26.5	2.8	22.2	0.6	15.5	23.7	1.5	0.1	3.8	30	10	
S3	Typic	A1	0–30	0.75	15.0	9.0	51	7.1	2.3	11.5	0.8	3.7	4.8	1.3	0.3	1.3	32	2	–
	Hapludand	A2	30–70	0.81	17.0	9.8	66	9.8	5.5	13.4	3.2	4.6	4.3	0.9	0.6	1.6	24	3	–
		Bw	70–110	0.72	20.0	10.0	86	15.2	3.5	17.2	1.5	3.5	11.6	3.3	0.2	2.4	17	nc[j]	–
S4	Humic	A	0–13	1.10	8.6	8.6	30	4.2	0.6	9.2	0.04	3.4	3.6	1.1	0.1	0.9	21	2	–
	Vitrixerand	Bw1	13–35	1.08	9.8	8.7	34	5.2	0.7	10.2	0.1	3.7	4.5	1.2	0.1	1.0	25	2	–
		Bw2	35–72	1.10	9.3	8.7	50	6.0	1.1	10.8	0.5	4.6	4.9	1.1	0.2	1.1	16	3	–
		2C	72–105	1.00	11.3	8.8	54	6.8	1.0	17.8	0.5	4.6	5.8	1.3	0.1	1.6	19	3	–
S5	Vitrandic	A1	0–5	1.12	11.7	7.7	15	2.2	0.4	12.5	0.3	2.0	1.8	0.9	0.2	0.8	31	1	
	Haploxeroll	A2	5–30	1.09	8.2	7.6	18	1.6	0.3	8.3	0.3	2.1	1.3	0.6	0.2	0.6	29	1	–
		Bw1	30–90	1.00	8.1	7.6	15	1.6	0.4	8.1	0.3	2.1	1.2	0.6	0.2	0.6	15	1	–
		Bw2	90–134	0.99	8.4	7.5	13	1.5	0.2	7.3	0.1	2.0	1.2	0.6	0.2	0.5	21	1	–
		2C	134+	1.26	7.7	7.8	18	1.7	0.8	9.7	0.6	2.6	0.9	0.3	0.5	0.7	20	1	–

[a] Al_o: acid oxalate extractable Al.

[b] Al_p: pyrophosphate extractable Al.

[c] Fe_o: acid oxalate extractable Fe.

[d] Fe_p: pyrophosphate extractable Fe.

[e] Si_o: acid oxalate extractable Si.

[f] Al_o–Al_p: Al present as allophane/imogolite.

[g] Al_p/Al_o: binary ratio (ranging 0=all allophane and 1=all humus–Al).

[h] Glass in the 0.02 to 2.0 mm fraction (percentage), by Holmgren (1967).

[i] nd: not determined.

[j] nc: not calculated, Al/Si >2.5.

Table 3
Chemical properties of soil samples

Study site	Soil classification (Soil Survey Staff, 1999)	Horizons	Depth (cm)	pH		Ca^{2+}	Mg^{2+}	K^+	Na^+	Σ	ECEC[a]	CEC[b]	Organic carbon	HAc[c]	FAc[d]	Hc[e]	C/N	HAc/FAc
				H_2O	KCl	(cmol(+) kg^{-1})							(g kg^{-1})					
S1	Thaptic Udivitrand	O	12–0	nd[f]	nd	1.6	1.0	1.1	0.9	4.5			147				25	
		C?	0–3	5.3	4.6	6.8	1.4	0.5	0.5	9.2	9.2	nd	73	nd	nd	nd	nd	nd
		2A1	3–13	5.5	4.8	7.6	0.6	0.3	0.4	9.0	9.1	nd	32	19.9	8.7	26.7	26	2.3
		2A2	13–35	5.6	5.0	6.8	0.2	0.3	0.5	7.8	7.9	nd	24	13.3	8.3	12.6	16	1.6
		2Bw1	35–54	5.4	5.3	5.2	0.2	0.3	0.5	6.1	6.2	nd	26	12.2	9.2	12.6	18	1.3
		2Bw2	54–70	5.1	5.1	4.0	1.3	0.2	0.5	6.0	6.1	nd	20	7.5	8.5	9.2	22	0.9
		2Bw3	70–90	5.2	5.2	5.2	tr[g]	0.2	0.4	5.9	6.0	nd	16	7.0	9.8	11.6	26	0.7
		3Ab	90–110	5.5	4.9	4.4	0.7	0.2	0.4	5.7	5.8	nd	30	8.1	7.7	7.5	nd	0.1
S2	Typic Hapludand	O	3–0	nd	nd	2.6	1.1	0.9	1.0	5.7			201				28	
		A1	0–30	5.4	5.1	18.0	0.6	0.7	0.5	19.8	19.9	nd	73	33.8	9.5	48.6	20	3.6
		A2	30–43	5.6	5.2	10.4	2.7	0.7	0.4	14.2	14.3	nd	44	22.6	10.2	28.6	18	2.2
		AB	43–55	5.7	5.1	9.6	1.2	0.4	0.5	11.7	11.8	nd	39	17.4	10.9	1.9	20	1.6
		Bw1	55–85	5.7	5.2	10.0	tr	0.4	0.5	10.8	10.9	nd	37	11.6	12.1	1.6	22	1.0
		Bw2	85–110+	5.8	5.2	7.2	1.4	0.4	0.6	9.6	9.7	nd	19	3.8	15.4	8.9	12	0.2
S3	Typic Hapludand	A1	0–30	4.9	5.3	18.7	0.1	0.7	0.4	19.9	20.0	nd	46	24.2	2.1	36.0	24	11.6
		A2	30–70	5.7	5.2	11.8	0.6	0.5	0.4	13.3	13.4	nd	40	13.5	nd	25.0	22	nd
		Bw	70–110	5.4	5.2	12.0	1.8	0.3	0.4	14.3	14.4	nd	41	15.7	nd	26.0	22	nd
S4	Humic Vitrixerand	A	0–13	6.4	5.5	6.7	1.7	0.2	0.9	9.5	9.6	nd	16	7.1	1.1	8.1	12	6.4
		Bw1	13–35	6.5	5.5	6.7	0.6	0.2	1.0	8.6	8.7	nd	17	8.3	1.0	9.3	12	8.6
		Bw2	35–72	6.4	5.3	6.3	0.6	0.3	0.9	8.0	8.1	nd	16	8.4	tr	11.0	15	nc[h]
		2C	72–105	6.3	5.1	9.0	1.2	0.3	1.6	12.1	12.2	nd	17	8.2	0.5	12.0	14	17.3
S5	Vitrandic Haploxeroll	A1	0–5	6.2	5.3	11.9	1.8	0.6	4.6	18.8	18.8	15.3	22	4.4	0.5	7.9	9	9.8
		A2	5–30	6.5	5.6	10.3	2.2	0.5	2.3	15.4	15.4	14.0	13	5.1	tr	16.0	10	nc
		Bw1	30–90	6.6	5.6	11.9	3.7	0.6	4.8	21.0	21.1	16.1	6	6.2	tr	6.0	6	nc
		Bw2	90–134	6.9	5.7	10.7	4.1	0.8	1.3	16.9	17.0	18.7	3	4.3	tr	3.0	4	nc
		2C	134+	6.6	5.4	19.0	5.3	0.9	2.4	27.6	27.7	26.6	1	3.4	tr	6.0	3	nc

[a] ECEC: effective cation exchange capacity.
[b] CEC: cation exchange capacity at pH 7.
[c] HAc: C content present as humic acids.
[d] FAc: C content present as fulvic acids.
[e] Hc: C content present as non extractable residue.
[f] nd: not determined.
[g] tr: traces.
[h] nc: not calculated.

Andisols under udic soil moisture regime to slightly acidic and almost neutral in the Xerand and Xeroll. There existed the opinion that a decrease in soil acidity was closely related with an increase in base saturation and also with the composition of colloid component (Shoji et al., 1988). The total exchangeable base content in S1 as compared to S5 was the only striking example, where an increase in amount of bases coincided with a decrease in soil acidity. The higher base concentration and the decrease in soil acidity in S5 were perhaps attributed to less leaching, hence lower losses of bases, due to lower MAP. However, the data also suggested that the higher pH_{water} values could perhaps be related to the lower Al activity and to lower organic matter content of the Xerand and Xeroll as compared to those in the Andisols with udic moisture regime (Tables 2 and 3). pH_{NaF} values were higher than 9.2 in all soil horizons of the Andisols with udic moisture regime indicating the presence of active Al (Saigusa et al., 1991). Relationships between pH_{water} and the factors which may explain its variation were examined by a simple and a multiple regression analysis (stepwise). pH_{NaF} was the variable which explained the greatest amount on variation in pH_{water} (R^2=0.6204, p<0.0000), followed by MPA (R^2=0.5868, p< 0.00001) and C_{org} (R^2=0.4282, p<0.0003). Total base content was not enough to explain the pH_{water} variation (R^2=0.095, p<0.07). When all factors were combined in a multiple regression analysis, only two variables were included–pH_{NaF} and C_{org}–which increased the explained variation of pH_{water} (R^2= 0.7806, p<0.0000). This confirms, to a certain extent, that soil acidity was closely related with Al activity and organic matter content, rather than with base content. On average, pH_{KCl} values were 0.6 units lower than those in water indicating a net negative charge for all horizons (Tan, 1996, 1998) except for A1-horizon in S3 in which an inverse relation was found. The exchange acidity was very low in all cases according to the pH range in which no exchangeable Al is expected to happen.

The ECEC of the pedons from west to east showed a tendency to vary according to the differences noted for exchangeable bases, which was also true for their differences noted at other depths in the pedon. In view of the definition of ECEC and the low and constant exchange acidity, this was to be expected.

The data in Table 3 indicated that C_{org} was high in the Andisols with udic soil moisture regime (A-horizon: 32 g kg^{-1} to 73 g kg^{-1}) as is usually the case in Andisols (Shoji et al., 1993), but lower in the Xerand and Xeroll (A-horizon: 13 g kg^{-1} to 22 g kg^{-1}) which were typical for those in Mollisols in Argentina (Rosell et al., 1978). Differences in the C/N ratios, with values in surface horizons ranging from 16 to 26 at S1, S2, and S3 versus 9 to 12 at S4 and S5, suggested that the rate of mineralization was faster with xeric moisture regime and higher mean annual temperature than with udic moisture regime and lower mean annual temperature. The humic C/fulvic C ratio (HAc/FAc) can be used as a suitable index for the degree of organic matter degradation. There was a remarkable difference in the HAc/FAc ratios among the A-horizons of Andisols, and this may be largely due to the differences in the nature of plant residues indicating a sensible contribution of the cover of grass-shrub steppe to the formation of humic substances. Ratios ranging from 1.6 to 3.6 were observed under *Nothofagus* forest (S1, S2); in contrast, the corresponding values were from 6.4 to 11.6 under grass-shrub steppe (S3, S4). In the Mollisol (S5) the HAc/FAc ratio was 9.8 where the vegetation was also grass-shrub steppe. In the *Nothofagus* forest the input of organic matter is mostly litterfall with a C/N ratio from 25 to 28 (Table 3) whereas in the grass-shrub steppe it is due to both litterfall and roots with a much higher C/N ratio—grasses from 86 to 227 and shrubs from 18 to 47 (Mazzarino et al., 1998).

The general belief is that one of the factors for organic matter stabilization and accumulation in Andisols is its interaction with Al, i.e. its preservation as Al-humates. However the present data failed to show a relationship between Al_o and organic matter content. The correlation with r=0.324 and df=21 was statistically non significant even at the 95% level.

3.2. Andic soil properties and classification

All soils showed andic properties with high glass content in the coarse fraction. S1, S2, S3, and S4 applying the first and/or the second criterion qualify as Andisols. S5 was the only case that did not qualify as Andisol, but qualified for Mollisol with a mollic epipedon and a base saturation higher than 50% in all horizons, meeting the vitrandic criterion at subgroup level (Soil Survey Staff, 1999). By using the average figures of the sum of Al_o+1/2Fe_o (for S1, S2, and S3 >2; for S4 and S5≤1) and glass percentage (%), we found that the glass % was almost constant (~25%) but andic features (Al_o+1/2Fe_o) decreased in soils from udic to xeric moisture regime. Al_o also decreased substantially from 7.1 to 26.7 g kg^{-1} in S1, S2, and S3, to 1.5–6.8 g kg^{-1} in S4 and S5 (Table 2), from which we may infer a decrease in weathering from udic to xeric moisture regime, also reflected in P-retention and pH_{NaF}. In contrast, the Fe_o showed only a slight decrease with values of (Fe_o–Fe_p) which indicate that Fe is present as amorphous Fe-oxy-hydroxides. In the Andisols under study, Al_o also increased within soil profiles implying a higher weathering of subsuperficial horizons. Parfitt and Henmi (1982) have shown that allophane contents can be estimated from extractable Si and Al and that such estimates agree with those of infrared analysis. The samples of soils, which qualified as Andisols in the present study, had low levels of Si_o (0.3% to 1.6%). From this the authors infer that the soils examined are probably in an early stage of development. The Si_o values also indicated a low rate of weathering, although higher under *Nothofagus* than under grass-shrub steppe with a certain independence from soil moisture regime (Tables 2 and 4). The estimated allophane soil content was highest under *Nothofagus* (S1, S2; 2% to 10%), decreased under grass-shrub steppe (S3, S4; 2% to 5%), and was lowest in S5 (1%). From this, a certain influence of vegetation on soil weathering may be inferred, being probably higher under *Nothofagus* than under grass-shrub steppe. This fact may be attributed to the differences in type and quantity of organic matter input, with a higher organic matter content and lower HAc/FAc ratio under *Nothofagus.* The lower HAc/FAc values indicate a more reactive organic matter due to the higher content of functional groups of fulvic acids (FA) which may be somewhat responsible for the weathering degree. S3 showed an intermediate case in which evidence of the effect of soil moisture regime and vegetation type are superposed.

Al_p/Al_o yield information about the relative composition of colloidal fraction, being 0.5 the ratio value used to separate Al-humus complexes (<0.5) from allophanic materials (>0.5; Shoji et al., 1988; Mizota and van Reeuwijk, 1989; Saigusa et al., 1991). The observation that these values were in average ≥0.5 in S1, S2, and S3 A-horizons suggest that much of the extractable Al was present in Al-humus complexes rather than in allophane. On the other hand, no relationship between Al_o and C_{org} was found suggesting that organically bond Al is not dominant, also supported by a nonsignificant correlation between Al_o and C_{org}. Since the allophane estimations were highest in soils with the highest C_{org} levels, e.g. S1 and S2, these results may indicate that the anti-allophanic hypothesis presented by Shoji et al. (1993) and Huang and Huang (1995), indicating that formation of Al-humates has prevented the formation of allophane, may not apply in these soils.

Table 4
Comparative table of mean values of some selected soil profile properties

Sites	S1	S2	S3	S4	S5
Soil moisture regime	udic			xeric	
Vegetation type	*Nothofagus* sp.		grass-shrub steppe		
Soil order	Andisol				Mollisol
Bulk density (Mg m^{-3})	0.73	0.70	0.76	1.07	1.09
pH_{Water}	5.4	5.6	5.3	6.4	6.6
pH_{NaF}	10.0	9.9	9.6	8.7	7.6
Al_o[a] (g kg^{-1})	14.6	19.3	10.7	5.6	1.7
P-ret.[b] (%)	92	84	59	38	15
Si_o[c] (g kg^{-1})	6.7	7.6	3.9	4.1	2.2
Estimated allophane (%)	4.5	7.6	2.1	2.5	1.0

[a] Al_o: acid oxalate extractable Al.
[b] P-ret.: phosphate retention.
[c] Si_o: acid oxalate extractable Si.

4. Conclusions

A recapitulation of the main findings of this study would be: (1) The change from an udic to a xeric soil moisture regime resulted in (i) a change from low bulk density into medium density values. The differences of bulk density of soils with xeric regime as compared to those with udic soil moisture regime were related to a lower rate of weathering probably coinciding with a lower content of allophane and higher clay crystallization and to a decrease in organic matter content. (ii) A change from moderately and strongly acidic to slightly acid and almost neutral which was closely related with Al activity and organic matter content, rather than with base content. (iii) A decrease in the C/N ratios in surface horizons suggests that the rate of mineralization was faster with xeric moisture regime and higher annual temperature than with udic moisture regime and lower annual temperature. (2) The differences between the vegetation types resulted in differences in HAc/FAc ratios which were higher under grass-shrub steppe than under *Nothofagus* forest indicating a sensible contribution of the cover of grass-shrub steppe to the formation of humic substances. Evidence was found about the possible effect that the differences in type of organic matter accumulating in various soils might have on expression on weathering, being higher under *Nothofagus* than under grass-shrub steppe. This was probably due to the higher content of functional groups of FA which may be somewhat responsible for the weathering degree. (3) No relationship between Al_o and C_{org} was found suggesting that organically bond Al is not dominant. Allophane content estimations, detected in highest amounts in soils with highest C_{org} contents, appeared to be contrary to the anti-allophanic hypothesis, indicating that formation of Al-humates has prevented the synthesis of allophane.

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