Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA)
Available online at www.inia.es/sjar
http://dx.doi.org/10.5424/sjar/2012102-351-11

Spanish Journal of Agricultural Research 2012 10(2), 513-520
ISSN: 1695-971-X
eISSN: 2171-9292

Fractionation of extractable aluminium and biomass production in an acid soil treated with calcareous amendments

M. Vidal-Bardán* and E. Villa-Bermejo

School of Agricultural Engineering, University of León, Avenida de Portugal 41, 24071 León (Spain)

Abstract

A Typic Palexerult in the *raña* formations of the northern plateau in the province of León (Spain) was subjected to acidity correction field tests over a period of three years. The experimental crop was a local rye variety (*Secale cereale* L. var. Petkus) and the amendments included gypsum, dolomite, limestone and sugar foam waste, all at a 6,000 kg ha^{-1} rate as $CaCO_3$. General analyses were integrated with specific tests for soluble and easily exchangeable Al forms (Al-$CaCl_2$) in addition to KCl, $BaCl_2$ and $CuCl_2$ extracted Al; adsorbed Al (NH_4AcO) and amorphous Al. Two types of multiple linear regression models (OLS) for production each year were established; some encompassed all studied variables and others the six Al forms only. As shown here, Al-KCl, Al-$CaCl_2$, base saturation and exchangeable Ca were the individual variables most strongly correlated with production, with R^2 = 0.865, within the topmost 12 cm of the soil layer receiving the calcareous amendments. A principal component analysis exposed a substantial share of pH-dependent charge in organic matter on the cation exchange capacity of the soil.

Additional key words: acidity; biomass; cation-exchange capacity; OLS equation; pH-dependent charge; pH increment.

Resumen

Fraccionamiento del aluminio extraíble y producción de biomasa en un suelo corregido con materiales calizos

Se han realizado unos ensayos de campo de tres años de duración encaminados a la corrección de la acidez de un Typic Palexerult de las formaciones de *raña* de la meseta norte de la provincia de León (España). El cultivo ensayado fue una variedad local (Petkus) de centeno (*Secale cereale* L.), empleándose como materiales calizos en la enmienda del suelo yeso, dolomita, caliza y espumas de azucarería, con dosis de 6.000 kg ha^{-1} de $CaCO_3$ equivalente. Además de la analítica general, se determinaron las formas de Al solubles y fácilmente intercambiables (Al-$CaCl_2$), además del Al extraído con KCl, $BaCl_2$ y con $CuCl_2$ estimándose también el Al-adsorbido (NH_4OAc) y el Al-amorfo. Se establecieron dos tipos de modelos de regresión lineal múltiple (OLS) de la producción anual de biomasa; el primero incluye todas las variables analizadas, mientras que en el segundo únicamente se consideran las seis formas de Al analizadas. Se comprueba que el Al-KCl, el Al-$CaCl_2$, el porcentaje de saturación de bases y el Ca de cambio son las variables más correlacionadas con la producción, alcanzándose valores de R^2 = 0,865, al considerar únicamente los 12 cm superficiales del horizonte en el que incorporó la enmienda caliza. Finalmente, mediante el análisis de componentes principales, se deduce el importante efecto de la carga dependiente del pH de la materia orgánica en el aumento de la CIC del suelo.

Palabras clave adicionales: acidez; biomasa; capacidad de intercambio catiónico; carga dependiente del pH; incremento de pH; regresión.

Introduction

Xerults are Ultisols possessing a xeric moisture regime in the Soil Taxonomy (Soil Survey Staff, 1999) and the equivalents, among others, of Alumic Acrisols in the WRB classification (FAO, 1998). Knowledge with the agricultural management of Ultisols under a Mediterranean climate is more limited than that with

*Corresponding author: mavidb@unileon.es
Received: 18-07-11. Accepted: 07-05-12

Abbreviations used: BS (base saturation); CEC (cation-exchange capacity); Dw (Darwin-Watson statistic); EC (electrical conductivity); ECEC (effective cation-exchange capacity); OLS (ordinary least-squares); OM (organic matter); PCA (principal component analysis).

the suborders Udults and Ustults, which are associated to regions with a subtropical (warmer, wetter) climate and more widely distributed worldwide (Soil Survey Staff, 1999). Palexerults are well represented in the central, western and northern regions of the Iberian Peninsula (Spain and Portugal). Most occur in old *raña* surfaces. A *raña* is a form of relief from the middle-upper Pliocene possessing a gentle slope and a continental detrital cover, and usually associated to quartzite ranges in nearby mountain range (Espejo, 1987).

Xerults are subject to two major agronomic shortcomings. One is the presence of argillic horizons with heavily altered minerals, a high content in exchangeable Al and, as a result, a low content in essential elements such as Ca, Mg, Cu, Zn and P. The content in phytotoxic Al^{3+} increases and pH decreases (particularly in underlying Bt horizons) with increasing horizon depth in the soil profile (Boul *et al*., 1997). The other limiting factor for the suborder Xerults in relation to Udults is a result of its xeric moisture regime, which is highly typical of the Mediterranean region. This regime governs water availability during plant growth, which is hindered by a high water stress during the summer.

The previous two limiting factors (*i.e.* an extreme acidity and prolonged drought in the soil moisture control section) require that soil management be aimed at two specific targets for success, namely: (a) reducing the contents in phytotoxic Al^{3+} and (b) facilitating growth and expansion of the rhizosphere (particularly in the AB and Bt horizons). The essentially clayey nature of the argillic horizon can be useful towards increasing the soil water reserve in the root zone (Ritchey *et al*., 1995).

As a rule, the low solubility of the calcareous materials used for agronomic liming (limestone and dolomite, mainly) hinders efficient reduction of Al^{3+} toxicity in sub-surface soil horizons (Reeve & Sumner, 1970, 1972). The low mobility of these materials can be overcome by replacing them with gypsum or sugar foam waste, which are more soluble and hence more efficient in reducing Al saturation in the Bt horizon (Shainberg *et al*., 1989). Specifically, gypsum is known to raise the Ca/Al ratio in soil (Lund, 1970; Noble *et al*., 1988; Kinraide *et al*., 1992) and also to facilitate the formation of $AlSO_4^+$ ion pairs (Pavan *et al*., 1982; Kinraide & Parker, 1987; Kinraide *et al*., 1992) in addition to boosting the self-liming effect reported by Reeve & Sumner (1970, 1972).

The primary aims of this field work were to identify the most suitable analytical variables for predicting biomass production in limed soil and establish their temporal changes, particularly as regards the exchange complex.

Material and methods

The experiment was conducted on an extremely acid Typic Palexerult from the Camposagrado *raña* (N León, Spain) over a period of three cropping years (2007-08, 2008-09 and 2009-10). The average annual temperature, annual rainfall and evapotranspiration of the study area are 10.2°C, 667 mm and 640 mm, respectively. Based on these figures, the soil temperature and moisture regimes are Mesic and Xeric respectively.

The experimental crop was a local rye variety (*Secale cereale* L.; Petkus) and the calcareous amendments used included limestone, mineral gypsum (white alabaster variety), dolomite and sugar foam. The last is a waste from the beet sugar industry. All amendments were applied in April 2007 and buried at a depth of 20 cm at an identical rate (6000 kg ha^{-1} as $CaCO_3$) (Vidal *et al*., 2003) for incorporation into the soil in a rotavator pass. The chemical composition of the four amendments was determined by atomic absorption spectrometry following alkaline fusion and digestion with HF and $HClO_4$ (Jackson, 1976). The experimental design was a randomized block with four replicates per treatment in addition to control plots. Each plot was 3 m × 5 m in size and separated from the next by a 2 m lane. The amount of seed per area unit employed in the rye field trial was 100 kg ha^{-1}. Background fertilizer was supplied in the form of an 8/15/15 complex to give 12.0 kg N ha^{-1}, 22.5 kg P_2O_5 ha^{-1} and 22.5 kg K_2O ha^{-1}. The cover fertilizer consisted of 38 kg N ha^{-1} as 33% calcium ammonium nitrate. This fertilization scheme coincides with the traditional choice of the local farmers. Broad-leaved adventitious plants were controlled with 40% MCPA at a rate of 1-L ha^{-1} during the spring. Plants were harvested 16 cm aboveground with a self-propelled mower, the aerial (collected) portion constituting the total biomass production for each plot and the uncut portion stubble.

Control measurements were made by periodically sampling the Ap and AB horizons with a 10 cm Riverside drill. To this end, the Ap horizon was split into two: Ap1 (0-12 cm) and Ap2 (12-25 cm). A total of six samplings were done over the studied period; three in March (shortly after establishment of the rye crop) and three after harvesting (October). The soil samples were air-dried and sieved through 2 mm mesh. Soil samples were analysed for pH in water and in 1 M KCl (1:2.5), electrical conductivity (EC) and organic matter (OM) (Walkley & Black, 1934). Soil texture was established according to Kilmer & Alexander (1949). Exchangeable bases were extracted with 1 M NH_4AcO at pH 7 and quantified by atomic absorption spectrometry (Ca and Mg) or flame emission spectrometry (Na and K). Cation-exchange capacity (CEC) was determined by titrating NH_4^+ in a Kjeldahl autotitrator. Aluminium was extracted with 1 M KCl (Al-KCl) according to Lin & Coleman (1960) and determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Soluble and easily exchangeable Al were extracted with 0.01 M $CaCl_2$ (Al-$CaCl_2$) according to Hoyt & Nyborg (1972), and so was Al-$BaCl_2$ with 0.1 M $BaCl_2$ (Peech *et al.*, 1947). Aluminum bound to organic matter (Al-$CuCl_2$) and outer sphere complexes (Al-sorbed or Al extracted with 1 M NH_4AcO at pH 4) was also determined. Amorphous Al oxide and hydroxide, and amorphous aluminosilicates (if present) extractable with 0.2 M ammonium oxalate at pH 3 were also quantified. Amorphous Al oxide and hydroxide were calculated from ammonium oxalate extractable Al minus (Al-KCl + Al-$CuCl_2$ + Al-sorbed), following the sequential scheme of Soon (1993). Aluminium in the previous fractions was determined by ICP-AES. The experimental data were used to calculate the percent base saturation (BS), effective cation-exchange capacity (ECEC) and percent Al saturation (Al-SAT).

The results thus obtained allowed empirical equations for rye biomass production to be constructed by ordinary least-squares (OLS) multiple linear regression in combination with the stepwise method. A total of twelve variables were studied, namely: pH_{water}, OM, ΔpH, CEC, Al-KCl, Al-$CaCl_2$, Al-$CuCl_2$, Al-$BaCl_2$, Al-sorbed, Al-amorphous, BS and Al-KCl/CEC. Variables were included or excluded in the model by using the stepwise method in accordance with preset criteria. The statistics determined for each equation included the coefficient of determination, R^2, and the ANOVA F, which was used to identify significant relationships between biomass production and each measured variable. In addition, stability and accuracy in the individual and standard regression coefficients were assessed by considering the significance of both the constant and the other regression coefficients. Finally, the Darwin-Watson statistic for each equation was used as an estimate of potential autocorrelation between errors. The multiple linear regression analysis was supplemented with principal component analysis (PCA) for multivariate data reduction. All statistical computations were done with the software SPSS v. 15.

Results

The results of the chemical analyses of the liming materials are shown in Table 1. Dolomite was the amendment containing the greatest amount of Mg, and limestone and sugar foam those containing the most Ca. Also, Al was present in increased amounts in limestone and dolomite by virtue of their containing silicates. Unlike the other amendments, sugar foam waste contained 79 g kg^{-1} OM with a C/N ratio of 11.0.

Tables 2 and 3 show the results of the physical and chemical characterization of the topmost three soil horizons. Texturally, the soil ranged from sandy loam in the Ap (umbric) horizon to sandy clayey loam in the AB (transition) horizon to clayey in the Bt (argillic) horizon.

Figure 1 shows the average total rye biomass production for each cropping year as obtained in the four replicates for the soil amended with limestone. The figure also shows the mean production per year for

Table 1. Chemical composition of the calcareous amendments

	CaO (g kg^{-1})	MgO (g kg^{-1})	Na_2O (g kg^{-1})	K_2O (g kg^{-1})	Al (mg kg^{-1})	Fe (mg kg^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	OM (g kg^{-1})
Sugar foam	403.8	14.7	0.4	1.0	2,469	1,420	121	32	12.0	79
Limestone	437.0	20.8	0.4	3.5	7,869	5,787	299	24	11.0	0
Dolomite	311.0	184.0	1.2	3.5	9,529	10,483	361	26	12.0	0
Gypsum	331.6	17.5	0.7	1.5	3,351	1,826	41	16	4.6	0

Table 2. General characterization of the studied soil

Horizon	Depth (cm)	pH-water	pH-KCl	ΔpH	Sand (%)	Silt (%)	Clay (%)	OM (g kg^{-1})	EC (dS m^{-1})
Ap	0-25	5.0	3.9	–1.1	57.7	23.1	19.2	24.6	0.031
AB	25-35	4.8	3.9	–0.9	54.3	18.4	27.3	6.5	0.035
Bt	35-55	4.7	3.6	–1.1	42.5	11.2	46.3	6.8	0.052

Table 3. Characteristics of the exchange complex. Aluminium extracted by KCl and bases extracted by NH_4AcO. All values are in cmol(+) kg^{-1}

Horizon	Ca	Mg	Na	K	Al	CEC	ECEC	BS (%)	Al-SAT(%)	Al-KCl/CEC
Ap	1.40	0.20	0.03	0.21	1.14	5.70	2.98	32.2	38.3	0.200
AB	1.32	0.18	0.02	0.13	1.64	5.48	3.29	30.1	49.8	0.299
Bt	1.87	0.30	0.03	0.12	3.10	9.45	5.42	24.7	57.1	0.328

each treatment in addition to the standard error of mean (SE), which was the statistic used to quantify scatter and estimate the variability of the mean between samples. Biomass production was clearly greater in the third year; also, sugar foam waste was the most effective amendment (up to 6,008 kg ha^{-1}), followed by dolomite and limestone. Figure 2 lists the mean values of pH-water and pH-KCl (ΔpH) of the three subhorizons (Ap1, Ap2 and AB) by effect of the treatments.

The results for each cropping year were used to develop two different equations. One included all measured variables (12), whereas the other only considered the six Al forms corresponding to the sequential extractions (*viz.* Al-KCl, Al-$CaCl_2$, Al-$CuCl_2$, Al-$BaCl_2$, adsorbed Al and amorphous Al). Only the data for the Ap1 subhorizon were used in both the first model and that considering the six Al forms alone.

If the average production (kg ha^{-1}) of the plots subjected to any of the four treatments is denoted by P, then the equations for the models including all

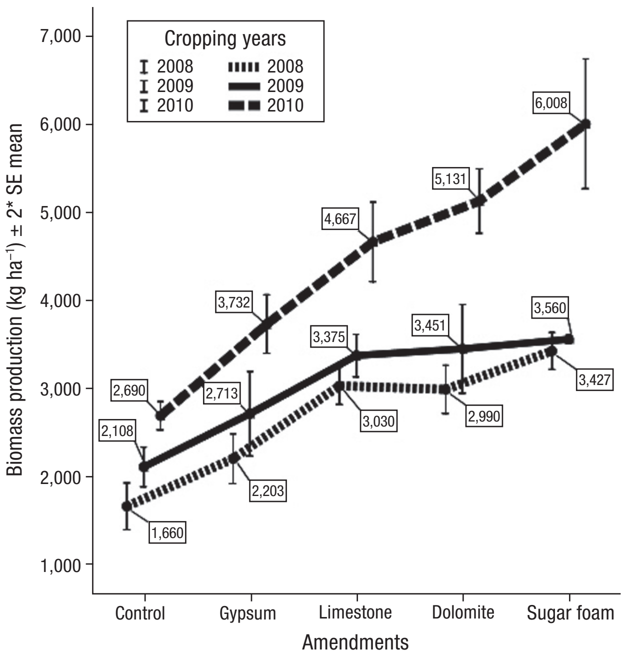

Figure 1. Average total biomass production (kg ha^{-1}). Standard errors (SE mean) are shown as bars at a double scale (± 2*SE mean).

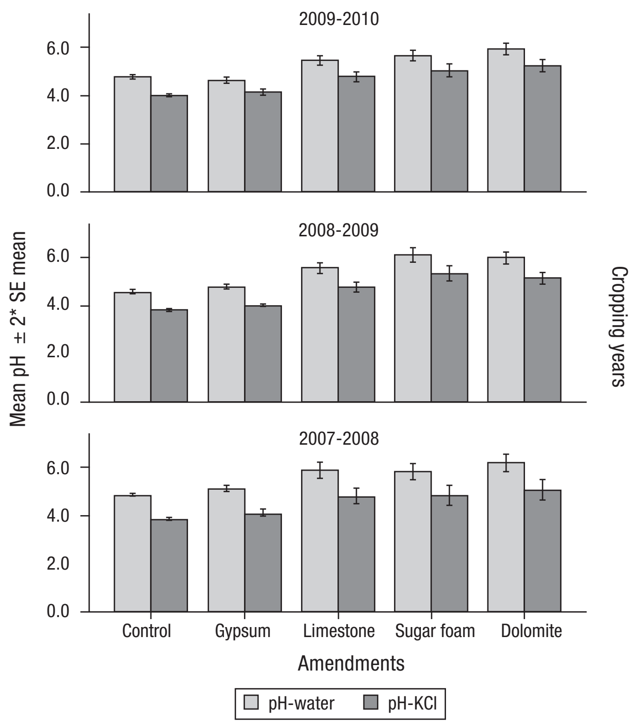

Figure 2. Variation of the average values of pH for Ap1, Ap2 and AB subhorizons during the three cropping years. Standard errors (SE mean) are shown as bars at a double scale (± 2*SE mean).

studied variables are (Dw is Darwin-Watson statistic):

$$P_{2007\text{-}08} = 3468.5 - 0.779\text{Al-KCl}$$
$$(R^2 = 0.606, F = 0.000, \text{Dw} = 1.423)$$

$$P_{2008\text{-}09} = -2053.7 + 662.2\text{pH}$$
$$(R^2 = 0.706, F = 0.000, \text{Dw} = 1.641)$$

$$P_{2009\text{-}10} = 2391.0 + 1.5\text{BS} - 0.678 \times \text{Ca}$$
$$(R^2 = 0.865, F = 0.000, \text{Dw} = 1.792)$$

And those for the models including the six Al forms only:

$$P_{2007\text{-}08} = 3362.0 - 0.810\text{Al-CaCl}_2$$
$$(R^2 = 0.656, F = 0.000, \text{Dw} = 2.218)$$

$$P_{2008\text{-}09} = 466.4 - 726.4\text{Al-KCl} + 252.5\text{Al-amorphous}$$
$$(R^2 = 0.704, F = 0.000, \text{Dw} = 1.978)$$

$$P_{2009\text{-}10} = 5374.5 - 0.858\text{Al-KCl}$$
$$(R^2 = 0.737, F = 0.000, \text{Dw} = 1.881)$$

Figures 3a and 3b show the factor saturation diagrams of the principal component analysis (PCA) for the first and third cropping year, respectively, and the four amendments in combination plus the control. PCA was applied to 12 analytical variables for the Ap1 subhorizon alone and included total biomass production in order to facilitate the analysis of temporal changes in the variables and their correlation with total annual biomass. The first two principal components (PCs) accounted for 69.6% of the total variance for the first year and 71.4% of that for the third. The first PC can be assigned to the axis reflecting pH and the factors governing it during the soil acidity correction process, whereas the second reflects the nature of the exchange complex in the Ap1 subhorizon and its changes.

Figure 4 shows the variation of the Al-KCl/CEC ratio as a function of pH-KCl for the two Ap subhorizons and the AB horizon in the control plots, which were only subject to the effect of the crop. The data correspond to the 24 samples from each of the three studied horizons (Ap1, Ap2 and AB) in the control plots, which were obtained in four replications of three yearly samplings; a total of 72 samples are thus included. Differences between horizons are clearly reflected in the substantial decrease in Al-KCl/CEC ratio observed in the Ap subhorizons and AB horizon.

Discussion

The differences between the pH values in KCl and water (ΔpH) were negative and amounted to approximately one unit (Table 2), which suggests the presence of net charge in the studied soil. Also, the relationship between pH and the degree of base saturation (BS) was very similar to that of kaolinite, which was the dominant mineralogical species (65%), followed by illite (20%) and vermiculite (5%) —the two minor species (Villa, 2005). Villa (2005) previously found gibbsite and goethite contents to increase with increasing horizon depth, and hematite to exhibit the opposite trend. As can be inferred from the Al-SAT values of Table 3, aluminum was the dominant cation in the exchange complex; thus, Al-SAT accounted for 38.3%,

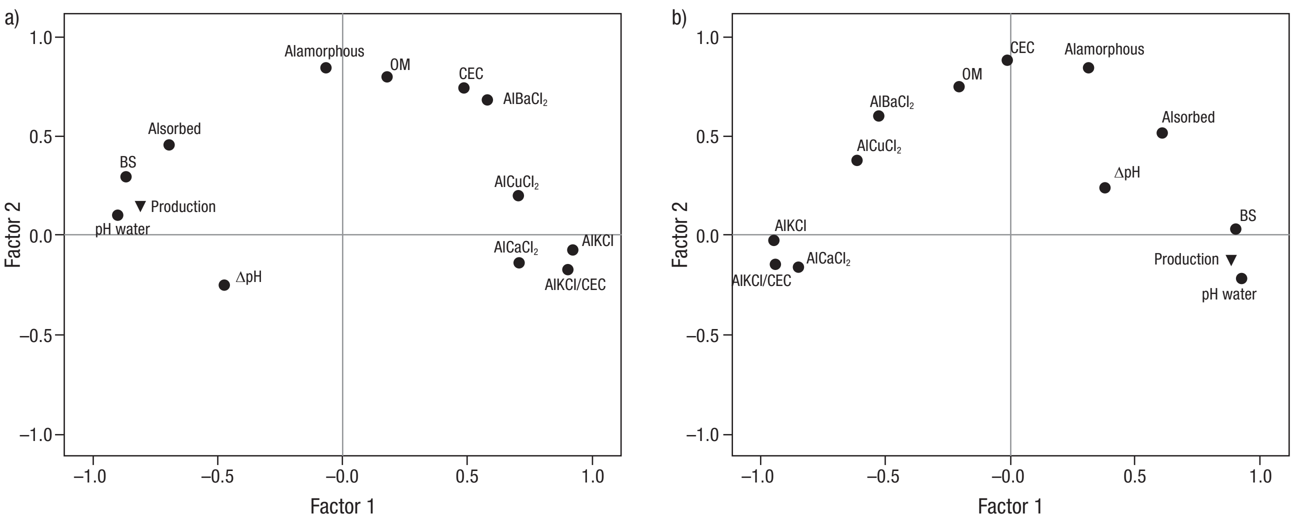

Figure 3. Factor saturation diagram for a) the first cropping year (2007-08) and b) the third cropping year (2009-10), and the Ap1 subhorizon. ΔpH-net charge; BS-base saturation; OM-organic matter; CEC-cation-exchange capacity.

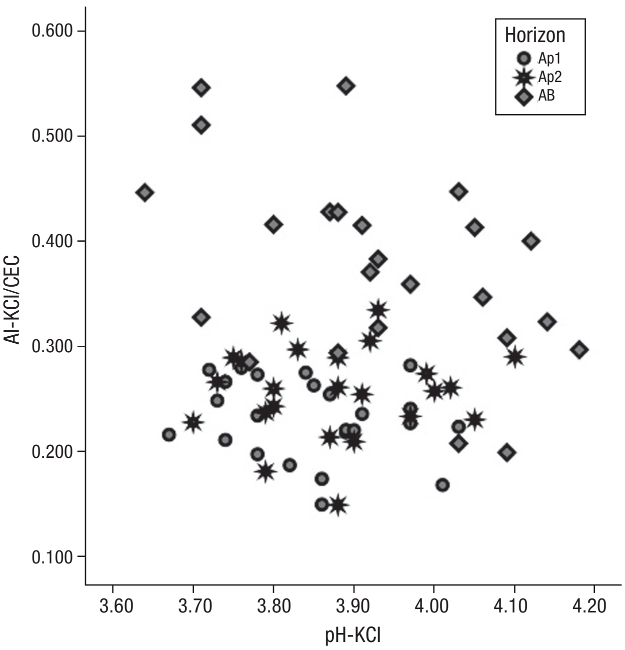

Figure 4. Exchangeable aluminium as a CEC fraction in the control plots.

49.8% and 57.1% in the Ap, AB and Bt horizon, respectively. All three horizons clearly exceeded the accepted phytotoxicity threshold for wet Spanish regions, which, according to Mombiela & Mateo (1984), is an Al-SAT level exceeding 20%. Although variable charge associated to organic matter in a highly acid soil is usually low (Thomas & Hargrove, 1984), we used the Al-KCl/CEC ratio as an estimate of pH-dependent charge in the soil organic fraction. As can be seen from Table 3, the Ap (umbric) horizon had a higher CEC and a lower exchangeable Al concentration than the AB horizon; as a result, the former exhibited a higher Al-KCl/CEC ratio. Likewise, the umbric horizon contained more OM and less clay than the AB and Bt horizons; therefore, variable, pH-dependent charge was a result mainly of organic matter in the Ap horizon. The superiority of this agroindustrial waste as an amendment is well documented (Espejo *et al.*, 1991) and has been ascribed to its increased content in active, readily dissolved limestone, and also to its fine texture —and increased surface/weight ratio as a result (Peregrina *et al.*, 2006). The increased total biomass production in the third year was due not only to the effect of the liming amendments —and hence, to the increased soil pH— observed in the plots receiving the liming amendments (Fig. 2), but also to the improved agroclimatic conditions and soil water balance. Thus, precipitation was 548.7 mm the first year (2007-08) and 958.5 mm the third (2009-10), the latter exceeding the mean annual rainfall for the study area (667 mm).

Only the regression equations for the Ap1 subhorizon are discussed since the highest R^2 values were invariably obtained in the topmost 12 cm of soil. Including the Ap2 subhorizon and/or the AB horizon in the calculations led to poorer multiple linear regression fitting, as well as to lower proportions of explained variance. These results suggest that the liming amendment and its final incorporation into the soil after three years were only effective within the topmost 12 cm.

The explained variance, R^2, increased gradually each year with both the 12-variable model and the 6-variable model, and peaked in the third year, once the liming material started to act and the acid correction effect on the topmost 12 cm of the Ap1 subhorizon increased. All F values were significant at the $p = 0.05$ level, which confirms the linear relationship between biomass production and the variables included in each regression model. Also, the residuals were independent, as reflected in Dw, which ranged from 1.4 to 2.2 (Dw is close to 2 for random, independent errors). Similarly apparent was the strongly adverse effect of the content in exchangeable Al (Al-KCl) during the first year, which was the sole variable present in the $P_{2007-08}$ linear regression equation corresponding the first group of OLS equations. The results for the second group confirmed that the most phytotoxic Al form was Al-$CaCl_2$ (*i.e.* soluble, readily exchanged aluminium) the first year ($P_{2007-08}$), but residual Al-KCl the second ($P_{2008-09}$) and third ($P_{2009-10}$). The beneficial effect of the transformation of displaced Al (Al-KCl) to Al-amorphous forms also reflected in the second group of OLS equations for the second year ($P_{2008-09}$), where Al-amorphous exhibited a positive regression coefficient. Finally, the negative sign of the regression coefficient for exchangeable calcium in the first group of equations for the third year ($P_{2009-10}$) can be ascribed to incomplete incorporation of the amendment into the soil and its partial dissolution during the time span of the experiment. Therefore, total biomass production was closely related to changes in Ap1 in the umbric horizon and scarcely influenced by the other horizons.

The multivariate analysis allowed the changes in Al forms obtained from the extraction sequence, and those in the soil exchange complex, to be interpreted. A comparison of Figs 3a and 3b, which show the final results for ACP in the first and second cropping year, respectively, reveals that biomass production, pH_{water} and BS saturated factor 1 very strongly and in the same direction; also, they were associated to a high content in exchangeable Al (Al-KCl and Al-$CaCl_2$). Likewise, amorphous Al and organically bound Al (Al-$CuCl_2$) exhibited substantial changes in factor 1. This can be ascribed to the combination of a reduced adverse, phytotoxic effect of Al-$CuCl_2$ and a simultaneous increase in amorphous Al during the third cropping year. Also, a comparison of the two figures reveals that Al-KCl/CEC, pH_{water}, and presence of net charge (ΔpH) saturated factor 2 differently. Thus, only during the third year did ΔpH and pH_{water} saturate factor 1 in the same direction as CEC and production. On the other hand, CEC and OM saturated factor 1 in the opposite direction to production, pH and ΔpH the first year. Similarly, saturation of the cation exchange capacity (BS) on the first PC increased during the third year as a result of the increase in pH-dependent charge (Al-KCl/CEC) derived mainly from the organic component.

Finally, the presence of pH-dependent charge in the Ap1 and Ap2 horizons was ascribed to organic matter in this umbric horizon, which was sandy loam in texture and consisted mainly of kaolinite and illite. Based on the CEC, clay and OM values for this epipedon, the fraction of CEC due to OM was 92 cmol(+) kg^{-1} [versus only 18 cmol(+) kg^{-1} for clay]. This was largely the result of the fulvic component (Vidal *et al*., 2006), as revealed by the mean results for the control plots during the three years. The results of Fig. 4 clearly expose a decreased Al-KCl/CEC ratio in the Ap1 and Ap2 subhorizons in relation to AB.

As final conclusions, ordinary least-squares (OLS) multiple linear regression models were used to predict total biomass production of rye on an extremely acid *raña* soil in the province of León (Spain). The soil was supplied with four different types of calcareous amendments: limestone, dolomite, gypsum and sugar foam waste. Based on the results of a three-year experiment, the accuracy of the models, and hence the explained variance, increased with decreasing number of horizons included in the model and was higher during the third year. Thus, the highest explained variance ($R^2 = 0.865$) was that obtained by considering the Ap1 subhorizon (0-12 cm) alone and the third cropping year only. The soil variables most strongly correlated with biomass production were BS, Al-KCl, Al-$CaCl_2$ and exchangeable Ca. The effect of the amendments only reached the topmost (12 cm) of soil during the three years of the field study. Finally, OM in the Ap (umbric) horizon was found to contain pH-dependent charge and the charge to have a substantial effect on the concomitant increase in CEC and decrease in positive charge in the soil.

Acknowledgements

The authors are grateful to the Education and University Council of the Castilla y León regional government for award of Project LE-04/01, the framework for the conduct of this research, and to the Neighbour Council of Rioseco de Tapia (León, Spain) for providing the land for the experimental plots.

References

Boul SW, Hole FD, Mc Craken RJ, Southard RJ, 1997. Soil genesis and classification. Iowa St Univ Press, Ames, IA, USA, 527 pp.

Espejo R, 1987. The soil and ages of the raña surfaces related to the Villuercas and Altamira mountain ranges. Catena 14: 399-418.

Espejo R, Barragán E, Díaz MC, Pérez J, 1991. Factores condicionantes del encalado en los Ultisoles del Oeste de España. Suelo y Planta 1: 195-202. [In Spanish].

FAO, 1998. World reference base for soil resources. World Soil Resources Report No. 84. FAO, ISRIC & ISSS, Rome.

Hoyt PB, Nyborg M, 1972. Use of dilute calcium chloride for the extraction of plant-available aluminum and manganese from acid soil. Can J Soil Sci 52: 163-167.

Jackson ML, 1976. Soil chemical analysis. Prentice-Hall. Englewood Cliffs, NJ, USA, 662 pp.

Kilmer VJ, Alexander LT, 1949. Methods of making mechanical analyses of soils. Soil Sci 68: 15-24.

Kinrade TB, Parker DR, 1987. Non-phytotoxicity of the aluminium sulfate ion $AlSO4^+$. Physiol Plantarum 71: 207-212.

Kinraide TB, Ryan PR, Kochian LV, 1992. Interactive effects of Al^{3+}, H^+ and other cations on root elongation considered in terms of cell-surface electrical potential. Physiol Plantarum 99: 1461-1468.

Lin C, Coleman MT, 1960. The measurement of exchangeable aluminum in soils. Soil Sci Soc Amer Proc 24, 444-446.

Lund ZF, 1970. The effect of calcium and its relation to several cations in soybean root growth. Soil Sci Soc Am Proc 34: 456-459.

Mombiela FA, Mateo ME, 1984. Necesidades de cal para praderas en terrenos "a monte". An INIA Ser Agricola 25: 129-143. [In Spanish].

Noble AD, Summer ME, Alva AK, 1988. The pH dependency of aluminium phytotoxicity alleviation by calcium sulphate. Soil Sci Soc Am J 52: 1398-1402.

Pavan MA, Bingham FT, Pratt PF, 1982. Toxicity of aluminium to coffee in Ultisols and Oxisols amended with $CaCO_3$, $MgCO_3$ and $CaSO_4·2H_2O$. Soil Sci Soc Am J 46: 1201-1207.

Peech M, Alexander LT, Dean LA, Reed JF, 1947. Methods of soil analysis for soil fertility investigations. USDA Circular 757, Washington DC, 25 pp.

Peregrina F, Santano J, Ordóñez R, Gónzález P, Espejo R, 2006. Agronomic implications of the supply of lime and gypsum by products to palexerults from western Spain. Soil Sci 171(1): 65-81.

Reeve NG, Summer ME, 1970. Effects of aluminium toxicity and phosphorus fixation on crop growth on oxisols in Natal. Soil Sci Soc Am Proc 34: 263-267.

Reeve NG, Sumner ME, 1972. Amelioration of subsoil acidity in Natal Oxisols by leaching of surface -applied amendments. Agrochemophisica 4: 1-6.

Ritchey KD, Feldhake, CM, Clarke, RB, 1995. Improved water and nutrient uptake from subsurface layers of gypsum-amended soils. In: Agricultural utilization of urban and industrial by-products (Karlen DL, Wright RJ & Kemper WO, eds.). ASA Special Pub. 58, Madison, WI, USA, pp: 157-181.

Shainberg I, Sumner ME, Miller WP, Pavan MA, Fey MV, 1989. Use of gypsum in soils: A review. Adv Soil Sci 13: 1-111.

Soon YK, 1993. Fractionation of extractable aluminum in acid soils: A review and a proposed procedure. Commun Soil Sci Plant Anal 24: 1683-1708.

Soil Survey Staff, 1999. Soil taxonomy. A basic system of soil classification for making and interpreting soil surveys. Agriculture Handbook No. 436. USDA, Washington, DC.

Thomas GW, Hargrove W, 1984. Soil acidity and liming, 2nd ed (Adams F.ed), Chap. 1*,* Agronomy*,* No. 12, Am. Soc. Agron, Madison.

Vidal M, López A, Espejo R, Blázquez R, 2003. Comparative analysis of the corrective action of various liming and gypsum amendments on a Palexerult. Commun Soil Sci Plant Anal 34: 709-723.

Vidal M, Garzon E, Garcia V, Villa E, 2006. Differentiating the amending effects of calcareous materials applied to acid soils by use of optimal scaling procedures. Agrochimica 50(3-4): 132-147.

Villa E, 2005. Incidencia de la aplicación de espumas de azucarería y otras enmiendas calizas sobre la producción de biomasa. Mejora a corto plazo de los condicionantes agronómicos de los suelos ácidos de raña del norte de León. Doctoral thesis. Universidad de León, León, Spain. [In Spanish].

Walkley A, Black IA, 1934. An examination of the Dejtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method*.* Soil Sci 37: 29-38.