Field application of industrial by-products as Al toxicity amendments: chemical and mineralogical implications

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Summary

Lime, gypsum and various gypsum-like by-products have long been applied to soil surfaces as ameliorants of soil acidity and aluminium and manganese toxicity. We examined changes in chemical and mineralogical properties at two different depths in two acid soils one year after the application of gypsum, phosphogypsum + dolomitic residue, red gypsum + dolomitic residue, sugar foam, and sugar foam + mined gypsum. All treatments were found to increase the proportion of Ca^{2+} and decrease those of Al^{3+} and Mn^{2+} in the exchange complex of the surface and subsurface horizons, thus reducing its effective Al and Mn saturation. However, the mined gypsum treatment resulted in losses of Mg^{2+} from the Ap horizon of the soils, and the sugar foam treatment was not so effective with the AB horizons as the other treatments. The combined application of both gypsum-like by-products and the dolomitic residue proved the most effective choice with a view to reducing the effective Al and Mn saturation of the exchange complex in the Ap and AB horizons. In addition, both treatments reduced Mg^{2+} losses at both depths. Finally, all treatments resulted in the formation and retention on mineral and organic surfaces of a large fraction of the Al^{3+} released by exchange with Ca^{2+} as Al polymers. This is quite consistent with the observed changes in the $CuCl_2$-, oxalate- and DTPA-extractable Al contents as well as by SEM and EDS analyses. Based on these results, the use of the appropriate mixtures of these by-products is an effective alternative to that of mined gypsum and lime to alleviate soil acidity and reduce toxic concentrations of Al^{3+} and Mn^{2+} in agricultural acid soils.

Introduction

Many agricultural soils are poorly productive as a result of their surface and subsurface soil acidity. Al and Mn phytotoxicity, which is the most salient outcome of acid pH levels, severely decreases the productivity of these soils by hindering root development (van der Watt *et al.*, 1991), causing nutrient and water stress in plants, and interfering with the active ion root uptake (Wright, 1989). As a consequence, vast areas of acid soils in the temperate zone are at risk of degradation and environmental impoverishment (Shainberg *et al.*, 1989).

In previous work, we examined the potential use of three industrial by-products (phosphogypsum (PG), red gypsum (RG) and sugar foam (SF)) to correct soil acidity and Al phytotoxicity in acid soils, using batch tests involving saturated solutions of the by-products (Garrido *et al.*, 2003). Similarly to Alva & Gascho (1991), we found an increase in exchangeable Ca^{2+} and a decrease in exchangeable Al, and also that both gypsum-like by-products (PG and RG) reduced

the concentrations of Mg^{2+} and K^+ in the exchange complex of the soils. With SF, the loss of Mg^{2+} was offset by the amount of Mg^{2+} contained in its saturated solution. We also detected the formation of hydroxy-Al polymers as a result of Al^{3+} being released into the soil solution. In this work, we have assessed and compared the potential use of four industrial by-products (namely PG, RG, SF and dolomitic residue (DR)) and mined gypsum (G) as soil acidity amendments. We have examined the effect of their use as individual (SF and G) or combined amendments (PG + DR, RG + DR and SF + G) on chemical and mineralogical properties, and nutrient availability, one year after their surface application to field plots of two acid soils. The results are discussed below.

Materials and methods

Soils and general analyses

We did field experiments on two acid soils (a Plinthic Palexerult (S1) and an Ultic Palexeralf (S2)) developed from Pliocene-Quaternary age formations (*rañas*) from two locations in Cáceres (eastern Spain). We chose these soils based on their

low productivity (a result of their moderate acidity, Al (S1 and S2) and Mn (S2) phytotoxicity) and of their differences in exchangeable Al^{3+} and Ca^{2+} contents (Table 1, Figure 1).

Soil pH was measured in deionized water (pH_w) and in 1 M KCl (pH_K) (in a 1:2.5 suspension), electrical conductivity (EC) was measured in a 1:5 suspension, and organic C (OC) was determined by wet digestion (Walkley & Black, 1934). Exchangeable bases were extracted with 1 M NH_4OAc (pH 7) (Thomas, 1982), and exchangeable Al^{3+} (Al_K) (Barnhisel & Bertsch, 1982) and Mn^{2+} (Mn_K) were determined with 1 M KCl. The effective capacity of the exchange complex (ECEC) was calculated as the sum of Al_K, Mn_K and the amounts of Ca, Mg, Na and K extracted by 1 M NH_4OAc at pH 7 (Shuman, 1990). We determined Al^{3+} and Mn^{2+} extractable in $CuCl_2$ (Al_{Cu} and Mn_{Cu}) by shaking 3 g of sample in 30 ml of 0.1 M $CuCl_2$ + 0.5 M KCl for 1 hour (Soon, 1993). Bioavailable Al and Mn were extracted with DTPA (Al_{DTPA}, Mn_{DTPA}) (Lindsay & Norvell, 1978). The Al^{3+} and Mn^{2+} contents in the poorly crystalline and amorphous fraction of the soils (Al_{ox} and Mn_{ox}) were extracted with 0.2 M ammonium oxalate + 0.2 M oxalic acid solution at pH 3 (McKeague & Day, 1966).

The mineralogical compositions of the total (≤ 2 mm) and clay ($\leq 2 \mu m$) fractions of the soil were identified by X-ray powder diffraction (XRD) on a Philips X'Pert diffractometer with graphite-monochromated $CuK\alpha$ radiation. The XRD patterns were obtained from random powder mounts and various oriented aggregates of the Mg- and K-clay (air-dried, ethylene glycol-solvated, heated at 300°C for 3 hours, and heated at 500°C for 3 hours). We obtained semi-quantitative estimates of the minerals from random powder and oriented aggregated patterns, using intensity factors reported by Schultz (1964).

Industrial by-products

Phosphogypsum (PG) is generated in the wet-acid production of phosphoric acid from rock phosphate. Red gypsum (RG) is a waste from the industrial production of titanium dioxide (TiO_2). Sugar foam (SF) is the waste produced by the sugar manufacturing industry as the beet juice is purified by flocculation of colloidal matter with a lime solution, followed by treatment with CO_2. Dolomitic residue (DR) results from the demolition of the thermal insulator material of an AOD (Argon Oxygen Decarburation)-type converter by the steel industry. Samples of the by-products were digested in a mixture of nitric and sulphuric acids and by alkaline fusion (sodium carbonate) after they had been dried at 45°C (RG and PG) or 105°C (SF and DR). The resulting solutions were analysed for major, minor and trace elements by ICP-AES, ICP-MS and ion chromatography. The chemical composition of the by-product samples used in these experiments is shown in Table 2.

The mineralogical composition of the by-products was identified by XRD from random powder patterns (Figure 1).

Gypsum is the main component of PG and RG, and is accompanied by small proportions of iron and titanium minerals in RG. An XRD study of the RG residue after dissolution of gypsum in deionized water revealed the presence of maghemite (γ-Fe_2O_3), goethite (α-FeOOH) and rutile (TiO_2). The DR consists mainly of magnesium oxide (MgO) and calcium hydroxide ($Ca(OH)_2$) with a small proportion of calcium oxide (CaO). Sugar foam contains calcium carbonate and traces of calcium oxide.

Field application of the amendments

The surface of ten 2×5 m plots per experimental site were randomly treated in duplicate with mined gypsum (G), phosphogypsum + dolomitic residue (PG + DR), red gypsum + dolomitic residue (RG + DR), sugar foam (SF) or sugar foam + mined gypsum (SF + G). An additional two control plots per site received no treatment. We established the application rates from preliminary batch tests involving the calculation of the amount of calcium (as calcium carbonate) required to neutralize acidity and raise pH_w for the surface horizons (Ap) of the soils to 6.2 (Arias & Serrano, 1997). Thus, in spite of the differential Ca^{2+} content of the by-products, we applied equivalent amounts of Ca^{2+} to all plots treated with G, PG + DR, RG + DR and SF (approximately 1.4 t ha^{-1} and 0.6 t 7ha^{-1} to S1 and S2, respectively). The SF + G treatment received G and SF at the same rates as applied to treatments receiving these amendments separately and therefore the SF + G treatment involved applying twice the amount of Ca^{2+} compared with the other treatments. The amendments were uniformly spread onto the entire surface of the plots and were not incorporated. After one year, duplicate samples from each plot were collected from the Ap horizon (5–20 cm) and the AB horizon (20–40 cm) using a spade and a hoe. The topmost 5 cm of the soil was discarded to avoid uncertainties due to the possible presence of undissolved amendment particles. No samples were collected from within 50 cm of the edge of the plot. Spontaneous plant growth was allowed during the one-year period. The annual rainfall rate (approximately 700 mm) was similar for the two experimental sites by virtue of their proximity. All samples were air-dried, crushed and sieved through a 2 mm mesh. We obtained homogeneous samples of the horizons for each treatment by mixing all samples from duplicate plots prior to the above-described analyses on triplicate subsamples. Similar to Garrido *et al.* (2003), we provide an estimate of the laboratory error by analysis of variance at the foot of Tables 3, 4 and 5. In addition, we used XRD to determine the variations in the mineralogical composition of the horizons resulting from the treatments.

Scanning electron microscopy observations

We investigated potential changes in the mineralogical characteristics of the soils due to the effect of the application of the
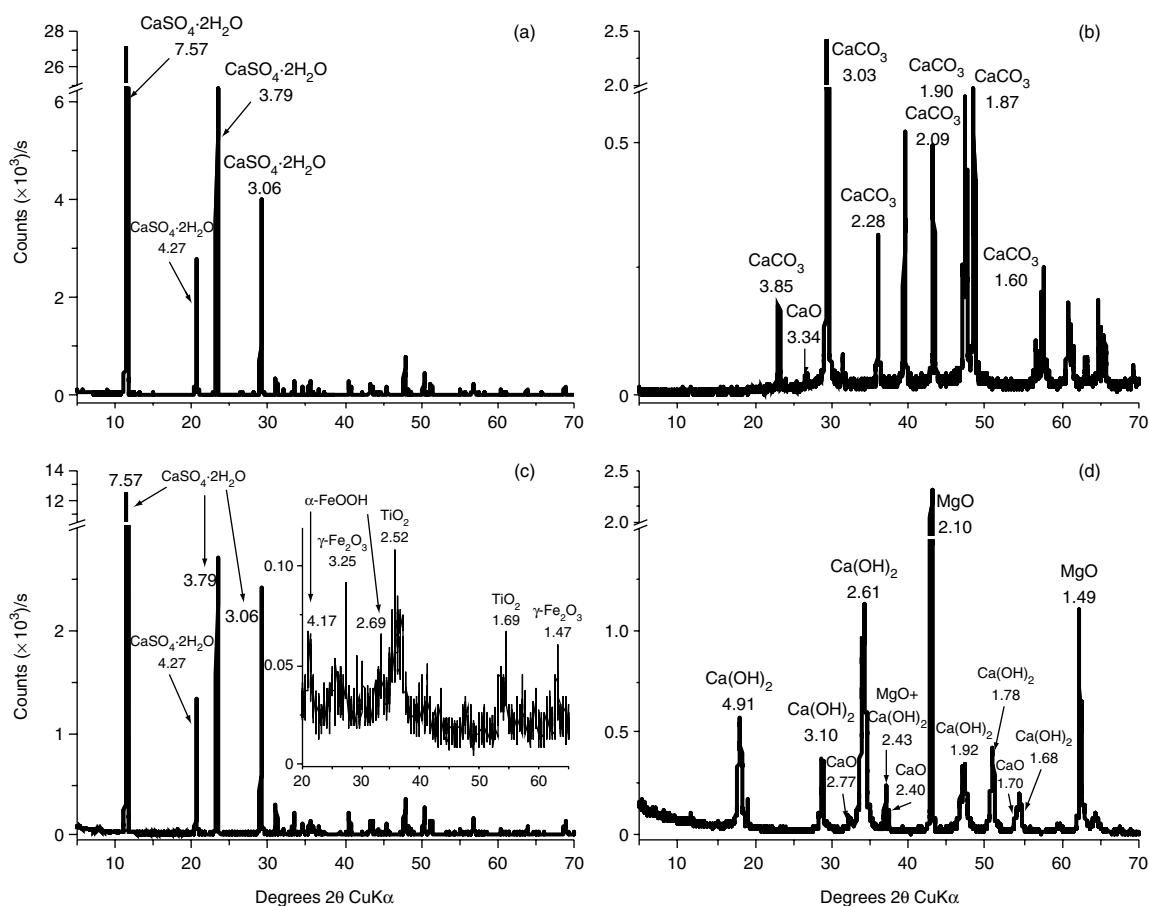
Table 1 Some physical, chemical and mineralogical properties of the soils

| | | | EC | OC | Sand | Silt | Clay | Ca^{2+} | Mg^{2+} | Na^+ | K^+ | Al^{3+} | Mn^{2+} | $ECEC^a$ | Al eff. sat.[b] | Mn eff. sat.[b] | Mineralogical properties[c] | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | ≤2 mm fraction | | | | | | ≤2 μm fraction | | | | | | | |
Soil	pH_w	pH_K	/mS cm^{-1}	/g kg^{-1}							/cmol$_{(+)}$ kg^{-1}				/%		Q	F_{Ca-Na}	F_K	G	H	Ph	Q	G	H	Ph	V	S	I	K
S1																														
Ap	5.2	4.2	0.03	22.4	675	250	75	0.32	0.08	0.04	0.09	1.26	–	1.79	70.3	–	74	tr	tr	4	3	19	12	6	6	76	8	ND	11	57
AB	4.9	4.1	0.02	6.5	643	201	156	0.16	0.05	0.08	0.08	1.56	–	1.92	80.9	–	65	tr	tr	4	3	28	24	7	2	67	6	ND	10	51
S2																														
Ap	5.5	4.2	0.04	13.4	651	225	124	1.58	0.50	0.34	0.19	0.68	0.51	3.81	5.07	13.4	80	tr	tr	tr	ND	20	22	7	3	68	ND	14	22	32
AB	5.2	3.9	0.03	3.2	598	262	140	2.13	0.71	0.04	0.14	0.29	0.27	3.59	3.78	7.58	75	tr	tr	tr	tr	25	27	5	4	64	ND	12	17	35

[a] ECEC, sum of exchangeable Ca, Mg, K, Na, Al and Mn.
[b] Effective saturation by Al and Mn of the exchange complex.
[c] Semi-quantitative mineralogical composition (relative % between samples) of the soils: Q, quartz; F_{Ca-Na}, calcium- and sodium-rich feldspars; F_K, potassium-rich feldspars; G, goethite; H, haematite; Ph, phyllosilicates; V, vermiculite; S, smectite; I, illite; K, kaolinite.
ND, not detected; tr, trace; –, not determined.

Figure 1 XRD patterns of the industrial by-products: (a) phosphogypsum, (b) sugar foam, (c) red gypsum, and (d) dolomitic residue. Inset figure corresponds to the undissolved residue of red gypsum after dissolution of gypsum. Numbers indicate the d-values ($\times 10^{-1}$ nm) of the main peaks.

amendments, using scanning electron microscopy in the back-scattered electron mode (SEM-BSE). Subsamples of the bulk soil samples from the Ap and AB horizons of all plots in the experimental sites were oven-dried (50°C) and embedded in low-viscosity acrylic resin (LR-White, medium grade). Blocks of resin-embedded samples were finely polished using a commercially available low viscosity oil/water emulsion as a lubricant and subsequently observed with a DMS940 A-Zeiss microscope equipped with a four-diode BSE detector. Microprobe analyses, including point analysis, and microprobe profiles, were made with a Link Isis energy dispersive spectrometry (EDS) microanalytical system on the SEM. The following microscopy and analytical operating conditions were used: a take-off angle of 35°, an accelerating voltage of 15 kV, a working distance of 25 mm, and a specimen current of 1–5 nA.

Results and discussion

Effect of the amendments on soil acidity

Consistent with the previous results of Shainberg *et al.* (1989) and Alcordo & Rechcigl (1993), pH_w in the G-treated plots

decreased slightly in the Ap horizons of both soils and in the AB horizon of S1 (Table 3). We found similar results in batch tests upon addition of PG and RG saturated solutions to the soils (Garrido *et al.*, 2003). However, this tendency was corrected by applying the gypsum-like by-products in combination with DR; thus, both the PG + DR and the RG + DR treatment caused little or no increase in pH_w of the soils. Only SF proved clearly effective in increasing pH_w in both the Ap and the AB horizons in S1 and in the Ap horizon of S2. By contrast, the joint use of SF and G, similarly to the gypsum-like by-product mixtures, caused little change in pH_w.

On the other hand, the treatments resulted in some differences in pH_K in both soils, that tended to be greater compared with differences in pH_w, probably due to the effective exchange of Al by Ca in the exchange complex. Except in the G-treated plots, the amendments increased pH_K in the Ap horizon of S1 but did not affect it in the AB horizon. With S2, all treatments increased pH_K in the Ap and AB horizons.

As a result of these changes in pH_w and pH_K, the differences between the two decreased in the Ap and AB horizons of S1 upon application of all treatments except SF, which increased the $pH_w - pH_K$ differences in both Ap and AB horizons. In

Table 2 Chemical composition of the by-products used

	PG	RG	DR	SF
		/g kg^{-1}		
Al$_2$O$_3$	2.31	8.43	3.55	7.31
CaO	322	253	477	407
Fe$_2$O$_3$	0.55	48.2	5.43	28.3
K$_2$O	< 0.29	0.75	< 0.29	1.51
MgO	0.103	1.79	375	10.5
MnO	< 0.13	1.07	0.890	0.318
Na$_2$O	1.18	1.51	< 0.27	0.956
P$_2$O$_5$	10.4	< 0.46	< 0.46	6.87
SiO$_2$	2.31	8.34	7.68	28.9
TiO$_2$	0.103	37.5	0.144	0.275
F$^-$	8.9	< 0.8	< 0.8	0.9
SO$_4^{2-}$	510	421	27.8	7.8
LOI[a]	215	235	111	445
pH[b]	3.8	7	12.6	9.3

	PG	RG	DR	SF
		/mg kg^{-1}		
As	< 3	7.4	< 3	7.23
B	< 20	< 20	< 20	<20
Ba	110	16.8	131	48.2
Be	< 1	< 1	< 3	0.22
Cd	1.9	5.54	< 1	< 0.5
Co	< 1.25	6.6	< 1.25	< 1.25
Cr	2.49	30.3	51.5	36.8
Cu	5.19	36.7	< 2	12.9
Mo	< 0.5	4.61	4.67	0.24
Ni	< 2	155	50.8	4.11
Pb	3.63	48.3	< 1	1.5
Sb	< 0.5	1.18	< 0.1	< 0.1
Se	< 2	< 2	< 2	7.02
Zn	< 3	171	14.7	25.9
Hg	0.19	0.07	0.04	< 0.02

[a]Loss on ignition (100–1000°C).
[b]pH of their saturated solution as explained in Garrido *et al.* (2003).

S2, however, all treatments including SF decreased the $pH_w - pH_K$ difference in the Ap horizon but increased it in the AB horizon.

These results are consistent with those found in earlier batch tests (Garrido *et al.*, 2003). The effect of G and the gypsum-like by-products (PG and RG) on the pH_w of the soils is the result of the opposing reactions of Al^{3+} and H$^+$ exchange by Ca^{2+}, and the ligand exchange of OH$^-$ by SO$_4^{2-}$ (Alcordo & Rechcigl, 1993; Smith *et al.*, 1994). As a consequence, pH_w varied little and pH_K increased due to the release of most available Al^{3+}, which decreased the resulting difference in both pH values. When the soil is treated with SF, the addition of OH$^-$ anions offsets the effect of the exchange of Al^{3+} by Ca^{2+}, so pH_w increased to a greater extent than did pH_K and the difference between the two increased as a result. The addition of DR (strongly alkaline, Table 2) in combination with the gypsum-like by-products compensated for the reduction in pH_w and increased pH_K, thereby decreasing the difference between both. The effect of the SF + G treatment on the pH values resulted from the opposing effect of both products separately; the addition of SF with G had no effect on the pH values in the Ap and AB horizons of S1, but increased pH_w and pH_K in the Ap and AB horizons of S2.

One year after the amendments were applied, SF was clearly the most effective treatment in raising pH_w in the Ap and AB horizons of S1, and the Ap horizon of S2. The moderate acidity of the AB horizon of S2 was corrected to a similar extent by all treatments. However, the lower solubility of the SF amendment relative to the others might account for its lesser effect on both pH_w and pH_K in the AB horizon of S2.

Effect of the amendments on the exchange complex

All treatments increased the amount of exchangeable Ca^{2+} in the Ap and AB horizons of S1 and S2 (Table 4). Obviously, the SF + G treatment provided the greatest increase in

Table 3 Effect of the amendments on the pH of the soils

	S1						S2					
	Ap			AB			Ap			AB		
Treatment	pH$_w$	pH$_K$	pH$_w$ − pH$_K$	pH$_w$	pH$_K$	pH$_w$ − pH$_K$	pH$_w$	pH$_K$	pH$_w$ − pH$_K$	pH$_w$	pH$_K$	pH$_w$ − pH$_K$
C	5.21	4.15	1.06	4.87	4.03	0.84	5.49	4.15	1.34	5.20	3.94	1.26
G	4.95	4.05	0.90	4.80	3.97	0.83	4.98	4.35	0.63	5.54	4.16	1.38
RG + DR	5.20	4.41	0.79	4.76	4.09	0.67	5.69	4.56	1.13	5.58	4.21	1.37
PG + DR	5.33	4.42	0.91	4.75	4.04	0.71	5.72	4.59	1.13	5.58	4.34	1.24
SF	5.70	4.41	1.29	5.21	4.09	1.12	6.16	5.49	0.67	5.29	3.98	1.31
SF + G	5.16	4.32	0.84	4.77	4.04	0.73	5.71	4.51	1.20	5.57	4.22	1.35
SE[a]	0.08	0.10										

[a]SE, pooled standard errors of the measurements of the Ap and AB horizons of both soils.

exchangeable Ca^{2+} in the Ap horizons of both soils as it involved the addition of twice the amount of Ca^{2+}. Also, the higher solubility of G might enhance SF dissolution as the pH slightly decreases. In the AB horizon of S1, however, the effect of this treatment was similar to those of the others. In the AB horizon of S2, the effect on exchangeable Ca^{2+} exceeded the increase observed with the other treatments. This treatment aside, PG + DR and RG + DR were the most effective amendments in increasing exchangeable Ca^{2+} in the Ap and AB horizons of S1. The SF treatment had a similar effect on the Ap horizon as the other amendments; in the AB horizon, however, it resulted in the smallest increase in exchangeable Ca^{2+} owing to its low solubility. Although the greatest exchangeable Ca^{2+} content in S2 was found in the Ap horizons of the SF-treated plots, this treatment resulted in the smallest increase in the AB horizon.

On the other hand, Al_K in the Ap and AB horizons was decreased by all treatments except SF, which hardly altered it in the AB horizons of S1 and S2 (Table 4). Once again, the greatest reduction was found in the Ap horizons of the SF + G-treated plots by virtue of the different application rate. However, the effect of this treatment on the AB horizon of both soils was similar to those of the other treatments. This finding, together with the above-described increase in exchangeable Ca^{2+}, suggests that the effect of the SF + G treatment on subsurface horizons one year after application is due mainly to the gypsum contained in the amendment; in the surface horizon, however, both compounds in the amendments combine their effects on the exchange complex.

In addition to decreasing Al_K, we found all treatments effective in reducing Mn_K in the Ap horizon of S2. However, the differences among treatments were small in the surface layer; also, as noted earlier, SF had no effect on Mn_K in the AB horizon.

The reduction of the amount of exchangeable Mg^{2+} by the application of G and gypsum-like by-products to the surface horizons has previously been encountered in batch (Garrido *et al.*, 2003) and field tests (Smith *et al.*, 1994; Arias & Serrano, 1997; Farina *et al.*, 2000); the Mg^{2+} is displaced by the large amounts of Ca^{2+} added in the amendments. Accordingly, the exchangeable Mg^{2+} content decreased in the topsoil of the G-treated plots of S1 and S2, and increased through leaching in the AB horizons (Table 4). The SF treatment increased the exchangeable Mg^{2+} content in S1 due to the Mg^{2+} content in the by-product, which offsets its displacement by Ca^{2+}. In fact, the Mg^{2+} content in the saturated solution of SF was one-half the amount of Ca^{2+} (Garrido *et al.*, 2003). However, the exchangeable Mg^{2+} content of the AB horizon of S1 upon treatment with SF was lower than that found in the AB horizons of the G-treated plots; in the latter case, however, the exchangeable Mg^{2+} content in the Ap horizon was reduced. In S2, SF had little effect on the exchangeable Mg^{2+} content of both the Ap and the AB horizon. On the other hand, the addition of DR to the gypsum-like by-products (PG + DR and RG + DR) resulted in the largest increases in exchangeable Mg^{2+}, both in the surface and in the subsurface horizons of the two soils. Therefore, the application of gypsum-like by-products in combination with DR was effective not only in reducing Al_K, but also in increasing the amount of exchangeable Mg^{2+} in the surface and subsurface horizons.

The overall effects of the amendments on the exchange complex are consistent with previously reported results

Table 4 Effect of the amendments on the exchange complex

	Treatment	Ap							AB						
		Ca^{2+}	Mg^{2+}	Al^{3+}	Mn^{2+}	ECEC	Al eff. sat.	Mn eff. sat.	Ca^{2+}	Mg^{2+}	Al^{3+}	Mn^{2+}	ECEC	Al eff. sat.	Mn eff. sat.
		/cmol$_{(+)}$ kg^{-1}					/%		/cmol$_{(+)}$ kg^{-1}					/%	
S1	C	0.32	0.08	1.26	–	1.79	70.3	–	0.16	0.05	1.56	–	1.92	80.9	–
	G	1.14	0.06	1.19	–	2.54	46.9	–	0.93	0.11	1.19	–	2.65	44.7	–
	RG + DR	1.84	0.12	0.67	–	2.81	23.8	–	1.69	0.14	1.22	–	3.24	37.8	–
	PG + DR	1.99	0.13	0.67	–	2.96	22.6	–	1.47	0.19	1.22	–	3.06	40.0	–
	SF	1.72	0.11	0.63	–	2.58	24.5	–	0.70	0.07	1.48	–	2.07	71.5	–
	SF + G	3.16	0.09	0.56	–	3.97	14.0	–	1.25	0.10	1.07	–	2.56	42.8	–
S2	C	1.58	0.50	0.19	0.51	3.81	5.07	13.4	2.13	0.71	0.14	0.27	3.59	3.78	7.58
	G	2.17	0.25	0.14	0.24	3.70	3.79	6.44	3.51	0.92	0.12	0.10	4.93	2.34	1.95
	RG + DR	2.67	0.93	0.10	0.28	5.20	1.92	5.01	3.71	1.31	0.10	0.10	5.85	1.71	1.64
	PG + DR	2.86	1.13	0.11	0.24	5.53	1.99	4.32	3.27	1.53	0.11	0.10	5.51	1.86	1.88
	SF	3.27	0.44	0.09	0.32	4.93	1.83	6.59	2.98	0.86	0.16	0.25	4.61	3.54	5.42
	SF + G	7.07	0.20	0.06	0.33	8.53	0.74	3.85	5.09	0.99	0.08	0.08	6.62	1.23	1.16
SE[a]		0.08	0.03	0.04	0.02	0.08	2.27	0.47							

[a]SE, pooled standard errors of the measurements of the Ap and AB horizons of both soils.

–, not determined.

(Shainberg *et al.*, 1989; Alcordo & Rechcigl, 1993; Vizcayno *et al.*, 2001) and with those of our batch tests (Garrido *et al.*, 2003). The changes involve a decrease in effective Al saturation in the exchange complex in both horizons of S1 and S2. Except for G, however, all treatments were more efficient in reducing Al saturation in the Ap horizon than in the AB horizon. Interestingly, the relative reduction with respect to the initial Al saturation was similar in both soils. Thus, both the PG + DR and the RG + DR treatment reduced the effective Al saturation by a factor of 3 and 2.6 with respect to the initial value for the Ap horizon of S1 and S2, respectively. In the AB horizons, these treatments reduced Al saturation by a factor of 2 in both soils. On the other hand, the effective Al saturation of the SF-treated plots was 2.9 and 2.8 times lower than that found in the Ap horizons of the control plots of S1 and S2, respectively, and these reduction factors decreased to approximately 1.1 in their AB horizons. The maximum reduction of the effective Al saturation was found in the Ap horizons of the SF + G-treated plots of both soils. However, the resulting values for this treatment on the AB horizons were not too different from those found in the other treated plots. This again confirms that the SF + G treatment, despite its doubled Ca^{2+} content relative to the other treatments, is not more effective at subsoil amelioration than the other amendments after one year. In addition, the effective Mn saturation in the exchange complex of S2 was also reduced by all treatments. With the exception of the SF-treated plots, however, the effective Mn saturation was reduced to a greater extent in the AB horizon than in the Ap horizon. Moreover, Mn saturation was 6.5 times lower in the AB horizon of the SF + G-treated plots; about 4 times lower in the G-, PG + DR- and RG + DR-treated plots; and 1.4 times

lower in the SF-treated plots. This differential capacity of the treatments to reduce the effective Mn saturation of the exchange complex warrants closer examination.

Effect of the amendments on Al and Mn bioavailability

We also identified the effect of the treatments on both Al_{DTPA} and Mn_{DTPA} as they can be related to a phytotoxic fraction of their corresponding total content in the soil (Table 5). SF proved the most effective treatment for the Ap horizon of S1, where it reduced Al_{DTPA} 4 times relative to the control plots. Both the PG + DR and the RG + DR treatment reduced Al_{DTPA} by a factor of 3.5, and SF + G and G by factors of 3.3 and 2.6, respectively. On the other hand, in the AB horizon SF caused only a slight decrease, whereas PG + DR and RG + DR reduced Al_{DTPA} 2.5 times, SF + G treatment 2, and G 1.2. As previously noted by Garrido *et al.* (2003), these results expose the 2-fold effect of the amendments in the soils. On the one hand, they reduce most of the available or readily exchangeable Al^{3+} fraction in the soil, mainly through exchange by Ca^{2+}, thus decreasing Al_{DTPA}. On the other, the polymerization of soluble monomeric Al forms decreases Al extractability in DTPA. This is supported by, among others, the fact that the SF caused the greatest reduction in Al_{DTPA} in the Ap horizon of S1, and also by the reduction of Al_{DTPA} in the AB horizon, which contained little organic matter. The polymerization process is promoted to a greater extent in the SF-treated plots exhibiting the largest increases in pH_w. In the AB horizon, SF was not so effective as the other treatments, so polymerization was not so apparent

Table 5 Effect of the amendments on the DTPA-, oxalate-extractable Al and Mn, and the difference between the KCl- and the $CuCl_2$-extractable Al and Mn

		Ap						AB					
	Treatment	Al_{DTPA}	Mn_{DTPA}	Al_{ox}	Mn_{ox}	Al_{Cu-K}	Mn_{Cu-K}	Al_{DTPA}	Mn_{DTPA}	Al_{ox}	Mn_{ox}	Al_{Cu-K}	Mn_{Cu-K}
		/mg kg^{-1}						/mg kg^{-1}					
S1	C	179	–	841	–	96.6	–	74.3	–	573	–	40	–
	G	67.6	–	2485	–	150	–	59.3	–	2022	–	103	–
	RG + DR	50.5	–	2773	–	217	–	28.6	–	2425	–	113	–
	PG + DR	46.6	–	2798	–	193	–	29.8	–	2075	–	90	–
	SF	44.9	–	2455	–	220	–	65.7	–	2218	–	60	–
	SF + G	53.2	–	2823	–	213	–	39.8	–	2230	–	127	–
S2	C	155	127	365	426	55.9	74	4.87	61.5	334	312	44.4	14.2
	G	39.1	77.9	1006	760	77.4	111	3.43	13.4	1007	353	56.2	30.0
	RG + DR	18.6	68.2	1256	759	87.7	107	2.73	13.8	1508	341	68.9	37.2
	PG + DR	25.3	73.8	1183	742	83.4	120	2.97	12.6	1521	393	71.4	37.0
	SF	42.8	89.7	1405	790	81.9	111	5.07	59.0	1631	282	32.3	18.5
	SF + G	41.2	81.2	1070	741	94.3	107	2.60	16.1	1441	436	73.8	25.2
SE[a]		3.47	1.94	46.08	19.54	4.53	3.33						

[a]SE, pooled standard errors of the measurements of the Ap and AB horizons of both soils.
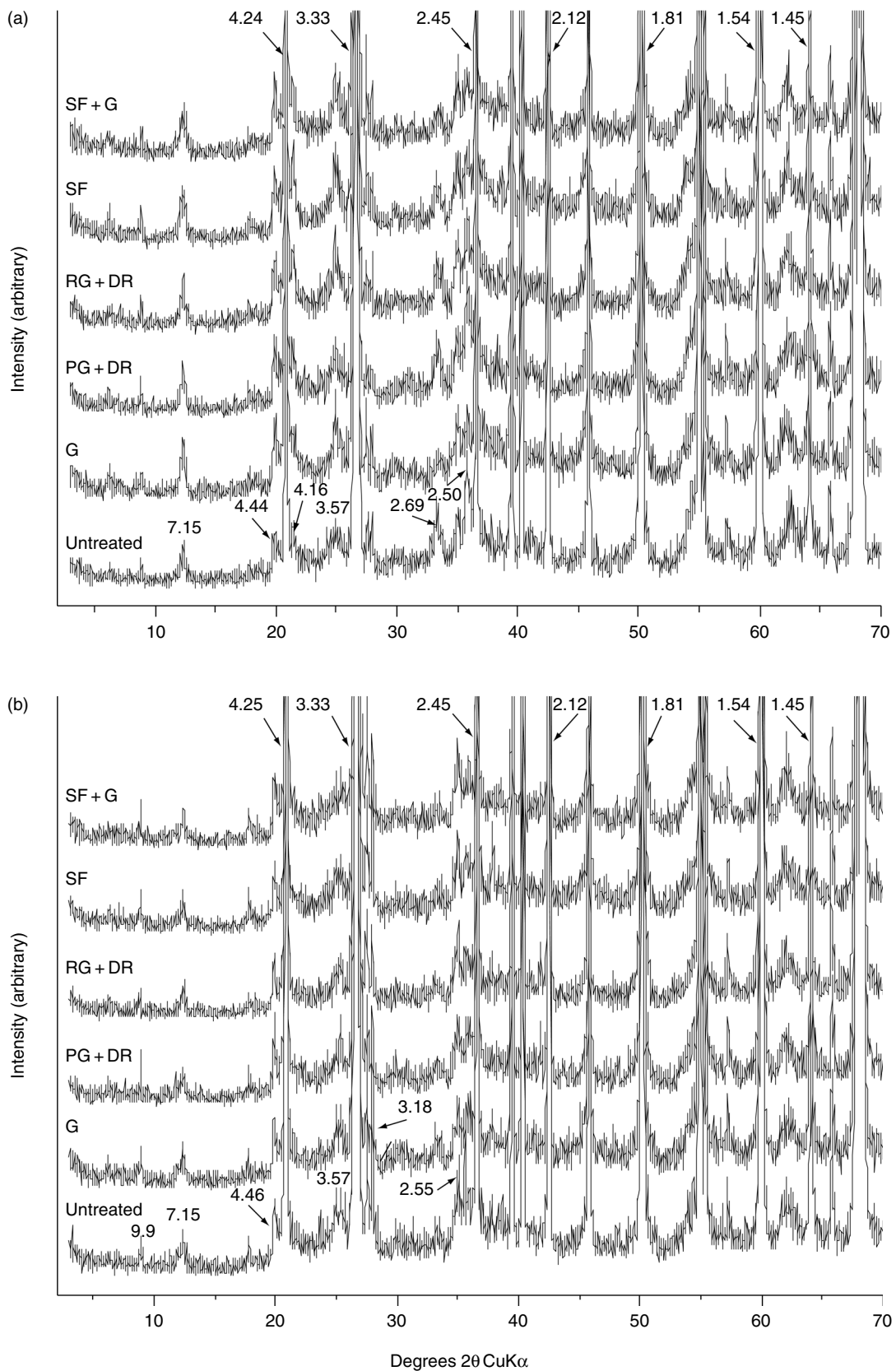
Figure 2 XRD patterns of the untreated and treated Ap horizons of (a) S1 and (b) S2 soils. Numbers indicate the d-values ($\times 10^{-1}$ nm) of the main peaks.

from the Al_{DTPA} value. Rather, both the PG + DR and the RG + DR treatment proved the most effective in displacing available and exchangeable Al^{3+} by Ca^{2+} in the AB horizon, the reduction of Al_{DTPA} being the greatest.

In addition, all treatments were effective in reducing Mn_{DTPA} in both horizons of soil S2 (Table 5). The Mn_{DTPA} was reduced to a greater extent in the AB horizon than in the Ap horizon, which is consistent with the decrease in effective Mn saturation of the exchange complex described above.

Formation of Al-hydroxy polymers

In previous experiments (Garrido *et al.*, 2003), we showed the formation and retention of hydroxy polymers of Al to be the principal mechanism through which Al phytotoxicity was alleviated upon application of gypsum- and lime-rich by-products. However, the batch conditions used probably gave rise to some inconsistencies in the results. In these field tests, the amount of oxalate-extractable Al (Al_{ox}) increased 3–4 times with respect to that found in the control plots in the surface and subsurface horizons of soils S1 and S2 by effect of all treatments (Table 5). However, XRD analyses of the untreated and treated samples showed that there were no modifications in the mineralogical composition of the soils resulting from the treatments (Figure 2a,b). All these results provide new evidence that all the treatments promote the polymerization of Al monomers upon exchange of most available and exchangeable Al.

In addition, the existence of these non-crystalline Al polymers could be observed by SEM-BSE and EDS analyses. Irrespective of the treatment applied to the soils, massive formations of Al polymers were frequently found associated with particles mainly composed of phyllosilicates and organic matter (Figures 3 and 4). As can be seen in the EDS spectra of these massive formations in the Ap horizon of S1 treated with PG + DR (Figure 4a,b), sulphate and phosphate anions were also detected associated with the Al polymers. This sorption phenomenon provides the soils with additional cation sorption capacity through the formation of ternary complexes (McBride, 1989; Illera *et al.*, 2004). In fact, the proportion of Ca^{2+} in these Al polymers as shown in the EDS spectra is greater in the horizons treated with gypsum-like by-products than in those treated with SF. The extent to which polymerization occurs depends both on the amount of Al^{3+} that is displaced by Ca^{2+} and available in the soil solution and on the amount of OH^- anions supplied by the amendments, so differences among treatments are difficult to assess. Alternative mechanisms have been proposed to account for the amelioration of Al toxicity including the formation of aluminium fluoride and aluminium sulphate complexes that can promote substantial Al leaching through the soil profile (Oates & Caldwell, 1985; Smith *et al.*, 1995) when the soil is treated with gypsum or gypsum-rich by-products. Based on our findings, however, we believe that, one year after the amendments are
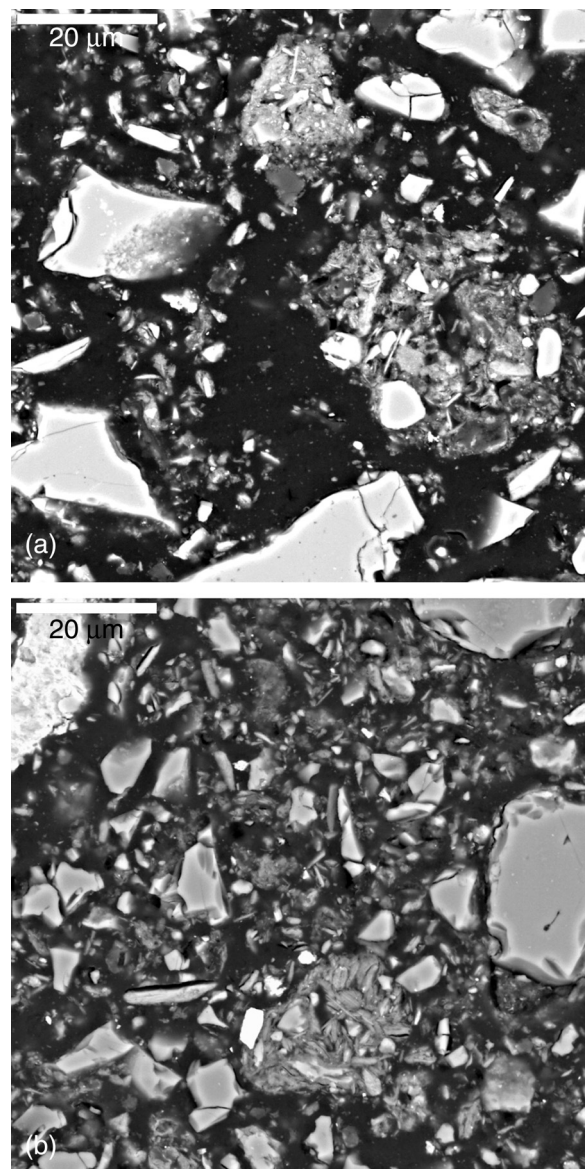

Figure 3 SEM-BSE image showing the untreated Ap horizons of (a) S1 and (b) S2 soils.

applied, the most salient result is that a large fraction of Al^{3+} in the soil remains within the soil matrix as Al-hydroxy polymers. Moreover, this result is shared by both lime-rich and gypsum-rich amendments.

On the other hand, Mn_{ox} also increased in the Ap horizon and, to a lesser extent, in the AB horizon of all treated plots of soil S2; differences among treatments were slight except for the SF treatment, which caused no change in the AB horizon (Table 5). The transformations of the Mn chemistry require further study as many soils of the temperate zone have higher Mn toxicity than Al toxicity.

Aluminium extracted into $CuCl_2$ (Al_{Cu}) has been used to estimate the potentially reactive Al pool on soils (Aitken,
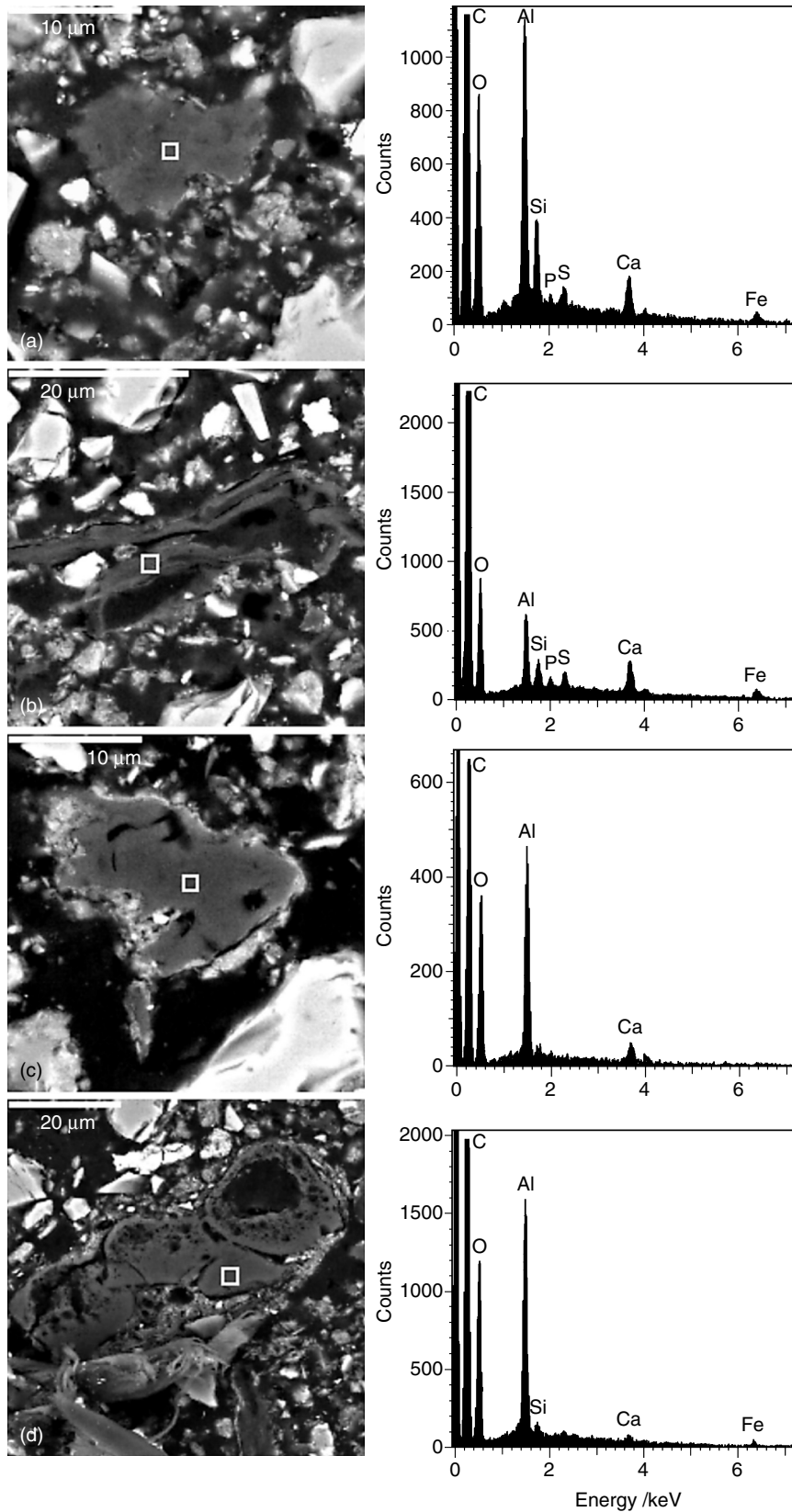
Figure 4 SEM-BSE image showing a massive formation of Al polymers associated with kaolinite crystals (a) and organic matter (b) in the Ap horizon of S1 treated with phosphogypsum + dolomitic residue, and Al polymers associated with kaolinite crystals (c) and organic matter (d) in the Ap horizon of S1 treated with sugar foam, with the EDS X-ray spectra of the corresponding zones marked with squares.

1992). However, this extraction method has been found to release Al from hydroxy-Al polymers, soluble amorphous Al and interlayer OH-Al in some clay minerals (Soon, 1993). For this reason, the difference between Al_{Cu} and Al_K (Al_{Cu-K}) has been attributed to Al-polymeric species and metastable forms of Al hydroxides in horizons containing little organic matter (Juo & Kamprath, 1979). Similarly to our previous experiments (Garrido *et al.*, 2003), Al_{Cu-K} increased in both horizons of soils S1 and S2. These results constitute further analytical evidence of the formation of Al polymers in soils treated with these by-products. On the other hand, Mn_{Cu-K} increased substantially in both horizons of soil S2 except with the SF treatment, which resulted in no variation with respect to the control plot.

Conclusions

The field application of mined gypsum, phosphogypsum + dolomitic residue, red gypsum + dolomitic residue, sugar foam, and sugar foam + gypsum treatments increased the amount of Ca^{2+} and decreased those of Al^{3+} and Mn^{2+} in the exchange complex of the surface and subsurface horizons of two acid soils. As a consequence, the effective Al and Mn saturation of the exchange complex was reduced and, one year after application, all treatments proved effective amendments for both Al and Mn toxicity in the studied soils. However, according to other authors, treatment with gypsum causes the loss of Mg^{2+} from the Ap horizon, and sugar foam, being a lime-rich amendment, is not so effective with AB horizons. Three additional combined options were tested with a view to solving Mg losses and improving the effectiveness in the AB horizon, namely: phosphogypsum + dolomitic residue, red gypsum + dolomitic residue, and the addition of a double amount of Ca by adding sugar foam and gypsum treatments in one combined amendment. Both gypsum-like treatments had similar effects and were the most effective treatments in reducing the effective Al and Mn saturation of the exchange complex in the Ap and AB horizons of the soils relative to the other treatments used at similar Ca rate. Only the addition of a double amount of Ca through application of the sugar foam and gypsum treatments in one amendment yielded better results than the other combined treatments on the surface horizon, the effect on the AB horizon being similar with all.

The most salient process after the release of available and exchangeable Al from the exchange complex is the formation and retention of Al-hydroxy polymers with all treatments. This is consistent with the results of our previous batch tests. The main analytical evidence of this result is the large increase in Al_{ox} in both horizons of the two soils. In addition, we could confirm this result using SEM-BSE observations and EDS analyses which showed the presence of massive formations of Al polymers associated with the clay minerals and organic matter irrespective of the amendment applied; additional evidence is provided by the $CuCl_2$ and DTPA extractions of Al^{3+} in the soils. The use of these by-products (particularly the combination of gypsum-rich by-products and the dolomitic residue) is an interesting alternative to other treatments. However, the solubility of these large pools of non-toxic Al polymers is highly sensitive to changes in the pH of the soil, so their long-term stability must be further studied and monitored.

References

Aitken, R.L. 1992. Relationships between extractable Al, selected soil properties, pH buffer capacity and lime requirement in some acidic Queensland soils. *Australian Journal of Soil Research*, **30**, 119–130.

Alcordo, I.S. & Rechcigl, J.E. 1993. Phosphogypsum in agriculture: a review. *Advances in Agronomy*, **49**, 55–118.

Alva, A.K. & Gascho, G.J. 1991. Differential leaching of cations and sulfate in gypsum amended soils. *Communications in Soil Science and Plant Analysis*, **22**, 1195–1206.

Arias, S. & Serrano, E. 1997. Effects of lime and gypsum amendments on cation redistribution and copper, zinc, and manganese availability in a Palexerult from SW Spain. *Agrochimica*, **XLI**, 233–240.

Barnhisel, R. & Bertsch, P.M. 1982. Aluminium. In: *Methods of Soil Analysis: Part 2, Chemical and Microbiological Properties* (eds A.L. Page *et al.*), pp. 275–300. American Society of Agronomy, Madison, WI.

Farina, M.P.W., Channon, P. & Thibaud, G.R. 2000. A comparison of strategies for ameliorating subsoil acidity. II. Long-term soil effects. *Soil Science Society of America Journal*, **64**, 652–658.

Garrido, F., Illera, V., Vizcayno, C. & García-González, M.T. 2003. Evaluation of industrial by-products as soil acidity amendments: chemical and mineralogical implications. *European Journal of Soil Science*, **54**, 411–422.

Illera, V., Garrido, F., Serrano, S. & García-González, M.T. 2004. Immobilization of the heavy metals Cd, Cu and Pb in an acid soil amended with gypsum- and lime-rich industrial by-products. *European Journal of Soil Science*, **55**, 135–145.

Juo, A.S.R. & Kamprath, E.J. 1979. Copper chloride as an extractant for estimating the potentially reactive aluminum pool in acid soils. *Soil Science Society of America Journal*, **43**, 35–38.

Lindsay, W.L. & Norvell, W.A. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Science Society of America Journal*, **42**, 421–428.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. *Advances in Soil Science*, **10**, 1–56.

McKeague, J.A. & Day, J.H. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science*, **46**, 13–22.

Oates, K.M. & Caldwell, A.G. 1985. Use of by-product gypsum to alleviate soil acidity. *Soil Science Society of America Journal*, **49,** 915–918.

Schultz, L.G. 1964. *Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale*. US Geological Survey Professional Paper 391-C, United States Government Printing Office, Washington, DC.

Shainberg, I., Sumner, M.E., Miller, W.P., Farina, M.P.W., Pavan, M.A. & Fey, M.V. 1989. Use of gypsum on soils: a review. *Advances in Soil Science*, **9,** 1–111.

Shuman, L.M. 1990. Comparison of exchangeable Al, extractable Al, and Al in soil fractions. *Canadian Journal of Soil Science*, **70,** 263–275.

Smith, C.J., Peoples, M.B., Keerthisinghe, G., James, T.R., Garden, D.L. & Tuomi, S.S. 1994. Effect of surface applications of lime, gypsum and phosphogypsum on the alleviating of surface and subsurface acidity in a soil under pasture. *Australian Journal of Soil Research*, **32,** 995–1008.

Smith, C.J., Goh, K.M., Bond, W.J. & Freney, J.R. 1995. Effects of organic and inorganic calcium compounds on soil-solution pH and aluminium concentration. *European Journal of Soil Science*, **46,** 53–63.

Soon, Y.K. 1993. Fractionation of extractable aluminum in acid soils: a review and a proposed procedure. *Communications in Soil Science and Plant Analysis*, **24,** 1683–1708.

Thomas, G.W. 1982. Exchangeable cations. In: *Methods of Soil Analysis: Part 2, Chemical and Microbiological Properties* (eds A.L. Page *et al.*), pp. 159–164. American Society of Agronomy, Madison, WI.

Van der Watt, H.V.H., Barnard, R.O., Cronje, I.J., Dekker, J., Croft, G.J.B. & Van Der Walt, M.M. 1991. Amelioration of subsoil acidity by application of a coal-derived calcium fulvate to the soil surface. *Nature*, **350,** 146–148.

Vizcayno, C., García-González, M.T., Fernández-Marcote, Y. & Santano, J. 2001. Extractable forms of aluminum as affected by gypsum and lime amendments to an acid soil. *Communications in Soil Science and Plant Analysis*, **32,** 2279–2292.

Walkley, A. & Black, A.I. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science*, **37,** 29–38.

Wright, R.J. 1989. Soil aluminium toxicity and plant growth. *Communications in Soil Science and Plant Analysis*, **20,** 1479–1497.