

Lime and phosphogypsum application and sulfate retention in subtropical soils under no-till system

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Abstract

This study reports long- and medium-term effects of the application of up to 12 Mg ha⁻¹ of phosphogypsum (PG) as soil conditioner and source of Ca and S, in two field trials, conducted under no-till systems. One field trial was located in Ponta Grossa, state of Paraná (PR), Brazil, on a loamy Oxisol, which received lime and PG applications in 1993. Another area of study was located in Guarapuava (PR), on a clayey Oxisol, which received PG in 2005. After thirteen years of surface-applied lime on the loamy Oxisol, we observed soil acidity reduction up to 80 cm depth, while PG effects Ca²⁺ and S-SO₄²⁻ contents were more pronounced at deeper soil layers. Sulfate distribution in soil profiles was mostly correlated with Fe_d and Fe_d-Fe_o. However, there was no long-term effect of lime and PG additions on no-till maize (*Zea mays*) and wheat (*Triticum aestivum*) yields. An appreciable movement of SO₄²⁻-S to the subsoil was observed in soil samples from the clayey Oxisol after surface-applied PG. This was observed even in the medium term (3.5 years) and despite the higher adsorption capacity of sulfate. In this case, PG addition had positive benefits on maize and triticale (*X Triticosecale*) yields due to the supply of Ca²⁺ and SO₄²⁻-S to the plants.

Keywords: sulfur, soil acidity, sulfate adsorption, weathered soil, subsoil acidity, cereal crops

1. Introduction

Acidity amelioration is one of the most important strategies in the management of highly weathered soils for an adequate crop growth. Approximately 70% of the Brazilian cultivated soils are highly acidic, showing toxic levels of aluminum (Al³⁺) and manganese (Mn²⁺), and low availability of exchangeable bases (Ritchey *et al.*, 1982). Therefore, the application of soil amendments is a primary strategy to achieve

satisfactory yields in Brazilian agricultural systems.

In such weathered tropical soils, lime and phosphogypsum (PG) are applied as soil amendments to alleviate Al³⁺ toxicity and improve the root environment, increasing the efficiency of applied nutrients and benefiting crop growth and yield (Toma *et al.*, 1999; Farina *et al.*, 2000a; Caires *et al.*, 2011b).

Under no-till systems (NTS), soil acidity is alleviated by surface-applied lime (without incorporation), there by maintaining soil aggregation. Nevertheless, in many cases, the amelioration of soil acidity by lime application may be restricted to the first soil layers (0 to 10 cm) due to soil conditions and the low mobility of lime products reaction. Subsoil acidity is also one of the major yield-limiting factors in acid soils (Toma *et al.*, 1999), since it restricts root growth decreasing the exploitation of water and nutrients. Under water deficient situations, the plant roots may need to explore the subsoil layers, thus improving soil layers below the topsoil can be beneficial for grain yield (Ritchey *et al.*, 1980).

Surface-applied PG ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is an alternative to provide Ca to crops and to decrease Al toxicity in soil subsurface layers (Oates and Caldwell, 1985) due to its relative higher solubility (0.24g/100g H_2O) when compared to lime. It is also a source of sulfur (minimum of 16% S) and provides a long-term residual effect when applied in large amounts, mainly in clayey soils (Toma *et al.*, 1999; Caires *et al.*, 2011b; Blum *et al.*, 2011).

Currently, the recommendation of PG requirements is based on clay content for most Brazilian agricultural soils. Due to the high operational costs of gypsum application (Toma *et al.*, 1999), high rates of the product are applied in the first year in order to promote long-term effects, especially in clayey soils. However, sulfate and cation losses must be considered for PG applications (Alves and Lavorenti, 2004b). There are many other factors governing sulfate adsorption and leaching. Some of these factors are for example: (i) soil pH (Hue *et al.*, 1985; Zhang and Yu, 1997), (ii) the presence of other anions such as phosphate (Bolan *et al.*, 1988), (iii) the presence of other cations in the soil solution (Chao *et al.*, 1963; Cichota *et al.*, 2007), and (iv) organic matter content (Ensminger, 1954; Couto *et al.*, 1979). The no-till soil surface layer presents unfavorable conditions for sulfate adsorption due to additions of phosphate fertilizers, the surface application of lime and practices that increase soil organic matter content. Therefore, it is important to

evaluate the subsoil conditions to measure SO_4^{2-} -S and cation leaching, especially when high amounts of PG are applied with the aim of achieving long-term effects.

During the 70's and 80's not only the research involving PG was intensified, but also the concern about the use of this phosphoric acid industry's by-product. In those decades many benefits of PG application were brought up, such as the increase of exchangeable Ca, the reduction of exchangeable Al, and the formation of deep rooting in the sub-soil (Reeve and Sumner, 1972; Ritchey *et al.*, 1980; Sumner *et al.*, 1986). A number of field studies have reported about the effects of PG application (Zambrosi *et al.*, 2007; Soratto and Crusciol, 2008; Caires *et al.*, 2011a; b; c). In these studies, however, the depth of sampling was commonly restricted to 60-80 cm, since 90% of the roots of the main crops are concentrated in this layer. However, there is still a lack of information about long-term of PG effects on the amelioration of sub-soil acidity and ion leaching of top soil.

This study reports long- and medium-term effects of PG applications conducted under a NT System in two field trials. Soil chemical attributes and factors related to SO_4^{2-} -S permanence in the soil [dithionite extractable Fe (Fe_d), oxalate extractable Fe (Fe_o), oxalate extractable Al (Al_o), pHNaF, remaining P (Prem) and remaining S (Srem)] were evaluated up to 200 cm depth. Grain yields of cereal crops *Z. mays*, *Taestivum* and *X Triticosecale* were also assessed after PG application of up to 12 t ha⁻¹.

2. Materials and Methods

2.1. Site description and soils

The experiments were carried out in two locations of the Brazilian state of Paraná: (i) Ponta Grossa (25°10'S, 50°18'W, 794 m a.s.l.) on a loamy Typic Hapludox, and Guarapuava (25°17'S, 51°48'W, 997 m.a.s.l.) on a clayey Typic Hapludox. The state of Paraná is the primary producer of cereals, legumes

and oil seeds in Brazil, where about 64.1 millions of tons were produced in 2010. This represented 21.6% of the national production (Brazil, 2011). The oxisols studied are widely distributed across the region and, therefore, are highly representative of the area. Table 1

shows the results obtained from the soil chemical and particle size distribution analyses at 0-20 cm depth, and some mineralogical attributes of the diagnostic soil horizon at 120 cm depth.

Table 1. Soil attributes for different depths before the establishment of the experiments.

Attribute	Typic Hapludox (Ponta Grossa, Paraná)	Typic Hapludox (Guarapuava, Paraná)
	-----Surfacelayer (0-20 cm)-----	
pH (0.01 M CaCl ₂)	4.5	5.9
¹ Organic C (g dm ⁻³)	19	28
² Exchangeable cations (mmol ₍₊₎ dm ³)		
Ca ²⁺	16	48
Mg ²⁺	10	22
K ⁺	1.4	4.3
Al ³⁺	6	0
Cation Exchange Capacity pH 7.0 (CEC) (mmol ₍₊₎ dm ³)	85.4	119
P, Mehlich-1 (mg dm ⁻³)	8.9	4.7
SO ₄ -S, 0.01 mol L ⁻¹ Ca(H ₂ PO ₄) ₂ (mg dm ⁻³)	19.1	5.9
Soil Texture	Loamy	Clayey
	-----Subsurface layer (≅120 cm)-----	

Organic C (g dm ⁻³)	8.1	10.2
SiO ₂ (g kg ⁻¹)	38	101
Al ₂ O ₃ (g kg ⁻¹)	144.36	294.3
Fe ₂ O ₃ (g kg ⁻¹)	53.7	175
MnO (g kg ⁻¹)	0.05	15.6
TiO ₂ (g kg ⁻¹)	2.1	482.4
Ki (SiO ₂ /60)/(Al ₂ O ₃ /102)	0.45	0.58
Kr (SiO ₂ /60)/(Al ₂ O ₃ /102)+(Fe ₂ O ₃ /160)	0.36	0.43
Mineralogy (relative distribution)	Gb>Kt>Hm=Gt	Gb>Kt>Gt>Hm
Kaolinite (%)	12.9	25.2
Gibbsite (%)	26.8	37.1
Hematite (%)	2.2	7.4
Goethite (%)	2.9	9.9

¹. Walkley-Black

². Ca, Mg and Al extracted by 1 M KCl and K extracted by Mehlich⁻¹.

³. Kt (kaolinite), Gb (gibbsite), Hm (hematite), Gt (goethite)

Iron (Fe) and Al were extracted with 9M H₂SO₄ solution, and Si was extracted with NaOH 30% (v/v) solution. Fe and Al contents were determined by atomic absorption spectrophotometry (AAS), and Si was quantified by gravimetry (Camargo *et al.*, 1986). It is assumed that the association of Fe, Al, Mn and Ti contents with secondary minerals are solubilized with 9 M H₂SO₄ solution, while Si is solubilized with NaOH 30% (v/v) solution. Taking these values into consideration, the weathering indexes Ki (SiO₂/60)/(Al₂O₃/102) and Kr (SiO₂/60)/[(Al₂O₃/102)+(Fe₂O₃/160)] were calculated. A mineralogical analysis of the clay fraction was conducted after treatment with Na-CBD (citrate-bicarbonate-dithionite) using X-ray analysis of oriented mounts on glass slides. The samples were saturated with either Mg or K, solvated with glycerol, heated to 350 and 550 °C, and X-rayed. The X-ray diffractograms were obtained in a diffractometer (Philips X'pert System) operating at 40 kV and 40 mA using Ni-filtered Cu-K α radiation, at 1.2 ° 2 θ min⁻¹ in the 3 to 45° 2 θ range. We also estimated the amounts of minerals, such as kaolinite, gibbsite, goethite and hematite, according to Kämpf and Schwertmann (1983).

Both soils are highly weathered, however, the Typic Hapludox from Guarapuava showed higher amounts of organic carbon, a higher degree of fertility, and no exchangeable Al. Moreover, the Guarapuava soil had a low Ca/Mg ratio (Caires *et al.*, 2004) and a low sulfate content. The Typic Hapludox from Ponta Grossa was highly acidic, with toxic amounts of Al³⁺ and low amounts of exchangeable bases. Both soils had gibbsite predominance in the clay fraction.

2.2. Experimental design, treatments and cropping studies

Before the establishment of the experiment both field sites were cultivated with grain crops under NTS during 15 years. The experiment in Ponta Grossa was established in 1993 on a randomized complete block design with three replications. The plot size was of

50.4 m² (6.3 × 8.0 m). The treatments consisted of dolomitic lime broadcast on the soil surface at 0 or 6 t ha⁻¹ in July 1993, and PG broadcast on the soil surface at 0 or 12 t ha⁻¹ in November 1993. Plots were unlimed or limed. Lime rate was calculated to increase the base saturation in the topsoil (0-20 cm) to 70%, as shown by Caires *et al.* (2005), while the PG rate was calculated to achieve the same equivalent in calcium content of the lime treatments. The experiment in Guarapuava was established in September 2005 with PG application at 0, 4, 8, and 12 t ha⁻¹ in a randomized complete block design with four replications. The plot size was of 49.0 m² (7.0 × 7.0 m). The PG rates were calculated to raise the exchangeable calcium/magnesium (Ca/Mg) ratio of the topsoil (0-20cm) to values between 4 and 8 based on data from previous studies (Caires *et al.*, 1999, 2004). More details concerning to the experimental site in Guarapuava can be found in Caires *et al.* (2011c).

In Ponta Grossa, *Z. mays* was sown in October 2008 (15 years after lime and PG applications) at a seeding density of rate of 6 seeds m⁻², and a row spacing of 0.85 m using the hybrid Pioneer 30F53. Cereal grains were harvested from a 10.8 m² plot. In July 2009 wheat (*T. aestivum* cv. Supera) was sown at a density of 175 kg ha⁻¹ and with a row spacing of 0.22m. The crop was harvested in November 2009 from a 4m² plot.

In Guarapuava, maize was sown in September 2008 (Pioneer 30R50) at a seeding rate of 5.5 seeds m⁻² with a row spacing of 0.75m. The harvest was performed in April 2009 from a 8.4-m² plot. In July 2009, triticale (*X Triticosecale* cv. IPR 111) was sown at a density of 240 kg ha⁻¹. This crop was harvested in November from a 4 m² plot. Cereal grain yields were corrected to a moisture of 130 g kg⁻¹ and the crop waste was left on the soil surface after the grain harvest.

The yield of cereal plants (maize, wheat or triticale) was evaluated in both areas of study. These cereal plants have shown stronger responses to PG application than leguminous plants as soybean or bean (Raij *et al.*, 1998; Toma *et al.*, 1999; Caires *et al.*, 1999; 2004;

Table 2. Cropping history and amounts of N, P, and K applied since the establishment of the experiments.

Agricultural year	Crop	N	P	K
			kg ha ⁻¹	
-----Ponta Grossa-----				
1993-1994	soybean	0	22	42
1994-1995	maize	65	30	33
1995-1996	soybean	0	22	42
1996	wheat	58	27	52
1996-1997	soybean	0	0	40
1997	triticale	60	32	62
1997-1998	soybean	0	0	40
1998-1999	soybean	0	28	54
1999-2000	soybean	0	13	25
2000-2001	maize	132	28	82
2001-2002	soybean	5	20	36
2002-2003	soybean	0	23	46
2003	wheat	80	0	33
2003-2004	soybean	0	26	50
2004-2005	maize	120	40	55
2005-2006	soybean	6	36	50
2006-2007	soybean	0	22	42
2007-2008	soybean	0	26	42
2008-2009	maize	134	36	89
2009	wheat	80	0	33
-----Guarapuava-----				
2005-2006	maize	195	39	62
2006-2007	soybean	0	0	0
2007-2008	soybean	5	22	42
2008-2009	maize	204	45	94
2009	triticale	66	24	60

2006; 2011b; c; Farina *et al.*, 2000a; Rheinheimer *et al.*, 2005; Soratto and Crusciol, 2008).

According to the soil test recommendations made for the state of Paraná, the rates of fertilization varied with the type of crop and year in both areas under study (Table 2). Nitrogen, P, and K were applied most times as urea, triple superphosphate, and potassium chloride, respectively.

Figure 1 shows the seasonal rainfall data observed in both areas under study during crop development. Guarapuava showed a higher mean annual rainfall (1,922 mm) than Ponta Grossa (1,554 mm). Ponta

Grossa showed its lower rainfall rate in December 2008 during maize flowering.

2.3. Soil sampling and chemical analysis

Soil samples were collected in Ponta Grossa in 2007, thirteen years after PG application. In Guarapuava samples were collected in 2009, three and half years after PG application. Twelve soil core samples per plot were taken with a soil probe sampler to obtain a composite sample of 0-5, 5-10, and 10-20 cm depths, and five cores of the 20-40 up to 180-200 cm depth.

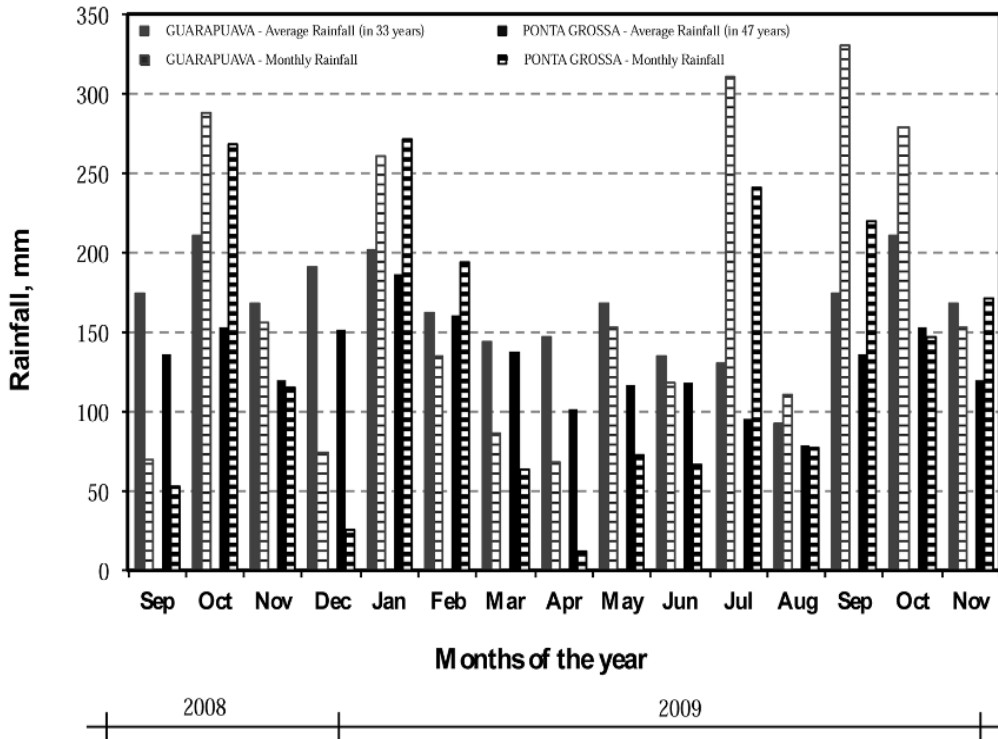


Figure 1. Monthly rainfall registered during the experiments and average monthly rainfall recorded for Ponta Grossa (47 years) and Guarapuava (33 years).

Samples were dried at 40°C, ground and sieved through a 2 mm sieve. Then the samples were stored in permeable plastic bags.

To evaluate the chemical alterations over the long and medium term of the treatments at both study sites, the soil pH was determined. This parameter was measured using 0.01 M CaCl₂ suspension and 1:2.5 v/v of soil/solution. The Δ pH was calculated by subtracting the pH measured in water from the one measured in 1 M KCl following the methodology proposed by Mekaru and Uehara (1972). The exchangeable Al³⁺ was extracted using 1 M KCl solution and determined by titration with 0.025 M NaOH solution, and Ca²⁺ and

Mg²⁺ were also extracted using 1 M KCl solution. These elements were determined by atomic absorption spectroscopy. The S-SO₄²⁻ soil contents were extracted with 0.01 M calcium phosphate (Fox *et al.*, 1964) in a 1:2.5 (v/v) soil/solution ratio. The suspension used (soil plus extracting solution) was shaken for 30 min, filtered and determined by turbidimetry. The use of calcium phosphate solution was first suggested by Fox *et al.* (1964), which contains sufficient P to displace most of the adsorbed sulfate in weathered soils. In selected layers of the control plots (without lime or PG application) adsorption isotherms were built by shaking 2.5 g of soil with 25 mL of CaCl₂ solutions, which contained SO₄²⁻ added as K₂SO₄, for 24h. After shaking

the sample, the suspensions were filtered through a filter paper (Whatman n° 42), and the solutions were analyzed for sulfate content using BaSO₄ turbidimetry. The amount of sulfate adsorbed was calculated as the difference between the initial and final sulfate concentrations. The results were fitted to the Langmuir and Freundlich isotherms, widely used for this purpose.

Other chemical attributes were obtained including organic carbon (Walkley Black) and clay content using the densimeter method (Gee and Or, 2002). “Free” iron oxides (Fe_d) were extracted using a Na-CBD solution as suggested by Mehra and Jackson (1960). Oxalate-extractable Fe and Al (which represent the poorly crystalline oxides) were determined according to methodology proposed by Loeppert and Inskeep (1996). The soil was equilibrated with 0.3 M ammonium oxalate at pH 3.25 on an end-over-end shaker. After centrifugation, the concentrations of Fe and Al in the equilibrium solution were measured by atomic absorption spectrophotometry. These forms of Fe and Al have been described as reactive or amorphous and are considered to exert a major influence on the P sorption capacity of many soils (Singh and Gilkes, 1991). Additionally the pH NaF (shaking 0.5 g of soil for 1 h with 20 mL of 1 M NaF) was determined following the methodology proposed by Bolland *et al.* (1996). The index proposed by these authors was created as a quick and economical procedure to access the P sorption capacity of soils. Thus, the increasing pH of extracts is an indirect measure of the P sorption capacity of soils (Singh and Gilkes, 1991). The same index was also used by Alves and Lavorenti (2004 a, b), which showed a suitable estimation of sulfate adsorption capacity for weathered sub-soils. The remaining P (Prem) and S (Srem) were obtained following the methodologies proposed by Alvarez *et al.* (2000) and Alvarez *et al.* (1983), respectively. The indexes Prem and Srem can also be used to predict S adsorption capacity, when compared to the pHNaF. The determination of Srem was performed shaking the soil samples with 0.01 M CaCl₂, which contained 20 mg L⁻¹ of S in the proportion 1:10 (soil/solution). The samples were centrifuged and filtered, and the suspension was quantified by turbidimetry.

2.4. Statistical Analysis

The effects of soil amendments (in both experiments) on soil chemical attributes and on crop grain yields were analyzed using analysis of variance with a randomized complete block design. Means were compared using Tukey test ($p \leq 0.05$) for the experiment conducted in Ponta Grossa, and using polynomial regression ($p \leq 0.05$) for the experiment conducted in Guarapuava. We used Pearson product moment to correlate the soil properties with the sulfate retained in the profile. The correlation coefficients were also used to explain increases in crop yield for the Guarapuava experiment.

3. Results and Discussion

3.1. Soil chemical attributes - thirteen years after lime and phosphogypsum application on a loamy Oxisol under no-till system

When the soil sampling was performed, after the surface application of lime and PG, the soil samples showed a high acidity and low pH values at all depths evaluated (Figure 2). Higher pH values were observed from 0-80 cm for the treatments that received lime application, either with or without PG. The effects of surface-applied lime in alleviating soil acidity below the point of placement have been reported in many field studies under NTS (Caires *et al.*, 2005; 2008; 2011b; Soratto and Crusciol, 2008) and these effects have been attributed to the benefits brought with the adoption of NTS, such as the use of plant debris on the soil surface (Miyazawa *et al.*, 2002; Franchini *et al.*, 2003) and the improvement in soil aggregation and aggregate stability (Six *et al.*, 1999). The aggregation improvement allows to the fine particles of surface-applied lime to move into and down of the profile along with water infiltration to alleviate the sub-soil acidity (Amaral *et al.*, 2004). Regardless of the mechanism involved, surface lime application is in many cases as effective as the incorporation of lime to reduce the sub-soil acidity in variable charge soils (Caires *et al.*, 2011b).

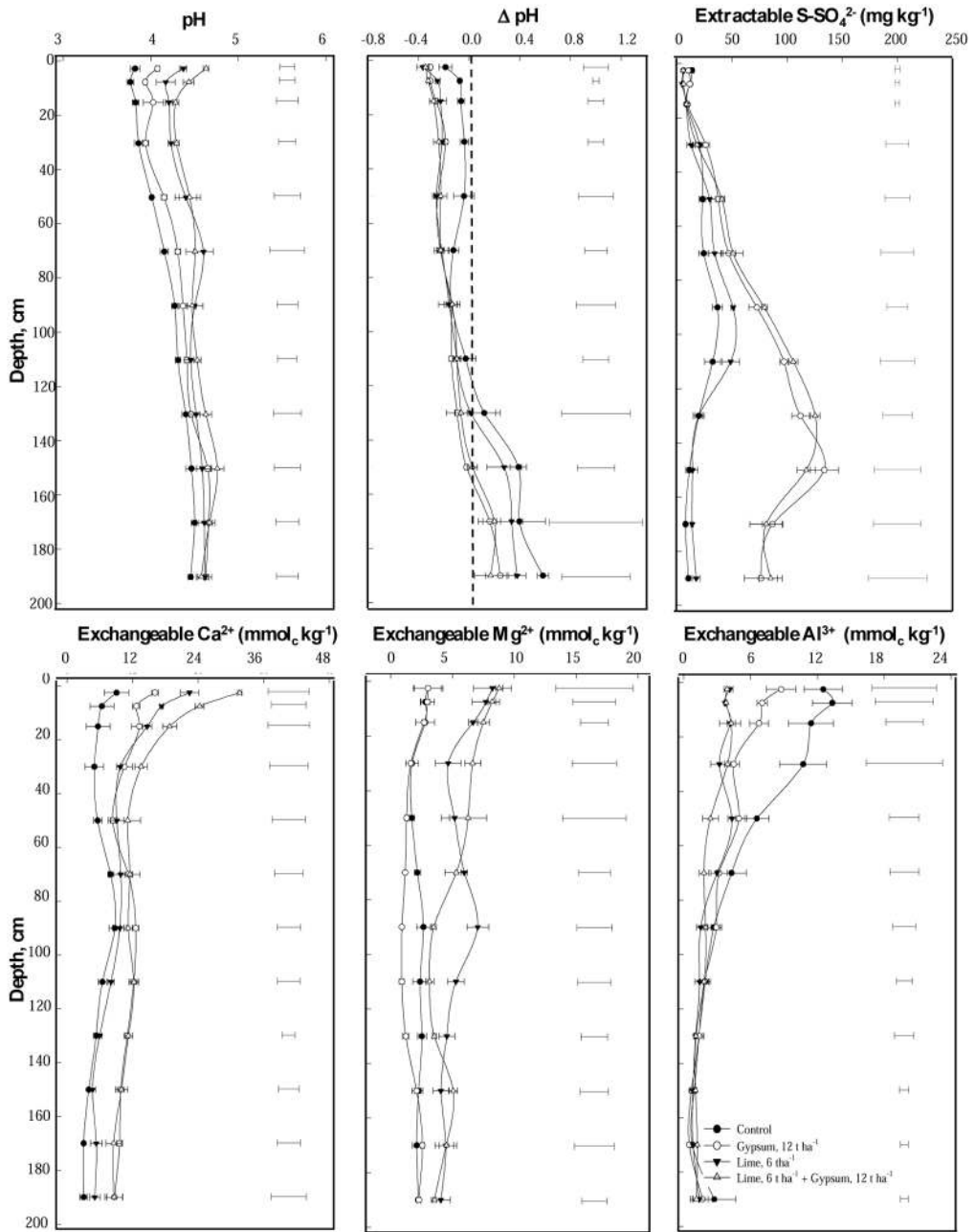


Figure 2. Effects of surface applied lime and phosphogypsum on soil attributes at different depths, 13 years after application. The bars at each depth indicate the LSD at $p = 0.05$.

The main effects of the treatments on acidity alleviation were observed up to 80 cm depth, and the soil pH of the plots that did not receive any amendment (control) was higher in the sub-soil than on the surface. This can be explained by the acidification caused by the use of high rates of N fertilizers (Table 2). Soils of the humid tropics used for grain cropping under NTS have become more acidic because of the use of increased rates of ammonium-based N fertilizers to obtain more intensive production of cereal crops, like wheat and maize (Juo *et al.*, 1995; Caires *et al.*, 2005; Garbuio *et al.*, 2011). In sub-surface soil samples (120-140 cm), slight increases in pH were observed in the plots that received PG. This increase can be attributed to the adsorption of sulfate on the surface of Fe and Al oxides, displacing OH⁻ and thus promoting partial neutralization of soil acidity (Reeve and Sumner, 1972). This is called “self-liming effect”, and was also reported by Toma *et al.* (1999) and Farina *et al.* (2000b).

The ΔpH (Figure 2) could be used to predict net soil charge (Mekaru and Uehara, 1972), which was affected by lime and PG application. Up to 80 cm depth, the soil profile had a negative ΔpH since management strategies employed in the area - like liming, fertilizer application, and conservation agriculture (preserving crop residues on the soil surface and increasing contents of soil organic matter) interfere with variable charge soils increasing the net negative charge. At depths greater than 120 cm we observed the dominance of positive charges, due to high amounts of Fe/Al oxides and lower content of organic matter (Table 1). In such layers, a ΔpH displacement (to the left region of the figure) was observed with the application of PG, due to the sulfate adsorption mechanism reported by Reeve and Sumner (1972). Lime effects on ΔpH were observed up to 80 cm depth.

After thirteen years of PG application, sulfur (SO₄²⁻-S) extracted by calcium phosphate was more concentrated at 100-160 cm depth (Figure 2). The lime application in 1993 increased the SO₄-S leaching due to increases in pH. This effect promotes more

negative charge and subsequent sulfate repulsion. A previous study that evaluated the same experiment after eight months of PG application showed that approximately 60% of the SO₄-S supplied by PG and extracted by 0.5 M ammonium acetate in 0.25 M acetic acid had leached to depths lower than 60 cm (Caires *et al.*, 1998). We choose to use the extractant 0.01 M Ca(H₂PO₄)₂ proposed by Fox *et al.* (1964), because it has enough phosphate to displace most of the adsorbed sulfate in many soils, and because we worked with highly weathered soils samples. Under the conditions previously described, the Ca can keep the ionic strength of the solution, and also depress the extraction of soil organic matter eliminating all possible contamination from the extractable organic S (Beaton *et al.*, 1968). At lower depths (between 120-160 cm), the higher sulfate adsorption persisted for many years after PG application, which could be attributed to the positive charges (as showed by ΔpH - Figure 2) attracting the negative charged sulfate ions. This result agrees with those observed by Farina *et al.* (2000b), who attributed the retardation of PG movement to the reversion of electric charge in sub-surface layers of an Ultisol in South Africa, as reflected by differences in ΔpH. In this study, part of this behavior could be attributed to the increases in clay content at deeper soil layers, which can be associated to the minerals present in the area (Table 1). Because of the solubility of PG and the soil texture, we would have expected that after thirteen years of application, it would have been completely leached from the soil profile.

We observed effects of the treatments on exchangeable Ca and Mg distribution in the entire soil profile (Figure 2). The higher increases of exchangeable Ca content in both surface and sub-surface layers were observed when lime + PG were applied. The surface application of lime in 1993 showed a residual effect up to 100 cm depth, while Ca movement up to 200 cm depth. These results were verified in plots that received PG. Increases in exchangeable Ca content due to PG application have been frequently reported (Toma *et al.*, 1999; Farina *et al.*, 2000b; Caires *et al.* 2004; 2006; 2011c), since each ton of PG provides around 5 mmol_c dm⁻³ of this nutrient.

However, the duration of the effect varies with the amount of product applied to the soil and the soil texture. In this experimental area, a previous study reported fast leaching of Ca^{2+} 24 months after PG application, where 40% of the applied Ca^{2+} had leached below 80 cm depth (Caires *et al.*, 2001).

There was an increase in exchangeable Mg content with the surface application of lime up to 100 cm depth (Figure 2). It was also observed a Mg^{2+} leaching at 80-120 cm depth when the combination of lime + PG was applied. After 13 years of PG application we were not able to see an effect of this amendment on the contents of exchangeable Mg. In the same experiment, higher losses of Mg^{2+} were reported even only twelve months after liming and eight months after PG application (Caires *et al.*, 1998). Moreover, the application of lime increased the Mg^{2+} levels in the soil solution making it very susceptible to leaching. At eight months after application of PG at 12 t ha^{-1} , exchangeable Mg contents were higher than those observed in this study (around $10 \text{ mmol}_e \text{ dm}^{-3}$ in the control plots and 30 mmol dm^{-3} in the ones that had received lime application). In a long-term experiment, losses of exchangeable Mg from the surface layers caused by PG application were relatively small when compared to the application of lime alone. These findings support the results obtained for Caires *et al.* 2011b.

We also observed toxic levels of Al^{3+} up to 100 cm depth, except for those treatments that received lime application (Figure 2). Exchangeable Al is responsible for the harmful effects of soil acidity due that this element is released in low pH conditions. On the other hand, the increases of pH due to lime application (Figure 2) caused hydrolysis of the Al ions, reducing their toxicity. It is important to mention that even after long-term applications it was possible to observe the effects of soil amendments on exchangeable Al^{3+} reduction up to 80 cm depth. Below this layer, Al contents were smaller than those observed in samples from the surface layer. The combined surface application of lime and PG under NTS was effective in maintaining the exchangeable Al at non-toxic levels for crops over the long term.

3.2. Soil chemical attributes - 3.5 years after phosphogypsum application on a clayey Oxisol, under no-till system

Surface-applied PG in 2005 did not affect the values of soil pH of samples collected in 2009, which were measured in 0.01 M CaCl_2 up to 60 cm depth (Figure 3). The lack of effect of PG on soil acidity was expected because PG is a neutral salt that does not have the ability of consume H^+ protons. Conversely, a linear increase in pH was observed at the lower depths (from 60 to 200 cm) as a response to PG rates, which can also be attributed to the self-liming mechanism previously reported by Reeve and Sumner (1972). It is note worthy that this increase in pH due to surface PG application was of small magnitude, and the soil utilized in this study had a relatively low acidity for a highly weathered soil. Consequently, very small amounts of exchangeable Al were found through out the investigated soil profiles (Figure 3).

The soil presented net negative charge (represented by ΔpH) up to 80 cm depth. Below this depth, the remaining charge was found to be predominantly positive. The effect of PG in the soil net charge took place from 80 to 200 cm, reducing the ΔpH (Figure 3). Differences between PG-treated and control plots in terms of ΔpH lend to support the important role played by SO_4^{2-} sorption-precipitation reactions, where the ΔpH differentials are clearly related to the quantities of SO_4 held in the soil, as found by Farina *et al.* (2000b). After the application of PG rates, the content of sulfate extracted with monocalcium phosphate increased in most depths evaluated ($p \leq 0.05$) (Figure 3). In most part of the profile where the samples were taken, the soil samples showed high clay content (700 g kg^{-1}). Unlike to the soil of the first experiment, however, which was also discussed in this review, the levels of Fe_d were constant along the profile (Table 3), and the prevalence of sulfate in the lower depths can be linked primarily to the effect of organic matter. This fact generated negative charges and promoted repulsion of the anions that moved to lower depths.

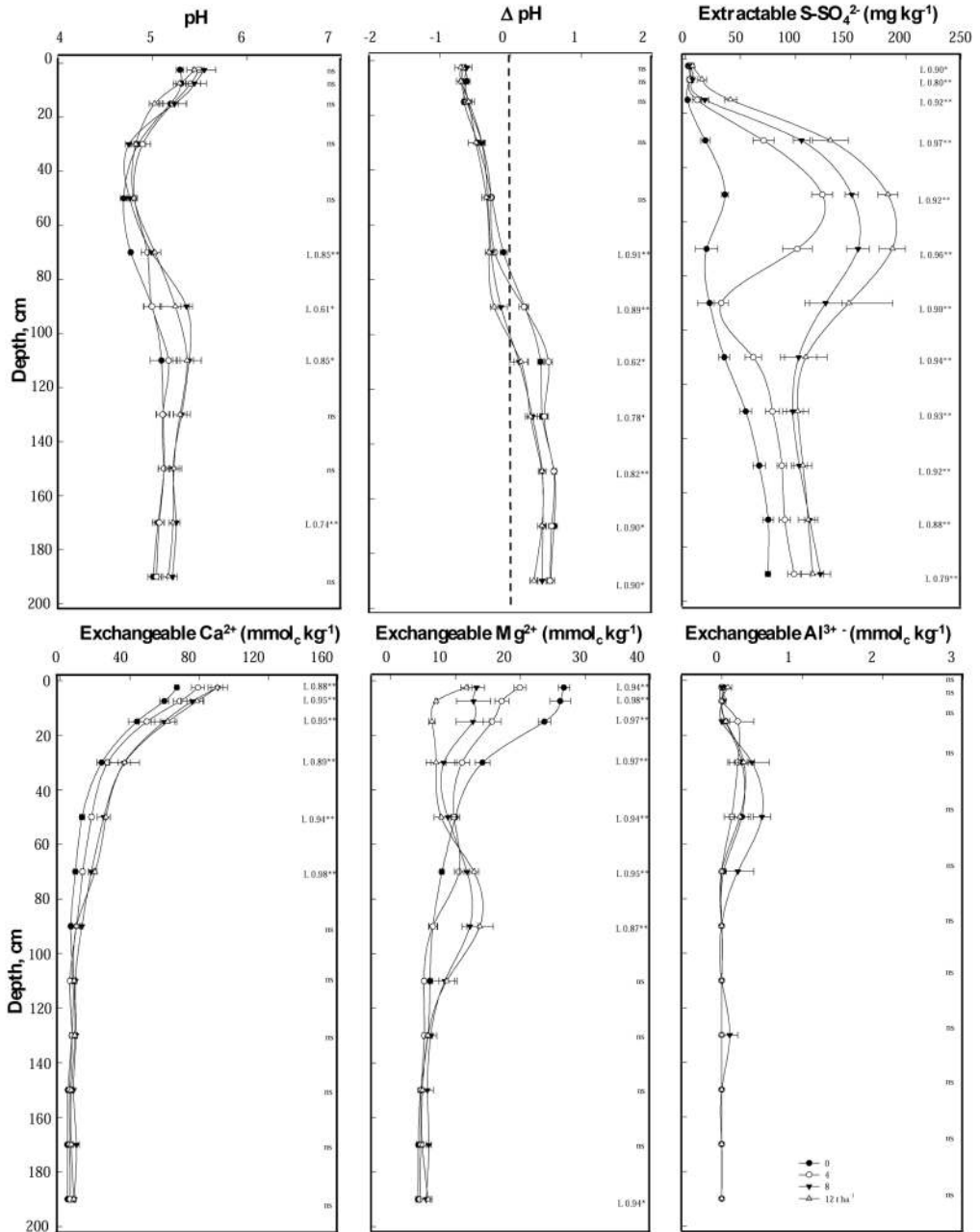


Figure 3. Effects of phosphogypsum rates on soil attributes at different depths, 3.5 years after application. L = significant by linear regression; * $p \leq 0.05$; ** $p \leq 0.01$; ns = not significant.

Table 3. Soil attributes related to sulfate adsorption.

Depth (cm)	Srem	Prem	OrganicC	Fe _d	Fe _o	Al _o	pH NaF
	-----mg L ⁻¹ -----		-----g kg ⁻¹ -----				
<i>LVd – Ponta Grossa/PR</i>							
0-5	14.9	21.9	23.6	36.2	1.7	3.9	9.5
5-10	14.7	18.0	19.3	38.0	1.7	3.5	9.8
10-20	14.8	15.7	17.4	37.3	1.9	4.4	9.9
20-40	12.2	13.2	14.6	42.0	1.6	4.6	10.0
40-60	10.6	8.7	11.6	45.9	1.5	4.7	10.3
60-80	10.0	7.0	10.9	46.2	1.4	6.1	10.4
80-100	9.4	5.1	10.4	47.5	1.4	5.8	10.5
100-120	7.7	3.9	9.2	50.8	1.6	6.0	10.5
120-140	6.5	2.8	8.1	50.1	1.6	4.7	10.6
140-160	4.8	1.6	7.4	49.8	1.6	4.8	10.5
160-180	4.2	1.3	8.2	48.3	1.5	3.6	10.4
180-200	4.1	1.4	7.4	49.4	1.6	4.7	10.5
<i>LVd – Guarapuava/PR</i>							
0-5	15.0	2.5	44.2	168.0	5.2	10.7	10.3
5-10	13.6	1.7	33.4	172.7	4.9	9.6	10.5
10-20	12.3	1.4	29.4	167.6	5.1	9.6	10.6
20-40	9.2	1.4	25.1	173.1	5.2	11.7	10.8
40-60	6.3	0.7	20.2	164.9	5.3	12.0	10.9
60-80	4.7	0.5	17.7	165.3	5.8	13.7	11.0
80-100	3.6	0.3	14.3	166.1	5.8	10.3	11.0
100-120	3.7	0.1	11.4	173.1	6.1	10.4	10.9
120-140	3.8	0.2	10.2	168.8	6.2	10.1	10.9
140-160	3.5	0.1	8.7	172.7	6.0	9.5	10.9
160-180	3.7	0.1	7.3	179.8	6.0	9.2	10.9
180-200	3.7	0.1	7.3	192.7	6.0	8.5	10.8

Since the values of ΔpH were zero or positive in the subsurface layers (Figure 3), combined with higher amounts of Al_2O_3 and Fe_2O_3 (175.0 and 294.3 g kg⁻¹, respectively) and lower Ki and Kr (Table 1), we can assume that the soil had reached an advanced degree of weathering. Under these circumstances, $\text{SO}_4^{2-}\text{-S}$ was rapidly leached to the sub-soil layers. Sulfate movement is dependent on the particle size distribution of the soil, the intensity of the rainfall after application, the amount of S supplied, and the presence of organic matter and other ions. In this case, the movement of sulfate in the soil profile can be attributed to the low soil acidity (Figure 3) and high levels of organic C (Table 1), as well as

fertilization with P (Table 2), especially in the first layers of the soil.

We found a linear increase in exchangeable Ca content up to 80 cm depth and leaching of exchangeable Mg up to 120 cm depth after application of PG rates (Figure 3). When high rates of PG were applied to clayey soils, the effects of increasing contents of Ca in the profile were very durable. In Georgia (USA), Toma *et al.* (1999) found an increase in levels of exchangeable Ca up to 120 cm after 16 years of 35 Mg ha⁻¹ of P G application in a kaolinitic soil. The levels of exchangeable Mg were reduced linearly with the PG rates applied from 0 to 40 cm depth (Figure 3). Leaching of exchangeable

Mg from the soil surface resulted in an increase surface of nutrient content at 60-120 cm depth after 3.5 years of PG application. According to Zambrosi *et al.*, 2007, the leaching of exchangeable Mg contents in the soil, with the addition of PG, is facilitated by the formation of the ionic-pair $MgSO_4$. This finding has been also reported in several field studies (Caires *et al.* 1998; 2004; 2006; 2011b; c; Toma *et al.*, 1999). For example, in the study performed by Toma *et al.* (1999), the Mg^{2+} leaching was observed from the 20-60 cm layer to the 100-120 cm layer, after sixteen years of PG application. The alleviation of soil acidity with dolomitic lime may be a viable alternative to minimize losses of exchangeable Mg caused by PG applications (Caires *et al.*, 2011b).

As the soil in this study presented low acidity, the levels of exchangeable Al found in the soil were lower than 1 mmol kg^{-1} , and were not influenced by the PG rates (Figure 3). After 3.5 years of the PG application, we did not observe an effect of the treatments on soil exchangeable K contents, although leaching of K^+ was observed in the first years of evaluation (Caires *et al.*, 2011c). Potassium contents were 8.6 mmol kg^{-1} in the control treatment (without PG addition) and 7.8 mmol kg^{-1} in the treatment that had received PG at 12 t ha^{-1} . K contents were, in average, 5.5 mmol kg^{-1} at 5-10 cm depth and 3.5 mmol kg^{-1} at 10-20 cm depth. Below the 60 cm depth, K contents were lower than 1.0 mmol kg^{-1} .

3.3. Factors related to sulfate retention

After thirteen years of PG application at 12 t ha^{-1} , 52% (503.6 mg kg^{-1}) of applied sulfate was recovered in the soil profile (0-200 cm) in the experiment carried out in Ponta Grossa (Figure 2). However, the remaining sulfate was leached to lower depths. In the experiment carried out in Guarapuava, we recovered 100% of the sulfate provided by the PG application at 12 t ha^{-1} in the soil profile (0-200 cm). A higher sulfate concentration was found in the 20-60 cm depth (Figure 3). The sulfate leaching losses may reduce the long-term possibility of maintaining the S supply of crops in low input farming (Eriksen and Askegaard, 2000), and may also remove cationic nutrients from the

root zone. Sulfate losses are a concern in agricultural and economic areas; however, they are not considered as a serious environmental problem. The presence of excessive amounts of sulfate can be a concern in water supplies, because of its cathartic effect upon humans (Jang; Townsend, 2001). Also, it may convert to hydrogen sulfide during some reuse scenarios, causing noticeable odors and tastes.

Table 3 shows soil attributes related to sulfate adsorption. Srem varied from 4.1 to 14.9 mg L^{-1} in the loamy Oxisol from Ponta Grossa, and from 3.5 to 15 mg L^{-1} in the clayey Oxisol from Guarapuava. Prem showed a wide variation between soil depths and the two experimental areas, varying from 1.3 to 21.9 mg L^{-1} in Ponta Grossa, and from 0.1 to 2.5 mg L^{-1} in Guarapuava (Table 3). Although both Srem and Prem normally present a close correlation with the maximum sulfate adsorption capacity in soils (Alves and Lavorenti, 2004a), Prem showed higher discriminatory capacity of sulfate adsorption in the soil profiles of our study. Based on these results, we selected depths with similar adsorption capacities and fitted adsorption isotherms for both experiments. The data presented a better fit to the Freundlich than to the Langmuir equation (Figure 4), and support the results presented by Bolan *et al.* (1988) and Alves and Lavorenti (2004b). The adsorption capacity increased with depth in both soils evaluated, and higher adsorption capacity was registered for the clayey Oxisol from Guarapuava. By fitting Langmuir isotherms to the data, we obtained a maximum adsorption of 56.8 mg kg^{-1} of SO_4^{2-} -S for the loamy Oxisol (Ponta Grossa) and 133.3 mg kg^{-1} for the clayey Oxisol (Guarapuava) at 0-20 cm depth. At the lowest depth, we found 217.4 and 384.6 mg kg^{-1} for Ponta Grossa and Guarapuava, respectively. These results obtained from this study agree with those previously reported for Prem (Alves and Lavorenti, 2004). Despite the fact that Prem had a higher discriminatory capacity of adsorption, the results must be carefully evaluated, especially when practical implications are envisaged. Since phosphate and sulfate do not present the same mechanism of adsorption (Goldberg, 2010), they can present different behaviors in agricultural and environmental systems.

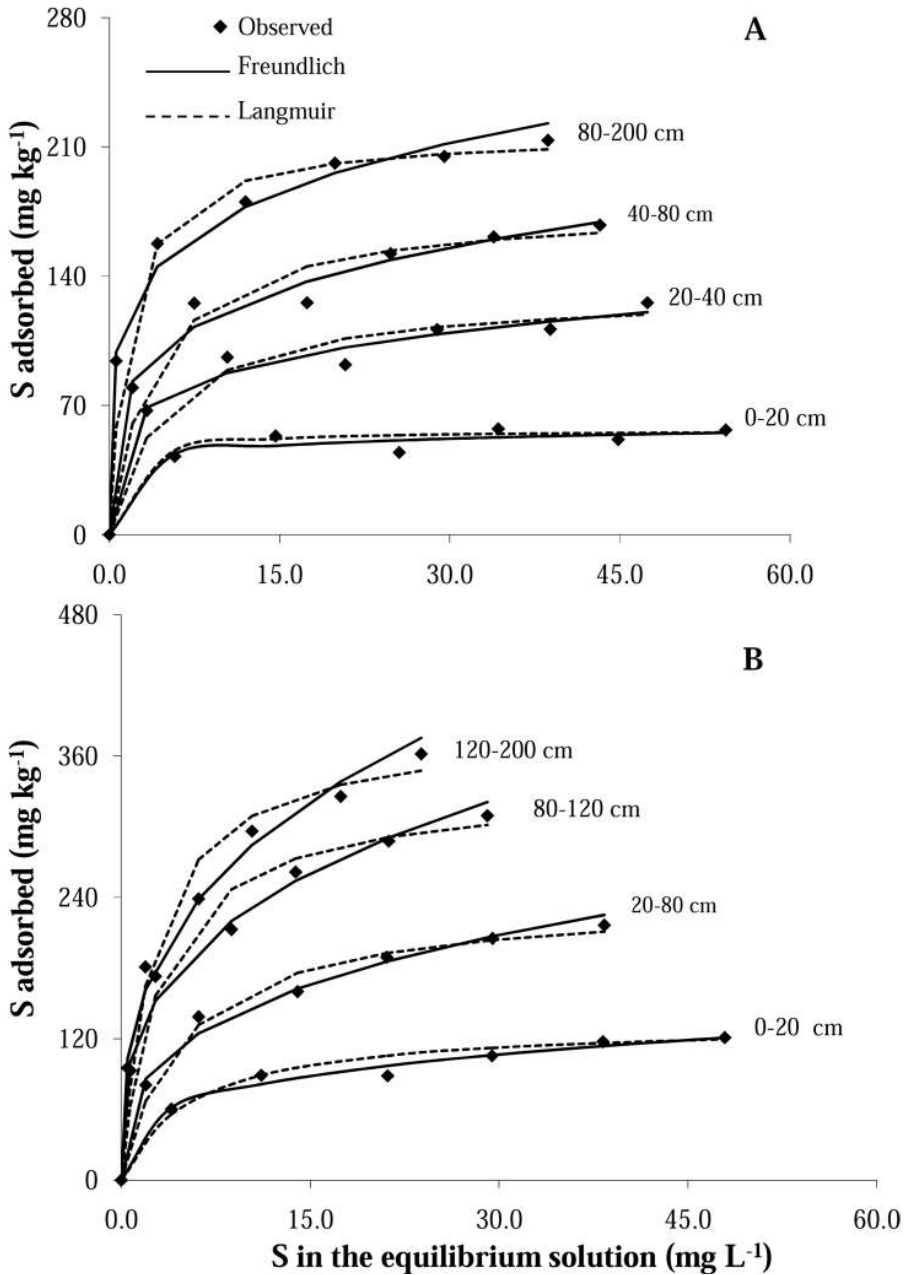


Figure 4. Experimental data of sulfate adsorption for the loamy Oxisol (A) and for the clayey Oxisol (B) at different depths, and adsorption curves drawn according to the Freundlich and Langmuir equations.

Higher levels of organic C were observed for the soil surface, and the soil from Guarapuava presented 55% more organic C than the soil from Ponta Grossa for all soil profiles evaluated. Higher amounts of organic C favor sulfate leaching due to the increase in negative charges and repulsion of $\text{SO}_4^{2-}\text{-S}$ (Couto *et al.*, 1979). Contents of Fe_d , Fe_o and Al- were higher in the Guarapuava soil. In both sites, the Fe_o/Fe_d ratio was lower than 0.07, which indicates the dominance of crystalline Fe hydroxides (Schwertmann *et al.*, 1982). Oxalate-soluble Fe and Al play an important role in sulfate adsorption in highly weathered sub-soils (Alves and Lavorenti, 2004b).

The retention of sulfate in soils is dependent on the nature of the colloidal system, soil pH, the concentration of sulfate and the concentration of other ions in solution. As a consequence, sulfate leaching may be subjected to considerable variation caused by differences in soil attributes or climatic conditions, and by differences in agricultural management (Eriksen and Askegaard, 2000).

The pH NaF values ranged from 9.5 to 10.6 for Ponta Grossa and from 10.3 to 11.0 for Guarapuava, suggesting that F⁻ replaces OH⁻ from the surface of soil colloids, thus increasing the pH value. However, pH NaF also showed a small discriminatory capacity for both soils, when compared to Prem, supporting the results previously reported by Alves and Lavorenti (2004a).

Even for soils with a marked capacity to retain sulfate, the strength of the retention seems to be weak. Chao *et al.* (1962) found that the adsorbed sulfate could be removed by repeated extraction with water. Since almost half of the applied sulfate was already leached to depths lower than 200 cm in the experiment conducted in Ponta Grossa, the sulfate extracted by calcium phosphate represents the soluble portion plus the retained $\text{SO}_4^{2-}\text{-S}$ remaining in the profile. By correlating the amounts of sulfate extracted by calcium sulfate and some soil attributes (Table 4), we verified that Fe_d , $\text{Fe}_d\text{-Fe}_o$ and pH NaF had positive correlations with $\text{SO}_4^{2-}\text{-S}$, while Srem, organic C and Prem were negatively correlated. We obtained lower coefficients of correlation for the Oxisol of Guarapuava (Table 5) since the PG was applied 3.5 years ago, and

it is still coming down in the profile. Moreover, we still observed high correlation coefficients between $\text{SO}_4^{2-}\text{-S}$ and pH measured in NaF, organic C and Srem.

3.4. Crop grain yields

Despite the decrease in exchangeable Al and the increase in exchangeable Ca contents after long-term applications of lime and PG (Figure 2), there was no significant increase in grain yield of cereal crops (maize + wheat) in Ponta Grossa (Figure 5). Many field trials conducted under NTS have shown increases in cereal crop grain yields with applications of lime (Ernani *et al.*, 2002; Caires *et al.*, 2005; 2008) and PG (Toma *et al.*, 1999; Farina *et al.*, 2000a; Caires *et al.*, 2011a;b; c).

In our study, both crops achieved good grain yields; the average was of 9,016 kg ha⁻¹ for maize and 2,553 kg ha⁻¹ for wheat. Based on the limited rainfall in December 2008 (Figure 1), we would expect to see positive effects of lime and PG applications on maize grain yields. However that did not occur. Water deficit usually potentiates the positive effects of lime and PG applications, especially when cereals are cropped (Caires *et al.*, 2008). Some authors have reported high crop grain yield in acid soils, under NTS even in the absence of lime (Brown *et al.*, 2008; Caires *et al.*, 2005; 2011a). Thus, the large grain yield found in acidic conditions is attributed to the lower concentration of toxic species of Al, and to the higher concentration of Al complexed with organic matter (Brown *et al.*, 2008; Alleoni *et al.*, 2010). Another possible explanation for the absence of crop response, is the short range of pH values (between 3.9 and 4.7), considering that the amendments were applied to the soil in 1993, and it did not longer had such significant effects. In a previous study carried out by Joris (2010), under similar conditions to those of this study, he observed the highest maize grain yield at pH of 6.1 (0.01 M CaCl₂). Ernani *et al.* (2002) observed that pH values above those required for Al neutralization have also contributed to the increase of maize yield. Increasing the PG rate applied to the soil surface led to a linear increase of cereal crop grain yields (maize+triticale) in Guarapuava (Figure 6). Based on the regression equation obtained, PG application at 12 t ha⁻¹ increased grain yield by 12%.

Table 4. Pearson Product Moment Correlation between the SO_4^{2-} -S in the soil profile and soil attributes related to S retention (n=12) for Ponta Grossa.

	$\text{SO}_4\text{-S}$	Organic C	Fe_d	Fe_o	Al_o	$\text{Fe}_d\text{-Fe}_o$	pH_{NaF}	Prem	Srem
SO_4^{2-}	-	-0.86**	0.90**	-0.39ns	0.34ns	0.90**	0.84**	-0.84**	-0.89**
Organic C		-	-0.96**	0.56ns	-0.46ns	-0.96**	-0.98**	0.99**	0.92**
Fe_d			-	-0.62*	0.53ns	0.99**	0.97**	-0.97**	-0.92**
Fe_o				-	-0.51ns	-0.63*	-0.61*	0.57ns	0.48ns
Al_o					-	0.53ns	-0.22ns	-0.43ns	0.58*
$\text{Fe}_d\text{-Fe}_o$						-	0.97**	-0.97**	-0.91**
pH_{NaF}							-	-0.97**	-0.86**
Prem								-	0.96**
Srem									-

Table 5. Pearson Product Moment Correlation between the SO_4^{2-} in the soil profile and soil attributes related to S retention (n=12) for Guarapuava.

	SO_4^{2-}	Organic C	Fe_d	Fe_o	Al_o	$\text{Fe}_d\text{-Fe}_o$	pH_{NaF}	P-rem	S-rem
$\text{SO}_4\text{-S}$	-	-0.62*	-0.09ns	0.45ns	0.54ns	-0.11ns	0.89**	0.66*	-0.75*
Organic C		-	-0.42ns	-0.88**	0.22ns	-0.37ns	-0.86**	0.99**	0.96**
Fe_d			-	0.33ns	-0.64*	0.99**	0.00ns	-0.32ns	-0.26ns
Fe_o				-	-0.18ns	0.27ns	0.70**	-0.87**	-0.90**
Al_o					-	-0.64*	0.24ns	0.16ns	0.03ns
$\text{Fe}_d\text{-Fe}_o$						-	-0.03ns	-0.27ns	-0.21ns
pH_{NaF}							-	-0.89**	-0.92**
Prem								-	0.97**
Srem									-

Positive responses of PG application on the yield of cereal crops, especially maize, have been obtained in several other studies conducted under diverse soil and weather conditions (Raij *et al.*, 1998; Toma *et al.*, 1999; Farina *et al.*, 2000a; Caires *et al.*, 1999; 2004; 2011a;c). In our study, where the soil had high exchangeable Ca levels and low exchangeable Al levels throughout the profile, the increases in grain yield due to the sub-soil improvement prompt by PG addition was an unexpected result.

Unlike the region of Ponta Grossa, no rainfall limitation was observed during crop growth (Figure 1). In our experiment, the increase in grain yield could be explained by the changes in the topsoil chemical attributes, which was due to PG application. The attributes most correlated to crop grain yield were (i) increases of SO_4^{2-} -S content; (ii) increases of exchangeable Ca content and Ca/Mg ratio; and (iii) decreases of exchangeable Mg and K contents (Table 6). Potassium data is not discussed here, because we did not observe effects of the soil

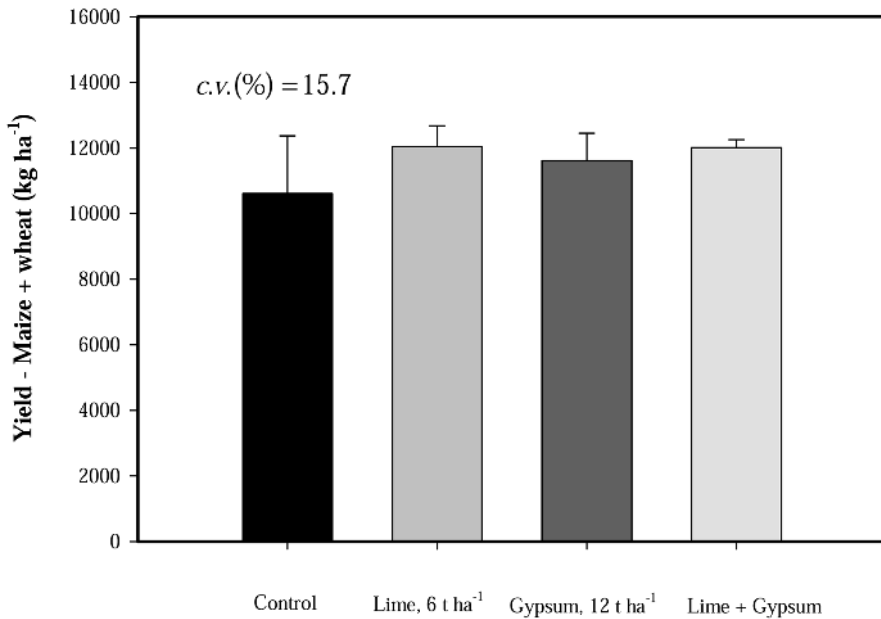


Figure 5. Accumulated yield (maize+wheat), grown in 2008-2009 in response to lime and phosphogypsum application in 1993 in Ponta Grossa.

conditioner on this ion after 3.5 years of PG application. However, intense leaching of K was registered in the first years after application of PG (Caires *et al.*, 2011c).

The attribute that most contributed to explain the increases of cereal yield occurred at 0-20 cm depth. However, effects of PG were also observed at deeper soil layers.

Higher correlation coefficients were verified for Ca and Mg contents, which were extracted by KCl, and for SO_4^{2-} -S extracted by calcium phosphate.

The data presented in this study support the findings previously discussed by Caires *et al.* (2011 b; c). For example, these authors reported that an increase of grain yield observed for cereal crops grown in soils without limitations imposed by acidic conditions are mainly related to the supply of Ca and S to the plants.

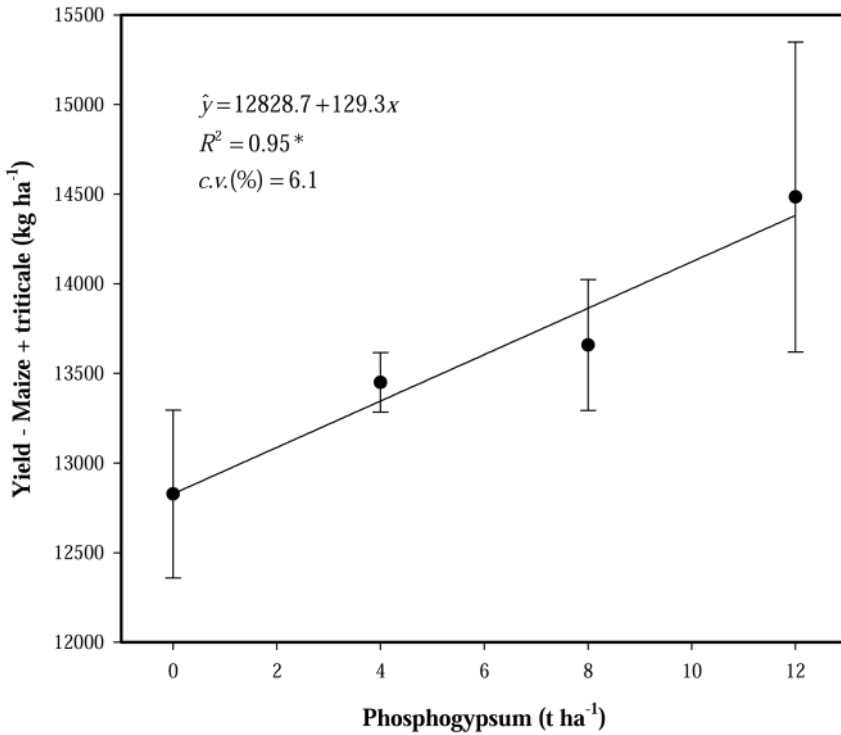


Figure 6 . Accumulated yield (maize+triticale), grown in 2008-2009 in response to phosphogypsum rates applied to the soil surface in 2005 in Guarapuava.

Table 6. Pearson Product Moment Correlation between the accumulated cereal yield and soil chemical attributes at different depths (n=16).

Depth (cm)	SO ₄ ²⁻ -S Ca(HPO ₄) ₂	SO ₄ ²⁻ -S NH ₄ OAc	Ca ²⁺ KCl	Ca ²⁺ Resin	Mg ²⁺ KCl	Mg ²⁺ Resin	K ⁺ Mehlich- 1	Ca/Mg KCl
0-5	0.69**	0.66**	0.60*	0.66**	-0.42ns	-0.31ns	-0.50*	0.52*
5-10	0.69**	0.79**	0.66**	0.23ns	-0.43ns	-0.35ns	-0.42ns	0.59*
10-20	0.63**	0.57*	0.65**	0.48ns	-0.46ns	-0.30ns	-0.62**	0.57*
20-40	0.29ns	0.32ns	0.39ns	0.41ns	-0.14ns	-0.20ns	-0.46ns	0.09ns
40-60	0.39ns	0.43ns	0.48ns	0.56*	0.14ns	0.36ns	0.27ns	0.20ns
60-80	0.46ns	0.46ns	0.40ns	0.31ns	0.70**	0.46ns	-0.13ns	0.01ns
80-100	0.14ns	0.54*	-0.06ns	0.02ns	0.21ns	0.19ns	-0.27ns	-0.30ns
100-120	0.21ns	0.28ns	-0.31ns	0.06ns	0.15ns	0.22ns	-0.22ns	-0.38ns
120-140	0.35ns	0.41ns	0.47ns	0.30ns	0.49ns	0.53*	-0.18ns	0.12ns
140-160	0.26ns	0.26ns	0.51*	0.38ns	0.46ns	0.24ns	-0.15ns	0.16ns
160-180	0.24ns	0.40ns	0.05ns	0.04ns	0.26ns	0.24ns	-0.30ns	-0.03ns
180-200	0.21ns	0.27ns	0.50ns	0.59*	0.54*	0.33ns	-0.39ns	0.15ns
0-20	0.67**	0.63**	0.67**	0.53*	-0.45ns	-0.33ns	-0.59*	0.58*

4. Conclusions

Applications of lime and phosphogypsum to the soil surface under no-till conditions provided long-term effects, ameliorating the root environment of plants. The effects of surface-applied lime reducing the soil acidity and increasing the exchangeable Ca and Mg contents were visible up to 80 cm depth, while the effects of phosphogypsum increasing Ca and SO_4^{2-} -S contents were more pronounced at deeper soil layers. Sulfate distribution in the soil profile was mostly correlated with Fe_d and Fe_d - Fe_o . No differences were found in maize + wheat yields in Ponta Grossa after long-term phosphogypsum application (15 years). In Guarapuava, the medium-term PG effects (3.5 years) showed a rapid SO_4^{2-} -S movement to the sub-soil, despite the soil higher adsorption capacity of sulfate. Surface-applied PG had positive benefits on maize + triticale yields due to increased Ca and SO_4^{2-} -S availability for the plants. Although the soils showed different capacities of sulfate adsorption, and were evaluated at different times, the crop responses to PG application under NTS were associated not only to the improvement of sub-soil conditions, but could also be related to the improvement of the soil chemical conditions of the soil surface layers.

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