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Effect of gypsum rates and lime with different reactivity on soil acidity and crop grain yields in a subtropical Oxisol under no-tillage

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ABSTRACT

The low solubility of lime ($CaCO_3$) and the absence of soil disturbance in fields under no-tillage (NT) may diminish the effectiveness of surface liming to reduce exchangeable Al^{3+} (toxic to plants) and increase the base saturation in deep soil layers. However, the effects of subsurface soil acidity can be attenuated by applying agricultural gypsum ($CaSO_4{\cdot}2H_2O$), which is more soluble than lime, and thus, can leached bases (exchangeable Ca^{2+}, Mg^{2+} and K^+) and S-SO_4^{2-} to deeper soil layers as well as decrease Al^{3+} toxicity to plants. Therefore, gypsum can be applied individually or in combination with lime. Herein, we conducted a field experiment aiming to evaluate short- (1 year) and long-term (11 years) effects of surface liming and gypsum application on the chemical properties of the 0.00–0.10, 0.10–0.20, 0.20–0.40 and 0.40–0.60 m soil layers and also on crop yield of 22 crop seasons (*i.e.,* 10 soybean, 3 maize, 4 white oat, 3 wheat and 2 barley crops). The study was performed in a clayey Typic Hapludox of moderate acidity managed under NT for more than 25 years in Guarapuava, Paraná State, southern Brazil. Three soil surface-applied lime strategies were tested in order to raise base saturation to 70%, namely: (*a*) 4.62 Mg ha^{-1} rate of lime of low effective calcium carbonate equivalent (ECCE = 75%); (*b*) 3.47 Mg ha^{-1} rate of lime with a high ECCE value (101%); and (*c*) the same rate of high-ECCE lime split in three applications (*i.e.*, 1/3 at the start of experiment; 1/3 after 1 year and 1/3 after 2 years). A control treatment without liming was also conducted. The liming strategies were combined with four rates of agricultural gypsum (*i.e.*, 0, 3, 6 and 9 Mg ha^{-1}) applied at the start of the experiment. Our findings did not reveal synergistic effect of lime and gypsum on soil chemical properties nor on crop yield. Gypsum resulted in very slight gains in grain yield (4% on average) and limited to just 25% of cereal (corn and winter cereals) crop seasons. On the other hand, liming increased soybean yields by 14% in 40% of crop seasons. Gypsum was more efficient than lime in raising exchangeable Ca^{2+} levels up to −0.60 m in the short term; however, lime promoted greater reduction of soil acidity and had a more marked residual effect on exchangeable Ca^{2+} contents than gypsum. The liming strategies did no promote substantial differences in crop yield, but low-ECCE lime sustained better soil chemical condition to plant growth for a longer period. Surface liming efficiently reduced subsurface acidity in a moderately acidic Oxisol managed under NT even in the short-term, promoting increments on soybean crop yields. In this case, the application of gypsum rates did not bring additional benefits to soil or plant yield.

1. Introduction

Crop yield in tropical and subtropical soils is limited mainly by soil acidity and low nutrient availability (Fageria and Nascente et al., 2014; Joris et al., 2016; Tiritan et al., 2016). Acid soils ($pH_{water} < 5.5$) account for about 78% of all potentially arable land in the world (Uexktill and Mutert, 1995). Liming, which is no doubt the most widespread soil acidity amendment strategy, reduces the toxic effects of exchangeable Al^{3+} and available Mn^{2+} ions (Tiritan et al., 2016; Rheinheimer et al., 2018), increases the availability of essential plant nutrients (Crusciol et al., 2016; Joris et al., 2016) and additionally, alters some physical (Bennett et al., 2014) and biological properties of soil (Holland et al.,

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2018).

Although the beneficial impact of liming on soil properties are well known (Fageria and Nascente et al., 2014), the intensity of the effects of lime amendments of variable reactivity (grain size) on soils under no-tillage (NT) have scarcely been explored in the short- and specially at long-term (Gonçalves et al., 2011; Rodrighero et al., 2015). The efficiency of split lime application in preventing surface alkalinization, micronutrient deficiencies (*e.g.,* Cu^{2+}, Zn^{2+}, Mn^{2+}) and/or concentration in plant roots also require further investigation (Bortoluzzi et al., 2014; Martins et al., 2014; Joris et al., 2016; Tiritan et al., 2016; Rheinheimer et al., 2018) owing to their potentially adverse impact of these conditions on crop yield (*e.g.,* particularly in water-deficient years) (Tiecher et al., 2018). Also, available knowledge on the effects of acidity in NT soils on crop yield is still limited and, unlike tilled soils, no direct relationship between acidity-related soil properties and crop production has to date been found (Martins et al., 2014). In fact, the response of crops to the surface application of lime to NT soils differs widely depending on the severity of the acidity, the soil organic carbon (SOC) content, structural quality of the soil, and the intrinsic acidity tolerance of the crop species and/or variety (Pauletti et al., 2014; Fageria and Nascente, 2014; Martins et al., 2014; Crusciol et al., 2016).

In the NT soil management system, which is used in approximately 157 Mha of land in the world and 32 Mha in Brazil alone (FAO, 2015), liming is usually applied to the soil surface without the traditional incorporation (Rheinheimer et al., 2018) promoting a rapidly alleviate acidity in the surface layers (Caires et al., 2011; Rampim et al., 2011; Dalla Nora et al., 2013; Calegari et al., 2013; Bortoluzzi et al., 2014; Crusciol et al., 2016; Joris et al., 2016). By contrast, the effects of lime on subsurface layers (*e.g.,* below -0.20 m) can be inconsistent and restrict plant root development through, for example, high Al saturation and low contents in alkaline cations, thereby leading to impaired water absorption, nutrient uptake and grain yield — particularly in dry years (Dalla Nora and Amado, 2013; Bortoluzzi et al., 2014; Pauletti et al., 2014; Zandoná et al., 2015; Dalla Nora et al., 2017b; Crusciol et al., 2016; Tiecher et al., 2018).

The low solubility and penetration of lime in soils has led to agricultural gypsum ($CaSO_4 \cdot H_2O$) being recommended as a soil conditioner (Ritchey et al., 1980), especially for NT soils. The solubility of agricultural gypsum (2.5 g L^{-1}) is roughly 170 times higher than that of lime (Bennett et al., 2014; Crusciol et al., 2016); as a result, the former efficiently increases the mobility of alkaline cations such as exchangeable Ca^{2+}, Mg^{2+} and K^+ bound to anions such as S-SO_4^{2-}, which disassociates and can bond to exchangeable Al^{3+} in the deeper soil layers decreasing its activity and toxic effects on plants (Pauletti et al., 2014; Crusciol et al., 2016; Dalla Nora et al., 2017b; Zocca and Penn, 2017). In addition to its conditioning role, agricultural gypsum provides a rich source of Ca^{2+} and S-SO_4^{2-} (Bennett et al., 2014; Zocca and Penn, 2017). Sulfur deficiency in agricultural soils has been widely examined in a number of locations in Europe (Ercoli et al., 2011), Africa (Kihara et al., 2017) and South America (Tiecher et al., 2013; Salvagiotti et al., 2017; Pias et al., 2019).

Studies evaluating the interaction of agricultural gypsum and liming on soil properties and crop grain yield are well documented in the literature, especially in soils under NT system (Caires et al., 2006, 2011; Pauletti et al., 2014; Crusciol et al., 2016; Costa and Crusciol, 2016; Dalla Nora et al., 2017a). However, so far to our knowledge, there is a lack of studies evaluating the effect of limestones with different reactivities and splitting lime rates combined with agricultural gypsum rates. Moreover, most of the studies evaluating the effects of gypsum and liming in a low number of crop seasons [two (Caires et al., 2006; Dalla Nora and Amado, 2013; Crusciol et al., 2016), four (Caires et al., 2011; Costa and Crusciol, 2016) and six crop seasons (Pauletti et al., 2014; Dalla Nora et al., 2017b)]. The results obtained in these studies are often contrasting. In common, all authors report the need to conduct long-term studies to evaluate the residual effect of limestone and gypsum, which may persist for more than two decades as reported for liming (Rheinheimer et al., 2018). Therefore, the present study presents a unique opportunity to evaluate the effect of liming strategies and agricultural gypsum rates on soil chemical properties and grain production of 22 crop seasons in a long-period of 13 years.

The currently recommended agricultural gypsum rate for soils in Brazil, which was developed under conventional tillage, is based on a critical Al saturation level above 20% and/or exchangeable Ca^{2+} content not greater than 0.5 $cmol_c$ Ca^{2+} dm^{-3} and/or an exchangeable Al^{3+} content not smaller than 0.5 $cmol_c$ Al^{3+} dm^{-3} (Pauletti and Motta, 2017). However, recent studies on NT soils have shown that agricultural gypsum also benefits crop grain yield in soils with Al saturation levels even below 10%, (Crusciol et al., 2016; Dalla Nora et al., 2017a; Tiecher et al., 2018), possibly as a result of an increased availability of alkaline cations and S-SO_4^{2-} in subsurface soil layers, and also to a potentially decreased acidity tolerance, increased production potential and decreased cycle duration of the current cultivars and hybrids leading to obviously increased nutrient requirements (Dalla Nora et al., 2017a). Whereas the response of crops to gypsum in soils with a high subsurface acidity (Al saturation > 20%) is well-documented (Pauletti et al., 2014; Caires et al., 2016; Costa and Crusciol, 2016), under conditions of low subsurface acidity (Al saturation ≤10%) remains poorly understood (Dalla Nora et al., 2017a).

The hypotheses tested in this study were as follows:

(i) Combining surface application of lime and agricultural gypsum in a long-term no-till Oxisol would determine better soil conditions in deeper soil layers in short-term induced by agricultural gypsum and the long-term effects of lime in attenuating soil acidity and increasing nutrient availability to crops.
(ii) Low-reactivity lime should be as efficient as highly reactive lime when applied to a moderately surface acidic soil in the short-term, but the former should have a more marked residual effect.
(iii) Splitting high-reactivity lime rate increases the residual effect on soil acidity properties and crop yields.

These three hypotheses were tested *via* a long-term study on an Oxisol under NT in Brazil. The primary aims were to assess the efficiency of different liming strategies and the use of agricultural gypsum in increasing crop yields and amending surface and subsurface soil acidity in short (1 year) and long term (11 years).

2. Material and methods

2.1. Experimental region and study area

The study was based on an experiment which had been running for 13 years (2004–2017) in an area of central coordinates 25°50′ S and 51°30′ W located in Guarapuava (Paraná State, Southern Brazil). The region has a humid subtropical climate falling in class Cfb of the Köppen–Geiger classification, and an average annual temperature and precipitation of 16.9 °C and 1956 mm yr^{-1}, respectively. Monthly cumulative precipitation data for each crop season were obtained from an automated weather station 2 km from the experiment site (see Fig. 1). The figure also shows the average precipitation for the previous 40 years for easier identification of values well above or below the historical means.

The soil was a clayey Typic Hapludox (Soil Survey Staff, 2014) which had been under NT for more than 25 years. The values of the soil chemical properties at the start of the experiment are shown in Table 1. Based on current recommendations, the soil (0.00 – 0.20 soil layer) had high available P and exchangeable K^+ contents; however, it required liming (*viz.*, base saturation < 60% and pH < 5.5; Pauletti and Motta, 2017).

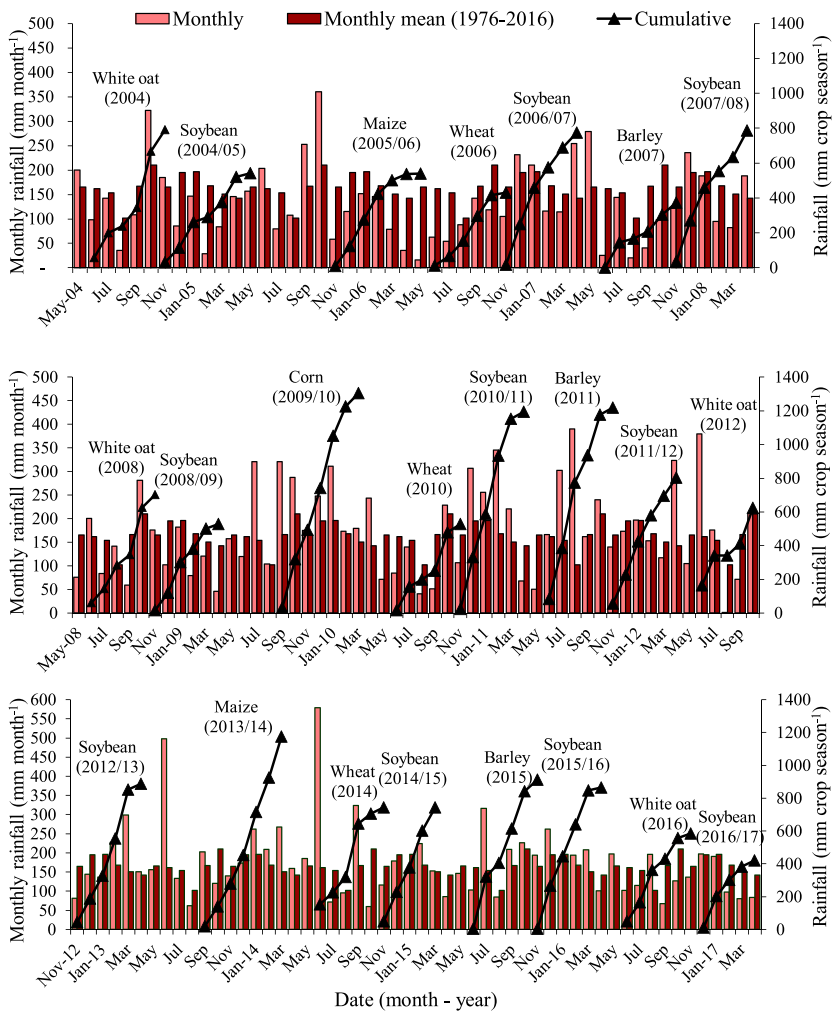

Fig. 1. Monthly rainfall for the experimental period (2004–2017), mean historical rainfall (1976–2016) and cumulative rainfall for each crop seasons in Guarapuava (Paraná State, southern Brazil).

2.2. Experimental design

A randomized block design consisting of subplots and three replications was used. The main plots (25.6 × 12.0 m = 307.2 m^2) were used for three different treatments intended to increase base saturation to 70% and involving application of (*a*) a 4.62 Mg ha^{-1} rate of dolomite lime of low effective calcium carbonate equivalent (ECCE = 76%); (*b*) a 3.47 Mg ha^{-1} rate of the same type of lime with a high-ECCE value (101%); and (*c*) the same rate of high-ECCE lime split in three times (*i.e.,* at the start and after 1 and 2 years). A control treatment without liming was also conducted in parallel. Subplots (6.4 × 12.0 m = 76.8 m^2) consisted of four different rates of agricultural gypsum (0, 3, 6 and 9 Mg ha^{-1}) that were applied in addition to the lime. Lime and agricultural gypsum were applied to the soil surface by hand in May 2004, the soil being kept under NT and no turnover throughout the study period. The composition of the lime and gypsum is shown in Table A1. The liming requirement (LR) was established by using the base saturation (*V*) method (Eq. (1)) to calculate the rate needed to increase *V* in the diagnostic soil layer (0.00–0.20 m) (Pauletti and Motta, 2017):

$$\text{LR (Mg ha}^{-1}) = \frac{[(V_2 - V_1) \times \text{CEC}_{\text{pH 7.0}}]}{\text{ECCE}} \quad (1)$$

where V_1 is the initial base saturation, V_2 the target saturation, $CEC_{pH\ 7}$ the potential cation exchange capacity of the soil and ECCE the effective calcium carbonate equivalent of the lime.

2.3. Cropping and yield assessment

A total of 26 crops were grown during the experimental period (May 2004–April 2017). Ten were soybean (Glycine max L.), three maize (*Zea*

Table 1
Soil chemical properties at the beginning of the field experiment in a Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil).

Soil layer (m)	pH_{water}	Al^{3+} $cmol_c\ dm^{-3}$	H + Al	Ca^{2+}	Mg^{2+}	K^+	CEC[(1)]	P mg dm^{-3}	S	SOC[(2)] g dm^{-3}	BS[(3)] %	AS[(4)]
0.00–0.10	5.3	0.1	7.8	5.8	2.3	0.5	16.4	28.0	9.0	31.1	52.9	0.0
0.10–0.20	5.4	0.1	7.8	5.1	1.8	0.3	15.0	8.9	11.0	24.1	48.2	0.7
0.20–0.40	5.2	0.1	8.4	3.5	1.9	0.2	14.0	3.5	14.0	21.4	40.6	2.1
0.40–0.60	5.1	0.3	9.0	2.4	1.6	0.1	13.1	1.7	26.0	17.1	33.7	6.7

[(1)]Cation exchange capacity at pH 7.0; [(2)]Soil organic carbon; [(3)]Base saturation; [(4)]Aluminum saturation.

Table 2
Agronomic information for the crop seasons of the period 2004–2017 in Guarapuava (Paraná State, southern Brazil).

Crop/year	Cultivar	Plant density (plants m^{-2})	Row spacing (m)	Seeding fertilization (kg ha^{-1})			N topdressing (kg N ha^{-1})
				N	P	K	
White oat (2004)	FAPA 4	250	0.17	–	–	–	30
Soybean (2004/05)	BRS Macota	30	0.40	–	38	38	–
Radish (2005)	–	120	0.17	–	–	–	–
Maize (2005/06)	P 30P34	7	0.80	39	78	78	150
Wheat (2006)	BRS UMBU	300	0.17	12	45	30	40
Soybean (2006/07)	CD 215	30	0.40	–	48	48	–
Barley (2007)	Not harvested	300	0.17	20	75	50	40
Soybean (2007/08)	CD 215	30	0.40	–	50	50	–
White oat (2008)	FAPA 4	250	0.17	16	60	40	30
Soybean (2008/09)	CD 215	30	0.40	–	60	60	–
Radish (2009)	–	120	0.17	–	–	–	–
Maize (2009/10)	P 30R50	7	0.80	28	105	70	150
Wheat (2010)	BRS GUAMIRIM	300	0.17	20	75	50	50
Soybean (2010/11)	FPS URANO	35	0.40	–	50	50	–
Barley (2011)	BRS CAUE	280	0.17	28	105	70	40
Soybean (2011/12)	FPS URANO	35	0.40	–	50	50	–
White oat (2012)	URS TAURA	250	0.17	8	30	20	36
Soybean (2012/13)	ROOS CAMINO	35	0.40	–	50	50	–
Radish (2013)	–	120	0.17	–	–	–	–
Maize (2013/14)	P 30F53YH	7	0.80	35	91	88	180
Wheat (2014)	BRS CAMPEIRO	300	0.17	28	105	70	67
Soybean (2014/15)	TMG 7262	25	0.40	–	50	50	–
Barley (2015)	BRS BRAU	280	0.17	24	90	60	45
Soybean (2015/16)	TMG 7262	22	0.40	–	50	50	–
White oat (2016)	URS Corona	250	0.17	–	–	–	45
Soybean (2016/17)	Produza Ipro	22	0.40	–	–	–	–

mays L.), four white oat (*Avena sativa* L.), three wheat (*Triticum aestivum* L.), three barley (Hordeum vulgare L.) and three forage radish (*Raphanus sativus* L.). Only 22 were assessed for grain yield, however, because one barley crop (2007) had to be excluded owing to frosts during the flowering stage, and so had three radish crops that were used as covers preceding maize in crop rotations. Phytosanitary measures were identical in all treatments and conformed to the technical recommendations for each crop type. Table 2 shows the cultivars and hybrids, sowing densities and spacings, and fertilizers used. Fertilizers were applied in the form of urea (45% N), triple superphosphate (42% P_2O_5) and potassium chloride (60% K_2O) as N, P and K source, respectively.

Plants and leaves from the soybean (2004/05, 2006/07, 2007/08 and 2008/09), maize (2005), wheat (2006) and white oat crops (2004 and 2008) were used to diagnose their status. Specimens were collected when each crop reached full flowering. A total of 20 plants (aerial portion) each of wheat and white oat were used to obtain a composite sample for each crop in addition to the first fully developed clovers of soybean and the intermediate leaf opposite the ear on maize. Soybean and maize leaves were obtained from 20 plants per plot (Pauletti and Motta, 2017). The samples were dried, ground, and analyzed for N, P, K, Ca, Mg and S leaf tissue content according to Malavolta (1997) and Tedesco et al. (1995).

Grain yield was assessed by using a mechanical collector specially designed for experimental plots. The assessed area was 32 m^2 (3.2 × 10 m) for soybean, 16 m^2 (1.6 × 10 m) for maize and 34 m^2 (3.4 × 10 m) for winter cereals. Grain yields were expressed at a moisture level of 13%. In order to evaluate the treatments effect on the group of crop seasons, the cumulative grain yield of soybean (10 crop seasons), cereals (12 crop seasons) and the body of crops (22 crop seasons) for each plot (treatments *vs* repetitions) was calculated. Then, a relative grain yield (% of the maximum crop yield) on the group of crop seasons of each plot was calculated in relation to the maximum cumulative grain yield of plot, according to the Eq. (2).

$$\text{Relative grain yield (\%)} = \frac{\text{Cumulative grain yield of plot (Mg ha}^{-1}\text{)}}{\text{Plot with maximum cumulative grain yield (Mg ha}^{-1}\text{)}} \times 100 \quad (2)$$

2.4. Soil sampling

The soil was subjected to short- and long-term sampling 1 and 11 years, respectively, after lime and agricultural gypsum were applied. Eight samples per plot were collected with a drill and combined to obtain a composite sample. Samples were obtained from four different layers across the soil profile (*viz.,* 0.00–0.10, 0.10–0.20, 0.20–0.40 and 0.40–0.60 m) and dried at 55 °C under circulating air prior to determining the following parameters according to Tedesco et al. (1995): pH in water at a 1:1 soil water ratio; exchangeable Ca^{2+}, Mg^{2+} and Al^{3+} as extracted by 1.0 mol L^{-1} KCl; available P and exchangeable K^+ as extracted by Mehlich-1 solution; available S-SO_4^{2-} as extracted by 0.01 mol L^{-1} calcium phosphate and the SMP index as a proxy for potential acidity (H + Al) (Kaminski et al., 2001). The previous parameters were used to estimate the sum of bases (*S*), potential cation exchange capacity {$CEC_{pH\ 7.0} = [Ca^{2+} + Mg^{2+} + K^+ + (H + Al)]$}, base saturation {$V$ (%) = $[(Ca^{2+} + Mg^{2+} + K^+)/CEC_{pH\ 7.0}] \times 100$} and Al saturation {$m$ (%) = $[Al^{3+} / (Ca^{2+} + Mg^{2+} + K^+ + Al^{3+})] \times 100$}.

2.5. Statistical analysis

The results were checked for normality by using the Shapiro–Wilk test at $p \leq 0{,}05$ in order to confirm homoscedasticity of the variance, those not meeting the condition being processed in logarithmic form. Data were then subjected to analysis of variance (ANOVA). Means of chemical properties of soil significantly differing at $p < 0.05$ between treatments were compared *via* Tukey's test at $p \leq 0.05$. Grain yields and nutrient contents were fitted to polynomial regression equations for the different agricultural gypsum rates and by Tukey's test at $p \leq 0.05$ in function of liming strategies. The relationship between the nutrient contents of leaf and plant tissues and crop yield was established by

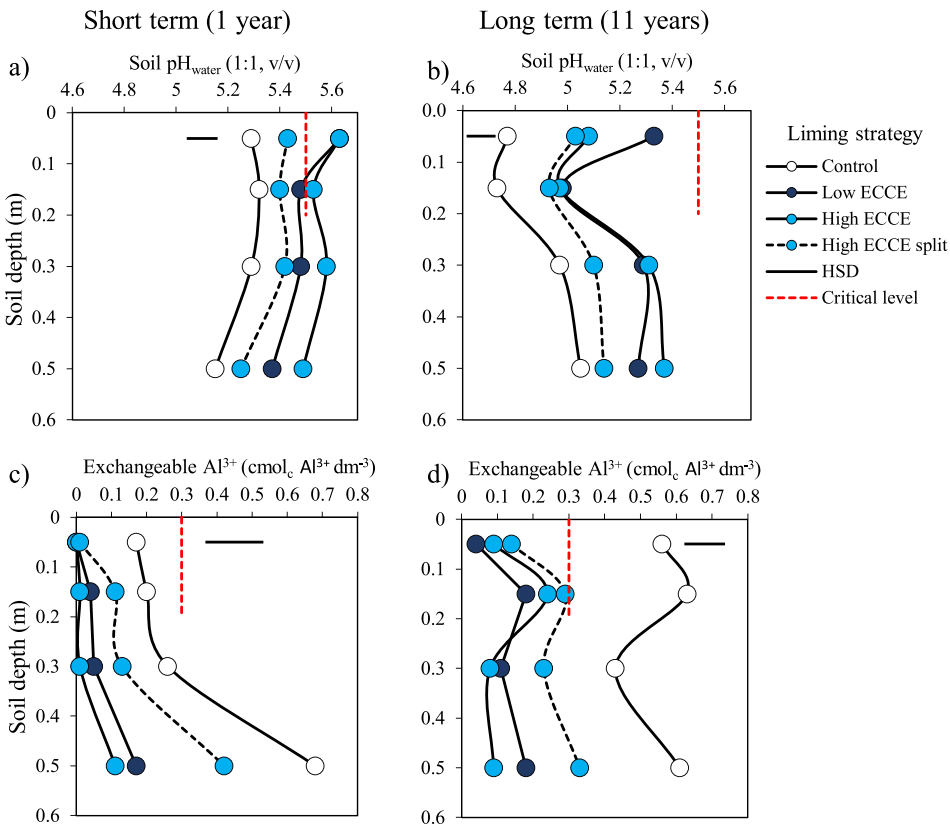

Fig. 2. Soil pH$_{water}$ (a, b) and exchangeable Al^{3+} (c, d) contents in the short (1 year) and long term (11 years) after surface liming with a low (76%) and high effective calcium carbonate equivalent (ECCE) (101%) at once or split into three applications to Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil). The horizontal solid line represents Tukey's honestly standard deviation (HSD) at $p < 0.05$ for the treatments and the dotted red line the critical values in the 0.00–0.20 soil layer for the grain crops: pH$_{water}$ = 5.5; exchangeable Al^{3+} = 0,3 cmol$_c$ Al^{3+} dm^{-3} (Pauletti and Motta, 2017).

Soil pH$_{water}$ (a, b) and exchangeable Al^{3+} (c, d) contents in the short (1 year) and long term

Pearson's linear correlation analysis. All statistical computations were done with the software Statistical Analysis System (SAS) v. 8.3 from SAS Institute (Cary, NC, USA).

3. Results

There was no interaction between liming strategies and gypsum rates as regards their effect on soil acidity (Table A2), grain yield (Table A3) and most of leaf-tissue macronutrient contents of crops (Table A4). For this reason, the results are discussed in terms of the main effects of the liming treatments on the means obtained at each agricultural gypsum rate and of those of the agricultural gypsum rates on the means for each liming treatment.

3.1. Response of soil acidity to lime

As can be seen from Fig. 2a and c, both the high- and the low-ECCE liming treatments raised pH and decreased the exchangeable Al^{3+} contents of the soil down to -0.60 m in the short term (1 year after application). Although the high-ECCE lime was more efficient in decreasing soil acidity than low-ECCE lime, there was no significant difference among this two lime strategies. The effect of split applying high-ECCE lime to the plots fell in between that of the control treatment (no lime) and those of the rest; in fact, this liming treatment supplied only one-third of the estimated amount required at the time it was applied. Low-ECCE lime exhibited greater persistence of its effects in the long term (11 years). This was especially so in the surface layer (0.00–0.10 m), where the pH was 5% higher than with the high-ECCE treatment (5.33 *vs* 5.08) (Fig. 2b). The other soil layers exhibited no significant differences in this respect. The treatment involving supplying high-ECCE lime in split applications was the least efficient in decreasing exchangeable Al^{3+} in the 0.40–0.60 m layer; however, the resulting exchangeable Al^{3+} content was 84% lower than with the control treatment (no liming) (Fig. 2d).

The short-term (1 year) effect of liming on exchangeable Ca^{2+} contents was limited to the surface soil layer (0.00–0.10 m), where both high- and low-ECCE lime increased them by 15% on average relative to the control treatment (Fig. 3a). The effect was more marked in the long term (11 years) and expanded to the 0.10–0.20 m soil layer with the low-ECCE lime (Fig. 3b). The effects on exchangeable Mg^{2+} were more marked than those on exchangeable Ca^{2+}. Thus, liming increased them down to the deepest soil layer (0.40–0.60 m) within 1 year after application of the amendments (Fig. 3c), the increase amounting to 90% on average in the surface layer. The low-ECCE treatment succeeded in maintaining Mg exchangeable 24% on average higher in relation to high-ECCE treatment down to 0.40 m after 11 years (Fig. 3d). Both the high- and the low-ECCE liming treatments substantially increased base saturation (*V*) down to -0.60 m within 1 year after application (Fig. 3e). After 11 years, the low-ECCE lime resulted in *V* values above the critical limit (66%) in the 0.00–0.10 m layer, whereas the high-ECCE lime led to 56% and the control treatment to only 39% (Fig. 3f).

3.2. Response of soil acidity to agricultural gypsum

Applying agricultural gypsum reduced soil pH after 1 year of it is application, however this decrease is very small, less than 4% (Fig. 4a). After 11 years of gypsum application no differences in the soil pH were observed (Fig. 4b). Also, the gypsum failed to decrease exchangeable Al^{3+} contents (Fig. 4c and d).

The contents in exchangeable Ca^{2+} resulting from gypsum application were 23% higher on average than with the control treatment (mean = 5.6 *vs* 4.5 cmol$_c$ dm^{-3}) (Fig. 5a). As can be seen from Fig. 5b, the effects persisted statistical significant in the long term but differences between treatments were smaller than in the short-term. On the other hand, the contents in exchangeable Mg^{2+} decreased with increasing gypsum rate. The short-term effects were significant down to

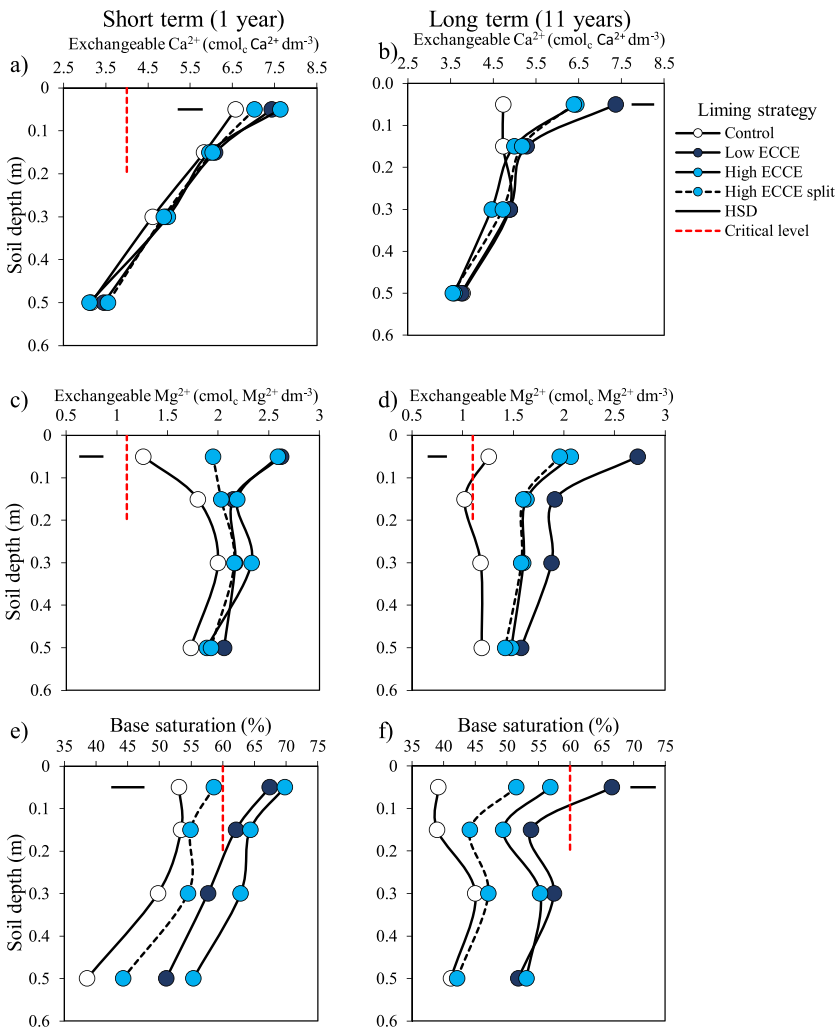

Fig. 3. Soil exchangeable Ca^{2+} (a, b) and Mg^{2+} contents (c, d), and base saturation (e, f) in the short (1 year) and long term (11 years) after surface liming with low- (76%) and high-ECCE (101%) applied at once of split into three annual applications to a Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil). The horizontal solid line represents Tukey's honestly standard deviation (HSD) at $p < 0.05$ for the treatments and the red dotted line the critical contents of the 0.00–0.20 m soil layer with the grain crops: exchangeable Ca^{2+} = 4 $cmol_c$ Ca^{2+} dm^{-3}, exchangeable Mg^{2+} = 1.1 $cmol_c$ Mg^{2+} dm^{-3} and base saturation = 60% (Pauletti and Motta, 2017).

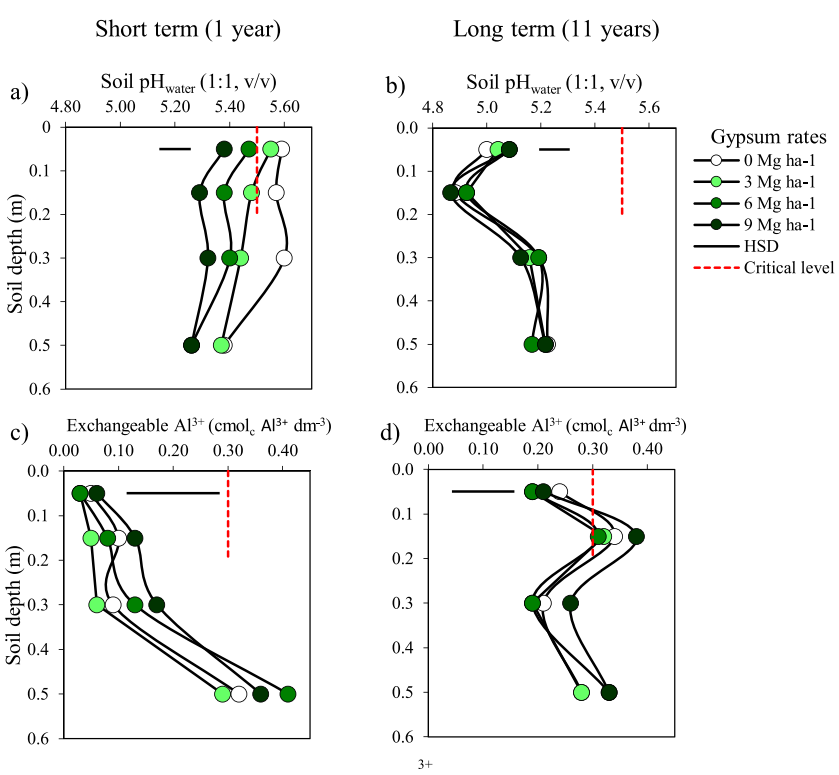

Fig. 4. Soil pH_{water} (a, b) and exchangeable Al^{3+} (c, d) contents in the short (1 year) and long term (11 years) after surface application of different rates of agricultural gypsum to a Typic Hapludox under no-tillage in Guarapuava (Paraná state, southern Brazil). The horizontal solid line represents Tukey's honestly standard deviation (HSD) at $p < 0.05$ for the treatments and the red dotted line the critical contents of the 0.00–0.20 m soil layer with the grain crops: Soil pH_{water} = 5.5, exchangeable Al^{3+} = 0.3 $cmol_c$ Al^{3+} dm^{-3} (Pauletti and Motta, 2017).

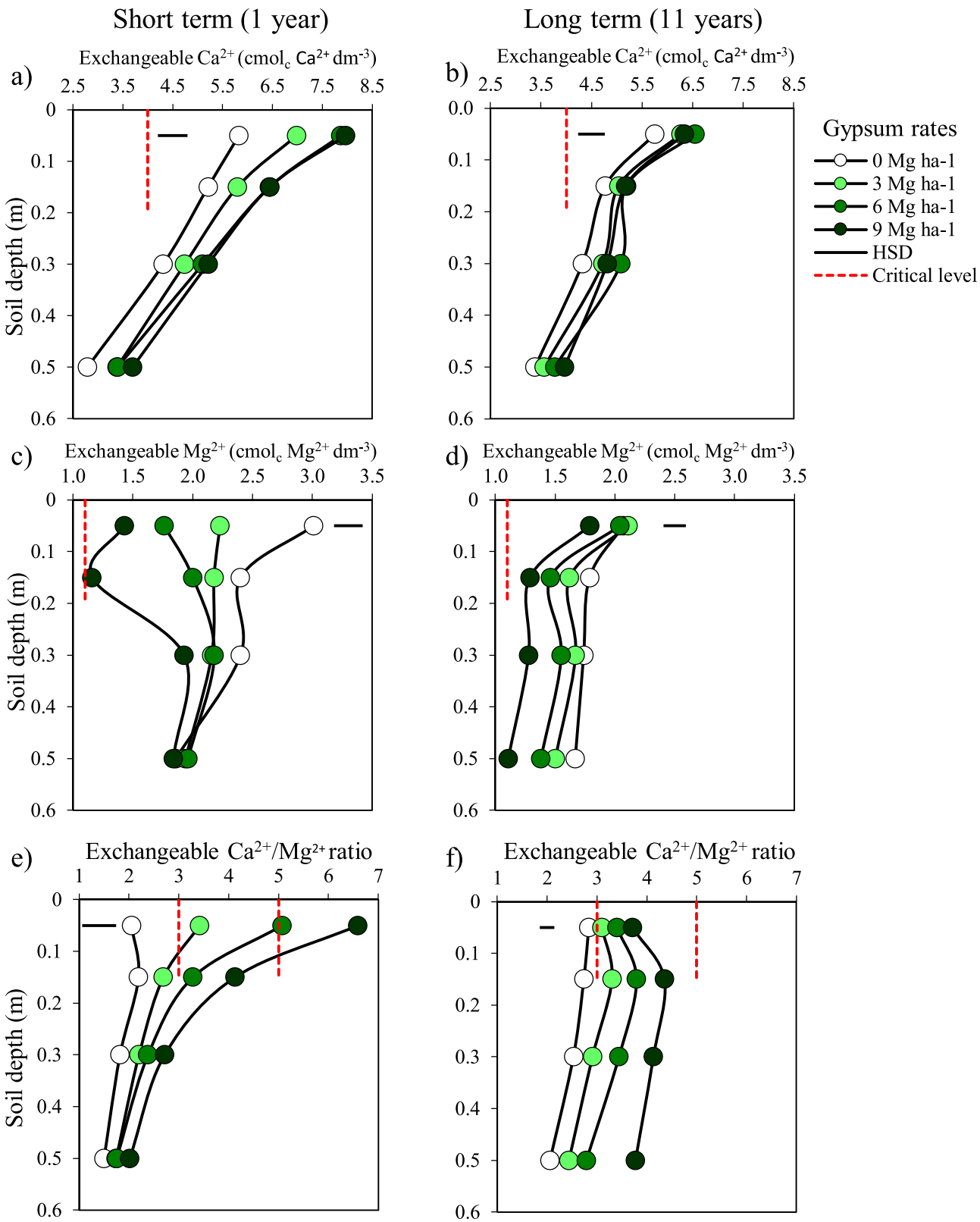

Fig. 5. Soil exchangeable Ca^{2+} (a, b) and Mg^{2+} contents (c, d), and exchangeable Ca^{2+}/Mg^{2+} ratio (e, f) in the short (1 year) and long term (11 years) after surface application of different rates of agricultural gypsum to a Typic Hapludox under no-tillage in Guarapuava (Paraná state, southern Brazil). The horizontal solid line represents Tukey's honestly standard deviation (HSD) at $p < 0.05$ for the treatments and the red dotted line the critical contents of the 0.00–0.20 m soil layer with the grain crops: Exchangeable Ca^{2+} = 4 $cmol_c$ Ca^{2+} dm^{-3}, exchangeable Mg^{2+} = 1.1 $cmol_c$ Mg^{2+} dm^{-3} and exchangeable Ca^{2+}/Mg^{2+} ratio = 3–5 (Pauletti and Motta, 2017).

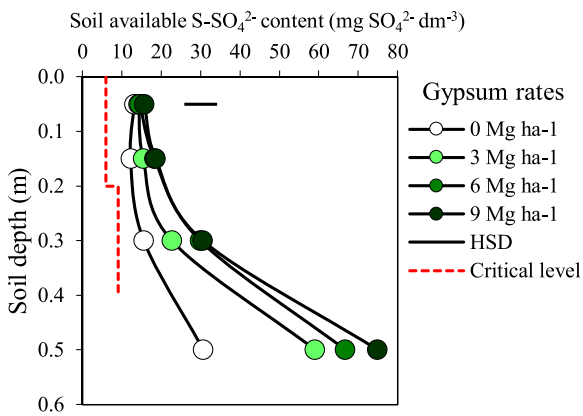

Fig. 6. Soil available S-SO_4^{2-} contents in the long term (11 years) after surface application of different rates of agricultural gypsum to a Typic Hapludox under no-tillage in Guarapuava (Paraná state, southern Brazil). The horizontal solid line represents Tukey's honestly standard deviation (HSD) at $p < 0.05$ for the treatments and the red dotted line the critical contents of available S-SO_4^{2-} in the 0.00–0.20 and 0.20–0.40 m soil layers for the grain crops, which are 6 and 9 mg SO_4^{2-} dm^{-3}, respectively (Pauletti and Motta, 2017).

-0.20 m (Fig. 5c), where the 9 Mg ha^{-1} rate decreased exchangeable Mg^{2+} contents by 52% relative to the control treatment (no gypsum): from 2.71 to 1.29 $cmol_c$ Mg^{2+} dm^{-3}. In the long term, exchangeable Mg^{2+} contents decreased in all soil layers below -0.10 m, which is suggestive of exchangeable Mg^{2+} leaching to even deeper layers than those examined here (*i.e.,* below -060 m; Fig. 5d).

As can be seen from Fig. 5e, gypsum significantly raised the exchangeable Ca^{2+}/Mg^{2+} ratio in the surface layer from 2 with the control treatment to 6.6 with the highest rate (9 Mg ha^{-1}). Increased leaching of exchangeable Ca^{2+} and solubilization of exchangeable Mg^{2+} from the amendments after 11 years led to a weaker, but significant effect on the exchangeable Ca^{2+}/Mg^{2+} ratio, especially in the deeper layers (Fig. 5f). Available S-SO_4^{2-} contents were only quantified 11 years after gypsum application, where they exhibited a substantial increase in subsurface layers (down to -0.20 m) with increase in gypsum rate (Fig. 6).

3.3. Response of macronutrients in plant tissues to lime and agricultural gypsum

Liming increased soybean leaf N contents by 15% on average relative to the control treatment in the 2006/07, 2007/08 and 2008/09 crop seasons, and leaf P contents by 11%, also on average, in the soybean 2008/09 crop and the white oat 2008 crop (Table 3). Increased leaf Mg contents relative to the control treatment were observed in the white oat 2004 and 2008 crops, and the soybean 2007/08 crops, receiving high-ECCE lime. As can be seen from Table A5, however, the contents of all macronutrients the soybean 2004/05, maize 2005/06 and wheat 2006 crops were not altered by liming.

Agricultural gypsum slightly increased P contents of plant tissue in the white oat 2004 crop (by 12% relative to the control with the 9 Mg ha^{-1} rate) (Fig. 7a). The Mg contents of plant tissue in white oat (2004) and those of leaves in three of the four soybean crop seasons (2004/05, 2007/08 and 2008/09) were linearly decreased by the gypsum rates application (Fig. 7b). On the other hand, the Ca contents of plant tissue exhibited the opposite trend in white oat (2004), maize (2005/06) and wheat (2006) (Fig. 7c). The S contents of plant tissue in white oat (2004), maize (2005/06) and soybean (2007/08) were increased by 117, 35 and 8% by the higher gypsum rate used (Fig. 7d). However, the other macronutrients (N and K) were not affected by gypsum in any crop (Table A6).

3.4. Response of grain yield to lime and agricultural gypsum

As can be seen from Table 4, only 6 of the 22 crop seasons assessed exhibited a favorable response to liming, namely: four soybean crops (2006/07, 2007/08, 2008/09 and 2012/13), one maize crop (2009/10) and one white oat crop (2012). The average increase by application of lime with low-ECCE in soybean yield for its four crops was 14% (0.38 Mg ha^{-1} yr^{-1}), which clearly exceeds those for maize (1%, 0.14 Mg ha^{-1} yr^{-1}) and white oat (9%, 0.34 Mg ha^{-1} yr^{-1}). Except for the barley 2011 crop, where the lime with high-ECCE treatment led to a 7% lower grain yield than the low-ECCE treatment, the crops exhibited no differences in this respect.

Agricultural gypsum increased grain yield only slightly, and exclusively in 3 of the 22 crops studied, namely: the white oat 2004 and 2012 crops (Fig. 8a) and the barley 2011 crop (Fig. 8d), with an average increase of 4% (0.20 Mg ha^{-1} yr^{-1}).

Jointly assessing the crops revealed a differential response of soybean to liming in relation to the other cereals (Fig. 9a). Thus, cumulative grain yield in soybean (10 crops) with the control treatment (no liming) was 88% of the maximum value and 9% lower than with the low-ECCE lime treatment (*viz.,* 96% of the highest yield) (Fig. 9a). By contrast, liming had no effect on grain yield in the cereals (12 crops) or the body of plant types (22 crops). With agricultural gypsum, grain yield was essentially identical for the three cereals (*viz.,* maize, wheat and barley) as a whole, soybean and the body of crops (Fig. 9b).

The leaf N contents of the soybean crop seasons (2006/07, 2007/08 and 2008/09) exhibited positive correlation ($r = 0.66^{**}$) with grain yield, the lowest contents being those for the control treatment, coinciding with the lowest grain yields (Fig. 10a). The leaf P contents also exhibited positive relationship ($r = 0.66^{**}$) with grain yield in the soybean 2006/07 and 2007/08 crop seasons (Fig. 10b). On the other hand, the P and Mg contents of plant tissue exhibited positive ($r = 0.31^{**}$) and negative relationship ($r = -0.39^{**}$), respectively, with grain yield in white oat (2004), where application of gypsum and lime increase P and Mg uptake, respectively, by the plants (Fig. 10c and d). For all other crop seasons there was no relationship between grain yields with the plant tissue nutrient contents (Table A7).

4. Discussion

4.1. Liming and soil acidity correction

Several studies have shown that soil acidity in subsurface layers (*e.g.,* below to −0.20 m) can only be completely amended after several years after surface liming in no-till soils (Rheinheimer et al., 2000; Caires et al., 2006; Calegari et al., 2013; Bortoluzzi et al., 2014; Martins et al., 2014; Pauletti et al., 2014; Joris et al., 2016). Based on our results, however, after only one year after surface liming a sensible increase of exchangeable Mg^{2+} contents, soil pH_{water} and base saturation, and also to decrease Al saturation down to −0.60 m, were observed (Figs. 2 and 3).

Such a rapid action of liming on an NT soil can be ascribed to small lime particles descending through biopores consisting of channels in roots and fauna, the presence of which is favored by high biological activity (*e.g.,* bioturbation), the adoption of crop rotations including plants of different volume and root architecture, and heavy supply of plant residues (Soratto and Crusciol, 2008; Tiritan et al., 2016). The high precipitation of the region (annual mean = 1956 mm yr^{-1}, Fig. 1) additionally facilitated dissolution and percolation of the amendment (Calegari et al., 2013; Dalla Nora et al., 2017b). Rapid mobilization of lime was also observed by Tiritan et al. (2016) in a Tropical Oxisol under an integrated crop–livestock system with NT, where liming decreased the acidity down to -0.30 m within 6 months after application. However, Rheinheimer et al. (2000) and Joris et al. (2016) found acidity correction in the deeper layers of soil previously under degraded grassland to be limited, where the soil to contain little SOC content, be

Table 3
Nutrient contents (g kg^{-1}) of leaf-tissue (means ± standard deviation) from white oat and soybean as affected by surface liming with a low and a high effective calcium carbonate equivalent (ECCE) amendment in a Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil).

Treatment	N		P		K		Ca		Mg		S	
	White oat (2004)											
Control	11.21 ± 1.10	ns	2.46 ± 0.28	ns	19.77 ± 1.96	ns	2.55 ± 0.35	ns	1.15 ± 0.15	b	1.27 ± 0.42	ns
Low-ECCE	10.32 ± 0.68		2.37 ± 0.21		18.88 ± 1.15		2.88 ± 0.50		1.23 ± 0.10	ab	1.23 ± 0.33	
High-ECCE	10.18 ± 0.79		2.44 ± 0.17		17.83 ± 2.56		2.86 ± 0.34		1.34 ± 0.17	a	1.41 ± 0.49	
High-ECCE, split[(1)]	11.22 ± 1.03		2.41 ± 0.19		19.50 ± 1.91		2.71 ± 0.23		1.13 ± 0.12	b	1.38 ± 0.42	
	Soybean (2006/07)											
Control	48.49 ± 2.20	b	4.73 ± 0.25	ns	26.42 ± 3.28	ns	11.65 ± 2.14	a	2.91 ± 0.66	ns	2.65 ± 0.16	ns
Low-ECCE	54.55 ± 1.68	a	4.84 ± 0.28		23.43 ± 4.69		9.86 ± 1.97	ab	3.06 ± 0.73		2.86 ± 0.30	
High-ECCE	53.03 ± 1.97	a	4.73 ± 0.27		24.71 ± 4.33		10.13 ± 0.76	ab	3.10 ± 0.68		2.84 ± 0.27	
High-ECCE, split	53.65 ± 1.34	a	4.88 ± 0.25		28.35 ± 3.92		9.12 ± 0.58	b	3.20 ± 0.46		2.89 ± 0.19	
	Soybean (2007/08)											
Control	42.47 ± 3.38	b	3.82 ± 0.42	ns	26.53 ± 1.62	ns	10.47 ± 0.87	ns	3.35 ± 0.21	b	2.89 ± 0.54	ns
Low-ECCE	52.09 ± 1.94	a	4.56 ± 0.43		25.12 ± 1.87		9.71 ± 1.72		3.46 ± 0.28	b	3.18 ± 0.32	
High-ECCE	51.15 ± 2.39	a	4.19 ± 0.44		23.94 ± 2.55		10.54 ± 1.54		3.76 ± 0.48	a	2.90 ± 0.30	
High-ECCE, split	51.53 ± 1.81	a	4.22 ± 0.32		26.24 ± 1.70		9.90 ± 0.97		3.51 ± 0.17	ab	3.14 ± 0.32	
	White oat (2008)											
Control	10.24 ± 0.69	ns	1.56 ± 0.23	b	22.63 ± 2.47	ns	2.54 ± 0.21	ns	1.35 ± 0.13	b	0.64 ± 0.10	b
Low-ECCE	10.67 ± 0.79		1.73 ± 0.21	ab	21.79 ± 3.53		2.70 ± 0.28		1.66 ± 0.21	ab	0.68 ± 0.09	ab
High-ECCE	9.93 ± 0.83		1.95 ± 0.27	a	17.34 ± 4.66		2.73 ± 0.17		1.75 ± 0.15	a	0.72 ± 0.12	a
High-ECCE, split	9.89 ± 0.61		1.78 ± 0.19	ab	21.88 ± 2.63		2.71 ± 0.21		1.64 ± 0.24	ab	0.69 ± 0.08	ab
	Soybean (2008/09)											
Control	44.76 ± 2.27	b	3.54 ± 0.29	b	24.99 ± 2.10	a	8.82 ± 1.00	ns	2.85 ± 0.30	ns	2.56 ± 0.19	ns
Low-ECCE	50.67 ± 1.93	a	3.72 ± 0.28	a	23.95 ± 2.03	ab	9.40 ± 1.39		2.98 ± 0.22		2.65 ± 0.43	
High-ECCE	49.50 ± 1.64	a	3.61 ± 0.25	ab	21.11 ± 2.82	b	10.03 ± 1.71		3.31 ± 0.47		2.58 ± 0.22	
High-ECCE, split	50.17 ± 1.66	a	3.76 ± 0.25	a	25.11 ± 2.22	a	9.21 ± 1.34		2.96 ± 0.28		2.79 ± 0.18	

[(1)]The rate was split into three applications. *Means followed by the same letter in a column for each crop were not significantly different as per Tukey's test at $p < 0.05$. ns = not significant.

highly acidic and possess a low structural quality. Thus, we can infer that the efficiency of surface liming in correcting subsurface acidity in NT soils is related to the management history of the soil (Calegari et al., 2013; Bortoluzzi et al., 2014).

Splitting application of the high-ECCE lime decreased its effect on the subsurface soil layers (*i.e.,* below to -0.20 m) —particularly as regards exchangeable Al^{3+}, soil pH_{water} and base saturation— in relation to application of the total rate at once (Figs. 2 and 3). While splitting amendments helps reduce losses by surface flow (Rheinheimer et al., 2018), how deep acidity can be corrected depends on the applied rate. Thus, the higher the liming rate is, the deepest will be the alkalizing effect (Rheinheimer et al., 2000; Álvarez et al., 2009; Calegari et al., 2013; Rodrighero et al., 2015; Tiritan et al., 2016) and the more advantageous will be applying the whole rate at once rather than in fractions (mainly with moderate acidic soils).

It is important to emphasize the long residual effect of liming observed here. This was especially so with the low-ECCE amendment, application of which led to soil pH_{water} values similar to the initial ones

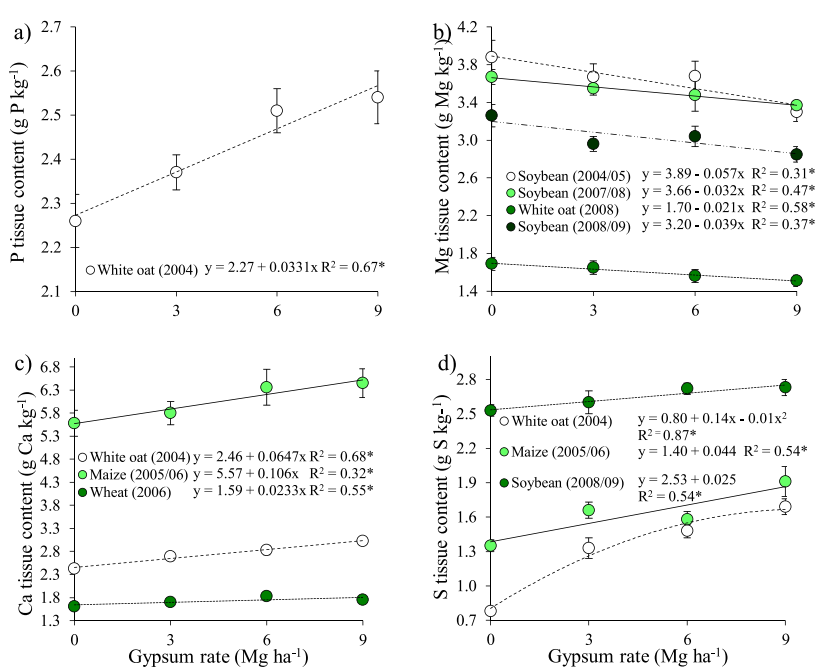

Fig. 7. Mean contents in P (a), Ca (b), Mg (c) and S (d) in soybean and maize leaves, and in wheat and white oat plant tissue as a function of the rate of agricultural gypsum surface applied to a Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil). Error bars are standard error, n = 12.

Table 4
Crop yields (means ± standard deviation, Mg ha^{-1}) as affected by surface liming with a low or high effective calcium carbonate equivalent (ECCE) amendment in a Typic Hapludox under no tillage in Guarapuava (Paraná State, southern Brazil).

Crop/year	Liming strategy								CV(2) (%)
	Control		Low-ECCE		High-ECCE		High-ECCE split[1]		
White oat (2004)	5.43 ± 0.39	ns	5.09 ± 0.39		4.71 ± 0.28		5.30 ± 0.68		11.21
Soybean (2004/05)	2.70 ± 0.25	ns	2.91 ± 0.29		2.95 ± 0.21		2.79 ± 0.29		15.06
Maize (2005/06)	12.89 ± 0.71	ns	12.29 ± 0.72		12.21 ± 0.84		12.97 ± 1.05		7.84
Wheat (2006)	3.81 ± 0.40	ns	3.68 ± 0.28		4.03 ± 0.56		3.75 ± 0.23		11.54
Soybean (2006/07)	3.66 ± 0.13	b	3.91 ± 0.09	ab	3.83 ± 0.17	ab	3.98 ± 0.11	a	3.89
Soybean (2007/08)	2.25 ± 0.17	b	2.74 ± 0.14	a	2.66 ± 0.18	ab	2.73 ± 0.25	a	11.63
White oat (2008)	5.44 ± 0.50	ns	5.40 ± 0.51		5.07 ± 0.90		5.55 ± 0.43		14.91
Soybean (2008/09)	2.08 ± 0.17	b	2.55 ± 0.26	a	2.55 ± 0.19	a	2.48 ± 0.20	a	8.08
Maize (2009/10)	14.08 ± 0.08	b	14.22 ± 0.11	a	14.11 ± 0.14	ab	14.17 ± 0.12	ab	0.65
Wheat (2010)	5.08 ± 0.34	ns	5.15 ± 0.36		4.92 ± 0.34		5.27 ± 0.28		10.57
Soybean (2010/11)	3.61 ± 0.15	ns	3.76 ± 0.14		3.78 ± 0.14		3.70 ± 0.14		3.41
Barley (2011)	5.07 ± 0.22	ab	5.17 ± 0.17	a	4.85 ± 0.24	b	5.12 ± 0.18	ab	4.42
Soybean (2011/12)	3.09 ± 0.23	ns	3.30 ± 0.15		3.31 ± 0.26		3.21 ± 0.14		8.58
White oat (2012)	4.10 ± 0.16	b	4.44 ± 0.14	a	4.40 ± 0.32	ab	4.29 ± 0.14	ab	5.32
Soybean (2012/13)	4.40 ± 0.28	b	4.90 ± 0.16	a	4.65 ± 0.24	ab	4.79 ± 0.30	ab	6.92
Maize (2013/14)	14.79 ± 0.48	ns	14.94 ± 0.46		14.42 ± 0.58		14.90 ± 1.14		5.28
Wheat (2014)	5.48 ± 0.21	ns	5.66 ± 0.22		5.56 ± 0.24		5.58 ± 0.14		4.04
Soybean (2014/15)	4.39 ± 0.25	ns	4.73 ± 0.25		4.49 ± 0.23		4.61 ± 0.16		7.90
Barley (2015)	4.12 ± 0.10	ns	4.14 ± 0.28		4.16 ± 0.12		4.15 ± 0.17		4.00
Soybean (2015/16)	4.34 ± 0.26	ns	4.37 ± 0.37		4.01 ± 0.32		4.36 ± 0.26		12.80
White oat (2016)	6.13 ± 0.57	ns	6.18 ± 0.71		6.06 ± 0.49		6.24 ± 0.66		10.10
Soybean (2016/17)	3.85 ± 0.32	ns	4.45 ± 0.36		4.16 ± 0.24		4.30 ± 0.26		13.47

[1]Total amount of 101% ECCE lime split into three applications. [2]Coefficient of variation. Means followed by the same letter in the line were not significantly different as per Tukey's test at $p < 0.05$. ns = not significant.

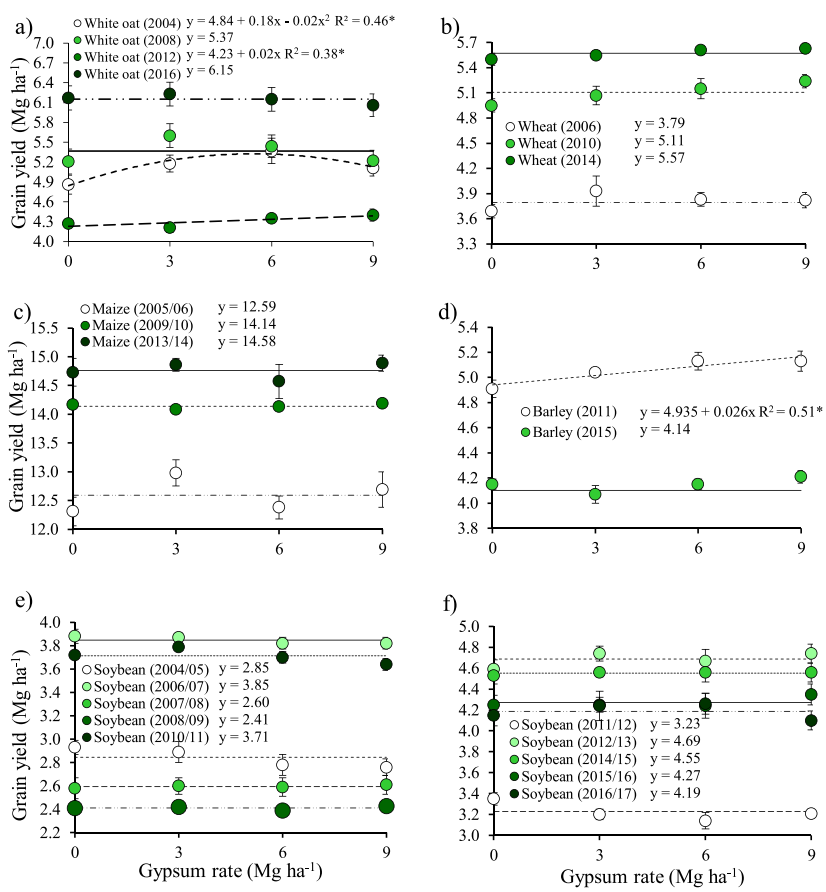

Fig. 8. Grain yield (Mg ha^{-1}) of white oat (a), wheat (b), maize (c), barley (d) and soybean (e, f) as a function of the rate of agricultural gypsum surface applied in 2004 to a Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil). Error bars are standard error, n = 12.

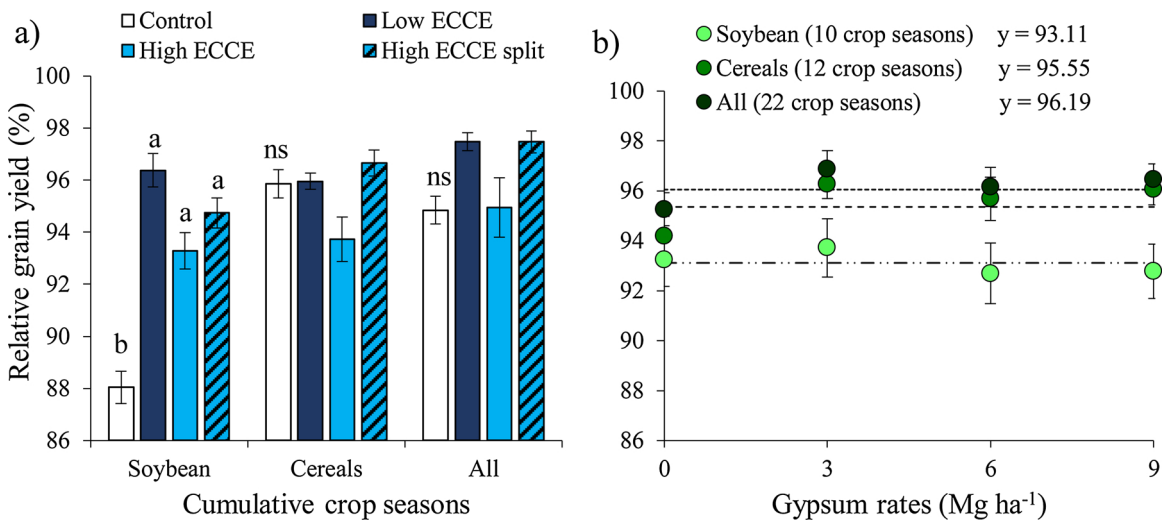

Fig. 9. Relative grain yield of soybean (10 crops), cereals (12 crops) and the body of crops (22) in response to surface liming with amendments of low- and high-ECCE (a) and to the surface application of different rates of agricultural gypsum (b) to a Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil). Error bars are standard error, n = 12.

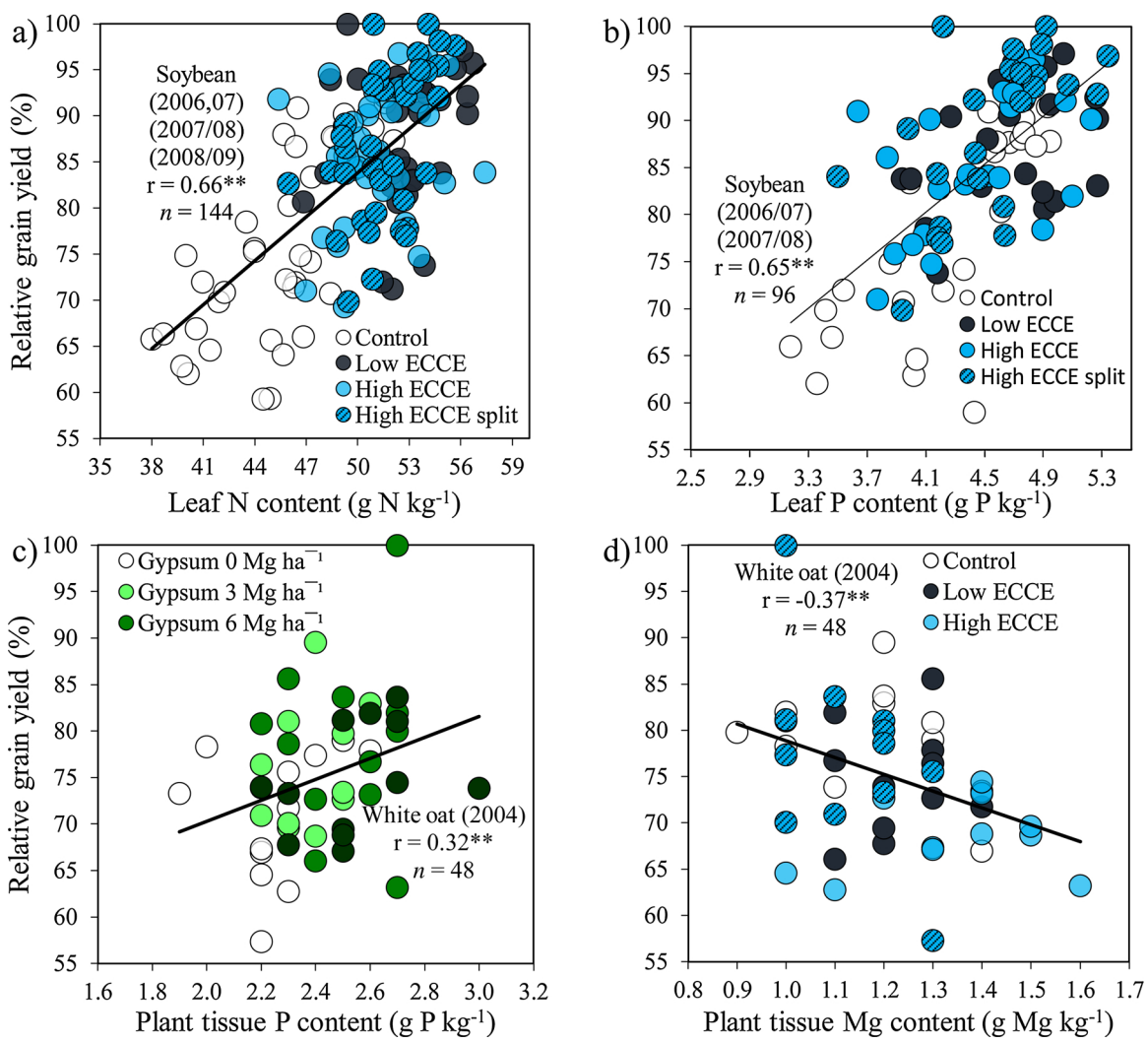

Fig. 10. Correlation of leaf N contents of soybean crops (2006/07, 2007/08 and 2008/09) (a), leaf P contents of soybean crops (2006/07 and 2007/08) (b), and P (c) and Mg (d) contents of plant tissue in white oat (2004) with the relative grain yield of the corresponding crops in a Typic Hapludox under no-tillage in Guarapuava (Paraná State, southern Brazil). n is the number of observations used in the correlation analysis. ** $p < 0.01$.

in addition to increased exchangeable Ca^{2+} and Mg^{2+} contents, and base saturation levels above 60% in the 0.00–0.20 m soil layer after 11 years (Fig. 3), all of which suggested that no further liming was required (Pauletti and Motta, 2017). Because lime requires an acid medium and low exchangeable Ca^{2+} contents to be efficiently dissolved (Zocca and Penn, 2017), moderately acidic soils such as ours can respond to liming over long periods. Consistent with previous results (Gonçalves et al., 2011), the residual effect of our amendments was more marked with the less reactive lime (*i.e.,* the low-ECCE lime). Eleven years after the high-ECCE amendment was applied, whether all at once or split, the soil pH_{water} and exchangeable Ca^{2+} and Mg^{2+} contents were similar to those before treatment, but base saturation was 48% and 55%, respectively, the fact that V < 60% justifying further liming.

Overall, our results show that the process by which NT soil is reacidified is slow and hence scarcely helped by external inputs. Thus, 11 years after application the soil had recovered 67 and 89% of its initial potential acidity (H + Al) with the low- and high-ECCE amendment, respectively, across the studied profile (0.00–0.60 m). Rheinheimer et al. (2018) found a sandy Ultisol recover barely 20% of its initial acidity 24 years after liming. The differences from the results of the previous authors can essentially be ascribed to the high initial acidity of their soils (*e.g., V* < 10%) and the need for high lime rates as a consequence.

4.2. Agricultural gypsum and soil acidity correction

The little reduction in soil pH_{water} obtained with gypsum in the short term (Fig. 4a) may have resulted from displacement of adsorbed exchangeable Al^{3+} and H^+ ions by exchangeable Ca^{2+} ions supplied by the gypsum (Zocca and Penn, 2017). In fact, the hydrolysis of each Al^{3+} relesead from the exchange sites generate 3 H^+ ions ($Al^{+3} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$) which reduce the soil pH_{water} substantially as a result. Small soil pH_{water} increases were also previously reported by other authors (Crusciol et al., 2016; Costa and Crusciol, 2016) and ascribed to exchange reactions between OH^- and S-SO_4^{2-}; however, gypsum is widely known not to correct soil acidity because their solubility products does not produce OH^- nor does it consume H^+ (Zocca and Penn, 2017).. +

Gypsum is known to efficiently reduce exchangeable Al^{3+} levels in soils with high contents of this element (Caires et al., 2016; Costa and Crusciol, 2016). This can occur by several mechanisms such as (i) exchangeable Al^{3+} leaching as an ion-pair for S-SO_4^{2-} (ii) by formation of precipitates like a $Al_2(SO_4)_3$. Ultimately, exchangeable Al^{3+} ions, which are detected in soil analyses when gypsum has been applied in the soil, can forms complexes such as $AlSO_4^+$ which reduces aluminum toxicity to plants as a result (Fageria and Nascente, 2014; Costa and Crusciol, 2016; Zocca and Penn, 2017). However, in our study exchangeable Al^{3+} contents were not altered by agricultural gypsum, this was possibly the result of the low content of this element in the soil (Fig. 5c and d).

In addition to its reducing soil acidity, agricultural gypsum is a good source of Ca^{2+} and S-SO_4^{2-} for soil, which increases their availability to plants (Figs. 4a, b and 5 e) (Crusciol et al., 2016; Costa and Crusciol, 2016; Dalla Nora et al., 2017b). However, partially hydrolyzed S-SO_4^{2-} is highly mobile in soil and can easily bond to accompanying ions such as exchangeable Ca^{2+}, Mg^{2+} and K^+, thus leading to nutrient deficiencies in the presence of excessive exchangeable Mg^{2+} and K^+ leaching (Pauletti et al., 2014). This is consistent with the observed reduction in exchangeable Mg^{2+} contents down to 0.40 m in the first year after application and even in the deepest layer examined (0.40–0.60 m) in the long term (11 years) (Fig. 5d). Consistent with previous results of Pauletti et al. (2014), there was no difference in soil exchangeable K^+ content among treatments. The higher leaching of exchangeable Mg^{2+} relative to exchangeable K^+ by effect of gypsum application is a result of S-SO_4^{2-} ions more easily bonding to exchangeable Mg^{2+} by effect of its higher bonding energy (Zocca and Penn, 2017).

Agricultural gypsum is recommended in areas where the soil has a high content in exchangeable Al^{3+} and a low content in exchangeable Ca^{2+} in the subsurface layer (0.20–0.40 m). Under these conditions, gypsum increases subsurface exchangeable Ca^{2+} levels and hence reduces exchangeable Al^{3+} activity, which in turn increases base saturation (Costa and Crusciol, 2016; Dalla Nora et al., 2017b). As can be seen in Table 1, our soil had low initial contents in exchangeable Al^{3+} (0.12 $cmol_c\ dm^{-3}$), and high exchangeable Ca^{2+} contents (3.5 $cmol_c\ Ca^{2+}\ dm^{-3}$) in the subsurface layer. Therefore, consistent with previous results of Crusciol et al. (2016), applying gypsum had no effect on base saturation (Fig. A1c and A1d) because the ensuing increase in exchangeable Ca^{2+} was offset by a decrease in exchangeable Mg^{2+} contents.

As can be seen from Fig. 5a, gypsum rapidly increased exchangeable Ca^{2+} contents in all soil layers within one year. Dalla Nora et al. (2017b) found application of gypsum to result in differences in exchangeable Ca^{2+} and available S-SO_4^{2-} contents among treatments after only six months. The residual effect of agricultural gypsum in increasing soil exchangeable Ca^{2+} and available S-SO_4^{2-} contents in the long term is well-documented (Caires et al., 2011; Costa and Crusciol, 2016; Dalla Nora et al., 2017b). However, in our study the long-term (11-year) changes in exchangeable Ca^{2+} contents by effect of gypsum were less expressive and restricted to the surface layer (Fig. 5b). Assessing the residual effect of agricultural gypsum is crucial because it allows the cost of the product to be divided among several seasons, thereby increasing the economic viability of this soil management practice (Dalla Nora et al., 2017b). Based on our results, the benefits of gypsum increasing soil exchangeable Ca^{2+} levels lasted less than 11 years even if the amendment was applied at a high rate (9 Mg ha^{-1}).

Gypsum increased exchangeable Ca^{2+} contents in the soil surface layer (0.00–0.10 m) in the short term by 38% relative to no application (Fig. 5a), whereas liming raised exchangeable Ca^{2+} levels merely by 16% (high-ECCE lime) relative to no lime (Fig. 3a). These results reveal that gypsum was more rapid than lime in rendering Ca^{2+} available, probably because of the higher solubility of the former (Bennett et al., 2014; Crusciol et al., 2016; Pauletti et al., 2014). In the long term, gypsum led to exchangeable Ca^{2+} contents barely 14% higher than control treatment (Fig. 5b), whereas low-ECCE lime resulted in 56% higher contents than no liming treatment (Fig. 3b). Therefore, lime had a much more marked residual effect than gypsum, these results corroborates with those reported by Costa and Crusciol (2016). According to Gonçalves et al. (2011), the response time of lime is inversely proportional to the strength of its residual effect. These results show that using gypsum in combination with low-ECCE lime can be effective to correct soils with high acidity.

4.3. Soil chemical properties, nutrient contents of plant tissue and crop yield as a function of liming strategy

Our hypothesis that applying agricultural gypsum and lime in combination to a moderately acidic soil would have a synergistic effect leading to increased crop yields was not confirmed. However, such a synergistic effect was previously observed by a number of authors in soils with a high subsurface acidity (Crusciol et al., 2016; Costa and Crusciol, 2016; Dalla Nora et al., 2017a).

Liming increased leaf P contents in the soybean crops (Table 3) even though it failed to also increase P availability in the soil (Fig. A2a and A2b). In fact, the control treatment showed higher available P contents in the superficial layer than in the lime treatments. This result can be related to the lower crop yield in the control, which in turns reduces P exportation. Crops with higher grain yield will extract a larger amount of nutrients from the soil, but on the other hand, will produces larger amount of residues which may increase the nutrient cycling and reduce

leaching, specially those nutrients whose ions have high mobility in the soil. Also, we need to consider that the effect of acidity correction of liming may have favored root growth, thereby increasing the soil volume explored by the plants and also their ability to absorb water and nutrients, particularly those scarcely mobile in soil such as P (Holland et al., 2018).

Liming also increased leaf N contents in the soybean crops (Table 3). The increased soil pH_{water} may affect the efficiency of N biological fixation, which is consistent with the increased leaf N contents observed with liming (Costa and Crusciol, 2016; Fageria and Nascente et al., 2014). According to Miransari (2016), soil $pH_{water} < 5.5$ considerably reduces N biological fixation by soybean, because it influences survival and growth of *Rizhobium*, infection, nodulation and N fixation. In the first year, soil pH_{water} only exceeded 5.5 in the treatments using low- or high-ECCE lime in a single application. Although all treatments decreased soil pH_{water} below 5.5 in the long term, that with low-ECCE lime successfully maintained soil $pH_{water} \approx 5.3$, which was the closest to the desirable value for an efficient N biological fixation (Fig. 2b). The soybean crops with substantially increased leaf N and P contents also increased grain yields (Table 3 and 4). This result suggests a relationship between the two variables that is supported by the high correlation of the leaf N ($r = 0.66$**) and P content ($r = 0.65$**) with the relative grain yield of the soybean crops (Fig. 10a and b). Thus, liming had a favorable effect on 40% of the soybean crops, whose grain yield was increased by 14% on average (0.38 Mg ha^{-1} yr^{-1} Table 4).

Despite the favorable effects on soil chemical properties (*e.g.,* increased soil pH_{water} values, exchangeable Ca^{2+} and Mg^{2+} contents, and base saturation, and decreased exchangeable Al^{3+} contents), grain yield in maize and the two winter cereals was scarcely affected by lime. In fact, less than 20% of cereal crops were affected and the average increase in grain yield was merely 5%. Our results thus confirm those of Joris et al. (2016), who found soybean crops to be more sensitive to soil acidity than cereals. High grain yields for crops grown on NT soils are widely documented even in highly acidic soils (Martins et al., 2014; Joris et al., 2016). In this work, the control treatment (no liming) led to an average yield of 3.4 Mg ha^{-1} $yr^{-1}$for soybean, 13.9 Mg ha^{-1} yr^{-1} for maize and 4.9 Mg ha^{-1} yr^{-1} for winter cereals. These values exceed the average yield for the last 5 years (2011–2016) in the Brazilian state of Paraná by 5,65 and 70%, respectively (CONAB, 2017). Accordingly, the increased cycling of nutrients and greater buffering capacity of NT soil relative to conventionally managed soil with tillage provide more favorable conditions for plant growth even at lower soil pH_{water} values, thereby alleviating the dependence on fertilizers and amendments —and hence, increasing the sustainability of production systems (Martins et al., 2014; Joris et al., 2016).

The fact that most of the crops ($\approx$ 73%) failed to respond to lime application can also be interpreted in terms of the soil chemical conditions under the control treatment 11 years after the experiment was started. Thus, the contents in exchangeable Al^{3+} of the control soil increased relatively little, even with a low pH_{water} value (4.75) in the 0.00–0.20 layer, and remained in the lower range (0.3–0.7 $cmol_c$ Al^{3+} dm^{-3}; Fig. 2b and d), moreover the exchangeable Ca^{2+} and Mg^{2+} contents of the soil were appropriate for crop growth (exchangeable $Ca^{2+} > 4$ $cmol_c$ Ca^{2+} dm^{-3} and exchangeable $Mg^{2+} > 1.1$ $cmol_c$ Mg^{2+} dm^{-3}; Fig. 3e and d) as per the diagnostic criteria proposed by the scientific community (Pauletti and Motta, 2017). Finally, the soil had high SOC contents, namely: 5.6 and 4.2% on average for the 0.00–0.20 m layer 1 and 11 years, respectively, after the treatments were applied.

Properly managing NT soils facilitates accumulation of SOC (Cherubin et al., 2018), which plays a number of roles ensuring correct soil performance and crop yield by increasing nutrient availability and reducing exchangeable Al^{3+} toxicity even in acid soils (Martins et al., 2014; Rheinhemer et al., 2018). Also, the decomposition of crop residues produces organic acids, which, together with other compounds released by plant roots, can form organometallic chelates with exchangeable Al^{3+} and alleviate its toxic and inhibitory effects on plant root growth (Alleoni et al., 2010; Martins et al., 2014; Holland et al., 2018). Even in an extremely acidic soil ($V = 10\%$ in the 0.00–0.20 m layer), Joris et al. (2016) observed no effect of liming on dry matter yield of black oat. Similarly, Martins et al. (2014) studied an Oxisol of moderate surface acidity ($V = 40\%$ in the 0.00–0.20 m layer) and high subsurface acidity (Al saturation = 60% in the 0.20–0.40 m layer) found no response to liming in three soybean crops.

The combined grain yield of the control treatment for the soybean crops (10 crop seasons) was approximately 9% lower (3.25 Mg ha^{-1}) than that of the low-ECCE lime treatment (Fig. 9a). Consistent with previous results of Rodrighero et al. (2015) for sandy and clayey soils, the lime strategies treatments exhibited no difference in grain yield. However, the low-ECCE amendment had a more marked residual effect on soil acidity that warrants using it to increase the liming return time —and hence agricultural benefits. Liming fail to alter both cumulative yield in cereals and total yield in grain crops. However, the liming treatments were especially influential on soybean, which is the main crop in the rotation systems typically used in NT soil areas in Brazil (CONAB, 2017) and one with high economic returns. For this reason, monitoring soil acidity in order to make the correct decision when to apply lime is always recommended with a view to ensuring appropriate conditions for crop growth and high grain yields.

4.4. Response of soil chemical properties, nutrient contents in plant tissue and grain yield to different rates of agricultural gypsum

The increased exchangeable Ca^{2+} (Fig. 5a) and available S-SO_4^{2-} (Fig. 6) content down to -0.60 m in the soil, and the increase of available P content in the surface layer (Fig. A1a), resulting from application of agricultural gypsum led to increased levels of these nutrients in plant tissue in the white oat 2004 crop (Fig. 7a and c), and also to an increase in grain yield by about 8% (Fig. 8a). The increase in grain yield for that white oat crop was positively correlated ($r = 0.31$**) with the P content of plant tissue (Fig. 10c). This was possibly a result of the absence of fertilization on the crop and on the plants grown under the control treatment therefore exclusively relying on soil available P content for growth; in contrast, the use of gypsum increased available P content as a result of its containing about 1% of this element. The increase in leaf S contents of the white oat 2004, maize 2005 and soybean 2008/09 crops resulting from application of gypsum is a frequent finding (Tiecher et al., 2013; Crusciol et al., 2016). However, as found here, the increase not always results in increased crop yields (see Fig. 8), but rather in "luxury uptake" by plants (Pias et al., 2019).

Previous studies (*e.g.*, Dalla Nora et al., 2017a; Tiecher et al., 2018) showed cereals to be more responsive than soybean to agricultural gypsum. Our results are consistent with this finding; thus, 25% of the cereal crops responded favorably to gypsum, whereas none of the soybean crops did. The average yield increase for the cereal crops exhibiting a positive response was merely 4% (Fig. 8a e d). The stronger response of cereals to agricultural gypsum in relation to soybean has been ascribed mostly to an increased efficiency of the former in using soil N (Caires et al., 2016), which is a highly dynamic nutrient and easily leached as N-NO_3^- form in deeper soil layers usually inaccessible to root plants.

Using agricultural gypsum reduced exchangeable Mg^{2+} contents (Fig. 5c and d) and raised the exchangeable Ca^{2+}/Mg^{2+} ratio in all soil layers as a result (Fig. 5e and f). However, soil exchangeable Mg^{2+} contents remained above the critical level for adequate growth of grain crops (*viz.,* 1.1 $cmol_c$ dm^{-3} according to Pauletti and Motta, 2017) in both the short and the long term. In fact, the exchangeable Ca^{2+}/Mg^{2+} ratio in the surface layer exceeded 6.5 already in the first year and this value considerably exceeds the levels recommended by Pauletti and Motta (2017): 3–5. The decrease in exchangeable Mg^{2+} contents was only observed in soybean leaves from the 2004/05, 2007/08 and 2008/09 crops, and in plant tissue from the white oat 2004 crop. However, in

any case, the Mg contents of both soybean and white oat remained within the recommended ranges. Under these conditions, applying gypsum to the soil had no adverse effect on grain yield.

In subtropical NT soils with a high subsurface acidity (Al saturation > 10%), the maximum increase in grain yield by effect of agricultural gypsum amount to about 17% on average and occur mainly in cereals (92% of crops) and also in soybean under conditions of water deficiency (100% of crops) (Tiecher et al., 2018). In fact, the response of crops to gypsum application is higher in crop seasons with water deficiency (Dalla Nora et al., 2017a; Tiecher et al., 2018) due to the reduction of Al^{3+} activity and the increase in the concentration of basic cations in the subsoil. In such conditions plants normaly has a better and deeper root development (Dalla Nora and Amado, 2013; Caires et al., 2016), which enables absorb water and nutrients in previously inaccessible soil layers. In our study, we observe the occurrence of some water deficiency in at least five crops seasons (soybean 2004/05, 2008/09, 2016/17, wheat 2010 and white oat 2012), but only in white oat 2004 there was an increase of 3% in grain yield on the treatment with the highest gypsum rate.

Our hypothesis that the increase in exchangeable Ca^{2+} and available S-SO_4^{2-} contents in subsurface layers resulting from gypsum application could lead to increased crop yields even in a soil of moderate subsurface acidity (*e.g.,* base saturation > 35% and Al saturation < 5%) was rejected. In fact, most of the crops (86%) failed and presented no response to gypsum. This was partly a result of the soil containing enough available S-SO_4^{2-} (> 10 mg SO_4^{2-} dm^{-3}) even 11 years after treatment without a new application, this results corroborates with those showed in a recent systematic rewiew of crop respose to sulfur fertilization in Brazil, where the authors observed that when soil available S-SO_4^{2-} are above the critical level the likehood to a positive crop response by sulfur fertilization is zero (Pias et al., 2019). Also, the good water availability for most crops (Fig. 1) helped reduce the likelihood of a response, but particularly that of soybean, to agricultural gypsum (Dalla Nora and Amado, 2013; Pauletti et al., 2014; Zandoná et al., 2015; Tiecher et al., 2018). Finally, the positive response of some crops to gypsum found in many studies (*e.g.,* Pauletti et al., 2014; Zandoná et al., 2015; Dalla Nora et al., 2017b) was probably more closely related to the amendment reducing exchangeable Al^{3+} toxicity than to its increasing the contents in available S-SO_4^{2-} and alkaline cations in the subsurface soil layer. In any case, the current recommendation for application of agricultural gypsum (*viz.,* Al saturation > 20% according to Pauletti and Motta, 2017) does not seem to hold for NT soils. As recently shown by Tiecher et al. (2018) in a systematic review of available literature, it is more appropriate to use an Al saturation value of 10% as the critical level for cereals on subtropical NT soils. Crusciol et al. (2016) and Dalla Nora et al. (2017a) also observed a positive response of grain crops to agricultural gypsum in soils with Al saturation of 5–10% in the subsurface layer.

5. Conclusions

The combined use of liming and agricultural gypsum had no synergistic effect in improving soil chemical properties and crop grain yields in a moderately acidic soil. Liming increased soybean yields by 14% on average in 40% of crop seasons, thus confirming the higher sensitivity of soybean to soil acidity in relation to cereals (maize and winter cereals). On the other hand, gypsum resulted in grain yield increase of only 4% on average in 25% in the cereal crops.

In the short term, agricultural gypsum proved to be more efficient than liming on increasing exchangeable Ca^{2+} contents in the soil profile. However, liming was more efficient in correcting soil acidity by altering several soil acidity properties (soil pH_{water}, base saturation and exchangeable Ca^{2+}, Mg^{2+} and Al^{3+}) and had a longer residual effect on exchangeable Ca^{2+} contents than agricultural gypsum. Spliting lime rate proved to be less efficient in correcting soil acidity in depth than the application at once. Although the liming strategies resulted in no difference in crop yield, the low-ECCE treatment exhibited a longer residual effect than the high-ECCE treatment and preserved appropriate soil acidity conditions for plant growth for 11 years. Surface liming of moderately acidic subtropical soils properly managed under NT provides an efficient method for lowering subsurface acidity up to -0.60 cm already within the first year after application. In this case, gypsum application did not bring additional benefits to soil or crop yields.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.still.2019.05.005.

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