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SOIL ACIDITY MANAG EMENT ON AN OXISOL QUALITY AND WHEAT -COMMON BEAN GROWTH UNDER A LONG TERM NO - TILLAGE SYSTEM

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I dedicate this thesis to my spouse Tais and all my family.

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ABSTRACT

Soil chemical and physical disorders are among major limiting factors to improve productive potential of tropical agriculture. The low productive capacity has been associated especially to soil acidity and macronutrient deficient, thus the development of strategies that improve production capacity of tropical acid soils are required. Lime and phosphogypsum (PG) are materials commonly used to improve soil chemical condition, but there is few information about the long-term effects of these products, applied superficially, especially on Oxisol physical properties and organic matter pools. Therefore, this research aimed to evaluate the effect of surface application of lime and PG on the soil chemical and physical attributes, root growth, plant nutrition, yield components, technological characteristics and yield of wheat and common bean, and soil organic matter (SOM) pools considered critical to make agricultural tropical systems sustainable and productive. A randomized complete block design was used and treatments were replicated four times. Four treatments were carried out: control (without lime and gypsum application); PG (2.1 Mg ha^{-1}); lime (2.0 Mg ha^{-1}); and a combination of lime and PG (2.0 and 2.1 Mg ha^{-1}, respectively). Since the experiment was established in 2002, the amendments rates have been applied three times (2002, 2004, and 2010). Superficial liming alleviated Oxisol acidity in the surface and subsurface layers after twelve years under soil acidity management, with positive results of PG associated to lime on soil pH, Ca^{2+} and Mg^{2+} levels, and base saturation in the topsoil layers (0-0.10 m). The surface application of lime is effective to improve root growth in subsurface layers, crop nutrition and wheat and common bean grain yield. The high correlation between soil chemical attributes and organic carbon pools shows that the soil organic matter (SOM) input was favored mainly by high levels of Ca and Mg and low levels of exchangeable Al in the soil. The combination lime and PG improved the SOM quality, increasing the formation and stabilization of humic substances in the soil. The use of both soil amendments combined also provided significant improvements on soil physical properties, manly in the formation and stabilization of large aggregates (>1.0 mm). This condition provided better physical protection of SOM, inducing higher organic carbon accumulation in these structures. Consequently, it was observed a better soil structure, resulting in greater macroporosity as well as lower soil bulk density and penetration resistance. Lime rate estimated to increase

the base saturation in the topsoil (0-0.20 m) to 70% was considered appropriate for surface liming recommendation in a tropical Oxisol under no-tillage system, but the combination with phosphogypsum provides major benefits on soil chemical and physical attributes and SOM quality.

Keywords: lime, phosphogypsum, plant nutrition, root growth, grain yield, grain quality, soil aggregates, organic carbon, humic substances.

RESUMO

Os distúrbios químicos e físicos do solo estão entre os principais fatores que restringem o potencial produtivo da agricultura tropical. A baixa capacidade produtiva tem sido associada principalmente à acidez do solo e deficiência de macronutrientes, portanto, é fundamental o desenvolvimento de estratégias que ampliem a capacidade de produção de solos ácidos tropicais. O calcário e o gesso agrícola (PG) são materiais comumente empregados na agricultura para melhorar as propriedades químicas do solo, mas existem poucas informações sobre os efeitos da aplicação superficial desses produtos nas propriedades físicas dos Latossolos e nas diversas frações da matéria orgânica do solo (SOM). Diante destes aspectos, este trabalho objetivou avaliar o efeito da aplicação superficial de calcário e PG sobre os atributos químicos e físicos do solo, crescimento radicular, nutrição de plantas, componentes de produção, características tecnológicas e produtividade de trigo e feijão e sobre as diversas frações de SOM, as quais são consideradas críticas para tornar os sistemas agrícolas tropicais sustentáveis e produtivos. O delineamento experimental foi em blocos casualizados com quatro repetições. Foram estabelecidos quatro tratamentos: controle (sem aplicação de calcário e gesso); PG (2,1 Mg ha^{-1}); calcário (2,0 Mg ha^{-1}); e uma combinação de calcário e PG (2,0 e 2,1 Mg ha^{-1}, respectivamente). Desde a instalação do experimento em 2002, as doses de calcário e PG foram aplicadas três vezes (2002, 2004 e 2010). A calagem superficial reduziu a acidez do solo nas camadas superficiais e subsuperficiais, com resultados positivos de adição de PG e calcário no pH do solo, teores de Ca^{2+} e Mg^{2+} e saturação de bases nas camadas superficiais do solo (0-0,10 m). A aplicação superficial de calcário é eficaz para aumentar o crescimento radicular do trigo e feijão nas camadas subsuperficias, além disso, favoreceu os aspectos nutricionais e rendimento de grãos de ambas as culturas. A alta correlação entre os principais atributos químicos do solo e as diversas frações da SOM demonstra que a adição de Ca e Mg e a redução na toxicidade do Al no solo são fundamentais para favorecer o acúmulo de SOM. A combinação de calcário e PG melhorou a qualidade da SOM, aumentando a formação e estabilização de substâncias húmicas no solo. Além disso, a associação de ambos os produtos também proporcionou melhorias significativas nas propriedades físicas do solo, induzindo maior formação e estabilização de macroagregados (> 1,0 mm). Esta condição proporcionou melhor proteção física da SOM, induzindo maior

acúmulo de carbono orgânico nessas estruturas. Consequente, foi observado uma significativa melhoria na estrutura do solo, resultando em maior macroporosidade, bem como menor densidade do solo e resistência à penetração. A dose de calcário calculada para aumentar a saturação de base no solo (0-0,20 m) a 70% foi considerada adequada para a recomendação de calagem superficial em um Latossolo tropical conduzido sob sistema plantio direto, porém a combinação com PG proporciona maiores benefícios nos atributos químicos e físicos do solo e qualidade da SOM.

Palavras-chave: calcário, gesso agrícola, nutrição de plantas, crescimento radicular, produtividade de grãos, qualidade de grãos, agregados de solo, carbono orgânico, substancias húmicas

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Chapter 2 – Root development and annual crop production as affected by lime and phosphogypsum application in a tropical Oxisol under no-tillage system

SUMMARY

Introduction

Soil acidity is one of the major limiting factors for crop production in several locations around the world, occurring mainly in tropical areas dominated by Ultisols and Oxisols. Among the main consequences of acid soils are the high toxicity of elements such as Al^{3+} and Mn^{2+} and the low availability of macronutrients, which affect severally root growth, water and nutrient uptake by plants, and consequently the crop yield and farm profitability.

In order to neutralize soil acidity and improve soil fertility, liming is the most common practice used by farmers due to low economic cost, in addition, is considered an important source of Ca and Mg for soils with low natural levels of exchangeable bases. Because of the chemical properties, lime has low solubility in water, reducing the mobility of the product down the soil profile. In conventional management systems, lime is usually incorporated into the soil during tillage processes, however, plowing and disking severally impact the physical, chemical, and biological attributes of soil, inducing transformations which contribute for land degradation.

The losses on productive capacity and soil health due to intensive tillage have affected drastically their capacity to sustain food production. As a result, in the last decades a massive conversion of conventional tillage to conservative ecosystems has occured, it minimizes the environmental impacts and increases soil capacity to produce food, fiber, and fuel, making the agricultural production more ecologically sustainable.

No-tillage (NT) system is the main conservative agricultural ecosystem spread and adopted in Brazil, however, the impact of soil acidity has restricted the benefits of the system in improving crop production. Due to environmental sustainability concepts, practices such as plowing and disking, commonly used for acidity amendments incorporation, are not recommended, thus lime is only applied superficially, which theoretically may limit limestone reaction below the point of placement.

Following up on this research, several long-term studies were conducted in subtropical areas, attesting the viability of lime applied superficially in NT system due to the greater accumulation of soil organic matter (SOM), which induces several physical and chemical mechanisms involved on lime action in subsurface layers. On

the other hand, limited information is available for tropical conditions, where rainfall distribution, soil physical attributes and SOM content are distinct compared to subtropical soils. Dry winter, high decomposition rates of SOM, frequent dry spells, and dense soil profile are important characteristics of tropical areas, which can affect the lime reaction applied superficially.

High acidity and low fertility of subsoils have been limiting crop production in several countries located in the tropics due to the chemical effect on root development of crops, limiting the growth and water and nutrient uptake by plants. Following up this information, further studies are required to evaluate the long-term effect of surface liming on tropical soil profile.

In order to improve root growth to subsurface layers severally affected by chemical disorders, the phosphogypsum (PG) can be an important strategy for improving lime reactions. The higher solubility, the capacity to neutralize Al^{3+} toxicity and increase the levels of basic cations (BC) at subsoil layers makes this by-product a possible complement to liming. In addition, the effect on improving root development may affects some soil attributes that can enhance lime reaction applied superficially.

The Brazilian Cerrado region has great potential to increase wheat and common bean production in Brazil, but Al toxicity and soil acidity has been considered one of the most important yield-limiting for both crops. Given these facts, liming has been recommended to improve crop production, but there is restrict information about the long-term effects of surface application of lime and PG combined on wheat and common bean growth, especially in tropical Oxisols managed under NT system.

We hypothesized that surface liming with PG addition play a crucial role in improving subsoil chemical attributes, SOM pools and soil physical attributes, being an important strategy to increase the crop production in regions with dry winter and frequent dry spells during rainy season. However, for tropical condition, there is restricted scientific information involving the long-term effects of surface application of lime and PG combined on SOM pools and soil physical attributes, considered critical factors to make agricultural tropical systems sustainable.

Therefore, this research aimed to evaluate the effect of surface application of lime and PG on the soil chemical and physical attributes, root growth, plant

nutrition, yield components, technological characteristics and yield of wheat and common bean, and soil organic matter pools considered critical to make agricultural tropical systems sustainable and productive.

Chapter 1

Soil acidity management under no-tillage system

Antonio C. A. Carmeis Filho and Carlos A. C. Crusciol

1.1. The No-Tillage System

The conventional agricultural practices and intensive crop production have intensified the degradation of soils in several regions of the world, reducing the sustainability and agricultural ecosystems potential in increasing food production. Among the major adverse long-term effects of conventional farming is the soil erosion, affecting by up to 40% of global cropland (WOOD et al., 2000), with significant losses of nutrients and biodiversity. In order to decrease soil degradation, efficient conservative technologies such as no-tillage (NT) systems were developed to maintain and improve the productivity potential, with minimal environmental impacts. For this, three basic and central principles are involved in the success of the NT systems: crop rotation, minimal soil disturbance, and permanent soil cover.

Among the major advantages of these conservative practices in combination are the soil structure maintenance, higher water retention, greater biological activity, greenhouse gas emissions mitigation, better nutrient cycling, erosion reduction, and smaller nutrient losses (HOBBS et al., 2008). Due to all these benefits, the conservative ecosystems such as NT system represents an important tool to recover areas highly degraded and avoiding deforestation caused by agricultural expansion. As a consequence of several benefits, it has been reported a big diffusion and adoption of technology over an area of approximately 160 million ha, distributed primarily, mainly in Latin America (66 million ha), North America (54 million ha), and Australia (18 million ha) (FAO, 2015).

Brazil is one of the leading countries in terms of adoption and expansion of the NT system. According to FEBRAPDP (Brazilian Federation of No-Tillage and Irrigation), this technology occupies approximately 32 million ha in the country, representing almost 60% of the management applied for grain production, a consequence of

the high potential of this system to build soil fertility, increase crop production, and reduce annual soil losses rate by erosion processes (HERNANI et al., 2002).

The several benefits of NT systems have been related as a result of conservative practices on soil organic matter accumulation, however, in tropical ecosystems is difficult to maintain high levels of soil organic matter, because the edaphic factors favor the high decomposition rates of organic compounds. In order to enhance the potential productivity and the sustainability of no-till tropical agricultural ecosystems, large input of organic residues is required, however, the low native fertility of highly weathered soils often constrain the amounts of biomass produced.

1.2. Soil acidity

It is estimated that around 4 billion ha of soils potentially arable are affected by soil acidity, being more predominant in soils located in tropical regions such as Ultisols and Oxisols, which represent more than 40% of the tropic soils (HAUG, 1983; SUMNER; NOBLE, 2003; FAGERIA; BALIGAR, 2008). South America is among the world's agricultural areas most affected by acid soils, with 15.1 million square kilometer or 85% of total area exhibiting some acid degree. Due to the negative impact of acidity on soil fertility, Fageria and Baligar (2001) estimate that about 850 million ha of South America`s soils are underutilized.

Soil acidity problems have been detected in approximately 70% of Brazilian agricultural areas, and in 40% of these cases, crop productivity is reduced by up to 50% due to a combination of chemical factors such as Al^{3+} toxicity and nutrient deficiency (FONTES et al., 2001; NORA; AMADO, 2013).

The Brazilian Cerrado, with more than 110 million ha potentially arable, plays a very important role for national agriculture/livestock/forestry production (LOPES et al., 2012), however, approximately 80% of this has chemical disorders proceeded from acidity, restricting agricultural productivity in this region (FAGERIA; STONE, 1999).

Soil acidity is characterized by hydrogen (H^+) ion concentration in soil solution, and several bio-chemical reactions contribute to acidify the soil. According to

Bolan et al. (1991) the most important processes involved in soil acidification are: i) CO_2 dissolution; ii) the uptake N by plants in different forms (ammonium, and N_2 fixation), iii) decomposition of organic residues, and iv) oxidation of N and S forms.

The respiration process by soil organisms represents the major source of CO_2, which reacts with water to produce carbonic acid (H_2CO_3) and H_3O^+, responsible by soil acidification. Due to high concentration of CO_2 into the soil, this process is considered to be the main responsible reaction for soil acidification (BOLAN et al., 1991). In an Alfisol, under high biological activity (root and soil organisms), Cheng et al. (2010) observed that CO_2 enrichment reduced soil pH values from 0.5 to 1.2 units, in addition, suggested that CO_2 effect on soil acidification can be higher than the values obtained, because under elevated CO_2 concentration some plants species exuded larger amounts of H^+ to soil solution. The reduction on soil redox potential by CO_2 enrichment had contributing for BC leaching in areas where rainfall exceeds evapotranspiration (BOLAN; HEDLEY, 2003).

The N input by fertilization is also an important factor involved in soil acidification, but the magnitude of effect varies according to the source of N-mineral and quantities applied in the soil. Several studies emphasized that the N mineral fertilization promoted significant reduces in soil pH values, with a concomitant effect on increasing exchangeable Al^{3+} (BOLAN et al., 1991; FAGERIA; BALIGAR, 2001; BOLAN; HEDLEY, 2003; CAIRES et al., 2015).

The application of fertilizers with high concentration of N-ammoniacal and N-amide have contributed significantly to accelerate soil acidification, and the high demand for food production associated with the price of fertilizer have intensified the use of these N sources, manly urea [$CO(NH_2)_2$] and ammonium sulfate [$(NH_4)_2SO_4$]. Verifying the effect of N fertilization as urea and ammonium sulfate on pH changes in tropical acid soils with moderately acidity, Stumpe and Vlek (1991) related that both N sources decreased soil pH, but the higher acidification potential were observed when ammonium sulfate was used.

In order to estimate soil pH changes in relation to N supply as $(NH_4)_2SO_4$, a quadratic regression model highly significant was suggested by Fageria and Baligar (2001) ($Y = 5.50 + 0.000039X - 0.000066X^2$, $R^2 = 0.93$), where N rates are

represented by X and soil pH by Y. However, Stumpe and Vlek (1991) emphasized that this effect can be changed according to acid conditions. In an Ultisol, the higher acidity prevented complete nitrification of the NH_4^+ derived from ammonium sulfate, and in this case the capacity of the urea in release protons can be higher.

Verifying the effect of N fertilization as urea and ammonium sulfate on pH changes in an Ultisol, Tong and Xu (2012) related greatest changes when urea was added. The authors observed pH decreases by up to 1.25, 1.54 and 1.84 units with 150, 300 and 400 mg/kg of urea-N added. These results are due to the urea effect in stimulating nitrification in soils with high acidity, accelerating soil acidification (ZHAO; XING, 2009), but according to Fenton and Helyar (2002) N added to the soil as urea only causes net acidification in medium- and long-terms if occurs significant losses of N as nitrate leaching.

In areas with high NO_3^- leaching, Fenton and Helyar (2002) recommend the addition of 3.6 kg of lime to neutralize the acidity generated for each kg of NO_3^- lost through leaching. Applying 180 kg ha^{-1} of NH_4NO_3 (ammonium nitrate) on an Oxisol, Caires et al. (2015) reported significant decreases on soil pH, and exchangeable Ca^{2+} and Mg^{2+} levels only at uppermost soil layer (0-0.05 m depth), but increases in exchangeable Al^{3+} levels were detected in all soil layers evaluated (0 to 0.60 m). Due to chemical changes, the authors related a decrease in cumulative grain yield of the crops. Based on the regression model, decreases of 5, 19, and 42% in cumulative grain yield would be expected with the annual applications of ammonium nitrate at 60, 120, and 180 kg N ha^{-1}, respectively.

The NH_4^+/NO_3^--N ratio in the soil solution plays a key role in alkali or acid production. If NO_3^- is leached, higher NH_4^+/NO_3^- -N ratio would stimulate nitrification (BOLAN et al. 1991), generating 2 mol H^+ for each mol NH_4^+ oxided (DE VRIES; BREEUWSMA, 1987). In addition, in order to maintain the neutrality of the root cells, when cation uptake exceeds anion uptake, larger amounts of H^+ is exuded by the roots resulting in reduction in soil pH. Conversely, when anion uptake exceeds cation uptake plant extrude net excess of OH^-/HCO_3^-. Imas et al. (1997) reported that H^+ efflux due to NH_4^+ uptake by some plants species can decrease soil pH by up to 1.7 units.

The cropping rotation systems can also affect soil acidification rates by introducing plants with different architecture and nutrient demand (HAYNES, 1983;

RENGEL et al., 2000). Vieira et al. (2008) related higher values of exchangeable Al and lower pH and base saturation index in soils under leguminous-based cropping systems compared with rotation systems composed essentially of gramineous species (by up to 0.117 pH unit/year). The authors describe this result due to the higher N inputs by legumes in the soil, in addition, minimal nitrate leaching would be expected due to the dense and abundant root system of the grass species, increasing the efficiency of nitrogen uptake. The N_2 fixation by legume species probably had also a significant effect on soil acidification, due to H^+ ions released into rhizosphere when actively fixing N_2. Jarvis and Robson (1983) described changes varying from 0.2 to 0.7 mol H^+ per mole of fixed N.

Some chemical reactions involving SOM dynamic can also contribute for soil acidification, but as acid and base reactions occur simultaneously, the H^+ balance is difficult to measure (STRAW et al. 2015). Usually, the contribution of SOM on release H^+ to soil solution is associated with mineralization processes. The deprotonation of acid groups, the CO_2 production and nitrification by higher biological activity are the most important processes involved in soil acidification (VAN BREEMEN et al., 1983).

The contribution of acid organics on releasing H^+ is soil pH-dependent, thus organic acid deprotonation vary according to the dissociation constants (pK) of the organic acids, which typically ranges from 2 to 7 (HELYAR, 1976; STRAW et al. 2015). The release of H^+ ions by organic acids will only occur if the soil pH is higher than the pK of the functional acid groups. Soil-solution acidity is typically generated by weak acids, therefore, soil acidification by organic compounds is dependent of the organic substance added and soil pH. If the organic acids with more than 50% dissociated are added to a soil with initial pH < pK, the pH would be increased by H^+ consuming (protonation). If the soil pH = pK, the pH would remain constant (RITCHIE; DOLLING, 1985). Due to low pK of carboxyl groups from humic and fulvic acids, Parfitt et al. (1977) related that the addition of this organics acids in the soil can displace hydroxyl groups from mineral surfaces. The dissociation of H^+ ions can contribute to soil solution acidification, but plays a fundamental role to increase cation exchange capacity of Oxisols.

Oxidation and reduction of sulfur forms can also be an important contributing factor of soil acidification. Golez and Kyuma (1997) observed a pH reduction from 8.5 to 3.4 due to presence of high H^+ ions released during pyrite oxidation, since for

each mole of pyrite oxidized 4 moles of H^+ ions are released to soil solution as result, the authors related significant losses of Ca, Mg, Zn, and Cu due to the acidification.

The large proportion of S in aerobic soils is found in organic forms, as sulfhydryl (-SH), and during the mineralization of SOM, this -SH forms are oxidized generates SO_4^{2-} and H^+. Otherwise, some results have shown that a portion of H^+ present in the soil can be neutralized by the OH- released with SO_4^{2-} adsorption, increasing the pH by ligand exchange mechanism called "self-liming effect" (SORATTO; CRUSCIOL, 2008; CRUSCIOL et al., 2016a).

Under acid soil, amorphous Al-OH depolymerize causing solubilization of Al into the soil solution, is considered one of the most important production-limiting factor for crops cultivated in acid soils. Several Al species are present in Oxisols and Ultisols solution, but only the soluble form (exchangeable Al^{3+}) is considered toxic for plants. Usually, the Al^{3+} is predominant below pH 4.7 ($CaCl_2$), and the main symptom of Al toxicity is the inhibition of root growth (manly root elongation and dry weight) (FOY, 1988). As a consequence, the reduction on cell division and the physiological damages in root cell membrane affect severally the uptake and transport of water and mineral ions (KOCHIAN, 1995). According to Ma et al. (2004), 10 µM Al was enough to inhibit 40% of root elongation in an Al-sensitive wheat cultivar within several hours due to changes in the cell wall viscosity and elasticity, however, in the roots exposed to a higher concentration of Al for a longer period, the plasma membrane, DNA, and enzymes may also be affected.

Based on a regression model between wheat root length and exchangeable Al^{3+} levels, Caires et al. (2008) related decreases on root length density of 5.8 and 6.2% at 0–0.10 and 0.10–0.20 m depths, respectively, for each increase of 1 $mmol_c$ dm^{-3} in exchangeable Al^{3+}. In addition, the authors suggested that Al^{3+} impact on root growth can be higher if water stress is more pronounced. Besides Al effect on reduces root growth, Nichol et al. (1993) suggested that Al inhibits the cation influx by reducing the net negative charge at the plasma membrane. The researchers observed for a sensitive barley cultivar that 100 µM of Al concentration inhibited the influx of Ca, NH_4, and K in the following order 69, 40, and 13%, respectively.

As the species of Al vary with pH, the neutralization of soil acidity is essential to reduce Al^{3+} toxicity which severely compromises root development and crop production. According to pH increments, the net positive charges (n) aluminum-hydroxyl species [$Al(OH)^n$] decreases, becoming insoluble (FAGERIA; BALIGAR, 2008). According to Marion et al. (1976), the exchangeable Al^{3+} ion (soluble) is predominant ion specie below pH 4.6, $Al(OH)_2^+$ at pH range 4.7 - 6.5, $Al(OH)_3^0$ at pH range 6.5 - 8.0.

Due to several mechanisms involved on soil acidification and indirectly on Al toxicity, the acid management plays a fundamental role to improve crop production and the sustainability of tropical agriculture systems.

1.3. Soil acidity management in no-till systems

Liming is the most common practice adopted to improve chemical fertility of soils affected by acidity. The preference of lime as an alkalization material is generally associated with the low cost and the efficiency of the product on reducing Al^{3+} toxicity; improving microbial activity, and consequently, N_2 fixation by legumes; contributing as an important source Ca^{2+} and Mg^{2+}; and improving nutrient availability due to pH increases (such as N, P, S, and Mo) (FAGERIA and ZIMMERMANN, 1998; QUAGGIO, 2000; TIRITAN et al., 2016).

The lime is characterized by ground limestone, and the major constituents are the calcium carbonate ($CaCO_3$) and the magnesium carbonate ($MgCO_3$). Lime quality is judged according to the amount of CO_3^{2-}, chemical base which is responsible for OH^- formation, however, the ionization constant value ($Kb = 2.2 \times 10^{-4}$) shows that the carbonate is a weak base, thus OH^- formation is relatively slow. In addition, the water solubility of the neutralizing species is considered extremely low (0.014 g/L^{-1} of $CaCO_3$ at 25°C; 0.106 g L^{-1} of $MgCO_3$ at 25°C), an important characteristic that influence in the lime efficiency on neutralizing soil acidity. Therefore, the surface contact area between lime particle and the soil plays a fundamental role to improve lime reaction.

In order to increase lime contact with the soil, in conventional tillage systems, lime has been incorporated into the soil by mechanical processes such as ploughing and disking (RHEINHEIMER et al., 2000; KAMINSKI et al., 2005). However,

for NT systems the soil disturbance practice is inadequate and posing a challenge to the basic principles of conservation agriculture (NICOLODI et al., 2008; CAIRES et al. 2008; SORATTO; CRUSCIOL, 2008b; COSTA; CRUSCIOL, 2016; CRUSCIOL et al., 2016a). Therefore, the application of lime on the soil surface, without incorporation, is the unique alternative to neutralize soil acidity in NT systems, but the alleviation of the soil acidity in the subsoil layers is generally slow, mainly in soils with pH-dependent charges (MIYAZAWA et al., 2002; ERNANI et al., 2004). In this case, some researchers suggest the application of finer materials with higher reactivity (HABY; LEONARD, 2002; RODRIGHERO et al., 2015), however, a result obtained by Melo et al. (2003) on a Red Distroferric Oxisol, showed that even 12 months after surface application of a lime with 100% of fineness factor (particles < 0.3 mm), the chemical soil attributes were not affected below to 0.10 m depth. In addition, the authors suggested that lime with larger particle sizes provided a prolonged residual effect, which would be important to reduce the effect of soil acidification processes. In a long-term field trial conducted in a soil with 290 g kg^{-1} of clay and low SOM content, Conyers et al. (2003) related that even 8 years after the surface application of 1.5 Mg ha^{-1} of a lime with 98% $CaCO_3$ and 99.5% of particles < 250 mm diameter it was not effective in neutralizing soil acidity below 0.10 m depth.

In the subtropical region of Brazil, Caires et al. (2000) conducted a field trial in a subtropical Oxisol to evaluate the extent of downward movement of three lime rates calculated to raise the soil base saturation to 50, 70 and 90% (2, 4, and 6 Mg ha^{-1}, respectively). Five years after the lime application, the authors related there were significant changes on soil pH, exchangeable Ca and Mg and soil base saturation up to 0.60 m depth, but the effects were variables (quadratic by up to 0.10 m and linear at 0.10 to 0.60 m depth). In addition, Caires et al. (2005) observed that the effect remaining constant at the 0 to 0.20 m depth for a period of up to 10 years after liming, showing that the lime rate estimated by soil base saturation method at 70% in the 0- to 0.20-m depth was appropriate, since provided maximum economic yield. However, the surface liming should only be recommended for soil with pH ($CaCl_2$) lower than 5.6 or base saturation inferior to 65%, in the 0-0.05 m layer (CAIRES et al., 1998).

Despite some studies conducted in the subtropical region of Brazil attested the feasibility of surface liming on reduce soil acidity and Al^{3+} toxicity, and

increasing levels of exchangeable Ca^{2+} and Mg^{2+} in the soil profile (CAIRES et al., 1998; 2000; 2005; 2008), the effect in tropical areas such as Cerrado region can be divergent. According to Ernani et al. (2004) soil organic matter content and the rainfall distribution are main mechanisms involved in the movement of alkaline compounds to subsoil layers, therefore variations in these characteristics can contest the feasibility of surface liming in tropical regions.

In order to verify the effect of surface liming in a recently established NT system, without previous soil disruption, in dry-winter region, Soratto and Crusciol (2008a) evaluated three dolomitic lime rates (1.1, 2.7, and 4.3 Mg ha^{-1}), intended to reach base saturation to 50, 70 and 90 %, respectively, similar as suggested by Caires et al. (2000). According to chemical analysis of soil samples taken 18 months after treatments establishment, the practice reduced soil acidity and increased exchangeable Ca levels, but only at topsoil layer (0-0.20 m). In addition, base saturation values were lower than those expected. Even with lime reapplication 24 months later (1.0, 2.0, and 4.0 Mg ha^{-1}), and soil samples taken four year after reapplication, Costa and Crusciol (2016) did not report differences on soil pH, phosphorus and exchangeable K^+ levels between control (0 Mg ha^{-1}) and standard treatment (2.0 Mg ha^{-1}) in the layers below 0.20 m depth. According to results obtained by Caires et al. (2015) and Rheinheimer et al. (2000) the absence effect on soil pH may suggest that the application frequency and lime rates calculated are not enough, considering higher intensity of soil acidification processes in topsoil layers, manly above 0.20 m depth, mainly due to nutrient extraction by the plants and the high rates of ammonium base nitrogen fertilizer.

Otherwise, comparing the rates 0 and 2.0 Mg ha^{-1} of lime, the long term results presented by Costa and Crusciol (2016) showed significant reductions on the H+Al contents and exchangeable Al^{3+} up to a depth of 0.40 m, and increases in Ca^{2+} and Mg^{2+} levels and base saturation values to the deeper soil layer (0.40-0.60 m). However, the authors emphasized that the effect in neutralizing Al toxicity and improve the availability of Ca and Mg at subsoil layers can promote over the time higher accumulation of organic matter, favoring mechanisms which stimulate surface liming reaction on alleviating subsurface acidity (RHEINHEIMER et al ., 2000; CORRÊA et al , 2007 SORATTO; CRUSCIOL , 2008a; TIRITAN et al., 2016)

Due to 75% of tropical soils be severally affected by poor chemical fertility of subsoil (SUMNER; NOBLE, 2003), the knowledge of the dynamics of all mechanisms involved on soil acidity neutralization, over the time, is required to improve crop production and the sustainability of tropical agricultural ecosystems.

1.4. Mechanisms involved on acidity neutralization of soils under no-till systems

1.4.1. Chemical factors

The mobility and/or reaction of basic anions (OH^- and HCO_3^-) in the soil is crucial to alleviate subsoil acidity. However, the displacement of these molecules through soil profile is variable according to the amount of acidic cations (such as H^+, Al^{3+}, Fe^{2+}, and Mn^{2+}) at uppermost layers. While there are acids cations, the acidity neutralization reactions would be limited to the surface layer, retarding effect in the subsurface. According to Rheinheimer et al. (2000), the effects of surface liming on soil pH at subsoil layers only occurred when the soil pH (H_2O) in the adjacent upper layer reach 5.2 - 5.6, necessary condition have formation of ionic pairs subsequently [$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$], which would be leached to deeper soil layers, promoting the acidity neutralization in the subsoil layers.

One important chemical mechanism, generally associate with the lime reaction below the point of placement, is the release of low molecular weight organic acids (i.e. oxalic, citric, malic, and tartaric acids) by decomposition of organic residues. According to Miyazawa et al. (2002) and Franchini et al. (2003), these organic substances have functional groups, especially carboxylic (-COOH) and phenolics (-OH) types, which play a role in various chemical reactions, including Fe^{2+} and Mn^{2+} complexation, reduction of Al^{3+} toxicity, and leaching of basic cations such as Ca^{2+} and Mg^{2+}, whose have restricted mobility due to high electrochemical attraction by negative charges determined by pH increases. In addition to the organic acids effect, the mobility of basic cations through soil profile, can also be influenced by complexation with inorganic ions such as SO_4^{2-} and NO_3^- (SORATTO; CRUSCIOL, 2008a; CRUSCIOL et al., 2011; 2016a; 2016b) .

Under NT system, when the soil pH was < 5.0, Alleoni et al. (2010) observed that approximately 80% of Al present in the soil solution at 0-0.20 m was complexed by organic molecules, however, most part of the proportion was associated to dissolved organic ligands (DOL) with a high molecular weight. For BC, Zambrosi et al. (2008) related that Ca and Mg complexation with DOL is predominant in the soil solution compared to inorganic ions. Among the inorganic anions, the interaction with SO_4^{2-} occurred in higher proportions compared with other ions, representing up to 1 and 1.5% of the total Ca and Mg species, respectively. Chaves et al. (1991) and Foloni et al. (2006) confirmed a higher affinity of Ca^{2+} and Mg^{2+} for SO_4^{2-}. Other associations of these BC with fluoride (BC-F), phosphate (BC-$HPO_{4(aq)}$), chloride (BC-Cl), and nitrate (BC-NO_3) are also involved in mobilization of these cations. Crusciol et al. (2011) showed a positive correlation between lime rates and NO_3^- contents in the 0.20-0.40 m layer, showing that nitrate was leached with K, Ca and Mg. The higher availability of macronutrients in deeper layers is crucial to improve root growth, nutrient and water uptake and grain yield, manly in tropical regions with dry seasons and frequent dry spells. Thus, N and S fertilization has been considered an important mechanism to intensify Ca and Mg movement through the profile of lime-amended tropical soils. In addition, Crusciol et al. (2011) related that N application on the soil surface may also contribute to reduce Al toxicity in the subsurface layers.

In a greenhouse experiment, evaluating lime percolation in an uncultivated Red Dark Oxisol, with 270 g kg^{-1} of clay and 7.6 g kg^{-1} of total organic carbon (TOC) content, Cassiolato et al. (2000) reported that the addition of lime on soil surface, in an amount required to neutralize 200% of the total soil acidity (H+Al), increased pH and Ca^{2+} level, and decreased exchangeable Al^{3+} in the up 0.10 m, but the addition of organic extracts increased the efficacy of surface applied, with benefits on soil pH and Ca levels by up to 0.20 m. Otherwise, contradictory results were presented by de Moraes et al. (2007), the authors did not reported influence of crop residues on improving lime efficiency, even in conditions with high amount of organic residues on the soil surface (20 Mg ha^{-1}). However, Miyazawa et al. (2002) suggested that the effect of these residues in increasing liming efficiency is highly variable and depended on chemical composition of organic materials. Therefore, the contribution of crop residues can be significant, improving the

efficiency of surface liming in alleviating subsoil acidity, however, it is essential their continual input into the soil (OLIVEIRA; PAVAN, 1996).

Other important chemical factor involving OH^- and HCO_3^- release in the root-soil interface is related to the anions level in the soil solution, mainly NO_3^-, which is the nutrient that is taken up at the highest rate by most annual plant species. In order to maintain cation-anion balance in root cells, a greater exuded of anions such as OH^- and HCO_3^- is generally found when the amount of uptake anions exceeds cations (HAYNES, 1990; MARSCHNER, 1995; QUAGGIO, 2000; HINSINGER et al., 2003). In a similar manner, taking up more cations than anions would have an excess of positive charges in cell cytoplasm, which leads higher release of H^+, decreasing pH in the rhizosphere. In an acidic soil, the application of N fertilizers as nitrate, roots of rape (*Brassica napus*) and tomato induced a large alkalization (≈0.7 pH unit) in their rhizosphere, compared with the control soil pH (CHAIGNON et al., 2002)

The chemical contribution of organic compounds, root activity, and inorganic complexes in acidity neutralization should be considered important chemical mechanisms to improve the efficiency of surface liming. However, some effects can also contribute indirectly, increasing the mobility of HCO_3, a product of the lime dissolution, through soil profile.

1.4.2. Physical factors

Among the major factors involved on subsoil acidity alleviation is the vertical displacement of lime, thus soil structure preservation play a fundamental role in this process due to lime particles percolation through water movement into soil porous structure (COSTA; ROSOLEM, 2007; GONÇALVES et al., 2011; CAIRES et al., 2011). Therefore, factors that influence soil aggregation can also favor lime reaction in subsurface soil layers.

The soil physical characterization, soil mineralogy, SOM content, and soil solution composition are the major factor involved on formation and stability of aggregates, and consequently on pore architecture. All these factors are directly related to cation exchange capacity (CEC) and electric double layer behavior, two of the main

mechanisms that influence flocculation and dispersion phenomes. Soils with thin double layers have greater flocculation power and the addition of cations with high valence is critical to push the double layer toward the particle surface, increasing attractive forces.

In acidic Oxisols, with high exchangeable Al^{3+} levels in the soil, clay flocculation is predominant due to high flocculation power of the trivalent cation. In addition, as the surface charge in soils highly weathered depends on activities of potential-determining ions (H^+ and OH^-) and electrolyte concentrations, these surfaces can be net negative, positive, or no charge. When the net total particle charge is zero (point of zero charge – PZC), the colloidal system exhibits maximum flocculation rate, due to the attraction between positively charged of mineral surface (e.g. kaolinite, goethite, hematite, etc.) and negatively charged of SOM, mainly humified compounds (ROTH; PAVAN, 1991). The lime effect on soil pH leads to an increase in negative charges density, increasing the repulsive forces. At the same time, Al^{3+} activity decreases and Ca^{2+} would occupy negative charge sites, which enlarge the cation cloud of double layer and may leads clay dispersion, however, the addition of high amounts of Ca^{2+} by liming allows that the van der Waals attractive forces overcomes the repulsive. Despite flocculation power of each cation being classified by valence, increasing according the following sequence: mono, di e trivalents, the ion hydrated radius and the concentration in the soil solution is also a preponderant factor in flocculation and dispersive mechanisms (RENGASAMY et al., 1986).

Due to chemical characteristics of Oxisols, theoretically lime application can increase colloid repulsion (CASTRO; LOGAN, 1991), affecting negatively important soil physical attributes, such as water infiltration and soil hydraulic conductivity, properties extremely important which can influence lime mobility into the soil. In an Oxisol, Roth et al. (1986) related that pH increase by liming (range from 5 to 7) reduced water infiltration due to higher clay dispersion. However, field measurements 2 years after lime application showed higher water infiltration in soil with liming. These results suggest that the detrimental effects of liming on clay dispersion have been observed in the short-term, however, the long-term effect of liming result in improve pore structure and infiltration capacity (CASTRO; LOGAN, 1991).

The solid-phase reaction between organic compounds (manly humified compounds), polyvalent metals (such as Ca^{2+}) and clays particles (kaolinite, oxides) has been considered as the first step for soil structure formation, since the microaggregates (20–250 μm) are the basic building blocks for the formation and stability of macroaggregates (>250 μm) (TISDALL; OADES, 1982; EDWARDS; BREMNER, 1967). According to Franzluebbers et al. (2002) stable macroaggregates in soil surface is very important for facilitating water infiltration, which can induce higher lime percolation to subsoil layers.

The labile organic matter (i.e. roots, fungal hyphae, microbial- and plant-derived polysaccharides) is the main binding agent involved on macroaggregation (TISDALL; OADES, 1982). Due to organic fractions associated with macroaggregates be less recalcitrant than those involved in microaggregation, continuous organic matter inputs is crucial to the stability of soil structure.

Root activity has many effects on soil aggregation and porous architecture. Many aggregates are formed around root system due to the amount of compounds, which have a cementing effect on soil particles. The exudation of some organic materials may lead to an instantaneous aggregate effect (i.e. mucilage such as polygalacturonic acid), however, some substances can contribute indirectly, improving microorganisms activity that provide extracellular compounds that bind particles together. Glomalin is a protein, produced by arbuscular mycorrhizal fungi, and the concentration in soil correlates positively with the percentage of water-stable aggregates (RILLIG et al., 2001). According to Rillig et al. (2002) the direct effect of glomalin can be much stronger than the direct effect of fungi structure, suggesting that this protein is involved in a very important mechanism for aggregates stabilization, due to its longer residence time in the soil.

The degree of influence by roots on soil structure through root exudation is very variable according to: (i) soil moisture, i.e. Watt et al. (1994) described that water stress can stimulate mucilage production in corn roots; (ii) plant species, i.e. Hutsch et al. (2002) related that corn exude more aggregate substances than wheat; (iii) root structure and distribution; i.e. Rillig et al. (2002) observed that grass species were associated with higher aggregation than legume plant types (iv) microbial associations, i.e.

Schutter and Dick (2002) suggests that bacterial activity may dominate in microaggregation while fungal activity dominates in macroaggregate formation; and (v) quality and amount of carbon inputs (SIX et al., 2004; BRONICK; LAL, 2005).

The porous channels formed by compressing action of growing roots and soil fauna (biopores) can play an important role for lime percolation. The root morphology has significant influence on porous architecture suggesting that plant species with vigorous root system can improve macroporosity and water infiltration. In a Sodosol with low hydraulic conductivity at the top of the B horizon (1.0-1.2 m depth), Mc Callum et al. (2004) showed that lucerne (*Medicago sativa*) and phalaris (*Phalaris aquatica*) increased macroporosity (total pores > 2.0 mm), however, lucerne provided a network of larger macropores (3 – 16 mm in diameter), increasing the water infiltration rate into the subsoil (9.3 mm h^{-1}) compared to control (2.3 mm h^{-1}) and phalaris (6.8 mm h^{-1}).

Soil management strategies that encourage root growth for subsoil layers and formation of biopores, manly those > 4 mm in diameter, may enhance the vertical water movement (BLACKWELL et al., 1990), and consequently, the vertical displacement of lime particles in crop production systems without soil mobilization.

Soil fauna can also improve aeration, porosity, water infiltration, and aggregate stability, according to the ability of macroorganisms to move into the soil and the capacity to produce biogenic structures that act in the formation of organo-mineral complexes. Compared to other animals, earthworms represent a key component in the biological strategies to improve structure due to direct and indirect influences on soil structure. Ehlers (1975) showed that after 10 years of earthworm inoculation, the water infiltration rate increased from 15 to 27 mm $hour^{-1}$, and this effect is related with high rhythm of activity of these organisms. In addition to mechanical activity, biogenic structures formed by ingest and egest soil material can act in the reorganization of soil particles (LAVELLE, 1988). According to Winsome and McColl (1998) earthworm activity increase significantly water-stable macroaggregates, and the influence of these macroorganisms are related to quality and quantity of organic residues added in the soil.

Soil organic matter content and soil biological activity are intimately linked with soil structural condition, thus both factors are strongly interrelated with the movement of lime particles into the soil profile, through water infiltration. Due to

being considered an important mechanism to alleviate subsoil acidity in NT systems, several researchers suggested that SOM input into the soil is crucial to improve the crop production and the sustainability of tropical acid soils, conducted under conservative agricultural ecosystems (AMADO et al., 2001; OLIVEIRA et al., 2003; BAYER et al., 2004; WENDLING et al., 2005; BORTOLUZZI et al., 2008; CORRÊA et al., 2009).

1.5. Lime plus phosphogypsum surface application: is it an effective strategy?

Due to low solubility of calcium and/or magnesium carbonate, generally has been detected high Al^{3+} toxicity and low availability of BC in the subsurface layers of soils without mobilization, both limiting factors for root growth. In tropical regions, with dry winter and frequent dry spells, restrictions on root elongation to deeper layers have limited annual crop yields. In order to provide better conditions for plant growth, the application of PG combined with lime may be a good strategy to improve the restrict effect of surface liming in subsurface layers. Each type of gypsum has specific chemical characteristics, but generally they are excellent sources of Ca^{2+} and SO_4^{2-}. In addition, the PG has high potential to reduce exchangeable Al^{3+} in the soil solution, stimulating the development of deep roots in acidic soils (CAIRES et al., 2003; CAIRES et al. 2005; SORATTO; CRUSCIOL, 2008a; CAIRES et al., 2011; CRUSCIOL et al., 2016a; 2016b).

Phosphogypsum is a by-product from phosphate fertilizer industry, thus the composition of material varies according to the source of rock phosphate and the process for manufacturing phosphoric acid (MAYS; MORTVEDT, 1986). The major constituent of PG are Ca (200-240 g kg^{-1}) and S (150-190 g kg^{-1}), however, among the chemical constituents are generally found: P (1-5 g kg^{-1}), F (5-38 g kg^{-1}), K (100-800 mg kg^{-1}), Mg (8-400 mg kg^{-1}), and Cd (0.23 mg kg^{-1}) (PAVAN et al., 1987; ALVA; SUMNER, 1989, 1990; SUMNER, 1990), but can contain trace metal contents (arsenic, silver, barium, cadmium, chromium, lead, mercury and selenium) (RUTHERFORD et al., 1994).

In view of the chemical composition of PG (more than 90% is $CaSO_4.2H_2O$), and the higher degree of solubility in water (2.0 - 2.5 g L^{-1} at 25ºC) when compared to limestone (15 mg L^{-1} at 25°C), the PG represent an excellent option to

improve rapidly subsoil chemical attributes in areas undisturbed. Among the major benefits of PG application on subsoil acidity: (i) increase Ca levels in subsurface layers; (ii) complex formation between Al^{3+} and sulfate (SO_4^{-2}) and fluoride (F^-), which are less toxic and more capable of being leached away; and (iii) SO_4^{-2} replaces hydroxyls (OH^-) on sesquioxide surfaces by ligand exchange, phenomenon known as "self-liming" (SINGH; MILES, 1978; RITCHEY et al., 1980; ALVA; SUMNER, 1988; FARINA; CHANNON, 1988; SHAINBERG et al. 1989; ALVA; GASCHO, 1991; CRUSCIOL et al., 2016a; 2016b).

Due to these benefits, recent studies has demonstrated the beneficial effects of surface application of gypsum on chemical properties of subsoil horizons. Soratto and Crusciol (2008), Caires et al. (2011), Crusciol et al. (2016a), and Costa and Crusciol (2016) related greater movement of Ca and SO_4–S throughout the soil profile, but in some cases it was reported significantly soil pH changes. The pH of an Oxisol, with kaolinite, gibbsite and goethite as the dominant mineral, increased from 4.2 to 4.5 at 0-0.15 m layer by application of 4 Mg ha^{-1} of gypsum (ISMAIL et al., 1993). Crusciol et al. (2016a) noticed that the addition of 3.0 Mg ha^{-1} of PG in an Oxisol led to an increase of 0.3 pH units in the 0–0.05 m soil layer. In subsoil layers (1.20-1.40 m), slight increases in pH were observed by Churka Blum et al. (2013) after 13 years after application of 12 Mg ha^{-1} of PG. Sixteen years after gypsum application, Toma et al. (1999) observed that pH (H_2O) was 0.1 to 0.2 units lower than the control at depths of 0.3 to 1.2 m. All these results suggest that the action of SO_4^{-2} in the displacement of OH^- from the soil colloids, promoting partial neutralization of soil acidity. According to Marsh et al. (1987) studies indicate that SO_4^{-2} binds more weakly to colloids surfaces than PO_4^{-2}, but more strongly than NO_3^- and Cl^-.

In most studies involving gypsum application have often been observed Mg and K leaching from the upper layers due to the formation of the ionic pair ($MgSO_4^0$ and KSO_4^+) (ALVA; GASCHO, 1991; OLIVEIRA; PAVAN, 1996; ZAMBROSI et al., 2007; SORATTO; CRUSCIOL, 2008a; CAIRES et al., 2011; CRUSCIOL et al., 2016a; 2016b). Over a period of 9 years, Caires et al. (2011) related that about 72% of the exchangeable Mg presented in the topsoil (0-0.20 m) moved to layers below to 0.20 m depth due to gypsum application. Compared to Mg^{2+} mobility, the authors observed that K^+ leaching were lower, but the addition of 6 Mg ha^{-1} of PG reduced significantly K^+ levels at

0- to 0.05- and 0.05- to 0.10-m depths one year after application. A lower Mg^{2+} and K^{+} availability in the 0.05-0.10 m depth was confirmed by Crusciol et al. (2016a) one year after the addition of 3 Mg ha^{-1} of PG. Zambrosi et al. (2007) also related the gypsum effect on increasing Mg^{2+} levels in the subsoil (0.4-0.8 m), following by reductions on exchangeable Mg^{2+} at the 0.05-0.2 m layer, however, no effect was observed on K levels, even with the addition of 9 Mg ha^{-1}. Thus, K movement due to gypsum application can be variable according to the gypsum rate, mineralogical and physical characteristics of soil, ionic strength, and rainfall rate (NAKAYAMA, 1971; OLIVEIRA; PAVAN, 1996; ZAMBROSI et al., 2007)

The capacity of PG on leaching exchangeable BC (Ca^{2+}, Mg^{2+}, and K^{+}) to the deep layers can be beneficial for root growth and water and nutrient uptake by plants, especially in tropical regions that suffer with dry seasons and frequent dry spells. According to Van Raij et al. (1996) and Ribeiro et al. (1999) PG should be recommended for areas with high levels of exchangeable Al^{3+} (> 5 $mmol_c$ dm^{-3}), and/or low availability of exchangeable Ca^{2+} (< 4 $mmol_c$ dm^{-3}).

The beneficial effect of gypsum on root growth was reported by several authors. Farina and Channon (1988) reported that the addition of 10 Mg ha^{-1} of mineral gypsum (86% $CaSO_4^{-2}.H_2O$), on a strongly acidic Plinthic Palcudul, increased corn root density at 0.40-0.60 m depth, however, this effect was observed only in the fourth growing season consecutive. According to Sumner et al. (1986) the long term effect would be expected due to insufficient time elapsed for the gypsum to move down the profile. Among the individual Al monomers, relative soybean root length was most highly correlated with the activity of $A1^{3+}$ (R^2 = -0.81) followed by $AIOH^{2+}$ (R^2 = -0.68), while $AlSO_4^{+}$ (R^2 = -0.33) gave the poorest correlation. From these data obtained by Noble et al. (1987) the addition of PG represents a good alternative to improve root growth, either through reduction in Al activity or by addition of Ca, or both. Caires and Rosolem (1991) confirmed a linear relationship between peanut root growth and exchangeable Ca levels in soil.

The gypsum effect in promoting deep rooting and improving soil chemical fertility have resulted in large production of several species. In a sandy clay loam soil (kaolinitic, thermic Typic Kanhapludult), Toma et al. (1999) showed benefits of

gypsum in improved crop yields of corn (29–50%) and alfalfa (≈50%), attributing these effects due to higher water extraction from the subsoil, reduction of exchangeable Al^{3+} and the increase in Ca^{2+} levels at deep layers. In a sandy clay loam (kaolinitic, thermic Typic Haplorthox) with 6.5 $mmol_c$ dm^{-3} of exchangeable Al^{3+} and SOM content of 20.9 g kg^{-1}, Soratto and Crusciol (2010) reported increases of 20% in grain yield of a upland rice cultivar, due to the application of 2,100 kg ha^{-1} of PG. In a silt loam soil (Typic Fragiudalf), with low SOM (25.4 g kg^{-1}), Chen et al. (2005) described that the application of 2,980 kg ha^{-1} of gypsum increased soybean grain yield by 12%, but in this case the authors attributed the effects due to the S supply, often requires for areas with low SOM content and with low S supply by mineral fertilization. According to Caires et al. (2011) higher response to gypsum in the cereal than in legume crops may be due to the lower cation exchange capacity of roots in grasses, however, regardless of the crop, the authors showed economic viability of PG use, even in soil containing a sufficient level of Ca^{2+} (≥8 $mmol_c$ dm^{-3}), low levels of exchangeable Al^{3+} (≤4 $mmol_c$ dm^{-3}), and Al saturation (≤15%) in the deep layers (0.20–0.60 m).

The results presented here provide clear evidence of gypsum benefits on root growth and crop production, manly in areas affected by Al^{3+} toxicity and low availability of BC in the deep layers. The increased plant biomass (root and shoot) due to gypsum application probably results in higher returns of organic residues to the soil. Increasing SOM content may induce important changes on soil physical attributes, with a tendency for an increase in the volume of pores (HAYNES; NAIDU, 1998), responsible for lime particles percolation to deeper soil layers. Therefore, in areas without soil mobilization, the application of gypsum combined with lime (at the same time) may increase alkalinization reaction rate at deep soil layers, improving water and nutrient uptake, and consequently annual crops productivity.

1.6. Soil Organic Matter Dynamics Affected by Lime and Phosphogypsum Application

Soil organic matter can be classified into two major types according to the structure and function. The light fraction consists of organic residues in

various stage of decomposition, which has a rapid turnover rate and serves as food for soil organisms and as a source of nutrients for plant development. The heavy fraction is the largest pool of soil organic carbon and includes organic recalcitrant compounds, involved in important mechanisms such as soil aggregation and cation exchange (GREENLAND, 1971).

Soil organic matter assumes an important role in many chemical, physical and biological processes, thus the adoption of strategies to build and maintain SOM are required to increase the sustainability of tropical agriculture ecosystems (HAYNES; NAIDU, 1998). Several studies have shown that the accumulation of SOM can be achieved by associations between conservative techniques and high input of organic residues (SIX et al., 1998; BAYER et al., 2001; BRIEDIS et al., 2012a; CASTRO et al., 2015).

Conservative practices as soil undisturbed can contribute to avoid SOM mineralization based on preserving aggregates structure, which protected physically organic matter against biological action. Some studies have reported that liming can accelerate decomposition of SOM. An experiment with an acid soil carried out in a laboratory incubation, Condron et al. (1993) reported that changes in soil pH from 4.5 to 6.6 by lime addition increased the mineralization of oak residues litter by 50%, from 3.2 to 4.7 mg C g^{-1}. Results obtained by Ekenler and Tabatabai (2003) showed that microbial carbon values increased significantly, with the increase of soil pH due to lime application. Expressed in mg kg^{-1}, the averages varied from 195 to 295 at 0-0.05 m depth, and from 116 to 382 at 0-0.15 m depth in soils under NT systems, being lime rates ranging from 0 to 6.72 Mg ECCE ha^{-1}. However, according to Fuentes et al. (2006) this effect tends to last only a short time, and the high mineralization rates are a consequence of the readily mineralizable fraction, which can be 7.5–12.5 times greater in limed than in non-limed soil. In addition, Fuentes et al. (2006) suggest that although microbial biomass increased with liming rate, the activity of these microorganisms slowly decreased with time.

Some results demonstrate that surface liming has a greater influence on SOM stocks. In a sandy clay loam Oxisol cultivated under a NT system for 15 years, Briedis et al. (2012b) related that the surface application of 9 Mg ha^{-1} of lime [6 Mg ha^{-1} (84% ECCE) at NT system establishment + 3 Mg ha^{-1} (90% ECCE) in reapplication seven

years later] increased the total organic carbon (TOC) contents of 6.5, 4.6, 2.0, and 1.6 g kg^{-1} at depths of 0 to 0.025, 0.025 to 0.05, 0.05 to 0.10, and 0.10 to 0.20 m, respectively, but the greatest impact was on the particulate organic carbon (POC) fraction due to the greater input of labile components resulted from crop residues. However, with the continuous flow of organic residues during the time, a higher input of organic compounds more stabilized were also observed (mineral-associated organic C - MOC), which provide a large contribution for soil aggregation and C storage. The authors suggested a strong correlation between POC and MOC ($r = 0.70$, $p < 0.001$).

In a clayey Oxisol, which was cultivated under a NT system for 5 years, Castro et al. (2015) observed that the surface application of 3.8 Mg ha^{-1} of lime (90% ECCE) led to greater TOC contents in the upper 0.10-m soil layer, but significant differences in MOC occurred only in the 0- to 0.05 m layer, resulting in 20% more MOC on average than the control treatment. According to authors this result may be related to the higher effect of soil acidity alleviation on increasing net negative charges by deprotonation of OH groups, facilitating the association between clay and humus due to polyvalent cations chemical bounds. The ability of Ca^{2+} sources to protect soil organic matter from mineralization has been demonstrated by several authors (OADES, 1988; BALDOCK; SKJEMSTAD, 2000; BRIEDIS et al., 2012b). The influence of Ca on soil aggregation plays a key role in the stabilization of SOM, since aggregate structure acts as barriers to microbial action.

In addition to physical-chemical complex which gives stability, chemical structure of soil organic fractions has also been used to predict rates of decomposition. An efficient strategy to increase SOM storage in the soil is to modify the C quality of residue. Organic residues such as sugar, hemicelluloses, carbohydrate, and protein are easily decomposable; however, compounds such as lignin and polyphenols tend to be more recalcitrant to biological decomposition (KONONOVA, 1966). Garbuio et al. (2011) suggest that liming may improve the quality of C sources available to microorganisms, leading to higher release of polyphenol fragments, which are considered the precursors for humic substances formation. Therefore, the adoption of strategies that increase the synthesis and stabilization of organic fraction more recalcitrant are essential to improve the sustainability of agricultural ecosystems, especially in tropical regions, where

the decomposition rates are generally high due to climate condition (JENKINSON; AYANABA, 1977).

The fraction of crop residues converted into more stabilized soil organic compounds is defined by "humification coefficient" (HÉNIN; DUPUIS, 1945), and the amount and quality of SOM play a fundamental role in the synthesis of organic fractions more stable. Recent studies has emphasized the importance of OC input via root compared with shoot (RASSE et al., 2005; JOHNSON et al., 2007).

Findings presented by Kätterer et al. (2011) showed that the humification coefficient for root-derived carbon was about 2.3 times higher than for aboveground plant residues. According to these researchers, these results can be explained due to the amount of extra-root C (defined as turnover and cell sloughing of epidermis root tissues, and soluble organic compounds exuded by the roots), which can be equivalent to about 65–100% of the measurable root biomass. In addition of the amount of OC, the chemical characterization of these structures can contribute for OC stabilization. Lignin is typically considered a recalcitrant material and precursor of humic substances (ZECH et al., 1997), and according to Johnson et al. (2007), some species as soybean showed higher concentration of total lignin in roots (212 g kg^{-1}) compared to the leaves (114 g kg^{-1}) and stems (173 g kg^{-1}). Therefore, in tropical wetlands where the decomposition rates of SOM are generally high, roots may play an important role in SOM dynamics

The high correlation coefficient between OC and Ca (r = 0.87), Mg (r = 0.82), and K (r = 0.70) were reported by Briedis et al. (2012b), which indicate that the application of lime and PG can contribute significantly to increase SOM through the soil profile. In a Rhodic Ferralsol (kaolinitic, thermic Typic Haplorthox), which had been cultivated under a NT system for 7 years, Costa and Crusciol (2016) confirmed the effect of surface application of lime + PG on improving SOM content up to 0.60 m, 48 months after last reapplication of amendment materials, however, after 60 months, the benefit was not observed at deeper layer (0.40-0.60 m), which can be explained by the labiality of organic material in this layer. The accumulation of labile SOM in the first soil sampling (48 months) probably is related to a greater biomass production by roots, which is a result of soil fertility improvements, such as increased pH, the supply of Ca and Mg, and Al^{3+}

reduction. However, as mentioned above, this effect tends to last only for the short term, may promote the accumulation of recalcitrant organic matter fractions in long-term.

1.7. Soil Physical Attributes Affected by Lime and Phosphogypsum Application

Changes in the soil physical attributes by surface application of lime and PG have often been attributed to electrochemical alterations in the soil and the effects of these soil amendments on SOM pools. Both mechanisms have a strong relationship with the formation and stabilization of micro- and macro-aggregates (ROTH et al., 1991; SIX et al., 2004; BRIEDIS et al., 2012b).

In an field experiment conducted for 12 years in an Oxisol under NT system, Bortoluzzi et al. (2010) related that the changes in soil electrochemistry, by liming, promoted significant changes on micro-aggregate stability due to Ca^{2+} acting as a cationic bridge between some organic fractions and clay fractions, both negatively charged due to mainly the dissociation of H^{+} (deprotonation). The Ca^{2+} effect on microagregation is generally related to SOM content, thus the organic C flow play a fundamental role for microaggregation (WUDDIVIRA; CAMPS-ROACH, 2007).

In ploughed systems, Ca^{2+} effect on the mechanisms of flocculation is not evident due to higher mineralization of SOM. Even after five years of lime incorporation (0.17 m depth into the soil), Albuquerque et al. (2000) related that liming increased the amount of clay dispersed in water ($R^2 = 0.93$, $p < 0.001$), probably caused by the decrease of SOM content. This result confirmed a negative correlation ($R^2 = -0.80$) between TOC and the amount of clay dispersed in water reported by Costa et al. (2004). As microaggregates have been considered the first hierarchical stage of soil aggregation, it is evident that the input of organic matter, manly compounds with high functional groups density (e.g. humic substances), and polyvalent cations such as Ca^{2+}, promotes extensive alterations in soil structure.

Within the hierarchical model, the rate of macroaggregate formation and stabilization occur in parallel. Corrêa et al. (2009) confirmed the close association between Ca and aggregates in 4–2 mm class, and the correlation coefficient obtained were: 0.33, 0.63, and 0.45 (p was <0.001) for 0-0.05-, 0.05-0.10-, and 0.10-0.20-m layers,

respectively, but it was not significant at layers below to 0.20 m depth. These results confirmed that the concept of microaggregates are basic structures for formation of larger aggregates. However, the greater level of aggregation demonstrated by lime application is a consequence of greater production of biomass. Briedis et al. (2012b) reported a high linear relationship between C input and mean weight diameter (MWD) (MWD = 0.92 C_{input} + 7.1, R^2 = 0.99, p<0.001) reinforcing the hypothesis that the surface liming provides a higher C flow in the soil due to increased biomass production, and according to the researchers, the roots can be considered as the most important agent to group micro- and meso-aggregates to form macroaggregates.

In a sandy loam (Typic Haplustalf), even with the lime incorporation (2.5 Mg ha^{-1}) once every 4 years, Haiti et al. (2008) also reported a significant increase of 15 and 44% in MWD with the addition of NPK in lime-amended soil compared with the application of NPK in unlimed soil and with the control treatment, respectively. In addition, to contribute directly and indirectly to the input of organic substances, the compressing action of growing roots and the high activity of microorganisms in the rhizosphere region help to hold soil particles together improving agregation (HAYNES; NAIDU, 1998). Bearden and Petersen (2000) reported significant contribution of arbuscular mycorrhizal, which are often associated with root systems in the formation of large aggregates, mainly with a size of 1-2 mm.

The fact that the SOM pools played an effective role in soil aggregation (MATOS et al., 2008), it is suggested that surface application of lime and PG significant changes in several physical attributes such as: total porosity, water infiltration, hydraulic conductivity, soil bulk density, and penetration resistance.

In a deep acid clayey Oxisol, two years after the application of 3.8 Mg ha^{-1} of dolomitic lime (ECCE = 90%), Castro et al. (2011) reported that the surface application of lime modify soil aggregation mechanisms, and even in a short term there was increases in macroporosity down to 0.10 m depth. In a long term experiment (29 years), Haiti et al. (2008) reported reduction in topsoil bulk density of 0.06 Mg m^{-3}, with application of NPK in lime-amended soil compared to control treatment (without NPK fertilization and lime application). As a consequence of nutrient management, total soil porosity and microporosity (equivalent pore diameter <30 μm) at 0–15 m depth was

significantly higher, and the effects are related due to higher organic matter input. According to Corrêa et al. (2009), surface application of lime at the rate 8 Mg ha^{-1}, 27 months after the application, allow the better aggregation of soil particles, down to 0.40 m depth, with positive effects on total soil porosity and water retention.

Gypsum can also provide significant changes on soil physical properties due to being considered an important source of Ca^{2+}. In addition, has a great potential to improve root proliferation in soil deep layers, which can favor soil aggregation. According to Souza et al. (2012), there is a significant interaction between soil management and the effect of gypsum on soil structure. In the soil treated with gypsum, the aggregation was higher in the conventional system, compared to NT system, however, despite the smaller effect of gypsum, the effect reflected in the higher stabilization of soil structure.

Rosa Junior et al. (2006) showed that the application of 2.0 Mg ha^{-1} of gypsum reduced the amount of water dispersible clay, however, higher proportion of the larger aggregates (>1.0 mm) only was observed with the application of lime rate to raise the base saturation in the topsoil (0-0.20 m) to 60%.

The addition of lime increases the net negative charges, which can affect the particles repulsion, however, the high concentration of Ca^{2+} in the soil solution leads compressing of the double layer sufficiently to enhance renewed flocculation (CASTRO FILHO, 1988). Although gypsum alone can reduce water clay dispersion (ROSA JUNIOR et al., 2006), on the other hand, this product can also increase clay dispersion and decrease water infiltration rate, which can be attributed due to the neutralization of Al^{3+}, considered an important flocculating agent (ROTH; PAVAN, 1991). Despite the impact of gypsum on electrochemical process, supposedly the gypsum potential on improving soil structure is more related to the production of biomass crops (COSTA et al., 2004; GRIÈVE et al., 2005; SORATTO; CRUSCIOL, 2008; SORATTO et al., 2010; COSTA; CRUSCIOL, 2016; CRUSCIOL et al., 2016a; 2016b).

As observed, the effects of the surface application of lime and PG on the soil physical attributes generally have been attributed to the greater accumulation of organic matter, however, in tropical areas with low SOM content, high decomposition rates of SOM, and low amount of straw on the surface, the long-term effects of soil amendments

remain poorly investigated, especially in tropical regions with dry winter and frequent dry spells during the rainfall season.

Soil management techniques improve physical properties of tropical soils, conducted under conservative principles, play a fundamental role to favor the vertical displacement of the soil acidity amendments with low mobility (AMARAL et al., 2004; BRIEDIS et al., 2012b). The alleviating subsoil acidity and the greater nutrient availability in subsurface soil layers, have been considered an important strategy to increase grain, fiber, and meat production in tropical soils affected by chemical disorders and dry periods.

1.8. Crops: Wheat and Common bean

Wheat (*Triticum aestivum* L.) is a cereal grain with an excellent option for crop rotation, however, weather aspects as drought stress has affected grain yield in different wheat cultivars. The cereal stands out among the main agricultural products, and it has been considered the second most important food crop in the developing world after rice.

Brazil produced, in the 2015/16 growing season, about 5.5 million tonnes of wheat for consumption estimated at 10.3 million tonnes. Faced with this data, it is inferred that Brazil is not self-sufficient in wheat production, with imports reaching about 50 % of the domestic wheat consumption needs. United States of America, Argentina and Uruguay supply most of Brazil's wheat imports (75%), however, due to logistics costs is expected that prices could rise up to 30 percent (CUNHA, 2005; CONAB, 2016).

Based on data from the Food and Agricultural Policy Research Institute (FAPRI), wheat production will grow at rates of 1.5 percent per year, between 2010 and 2019. FAO's global wheat production growth rates of 1.1 percent to 2030 and 0.5 percent between 2030 and 2050, placing Brazil's production at 7.3 million tonnes in 2050 (WEIGAND, 2011). These projections demonstrate the necessity of expansion of cropland area and sustainable strategies that increases wheat production and yield stability.

The Brazilian Cerrado region has great potential to increase wheat production in Brazil, with favorable weather conditions and strategic location for logistics. Among the Brazilian states, São Paulo has great potential to expand wheat production,

since the major wheat flour manufacturing industries are located in this region. Wheat production in this state can contribute to supply the high demand of the cereal during the off-season production (ALBRECHT et al., 2005). In addition, the development of modern cultivars adapted to climate and soil conditions of the region, favors the expansion of this crop in the State of São Paulo (TRINDADE et al., 2006).

In order to maximize wheat production in Cerrado areas, it is extremely important the adoption of modern farming techniques that favor the development of the plants, since most of the soils in this area are highly weathered, presenting serious chemical limitations for crop production, which inhibits growth of most wheat cultivars, bringing as a result little tillering and low grain yields (HANSON et al., 1982).

In a long-term field trial carried out on a loamy dystrophic Oxisol at the State of Paraná, Caires et al. (2006c) evaluated the grain yield and root growth of wheat in acid soil after 10 years from surface liming and three years after re-liming. The authors reported a positive effect of liming on crop development. According to polynomial regression analyses, the length density of wheat roots (y, in cm cm^{-3}) increased linearly according to the surface-applied lime rates (x, in Mg ha^{-1}), at depths of 0–0.10 m ($y = 5.65 + 0.534x$, $R^2 = 0.91$), 0.10–0.20 m ($y = 0.91+ 0.122x$, $R^2 = 0.94$), and 0.20–0.60 m ($y = 0.57 + 0.047x$, $R^2 = 0.81$). As a consequence, wheat grain yield also increased linearly with the application of lime on the soil surface, however, the authors emphasized that the crop response to liming can be variable according the water regime that occurs during the growing cycle of the plants.

Considering the low natural soil fertility and the dry winter, Cerrado soils require appropriate acid management technologies to increase wheat potential yield. In a region with low rainfall, Caires et al. (2008) reported high correlation between wheat grain yield and total root length per soil surface area to a depth of 60 cm. The Al toxicity has been considered a major factor to reduce root growth in Oxisols, and according to these authors the soil exchangeable Al^{3+} level of 3 $mmol_c$ dm^{-3} should be considered critical for wheat root growth because it provided a decrease in root length density of the order of 20%.

In a trial conducted in an Australian region with low rainfall regime, subsoil Al toxicity was also considered one of the most important wheat yield-

limiting (TANG et al., 2002). However, the effect of surface liming can also be variable according to the genotype used (SA et al., 1999; COSTA; ROSOLEM, 2007). Given these facts, further work is required to evaluate genotype performance in Cerrado region, especially in the State of São Paulo, regarding the long-term effect of acid management in tropical soils under NT system.

The common bean (*Phaseolus vulgaris* L.) stands out among the major crops grown in São Paulo Southwest region. Among several genders of beans, *Phaseolus* is the most cropped in Brazil and in the world, producing about 24 million tons of grain annually. Brazil, India, Myanmar, United States of America, and Mexico are the top five producer countries of *Phaseolus*, which together account about 55% of world production. Among them, Brazil is the third largest producer of beans, accounting for approximately 13% of world production (FAO, 2014).

In the 2015/2016 growing season, the Southeast region stands out as the second largest Brazilian producer, with approximately one million tons of grain and accounting for 24% of national production. However, as in most of the cases the specie is considered secondary crop, the annual average grain yield in Brazil is very low (around 1,000 kg ha^{-1}) (CONAB, 2016), considering that the common bean grain yields in some cases are <20% of yield potential. Among the factors related to low grain yield, the crop growth in degraded soils with low natural fertility, and low investment in production technology, such as the application of lime and fertilizers (CIAT, 1991; BARBOSA FILHO et al., 2005).

Most of the Cerrado areas planted with common bean, including at State of São Paulo, presenting serious chemical limitations for crop production. These soils are generally acid with high concentrations of exchangeable Al^{3+}, which makes them chemically poor, with little capacity for cation retention and low nutrient availability (COSTA; CRUSCIOL, 2016). As related for wheat, these factors are the most important common bean yield-limiting (FAGERIA; BALIGAR, 2001; CRUSCIOL et al., 2016b). In this case, the adoption of soil management practices is required to increase the yield potential of the crop.

In a field trial conducted under NT system in São Paulo Southwest region, Silva et al. (2011) reported that the surface application of lime increased linearly the

grain yield of the cultivar IAPAR 81 according to the increasing lime rate, showing the beneficial effects of the conservative practice on improving crop production. The results presented here are attributed to the effect of liming on increasing soil pH and the exchangeable Ca^{2+} and Mg^{2+} levels down to a 0.10 m depth.

In other field trial carried out in NT system to evaluate the effects of lime and PG surface application on yield components and common bean grain yield, Soratto et al. (2010) related that the liming, regardless of PG addition, increased the number of pods per plant and grain yield of two bean cultivars (‘Carioca’ and ‘Pérola’). Otherwise, Crusciol et al. (2016b) related positive effect of PG and lime mixture on yield components and common bean grain yield, indicating that it is possible to improve NT common bean production using mixtures of soil acidity amendments.

Silva et al. (2012) concluded that the effect of liming on common bean grain yield is influenced by genetic characterizes. Comparing five cultivars the authors related that IAPAR 81 showed better grain yield with the increase of lime rates, obtaining a significant increase of 31% in grain yield with application of 5.4 Mg ha^{-1} of dolomitic lime. Chemical attributes of an Oxisol for maximum common bean grain yield were estimated by Fageria and Stone (2004), and the adequate values for 0-0.20 m layer were: pH, 6.6; exchangeable Ca and Mg, 40, and 12 $mmol_c\ kg^{-1}$; total acidity in pH 7.0 (H + Al) 24 $mmol_c\ kg^{-1}$; cation exchange capacity (CEC), 79 $mmol_c\ kg^{-1}$; base saturation, 69%. However, the acidity condition at below of the topsoil layer (0-0.20 m) can affect crop growth and grain yield mainly during drought periods.

Phosphogypsum can be an important complement to liming, promoting higher crop yields in NT systems established in tropical regions, mainly in areas and seasons with low rainfall regime. Furthermore, there is restrict information about the long term effects of soil acidity management on yield potential of wheat and common bean growth under NT condition. However, it is possible that the joint application of lime and PG provide greater chemical and physical conditions that improve crop production and agricultural sustainability in tropical areas with low natural fertility.

1.9. References

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Chapter 2

Root development and annual crop production as affected by lime and phosphogypsum application in a tropical Oxisol under no-tillage system

Antonio C. A. Carmeis Filho, Carlos A. C. Crusciol

2.1. Abstract

In tropical conservation agriculture systems, the yield of annual crops has been limited by several factors, including the poor soil chemical fertility, high acidity levels, and poor root growth. These problems increase the susceptibility of plants to water stress and nutrient deficiencies, particularly in regions with frequent dry spells. In order to improve crop productivity in tropical areas with acidic soil, this study evaluated the effect of surface applications of lime and phosphogypsum (PG) on the soil chemical properties, root growth, plant nutrition, yield components, technological characteristics, and grain yield of wheat (*Triticum aestivum*) and common bean (*Phaseolus vulgaris* L.) cultivated in two growing seasons (2013/2014 and 2014/2015). A long-term field experiment (12 years) was conducted under a no-tillage system with an annual crop rotation scheme. The experimental design was a completely randomized block with split-plot arrangement and four replications. The experiment consisted of four treatments (control without soil amendment application; PG at 2.1 Mg ha^{-1}; lime at 2.0 Mg ha^{-1}; and lime and PG at 2.0 and 2.1 Mg ha^{-1}, respectively) and two growing seasons (2013/2014 and 2014/2015). Since the experiment establishment, lime and PG rates were applied three times (2002, 2004, and 2010). The surface application of lime and PG combined reduced the soil acidification at 0 to 0.10 m and provided the highest levels of exchangeable Ca^{2+} in the uppermost surface layers (36.4 and 27.3 $mmol_c$ dm^{-3} at 0-0.05- and 0.05-0.10-, respectively), even four years after the last reapplication of soil amendments. This strategy was also effective to decrease aluminum toxicity, increasing the base saturation to a 0.40 m depth. Surface liming, regardless of PG addition, was sufficient to improve root elongation up to 370% and 127% for wheat and common bean, respectively, providing better length distribution in soil profile (0 to 0.60 m depth). However, a more pronounced effect was observed in the growth of common bean roots when PG was applied with liming. For both

species, the crop nutrition and grain yield results suggest that lime rate estimated to increase the base saturation in the topsoil (0-0.20 m) to 70%, with reapplications when base saturation reached ≤ 50%, was appropriate for liming recommendation in Oxisols managed under no-tillage system. The combination of lime and PG resulted in highest common bean grain yield (2,061 kg ha^{-1}).
Key words: *Phaseolus vulgaris* L., *Triticum aestivum*, plant nutrition, acidity management

2.2. Introduction

The degradation of tropical soils caused by climate conditions, land-use intensity, and inadequate management techniques are among the most important factors limiting agriculture production in regions such as Central and South America and the African Savanna (LAL et al., 1988; TILMAN et al. 2002). The major physical-chemical characteristics of the soil groups that are dominant in highly weathered regions include low cation exchange capacity (CEC), low availability of macronutrients, low soil organic matter (SOM), and excessive compaction (FELLER; BEARE, 1997; GLASER et al., 2002). To improve soil fertility and agricultural system sustainability, several studies have focused on developing conservation techniques for increasing crop productivity in tropical regions.

The no-tillage (NT) concept innovated agriculture in several parts of the world by allowing agricultural development in areas considered inadequate for crop growth because of serious physical and chemical problems. The excellent performance in increasing yield and preserving natural resources, NT technology has been adopted over approximately 160 million ha of land (FAO, 2016). However, in areas affected by high H^+ and Al^{3+} activity in the soil solution, reducing soil acidity is required to achieve high production potentials (FARHOODI; COVENTRY, 2008).

Liming is an effective method of improving the chemical attributes of soils affected by acidity; however, because of its low reactivity and solubility in the soil, incorporating lime through physical disruption is generally recommended despite posing a challenge to the basic principles of conservation agriculture. Therefore, Caires et al. (2005) conducted a study in a subtropical humid ecosystem to verify the long-term effects of surface liming, and their results indicated that after one year of application, significant

effects were observed in the acidity components in the 0 to 0.10 m soil layer, with the effects reaching the 0.10 to 0.20 m soil layer after only 2.5 years.

Certain soil physical properties, such as pore arrangement, infiltration capacity, and hydraulic conductivity, are considered key factors for improving the physical displacement of lime particles through the soil profile, which favors timely reactions and indicates the viability of this practice (AMARAL et al., 2004). In highly weathered areas, SOM is postulated as the major agent for the formation and stabilization of a porous structure, which is responsible for water flow and vertical nutrient percolation, including alkaline compounds (SIX et al., 2004). In addition to their physical effects, certain organic substances can contribute to Ca^{2+} and Mg^{2+} mobilization and soil acidity alleviation because of chemical reactions between organic functional groups and polyvalent cations such as Al^{3+} (FRANCHINI et al., 2003).

Compared with the climate conditions at the study sites of Caires et al. (2005; 2006a; 2006b), in tropical areas with dry winters and higher average air temperatures, the effect of surface liming is uncertain and may require a longer period because of the lower SOM content, resulting from the effect of high temperatures and humidity on the decomposition of organic residues (FRANZLUEBBERS et al., 2001). However, as observed in subtropical regions, surface liming may be an important strategy for increasing agriculture production in tropical NT systems. Thus, the adoption of appropriate techniques may improve the efficiency and the effects of surface applications in these areas.

The addition of PG may be an interesting alternative for improving lime reactions. Although this by-product has little to no effect on the soil pH (SUMNER et al., 1986), the higher solubility of calcium sulfate helps alleviate Al^{3+} toxicity (CARVALHO; VAN RAIJ, 1997) and increase basic cation availability at deeper soil layers over a shorter period compared with limestone (CHURKA BLUM et al., 2013). In addition, the ability of PG to improve root development affects several physical-chemical mechanisms that can influence lime mobility, including the formation and stability of pores, biological activity, and the exudation of organic substances involved in soil aggregation and Al^{3+} complexation (FRANCHINI et al., 2003; SIX et al., 2004; WATT et al., 2006).

Therefore, PG applications in lime-amended soils may have a synergetic effect in improving the reaction and lime effect to alleviate subsoil infertility in tropical areas with low SOM contents (SUMNER et al., 1986). Furthermore, in regions with dry spells, scientific information is lacking on the effect of both soil amendments for wheat and common bean root architecture. This knowledge is important for avoiding water stress for these species cropped in tropical areas. In addition, because of the effects on SOM content, this strategy may help improve the sustainability of tropical agronomic systems.

This study aimed to evaluate the effect of surface applications of lime and PG on the soil chemical properties, root growth, plant nutrition, yield components, technological characteristics, and grain yield of wheat and common bean in a long-term experiment under NT system.

2.3. Materials and Methods

2.3.1. Site Description

This experiment was performed in Botucatu, São Paulo State, Southeastern Brazil (48º 23' W, 22º 51' S, 765 m above sea level) during two growing seasons in an area under NT over a 14-year experimental period. According to the Köppen classification system, the climate of the study area is Cwa, with dry winters and hot and rainy summers. The rainfall and the mean maximum and minimum temperatures recorded over the two growing seasons are shown in Figure 1.

The soil is a sandy clay loam kaolinitic thermic Typic Haplorthox (USDA, 1999). At the beginning of the experiment (2002) the topsoil (0-0.20 m) showed the following chemical (VAN RAIJ et al., 2001) and textural characteristics: organic matter, 20.9 g dm^{-3}; pH (1:2.5 soil/$CaCl_2$ suspension 0.01 mol L^{-1}), 4.2; P (resin), 9.2 mg dm^{-3}; exchangeable K, Ca, and Mg 1.2, 14, and 5 $mmol_c$ dm^{-3}, respectively; total acidity in pH 7.0 (H + Al) 37 $mmol_c$ dm^{-3}, cation exchange capacity (CEC) 58 $mmol_c$ dm^{-3}; base saturation 37%; sand, silt, and clay contents of 54, 11, and 35%, respectively. In the subsoil (0.20-0.40 m) clay content was 36%.

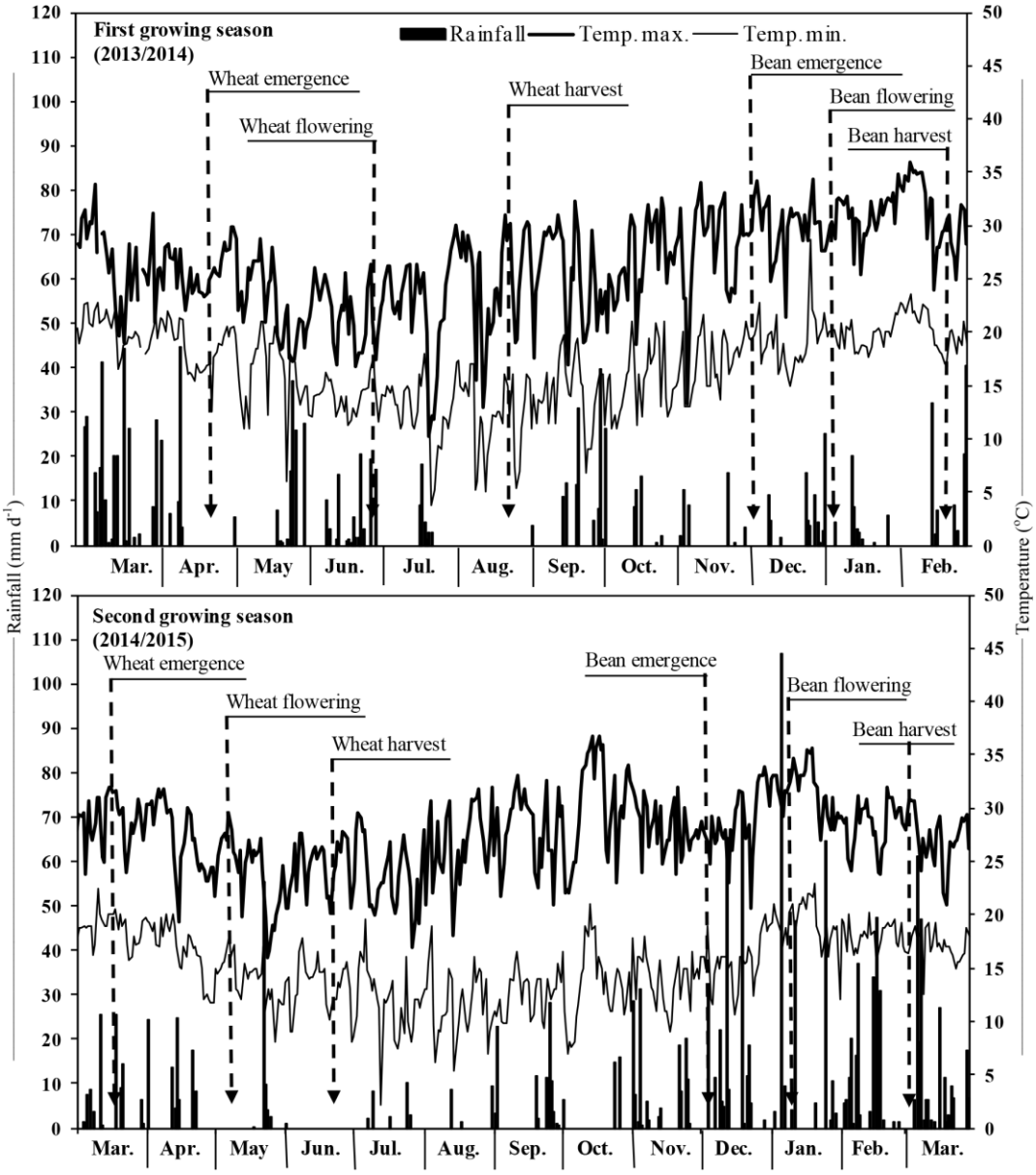

Figure 1. Daily rainfall, maximum and minimum temperatures, and growth dates of the crops at Botucatu, São Paulo State, Brazil, during the experimental period, in the agricultural years of 2013/2014 and 2014/2015.

2.3.2. Experimental Design and Treatment Establishment

The experiment was arranged in a randomized complete block design with split-plot arrangement and four replications. Each plot covered an area of 46.8 m^2 (5.2 m x 9.0 m). The plots were as follows: (i) control (no lime or PG), (ii) PG (2.1 Mg ha^{-1}), (iii) lime (2.0 Mg ha^{-1}) and (iv) lime and PG (2.0 Mg ha^{-1} and 2.1 Mg ha^{-1}, respectively). Subplots comprised two growing seasons (2013/2014 and 2014/2015). The

dolomitic lime rate (R) was calculated to increase the base saturation in the topsoil (0 to 0.20 m) to 70% using Eq. [1] as described by Cantarella et al. (1998).

$$R\ (Mg\ ha^{-1}) = (BS_2 - BS_1).CEC / (ECCE.10)\ [1]$$

where ECCE is the effective calcium carbonate equivalent of the dolomite; BS_2 is the estimated base saturation (70%); and BS_1 is the base saturation determined by the soil chemical analysis and calculated using Eq. [2].

$$BS_1(\%) = (Ca_{ex} + Mg_{ex} + K_{ex}).100 / CEC\ [2]$$

where Ca_{ex}, Mg_{ex}, and K_{ex} are the levels of basic exchangeable cations in the soil, and CEC is the total cation exchange capacity, which was calculated using Eq. [3].

$$CEC\ (mmol_c\ dm^{-3}) = Ca_{ex} + Mg_{ex} + K_{ex} + \text{total acidity (H+Al)}\ [3]$$

The PG rate (PR) was calculated using Eq. [4] according to the method proposed by van Raij et al. (1997).

$$PR\ (kg\ ha^{-1}) = 6.CL\ [4]$$

where CL is the clay content ($g\ kg^{-1}$) in the soil layer at 0.20 to 0.40 m.

During the study period, the treatments were applied three times, and different species were cropped in season and off season from 2002 to 2015. Details of the crop sequences and fertilizer management are shown in Table 1.

Table 1. Crops grown during the study period and the treatment application scheme during the experimental period (from 2002 to 2015).

Season	Crops		Treatment application
	Summer crop	Autumn-winter-spring crop	
2002/2003	***Oriza sativa*** **(cv. Caiapó)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 50 kg of N ha^{-1}	***Avena strigosa*** **(cv. Comum)** BF: 200 kg ha^{-1} of NPK 10–20–10 + 4.5% S	Lime: 2,700 kg ha^{-1} (71% ECCE)† Gypsum: 2,100 kg ha^{-1}
2003/2004	***Phaseolus vulgaris*** **(cv. Pérola)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 110 kg of N ha^{-1}	***Avena strigosa*** **(cv. Comum)** BF: 200 kg ha^{-1} of NPK 04–20–20 + 7% S	
2004/2005	***Arachis hypogaea*** **(cv. Runner IAC 886)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn.	***Avena sativa*** **(cv. IAC 7)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 110 kg of N ha^{-1}	Lime: 2,000 kg ha^{-1} (71% ECCE) Gypsum: 2,100 kg ha^{-1}
2005/2006	***Arachis hypogaea*** **(cv. Runner IAC 886)** BF: 24	***Avena sativa*** **(cv. IAC 7)** BF: 8 kg ha^{-1} of N + 40 kg ha^{-1}	

	kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn.	P_2O_5 + 20 kg ha^{-1} of K_2O + 7% S	
2006/2007	***Zea mays*** **(cv. 2B570)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn. TF: 90 kg of N ha^{-1}	***Urochloa brizantha*** **(cv. Marandu)** The forage seeds were simultaneously sown with corn.	
2007/2008	***Zea mays*** **(cv. 2B570)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn. TF: 90 kg of N ha^{-1}	***Urochloa brizantha*** **(cv. Marandu)** The forage seeds were simultaneously sown with corn.	
2008/2009	***Glycine max*** **(cv. MGBR-46)** BF: 250 kg ha^{-1} of NPK 04–20–20 + 4.5% S + 0.5% Zn.	***Avena strigosa*** **(cv. Comum)** No fertilizer was applied	
2009/2010	***Glycine max*** **(cv. CD216)** BF: 250 kg ha^{-1} of NPK 04–20–20 + 4.5% S + 0.5% Zn.	***Sorghum vulgare*** **(cv. AG1020)** No fertilizer was applied	
2010/2011	***Zea mays*** **(cv. 2B433)** BF: 350 kg ha^{-1} of NPK 08–28–16. TF: 150 kg of N ha^{-1}	***Crambe abyssinica*** **(cv. FMS Brilhante)** BF: 150 kg ha^{-1} of NPK 08–28–16	Lime: 2,000 kg ha^{-1} (88% ECCE) Gypsum: 2,100 kg ha^{-1}
2011/2012	***Zea mays*** **(cv. 2B433)** BF: 350 kg ha^{-1} of NPK 08–28–16. TF: 150 kg of N ha^{-1}	***Crambe abyssinica*** **(cv. FMS Brilhante)** BF: 150 kg ha^{-1} of NPK 08–28–16	
2012/2013	***Pennisetum glaucum*** **(cv. ADR300)** No fertilizer was applied	***Triticum aestivum*** **(cv. CD116)** BF: 75 kg ha^{-1} of N + 70 kg ha^{-1} P_2O_5 + 40 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn.	
2013/2014	***Phaseolus vulgaris*** **(cv. Pérola)** BF: 10 kg ha^{-1} of N + 50 kg ha^{-1} P_2O_5 + 50 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn. TF: 100 kg of N ha^{-1}	***Triticum aestivum*** **(cv. CD116)** BF: 75 kg ha^{-1} of N + 70 kg ha^{-1} P_2O_5 + 40 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn.	
2014/2015	***Phaseolus vulgaris*** **(cv. Pérola)** BF: 10 kg ha^{-1} of N + 50 kg ha^{-1} P_2O_5 + 50 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn. TF: 100 kg of N ha^{-1}		

†The reapplications in October of 2004 and 2010 were performed when the standard treatment (calculated rate) reached base saturation ≤ 50%. BF: base fertilization; TF: topdressing fertilization.

2.3.3. Soil Sampling and Chemical Analysis

Three (36 months) and four (48 months) years after the last reapplication of lime, eight individual soil samples were randomly collected at depths of 0.00–0.05, 0.05–0.10, 0.10–0.20, 0.20–0.40, and 0.40–0.60 m from the experimental area of each plot to form a composite sample. The samples were dried, sieved (2-mm sieves) and analyzed according to Cantarella et al. (1998) and van Raij et al. (2001) to determine the soil chemical attributes (pH, Al^{3+}, P, SOM, S-SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^{+}, and base saturation).

The soil pH was determined in a 0.01 mol L^{-1} $CaCl_2$ suspension (1:2.5 soil/solution), and the exchangeable Al was extracted with a neutral 1 mol L^{-1} KCl solution (1:10 ratio of soil:solution) and determined by titration with a 0.025 mol L^{-1} NaOH solution. The SOM was determined by the colorimetric method using a sodium dichromate solution according the method proposed by Heanes (1984). Soil S-SO_4^{2-} analyses were performed through extraction using calcium phosphate (0.01 mol $L^{-}1$) in a 1:2.5 soil:solution ratio, which was followed by the turbidimetric method using a $BaSO_4$ solution (BARDSLEY; LANCASTER, 1960). The available P and exchangeable basic cations (Ca^{2+}, Mg^{2+}, and K^{+}) were extracted using an ion-exchange resin (VAN RAIJ et al., 1986). Phosphorus in the extractable solution was determined by the colorimetric method proposed by Murphy and Riley (1962) using a FEMTO 600S spectrophotometer. To determine the Ca^{2+}, Mg^{2+}, and K^{+} contents, a Shimadzu AA-6300 atomic absorption/flame-emission spectrophotometer was used. The CEC was obtained by summing the individual cations (H, Al, K, Ca, and Mg). The base saturation (BS) values were calculated by dividing the sum of the K, Mg, and Ca contents (the bases) by the CEC and multiplying the result by 100% (VAN RAIJ et al., 2001).

2.3.4. Crop Management

Before sowing both crops (approximately 20 days), weed control was performed with a glyphosate application [1440 g of active ingredient (a.i.) ha^{-1}] using a tractor-mounted boom sprayer (Condor 600 M14 JACTO) with a spraying pressure of 5 bars and a spray volume of 250 L ha^{-1}.

The wheat cultivar ‘CD116’ was sown on Apr. 18, 2013, and Mar. 12, 2014. The wheat seeds were sown in both growing seasons at a within-row spacing of 0.17 m and rows of 80 seeds m^{-1} using NT seeding (Semeato model SHM 15/17, Passo Fundo, RS, Brazil). The seeds were treated with 52 g a.i. of thiamethoxam {3-(2-chloro-thiazol-5-ylmethyl)-5-methyl-1,3,5 oxadiazinan-4-ylidene (nitro) amine}, 60 g a.i. of carboxin (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxamide), and 60 g a.i. of thiram (tetramethylthiuram disulfide) to 100 kg of seeds. Fertilization was performed at sowing with 40 kg N ha^{-1} as urea + 250 kg ha^{-1} of NPK 14–28–16 + 0.5% Zn + 4.5% S (CANTARELLA et al., 1997). Before fertilization, the products were mixed using a

mechanical mixer. The weeds were controlled using 0.8 kg a.i. ha^{-1} of 2,4-D, sal dimetilamina {dimethylammonium (2,4-dichlorophenoxy) acetate} and 58 g a.i. ha^{-1} of clodinafope-propargil {(R)-2-[4-(5-chloro-3-fluoro-pyridin-2-yloxy)-phenoxy]-propionic acid prop-2-ynyl ester} 10 d after sowing. The emergence of 50% of the plants occurred 5 d after sowing in the first growing season and 4 d after sowing in the second season.

On November 28, 2013, and December 01, 2014, the common bean cultivar 'Pérola' was sown at a density of 15 seeds m^{-1} and between-row spacing of 0.45 m using a mechanical seeder (Semeato Model Personale Drill-13, Passo Fundo, RS, Brazil). To treat 100 kg of seeds, 105, 60, and 60 g a.i. of thiamethoxam, carboxin, and thiram, respectively, were used. Base fertilization was performed at sowing with 250 kg ha^{-1} of NPK 04–20–20 + 4.5% S + 0.5% Zn. The emergence of 50% of the plants occurred 4 d after sowing in the first growing season and 5 d after sowing in the second season. Nitrogen topdressing fertilization as ammonium nitrate (31% N) was performed with 100 kg N ha^{-1} when the plants reached stage V_4 (third trifoliate leaf expanded) according to the recommendations of Ambrosano et al. (1997).

2.3.5. Root Sampling and Analyses

In both crops and growing seasons, the root characteristics (length and diameter) at each flowering stage were measured via eight individual soil samples randomly collected from in-row (4) and between row (4), of each plot, to form a composite sample. For wheat, the samples from row and between row were mixed to form one due to reduced row spacing. A galvanized-steel probe with a 69-mm diameter cutting tip was used at depths of 0 to 0.05, 0.05 to 0.10, and 0.10 to 0.20 m. For samples collected at 0.20 to 0.40 and 0.40 to 0.60 m, the probe had a 49-mm diameter cutting tip. The roots were carefully separated from the soil and other residues by washing under a flow of swirling water over a 0.5-mm mesh sieve according to Oussible et al. (1992). The root samples were immersed in a 50% ethyl alcohol solution in plastic pots with lids and stored under refrigeration at 2°C until evaluation. To evaluate the root length density (km m^{-3}) and diameter (mm), the roots were digitalized using an optical scanner (Scanjet 4C/T, HP) at high resolution (600 dpi) and then analyzed using the software program 'WinRhizo' version 3.8-b (Regent Instrument Inc., Quebec, Canada). The root length distribution was

calculated by the ratio between the root length density data in each layer and the total amount of root length, and then the product was multiplied by 100.

2.3.6. Plant Sampling and Analyses

In the flowering stage of both crops, leaf samples were collected to determine the nutrient concentration, which was performed according to the method proposed by Cantarela et al. (1997) and Ambrosano et al. (1997). At the same stage, 10 random plants per plot were collected for to determine the shoot dry matter. All of the samples were dried in a forced air oven at 65°C for 72 h. The plants were weighed and the leaves ground (to pass a 40-mesh stainless steel screen) and analyzed to determine the nutrient concentration according to the methods described by Malavolta et al. (1997). All of the macronutrients (P, K, Ca, Mg, and S), except N, were extracted by nitroperchloric digestion. Nitrogen was extracted using a H_2SO_4 extract solution and determined by the Kjeldahl distillation method. From the digested solution, P and S were determined by colorimetry and turbidimetry methods, respectively, and, K, Ca, and Mg were determined by atomic absorption spectrophotometry.

At physiological maturity, 20 plants were evaluated at the experimental area to determine the plant height (measuring from the soil surface to the tip of the ear). Wheat was harvested on August 22, 2013 and June 24, 2006 in the first and second growing seasons, respectively, and the following parameters were determined: ear length (obtained by measuring 20 ears at each plot), yield components [number of ears per square meter, which was obtained by counting the number of panicles in 2.0 m of plants in two central rows from the usable area of each plot), number of spikelets per ear (obtained by counting the number of spikelets in 20 ears at the experimental area), grain per spikelet (obtained using the following function: number of grains in 20 ears/total number of spikelets in 20 ears) and 1000-grain weight (evaluated by the random collecting and weighing of four samples of 1000 grains from each plot)], volumetric mass (obtained by weighing four samples of grain for the 0.25 L volume, with data converted to 100 L volumes) and grain yield [obtained by the grain weight mechanically harvested from the usable area, with data transformed to grain yield per hectare (130 g kg^{-1} wet basis)].

Common bean was harvested manually on February 17, 2014 and March 03, 2015 in the first and second growing seasons, respectively. The yield components [final population of plants (counting the number of plants in the two central rows in 7-m rows in each plot and then extrapolated to the hectare), number of pods per plant (obtained by counting the number of pods in 10 plants randomly collected at the experimental area), number of grains per pod (obtained using the following function: total number of grains in 10 plants/total number of pods in 10 plants), 100-grain weight (evaluated by randomly collecting and weighing four samples of 100 grains from each plot)], plant survival (obtained using the following function: final population of plants/number of emerged plants x 100), and grain yield [obtained by the grain weight manually harvested from seven central 7-m rows, with data transformed to the grain yield per hectare (130 g kg^{-1} wet basis)] were determined.

The technological quality of the common bean grains was analyzed 60 days after harvest. For each plot, four grain samples were randomly collected and then classified using a sieve with oblong holes of 12/64" x ¾ (4.76 x 19.05 mm). After one minute of shaking, the sieve yield (%) was calculated by the ratio between the weight of the grains retained on the sieve and the total sample weight multiplied by 100. Following this assessment, the classified grains (commercial grains) were ground and submitted to a N determination procedure (MALAVOLTA et al., 1997). The protein content was obtained by multiplying 6.25 by the N concentration in the grains.

2.3.7. Statistical Analyses

All data were initially tested for normality using the Shapiro-Wilk test from the UNIVARIATE procedure of SAS (version 9.3; SAS Inst. Inc., Cary, NC), and the results indicated that all data were distributed normally ($W \geq 0.90$). The treatments, growing seasons and resultant interaction were considered fixed effects. The treatments and growing seasons (only for the plant results) means were compared via Fisher's protected LSD test. The effects were considered statistically significant at $P \leq 0.05$. As the root characteristics data were considered statistically significant at $P \leq 0.10$. A higher probability for the root system evaluation was used because these characteristics are more variable (FAGERIA; MOREIRA, 2011).

2.4. Results

2.4.1. Soil Chemical Characteristics

The soil amendments had different effects on each soil chemical attribute. In both soil samplings, the soil pH; exchangeable Al^{3+} and $S\text{-}SO_4^{2-}$; exchangeable Ca^{2+}, Mg^{2+}, and K^{+}; and BS were significantly ($P \leq 0.05$) influenced by the treatments in all of the evaluated soil layers (Table 2). The surface liming, regardless of PG addition, reduced soil acidity, even in the deeper soil layers (Fig. 2A). The application of PG and lime in a combination was effective at alleviating the soil acidification in the uppermost soil layers, and the soil pH ranged from 4.6 to 5.3 at depths of 0 to 0.05 m and from 4.5 to 5.1 at depths of 0.05 to 0.10 m during the twelve-month period between both soil samplings (Fig. 2B).

Table 2. Probabilities of the calculated F-value for soil chemical properties at the depths of 0–0.05, 0.05–0.10, 0.10–0.20, 0.20–0.40 and 0.40–0.60 m at 36 and 48 months after reapplication of lime and phosphogypsum.

	Treatments†				
	0-0.05 m	0.05-0.10 m	0.10-0.20 m	0.20-0.40 m	0.40-0.60 m
			36 months		
pH	<0.0001	0.0013	<0.0001	0.0016	0.0005
Al^{3+}	<0.0001	<0.0001	<0.0001	0.0048	0.0469
P resin	0.2122	0.1975	0.3618	0.1860	0.6984
SOM‡	0.0873	0.3492	0.2235	0.5459	0.0046
$S\text{-}SO_4^{2-}$	0.0487	0.0211	0.0364	0.0377	0.0453
Ca^{2+}	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Mg^{2+}	<0.0001	<0.0001	<0.0001	0.0053	0.0020
K^{+}	0.0264	0.0402	0.0236	0.0328	0.1156
BS§	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
			48 months		
pH	<0.0001	<0.0001	0.0004	0.0005	0.0021
Al^{3+}	<0.0001	<0.0001	<0.0001	<0.0001	0.0090
P resin	0.9794	0.0056	0.3000	0.1849	0.1245
SOM	0.0287	0.0001	0.0021	0.0352	0.0006
$S\text{-}SO_4^{2-}$	0.0003	0.0062	0.0243	<0.0001	<0.0001
Ca^{2+}	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Mg^{2+}	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
K^{+}	0.0059	<0.0001	0.0002	<0.0001	<0.0001
BS	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

†Treatments: control, phosphogypsum, lime, and lime + phosphogypsum. The amendments rates have been applied three times (2002, 2004, and 2010).

‡SOM: soil organic matter
§BS: base saturation

As observed for the soil pH, lime + PG applications produced positive effects that were also observed in the exchangeable Al^{3+} levels at the second soil sampling (Fig. 2D). Although a positive effect of the products combination was not confirmed previously (36 months), the individual application of lime significantly reduced pH and exchangeable Al^{3+} levels from depths of 0 to 0.60 m (Figs.2A and 2C).

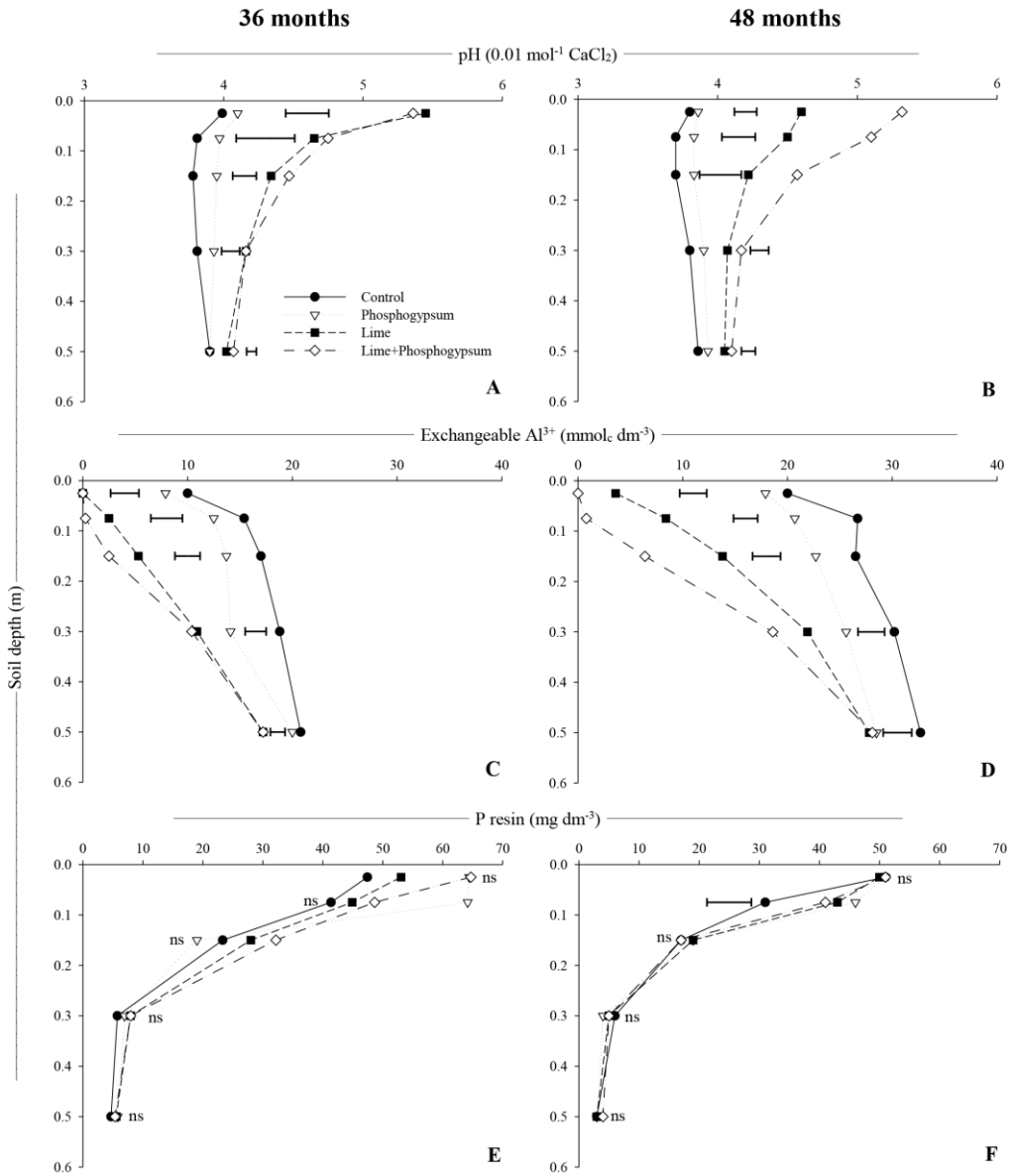

Figure 2. Soil pH (0.01 mol L^{-1} $CaCl_2$), exchangeable Al, and phosphorus levels in the soil samples taken 36 and 48 months after last reapplication lime (■), phosphogypsum (▽), and limestone + phosphogypsum (◊) and the corresponding levels of the control (●).The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars represent the least significant difference by the LSD test at $P = 0.05$; ns: non-significant.

The P level was not influenced by the soil amendments application during the evaluation period except at the 0.05 to 0.10-m layer, where the lowest P availability was observed in the control treatment (Figs. 2E and 2F). In the first soil sampling, liming increased the SOM levels in the deepest soil layer (0.40 to 0.60 m), regardless of PG addition as a complement (Fig. 3A). The greatest impact on the SOM was observed in the lime-amended soil after 12 years of experimentation (Fig. 3B).

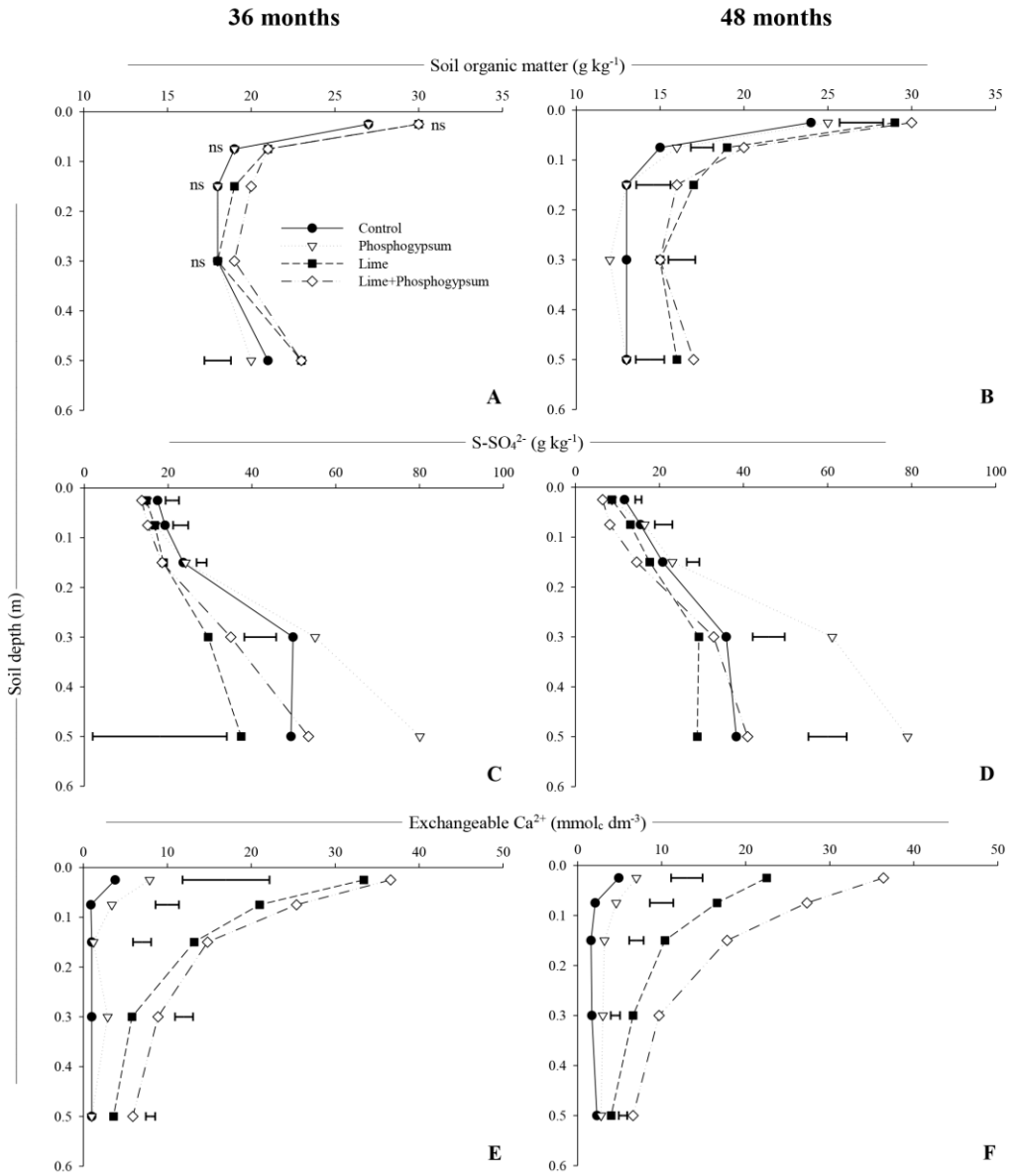

Figure 3. Soil organic matter, $S\text{-}SO_4^{2-}$, and exchangeable Ca levels in the soil samples taken 36 and 48 months after last reapplication lime (■), phosphogypsum (▽), and limestone + phosphogypsum (◊) and the corresponding levels of the control (●).The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars represent the least significant difference by the LSD test at $P = 0.05$; ns: non-significant.

In both soil samplings, a decrease in the $S\text{-}SO_4^{2-}$ levels was observed for all soil layers when PG was applied in a combination with limestone (Figs. 3C and 3D). The untreated plots (control) exhibited higher S availability in the 0 to 0.20-m layer compared with the soil treated with lime and PG together. In the deeper soil layers

(0.20 to 0.40 and 0.40 to 0.60 m), the highest levels of S-SO_4^{2-} were observed in the plots treated with individual applications of PG.

Regardless of the soil sampling and depth, the surface application of lime increased the exchangeable Ca^{2+} and Mg^{2+} levels (Figs 3E, 3F, 4A, and 4B). However, the PG addition as a complement resulted in the greatest availability of these nutrients in topsoil layers (0- to 0.10-m). Although gypsum is considered a good source of Ca, our long-term results showed that individual applications of this product were ineffective at increasing Ca in the soil profile. Exchangeable K^+ was influenced differently by the treatments according to the soil sampling (Figs 4C and 4D). In the first soil sampling, the association of both products provided higher K levels in the 0- to 0.40-m layer compared with the control treatment. However, a decrease in K availability was observed twelve months later (48 months) in the soil treated with PG and lime.

The surface application of lime was considered an effective acidity management practice for increasing the base saturation of soil profile (from 0 to 0.60 m) (Figs 4E and 4F). Although the effect of PG as liming complement was not observed in the first soil sampling, our results suggest that the use of gypsum has a long-term positive effect on the base saturation index, which indicates that this practice a good alternative for improving the subsoil chemical fertility.

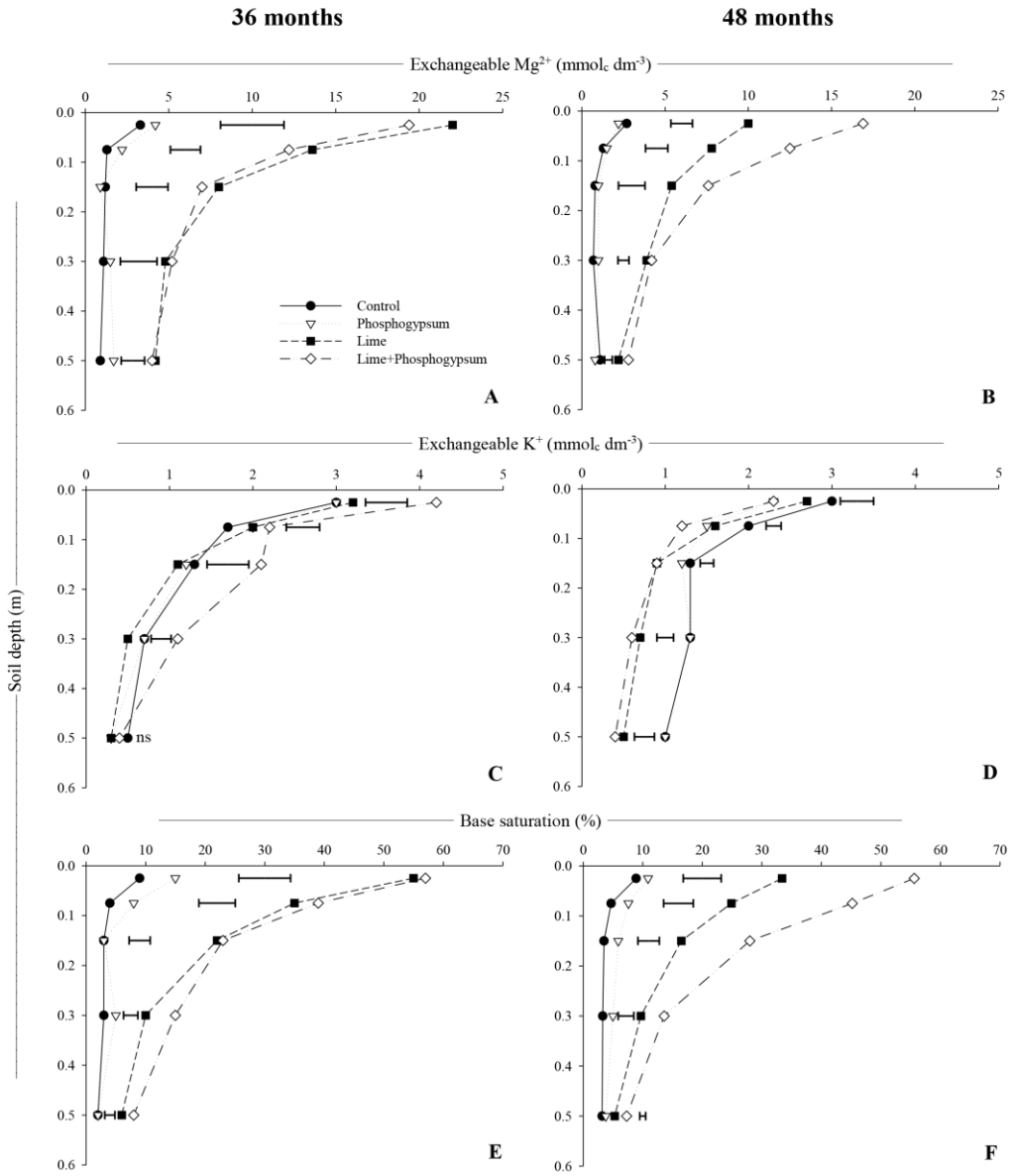

Figure 4. Exchangeable Mg and K, and base saturation levels in the soil samples taken 36 and 48 months after last reapplication lime (■), phosphogypsum (▽), and limestone + phosphogypsum (◊) and the corresponding levels of the control (●).The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars represent the least significant difference by the LSD test at $P = 0.05$; ns: non-significant.

2.4.2. Wheat

2.4.2.1. Root development

The wheat root characteristics were highly influenced by the surface application of the soil amendments and the growing seasons, and significant interactions were not observed among the factors (Table 3). The root length density was higher in the

lime-amended soil, regardless of whether PG was added, in all of the evaluated soil layers (Fig. 5A). In the 0- to 0.05-m layer, the surface application of lime resulted in a lower percentage of root length distribution compared with the control treatment. However, a higher root system concentration was observed at the subsoil layer, specifically in the 0.20- to 0.40-m layer (Fig. 5B). A similar result was observed for the root diameter, with the limed plots resulting in root development with a smaller diameter in the uppermost soil layer (0- to 0.05-m depth) and root growth with a greater caliber in the 0.40- to 0.60-m soil layer when PG was applied as a complement (Fig. 5C).

Table 3. Length density, length distribution, and diameter of wheat root system as affected by surface application of lime and phosphogypsum and growing season, and probabilities of the calculated F-values at Botucatu, São Paulo State, Brazil.

	0-0.05 m	0.05-0.10 m	0.10-0.20 m	0.20-0.40 m	0.40-0.60 m
			Root length density, km m^{-3}		
Growing season					
2013	78.7 a[†]	29.1 a	3.5 b	3.4 b	1.5 a
2014	29.7 b	17.6 b	8.8 a	4.4 a	1.5 a
F probability					
Blocks	0.1453	0.8142	0.5457	0.3285	0.6817
Treatments (T)[‡]	<0.0001	<0.0001	<0.0001	<0.0001	0.0088
G. Season (G)	<0.0001	0.0017	<0.0001	0.0989	0.9753
T x G	0.8824	0.6376	0.2120	0.8159	0.3009
			Root length distribution, %		
Growing season					
2013	69.3 a	23.8 a	2.7 b	2.8 b	1.3 a
2014	51.3 b	27.3 a	13.6 a	5.9 a	1.9 a
F probability					
Blocks	0.5658	0.4359	0.9361	0.1657	0.6032
Treatments (T)	0.1594	0.3293	0.7946	0.0198	0.6354
G. Season (G)	0.0001	0.1985	<0.0001	0.0002	0.2055
T x G	0.8820	0.5032	0.8710	0.1953	0.2865
			Root diameter, mm		
Growing season					
2013	0.22 b	0.25 a	0.26 a	0.28 a	0.28 a
2014	0.27 a	0.25 a	0.26 a	0.27 a	0.29 a
F probability					
Blocks	0.2654	0.3122	0.2917	0.3709	0.6046
Treatments (T)	<0.0001	0.2569	0.2310	0.1682	0.0757
G. Season (G)	<0.0001	0.9024	0.9053	0.5076	0.3875
T x G	0.5099	0.1419	0.7588	0.1205	0.5483

†Values followed by the same letter within a column are not significantly different at $p \leq 0.10$ according to the LSD test.

‡Treatments: control, phosphogypsum, lime, and lime + phosphogypsum. The amendments rates have been applied three times (2002, 2004, and 2010).

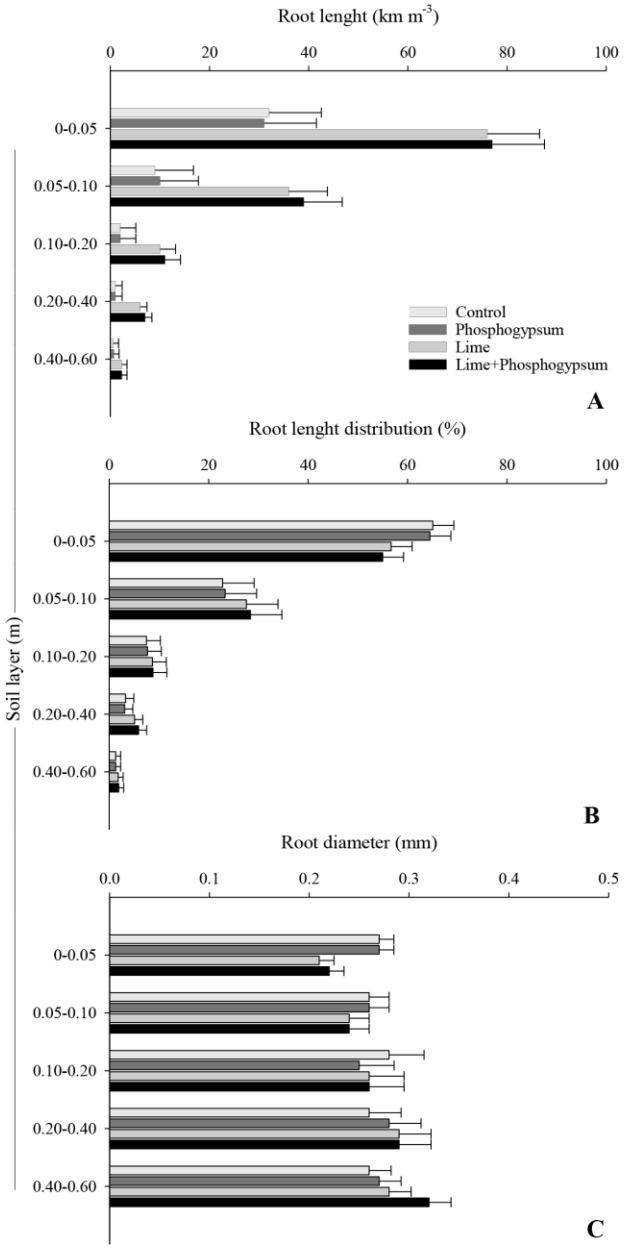

Figure 5. Root length density (a), percent distribution of root length density (b), and root diameter (c), of wheat as affected by lime (□), phosphogypsum (▩), and limestone + phosphogypsum (■) and the corresponding levels of the control (□), at different depths. The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars indicate the least significant difference for each depth at $P \leq 0.10$ according to the LSD test.

Regarding the growing season effect on the root development, a greater length density in the layer at 0 to 0.10 m was observed in the first growing season, and higher root growth was observed in the subsurface layers (0.10 to 0.20 and 0.20 to 0.40 m) during the second growing season (Table 3). Consequently, a higher root system concentration was observed in the 0 to 0.05-m layer, which resulted in a smaller distribution in the subsoil layers, specifically in the 0.10- to 0.40-m layer. With the exception of the surface soil layer (0- to 0.05-m depth), where a greater caliber of roots was observed in the second growing season, these factors did not affect the root diameter.

2.4.2.2. Aboveground biomass and plant nutrition

The shoot dry matter and macronutrient concentration in the flag leaves of the planted wheat were significantly affected by the surface application of the soil amendments and growing season; however, the probabilities of the calculated F-values did not confirm any interactions between the factors (Table 4). Soil acidity alleviations caused by liming increased the plant development and, consequently, the aboveground biomass production of wheat with additions of up to 125%, when PG was added.

The leaf concentrations of N, Ca, and Mg were positively influenced by the surface application of lime, otherwise this effect reduced the K concentration in the flag leaves. Compared with the control treatments, the individual application of PG was effective at increasing the N and Ca concentrations, although it resulted in a lower Mg concentration in the flag leaves. The phosphorus and S concentrations were not affected by the main treatments. This specie showed higher growth of the aboveground biomass in the first growing season; however, the lowest concentrations of N, K, Ca, and Mg in the flag leaves were observed in this cycle.

Table 4. Shoot dry matter (SDM) and macronutrient concentration (N, P, K, Ca, Mg, and S) in flag leaves of wheat, plant height (PH), ear length (EL), number of ear per square meter (NE), spikelets per ear (SE), grain per spikelet (GS), weight of 1,000 grains (W1000), volumetric mass (VM), and grain yield (GY) of wheat as affected by surface application of lime and phosphogypsum and growing season, and probabilities of the calculated F-values at Botucatu, São Paulo State, Brazil.

	SDM	N	P	K	Ca	Mg	S
Treatments	**kg ha^{-1}**	**---------- g kg^{-1} ----------**					
Control	1,547 c†	42 c	3.0 a	20 a	2.8 c	1.4 c	1.8 a
Phosphogypsum	1,305 d	46 b	3.1 a	20 a	4.0 b	1.1 d	2.1 a
Lime	3,306 b	51 a	3.1 a	16 b	5.5 a	2.3 a	2.2 a
Lime + Phosphogypsum	3,484 a	53 a	3.1 a	16 b	5.9 a	2.1 b	2.2 a
Growing season							
2013	2,726 a	42 b	3.2 a	16 b	3.6 b	1.4 b	2.1 a
2014	2,095 b	54 a	2.9 a	20 a	5.5 a	2.0 a	2.1 a
F probability							
Treatments (T)‡	<0.0001	<0.0001	0.4036	<0.0001	<0.0001	<0.0001	0.3684
Growing season (G)	<0.0001	<0.0001	0.5001	<0.0001	<0.0001	<0.0001	0.8729
T x G	0.5472	0.1371	0.0991	0.6822	0.1829	0.1911	0.1128

	PH	EL	NE	SE	GS	W1000	VM	GY
Treatments	**------ cm ------**		**---------- nº ----------**			**g**	**kg 100L^{-1}**	**kg ha^{-1}**
Control	59 b	5.2 b	113 b	11 b	1.6 b	35.6 b	80.3 b	822 b
Phosphogypsum	60 b	5.1 b	121 b	11 b	1.7 b	36.0 b	79.9 b	855 b
Lime	74 a	6.1 a	286 a	13 a	2.5 a	41.4 a	82.0 a	3,563 a
Lime + Phosphogypsum	74 a	6.3 a	288 a	14 a	2.6 a	41.3 a	81.7 a	3,808 a
Growing season								
2013	80 a	6.3 a	227 a	14 a	2.1	41.7 a	78.3 b	2,768 a
2014	54 b	5.0 b	177 b	11 b	2.2	35.5 b	83.6 a	1,755 b
F probability								
Treatments (T)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Growing season (G)	<0.0001	<0.0001	<0.0001	<0.0001	0.4384	<0.0001	<0.0001	<0.0001
T x G	0.2587	0.2165	0.1121	0.2050	0.2255	0.1754	0.1243	0.6916

†Values followed by the same letter within a column are not significantly different at $p \leq 0.10$ according to the LSD test.

‡The amendments rates have been applied three times (2002, 2004, and 2010).

2.4.2.3. Plant and technological characteristics, yield components, and grain yield

All of the evaluated wheat characteristics were affected by surface applications of lime, and all of the parameters except grains per spikelet were also influenced by the growing season; however, an interaction between the two factors was not observed (Table 4). Compared with the control treatment, only the lime-amended soil, regardless of whether PG was applied, favored plant growth during the reproductive stages and resulted in a higher number and size of the ears and quantity of inflorescences (spikelets) in each ear. The benefits of alleviating soil acidity were also reflected in the

grain development, with improvements observed in the number per ear, the weight of these structures and the volumetric mass, which is considered an important quality parameter. Because of environmental conditions, wheat development was greater during the first growing season, although a reduction in volumetric mass was observed relative to the subsequent season.

2.4.3. Common Bean

2.4.3.1. Root development

Similar to the wheat root characteristics, interaction effects between the main treatments and growing season were not observed for the common bean root attributes in the in-row and between-row locations; however, significant single effects were observed for these factors (Table 5). The surface application of lime significantly increased the root length density in both locations (in row and between row) at all evaluated soil layers (Figs. 6A and 6B), and a positive effect of PG was observed in the between-row locations in the 0- to 0.10-m layer when this by-product was applied in a combination with lime. In addition, compared with the control treatment, a positive effect was also observed from the individual application of PG, which resulted in increased growth of the common bean root system in the subsoil, specifically in the 0.20- to 0.40-m layer. Consequently, a smaller percentage of the root length distribution was found in the 0.10- to 0.20-m layer, and a greater concentration occurred in the 0.20- to 0.40-m layer in both the in-row and between-row locations (Figs. 6C and 6D).

Table 5. Length density, length distribution, and diameter of common bean root system within rows (R) and between rows (BR), as affected by surface application of lime and PG and growing season, and probabilities of the calculated F-values at Botucatu, São Paulo State, Brazil.

	0-0.05 m		0.05-0.10 m		0.10-0.20 m		0.20-0.40 m		0.40-0.60 cm	
	R	BR	R	BR	R	BR	R	BR	R	BR
	Root length density, km m^{-3}									
Growing season										
2013	12.3 a†	10.1 a	14.5 a	7.1 a	4.4 a	1.8 b	1.35 a	0.9 a	0.6 a	0.34 a
2014	5.5 b	5.3 b	10.3 b	5.4 b	4.4 a	2.7 a	0.83 b	0.9 a	0.7 a	0.28 b
F probability										
Blocks	0.8946	0.4152	0.2693	0.4615	0.4594	0.6344	0.6090	0.3975	0.2913	0.2993
Treatments (T)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0003	<0.0001	<0.0001
G. Season (G)	<0.0001	<0.0001	<0.0001	<0.0001	0.8817	<0.0001	0.0017	0.8892	0.0783	<0.0001
T x G	0.3569	0.5578	0.6591	0.7824	0.3981	0.3874	0.5646	0.8019	0.6273	0.7284
	Root length distribution, %									
Growing season										
2013	37.2 a	51.8 a	44.2 a	34.4 a	13.3 b	8.2 b	3.7 a	4.1 b	1.7 b	1.5 b
2014	23.7 b	35.2 b	45.5 a	37.2 a	24.4 a	18.6 a	3.6 a	7.0 a	2.8 a	2.0 a
F probability										
Block	0.4792	0.9069	0.5194	0.9344	0.5735	0.6782	0.9573	0.8619	0.6277	0.2375
Treatments (T)	0.1519	0.3586	0.0010	0.5143	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.3575
G. Season (G)	<0.0001	<0.0001	0.2292	0.0722	<0.0001	<0.0001	0.7978	<0.0001	<0.0001	<0.0001
T x G	0.8920	0.7132	0.3028	0.2598	0.3512	0.4752	0.5780	0.3741	0.2851	0.3684
	Root diameter, mm									
Growing season										
2013	0.22 b	0.24 b	0.25 b	0.24 a	0.28 a	0.27 a	0.27 b	0.26 a	0.28 a	0.24 b
2014	0.29 a	0.27 a	0.29 a	0.26 a	0.27 a	0.27 a	0.32 a	0.28 a	0.29 a	0.28 a
F probability										
Block	0.2462	0.1386	0.6484	0.7631	0.4305	0.3938	0.3278	0.8743	0.8626	0.2587
Treatments (T)	0.0027	0.1963	0.0819	0.9057	<0.0001	<0.0001	<0.0001	0.0741	0.0006	0.1088
G. Season (G)	<0.0001	<0.0001	<0.0001	0.0909	0.4923	0.2815	<0.0001	<0.0001	0.8570	<0.0001
T x G	0.5263	0.5693	0.3287	0.4562	0.2189	0.7492	0.8269	0.4803	0.3367	0.5871

†Values followed by the same letter within a column are not significantly different at $p \leq 0.10$ according to the LSD test.

‡Treatments: control, phosphogypsum, lime, and lime + phosphogypsum. The amendments rates have been applied three times (2002, 2004, and 2010).

In the between-row locations, with the exception of the 0.10- to 0.20-m layer, the surface liming, regardless of whether PG was added, did not affect the root length distribution compared with the control treatment. Within rows, the alleviation of soil acidity decreased the common bean root system concentration in the 0.10- to 0.20-m layer and significantly increased the distribution in the 0.05- to 0.10-m and 0.20- to 0.60-m soil layers. In addition, in the 0.10- to 0.40-m layer, these treatments promoted greater root diameters in the between-row locations and lower root diameters in-row locations (Figs 6E and 6F). The control treatment showed a greater mean root diameter in the 0- to 0.05-m layer and lower diameters in the 0.40- to 0.60-m layer.

In the first growing season, the root length density was higher in the uppermost soil layers (0 to 0.05 m and 0.05 to 0.10 m) in both locations (Table 5). In

addition, the environmental conditions in this season stimulated the root growth in the 0.40 to 0.60-m layer between rows and in the 0.20- to 0.40-m layer within rows. Higher concentration of the common bean root system was observed at the surface layer (0 to 0.05 m), consequently, a lower proportion was observed in the deeper layers to a depth of 0.10 m. The root diameter was also significantly affected by the growing season, and the common bean cultivated in the second year presented thicker roots at the 0- to 0.10-m layer and in the subsurface soil layers (0.20 to 0.40 m and 0.40 to 0.60 m).

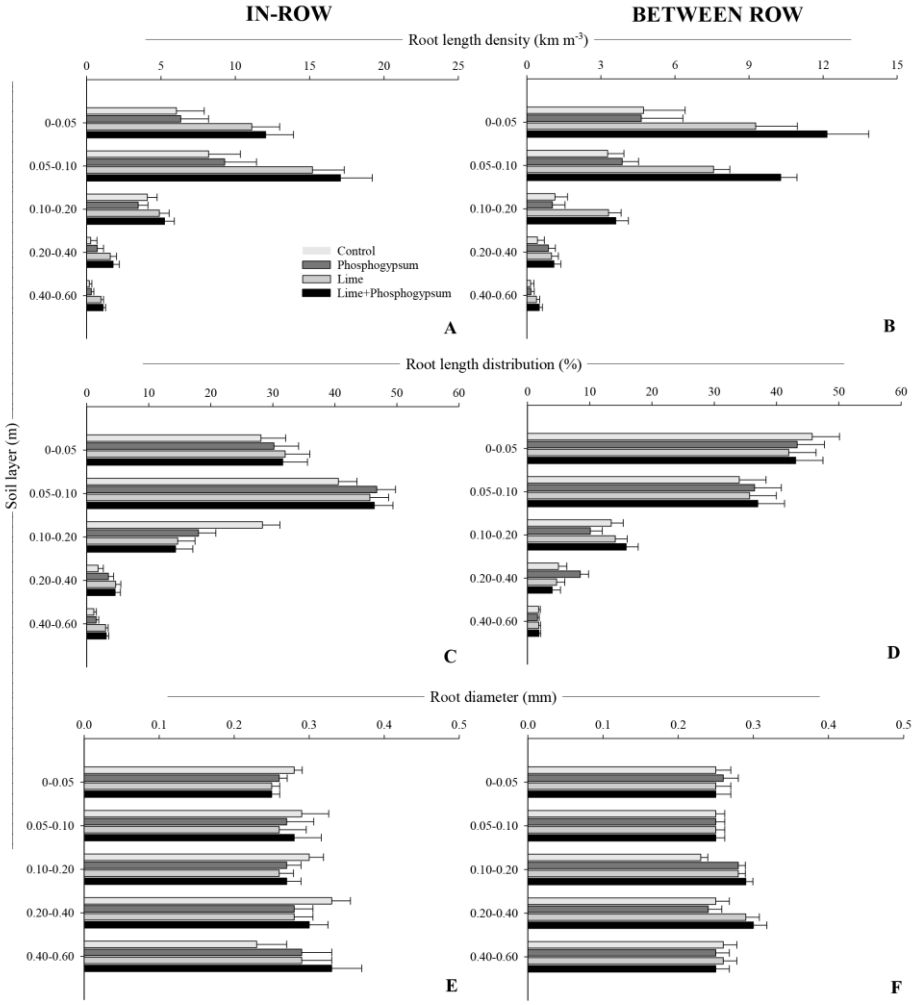

Figure 6. Root length density (a and b), percent distribution of root length density (c and d), and root diameter (e and f), of common bean within rows (a, c, and e) and between rows (b, d, and f), as affected by lime (□), phosphogypsum (▩), and limestone + phosphogypsum (■) and the corresponding levels of the control (□), at different depths. The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars indicate the least significant difference for each depth at $P \leq 0.10$ according to the LSD test.

2.4.3.2. Aboveground biomass and plant nutrition

The lime-amended soil contributed to the common bean growth and plant nutrition (Table 6), and the amelioration of chemical attributes increased the shoot dry matter production by up to 94%, regardless of whether PG was added. The surface liming significantly increased the N, P, Ca, Mg, and S concentrations in the common bean leaves, although the K uptake was not affected by the treatments. Except for Ca, the results indicated that the PG application had no effect on the macronutrient uptake by the plants. The planted common bean showed the highest shoot dry matter growth and concentration of N, P, Ca, and Mg in the leaves during the first growing season.

Table 6. Shoot dry matter (SDM), macronutrient concentration (N, P, K, Ca, Mg, and S) in common bean leaves, plant population (POP), plant survival (PS), pods per plant (PP), grains per pod (GP), weight of 100 grains (W100), protein content (PC), grain yield (GY), and sieve yield (SY) of common bean as affected by surface application of lime and phosphogypsum and growing season, and probabilities of the calculated F-values at Botucatu, São Paulo State, Brazil.

	SDM	N	P	K	Ca	Mg	S
Treatments	**kg ha^{-1}**			**g kg^{-1}**			
Control	1,142 b†	50 b	2.7 b	19 a	8 d	3.9 b	2.4 b
Phosphogypsum	1,133 b	50 b	2.7 b	20 a	10 c	3.6 b	2.4 b
Lime	1,934 a	54 a	2.9 a	18 a	16 b	6.4 a	2.7 a
Lime + Phosphogypsum	2,203 a	55 a	3.0 a	19 a	18 a	6.1 a	2.7 a
Growing season							
2013	1,766 a	57 a	3.4 a	19 a	17 a	5.7 a	1.7 b
2014	1,440 b	48 b	2.2 b	19 a	10 b	4.2 b	3.4 a
F probability							
Treatments (T)‡	<0.0001	0.0047	0.0005	0.0786	<0.0001	<0.0001	0.0205
Growing season (G)	0.0254	<0.0001	<0.0001	0.1131	<0.0001	<0.0001	<0.0001
T x G	0.9781	0.4769	0.1249	0.1872	0.0981	0.2947	0.9240

	POP	PS	PP	GP	W100	PC	GY	SY
Treatments	**(x10^3 ha^{-1})**	**%**	**------- nº -------**		**g**	**g kg^{-1}**	**kg ha^{-1}**	**%**
Control	87 c	41 b	8.4 c	3.4 c	24.8 a	265 b	591 c	76 a
Phosphogypsum	80 c	37 b	8.8 c	3.3 c	23.3 a	249 c	492 c	78 a
Lime	139 b	56 a	13.0 b	3.9 a	24.3 a	283 a	1,630 b	60 b
Lime + Phosphogypsum	150 a	55 a	15.5 a	3.8 a	24.5 a	283 a	2,061 a	58 b
Growing season								
2013/2014	116 a	56 a	9.3 b	3.6 a	23.7 a	289 a	950 b	69 a
2014/2015	111 a	39 b	13.6 a	3.5 a	24.8 a	251 b	1,438 a	67 a
F probability								
Treatments (T)	<0.0001	<0.0001	<0.0001	0.0033	0.2069	<0.0001	<0.0001	0.0001
Growing season (G)	0.0918	<0.0001	<0.0001	0.2594	0.0999	<0.0001	<0.0001	0.2055
T x G	0.2163	0.5671	0.0867	0.1233	0.7230	0.9763	0.0983	0.2685

†Values followed by the same letter within a column are not significantly different at $p \leq 0.05$ according to the LSD test.

‡The amendments rates have been applied three times (2002, 2004, and 2010).

2.4.3.3. Yield components, technological characteristics, and grain yield

As observed for wheat, the soil amendments treatments and growing season affected the common bean development (Table 6). Compared with the control treatment, the results indicated that surface application of lime + PG was effective at increasing the plant population, plant survival, pods per plant, grains per pod, protein content, and grain yield by up 72%, 34%, 84%, 12%, 7%, and 248%, respectively. However, compared with what was observed for wheat, the combination of both soil amendments provided greater final plant populations and pods per plant compared with the application of lime alone and resulted in the greatest grain yields. Despite these results, the lime application negatively affected the grain size and reduced the sieve yield (grains retained on the 12/64" x ¾ sieve).

The plant population was not affected by the growing season, although the plant survival was greater during the first year. Despite a similar plant population for both seasons, the grain yield was higher in the second growing season because of a greater development of pods per plant; however, the protein concentration in the grains was lower.

2.5. Discussion

The surface application of lime to undisturbed acid soil was considered a viable practice for improving the chemical attributes and alleviating the acidity of a tropical Oxisol profile conducted under NTS over a 12-year experimental period in a region with dry winters, frequent dry spells during rainy season, and an annual average maximum temperature of 26ºC. In a trial conducted under a clayey Oxisol, in a region with distinct climate characteristics, frequent frosts during winter, and an annual average maximum temperature of 22ºC, Caires et al. (2006a) found a limited effect of surface liming above a depth of 0.10 m five years after the amendment application, which indicated the slower reaction of calcium carbonate in deeper soil layers. In the same trial, Caires et al. (2011) confirmed a positive effect of lime applied superficially to a depth of 0.60 m eight years after application. However, the authors emphasize that no benefits of PG application were observed for the important soil chemical attributes of the acidic soils. Our long term results, however, suggest that PG is an important complement to liming, since the

PG reaction in lime-amended soil provided indirect effects that reduce the magnitude of soil acidification within the 0- to 0.10-m layer, which is where most of the wheat and common bean root systems are located (Figures 5B, 6C, and 6D), and it significantly reduced the exchangeable Al^{3+} levels in the 0 to 0.40 m layer.

Phosphogypsum is not considered effective at alleviating soil acidity (CAIRES et al., 2011), however several hypotheses have been advanced to explain how PG reduces soil acidification over time. Alva et al. (1990) attributed the result to a ligand exchange reaction between SO_4^{2-} and OH^- ions. According to these authors, a greater depletion of SO_4^{2-} in the soil solution by gypsum dissociation induced changes in the ionic strength of the solution, thereby increasing the adsorption of this anion on the soil colloid surface and affecting hydroxyl (OH^-) desorption from Al and Fe oxyhydroxides. Toma et al. (1999) only observed this effect for highly weathered soils with low levels of exchangeable Al, such as in the uppermost soil layers for the soil treated with lime and PG combined (Figure 2D). This hypothesis may explain why PG alone did not cause variations in the soil pH because high levels of exchangeable Al (> 7.5 $mmol_c\ dm^{-3}$) were observed in both soil samplings in this treatment (Figures 2C and 2D).

Other mechanisms underlying the reduction in soil acidification may be attributed to root proliferation and the metabolic function of root cells to maintain a cytoplasm pH close to neutrality (7.0-7.5). The increase in SO_4^{2-} and NO_3^- availability in the soil solution via the gypsum reaction (CRUSCIOL et al., 2016) may have improved the uptake of these anions by the root cells, resulting in higher OH- exudation in the rhizospheric zone (NYE, 1981). This theory can be confirmed by the lower SO_4^{2-} levels in the soil solution in the second soil sampling (48 months) and the higher plant development for the treatment that received PG in a combination with lime. Factors that affect the input of organic residues may also provide cation exchange surfaces, which contribute to reduced amounts of Al^{3+} and H^+ in the soil solution (GARBUIO et al., 2011).

Although PG is considered a good source of sulfate, lower levels of SO_4^{2-} were observed in the uppermost soil layers, when lime was applied together with PG (Figures 3C and 3D). This effect may have been caused by SO_4^{2-} uptake and a higher removal of S from the area because the plant development and grain yield were also higher in this treatment compared with the control, particularly for the common bean crop. Soratto

et al. (2013) reported a higher relative exportation of S by the crop, with the removal of almost 50% of all absorbed S along with the grains. Higher SO_4^{2-} levels were observed from 0.20 to 0.60 m for the treatments that received PG alone because the S removal in this treatment was lower compared to lime-amended soils. Churka Blum et al. (2013) observed significant SO_4^{2-} movement 3.5 years after surface application, even in a loamy Oxisol with a higher adsorption capacity.

The surface application of PG alone reduced the exchangeable Al^{3+} and had a more pronounced effect in the second soil sampling (48 months) (Figures 2C and 2D). Considering the amounts of SO_4^{2-} in the soil, this effect may have been caused by the reaction between SO_4^{2-} and Al^{3+}, which induced the formation of molecules such as $AlSO_4^{+}$. In addition, Carvalho and van Raij (1997) related that the PG effect of reducing the toxicity of Al^{3+} may be related to the presence of F^{-}, which is responsible for the formation of more stable molecules with Al compared with SO_4^{2-}. The lowest values of exchangeable Al^{3+} were obtained with the association of both soil amendments, and this effect may have been caused by the beneficial effect of lime and PG combined on soil pH changes because soluble Al^{3+} is negatively correlated with soil pH (-0.63; $p < 0.0001$) (ABREU JUNIOR et al., 2003). In addition to the direct pH effects, the lower levels of exchangeable Al^{3+} in the lime-amended soil may have been related to the high input of SOM (via the roots and shoots). In a trial conducted in two acidic soils at a soil solution with pH <5.0, Alleoni et al. (2010) observed that most of the Al present in the soil solution (approximately 70-80% of the total) was complexed to organic compounds exuded by the root cells or released by organic residue decomposition.

Although the statistical analysis did not show a significant effects of surface liming on the SOM content at first soil sampling (Figure 3A), significant increases was observed at 48 months, including in the deeper soil layers (Figure 3B). Plant growth (shoots and roots) represents a key process for increasing this important soil component (GARBUIO et al., 2011). Our results showed that liming significantly stimulated the root volume and increased the length density of both evaluated species (Figures 5A, 6A, and 6B), which increased the source of SOM. Based on previous studies, reducing soil acidity and neutralizing Al^{3+} activity are preponderant factors involved in root development. In a period with irregular rainfall and water stress, Caires et al. (2008) established that 3 $mmol_c$

dm^{-3} of exchangeable Al^{3+} was a critical value for wheat root growth, and it affected the root length density by up 20%. In addition to the root effects, the application of lime increased the quantity of aboveground biomass (shoot dry matter) of wheat and common bean by 125% and 93%, respectively.

In addition to the effect of lime on alleviating soil acidity and reducing Al^{3+} toxicity, the amelioration of other chemical attributes, such as exchangeable Ca^{2+} and Mg^{2+} and base saturation, also contributed to the SOM inputs. Regardless of whether PG is applied, surface liming is considered an effective practice for increasing Ca^{2+} and Mg^{2+} availability in all Oxisol profiles (Figures 3E, 3F, 4A, and 4B). In a subtropical Oxisol, similar results were observed by Caires et al. (2005) over a period of 10 years after liming. The authors indicated that the practice was viable at a depth of 0 to 0.20 m, which is appropriate for regions with a low probability of water stress. In regions such as the Brazilian Cerrado and African Savannah, the amelioration of subsoil chemical attributes is essential for improving root development and reducing plant stress during dry spells periods.

The vertical displacement of basic cations, such as Ca^{2+} and Mg^{2+}, may be explained using the following theories: mobilization induced by complexation with organic species, physical migration of lime particles, and decomposition of Ca/Mg-organic molecules (FRANCHINI et al., 2003; AMARAL et al., 2004). In a trial conducted in a dystrophic clayey Oxisol, with high accumulation of organic residues on the soil surface, Zambrosi et al. (2008) observed an important contribution of organic anions to Ca leaching down to a depth of 0.6 m, since associations with inorganic ions, such as F^-, PO_4^{2-}, Cl^-, and NO_3^-, representing less than 1% of the total Ca complexed. However, because the reaction with polyvalent cations can change according to the variety of organic acids in the soil solution, certain organic residues may be more effective at forming stable complexes with these cations (FRANCHINI et al., 2003). Crop rotation is an important strategy for improving the efficiency of surface liming. The cultivation of species that have different plant architectures, associated with other management practices such as high organic residue inputs and minimum soil mobilization, help to improve the soil structure, which positively affects the formation of vertical porous channels through chemical interactions

and biological activity (MACHADO; SILVA, 2001), with these channels physically displacing basic cations, such as Ca^{2+} and Mg^{2+}.

Despite the application of high rates of K fertilizer since the experiment was initially set up, the benefits of PG + lime observed in first soil sampling may have been related to the amount of organic residue added to the soil over time, which it would contribute to a higher rate of K cycling (Figure 4C). To prevent K losses, Rosolem and Calonego (2013) suggested that soil should remain cultivated or covered with organic residues, and in tropical regions, the quantity and quality of the mulch is essential to providing maximum soil protection. In addition, the authors emphasized that management practices that influence the concentration of organic acids in the soil solution help to prevent K^+ losses because these compounds can form stable complexes with K^+. However, due to K dynamics, in the second soil sampling (48 months), lowest K^+ levels were observed in the soil treated with lime + PG (Figure 4D). The effect of soil amendments combination on the plant development and shoot dry matter production, as observed for wheat, and the amount of K extracted by Poaceas species show that a considerable amount of K may exist in crop residues pool. In a red distroferric Oxisol with 0.4 $mmol_c\ dm^{-3}$ of K, Rosolem et al. (2005) observed a significant amount of K extracted by pearl millet (equivalent to 26.2 $kg\ ha^{-1}$ for each 8.0 t of residue produced).

Variations in the reduction of H^+ and exchangeable Al^{3+} and increase of basic cation levels (Ca^{2+}, Mg^{2+}, and K^+) had a positive effect on the base saturation (Figures 4E and 4F). Significant effects of PG and lime combination in the uppermost soil layers (from 0 to 0.20 m) were observed. Caires et al. (2006a) emphasized a close relationship between pH ($CaCl_2$) and base saturation in the same soil depths (0 to 0.05 m, $r^2 = 0.92$; 0.05 to 0.10 m, $r^2 = 0.90$; and 0.10 to 0.20 m, $r^2 = 0.82$), whereas our results showed significant changes in the soil pH. The amelioration of the cation exchangeable complex (increasing proportion of basic cations) was essential to improving the plant development of both crops, particularly the root structure. In addition to base saturation, Caires et al. (2006b) observed that root growth was primarily favored by reductions in the soil acidity and increases in the exchangeable Ca^{2+}. This theory can be confirmed by the root development of common bean observed here.

The combination of PG and lime did not affect the wheat root length density (Figure 5A), although it promoted greater root development for the common bean crop at the between row locations in the 0- to 0.05- and 0.05- to 0.10-m layers (Figure 6B). This effect may have been caused by the higher Ca availability in the uppermost soil layers and the nutritional requirements for each species. Compared with the wheat plants, the common bean crops showed a higher demand for this cation. According to Soratto et al. (2013), the absorption per hectare may range from 34 to 69 kg for Ca. Otherwise, the amount of Ca accumulated by winter wheat plants during all cycles was approximately 33 kg ha^{-1}, although the demand can change according to the soil type, cultivar, weather conditions and irrigation and fertilization levels (PREEZ; BENNIE, 1991). Wissemeier and Horst (1995) observed that increasing the Ca supply through $CaSO_4$ additions enhanced the soybean root elongation in the presence and absence of exchangeable Al^{3+}, which can be explained by the increased common bean root length in the 0.20- to 0.40-m layer through the addition of PG alone.

The amelioration of chemical attributes throughout the entire soil profile provided a significantly greater root architecture for both species, particularly in the wheat crop, which presented a lower root system concentration at the soil surface and a higher concentration at deeper layers (Figures 5B and 6D). In a region with better rainfall distributions and lower water evaporation rates, Caires et al. (2008) observed an increase in the proportion of roots below the 0.20-m layer, which is a fundamental characteristic for reducing the negative effects of dry spells on grain yield, particularly in regions such as the Brazilian Cerrado and the African Savannah, where dry spells are commonly observed during the rainy season. In addition, Caires et al. (2006b) suggested that exchangeable Al^{3+} and Al^{3+} saturation are the most closely correlated chemical factors with root growth.

Compared with the control treatment, the lower root diameter at the 0- to 0.05-m layer observed in the soil treated with lime (for common bean at the in-row location only) may have been caused by the physiological mechanism that prevents root cell damage under high levels of exchangeable Al^{3+} ($\geq$ 10 $mmol_c$ dm^{-3}). In a study conducted using snapbean cultivars, Miyasaka and Hawes (2001) observed that Al toxicity induces the synthesis of a mucilage layer in the root border cells, and this layer may influence the physical characteristics of the roots. This physiological response can also

explain the effect of growing season on the root diameter because the exchangeable Al^{3+} levels in the soil increased over time between both soil samplings (Tables 3 and 5). The effect of soil amendments on the root diameter can also be explained by a regulatory mechanism between the root elongation rates and root diameter, and these characteristics may vary according to the balance of root types in each soil layer (CAHN et al., 1989). This theory may explain the higher root diameter in the deeper layers of soil treated with the amendments.

The growing season also had a significant effect on the root growth of both species. In the case of wheat, although both growing seasons received similar rainfall amounts, the higher root length density observed in the 0- to 0.05- and 0.05- to 0.10-m layers in the first year may be a result of variations in the soil temperature (Table 3). Our results showed an average maximum air temperature of 23.1ºC in the first growing season and 26.0ºC in the second season, and these temperatures can be related with soil temperature (Figure 1). Because the optimal soil temperature for wheat root growth is below 20°C (PORTER; GAWITH, 1999), this climatic variability promoted lower root length densities at the uppermost surface layers during the second growing season; however, greater development occurred in the deeper soil layers.

The higher common bean root length density observed in the first growing season (Table 4) may have occurred because of rainfall precipitation levels, which were lower (185 mm) than the rainfall levels during the second cycle (772 mm) (Figure 1). Higher root length density is considered to be important defense mechanism against water deficits during stages with high metabolic activity. Studying the effects of water limitation on *Lupinus albus* root growth, Chaves et al. (2002) observed that water stress may stimulate the fine root length of herbaceous annuals species, including in the deeper soil layers, including the 0.20- to 0.40-m and 0.40- to 0.60-m layers. The greater intensity of root growth at the uppermost layer (0 to 0.05 m) resulted in a higher root concentration in the soil surface during the first growing season.

As observed for the roots, the aboveground plant growth of wheat and common bean was positively influenced by the surface application of lime (Tables 4 and 6). For common bean, the absence of a PG + lime effect may have been caused by the reduced soil acidity and improved root structure associated with the adequate mineral

nutrition observed in both treatments. In wheat, the concentrations of N, Ca, and Mg in the flag leaves increased in the soil treated with lime only, and regardless of the PG addition, these nutrients were within the adequate range (for Ca and Mg) or above the adequate range (for N) (CANTARELLA et al., 1997). Despite the lower concentration of K in the flag leaves of the lime-amended treatments compared with the control treatment, 16 g of K kg^{-1} is considered appropriate according to Cantarella et al. (1997). Castro and Crusciol (2013) suggested that competition may occur in the cation uptake, however, this result was most likely caused by a dilution effect resulting from the higher shoot growth, which can also explain the lower concentration of N, K, Ca, and Mg in the leaves in the first growing season, which presented higher aboveground plant growth compared with the second year. Although the results did not indicate effects of the growing season or soil amendments on the P and S concentrations in the leaves, these nutrients are also considered to fall within the adequate range in both years (CANTARELLA et al., 1997), which may have been associated with the small effect of the soil amendments on the availability of these nutrients in the soil. In upland rice sown one month after PG application, Soratto and Crusciol (2008) observed a higher concentration of S in the flag leaves because of the addition of gypsum to the soil; however, our long-term results did not emphasize this effect. The authors also emphasized that the P concentration in the rice flag leaves was not influenced by recent applications of lime and PG combined.

The effects of surface liming on the shoot dry matter and concentrations of N, Ca, and Mg were also observed in the common bean leaves, however, in this specie, lime additions improved the S uptake by the plants. In the lime-amended soil, the macronutrient concentrations in the leaves were within (for P, Ca and S) or above (for N and Mg) the adequate range (AMBROSANO et al., 1997) except for K, which showed concentrations that were below the range. In a short-term experiment conducted in an acid clayey Oxisol under similar climate conditions, Castro and Crusciol (2013) did not observe improvements in the concentrations of N, P, Mg, and S in the common bean leaves at 18 months after surface application of lime and silicate. However, the authors emphasized that both soil amendments favored the shoot dry matter production.

The higher concentrations of N, P, Ca, and Mg in the common bean leaves during the first growing season may have been related to the high transpiratory flux

caused by the higher leaf mass per area. In the common bean cycle, rainfall occurred at lower levels (185 mm) than in the second growing season (772 mm); however, certain plant species, such as soybean, maintain a high leaf-water potential, which is responsible for dry matter accumulation and nutrient uptake (TANGUILIG et al., 1987). In addition, the higher root length density at the surface soil layers (0 to 0.05 m and 0.05 to 0.10 m) observed in the first growing season could have increased the water and macronutrient uptake. Despite these mechanisms, the S concentration in the common bean leaves was reduced, which may have been related to antagonistic processes that most likely involve anion uptake.

Our study sites were located in a tropical region with dry winters, and our long-term results showed that surface liming in an Oxisol with low levels of CEC and SOM is an effective method of increasing plant growth and positively influencing the plant nutrition, technological characteristics, yield components, and grain yield (Tables 4 and 6). Several factors contributed to the increased production and quality of the wheat and common bean grains, particularly the reduction in soil acidity (H^+ activity and exchangeable Al^{3+}), higher accumulation of organic matter and supply of Ca and Mg, increase in the base saturation, and improvements to the root growth (CAIRES et al., 2005; FARHOODI; COVENTRY, 2008; CASTRO; CRUSCIOL, 2013). Caires et al. (2006b) observed that the root length density and certain soil chemical attributes, such as pH and exchangeable Al^{3+} and Ca^{2+} levels, were the main determining factors for the crop yield potential, which may directly impact the grain quality.

Under limited rainfall during wheat development, Caires et al. (2008) showed that root elongation to a depth of 0.20 m is essential for improving wheat grain yields. Our results showed that despite a higher wheat root length density and better root distribution in the subsurface layers (0.10 to 0.20 m and 0.20 to 0.40 m), the wheat grain yield was lower in the second growing season, which was most likely related to the amount of water available in the soil during the different development stages of the crop. Therefore, despite a similar amount of rainfall registered in both growing seasons (269 and 253 mm, respectively), the higher number of rain episodes preceding the wheat flowering phase increased the plant height, ear length, ear number per square meter, spikelets per ear, 1,000-grain weight and grain yield. According to Gupta et al. (2001), these results may be

related to water availability in the soil during the boot and anthesis stages, which are more sensitive to water stress.

As observed for the wheat crop, surface liming improved the quality (protein content) of the common bean grains. However, the effects of liming on certain main yield components, such as the final population and number of pods per plant, and the grain yield were increased when PG was associated with lime (Table 6). This effect was most likely related to the effect of PG on root growth in the between-row locations, specifically in the 0- to 0.05-m and 0.05- to 0.10-m layers, with the application promoting improved exploration of the soil volume and affecting the water absorption in these soil layers. Usually, reduced grain yields in common bean cultivars are related to water stress during the flowering and pod-filling stages (BOUTRAA; SANDERS, 2001). The lower grain yield observed in the first growing season may have been caused by the lower rainfall regime during the first common bean cycle (185 mm) compared with that of the second growing season (772 mm) (Fig. 1).

The contribution of soil amendments to the improved common bean yield per plant negatively affected the grain size and reduced the percentage of grains retained on the sieve (12/64" x ¾; 4.76 x 19.05 mm) (Table 6). In the treatments without lime application, the number of grains per plant was reduced. Consequently, the competition among photoassimilates in these structures was lower, which resulted in a proportionally greater grain volume for the common bean cultivated in soils with higher acidity. This physiological mechanism was confirmed by Cancellier et al. (2011).

2.6. Conclusions

Surface application of lime was considered an appropriate practice in alleviating subsoil acidity, reducing Al^{3+} toxicity, improving Ca^{2+} and Mg^{2+} availability, and increasing SOM accumulation in all soil profiles at depths of up to 0.6 m. Our results suggested that phosphogypsum is an important complement to liming because soil amendments combination reduced the soil acidification process and promoted the highest levels of Ca^{2+} and Mg^{2+} and highest values of base saturation in the topsoil layers (0 to 0.10 m) over time. Despite the beneficial effects of PG on the soil fertility, positive effects of its combination with lime were only observed for common bean root growth, which showed

higher root length densities per soil volume at the uppermost soil layer (0 to 0.10 m). For common bean, the effects of adding PG included the increased development of the plants and reproductive structures, which increased the common bean grain yield. For wheat, adding PG did not have an effect, whereas surface liming was essential to improving the plant nutrition, grain yield, and wheat grain quality. Therefore, surface liming was an excellent strategy for improving tropical soil fertility, which can contribute to the sustainability of agriculture systems in highly weathered areas.

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Chapter 3

Impacts of lime and phosphogypsum applications on soil organic matter pools of a tropical Oxisol under long-term no-tillage system

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3.1. Abstract

Developments of strategies that improve soil organic matter (SOM) quality in tropical acid soils are considered a key factor to improve sustainability of agricultural ecosystems. This research aimed to evaluate the effect of surface application of lime and phosphogypsum (PG) on the quality and amount of SOM in a long-term no-till crop rotation. A field experiment was performed in an Oxisol which had been conducted under no-tillage system for 12 years with annual crop rotation. A randomized complete block design was used and four treatments (control, no soil amendments; 2.1 Mg PG ha^{-1}; 2.0 Mg lime ha^{-1}; and 2.0 + 2.1 Mg lime and PG ha^{-1}, respectively) were replicated four times. Since the experiment establishment, lime and PG rates were applied three times (2002, 2004, and 2010). Surface liming effectively increased SOM input via shoot and root growth up to 195 and 449%, according the specie and growing season. Although PG had no effect on plant biomass production, combination of PG with lime showed potential to increase N up to 50%, mainly in the surface. Surface liming increased total organic carbon (TOC) up to 30% from 0 to 0.40 m, while the combination with PG did not. However, PG addition in lime-amended soil increased the proportion of particulate organic carbon (POC) in TOC, which contributed to higher amounts of C mineralized (16.1, 14.7, and 11.6% of TOC at 0-0.05-, 0.05-0.10-, and 0.10-0.20-m, respectively). The proportion of TOC as humic and fulvic acid increased with surface application of lime and PG combined at depths above 0.10 m. Overall results suggested that PG is considered an important complement of surface liming, increasing labile and proportion of stable organic C pools.

Key words: limestone, phosphogypsum, root dry matter, humic substances

3.2. Introduction

The expansion of conservation agriculture is considered important for reducing soil degradation. Due to the environmental advantages, management systems such as no-till (NT) stands out among many agricultural practices adopted in several global regions, especially in areas with dry seasons. Widespread adoption of NT is extensive throughout the world, especially in South America (66 million ha) and North America (54 million ha), growing by 19 and 35%, respectively, over the last eight years (FAO, 2015).

Positive results of tropical conservation agriculture are related to increased soil organic matter (SOM) pools, which is considered the main indicator of soil quality (Castro et al., 2015). In highly weathered soils, such as Oxisols and Ultisols, which are naturally infertile, SOM is the largest source of cation exchange capacity (CEC), and therefore influences nutrient availability. The CEC from SOM is a due to certain SOM pools (humic substances) that are rich in functional groups comprising 70-90% of CEC in these soils (ILLÉS; TOMBÁCZ, 2006). In addition, SOM has significant effects on soil physical properties that can improve crop productivity and prevent land degradation processes. In tropical areas with low SOM storage due to high decomposition rates of organic residues, the environmental and economic benefits of conservative agriculture have not been fully realized because of soil acidity issues that additionally reduce SOM input.

Soil acidity affects approximately 30-40% of the world's arable land (VON UEXKUELL; MUTERT, 1995). Chemical characteristics associated with acid soils such as deficiencies of essential nutrients (such as Ca^{2+} and Mg^{2+}), and Al and/or Mn toxicity are considered major factors that reduce SOM input (GARBUIO et al., 2011). Caires et al. (2006) showed that low availability of basic cations associated with high levels of exchangeable Al in highly weathered soil frequently limited plant growth, and consequently reduced the amount of organic residues added to the soil. In addition to SOM input, Briedis et al. (2012) found that polyvalent cations are fundamental to stabilize SOM by physio-chemical mechanisms. Therefore, increasing SOM storage in these soils will require management techniques to alleviate soil acidity, neutralize toxic elements, and increase base saturation throughout the soil profile.

Application of lime materials is the most common and efficient practice for reducing soil acidity in NT systems; in addition, the liming material is often a good source of Ca and Mg for deficient soils (FAGERIA; NASCENTE, 2014). However,

since Ca and Mg carbonates have relatively low solubility in soils, PG has been studied by several researchers as a possible complement to liming. Phosphogypsum may reduce Al toxicity and increase Ca availability in subsurface soil layers (SUMNER et al., 1986; SORATTO; CRUSCIOL, 2008; CAIRES et al., 2011; CRUSCIOL et al., 2016), improve root growth, and as a consequence, shoot development. This increased root and shoot growth serves as an input source for SOM (OATES; CALSWELL, 1985; HAYNES et al., 1998).

Some long-term studies have confirmed the potential of surface lime applications to increase organic carbon (OC) storage in highly weathered tropical soils by increasing plant growth and therefore SOM input (BRIEDIS et al., 2012; CASTRO et al., 2015). However, there is few scientific information supporting improvements on OC quality and stability by surface application of lime and PG in tropical areas with frequent dry spells. Furthermore, authors such as Garbuio et al. (2011) stress the importance and necessity of scientific studies that determine the long-term impact of soil amendments on OC stability. New strategies that increase OC storage in soil profile, and increased agriculture sustainability is considered a key factor to reduce economic costs and environmental impacts of agricultural production. Therefore, this study aimed to evaluate the effect of surface application of lime and PG on the content and quality of SOM in a long-term experiment under no-tillage.

3.3. Material and Methods

3.3.1. Site Description

The experiment was conducted in São Paulo State, Brazil (48° 23′ W, 22° 51′ S and 765 m), under no-till management during a 12-year experimental period. Soil was classified as a sandy clay loam kaolinitic, thermic Typic Haplorthox (USDA, 1999). According to Köeppen's classification, the climate is Cwa, with a dry winter and hot wet summer. The annual average maximum and minimum temperature are 15.3 and 26.1ºC, respectively, with monthly rainfall averages between 37.7 and 224 mm, and accumulated precipitation of 1,359 mm in which 75% occurs from October to March.

Before the establishment of the experiment (2002), chemical attributes were determined (0-0.20 m) according to the methodology proposed by van Raij

et al. (2001), and granulometric analysis according to Kiehl (1979). The soil pH was determined in a 0.01 mol L^{-1} $CaCl_2$ suspension (1:2.5 soil:solution). Soil organic matter was determined by chromic acid digestion, according to the method proposed by Heanes (1984). The total acidity at pH 7.0 (H, Al) was extracted by calcium acetate 0.5 mol L^{-1} at pH 7.0 and determined by titration with 0.025 mol L^{-1} NaOH solution. Exchangeable Al was extracted with neutral 1 mol L^{-1} KCl at a 1:10 soil:solution ratio and determined by titration with 0.025 mol L^{-1} NaOH solution. The available P and exchangeable basic cations (Ca_{ex}, Mg_{ex}, and K_{ex}) were extracted using an ion-exchange resin (VAN RAIJ et al., 1986). Phosphorus concentrations in extracts were determined by a colorimetric method (MURPHY; RILEY, 1962) with a FEMTO 600S spectrophotometer. Concentrations of Ca^{2+}, Mg^{2+}, and K^{+} in extracts were determined by an atomic absorption/Flame-Emission spectrophotometer (Shimadzu AA-6300). Cation exchange capacity (CEC) was obtained by sum of the individual cations (H, Al, K, Ca, and Mg). The base saturation (BS) values were calculated by dividing the sum of the equivalents of K, Mg, and Ca (the bases) by the CEC and multiplying by 100 (VAN RAIJ et al., 2001).

At the beginning of the experiment (2002) the topsoil (0-0.20 m) showed the following chemical and textural characteristics: organic matter, 20.9 g dm^{-3}; pH (1:2.5 soil/$CaCl_2$ suspension 0.01 mol L^{-1}), 4.2; P (resin), 9.2 mg dm^{-3}; exchangeable K, Ca, and Mg 1.2, 14, and 5 $mmol_c$ dm^{-3}, respectively; total acidity in pH 7.0 (H + Al) 37 $mmol_c$ dm^{-3}, cation exchange capacity (CEC) 58 $mmol_c$ dm^{-3}; base saturation 35%; sand, silt, and clay contents of 54, 11, and 35%, respectively. In the subsoil (0.20-0.40 m) clay content was 36%.

3.3.2. Experimental Design and Treatments Establishment

A randomized complete block design was used with four replications. Each plot was 46.8 m^2 (5.2 m x 9.0 m). The treatments were composed of: (i) control (no lime and PG), (ii) PG (2.1 Mg ha^{-1}), (iii) lime (2.0 Mg ha^{-1}) and (iv) 2.0 Mg ha^{-1} lime and 2.1 Mg ha^{-1} PG. The lime rate (R) was chosen to increase the base saturation in topsoil (0-0.20 m) to 70%, as calculated in Eq. [1] (CANTARELLA et al., 1998).

$$R\ (Mg\ ha^{-1}) = (BS_{target} - BS).CEC\ /\ (ECCE.10) \quad [1]$$

where ECCE is the effective calcium carbonate equivalent of the dolomite; BS_{target} is the target base saturation (70%); BS is the base saturation determined in soil chemical analysis.

The PG rate (PR) was calculated using Eq. [2], according method proposed by van Raij et al. (1997).

$$PR\ (kg\ ha^{-1}) = 6.CL \quad [2]$$

where CL is the clay content (g kg^{-1}) in the 0.20- to 0.40-m soil layer.

During the study period, the treatments were applied three times, and different species were cropped in season and off season from 2002 to 2015. Details of the crop sequences and fertilizer management are shown in Table 1.

Table 1. Crops grown during the study period and the treatment application scheme during the experimental period (from 2002 to 2015).

Season	Crops		Treatment application
	Summer crop	Autumn-winter-spring crop	
2002/2003	***Oriza sativa*** **(cv. Caiapó)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 50 kg of N ha^{-1}	***Avena strigosa*** **(cv. Comum)** BF: 200 kg ha^{-1} of NPK 10–20–10 + 4.5% S	Lime: 2,700 kg ha^{-1} (71% ECCE)† Gypsum: 2,100 kg ha^{-1}
2003/2004	***Phaseolus vulgaris*** **(cv. Pérola)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 110 kg of N ha^{-1}	***Avena strigosa*** **(cv. Comum)** BF: 200 kg ha^{-1} of NPK 04–20–20 + 7% S	
2004/2005	***Arachis hypogaea*** **(cv. Runner IAC 886)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn.	***Avena sativa*** **(cv. IAC 7)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 110 kg of N ha^{-1}	Lime: 2,000 kg ha^{-1} (71% ECCE) Gypsum: 2,100 kg ha^{-1}
2005/2006	***Arachis hypogaea*** **(cv. Runner IAC 886)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn.	***Avena sativa*** **(cv. IAC 7)** BF: 8 kg ha^{-1} of N + 40 kg ha^{-1} P_2O_5 + 20 kg ha^{-1} of K_2O + 7% S	
2006/2007	***Zea mays*** **(cv. 2B570)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn. TF: 90 kg of N ha^{-1}	***Urochloa brizantha*** **(cv. Marandu)** The forage seeds were simultaneously sown with corn.	
2007/2008	***Zea mays*** **(cv. 2B570)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn. TF: 90 kg of N ha^{-1}	***Urochloa brizantha*** **(cv. Marandu)** The forage seeds were simultaneously sown with corn.	
2008/2009	***Glycine max*** **(cv. MGBR-46)** BF: 250 kg ha^{-1} of NPK 04–20–20 + 4.5% S + 0.5% Zn.	***Avena strigosa*** **(cv. Comum)** No fertilizer was applied	
2009/2010	***Glycine max*** **(cv. CD216)** BF: 250 kg ha^{-1} of NPK	***Sorghum vulgare*** **(cv. AG1020)** No fertilizer was applied	

	04–20–20 + 4.5% S + 0.5% Zn.		
2010/2011	***Zea mays*** **(cv. 2B433)** BF: 350 kg ha^{-1} of NPK 08–28–16. TF: 150 kg of N ha^{-1}	***Crambe abyssinica*** **(cv. FMS Brilhante)** BF: 150 kg ha^{-1} of NPK 08–28–16	Lime: 2,000 kg ha^{-1} (88% ECCE) Gypsum: 2,100 kg ha^{-1}
2011/2012	***Zea mays*** **(cv. 2B433)** BF: 350 kg ha^{-1} of NPK 08–28–16. TF: 150 kg of N ha^{-1}	***Crambe abyssinica*** **(cv. FMS Brilhante)** BF: 150 kg ha^{-1} of NPK 08–28–16	
2012/2013	***Pennisetum glaucum*** **(cv. ADR300)** No fertilizer was applied	***Triticum aestivum*** **(cv. CD116)** BF: 75 kg ha^{-1} of N + 70 kg ha^{-1} P_2O_5 + 40 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn.	
2013/2014	***Phaseolus vulgaris*** **(cv. Pérola)** BF: 10 kg ha^{-1} of N + 50 kg ha^{-1} P_2O_5 + 50 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn. TF: 100 kg of N ha^{-1}	***Triticum aestivum*** **(cv. CD116)** BF: 75 kg ha^{-1} of N + 70 kg ha^{-1} P_2O_5 + 40 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn.	
2014/2015	***Phaseolus vulgaris*** **(cv. Pérola)** BF: 10 kg ha^{-1} of N + 50 kg ha^{-1} P_2O_5 + 50 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn. TF: 100 kg of N ha^{-1}		

†The reapplications in October of 2004 and 2010 were performed when the standard treatment (calculated rate) reached base saturation ≤ 50%. BF: base fertilization; TF: topdressing fertilization.

3.3.3. Plant sampling and analyses

Plant analyses were performed on wheat and common bean grown in 2013/2014 and 2014/2015 seasons. Wheat cultivar, CD 116, was sown on 18 Apr. 2013 and 12 Mar. 2014 (fall-winter growing period), at a density of 80 seeds m^{-1}, with 0.17 m spacing between rows. Wheat fertilization was performed at sowing with 40 kg N ha^{-1} as urea + 250 kg ha^{-1} of NPK 14–28–16 + 0.5% Zn + 4.5% S (CANTARELLA et al., 1997). Common bean cultivar Pérola was sown on 28 Nov. 2013 and 01 Dec. 2014 (summer growing period) using a row spacing of 0.45 m with 16 seeds m^{-1} in each row. Fertilizer was applied at sowing at the following rate: 250 kg ha^{-1} of N-P_2O_5-K_2O 4-20-20 + 0.5% Zn. Nitrogen (N) topdressing was performed at a rate of 100 kg N (as ammonium nitrate) ha^{-1} at stage V_4 (third trifoliate leaf expanded), as recommended by Ambrosano et al. (1997).

In both crops, growing seasons, and at each flowering stage, shoot and root parts were collected. Ten random plants per plot were removed for shoot dry matter determination. Root growth was measured via eight individual soil samples randomly collected from in-row (4) and between row (4), of each plot, to form a composite

sample. Soil samples were taken at 0-0.05, 0.05-0.10, and 0.10-0.20 m depths with a 69-mm diam. cutting tip soil probe. For soil samples collected at 0.20-0.40 m, a 49-mm diam. cutting tip probe was used. Roots were carefully separated from the soil and other residues by washing under a flow of swirling water, according to the method described by Oussible et al. (1992). Shoot and roots samples were dried in a forced air oven at 65 ºC for 72 h and weighed for dry mass determination.

3.3.4. Soil sampling and chemical analyses

Twelve years after experiment establishment, soil samples were randomly collected from 0 to 0.40 m depth with a soil probe two months after wheat harvest (Oct. 2014). The samples were air-dried, sieved (2-mm) and analyzed according to van Raij et al. (2001) to determine chemical properties (exchangeable Al^{3+}, Ca^{2+}, Mg^{2+}, and base saturation).

Total organic carbon (TOC) and total nitrogen (TN) was measured using an elemental analyzer (LECO-TruSpec1 CHNS). Soil organic matter physical fractionation was performed according to the method proposed by Cambardella and Elliot (1992). A 20 g soil sample (air-dried and sieved through 2-mm mesh) was homogenized in 80 mL sodium hexametaphosphate solution (5 g L^{-1}). Samples were shaken horizontally for 15 h, and sieved through 0.053-mm mesh sieves using deionized water. Retained material was transferred to aluminum dishes and dried at 45º C in a forced-air oven until constant mass, followed by grinding with a porcelain mortar and pestle and homogenized. Particulate nitrogen (PN) and particulate organic carbon (POC) was measured via dry combustion with the elemental analyzer, and is the N and C content in the 0.053-2 mm soil fraction. The mineral-associated organic carbon (MOC) was calculated by the difference between TOC and POC.

Chemical fractionation of soil organic matter was determined according to the method described by Ciavatta et al. (1990), using Superlite DAX-8 resin to separate non-humified substances from humic fractions. Ten g soil samples (air-dried, sieved through 2-mm mesh, and without litter fraction) were weighed in 250-mL centrifuge tubes, in which 100 mL of 0.1 M NaOH plus 0.1 M $Na_4P_2O_7$ was added. Nitrogen gas was bubbled through the solution for 2 min to purge carbon dioxide, and then the samples were

shaken for 2 h at 160 oscillations per minute followed by centrifugation at 14,000 RPM for 25 min. The suspension was filtered through a 0.45-µm millipore filter. The remaining solids (humin and minerals matter) were stored for subsequent analysis. Twenty-five mL of the extract was transferred into a centrifuge tube and acidified to pH < 2 by slowly adding 9-10 mL of 0.5M H_2SO_4, followed by centrifuging at 9,000 RPM for 25 minutes. The precipitate (humic acid fraction, HA) was separated and redissolved with 20 mL of 0.3M NaOH and stored for C determination. The supernatant solution was slowly applied to a column (a common 60-ml plastic syringe) containing about 6 cm^3 of Superlite DAX-8 resin previously equilibrated in 0.005 M H_2SO_4. The eluate (non-humic substances) was discarded and the column was eluated with 20 ml of 0.005 M H_2SO_4. The retained fraction (fulvic acid fraction, FA), generally brown in color, was eluated using 20 mL of 0.5 M NaOH, discarding the first 3 ml, and collected in 125-mL glass bottle for C determination.

Organic C in humin (C-HU), humic (C-HA) and fulvic acid (C-FA) solutions were determined by a wet oxidation method adapted from Heanes (1984). One g (for solid) or 15-mL (for liquid) of each sample was placed in a 125-mL Erlenmeyer flask, in which 10 mL of $K_2Cr_2O_7$ solution (49.02 g L^{-1}) and 20 mL of 98% H_2SO_4 were carefully added while manually agitating. After three hours, DI water was added to approximately the 50 mL mark of the Erlenmeyer flask. The solution was transferred to a volumetric flask and the final volume was adjusted to 100 mL with DI water. Organic carbon was measured using a Milton Roy Spectronic 21D spectrophotometer at 600nm. A standard curve was prepared using sucrose solution (4.754 g L^{-1}) containing 2 mg organic-C mL^{-1}.

Carbon mineralization was analyzed according to methodology described by Bernal et al. (1998). One-hundred g soil sample (air-dried and sieved through 2-mm sieve) was placed in incubation flasks (0.925-L Mason jars®). Distilled water was added to adjust the soil moisture to 70% of field capacity. To determine the amount of C released (i.e. OC mineralized), a 50-ml beaker with 20 ml of 0.3 M NaOH was placed on top of the soil in each incubation flask. Each incubation flask was kept sealed between sampling events. Periodically, the trapped OC was quantified by NaOH titration (using 0.5 M HCl as titrant) after 10 ml of 0.05 M $BaCl_2$ was added to the solution.

3.3.5. Statistical analyses

To further estimate OC in humic substances (C-HA, C-FA and C-HU) and COT, a conversion factor of 1.14 was used to convert the wet C analysis method to values from the dry combustion, as proposed by Rheinheimer et al. (2008). All data were analyzed using two-way ANOVA. The treatments were considered fixed effects. Significant differences between the means were determined using Fisher's protected LSD test. Effects were considered significant at $P \leq 0.05$ for shoot dry matter and SOM parameters, and $P \leq 0.10$ for root dry matter data. A higher probability for the root system evaluation was used because these characteristics are naturally more variable (FAGERIA; MOREIRA, 2011). Pearson's correlation analysis was conducted to investigate the relationship between soil chemical properties (pH, Al, Ca, Mg and base saturation) and OC pools in soil profile (0 to 0.40 m).

3.4. Results

In both crop species the shoot dry matter production was affected by treatments (Table 2). Regardless of growing season, shoot production from wheat and common bean were positively influenced by surface application of lime, with no significant effects from lime and PG combination. This demonstrated that lime alone provided better conditions for crop growth than PG alone, at 12 years after treatment establishment and 48 months from last reapplication. With regard to the influence of soil amendments on root dry matter development, significant effects were confirmed by probabilities of the calculated F-value ($p \leq 0.05$) (Table 3).

Table 2. Shoot dry matter of wheat and common bean affected by surface application of lime and phosphogypsum in a tropical Oxisol under no-tillage system. Lime and phosphogypsum rates were applied in 2002, 2004, and 2010.

Treatments	Shoot dry matter (kg ha^{-1})			
	Wheat (2013)	Wheat (2014)	Common bean (2013/2014)	Common bean (2014/2015)
	kg ha^{-1}			
Control	2,072 b†	1,021 b	1,303 b	980 b
Phosphogypsum	1,454 b	1,154 b	1,256 b	1,011 b
Lime	3,428 a	3,183 a	2,141 a	1,727 a
Lime + Phosphogypsum	3,949 a	3,020 a	2,362 a	2,044 a
ANOVA (*F probability*)				
Blocks	0.3525	0.3697	0.3242	0.5879
Treatments	<0.0001	<0.0001	0.0035	0.0019

† Values followed by the same letter are not significantly different between treatments (i.e. within column) at $P \leq 0.05$ according to the LSD test.

Table 3. Probabilities of the calculated F-value, coefficient of variation (CV), and least significant difference (LSD) for root dry matter of wheat and common bean at four different soil depths, sampled at the flowering stage for two growing seasons (2013/2014 and 2014/2015).

Layer (m)	*F probability*				CV(%)		LSD	
	Blocks		Treatments†					
	2013/2014	2014/2015	2013/2014	2014/2015	2013/2014	2014/2015	2013/2014	2014/2015
				Wheat				
0-0.05	0.2146	0.5719	0.0246	<0.0001	23.2	21.6	155.3	80.8
0.05-0.10	0.2174	0.4647	0.0001	0.0016	17.9	27.8	57.1	111.0
0.10-0.20	0.6065	0.8864	<0.0001	<0.0001	22.7	25.8	12.2	14.9
0.20-0.40	0.3203	0.3113	0.0014	<0.0001	33.1	29.5	10.8	19.1
				Common bean				
0-0.05	0.1626	0.5414	<0.0001	<0.0001	22.6	26.4	28.3	36.2
0.05-0.10	0.5689	0.2950	<0.0001	<0.0001	18.2	25.3	22.3	32.2
0.10-0.20	0.2513	0.3365	<0.0001	0.1218	15.4	20.3	14.4	26.3
0.20-0.40	0.3001	0.4903	<0.0001	<0.0001	23.4	18.1	9.3	5.5

†Treatments: control, phosphogypsum, lime, and lime + phosphogypsum.

Similar to shoot dry matter production, limestone provided a higher production of root dry matter in all soil layers evaluated, regardless of crop and growing season (Figures 1A, 1B, 1C, and 1D). As observed for shoot growth, the PG and lime combined did not significantly increase root dry matter, with exception in the first common bean season at the 0.05- to 0.10-m soil depth (Figure 1C). However, the application of PG alone did not significantly increase root production of common bean.

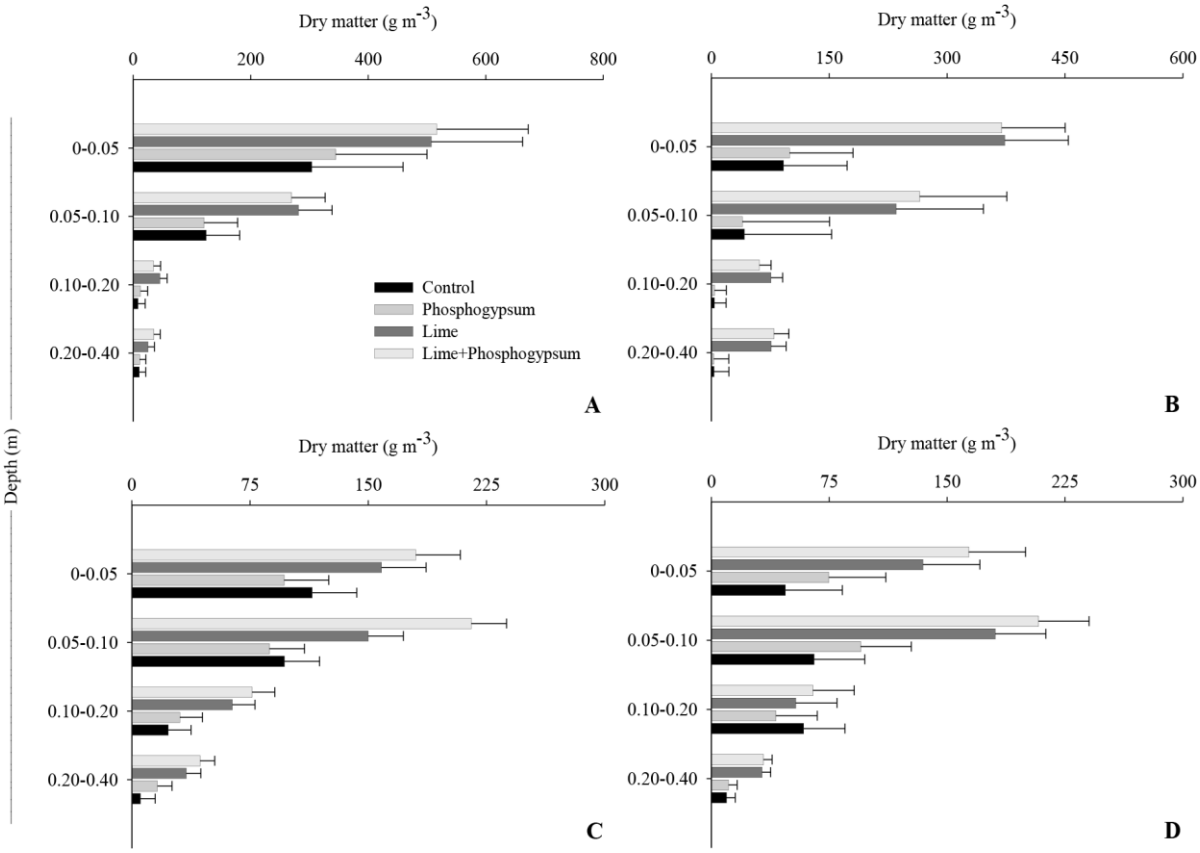

Figure 1. Root dry matter at several depths for wheat (A and B) and common bean (C and D) cultivated in two growing seasons (A and C: 2013/2014, B and D: 2014/2015) as affected by lime (□), phosphogypsum (▩), and limestone + phosphogypsum (■) and the corresponding levels of the control (□), at different depths. The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars indicate the least significant difference between amendments within each soil depth at $p \leq 0.10$.

There were significant effects ($p \leq 0.05$) of the treatments on nitrogen and organic pools in all soil layers evaluated (Table 4). Surface application of lime increased PN in the 0- to 0.05-m depth (Figure 2A), whereas this effect was not observed in the next lower depth (0.05 to 0.10-m), but the soil amendments application reduced PN below 0.10 m depth. Otherwise, the combination of both products increased the TN in all soil layers evaluated (Figure 2B), which was positively correlated to exchangeable basic cations (Ca^{2+} and Mg^{2+}) and negatively correlated to exchangeable Al in the soil profile (Table 5).

Table 4. Probabilities of the calculated F-value, coefficient of variation (CV), and least significant difference (LSD) for nitrogen and organic carbon pools at the soil depths of 0–0.05, 0.05–0.10, 0.10–0.20, and 0.20–0.40 m at 12 years after initial establishment of treatments[†].

Layer	*F probability*		CV(%)	LSD
(m)	Blocks	Treatments[‡]		
		N-Particulate		
0-0.05	0.5026	<0.0001	3.1	0.017
0.05-0.10	0.3482	<0.0001	5.1	0.016
0.10-0.20	0.2851	<0.0001	10.3	0.020
0.20-0.40	0.3112	<0.0001	8.8	0.025
		N-Total		
0-0.05	0.2629	<0.0001	2.9	0.033
0.05-0.10	0.7135	0.0002	6.1	0.047
0.10-0.20	0.8616	<0.0001	7.1	0.047
0.20-0.40	0.5800	0.0020	8.4	0.055
		C-Particulate		
0-0.05	0.2658	0.0027	9.4	1.372
0.05-0.10	0.5948	<0.0001	10.6	0.630
0.10-0.20	0.4738	<0.0001	8.3	0.159
0.20-0.40	0.6350	<0.0001	9.1	0.151
		C-Total		
0-0.05	0.3363	0.0016	6.8	1.863
0.05-0.10	0.2189	<0.0001	5.2	0.888
0.10-0.20	0.2047	0.0006	9.0	1.265
0.20-0.40	0.2321	0.0039	11.4	1.516
		C-Mineral-associated		
0-0.05	0.5742	0.0027	5.4	1.027
0.05-0.10	0.3472	0.0168	9.0	1.168
0.10-0.20	0.2873	0.0066	10.3	1.255
0.20-0.40	0.3499	0.0034	9.0	1.051
		POC/TOC ratio		
0-0.05	0.4234	0.0026	4.5	3.162
0.05-0.10	0.7725	<0.0001	7.1	2.631
0.10-0.20	0.1379	<0.0001	5.2	1.125
0.20-0.40	0.5972	<0.0001	8.1	1.573
		C-Humin		
0-0.05	0.9802	0.0004	12.2	2.781
0.05-0.10	0.6749	0.9212	11.6	1.192
0.10-0.20	0.2402	0.0201	14.1	0.689
0.20-0.40	0.5875	0.0125	13.9	0.870
		C-Humic acids		
0-0.05	0.3722	0.0011	5.8	0.111
0.05-0.10	0.3028	0.0011	10.5	0.102
0.10-0.20	0.1317	<0.0001	11.1	0.080
0.20-0.40	0.3044	0.0004	12.5	0.092

		C-Fulvic acids		
0-0.05	0.8780	0.0001	7.5	0.028
0.05-0.10	0.8976	0.0064	15.2	0.031
0.10-0.20	0.4168	<0.0001	5.9	0.022
0.20-0.40	0.9301	0.0013	13.1	0.032
		C-HU/TOC ratio		
0-0.05	0.4078	<0.0001	8.0	9.961
0.05-0.10	0.2868	0.0430	12.7	12.453
0.10-0.20	0.2398	0.5292	15.6	17.148
0.20-0.40	0.5806	0.8643	17.6	13.411
		C-HA/TOC ratio		
0-0.05	0.3442	0.4945	8.4	0.989
0.05-0.10	0.4622	0.2360	10.8	1.523
0.10-0.20	0.2724	0.0019	9.5	0.773
0.20-0.40	0.5636	0.0014	11.4	0.710
		C-FA/TOC ratio		
0-0.05	0.3077	0.0360	7.7	0.149
0.05-0.10	0.9613	0.0037	9.5	0.503
0.10-0.20	0.5065	0.0043	6.6	0.581
0.20-0.40	0.6157	0.0005	12.7	0.304

†POC: particulate organic carbon; TOC: total organic carbon; HU: humin; HA: humic acids; FA: fulvic acids.
‡Treatments: control, phosphogypsum, lime, and lime + phosphogypsum. The amendments rates have been applied three times (2002, 2004, and 2010).

Lime application, alone or in combination with PG, generally resulted in an increase in organic carbon (OC) pools in this Oxisol, as illustrated by higher POC, TOC, and MOC contents within 0- to 0.40-m depth, but the effect varied with soil depth (Figures 2C, 2D, and 2E). The application of PG alone did not result in greater inputs of crop residues (Table 2 and Figure 1), however, the combined application with lime provided a positive effect on POC, resulting in higher contents in the 0.05- to 0.10- and 0.20- to 0.40-m depth. In addition, it was observed that the POC/TOC ratio was greater when PG was applied combined to liming, suggesting the formation of SOM with greater lability. There were significant relationships between OC pools (except for MOC) and some soil chemical attributes (pH, exchangeable Al^{3+}, Ca^{2+}, Mg^{2+}, and base saturation) in all soil layers evaluated (Table 5).

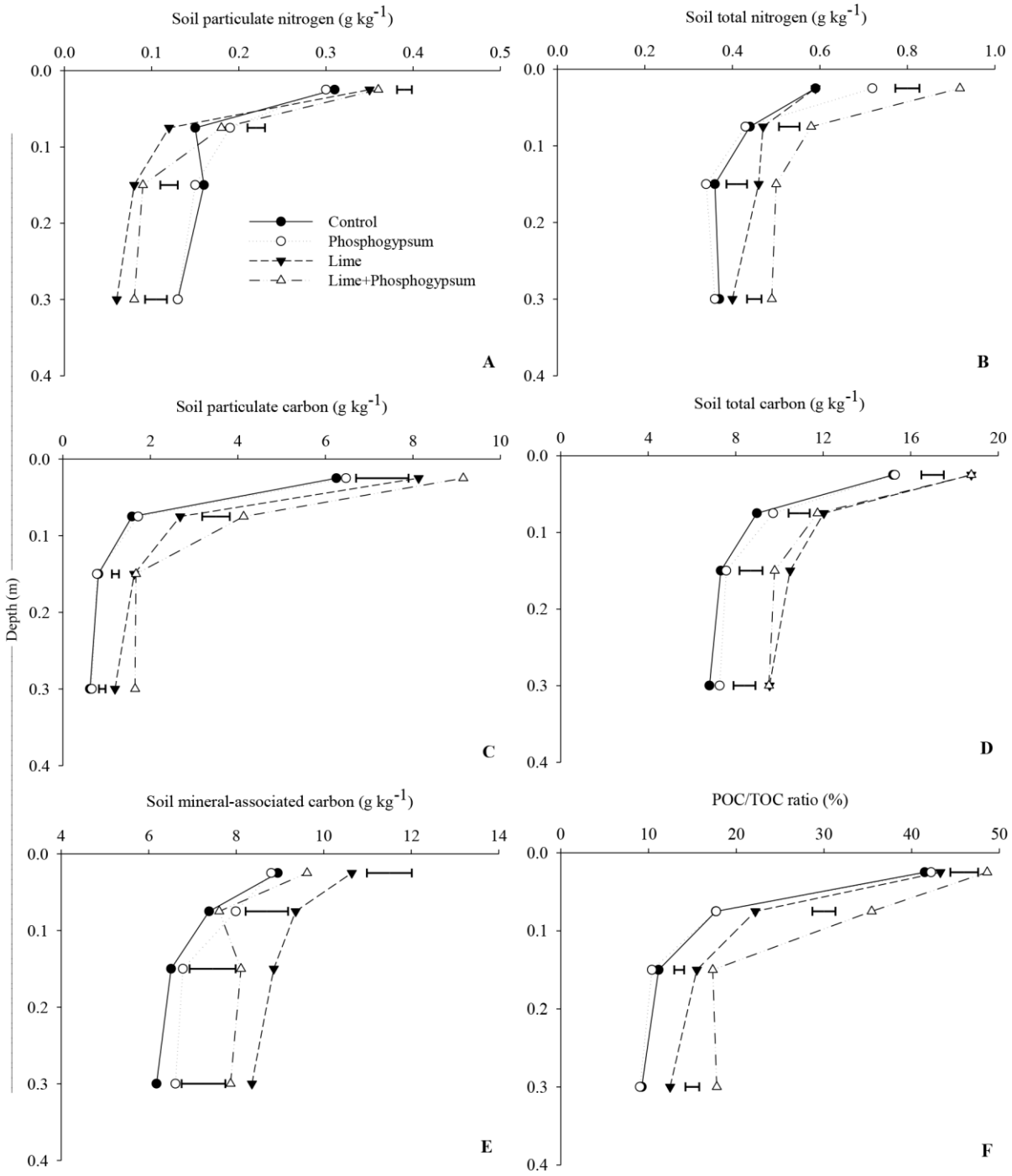

Figure 2. Soil particulate nitrogen (A), soil total nitrogen (B), soil particulate organic carbon (C; POC), soil total organic carbon (D; TOC), soil mineral-associated carbon (E), and POC/TOC ratio (F) as affected by lime (▼), phosphogypsum (○), and limestone + phosphogypsum (△) and the corresponding levels of the control (●).The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars indicate the least significant difference between treatments within each soil depth at $p \leq 0.05$.

Table 5. Probabilities of the calculated F-value (P) and Pearson correlation coefficients (r) between soil organic matter pools and soil chemical properties in soils treated with lime and gypsum applications in an Oxisol under long-term no-tillage experiment†.

	TOC		POC	
Parameter‡	**r**	**P**	**r**	**P**
pH	0.7852	<0.0001	0.9241	<0.0001
Al^{3+}	-0.8433	<0.0001	-0.9205	<0.0001
Ca^{2+}	0.8039	<0.0001	0.9448	<0.0001
Mg^{2+}	0.8376	<0.0001	0.9468	<0.0001
Base saturation	0.7870	<0.0001	0.9258	<0.0001
	MOC		**C-HA**	
	r	**P**	**r**	**P**
pH	0.4565	0.0752	0.8722	<0.0001
Al^{3+}	-0.5680	0.0224	-0.9180	<0.0001
Ca^{2+}	0.4599	0.0739	0.8645	<0.0001
Mg^{2+}	0.5186	0.0403	0.9013	<0.0001
Base saturation	0.4503	0.0807	0.8528	<0.0001
	C-FA		**C-HU**	
	r	**P**	**r**	**P**
pH	0.9012	<0.0001	0.8520	<0.0001
Al^{3+}	-0.9133	<0.0001	-0.8934	<0.0001
Ca^{2+}	0.9177	<0.0001	0.8583	<0.0001
Mg^{2+}	0.9418	<0.0001	0.8283	<0.0001
Base saturation	0.9187	<0.0001	0.8636	<0.0001

†Treatments: control, phosphogypsum, lime, and lime + phosphogypsum. The amendments rates have been applied three times (2002, 2004, and 2010).

‡TOC: total organic carbon; POC: particulate organic carbon; MOC: mineral-associated organic carbon; C-HA: organic carbon as humic acid; C-FA: organic carbon as fulvic acid; C-HU: organic carbon as humin.

Analysis of humic substances revealed important effects of the soil amendments on C-HA, C-FA, and C-HU in an Oxisol profile (Figures 3A, 3B, and 3C). Pearson's correlation analysis between the soil chemical properties and the amounts of OC in the form of humic substances shows that humification was favored by the increase in pH, exchangeable Ca^{2+} and Mg^{2+}, and base saturation, and by reduction of toxicity by exchangeable Al^{3+}. Phosphogypsum and lime applied in combination provided the highest values of C-FA and C-HU at 0- to 0.05-m and below to 0.10 m depth. In addition, the C-HA/TOC ratio and C-FA/TOC ratio showed that the simultaneous use of both products provided the greatest proportion of OC of lower lability in the subsurface layers (0.10- to 0.30-m depth), and positively affected the quality of SOM at 0-0.05 m layer through higher proportions of OC as humic substances (FA and humin) (Figures 3D, 3E, and 3F).

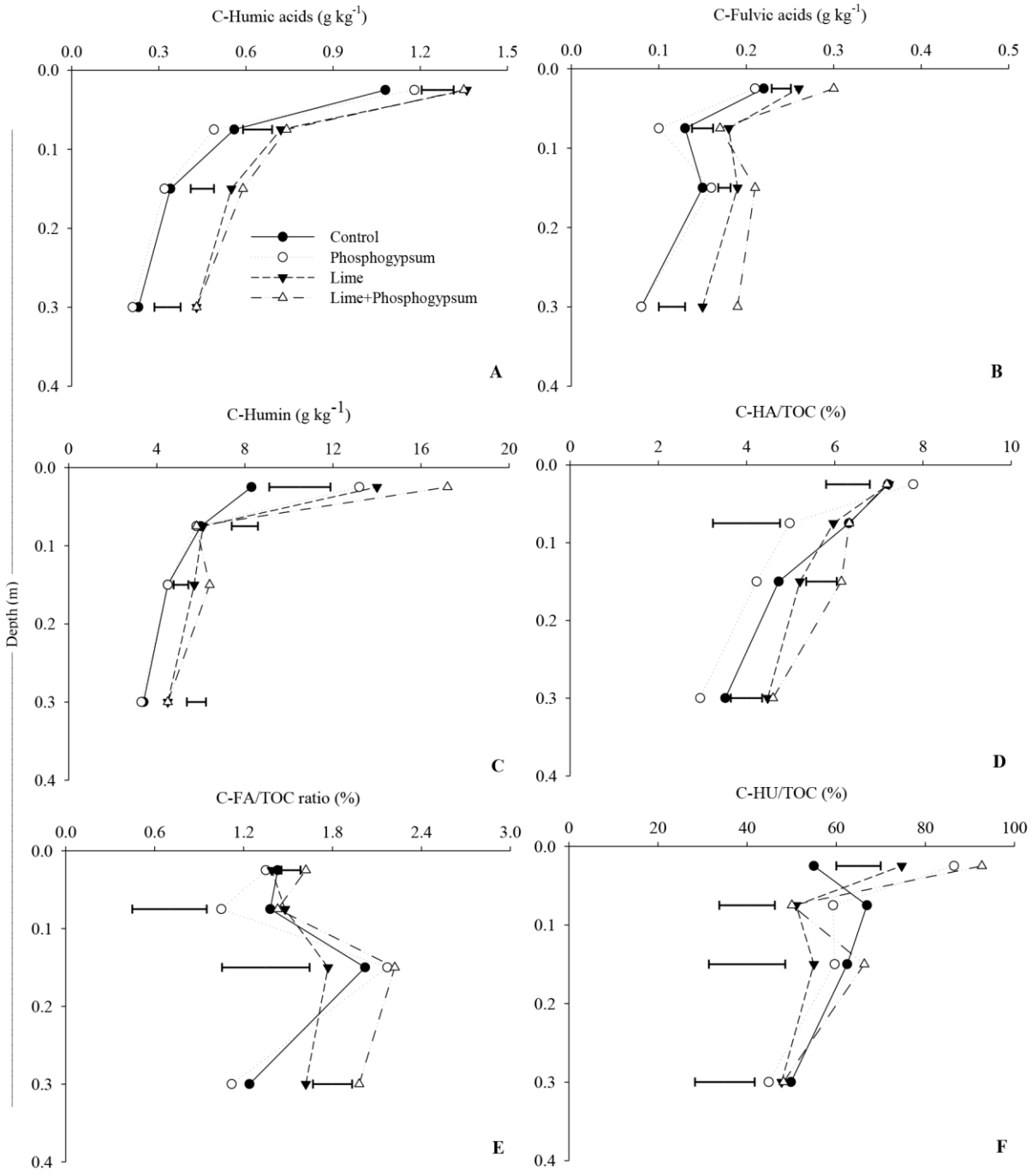

Figure 3. Soil organic carbon in the form humic acid (A; C-HA), fulvic acids (B; C-FA), humin (C; C-Humin), C-HA/TOC ratio (D), C-FA/TOC ratio (E), and C-HU/TOC (F) as affected by lime (▼), phosphogypsum (○), and limestone + phosphogypsum (△) and the corresponding levels of the control (●).The amendments rates have been applied three times (2002, 2004, and 2010). Horizontal bars indicate the least significant difference between treatments within each soil depth at $p \leq 0.05$. TOC: Total organic carbon

As PG + lime combined resulted in greater POC/TOC ratios, the combination of amendments allowed for a greater proportion of TOC that was mineralized after 73 days of incubation, for all soil depths evaluated (16.06%, 14.73%, and 11.59% of TOC at 0- to 0.05-, 0.05- to 0.10-, and 0.10- to 0.20-m, respectively) (Figures 4A, 4B, and 4C). Initially for 0-0.05 and 0.05-0.10-m soil depths, all treatments released similar amounts of C (estimate averages: 2.0% and 2.5 % of TOC, respectively). At the 0.10-0.20-m soil depth, the combination of PG and lime showed higher mineralization (2.5% of TOC in the first three days), compared to the control treatment (1.4% of TOC). At the soil surface, the total amount of OC released was similar among treatments after 9 days of incubation (approximately 4.4% of TOC). After this period, the surface application of lime + PG showed higher cumulative C mineralized, compared to other treatments for all soil layers.

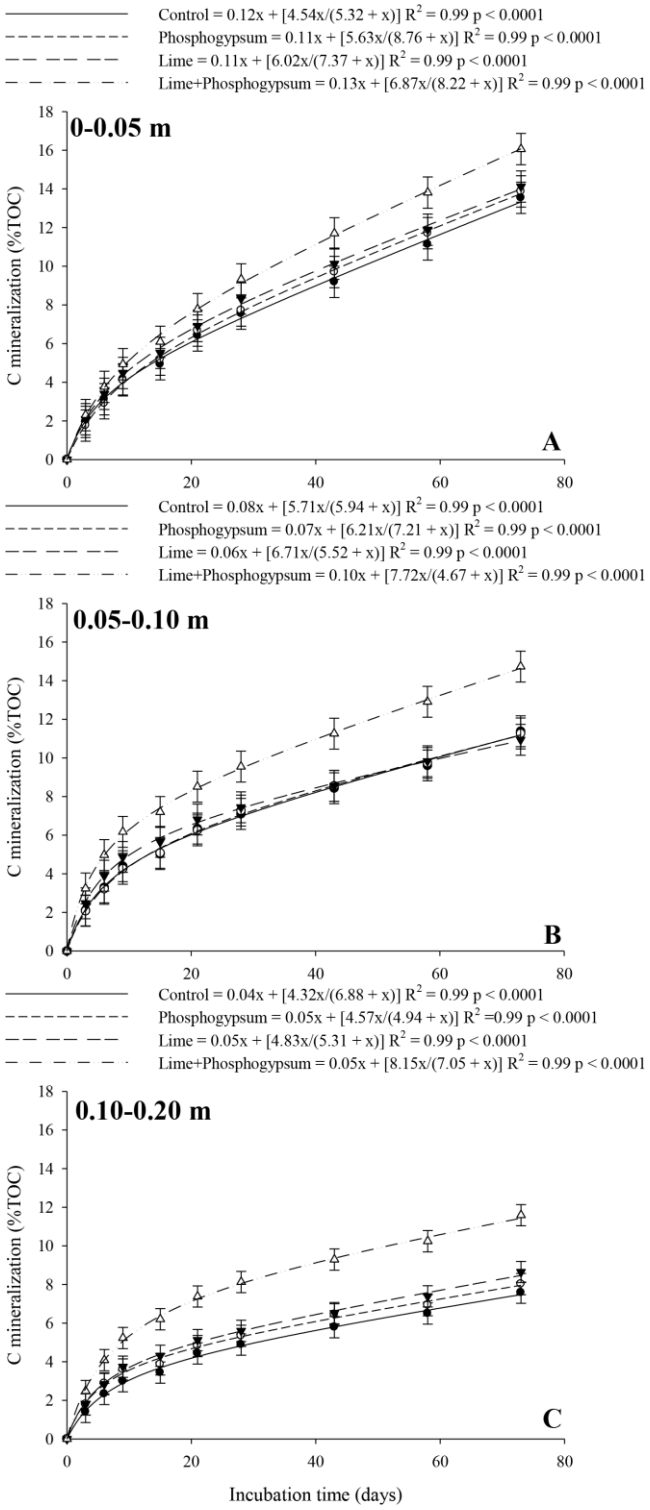

Figure 4. Cumulative carbon mineralized at soil depths of 0-0.05 m (A), 0.05-0.10 m (B), and 0.10-0.20 m (C), as affected by lime (▼), phosphogypsum (○), and limestone + phosphogypsum (△) and the corresponding levels of the control (●). The amendments rates have been applied three times (2002, 2004, and 2010). Vertical bars indicate the least significant difference between treatments within each time sampling at $p \leq 0.05$.

3.5. Discussion

The increased biomass production (shoot and roots) were a function of the alleviation of soil acidity and soil fertility amelioration from 0 to 0.40 m depth (Table 2). However, while PG is often considered an important soil amendment and a source of Ca and S, the application of the by-product alone did not increase the shoot and root dry matter in both crops and growing seasons. This lack of impact of PG alone may be due to the low magnitude of residual effect and high soil acidity levels (pH). This is similar to Weir et al. (1963), who found no residual effects of gypsum at 16 months after application in a Podzolic soil. According to Caires et al. (2011), on a clayey Oxisol previously used for pasture, more than 50% of the applied exchangeable Ca from gypsum was leached into the soil layers deeper than 0.60 m after 27 months.

In contrast, surface application of lime significantly increased the input of organic residues into the soil (shoot and root), which may be partly due to soil acidity alleviation and the higher residual effect of the lime compared to gypsum (Table 2 and Figure 1). In a trial conducted on a clayey Oxisol, Caires et al. (2006) observed that the liming effect remained consistent for a period of 60 months. The higher input of organic compounds, resulting from acid neutralizing amendments, contribute to reduce soil acidification over time by decomposition of Ca-organic molecules, which may provided an alkaline effect on soil (POCKNEE; SUMNER, 1997). As consequence the authors related that the pH index may remain constant for a prolonged time, with minor variation, compared to agriculture systems with low input of SOM. Several studies have reported mechanisms to explain increases in soil pH resulting from SOM addition including: contribution to increase CEC (adsorption of acid ions), displacement of OH^- from minerals, and input of basic cations (McBRIDE, 1982; RITCHIE, 1985; BESSHO; BELL, 1992; WONG et al., 1998; INAGAKI et al., 2016).

Pearson's correlation analysis between soil chemical properties (exchangeable Al^{3+}, Ca^{2+}, Mg^{2+}, and base saturation) and SOM pools confirmed that the concentrations of basic cations and the reduction of exchangeable Al^{3+} are important for increasing input of SOM to the soil, thereby increasing soil TOC, POC, and MOC (Table 5 and Figures 2C, 2D, and 2E). The reduction of Al^{3+} toxicity and increasing Ca and Mg

through surface application of lime has been shown by several authors to play a fundamental role in increasing crop development in no-tillage systems (CAIRES et al., 2006; SORATTO; CRUSCIOL, 2008; BRIEDIS et al., 2012; FAGERIA; NASCENTE, 2014). When lime applications are combined with no-till, there is the additional advantage of increasing the OC supply to soil, mainly via roots, considered the major source of organic material since shoot residues are rapidly decomposed (HAYNES et al., 1998). Thus, the application of soil amendments, which are also sources of Ca and Mg, are considered good strategies to increase the input of SOM.

There was no significant effect of PG application on soil TOC at 12 years after treatment establishment (Figure 2D). However, the highest amount of POC was in the 0.05 to 0.10 and 0.20 to 0.40-m soil layers when gypsum was applied with lime in a combination (Figure 2C). In addition, based on the POC/TOC ratio, PG + lime contributed to increase the proportion of litter organic matter fraction in soil. Inagaki et al. (2016) also observed that gypsum application increase the stocks of labile OC pools, and consequently stimulated higher biological activity.

Our C mineralization results were highly influenced by labile OC pool. After 73 d of incubation, at all soil layers evaluated (Figures 4A, 4C, and 4E), the PG addition with liming increased soil respiration and the amount of C mineralized. Alvarez and Alvarez (2000) showed a high positive relationship between C mineralization and the light fraction C ($r^2 = 0.83$; $p<0.001$). According to authors, the higher proportion of labile compounds in the soil induces changes on biological activity. In addition, Carter (1985) and Inagaki et al. (2016) confirmed that gypsum application may improve microbial activity due to changes in soil chemistry attributes, with benefits related to root growth (via root exudates), mainly during drought periods (Farina and Channon, 1988).

The positive effect of PG + lime application on increasing the proportion of labile OC pools (POC/TOC ratio), and consequently soil respiration, is especially important considering the higher levels of TN at the 0 to 0.10-m and 0.20 to 0.40-m soil depths, since organic residues decomposition may be considered a primary source of N in the soil (Figure 2B). Regardless of mechanisms involved, the relatively higher TN levels and amounts of non-recalcitrant organic compounds in soils, mainly residues containing easily degradable

materials (RAPHAEL et al., 2016), are considered important characteristics to maximize microbial activity, and consequently the C mineralization rates.

Despite the PG effect on the amounts of C mineralized, higher input of organic residues mainly via roots contribute significantly to increase the OC stored in tropical soils. This is because decreased mineralization rates of belowground SOM compared to aboveground biomass increases the probability to be stabilized by mineral particles (ZECH et al., 1997). Johnson et al. (2007) found that the majority of OC contributed by corn was from roots since they had a longer half-life (more than 10 years), compared with corn leaves and stems (6 to 7 years).

Regardless of PG application, liming alone was a viable strategy to increase TOC in the soil profile, including the fraction considered more stable (MOC), which may be due to improving soil fertility (BRIEDIS et al., 2012; CASTRO et al., 2015). Despite lower correlation between exchangeable base cation availability and MOC compared with other OC pools, base cations are generally believed to increase bonding between charged mineral surfaces and organic functional groups (BRONICK; LAL, 2005).

The effect of soil amendments on soil MOC may be related to pH changes. Decreased pH increases the solubility of Fe and Al in Oxisols, and according to Greenland (1971), Alberts and Filip (1998), and Clemente and Bernal (2006) the bond formed between metallic ions and carboxyl groups found on SOM tends to be very strong with high stability, increasing the interactions between mineral particles and organic molecules. Although gypsum is not and acid neutralizing material (OATES; CALSWELL, 1985; SUMNER et al., 1986), our results showed that the magnitude of acidification was lower in lime-amended soil treated with PG (pH 5.0), compared with application of lime alone (pH 4.5) after 48 months from last reapplication.

Several authors have been reported that gypsum application to highly weathered-variable charged soils can release hydroxyl (OH^-) by specific adsorption of SO_4^{2-}, similar to effects of phosphate ($H_2PO_4^{2-}$) application (RAJAN, 1978; ALVA et al., 1990). In addition, as consequence of higher root growth, the volume of soil explored is larger, and the contribution of alkaline ions as HCO_3^- and OH^- exuded by roots (RILEY; BARBER, 1969) may be increased with gypsum application, due to higher availability of anions in soil solution, such as sulfate (SO_4^{2-}) and nitrate (NO_3^-). Crusciol et

al. (2016) confirmed the ability of PG to increase the levels of these anions in Oxisol solutions, compared with the individual application of lime. In addition, Garbuio et al. (2011) emphasized that higher input of plant residues can increase cation exchange surfaces and proton-bearing functional groups, which suggests higher adsorption of H^+, contributing to buffering the acidification process over time.

The PG effect of improving microbial activity can favor decomposition of non-recalcitrant compounds, inducing synthesis of more stable molecules (i.e. humin and humic/fulvic acids), and improving the quality of SOM (STEVENSON, 1982) (Figure 3). However, the intensity of humification is significantly influenced by soil chemical factors (ZECH et al., 1997). According to Zech et al. (1997) the chemical structure of humic substances are characterized by higher aromatic functional group composition, and soils with low C/N ratios and higher pH values tend to increase the aromaticity of humic substances.

For the highly weathered tropical soil used in this study, acidity amelioration by surface liming was considered effective for increasing SOM quality by increasing humin (C-HU), humic (C-HA) and fulvic acids (C-FA) contents (Figues 3A, 3B, and 3C). The results showed significant correlations between soil chemical properties and the amount of humic substances, which may have had an impact on the synthesis and stabilization of these compounds in tropical soils (Table 5). In acid soils, Fuentes et al. (2006) demonstrated that lime applications increased decomposition of the readily mineralizable C pool 7.5 to 12.5 times compared to non-limed soil, with less impact on decomposition at deeper soil depths. However, less information is available regarding the effect of soil amendments on the synthesis of humic substances. To understand the short-term effects of surface lime application on OC pools, Garbuio et al. (2011) collected soil samples of a sandy clay loam Oxisol that had been under a no-till regime for 26 yr. At 30 months after dolomite application, the authors found that microbial biomass and the amount of water-soluble organic substances increased at 0 to 0.10-m soil depths. In addition, the authors highlighted that soil management techniques that influence the quality of OC sources may increase the activity and diversity of the microbial community, and consequently the synthesis and stabilization of these substances.

The PG effect on increasing the amounts of C-FA and C-HU in the lime-amended soil suggested that this by-product also affected some oxidation and enzymatic reactions, considered key factors associated with metabolic pathway of these molecules in tropical soils conducted under a long-term NT system. Higher input of organic materials rich in lignin and phenolic polymers are considered important for FA formation (OGNER; SCHNITZER, 1970). Oades (1988) demonstrated a positive correlation between organic compounds such as lignin, and the amount and quality of organic residues input, with the proportion of different plant parts that influence the composition of organic substrate. Zech et al. (1997) suggested that the addition of materials rich in lignin, considered resistant to biological degradation, contribute to the pathway of humic substances. According to Johnson et al. (2007), the amount of total lignin varies between plant species and plant parts within species. In the case of soybean, the authors showed that the leaves (114 g kg^{-1}) and stems (173 g kg^{-1}) had a lower concentration of total lignin compared with roots (212 g kg^{-1}).

The oxidation and decarboxylation reactions, followed by microbiological action on lignin and others phenolic polymers, are considered essential for formation of humic substances. Soil acidity alleviation appears to increase the reactivity of some precursor compounds, such as tri-hydroxy phenols (HAIDER et al., 1975; STOTT; MARTIN, 1990).The application of both amendments combined reduced soil acidification over time resulted in a significant increase in the proportion of TOC in the form of humic substances (C-HA/TOC, C-FA/TOC and C-HU/TOC) affecting the OC quality, which may be an important strategy to increase C stored in soil (Figures 3D, 3E, and 3F). In addition to the pH effect, this result may be partly due to the interactions of polyvalent cations (such as Ca^{2+} and Mg^{2+}) with functional groups of minerals and organic matter, which constitute an important physical-chemical complex (ZECH et al., 1997) that prevent losses of OC, via microbial decomposition and leaching. The high amount of charged functional groups on humic substances (3,000–14,200 $mmol_c$ dm^{-3}) (STEVENSON, 1994) provide ideal conditions for formation of chemical bonds with soil minerals for stabilizing humic compounds in tropical soils. Belkacem and Nys (1995) showed a significant correlation (R^2 = 0.72) between Ca and dissolved OC (such as FA). Ultimately, many factors may affect

the distribution of SOM pools, the quality and amount of organic residues, stability and characteristics of each fraction, biological activity, and soil physical-chemical properties.

In general, as SOM accumulates at the soil surface, the biological activity becomes more intense in this zone, and as a consequence more humic substances are synthesized and complexed with mineral particles, which may explain the highest C-FA/TOC ratio observed in the 0 to 0.05-m. However, for humic substances not stabilized with minerals, such as FA, may have leached downward due to the higher pH conditions at the surface (STEVENSON, 1994). Leaching of FA from the surface may explain higher contribution of humic compounds to TOC at the 0.10 m depth. On the other hand, the humin fraction, which is considered insoluble at all pH levels, did not appear to be impacted by the soil amendments below the 0.10 m depth.

The higher C-HU/TOC ratio in the 0-0.05 and 0.05-0.10-m in the PG and control treatments, respectively, may be related to the quality of substrate input (root and shoot residues). This substrate may provide low molecular weight compounds such as polyphenols associated with N molecules, considered an important humification pathway for humin formation (STEVENSON, 1994). In addition to variation among species, Kraus et al. (2004) showed that soil fertility and pH have a significant influence on secondary compounds synthesis in perennial species, such as polyphenols, considered important precursor molecules for humus formation. Therefore, soil acidity and low input of OC sources may reduce the synthesis of humin, but increase the stability of it. Grasset et al. (2002) suggested that humin is more resistant to biodegradation than HA and FA acids, due to its more complex structure. Similar to HA and FA, chemical bonds between humin, polyvalent ions and mineral particles may help to preserve humin. For this study, the low contribution of above ground organic residues is also influenced by the low fertility of the control, and the association of these factors may have increased the proportion of TOC as humin.

Based in our results, the use of lime + PG was considered an appropriate practice for improving soil fertility with positive effects on SOM quality. Surface application of lime + PG may improve environmental quality of agricultural ecosystems due to the contribution of increased OC stability, especially in a tropical region with climate conditions favorable to high rates of C losses.

3.6. Conclusions

Surface liming is considered an important tool to increase SOM input in tropical acid soils conducted under long-term NT systems. The maintenance of high concentrations of basic cations (such as Ca and Mg) and low levels of exchangeable Al in soil solution demonstrated high correlation to quantity and quality of SOM. Although PG had no effect on plant growth, the combination of PG with lime increased the formation and stabilization of humic substances, mainly as fulvic and humic acids, which can be attributed to soil fertility improvement and the higher input of organic residues. Therefore, surface application of lime and gypsum, associated with conservative practices, are considered key factors to improve soil health and consequently the sustainability of agricultural systems in tropical regions.

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RESEARCH ARTICLE

Impact of Amendments on the Physical Properties of Soil under Tropical Long-Term No Till Conditions

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Abstract

Tropical regions have been considered the world's primary agricultural frontier; however, some physico-chemical deficiencies, such as low soil organic matter content, poor soil structure, high erodibility, soil acidity, and aluminum toxicity, have affected their productive capacity. Lime and gypsum are commonly used to improve soil chemical fertility, but no information exists about the long-term effects of these products on the physical attributes and C protection mechanisms of highly weathered Oxisols. A field trial was conducted in a sandy clay loam (kaolinitic, thermic Typic Haplorthox) under a no-tillage system for 12 years. The trial consisted of four treatments: a control with no soil amendment application, the application of 2.1 Mg ha^{-1} phosphogypsum, the application of 2.0 Mg ha^{-1} lime, and the application of lime + phosphogypsum (2.0 + 2.1 Mg ha^{-1}, respectively). Since the experiment was established in 2002, the rates have been applied three times (2002, 2004, and 2010). Surface liming effectively increased water-stable aggregates > 2.0 mm at a depth of up to 0.2 m; however, the association with phosphogypsum was considered a good strategy to improve the macroaggregate stability in subsoil layers (0.20 to 0.40 m). Consequently, both soil amendments applied together increased the mean weight diameter (MWD) and geometric mean diameter (GMD) in all soil layers, with increases of up to 118 and 89%, respectively, according to the soil layer. The formation and stabilization of larger aggregates contributed to a higher accumulation of total organic carbon (TOC) on these structures. In addition to TOC, the MWD and aggregate stability index were positively correlated with Ca^{2+} and Mg^{2+} levels and base saturation. Consequently, the increase observed in the aggregate size class resulted in a better organization of soil particles, increasing the macroporosity and reducing the soil bulk density and penetration resistance. Therefore, adequate soil chemical management plays a fundamental role in improving the soil's physical attributes in tropical areas under conservative management and highly affected by compaction caused by intensive farming.

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Introduction

The loss of basic cations due to leaching and crop removal associated with the application of high rates of ammoniacal and nitric fertilizers is considered the primary factor leading to soil acidification [1,2], which affects crop production in several agricultural soils worldwide, such as Ultisols and Oxisols [3]. Typically, the problems resulting from soil acidity are linked to poor chemical fertility, such as aluminum (Al^{3+}) toxicity and macronutrient deficiency; however, inadequate soil physical properties may also affect the potential productivity of these soils [1].

Due to their mineral properties, such as a low density of electrical charges on clay minerals, low organic matter content, and low cation exchange capacity, Ultisols and Oxisols are susceptible to surface crusting and subsoil compaction, reducing their macroporosity and hydraulic conductivity, which increases the risk of erosion and land degradation [4]. Therefore, management interventions play an important role in enhancing the physical quality of these soils.

Economically, the application of limestone is the most feasible strategy for alleviating soil acidity and for correcting chemical deficiencies [3]. In addition to its effect on pH, lime is a good source of Ca and Mg and can effectively increase fertilizer efficiency. However, due to the chemical characteristics of limestone, such as low solubility and dissolution rates, the method of product incorporation has been recommended to improve the reaction time in soil subsurface layers [5]. According to conservation principles, soil disturbances severely damage the soil structure, accelerating erosion and land degradation processes [6]; therefore, in areas under a no-tillage (NT) system, liming is usually performed superficially [1,7]. Studies conducted by Caires et al. [8], Castro and Crusciol [9] and Caires et al. [2] showed the feasibility of surface liming in improving soil chemical attributes and grain yields; however, according to these authors, the magnitude of the effect varies according to soil texture, lime rates, reaction time, crop rotation, water regime, and the combined use with more soluble materials, such as phosphogypsum. In a tropical area under a no-tillage system and with a minimal disturbance of soil, Crusciol et al. [10] suggested the technique of combining both soil amendments as a good strategy to neutralize Al^{3+} toxicity and to increase the number of basic cations available in subsoil layers in a shorter period compared to an application of lime alone.

Despite studies that reveal the benefits of lime and phosphogypsum on soil chemical properties and crop grain production [11,12], there have been conflicting results regarding the effects of soil amendments on the physical attributes of highly weathered soils. In a short-term study, Roth and Pavan [7] reported that lime incorporation increased clay dispersion and lowered infiltration rates of an Oxisol soil, and these effects were attributed to lower Al^{3+} and H^{+} activities in the soil solution, promoting the compression of the diffuse double layer and the flocculation of particles. Due to the effect of reducing free Al^{3+}, the authors also observed clay dispersion effects in treatments with phosphogypsum. Haynes and Naidu [13] suggested that higher Ca^{2+} levels in the soil solution might cause compression of the double layer, consequently promoting particle flocculation; therefore, the application of materials as Ca sources may favor aggregation mechanisms, which are important for improving the soil structure.

In Oxisols and Ultisols, the soil organic matter content has a profound effect on the soil's physical attributes because physico-chemical reactions with inorganic compounds play a fundamental role in aggregate formation and soil structure [14]. Roots, fungal hyphae, humic substances, soil organisms, and polysaccharides are important binding agents involved in aggregate formation [15,16], and because these fractions can be influenced by agricultural management [13], the long-term benefits of amendment practices may improve the structure of the entire soil profile, including deeper soil layers.

Based on this information, the following hypotheses were proposed: a) surface liming can increase the water stability of aggregates because of the effect on the cation exchange capacity

and Ca availability; b) soil acidity alleviation can influence several mechanisms acting on the formation and stability of aggregates; c) the addition of phosphogypsum in lime-amended soil can favor root growth, which is an important source of biocompounds involved in soil aggregation and porous structure formation; and d) the application of soil amendments can favor C protection mechanisms. There is no information regarding the effect of both soil amendments on improving the physical fertility of the tropical soil profile under a long-term no-tillage system. This study aimed to evaluate the long-term effect of the superficial application of lime and phosphogypsum on the soil's physical attributes and on the protection mechanisms of total organic carbon (TOC) in a tropical Oxisol under an NT system in a dry winter region.

Materials and Methods

Site description

The experiments were conducted in Botucatu, SP, Brazil (48° 23′ W, 22° 51′ S and 765 m) in an area under a no-till system over a 12-year period. The soil was classified as a sandy clay loam (kaolinitic, thermic Typic Haplorthox) [17]. According to Köeppen's classification, the climate is Cwa, with a dry winter and a hot, wet summer. The rainfall values as well as the mean maximum and minimum temperatures recorded over a long period (50 years) are shown in Table 1. Prior to establishing the experiment in 2002, the chemical and physical properties were determined (0–0.2 m), according to the methodology proposed by van Raij et al. [18] and Kiehl [19], respectively. The following results were obtained: organic matter, 21 g dm^{-3}; pH (1:2.5 soil/$CaCl_2$ suspension 0.01 mol L^{-1}), 4.2; P (resin), 9.2 mg dm^{-3}; exchangeable K, Ca, and Mg 1.2, 14, and 5 $mmol_c$ dm^{-3}, respectively; total acidity at pH 7.0 (H + Al) 37 $mmol_c$ dm^{-3}, cation exchange capacity (CEC) 57 $mmol_c$ dm^{-3}; base saturation 35%; sand, silt, and clay contents of 54, 11, and 35%, respectively. In the subsoil (0.20–0.40 m), the clay content was 36%.

Experimental design and treatment establishment

A complete randomized block design was used with four replications. Each plot covered an area of 46.8 m^2 (5.2 m x 9.0 m). The plots were composed of four treatments: (i) a control (no lime or phosphogypsum), (ii) phosphogypsum (2.1 Mg ha^{-1}), (iii) lime (2.0 Mg ha^{-1}) and (iv) lime + phosphogypsum (2.0 Mg ha^{-1} + 2.1 Mg ha^{-1}, respectively). The dolomitic limestone (Embracal®, Saltinho, São Paulo, Brazil) was composed of 23.3% CaO and 17.5% MgO, and the rate (R) was calculated using Eq (1) to increase the base saturation in the topsoil (0–0.20 m) to 70%, as described by Cantarella et al. [20]:

$$R(Mg.ha^{-1}) = \frac{(BS_2 - BS_1).CEC}{(ECCE/100)} \quad (1)$$

Table 1. Rainfall and maximum and minimum temperatures in Botucatu, São Paulo, Brazil, over a long period.

Climate characteristics	Month											
	Jan.	Feb.	Mar	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
	Long-term (50-yr) avg.											
Monthly rain, mm	224.0	203.2	140.9	66.5	75.8	55.9	37.7	38.9	71.3	126.5	133.3	184.6
Mean max. temp., ˚C	28.1	28.0	28.0	27.0	24.0	23.0	23.0	25.0	26.2	26.7	27.2	27.2
Mean min. temp., ˚C	17.1	17.4	19.0	17.0	15.0	13.0	13.0	14.0	12.4	14.2	15.1	16.4

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where ECCE is the effective calcium carbonate equivalent of the dolomite and BS_2 is the estimated base saturation (70%). BS_1 is the base saturation determined by the soil chemical analysis and calculated using Eq (2):

$$BS_1(\%) = \frac{(Ca_{ex} + Mg_{ex} + K_{ex}).100}{CEC} \quad (2)$$

where Ca_{ex}, Mg_{ex}, and K_{ex} are the levels of basic exchangeable cations in the soil. CEC is the total cation exchange capacity, calculated according to Eq (3):

$$CEC(mmol_c.dm^{-3}) = Ca_{ex} + Mg_{ex} + K_{ex} + (H + Al) \quad (3)$$

The phosphogypsum (Embracal®, Saltinho, São Paulo, Brazil) was composed of 20% Ca, 16% S and residual P and F (0.1%). Minor heavy metal contents were detected, including Cd, Ni, Pb, Cr, and Hg at levels of 3.1, 53.6, 12.6, 990, and <0.1 mg kg^{-1}, respectively, according to the US Environmental Protection Agency definition of trace element pollution levels in by-product materials. The phosphogypsum rate (PR) was calculated using Eq (4), according to the method proposed by van Raij et al. [21]:

$$PR(Mg.ha^{-1}) = 6.CL \quad (4)$$

where CL is the clay content (g kg^{-1}) in the soil layer at a 0.20- to 0.40-m depth.

During the study period, the treatments were applied three times, and different species were cropped in season and off season from 2002 to 2015. Details of the crop sequences and fertilizer management are shown in Table 2.

Additional details about the accumulated shoot and root dry matter of wheat and common bean cropped in the 2013/2014 and 2014/2015 growing seasons, respectively (Table 2), exchangeable Al and Ca, and soil pH for each soil layer (determined two months after the wheat harvest) as a function of the treatments are shown in Table 3. The soil chemical attributes were measured according to the methodology proposed by van Raij et al. [18].

Soil sampling

Twelve years after treatment establishment, in 2014 (two months after the wheat harvest), a trench measuring 0.50 m wide, 0.80 m deep and 0.80 m long was dug in each plot. Soil samples were randomly collected using the trench profile. To determine the aggregate stability and particle density at each soil layer, four clod samples were excavated from the trench wall at depth layers of 0.00–0.05, 0.05–0.10, 0.10–0.20, 0.20–0.40, and 0.40–0.60 m to form a composite sample as described by Castro Filho et al. [22]. On the same day, using volumetric rings (height 5.0 cm, internal diameter 4.8 cm), two undisturbed samples were collected at the center of each soil layer to determine the soil bulk density, the total, macro-, and micro-porosity, and the soil penetration resistance (PR) [23].

Soil physical attributes and C analysis

For the soil's water-stable aggregate analysis, undisturbed soil monolith samples were air-dried, gently sieved through 8.0-mm sieves and retained on a 4.0-mm sieve. A 25-g aliquot of the retained air-dried aggregate fraction was pre-wetted (using a spray bottle) and was subjected to a wet-sieving procedure for 15 min using a nest of sieves with 4.00, 2.00, 1.00, 0.50, 0.25, and 0.105-mm mesh sizes linked to mechanical equipment adjusted to 31 vertical oscillations min^{-1} [24]. The procedure was performed on six separate classes of water-stable aggregates: >2.0–8.0 mm, >1.0–2.0 mm, >0.5–1.0 mm, >0.25–0.5 mm, >0.105–0.25 mm, and <0.105 mm. The fractions retained on each sieve were transferred to aluminum dishes and

Table 2. Crops grown during the study period and the treatment application scheme during the experimental period (from 2002 to 2015).

Season	Crops		Treatment application
	Summer crop	Autumn-winter-spring crop	
2002/ 2003	***Oriza sativa* (cv. Caiapó)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 50 kg of N ha^{-1}	***Avena strigosa* (cv. Comum)** BF: 200 kg ha^{-1} of NPK 10–20–10 + 4.5% S	Lime: 2,700 kg ha^{-1} (71% ECCE)† Gypsum: 2,100 kg ha^{-1}
2003/ 2004	***Phaseolus vulgaris* (cv. Pérola)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 110 kg of N ha^{-1}	***Avena strigosa* (cv. Comum)** BF: 200 kg ha^{-1} of NPK 04–20–20 + 7% S	
2004/ 2005	***Arachis hypogaea* (cv. Runner IAC 886)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn.	***Avena sativa* (cv. IAC 7)** BF: 300 kg ha^{-1} of NPK 08–28–16 + 4.5% S + 0.5% Zn. TF: 110 kg of N ha^{-1}	Lime: 2,000 kg ha^{-1} (71% ECCE) Gypsum: 2,100 kg ha^{-1}
2005/ 2006	***Arachis hypogaea* (cv. Runner IAC 886)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn.	***Avena sativa* (cv. IAC 7)** BF: 8 kg ha^{-1} of N + 40 kg ha^{-1} P_2O_5 + 20 kg ha^{-1} of K_2O + 7% S	
2006/ 2007	***Zea mays* (cv. 2B570)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn. TF: 90 kg of N ha^{-1}	***Urochloa brizantha* (cv. Marandu)** The forage seeds were simultaneously sown with corn.	
2007/ 2008	***Zea mays* (cv. 2B570)** BF: 24 kg ha^{-1} of N + 84 kg ha^{-1} P_2O_5 + 48 kg ha^{-1} of K_2O + 10% S + 0.5% Zn. TF: 90 kg of N ha^{-1}	***Urochloa brizantha* (cv. Marandu)** The forage seeds were simultaneously sown with corn.	
2008/ 2009	***Glycine max* (cv. MGBR-46)** BF: 250 kg ha^{-1} of NPK 04–20–20 + 4.5% S + 0.5% Zn.	***Avena strigosa* (cv. Comum)** No fertilizer was applied	
2009/ 2010	***Glycine max* (cv. CD216)** BF: 250 kg ha^{-1} of NPK 04–20–20 + 4.5% S + 0.5% Zn.	***Sorghum vulgare* (cv. AG1020)** No fertilizer was applied	
2010/ 2011	***Zea mays* (cv. 2B433)** BF: 350 kg ha^{-1} of NPK 08–28–16. TF: 150 kg of N ha^{-1}	***Crambe abyssinica* (cv. FMS Brilhante)** BF: 150 kg ha^{-1} of NPK 08–28–16	Lime: 2,000 kg ha^{-1} (88% ECCE) Gypsum: 2,100 kg ha^{-1}
2011/ 2012	***Zea mays* (cv. 2B433)** BF: 350 kg ha^{-1} of NPK 08–28–16. TF: 150 kg of N ha^{-1}	***Crambe abyssinica* (cv. FMS Brilhante)** BF: 150 kg ha^{-1} of NPK 08–28–16	
2012/ 2013	***Pennisetum glaucum* (cv. ADR300)** No fertilizer was applied	***Triticum aestivum* (cv. CD116)** BF: 35 kg ha^{-1} of N + 70 kg ha^{-1} P_2O_5 + 40 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn.	
2013/ 2014	***Phaseolus vulgaris* (cv. Pérola)** BF: 10 kg ha^{-1} of N + 50 kg ha^{-1} P_2O_5 + 50 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn. TF: 100 kg of N ha^{-1}	***Triticum aestivum* (cv. CD116)** BF: 35 kg ha^{-1} of N + 70 kg ha^{-1} P_2O_5 + 40 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn.	
2014/ 2015	***Phaseolus vulgaris* (cv. Pérola)** BF: 10 kg ha^{-1} of N + 50 kg ha^{-1} P_2O_5 + 50 kg ha^{-1} of K_2O + 11 kg of ha^{-1} S + 12 kg of ha^{-1} Zn. TF: 100 kg of N ha^{-1}		

† The reapplications in October of 2004 and 2010 were performed when the standard treatment (calculated rate) reached base saturation ≤ 50%. BF: base fertilization; TF: topdressing fertilization.

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were dried in a forced air oven at 45˚C for 72 h for later weighing. Based on the weight and initial soil moisture content of each fraction, the values were adjusted to a dry soil weight, which was used to calculate the aggregate distribution (AD%), aggregate stability index (ASI) mean weight diameter (MWD) and geometric mean diameter (GMD), as follows in Eqs (5), (6), (7) and (8), respectively, as described by Kemper and Chepil [24]:

$$AD\% = \frac{(100.wi)}{\sum wi} \quad (5)$$

$$ASI\% = \frac{(yi - zi).100}{yi} \quad (6)$$

Table 3. Accumulated shoot and root dry matter (wheat and common bean), exchangeable Al and Ca, and soil pH at several depths as a function of the surface application of lime and phosphogypsum in a tropical Oxisol under a no-tillage system.

	Treatments			
	Control	Phosphogypsum	Lime	Lime + Phosphogypsum
	Shoot dry matter accumulated (wheat + common bean), kg ha^{-1}			
Total	2,001.5	2,164.7	4,910.5	5,064.1
Soil layer (m)				
	Root dry matter accumulated (wheat + common bean), g m^{-3}			
0–0.05	139.0	174.2	508.0	533.1
0.05–0.10	107.4	134.4	415.9	473.2
0.10–0.20	62.6	45.1	129.5	125.7
0.20–0.40	12.9	14.0	108.2	112.7
0.40–0.60	2.7	5.6	40.0	28.9
	Exchangeable Al, $mmol_c$ dm^{-3}			
0–0.05	20.0	17.9	3.6	0.0
0.05–0.10	26.7	20.7	8.4	0.8
0.10–0.20	26.5	22.7	13.8	6.4
0.20–0.40	30.2	25.6	21.9	18.6
0.40–0.60	32.7	28.5	27.8	28.1
	Exchangeable Ca, $mmol_c$ dm^{-3}			
0–0.05	4.9	7.0	22.5	36.4
0.05–0.10	2.1	4.6	16.6	27.3
0.10–0.20	1.6	3.2	10.4	17.8
0.20–0.40	1.7	3.0	6.6	9.7
0.40–0.60	2.3	2.8	4.0	6.6
	Soil pH			
0–0.05	3.8	3.9	4.6	5.3
0.05–0.10	3.7	3.8	4.5	5.1
0.10–0.20	3.7	3.8	4.2	4.6
0.20–0.40	3.8	3.9	4.1	4.2
0.40–0.60	3.9	3.9	4.1	4.1

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$$MWD = \sum_{i=1}^{n} (xi.wi) \tag{7}$$

$$GMD = \exp\left(\frac{\sum wi \ln xi}{\sum wi}\right) \tag{8}$$

where *wi* is the weight of the aggregates of each size class; *xi* is the mean diameter of the size class (mm); *yi* is the weight of the dry soil sample (105˚C); and *zi* is the weight of aggregates smaller than 0.25 mm.

To evaluate the amount of TOC within the soil aggregate classes, the fractions were classified into three groups according to the classification proposed by Dube et al. [25]: >2.0–8.0 mm (macroaggregates), >0.25–2.0 mm (mesoaggregates) and >0.105–0.25 mm (microaggregates). The samples of each group were ground in a porcelain mortar and homogenized, and then, the C content was determined using an elemental analyzer.

In the laboratory, the undisturbed samples were saturated by gradually increasing the water level for 48 h. Then, all saturated samples were weighed and subjected to a 0.006-MPa tension

on porous plates in Richard's pressure chamber [26]. Upon reaching stability, the samples were weighed and subjected to a 0.03-MPa tension. Once the samples were at equilibrium, PR analysis was performed using a Marconi electronic penetrometer (model MA933) constructed with a metal vertical probe with a 30° cone and a base area of 0.1256 cm^2. Penetration into the samples was performed with a constant penetration velocity of 10 mm min^{-1}, using a charge cell of 20 kg, to a depth of 40 mm. PR data were acquired with TexturePro CT V1.4 software, and the measurements obtained from the surface of the sample to a 10-mm depth were discarded, as suggested by Tormena et al. [27]. After the PR test, the samples were dried in a forced air oven at 105°C for 48 h and weighed to determine the soil bulk density. The total porosity was the difference between the weighed samples (water-saturated and dried), macroporosity was determined as the water content difference between the water-saturated samples and those subjected to a 0.006-MPa tension, and microporosity was calculated by the difference between the total porosity and macroporosity [28].

The particle density (PD) was obtained using a 20-g aliquot of disturbed samples, which were dried in a forced air oven at 105°C for 24 h. Dried samples were transferred to a 50-ml volumetric flask, and the volume was adjusted with ethyl alcohol (95% v/v) while shaking gently to remove air bubbles. The particle density was calculated using Eq (9), according to the method proposed by Blake and Hartge [29]:

$$PD(kg.dm^{-3}) = \frac{x}{(50 - y)} \quad (9)$$

where x is the weight of the dried samples (105°C) and y is the ethyl alcohol volume used.

Statistical analyses

All data were initially tested for normality using the Shapiro-Wilk test from the UNIVARIATE procedure of SAS (version 9.3; SAS Inst. Inc., Cary, NC), and the results indicated that all data were distributed normally ($W \geq 0.80$). The data were then analyzed using the PROC MIXED procedure of SAS and the Satterthwaite approximation to determine the degrees of freedom for the tests of fixed effects. The treatments were considered fixed effects. Significant differences between the means were determined using Fisher's protected LSD test. Effects were considered significant at $P \leq 0.05$.

Results

The results showed significant effects ($p \leq 0.05$) of soil amendments on the soil physical attributes and on the stabilization of organic carbon via aggregation mechanisms (Tables 4 and 5). The surface application of the combination of lime and phosphogypsum increased the amount of water-stable aggregates >2.0 mm, consequently reducing the classes of >0.25–0.5 and >0.105–0.25 mm in all soil layers (Fig 1, S1 Table). Compared with the control, the effect of association on both soil amendments was more pronounced in the subsurface (below 0.05 m), and the observed increase was 82, 145, 273, and 152% in the 0.05–0.10-, 0.10–0.20-, 0.20–0.40-, and 0.40–0.60-m soil layers, respectively. Liming was the only practice that increased the level of aggregation (classes larger than 1.0 mm), but the product alone had no positive influence on increasing the proportion of macroaggregates in the 0.40–0.60-m layer. At a 0.05- to 0.40-m depth, a reduced effect of the application of phosphogypsum alone was observed, primarily in the aggregate classes of >2–8 mm and >0.105–0.25 mm, which showed increased MWD and GMD (Fig 2, S2 Table).

The soil amendment combination (lime + phosphogypsum) was considered a highly effective technique to improve the level of soil aggregation, providing the highest MWD and GMD

Table 4. ANOVA significance for soil physical attributes and total organic carbon (TOC) content in the water-stable aggregate classes.

Soil layer (m)	F probability		F probability	
	Blocks	Treatments	Blocks	Treatments
	Aggregate-size (>2.0–8.0 mm)		Mean weight diameter	
0–0.05	0.5458	0.0040	0.4979	0.0025
0.05–0.10	0.2906	<0.0001	0.2762	<0.0001
0.10–0.20	0.7876	<0.0001	0.4353	<0.0001
0.20–0.40	0.4396	<0.0001	0.5231	<0.0001
0.40–0.60	0.2538	<0.0001	0.1666	<0.0001
	Aggregate-size (>1.0–2.0 mm)		Geometric mean diameter	
0–0.05	0.4151	0.0524	0.6207	0.0002
0.05–0.10	0.6515	0.0065	0.2232	<0.0001
0.10–0.20	0.8471	<0.0001	0.3541	0.0001
0.20–0.40	0.7006	0.0007	0.1905	0.0002
0.40–0.60	0.9271	0.0021	0.2091	0.0004
	Aggregate-size (>0.5–1.0 mm)		Penetration resistance	
0–0.05	0.8771	0.4191	0.1499	<0.0001
0.05–0.10	0.8540	0.0009	0.9612	0.0246
0.10–0.20	0.9840	0.2724	0.9960	0.0088
0.20–0.40	0.3032	0.0141	0.4761	0.2264
0.40–0.60	0.5779	0.0015	0.6347	<0.0001
	Aggregate-size (>0.25–0.5 mm)		TOC in macroaggregates (>2.0–4.0 mm)	
0–0.05	0.3058	0.0010	0.8736	0.0003
0.05–0.10	0.8010	0.0015	0.5062	0.0002
0.10–0.20	0.5053	<0.0001	0.2856	0.4491
0.20–0.40	0.2961	<0.0001	0.3151	0.0334
0.40–0.60	0.4827	0.0005	0.9912	0.2712
	Aggregate-size (>0.105–0.25 mm)		TOC in mesoaggregates (>0.25–2.0 mm)	
0–0.05	0.5013	0.0009	0.6179	<0.0001
0.05–0.10	0.2795	<0.0001	0.1302	<0.0001
0.10–0.20	0.4863	0.0004	0.6788	<0.0001
0.20–0.40	0.3602	0.0049	0.5174	0.0004
0.40–0.60	0.1449	0.0069	0.3126	0.0005
	Aggregate-size (<0.105 mm)		TOC in microaggregates (>0.105–0.25 mm)	
0–0.05	0.1804	<0.0001	0.1409	0.4698
0.05–0.10	0.7101	0.0075	0.4096	0.0108
0.10–0.20	0.1554	0.0005	0.2187	<0.0001
0.20–0.40	0.7024	0.0216	0.5365	0.0064
0.40–0.60	0.9636	0.0075	0.3877	0.0004

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values in all soil layers (S2 Table), with a high correlation observed between MWD and soil chemical parameters. Compared with liming alone, the synergistic effect of phosphogypsum applied with lime only was not observed at the soil surface (0- to 0.05-m depth). In addition, the combination of both soil amendments contributed to the increase in MWD and GMD in deeper soil layers.

The combined application of lime and phosphogypsum effectively increased the organic C content in different classes of aggregates (>2.0–8.0, >0.25–2.0, and >0.105–0.25 mm) (Fig 3, S3 Table). In soil surface layers (0–0.05 and 0.05–0.10 m), the amendment materials resulted in the highest accumulation of organic C on macro- and meso-aggregates, i.e., 68 and 80% from 0

Table 5. Aggregate stability index, soil bulk and particle density, total porosity, macroporosity, and microporosity of soil as affected by the surface application of lime and phosphogypsum in different soil layers in a tropical no-tillage system.

Treatments	Soil layers (m)				
	0–0.05	**0.05–0.10**	**0.10–0.20**	**0.20–040**	**0.40–0.60**
	Aggregate stability index (%)				
Control	79.3 b†	66.3 c	68.3 c	66.5 b	59.3 b
Phosphogypsum	75.7 c	73.5 b	75.4 a	65.8 b	60.4 b
Lime	85.0 a	73.7 b	71.1 b	67.5 b	54.1 c
Lime + Phosphogypsum	83.8 a	77.6 a	75.4 a	72.3 a	63.3 a
F probability					
Block	0.6813	0.5679	0.8518	0.5055	0.3745
Treatments	<0.0001	<0.0001	0.0001	0.0041	<0.0001
	Soil bulk density (kg dm^3)				
Control	1.60 a	1.78 a	1.79 a	1.73 a	1.56 a
Phosphogypsum	1.54 a	1.69 ab	1.77 a	1.61 b	1.56 a
Lime	1.66 a	1.68 ab	1.62 b	1.53 c	1.39 b
Lime + Phosphogypsum	1.56 a	1.62 b	1.56 b	1.48 c	1.36 b
F probability					
Block	0.5089	0.5288	0.3377	0.2837	0.5278
Treatments	0.4473	0.1531	0.0059	<0.0001	0.0016
	Particle density (kg dm^3)				
Control	2.28 a	2.46 a	2.46 a	2.42 a	2.26 a
Phosphogypsum	2.27 a	2.34 ab	2.46 a	2.32 ab	2.24 a
Lime	2.34 a	2.34 ab	2.32 ab	2.23 b	2.09 b
Lime + Phosphogypsum	2.24 a	2.29 b	2.21 b	2.14 b	2.04 b
F probability					
Block	0.2660	0.2958	0.3301	0.2782	0.9001
Treatments	0.5936	0.0710	0.0135	0.0437	0.0045
	Total porosity (%)				
Control	42.0 a	37.8 a	37.1 b	39.5 b	45.1 b
Phosphogypsum	47.1 a	38.8 a	39.3 b	43.7 ab	44.6 b
Lime	41.5 a	39.8 a	43.0 a	46.5 a	50.3 a
Lime + Phosphogypsum	44.1 a	41.6 a	42.0 a	45.3 a	50.6 a
F probability					
Block	0.9190	0.2948	0.7681	0.8302	0.2173
Treatments	0.4157	0.4718	0.0041	0.0670	0.0122
	Macroporosity (%)				
Control	12.0 b	6.8 b	5.5 b	6.0 c	10.3 b
Phosphogypsum	16.9 a	10.8 a	8.5 a	14.5 a	11.5 b
Lime	9.0 b	7.0 b	8.7 a	10.5 b	14.3 a
Lime + Phosphogypsum	11.8 b	9.8 a	8.5 a	9.0 b	14.8 a
F probability					
Block	0.2635	0.1262	0.6010	0.5886	0.9296
Treatments	0.0023	0.0047	0.0029	0.0001	0.0005
	Microporosity (%)				
Control	30.0 a	31.0 a	31.8 a	33.3 ab	34.8 a
Phosphogypsum	30.3 a	28.0 a	31.0 a	29.0 b	32.8 a
Lime	32.5 a	32.8 a	34.5 a	36.5 a	36.0 a
Lime + Phosphogypsum	32.3 a	31.8 a	33.5 a	36.0 a	35.8 a

(*Continued*)

Table 5. (*Continued*)

Treatments	Soil layers (m)				
	0–0.05	0.05–0.10	0.10–0.20	0.20–040	0.40–0.60
F probability					
Block	0.6779	0.9699	0.4261	0.8588	0.5265
Treatments	0.7041	0.2948	0.2272	0.0433	0.5257

† Values followed by the same letter within a column are not significantly different at $p \leq 0.05$ according to the LSD test.

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to 0.05 m and 76 and 58% from 0.05 to 0.10 m, respectively, compared with the control treatment. A greater TOC content in the microaggregates was also observed; however, only the combination of both soil amendments was considered effective for increasing the TOC content in this class of aggregates in all soil layers because surface liming alone did not increase the TOC in microaggregates at a depth of up to 0.1 m. Despite the positive effect of phosphogypsum on the protection mechanisms and the promotion of organic C accumulation in an Oxisol, the benefits were only effective when phosphogypsum was applied in combination with lime.

The ASI was positively affected by a combination of lime and phosphogypsum, with gains of 6%, 17%, 10%, 8%, and 7% in the aggregate stability in the soil layers of 0–0.05, 0.05–0.10, 0.10–0.20, 0.20–0.40, and 0.40–0.60-m, respectively (Table 5, S4 Table). This finding may result from the direct effect of these materials on increasing the pH and the Ca exchange levels because there was a high correlation between these parameters and the aggregate stability index (S4 Table). The surface application of lime increased the aggregate stability at a depth of up to 0.40 m, but in the deeper layer (from 0.40 to 0.60 m), this practice increased the proportion of unstable aggregates compared with the control treatment. The surface application of lime, alone or combined with phosphogypsum, was considered an efficient strategy to increase macroporosity (pores with a diameter $\geq$30 μm) in the soil profile, resulting in an increase in total porosity to a depth of 0.10 m, reducing soil bulk density by up to 16% in subsurface soil layers. Microporosity (pores with a diameter $<$30 μm) was not affected by the addition of both amendments in a combination; however, in a no-till system, management practices that positively influence the macropore distribution are considered fundamental because these pores directly affect root growth, primarily in regions with dry seasons. Some studies consider a critical degree of compaction when the total macroporosity is less than 10% [30,31].

The lower distribution of macropores in lime-amended soil compared with the application of phosphogypsum alone from a 0- to 0.10-m depth was not associated with penetration resistance because the results obtained showed that only surface liming reduced the ratio of penetration resistance by up to 39% in the uppermost soil layers (S4 Table), which may be related to the formation of biopores via biological activity.

In all soil layers, except at the 0.20–0.40-m depth, lower penetration resistance rates were obtained by applying a combination of lime and phosphogypsum (Fig 4, S5 Table). The application of lime alone had a substantial effect on the uppermost soil layer because this treatment provided the lowest penetration resistance value (1.55 MPa) for a 0- to 0.05-m depth. Both soil amendments, alone or combined, had different effects according to the soil depth but were useful for ameliorating the Oxisol soil structure cultivated under NT systems.

Discussion

The indirect effect of soil amendments on increasing the input of above- and under-ground residues has been considered to play a fundamental role in improving soil physical attributes

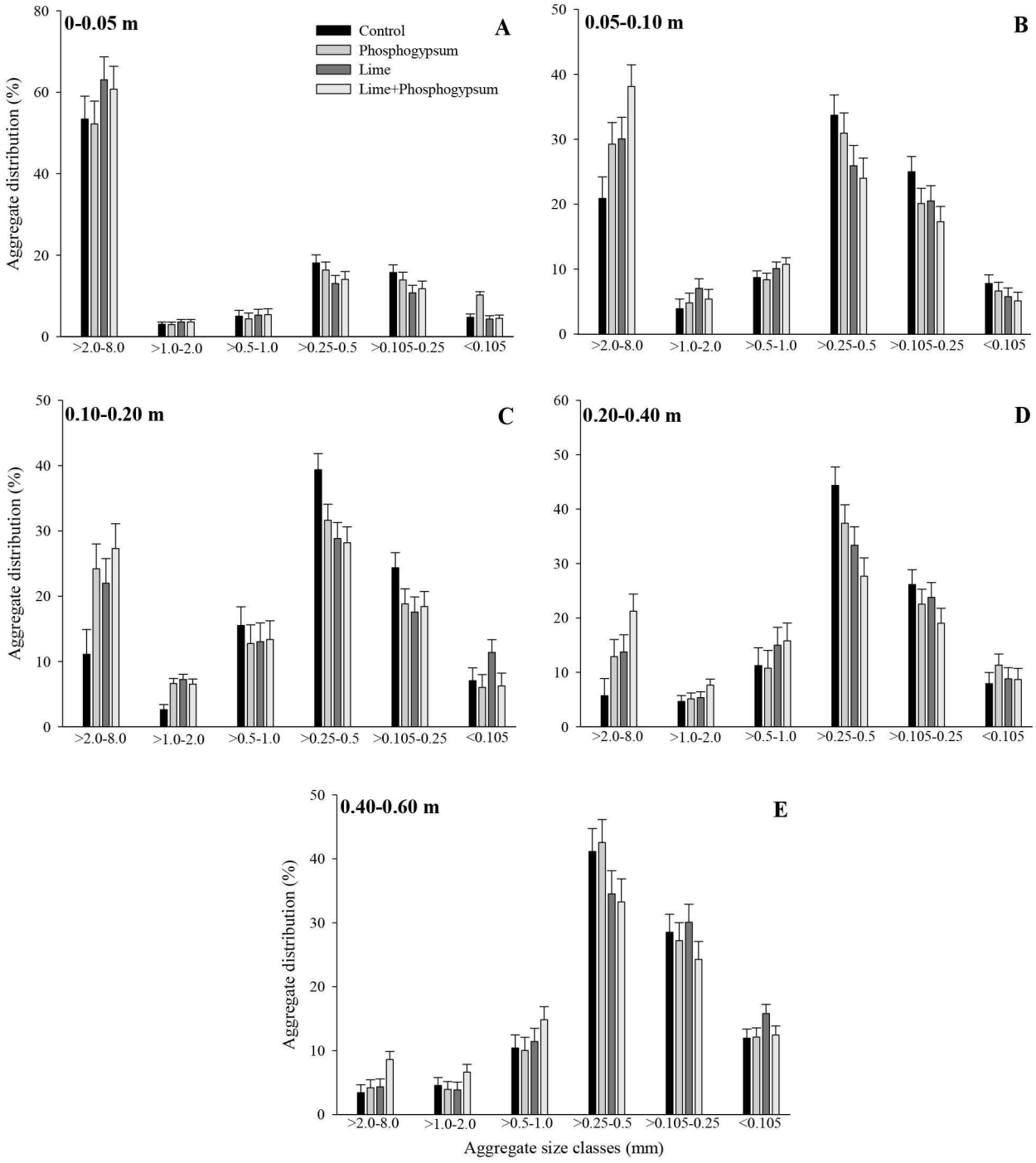

Fig 1. Water-stable aggregate distribution as affected by the surface application of lime and phosphogypsum in different soil layers in a tropical no-tillage system. The vertical bars indicate the least significant difference at $p \leq 0.05$.

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(Table 3) [13,32,33]. In a long-term study conducted using a kaolinitic, thermic Typic Hapludox soil, Briedis et al. [33] reported a greater influence of surface liming on the soil structural organization due to the high input of organic C by crop residues and the microbial activity with soil acidity alleviation; however, there is no information available about this influence

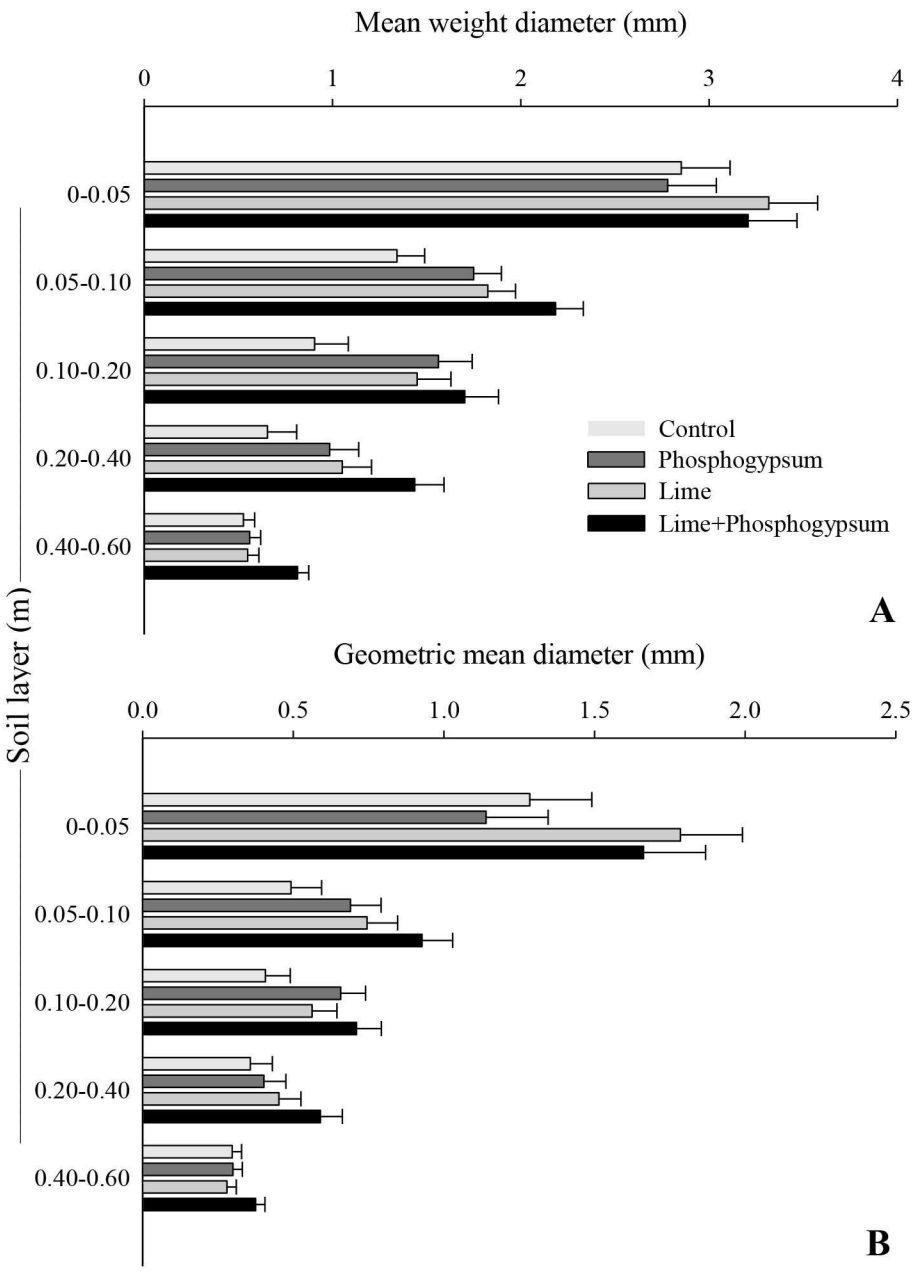

Fig 2. Mean weight diameter and geometric mean diameter of aggregates as affected by the surface application of lime and phosphogypsum in different soil layers in a tropical no-tillage system. The horizontal bars indicate the least significant difference at $p \leq 0.05$.

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under tropical conditions. As mentioned, the input of crop residues plays a fundamental role in increasing the formation and stability of larger aggregates, primarily those with a diameter >1 mm [34]; however, in tropical regions, the high temperature and humidity favor the decomposition of organic residues, affecting organic C storage.

Several organic and inorganic compounds increase water-stable aggregation, and according to the aggregate hierarchy concept, each stage of formation is associated with different binding agents [15]. The chemical-physical interaction between some organic molecules and

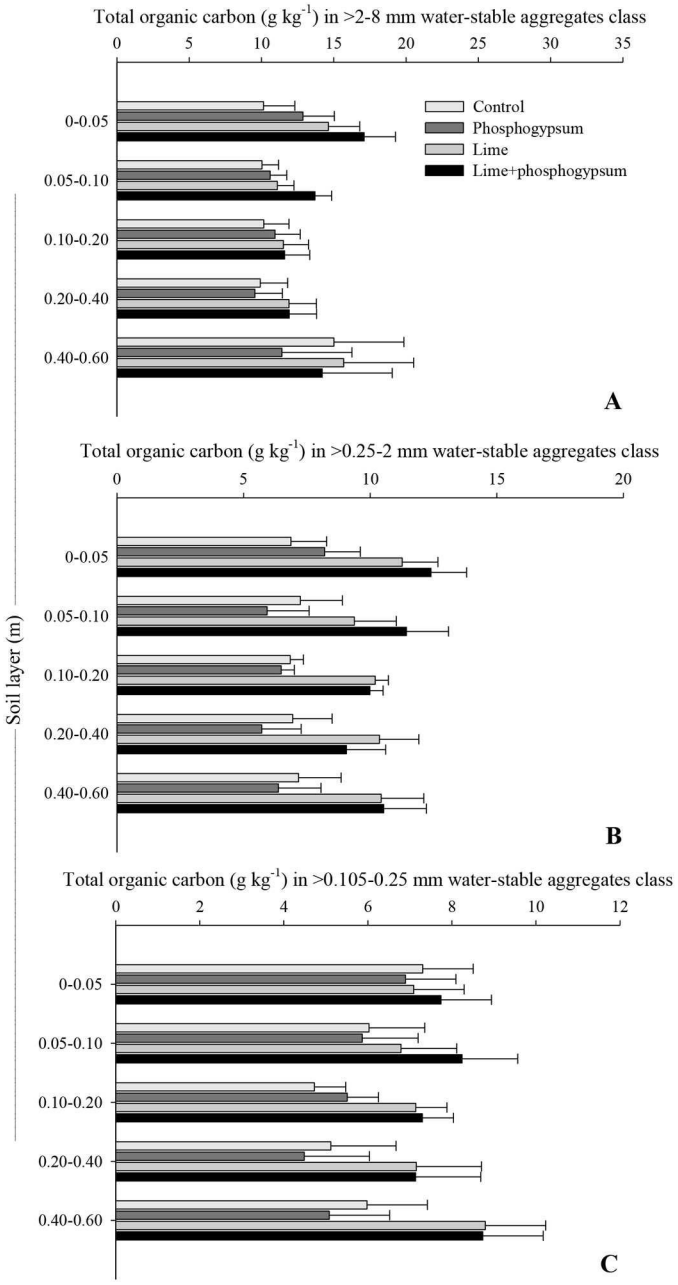

Fig 3. Total organic carbon content in the water-stable aggregate classes as affected by the surface application of lime and phosphogypsum in different soil layers in a tropical no-tillage system. The horizontal bars indicate the least significant difference at $p \leq 0.05$.

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polyvalent cations and mineral particles was proposed by Edwards and Bremner [35] to describe microaggregation (<0.25 mm). Sequentially, due to the action of soil organisms, roots, litter fragments, and non-humic substances (such as carbohydrates), larger aggregates are formed and stabilized [14,36]. Consequently, management practices that enhance SOM input are considered highly effective for the improvement of the soil structure.

Several researchers considered that the high input of labile organic matter (shoot and root fragments) is an important agent for the formation and stability of larger aggregates

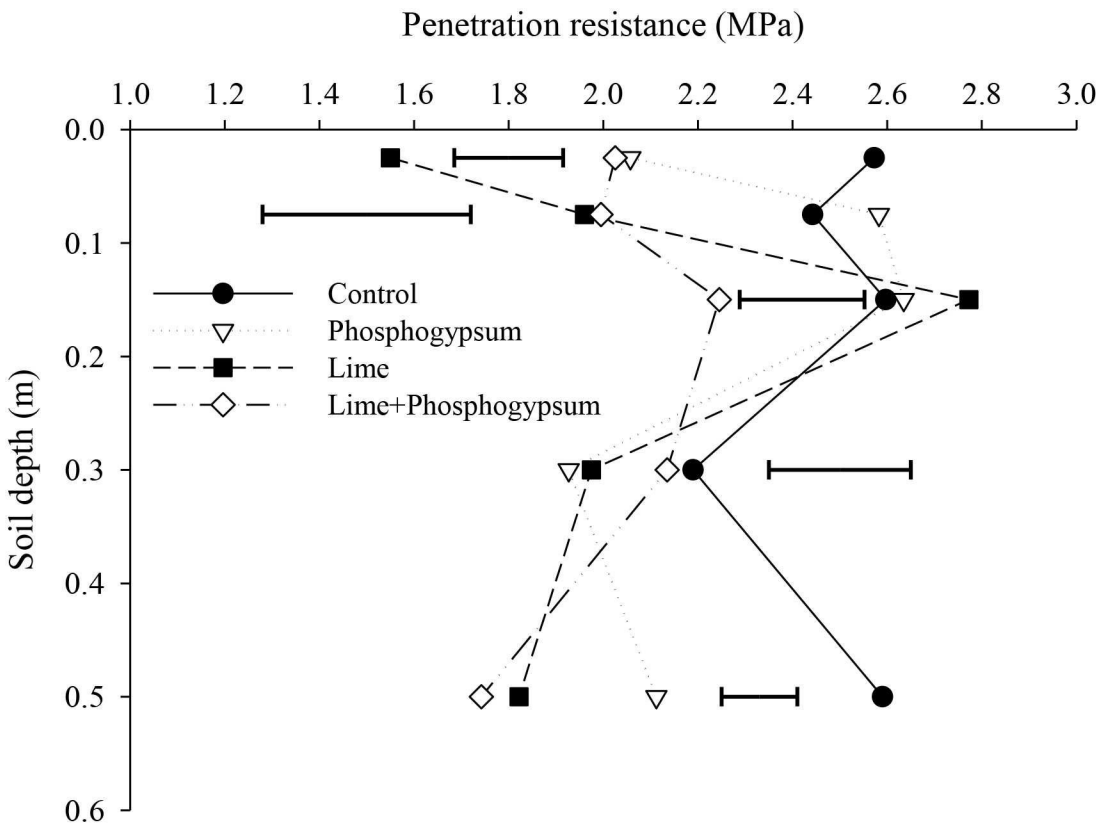

Fig 4. Penetration resistance as affected by the surface application of lime and phosphogypsum in different soil layers in a tropical no-tillage system. The horizontal bars indicate the least significant difference at $p \leq 0.05$.

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[13,33,36,37]. Because this organic fraction is highly sensitive to soil acidity and management practices, amendment procedures that improve soil chemical properties without the disruption of soil structure are desirable. In a clay Typic Rhodudalf soil, Castro et al. [9] reported that surface liming could increase labile organic matter in the soil surface layer six years after the treatment establishment; however, the authors did not observe positive results in subsurface layers due to the low effect of lime on acidity alleviation [5]. Roots are considered the most important source of labile organic matter for subsoil layers; thus, practices that increase root growth into subsoil layers play a fundamental role in the formation and stability of larger aggregates in the subsoil. In addition, the root structures are considered a more effective approach to improve the soil structure than above-ground residues [33].

Our long-term results showed the benefits of soil amendments on the stability of the largest aggregate class (>2.0–8.0 mm) (Fig 1), and this effect may be explained by the effect on root growth at deeper soil layers (Table 3). Six et al. [14] reported a strong effect of root development on the proportion of macroaggregates and described the effect on the soil water regime, root exudation, and root biomass as the result of important mechanisms involved in the stability of macroaggregates. Evaluating the effect of root-released substances on aggregate properties over 30 days of incubation, Traoré et al. [38] reported that the proportion of stable aggregates increased 3.8-fold due to the root mucilage effect. Changes in aggregate properties by water regime and microbial community dynamics were reported by Denef et al. [39]. In a soil with 30% of dry weight composed of macroaggregates, these authors reported a reduction in the amount of large aggregates to 21% after the first cycle of drying and wetting, but after

two cycles, the macroaggregates became more resistant. In addition, these authors observed a high linear correlation between fungal biomass and the percentage of large aggregates (r^2 = 0.93), suggesting that the amount of fresh residues via the roots is fundamental to enhance fungal growth, consequently enhancing the structural stability.

In conclusion, due to the effect of soil chemical deficiencies on root growth, the structural stability of the aggregates can be affected. Several studies described Al^{3+} toxicity as the major root growth-limiting factor [12,40]; thus, the modifications caused by lime and phosphogypsum application (alone or combined) on exchangeable Al^{3+} levels may result in differences in the root architecture, thus, in the amounts of stabilization agents. Based on the regression models, Caires et al. [41] observed a highly negative correlation between wheat root length density and exchangeable Al^{3+} levels. At topsoil layers (0–0.20 m), the authors reported a decrease of approximately 6.0% in root length density for each increase of 1 $mmol_c$ dm^{-3} in exchangeable Al^{3+}. This result can explain the benefits of the lime + phosphogypsum application, showing the highest aggregate stability in the largest aggregate class in the 0.05–0.10-, 0.20–0.40-, and 0.40–0.60-m layers. In a sodic soil with a low infiltration rate, Valzano et al. [42] also reported that the combination of lime and gypsum provided a higher accumulation of SOM, which reduced the degree of dispersion of mineral particles, increasing the proportion of more stable, larger aggregates.

In addition to the indirect effect of the lime + phosphogypsum treatment on enhancing the proportion and stability of macroaggregates (Fig 1), the chemical effects of the different treatments (Table 3) can also induce divergent changes in the flocculation mechanisms. According to Roth and Pavan [7], in soils with variable charges, the addition of lime alone increases the pH, favoring repulsive forces between particles and leading to a dispersion phenomenon; however, because Ca acts as a binding agent, practices that increase Ca levels in the soil enhance the formation and stability of microaggregates, which is essential for large aggregate arrangements. Therefore, the phosphogypsum effect in lime-amended soil can also explain the greater stability of large aggregates, primarily in deeper soil layers (0.20–0.40 and 0.40–0.60 m) in the size classes from >1.0 to 2.0 mm and from >2.0 to 8.0 mm. Baldock et al. [43] reported that dispersive mechanisms in a red-brown soil (Rhodoxeralf) were significantly reduced by the addition of lime and gypsum, but a better effect was observed when higher amounts of Ca^{2+} were added. Corrêa et al. [44] found a significant correlation between Ca and soil aggregation, which was positive for aggregate classes of 4–2 mm and negative for the 0.5–0.25 mm class. Although microaggregate stability plays a fundamental role in macroaggregate arrangements, Baldock et al. [43] emphasized that labile organic matter is essential for the formation and stabilization of larger aggregates because in soil without the addition of organic residues, the authors did not report an effect of lime and gypsum addition on macroaggregate stability.

Due to the better level of organization, a reduction in the proportion of smaller aggregates was observed, primarily in the size classes from >0.105 to 0.25 mm and from >0.25 to 0.5 mm, as reported by Muneer and Oades [45]. Therefore, a higher proportion of water-stable aggregates > 1 mm was observed with soil amendments applied in combination, which resulted in an increase in MWD and GMD (S2 Table). Briedis et al. [33] reported a strong linear relationship between MWD and organic C input ($MWD = 0.92\ C_{input} + 7.1$, $R^2 = 0.99$), reinforcing the hypothesis that management techniques that contribute to the increase in soil organic matter (via above- and below-ground biomass) are important for improving the soil structure. In addition to the quantity of C, Martins et al. [36] suggested that the quality of the organic residues might contribute to an increase in the proportion of large water-stable aggregates in Oxisols. The researchers reported a close relationship between MWD and the pentose ($r^2 = 0.88$, $p<0.001$) and hexose ($r^2 = 0.77$, $p<0.01$) contents because these substances stimulate the activity of specific decomposers that are associated with macroaggregation. Because

the hydrolysable carbohydrate contents are often associated with soil chemical properties, factors such as soil acidity and nutrient deficiency have limited the supply of these organic molecules [46].

Several organic C compounds, such as humic substances, mucilages, and polysaccharides, are considered important binding agents for the formation and stabilization of aggregates, which provide a protective physical barrier against the action of decomposers, preventing the oxidation of SOM. Each aggregate class is involved in the protection of specific fractions [47]. The fact that most of the organic C is present in the >0.105–0.25 mm water-stable aggregate class is most likely related to the amounts of humic substances because these compounds have a strong chemical interaction with the clay mineral fraction and are considered important binding agents for microaggregation. Due to the high stability of humic compounds, no changes in TOC in the 0–0.05-m layer were observed, and the chemical changes induced by the combined application of lime and phosphogypsum were not enough to induce changes in the SOM dynamics in this layer (Table 3). However, in deeper layers, the soil amendments applied in a combination may influence the metabolic pathway of humic substances, possibly contributing along with the addition of organic residues (via above- and below-ground biomass), mainly those rich in lignin, considered a precursor of these compounds [48]. Roots have been reported to be rich in lignin compared with the aboveground residues [49], and Caires et al. [41] reported the benefits of surface liming on root growth. Our results suggest that soil amendments can modify the amounts of these substances in the soil due to the addition of organic residues, contributing to an increase in TOC in smaller aggregates. Lehmann et al. [50] observed that organic C in soil microaggregates is more closely related to the high stability of these organic molecules on mineral surface charges than to C physical protection.

As mentioned above, the larger aggregates (from >0.25 to 8.0 mm) are formed by the union of small aggregates (from >0.105 to 0.25 mm), and transitory and temporary organic fractions, such as polysaccharides, microorganism cells, and crop residues (roots and shoots), play an important role in this process [51]. Therefore, the major reason that the combined application of lime + phosphogypsum improves TOC stored in larger aggregates (from >0.25 to 2.0 and >2.0 to 8.0 mm) in the surface (0–0.05 and 0.05–0.10 m) and subsurface layers (0.10–0.20 and 0.20–0.40 m) is the effect of soil amendments on root and shoot growth [13] (Fig 3). However, most of the organic C stored in larger aggregates is attributed to aboveground residues (biomass senescence and compounds exuded) [34], and the Al^{3+} complexation and soil acidity alleviation is fundamental for an increase in the C flow. In medium-textured soils, a positive relationship between the amounts of C physically protected and the C input was reported by Chevallier et al. [52]. Because the indirect effect of the surface application of lime and phosphogypsum is to modify different size fractions of SOM [9,13,31], the amendment practices were considered to enhance C storage in tropical acid soils that are naturally low in organic matter content.

The contribution of soil amendments to the formation and stability of large macroaggregates through different SOM fractions has a positive effect on the soil structure over time, primarily increasing the macroporosity and reducing the soil bulk and particle density in subsurface soil layers (below a 0.10-m depth) (Table 5). Similar results were obtained by Haiti et al. [53] in Alfisol soil of sub-humid tropics. The authors primarily attributed the positive effect on the soil's physical attributes to changes in the TOC content at a 0–0.30-m soil depth, highlighting a significant ($P<0.01$) and positive linear relationship with total porosity and a negative linear relationship with soil bulk density. Therefore, due to soil amendments application, soil aggregation increased the volume of macropores, which serve as channels for water to flow through a soil profile. Changes in the pore size distribution and SOM content affected the soil bulk and particle density. According to Rühlmann et al. [54], in addition to the

Table 6. Pearson correlation coefficients among soil physical attributes (aggregate stability index, soil bulk density, mean weight diameter, and penetration resistance) and soil chemical properties (pH, exchangeable Al^{3+}, and Ca^{2+}) affected by lime and phosphogypsum application in an Oxisol under a long-term no-tillage experiment.

Chemical parameter†	Soil physical attributes							
	Aggregate stability index		Soil bulk density		MWD		Penetration resistance	
	r	*P*	*r*	*P*	*r*	*P*	*R*	*P*
pH	0.8851	<0.0001	-0.5600	0.024	0.8728	<0.0001	-0.7899	<0.0001
Al^{3+}	-0.9072	<0.0001	0.5926	0.0162	-0.9140	<0.0001	0.8761	<0.0001
Ca^{2+}	0.9194	<0.0001	-0.5898	0.0159	0.9014	<0.0001	-0.8025	<0.0001

†MWD: mean weight diameter;

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quantity of SOM, the factors influencing the composition (ranging from 1.10 to 1.50 g cm^{-3}) and the distribution of different organic components in soils significantly affect the soil particle density. Thus, soil acidity management practices in acidic soils are considered a key factor to increase the SOM pool, translating into benefits for the soil's physical attributes.

The positive effect of phosphogypsum alone on increasing the macroporosity in the uppermost soil layers (0–0.05- and 0.05–0.10-m depths) may be attributed to the ratio between positive and negative charges. As mentioned above, the liming effect of increasing the CEC may induce dispersive forces, which can increase clay dispersion, sealing the surface macropores [7]. Because phosphogypsum does not change the CEC, these dispersive mechanisms were not observed. However, the primary effect is most likely related to the gypsum effect of increasing the root growth, which can affect the volume of biopores formed by root senescence [11,40]. McCallum et al. [55] reported significant benefits from perennial pasture root growth to increase the soil macroporosity (pores >2 mm); in addition, the authors considered management strategies for root growth as an important tool to ameliorate the porosity in undisturbed soil.

Marsili et al. [56] found a significant correlation between the volume of larger pores and soil penetration resistance in the surface layer (0–0.10 m), whereas our results demonstrated the lowest values of penetration resistance in treatments involving the application of lime without gypsum (Table 6). This effect is most likely related to the higher aggregate stability index in lime-amended soil compared with the index in soil treated with only a surface application of phosphogypsum. At the sampling time, phosphogypsum treatments had a higher macroporosity at the soil surface; however, our results suggested that these structures were formed by aggregates with low stability, which characterizes the macropores as fragile structures that are easily affected by anthropogenic and environmental factors. Thus, amendment practices that alleviate soil acidity and increase the amount of stabilizing substances (such as Ca^{2+} levels and crop residues) are considered effective for improving soil structure stability and reducing soil penetration resistance.

In subsoil layers, the results obtained by the lime + phosphogypsum treatment demonstrated the viability of the combined use of both soil amendments. The additive effect of phosphogypsum can be related to the root growth and to the supply of Ca on the subsurface, considering the importance of binding agents between organo-mineral particles. In a Panoche soil irrigated with saline water, Mitchell et al. [57] reported a positive effect of a surface gypsum application on some soil physical attributes, reducing the soil crust strength by an average of 14% and increasing the soil aggregate stability by an average of 46%. However, there is limited information regarding the effect of the combined surface application of lime and phosphogypsum on the physical attributes of the Oxisol profile.

Conclusion

The surface application of lime and phosphogypsum in a tropical acid soil induced significant changes to the soil physical structure. Our long-term findings showed that the combination of both soil amendments plays an important role in improving the physical properties of tropical acid soils treated with conservative principles, without soil mechanical mobilization. The combined application of lime and phosphogypsum provided a positive effect on the formation and stabilization of large aggregates (>1.0 mm), inducing the complexation of organic carbon in these structures, which is fundamental for the enhancement of soil structure. A better aggregation level promoted larger MWD and GMD, even in deeper soil layers, which may have resulted in greater macroporosity as well as lower soil bulk density and penetration resistance.

Supporting Information

S1 Table. Water-stable aggregate distribution as affected by surface application of lime and phosphogypsum in different soil layers, in a tropical no-tillage system.
(PDF)

S2 Table. Mean weight diameter and geometric mean diameter of aggregates as affected by surface application of lime and phosphogypsum in different soil layers, in a tropical no-tillage system.
(PDF)

S3 Table. Total organic carbon in the water-stable aggregate classes as affected by surface application of lime and phosphogypsum in different soil layers, in a tropical no-tillage system.
(PDF)

S4 Table. Aggregate stability index, soil bulk and particle density, total porosity, macroporosity, and microporosity of soil as affected by the surface application of lime and phosphogypsum in different soil layers in a tropical no-tillage system.
(PDF)

S5 Table. Penetration resistance as affected by surface application of lime and phosphogypsum in different soil layers, in a tropical no-tillage system.
(PDF)

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General conclusions

Superficial liming alleviated the surface and subsurface soil acidity, whereas the combination with phosphogypsum provides major benefits on soil pH, exchangeable Ca and Mg levels, and base saturation in the topsoil layers (0 to 0.10 m).

The surface application of lime is effective to improve root growth, crop nutrition and wheat and common bean grain yield, but the combination with phosphogypsum provides positive effects only for common bean growth.

Soil acidity alleviation increased soil organic matter input in an Oxisol conducted 12 years under no-tillage system. The high correlation between organic carbon pools and soil chemical attributes shows that soil organic matter input was favored mainly by maintenance of high levels of exchangeable Ca and Mg and low levels of exchangeable Al. The combination of lime and phosphogypsum improved soil organic matter quality, increasing the formation and stabilization of humic substances.

The combination of lime and phosphogypsum also plays an important role in improving the physical properties of the tropical Oxisol conducted 12 years under no-till procedures. The use of phosphogypsum associated with lime provided benefits on the formation and stabilization of large aggregates (>1.0 mm), inducing the complexation of organic matter in these structures, contributing to the organic carbon accumulation in the soil. These results promoted a better physical condition of the soil, even in subsoil layers, resulting in greater macroporosity as well as lower soil bulk density and penetration resistance.

Lime rate estimated to increase the base saturation in the topsoil (0-0.20 m) to 70% was considered appropriate for surface liming recommendation in a tropical Oxisol under no-tillage system, but the combination with phosphogypsum provides major benefits on soil chemical and physical attributes and SOM quality.