Adsorption and desorption of phosphorus in subtropical soils as affected by management system and mineralogy

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A B S T R A C T

Phosphorus added to soil is only partly available to crops because it is sorbed to some extent by various soil components. The aim of this study was to assess the influence of mineralogy and soil management (either conventional tillage, CT, or no-tillage, NT) on the maximum P adsorption capacity (P_{max}), remaining P (P_{rem}), and maximum desorbable P (β) in a Rhodic Paleudult, a Rhodic Hapludox and a Humic Hapludox, all from southern Brazil. P_{max} was estimated from the Langmuir equation describing the sorption curve for soil samples and β from a first-order kinetic equation describing successive P extraction with an anion-exchange resin following incubation of the soils with an amount of P equivalent to 30% of P_{max} (P_{added}). P_{max} and P_{rem} were significantly correlated with the content of iron oxides (mainly in goethite, Gt). P_{max} was lower under NT than under CT in the Rhodic Paleudult and Rhodic Hapludox. On the other hand, P_{rem} was lower under CT than under NT, and exhibited significant differences between the 0–5 and 5–10 cm layers under NT. Parameter β peaked in the soil with the highest P_{max} but the β/P_{added} ratio was highest in the Rhodic Paleudult, which was the soil with the lowest content in iron oxides. These results suggest that the soil with the highest P_{max} and Gt content (viz., the Humic Hapludox) supplies plants with P at a lower rate than the other two despite its high P desorption potential.

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1. Introduction

Phosphorus (P) in soil is an important limiting nutrient to agricultural production and, due its scarcity, was considered by Cordell and Neset, (2014) as one of global environmental challenges of the 21th century. The efficient use and management of P in farming systems is fundamental to reach large agricultural productivity without threatening the environmental quality (MacDonald et al., 2011; Mihailescu et al., 2015).

Strongly weathered soils sorb large amounts of phosphorus (P) and limit plant growth as a result (Vitousek et al., 2010). The degree of interaction between phosphate and soil minerals can be measured via the maximum phosphorus adsorption capacity (P_{max}; Olsen and Watanabe, 1957) or remaining phosphorus (P_{rem}; Alvarez and Fonseca, 1990). P_{max} is generally estimated from a Langmuir equation fitting P sorption data, whereas P_{rem} represents the amount of P remaining in solution at equilibrium after addition of a known amount to a soil suspension.

Some studies indicate that P sorption is correlated to the clay fraction content of the soil (Barbieri et al., 2013; Oliveira et al., 2014). However, this correlation is substantially influenced by the content and crystallinity of iron oxides [particularly hematite (Hm), goethite (Gt) and maghemite (Mh)] and aluminum hydroxides [particularly gibbsite (Gb)] (Barrón and Torrent, 1996; Lair et al., 2009; Broggi et al., 2010; Yoon et al., 2014; Bortoluzzi et al., 2015). Goethite generally sorbs more P than paragenetic Hm by virtue of its higher surface area (Torrent et al., 1994; Wang et al., 2013; Bortoluzzi et al., 2015). Thus, P_{max} in some Brazilian soils has been positively correlated with Gt and Gb contents (Barbieri et al., 2009; Barbieri et al., 2009b) and negatively correlated with P_{rem} (Andrade et al., 2002). Therefore, fertilizer P recommendations based on clay content may not be accurate (Pinto et al., 2013).

The extent of desorption of P sorbed in soil depends on the chemical nature and energy of the bonds between phosphate and soil components (Guppy et al., 2005; Antelo et al., 2007). One method for evaluating maximum desorbable P (β) involves successive extraction of the soil with an anion-exchange resin (AER; McKean and Warren, 1996; Tiecher et al., 2012). Organic acids compete with phosphate for sorption sites and modify the

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bonding energy of sorbed P (Schwertmann et al., 1986; Mikutta et al., 2006; Lindegren and Persson, 2009). Lemare et al. (1987) found the addition of organic residues to soil to have no effect on P_{max} but to increase β in previously fertilized soils, probably because of the decrease in adsorption energy between iron oxides and phosphate (Kreller et al., 2003). A similar effect can result from long-term conservation management practices increasing soil organic matter such as no-tillage (NT) (Duiker and Beegle, 2006; Souza et al., 2014). For example, Tiecher et al. (2012) and Pavinato et al. (2010) found P desorption from Brazilian Oxisols to be greater under NT than under conventional tillage (CT), suggesting a way to improve the efficiency of P fertilizers in soils with high P_{max}.

Characterizing P sorption and desorption in soils under different management systems may be useful to develop effective fertilizer use strategies. The primary aim of this study was to assess the influence of mineralogy and soil management on P_{max}, P_{rem} and β in three types of subtropical soils under long-term NT or CT.

2. Material and methods

2.1. Description of sites and soil sampling

Soil samples were collected in 2013 from three different Brazilian subtropical soils, namely: (1) a Rhodic Paleudult (RP; Soil Survey Staff, 2010) on granite located at the Agronomic Experimental Station of the Federal University of Rio Grande do Sul; (2) a Rhodic Hapludox (RH; Soil Survey Staff, 2010) on basalt located on a commercial farm (Rio Grande do Sul State) and (3) a Humic Hapludox (HH; Soil Survey Staff, 2010) on basalt located at the Experimental Station of the Agrarian Foundation for Agricultural Research in Paraná State. A randomized block experimental design with three blocks and two treatments (CT and NT) was used at the three sites.

The experiment on RP was installed in 1985 in a field where CT had been in practice since 1970. Soil in the NT plots was managed with a seeder/fertilizer machine with dual discs, and that in the CT plots was plowed with a ripper to a depth of 20 cm followed by disking in spring. Vetch (*Vicia sativa*) + black oats (*Avena strigosa*) in winter and maize (*Zea mays*) + cowpea (*Vigna unguiculata*) in summer were cultivated under NT, and only black oats and maize under CT. Winter crops were sown directly in both NT and CT plots. In the RH experiment, NT was implemented in 1997 after 27 years under CT with ripping and disking for soil disturbance. Crops were planted with a seeder/fertilizer furnished with a cutter disc in both NT and CT plots. The crop rotation used included wheat (*Triticum*
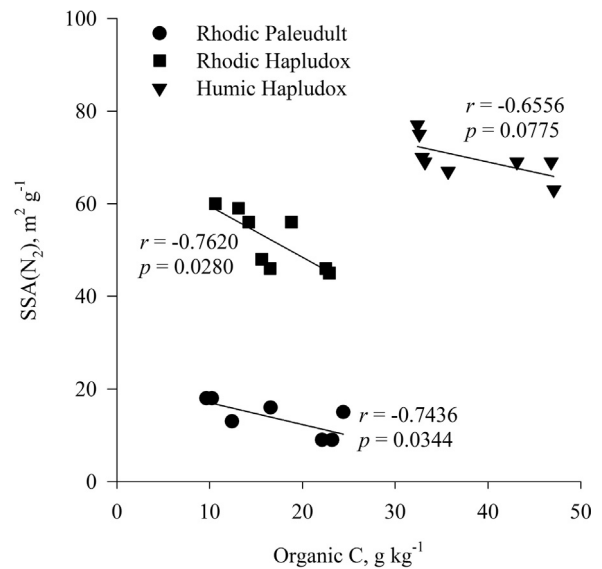
aestivum), soybean (*Glycine max*), wild radish (*Raphanus sativus*), black oat, vetch and maize. The soil for the HH experiment had been under CT with plowing to a depth of about 25 cm, and then disked in winter and summer, since 1950. NT was installed on one half of the area in 1978 and a seeder/fertilizer with a cutter disc used to seed wheat, barley (*Hordeum vulgare*), oats, wild radish, soybean, vetch and maize in a rotation system. In both experimental fields, fertilizers were applied in rows at a depth of 5–8 cm. P, K and N fertilizer were applied at the recommended rates for each crop (CFS RS/SC, 1995; CQFS RS/SC, 2004).

Thirty-six composite soil samples corresponding to 3 fields, 3 blocks, 2 treatments and 2 depths (0–5 cm and 5–10 cm) were studied. All samples had a high available P content (Mehlich-I), i.e., higher than the sufficiency or critical level (CQFS RS/SC, 2004), at the time of collection.

2.2. Soil analyses

Disturbed soil samples were air-dried, gently ground and passed through a 2-mm sieve to obtain the air-dried fine fraction for all subsequent analyses. Particle size analysis was performed by using the pipette method after dispersing particles in 1 mol $NaOH\,L^{-1}$. Then, the total clay fraction ($\emptyset < 0.002$ mm) of each soil sample was collected by sedimentation according to Stokes' law for mineralogical analysis. The clay suspension was flocculated with 1 mol $HCl\,L^{-1}$, washed with a 1:1 ethanol/water mixture, dried at 50 °C and gently ground in an agate mortar.

Total organic carbon (organic C) was determined by dry combustion in a Shimadzu VCSH carbon analyser. Specific surface area (SSA) was determined by using (1) water at a relative humidity of 20% as adsorbate (Quirk, 1955); and (2) the BET method with N_2 as adsorbate (Gregg and Sing, 1982) in a Micromeritics ASAP 2010 analyser.

Iron in pedogenic iron oxides was obtained by double extraction with a dithionite–citrate–bicarbonate mixture at 80 °C (Fe_d; Mehra and Jackson, 1960) and Fe in poorly crystalline Fe oxides (basically ferrihydrite) was extracted with 0.2 mol L^{-1} ammonium oxalate at pH 3.0 in the dark (Fe_{ox}; Schwertmann, 1964). Dissolved Fe was determined by atomic absorption spectroscopy (AAS). Selective dissolution of Mh ($\gamma\text{-}Fe_2O_3$) was accomplished by applying 1.8 mol $H_2SO_4\,L^{-1}$ at 80 °C to the clay fraction for 27 min (Schwertmann

Fig. 1. Pearson's correlation coefficient (r) between organic C and surface specific area with N_2 as adsorbate (SSA-N_2), and p value.

Table 1
Physico-chemical properties of the three soils under no-tillage system (NT) and conventional tillage (CT).

Soil	Rhodic Paleudult		Rhodic Hapludox		Humic Hapludox	
Depth	NT	CT	NT	CT	NT	CT
cm	Clay, g kg^{-1}					
0–5	210	225	572	588	638	635
5–10	197	212	571	583	630	627
	Organic C, g kg^{-1}					
0–5	23.6 a	10.0 b	23.2 aA	16.4b	48.9 aA	31.9b
5–10	17.0	10.1	16.2 B	12.1	36.1 B	31.6
	SSA(H$_2$O), m^2 g^{-1}					
0–5	26	22	58 a	61 b	73	72
5–10	21	25	56	59	71	73
	SSA(N$_2$), m^2 g^{-1}					
0–5	9 a	16 b	46 a	56 bB	66	72
5–10	11	17	47	59A	68	73

SSA(H$_2$O) and SSA(N$_2$) N$_2$ specific surface area as determined with water and nitrogen as adsorbate, respectively. Lowercase letters compare soil management systems and uppercase letters soil layers; absence of letters indicates no significant difference.