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Short communication

Paddy cultivation significantly alters the forms and contents of Fe oxides in an Oxisol and increases phosphate mobility

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ABSTRACT

To evaluate the effect of paddy cultivation on phosphorus environmental risk in an Oxisol–derived paddy soil, we examined phosphate (P) affinity on bulk soils and their different–size fractions with adsorption/desorption isotherms. The results showed that intermittent flooding in Oxisol–derived paddy soil, led to a significant decrease in free Fe oxides and an increase in amorphous Fe oxides in the surface (0–20 cm) and subsurface (20–40 cm) soils. A disproportional ratio of P adsorption capacities to the contents of free Fe oxides was observed in the studied Oxisol, when compared with that in the paddy soil, owing to more reactive sites exposed on amorphous Fe oxides than on crystalline Fe oxides. Furthermore, P adsorption/desorption isotherms revealed that non–electrostatic adsorption was the main mechanism responsible for P binding to the Oxisol and its derived paddy soil, representing 83.94%–99.62% of the adsorption capacities. Examination of P adsorption by different–size soil fractions further revealed that an equivalent mass of Fe oxides in the paddy soil particles retained more P than those in the Oxisol.

1. Introduction

The solid components of paddy soils, involving clay minerals, organic matter, microorganisms, particularly for the Fe oxides are intensively influenced by alternative submerged conditions in (sub)tropical areas (Kögel-Knabner et al., 2010). The intermittently waterlogged soils undergo segregation, gleying, and chloritisation, which affect the forms and contents of Fe oxides (Singh et al., 1998). These characteristics have a profound impact on the transport and mobility of contaminants (heavy metals, organic pollutants, pesticides, etc.) as well as nutrients. However, little information is available concerning the effect of intermittent flooding on the intrinsic characteristics of paddy soils derived from variable–charge soils (Jiang et al., 2017).

Phosphorus is associated with excessive growth of phytoplankton in freshwater bodies (Zamparas and Zacharias, 2014), and increasing phosphorus concentration in surface waters is a major cause of eutrophication, producing detrimental impacts on the quality of these waters. Source and transport control strategies can help in decreasing non–point phosphorus runoff and leaching losses, and studies on phosphate (P) adsorption affinity and capacity of soils, which are primarily affected or determined by soil surface properties, are important to understand the environmental risk of phosphorus. In general, the availability, transport, and fate of P are strongly dependent on adsorbents such as Fe/Al oxides in variable–charge soils (Zou et al., 2011), and calcium carbonate in calcareous soils (Lombi et al., 2004). Intermittent flooding in an alternating flooding–drying Oxisol–derived paddy soil results in a significant decrease in free Fe oxides and increase in amorphous Fe oxides (Zou et al., 2011; Jiang et al., 2017). Free Fe oxides are generally recognized as the main adsorbents for P in variable–charge soils. Among them, amorphous Fe oxides have higher specific surface area and more reactive sites exposed to multivalent oxyanions than crystalline Fe oxides (Jiang et al., 2017). Therefore, in addition to the contents of free Fe oxides in soils, transformation of Fe oxides should also be taken into account, which further complicates the comparison of P adsorption on paddy soil and its parent Oxisol.

Although surface properties of different–size soil fractions had been extensively studied (Qafoku, 2010; Tang et al., 2015), the contents and forms of Fe oxides and P affinity on different–size particles extracted from paddy and upland soils need further investigation to evaluate the effect of intermittent flooding on the fate, transport and mobility of phosphorus in these soils as well as in Oxisol. Thus, the objectives of the

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Table 1
Basic properties of the studied soils.

Soils	Depth cm	Clay g kg^{-1}	Silt	Sand	pH	Organic matter %	CEC $cmol_c\ kg^{-1}$	Olsen-P mg kg^{-1}	Total Fe_2O_3 g kg^{-1}	Free Fe_2O_3	Amorphous Fe_2O_3
Paddy soil	0–20	372.8	196.8	430.4	7.33 ± 0.00	2.70 ± 0.01	18.0 ± 0.05	16.84 ± 0.20	76.63 ± 2.60	63.07 ± 0.29	7.86 ± 0.14
Paddy soil	20–40	437.7	164.1	398.2	7.45 ± 0.00	1.38 ± 0.01	17.4 ± 0.00	4.52 ± 0.24	87.88 ± 0.22	71.88 ± 0.17	9.90 ± 0.04
Oxisol	0–20	672.4	73.1	254.5	5.04 ± 0.00	2.06 ± 0.00	15.1 ± 0.05	3.08 ± 0.07	108.12 ± 3.82	105.87 ± 0.05	6.40 ± 0.02
Oxisol	20–40	660.7	143.2	196.1	5.12 ± 0.02	1.50 ± 0.01	14.0 ± 0.10	1.70 ± 0.14	111.32 ± 2.54	106.21 ± 1.24	6.41 ± 0.07

Data are means ± standard deviation of duplicates.

present study were to (1) determine the effect of intermittent flooding on P sorption–desorption by Oxisol and derived paddy soil, and their different–size particles, and (2) assess the environmental risk of phosphorus in Oxisol and derived paddy soil.

2. Materials and methods

Paddy soil and original Oxisol were sampled from the experimental fields of Guangdong Ocean University (GDOU), Zhanjiang City, Guangdong Province, China (21°9′N, 110°17′E). The selected basic properties and variance analysis of the bulk soils and different–size soil fractions are presented in Tables 1 and S1, Tables 2 and S2, respectively. Batch P adsorption/desorption experiments with bulk soils and different–size soil fractions were performed in duplicate. The Gibbs free energy ($\triangle G$) of P adsorption was calculated using the adsorption coefficient k (g L^{-1}). The detailed experimental procedures along with statistical analysis are given in the Supplementary Material.

3. Results and discussion

3.1. Properties of the studied soils with respect to P affinity

As mentioned in our previous work (Jiang et al., 2017), the physical and chemical properties of the paddy soil significantly change after dozens of years of rice cultivation. The main changes in the intermittent flooding Oxisol derived paddy soil include losses of Fe oxides and fine particles, along with transformation of Fe oxides. The free Fe oxides are the major effective adsorbents of multivalent oxyanions (Qafoku et al., 2004). In the present study, the contents of total and free Fe oxides significantly decreased in the paddy soil colloid, when compared with those in the original Oxisol (Tables 1 and S1). Among free Fe oxides, amorphous Fe oxides have been reported to have higher affinity for multivalent oxyanions adsorption because of their large surface area and reactivity of surface functional groups (Bowell, 1994; Jackson and Miller, 2000). The amount of amorphous Fe oxides in the surface paddy soil examined in the present study was much higher than that in the original Oxisol (Tables 1 and S1, DF = 1, F = 936.00, P = 0.000). Consequently, both the form and content of Fe oxides were taken into account for assessing the effect of intermittent flooding on P adsorption by paddy soil and Oxisol.

The results of clay mineralogical analysis indicated that the abundance of goethite increased and hematite decreased in the paddy soil, when compared with that in the Oxisol colloid (Fig. S1, Jiang et al., 2017). Moreover, the peak intensities of illite and vermiculite increased and decreased in the paddy soil colloid, respectively, when compared with those in Oxisol, indicating that the quantities of illite increased at the expense of vermiculite, probably owing to K absorption by vermiculite (Barre et al., 2008). Besides, paddy cultivation led to progressive loss of fine particles by vertical illuviation and lateral runoff, as well as lower content of colloid fractions in the paddy soil (Table 1). In general, soil colloid fractions have higher density of reactive surface sites and larger specific surface area, and thus have higher P adsorption potential. In addition, an increase in paddy soil organic matter, pH value, and cation exchange capacity (CEC) can result in greater inhibition of P adsorption owing to competition for analogy adsorption sites and stronger electrostatic repulsion. Thus, we presumed that P affinity, transport and mobility in variable–charge soil would differ as a result of paddy cultivation.

3.2. P adsorption and desorption on bulk soils

The P adsorption and desorption isotherm curves for two layers of Oxisol and derived paddy soil at pH 5.1 and 7.0 are presented in Fig. S2. It can be observed from the figure that the P adsorption data followed a Langmuir–type isotherm (R^2 = 0.99–1.00, Table 3). The Langmuir adsorption capacities of P (Q_m^{ad}) on the surface and subsurface paddy soil increased by 45.08% and 28.18%, respectively, when compared with those of the corresponding layers of upland Oxisol at pH 5.1. The

Table 2
Contents of total Fe_2O_3 (Fet), free Fe_2O_3 (Fed) and amorphous Fe_2O_3 (Feo), as well as Langmuir equation simulated maximum P adsorption capacity (Q_m^{ad}) by different–size particles of the bulk Oxisol and derived paddy soil.

Soils	Depth	Particles	Fet g kg^{-1}	Fed	Feo	Crystalline Fe_2O_3	Q_m^{ad*} g kg^{-1}	k L g^{-1}	R^2
Paddy soil	0–20 cm	clay	110.64 ± 7.91	94.50 ± 0.55	7.43 ± 0.07	87.07	2.25	0.66	1.00
		silt	98.05 ± 2.71	83.81 ± 0.37	11.14 ± 0.07	72.67	1.60	0.44	1.00
		sand	29.52 ± 0.14	29.60 ± 2.07	3.74 ± 0.04	25.86	0.28	0.29	0.98
Paddy soil	20–40 cm	clay	106.34 ± 2.63	92.81 ± 0.55	7.35 ± 0.07	85.46	3.30	2.33	1.00
		silt	103.86 ± 1.73	88.24 ± 0.53	7.22 ± 0.13	81.02	1.73	0.77	1.00
		sand	49.56 ± 0.38	45.71 ± 0.53	10.93 ± 0.00	34.78	0.61	0.34	1.00
Oxisol	0–20 cm	clay	139.45 ± 0.69	122.02 ± 1.22	6.99 ± 0.14	115.03	2.32	0.77	1.00
		silt	137.43 ± 5.97	115.86 ± 4.27	6.71 ± 0.15	109.15	1.85	0.48	1.00
		sand	95.18 ± 3.24	85.56 ± 0.55	4.98 ± 0.06	80.58	1.44	0.23	0.99
Oxisol	20–40 cm	clay	138.29 ± 2.11	124.73 ± 0.45	6.92 ± 0.02	117.81	2.05	0.43	0.99
		silt	138.17 ± 0.18	122.43 ± 0.21	7.05 ± 0.02	115.38	2.01	0.47	0.99
		sand	98.33 ± 3.18	92.78 ± 0.05	5.29 ± 0.06	87.49	1.56	0.27	0.99

Data are means ± standard deviation of duplicates. *Q_m^{ad}: P adsorption capacity obtained at pH 5.1.