



# Mobilization of phosphate in variable-charge soils amended with biochars derived from crop straws



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## ABSTRACT

The content of available phosphorus in variable-charge soils is often low due to the strong adsorption of phosphate by the soils. The application of crop straw-derived biochars can change surface chemical properties of variable-charge soils, and thus, should affect phosphate adsorption and phosphorus availability in the soils. However, little information is available on the effect of biochars on the mobility and bioavailability of phosphate in variable-charge soils. The objectives of this study were to investigate the effect of crop straw-derived biochars incorporated on phosphate adsorption by variable-charge soils, and then gain insight into the mechanisms for the effect of biochars on phosphate adsorption. Results showed that crop straw-derived biochars are characterized by large specific surface area, highly negative charged surface, ample of anionic functional groups, and moderate concentrations of divalent  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The incorporation of the biochars increased soil CEC (cation-exchange capacity), thus, increased the repulsion of soil surfaces to phosphate, and subsequently decreased the phosphate adsorption by the soils. The ample anionic functional groups on added biochars competed for the adsorption sites on the variable-charge soils with phosphate, and thus, inhibited phosphate adsorption by the soils. The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the biochars formed precipitates with phosphate in the soils and have the potential to increase apparent phosphate adsorption. Rice straw biochar with the higher CEC and the lowest contents of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  showed the greatest inhibition on the phosphate adsorption, and thus, could likely be the best choice as amendment to mobilize phosphate in the variable-charge soils. The phosphate adsorption by both control soil and biochars-amended soils decreased with rising pH. Incorporation of the biochars increased the pH of the amended soils, thereby, further mobilizing phosphate in the soils.

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## 1. Introduction

Large areas of variable-charge soils are distributed in tropical and subtropical regions in the south of China. They are rich in iron (Fe) and aluminum (Al) oxides as a result of intensive weathering and leaching conditions (Yu, 1997; Qafoku et al., 2004). Available phosphate contents of these soils are often low because phosphate is strongly bound by Fe/Al oxides (Guzman et al., 1994). Formation of inner-sphere surface complexes of phosphate on soil surfaces is the main mechanism for inorganic phosphate binding to Fe/Al oxides surfaces of the soils (Mott, 1981; Tejedortejedor and Anderson, 1990), which makes phosphate unavailable for plant use. Commonly, phosphate is deficient in acid tropical soils and often limits crop production (Hartono et al., 2005; Johnson and

Loeppert, 2006). Meanwhile, the preservation and the use of crop straw are important to a sustainable agriculture, for the purposes of soil and water conservation, returning surplus nutrients (Lal, 1995; Sharratt et al., 2006), aqueous and atmospheric environment protection in rural areas, in addition to mitigating the air-pollution effects of traditional slash-and-burn practices.

Previous studies have shown that application of biochar improves soil fertility by changing several important soil physical and chemical properties. For example, incorporation of biochars decreases soil bulk density and increases soil water holding capacity, specific surface area, soil pH, and cation-exchange capacity (Novak et al., 2009; Laird et al., 2010; Xu et al., 2012). Biochar can also increase the contents of soil nutrients as biochar itself contains Ca, Mg, K, and phosphate (Novak et al., 2009; Laird et al., 2010; Deenik et al., 2011; Glaser and Birk, 2012; Rajkovich et al., 2012), and its addition can also encourage some beneficial microorganisms (Chen et al., 2011). Thus, the application of biochar has the effect of promoting plant growth and increasing crop yields

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in tropical and subtropical regions (Deenik et al., 2011). The effect of biochar on available phosphate in permanently charged soils has been investigated recently (Novak et al., 2009; Laird et al., 2010). However, little information is available on the effect of biochar on the mobility and bioavailability of phosphate in variable-charge soils.

Fourier-transform infrared spectroscopy (FTIR) and adsorption–desorption experiments have shown that anionic functional groups from agricultural residue-based biochars can inhibit the adsorption of phosphate on Fe-(hydr)oxides by competing for adsorption sites with phosphate (Chen et al., 2011; Cui et al., 2011). Thus, we hypothesize that the incorporated biochar may reduce the adsorption of phosphate by authentic variable-charge soils through the similar mechanism with pure Fe (hydr)oxide systems, because these soils contain large amounts of Fe and Al oxides (Yu, 1997). In addition, biochar carries large amount of negative charge on its surface (Yuan et al., 2011). Incorporation of biochar can increase the CECs of variable-charge soils, and thus, the repulsion of soil surfaces to anion, subsequently decreases phosphate adsorption by the soils.

The objectives of this study were: (1) to examine the change in surface chemical properties of variable-charge soils induced by the incorporation of biochars; (2) to elucidate the relationship between phosphate adsorption and surface chemical properties of variable-charge soils amended with biochars; and (3) to gain insight into the mechanisms of how biochars may affect phosphate adsorption by soils. We determined the surface chemical properties and element composition of the biochars derived from the straws of rice, canola, soybean, and peanut at first, and then evaluated the effect of these biochars on phosphate adsorption by two variable-charge soils: an Oxisol and an Ultisol.

## 2. Materials and methods

### 2.1. Soils and biochars

Subsoil samples of an Oxisol (Typic Acrorthox) and an Ultisol (Typic Paleudults) derived from basalt and granite were collected under natural trees in pristine areas of Chengmai (19°46'6b 110°00'E) and Kunlun (19°31'N, 109°49'E), respectively, in the Hainan province, China. These soils represent the main types of variable-charge soils in tropical regions of Southern China. In order to avoid the influence of organic matter on the results, the subsoil was selected and used in the present study. The soil samples were air dried and ground to pass through a 60-mesh sieve (0.25 mm). Selected properties of the soils are listed in Table 1.

Straw residues from rice (*Oryza sativa* L.), peanut (*Arachis hypogaea* L.), canola (*Brassica campestris* L.), and soybean (*Glycine max* L.) were collected from cropland in a suburb of Nanjing, China. The straw samples were air dried at room temperature and ground to pass through a 10-mesh sieve (2.00 mm). The ground straw samples were then placed in ceramic crucibles, each covered with a fitted lid, and pyrolyzed under oxygen-limited conditions in a muffle furnace (Shanghai Xinmiao Electricity Furnace Inc., Shanghai, China). The furnace temperature was raised to 400 °C at a rate of approximately 20 °C per min and then held constant for

4 h. The biochars were allowed to cool at room temperature and were then ground to pass through a 60-mesh (0.25-mm) sieve (Chun et al., 2004; Yuan et al., 2011). A commercial activated carbon is obtained from Shanghai Tongshi Chemical Engineering Company, China was used as a standard for comparison purpose.

### 2.2. Incubation experiments

Air-dried soil samples of 190.0 g were placed in polyethylene cups and 10.0 g of biochar was added at 5% (w/w) rate of application (120 t/ha) (Jiang et al., 2012). The soil and biochar were mixed thoroughly and were then wetted with deionized water to 70% of field water holding capacity of the soil (about 18.5% and 20.4% for the Oxisol and the Ultisol, respectively). The field water holding capacity of the soils was estimated on disturbed soil samples (<2 mm) by measuring moisture retention at –33 kPa on repacked samples in laboratory (Klute, 1986). A treatment without biochar was used as a control. All cups were covered with a plastic lid, and a small hole (diameter <5 mm) was made on top of the lid to allow gas exchange while minimizing moisture loss. The cups were incubated at 25 °C and were weighed every 5 days, with the necessary amount of water added to maintain constant moisture content throughout the incubation period. After 30 days of incubation, the soil samples were removed from the cups. Samples were then air-dried and ground to pass through a 60-mesh sieve (0.25 mm) for adsorption experiments.

### 2.3. Characterization of the biochars and activated carbon

The sample of rice straw biochar was coated with a thin layer of gold and mounted on a copper slab using a double-stick carbon tape and was then examined using a LEO 1530 VP scanning electron microscope (SEM) (Lehmann and Joseph, 2009). Samples for transmission electron microscopy (TEM) were dispersed in anhydrous alcohol ultrasonically for 20 min, and then a drop of suspension was deposited onto a carbon-coated copper grid. After being air-dried, the morphology of the biochar was recorded using a JEOL 2100 200 kV transmission electron microscope (Lehmann and Joseph, 2009). Surface areas were measured using ASAP 2020 (Micromeritics) and NOVA 4200e (Quantachrome) sorption instruments, using N<sub>2</sub> and CO<sub>2</sub>, respectively. Samples of biochar and activated carbon were degassed under vacuum (200 °C, 24 h) prior to N<sub>2</sub> and CO<sub>2</sub> adsorption. The N<sub>2</sub>-BET surface areas were evaluated from the N<sub>2</sub> adsorption isotherms by applying the BET equation in the relative pressure ( $P/P_0$ ) range of 0.05–0.35 (Mukherjee et al., 2011). Because the measurement of CO<sub>2</sub> adsorption was conducted at a higher temperature (0 °C), a lower kinetic limit compared with N<sub>2</sub>,  $P/P_0$  was in the range 0.001–0.05. The CO<sub>2</sub> surface area, micropore surface area, and pore diameter were evaluated using multi-point BET (MBET), Dubinin–Radushkevich (D–R), and Dubinin–Astakhov (D–A) equations, respectively (Mukherjee et al., 2011).

The FTIR spectrum of the biochar was recorded using a PE 100 spectrophotometer (PerkinElmer), scanning from 4000 to 800 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> (Yuan et al., 2011). Acidic functional groups on the surface of biochar were evaluated using

**Table 1**  
Basic properties of the tested soils.

Soil	Location	Parent material	Organic matter g kg <sup>-1</sup>	Free oxides		Amorphous oxides		pH	CEC cmol <sub>c</sub> kg <sup>-1</sup>
				Fe <sub>2</sub> O <sub>3</sub> g kg <sup>-1</sup>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>		
Oxisol	Chengmai, Hainan	Basalt	7.86	145.93	23.70	2.93	5.17	5.04	6.54
Ultisol	Kunlun, Hainan	Granite	8.42	33.83	12.41	0.67	3.25	4.96	6.80

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