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Roles of biochar in improving phosphorus availability in soils: A phosphate adsorbent and a source of available phosphorus

Hanzhi Zhang [a], Chengrong Chen [a,*], Evan M. Gray [b], Sue E. Boyd [c], Hong Yang [d], Dongke Zhang [d]

[a] Environmental Futures Research Institute, Griffith School of Environment, Griffith University, Nathan, QLD, 4111, Australia
[b] Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, QLD, 4111, Australia
[c] Environmental Futures Research Institute, School of Natural Sciences, Griffith University, Nathan, QLD, 4111, Australia
[d] Centre for Energy (M473), School of Mechanical and Chemical Engineering (M050), The University of Western Australia, 35 Stirling Highway, Crawley, WA, 6009, Australia

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ABSTRACT

In this study, the amounts of phosphorus (P) in nine types of biochar (one natural woody biochar and eight manufactured plant derived biochars) extractable by deionized water, 0.5 N $NaHCO_3$ (pH = 8.5) and 0.5 N H_2SO_4, respectively, and P adsorption on single biochar or soil/biochar mixtures were examined to investigate the potential effect and role of biochar in improving P availability in soils. Results indicated that biochars were able to bring available P into soils, but the amount and form of available P was dependent on biochar types. The results from P adsorption experiments (in phosphate solutions of 100 and 200 mg P L^{-1}, respectively) revealed that not all the biochars showed favourable P retention abilities and the amount of P retained by each biochar varied with the P concentration in the solution used. Among the nine biochars studied, only biochar derived from Mallee (*Eucalyptus polybractea*) at 720 °C with a solid residence time of 20 min showed a high P retention ability. Soils amended with Mallee biochar (5% w/w) showed an increase in the P retention ability by 16% after treatment with 200 mg P L^{-1} phosphate solution. 55% of the retained P on Mallee biochar was still available for plant uptake. Results from the kinetic study of P adsorption on Mallee biochar indicated that there were two stages in P adsorption on Mallee biochar, a rapid chemisorption stage followed by a surface-diffusion-controlled stage when the surface adsorption sites were saturated. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy and attenuated total reflectance-Fourier transform infrared spectroscopy revealed that calcium carbonate was mainly responsible for P chemisorption on Mallee biochar.

1. Introduction

Phosphorus (P) is an essential element for plant growth and its deficiency in soil restricts crop yield. Many agricultural lands throughout the world are suffering P deficiency, especially in tropical and subtropical areas as a result of high rainfall and high P fixation (Blake et al., 2000; Kamh et al., 1999). In order to meet plant P requirements, approximately 15 million tons of P fertilizer is globally applied to agricultural land each year (Wang et al., 2012). However, only 5–30% of P applied is taken up by the crop in the year following application (Price, 2006). A substantial amount of the applied ortho-phosphate is often lost to the aqueous environment via runoff. Liang et al. (2005) reported that natural runoff due to rainfall accounts for approximately 79% of P loss from rice fields. Currently, the majority of P fertilizer is derived from mined rock phosphate, a non-renewable resource. It has been predicted (Streubel et al., 2012) that supplies of rock phosphate may be depleted by the end of this century, as international demand for P further increases over the next 50 years, in response to global population growth. Thus, there is a pressing need to explore new strategies that can provide P in forms available for plant uptake, which can supplement and enhance or supersede traditional P fertilizer treatments, reducing the loss of plant-available P from soils and thereby overcoming P deficiency in the short term.

Biochar is attracting increasing attention in recent years as a potential soil amendment. Numerous researches internationally have now shown that biochars can function as a reservoir of P for soils and that a certain fraction of this P is in a suitable form available for plant uptake. Feedstock type and manufacture conditions of biochar are critical to the amount of total P and available P in biochar. Siebers and Leinweber (2013) reported that the amount of P in a biochar derived from animal bone chips could be 152.0 g kg^{-1} and that water-extractable P was 6.6 g kg^{-1}. Uzoma et al. (2011) reported that the amount of Olsen-P in a woody biochar produced at 500 °C was as high as 23 g kg^{-1}, while there was only 1.2 g kg^{-1} of Olsen-P in the biochar produced from the same feedstock but at 300 °C. Available P in biochar is generally extracted with water, sodium bicarbonate ($NaHCO_3$) or acid (e.g. sulfuric acid, formic acid and citric acid; Chintala et al., 2014; Gaskin et al., 2008; Parvage et al., 2013; Wang et al., 2012). Water-extractable P is readily plant-available P, while $NaHCO_3$-extractable P also includes

* Corresponding author.
E-mail address: c.chen@griffith.edu.au (C. Chen).

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labile P adsorbed on the surface of iron (Fe) and aluminium (Al) oxides or hydroxides or calcium carbonate ($CaCO_3$). Acid extracts readily plant-available P and available P in Ca, Fe and Al phosphates (Mehlich, 1978). After the application of biochar to acidic soil, phosphates bound with free cations such as Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+} dissolve and released P is available for plant uptake again. In addition to being a potential P source, some biochars can also adsorb phosphate efficiently from solutions (Peng et al., 2012; Streubel et al., 2012; Yao et al., 2013b), suggesting that biochar could play a role in retaining P applied as fertilizer. At the present time, however, information concerning the effect of biochars on soil phosphate retention is rather limited.

Against the above backdrop, this study was aimed to determine (a) the availability of P in nine biochars derived from different plant materials at different pyrolysis temperatures, (b) the effects of the biochars on phosphate adsorption on soils, and (c) the mechanisms for phosphate adsorption on the biochars.

2. Materials and methods

2.1. Materials

The nine biochars used in this study included both natural and manufactured biochars. The wildfire biochar (WFB) was produced from a stem of *Eucalyptus pilularis* during a wild fire at Peachester State Forest, southern Queensland in 1969 (350–500 °C). The sugarcane bagasse biochar (SBB) was produced in a muffle furnace at 350 °C under an oxygen limited condition with a solid residence time of 1 h. The biochars derived from peanut shell (PSB), greenwaste (GWB) and blady grass (*Imperata cylindrical*, BGB) were all produced in a muffle furnace at 450 °C under an oxygen limited condition with a solid residence time of 1 h, while the other four biochars were obtained by pyrolysing Jarrah (*Eucalyptus marginate*, JB), Mallee (*Eucalyptus polybractea* from Narrogin of Western Australia, MB), Pine (*Pinus radiate* from South West Plantations, PB), and timber (mixtures of soft wood from Western Australia, TB) in an indirectly heated rotary kiln operating at 720 °C and with a solid residence time of 20 min. All biochars were finely ground to <1 mm by a mortar and pestle and sealed in containers before use. The soils used in this study were sandy clay loam and were collected from northern Queensland. Soil pH is 4.3, total C 2.9%, total N 0.20% and total P 1320 mg kg^{-1}. The soil samples were air dried and passed through a 2 mm sieve before use. The pH of the biochar and soil samples were determined using a solid:water ratio 1:30 and 1:5, respectively. Basic properties of the biochar samples are shown in Table 1. Phosphate solutions were prepared by dissolving potassium dihydrogen phosphate (KH_2PO_4) in 0.01 N potassium chloride (KCl) solutions.

2.2. Extractable P in biochars

Both sulfuric acid and hydrochloride acid are widely used in the extraction of P from biochar in addition to water and sodium bicarbonate ($NaHCO_3$) solution. However, sulfate ions in H_2SO_4 solution can also release orthophosphate adsorbed on colloidal surfaces in biochar, which cannot be achieved by chloride ions. Thus, in this study, each biochar was subjected to extraction with deionized (DI) water, 0.5 N $NaHCO_3$ solution with pH of 8.5 and 0.5 N sulfuric acid (H_2SO_4) solution respectively, to verify the amount of extractable P. A suspension of 0.1 g biochar and 30 mL of extractant solution was shaken in an end-to-end shaker at 120 rpm for 48 h in 50 mL centrifuge tubes. The suspension was then centrifuged (4000 rpm, 15 min) and the resulting supernatant filtered through a Whatman No. 42 filter paper. The filtrate was analysed for the amount of P extracted according to the colorimetric molybdenum-blue method (John, 1970). All the extractions were repeated three times. The average data and standard deviations are reported.

2.3. P adsorption on biochars and soil/biochar mixtures

The P adsorption of each biochar was examined by placing 0.1 g of biochar in 30 mL phosphate solution (100 and 200 mg P L^{-1}, respectively) in 50 mL centrifuge tubes and then shaken in an end-to-end shaker for 48 h at room temperature. The suspension was then centrifuged (4000 rpm, 15 min) and the resulting supernatant filtered through a Whatman No. 42 filter paper. The amount of P adsorbed on biochar samples was determined by the difference between the initial P amount in the phosphate solution and the remaining P amount in the filtrate.

In order to determine whether or not the adsorbed P on biochars was still available for plant uptake, a P desorption experiment was conducted on P-load Mallee biochar samples treated with 200 mg P L^{-1} phosphate solution as Mallee biochar (MB) sample adsorbed the highest amount of P from the solution among all tested biochars. After adsorption treatment, the P-loaded MB was rinsed four times with DI water. After washing, drying and weighing, the biochar was placed in a 50 mL centrifuge tube and extracted with 30 mL 0.5 N $NaHCO_3$ (pH = 8.5) on an end-to-end shaker (120 rpm, RT, 48 h). The suspension was then centrifuged (4000 rpm, 15 min) and the resulting supernatant filtered through a Whatman No. 42 filter paper. The colorimetric molybdenum-blue method (John, 1970) was then applied to the filtrate to determine the amount of P desorbed from the P-loaded biochar.

P adsorption in soil/biochar mixtures was examined to assess the efficacy of biochar amendments as a method for increasing P retention in soils. MB was used in this experimentation, due to its extraordinary P adsorption ability (Fig. 2). The extent of P adsorption within soils amended with MB was examined by mixing an amended soil (with a ratio of 2 g of soils to 0.1 g of MB) sample with portions of phosphate solutions (30 mL, 200 mg P L^{-1}) in 50 mL centrifuge tubes. The tubes were then shaken end-to-end at 120 rpm at room temperature. A tube was withdrawn after the shaking was conducted for 48 h. The suspension was then centrifuged (4000 rpm, 15 min) and immediately filtered through a Whatman No. 42 filter paper. The amount of P adsorbed on the soil/biochar mixture was calculated by the differences between the initial P concentration in the phosphate solution and the remaining P concentration in the filtrate. A soil sample without biochar was set up as control.

Table 1
Basic properties of nine biochars used in this study.

Samples	Temperature (°C)	pH_{water}	EC (μS cm^{-1})	Total C (%)	Total N (%)	Total P (mg kg^{-1})	BET–N_2 surface area (m^2 g^{-1})
Wildfire biochar (WFB)	350–500	3.1	110	69.7	0.22	15	109
Jarrah biochar (JB)	750	10.8	315	86.0	0.23	61	206
Pine biochar (PB)	750	8.6	321	84.2	0.15	266	322
Timber biochar (TB)	750	9.6	474	84.7	0.23	236	382
Mallee biochar (MB)	750	10.2	1373	69.0	0.43	1877	233
Greenwaste biochar (GWB)	450	9.6	720	59.7	0.51	1596	271
Peanut shell biochar (PSB)	450	8.7	495	35.1	0.73	640	112
Blady grass biochar (BGB)	450	7.1	978	64.0	1.24	1810	Not detected
Sugarcane bagasse biochar (SBB)	350	5.9	614	70.8	0.34	1761	Not detected