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The effect of different pyrolysis temperatures on the speciation and availability in soil of P in biochar produced from the solid fraction of manure

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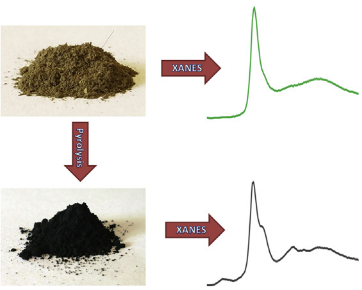
HIGHLIGHTS

- Pyrolysis temperatures above 600 °C result in gradually less soluble P species.
- Biochar has lower immediate P availability in soil compared to the feedstock.
- For most biochars P availability in soil increases with time after application.
- Only exception are high temperature biochar in pH neural and high clay soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar application to agricultural land has been proposed as a means for improving phosphorus (P) availability in soil. The purpose of the current study was to understand how pyrolysis temperature affects P speciation in biochar and how this affects availability of P in the amended soil. Biochar was produced at different temperatures from digestate solids. The primary species of P in digestate solids were simple calcium phosphates. However, a high co-occurrence of magnesium (Mg) and P, indicated that struvite or other magnesium phosphates may also be important species. At low temperatures, pyrolysis had little effect on P speciation; however, as the temperature increased above 600 °C, the P gradually became more thermodynamically stable in species such as apatite. At very high temperatures above 1000 °C, there were indications of reduced forms of P. Biochar production decreased the immediate availability of P in comparison with the original digestate solids. However, for biochar produced at low temperatures, availability quickly increased to the same levels as in the digestate solids. For biochar produced at higher temperatures, availability remained depressed for much longer. The low availability of P in the biochar produced at high temperatures can probably be explained by the formation of less soluble P species in the biochar. In contrast, the transient decrease of availability of the P in the biochar produced at low

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temperatures can be explained by mechanisms, such as sorption on biochar, which gradually decreases because of oxidation of the biochar surfaces or changes in pH around the biochar particles.

1. Introduction

Biochar is the charcoal-like product obtained from the pyrolysis of biomass. Biochar addition to agricultural land has been proposed as a way of improving the quality of soil and has been intensively investigated during the past decade. Biochar application to agricultural land offers at least two potential advantages. Biochar is very stable, which means that some of the carbon stays in the soil for a long time. This means that the improvements may also be sustained and that the carbon contained in it is sequestered from the atmosphere for centuries (Lehmann et al., 2006; Bruun et al., 2008). This idea is inspired from the *terra preta* soils of South America. These old, anthropogenic soils were created by the people who inhabited the area before the arrival of Europeans through the addition of charcoal and other organic waste products and still sustain productivity at much higher levels than the surrounding soils (Glaser and Birk, 2012).

There are several ways in which biochar can potentially improve soil quality. These include improved water-holding capacity and cation exchange capacity and a reduction in the susceptibility to erosion (Glaser et al., 2002; Joseph et al., 2010). Furthermore, biochar can improve soil fertility through its beneficial effects on phosphorus (P) availability (Lehmann et al., 2003; Yamato et al., 2006; Zhang et al., 2016). The mechanisms leading to increased availability may be due to the P supplied with the biochar but may also be due to other mechanisms envisioned for other types of organic matter such as competitive sorption and metal complexation (Guppy et al., 2005).

Kruse et al. (2015) recently reviewed methods that are useful for analyzing P speciation in environmental samples, but only a limited number of these techniques have been used to analyze biochar. A useful technique that has the advantage of not requiring P extraction, does not rely on the crystallinity of the phase under investigation and can be directly applied to dilute, solid samples is synchrotron based X-ray absorption near edge structure (XANES) spectroscopy. Phosphorus K-edge XANES has been used to investigate P speciation in soils (Beauchemin et al., 2003,Lombi et al., 2006; Rivard et al., 2016) manures (Toor et al., 2005; Sato et al., 2005; Shober et al., 2006; Güngör et al., 2007) and sewage sludge (Shober et al., 2006; Ajiboye et al., 2007; Kruse et al., 2010). Zwetsloot et al. (2015) used K-edge XANES to analyze the effect of pyrolysis temperature on the speciation of P in biochar produced from slaughterhouse waste and various combinations of slaughterhouse waste and energy crops. However, our general understanding of P speciation in biochar and how it is affected by pyrolysis temperature is still incomplete.

The assessment of P plant availability in soil presents a challenge due to the range of equilibrium reactions involving adsorption, precipitation and biological immobilization that control the activity of plant-available phosphate in solution (Hinsinger et al., 2011). The diffusive gradients in thin films (DGT) technique shows promise for the assessment of plant availability of phosphate in soil (Tandy et al., 2011; Six et al., 2013). The DGT devices consist of a ferrihydrite-containing phosphate binding layer with a diffusive gel and filter membrane mounted on top. When applied in a soil, the DGT will decrease the concentration of phosphate locally in much the same way as a plant root, and in that way mobilize the same fractions of phosphate which can also be mobilized by the plant root. This technique is therefore a rapid method that is much easier to apply than plant trials. Furthermore the technique can provide a higher resolution of measurement in time. The DGT technique has been used to assess the availability of P in biochar (Christel et al., 2014, 2015, 2016), but there have been very few investigations into the interactions of biochar with different soil types and the effect of P speciation.

The purpose of the current study was to combine relatively well-known methods, such as X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), XANES spectroscopy at the K and L-edges to understand how pyrolysis temperature affects P speciation in biochar produced from digestate solids. Furthermore, DGT was used to elucidate how P speciation in biochar affects the availability of P in biochar-amended soils.

2. Materials and methods

2.1. Biochar production

Biochar was produced from the solid fraction of a digestate collected from the Fangel biogas plant in Denmark. The plant is using approximately 75% animal slurry from pig and dairy farms and 25% waste from the food industry. After digestion, the effluent digestate was separated into a liquid and solid fraction using a decanting centrifuge (GEA Westfalia Separator A/S) installed at the plant. A sample of the solid fraction was taken after separation and dried in an oven at 80 °C.

Biochar was produced by the method described in Christel et al. (2014). Briefly, two crucibles were fitted on top of each other with the upper crucible turning downward so that the edges of the crucibles were meeting to create an egg shaped container with a closed cavity. The cavity was tightly packed with digestate solid fraction to have as little residual air inside as possible. The containers were placed in an oven at 300, 450, 600, 750, 900 or 1050 °C for 1 h after which the oven was turned off and allowed to cool. The mass loss during the process was determined and the samples were ground using a zirconium ball mill. Subsequently all samples were analyzed for C, N and S using an elemental analyzer (vario MACRO cube CNS, Elementar). Other elements were analyzed after digestion in 3.5% HF and H_2O_2, using inductively coupled plasma optical emission spectrometry (ICP–OES, Optima 5300 DV, Perkin Elmer, Ontario, Canada).

2.2. P $L_{2,3}$-edge XANES

All samples were ground using a mortar and pestle and a thin layer was mounted on carbon tape and excess material was removed with compressed air. The standards included: struvite, hydroxyapatite, calcium phosphate dibasic, calcium phosphate amorphous, calcium phosphate tribasic, iron phosphate, calcium phosphate dibasic dihydrate, and calcium pyrophosphate as well as two organic P compounds asolectin and phytic acid (Sigma-Aldrich). Finally, natural phosphorus-containing minerals were included, i.e. apatite, strengite and variscite, which were supplied by the South Australian Museum. See Table S1 in the supplementary information for more information.