Phosphorus bioavailability from ash-rich biochars produced at different pyrolysis temperatures

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Introduction

Biochars are highly variable in nutrient composition and availability, this being determined by type of feedstock and pyrolysis conditions [1]. Knowledge of the amount of available P in biochar is essential to determining the rate to be applied to meet crop P requirement, while ensuring a low risk of water eutrophication [2]. Phosphorus availability in fertilizers can be determined using either (i) bioassay tests or (ii) chemical methods. Bioassays are the most reliable methods to predict P availability; however, these methods are soil specific and time and cost consuming. Therefore, a robust chemical method is needed developing to measure the P availability in biochars. Extraction of P by 2% citric acid, 2% formic acid, or 1M ammonium citrate at pH 7 are the three most adopted methods to examine available inorganic P in phosphate rocks. Phosphorus in both biosolids and manure is predominantly in inorganic form [3], and so it will be in biochars. It is thus hypothesized that the above-mentioned chemical methods can be useful for P bioavailability testing of biochars. In the present study, chemical analysis –including total P (TP, 10%HCl:10%HNO₃ mixture), extractable P (2% citric acid, CA-P; 2% formic acid, FA-P; and neutral ammonium citrate, NAC-P) – and a bioassay test using rye-grass grown in a P deficient sandy soil were used to compare P bioavailability of different biochars and two kinds of P fertilizers [phosphate rock (PR) and calcium dihydrogen phosphate (CaP)]. Biochars were produced from two different feedstocks (cattle manure-wood mixture and biosolid-wood mixture) at four different pyrolysis temperatures (250, 350, 450 and 550 °C).

Results and Discussion

Feedstock P was fully recovered in the biochars produced. 98–119% of the initial P was recovered in MA biochars, and 93–108% in BS biochars. High temperature biochars showed
higher total P recovery than low temperature biochars. This could be due to the interference of organic P in feedstocks which could not be digested by the acid mixture used in this study. However, pyrolysis cleaves the organic P bonds present in the feedstocks resulting in an increase of acid soluble P salts [4], recovery of P improved with final pyrolysis temperatures above 250°C.

A good correlation was found between TP concentrations (Figure 1) and ash contents in biochars indicated that P existed mainly in the ash fractions as cation-phosphate complexes which were probably amorphous in nature, as no clear peaks of P compounds were identified by XR-diffraction. Results from a stepwise regression between the cation and P concentrations from the extractability test (data not shown) showed that Mg-P dominated in the dairy manure (MA) biochars, whereas Al-P and/or adsorbed P were the main P species in biochars made from biosolids (BS).

Both ryegrass yield and P uptake increased significantly (p<0.05) with the addition of biochars compared with the un-amended soil treatment, and the pots amended with feedstocks in terms of similar application rates. Both yields and P uptake data vs TP were fitted to a Mitscherlich equation, which can be written as:

\[ Y = Y_0 + \frac{Y_{\text{max}}}{1 + e^{-\Delta Y}} \]

This equation assumes that only the nutrient under consideration is limiting crop yield, and predicts that yields increase with increasing fertilizer rates until they asymptotically reach a maximum [5]. In this study, the P free complete nutrient solution ensured P was the only nutrient limiting the grass growth, which allowed the use of the Mitscherlich equation. Regarding the dry matter yield modelling, all groups shared a maximum dry matter yield \( (Y_{\text{max}}=Y_0+\Delta Y) \), and the activity coefficient \( (\Delta) \) followed a descending order as CaP>MA>PRs>BS, suggesting that CaP was the most available P (as expected, given the high solubility of CaP in water), followed by MA, PRs and BS. This is consistent with the chemical stability constants.

The Mitscherlich equation was also used to fit yields and P uptake vs different extractable P (data not shown), but only FA-P showed significant results (Figure 2). Yields were not so sensitive as P uptake (Figure 2). Compared to TP, FA-P decreased the deviation between biochar and CaP treatment (Figure 2b). More interesting, the PR treatment data fell in the same curve as the biochar treatments, suggesting FA-P was a good indicator of P bioavailability in biochars.

**Conclusion**

Phosphorus as enriched in the ash fraction during pyrolysis could be fully recovered in biochars. Both extractability and bioavailability of P primarily depended on P composition in the feedstocks and to a less extent on final pyrolysis temperature. In this study, Mg-P dominated in the dairy manure (MA) biochars, whereas amorphous Al-P and/or adsorbed P were the main P species in biochars made from biosolids (BS). Mg-P forms had higher extractability and bioavailability. Plant growth response modelling based on a Mitscherlich equation indicates 2% formic acid extractable P (FA-P) is the recommended measure of P availability in biochars. Biochars –especially those made at high temperature – had comparable agronomic efficiency on a FA-P basis to commercial fertilisers. In summary, high-ash biochars with high P concentrations are potential slow-release P sources with high agronomic efficiency and low water eutrophication risks. Their suitability as P fertilizers should be assessed using the standard chemical extraction methods already used to characterize manufactured P fertilizers.

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