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Response of soil alkaline phosphatase to biochar amendments: Changes in kinetic and thermodynamic characteristics

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ABSTRACT

Biochar addition to soil often increases the activity of alkaline phosphatase (ALP) involved in phosphorus (P) cycling, but the underlying mechanisms of its effect is poorly understood. This study investigated the response of kinetic parameters including maximal velocity (V_{max}) and Michaelis–Menten constant (K_m), and thermodynamic parameters including activation energy (E_a), enthalpy (ΔH_a) and temperature coefficient (Q_{10}) of ALP to addition of two maize biochars (400 and 600 °C) in two calcareous (Typic Haplocalcid) soils with clayey and sandy loam texture. The biochars were added to the soils at 1% (w/w) and the mixtures were incubated for 90 days under laboratory conditions (25 ± 1 °C and 70% of water holding capacity). Soils with addition of raw residue were used as positive controls and soils without biochar and raw residue were included as negative controls. The potential activity of ALP was assayed at the end of incubation period. The kinetic parameters of ALP were estimated using non-linear regression techniques and the thermodynamic characteristics were determined at different incubation temperatures (17, 27, 37, 47 and 57 °C) using the Arrhenius equation. Compared with the negative control, the addition of raw residue and biochars increased ALP activity (3.1- to 4.4-fold) after the 90-day incubation, depending upon the pyrolysis temperature and soil texture. The positive effect of biochar addition on soil ALP was greater with low than high temperature biochars and in sandy loam than clayey soils. Biochar addition increased the K_m and V_{max} values of ALP in the clayey soil but decreased these parameters in the sandy loam soil compared with the corresponding negative controls. Generally, application of maize raw residue and biochars increased the E_a, ΔH_a and Q_{10} values of ALP compared with the negative controls, and the increases were similar for the two pyrolysis temperatures. Soil ALP can be strongly adsorbed by biochar particles; increasing its thermal stability and decreasing its sensitivity to elevated temperatures. In conclusion, application of maize biochar to arid-soils has a high potential to improve the ALP activity, with implications for organic P mineralization and availability. Biochar would change ALP kinetic and thermodynamic characteristics differently, depending mainly on soil texture, through the surface adsorption of this enzyme on biochar particles. These changes will be useful for modeling P mineralization and biochemical processes in biochar-amended calcareous soils.

1. Introduction

Recent interests in sustainable management practices in agroecosystems have been focused on the application of carbonized organic feedstocks produced through pyrolysis to increase soil biochemical processes and soil quality (Paz-Ferreiro et al., 2014; Masto et al., 2013; Mukherjee and Lal, 2016; Khadem and Raiesi, 2017b), plant growth and productivity (Masto et al., 2013; Kumar et al., 2013; Xu et al., 2016), and to mitigate climate change effect through carbon (C) sequestration in the soil (Spokas, 2010; Brassard et al., 2016). Biochar, the product of biomass pyrolysis at different temperatures under low oxygen, is a valuable soil amendment because of its multiple beneficial effects on physical, chemical and biological indicators of soil quality and health (Masto et al., 2013; Paz-Ferreiro et al., 2014; Mukherjee and Lal, 2016; Khadem and Raiesi, 2017b).

Alkaline phosphatase (ALP) enzyme is an important soil hydrolase that catalyzes the hydrolysis of both esters and anhydrides of phosphoric acid; therefore, it has an important function in organic P mineralization and plant P nutrition, especially in P-limited calcareous soils (Chapuis-Lardy et al., 2006; Acosta-Martínez et al., 2008; Bera et al., 2016). This enzyme is sensitive to agricultural management practices and changes in environmental conditions (Acosta-Martínez et al., 2008; Trasar-Cepeda et al., 2008). Biochar has been reported to increase the potential activity of ALP by improvements in soil physical (e.g., aggregation, aeration,

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water retention), chemical (e.g., pH, nutrient retention) and biological (e.g., labile carbon, microbial activity and biomass, community structure) properties (Masto et al., 2013; Oleszczuk et al., 2014; Jin et al., 2016; Abujabhah et al., 2016; Bhaduri et al., 2016; Bera et al., 2016; Al Marzooqi and Yousef, 2017) and co-location of enzyme and substrate (Lehmann et al., 2011; Gul et al., 2015). Nevertheless, biochar application can also have a negative (Kumar et al., 2013; Noyce et al., 2017) or even no (Zhang et al., 2017) effect on soil ALP activity. The conflicting results regarding biochar impacts on soil ALP have been ascribed to differences in the type of soil and biochar (feedstock source), biochar production conditions (pyrolysis temperature, particle size), application rate and the experimental conditions and duration (Jin et al., 2016; Noyce et al., 2017; Song et al., 2018).

The potential enzyme activities assayed using current soil enzyme procedures reflect the total amount of an enzyme present in the soil and are indeed indicative of overall enzyme concentrations (Wallenstein and Weintraub, 2008). Although biochar has a great potential for increasing the activity of most soil enzymes including ALP, its impact on the kinetic and thermodynamic parameters remains poorly characterized (Jin, 2010; Khadem and Raiesi, 2017a). Enzyme activity is usually described by the kinetic parameters, which link the enzymatic reaction rate to substrate concentration (Perucci and Scarponi, 1984; Tabatabai and Dick, 2002; Marx et al., 2005; German et al., 2011). The kinetic parameters of an enzyme include maximal velocity (V_{max}) and the Michaelis–Menten (K_m) constant, which can provide an indication of the nature, stability of the enzyme and enzyme-substrate complex (Marx et al., 2005; Wallenstein and Weintraub, 2008); and thus advance our knowledge regarding the status of the active enzyme and catalytic reaction (Farrell et al., 1994; Marx et al., 2005). K_m reflects the affinity of the enzyme for substrate and enzyme efficiency, and is independent of the amount of enzyme present, whereas V_{max} represents the total amount of an enzyme in the soil (Perucci and Scarponi, 1984; Marx et al., 2005; German et al., 2011). An increase in K_m (i.e., low substrate affinity) can indicate a decrease in the overall enzyme function (German et al., 2011), and this constant may even be used as an indication for the level of enzyme adsorption or accessibility (Marx et al., 2005). The V_{max} and K_m values for soil enzymes are known to change with addition of organic amendments such as biochar (Jin, 2010; Chintala et al., 2015) and crop residues (Perucci and Scarponi, 1984). For instance, the V_{max} and K_m values for ALP increased due to the high adsorption capacity of biochar for its substrate, while those for β-glucosidase and cellobiosidase decreased with addition of 1 and 12 t h^{-1} corn stover biochar to a temperate soil in a field experiment (Jin, 2010). Similarly, the V_{max} and K_m values for the denitrification enzyme activity were reduced by addition of different biochar sources to soils from two different landscape positions (Chintala et al., 2015). However, the underlying mechanisms responsible for the reduction of the kinetic parameters in biochar-amended soils were not elucidated. In particular, enzyme kinetic behavior and the derived kinetic parameters (V_{max} and K_m) can be indirectly influenced by changes of soil structure, organic matter quantity and quality due to the addition of organic amendments (Perucci and Scarponi, 1984). Biochar was reported to adsorb soil enzymes, enzyme substrate or both due to its high surface area and abundant oxidized functional groups (Paz-Ferreiro et al., 2014; Sun et al., 2014). The adsorption and immobilization of an enzyme may increase its V_{max} and K_m values, with a reduction in its potential activity (Kandeler, 1990; Nannipieri et al., 2011; Sun et al., 2014). The adsorption of an enzyme on biochar surfaces may change the structure of the enzyme functional groups or active site, resulting in a decreased enzyme activity (Chintala et al., 2014). Conversely, enzyme adsorption may increase the contact between enzyme and adsorbed substrate in and around biochar particles through their co-location, resulting in enhanced enzyme activity (Jin, 2010; Lehmann et al., 2011).

On the other hand, thermodynamic parameters of soil enzymes; e.g., activation energy (E_a) and temperature coefficient (Q_{10}), are important characteristics for a better understanding of the temperature sensitivity of soil enzymes (Trasar-Cepeda et al., 2007; Menichetti et al., 2015) and, therefore, changes in nutrient cycling following temperature fluctuations and global warming. At present, the necessary information on how biochar affects the thermodynamic characteristics of soil enzymes is also very limited. Biochar amendments have been reported to reduce E_a and Q_{10} values for several soil hydrolases including phosphomonoesterase (Paz-Ferreiro et al., 2015) or increase E_a and enthalpy of activation (ΔH_a) values for denitrifying enzyme activity (Chintala et al., 2015). The reductions in E_a and Q_{10} were attributed to the release of different isoenzymes or the conformation changes due to enzyme adsorption on biochar surfaces (Paz-Ferreiro et al., 2015). Thermodynamic characteristics provide more information about the thermal and proteolytic stability of enzymes, and also their resistance to pH and other environmental changes (Allison, 2006; Nannipieri et al., 2011).

Nevertheless, the mechanisms involved in soil enzyme-biochar interaction still remain largely unclear, and the link between biochar properties and enzyme kinetics and thermodynamics, remains a research priority in soil enzymology (Chintala et al., 2015; Khadem and Raiesi, 2017a). Specifically, it is not clear how biochar affects the kinetic and thermodynamic behavior of ALP in soil, and to our knowledge, there is very little information regarding the response of ALP kinetics and thermodynamics in biochar-treated soils (Jin, 2010). Understanding the kinetics and thermodynamics of soil ALP in biochar-amended soils is necessary for a better understanding of its function in P cycling and modeling the decomposition of soil organic matter (Wallenstein and Weintraub, 2008; Hui et al., 2013; Paz-Ferreiro et al., 2015).Therefore, the main objectives of the current study were to (1) quantify the effects of maize biochars produced at two pyrolysis temperatures on the potential activity, kinetic and thermodynamic parameters of soil ALP, (2) compare the ALP activity, kinetic and thermodynamic characteristics between the soils amended with uncharred corn feedstock and its biochars; and (3) establish whether maize biochar effects would depend on soil texture. We tested two working hypotheses: (1) biochar addition to the soil would modify ALP kinetic and thermodynamic parameters and (2) these biochar effects would differ with pyrolysis temperature and soil texture.

2. Materials and methods

2.1. Soil sampling and biochar production

The experimental soils used for this study were collected from agricultural fields located in Alborz province (50° 15′ 1.2″ N, 35°44′ 11.7″ E and 50° 42′ 27.2″ N, 35° 49′ 4.03″ E), northwest Iran. The study area is dominated by a cold and dry continental climate with mean annual temperature of 21 °C and average annual precipitation of < 250 mm. The soils in the study area are developed on andesite and pyroclastic parent materials and classified as Typic Haplocalcid. Soil samples were collected from 0 to 30 cm, air-dried and passed through a 2-mm sieve for homogenization and to exclude large stone and organic fragments. Subsamples were initially analyzed for the determination of soil particle-size distribution. The sand, silt and clay contents were 80%, 10% and 10% for the sandy loam soil and 10%, 38% and 52% for the clayey soil, respectively. Additional details regarding the soil sampling, preparation and analysis are provided in Khadem and Raiesi (2017b) and the selected soil characteristics are reported in Table 1.

The raw maize stalks (residues) were initially air-dried and milled to pass a 2-mm sieve. The biochars were then produced over a 2 h period by slow pyrolysis process at the temperatures of 400 and 600 °C in a thermal furnace. Subsamples of the biochars were used for chemical analysis. Detailed information for biochar analysis is provided in Khadem and Raiesi (2017b), and the selected properties of the raw biomass and laboratory-produced biochars are summarized in Table 2.