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Research article

The impact of biochars prepared from agricultural residues on phosphorus release and availability in two fertile soils

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A B S T R A C T

Biochars have a high variability in chemical composition, which is influenced by pyrolysis conditions and type of biomass. Essential macronutrient P retained in biochar could be released and made available to plants, enhancing plant growth. This study was conducted in order to evaluate whether biochar, produced from agricultural residues, could release P in water, as well as study its potential effect on plant growth and P uptake. Biochar samples were prepared from rice husks, grape pomace and olive tree prunings by pyrolysis at 300 °C and 500 °C. These samples were used for P batch successive leaching experiments in order to determine P release in water. Subsequently, rice husk and grape pomace biochars, produced by pyrolysis at 300 °C, were applied to two temperate soils with highly different pH. A three-month cultivation period of ryegrass (*Lolium perenne* L.) was studied in threefold replication, while three harvests were accomplished. Treatments comprised control soils (without amendment) and soils amended only with biochar. Results of P leaching tests showed a continuous release of P from all biochars as compared to raw biomass samples, for which the highest P concentrations were detected during the first extraction. Grape pomace and rice husk biochars pyrolyzed at 500 °C showed higher levels of water-extractable P, as compared to their corresponding raw biomass. Biochars, at 500 °C, leached more P in all four extractions, compared to biochars at 300 °C, apart from olive tree prunings biochars, where both pyrolysis temperatures presented a similar trend. Concerning plant yield of ryegrass, rice husk and grape pomace biochars showed positive statistically significant effects on plant yield only in slightly acidic soil in second and third harvests. In terms of P uptake of ryegrass, grape pomace biochars depicted positive significant differences ($P < 0.05$) in third harvest, in slightly acidic soil, while in first and second harvests positive significant differences were observed in alkaline soil. These results suggest that biochars derived from agricultural residues may act as a source of P in agronomic applications and improve plant growth, although soil conditions may play a significant role.

1. Introduction

Intensive agriculture generates large quantities of nutrient-rich agricultural residues whose management and disposal may create environmental problems (Smider and Singh, 2014). Greece produces approximately 4.6 million tonnes of agricultural residues per year from different crops (olive, grape, maize, rice, cereals, cotton etc.) (Boukis et al., 2009). As agriculture is looking for nutrient recycling through practical and feasible strategies for utilization of the agricultural wastes, production of biochar may be an alternative solution.

Conversion of agricultural residues into biochar through pyrolysis has more advantages than the usual methods of disposal. The waste volume decreases through pyrolysis, the risk of pathogens, organic pollutants and heavy metal availability is practically eliminated, and, most important, this highly recalcitrant form of carbon increases carbon storage in the soil, thus facilitating carbon dioxide removal from the atmosphere (Lehmann et al., 2006). Converting these residues into biochar for soil amelioration suggests an alternative option for long-term C storage and recycling of nutrients (Smider and Singh, 2014). Biochar applied to soil increases soil pH, soil cation exchange capacity, CEC (Liang et al., 2006), and soil water holding capacity (Glaser et al., 2002). Biochars usually have a high surface charge density, while CEC values up to 112 $cmol_c\ kg^{-1}$ have been reported (Cheng et al., 2008). This high surface charge density allows biochars to retain cations by cation exchange and internal

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porosity. Adsorption of nutrients takes place on polar and non-polar sites present on biochar surface (Laird et al., 2010). Moreover, biochars can contain and release essential nutrients themselves, which subsequently can be utilized by plants (Laird et al., 2010). Inorganic elements, such as N, P, K and Ca, retained in biochar could provide essential macro and micro-nutrient elements to the plants (Tan and Lagerkvist, 2011).

Among nutrients, phosphorus has recently received considerable attention compared with other elements due to the fact that P is a non-renewable resource and irreplaceable in crop growth and development. Studies have shown that the reserves of phosphorus-rich ores will become depleted in 50–100 years (Driver et al., 1999) with severe loss of P in agricultural fields and very slow recycling rate of P by natural processes (Weikard and Seyhan, 2009). It is estimated that about 80% of phosphates are currently used in fertilizer production (Shu et al., 2006). Therefore, methods and strategies of reusing and recovering P are of interest a lot more often than before. Concentrations of P in biochars are several times higher than in unpyrolyzed organic materials rendering biochar a potential P soil amendment (Brewer et al., 2009). Many studies reported on biochar itself being a potential P source (Silber et al., 2010; Cao and Harris, 2010; Angst and Sohi, 2013; Hale et al., 2013; Mukherjee and Zimmerman, 2013).

Generally, the positive effect of biochar has been investigated mostly on tropical soils with low fertility and high acidity (Glaser et al., 2002). However, plant responses to biochar application on temperate and alkaline soil may be limited or even detrimental, as reported by Borchard et al. (2014) and Jay et al. (2015). Therefore, more studies need to be conducted in order to understand P release kinetics of different types of biochar in water and subsequently in temperate soil, in order to evaluate its potential as a fertilizer. To this end, we chose rice husks, grape pomace and olive tree prunings as biomass for biochar production to study: (i) the release of P already present in biochar and raw biomass in water, and (ii) whether biochars from grape pomace and rice husk pyrolyzed at 300 °C (a) affect P uptake of *Lolium perenne* L. on fertile soils with contrasting pH and (b) improve plant growth.

2. Materials and methods

2.1. Biomass and biochar preparation and characterization

Grape pomace (GP) was obtained from a local winery in Chania, rice husks (RH) from a rice mill in northern Greece, while olive tree prunings (OP) from an olive orchard at the Technical University's Park for the Preservation of Flora and Fauna. The biomass, prior to use, was dried at 105 °C for 24 h, ground and sieved to 500 μm in order to ensure uniformity of samples during pyrolysis.

Biochar samples were produced using a muffle furnace (Linn High Therm). To maintain an oxygen-free atmosphere during the process, 99% pure nitrogen gas was supplied to the system at a 200 mL min^{-1} flow rate. The temperature increase rate was set at 6 C min^{-1}. After reaching the target temperature, the sample was kept in the operating furnace for 60 min (residence time). The biochars were then removed from the furnace, cooled in a desiccator, weighed and stored in airtight plastic containers. Biochar samples from different biomass (GP, RH, OP) and temperature regimes (300 °C and 500 °C) will be referred to as GP-300, GP-500, RH-300, RH-500, OP-300, OP-500, while raw (unpyrolyzed) biomass samples as GP-R, RH-R and OP-R. The yield of biochars was determined as the ratio of the produced biochar weight to the dry weight of biomass subjected to pyrolysis as presented by Agrafioti et al. (2013). The pH and electrical conductivity (EC) was measured in a suspension of biochar or biomass in deionized water (ratio of 10% w/v) after shaking it for 24 h at 60 rpm (Marks et al., 2014). Ash content of biochars and raw agricultural wastes was determined by dry combustion in a muffle furnace at 750 °C for 6 h (ASTM, 2007). Total C and N concentrations were determined using a CHNS-O EA 3000 (EuroVector) analyzer. Nutrient elements in feedstock and biochars were identified using ICP-MS. Specifically, 9 mL HNO_3 were added to 0.2 g biochar, followed by microwave digestion at 150–180 °C (Multiwave 3000 Digestor). Supernatant solutions were diluted with MilliQ water and analyzed by ICP-MS (Agilent-CX).

2.2. Soil characterization

Agricultural soils from two different sites in Chania were sampled in summer 2014. The soils used for the experiment were collected from the topsoil (0–20 cm). From the bulk soil samples, stones and plant tissues were removed, and the samples were homogenized, air dried, crushed, and passed through a 10 mm and 2-mm sieve. The features of soil samples are presented in Table 1. Soil pH and electrical conductivity (EC) were determined using the relevant electrodes in a multi-meter (SevenMulti, Mettler-Toledo, Switzerland) in 1:2 and 1:1 soil pastes respectively. Soil texture was determined using the Bouyoucos hydrometer method. Percentage of organic matter was determined using the Walkley-Black method, carbonate content (total $CaCO_3$ percentage) was determined using the volumetric calcimeter method, while available P by the Olsen method (Black et al., 1965). Nitrate-N was determined colorimetrically at 400 nm, after KCl extraction (20 g of soil in a final 1:2.5 dilution) and use of Nitraver reagent (Hach-Lange, Germany). Exchangeable K, Ca and Mg were determined after ammonium acetate extraction (2.5 g of soil in a final 1:20 dilution) and measurement in an ICP-OES (Optima 8300, Perkin-Elmer, USA). Exchangeable Fe, Zn, Mn and Cu were determined after DTPA extraction (10 g of soil in a final 1:2.5 dilution) and measured by ICP-OES.

2.3. Phosphorus leaching tests

To investigate phosphate release, successive P leaching experiments took place in order to quantify the maximum amount of phosphorus likely to be released by both biochar and raw biomass samples into the natural environment. For each one of the successive batch extractions of P from the six biochar and the three raw biomass samples, the contact time was 24 h. 1.5 g of material was added in 150 mL of water (1:100 ratio) and the suspensions

Table 1
Characteristics of the two soils used in the pot experiments.

Characteristic	Units	Soil	
		Loam	Sandy loam
pH		8.21	6.75
$CaCO_3$	(%)	25.87	5.81
OM	(%)	2.88	5.49
EC	(dS m^{-1})	0.44	0.78
Sand	(%)	45.60	55.60
Silt	(%)	40.00	30.00
Clay	(%)	14.40	14.40
N	(mg kg^{-1})	16.30	22.60
P	(mg kg^{-1})	13.30	35.40
K	(mg kg^{-1})	860.00	206.00
Ca	(mg kg^{-1})	6897.00	4795.00
Mg	(mg kg^{-1})	298.00	234.00
Fe	(mg kg^{-1})	1.54	25.00
Zn	(mg kg^{-1})	0.28	1.01
Mn	(mg kg^{-1})	4.14	9.06
Cu	(mg kg^{-1})	0.24	0.79