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Effect of biochar amendment on nitrate retention in a silty clay loam soil

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Abstract

Biochar incorporation into agricultural soils has been proposed as a strategy to decrease nutrient leaching. The present study was designed to assess the effect of biochar on nitrate retention in a silty clay loam soil. Biochar obtained from the pyrogasification of fir wood chips was applied to soil and tested in a range of laboratory sorption experiments. Four soil treatments were considered: soil only (control), soil with 2, 4 and 8% of biochar by mass. The Freundlich sorption isotherm model was used to fit the adsorbed amount of nitrate in the soil-biochar mixtures. The model performed very well in interpreting the experimental data according to a general linear regression (analysis of co-variance) statistical approach. Nitrate retention in the soil-biochar mixtures was always higher than control, regardless the NO_3^- concentration in the range of 0-400 mg L^{-1}. Different sorption capacities and intensities were detected depending on the biochar application rate. The highest adsorption capacity was observed in the soils added with 2 and 4% of biochar, respectively. From the results obtained is possible to infer that nitrate retention is higher at lower biochar addition rate to soil (2 and 4%) and at lower nitrate concentration in the soil water solution. These preliminary laboratory results suggest that biochar addition to a typical Mediterranean agricultural soil could be an effective management option to mitigate nitrate leaching.

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Introduction

Large fertilising applications in intensive cropping systems are the main cause of nutrient loss from agricultural soils to aquatic systems (Yao *et al*., 2012). Among these nutrients, nitrogen is of prime concern. Nitrogen in the form of nitrate (NO_3^-) is highly soluble within the soil water solution, poorly adsorbed by the soil particles and therefore prone to be leached away by the water percolating along the soil profile. NO_3^- leaching depletes soil fertility, limits the nitrogen utilisation efficiency by the plants, reduces crop yields and represents a significant economic cost for farmers. Moreover, adverse impacts on environmental and human health might be developed by nitrate leaching. It is therefore very important to develop effective technical solution able to mitigate nitrate leaching from agricultural fields. Increasing the NO_3^- retention capacity of soil has the potential to reduce nitrate losses and improve nitrogen utilisation efficiency for a sustainable crop production. On this respect, the use of biochar is currently raising interest as a potential means to increase the capacity of soils to retain nutrients (Atkinson, 2010). Biochar is the solid, carbonaceous product obtained by the thermochemical processes (pyrolysis or gasification) of biomass conversion into renewable energy products (Laird *et al*., 2009). The use of biochar as soil amendment has gained attention as a valid strategy to mitigate global climate change, by sequestering atmospheric CO_2 and reducing greenhouse gas emissions (Laird, 2008), improve physicochemical and microbiological soil properties (Gul *et al*., 2015), enhance plant growth and crop yield (Vaccari *et al*., 2011). What is specifically relevant to our study is that biochar seems to have the potential to reduce NO_3^- leaching (Knowles *et al*., 2011). Mechanism of decreased nitrate leaching were found to be the adsorption of NO_3^- on anion exchange surface of biochar, particularly when biochar was obtained at high temperatures (>600°C); the inhibited nitrification and thus the decreased nitrate production; the N immobilisation due to the presence of labile C in biochar; the incorporation of NO_3^- present in soil solution into biochar pores; the increased water retention in the soil which may reduce NO_3^- leaching (Lone *et al*., 2015). Recently, a number of studies, carried out in open field (Ventura *et al*., 2013), in pots experiment (Buecker *et al*., 2016) or using columns leaching (Bradley *et al*., 2015; Kanthle *et al*., 2016; Yuan *et al*., 2016), indicated that biochar is an effective option of nitrate leaching mitigation. However, other studies oppositely showed a limited or no ability of biochar to retain NO_3^-. Yao *et al*. (2012) found the poor ability of nine out of thirteen biochars tested to adsorb nitrate. Hollister *et al*. (2013), in sorption experiments carried out using biochar from corn or oak, observed the inability of biochar to retain NO_3^-. Eykelbosh *et al*. (2015) found that biochar from sugarcane filtercake did not lessen NO_3^- leaching from the soil. These contradictory results are likely because of the differences in type of biochar, type of soil and level of biochar applied. Therefore, the nitrate sorption effectiveness of biochar need to be studied prior to its application aimed at controlling nitrogen losses from agricultural soil.

In this study, we investigated the effect of fir wood biochar application on nitrate retention in a silty clay loam soil. A range of laboratory experiments was carried out with the aim to assess whether soil amendment with several amounts of biochar can affect the ability to retain NO_3^- and, eventually, the most effective biochar application rate.

Materials and methods

Soil and biochar

Topsoil (from 0 to 20 cm of depth) was collected from an agricultural field in the Foggia district (Apulia Region, southern Italy). Before the experiments started, a soil physicochemical characterisation was carried out. The particle-size distribution was determined using the pipette-gravimetric method. The water holding capacities at –0.03 MPa (field capacity) and –1.5 MPa (wilting point) were obtained using a pressure-plate apparatus (Soilmoisture Equipment Corp.). The pH and electrical conductivity were measured on 1:2.5 (w/v) aqueous soil extracts and saturated soil paste extracts, by a GLP 22+ pH-meter and a GLP 31+ EC-meter (Crison Instruments, Barcelona), respectively. The available phosphorus was determined by the sodium bicarbonate method (Olsen *et al.*, 1954), and the total organic carbon by the Walkley-Black (1934) acid dichromate digestion technique. The total nitrogen was obtained according to the Kjeldahl method (Bremner 1996) and the NO_3^--N content was determined by soil extraction with 2 M KCl, followed by spectrophotometric analysis of the extract (Keeney and Nelson, 1982). Soil had a silty clay loam texture (United States Department of Agriculture classification), with a field capacity of 38.0% dry weight (dw), a wilting point of 20.3% dw. The main characteristics were: clay, 27.6%; silt, 55.8%; sand, 16.6%; organic matter, 0.4%; total nitrogen, 0.4‰; NO_3^--N, 2.6 mg N kg^{-1}; P_2O_5, 41.8 ppm; pH 8.4; and electrical conductivity, 0.3 dS m^{-1}.

Biochar was purchased from a commercial producer. It was obtained by pyrogasification of fire wood chips. Biomass pyrogasification occurred at temperature up to 1200°C in a gasifier unit rated at 200 kWe in delivered power capacity. A set of chemical analyses was conducted on biochar. Proximate analysis determined the relative content in total solid (TS), volatile solid (VS), ash (AS) and fixed carbon (FC), using a TGA analyser unit (LECO-TGA701), according to the ASTM D7582 method. pH and electrical conductivity were determined using a biochar to deionised water mass ratio 1:20, followed by shaking and waiting an equilibrium time of 5 min before measurement by a GLP 22+ pH-meter and a GLP 31+ EC-meter (Crison Instruments, Barcelona), respectively. Ultimate analysis determined the C, N, H and S content using a CHNS Elemental Analyser (CHN LECO 680), according to the method LECO-ASTM D5373. O content was calculated by the difference: oxygen (O) (%) = 100-C-H-N-S-ash. From hydrogen (H), carbon (C) and O content, the molar ratios of hydrogen to organic carbon (H/C_{org}) and oxygen to organic carbon (O/C_{org}) were obtained. Micro- and macro-elements analysis was performed by digesting 0.25 g of sample in 10 mL of HNO_3 in a closed vessel microwave digester (CEM-Mars6) for 20 min at 220°C. The metals in the solution were analysed by inductively coupling plasma spectrometry-optical emission spectroscopy (ICP-OES Agilent 720). Biochar was alkaline with a pH of 9.4 and showed a salinity level of 300 mSm^{-1}. Proximate analysis indicated that biochar contained 88.0% FC, 8.7% VS and 3.3% AS. Ultimate analysis showed that biochar was carbon-rich, with a C content of 83.2% by mass, and 1.7% H, 0.4% nitrogen (N), 0.05% sulphur (S) and 11.4% O by mass. H/C_{org} and O/C_{org} were equal to 0.25 and 0.10, respectively (lower values of these ratios are correlated with greater carbon stability). ICP-OES analysis revealed the presence of inorganic nutrients such as potassium (K) (25244.8 mg kg^{-1}), calcium (Ca) (4392.5 mg kg^{-1}), magnesium (Mg) (1043.5 mg kg^{-1}) and iron (Fe) (1023.6 mg kg^{-1}). Heavy metals concentrations ranged from not detectable amount for cadmium (Cd), copper (Co) and lead (Pb) to amounts as high as 286.6 mg kg^{-1} for manganese (Mn). According to the technical specifications published by the Italian Ministry of Agriculture which has recently approved the inclusion of biochar in the list of soil amendments allowed in Italian agriculture (Italian Official Journal - General Series No 186, 12-8-2015), biochar is assigned to a *class* on the basis of its percentage content of organic C and ash. Biochar used in our experiments belonged to the Class 1 (C_{org} >60%; ash <10%). Moreover, all the requirements of the Italian technical specifications (salinity ≤1000 mSm^{-1}, pH = 4-12, H/C_{org} ≤0.7) were fully complied.

Before laboratory experiments started, subsamples of air-dried soil were respectively added and homogeneously mixed with subsamples of air-dried biochar. Biochar and soil were preliminary sieved at 1 mm in order to increase the area:volume ratio of the respective particles thus maximising their reciprocal interaction. Biochar was applied at rates of 2, 4 and 8% of dry soil weight. Rates of biochar application could be considered equivalent to 48, 96 and 192 Mg ha^{-1}, assuming a soil bulk density of 1.2 Mg m^{-3} and a soil depth of 0.20 m. The obtained mixtures were maintained at room temperature (22±0.5°C) until their utilisation.

Nitrate sorption experiments

A range of laboratory experiments was performed comparing four soil treatments: soil only (control, B0); soil + 2% biochar (g biochar per g soil, B2); soil + 4% biochar (B4); soil + 8% biochar (B8). A stock solution of 5 mg NO_3^- L^{-1} was prepared by dissolving 8.20 g of KNO_3 in 1 L of deionised water and serial dilutions were applied to obtain concentrations of 5, 10, 50, 100, 200, 300 e 400 mg NO_3^- L^{-1}. At room temperature (22±0.5°C) and for each soil treatment, 100 mg of soil was added into a vessel and mixed with 50 mL of each nitrate solution. The mixtures were stirred for 24 h with a mechanical shaker. After reaching equilibrium, the soil-biochar suspensions were filtered with a 0.22 μm nylon membrane filter. The filtrate NO_3^- concentration at equilibrium was then analysed by ion-exchange chromatography (Dionex ICS-1100, Dionex Corp., Sunnyvale, CA, USA). All the experiments were carried out in duplicate.

For each sample, sorbed nitrate was calculated by applying the following equation:

$$Q_e = (V/W) * (C_i - C_e) \qquad (1)$$

where: Q_e = amount of NO_3^- adsorbed per unit weight of sample at equilibrium (mg g^{-1}); V = volume of the liquid phase (mL); W = soil sample weight (mg); C_i e C_e= initial and final (at equilibrium) concentrations of NO_3^- in the liquid phase (mg L^{-1}).

To describe the empirical relationship between the amount of adsorbed and dissolved NO_3^-, considering the soil-biochar mixtures at equilibrium and constant temperature, the Freundlich sorption model was applied as follow:

$$Q_e = K_f * C_e^{1/n} \qquad (2)$$

where: K_f (mg g^{-1}) and 1/n (L mg^{-1}) are experimentally derived coefficients specifically related to the sorbent-sorbate system. K_f stands for the initial adsorption capacity, while 1/n corresponds to the sorption intensity. The higher K_f, the greater the adsorption capacity; the higher 1/n, the higher the sorption intensity; if n = 1, then sorption is linear. The values of these empirical coefficients were obtained from the linearised form of the Freundlich model:

$$\log Q_e = \log K_f + 1/n \log C_e \quad (3)$$

where: $\log K_f$ is the intercept while 1/n is the slope of the regression line.

The log-transformed data set was processed as a whole by applying an analysis of co-variance (ANCOVA), *i.e.*, a general linear model which processes together levels of a categorical independent variable (the soil-biochar treatments) with a continuous variable, known as covariate or regressor (the C_e liquid phase concentrations). According to this procedure, a statistical discrimination among the values of intercepts and slopes of the regression lines becomes viable.

Results and discussion

Figure 1 shows the NO_3^- sorption isotherms of the four soil treatments according to the linear form of the Freundlich model, resulting from the ANCOVA statistical procedure and obtained by plotting log Qe against log Ce. Nitrate retention in the soil mixed with biochar was always higher than the control, regardless the NO_3^- concentration in the range of 0-400 mg L^{-1}. Different sorption capacities and intensities were detected depending on the biochar application rate. Indeed, as resulting from the values of intercepts and slopes of the linear Freundlich model reported in Table 1, soil treatments B2 and B4 were not statistically different each other, while B8 showed different K_f and 1/n values in respect to both B2 and B4 as well as compared to B0. In particular, the nitrate sorption capacity (the K_f intercept value) for B2 and B4 resulted significantly higher than the other two soil treatments, highlighting the enhanced NO_3^- adsorption capacity of the soil when treated with 2 and 4% of biochar by mass. Conversely, the intensity of nitrate retention (the 1/n slope value) in the soil without biochar addition (B0) was significantly higher than in the soil-biochar mixes (B2, B4 and B8). By observing Figure 1 is easy to note that the four lines tend to converge at higher nitrate equilibrium values. From the results obtained is possible to reasonable infer that nitrate retention is higher at lower biochar addition rate to soil (B2 and B4) and at lower nitrate concentration in the soil water solution.

A straightforward explanation for the effect of biochar on nutrient retention is that it acts as an adsorbent (Clough *et al*., 2013). Organic material generally has some adsorption capacity and the charring process, especially at higher temperatures, usually increases this feature (Bhatnagar and Sillanpaa, 2010). The nitrate retention observed in the soil-biochar mixtures might indicate a NO_3^- adsorption process due to the high temperature at which biochar was obtained. As observed by Cheng *et al.* (2008), biochars produced at high temperatures have a greater specific surface area and are positively charged. Kameyama *et al*. (2012) reported that NO_3^- sorption to biochar increased with greater biochar production temperatures, due to the formation of basic functional groups. The findings of this study are consistent with the results of other biochar researches carried out under controlled laboratory-based conditions (Mizuta *et al*., 2004; Yao *et al*., 2012; Liang *et al*., 2014), which observed some nitrate adsorption with some high temperature biochars. They are also in line with the results of a field experiment recently reported by Haider *et al*. (2016). The authors observed that on a cultivated temperate sandy soil biochar reduced nitrate leaching. NO_3^- sorption in biochar amended soil was attributed to several mechanisms, such as solution mass flow into biochar particles, where the NO_3^- ions are physically entrapped within biochar pores; non conventional H bonding and bonding between NO_3^- and functional groups or positively charged cations on biochar surface.

Conclusions

Based on a preliminary laboratory assessment, the obtained results showed the positive effect of biochar on soil nitrate retention. The addition of a biochar from fir wood to a silty clay loam soil, particularly at the rate of 2 and 4%, enhanced the soil NO_3^- sorption. The present findings will be extend to long-term experimental trials under field conditions in order to fully investigate the effects of biochar characteristics and soil properties interactions on nitrate retention. Elucidating these aspects may enable the optimisation of large-scale application of biochar to agricultural fields as an effective option of nitrate leaching mitigation.

Table 1. Analysis of co-variance results. Coefficients of the linearised Freundlich sorption model as applied to nitrate for the four experimental soil-biochar mixtures (B_i). The reported Δ values are the incremental effects due to soil treatments with respect to the average values of the intercept ($\log K_f$) and slope (1/n), respectively.

Term	Estimate	*	Standard error	P
Intercept - log Kf	−0.48		0.06	<0.0001
Δ B2	+0.46	a	0.11	<0.0001
Δ B4	+0.29	a	0.11	0.0095
Δ B8	−0.16	b	0.11	0.1791
Δ B0	−0.60	c	0.12	<0.0001
Slope - 1/n	1.02		0.04	<0.0001
Δ B2	−0.12	a	0.06	0.0625
Δ B4	−0.10	a	0.06	0.1389
Δ B8	+0.04	b	0.07	0.5582
Δ B0	+0.18	c	0.07	0.0129
R^2	-		0.94	
RMSE	-		0.19	
CV (%)	-		16.16	

*Values followed by the same letters are not significantly different (P≤0.05). RMSE, root mean square error; CV, cultivar.

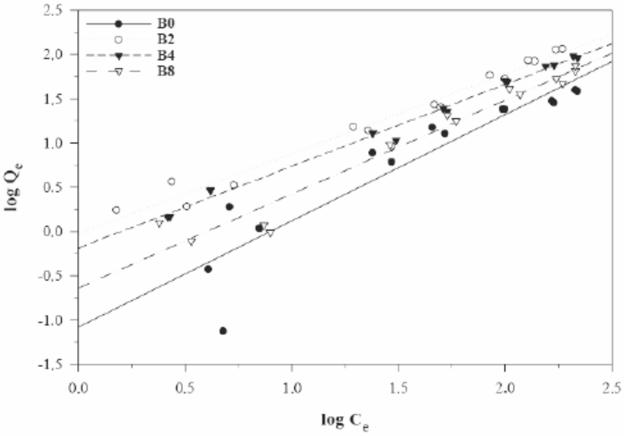

Figure 1. Linearised sorption isotherms according to the Freundlich model as applied to nitrate for the four experimental soil-biochar mixtures.

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