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Gasifier biochar effects on nutrient availability, organic matter mineralization, and soil fauna activity in a multi-year Mediterranean trial

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ABSTRACT

Gasifier pine biochar is a carbon-rich material which may be useful as a soil amendment. In Europe and elsewhere there may be potential added value of char produced in industrial gasifiers, up to now considered as wastes. Pine gasification biochar was tested as a soil amendment in a multi-year Mediterranean barley crop field trial, applied at 12 and 50 t ha^{-1} while applying half the usual N rate at 50 kg ha^{-1}, contrasted with a full 100 kg ha^{-1} N fertilizer treatment without biochar. Over the 6–30 month period following the application, biochar treatments did not have any significant effect on soil microbial biomass, respiration, or metabolic coefficient. N mineralization as NO_3^- was decreased by biochar at 6 and 12 months from experiment start and coincided with ammonium accumulation. Biochar increased overall soil concentrations of K^+ and SO_4^{2-}, attributed to a direct additive effect, agreeing with data from other sources. Biochar treatments (with half usual N fertilization) did not have any significant effects on barley crop parameters, and when biochar treatments were contrasted against full N fertilization with no biochar, the usual N dosage was clearly more beneficial to crop development. Finally, soil fauna activity was negatively impacted by gasifier biochar treatments in years two and three, indicating a risk to soil processes mediated by soil invertebrates. Though this gasifier biochar is expected to be highly stable and therefore of interest for carbon sequestration, its utilization therefore risks negative effects on some biologically-mediated soil processes at high application rates.

1. Introduction

Crop residues or other biomass waste streams can be pyrolyzed to produce char, a carbon-rich, highly recalcitrant material, which when applied as a soil amendment is called 'biochar' (Lehmann and Joseph, 2015). While there is increasing evidence that biochar has the capacity to improve crop yields in highly weathered soils due to enhancement of important parameters of soil fertility including cation exchange capacity (CEC) and soil organic carbon (SOC), studies in alkaline soils are not particularly abundant and different results in crop status have been documented (Lentz and Ippolito, 2012; Zhang et al., 2012; Schmidt et al., 2014; Zhao et al., 2014). In some of these cases a positive effect of biochar on crop yields has been associated with an improved nutrient status. Apart from direct nutrient release, it has been suggested that biochar can indirectly improve fertilizer use efficiency (Zhao et al., 2014). Biochar may also indirectly affect soil nutrient dynamics by influencing microbial abundance and causing community shifts (Lehmann et al., 2011; McCormack et al., 2013). A recent proliferation of studies has shown diverse indirect effects of biochar on soil N, with important potential consequences for N cycling and plant nutrition (Clough et al., 2013). Of these studies, a few have been conducted on calcareous soils where reduced soil NO_3^- concentrations have been reported (Ventura et al., 2013; Ducey et al., 2013; Ippolito et al., 2014). With regards to biochar effects on soil biology and crucial biotically-mediated processes, significant evidence of effects exist, though a synthesis of the currently available information into generalizations or patters has been an elusive task, and remains a top research priority (Lehmann et al., 2011; Ameloot et al., 2013).

The above uncertainties underscore the need for a better understanding of how biochar can affect soil chemical properties

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and biologically-mediated soil processes of agronomic importance. Firstly, there is a need for medium to long-term data in the Mediterranean. Second, there are few studies of gasifier biochars, and even fewer field studies: these points are key contributions of our study. We postulated that gasifier biochar application to a barley cropping system on a Mediterranean calcareous soil may ease typical limiting factors to crop growth such as nutrient availability and water availability. To understand effects on biologically-mediated processes, microbial biomass, microbial respiration, mineralization, and fauna activity were monitored since these are indicators of impacts on soil quality and processes such as litter decomposition, nutrient cycling, and energy flow in soil ecosystems (Wardle, 1992; Filzek et al., 2004).

2. Materials and methods

2.1. Biochar production and characterization

A pine (*Pinus pinaster* + *Pinus radiata*) chip gasifier biochar was obtained from an industrial gasification facility in Vitoria, Basque Country, N Spain. Production conditions at the facility range from 600 to 900 °C, with an approximate holding time of 10 s. Characterization was largely following test methods described in Camps-Arbestain et al. (2015). Briefly, C, N, H, S were determined by elemental analysis (LECO TruSpecCHN and LECO SC-144 DR); oxygen content was estimated as difference of sum of elemental analysis and ash; ash gravimetrically following combustion at 550 °C; volatiles gravimetrically following 950 °C for six minutes in a reducing atmosphere; for major nutrients, ash was analyzed for Na and K by flame photometry and for Ca and Mg by atomic absorption spectroscopy, and P was determined colorimetrically following microwave-assisted attack of biochar with HCl and HNO_3; pH and electrical conductivity (EC) from 1:20 aqueous extracts; $CaCO_3$ and C-CO_3 as described in Wang et al. (2014). Functional groups were evaluated with Fourier-transform infrared spectroscopy (FTIR); cation exchange capacity (CEC) was evaluated with a modified ammonium acetate adsorption method (Lavkulich, 1981).

Biochar heavy metal loadings were determined using inductively coupled plasma-mass spectrometry (ICP-MS) in an accredited external laboratory (GTS, Bellaterra, Spain). Extraction and quantification of biochar polycyclic aromatic hydrocarbons (PAH) was performed by the same accredited external laboratory. Analysis was in duplicate. Following 24-h microwave-assisted 1:1 acetone:hexane extraction, gas chromatography-mass spectrometry (GC–MS) was employed to quantify concentrations 16 PAHs classified by the USEPA as priority contaminants. Calibrations were established using a commercial standard.

By weight, the gasifier biochar's particle sizes were largely in the 500–2000 μm (42%) and 50–100 μm (28%) fractions. Elemental composition, nutrient content, and chemical properties are shown in Table 1. FTIR-evaluated functional groups were barely apparent, and also notable was the high absorbance offset in the absorbance spectrum, attributable to the high abundance of condensed aromatic structures (Fig. S1; Mochidzuki et al., 2003). The H:C_{org} ratio, which was relatively quite low for a biochar (Table 1), also indicated high condensation. CEC was also low for a biochar (Table 1).

With regards to contaminants, heavy metals are not typically a concern for wood biochars, however gasification results in high condensation, increasing the concentrations of metals present. As seen in Table 1, the biochar's heavy metal loadings were below thresholds for the Premium grade according to the European Biochar Certificate (EBC), with the exception of Cd, which was still below the threshold for Basic grade. Biochar PAHs have received increased attention due to important environmental consequences. The EBC has established limits of $<12\ \mu g\ g^{-1}$ for Basic Grade biochar, and $<4\ \mu g\ g^{-1}$ for Premium Grade. The gasifier biochar's EPA PAH concentrations are shown in Table S1. The overall concentration of $321\ \mu g\ g^{-1}$ was high for a biochar, far surpassing EBC thresholds, and exceeding most values found in the literature; however, within the same order of magnitude Rogovska et al. (2012) reported total PAHs of $255\ \mu g\ g^{-1}$ for a corn gasification biochar produced at 845 °C.

Table 1
Elemental composition, proximate analyses, main nutrients, heavy metal content, and chemical characterization of the pine gasification biochar.

Parameter	Unit	Value
C[a]	%	79.34
N[a]	%	0.02
H[a]	%	1.22
S[a]	%	0.15
O[b]	%	8.48
O/C_{org}[a]	%	0.08
H/C_{org}[a]	%	0.19
Ash[d]	%	10.79 ± 0.26
Volatile matter[d]	%	8.0 ± 0.28
P[a]	$mg\ kg^{-1}$	1337
Na[a]	$mg\ kg^{-1}$	480
K[a]	$mg\ kg^{-1}$	9360
Ca[a]	$mg\ kg^{-1}$	20520
Mg[a]	$mg\ kg^{-1}$	2100
Cu[a]	$mg\ kg^{-1}$	12
Co[a]	$mg\ kg^{-1}$	8
Cr[a]	$mg\ kg^{-1}$	34
Ni[a]	$mg\ kg^{-1}$	25
Pb[a]	$mg\ kg^{-1}$	16
Zn[a]	$mg\ kg^{-1}$	256
As[a]	$\mu g\ kg^{-1}$	906
Cd[a]	$\mu g\ kg^{-1}$	1383
Sb[a]	$\mu g\ kg^{-1}$	435
$CaCO_3$[d]	$g\ kg^{-1}$	33.4 ± 0.62
C–CO_3[d]	$g\ kg^{-1}$	4 ± 0.62
pH (1:20)[d]	–	11.5 ± 0.04
EC[d]	$dS\ m^{-1}$ 25 °C	0.69 ± 0.02
CEC[c]	$mmol_c\ kg^{-1}$	21.1 ± 6.6

[a] Single determination.
[b] Estimated by difference.
[c] Reported value mean of two determinations, error as standard deviation.
[d] Reported value mean of three determinations, error as standard deviation.

2.2. Mesocosm construction and field trial

Field mesocosms were constructed in March 2011 at the IRTA Torre Marimón experimental station (Caldes de Montbui, Barcelona, NE Spain; mean annual precipitation = 616 mm, mean annual temperature = 14.7 °C, annual potential evapotranspiration (Thornthwaite) = 787 mm). Here the climate is sub-humid coastal Mediterranean, with two rainy periods in spring and autumn, winter and summer being dry periods. The temperature and pluvial meteorological conditions over the campaign were recorded at a meteorological station installed at experiment's location, and are shown in Fig. 1 (in this figure samplings are indicated in their temporal succession). The site is situated on a calcareous *Fluventic haploxerept* (Soil Survey Staff, 2010), whose main properties are reported in Table 2. Eighteen 1 m^2 mesocosms were constructed by excavating the upper 20 cm, delimiting horizontally on each side with four 30 cm-height steel plates protruding to 10 cm above ground level. Three treatments of gasifier pine (*Pinus pinaster* and *P. radiata*) biochar additions of 0, 12, and 50 t ha^{-1} were assigned in a complete random block. Excavated soil was thoroughly mixed with biochar before refilling, and controls were also excavated, mixed, and refilled. To test the gasifier biochar's potential for improving fertilization efficiency, in these plots N was applied at half the usual rate or 50 kg N ha^{-1}