High concentrations of polycyclic aromatic hydrocarbons (naphthalene, phenanthrene and pyrene) failed to explain biochar's capacity to reduce soil nitrous oxide emissions

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A B S T R A C T

The presence of polycyclic aromatic hydrocarbons (PAHs) has been postulated as a mechanism by which biochar might mitigate N_2O emissions. We studied whether and to what extent N_2O emissions were influenced by the three most abundant PAHs in biochar: naphthalene, phenanthrene and pyrene. We hypothesised that biochars contaminated with PAHs would show a larger N_2O mitigation capacity and that increasing PAH concentrations in biochar would lead to higher mitigation potentials. Our results demonstrate that the high-temperature biochar (550 °C) had a higher capacity to mitigate soil N_2O emissions than the low-temperature biochar (350 °C). At low PAH concentrations, PAHs do not significantly contribute to the reductions in soil N_2O emissions; while biochar stimulated soil N_2O emissions when it was spiked with high concentrations of PAHs. This study suggests that the impact of biochar on soil N_2O emissions is due to other compositional and/or structural properties of biochar rather than to PAH concentration.

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1. Introduction

The increase of anthropogenic N_2O emissions is a major environmental concern since it contributes considerably to stratospheric ozone depletion and climate change (Ravishankara et al., 2009; UNEP, 2013). Agriculture is the largest source of anthropogenic N_2O emissions, with about 4 Tg N_2O–N per year, which represent more than 65% of the total anthropogenic N_2O emissions (UNEP, 2013). Therefore, the reduction of N_2O emissions from agricultural sources constitutes a critical research challenge (Venterea et al., 2012).

Biochar is a charcoal-like substance produced from the pyrolysis of residual biomass with a high potential to be used as a valuable soil amendment (Biederman and Harpole, 2013; Jeffery et al., 2013). Biochar addition to soil has been found to decrease nitrous oxide emissions (Case et al., 2012; Spokas and Reikosky, 2009; Stewart et al., 2013). Cayuela et al. (2014) reported an average reduction of 54% in diverse soils and environmental conditions. The causes and mechanisms of this reduction are still controversial (Borchard et al., 2014; Sánchez-García et al., 2014; Spokas, 2012). One of the proposed hypotheses was the temporary release of polycyclic aromatic hydrocarbons (PAHs), which are commonly present in biochar as a result of the pyrolysis process (Cayuela et al., 2014; Wang et al., 2013). PAH concentrations, ranging from negligible (below the detection limits) up to 355 mg kg^{-1}, have been found in biochar samples (Fabbri et al., 2013; Hale et al., 2012; Hilber et al., 2012; Quilliam et al., 2013). Naphthalene is recognised as the most abundant PAH in biochar, followed generally by phenanthrene and pyrene (Freddo et al., 2012; Hale et al., 2012; Hilber et al., 2012; Keiluweit et al., 2012).

Several ecotoxicological studies have reported the impact of PAHs on soil N transformations mediated by microorganisms. For instance Chang et al. (2002) found that naphthalene strongly inhibits ammonia oxidation by nitrifying bacterium *Nitrosomonas europaea* and Sverdrup et al. (2002) and Maliszewska-Kordybach et al. (2007) demonstrated the toxicity of phenanthrene and pyrene to nitrifying microorganisms in soil. Denitrification activity has also been found to be inhibited by PAHs. For example, Guo et al. (2011) showed that pyrene reduced denitrification activity and altered the soil denitrifying community. Nonetheless, the impact of PAHs on soil N_2O emissions is still a largely unexplored field. In an incubation study, Contreras-Ramos et al. (2009) showed that

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contamination with PAHs did not modify N_2O emissions in a sandy loam soil, whereas Álvarez-Bernal et al. (2009) found that pollution of soil with PAHs increased N_2O emissions. In addition, little information is found about the impact of PAHs in biochar on soil N_2O emissions. Recently, Wang et al. (2013) indicated a correlation between the concentration of PAHs in low temperature biochars (300–400 °C) and the decrease in soil N_2O emissions. These authors postulated that the presence of PAHs in biochars might play a major role in reducing nitrous oxide emissions by decreasing total denitrification activity in soil.

The aim of this study was to evaluate the impact of PAHs on biochar's N_2O mitigation capacity. Two hypotheses were tested: (i) PAHs contribute significantly to the decreased N_2O emissions observed in biochar amended soils, and (ii) increasing PAHs concentrations in biochar would lead to higher N_2O mitigation in soil.

2. Materials and methods

2.1. Soil and biochar samples

The soil, classified as Haplic Calcisol (FAO, 2006), was collected from the topsoil (0–25 cm) of a commercial table grape orchard managed under drip irrigation and no tillage cropping system (37°45′55.5″, -1°31′33.3″, Murcia, Spain), air-dried and sieved (<2 mm) before its use. It had a loam texture (32% sand, 42% silt, and 26% clay), pH of 7.8, 501.1 g kg^{-1} CaCO$_3$, 8.1 g kg^{-1} organic-C, 0.8 g kg^{-1} total N, 3.1 mg NH$_4^+$-N kg^{-1} and 26.8 mg NO$_3^-$-N kg^{-1}. Two biochar samples, produced from pine wood in the framework of the project "Proyecto Biocar: Estudio del Biocarbón como Sumidero de Carbono" (IPT-440000-2010-8) by slow pyrolysis at highest treatment temperature (HTT) 350 and 550 °C (named B350 and B550, respectively) were used. The biochar production was carried out in a semi-continuous, electrically-heated reactor, with a design to ensure oxygen-free conditions, at the University of León (Sánchez et al., 2007). The biochars were homogenised and ground in a stainless steel mill to <2 mm before analysis and use. B550 showed higher pH, liming capacity, degree of aromaticity (lower H/C_{org} and O/C_{org} ratios), surface area, ash content, nutrient and PAH

Table 1
Main characteristics of the two pine wood biochars produced by slow pyrolysis at 350 °C (B350) and 550 °C (B550), respectively (on a dry weight basis).

Parameters	B350	B550
pH[a]	7.22	8.24
Liming equivalence (g CaCO$_3$ kg^{-1})	6.3	16.9
Electrical conductivity[a] (dS m^{-1})	0.26	0.51
Volatile matter (g kg^{-1})	301.6	131.7
Ash (g kg^{-1})	13.6	24.8
C_{org} (g kg^{-1})	783.0	860.2
Water-soluble C_{org} (mg kg^{-1})	1431	335
N (g kg^{-1})	3.4	4.2
Water-soluble N (mg kg^{-1})	10	15
NH$_4^+$-N (mg kg^{-1})	0.6	nd
NO$_3^-$-N (mg kg^{-1})	0.4	0.6
Specific surface area (m^2 g^{-1})	254	399
Cation exchange capacity (cmol kg^{-1})	17.6	10.2
C_{org}/N	230	205
molar H/C_{org}	0.55	0.34
molar O/C_{org}	0.16	0.07
PAHs (mg kg^{-1})	2.1	8.9
Naphthalene (mg kg^{-1})	1.2	5.6
Phenanthrene (mg kg^{-1})	0.4	1.4
Pyrene (mg kg^{-1})	0.1	0.5

[a] Water extract 1:10 (w/v); nd: non detected; C_{org}: organic carbon; N: total nitrogen; and PAHs: polycyclic aromatic hydrocarbons (sum of the EPA's 16 priority pollutants).

concentrations compared to B350; but lower C_{org}/N, volatile matter and water-soluble organic carbon contents and cation exchange capacity. Both biochars showed a low content of inorganic-N (Table 1).

2.2. Analytical methods

In the soil, pH was determined in a 1:10 (w/v) soil/water extract, soil texture was determined using the pipette method according to Kettler et al. (2001) and CaCO$_3$ content was measured with a Bernard calcimeter. Soil organic carbon and total nitrogen were determined according to the Walkley-Black method and the Kjeldahl procedure, respectively. NH$_4^+$-N was extracted with 2 M KCl at 1:10 (w/v) and determined by a colorimetric method based on Berthelot's reaction; while NO$_3^-$-N and NO$_2^-$-N were extracted with water 1:10 (w/v) and determined by ion chromatography (Dionex ICS-2100, Sunnyvale, USA).

In the biochar samples, pH and electrical conductivity (EC) were determined in the 1:10 (w/v) extract after shaking the mixture mechanically for 2 h. Proximate analysis was performed according to ASTM 3302, UNE 3219 and UNE 32004 for total moisture, volatile matter and ashes. The total contents of C, N and H were measured with an elemental analyser (LECO CHN-600, Leco Corporation, St. Joseph, USA), according to ASTM 5373, and total S with a LECO SC-132 analyser (Leco Corporation, St. Joseph, USA), according to ASTM 4239. The O content was calculated by subtracting the sum of the percentages of C, H, N, S (on a dry ash-free basis) from 100%; while the organic-C (C_{org}) by subtracting the inorganic C from the total C. The inorganic C was measured as calcium carbonate (inorganic C), according to the 04.08-A method (TMECC, 2002). The water-soluble organic carbon (WSC$_{org}$), water-soluble inorganic carbon and water-soluble nitrogen (WSN) were determined using an automatic analyser for liquid samples (TOC-V CSN + TNM-1 Analyzer, Shimadzu Corporation, Tokyo, Japan). Mineral N (NH$_4^+$-N and NO$_3^-$-N) was extracted with 2 M KCl and the amounts of NH$_4^+$-N and NO$_3^-$-N determined by colorimetry using a microplate reader. The cation exchange capacity (CEC) was measured by a modified ammonium-acetate compulsory displacement method (Gaskin et al., 2008). The surface area was determined by using the CO$_2$ adsorption method (273 K, Micromeritics ASAP 2020 instrument, Norcross, USA). All samples were degassed under vacuum at 200 °C for 8 h, prior to analysis.

The polycyclic aromatic hydrocarbon content in biochar and biochar-soil mixtures (PAHs, sum of the EPA's 16 priority pollutants) was determined by Eurofins Umwelt Ost GmbH (Freiberg, Germany) according to DIN EN 15527. The PAHs were analysed and identified after a 2-h hot extraction with toluene (Hilber et al., 2012) by using gas chromatography-mass spectrometry.

2.3. Soil incubations

The incubations were carried out in 250 mL polycarbonate jars (Sarstedt AG & Co., Nuremberg, Germany), containing 100 g (oven-dry weight basis) of soil or biochar-soil mixture. The biochars were mixed thoroughly with the soil in a proportion of 2% (w/w on a dry weight basis) and a solution with KNO$_3$ was added to soil in order to adjust moisture to 90% of the water filled pore space (WFPS) and also to apply 50 mg N kg^{-1} soil. The jars were incubated in darkness under aerobic conditions at 25 °C for 21 days in a Heraeus "B12 Function Line" incubator (Hanau, Germany). The soil moisture was gravimetrically adjusted to maintain 90% WFPS every day with deionised water for each individual jar.

Three incubation experiments were carried out under the above mentioned experimental conditions to assess the effects of: 1) two contrasting biochars without PAH addition; 2) the same biochars