



Pine sawdust biomass and biochars at different pyrolysis temperatures change soil redox processes

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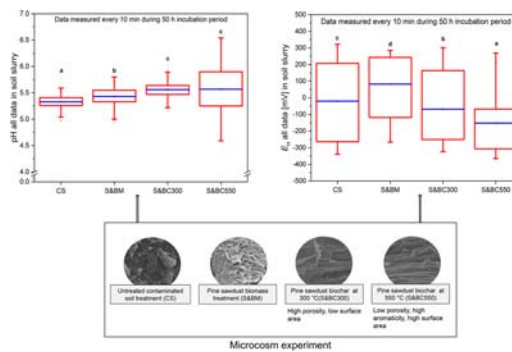
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HIGHLIGHTS

- First study of the effects of biochars on soil redox potential (E_H) and pH
- The most rapid E_H change per hour was in soil treated with biochar made at 550 °C.
- This E_H decline occurs after 10 h during the redox experiment.
- The second rapid E_H change was found in soil treated with pine sawdust biomass.
- At low E_H , biochar made at 550 °C increased PLFA biomass compared to untreated soil.

GRAPHICAL ABSTRACT



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ABSTRACT

To date, no investigation has been carried out to explore the effects of biochars produced at different pyrolysis temperatures on the dynamics of redox potential (E_H) and pH in a contaminated floodplain soil. Thus, we aimed to quantify the dynamics of E_H and pH in contaminated flooded soils treated with 70 t ha⁻¹ of pine sawdust biomass (S&BM) and biochars pyrolyzed at 300 °C (S&BC300) and 550 °C (S&BC550) and pre-incubated for 105 days in an automated biogeochemical microcosm system. Microbial community composition was also determined via analyzing phospholipid fatty acid (PLFA). We found that BC300 and BC550 treatments substantially decreased (3–6.5%) and BM increased (~37%) the mean of soil E_H compared to the untreated contaminated soil (CS). The largest E_H decline in S&BC550 was at the rate of -80 mV h^{-1} at 10 h while it was observed at 25 h in S&BC300 and 20–25 h in S&BM or CS, respectively. At high E_H , a higher total PLFA biomass and microbial groups in the CS (71–87%) were found in comparison to treated soils. Higher aromaticity and ash content in BC550 than

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Soil microbial community
Redox potential

BC300 and BM led to the greater PLFA biomass and microbial groups which contributed to higher capacity of accepting and donating electrons in soil slurry and were probably one reason for the largest decrease in E_H . Pine sawdust biomass and BCs have a noticeable influence in soil biogeochemical processes relevant to fluctuating redox conditions.

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1. Introduction

As a current research agenda, cost-effective methods to meet the remediation needs become a global concern (Rinklebe et al., 2016a; Shaheen and Rinklebe, 2015; Tsang and Yip, 2014). Applicable and economic treatments with high adsorption capacity to stabilize potentially toxic elements in contaminated soil have become essential for environmental remediation and restoration (Kumpiene et al., 2008; Ok et al., 2011).

Understanding of biogeochemical processes in contaminated wetland soils that control the presence and bioavailability of toxic elements (TEs) is a key to select the best management practices. Within this context, soil redox potential (E_H) is considered a reliable indicator of the oxidation-reduction status covering entire soil biogeochemical processes which also have an impact on different TEs, anions and organic compounds under fluctuating oxic and anoxic conditions (Yu et al., 2007; Yu and Rinklebe, 2013).

Biochar (BC) is a carbon-rich material produced by pyrolysis of biomass such as wood, crop residues and manure under limited oxygen environment (Ok et al., 2015; Rajapaksha et al., 2016). Biochar is known as a suitable soil amendment for sustaining soil fertility and productivity, remediating metal contaminated sites, sequestering carbon and reducing greenhouse gas emission (Kim et al., 2016; Novak et al., 2016). The pyrolysis conditions (e.g., temperature) and feedstock type influence the physicochemical properties of BCs and perform a crucial role in determining how different BCs affect soil processes and functions as well as microbial communities (Cho et al., 2017a; Cho et al., 2017b; Lou et al., 2016a, 2016b; Oleszczuk et al., 2016). Biochars can lead to an increase or decrease of soil microbial biomass due to the interactions of BC with soil mineral and organic matter (Lehmann et al., 2011). Therefore, further investigations on BC impacts on soil microbial biomass and composition related to redox reactions under flooding conditions have recently received a noteworthy interest (Joseph et al., 2010; Lehmann et al., 2011).

The BC can donate and accept electrons and its electrochemical properties as a reductant is a function of pyrolysis temperature because it contains amorphous C, aromatic C, and labile OC (Joseph et al., 2015; Prévotau et al., 2016). Furthermore, Klüpfel et al. (2014) revealed that grass and wood BCs pyrolyzed at 700 °C had higher electrons accepting or donating capacity in suspensions of BCs and anoxic buffer solutions compared to BCs produced at 400 °C. Therefore, our hypothesis was that redox properties of BCs produced at various pyrolysis temperatures from pine sawdust biomass may alter the dynamics of E_H and pH in a floodplain soil. In particular, the E_H might decrease in the biochar-treated soil compared to biomass-treated and untreated soils because BC could increase soil pH and the retention of anions and cations, owing to substantial changes in redox processes and reactions of TEs and other solutes in the soil solution.

Thus, we aimed i) to quantify the impact of pine sawdust biomass and biochars pyrolyzed at 300 °C and 550 °C on the dynamics of E_H and pH in a contaminated floodplain, ii) to evaluate the effects of E_H -conditions and treatments on soil microbial community composition by means of phospholipid fatty acids (PLFA), and iii) to elucidate the underlying redox-driven processes using the predominant functional groups of aliphatic and aromatic carbon in biomass and biochars using the ^{13}C Nuclear Magnetic Resonance (NMR) spectra.

2. Materials and methods

2.1. Materials

The soil sample was collected from the upper 30 cm of an agricultural field located in Gongju, Chungcheongnam-do Province, Korea (36°31.87'66"N, 127°04.04'31"E). Particularly, a composite soil sample (~200 kg) was collected from ten representative points at field location following the systematic unaligned grid sampling method. The field was located near the Tancheon mine and planted with vegetables a few years ago before banning its cultivation due to high contamination with As and Pb (Igalavithana et al., 2017). Details about physicochemical properties of soil are provided in Supporting information No. S1. The soil was air-dried, and passed, after removing debris, through a 2-mm sieve. Sawdust biomass (BM) from pine trees was obtained from a sawmill company, Korea. Air dried pine sawdust with a particle size <1.0 mm was used as a feedstock to produce two biochars at 300 °C (BC300) and 550 °C (BC550) pyrolysis temperatures with a heating rate of 7 °C min⁻¹ for 2 h under limited oxygen in a Nabertherm furnace (Lou et al., 2016a, 2016b).

2.2. Incubation experiment

The incubation experiment was performed in four treatments: soil mixed with pine sawdust biomass (<2 mm) (S&BM), biochars pyrolyzed from pine sawdust as feedstock at 300 °C (S&BC300), and 550 °C (S&BC550) at 70 t ha⁻¹, along with the untreated contaminated soil (CS). Soils were incubated at 25 °C for 105 days. Soil moisture at 70% water holding capacity was maintained throughout the incubation period. At the end of incubation, the soil was characterized physically, chemically and microbiologically. Details about physicochemical analysis of untreated and treated soils can be found in Supporting information No. S1. Major properties of the soils are presented in Table 1.

Table 1

Selected properties and element concentrations (microwave digestion) of contaminated soil (CS), and soils treated with pine sawdust biomass (S&BM), biochar 300 °C (S&BC300), and biochar 550 °C (S&BC550) after 105 days of incubation.

Unit	CS	S&BM	S&BC300	S&BC550
Basic properties				
pH [CaCl ₂] ^a	4.24	4.42	4.48	5.66
EC [μS cm ⁻¹]	223.0	72.2	163.5	156.0
C _t ^b [%]	1.28	2.19	6.69	7.53
Concentrations ^c				
Al [g kg ⁻¹]	46.23	39.34	50.98	58.16
Fe	46.87	44.36	39.89	44.30
Mn	0.72	0.70	0.57	0.63
Ca	1.51	4.78	1.54	2.08
Mg	4.91	4.48	4.54	5.19
K	6.99	6.49	12.34	13.29
P	1.40	1.23	1.15	1.30
S	0.48	0.46	0.41	0.45

^a pH determined in a 1:5 soil-CaCl₂ suspension according to (DIN EN 15933, 2012).

^b C_t: total carbon.

^c According to (U.S. EPA Method 3051A, 2007).

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