



Effects of softwood biochar on the status of nitrogen species and elements of potential toxicity in soils

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ABSTRACT

The effects of softwood-derived biochar materials on the chemical behaviour of environmental contaminants in soils were examined in two microcosm scenarios. Addition of the biochar materials into an alkaline sandy soil significantly reduced NH_3 volatilization and made it available for conversion into NO_3^- via nitrification. This process could be enhanced by an increased application rate of biochar produced at a higher pyrolysis temperature. Under the alkaline conditions encountered in the experiment, the biochar surfaces tended to be negatively charged which disfavours the adsorption of NO_3^- . Therefore, in a fully open system, the addition of biochar materials was likely to contribute to nitrate leaching from the fertilized alkaline sandy soil. The effects of the biochar materials on the immobilization of Fe^{2+} generated via anaerobic iron reduction in the inundated contaminated soil were not observed, except for the treatment with a higher dose of biochar material produced under pyrolysis temperature at 700°C after the 240th h of incubation. Arsenic showed similar behaviour to Fe. Zn tended to have a higher affinity to the biochar, as compared to Mn. Immobilization of Pb occurred regardless of whether or not the biochar is present.

1. Introduction

Biochar produced from pyrolysis of biomass is thought to be an ideal product for improvement of soil fertility, remediation of contaminated soils, and long-term storage of carbon (Beesley et al., 2011; Jeffery et al., 2011; Tang et al., 2013; Ahmad et al., 2014). In recent years, there have been increasing investigations into the effects of biochar on removing a range of environmental pollutants from water and soil environments (Beesley et al., 2010; Ahmad et al., 2016). So far, the available publications reveal mixed results, showing that biochar may enhance, inhibit or have no effects on a pollutant of concern, depending on the biochar type used and the environmental conditions under investigation (Ahmad et al., 2014).

Biochar can be produced using a wide variety of organic feedstock such as woods, grasses, manures and organic waste materials (Mukome et al., 2013). The nature of feedstock, together with the operational conditions for pyrolysis, could markedly affect the physical and chemical characteristics of biochar (Aller, 2016). This explains the inconsistent observations on biochar-driven pollutant immobilization by different researchers who used different types of biochar in their experiments. To date, despite increased available information on biochar, there has still been insufficient understanding to allow generalization of biochar functions in terms of their uses for environmental remediation.

This demands substantial further study to cover a wider range of biochar types in various environmental scenarios.

In this study, biochar materials produced from softwood pellets at two different pyrolysis temperatures were selected to observe their effects in two scenarios: (a) chemical behaviour of added ammonium in sandy soil and (b) immobilization of arsenic and heavy metals in a contaminated soil under water inundation conditions. The abundant organic waste from wood processing is an important source of biomass for biochar production (Komkiene and Baltreinaite, 2016). Wood-derived biochar materials also tend to contain less polycyclic aromatic hydrocarbons (PAHs), as compared to those produced from other biomass types (Buss et al., 2016). This makes wood-originated biochars more attractive for being used as a remediating agent for soil contamination.

Ammonium-based chemical fertilizers are widely used for agricultural production (Fowler et al., 2013). Upon application, ammonium may be lost from soils through volatilization of ammonia if the soil pH is sufficiently high (Cameron et al., 2013). Microbially-mediated oxidation of ammonium (nitrification) can lead to the emission of gaseous nitrogen species and formation of nitrate (NO_3^-). Nitrate has a weak affinity to soil colloids and therefore is easier to mobilize under most soil conditions (Barber, 1995; Dickinson and Murphy, 2008). Under anaerobic conditions, nitrate can be reduced to form nitrogen gas

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(denitrification), leading to further nitrogen loss from soils (Cameron et al., 2013). Alkaline sandy soils are particularly prone to loss of nitrogen due to their weak capacity to adsorb ammonium and high water permeability. Furthermore, alkaline soils have favourable pH conditions for ammonia volatilization (Schomberg et al., 2012). The better availability of free ammonium in sandy soils owing to weak ammonium adsorption may also enhance nitrification. A few studies have shown that biochar can enhance retention of nitrogen in coarse-textured soils. Yao et al. (2012) reported that application of Brazilian pepperwood and peanut hull biochar (pyrolyzed at 600 °C) reduced NO_3^- leaching by 34.3% and 34%, respectively. Jarrah wood biochar (pyrolyzed at 600 °C) has also been found to significantly reduce NO_3^- leaching from sandy soil by 25% (Dempster et al., 2012). It is widely believed that a pyrolysis temperature > 600 °C tends to be more favourable for producing biochar with a greater capacity to retain NO_3^- (Hale et al., 2013; Hollister et al., 2013). Higher production temperatures are known to increase biochar surface areas and possibly the number of adsorption sites for nitrogen species. This could also increase water holding capacity of soils and consequently reduce the degree of nitrogen leaching (Uzoma et al., 2011). However, Gai et al. (2014) found that the biochar produced at 600–700 °C using different feedstock in an aqueous batch study was ineffective for NO_3^- retention. Therefore, the efficacy of biochar to retain N species could also be markedly affected by the inherent physiochemical properties of individual biochar and the environmental conditions into which the biochar is applied.

In a previous investigation, it was found that arsenic and heavy metals present in contaminated soils could be released under water inundation conditions in the presence of grass clippings (Mukwaturi and Lin, 2015). This represents a potential threat to the environment surrounding the contaminated sites. To minimize the environmental risk from contaminated sites, appropriate remediation measures need to be taken. It has been demonstrated that biochar has the capacity to immobilize a range of environmental pollutants (Park et al., 2016). It is therefore considered that biochar may have the potential for being used as a soil conditioner for minimizing the mobilization of elements of potential toxicity from the contaminated soils during flood inundation, which is worthy of investigation.

2. Materials and methods

2.1. The biochar materials used in the experiments

Two softwood-derived biochar materials with pyrolysis temperatures at 550 °C and 700 °C (labelled as SWP550 and SWP700, respectively) were used for the microcosm experiments in this study. These biochar materials were purchased from the United Kingdom Biochar Research Centre (UKBRC). The major physical and chemical characteristics, as provided by the manufacturer, are given in Supplementary Table S1. Prior to their uses in the experiments, the biochar samples were oven-dried at 40 °C for 48 h and then ground using a mortar and a pestle to pass through a 2 mm sieve with a portion of the sample being further ground and passed through a 63 µm sieve for FTIR analysis.

2.2. The sandy soil used in Experiment 1

The sandy soil sample was collected from a construction site at the University of Salford, Manchester. After collection, the soil was oven-dried at 40 °C for 48 h, gently crushed using a mortar and a pestle, and passed through a 2 mm sieve. All gravels with a particle diameter > 2 mm were discarded. Some of the major physical and chemical characteristics are provided in Supplementary Table S1.

2.3. The contaminated soil used in Experiment 2

The contaminated soil sample was collected from a closed landfill

site in the Greater Manchester region, United Kingdom. After collection, the soil was oven-dried at 40 °C for 48 h, gently crushed using a mortar and a pestle to pass through a 2 mm sieve. All gravels with a particle diameter > 2 mm were discarded. Some major physical and chemical characteristics are provided in Supplementary Table S1.

2.4. Experiment 1: nitrogen in sandy soil

Plastic bottles (125 mL) were used as batch reactors. For each biochar type, one control and two treatments were used (see Supplementary Table S2). Appropriate amounts of biochar, sand and NH_4Cl were placed in each bottle and thoroughly mixed using a glass rod, followed by adding 10 mL of ultrapure water. The reactors were then allowed to stand for 24 h. At the end of the experiment, 100 mL of ultrapure water was added into each bottle and shaken for 1 h on a rotary shaker. After shaking, 15 mL of the supernatants were removed for measurement of water-soluble ammonium and nitrate. The supernatant was then decanted by passing it through a filter paper (Whatman 40). All residues retained on the filter paper were put back into each bottle for further extraction by a KCl solution. 100 mL of 1 M KCl solution was added into each bottle and shaken again on a rotary shaker for 1 h. 15 mL of supernatant was then taken for measurement of the KCl-extractable ammonium and nitrate. All the water and KCl extracts taken for measurements of different nitrogen species were frozen before analysis by ion chromatography.

2.5. Experiment 2: arsenic and heavy metals in contaminated soil

A microcosm experiment was conducted to observe the temporal variation in several parameters following water inundation. Plastic bottles (500 mL) were used as batch reactors. Prior to the experiment, the bottles were washed with nitric acid and rinsed with deionised water, followed by drying. One control (added grass clippings but no added biochar, labelled as C) and two biochar treatments were set for each biochar type. Details on experimental set-up are shown in Supplementary Table S3. In each reactor, 50 g of soil was placed into the bottle. For C, Treatment 1 and Treatment 2, 5 g of fresh grass clippings (chopped to 1 cm in length) was added into the bottle. For Treatment 1 and Treatment 2, 0.5 or 2 g of biochar was added, respectively. The contents of each bottle were thoroughly mixed by a glass rod and then 200 mL of ultrapure water (18.2 MΩ cm) was poured into the bottle to create water inundation conditions. The bottles were capped and agitated by hand for 1 min and then allowed for standing on the laboratory bench. The experiment was run for 15 days. During the incubation experiment, monitoring of various parameters were made from the 1st h of the experiment. Subsequent sampling was performed at the 24th, 48th, 120th, 240th and 360th h following the commencement of the experiment. pH, electrical conductivity (EC) and dissolved oxygen (DO) were measured in-situ using a pH meter (Jenway-3510), EC meter (Mettler Toledo) and DO meter (Oxyguard Handy MK1 DO), respectively. After this, 10 mL of the overlying water later was taken for measurements of different trace elements. The samples were passed through a 0.22 µm syringe filter and acidified by adding 2 drops of nitric acid. The solution was then stored in the fridge at 4 °C before analysis.

2.6. Analytical methods

The surface morphology and structure of the biochar samples were observed using a Philips XL30 SFEG scanning electron microscope (SEM). The micrographs were acquired using an accelerating voltage of 7 kV with a spot size of 3 and secondary electron detection (SE). Surface functionality of the biochar samples was analysed by Fourier transform infrared spectroscopy (FTIR) (Thermo Fischer Nicolet IS10) with a spectral resolution of 16 cm^{-1} . Spectrograph v1.0.5 software was used to assist in the interpretation of the results. Pre-analysis was done using

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