Chemosphere 142 (2016) 100–105

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Biochar amendment to soil changes dissolved organic matter content and composition

Andreas Smebye [a,b,*], Vanja Alling [a,1], Rolf D. Vogt [b], Tone C. Gadmar [b], Jan Mulder [c], Gerard Cornelissen [a,c,d], Sarah E. Hale [a]

[a] Norwegian Geotechnical Institute (NGI), P.O. Box 3930, Ullevål Stadion, NO-0806 Oslo, Norway
[b] Department of Chemistry, University of Oslo (UiO), P.O. Box 1033, Blindern, NO-0315 Oslo, Norway
[c] Department of Environmental Sciences (IMV), Norwegian University of Life Sciences (NMBU), P.O. Box 5003, NO-1432 Ås, Norway
[d] Department of Applied Environmental Sciences (ITM), Stockholm University, 10691 Stockholm, Sweden

HIGHLIGHTS

- Biochar increased the pH and released dissolved organic matter from the soil.
- Biochar sorbed more small aliphatic than large aromatic dissolved organic molecules.
- A size exclusion effect in biochar's micropores could explain the sorption pattern.

ARTICLE INFO

Article history:
Received 30 November 2014
Received in revised form 23 April 2015
Accepted 24 April 2015
Available online 13 May 2015

Keywords:
Biochar
Dissolved organic matter
Sorption
Soil amendment
Acrisol

ABSTRACT

Amendments of biochar, a product of pyrolysis of biomass, have been shown to increase fertility of acidic soils by enhancing soil properties such as pH, cation-exchange-capacity and water-holding-capacity. These parameters are important in the context of natural organic matter contained in soils, of which dissolved organic matter (DOM) is the mobile and most bioavailable fraction. The effect of biochar on the content and composition of DOM in soils has received little research attention. This study focuses on the effects of amendments of two different biochars to an acidic acrisol and a pH-neutral brown soil. A batch experiment showed that mixing biochar with the acrisols at a 10 wt.% dose increased the pH from 4.9 to 8.7, and this resulted in a 15-fold increase in the dissolved organic carbon concentration (from 4.5 to 69 mg L^{-1}). The pH-increase followed the same trend as the release of DOM in the experiment, causing higher DOM solubility and desorption of DOM from mineral sites. The binding to biochar of several well-characterised reference DOM materials was also investigated and results showed a higher sorption of aliphatic DOM to biochar than aromatic DOM, with DOM-water partitioning coefficients (K_d-values) ranging from 0.2 to 590 L kg^{-1}. A size exclusion occurring in biochar's micropores, could result in a higher sorption of smaller aliphatic DOM molecules than larger aromatic ones. These findings indicate that biochar could increase the leaching of DOM from soil, as well as change the DOM composition towards molecules with a larger size and higher aromaticity.

1. Introduction

Soil organic matter (SOM) is essential for soil quality as it retains nutrients and water in soils (Brady and Weil, 2008). Due to these properties, low levels of SOM in tropical agricultural soils can be a main cause of poor soil fertility (van Wambeke, 1992). Amendments of pyrolysed agricultural residues, referred to as biochar, have been promoted to improve soil quality (Lehmann, 2007). In recent years, field trials have shown both beneficial and negative effects of biochar amendments on plant growth (Jeffery et al., 2011). The largest yield ameliorations following biochar amendments have been observed in acidic and pH-neutral soils of medium to coarse textures (Asai et al., 2009; Major et al., 2010). In addition, biochar amendments increase carbon sequestration, a co-benefit contributing to the mitigation of climate change (Lehmann, 2007).

* Corresponding author at: Norwegian Geotechnical Institute (NGI), P.O. Box 3930, Ullevål Stadion, NO-0806 Oslo, Norway.
E-mail address: and@ngi.no (A. Smebye).
[1] Current address: Norwegian Environment Agency, P.O. Box 5672 Sluppen, NO-7485 Trondheim, Norway.

http://dx.doi.org/10.1016/j.chemosphere.2015.04.087
0045-6535/

Studies of sites amended with biochar more than 800 years ago in the Amazon have demonstrated that biochar can sorb natural organic matter (Liang et al., 2006) and thereby preserve SOM (Kaiser and Guggenberger, 2000). Dissolved organic matter (DOM), the more mobile and bioavailable fraction of organic matter in soil, is commonly defined as the organic matter remaining in solution after 0.45 μm filtration (Perdue and Ritchie, 2003). The extent of sorption of DOM to biochar will, as for mineral surfaces, depend on the ionic strength and pH of the soil solution (Kaiser and Guggenberger, 2000), as these parameters affect both the DOM solubility (de Wit et al., 2001) and available sorption sites (Kennedy and Billett, 1996).

The porous structure of biochar results in a large surface area and dominance of micropores (Downie et al., 2009) that sorbs and thereby immobilizes both organic and inorganic pollutants in contaminated water and soils (Ahmad et al., 2014; Beesley et al., 2011; Mohan et al., 2014). These micropores are also responsible for the sorption of DOM to biochar (Kasozi et al., 2010). Furthermore, a size exclusion effect can be exhibited by the micropores resulting in a larger sorption of smaller aliphatic DOM molecules than larger aromatic ones, as the latter are too big to enter the micropores (Kasozi et al., 2010). Alkaline ash that is also formed in the pyrolysis process along with the biochar will also affect the sorption to biochar as it could change the solubility of DOM by increasing the soil pH. Previous studies investigating the effect of biochar on DOM content and composition (Kasozi et al., 2010; Mukherjee and Zimmerman, 2013) have attempted to remove the confounding effect of ash by washing the biochar prior to performing experiments. Field trials have shown that biochar addition to soils can increase the soil pH (Martinsen et al., Unpublished results; Yamato et al., 2006). If biochar amendments lead to a higher DOM solubility this may result in a release of DOM sorbed to the soil thus increasing the carbon flux and bioavailability of DOM in soil.

In addition, biochar itself contains DOM, where content and composition depends on both the biochar feedstock material and biochar pyrolysis conditions as demonstrated by Uchimiya et al. (2013) and Yun et al. (2012). One side effect of this native biochar DOM is that it could lead to mobilization of heavy metals following application of biochar amendments in soils (Beesley and Dickinson, 2011; Uchimiya et al., 2010). Changes in DOM could also affect the response of microbial diversity to biochar amendments, one of the remaining knowledge gaps in this research area (Lehmann et al., 2011).

This mechanistic study is the first to test the effect of both untreated and washed biochar on soil DOM content and composition. Biochar was added to two different agricultural soils (an acidic acrisol and a pH-neutral brown soil) in a batch experiment to investigate the effect of biochar on DOM content. Biochar was used (i) untreated, (ii) after washing with water to reduce the DOM released from the biochar itself or (iii) after acid-washing to reduce the alkalinity of the biochar. Our first hypothesis is that biochar amendments will release DOM from the soil. Biochar has previously been observed to possess a selective sorption of DOM (Kasozi et al., 2010), which necessitates the need to look at both DOM content and composition. To test the effects of biochar on DOM composition, biochar was mixed with well-characterised reference dissolved organic matter (RefDOM) of varying aromaticity and aliphaticity (Vogt et al., 2004). Our second hypothesis is that sorption of DOM to biochar will change the composition of the DOM remaining in solution. The scope of the study did not therefore include detailed characterisation of the DOM released from biochar *per se*, but rather changes induced by biochar sorption in a solution with a known composition. The results of this study will provide novel information as to how the presence of biochar can change the amount and composition of DOM in soil.

2. Materials and methods

2.1. Materials

Two biochar feedstocks, cacao shell and rice husk, were pyrolysed for 3.5 h at around 600 °C and 500 °C, respectively (pyrolysis temperatures deduced from calibrated thermogravimetric analysis, see Supporting Information). The pyrolysis was conducted in simple kilns at the Indonesia Soil Research Institute in Bogor (Hale et al., 2013a) (for further pyrolysis details, see SI). Pyrolysis yield was 30.4 wt.% and 22.0 wt.% of the original dry weight of the cacao shell and rice husk biochar feedstock, respectively. The biochars were stored in air-tight jars and were sieved through a 2 mm mesh before use (for physicochemical properties of the biochars, soils and RefDOMs used in this study, see SI).

The biochars were treated in two ways prior to starting the experiments; (i) washing with water and (ii) washing with acid. The washing was carried out using 50 ml of water per gram biochar. Washing with water in flow-through columns generated a biochar with a low release of DOM. A subsample of this washed biochar was further acid-washed (0.1 M HCl). This served to dissolve all carbonates and oxides in the ashes found in biochar, removing its alkalinity. After acid-washing the cacao shell and the rice husk biochar with 20 and 10 mL acid per gram biochar, respectively, the pH of both biochar leachates had dropped from approximately 9 to 2. All washing was performed at a low flow (<0.13 L h^{-1}) to prevent physical damage of the material. A 0.45 μm cellulose nitrate filter (Sartorius, Germany) prevented loss of particulate material. After the pre-treatments each biochar was then used as: "untreated", "washed" and "acid-washed" (and is referred to in this way throughout the manuscript).

Two different agricultural soils were used in the study; (i) an acidic acrisol from Lampung in Indonesia (Tamanbogo; 0.89570N, 112.55680E), and (ii) a pH-neutral brown soil from Norway (Norderås; 59.67945N, 10.76888E). Each soil was collected from the 0–15 cm top soil layer from five different points mixed thoroughly and kept in air-tight plastic bags during shipping. The soil samples were sieved through a 2 mm mesh before use.

Three different well-characterised RefDOMs were included to study the effects on DOM composition by the sorption of DOM to biochar. The RefDOMs were produced through reverse-osmosis and freeze-drying of forested fresh water catchment in Scandinavia by Vogt et al. (2004). The freeze-dried powders of the RefDOM were dissolved in water and stirred for three days before use. Based on their specific UV absorbency (sUVa; for explanation see Section 2.3) the RefDOMs ranged from rather aliphatic to relatively aromatic; (i) aliphatic RefDOM with a sUVa of 2.5, (ii) intermediate RefDOM with a sUVa of 3.5, and (iii) aromatic RefDOM with a sUVa of 3.9.

All chemicals used were of pro analysis quality (>99.5%) and only ultra-pure (>1 MΩ cm^{-1}) water ion-exchanged with Elix-5 system (Millipore, USA) was used for sample preparations.

2.2. Batch experiments

Two separate batch experiments were conducted; one where the effect of biochar on DOM content was studied by adding biochar to soils, and one where the effect of biochar on DOM composition was studied by adding biochar to RefDOM solutions. All mixtures were shaken for 72 h in order to reach sorption equilibrium between the DOM and the biochar (Kasozi et al., 2010). The dissolved fraction was then collected for analyses by filtering through a 0.45 μm filter. All analyses of DOM were conducted within two days of filtration (for filtration details, see SI).