



Ecotoxicological characterization of biochars: Role of feedstock and pyrolysis temperature



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HIGHLIGHTS

- Soil respiration was explained by the volatile content of the materials applied.
- Collembolan toxicity was generally not observed at typical application rates.
- Toxicity was feedstock dependent and generally unaffected by charring temperature.
- The toxicity observed in some materials was mostly explained by soluble Na.
- Bioassays were shown to be useful in biochar quality evaluation schemes.

ARTICLE INFO

Article history:

Received 15 October 2014

Received in revised form 10 December 2014

Accepted 14 December 2014

Available online xxx

Editor: Mark Hanson

Keywords:

Biochar
Ecotoxicity
Bioassays
Microorganisms
Soil basal respiration
Fauna
Collembolans
Reproduction

ABSTRACT

Seven contrasting feedstocks were subjected to slow pyrolysis at low (300 or 350 °C) and high temperature (550 or 600 °C), and both biochars and the corresponding feedstocks tested for short-term ecotoxicity using basal soil respiration and collembolan reproduction tests. After a 28-d incubation, soil basal respiration was not inhibited but stimulated by additions of feedstocks and biochars. However, variation in soil respiration was dependent on both feedstock and pyrolysis temperature. In the last case, respiration decreased with pyrolysis temperature ($r = -0.78$; $p < 0.0001$, $n = 21$) and increased with a higher volatile matter content ($r = 0.51$; $p < 0.017$), these two variables being correlated ($r = -0.86$, $p < 0.0001$). Collembolan reproduction was generally unaffected by any of the additions, but when inhibited, it was mostly influenced by feedstock, and generally without any influence of charring itself and pyrolysis temperature. Strong inhibition was only observed in uncharred food waste and resulting biochars. Inhibition effects were probably linked to high soluble Na and NH_4 concentrations when both feedstocks and biochars were considered, but mostly to soluble Na when only biochars were taken into account. The general lack of toxicity of the set of slow pyrolysis biochars in this study at typical field application rates ($\leq 20 \text{ Mg ha}^{-1}$) suggests a low short-term toxicity risk. At higher application rates ($20\text{--}540 \text{ Mg ha}^{-1}$), some biochars affected collembolan reproduction to some extent, but only strongly in the food waste biochars. Such negative impacts were not anticipated by the criteria set in currently available biochar quality standards, pointing out the need to consider ecotoxicological criteria either explicitly or implicitly in biochar characterization schemes or in management recommendations.

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1. Introduction

Biochar use as soil conditioner is currently an important topic of research (Gurwick et al., 2013) and related to potential benefits in the context of agricultural yield, carbon sequestration, waste management and clean energy production (Lehmann and Joseph, 2009; Sohi et al.,

2009; Kookana et al., 2011), as well as the more recently claimed role in land reclamation (Beesley et al., 2011; Xie et al., in press). The capacity of biochar technologies to process any carbon-rich waste may allow upcycling of waste surplus or low quality wastes such as sewage or tannery sludges (Muralidhara et al., 1982; Bridle and Pritchard, 2004; Hossain et al., 2010; Méndez et al., 2013). Pyrolysis technologies have been shown to change pollutant burden of the original feedstocks, such as the usual potentially toxic element concentration increases due to mass losses (Koppolu et al., 2003; Méndez et al., 2012; Farrell et al., 2013) and the formation of PAH or dioxins (Schimmelpfennig

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and Glaser, 2012; Hale et al., 2012). More recently, toxic effects of volatile organic compounds (VOCs) resulting from the re-condensation of pyrolysis liquids and gases on biochar have been demonstrated (Buss and Mašek, 2014). The variety of usable feedstocks and pyrolysis procedures leads to a wide range of resulting biochars in terms of pollutant composition and burden, including biochars with unsuitable properties as a soil amendment, though still useful for other environmental benefits, e.g. charcoal use, bioenergy generation and carbon sequestration without soil application.

The soil application of some biochars might unfavorably impact soil quality. Some authors suggest a need to demonstrate both the benefits of biochar to soil health and lack of detrimental effects to the environment (Verheijen et al., 2010). However, research about possible negative impacts of biochars on soil biota is rarely addressed despite the existence of large-scale field trials and sales of biochar products in the market place (Busch et al., 2013). The potential impacts on soil biota might be roughly separated into those mediated by direct negative effects such as pollutant release and excessive salinization or liming (Liesch et al., 2010; McCormack et al., 2013), but also by indirect effects, such as a decreased albedo (Genesio and Miglietta, 2012) if associated with excessive soil heating or drying.

Most products used in agriculture conform to industrial or regulatory standards to ensure that they can be safely used in soil, although for biochar this would require an agreement on the main characteristics to be taken into account (Joseph et al., 2009). Several biochar quality guidelines have been recently proposed such as the IBI Biochar Standard (IBI, 2013), the European Biochar Certificate (EBC, Schmidt et al., 2012) or the UK Biochar Quality Mandate (BQM, Shackley et al., 2013). In these standards, environmental risks are accounted for by the inclusion of limit values for physicochemical properties, including pollutants such as heavy metals, dioxins/furans, PAHs, PCBs or BTEX. However, the use of chemical analyses for this purpose has several limitations such as the fact that total concentrations do not necessarily relate to the bioavailable fraction or the final uptake by organisms (Van Straalen et al., 2005); that non-target toxic substances might also be present and not assessed; and that the combined toxicity of all the chemicals present cannot be assumed to be easily predicted since additive, synergistic and antagonist effects can occur. The use of bioassays for biochar characterization overcomes such limitations, since biochar effects on indicator organisms integrate any of the processes previously described. Although bioassays have also some intrinsic limitations such as a low ecological relevance, because only short-term effects for particular cultured species are assessed, they offer a genuine possibility to assess the actual effects in exposed individuals. Bioassays are increasingly used as a tool for the prospective assessment of environmental risks of substances before its marketing, release, or agricultural use (Brock, 2013), and a necessary complement to the traditional chemical characterization. Bioassay-based approaches may complement physicochemical characterization for the quality assessment of biochars, similar to what has been proposed for the characterization of wastes in the EU (Moser and Römbke, 2009).

Bioassays are not included in all of the currently available biochar quality standards, with the exception of the germination assay which is mandatory in the IBI standard (IBI, 2013). Studies exist utilizing plants (Solaiman et al., 2012; Rogovska et al., 2012; Busch et al., 2013), soil fauna (Liesch et al., 2010; Van Zwieten et al., 2010; Busch et al., 2012; Hale et al., 2013; Marks et al., 2014), as well as aquatic organisms (Hale et al., 2013; Oleszczuk et al., 2013), but the utility of bioassays potentially used in the context of biochar ecotoxicological characterization is still to be rigorously assessed. Furthermore, while ample data exist on the influence of the feedstock and/or the pyrolysis procedure on biochar composition, recalcitrance, or nutrient retention (Novak et al., 2009; Bruun et al., 2011; Hossain et al., 2011; Singh et al., 2012; McBeath et al., 2014; Nelissen et al., 2014), their influence on ecotoxicological effects is not yet well understood.

Therefore, we investigated the effects of a diverse set of biochars on soil basal respiration and collembolan reproduction in a bioassay. The specific objectives of the study were to assess whether charring changes the ecotoxicity of organic soil amendments; how feedstock and pyrolysis temperature affect ecotoxicity; and which amendment properties relate to negative effects.

2. Materials and methods

2.1. Soil, feedstocks and biochars

The soil used in this study was collected in April 2008 in the Cornell Musgrave Research Farm (Aurora, New York). The soil was continuously cropped to corn for decades under standard, regional agricultural management practices. Soil had a 42% sand, 31% silt and 27% clay, total C content of 16.2 g kg⁻¹, total N of 1.6 g kg⁻¹, and a pH around 7 (see Rajkovich et al., 2012 for a more detailed description). Soil was collected after snowmelt and before any pesticide or fertilization was applied. After collection, soil was air-dried, homogenized, and sieved to 5 mm. Soil was stored for two years and before the beginning of the experiment two freezing–thawing cycles (24 h at –20 °C, 24 h at 20 °C) were carried out, ensuring that no fauna remained.

Bull manure with sawdust, corn stover, oak wood and pine wood were obtained from local suppliers in Wisconsin. Digested dairy manure was supplied by AA Dairy (Candor, NY, USA), obtained after the anaerobic digestion of dairy manure and removal of the liquid fraction by a screw press. Food waste was collected from Cornell University dining halls (Ithaca, NY, USA), and included discards from food preparation, unconsumed food and paper plates and napkins. White paper mill waste was obtained in Mohawk Fine Papers Inc. (Cohoes, NY, USA). The materials were dried at 60 °C until constant weight and processed to pass a 2-mm sieve.

Two biochars were obtained from each feedstock (Table 1), obtained by slow pyrolysis at Best Energies (Cashton, WI, USA), and produced at low (300 or 350 °C) and high temperature (550 or 600 °C). A detailed description of the pyrolysis procedure is provided in Enders et al. (2012). The set of biochars in this study was considered as representative, since slow pyrolysis is the most common technology to produce biochar due to its moderate operating conditions and optimization of biochar yields (Xie et al., in press).

Table 1
Source of feedstocks, and pyrolysis procedure to obtain the corresponding biochars.

Material	Feedstock and source	Treatment
BM		Feedstock
BM350	Bull manure w/sawdust, WI local supplier	Slow pyrolysis, 350 °C
BM550		Slow pyrolysis, 550 °C
CS		Feedstock
CS350	Corn stalks, WI local supplier	Slow pyrolysis, 350 °C
CS550		Slow pyrolysis, 550 °C
DDM		Feedstock
DDM300	Digested Dairy Manure Screw Pressed, AA Dairy, Candor, NY	Slow pyrolysis, 300 °C
DDM600		Slow pyrolysis, 600 °C
FW		Feedstock
FW300	Food waste, Cornell dining hall	Slow pyrolysis, 300 °C
FW600		Slow pyrolysis, 600 °C
OW		Feedstock
OW350	Oak, WI local supplier	Slow pyrolysis, 350 °C
OW550		Slow pyrolysis, 550 °C
PMW		Feedstock
PMW300	Paper Mill Waste, Mohawk Fine Papers Inc., Cohoes, NY	Slow pyrolysis, 300 °C
PMW600		Slow pyrolysis, 600 °C
PW350		Feedstock
PW350	Pine, WI local supplier	Slow pyrolysis, 350 °C
PW550		Slow pyrolysis, 550 °C

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