



# Inherent organic compounds in biochar—Their content, composition and potential toxic effects



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## ABSTRACT

Pyrolysis liquids consist of thermal degradation products of biomass in various stages of its decomposition. Therefore, if biochar gets affected by re-condensed pyrolysis liquids it is likely to contain a huge variety of organic compounds. In this study the chemical composition of such compounds associated with two contaminated, high-volatile organic compound (VOC) biochars were investigated and compared with those for a low-VOC biochar. The water-soluble organic compounds with the highest concentrations in the two high-VOC biochars were acetic, formic, butyric and propionic acids; methanol, phenol, o-, m- and p-cresol, and 2,4-dimethylphenol, all with concentrations over  $100 \mu\text{g g}^{-1}$ . The concentrations of 16 US EPA PAHs determined by 36 h toluene extractions were  $6.09 \mu\text{g g}^{-1}$  for the low-VOC biochar. For high-VOC biochar the total concentrations were  $53.42 \mu\text{g g}^{-1}$  and  $27.89 \mu\text{g g}^{-1}$ , while concentrations of water-soluble PAHs ranged from  $1.5$  to  $2 \mu\text{g g}^{-1}$ . Despite the concentrations of PAHs exceeding biochar guideline values, it was concluded that, for these particular biochars, the biggest concern for application to soil would be the co-occurrence of VOCs such as low molecular weight (LMW) organic acids and phenols, as these can be highly mobile and have a high potential to cause phytotoxic effects. Therefore, based on results of this study we strongly suggest for VOCs to be included among criteria for assessment of biochar quality.

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## 1. Introduction

It is well known that char from natural forest fires and organic compounds released from such processes can promote seed germination and plant growth (Brown and Staden, 1997; Keeley and Pizzorno, 1986). However, negative effects of compounds generated during forest fires have also been observed and various organic compounds like phenolics and naphthalene can be responsible (Nelson et al., 2012). Recent work has shown that

*Abbreviations:* GC biochar, gas contaminated biochar; LC biochar, liquid contaminated biochar; NC biochar, non-contaminated biochar; VOC, volatile organic compound; LMW, low molecular weight; HMW, high molecular weight; PAH, polycyclic aromatic hydrocarbon; BTEX, benzene, toluene, ethylbenzene, and xylenes; TEF, toxicity equivalency factors; TEQ, toxic equivalents; PTE, potentially toxic elements;  $\log K_{oc}$ , logarithm of soil organic carbon-water partitioning coefficient.

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biochar, a carbon-rich material formed from biomass by pyrolysis (a thermochemical conversion process carried out in the absence of oxygen) can be used to improve soil properties, to remediate soil contamination and for long-term carbon storage (Buss et al., 2012; Lehmann and Joseph, 2009). Similar to natural char, besides positive effects of biochar, negative effects have also been reported (Bernardo et al., 2010; Buss and Mašek, 2014; Gell et al., 2011; Kloss et al., 2014; Oleszczuk et al., 2013; Quilliam et al., 2012; Rogovska et al., 2012; Smith et al., 2013), however, detailed understanding of causes of such negative effects is yet lacking. The authors have previously shown that pyrolysis liquids condensed on biochar can have toxic effects on plants (Buss and Mašek, 2014); and this study further investigated the causes of this toxicity resulting from this contamination pathway.

Contaminants within biochar may present a risk following application to soil, thus, several studies have determined the total and bioavailable concentrations of potentially toxic elements (PTE) (e.g., Cd, Cu, Pb, Zn) and polycyclic aromatic hydrocarbons (PAHs) in

biochars from various feedstocks and produced under various pyrolysis conditions. As low total levels and much lower levels of bioavailable PAHs and PTEs have generally been detected in biochars, these are not usually considered as a threat to plants and the environment (Hale et al., 2012; Singh et al., 2010). Nevertheless, in some studies, PAHs in biochar were suspected to have been responsible for acute toxicity to various organisms (Oleszczuk et al., 2013; Rogovska et al., 2012).

During pyrolysis, organic matter is broken down and new compounds are formed that are either transformed and incorporated into char or are volatilised and end up in the pyrolysis liquid/gas phases (Antal and Grønli, 2003; Spokas et al., 2011). Small amounts of compounds with a boiling point lower than the pyrolysis temperature naturally end up in the solid pyrolysis fraction, depending on the extent and nature of interaction between pyrolysis gases and solids. However, re-condensation and trapping in biochar pores are among the mechanisms responsible for enhancing biochar's concentration of compounds that are normally associated with the pyrolysis liquid fraction (Fagernäs et al., 2012; Spokas et al., 2011). The amount of re-condensation is highly variable and is related to the design of different pyrolysis units, where influences such as cold spots can cause vapour re-condensation and a contamination by liquids (Buss and Mašek, 2014; Gundale and DeLuca, 2006; Spokas et al., 2011). A huge variety of organic thermal degradation intermediates of various chemical classes have been found in pyrolysis liquids (Cordella et al., 2012; Sánchez et al., 2009). Among these are volatile organic compounds (VOCs), e.g. low molecular weight (LMW) organic acids, alcohols, ketones and phenols (Cordella et al., 2012). In addition, PAHs have also been reported in pyrolysis liquids and biochar, in much higher levels in the former than the latter (less than 1% of the total PAHs produced are present in pyrolysis solids) (Fagernäs et al., 2012). Although levels of VOCs in biochar show a decrease with a rise in pyrolysis temperature (more volatilization from solid product), the picture for PAHs is more complex (Fabbri et al., 2013; Hale et al., 2012).

Since there are only a limited number of reported studies on the topic of VOCs and biochars and to our knowledge no quantitative studies, there is a need to investigate the composition and concentration of organics sorbed to biochar. This is especially important since highly varied responses have been reported for biochar application to soil (Jeffery et al., 2011) and VOCs within the biochar may be responsible for some of the positive and negative effects that cannot be explained by factors like nutrients, pH or soil structure improvements (Elad et al., 2011; Nelson et al., 2012; Spokas et al., 2011).

In the current study, biochars contaminated by a high dose of re-condensed pyrolysis liquids and gases (high-VOC biochars) were analysed for low molecular weight (LMW) organics and priority PAHs as potentially toxic compounds and compared to a low-VOC biochar. These samples represent the worst-case scenario of uncontrolled pyrolysis and production in poorly designed or operated pyrolysis units. In a previous study, phytotoxicity of these high-VOC biochars on cress seeds was already demonstrated and the mechanisms investigated (Buss and Mašek, 2014). The objectives of this study were to assess the nature of condensed compounds on biochar, to identify classes of compounds with the highest potential for adverse impact after soil application and to explain the toxic effects of this specific set of biochars. The two working hypotheses behind this research were as follows: a) Re-condensation of pyrolysis liquids on biochar simultaneously increases concentration of two classes of organic contaminants, PAHs and VOCs; b) VOCs, not PAHs are responsible for the main negative effects of biochar affected by pyrolysis liquid re-condensation.

## 2. Materials and methods

### 2.1. Biochars

All biochar samples were produced from the same feedstock, softwood pellets, pyrolysed at the same nominal highest treatment temperature of 550 °C, with the same mean residence time of 20 min in the same pyrolysis unit. Re-condensation of pyrolysis liquids and gases on biochar during production led to two differently contaminated high-VOC biochars, a liquid contaminated (LC) biochar and a gas contaminated (GC) biochar. Furthermore, one low-VOC, non-contaminated (NC) biochar was investigated that originated from a production run with minimal re-condensation. More details about the pyrolysis unit, how the contamination occurred and the properties of all three biochars can be found in Buss and Mašek (2014).

### 2.2. Extractions and analyses

The concentrations stated in this study are not reported on a dry weight basis due to the high-VOC content of two of the samples. It was not possible to either remove the biochar moisture content without releasing VOCs or to determine the moisture content of the samples. The following extractions and analyses were performed for the NC (low-VOC) biochar and the two high-VOC biochars. If not stated otherwise the analysis were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), laboratories accredited by United Kingdom Accreditation Service (UKAS). Validation/quality control of the analyses are stated in Table S1 as percentage standard deviation of the concentration of (low, high) standards analysed in replicates.

#### 2.2.1. Total PAH extraction and analysis

The total concentrations of the 16 US EPA PAHs were determined according to Hilber et al. (2012) by 6 h and 36 h soxhlet extractions using toluene, followed by a GC–MS analysis (6890 GC plus autosampler and Agilent 5975c MS). Both extractions were performed to compare the extractability of different PAHs with time and to compare total PAH levels with literature values based on the same extraction duration. The limit of detection for PAHs was 0.10 µg g<sup>-1</sup>.

#### 2.2.2. Water extractable phenols

According to the method of Hildebrand (1979), 5 g solid material was extracted with 500 mL deionised water (solid-to-liquid ratio of 1:100) for 12 h in a closed bottle to prevent the loss of volatiles. Instead of using a soxhlet apparatus, a magnetic stirrer was used since it resulted in higher phenol recoveries and gave results with lower standard deviations. The mixtures were filtered under vacuum and the LCK 345 phenol index test (Hach, Loveland, Colorado, USA) was used for analysis of the phenol index in the extracts using a DR5000 Spectrophotometer UV-VIS (Hach, Loveland, Colorado, USA). Furthermore, the samples were analysed for methylated and chlorinated phenols according to BS EN 12673:1999/BS 6068-2.65:1999 (2008) using a Restek Rxi – XLB column in an Agilent 7890 GC – 5975c MS. Analyses were performed by EUROFINIS Umwelt West (Wesseling, Germany), accredited laboratory by Germany's National Accreditation Body (DakkS). Compounds below the detection limit and phenol index results from a different solid-to-liquid ratio than 1:100 are stated in Tables S2 and S3.

#### 2.2.3. Water extractable PAHs, organic acids, alcohols and ketones

10 g of biochar was extracted with 100 mL of deionised water (solid-to-liquid ratio of 1:10) for 24 h on a reciprocal shaker at 150 rpm. samples were then vacuum filtered using Whatman no. 1

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