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Risks and benefits of marginal biomass-derived biochars for plant growth

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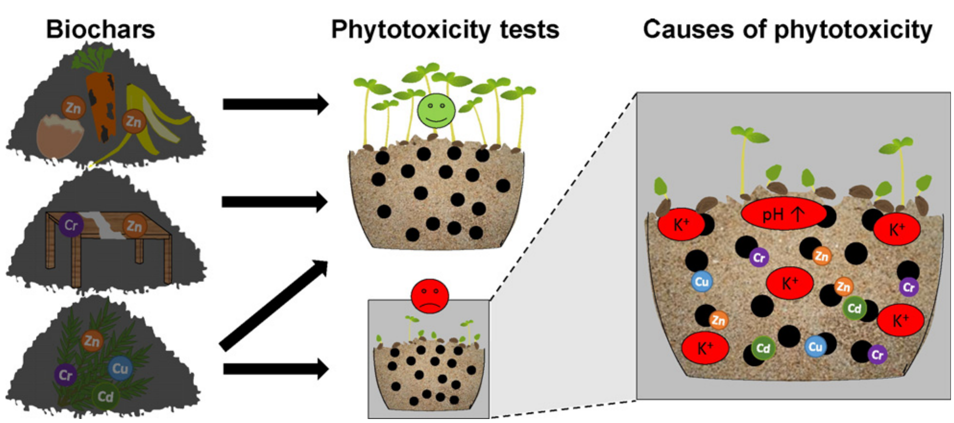
HIGHLIGHTS

- The availability of PTEs was highest in the highest temperature biochars.
- The availability of PTEs in the biochars were comparable to that in soil at same pH.
- Total and available concentrations of PTEs did not reflect phytotoxicity.
- Available K concentration and pH were largely responsible for observed phytotoxicity.
- The effect of available K could be attributed to influence on osmotic potential.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, 19 biochars from marginal biomass, representing all major biomass groups (woody materials, grass, an aquatic plant, anthropogenic wastes) were investigated regarding their content of available potentially toxic elements (PTEs) and nutrients (determined by NH_4NO_3-extractions) and their effects on cress (*Lepidium sativum*) seedling growth. The objective was to assess the potential and actual effects of biochar with increased PTE content on plant growth in the context of use in soil amendments and growing media. It showed that the percentage of available PTEs was highest for biochars produced at the highest treatment temperature (HTT) of 750 °C. On average, however, for all 19 biochars, the percentage availability of Cu, Cr, Ni and Zn (<1.5% for all) was similar to the percentage availability reported in the literature for the same elements in soils at similar pH values which is a highly important finding. Most biochars exceeded German soil threshold values for NH_4NO_3-extractable PTEs, such as Zn (by up to 25-fold), As and Cd. Despite this, cress seedling growth tests with 5% biochar in sand did not show any correlations between inhibitory effects (observed in 5 of the 19 biochars) and the available PTE concentrations. Instead, the available K concentration and biochar pH were highly significantly, negatively correlated with seedling growth (K: $p < 0.001$, pH: $p = 0.004$). K had the highest available concentration of all elements and the highest percentage availability (47.7 ± 19.7% of the total K was available). Consequently, available K contributed most to the osmotic pressure and high pH which negatively affected the seedlings. Although a potential risk if some of these marginal biomass-derived biochar were applied at high concentrations, e.g. 5%

Abbreviations: PTE, Potentially toxic elements; LOD, limit of detection; LOQ, limit of quantification; SD, standard deviation; MLV-index, Munoo-Liisa-Vitality index; CEC, cation exchange capacity; HTT, highest treatment temperature.

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(>100 t ha^{-1}), when applied at agriculturally realistic application rates (1–10 t ha^{-1}), the resulting smaller increases in pH and available K concentration may actually be beneficial for plant growth.

1. Introduction

Biochar can improve soil chemical properties (e.g. pH, cation exchange capacity (CEC)), soil biological properties (e.g. stimulate microbial growth) and soil physical properties (e.g. water holding capacity) (Lehmann and Joseph, 2015) and in addition, supply nutrients directly to the soil (Ippolito et al., 2015). Consequently, among other things, biochar is being tested for plant growth promotion in agriculture, horticulture and viticulture. However, inhibiting effects caused by biochar could negate any positive effects and so biochar should not contain contaminants which pose a risk to plant growth.

The contaminants in biochar which have been reported to be present at sufficient concentrations to affect plant growth are: polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and potentially toxic elements (PTEs). These can originate from the feedstock (predominantly PTEs) and/or the production process itself (VOCs, PAHs and some metals) (Buss et al., 2015, 2016; Hale et al., 2012; Hilber et al., 2012). While process conditions can be adjusted and pyrolysis units can be built to minimise contamination resulting from the production process (Buss et al., 2016; Hale et al., 2012), contaminants in the feedstock are source-dependent, and therefore careful selection of biomass is necessary.

From an economic and sustainability perspective, the ideal feedstock for biochar production is biomass or organic waste that would otherwise be landfilled or incinerated (Shackley et al., 2011). However, these materials are likely to contain contaminants, e.g. originating from the soil or water bodies in which the biomass was grown or from direct anthropogenic influences (e.g. wood from demolition sites, sewage sludge and food waste). Such material of limited economic value is henceforth referred to as "marginal biomass". Biochars produced from marginal biomass containing organic contaminants, e.g. PAHs or dioxins, have been shown to pose a low risk as such contaminants tend to be largely destroyed or evaporated during pyrolysis (Wijesekara et al., 2007; Zielińska and Oleszczuk, 2015).

PTEs, on the other hand, mostly remain in the solids (feedstock/biochar) during biochar production and only a few are partially evaporated (Buss et al., 2016). Consequently, guideline values for total concentrations of PTEs have been introduced and biochars can be tested for compliance against these guidelines (EBC, 2012; International Biochar Initiative, 2011). However, when biochar is applied to a soil or a plant growth medium, only a fraction of the PTEs (and nutrients) are present in forms which can be taken up by plants. This proportion is usually termed the 'bioavailable' fraction and, since it usually does not correlate with total elemental content (Ippolito et al., 2015), methods to assess the extent of PTE bioavailability have been developed.

Numerous chemical extraction methods using a wide range of extractants including deionised (DI) water, salt solutions, complexing agents or weak acids have been used to approximate the bioavailable fraction of PTEs (and nutrients) in soils and biochar (Farrell et al., 2013; McLaughlin et al., 2000; Monter Roso et al., 1999; van Raij, 1998). BS ISO 19730:2008 (2008) describes soil extraction with 1 mol L^{-1} NH_4NO_3 for assessing the fraction of trace elements able to interact and affect crop growth and was used to establish German legislation threshold values for PTEs for protecting plant growth and crop quality (German Federal Soil Protection and Contaminated Sites Ordinance, 1999). In addition to extraction of PTEs in soil, the method has also been tested and recommended for extractable cationic nutrients (Schöning and Brümmer, 2008; Stuanes et al., 1984) and for extracting PTEs and nutrients in biochar/biochar-amended soils (Alling et al., 2014; Karer et al., 2015; Kim, 2015; Kloss et al., 2014b; Park et al., 2011). The proportion recovered by such extractants has been described using various terms; in this study, the term "available" will be used throughout.

Previous studies determining the available concentration of PTEs in feedstocks and biochars have revealed that the pyrolysis process itself can immobilise various PTEs already present in the feedstock; this resulted in pyrolysis being recommended for waste treatment prior to landfilling (Farrell et al., 2013; Hwang and Matsuto, 2008; Khanmohammadi et al., 2015; Liu et al., 2014; Meng et al., 2013). The immobilisation was reported to result from different binding of PTEs to the carbon lattice after pyrolysis and through increase in pH of the material when converted into biochar (Gu et al., 2013; Liu et al., 2014). Yet, it remains unclear if biochars resulting from feedstocks that are heavily contaminated with PTEs, e.g. plants grown on soil which exceed soil threshold values or PTE-contaminated anthropogenic wastes, are suitable for amendment of soil and growing media.

In a previous study, the total concentrations of nutrients and PTEs were analysed in 19 marginal biomass-derived biochars and PTE concentrations were tested for compliance with threshold values for total PTEs (Buss et al., 2016). In the current study, cress germination and early seedling growth tests were conducted to assess the risk of PTEs in biochar for plant growth. Furthermore, available PTEs were determined using NH_4NO_3 and compared to German legislation threshold values. To complete the risk-benefit analysis of application of marginal biomass-derived biochar to soil and growing media, the availability of nutrients was determined to assess the potential fertiliser value. In addition, the effect of highest treatment temperature (HTT) and feedstock on percentage available of total PTEs and nutrients was examined. Ultimately, the available elemental content of the biochars (and biochar pH and EC values) were correlated with phytotoxic effects to identify the parameter with the greatest potential to affect plant growth adversely.

2. Materials and methods

2.1. Biochars

Nineteen biochars produced from 10 marginal biomass feedstocks from all major biomass categories, including woody materials, grass, an aquatic plant and anthropogenic wastes (non-virgin feedstocks), were used for this study. As all these materials were described in detail in Buss et al. (2016), only a short description is provided in Table 1. Feedstock effects were studied for all 10 biomasses where pyrolysis at 550 °C was used as a typical medium HTT. To study the effects of temperature, 2 feedstocks (ADX, DW) were pyrolysed at HTTs of 350, 450, 550, 650 and 750 °C and 1 (WLB) was pyrolysed at 550 °C and 700 °C. In all cases, the biochars were produced using the continuous screw pyrolysis unit described in Buss et al. (2016). All biochars are termed according to their feedstock as abbreviated in Table 1 and their respective production temperature (°C).

2.2. Ammonium nitrate (NH_4NO_3) extractions

According to BS ISO 19730:2008 (2008) the recommended soil-to-NH_4NO_3-solution ratio is 1:2.5 (m/v); however, due to its low bulk density and high water sorption capacity, the ground biochar did not mix well with the small amount of water and the mixture was too viscous to ensure proper extraction. Different solid-to-solution ratios were tested and thorough mixing of the sample was ensured by using a ratio of 1:10 (m/v). In short, representative samples were taken from each biochar container by taking sub-samples, grinding those with mortar and