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Difficulties in using soil-based methods to assess plant availability of potentially toxic elements in biochars and their feedstocks

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HIGHLIGHTS

- Soil PTE extractability assays are unsuitable for risk assessment of biochars.
- Pyrolysis increases PTE concentrations and reduces PTE availability.
- Germination assays may be useful as a dual-purpose tool to assess PTE phytoavailability.

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ABSTRACT

The use of biochars in agriculture to improve soil function and carbon sequestration is expected to increase into the future. We aimed to identify the most suitable chemical extractants for the risk assessment of potentially toxic element (PTE) availability in biochars produced from a range of feedstocks, and to investigate the changes in PTE extractability that occur as a result of feedstock pyrolysis using five common extraction methods. We evaluated these methods with regard to their ability to predict PTE phytoavailability in four different biochars against metal uptake by wheat. No single extractant significantly correlated well with ≥4 PTEs from the 10 examined, highlighting that the availability and binding mechanism of individual PTEs differed by biochar type. Commonly used PTE extraction methods need to be reviewed for use with biochars, and that some biochars may be able to stabilise PTEs, reducing risks of contamination upon land application.

1. Introduction

Biochars are defined as biomass-derived carbon (C) produced by the thermal decomposition of a feedstock by pyrolysis in the partial or total absence of oxygen, which are intended specifically for application to soil [1]. In recent years, the main focus of biochar research has been its potential for C sequestration in soils, as evidenced by Lehmann [2]. There has also been significant interest in the potential of biochars to increase agronomic yields though the amelioration of physico-chemical soil constraints [3], direct increases in nutrient availability though the presence of available nutrients within biochars, and increasing mycorrhizal symbioses [4].

As biochars may be produced from a wide range of organic feedstocks, including crop stubble, woody material, biosolids and urban wastes [5], it is likely that in addition to C and nutrients, they will also contain a wide range of other elements, including potentially toxic elements (PTEs) such as Cu, Pb and As. Given the recalcitrant nature of biochar, it is a possibility that these PTEs are less bioavailable if applied to soils in pyrolysed rather than as the original feedstock. This is due to pyrolysed organic matter being harder to mineralise [6] and subsequently release of contaminants bound in the macromolecular structure may be expected to be slower. Biochars can be produced from a wide range of organic feedstocks of varying quality, from virgin woods and grasses to urban biosolids [7].

As biochars are still a novel soil amendment, there are no legislative standards available prescribing limits of the concentrations of PTEs in biochars to be applied to soils. Consequently, controls on their application to agricultural land will either follow existing regulations for composts or biosolids, waste-to-land regulations; or alternatively application is unregulated, dependent upon local legislation. Conventional biowastes and their products such as composts and biosolids consist primarily of easily degradable C, and regulations and standards such as AS-4454 in Australia [8] or the PAS100 in the UK [9] are based upon an assessment of the total concentration of metals within composts, with no consideration given for their actual bioavailability. This may be overly restrictive as such an approach does not take into consideration the fact that at the point of application, only a small proportion of PTEs may be

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bioavailable in soils, potentially limiting the use of these nutrient-rich bioresources [10]. However, there are equal concerns that any addition of PTEs to agricultural land through the use of biowastes as amendments is undesirable due to the potential for their release and subsequent uptake and contamination by crops in the longer term [11].

Unlike other biowastes and their products, most biochars are very stable [1,5,6], with estimates of mean residence time in the order of 2000 years [12]. As such, concerns about longer-term release of PTEs from biochars applied in agricultural systems should be assessed in relation to the potential benefits of biochar application from a C sequestration, agricultural productivity, and waste management perspective. The application of existing regulations, guidelines and standards and the associated methodologies for degradable biowastes such as composts and biosolids may therefore not be suitable to assess the risks and/or benefits of the application of biochars. This is especially true given the expected low application rates of biochars relative to other organic amendments such as composts or biosolids. Additionally, the pyrolysis process may alter the oxidation state of some PTEs such as Cr(III) or Cr(VI), greatly increasing or decreasing their chemical toxicity. There is a requirement to understand the potential risk of PTEs within biochars to allow environmental guidelines to be produced (or amended) which accurately reflect the environmental risk of the application. Accordingly, such an assessment should not be based on total metal content but on PTE phytoavailability, and feedstock type should not be an *a priori* limiting factor.

The assessment of PTE phytoavailability in soils is generally based upon chemical extractability assays, utilising various strengths of aqueous extracts to remove different fractions of PTEs, from water soluble to weakly and strongly sorbed or complexed to solid phases. These range from 18.2 MΩ ultra-pure water, through dilute neutral salts and chelating agents, to dilute mineral and organic acids; each of these methods has success within the target system/soil type [13]. From an analytical perspective, water [14] and 0.01 M $CaCl_2$ [15] extracts are low risk and high throughput, allowing rapid multi-elemental analysis not only for PTE risk assessment, but also for the analysis of micro- and macro- nutrient availability. However, compared to stronger extracts such as 0.05 M ethylenediaminetetraacetic acid (EDTA) or 0.5 M acetic acid (HOAc), water or weak salt solutions may under-estimate phytoavailability by failing to take into consideration mechanisms such as enzymes and exudation of organic acids by plants and microorganisms in order to facilitate micronutrient (and inadvertently PTE) uptake [10]. As an intermediate to these two extremes, 1 M NH_4NO_3 has been adopted as a German standard to assess phytoavailability of PTEs in soils, and has been found to give good agreement with plant uptake for a number of elements in several food-crop species, but struggled to predict Pb, As, Hg and Cu uptake in wheat [16].

As can be seen from the literature, there are difficulties in establishing true phytoavailability availability assessments using chemical extracts alone. These can be attributed to several factors, including the accurate replication of solubilisation and uptake of plants and microorganisms, the different chemical properties of each PTE when a single extractant and multi-elemental analysis is preferred, and sorption/desorption dynamics [10,13]. Consequently, it is desirable to carry out an additional assessment of either plant toxicity [17] or plant uptake and accumulation [10]. One major issue with carrying out a phytoavailability analysis as part of a risk assessment for organic amendments such as biochars is the cost and time taken to grow a plant to a sufficient size to allow its metal content to be assessed. Consequently, it is desirable to identify chemical extractants which best correlate with plant uptake in a target species [13].

The aim of this work was to identify the most suitable chemical extractants for the risk assessment of PTE availability in biochars produced from a range of feedstocks, and to investigate the changes in PTE extractability that occur as a result of pyrolysis of the raw feedstock. We used wheat as a phytoassay to assess plant uptake of PTEs, and related this back to their chemical extractability. This information will be applicable to risk assessments for biochar on plant growth and human/animal health. We hypothesised that whilst many PTEs would be concentrated by the process of pyrolysis, leading to an increase in total PTE concentrations in biochars relative to the feedstocks, PTE availability would greatly decrease as a result of the conversion of organic matter to the form of aromatic carbon during the pyrolysis process. We also hypothesised that neutral salt solutions would most accurately predict PTE phytoavailability than stronger extractants such as EDTA.

2. Experimental

2.1. Biochar production

In order to investigate PTE phytoavailability and changes in availability as a result of pyrolysis, we obtained four feedstocks for use in this study. Poultry litter feedstock (PLF) was collected from near Gosford, NSW, in early 2010, and comprised a mixture of wood chips and chicken faeces. It is commonly used throughout Australia as a nutrient-rich fertiliser. Wheat straw feedstock (WSF) was purchased from Coastal Rural Trader, Ourimbah, NSW in early 2010, and consisted mainly of dry *Triticum aestivum* straw with some seed husks and leaves present. Oil mallee feedstock (OMF) is the woody residue from *Eucalyptus oleosa* trees after eucalypt oil steam extraction, and was collected from western NSW in July 2010. Finally, municipal tertiary treated biosolids (BSF) were collected from Ballina Shire Council, NSW in mid 2009. This biosolid is from a rural and peri-urban environment with some light industry, and as such was expected to have moderate concentrations of PTEs.

All biochars were produced at 550 °C in a Pyrochar300 continuous reactor with a mean residence time of 20 min (Pacific Pyrolysis Pty Ltd., Somersby, NSW, Australia). Poultry litter biochar (PLB) contained 44.1% C, 1.71% N, and had a pH of 9.57. Wheat straw biochar (WSB) contained 56.6% C, 2.1% N, and had a pH of 9.00. Oil mallee biochar (OMB) contained 67.0% C, 0.5% N, and had a pH of 7.51. Finally, biosolids biochar (BSB) contained 28.7% C, 3.8% N, and had a pH of 7.42.

2.2. PTE extraction methods

Total PTE concentration of the biochars and feedstocks was determined in quadruplicate by $HClO_4/HNO_3$ digestion in open digestion tubes in a heated block [18] before filtration to 0.45 μm and analysis by ICP-MS (7500cx, Agilent Technologies, CA, USA). Concentration factors were calculated to determine the relative increase in concentration in the biochars relative to their feedstocks. Where concentrations were below limit of detection, a nominal concentration of 0.01 mg kg^{-1} was used to facilitate this calculation. Five commonly used aqueous soil extraction methods were chosen for the assessment of extractable PTEs as an assessment of their suitability to predict phytoavailablility. Water soluble and 0.01 M $CaCl_2$ extractable PTEs were extracted in a sample:extractant ratio of 1:10 by shaking for two hours on a reciprocal shaker [14,15]. 0.05 M EDTA extractable PTEs were extracted in a sample:extractant ratio of 1:10 for one hour, and 0.5 M HOAc extractable PTEs were extracted in a sample:extractant ratio of 1:5 for one hour [19]. 1 M NH_4NO_3 extractable PTEs were extracted in a sample:extractant ratio of 1:2.5 for two hours [16]. All extracts were carried out in quadruplicate with fresh biochars/feedstocks and were centrifuged for 10 min at 850 *g* before filtration to 0.45 μm, and were analysed by ICP-MS as above. Data are reported on a dry weight basis.