Agriculture, Ecosystems and Environment 191 (2014) 133–141

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

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

Response of plant and soil microbes to biochar amendment of an arsenic-contaminated soil

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ARTICLE INFO

Article history:
Received 31 July 2013
Received in revised form 17 March 2014
Accepted 18 March 2014
Available online 18 April 2014

Keywords:
Biochar
Arsenic
Soil Microbial Activity
Phytoextraction
Soil Remediation
Environmental Risk

ABSTRACT

The historical treatment of livestock with arsenical-based pesticides has resulted in large areas of pastoral land being highly contaminated with arsenic. This study investigated the effect of biochar on soil microbial activity and arsenic phytoextraction in an arsenic-contaminated soil during a 180 d glasshouse experiment. Biochar made from willow feedstock (*Salix sp*) was pyrolysed at 350 and 550 °C (representing a low- and high-temperature biochar) and amended to soil at rates of 30 t ha^{-1} and 60 t ha^{-1} to 30 cm depth (10 and 20 g biochar kg^{-1} soil, respectively). Ryegrass (*Lolium perenne* L.) was seeded and plant growth was monitored. Soil microbial activity, quantified using the dehydrogenase activity (DHA) assay, was significantly increased ($P < 0.01$) under all biochar treatments. This increase was in excess of 100% after 30 d of treatment and was significantly higher ($P < 0.05$) than the control throughout the trial for 350 °C amended soils. The increase for the 550 °C amended soils relative to the control was greater than 70%. No negative effect of biochar amendments on ryegrass germination was observed. Biochar promoted a 2-fold increase in shoot dry weight (DW) and a 3-fold increase in root DW after 180 d under all biochar amendments and this was attributed, at least in part, to the fertility value of biochar. By increasing dose rates of biochar amendment from 30 t ha^{-1} to 60 t ha^{-1} shoot tissue of ryegrass extracted significantly higher ($P < 0.05$) concentrations of arsenic. Through extrapolation, 350 °C biochar-amended soils were estimated to have the potential to increase ryegrass sward DW growth by 0.68 t ha^{-1} compared to ryegrass grown on unamended soils. This would correspond to an increase in the extraction of total arsenic by 14,000 mg ha^{-1} compared to unamended soils and in doing so decreasing soil remediation times by over 50%. This investigation provides insight into the beneficial attributes of biochar in contaminated soil, and specifically that produced from willow wood, and its potential to reduce the time needed to remediate arsenic-contaminated soil. However, more studies are needed to understand the mechanisms through which these benefits are provided.

1. Introduction

Soil contamination is a global problem and occurs when the concentration of an element or compound in soil exceeds a natural background threshold value (Chapman, 2007). Contamination can occur through geogenic or anthropogenic processes (Beesley et al., 2011a). The agricultural development of New Zealand through the 20th century saw the use of a range of inorganic and organic compounds as pesticides to control production-limiting insects. These pesticides included arsenicals and a range of organochlorines used specifically to control parasites on sheep. Animals would be submerged in baths containing these chemicals with the leftover solution pumped onto surrounding soil. Today an estimated 50,000 contaminated sheep dip sites exist in New Zealand with soil concentrations of arsenic reaching as high as 11,000 mg kg^{-1} to a depth of 30 cm (NZ Ministry for the Environment, 2006).

Dipping with arsenic is no longer practiced. Today organophosphate compounds are topically applied to animals to control parasites. However, historically-contaminated soil (as a present day risk) can negatively affect water quality where arsenic leaches through the soil profile and becomes a diffuse source of pollution to streams and rivers. Arsenic in soil can also detrimentally affect soil microbial activity and thus affect nutrient cycling and soil biodiversity (Klose & Ajwa, 2004; Pampulha & Oliveira, 2006; Zhou et al., 2006; Anderson et al., 2009). Therefore, the

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http://dx.doi.org/10.1016/j.agee.2014.03.035
0167-8809/

remediation of historically contaminated sheep-dip sites has been defined as an important goal for future environmental sustainability in New Zealand (NZ Ministry for the Environment, 2006). Two technology-based concepts that have the potential to manage and/or remediate arsenic in soil are biochar and phytoextraction.

Plants have a natural ability to take up metals and metalloids from soil by either passive or active means, but the technological application of this trait to remediate contaminated areas can take hundreds of years depending on the severity of contamination (Tsao, 2003; Saleh et al., 2004; Meers et al., 2008; Zhao et al., 2009). The plant species that have been most commonly used to extract arsenic from soil (phytoextraction) are arsenic hyperaccumulating ferns such as *Pteris vittata* and *Pteris cretica*. These plants have been used for arsenic remediation under both greenhouse and field conditions (Zhao et al., 2002; Xiao et al., 2008). Niazi et al. (2010) reported that hyperaccumulator ferns grown in the field at a historic cattle dip site had an arsenic concentration of more than 3500 mg kg^{-1} after 6 months of growth (Niazi et al., 2010). Ferns, however, have slow growth rates and require low light-intensity conditions to flourish. Their use in field applications may therefore be limited.

The target characteristics for a plant species being used in phytoextraction include adequate rates of growth and biomass production (including the development of root biomass) along with tolerance to the metal (metalloid) being targeted for remediation (Vamerali et al., 2010). Any strategy that can increase the rate of plant growth and that can manipulate soil chemistry and biology to increase arsenic bioavailability for plant uptake may improve the potential and timeframe for phytoremediation. It is in the context of optimised phytoextraction using a non-hyperaccumulator but high biomass and growth rate species that biochar may be a soil amendment that can reduce the timeframe of remediation.

Biochar is charcoal added to soil to improve soil functions and to reduce emissions from organic material that would otherwise naturally degrade to greenhouse gases (Sohi et al., 2010). The potentially useful surface properties of biochar can lead to contaminant control and nutrient retention and release. Fresh biochars usually have a low cation exchange capacity (CEC). However, with time its surface will tend to oxidise as a result of weathering and increase CEC (Cheng et al., 2006; Cheng et al., 2008; Calvelo Pereira et al., 2011). High CEC will lead to the retention of many heavy metals in soil but not that of metalloids such as arsenic which mainly exists as an oxyanion. Biochar can also have high liming equivalence which may raise the soil pH and thus has the potential to increase the mobility of arsenic making it more available for uptake by plants (Hartley et al., 2009; Joseph et al., 2010). This scenario can increase the extraction efficiency for arsenic uptake into plants and reduce remediation times for contaminated soil. Therefore, a coupled biochar and phytoextraction remediation system could potentially reduce the remediation time due to the alkaline properties of biochar increasing the elemental solubility of arsenic within the soil (Beesley et al., 2011a).

Previous studies investigating the interactions between biochar and soil contaminants in a contaminated soil have focussed on metal availability and retention (Namgay et al., 2010; Beesley et al., 2011b). Less attention has been paid to the dual effect of biochar on plant growth and soil microbial activity, and the effect that these may have in the stimulation of arsenic phytoextraction. Here, we investigate the influence of biochar on soil chemistry and biology when applied to a highly arsenic-contaminated soil in the presence of plants. We have used *Lolium perenne* L. (perennial ryegrass) as a model non-arsenic accumulator plants species. Ryegrass is a common species grown in New Zealand pastoral systems that thrives on soil with a pH between 5.5 and 7.5 (Sartie, 2006). Ryegrass is routinely used to investigate plant growth responses (germination, root and shoot growth) to changing environmental conditions, and has been used in this study to better understand plant–soil dynamics in a biochar amended soil.

The specific objectives of our study were (i) to determine whether biochar produced at 350 °C and 550 °C added to an arsenic-contaminated soil would promote arsenic uptake in *L. perenne* L., (ii) to investigate whether biochar additions would affect soil microbial activity in such a system, and (iii) to ascertain the potential that biochar amendment of sheep-dip contaminated soil has to improve the efficacy of phytoextraction for soil remediation and management.

2. Materials and methods

2.1. Sample collection and pre-treatment

A sheep dip site that was operational from 1860 to 1980 was identified on the east coast of the North Island of New Zealand. Previous analysis of soil from this location defined the presence of heterogeneous arsenic contamination ranging from 200 to 2000 mg kg^{-1} in the proximity of the dip (Gregory, 2013) along with moderate concentrations of organochlorines (dieldrin, aldrin, DDT, lindane) which were not investigated as part of the current study. A bulk sample of soil (300 kg) was taken from the top soil (0–20 cm) across a 2 m × 2 m area identified as where the remaining arsenical solution was disposed of at the end of dipping. The soil was mixed to obtain homogeneity using a nursery grade mixer with two sets of revolving sleeves that slowly fold the soil, and finally sieved through a 5 mm-mesh.

2.2. Biochar production

Wood from one-year-old willow (pyrolysed at 350 °C) and five-year-old willow (pyrolysed at 550 °C) (*Salix sp.*) was collected from a commercial willow farm and chipped into approximately 0.5 cm size fragments and dried at 30 °C until constant weight. The wood was pyrolysed using a 25 L gas-fired rotating drum kiln with an average heating rate of 23.3 and 36.6 °C min^{-1} for the 350 °C (low temperature) and 550 °C (high temperature) biochars respectively. The peak temperatures were achieved by controlled release of pyrolysis gases in the kiln, and were maintained for 1–2 min followed by a 1 h cooling period prior to discharge into a sealed plastic bag.

2.3. Glasshouse experiment

Pot experiments were conducted under glasshouse conditions using square plastic pots measuring 20 × 20 cm and 30 cm deep, with drainage holes drilled at the base of the containers. Analysis of the soil showed that soil fertility was within agronomic guideline parameters, and therefore fertiliser (N:P:K) was not applied. Two doses of biochar were selected: 10 and 20 g biochar kg^{-1} soil, which when incorporated to 30 cm depth corresponds to a loading of 30 t ha^{-1} and 60 t ha^{-1}, respectively. These doses are higher than those used in agronomic studies, and probably not feasible for large areas of land. However, sheep dip sites are commonly small (30 m^2) but highly contaminated, and may be amenable to high rates of biochar application. Biochar was manually mixed with soil prior to filling of the pots. All pots were kept at 70% water holding capacity (WHC) with the addition of distilled water and left for 1 week to incubate prior to planting with ryegrass. Fifty (*Lolium perenne* L. cv *Nui*) seeds obtained from AgResearch Grasslands NZ (Accession No: A13509 Nil Endophyte), that were imbibed overnight in distilled water, were then placed on top of the soil using forceps (representing $T = 0$) and lightly sprayed with distilled water daily. The growth experiment was conducted over 6 months with three replicate pots per treatment. Germination rate was recorded over