USE OF BIOCHAR FOR THE SUSTAINABLE REMEDIATION OF SHEEP DIP SITES

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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., 2011). 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).

Current-day environmental concern over historic sheep-dip sites relates to arsenic and organochlorine residues in soil. These chemicals are known to be persistent and very damaging to a number of ecological indicators such as stream ecosystems and wildlife (McBride et al., 1998; NZ Ministry for the Environment, 2006). Most historic sheep dip sites can today be considered as co-contaminated. At present, dipping with arsenic and

organochlorines is no longer practiced with organophosphate compounds being applied to animals to control parasites.

The current conversion of past agricultural land (land on which sheep dip sites are located) into lifestyle and rural sub-division blocks is increasing the likelihood of humans and food crops from being subjected to the soil contamination from this past agricultural practice. Therefore, the 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).

Organochlorines in soil will break down with time, and can be degraded or volatilised from soil through a number of reactive steps such as dechlorination, dehydrochlorination, isomerisation and oxidation (Lal & Saxena, 1982; Aislabie et al., 1997; van Zwieten et al., 2003). These degradative processes can be facilitated by microbiological activity in soil, and the technology of promoting the degradation of a soil contaminant is known as bioremediation. The effectiveness of bioremediation techniques can be increased through the addition of specific amendments to soil (Quilty & Cattle. 2011). Yet the effectiveness of bioremediation on arsenic contamination is not as clear and requires another method.

Two technologies that have the potential to manage and/or remediate arsenic and organochlorines in soil are biochar and phytoextraction. Biochar is charcoal (a stable form of carbon) intended to be added to soil to improve soil functions and to reduce emissions from parent organic material that would otherwise naturally degrade to greenhouse gases (Kookana et al., 2011). Depending on pyrolysis conditions (which form the biochar) different biochars with different properties can be produced. Low temperature biochars have a considerable fraction of volatile carbon, which represents a potential energy source for soil microbiological activity (Warnock et al., 2007). Amendment of soil with labile carbon has the potential to stimulate microbial activity promoting dechlorination of organochlorines and a subsequent reduction in the half-life of these chemicals in soil (Kolb et al., 2009; Kuzyakov et al., 2009; Anderson et al., 2011). This property of biochar may lead to beneficial attributes such as bioremediation of contaminated soil.

Phytoextraction utilises the natural ability of plant species to extract metals out of the soil and into plant parts. This process is usually very slow and can require decades to completely

remediate soils contaminated with metals. Its use in this case is designed to reduce remediation times by being coupled with biochar. Biochar can 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 at al., 2010). This scenario can increase the extraction efficiency for arsenic uptake into plants and reduce remediation times for contaminated soil. Therefore, a coupled remediation system between biochar and phytoextraction can reduce this remediation time due to the alkaline properties of biochar increasing the elemental solubility of arsenic within soil for plant extraction (Beesley et al., 2011).

To our knowledge no studies have analysed the specific response of soil microbes to carbon amendment of a co-contaminated soil. In particular, the biochar-promoted degradation of organochlorines in an arsenic contaminated soil and increased phytoextraction of arsenic is poorly defined in literature. The objectives of our study were to investigate if biochar produced from willow at two temperatures of pyrolysis (350 and 550°C) (i) has an effect on microbial activity (ii) promotes the degradation of organochlorines in soil and iii) its coupled use with plant species used for metal uptake can increase the phytoextraction potential of arsenic and in doing so, decrease remediation times at dip sites.

METHODS

Due to space constraints the methods for the complete analysis of the field study and glasshouse experiment are described in Gregory (2013) and Gregory et al. (2013a,b,c). For reference, control soils mentioned are those that have not been amended with biochar.

RESULTS

Soil Microbial Activity Stimulated

Dehydrogenase activity was significantly increased with the addition of both types of biochar at both 30 t ha^{-1} and 60 t ha^{-1} for all time points relative to the control ($P<0.05$) (Figure 1). Dehydrogenase activity also increased with time for the control treatment. This increase was of 155 µg g^{-1} DM (dry matter) in the control soil over 180 d. Biochar (350°C) added at 30 t ha^{-1} increased dehydrogenase activity by 163 µg g^{-1} DM and 235 µg g^{-1} DM (30 t ha^{-1} and 60 t ha^{-1} respectively). Biochar (550°C) added at 30 t ha^{-1} increased by 169 µg g^{-1}

DM and 60 t ha^{-1} by 175 µg g^{-1} DM. In general, biochar-amended soils had higher dehydrogenase activity compared to the control yet the relative rate of increase was the same for all three treatments.

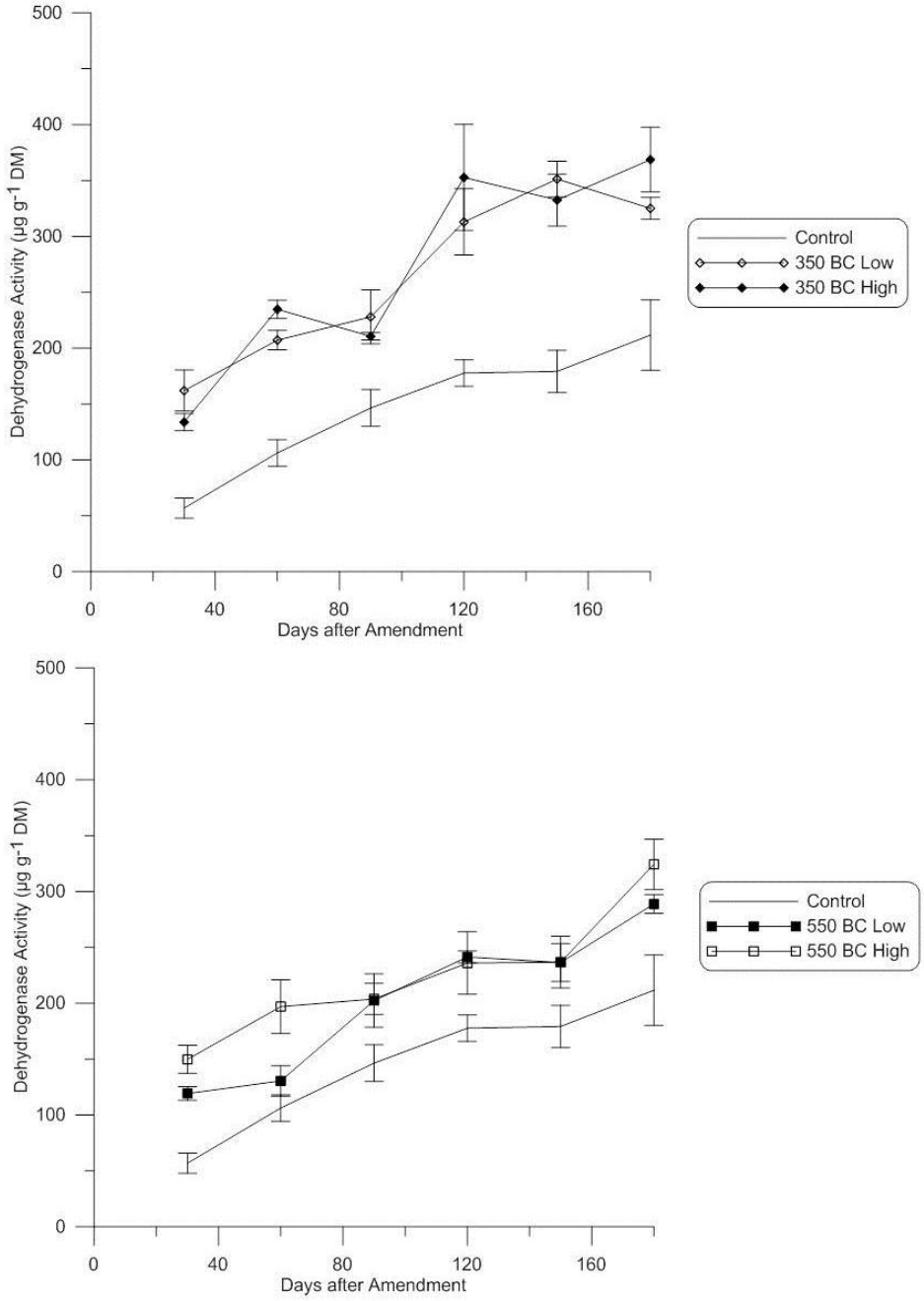

Figure 1. Soil dehydrogenase activity measured in µg per g of dry matter (DM) as a function of 350°C and 550°C biochar treatment (mean *n* = 3 ; ± s.e.).

Organochlorine Degradation Promoted with Biochar

Additions of both types of biochar at both rates caused a significant decrease in the soil concentration of two isomers of HCH, alpha-HCH (Figure 2A) and gamma-HCH (Figure 2B) ($P<0.01$). Alpha HCH was observed to undergo nearly a 10-fold reduction under all biochar treatments compared to the control while lindane underwent a 4-fold reduction under all biochar treatments. There was no significant difference ($P<0.05$) in the extent of reduction between the four biochar treatments. Delta HCH concentrations also reduced slightly but not significantly under each biochar treatment (Figure 2D) and there was no difference attributable to the biochar treatment used. The isomer beta HCH was unaffected by biochar amendment and after 6 months of treatment did not significantly differ ($P<0.05$) in concentration compared to the control.

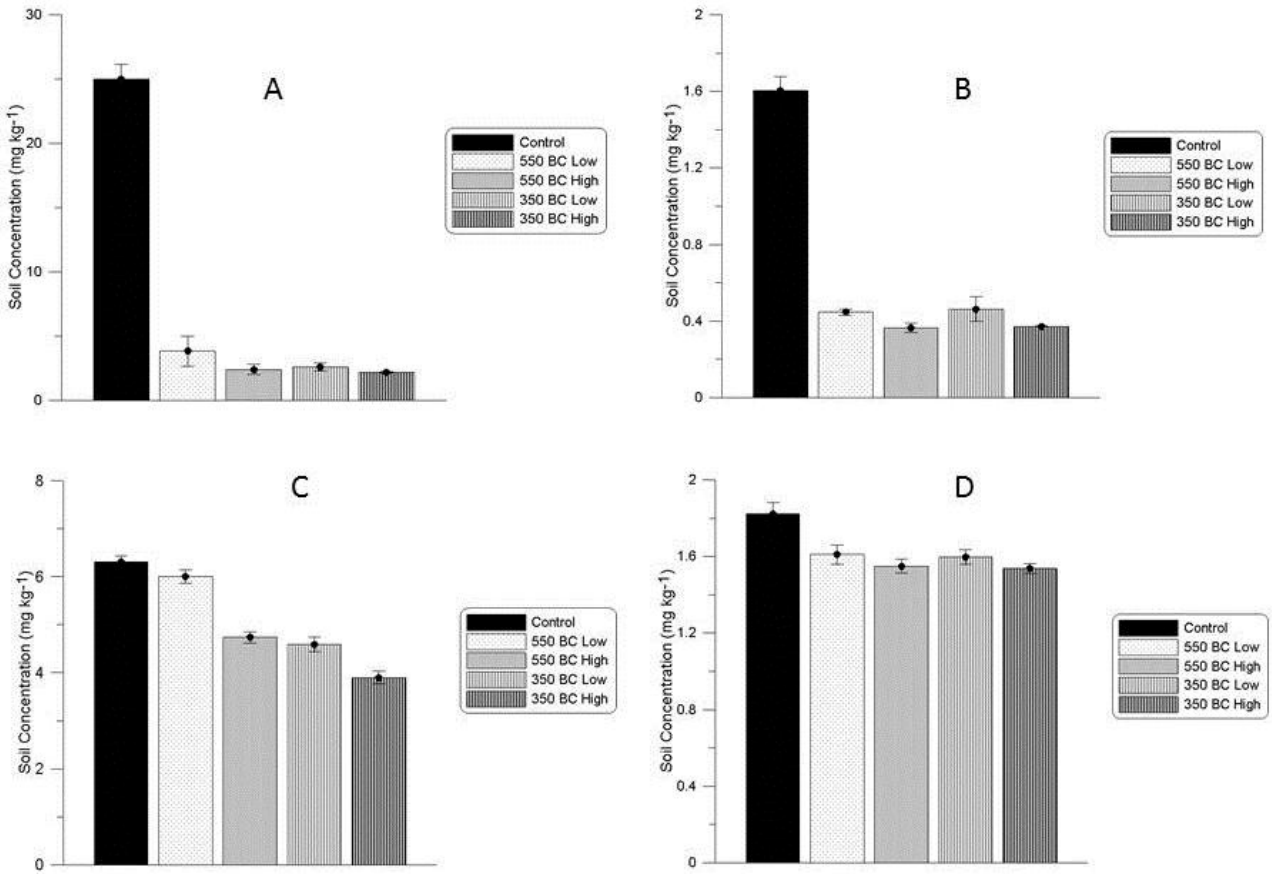

Figure 2. Soil concentrations (mg kg^{-1}) for A) Alpha-HCH B) Lindane C) DDT and D) Delta-HCH at the termination of the glasshouse trial under different treatments. Significant differences are observed between all biochar types and the control ($P<0.01$) (mean $n = 3$; ± s.e.)

A decrease in the soil concentration of DDT (including its breakdown products: sum DDT) was also significantly affected (P<0.01) by three of the four treatments under study (350°C biochar at 30 t ha^{-1} and 60 t ha^{-1} and also 550°C biochar at 60 t ha^{-1}) compared to the control (Figure 2C). The magnitude of the decrease in DDT concentration was influenced by the biochar treatment used. 350°C biochar at 60 t ha^{-1} resulted in a reduction of 38% of total DDT in soil compared to the control, with 350°C biochar (30 t ha^{-1}) and 550°C biochar (60 t ha^{-1}) reduced total DDT concentrations by 27 and 25% respectively compared to the control.

Increased Phytoextraction of Arsenic under Biochar Amendment

Arsenic concentrations in ryegrass shoot biomass was significantly increased as a function of both biochar treatments at 60 t ha^{-1} relative to the control (Figure 3). However no change was apparent for biochar applied at a rate of 30 t ha^{-1} compared to the control (P<0.05). The maximum concentration of shoot arsenic was 15.3 mg kg^{-1} for the 60 t ha^{-1} application of 350°C biochar. This was an increase of 33% over the control concentration (11.5 mg kg^{-1}). Under field conditions (using willow as a high biomass crop) arsenic concentration of the control willow stem was 0.11 mg kg^{-1} while that grown on soil amended with 350°C and 550°C biochar was 1.27 and 0.14 mg kg^{-1} respectively.

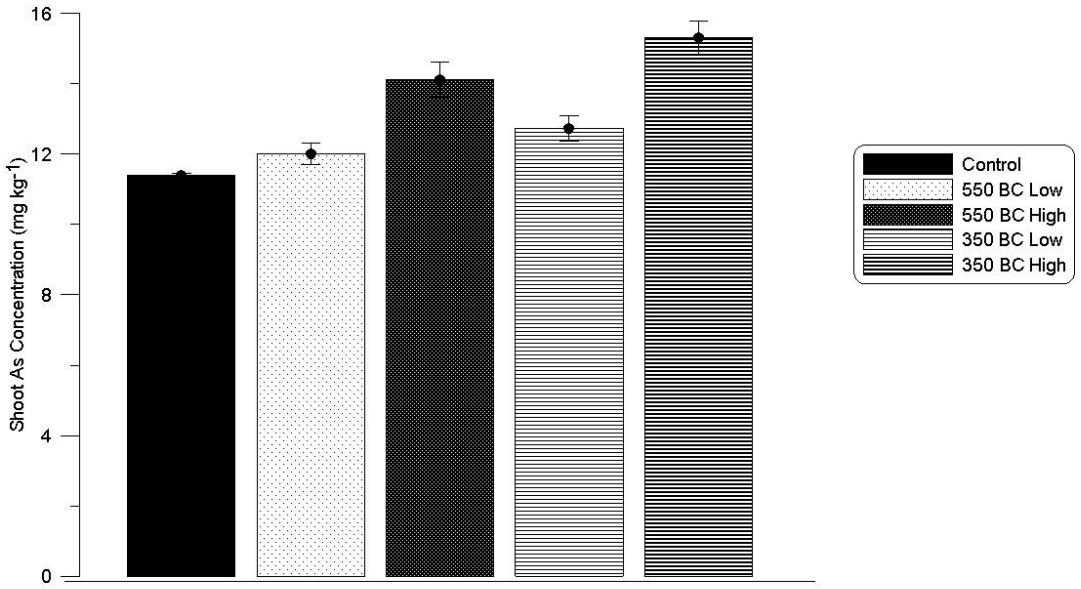

Figure 3. Total average arsenic concentration (mg kg^{-1}) in ryegrass shoot biomass as a function of biochar treatment (mean *n* = 3 ; ± s.e.).

CONCLUSION

We have shown that in a highly arsenic/organochlorine-contaminated soil microbial activity can be stimulated by the addition of biochar amendment and results in significant degradation of a number of organochlorines after 180 d. Isomers of the organochlorine hexachlorocyclohexane (HCH), particularly alpha-HCH and gamma-HCH (lindane), underwent 10-fold and 4-fold reductions in soil concentrations respectively (2.2 mg kg^{-1} and 0.4mg kg^{-1}) compared to the control (25 mg kg^{-1} and 1.6 mg kg^{-1} respectively). Amendment of soil with biochar also caused a significant reduction ($P<0.01$) in soil DDT levels. Further, biochar promoted an increase in arsenic phytoextraction and based on data extrapolation resulted in a decrease in remediation time of 92% under field conditions. Calculation by tonnage revealed that willow poles, acting as a high biomass crop under biochar amendment, has the potential to decrease remediation times by as much as ~60 years. These results provide evidence for the beneficial properties of a coupled biochar-phytoextraction system for the sustainable remediation of contaminated soil in New Zealand.

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