



Influence of biochars, compost and iron grit, alone and in combination, on copper solubility and phytotoxicity in a Cu-contaminated soil from a wood preservation site

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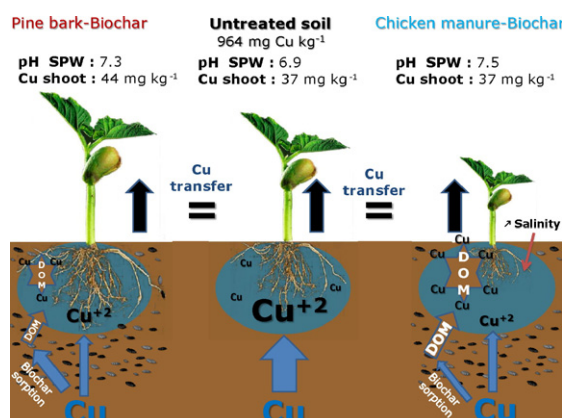
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HIGHLIGHTS

- The contaminated soil displayed high soluble Cu concentration.
- All tested amendments decreased the Cu^{2+} concentration in the soil pore water.
- Poultry manure-derived biochar increased Cu concentration in the soil pore water.
- Pine bark-derived biochar mixed with iron grit decreased Cu in the soil pore water.
- None of the tested amendments has significantly improved plant yields.

GRAPHICAL ABSTRACT



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ABSTRACT

Two biochars, a green waste compost and iron grit were used, alone and in combination, as amendment to improve soil properties and in situ stabilize Cu in a contaminated soil ($964 \text{ mg Cu kg}^{-1}$) from a wood preservation site. The pot experiment consisted in 9 soil treatments (% w/w): untreated Cu-contaminated soil (Unt); Unt soil amended respectively with compost (5%, C), iron grit (1%, Z), pine bark-derived biochar (1%, PB), poultry-manure-derived biochar (1%, AB), PB or AB + C (5%, PBC and ABC), and PB or AB + Z (1%, PBZ and ABZ). After a 3-month reaction period, the soil pore water (SPW) was sampled in potted soils and dwarf beans were grown for a 2-week period. In the SPW, all amendments decreased the Cu^{2+} concentration, but total Cu concentration increased in all AB-amended soils due to high dissolved organic matter (DOM) concentration. No treatment improved root and shoot DW yields, which even decreased in the ABC and ABZ treatments. The PBZ treatment decreased total Cu concentration in the SPW while reducing the gap with common values for root and shoot yields of dwarf bean plants. A field trial is underway before any recommendation for the PB-based treatments.

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1. Introduction

Since the 18th century, Cu-based salts are used as wood preservatives to control insects and fungi (Karjalainen et al., 2009). Long time use of Cu-based salts such as CuSO_4 and chromated copper arsenate (CCA) combined with washings of treated wood often results in soil Cu contamination (Bes and Mench, 2008). Copper in moderately and highly organic contaminated soils is present in less mobile and bioavailable forms, whereas in mineral soils, the labile fraction is often higher (Mench and Bes, 2009). Copper excess in topsoils can enhance its concentration in the labile soil pool (environmental availability) and in tissues of biological receptors (bioavailability) (Bolan et al., 2014). This can force plants to adapt their cellular Cu homeostasis (Ravet and Pilon, 2013), impact their growth (Cuypers et al., 2000; Bes et al., 2013; Kolbas et al., 2015) and select Cu-tolerant plant species and populations (Hego et al., 2015). It can also decrease soil biodiversity, e.g. abundance and species composition of earthworm, bacteria and fungi communities (Lagomarsino et al., 2011; Qiu et al., 2013; Mackie et al., 2015), and inhibit activity of hydrocarbon-degrading microorganisms thus impairing C and N cycles (Mackie et al., 2015). In addition, wood preservation sites are often characterized by unfavourable soil properties, e.g. lack of structure with low organic matter (OM) content, low nutrient availability and acidic pH (Mench and Bes, 2009; Bes et al., 2010; Hattab et al., 2014; Thaler and Humar, 2014).

In situ stabilization of contaminants through mineral and organic soil amendments is one of the feasible gentle remediation options (GRO) which can be implemented at contaminated sites (Kidd et al., 2015). This option aims at (1) improving soil biophysical and chemical properties such as OM and nutrient contents (2) reducing the pollutant linkages (here the combination of a source-pathway-receptor, Cundy et al., 2015) and (3) restoring the cascade of biological processes and functions which in turn promotes ecosystem services (Mench et al., 2010; Bolan et al., 2014). The soil amendments can lead to immobilize Cu in the solid phase through various reactions, i.e. sorption, precipitation, complexation, ion exchange and redox process, thereby decreasing Cu environmental (bio)availability (Kumpiene et al., 2008).

Biochars (biologically derived charcoal) are carbon-rich carbonized residues produced by waste biomass pyrolysis (thermal treatment) under high temperatures (450 to 650 °C) and mid to low oxygen (Lehmann, 2007; Ahmad et al., 2014). Amending soils with biochar has gained attention due to its ability to (1) improve soil fertility and plant yields (2) resist to chemical/biological degradation and thus serve as a long-term storage of carbon, (3) increase cation exchange capacity (CEC), pH, and water and nutrient retention, and (4) promote microbial communities able to degrade xenobiotics (Zhang et al., 2013). In addition, an increased number of studies reports the biochar ability to immobilize trace elements (TE), including Cu, and to reduce the phytotoxicity of TE-contaminated soils (Park et al., 2011; Luo et al., 2014). Biochar effects on Cu-contaminated soils depend on many parameters such as biochar properties (i.e. raw material, initial carbon content, pyrolysis temperature and sorption capacity) and characteristics of soils to be remediated (e.g. pH, soil texture, and OM content) (Park et al., 2011). Biochar made from oak, ash, sycamore and birch was the more effective treatment at reducing pore water Cu concentrations of a Cu mine in Cheshire, UK (Karami et al., 2011). Negatively-charged biochar surfaces sorb Cu, improve water supply, and ameliorate Cu toxicity in sandy soils (Buss et al., 2012). The Cu leaching was reduced following biochar addition in a $\text{Cu}(\text{NO}_3)_2$ -spiked soil (Bakshi et al., 2014). Water soluble Cu was decreased by hardwood-derived biochar at a gasworks site in Brighton, UK (Gomez-Eyles et al., 2011). Addition of a bamboo and

rice straw biochar resulted in 97% reductions of extractable Cu in a polycontaminated paddy field (Yang et al., 2016).

Conversely negative effects of biochar are reported (Buss et al., 2015). During the pyrolysis process, polycyclic aromatic hydrocarbons (PAHs), dioxins and furans are likely formed and conservative TE accumulate in the residual material. Usually, bioavailable PAH and TE concentrations in biochars are sufficiently low for not being considered as a threat to plants and the environment (Singh et al., 2010; Hale et al., 2012). However, depending on their concentrations, PAHs and TE are suspected to induce acute toxicity to various organisms (Rogovska et al., 2012; Oleszczuk et al., 2013). Uchimiya and Bannon (2013) reported Cu mobilization after inactivated plant biochar addition in a sandy soil induced by either metal ion-coordinating organic fractions or competition between dissolved organic matter (DOM) and metal ions for the sorption sites of biochar and soil components. Hardwood-derived biochar can enhance 30 times the Cu concentration in the soil pore water (SPW) due to increased dissolved organic carbon (DOC) in a soil contaminated by As, Cu, Zn and Cd, Kids Grove, Staffordshire, UK (Beesley et al., 2010). A hardwood biochar and a compost, alone and in combination, as soil amendment did not reduce the DTPA-extractable Cu fraction in a vineyard Cu contaminated soil but influenced the microbial community composition (Mackie et al., 2015). In degraded soils only amended with biochars, TE (i.e. As, Cu, and Pb) solubility can increase by co-mobilization with DOM. According to Beesley and Marmiroli (2011), the combination of amendments such as compost and iron oxides with biochar may be more suitable than biochar alone for the remediation and revegetation of contaminated land as it may promote TE immobilization and buffer nutrient depletion.

Compost inputs into depleted Cu-contaminated soil can (1) improve soil texture and structure, (2) promote microbial community functioning, (3) stimulate OM cycle and humification process, notably if the soil mesofauna is present or can colonize, (4) form immobilized complexes between humic acids and Cu, (5) increase nutrient status and water retention, and (6) change soil pH and CEC (Kumpiene et al., 2008). Its effects on Cu environmental bioavailability depend on the composted material, its microbial degradability (i.e. C/N ratio), the salt content, soil pH and Eh, and soil type (Beesley et al., 2010). Biochar-compost blends can increase total carbon, nitrogen and phosphorus in soils and stabilize soil aggregates, as well as stimulate microorganisms (Sizmur et al., 2011; Schulz et al., 2013). Compost and biochar mixtures can promote Cu sorption and reduce plant Cu content compared to biochar alone (Sizmur et al., 2011; Borchard et al., 2012).

Iron grit mainly consists of zerovalent Fe(0) (e.g. 97%) and some impurities (e.g. Mn 3%). Once in the soil, iron grit corrodes to form newly Fe/Mn oxo(hydro)oxides, which can sorb TE such as Cu (Tiberg et al., 2016). Such oxides can reduce the available fraction of metal(loid)s, notably in the root zone, and thus lower the pollutant linkages associated with their leaching, ecotoxicity, plant uptake and human exposure (Komárek et al., 2013). Single use of iron grit is usually insufficient to remediate Cu-contaminated soils. Its combination with other amendments, mainly organic, is recommended to enhance plant growth on these soils (Bes and Mench, 2008).

Information is scarce on the combined effect of amending a Cu-contaminated soil from a wood preservation site with biochar and either compost or iron grit. This study aimed at assessing the potential benefits and drawbacks posed by adding biochar derived from either animal or plant feedstocks, i.e. poultry manure and pine bark chips, compost and iron grit, alone and in combination, in a Cu-contaminated soil from a wood preservation site. The novelty of this study was to quantify the influence of these treatments on (1) Cu and nutrient mobility, sorption and/or leaching; (2) dwarf bean (*Phaseolus vulgaris* L.) yield; and (3)

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