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Compost and biochar interactions with copper immobilisation in copper-enriched vineyard soils

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ABSTRACT

Applications of Cu-based fungicides against downy mildew of grapevines have led to Cu accumulation in the topsoil of vineyards. In such soils, Cu may reach levels high enough to exert adverse effects on soil microorganisms, soil fauna and plant roots. This study aimed to test combinations of compost and biochar for their potential to decrease the bioavailability of Cu in Cu-enriched vineyard soils.

Grapevine plants (*Vitis vinifera* L. cv. Grüner Veltliner) were cultivated in soil columns equipped as microlysimeters during two vegetation periods under greenhouse conditions. The two experimental soils differed in pH (6.2 and 7.2, resp.), organic carbon (2.7 and 0.9%, resp.) and EDTA-Cu (97 and 198 mg kg^{-1}, resp.). Treatments differed in the mixing ratio of compost and biochar, feedstock for biochar and post-pyrolysis modification of biochar. Standard addition rates amounted to 4 kg additive m^{-2}.

Cu uptake into the grapevine shoots and leaves hardly responded to the different soil additive treatments. The roots buffered different Cu availability with increased Cu accumulation and largely prevented excessive translocation to aerial plant parts. The soil with lower pH and higher organic carbon content showed more vigorous shoot growth and higher leaf Cu concentrations than the soil of neutral pH in spite of lower EDTA-Cu concentrations of the soil. Soil analyses at the end of the experiment showed that the $CaCl_2$-extractable fraction of Cu was lower in the neutral soil (3% of EDTA-Cu) than in the more acidic soil richer in C_{org} (8%).

The novelty of this study is the inclusion of Cu speciation for investigating the effects of the soil additives. Differences between treatments were more pronounced for Cu^{2+} than for $CaCl_2$-extractable Cu. All tested additive treatments in the acidic soil showed clear reductions of Cu^{2+} compared to the control without additives whereas this effect was less expressed but still recognizable in the neutral soil. In the soil pore water the Cu concentrations showed a Cu-mobilizing effect of the additives in the neutral soil, a mostly not significant effect in the acidic soil and a clear decrease of the Cu^{2+} fraction that was more distinct in the acidic than in the neutral soil. Although the Cu^{2+} fraction that was successfully reduced by the tested additives usually constitutes only <1% of total Cu in soil, this fraction is ecotoxicologically more relevant than the prevailing organically bound fraction.

1. Introduction

Downy mildew (*Plasmopara viticola* Berk. & Curt. (Berl. and de Toni)) is a fungal disease that has spread in Europe since 1878 and that still is causing widespread leaf and fruit damages in grapevine (*Vitis vinifera* L.) if left untreated (Jermini et al., 2010). The first effective countermeasures were based on the discovery of a mixture of copper sulfate and lime that successfully prevented the leaf infection by *Plasmopara viticola* (Millardet, 1885). This

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suspension provided Cu^{2+}-ions that acted as enzymatic toxin for the germinating fungal spores (Weaver et al., 2010). The success story of copper sulfate as fungicide initially lead to high application rates of 8 up to 50 kg Cu ha^{-1} with the unavoidable side-effect of Cu accumulation in the top soil as Cu is mostly bound to mineral-associated soil fractions in the long-term, especially in old vineyards, and therefore is rather immobile (Brunetto et al., 2014). First warnings about the ecotoxicological risks of elevated Cu concentrations in the soil date back to the 1960ies (Delas, 1963), but only in the 1980ies and 1990ies reports about Cu accumulations in vineyards and orchards made the public aware of potential problems and the necessity to look for alternatives to Cu-based fungicides (Merry et al., 1983; Deluisa et al., 1996).

For organic agriculture up to now no satisfying replacements for Cu-fungicides are available. Therefore the deposition of Cu continues although at a much lower level (2–3 kg ha^{-1}) than the maximum application rates in the first half of the 20th century. In vineyards with Cu-concentrations of 100–300 mg kg^{-1} in the top soil these concentrations are less relevant for grapevines that are usually rooting much deeper (up to 5 m) and exclude excessive Cu uptake by the roots (Juang et al., 2012). However, soil microorganisms, soil fauna and annual soil cover crops with shallow rooting systems are more directly exposed to and impaired by the impacts of fungicide applications. Starting at concentrations of 60–100 mg Cu kg^{-1}, enzymatic activities of soil bacteria are reduced and earthworm reproduction and abundance are inhibited (Jänsch and Römbke, 2009; Mackie et al., 2012).

Cu existing at such high concentrations in extended acreages of vineyards can neither be removed by soil exchange nor by phytoextraction methods at reasonable costs and in a manageable time scale, even if Cu extraction is supported by specific microorganisms (Mackie et al., 2012). If Cu uptake by fast growing bioenergy crops was enhanced severalfold by various inorganic and organic soil amendments, Rinklebe and Shaheen (2015) report the example of a heavily contaminated floodplain soil where a significant bioremediation success still would take hundreds of years. Another option is the reduction of Cu bioavailability by *in-situ* methods which incorporate organic or inorganic additives with promising Cu sorption capacity into polluted soils. Organic soil amendments like biochar have a high specific surface area and functional groups that increase the sorption potential for cationic elements in soil like Cu (Hua et al., 2009; Karami et al., 2011; Trakal et al., 2011; Aran et al., 2016). Additionally, biochar amendments to agricultural soils may be beneficial for physical soil characteristics (Burrell et al., 2016) and for reducing nutrient losses (Bücker et al., 2016).

Freshly produced biochar originally has only few functional surface groups when produced under high temperatures (>500 °C). But as a consequence of atmospheric oxidation or microbial modification soon functional groups (carboxyl-, hydroxyl-, carbonyl-, phenolic groups) are attached that provide negative surface charges and high cation exchange capacity (Beesley and Marmiroli, 2011). Cationic trace elements can then be sorbed to biochar surfaces electrostatically or chemically, accompanied by a release of protons (Uchimiya et al., 2010). Although functional groups which remain on biochar surfaces after low temperature pyrolysis (<500 °C) can be modified during long-term storage in the soil, thereby releasing already sorbed elements, this effect is compensated by the continuous creation of new sorption sites and functional groups (Mukherjee et al., 2011). The formation of new oxygen-containing functional groups, especially carboxyl groups that are important for Cu-sorption (Uchimiya et al., 2012a), during ageing is a pH-dependent process that facilitates Cu-sorption at low pH but not at neutral pH (Guo et al., 2014). Additionally, the high pH of most biochars and mineral residues in the biochar facilitate precipitation of metals as phosphates or carbonates (Liang et al., 2014; Beesley et al., 2015), including the formation of copper carbonate (Rinklebe and Shaheen, 2015).

Dissolved organic carbon (DOC) can originate from soil organic matter but also from organic soil amendments like compost and biochar. In spite of the general recalcitrance of biochar against degradation in soil, a minor fraction of biochar carbon (about 3%; Wang et al., 2016) is a labile pool that may temporarily increase DOC forming complexes with metals and metalloids like Cu and As (Kloss et al., 2015). Biochar produced at lower pyrolysis temperature provides more DOC that may mobilize Cu whereas higher temperatures (700 °C) rather promote retention of Cu (Uchimiya et al., 2012b).

The use of combinations of biochar and compost as soil amendments has been suggested to have superior agronomic value than biochar alone (Schulz et al., 2013). The role of compost of such mixtures is to supply nutrients to plants which is an essential standard strategy in organic crop production (Quilty and Cattle, 2011) and also in organic grape production (Schmidt et al., 2014). Considering the potential problems with Cu-enriched vineyard top soil, such recommendations raise the question if either the mobilizing effect of DOC from compost additions or the sorption capacity of biochar will prevail when both components are incorporated into soils afflicted by the heritage of historic Cu-fungicide applications.

This study had the objective to analyze the Cu-immobilization potential of biochar in historically Cu-enriched vineyard soils when applied with or without compost. As innovative contribution to existing literature, the study should include Cu speciation to differentiate between the effects on total Cu concentrations in soil pore water and on Cu^{2+} which constitutes an ecologically important sub-fraction of Cu_{total} and extractable Cu. In the frame of this study two hypotheses were tested:

1. Organic soil amendments reduce Cu translocation from soil to plant tissues of grapevine (roots, stems, leaves)
2. Organic soil amendments reduce phytotoxic Cu^{2+} in soil pore water.

2. Material and methods

2.1. Experimental installation

Soil columns were installed in PVC pipes with a diameter of 0.2 m and a height of 0.5 m. Each container was filled with 15 kg of dry soil or soil-additive mixture. The basic characteristics of the two soils and the soil additives are listed in Table 1 and Table 2. The experimental soils were taken from two vineyards in traditional winegrowing regions in Styria (St. Stefan) and Lower Austria (Rossatz). The soils were selected according to their Cu concentrations (Table 1) which may appear low in comparison with contaminated mine tailings or polluted floodplain soils but which are high in comparison with average vineyard or field soils and which exceed the guide values for unrestricted agricultural use according to ÖNORM L 1075.

The different treatments consisted of varying amounts and mixing ratios (dry matter-based) of compost and biochar. The calculations of the additive addition rates were based on the assumption of the area-based application rate to an incorporation depth of 0.2 m in field experiments and a soil bulk density of 1.3 kg dm^{-3}. Details of the treatment-specific addition rates are indicated in Tables 3 and 4 The selection of the treatments was guided by the aim to differentiate between the roles of compost and biochar (different mixing ratios) and the effect of biochar carboxylation by two methods (citric acid and tartaric acid modification).