Chemosphere 162 (2016) 293–307

Contents lists available at ScienceDirect

Chemosphere

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

Review

Copper accumulation in vineyard soils: Rhizosphere processes and agronomic practices to limit its toxicity

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HIGHLIGHTS

- Speciation of Cu in soil solution is crucial to determine its toxicity to organisms.
- Root exudation is involved in both Cu exclusion and Cu accumulation in plants.
- Agronomic practices might either alleviate or exacerbate Cu toxicity

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
28 July 2016
Accepted 31 July 2016
Available online 16 August 2016

Handling Editor: X. Cao

Keywords:
Copper
Rhizosphere processes
Vineyard soils
Cu toxicity

ABSTRACT

Viticulture represents an important agricultural practice in many countries worldwide. Yet, the continuous use of fungicides has caused copper (Cu) accumulation in soils, which represent a major environmental and toxicological concern. Despite being an important micronutrient, Cu can be a potential toxicant at high concentrations since it may cause morphological, anatomical and physiological changes in plants, decreasing both food productivity and quality. Rhizosphere processes can, however, actively control the uptake and translocation of Cu in plants. In particular, root exudates affecting the chemical, physical and biological characteristics of the rhizosphere, might reduce the availability of Cu in the soil and hence its absorption. In addition, this review will aim at discussing the advantages and disadvantages of agronomic practices, such as liming, the use of pesticides, the application of organic matter, biochar and coal fly ashes, the inoculation with bacteria and/or mycorrhizal fungi and the intercropping, in alleviating Cu toxicity symptoms.

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http://dx.doi.org/10.1016/j.chemosphere.2016.07.104
0045-6535/

1. Introduction

Among the processed crops, which include all agricultural and food products that are derived from their respective primary commodities, wine is one of the most important in the world (FAOSTAT, 2012). The world viticulture regions are generally located in climatic areas that are, however, favourable to the occurrence of fungal diseases, including downy mildew (*Plasmopara viticola*). The regular use of copper (Cu)-based fungicides (e.g. Cu sulfate, Cu oxychloride) to protect grapevine plants from these pests has led to a long-term accumulation of Cu in vineyard soils (particularly in the upper layers), reaching concentrations that are far higher as compared to the trace amounts that are required for healthy plant growth (Pietrzak and McPhail, 2004) and, in some circumstances, even exceeding the limits imposed in the EU for agricultural soils (Komárek et al., 2010). Besides Cu-containing fungicidal and bactericidal sprays, substantial Cu addition to soils can occur from the addition of contaminated wastes (Liu et al., 2007) and/or mineral- and organic-fertilizers (Xiaorong et al., 2007), including organic residues (e.g. pig and poultry manure and organic composts, Brunetto et al., 2014; Couto et al., 2015). It should be emphasized that Cu is an essential element for plants and, by definition, it is necessary for an organism to function properly, since it plays key roles in several biochemical and physiological processes connected to plant growth and development (Yruela, 2005). Nonetheless, depending on the concentration and on the bioavailable fraction, Cu could also exert toxic effects on plants. In particular, when its bioavailable concentration is very high, the growth of plants (Ambrosini et al., 2015a) and their productivity could be severely impaired. For instance, in grapevine plants grown in acidic soils, Cu toxicity, besides affecting plants growth and productivity (Gupta and Aten, 1993), can also worsen the quality and the nutritional value of the products (Cambrollé et al., 2013; Juang et al., 2014; Komárek et al., 2010; Tanyolaç et al., 2007; Toselli et al., 2009). For this reason, the deeper understanding of Cu dynamics in soil, particularly considering the complexity of rhizosphere processes driving Cu acquisition mechanisms by plants, could represent a prerequisite for the development of agronomic strategies aimed at limiting soil Cu-availability. These aspects are even more relevant in relation to other common agricultural practices, such as herbicide applications for weed control in vineyards.

Therefore, this review will discuss the main Cu processes occurring at the soil-microbe-root interface (*i.e.* rhizosphere) that could play a role in the tolerance mechanisms adopted by plants when grown in soil characterized by high Cu availability. For this purpose, Cu fractions in soils, mechanisms of root Cu uptake and its allocation in shoot as well root exudation phenomenon will be discussed in relation to the processes underlying the agronomic practices commonly adopted, also considering the role that herbicides or their residues in the soil could exert. Strategies to improve agronomic practices aimed at mitigating Cu toxic effects will also be discussed.

2. Copper in the rhizosphere

It is well known that the Cu-available fraction for plants strongly depends on mineral and organic forms in the soil and on biogeochemical cycles, which the different Cu sources undergo. Moreover, in the rhizosphere these cycles are strongly influenced by the intensive interactions between roots and microorganisms, which, in turn, shape the mineral and organic Cu fractions. In addition, the amount of Cu absorbed by plants depends on both its availability in the rhizosphere and the functionality of the protein systems committed to the nutrient acquisition at root level and, then to the allocation into shoot tissues. In other words, Cu forms, which can be taken up, are closely dependent on the selectivity of those proteins, which mediate nutrients' transport across the plasma membranes.

2.1. Soil Cu forms and their biogeochemical cycles

Copper is a metallic element and its natural concentration in soil depends on its concentration in rocks. The average Cu concentration in soils registered worldwide ranges from 6 to 80 mg kg^{-1}. Soils with a Cu concentration lower than 8 mg kg^{-1} may because of the onset of Cu deficiency symptoms in crops (McBride, 1994).

The distribution of Cu between solid phase and soil solution depends on precipitation/dissolution, adsorption/desorption and redox reactions (Fig. 1). In the soil solution, Cu may be in free form as Cu^{2+} or, in most cases, complexed. The complexation may occur with either inorganic anionic binders or organic molecules. The formation of stable complexes in the soil solution can delay the adsorption of Cu with functional groups on the surface of reactive particles (Alleoni et al., 2005; Sparks, 2003). In the solid phase, Cu can be sorbed through mechanisms such as ion exchange (non-specific adsorption), specific adsorption and complexation with soil organic matter (Alloway, 1995; Sposito, 1989). Non-specific adsorption is weak and unstable. This type of adsorption weakly affects the availability of Cu. In this type of sorption, Cu can retain its internal hydration sphere and a high degree of rotational mobility on exchange sites (Alleoni et al., 2005; McBride, 1979). In specific adsorption on functional groups of inorganic particles, the metal partially or completely loses its hydration water forming an inner sphere complex with either OH^- or a H_2O molecule bound to a metal ion of the crystalline lattice on the surface of Fe, Mn and Al oxides, non-crystallized aluminosilicates and edges of clay minerals (Alleoni et al., 2005; Bradl, 2004; Ferreira et al., 2014).

The nature of Cu interactions with soil components has been