Journal of Environmental Management 92 (2011) 1849–1857

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Effect of spent mushroom substrate applied to vineyard soil on the behaviour of copper-based fungicide residues

E. Herrero-Hernández [a], M.S. Andrades [b], M.S. Rodríguez-Cruz [a], M.J. Sánchez-Martín [a,*]

[a] Instituto de Recursos Naturales y Agrobiología (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, Spain
[b] Departamento de Agricultura y Alimentación, Universidad de La Rioja, Madre de Dios 51, 26006 Logroño, Spain

ARTICLE INFO

Article history:
Received 29 July 2010
Received in revised form
1 February 2011
Accepted 8 March 2011
Available online 1 April 2011

Keywords:
Copper distribution
Vineyard soil
Spent mushroom substrate
Chemical forms

ABSTRACT

The effect of the addition of spent mushroom substrate (SMS) to the soil as an amendment on the distribution and/or fate of copper from a copper-based fungicide applied to a vineyard soil in La Rioja (N. Spain) was studied. The study was carried out on experimental plots amended or not with SMS at rates of 40 and 100 t ha^{-1}. The variation in total Cu content in the topsoil (0–10 cm) and in the soil profile (0–50 cm), and the distribution of Cu in different fractions of the topsoil were studied as a function of the dose of Cu added (5 and 10 kg ha^{-1}) and of the time elapsed since application (0–12 months). In addition, the changes in the chemical properties (solid organic carbon (OC), dissolved organic carbon (DOC) and pH) of the soils were studied. A greater capacity for Cu retention by the amended soils than by the unamended one was observed only when the fungicide was applied at the high dose. No effect of the amendment rate was noted on this retention capacity. The metal content in the topsoil decreased over time in step with the disappearance of the OC in the amended soil due to its oxidation, mineralization and/or leaching. This decrease in total Cu content was possibly due to the formation of soluble Cu complexes with the DOC, which facilitated its transport through the soil. A re-distribution of Cu in the different soil fractions was also observed over time, mainly from the organic to the residual fraction. The results obtained indicate that the increase in OC due to the application of SMS at the rates used does not lead to any significant increase in the persistence of Cu in the soil over time. Of greater interest would be the assessment of the risk for groundwater quality, owing to possible leaching of the fungicide enhanced by the SMS when SMS and Cu-based fungicides are jointly applied to vineyard soils.

1. Introduction

The use of organic and inorganic fungicides in vineyards is a common practice in many wine-producing countries (Komárek et al., 2010). Copper-based fungicides have been intensively used to control fungal vine diseases such as downy mildew, caused by *Plasmopara viticola*. They are even used for organic vine cultivation, where the application of organic fungicides is prohibited (EC regulation 473/2002). Although copper-based fungicides are effective for the control of fungal diseases, their long-term use can result in increased copper levels in surface soils with respect to natural background Cu concentrations (<30 mg kg^{-1}) (Adriano, 2001). Cu concentrations varying over a broad range have been detected in the surface horizons of vineyard soils in Europe (14–1280 mg kg^{-1}), Australia (6–249 mg kg^{-1}), and Brazil (37–3216 mg kg^{-1}) (Komárek et al., 2010; Wightwick et al., 2008). They depend on factors such as the parent soil material (Adriano, 2001), the age of the vineyard (Fernández-Calviño et al., 2008; Pietrzak and McPhail, 2004), the landform of the soil (terrace, plateau or plain) (Rusjan et al., 2007), and the influence of climate (Fernández-Calviño et al., 2009). Most published values exceed the warning and critical legislative limits (50 and 140 mg kg^{-1}, respectively) established in the EU for Cu concentrations in agricultural soils (Komárek et al., 2010). These data indicate that potential soil contamination could occur through the use of copper-based fungicides, although data on Cu mobility in soils and its availability to biota are also necessary for the assessment of its environmental impact (Ahumada et al., 2009; Brun et al., 1998; Flores-Vélez et al., 1996).

Increases in Cu content in soils occur as a result of its retention through mechanisms of specific adsorption, cation exchange, and the precipitation of new solid phases. Factors such as pH, clay mineral content, carbonates and organic matter (OM) content are important in this process (Arias et al., 2004; Komárek et al., 2009;

* Corresponding author. Tel.: +34 923 219 606; fax: +34 923 219 609.
E-mail address: mjesus.sanchez@irnasa.csic.es (M.J. Sánchez-Martín).

0301-4797/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jenvman.2011.03.011

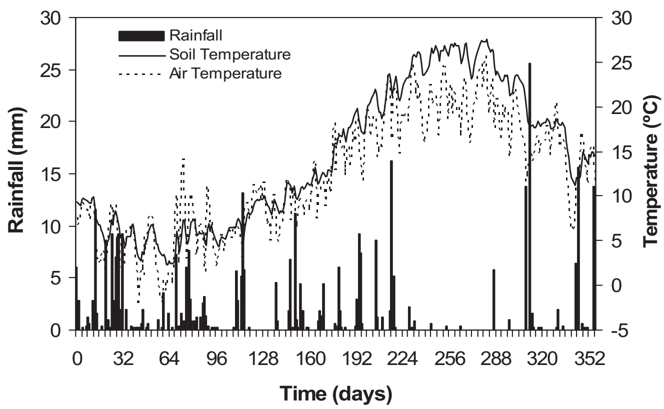

Fig. 1. Weather conditions at the site throughout the experiment.

Rodriguez-Rubio et al., 2003). The adsorption of Cu by solid OM through complexation, especially with humic and fulvic acids (inner-sphere complexes), is one of the most important mechanisms involved in the retention of this element by the soil (Boudesocque et al., 2007). However, dissolved OM (DOM) may also form soluble complexes with Cu and thus increase its mobility, especially at alkaline pH (Doelsch et al., 2010; Stevenson, 1994; Temminghoff et al., 1997), and its possible leaching/transport to groundwater and surface waters.

Vine cultivation is the main agricultural activity in the region of La Rioja (N. Spain). Its importance lies in the considerable economic activity it generates (D.O. Ca. Rioja, 2009). Some of these soils have low OM contents, and attempts are currently being made to improve their fertility through the application of organic amendments. Spent mushroom substrate (SMS) is the pasteurized organic material remaining after a mushroom crop has been harvested. In the La Rioja region, this spent substrate is produced in large amounts (>183,000 tons in 2005) and for many years SMS was disposed of in landfills. However, this method has recently become an environmental issue and industries are now proposing to reuse these materials as soil amendments. The addition of such residues to vineyard soils may be beneficial because they are rich in nutrients and OM (Paredes et al., 2009). However, the application of SMS involves the addition of the solid and liquid OM from these residues to the soil, which could affect Cu dynamics when it is applied as a fungicide in vineyard soils.

The high affinity of Cu for OM has led many authors to study the influence of organic amendments such as sewage sludge, urban compost, biochar, greenwaste compost or agro-industrial byproducts in the fate of Cu in the soil, since both the solid OM from these organic residues (Ramos, 2006; Vega et al., 2009; Xiao and Huang, 2009) and their dissolved fractions, DOM (Ashworth and Alloway, 2004; Gondar and Bernal, 2009; Beesley et al., 2010) may modify the sorption and/or mobility of Cu in soils. However, only a few authors have included SMS among the organic residues studied (van Herwijnen et al., 2007). Moreover, these studies were generally conducted in the laboratory, and there are far fewer studies that have explored the situation under field conditions (Besnard et al., 2001). Accordingly, additional research is needed because results in laboratory systems may differ from those obtained under field conditions.

The objective of this work has been to study the effect of adding SMS used as an amendment on the distribution and/or fate of Cu from a Cu-based fungicide applied to a vineyard soil. The study was carried out at experimental field plots, determining over one year: 1) the variation in the parameters of the unamended and amended soils (pH, OC, and DOC) that can modify the behaviour of Cu; 2) the changes in the total Cu content in the topsoil and in the soil profile to assess its possible accumulation and/or transfer to groundwater, and 3) the re-distribution of Cu in the different fractions of the topsoil as estimated by a sequential extraction procedure to determine the evolution of its potential (bio)-availability for plants and other organisms. Two rates of SMS (40 and 100 t ha^{-1}) and two doses of a Cu-based fungicide (5 and 10 kg ha^{-1}) were used to approximate the results of the experiments conducted to the agricultural conditions usually employed.

2. Materials and methods

2.1. Site description and experimental design

A field experiment was conducted in a vineyard soil located in Sajazarra (SA), La Rioja, Spain, (42°35′0″N latitude and 2°57′0″W longitude). Sajazarra lies at an altitude of 500 m above sea level, with a temperate climate and gentle topography. Experimentation was conducted in a sandy clay loam soil developed on calcareous sandstones and classified as Typic Calcixerept according to the Soil Survey Staff (2006).

An experimental layout of randomized complete blocks was designed with six treatments (unamended and amended soils at two rates of SMS treated with two doses of Cu) and three replicates per treatment (18 plots of 1.50 × 3.90 m). Prior to soil amendment, the soil was tilled using a field cultivator. Unamended vineyard soil and the same soil amended with SMS at rates of 40 t ha^{-1} (SA-40) or 100 t ha^{-1} (SA-100) (dry weight) were prepared on 10 November 2008. SMS was manually mixed with the topsoil (0–10 cm) in each plot. Three more plots (unamended, and amended with low and high rates of SMS) did not receive Cu application and were used as untreated control SA soils. Solutions of Cu at two doses (5 and 10 kg ha^{-1}) corresponding to the recommended dose and twice this dose were prepared from the commercial formulation Cuprosan 500 (50% w/w of Cu as copper oxychloride). They were applied to the plots by surface soil spraying the day after soil was amended using a manual backpack sprayer. Thus, nine of the plots were treated with the low dose and the other nine plots were treated with the high dose of the Cu-based fungicide. The plots did not receive any other treatment until the experiment was completed (November 2009).

Weather conditions (precipitation and soil and air temperature) were monitored at the site throughout the experiment (Fig. 1). The data recorded gave an annual mean temperature for the air of 12 °C

Table 1
Selected properties of soil used.

Depth (cm)	Soil texture	pH	OC g kg^{-1}	N g kg^{-1}	$CaCO_3$ g kg^{-1}	Sand g kg^{-1}	Silt g kg^{-1}	Clay g kg^{-1}	Total Cu mg kg^{-1}
0–10	Sandy loam	7.7	13.1	1.3	295	607	202	171	25.8 ± 2.29
10–20	Sandy loam	7.8	12.9	1.3	292	626	183	191	16.3 ± 0.43
20–30	Sandy loam	7.8	12.1	1.3	296	641	214	145	18.4 ± 1.15
30–40	Sandy loam	7.8	10.9	1.2	305	636	230	134	10.9 ± 2.24
40–50	Sandy clay loam	7.9	8.4	0.9	436	633	157	210	6.60 ± 3.16