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Effect of different rates of spent mushroom substrate on the dissipation and bioavailability of cymoxanil and tebuconazole in an agricultural soil

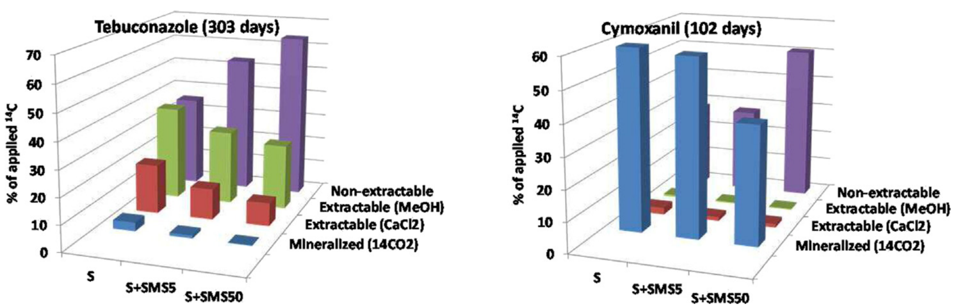
Alba Álvarez-Martín, María Jesús Sánchez-Martín, Eva Pose-Juan, María Sonia Rodríguez-Cruz *

Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), Cordel de Merinas 40-52, 37008 Salamanca, Spain

HIGHLIGHTS

- Fungicide dissipation rate was higher in the amended soil than in the unamended one.
- Dissipation occurred in the amended soil due to the formation of bound residues.
- Bound residues increased with incubation time for tebuconazole.
- An increasing fraction of bound cymoxanil was bioavailable for mineralization.
- Soil dehydrogenase activity was affected by SMS application and incubation time.

GRAPHICAL ABSTRACT



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ABSTRACT

Physicochemical methods to immobilize pesticides in vulnerable soils are currently being developed to prevent water contamination. Some of these methods include the use of different organic residues to modify soils because they could limit the transport of pesticides and/or facilitate their dissipation. Spent mushroom substrate (SMS) may be used for these purposes. Accordingly a study was conducted under laboratory conditions to know the dissipation and bioavailability of the fungicides cymoxanil and tebuconazole over time in a vineyard soil amended with two rates of spent mushroom substrate (SMS) (5% and 50% (*w/w*)), selected to prevent the diffuse or point pollution of soil. The dissipation of cymoxanil was more rapid than that of tebuconazole in the different soils studied. The dissipation rate was higher in the amended soil than in the unamended one for both compounds, while no significant differences were observed between the amended soils in either case. An apparent dissipation occurred in the amended soil due to the formation of non-extractable residues. Bound residues increased with incubation time for tebuconazole, although a proportion of this fungicide was bioavailable after 303 days. The major proportion of cymoxanil was tightly bound to the amended soil from the start, although an increasing fraction of bound fungicide was bioavailable for mineralization. Soil dehydrogenase activity was significantly affected by SMS application and incubation time; however, it was not significantly modified by fungicide application. The significance of this research suggests that SMS applied at a low or high rate to agricultural soil can be used to prevent both the diffuse or point pollution of soil through the formation of non-extractable residues, although more research is needed to discover the time that fungicides remain adsorbed into the soil decreasing either bioavailability (tebuconazole) or mineralization (cymoxanil) in SMS-amended soils.

1. Introduction

Pesticide residues are now being detected in waters and soils in different areas around the world due to the intensive application of these

* Corresponding author.
E-mail address: msonia.rodriguez@irnasa.csic.es (M.S. Rodríguez-Cruz).

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compounds in agriculture (Rabiet et al., 2010; Herrero-Hernández et al., 2013; Pose-Juan et al., 2015a). Consequently, soil and water contamination is a growing concern, as these compounds could be toxic and cause health and environmental problems. European and Spanish legislation (Directive 2009/128/EC and Royal Decree 1311/2012, respectively) on this matter advises introducing specific measures to prevent soil contamination and limit the transport of contaminants through water resources, especially groundwater, to reduce the risks and impacts of pesticide use (EC, 2009; MPR, 2012).

Pesticide application and management in agriculture may cause the diffuse and point pollution of soil and water bodies. Diffuse sources of soil pollution include spray drift, run-off, leaching, etc., whereas point sources include farmyard activities, direct contamination, and overspray, among others (Carter, 2000; Balderacchi et al., 2013). Physicochemical methods to immobilize pesticides in vulnerable soils are currently being developed to prevent water contamination. Some of these methods include the use of different organic residues to modify soils, as their high organic matter (OM) content could limit the transport of pesticides from soil to groundwater and/or facilitate their dissipation, avoiding the diffuse or point pollution of waters due to the intensive use of these compounds (Rodríguez-Cruz et al., 2012; Álvarez-Martín et al., 2016).

Spent mushroom substrate (SMS) is an organic residue from mushroom production. In 2012, Spain was the fourth largest producer of mushrooms in Europe, with an output of 146,000 t (FAOSTAT, 2015). Mushroom production generates 170,000 t of SMS per year (MAGRAMA, 2015). SMS has a high content of OM and nutrients, and can be used as an amendment to improve soil properties and quality (Brunetti et al., 2009; Peregrina et al., 2012). Furthermore, due to its high OM content, SMS could be a useful tool to control the behavior of pesticides in soils modified with this residue. Previous works have studied the use of SMS to immobilize pesticides in amended soils (Marín-Benito et al. 2012a) or in biobeds (Karanasios et al., 2010; Gao et al., 2015), as well as its effect for controlling the leaching or biodegradation of pesticides (Kadian et al., 2012) and PAHs (García-Delgado et al. 2013).

Cymoxanil and tebuconazole are two fungicides with very different properties that are widely used on vineyards. Previous studies have reported the dissipation of some fungicides in a vineyard soil amended with fresh and re-composted SMS (Marín-Benito et al., 2012b). Furthermore, Herrero-Hernández et al. (2011) have studied the dissipation of tebuconazole in a vineyard soil amended with SMS under field conditions. Both studies highlight the effect of SMS characteristics on the dissipation of fungicides. However, the effect of SMS on the bioavailability and dissipation mechanism of fungicides in amended soil when SMS is applied at two contrasting rates in order to predict their persistence in the soil has not been reported. SMS contrasting rates could be used to prevent diffuse or point soil pollution and results could provide relevant knowledge about these processes. The dissipation of pesticides in soils amended with different rates of other organic residues has hardly been studied (Karanasios et al., 2010), and, in general, a very low range of amendment rates was applied to the soil in these experiments (López-Piñeiro et al., 2013; Sopeña and Bending, 2013).

Cymoxanil [1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea] is an aliphatic nitrogen fungicide that is effective against grape downy mildew. The dissipation of this fungicide has scarcely been studied (Liu et al., 2014). It is considered a non-persistent compound that degrades rapidly, with a time to 50% degradation (DT_{50}) value of 1.2 days in soils under laboratory aerobic conditions (PPDB, 2015). Tebuconazole [(*RS*)-1-*p*-chlorophenyl-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol] belongs to the fungicide group of triazoles, which is used to control smut and bunt diseases of cereals and other field crops and powdery mildew in grapevines. Tebuconazole is a hydrophobic fungicide with low solubility in water, and it degrades slowly in soil ($DT_{50} > 365$ days; very persistent), being slightly mobile (Kfoc = 769) (PPDB, 2015). Tebuconazole dissipation has been studied mainly in unamended soils (Strickland et al., 2004; Potter et al., 2005; EFSA, 2008b, Fenoll et al., 2011), but there is little information on its dissipation in amended soils (Herrero-Hernández et al., 2011). Tebuconazole and cymoxanil have been detected at concentrations of up to 3.2 μg L^{-1} and 0.9 μg L^{-1} in surface and ground waters, respectively, from La Rioja region (Spain), exceeding the EU's 0.1 μg L^{-1} limit (Herrero-Hernández et al. 2013).

The bioavailability of pesticides in soils and the dissipation mechanism from a mass balance including aqueous and organic extractable fractions and mineralized and non-extractable fractions have been studied in recent years under different environmental conditions and agricultural practices (Mamy et al., 2005, Alonso et al., 2015). However, as far as we know, there are no studies on amended soils under laboratory conditions for cymoxanil and tebuconazole.

The aim of this paper was to study the impact that the SMS applied to soil at two different rates (5% and 50% on a dry weight basis) had on the bioavailability and dissipation mechanism of two fungicides with very different characteristics, namely, tebuconazole and cymoxanil. Studies were therefore carried out on dissipation kinetics (i) and mass balance (ii). Furthermore, soil dehydrogenase activity was assessed (iii) as a soil biochemical parameter to evaluate the impact of organic amendment and fungicides on soil microbial communities, and its possible effect on their dissipation (Muñoz-Leoz et al., 2012; Pose-Juan et al., 2015b). Our findings support the development of strategies for optimizing the dissipation of these fungicides in amended soils in order to restrict the contamination of water by these compounds.

2. Materials and methods

2.1. Pesticides and reagents

Unlabeled analytical standards of tebuconazole PESTANAL® and cymoxanil PESTANAL® (>99% purity) were supplied by Sigma-Aldrich Química S.L. (Madrid, Spain). Labeled [triazole-U-^{14}C]-tebuconazole and [acetyl 2-^{14}C]-cymoxanil (specific activities of 4.72 and 10.08 MBq mg^{-1} and 98.06% and 97.79% purities, respectively) were supplied by IZOTOP Co. Ltd. (Budapest, Hungary). The characteristics of the fungicides are included in Table 1 (PPDB, 2015).

HPLC grade acetonitrile and chloroform anhydrous (>99% purity) were supplied by VWR International Eurolab (Spain). 2,3,5-Triphenyltetrazolium chloride (TTC) and 2,3,5-triphenylformazan (TPF) were supplied by Sigma-Aldrich Química S.L. (Madrid, Spain).

2.2. Organic amendment

Spent mushroom substrate (SMS) from *Agaricus bisporus* cultivation is a pasteurized mixture of wheat straw, poultry manure, urea, and gypsum. This residue was supplied by Sustratos de La Rioja S.L. (Pradejón, Spain). The characteristics of SMS were determined in air-dried samples. The pH was determined in a residue/water suspension (1/2.5 *w*/*v* ratio). Organic carbon (OC) content was determined by oxidation (Walkley–Black method). Dissolved organic carbon (DOC) was determined in a suspension of residue in Milli-Q ultrapure water (1/100 *w*/*v* ratio), as described by Marín-Benito et al. (2012b). Total N content was determined according to the Kjeldahl method. The organic amendment applied had the following characteristics (on a percentage dry weight basis): pH 6.97, ash content 33.6%, OC content 24.5%, DOC content 1.91%, N content 1.75% and C/N 13.9. Moisture content was 64.5%.

2.3. Unamended and amended soil characterization

A soil sample (S) was collected from the surface horizon (0–30 cm) of a vineyard located in Sajazarra (La Rioja, Spain). The soil was sieved (<2 mm), and the characteristics were determined by standard analytical methods (MAPA, 1986), and they are included in Table 2. The pH