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Leaching of two fungicides in spent mushroom substrate amended soil: Influence of amendment rate, fungicide ageing and flow condition

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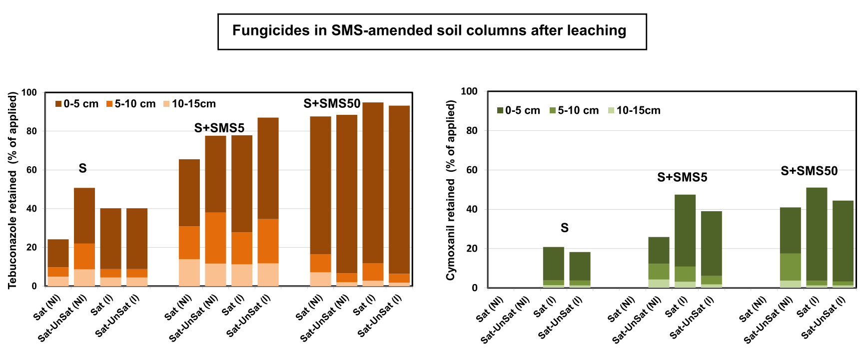
HIGHLIGHTS

- Influence of different factors on the leaching of fungicides in a soil was studied.
- Soil amendment decreased leaching of tebuconazole under different flow conditions.
- Leaching of cymoxanil decreased in amended soil under saturated-unsaturated flow.
- Ageing favours retention decreasing tebuconazole leaching or cymoxanil mineralization.
- Leaching is important when organic amendment is used to prevent water contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

A study has been conducted on the leaching of two fungicides, tebuconazole and cymoxanil, in a soil amended with spent mushroom substrate (SMS), with an evaluation of how different factors influence this process. The objective was based on the potential use of SMS as a biosorbent for immobilizing pesticides in vulnerable soils, and the need to know how it could affect the subsequent transport of these retained compounds. Breakthrough curves (BTCs) for ^{14}C-fungicides, non-incubated and incubated over 30 days, were obtained in columns packed with an unamended soil (S), and this soil amended with SMS at rates of 5% (S + SMS5) and 50% (S + SMS50) under saturated and saturated-unsaturated flows. The highest leaching of tebuconazole (>50% of the total ^{14}C added) was found in S when a saturated water flow was applied to the column, but the percentage of leached fungicide decreased when a saturated-unsaturated flow was applied in both SMS-amended soils. Also a significant decrease in leaching was observed for tebuconazole after incubation in the column, especially in S + SMS50 when both flows were applied. Furthermore, cymoxanil leaching was complete in S and S + SMS when a saturated flow was applied, and maximum peak concentrations were reached at 1 pore volume (PV), although BTCs showed peaks with lower concentrations in S + SMS. The amounts of cymoxanil retained only increased in S + SMS when a saturated-unsaturated flow was applied. A more relevant effect of SMS for reducing the leaching of fungicide was observed when cymoxanil was previously incubated in the column, although mineralization was enhanced in this case. These results are of interest for extending SMS application on the control of the leaching of fungicides with different physicochemical characteristics after different ageing times in the soil and water flow conditions applied.

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1. Introduction

The application of fungicides is usually intensive in different crops, and the presence of these compounds and their residues has frequently been detected in recent years in waters (Herrero-Hernández et al., 2016; Papadakis et al., 2015; Reilly et al., 2012) and soils (Bermúdez-Couso et al., 2007; Pose-Juan et al., 2015). Therefore, new tools need to be developed to avoid pesticides entering groundwater.

Only strong adsorption (binding) would be an efficient technique for preventing diffuse and/or point water pollution. Because of this, the use of low-cost adsorbent materials for these purposes has recently led researchers to explore the adsorption capacity of organic wastes (Gupta et al., 2009; Kurniawan et al., 2006). Although these wastes are expected to have less adsorption capacity than synthetic adsorbents, their low cost makes them competitive alternatives (Kyzas and Kostoglou, 2014). Some of these cheap biomaterials are sourced from agricultural activities or from industrial activities. They are characterized by a high organic carbon (OC) content and they are used simultaneously both as organic soil amendments to increase agricultural productivity (Courtney and Mullen, 2008; Udom et al., 2016) and as adsorbents of organic contaminants in soils, considering that OC is one of the most important soil factors influencing the adsorption process (Tran et al., 2015; Zolgharnein et al., 2011). The use of different organic residues with the potential to increase the adsorption of pesticides by soils has been reported in the literature (Ahmad et al., 2014; Marín-Benito et al., 2012; Rodríguez-Cruz et al., 2012).

However, adsorption is not the only process controlling the future behavior of pesticides in soils. An understanding of the influence that the organic amendments have on the leaching of adsorbed pesticides in the soil profile is required, as it has been less explored than other processes. Investigations in this direction have frequently involved columns packed with soil after the application of organic amendments such as sewage sludge, grape marc or SMS (Marín-Benito et al., 2013), winery vermicompost (Fernández-Bayo et al., 2015), agro-industrial and composted organic wastes (Fenoll et al., 2015), olive mill waste (Lopez-Piñeiro et al., 2013), biochar (Cabrera et al., 2011; Khorram et al., 2015; Larsbo et al., 2013) or green compost (Kodesova et al., 2012). The leaching of herbicides in general has been addressed in these works, although few have included fungicides. These studies have reported decreasing leaching of pesticides in soils by the effect of organic amendments, although they have usually been conducted under similar flow conditions (saturated or saturated-unsaturated) and ageing state of the pesticide in the amended soil.

Leaching of fungicides under changing conditions could be of interest because these factors together with the characteristics of pesticides determine, to a greater or lesser extent, the mobility of these compounds and the possible contamination of groundwater. In addition, the study of fungicides leaching under these flow conditions is closer to real field conditions than unchangeable flow conditions.

Tebuconazole and cymoxanil are two fungicides that are widely used and are effective against various foliar diseases in grapes, cereals and other field crops. Both fungicides have been approved for use in most European countries, with an expiry date of 2019. They are non-polar (tebuconazole) and polar compounds (cymoxanil) with different chemical structures and properties, but a similar threshold of toxicological concern (high class III) (PPDB, 2015). Tebuconazole is a synthetic triazole, and it is considered a moderate-persistent fungicide with a moderate GUS index (2.85). Cymoxanil is a synthetic cyanoacetamide oxime compound, and it is considered a non-persistent fungicide with a low GUS index (0.34).

Both fungicides enter the soil after their application to plants, and in areas of intense fungicide use in Spain they have been detected in surface and ground waters in higher concentrations than those permitted by EU legislation (0.1 μg L^{-1}) (Herrero-Hernández et al., 2013, 2016), as well as in other areas of the world (Battaglin et al., 2011; De Gerónimo et al., 2014; Montagner et al., 2014). These results provided support for the studies on the immobilization and dissipation of both fungicides in soil amended with the organic SMS residue considered by Álvarez-Martín et al. (2016a and 2016b) for proposing a strategy to prevent water contamination by these compounds. A range of SMS doses were used in these studies, and an increase in the adsorption coefficients of up to >20 times (tebuconazole) or >40 times (cymoxanil) was obtained for soils amended with SMS at rates between 2% and 75%. On the other hand, the dissipation of tebuconazole and cymoxanil in SMS-amended soils revealed that SMS reduces the extractable fraction of fungicides through the formation of non-extractable residues. Although the immobilization of these compounds may be the first step to avoid water contamination, other processes such as fungicide leaching should be explored to investigate the time that fungicides remain adsorbed, decreasing their potential for biodegradation and/or their bioavailability in SMS-amended soils.

Accordingly, the aim of this work was to study the leaching of tebuconazole and cymoxanil in an unamended vineyard soil and in one amended with SMS. The leaching of both fungicides was carried out using packed soil columns and to gain a better understanding of the effect of the proposed soil amendment strategy the following factors were evaluated: i) the rate of SMS applied to the soil, with a low rate (5%) and a high rate (50%) being applied to simulate the application of SMS as a soil amendment or as a barrier; ii) the water flow regime applied; a similar water volume was applied under saturated or steady flow or under intermittent saturated-unsaturated flow; and iii) the incubation (or ageing) time of the fungicide in the soil (1 and 30 days) prior to leaching. The influence of these factors jointly evaluated (adsorbent, water flow regime and ageing of fungicide) on the mobility of the fungicides tebuconazole and cymoxanil, with different characteristics, has been not reported to our knowledge.

2. Materials and methods

2.1. Chemicals

The fungicides tebuconazole and cymoxanil were used as unlabeled and labeled compounds. The unlabeled compounds (analytical standards of PESTANAL purity >99%) were supplied by Sigma-Aldrich Química S.A. (Madrid, Spain), and the labeled compounds were supplied by IZOTOP Co., Ltd., (Budapest, Hungary). [Triazole-U-^{14}C]-tebuconazole had a specific activity of 4.72 MBq/mg, and a chemical and radiochemical purity of 98% and 95%, respectively, and [acetyl-2-^{14}C]-cymoxanil had a specific activity of 10.08 MBq/mg, and both chemical and radiochemical purity of 98%.

Table 1 shows their physicochemical properties and environmental fate parameters (PPDB, 2015). Tebuconazole is classified as non-polar and immobile with low water solubility (36 mg L^{-1}), while cymoxanil is polar and mobile with high water solubility (780 mg L^{-1}), according to the classification of non-polar when the log K_{ow} value is >3.0, and as mobile when the log K_{oc} is <2.5 (Delle Site, 2001).

2.2. Soil and amendment

SMS from *Agaricus bisporus* cultivation was supplied by Sustratos de La Rioja S.L. (Pradejón, Spain). Its physicochemical characteristics, as described by Marín-Benito et al. (2012), are pH 6.97, ash content 33.6%, OC content 24.5%, dissolved organic carbon (DOC) content 1.91%, and moisture content 64.5%.

A soil sample was collected from the surface horizon (0–30 cm) in a vineyard located in Sajazarra (42°35′18″N, 2°57′41″W) in Spain's La Rioja region. The soil was air-dried and sieved (<2 mm) to determine its characteristics using standard analytical methods (Sparks, 1996). Soil texture was classified as sandy clay loam (67.0% sand, 11.9% silt, 21.1% clay and 51.0% carbonate content). The soil was amended with SMS at 5% and 50% (w/w) on a dry weight basis. The pH, OC and DOC content were 7.52, 0.67% and <0.01% (unamended soil, S), 7.26, 1.73%