Ecotoxicology and Environmental Safety 74 (2011) 1480–1488

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Field-scale dissipation of tebuconazole in a vineyard soil amended with spent mushroom substrate and its potential environmental impact

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ARTICLE INFO

Article history:
Received 23 September 2010
Received in revised form
12 April 2011
Accepted 16 April 2011
Available online 2 May 2011

Keywords:
Tebuconazole
Vineyard soil
Spent mushroom substrate
Dissipation
Soil dehydrogenase activity

ABSTRACT

The persistence, mobility and degradation of tebuconazole were assessed under field conditions in a sandy clay loam soil amended with spent mushroom substrate (SMS) at two rates. The aim was to evaluate the environmental impact of the simultaneous application of SMS and fungicide in a vineyard soil. SMS is the pasteurized and composted organic material remaining after a crop of mushroom is produced. SMS is generated in increasing amounts in La Rioja region (Spain), and could be used as soil amendment in vineyard soils, where fungicides are also applied in large amounts. The study was carried out in 18 experimental plots (6 treatments and 3 replicates per treatment) over one year. Laboratory experiments were also conducted to verify the changes over time in the adsorption of fungicide by soils and in soil dehydrogenase activity caused by the fungicide and/or SMS. Tebuconazole dissipation followed biphasic kinetics with a rapid dissipation phase, followed by a slow dissipation phase. Half-life (DT50) values ranged from 8.2 to 12.4 days, with lower DT50 for amended soils when compared to the non-amended controls. The distribution of tebuconazole through the soil profile (0–50 cm) determined at 124, 209 and 355 days after its application indicated the higher mobility of fungicide to deeper soil layers in amended soils revealing the influence of solid and dissolved organic matter from SMS in this process. Tebuconazole might be available for biodegradation although over time only chemical or photochemical degradation was evident in surface soils. The results obtained highlight the interest of field and laboratory data to design rational applications of SMS and fungicide when they are jointly applied to prevent the possible risk of water contamination.

1. Introduction

Tebuconazole ((*RS*)-1-p-chlorophenyl-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl) pentan-3-ol) is a systemic fungicide, which is effective against various diseases affecting cereals and maize and controls numerous pathogens in various crops including grapevines and vegetable crops (Fenoll et al., 2009; Rial-Otero et al., 2005). It is used on grapevines to combat powdery mildew fungi (*Uncinula necator*). Tebuconazole is persistent in soils and presents low to moderate mobility, thereby posing a low risk of groundwater contamination (EFSA, 2008). However, tebuconazole has been detected in streams, wastewaters and lakes at concentrations of up to 9.1 $\mu g\,L^{-1}$ (Berenzen et al., 2005; Kahle et al., 2008), which exceeds the EU's 0.1 $\mu g\,L^{-1}$ limit, and hence the fungicide poses a risk of runoff into river basins and streams. Tebuconazole is highly adsorbed by soils and mainly concentrated in the topsoil layer. Tebuconazole degraded slowly in soil in laboratory studies, but under field conditions the compound degraded much more rapidly (EFSA, 2008). Its degradation is influenced by the organic carbon (OC) content because it has a high affinity for soil organic matter (OM). Low OC content contributes to decreased adsorption and therefore encourages the microbial degradation of the fungicide. Several authors have studied the degradation of this fungicide in soils under laboratory conditions (Bending et al., 2007; Potter et al., 2005; Strickland et al., 2004; White et al., 2010), but the dissipation of tebuconazole under field conditions has scarcely been studied and no published data are currently available on the extent and rate at which this compound degrades in soil amended with organic residues.

Organic residues are commonly added to soil through agricultural practices. Pesticides are frequently applied jointly with amendments or sequentially during the crop growing season. This practice may give rise to a potential interaction between pesticide and amendment, and the environmental fate and behavior of pesticides in soil can be modified (Briceño et al., 2007). Amendments may increase pesticide persistence in the soil, which has the potential to

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doi:10.1016/j.ecoenv.2011.04.023

increase runoff and leaching risks. Some studies have suggested that the addition of amendments to soil might also lead to an increase in pesticide adsorption (Dolaptsoglou et al., 2009). Most of the studies researching the effect of organic amendments on the adsorption, mobility and degradation of pesticides in soils have been conducted under laboratory conditions (Kandian et al., 2008; Marín-Benito et al., 2009a, 2009b; Wang et al., 2009). Beulke et al. (2005) studied whether the degradation of pesticides in simple laboratory systems differed from that in the field, and how some of the simplifications inherent to laboratory studies present serious shortcomings. Some authors have indicated that the extension of laboratory-derived kinetic data to field settings should be addressed with caution (Potter et al., 2005). In general, dissipation field studies are scarce (Guo et al., 2010; Laabs et al., 2000), and only a few studies have examined the influence of different organic amendments on pesticide dissipation (Cabrera et al., 2009; Dolaptsoglou et al., 2009). Accordingly, additional research is needed to investigate the effect of organic amendments on pesticide dissipation in soils over time under field conditions.

In La Rioja region (NW Spain), mushroom production is the second major activity after vineyard farming, generating large amounts of spent mushroom substrate (SMS) (Martín et al., 2009). SMS is the pasteurized and composted organic material remaining after a crop of mushroom is produced. Mushroom farming is seeking environmental, agricultural and industrial uses for the SMS generated on the farm in increasing quantities (Wuest et al., 1995). SMS could be exploited as a soil fertilizer and an amendment to increase the OM content of vineyard soils, which is generally low. Fungicides are applied in large amounts in vineyards, and their behavior in vineyard soils amended with SMS could be modified, with implications for their persistence in soil and transport to groundwater.

As part of the ongoing project on the evaluation of the environmental impact on soil and water of fungicides applied to vineyards when previously amended with SMS, the persistence, mobility and degradation of tebuconazole was assessed under field conditions in a vineyard soil (Sajazarra, La Rioja, Spain), both unamended and amended with SMS at two rates. Field experiments were supplemented by laboratory experiments to shed light on the changes in the adsorption of fungicide by unamended and SMS-amended soils over time and the changes in dehydrogenase activity of soils due to the impact of tebuconazole and SMS amendment. A long-term study on the impact SMS amendment in vineyard soils has on fungicide fate is needed to assess the environmental risk for groundwater contamination. Our literature review did not find any studies on the dissipation of tebuconazole in SMS-amended soils under field conditions.

Table 1
Characteristics of the spent mushroom substrate (SMS) given on a dry weight basis.

	pH	Moisture (%)	Ash (%)	OM (g kg^{-1})	OC (g kg^{-1})	DOC (g kg^{-1})	*N* (g kg^{-1})	*C/N*
SMS	7.5	53.0	44.4	556	271	12.2	22	12.3

2. Materials and methods

2.1. Chemicals

An analytical standard of tebuconazole was purchased from Dr. Ehrenstorfer, Germany (98.5% purity), and the commercial formulation of tebuconazole, Folicur 25 EW (Bayer Crop Science, Germany), was used. Tebuconazole is a fungicide with a water solubility of 36 mg L^{-1} and a log Kow of 3.7 (Tomlin, 2000). HPLC grade methanol was supplied by Merck (Germany), and acetone was supplied by Panreac (Spain). 2,3,5-Triphenyltetrazolium chloride (TTC) and 2,3,5-triphenyl formazan (TPF) were supplied by Sigma-Aldrich Química SA (Spain).

2.2. Organic amendment

Spent mushroom substrate (commercial name: INTRACOMPOST SPCH-SPC), from *Agaricus bisporus* (75%) and *Pleurotus sp.* (25%) cultivation, was kindly supplied by INTRAVAL Environmental Group TRADEBE S.L. (Spain). SMS is initially composed by a mixture of cereal straw and poultry litter, ammonium nitrate, urea and minerals (gypsum and/or calcium carbonate). After mushrooms are produced, the remaining substrate is pasteurized previous to its use as amendment. Therefore, presence of spores in the SMS was not evident. Moreover, SMS used in this work is composted and this process is carried out in piles (2.5 m high) for several weeks under aerobic conditions. Previously, the material is mixed with woodchips to favor its aeration, and it is regularly turned to favor maturation and decomposition, which increase the residue's uniformity and stability level. The physicochemical characteristics of SMS are given (on a dry weight basis) in Table 1. The pH was determined in a SMS/water suspension (1/2), and ash percentage was determined by weight difference on ignition at 540 °C for 24 h. OM was calculated as 100-% ash. OC content was determined by the modified Walkley-Black method (Prat Pérez and Sánchez, 1973). Dissolved organic carbon (DOC) was determined in a suspension of soil in deionized water (1:2) after shaking (24 h), centrifugation (20 min at 10,000 rpm) and filtering. The DOC content was determined using a Shimadzu 5050 (Shimadzu, Columbia, MD, USA) organic carbon analyzer. Total *N* was determined by the Kjeldahl method (Bremner, 1996).

2.3. Field site and soil preparation

The field experiment was conducted in a vineyard soil in Sajazarra, La Rioja, Spain (42°35′0″N latitude and 2°57′0″W longitude). Weather conditions (rainfall and soil and air temperature) were monitored over the 355 days of experimentation at a weather station close to the study site (about 4 km east) (Fig. 1). Experimentation was conducted in a sandy clay loam soil (Typic Calcixerept). The soil samples were air dried and sieved (< 2 mm). The principal soil characteristics

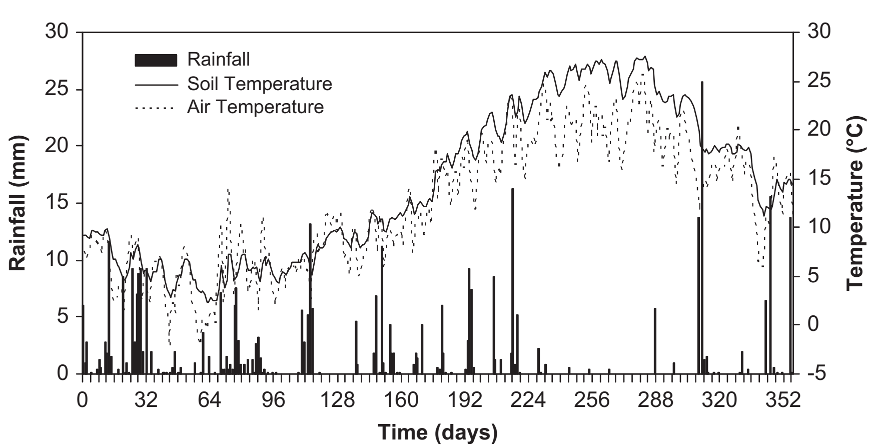

Fig. 1. Rainfall and temperature evolution over time.