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Modeling fungicides mobility in undisturbed vineyard soil cores unamended and amended with spent mushroom substrates

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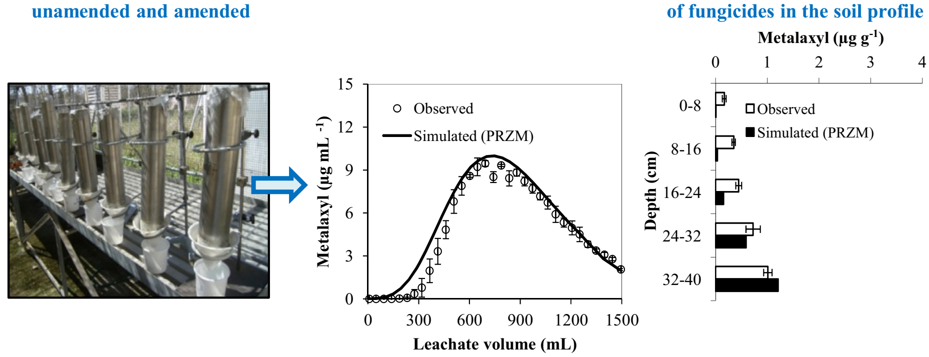
HIGHLIGHTS

- The PRZM performance to assess the fate of fungicides in amended soils was tested.
- The key parameter was the hydrodynamic dispersion coefficient.
- PRZM predicted satisfactorily the leaching and vertical distribution of penconazole.
- PRZM described well the metalaxyl and CGA-62826 leaching after calibration.
- PRZM correctly simulated the vertical distribution of metalaxyl, not of CGA-62826.

GRAPHICAL ABSTRACT

Undisturbed soil cores, unamended and amended | Leaching of fungicides | Vertical distribution of fungicides in the soil profile



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ABSTRACT

The performance of the pesticide fate model PRZM to predict the fate of two fungicides, penconazole and metalaxyl, and the major metabolite of metalaxyl (CGA-62826), in amended and unamended vineyard soils was tested from undisturbed soils columns experiments. Three different treatments were tested in two soils: control soil (unamended), and soil amended with fresh or composted spent mushroom substrates, which correspond to common agricultural practices in Spain. Leaching experiments were performed under non-saturated flow conditions. The model was parameterized with laboratory and literature data, and using pedotransfer functions. It was first calibrated for water flow against chloride breakthrough curves. The key parameter was the hydrodynamic dispersion coefficient (DISP). No leaching of penconazole, the most hydrophobic fungicide, was observed. It remained in the top 0–8 cm of the column. In any case, simulations were highly correlated to the experimental results. On the contrary, metalaxyl and its metabolite were consistently found in the leachates. A calibration step of the K_d of metalaxyl and CGA-62826 and of DISP for CGA-62826 was necessary to obtain good prediction of the leaching of both compounds. PRZM generally simulated acceptable metalaxyl vertical distribution in the soil profiles although results were overestimated for its metabolite. Nevertheless, PRZM can be reasonably used to assess the leaching (through breakthrough curves) and vertical distribution of fungicides in amended soils, knowing their DISP values.

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1. Introduction

Fungicides are used on a wide range of crops (vine, cereal, fruit, ornamental, vegetable, etc.) to prevent foliar diseases such as powdery mildew, downy mildew or botrytis. They are usually applied before appearance of infections because of their higher efficiency in preventive than in curative treatments. Fungicides are the second most used pesticides in Spain after insecticides: in 2011, 29% of the 37 512 tons of crop protection products applied were fungicides (MAGRAMA, 2014). The use of these compounds is very common and crucial in wine-growing to maintain/increase the economic benefits of the sector. One of the most important Spanish area of vineyards is the rooted wine region of La Rioja (northern Spain) where 34.6% of the total area cultivated (156 869 ha) is dedicated to vineyards (Estadística Agraria Regional, 2011). Wine sales reached 277 million L in 2013 after an extraordinary yield of 41 L of wine ha^{-1} (Rioja DOCa – Qualified Designation of Origin, 2014). However, vineyards soils are generally poor in organic matter (OM) and organic amendments are usually needed. Recently, in Spain, and especially in La Rioja region, spent mushroom substrate (SMS) has become a major organic amendment because of its high OM content, and the huge amounts of residues annually generated by mushroom industries (325 000 tons of SMS in 2007; Martín et al., 2009). As most of the drinking water of La Rioja is provided by groundwater (Navarrete et al., 2008), the assessment of the fate of fungicides in SMS amended soils is critical. Some studies showed that the adsorption, desorption, mobility, and degradation of fungicides is modified by the presence of SMS (Herrero-Hernández et al., 2011; Marín-Benito et al., 2009a, 2009b, 2012, 2013). However, a high diversity of fungicides can be used and applied in a high diversity of soils, so they cannot be studied on case-by-case basis because laboratory and field experiments are time-consuming and cost prohibitive.

Numerical models describing the fate of pesticides in the environment are useful tools to help prevent the contamination of water bodies, and four of them are used at the European level for risk assessment of pesticides for their registration (FOCUS, 2000). However, although the performance of numerous models to assess the fate of pesticides in amended soils was tested (Filipović et al., 2014; Marín-Benito et al., 2013), that of the models used for pesticides registration has been rarely studied (Jarvis et al., 2000). Among these models, PRZM (Pesticide Root Zone Model, Carsel et al., 1998) takes into account most of the processes involved in the fate of pesticides in the environment, it is widely used, and it has been shown to provide reliable results in a number of instances (e.g. Jackson, 2003; Mamy et al., 2008).

Two of the most used fungicides in vineyards, penconazole (1-[2-(2,4-diclorophenyl)pentyl]-1H-1,2,4-triazole) and metalaxyl (methyl-N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-D,L-alaninate), were selected to test the performance of PRZM. They have

Table 1
Physicochemical characteristics of unamended (control) and amended soils, and main PRZM soils and substances input parameters.

Parameter (units)/treatment	AL		AL+F-SMS		AL+C-SMS		V		V+F-SMS		V+C-SMS	
Soil layer (cm)	0–30	30–40	0–30	30–40	0–30	30–40	0–30	30–40	0–30	30–40	0–30	30–40
Sand (%)[a]	64.4	43.6	56.3	45.8	59.1	60.9	51.8	51.3	48.8	47.3	50.5	52.0
Silt (%)[a]	14.2	19.5	18.3	22.4	15.2	14.2	13.5	15.1	13.9	16.1	14.3	16.1
Clay (%)[a]	21.4	36.9	25.4	31.8	25.7	24.9	34.7	33.6	37.3	36.6	35.2	31.9
Bulk density ($g\ cm^{-3}$)[b]	1.408	1.408	1.456	1.456	1.395	1.395	1.184	1.184	1.200	1.200	1.007	1.007
OM (%)[a]	1.04	0.85	1.46	0.91	1.41	0.76	2.54	1.58	2.96	1.85	2.83	1.31
pH (water)[a]	7.8	7.9	7.8	7.8	7.8	7.7	7.8	7.7	7.6	7.6	7.7	7.7
$CaCO_3$ (%)[a]	11.3	10.6	11.2	11.6	11.3	12.2	34.6	40.0	30.3	32.6	30.7	36.1
θ_{FC} ($cm^3\ cm^{-3}$)[c]	0.236	0.329	0.272	0.303	0.272	0.250	0.361	0.336	0.385	0.360	0.385	0.335
θ_{WP} ($cm^3\ cm^{-3}$)[c]	0.141	0.215	0.166	0.192	0.167	0.154	0.227	0.210	0.244	0.228	0.236	0.203
$\theta_{initial}$ ($cm^3\ cm^{-3}$)[d]	0.236	0.329	0.272	0.303	0.272	0.250	0.361	0.336	0.385	0.360	0.385	0.335
υ_m ($cm\ h^{-1}$)[e]	0.131		0.119		0.125		0.094		0.088		0.090	
Hydrodynamic dispersion coefficient ($cm^2\ h^{-1}$)												
Chloride ion, penconazole, metalaxyl[f]	0.333		0.104		0.208		0.250		0.167		0.083	
CGA-62826 metabolite[g]	0		0		0		0		0		0	
Parameterization specific to substances												
Sorption												
K_d ($L\ kg^{-1}$)												
Penconazole[a]	3.68	1.82	6.82	2.78	4.35	1.64	11.4	5.83	12.1	6.72	12.0	4.34
Metalaxyl	0.15[a]	0.08[a]	0.20[g]	0.14[g]	0.14[a]	0.10[a]	0.42[g]	0.19[g]	0.28[g]	0.39[g]	0.57[g]	0.30[g]
CGA-62826 metabolite[g]	0.08	0.04	0.10	0.07	0.07	0.05	0.21	0.10	0.14	0.20	0.29	0.15
Degradation												
DT_{50} (days)												
Penconazole	192[h]	384[i]	235[h]	470[i]	1733[h]	3466[i]	192[j]	384[i]	235[j]	470[i]	1733[j]	3466[i]
Metalaxyl	31.1[h]	62.2[i]	31.4[h]	62.8[i]	56.7[h]	113.4[i]	31.1[j]	62.2[i]	31.4[j]	62.8[i]	56.7[j]	113.4[i]
CGA-62826 metabolite	31.2[k]	62.4[i]	42.4[l]	84.8[i]	76.6[l]	153.2[i]	31.2[k]	62.4[i]	42.4[m]	84.8[i]	76.6[m]	153.2[i]
θ_{ref} ($cm^3\ cm^{-3}$)[n] (all substances)	0.094		0.108		0.108		0.144		0.154		0.154	

[a] From Marín-Benito et al. (2009a).
[b] From Marín-Benito et al. (2009b).
[c] Soil water content at field capacity (θ_{FC}, 33 kPa) and at wilting point (θ_{WP}, 1500 kPa) estimated from Rawls et al. (1982).
[d] Initial soil water content.
[e] Pore water velocity.
[f] Estimated from chloride BTCs (Carsel et al., 1998).
[g] Calibrated.
[h] From Marín-Benito et al. (2012).
[i] Variation of the degradation rate k (k (d^{-1}) = ln (2)/DT_{50}) with depth: k for 0–30 cm and $k \times 0.5$ for 30–40 cm (FOCUS, 2000).
[j] Assumed equal to measured DT_{50} of metalaxyl for control and amended AL soils.
[k] From PPDB (2015).
[l] Estimated from the DT_{50} CGA-62826/DT_{50} metalaxyl ratio (PPDB, 2015).
[m] Assumed equal to the estimated DT_{50} of CGA-62826 in amended AL soils.
[n] Reference soil moisture content in the degradation experiments.

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