Effect of the Addition of Wine Distillery Wastes To Vineyard Soils on the Adsorption and Mobility of Fungicides

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In the present work, a study was made of the effect of the addition of liquid and solid wine distillery wastes (WLW and WSW) to vineyard soils on the adsorption and leaching of penconazole and metalaxyl, two fungicides of different hydrophobic character that are widely used in vine cultivation. The study of these processes is of great interest, since currently the green filter system is implemented simultaneously in vine cultivation and as an alternative to classic purification methods of such organic wastes. Three vineyard soils selected from the La Rioja region (NW Spain) were used. Adsorption isotherms of the ^{14}C-labeled fungicides by the soils in aqueous medium and in WLW medium were obtained, together with the percolation curves of the fungicides in packed soil columns under saturated flow conditions. The adsorption and leaching of metalaxyl in a soil amended with WSW were also studied. The Freundlich Kf constants indicated an increase in the adsorption of both fungicides by the soils in WLW medium as compared to aqueous medium. The amounts of penconazole leached in the three soils when they were washed with water and WLW ranged between 3.18 and 39.3% and between 2.00 and 10.4%, respectively, of the total fungicide added to the columns. In the case of metalaxyl, these amounts represented 69.1−100 and 91.6−117%. Variations were also observed in the shape and parameters of the breakthrough curves obtained in both systems and in the presence of WSW. The soluble organic compounds of WLW must be retained by the soil components, creating new adsorbent hydrophobic surfaces, which increase the retention in the soil of the highly hydrophobic compound penconazole. In the case of metalaxyl, which is very water soluble, the soluble organic compounds of WLW seem to contribute to the increase in its leaching, whereas the WSW favors the opposite effect. The results obtained, indicating modifications in the adsorption and leaching of penconazole and metalaxyl in the presence of WLW and WSW, show that further studies should be carried out on the adsorption and mobility of the fungicides in soils from the vineyard zone, which in turn are used as a green filter purification system of wine wastes.

KEYWORDS: Wine wastes; green filter; vineyard soils; adsorption; mobility; fungicides

INTRODUCTION

Wastewaters from the wine-producing agroindustry (vinasses) are a significant source of pollution of surface waters. They are often discharged directly into rivers with no previous treatment, and because of their high organic load and their oxygen demand, they cause the death of fish and other aquatic animals (1−3). With increasing public awareness about the problems caused by such discharges, these are now prohibited (4−6), and it is now the responsibility of industrial enterprises to find alternative methods, which are sometimes very costly, to purify their wastewaters.

The green filter system, as a purification system of these residues in controlled doses in the soil, is currently being tested as an alternative to classic methods of purifying the solid and liquid organic residues generated in the wine production process. This system could be a technically recommendable solution since it would reduce the environmental impact of such wastes. Furthermore, the system would also offer an improvement to the structure and fertility of the soils where the wastes are applied since these are of considerable agronomic interest because of their high levels of OM (sugars, alcohols, tartrates, etc.) and of potassium, phosphorus, and calcium (7−9).

However, it should be borne in mind that the behavior of fungicides, which are widely applied in vineyards, may be affected by the OM content in suspension and in soluble form of wine wastes. This effect will occur when both fungicides

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Table 1. Selected Characteristics of the Soils

soils	soil type	soil texture	pH	OM (%)	sand (%)	silt (%)	clay (%)	CaCO$_3$ (%)	clay mineralogy[a]
soil 1		calcixerollic xerochrept	7.7	3.88				31.6	
soil 2	sandy loam	typic dystrochrept	4.6	1.76	58.8	25.1	16.2		I, K, V–Cl
soil 3	sandy loam	calcixerollic xerochrept	8.2	0.65	71.4	9.30	19.3	18.7	I, K
soil 3 + WSW	sandy loam	calcixerollic xerochrept	7.8	3.40	71.4	9.30	19.3	18.7	I, K

[a] In order of abundance: I, illite; K, kaolinite; V–Cl, vermiculite–chlorite intergrade.

and wastes are applied to soils subjected simultaneously to vine cultivation and to the green filter depuration system. The main processes governing the behavior of nonionic pesticides in soils, such as adsorption and mobility, essentially depend on the soil OM content (*10, 11*). A correlation between adsorption and soil OM contents has been found for different pesticides (*12−14*). Despite this, studies on the interaction of pesticides with dissolved OM (DOM) (*15−17*) have reported a decrease in the adsorption of these compounds by the soil, facilitating their mobility in this system. In the presence of exogenous OM, added to the soil as amendments in agricultural practices, an increase in the adsorption or mobility of pesticides depends on the nature of the amendment and on the characteristics of the pesticide used (*14, 18−24*). The most widely used organic amendments are peat, sewage sludges, or city refuse compost, but as far as we are aware, no studies have addressed the effect of wine wastes on the behavior of pesticides in soils.

In the La Rioja region (NW Spain), whose main activity is agriculture, 10.5% of the total area cultivated (57 000 hectares) is devoted to vineyards. This activity is of huge economic importance in the region because of the vast quantities of wine (250 million L) produced (*25*). As a result, the application of fungicides is very high: 49.3% of the total pesticides applied in the area (2345 t), most of them used in vineyards (*26*). The green filter depuration system is now beginning to be used in certain zones of the Rioja region.

The objective of the present work was to study the influence of the WLW and WSW generated in the wine production process on the adsorption and mobility of the fungicides penconazole and metalaxyl in soils. These fungicides are very different as regards their hydrophobicity (Kow) and aqueous solubility, and they are widely used in vineyards in the region. The soils employed were also from vineyard areas with different characteristics. Additionally, in the soil with the lowest OM content, the adsorption and mobility of metalaxyl, as the most water soluble one of the two fungicides assayed, were studied in the presence of WSW.

MATERIALS AND METHODS

Chemicals. Unlabeled penconazole and metalaxyl (>97% purity) and ^{14}C-labeled penconazole (specific activity 1.02 MBq mg^{-1}, >98.1% purity) and ^{14}C-labeled metalaxyl (specific activity 1.37 MBq mg^{-1}, >97.2 purity) were supplied by Novartis Crop Protection AG (Basel, Switzerland). Penconazole is a solid compound with a water solubility of 73 μg mL^{-1} and a log Kow of 3.72, while metalaxyl is a solid compound with a water solubility of 8.4 mg mL^{-1} and a log Kow of 1.75 (*27*).

Soils. Table 1 lists the types of soils used (*28*) and some selected characteristics. These soils were from different vineyard areas of the Rioja region. Samples of soils (0−30 cm) were collected, air-dried, and sieved through 2 mm mesh. Their particle size distribution was determined using the pipet method (*29*). OC was determined according to a modified version of the Walkley−Black procedure (*30*), and the results were multiplied by 1.72 for conversion into OM contents. Soil pH values were measured in slurries made up at a 1:1 soil/water ratio. Inorganic carbon (as CaCO$_3$) was determined using a Bernard calci-

meter. Clay minerals were qualitatively identified by the X-ray diffraction technique (*31*). The soil with the highest sand content of the three soils selected (soil 3) was amended with WSW (40 t ha^{-1} dose as total carbon).

Amendments. WLW and WSW generated in the wine production in Bodegas Viña Ijalba S. A. (La Rioja, Spain) were employed. They have a low pH (*4, 5*), a high concentration of organic acids (tartaric and malic acids), and in lesser amounts, sulfuric acid and phosphoric acid. However, they do not contain persistent hydrocarbons, heavy metals, or organic solvents (Viña Ijalba 2001, personal communication). The OC contents of WLW and WSW as determined by a Shimadzu 5050 Total Organic Carbon Analyzer (Shimadzu, Columbia, MD) were 0.15 and 43.5%, respectively.

Adsorption. Adsorption experiments were carried out using the batch equilibration technique with ^{14}C-penconazole and ^{14}C-metalaxyl. Triplicate 5 g samples of natural soils and soil 3 amended with WSW were equilibrated with 10 mL of aqueous solutions or WLW solutions of each pesticide. The concentrations of pesticide used were 20, 30, 40, 50, and 60 μg mL^{-1}, and the activity of the solution was 83 Bq mL^{-1}. The suspensions were kept at 20 ± 2 °C for 24 h in a thermostated chamber with intermittent shaking (2 h every 4 h). Preliminary experiments revealed that a contact time of 24 h was long enough for equilibrium to be reached. Subsequently, the suspensions were centrifuged at 3300 rpm for 30 min. To determine the concentrations, a 1.0 mL aliquot of supernatant was withdrawn by duplicate from each tube and added to 4 mL of scintillation liquid and its activity was measured in disintegrations per minute (dpm) on a Beckman LS 6500 Liquid Scintillation Counter (Beckman Instruments Inc., Fullerton, CA). The dpm recorded for the supernatant aliquot was related to the dpm obtained for the aliquots of the respective standard solutions of penconazole or metalaxyl, and the fungicide equilibrium concentration was determined. The amount of pesticide adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the soil. The experiments were conducted with standards and blanks in water and in WLW included in each series. The adsorption data were fitted to the linearized form of the Freundlich equation: log Cs = log Kf + nf log Ce, where Cs (μg g^{-1}) is the amount of adsorbed fungicide, Ce (μg mL^{-1}) is the equilibrium concentration of fungicide in solution, and Kf and nf are two characteristic constants of pesticide adsorption.

Soil Column Leaching. Glass leaching columns of 3 cm (i.d.) × 20 cm (length) were packed with 100 g of natural soil or soil amended with WSW (soil 3) previously sieved through a 4 mm screen. Then, each column was saturated with water and allowed to drain for 24 h so that it could attain humidity conditions equivalent to field capacity (*32*). The PV of the packed columns was estimated by the weight difference of water-saturated columns vs dry columns. Then, 1 mL of a solution of ^{14}C-penconazole or ^{14}C-metalaxyl at 100 μg mL^{-1} in methanol and a specific activity of 8 KBq mL^{-1} was added to the top part of the columns. The columns were next washed with 300 mL (42 mm) of water or WLW under a saturated flow regime, collecting successive 15 mL leach fractions in which the concentrations of penconazole or metalaxyl were measured as indicated above. After being allowed to drain for some time, the columns were cut into three segments. Five samples of 5 g each were taken from each segment; two such samples were used to determine the moisture content of the soil, and the other three samples were employed to determine pesticide contents. To quantify the ^{14}C in the different segments, a Harvey OX-500 Biological Oxidizer (Harvey Instruments Corp., Hillsdale, NJ) was used and the activities of the radioactive solutions were determined on a Beckman LS 6500 Liquid
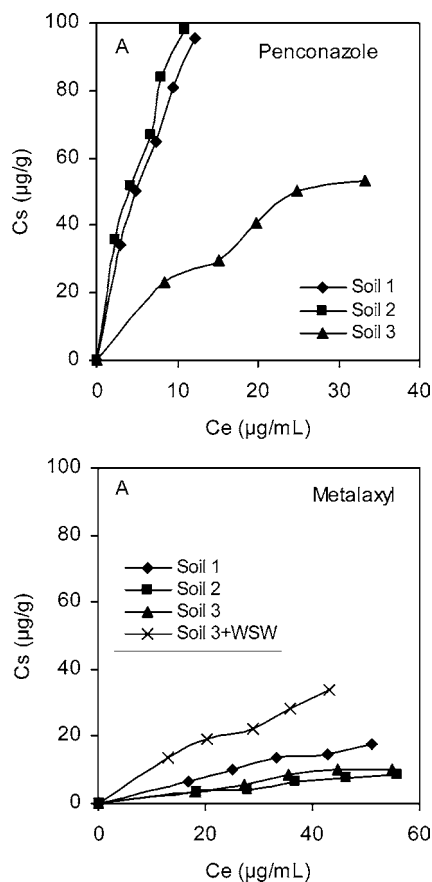
Figure 1. Adsorption isotherms of penconazole and metalaxyl in water by the soils studied.

Table 2. Freundlich Constants (Kf, nf) for the Adsorption of Penconazole and Metalaxyl by Soils

soils	water			WLW		
	Kf	nf	r	Kf	nf	r
	penconazole					
soil 1	15.9 ± 0.31[a]	0.71 ± 0.01[a]	0.99	16.7 ± 0.40[a]	0.72 ± 0.04[a]	0.99
soil 2	20.7 ± 0.42	0.65 ± 0.00	0.99	22.3 ± 0.50	0.62 ± 0.01	0.99
soil 3	5.35 ± 0.06	0.67 ± 0.00	0.98	9.03 ± 0.48	0.60 ± 0.03	0.99
	metalaxyl					
soil 1	0.59 ± 0.15	0.87 ± 0.19	0.98	1.27 ± 0.01	0.63 ± 0.01	0.99
soil 2	0.24 ± 0.14	0.89 ± 0.05	0.97	0.44 ± 0.01	0.60 ± 0.00	0.97
soil 3	0.22 ± 0.08	0.99 ± 0.10	0.97	0.26 ± 0.17	0.96 ± 0.13	0.90
soil 3 + WSW	2.05 ± 0.55	0.73 ± 0.08	0.99	1.99 ± 0.70	0.76 ± 0.21	0.99

[a] Mean values ± SD of three replicates.

Scintillation Counter (Beckman Instruments Inc.). Each experiment was performed in triplicate.

Conservative tracer transport, using chloride as an ion tracer (KCl), was implemented to describe the dispersive characteristics of each column used for the pesticide transport studies. The amount of chloride ion applied was 40 mg, and the water flow rate was the same as that used in the pesticide leaching studies. The chloride ion concentration was determined using a Metrohm Ion Chromatograph (Metrohm Ltd., Switzerland).

The chemical identities of penconazole and metalaxyl were determined in randomly selected samples of leachates and/or soil extracts in methanol by thin-layer chromatography, using a Berthold TLC Tracemaster 20 Linear Detector. No degradation products were observed.

The leaching of C from WLW was controlled in parallel experiments carried out without the fungicides added to the soils. Dissolved C in successive 15 mL fractions was determined as indicated above for WLW.

Statistical Analysis. Analysis of variance (ANOVA) was used to evaluate the effects of the different soils and treatments. Standard deviation (SD) was used to indicate variability, and the least significant difference (LSD) test at a significance level of 5% was used to separate means.

RESULTS AND DISCUSSION

Adsorption Studies. Adsorption isotherms of penconazole and metalaxyl by the three soils studied were obtained in aqueous medium and in WLW medium. **Figure 1** shows only those obtained in aqueous medium because they were very similar to those obtained in WLW medium. All of the isotherms were of the L type of the classification of Giles et al. (*33*), but the initial curvature was very different for both fungicides. This type of curve indicates a high affinity of the adsorbent for the adsorbate, and it is increasingly harder for the compound to

find sites vacant for adsorption as the concentration increases. All of the isotherms fitted the Freundlich equation, with *r* values between 0.90 and 0.99. The values of the Kf and nf constants determined from that equation are shown in **Table 2** and were used to compare the adsorption of penconazole and metalaxyl by the different soils and to compare the adsorption of both fungicides by the soils in aqueous medium and in WLW medium. Kf refers to the amount adsorbed for an equilibrium concentration of 1 μg mL^{-1} and hence represents adsorption at low concentrations, while nf reflects the variation in adsorption with the concentration (curvature of the isotherms).

The Kf values obtained for the adsorption of penconazole by the soils ranged between 5.35 and 20.7 when adsorption was studied in aqueous medium and increased (9.03−22.3) when adsorption was performed in WLW. The Kf values obtained in both media were significantly different (LSD = 0.55, $p < 0.05$). The nf values were always lower than 1 and varied across a narrow range (0.60−0.72), in agreement with the curvature of the isotherms. The lowest adsorption of penconazole in both water and in the presence of WLW was observed in the soil with the lowest OM content, soil 3. Kf increased in soil 1 and soil 2, with higher OM contents than soil 3, although not linearly. Sánchez-Martin el al. (*34*) found a highly significant correlation between the Kf and the OM content on studying the adsorption of penconazole by 26 soils with a broad range of OM contents (0.31−8.24%). However, in the present work, we did not observe a stronger adsorption of penconazole by the soil with the highest OM content (soil 1); instead, this was observed for soil 2, with a midrange content in this fraction. This indicates, at least in principle, that penconazole adsorption by the soils studied could be related not only to the OM content but also to the nature of the OM involved and to other soil properties such as pH. The penconazole molecule contains a five-membered ring, with three heterocyclic nitrogen atoms, and some or all of these nitrogen atoms could be protonated in soil 2, which has an acid pH (4.6). This would definitely help to increase the adsorption of penconazole by the active soil fractions (clay and OM). Consistent with this, some authors have reported that the sorption of weakly basic pesticides such as imazaquin (*35*), imazethapyr (*36*), or propiconazole (*37*), with heterocyclic rings in their structure, can occur through ionic bonds and/or physical adsorption, depending on the pH of the system.

The increase in the adsorption of penconazole in WLW medium can be explained in terms of the notion that the soluble organic compounds present in WLW must be adsorbed by the soil components, particularly clay, giving rise to the formation of new hydrophobic surfaces that will allow the adsorption of the fungicide to increase. The adsorption of wine wastes

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(vinasses) and of the organic compounds present in these residues, such as sugars, alcohols, and tartrates, by natural montmorillonite or this clay modified with tetramethylammonium bromide has also been observed by Büchler (*38, 39*). Other authors (*40*) have performed studies on the adsorption of dissolved OC from wine wastes by soils, finding a positive correlation between the adsorption and the soil clay content and a negative correlation between the adsorption and the soil OM content. In agreement with this, the highest adsorption of organic compounds present in WLW could be in soil 3, with the highest clay content and the lowest OM content, and because of this, the highest increase in the adsorption of penconazole in this medium is also seen in soil 3.

The Kf values obtained for the adsorption of metalaxyl by the soils ranged between 0.22 and 0.59 (aqueous medium) and between 0.26 and 1.27 (WLW medium) (**Table 2**). The nf values were also lesser than unity, although they fluctuated across a broader range. The values of these constants indicate a low adsorption of metalaxyl by the soils in both media, the lowest values consistently being found in soil 3, with the lowest OM content. The results obtained also point to the influence of the OM content in the adsorption of metalaxyl, even though the hydrophobicity of this fungicide is low. A highly significant correlation between the Kf values for metalaxyl adsorption and the soil OM content has been reported by Andrades et al. (*41*) in a study on the adsorption of metalaxyl by soils with OM contents ranging between 0.31 and 8.24%. However, in this study, the authors indicated a similar contribution of the contents of OM and clay to the variance in adsorption for vineyard soils with a low OM content (0.3−1.37%). Also, Fernandes et al. (*42*) have shown that the OM content is the most important soil property in the adsorption of metalaxyl at low concentrations of the fungicide.

A significant increase in adsorption was also observed in WLW medium (LSD = 0.16, *p* < 0.05), although the strongest increase in adsorption was not found in soil 3, as in the case of penconazole. This is probably due to a more reduced interaction of metalaxyl, which is less hydrophobic than penconazole, with the hydrophobic surfaces created by the adsorption of the organic compounds present in WLW by the clay fraction of soil 3. This is consistent with the results of other authors (*43, 44*) concerning the adsorption of pesticides and organic compounds by soils modified with hydrophobic surfactants that show low or no adsorption when the degree of hydrophobicity is very low.

In view of the low capacity of metalaxyl adsorption by the soils selected, we studied the influence of the solid amendment (WSW) in the adsorption of this fungicide. Soil 3 amended with 40 t/ha of WSW (as total carbon) was used. The adsorption isotherm obtained in aqueous medium is shown in **Figure 1**. The Kf values obtained, 2.05 (water) and 1.99 (WLW), indicate that the addition of the solid amendment elicits an increase (10-fold) in the adsorption of the fungicide in both media, despite the low hydrophobicity of metalaxyl.

In the literature, no references have been found concerning the effect of wine wastes on adsorption of pesticides. The results obtained by different authors for soils modified with other solid organic amendments (*21, 23, 24*) also point to an increase in the adsorption of pesticides. In general, in the presence of liquid organic amendments, decreases in the adsorption of pesticides by soils have been found (*17, 19, 21, 45*). Notwithstanding, in some of these studies, the authors reported increases in the adsorption of herbicides such as dimefuron, atrazine, and carbetamide by soils in the presence of DOM from straw fermentation compounds (*19*): 2,4D in the presence of DOM

from a commercial liquid amendment (*24*), and MCPA in the presence of fulvic acids (*46*).

Mobility Studies. Figure 2 shows the BTCs and cumulative curves of penconazole leaching in the soil columns with water and with WLW. The figure also includes the curves of chloride tracer ion in water for each of the soils. The chloride tracer ion BTCs were almost identical in the three soils assayed. The percolation of Cl⁻ conservative ion did not undergo retention or degradation in soils, and this indicates that the movement of water begins at 0.5 PV and reaches a maximum at about 1 PV, as is generally expected to occur in the percolation of conservative ions (*47*).

The BTCs corresponding to the percolation of penconazole in soils 1 and 2 were very similar in shape when the leaching was carried out with water and when using WLW. The curves corresponding to leaching with water show a concentration peak of 0.43 (soil 1) and 0.22% (soil 2) at a water volume of 0.5−1.5 PV, similar to the percolation of the conservative ion. This small effect could be due to preferential flow paths. The curves obtained upon washing with WLW do not show a breakthrough for the added water flow (7.5 PV) but instead a plateau. The concentration of penconazole was almost constant in the different leached fractions and was always <0.2% of the amount initially applied. The total amounts leached with water were very low, 4.25 (soil 1) and 3.18% (soil 2) of the amount initially applied to the columns, and were lower when washing was performed with WLW (**Figure 2**).

The BTCs of penconazole in soil 3 (with a lower OM content) in both aqueous and WLW medium show a maximum peak. When the columns were washed with water, the fungicide began to appear at 2.25 PV and reached a maximum concentration of 4.25% after 6.2 PV had been applied, whereas when washing was carried out with WLW the leaching kinetics were altered and the peak appeared at 6.6 PV, with a concentration of 1.57%. The presence of WLW gave rise to a 3-fold decrease in the concentration of the maximum peak as well as a delay in the PV corresponding to this peak (0.4 PV). The amounts of penconazole leached represent 39.3 and 10.4% of the amount initially added to the columns after leaching with water and with WLW, respectively (**Figure 2**).

The overall balance of penconazole leached and retained in the columns was ≥100%, and an accumulation of penconazole was observed in the first segment of the column for soils 1 and 2 after washing with water or WLW (**Table 3**). In soil 3, the percentage of residual penconazole decreased, the fungicide showing a similar distribution in all three segments of the column (water) or an accumulation in the lower segments (WLW).

Figure 3 shows the BTCs and cumulative curves for the leaching of metalaxyl in soil columns with water and with WLW. The curves corresponding to soils 2 and 3 show that the breakthrough of metalaxyl occurs rapidly at 1.2 PV (soil 2) and at 1.5 PV (soil 3); the fungicide exhibits a similar behavior in these soils to that shown by the conservative solute. The shape of the curves obtained after leaching with water and WLW was symmetric, indicating a weak interaction between the solute and the adsorbent. Moreover, they were similar, and almost no differences were observed as regards the concentration of the maximum peak, which was higher in soil 3 [51.3 (water) and 46.3% (WLW)] than in soil 2 [35.4 (water) and 37.4% (WLW)]. The amounts leached were ≥100% of the fungicide initially added, both when water and when WLW were used for washing.

In soil 1, with a higher OM content, BTCs with peaks at 1 PV or 1.75 PV were obtained when the columns were washed
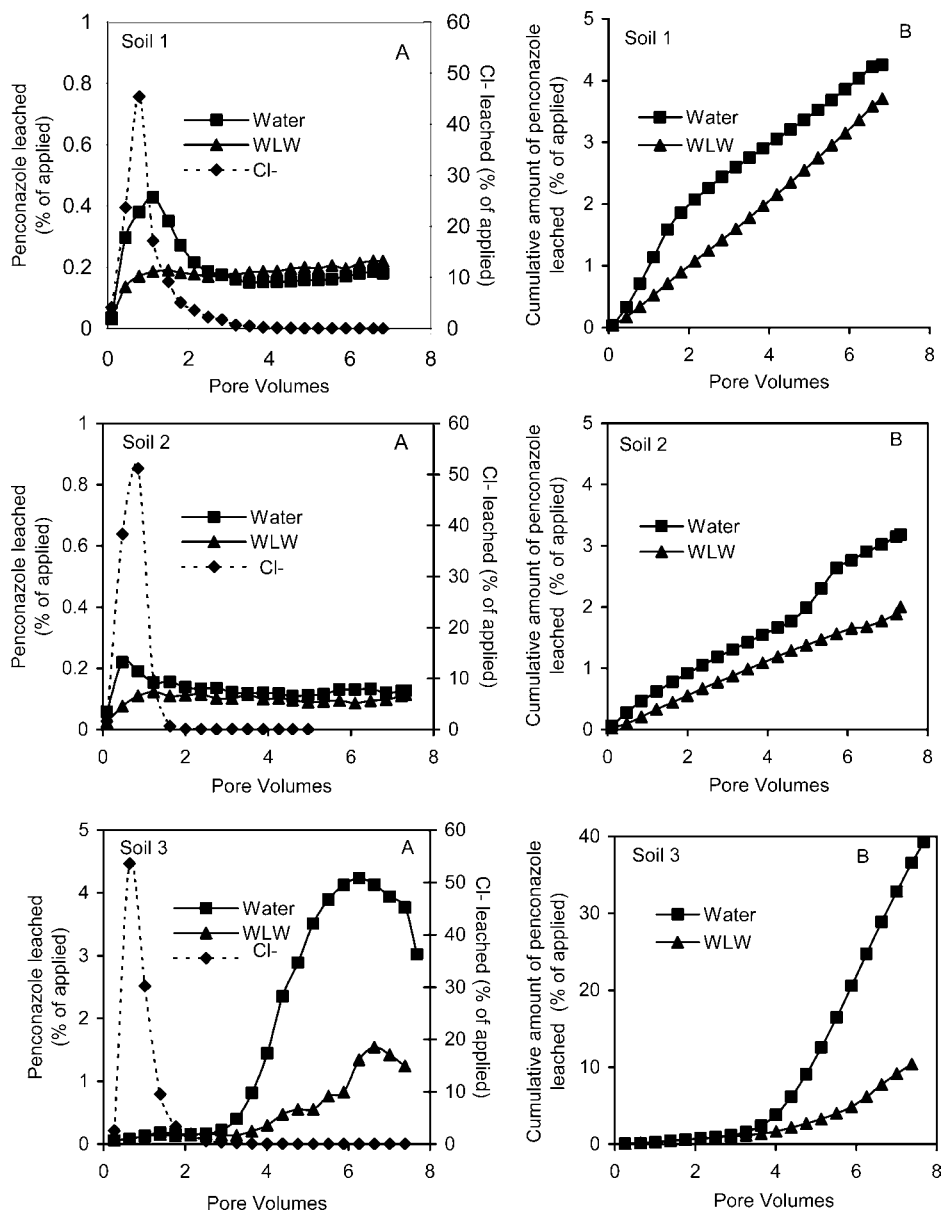
Figure 2. Breakthrough (**A**) and cumulative (**B**) curves for penconazole leaching in soils washed with water and with WLW.

Table 3. Amounts of Penconazole and Metalaxyl Retained and Leached (% of Applied) in Soil Columns Washed with Water and with WLW

	water				WLW			
segment (cm)	soil 1	soil 2	soil 3	soil 3 + WSW	soil 1	soil 2	soil 3	soil 3 + WSW
				penconazole				
0–5	83.1 ± 6.31[a]	93.3 ± 2.51[a]	21.9 ± 4.62[a]		74.4 ± 4.37[a]	95.2 ± 5.74[a]	19.4 ± 3.23[a]	
5–10	20.2 ± 0.82	16.1 ± 1.69	26.8 ± 0.79		22.1 ± 0.33	8.03 ± 1.69	31.6 ± 4.97	
10–15	5.36 ± 2.62	3.48 ± 2.89	25.0 ± 6.99		11.1 ± 3.08	1.34 ± 0.39	31.5 ± 5.12	
total soil	108 ± 2.84	112 ± 5.45	73.9 ± 2.77		107 ± 0.96	104 ± 3.62	82.5 ± 3.08	
total leached	4.25 ± 2.43	3.18 ± 1.19	39.3 ± 2.36		3.70 ± 0.77	2.00 ± 0.03	10.4 ± 5.35	
				metalaxyl				
0–5	3.76 ± 0.50	2.83 ± 1.33	4.15 ± 0.70	1.62 ± 0.60	2.26 ± 0.77	3.03 ± 0.16	1.91 ± 0.04	1.29 ± 0.01[a]
5–10	4.10 ± 1.25	1.22 ± 0.07	1.35 ± 0.12	1.01 ± 0.13	2.29 ± 1.62	1.18 ± 0.24	1.32 ± 0.02	1.31 ± 0.19
10–15	19.1 ± 9.84	1.08 ± 0.08	1.10 ± 0.24	1.79 ± 0.20	2.77 ± 1.76	0.89 ± 0.01	1.20 ± 0.38	1.75 ± 0.02
total soil	27.1 ± 11.6	5.15 ± 1.49	6.63 ± 0.56	4.45 ± 0.52	7.33 ± 4.16	5.11 ± 0.06	4.45 ± 0.30	4.37 ± 0.22
total leached	69.1 ± 1.32	116 ± 1.25	100 ± 6.09	85.1 ± 3.46	91.5 ± 8.97	117 ± 1.85	107 ± 1.14	86.2 ± 0.62

[a] Mean values ± SD of three replicates.

with water or with WLW, respectively. The curves obtained are not symmetric; instead, they show tails, which indicates a continuous leaching of the compound after the maximum peak had been attained, corresponding to slower adsorption−desorp-

tion kinetics (*48*). The concentration of the maximum was lower when leaching with water (7.26%) than when leaching with WLW (11.4%). The presence of WLW led to a delay of 0.75 PV in the appearance of the maximum peak, although the
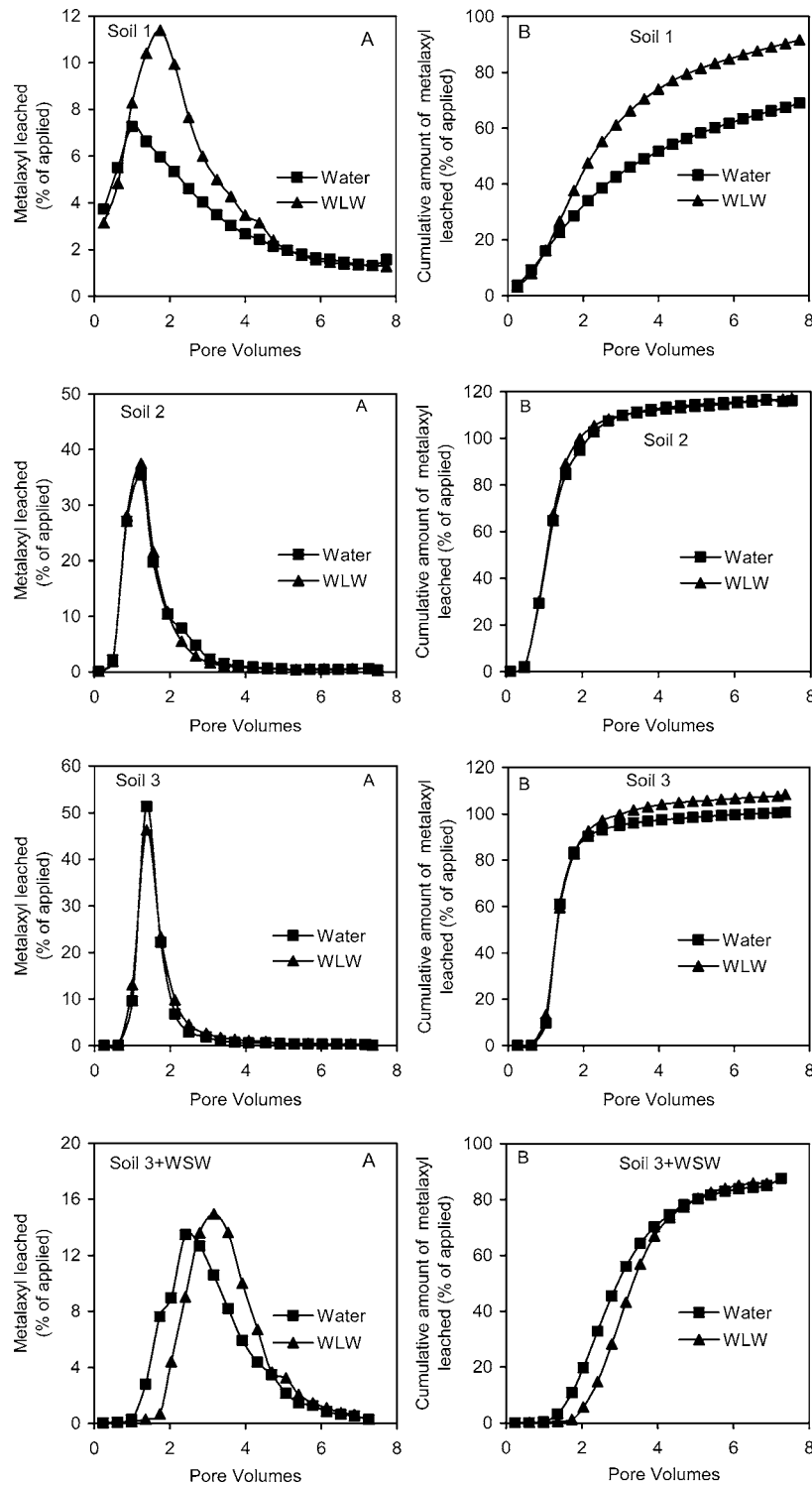
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Figure 3. Breakthrough (**A**) and cumulative (**B**) curves for metalaxyl leaching in soils washed with water and with WLW.

concentration of this peak was higher. The amounts of metalaxyl leached were 69.1 (water) and 91.5% (WLW) of the amount initially added to the columns.

With a view to confirming the adsorption of WLW by the soils in the washing of the columns, these were subjected to a washing with WLW without applying the fungicide. The decrease found in the OC content after 2 PV in the successive leached fractions with respect to the WLW concentration (**Figure 4**) confirmed the incorporation of C into the soil. According to the decrease in the amount of penconazole leached in the presence of WLW in all three soils, this increase in C

would favor the adsorption of the hydrophobic fungicide penconazole by the soil to a greater extent than by the C in solution. In the case of metalaxyl, a more soluble compound in water, the adsorbed C may initially favor its adsorption by the soil, giving rise to a delay in leaching, although the total balance of compound leached increased in the presence of WLW. The results on the adsorption of pesticides by DOM and increases in the leaching of the pesticide adsorbed have been reported by several authors (*14, 22*).

In a study of the removal of dissolved OM following the addition of vinasse to soils, Chapman et al. (*49*) also indi-
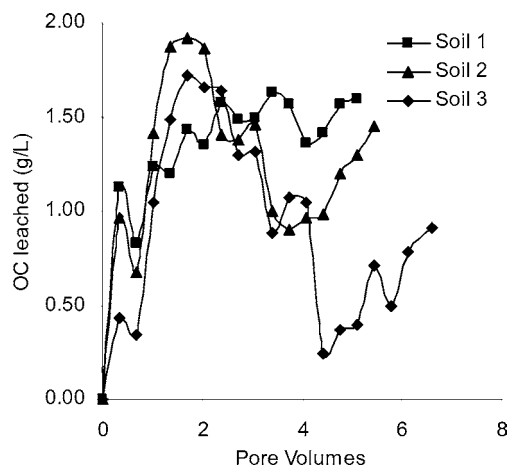
Figure 4. BTCs for OC leaching in soils washed with WLW.

cated a rapid decrease in C in leachates, attributable to the adsorption of this element by the soil followed by a varying period of little change in the concentration of C.

The addition of WSW to soil 3 significantly altered the leaching kinetics of metalaxyl, causing a delay in the appearance of the maximum peak (2.5 PV, water, and 3 PV, WLW) and a 3-fold decrease in its concentration (13.4%, water, and 14.9%, WLW) with respect to the unamended soil. However, the residual concentration of metalaxyl after leaching was low; the compound was distributed in a similar way in all three segments of the column (**Table 3**).

The results obtained in this work reveal the degree of modification in the adsorption and mobility of the fungicides penconazole and metalaxyl in soils amended with wine distillery wastes. These modifications occur as a function of the water solubility and/or the hydrophobicity of the fungicides, the nature of the soils (especially their OM content), and the nature of the solid or liquid state of the residue employed. The results point to the need to carry out further studies on the adsorption and mobility of fungicides for use in vineyard soils that in turn are employed as a green filter purification system for wine wastes. However, the effect of the enrichment in OM of the soils on the behavior of fungicides applied later on is not easy to deduce. This would require other studies addressing the variation in the adsorption and mobility of fungicides with the evolution of the OM content as a function of time.

ABBREVIATIONS USED

WLW, wine liquid wastes; WSW, wine solid wastes; OC, organic carbon; OM, organic matter; PV, pore volume; BTC, breakthrough curve.

ACKNOWLEDGMENT

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