

Effect of Spent Mushroom Substrate Amendment of Vineyard Soils on the Behavior of Fungicides: 1. Adsorption–Desorption of Penconazole and Metalaxyl by Soils and Subsoils

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The effect of the addition of fresh and composted spent mushroom substrates (F-SMS and C-SMS) to vineyard soils on the adsorption–desorption of penconazole and metalaxyl was studied under laboratory conditions. SMS is a promising agricultural residue as an amendment to increase the soil organic matter (OM) content. It may also modify the behavior of fungicides applied to vineyards. Freundlich K_f adsorption constants of both fungicides by soils and subsoils from three experimental plots unamended and amended in the field ranged between 2.78 and 13.4 (penconazole) and 0.14 and 0.67 (metalaxyl) with scant differences for unamended soil and subsoil. However, K_f values of amended soils were higher than those corresponding to subsoils and generally higher than those of unamended soils (up to 2.3 times for penconazole and 1.3 times for metalaxyl). The influence of SMS treatment (fresh or composted) was observed in the adsorption of the most hydrophobic fungicide penconazole. Simple and multiple correlations between soil and subsoil properties and adsorption constants indicated the influence of the OM on the adsorption of both fungicides, together with the clay, silt, and CaCO_3 content for metalaxyl and the pH for penconazole. The results revealed changes in the adsorption–desorption processes of these fungicides, which could give rise to a decrease in the mobility of metalaxyl (highly water-soluble) and an increase in the retention of penconazole (more hydrophobic). These effects could have an impact on surface and/or groundwater contamination.

KEYWORDS: Fungicide; soil; subsoil; vineyard; spent mushroom substrate; adsorption–desorption; soil properties

INTRODUCTION

In recent years, the proper use and disposal of all kinds of organic residues (forest, agriculture, urban, and industrial) have attracted considerable attention in developed countries. These materials can be considered as renewable resources contributing to solve the environmental problems deriving from their uncontrolled accumulation. Spent mushroom substrates (SMS) (also named mushroom compost) are one of the most promising renewable agricultural organic resources. This spent substrate is the pasteurized organic material remaining after a crop of mushrooms has been harvested. It is rich in nutrients and organic matter (OM) and can provide benefits to other agricultural sectors (1, 2).

In 1997, the world production of mushrooms exceeded 6 million tons, with an annual increase of 12% between 1981 and

1997 (3). Three main types of mushrooms, *Agaricus bisporus*, *Pleurotus* spp., and *Lentinula edodes*, account for 70% of the world's production and generate millions of tons of spent substrate that accumulates over the years. For each ton of mushrooms produced, at least an equivalent amount of SMS (dry weight) is generated and must be disposed of (4). Thus, a more effective use and exploitation of this residual material represents an issue of paramount importance. In different parts of the world, SMS have been used as biofuel and animal feed and for soil bioremediation. However, their most frequent use has been as an organic soil amendment in greenhouses and open-field settings (1, 5).

Recently, the production of mushrooms in the region of La Rioja (northern Spain), increased from 51 372 tons in 1999 to 83 500 tons in 2005. For many years, the SMS produced in this region (>183 000 tons in 2005) (6) were disposed in landfills. However, recently, this method has generated an environmental problem and the industries are now proposing the reuse of such materials as soil amendments. The addition of these residues to

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the vineyard soils of the studied region is of great interest to increase the low original OM levels. This is of great relevance because vineyard cultivation is of huge economic importance in the region. These soils represent 34% of the total area cultivated (159 127 ha) of the region (7), and the vineyards generate huge economic benefits (270 million L of wine produced in 2008) (8).

However, the application of SMS involves an addition of solid and liquid OM from these residues to the soil, which could affect other agricultural practices, such as the application of fungicides. Fungicides are applied in large amounts in vineyard cultivation, representing about 9.70 kg ha⁻¹ annually or 51% of pesticides applied in the area in 2006 (9). As it is known, the main processes affecting pesticide behavior in soil, such as adsorption, mobility, and degradation, are largely related to the soil OM content. This is especially the case when the pesticides are non-ionic hydrophobic compounds with low water solubility. The adsorption of these compounds is related to the solid OM content of the soil, whereas mobility is related to the dissolved organic matter (DOM) content in general (10). These hydrophobic pesticides are able to establish hydrophobic interactions with the DOM, increasing the pesticide solubility in water and, hence, the transport to groundwater. In fact, the presence of pesticides in groundwater is becoming very frequent (11), and this has arisen considerable environmental concern.

Many authors have studied the influence of solid OM from different organic residues, such as sewage sludge, city refuse compost, woods, or agro-industrial byproduct (12–15), and their dissolved fractions, DOM (16–19), on the adsorption and/or mobility of pesticides in soils. However, no studies addressing the influence of the application of SMS on fungicide behavior in soils have been published thus far. In some papers, the influence of these substrates on the degradation and mineralization of organic compounds, such as benzene (20) and polycyclic aromatic hydrocarbons (PAHs) (21), have been studied. Other studies have considered the effectiveness of the residues for use as adsorbents for the removal of carbamate pesticides from washing machine devices (22) or to remove organic contaminants, such as pentachlorophenol, in water systems (23).

The objective of the present work was to study the influence of fresh and composted SMS (F-SMS and C-SMS) generated by the mushroom *A. bisporus* production in the region of La Rioja on the adsorption–desorption of the fungicides penconazole and metalaxyl by soil and subsoil. These fungicides are very different with regard to their hydrophobicity (K_{ow}) and water solubility, and they are widely used in the vineyards. Soils were from experimental plots in vineyard areas, unamended and amended with SMS in the field. The influence of their characteristics on pesticide adsorption was studied using a statistical approach.

MATERIALS AND METHODS

Fungicides. The fungicides penconazole (1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazol) and metalaxyl (methyl-*N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-*D,L*-alaninate) used in this work are solids with water solubility and log K_{ow} values of 73 mg L⁻¹ (20 °C) and 3.72 (pH 5.72, 25 °C) for penconazole and 8400 mg L⁻¹ (22 °C) and 1.75 (25 °C) for metalaxyl (24). Penconazole was used unlabeled (> 98% purity) and ¹⁴C-labeled (specific activity of 1.02 MBq mg⁻¹ and 98% purity), and metalaxyl (97.2% purity) was used unlabeled. All compounds were kindly supplied by Novartis Crop Protection AG (Basel, Switzerland).

Soils. Surface soils and subsoils were taken from vineyard experimental plots of the La Rioja region located in Aldeanueva (AL) (42°14'0"N latitude and 1°53'0"W longitude), Sajazarra (SA) (42°35'0"N latitude and 2°57'0"W longitude), and Viana (V) (42°30'0"N latitude and 2°20'0"W longitude). The locations were selected for their different altitudes, topographies, and climates. Their geology is rich in alluvial and colluvial detritic materials from the Pleistocene–Holocene. Each plot of 2.03–2.74 ha area was divided into three subplots corresponding to unamended and amended soil with F-SMS or C-SMS. F-SMS and C-SMS were added in April, 2006, in the field at a recommended rate (similar to other organic amendments) of 25 tons ha⁻¹ (dry weight) to study the agronomic effect of SMS on vineyards simultaneously (25). Soil samples were taken 6 months later from 27 sites (3 sites per subplot) over the experimental plot. At each site, three soil cores (0–60 cm) were taken to make a soil (0–30 cm) and subsoil (30–60 cm) composite sample representative of each site. AL soil is a Fluventic Haplocambids; SA soil is a Typic Calcixerepts; and V soil is a Typic Xerorthents (26).

Soil characteristics (mean values of three sites), determined by usual analytical methods (27), are shown in Table 1. The soil samples were

Table 1. Selected Properties of Soils and Subsoils

| soils | soil texture | pH | OM (%) | DOC ^a (mg L ⁻¹) | CaCO ₃ (%) | sand (%) | silt (%) | clay (%) | clay mineralogy ^b |
|-------------------------|-----------------|-----|--------|--|-----------------------|----------|----------|----------|------------------------------|
| Soils | | | | | | | | | |
| AL ^c | sandy clay loam | 7.8 | 1.04 | 35.7 | 11.3 | 64.4 | 14.2 | 21.4 | I, K, M, Chl |
| AL + C-SMS ^d | sandy clay loam | 7.8 | 1.41 | 43.1 | 11.3 | 59.1 | 15.2 | 25.7 | I, K, M, Chl |
| AL + F-SMS ^e | sandy clay loam | 7.8 | 1.46 | 48.5 | 11.2 | 56.3 | 18.3 | 25.4 | I, K, M, Chl |
| SA ^c | sandy clay loam | 7.7 | 1.74 | 33.2 | 27.9 | 57.9 | 10.5 | 31.6 | I, K, Chl–I |
| SA + C-SMS ^d | sandy clay loam | 7.8 | 1.74 | 36.8 | 32.0 | 51.3 | 23.3 | 25.4 | I, K, Chl–I |
| SA + F-SMS ^e | sandy clay loam | 7.8 | 1.81 | 37.2 | 29.9 | 54.7 | 10.4 | 34.9 | I, K, Chl–I |
| V ^c | sandy clay loam | 7.8 | 2.54 | 65.7 | 34.6 | 51.8 | 13.5 | 34.7 | I, K, Chl–I |
| V + C-SMS ^d | sandy clay | 7.7 | 2.83 | 66.7 | 30.7 | 50.5 | 14.3 | 35.2 | I, K, Chl–I |
| V + F-SMS ^e | sandy clay | 7.6 | 2.96 | 74.8 | 30.3 | 48.8 | 13.9 | 37.3 | I, K, Chl–I |
| Subsoils | | | | | | | | | |
| AL ^c | clayed loam | 7.9 | 0.85 | 23.7 | 10.6 | 43.6 | 19.5 | 36.9 | I, K, M, Chl |
| AL + C-SMS ^d | sandy clay loam | 7.7 | 0.76 | 20.1 | 12.2 | 60.9 | 14.2 | 24.9 | I, K, M, Chl |
| AL + F-SMS ^e | sandy clay loam | 7.8 | 0.91 | 24.9 | 11.6 | 45.8 | 22.4 | 31.8 | I, K, M, Chl |
| SA ^c | sandy clay loam | 7.9 | 1.41 | 35.1 | 39.2 | 59.7 | 10.0 | 30.3 | I, K, Chl–I |
| SA + C-SMS ^d | clayed loam | 8.0 | 1.07 | 29.2 | 48.9 | 41.8 | 19.9 | 38.3 | I, K, Chl–I |
| SA + F-SMS ^e | sandy clay loam | 7.9 | 1.33 | 33.5 | 42.6 | 60.3 | 9.7 | 30.0 | I, K, Chl–I |
| V ^c | sandy clay loam | 7.7 | 1.58 | 66.2 | 40.0 | 51.3 | 15.1 | 33.6 | I, K, Chl–I |
| V + C-SMS ^d | sandy clay loam | 7.7 | 1.31 | 42.4 | 36.1 | 52.0 | 16.1 | 31.9 | I, K, Chl–I |
| V + F-SMS ^e | sandy clay | 7.6 | 1.85 | 59.9 | 32.6 | 47.3 | 16.1 | 36.6 | I, K, Chl–I |

^a Determined in soil extracts (1:2 ratio) after 24 h of agitation at 20 °C. ^b I, illite; K, kaolinite; M, montmorillonite, Chl–I, chlorite–illite interstratified. ^c Unamended soil. ^d Soil amended with C-SMS. ^e Soil amended with F-SMS.

Table 2. Characteristics of F-SMS and C-SMS

| parameter | F-SMS | C-SMS |
|------------------------|-------|-------|
| pH | 6.7 | 7.4 |
| ash (%) | 41.7 | 51.9 |
| moisture (%) | 60.8 | 39.6 |
| OC (%) | 28.8 | 27.4 |
| DOC (%) ^a | 13.3 | 4.34 |
| N (%) | 2.36 | 1.95 |
| C/N | 14.2 | 14.2 |
| Al ($\mu\text{g/g}$) | 1733 | 6318 |
| Ca (%) | 8.64 | 9.8 |
| Mg (%) | 0.92 | 1.48 |
| P (%) | 0.87 | 0.85 |
| K (%) | 2.83 | 2.23 |
| Na ($\mu\text{g/g}$) | 3373 | 2995 |
| Fe ($\mu\text{g/g}$) | 1438 | 8941 |
| Mn ($\mu\text{g/g}$) | 315 | 421 |
| Cd ($\mu\text{g/g}$) | 0.06 | 0.65 |
| Cr ($\mu\text{g/g}$) | 8 | 5 |
| Cu ($\mu\text{g/g}$) | 53 | 63 |
| Ni ($\mu\text{g/g}$) | 4 | 29 |
| Pb ($\mu\text{g/g}$) | 2 | 28 |
| Zn ($\mu\text{g/g}$) | 257 | 273 |

^a Expressed as a percentage of the total OC.

air-dried and sieved (<2 mm). The pH of the soils was determined in water/soil suspensions (ratio of 1:2.5), and their particle size distribution was determined using the pipet method. Organic carbon (OC) contents were determined by the modified method of Walkley–Black, and the results were multiplied by 1.72 to convert the carbon into OM. Inorganic carbon was determined as CaCO₃ with a Bernard calcimeter. The dissolved organic carbon (DOC) content was determined using a Shimadzu 5050 (Shimadzu, Columbia, MD) organic carbon analyzer. Clay minerals were identified qualitatively by the X-ray diffraction technique, using a Philips PW 1710 diffractometer (Eindhoven, The Netherlands).

SMS. The spent substrate was collected after the cultivation of *A. bisporus* mushroom and was kindly supplied by INTRAVAL Environmental Group TRADEBE, S.L. (La Rioja, Spain). This residue was used fresh (F-SMS) and composted (C-SMS). F-SMS is obtained immediately after it is removed from mushroom houses and may have a heterogeneous composition, depending upon its origin (28). Alternatively, SMS can be further composted under aerobic conditions to obtain C-SMS to increase the uniformity and stability level of the SMS. The characteristics of the SMS used are shown in Table 2. The pH was determined in a water/SMS suspension (1:5), and ash was determined by ignition at 540 °C. OC and DOC were determined as previously indicated. Total N was determined with the Kjeldahl method. Determination of inorganic elements was carried out by aqua regia extraction in a Ethos Sel model microwave system (Milestone, Shelton, CT), and analysis was performed on a Varian model 720-ES inductively coupled plasma–optical emission spectrometer (Varian Instruments, Palo Alto, CA). No pesticides were detected in the SMS used (CTICH 2007, personal communication).

Adsorption–Desorption Experiments. Adsorption–desorption isotherms of fungicides by soils and subsoils (from one site per subplot) were obtained using the batch equilibrium technique. Duplicate soil samples of 5 g were equilibrated with 10 mL of a Milli-Q ultrapure water solution of each fungicide at concentrations of 1, 5, 10, 15, 20, and 25 mg L⁻¹ and an activity of 150 KBq L⁻¹ for the ¹⁴C-penconazole. The suspensions were shaken at 20 ± 2 °C for 24 h in a thermostatted chamber, with intermittent shaking for 2 h at 3 h intervals. Preliminary experiments revealed that contact for 24 h was long enough for equilibrium to be reached. The suspensions were subsequently centrifuged at 5045 g for 15–30 min, and the equilibrium concentrations of fungicide were determined. The amount of fungicide adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the soil. Calculations were based on the assumption that no degradation of fungicides occurred during adsorption studies.

The desorption isotherms of the fungicides were studied in soil samples initially treated with 15 and 25 mg L⁻¹ solutions of each fungicide during

the adsorption study in four sequential withdraw–replace steps. In each desorption step, after adsorption equilibrium had been reached, a 5 mL aliquot was withdrawn from the solution and immediately replaced by 5 mL of Milli-Q water. The resuspended samples were shaken as indicated above, after which the suspensions were centrifuged and the desorbed fungicide was calculated as the difference between that initially sorbed and the amounts desorbed measured.

Adsorption of fungicides by soils and subsoils (from three sites per subplot) was also studied at an initial concentration of 15 mg L⁻¹. The experimental conditions were similar to those used to obtain the adsorption isotherms, and distribution coefficients (K_d) were determined.

Fungicide Analysis. The ¹⁴C-penconazole equilibrium concentration was determined by mixing 1 mL of supernatant solution with 4 mL of scintillation liquid, and the activity of the fungicide was measured in disintegrations per minute (dpm) on a Beckman LS6500 liquid scintillation counter (Beckman Instruments, Inc., Fullerton, CA). The dpm value recorded was related to the dpm obtained for the aliquots of the respective standards of the pesticide solutions. In all solutions, determinations were carried out in duplicate and the coefficient of variation was always <2%. Metalaxyl analysis was accomplished by high-performance liquid chromatography (HPLC). The apparatus used was a Waters chromatograph (Waters Association, Milford, MA), equipped with a model 600E multisolute delivery system attached to a model 717 autosampler, a model 996 photodiode array detector (DAD), a ZQ mass spectrometer detector (MS), and Empower software as the data acquisition and processing system. A Waters Symmetry C18 column (75 × 4.6 mm inner diameter, 3.5 μm) was used at ambient temperature, and the mobile phase was 30:70 acetonitrile/water in a 0.1% formic acid solution. The flow rate of the mobile phase was 0.3 mL min⁻¹, and the sample injection volume was 10 μL . Detection by HPLC/DAD was carried out at 194 nm, and detection with HPLC/MS to confirm the identity of the compound was carried out by monitoring the positive molecular ion (m/z) 280.21 for metalaxyl. Under these conditions, the retention time of the fungicide was 4.3 min.

Data Analysis. The adsorption and desorption data of the fungicides were fitted to the linearized form of the Freundlich equation: $\log C_s = \log K_f + n_f \log C_e$ or $\log C_s = \log K_{fd} + n_{fd} \log C_e$, where C_s (mg kg⁻¹) is the amount of adsorbed fungicide; C_e (mg L⁻¹) is the equilibrium concentration of fungicide in solution, and K_f or K_{fd} (mg¹⁻ⁿ kg⁻¹ Lⁿ) and n_f or n_{fd} are the Freundlich adsorption or desorption coefficients and nonlinearity coefficients, respectively. Distribution coefficients, K_d , were calculated from the relationship between C_s and C_e . K_{dom} values were also calculated as 100 K_d /MO. The K_f and K_d values were subjected to analysis of variance (ANOVA). Standard deviation (SD) was used to indicate variability in the adsorption coefficient values among replicates, and the least significant difference (LSD), at a confidence level of 95%, was determined to evaluate the effects of different soils or treatments on the adsorption of fungicides by soils. Simple and multiple linear regression models were used to relate adsorption to the soil characteristics.

RESULTS AND DISCUSSION

Adsorption–Desorption of Fungicides by Vineyard Soils.

Figures 1 and 2 include the adsorption–desorption isotherms of penconazole and metalaxyl by unamended soils and subsoils and soils and subsoils amended with C-SMS and F-SMS. These isotherms fitted the Freundlich equation [r^2 values ≥ 0.97 ($p < 0.01$) (adsorption) and ≥ 0.90 ($p < 0.01$) (desorption)]. The K_f , n_f and K_{fd} , n_{fd} parameters determined from this equation are shown in Tables 3 and 4.

In general, all isotherms obtained were nonlinear and n_f values are lower than unity, in agreement with the L shape of the isotherms (29), showing a high initial affinity of the adsorbent for the adsorbate. For metalaxyl, some isotherms were of S type and the n_f values are higher than unity, indicating a strong competition for adsorption sites by water molecules at low fungicide concentrations. Nonlinear isotherms are obtained when specific interactions are involved in the adsorption of pesticides by the soils (30), and they appear frequently in the literature addressing other pesticides with triazole or imidazole groups in

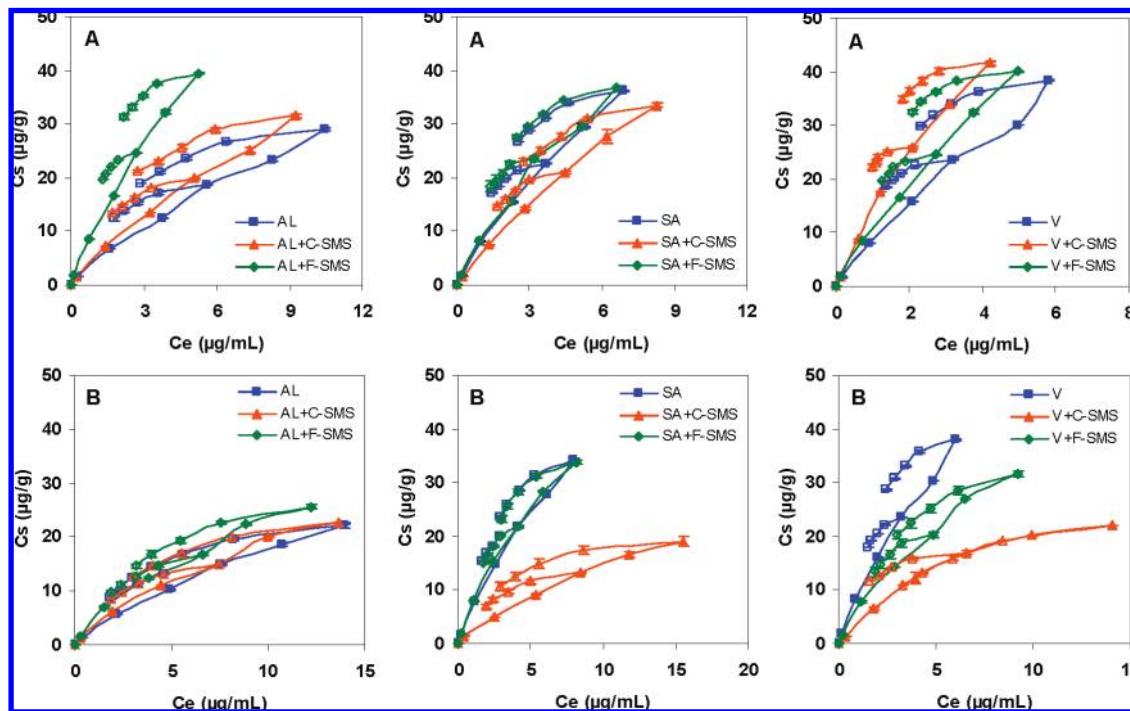


Figure 1. Adsorption–desorption isotherms of penconazole by unamended and amended (A) soils and (B) subsoils. Error bars represent the standard error of the mean C_s value ($n = 2$).

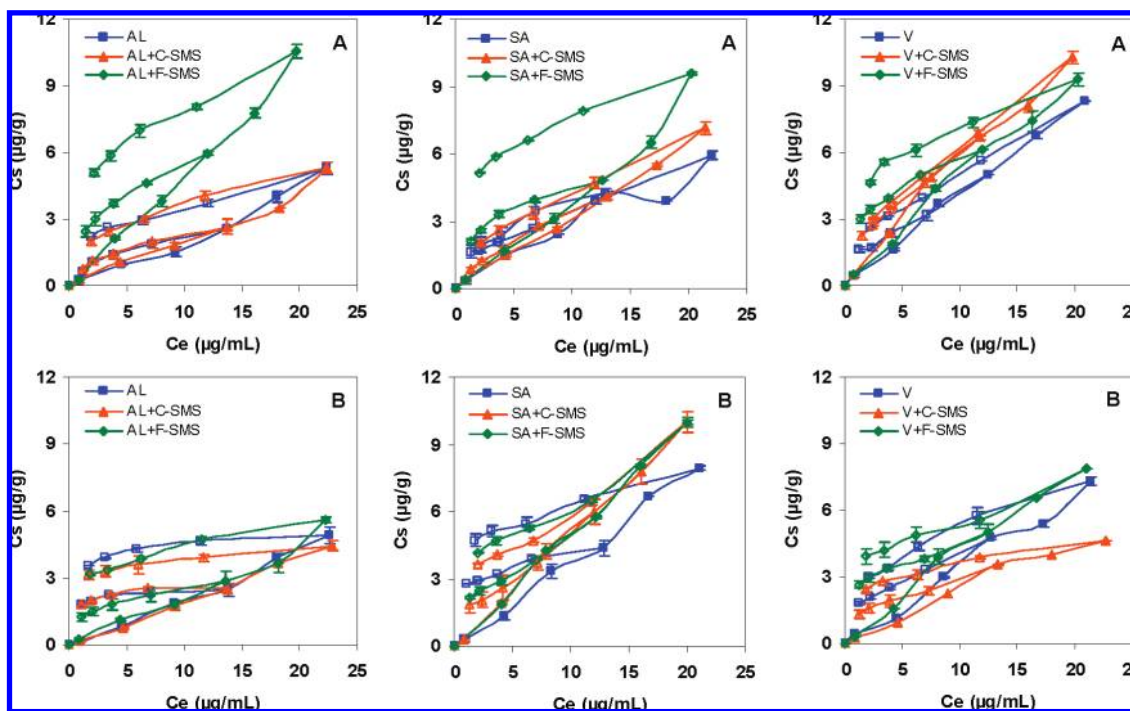


Figure 2. Adsorption–desorption isotherms of metalaxyl by unamended and amended (A) soils and (B) subsoils. Error bars represent the standard error of the mean C_s value ($n = 2$).

their molecules, such as penconazole, or with polar groups, such as metalaxyl (31).

The K_f values obtained for the adsorption of penconazole by soils (4.33–13.4) were higher than those obtained for subsoils (2.78–8.85). For unamended soils, these K_f values increased in the order $V > SA > AL$ ($LSD = 0.77$, $p < 0.001$) and were not significantly different ($LSD = 0.63$, $p < 0.1$) for soils and subsoils. However, the K_f values for the amended soils were higher than those corresponding to the subsoils ($LSD = 1.64$,

$p < 0.001$), and in general, they were also higher than those for unamended soils (up to 2.3 times). Furthermore, the adsorption constants of penconazole by F-SMS soils were relatively higher than for C-SMS soils. The addition of these residues did not seem to affect the adsorption of the fungicide by the subsoils, and K_f values followed the order unamended soil \geq F-SMS soil $>$ C-SMS soil for V soil.

F-SMS had a higher OM content than C-SMS and provided a higher OM content to the amended soils (Table 1), which suggests

Table 3. Freundlich Constants for Adsorption (K_f and n_f) and Desorption (K_{fd} and n_{fd}) of Penconazole by Soils and Subsoils and Hysteresis Coefficients (H)

| soils | $K_f \pm SD^a$ | $n_f \pm SD$ | r^2 | $K_{fd} \pm SD$ | $n_{fd} \pm SD$ | r^2 | H^b |
|-------------------------|----------------|--------------|-------|-----------------|-----------------|-------|-------------|
| Soils | | | | | | | |
| AL ^c | 4.33 ± 0.05 | 0.82 ± 0.00 | 0.99 | 13.6 ± 0.06 | 0.34 ± 0.01 | 0.96 | 2.41 ± 0.06 |
| AL + C-SMS ^d | 5.19 ± 0.00 | 0.81 ± 0.02 | 1.00 | 15.1 ± 0.08 | 0.34 ± 0.01 | 0.97 | 2.37 ± 0.02 |
| AL + F-SMS ^e | 10.2 ± 0.10 | 0.85 ± 0.00 | 0.99 | 26.2 ± 1.66 | 0.26 ± 0.03 | 0.94 | 3.24 ± 0.40 |
| SA ^c | 7.72 ± 0.12 | 0.82 ± 0.00 | 0.99 | 20.6 ± 0.06 | 0.30 ± 0.00 | 0.95 | 2.69 ± 0.00 |
| SA + C-SMS ^d | 5.72 ± 0.11 | 0.86 ± 0.04 | 0.99 | 16.4 ± 1.20 | 0.35 ± 0.02 | 0.96 | 2.45 ± 0.29 |
| SA + F-SMS ^e | 8.27 ± 0.27 | 0.81 ± 0.00 | 0.99 | 21.4 ± 1.09 | 0.30 ± 0.02 | 0.96 | 2.70 ± 0.23 |
| V ^c | 8.44 ± 0.12 | 0.85 ± 0.01 | 0.99 | 24.4 ± 0.19 | 0.27 ± 0.00 | 0.94 | 3.12 ± 0.02 |
| V + C-SMS ^d | 13.4 ± 0.19 | 0.85 ± 0.00 | 0.99 | 31.8 ± 1.45 | 0.20 ± 0.02 | 0.90 | 4.21 ± 0.36 |
| V + F-SMS ^e | 10.4 ± 0.14 | 0.85 ± 0.00 | 0.99 | 28.2 ± 1.04 | 0.23 ± 0.02 | 0.90 | 3.68 ± 0.28 |
| Subsoils | | | | | | | |
| AL ^c | 3.01 ± 0.04 | 0.77 ± 0.01 | 0.99 | 8.51 ± 0.55 | 0.38 ± 0.01 | 0.98 | 2.05 ± 0.09 |
| AL + C-SMS ^d | 3.56 ± 0.08 | 0.73 ± 0.01 | 0.99 | 8.50 ± 0.23 | 0.39 ± 0.01 | 0.97 | 1.87 ± 0.01 |
| AL + F-SMS ^e | 4.43 ± 0.26 | 0.73 ± 0.01 | 0.99 | 9.40 ± 0.83 | 0.42 ± 0.03 | 0.97 | 1.76 ± 0.09 |
| SA ^c | 6.75 ± 0.06 | 0.80 ± 0.01 | 0.99 | 16.7 ± 0.85 | 0.36 ± 0.03 | 0.96 | 2.23 ± 0.17 |
| SA + C-SMS ^d | 2.78 ± 0.55 | 0.71 ± 0.11 | 0.99 | 7.75 ± 0.99 | 0.35 ± 0.02 | 0.94 | 2.04 ± 0.43 |
| SA + F-SMS ^e | 7.37 ± 0.16 | 0.76 ± 0.00 | 0.99 | 16.3 ± 0.99 | 0.36 ± 0.01 | 0.94 | 2.09 ± 0.09 |
| V ^c | 8.85 ± 0.20 | 0.81 ± 0.00 | 0.99 | 22.2 ± 0.07 | 0.31 ± 0.01 | 0.95 | 2.60 ± 0.10 |
| V + C-SMS ^d | 3.65 ± 0.15 | 0.76 ± 0.03 | 0.98 | 6.47 ± 0.02 | 0.48 ± 0.00 | 0.97 | 1.58 ± 0.07 |
| V + F-SMS ^e | 6.06 ± 0.45 | 0.78 ± 0.01 | 0.99 | 13.2 ± 1.31 | 0.40 ± 0.02 | 0.98 | 1.93 ± 0.09 |

^aSD = standard deviation of replicates. ^b $H = n_f/n_{fd}$. ^cUnamended soil. ^dSoil amended with C-SMS. ^eSoil amended with F-SMS.

Table 4. Freundlich Constants for Adsorption (K_f and n_f) and Desorption (K_{fd} and n_{fd}) of Metalaxyl by Soils and Subsoils and Hysteresis Coefficients (H)

| soil | $K_f \pm SD^a$ | $n_f \pm SD$ | r^2 | $K_{fd} \pm SD$ | $n_{fd} \pm SD$ | r^2 | H^b |
|-------------------------|----------------|--------------|-------|-----------------|-----------------|-------|-------------|
| Soils | | | | | | | |
| AL ^c | 0.26 ± 0.00 | 0.91 ± 0.07 | 0.98 | 1.67 ± 0.05 | 0.34 ± 0.04 | 0.96 | 2.65 ± 0.50 |
| AL + C-SMS ^d | 0.29 ± 0.03 | 0.88 ± 0.01 | 0.99 | 1.46 ± 0.14 | 0.41 ± 0.01 | 0.99 | 2.13 ± 0.03 |
| AL + F-SMS ^e | 0.34 ± 0.02 | 1.16 ± 0.24 | 0.99 | 3.89 ± 0.21 | 0.32 ± 0.01 | 0.99 | 3.59 ± 0.68 |
| SA ^c | 0.36 ± 0.07 | 0.89 ± 0.20 | 0.98 | 2.40 ± 0.01 | 0.54 ± 0.02 | 0.98 | 1.67 ± 0.32 |
| SA + C-SMS ^d | 0.47 ± 0.04 | 0.85 ± 0.05 | 0.99 | 1.29 ± 0.08 | 0.54 ± 0.02 | 0.99 | 1.57 ± 0.04 |
| SA + F-SMS ^e | 0.40 ± 0.06 | 1.00 ± 0.06 | 0.99 | 4.18 ± 0.03 | 0.27 ± 0.00 | 0.99 | 3.71 ± 0.21 |
| V ^c | 0.54 ± 0.03 | 0.89 ± 0.12 | 0.99 | 1.63 ± 0.00 | 0.51 ± 0.00 | 0.97 | 1.74 ± 0.24 |
| V + C-SMS ^d | 0.67 ± 0.00 | 0.93 ± 0.01 | 0.99 | 3.21 ± 0.08 | 0.58 ± 0.02 | 0.99 | 1.61 ± 0.07 |
| V + F-SMS ^e | 0.60 ± 0.01 | 0.91 ± 0.00 | 0.99 | 3.73 ± 0.07 | 0.29 ± 0.01 | 0.98 | 3.12 ± 0.12 |
| Subsoils | | | | | | | |
| AL ^c | 0.14 ± 0.01 | 1.15 ± 0.01 | 0.99 | 3.36 ± 0.14 | 0.13 ± 0.05 | 0.99 | 9.02 ± 3.55 |
| AL + C-SMS ^d | 0.18 ± 0.03 | 1.03 ± 0.11 | 0.99 | 2.89 ± 0.37 | 0.13 ± 0.02 | 0.97 | 7.90 ± 1.67 |
| AL + F-SMS ^e | 0.30 ± 0.03 | 0.88 ± 0.05 | 0.99 | 2.63 ± 0.03 | 0.24 ± 0.00 | 0.97 | 3.74 ± 0.20 |
| SA ^c | 0.32 ± 0.01 | 1.06 ± 0.20 | 0.99 | 3.99 ± 0.50 | 0.21 ± 0.04 | 0.95 | 4.99 ± 0.10 |
| SA + C-SMS ^d | 0.38 ± 0.02 | 1.11 ± 0.04 | 0.99 | 2.41 ± 0.07 | 0.43 ± 0.03 | 0.91 | 2.61 ± 0.07 |
| SA + F-SMS ^e | 0.44 ± 0.02 | 1.05 ± 0.02 | 0.99 | 3.00 ± 0.10 | 0.36 ± 0.01 | 0.90 | 2.94 ± 0.14 |
| V ^c | 0.44 ± 0.00 | 0.89 ± 0.01 | 0.97 | 2.14 ± 0.03 | 0.40 ± 0.02 | 0.99 | 2.23 ± 0.06 |
| V + C-SMS ^d | 0.29 ± 0.00 | 0.91 ± 0.03 | 0.99 | 2.04 ± 0.17 | 0.26 ± 0.03 | 0.99 | 3.55 ± 0.28 |
| V + F-SMS ^e | 0.42 ± 0.01 | 0.99 ± 0.00 | 0.99 | 3.09 ± 0.52 | 0.28 ± 0.04 | 0.95 | 3.57 ± 0.52 |

^aSD = standard deviation of replicates. ^b $H = n_f/n_{fd}$. ^cUnamended soil. ^dSoil amended with C-SMS. ^eSoil amended with F-SMS.

the influence of this soil parameter in penconazole adsorption. However, the DOC content (slightly higher in soils amended with F-SMS than those amended with C-SMS, owing to the nature of both residues) did not seem to affect the decrease in the adsorption of fungicide determined by the batch equilibrium technique. Some authors have indicated a decrease in the adsorption of hydrophobic organic compounds by soils in the presence of DOC (19), whereas others suggest that soluble organic compounds could be adsorbed by soil components, in particular, clays, giving rise to the formation of new hydrophobic surfaces that would allow for the adsorption of pesticides to increase (16, 17). Gu et al. (32) in studies addressing the washing of SMS in field settings or during the composting process indicated that a

fraction of the DOC from SMS could be adsorbed by soil components. An increase in the adsorption of penconazole by soils in liquid wine distillery waste medium as compared to aqueous medium was also described by Andrades et al. (33) and explained as being due to the adsorption of soluble organic compounds from this residue by soil components.

The K_f values obtained were in all cases lower than those reported by Sánchez-Martín et al. (34) for the adsorption of penconazole by vineyard soils with an OM content between 0.31 and 1.98%, possibly because of the different experimental conditions used in this study.

The K_f values obtained for the adsorption of metalaxyl by soils ranged between 0.26 and 0.67, and those obtained for subsoils

were between 0.14 and 0.44. As in the case of penconazole, the K_f values for the unamended soils also increased in the order $V > SA \geq AL$ ($LSD = 0.17, p < 0.05$), and no significant differences were observed between those corresponding to soils and subsoils ($LSD = 0.14, p > 0.1$). The K_f values of SMS-amended soils were also higher than those of subsoils ($LSD = 0.08, p < 0.01$) and, in general, higher than those of unamended soils. No significant differences were observed between F-SMS and C-SMS soils. The increase in the OM content because of the addition of SMS also gave rise to a lower increase in the adsorption of metalaxyl (up to 1.3 times) than for penconazole. The mean K_f values obtained for the adsorption of this fungicide, more water soluble and less hydrophobic, were 19 and 16 times lower than those of penconazole for both the soils and subsoils, respectively. Fernandes et al. (35) reported similar values for the adsorption of metalaxyl by natural soils from the south of Spain and Portugal, with OM contents of 0.45 and 2.54, but results obtained here are lower than those reported by Andrades et al. (36) for the adsorption of fungicide by natural soils, with an OM content between 3.30 and 8.24%.

No evidence of metalaxyl adsorption by the hydrophobic surfaces possibly created by the adsorption of soluble organic compounds from F-SMS addition was observed. This agrees with our studies (37) concerning the adsorption of pesticides by soils physicochemically modified by the addition of hydrophobic surfactants. Results indicate little or no adsorption when the degree of hydrophobicity was very low.

Desorption isotherms were obtained after fungicide adsorption at initial concentrations of 15 and 25 mg L⁻¹ (Figures 1 and 2). In all cases, the isotherms exhibited hysteresis to a greater or lesser extent, because desorption data did not coincide with those of the adsorption isotherms. K_{fd} values of penconazole ($C_i = 25$ mg L⁻¹) from soils were higher than those from subsoils for both the unamended ($LSD = 0.99, p < 0.001$) and amended ($LSD = 3.59, p < 0.001$) soils (Table 3). These values varied in the same sense as the adsorption constants ($V > SA > AL$) and were also higher for F-SMS soil than for C-SMS soil. The hysteresis coefficients also indicated a greater irreversibility of the

adsorption of penconazole from soil than from subsoil (Table 3). Results indicate that the desorption process is similar whatever the initial concentration was for the adsorption ($C_i = 15$ mg L⁻¹, data not shown, and $C_i = 25$ mg L⁻¹).

K_{fd} desorption constants of metalaxyl from soil and subsoil varied between 1.29 and 4.18 and 2.04 and 3.99, respectively (Table 4). Statistically, the K_{fd} values corresponding to desorption from the unamended subsoils were higher than those corresponding to unamended surface soils ($LSD = 0.843, p < 0.01$). This, together with the hysteresis coefficients, indicated that the irreversibility of the adsorption of metalaxyl from subsoil was greater than that from soil. However, the K_{fd} desorption values from the amended soil and subsoil were not statistically different ($LSD = 0.546, p > 0.1$). This different behavior suggests different interaction mechanisms for both fungicides with the soil OM or the involvement of different soil components in this process.

Taking into account that no references have been found in the literature concerning the effect on adsorption of fungicides by SMS amended soils, it was considered of interest to broaden this study to know the influence of soil properties on this process. The adsorption of fungicides by soils and subsoils from three sites per subplot at an initial concentration of 15 mg L⁻¹ was carried out, and K_d distribution coefficients were determined (Table 5). K_d values varied in the same sense as the K_f constants ($V > SA > AL$), although the values were lower, as would be expected from the shape of the isotherms. There were significant differences between the K_d values corresponding to soil and subsoil [unamended ($p < 0.01$) or amended with SMS ($p < 0.05$)] (Table 5), but there were not significant differences between the K_d values corresponding to the adsorption of both fungicides by F-SMS soil and C-SMS soil.

A relative variability of K_d , expressed by their CV (Table 5), was found for both groups of soils. The CV of K_d values were similar for both fungicides and fluctuated across a greater range for subsoil than for soil. Variability in adsorption for the unamended soil (CV ranged between 11.2 and 31.1%) and F-SMS soil (CV ranged between 29.0 and 59.5%) was greater than for C-SMS soil (CV < 9% for penconazole and < 15% for

Table 5. Distribution Coefficients K_d (mL g⁻¹) and K_{dom} for Adsorption of Penconazole and Metalaxyl by Soils and Subsoils and Variation Coefficients (CV)

| soil | soil properties (CV %) | | | | | penconazole | | | metalaxyl | | |
|-------------------------|------------------------|------|------|------|-------------------|----------------|--------|-------------|--------------|--------|-------------|
| | pH | OM | clay | silt | CaCO ₃ | $K_d \pm SD^a$ | CV (%) | K_{dom}^b | $K_d \pm SD$ | CV (%) | K_{dom}^b |
| Soils | | | | | | | | | | | |
| AL ^c | 0.7 | 5.01 | 7.28 | 23.9 | 4.03 | 3.68 ± 0.41 | 11.2 | 2.55 | 0.19 ± 0.04 | 18.8 | 1.26 |
| AL + C-SMS ^d | 0.7 | 9.06 | 14.2 | 22.5 | 6.68 | 4.35 ± 0.39 | 8.91 | 2.54 | 0.21 ± 0.07 | 9.76 | 1.24 |
| AL + F-SMS ^e | 1.4 | 22.5 | 2.95 | 9.85 | 3.61 | 6.82 ± 1.98 | 29.0 | 2.66 | 0.34 ± 0.14 | 42.4 | 1.34 |
| SA ^c | 3.2 | 18.5 | 11.7 | 23.7 | 30.1 | 4.79 ± 1.28 | 26.8 | 2.43 | 0.26 ± 0.06 | 24.7 | 1.17 |
| SA + C-SMS ^d | 0.7 | 14.5 | 23.2 | 94.0 | 41.2 | 5.08 ± 0.31 | 6.14 | 2.46 | 0.27 ± 0.04 | 14.8 | 1.19 |
| SA + F-SMS ^e | 0.7 | 19.0 | 25.8 | 21.2 | 21.5 | 5.51 ± 1.78 | 32.4 | 2.47 | 0.28 ± 0.09 | 32.0 | 1.17 |
| V ^c | 0.7 | 21.5 | 11.1 | 9.85 | 14.6 | 11.4 ± 3.56 | 31.1 | 2.64 | 0.52 ± 0.10 | 19.6 | 1.31 |
| V + C-SMS ^d | 0.7 | 5.01 | 6.72 | 18.8 | 6.90 | 12.0 ± 0.33 | 2.77 | 2.63 | 0.57 ± 0.01 | 1.01 | 1.31 |
| V + F-SMS ^e | 2.0 | 49.7 | 8.86 | 17.4 | 18.1 | 12.1 ± 7.20 | 59.5 | 2.60 | 0.62 ± 0.34 | 55.6 | 1.31 |
| Subsoils | | | | | | | | | | | |
| AL ^c | 0.7 | 14.2 | 42.1 | 21.3 | 10.0 | 1.82 ± 0.53 | 28.8 | 2.32 | 0.13 ± 0.05 | 36.5 | 1.16 |
| AL + C-SMS ^d | 1.4 | 30.4 | 15.6 | 44.0 | 19.6 | 1.64 ± 0.36 | 21.9 | 2.34 | 0.15 ± 0.05 | 31.2 | 1.29 |
| AL + F-SMS ^e | 0.0 | 11.6 | 25.1 | 27.8 | 10.9 | 2.78 ± 0.35 | 12.5 | 2.48 | 0.18 ± 0.04 | 19.9 | 1.28 |
| SA ^c | 1.4 | 40.4 | 28.8 | 39.1 | 30.5 | 3.51 ± 1.79 | 51.1 | 2.38 | 0.26 ± 0.11 | 40.7 | 1.26 |
| SA + C-SMS ^d | 0.7 | 51.2 | 25.7 | 43.8 | 28.4 | 2.52 ± 1.61 | 64.1 | 2.35 | 0.28 ± 0.20 | 69.0 | 1.38 |
| SA + F-SMS ^e | 1.9 | 31.3 | 21.9 | 25.8 | 14.8 | 3.46 ± 1.61 | 46.5 | 2.40 | 0.28 ± 0.18 | 66.7 | 1.26 |
| V ^c | 1.4 | 15.3 | 15.3 | 15.2 | 21.0 | 5.83 ± 1.36 | 23.3 | 2.56 | 0.28 ± 0.09 | 30.8 | 1.25 |
| V + C-SMS ^d | 1.9 | 36.3 | 6.17 | 23.7 | 29.8 | 4.34 ± 1.87 | 43.0 | 2.51 | 0.30 ± 0.04 | 11.6 | 1.38 |
| V + F-SMS ^e | 1.5 | 22.6 | 11.7 | 1.57 | 16.7 | 6.72 ± 2.65 | 39.4 | 2.54 | 0.41 ± 0.02 | 4.22 | 1.35 |

^a SD = standard deviation of three-site distribution coefficients. ^b $K_{dom} = 100K_d/\%$ OM. ^c Unamended soil. ^d Soil amended with C-SMS. ^e Soil amended with F-SMS.

metalaxyl). K_d variability in subsoil was, in general, higher than in soil, regardless of the amendment treatment. This could be due to the greater variability of the physicochemical properties of subsoil (Table 5) and also the limited effect of the amendment addition on subsoil properties. These results agree with those reported by other authors (38, 39), who indicated a relationship between the variability in the adsorption of pesticides by soil and the variability in soil properties.

The observed decrease of the adsorption variability of C-SMS soils suggests that the effect of this amendment was predominant with respect to other soil properties even for metalaxyl, which is less hydrophobic than penconazole. Furthermore, the greater uniformity of the nature of the composted material (40) would also account for the lesser variability of the adsorption with respect to F-SMS soil. F-SMS even increased the adsorption variability with respect to the unamended soil.

Influence of Soil Properties on the Adsorption of Fungicides by Vineyard Soils. The simple correlation coefficients (r) shown in Table 6 revealed the existence of a highly or very significant positive correlation between the K_f and K_d constants and the OM content for both fungicides. There was also a significant positive correlation between K_f and K_d and the clay content for the adsorption of penconazole by soil and for the adsorption of metalaxyl by soil and subsoil. In addition, a significant negative correlation between K_d and pH for both fungicides in soil and for penconazole in subsoils was found. A significant correlation between OM and pH ($r = 0.567$, $p < 0.01$) was seen in the soil but not in the subsoil.

On the basis of the determination coefficient, r^2 , OM would account for 75–89 or 91–89% of the variance of the adsorption

Table 6. Simple Correlation Coefficients (r) between Freundlich Constants (K_f) and Distribution Coefficients (K_d) of Fungicides and Soil and Subsoil Properties

| constant/fungicide | pH | OM | CaCO ₃ | sand | silt | clay |
|---------------------------------|---------------------|--------------------|--------------------|---------------------|---------------------|--------------------|
| Soils | | | | | | |
| K_f /penconazole ($n = 9$) | 0.053 | 0.864 ^a | 0.342 | -0.144 | -0.394 | 0.830 ^a |
| K_d /penconazole ($n = 27$) | -0.469 ^b | 0.945 ^c | 0.315 | -0.330 ^d | -0.026 | 0.421 ^b |
| K_f /metalaxyl ($n = 9$) | 0.054 | 0.787 ^b | 0.815 ^a | -0.540 | -0.061 | 0.778 ^b |
| K_d /metalaxyl ($n = 27$) | -0.496 ^a | 0.926 ^c | 0.329 ^d | -0.418 ^b | 0.046 | 0.443 ^b |
| Subsoils | | | | | | |
| K_f /penconazole ($n = 9$) | -0.072 | 0.954 ^c | 0.102 | 0.368 | -0.644 ^d | 0.014 |
| K_d /penconazole ($n = 27$) | -0.466 ^b | 0.943 ^c | 0.139 | -0.008 | -0.158 | 0.128 |
| K_f /metalaxyl ($n = 9$) | 0.045 | 0.631 ^d | 0.648 ^d | -0.292 | -0.316 | 0.675 ^b |
| K_d /metalaxyl ($n = 27$) | -0.138 | 0.676 ^c | 0.336 ^d | -0.240 | -0.022 | 0.368 ^d |

^a $p < 0.01$. ^b $p < 0.05$. ^c $p < 0.001$. ^d $p < 0.1$.

of penconazole by soil or subsoil expressed by K_f and K_d . This indicates the influence of the soil OM content (natural or from SMS) in the adsorption of this highly hydrophobic fungicide, and it is in agreement with the narrow range found for the K_{dom} values (Table 5). However, the OM content would account for a lower percentage of variance in the adsorption of metalaxyl by soil and subsoil (62–86 and 40–46%, respectively). This suggests that other soil parameters may influence the adsorption of this fungicide, although this was not noticed in the K_{dom} values, which were very close.

The results were also subjected to multiple linear regression analysis by combining two or more variables to determine the relative importance of soil parameters when they vary simultaneously. Table 7 shows the multiple linear regression models for the adsorption of fungicides by soil and subsoil, which gave rise to a combination of higher adjusted r^2 and lower mean square errors. The significance levels for the related variables were also included. All equations reveal significant relationships ($p < 0.001$) between the K_f and K_d adsorption constants and the variables of the models. In each of them, the coefficient of determination, r^2 , accounts for a percentage of variability of K_f or K_d of 91–98% (penconazole) or 57–93% (metalaxyl), that is, higher than that explained when only the OM content is considered as the responsible variable.

The OM regardless of its origin (natural or exogenous) revealed to be the soil parameter that most influences the adsorption of fungicides by both soil and subsoil, unamended and amended with SMS, with OM contents of < 0.85 and $< 2.96\%$, respectively, despite different characteristics of both compounds. Other parameters, such as the content in clay, silt, and carbonates, also affected the adsorption of metalaxyl by soil and subsoil at both low concentrations (K_f) and higher concentrations (K_d) of fungicide in solution. These variables affected penconazole adsorption only at low concentrations of fungicide in solution (K_f), whereas pH had a greater importance, possibly because of the chemical structure of this fungicide (33, 41).

Consequently, the results obtained here show that the use of F-SMS or C-SMS as an amendment at relatively low agronomic doses elicits an increase in the OM content of soils. This could be of great importance for vineyard soils, especially when C-SMS, which is more homogeneous than F-SMS, is used. Nevertheless, this increase in the OM content also may modify the adsorption–desorption of penconazole and metalaxyl. The increase in adsorption of metalaxyl, which is highly soluble, should give rise to a decrease in its mobility. However, for penconazole, it could elevate its retention. This can have an impact on surface and/or ground water contamination. However, studies addressing the mobility and degradation of these two fungicides in the same soils

Table 7. Multiple Regression Equations between Freundlich Constants (K_f) and Distribution Coefficients (K_d) of Fungicides and Soil and Subsoil Properties

| constant/fungicide | regression equation | significance level | | | | | r^2 |
|--------------------|--|--------------------|-------|-------|-------|-------------------|-------|
| | | pH | OM | clay | silt | CaCO ₃ | |
| Soils | | | | | | | |
| K_f /penconazole | $-6.843 + 5.008\text{OM} + 0.319\text{clay} + 0.135\text{silt} - 0.224\text{CaCO}_3$ | | 0.05 | 0.013 | 0.011 | 0.004 | 97.7 |
| K_d /penconazole | $-35.87 + 5.539\text{OM} + 4.340\text{pH} - 0.051\text{CaCO}_3$ | 0.091 | 0.000 | | | 0.061 | 91.5 |
| K_f /metalaxyl | $-0.436 + 0.024\text{clay} + 0.009\text{silt}$ | | | 0.000 | 0.000 | | 95.0 |
| K_d /metalaxyl | $-0.240 + 0.226\text{OM} + 0.005\text{clay} + 0.006\text{silt} - 0.004\text{CaCO}_3$ | | 0.000 | 0.077 | 0.005 | 0.026 | 90.5 |
| Subsoils | | | | | | | |
| K_f /penconazole | $20.31 + 4.379\text{OM} - 2.643\text{pH}$ | 0.273 | 0.000 | | | | 92.7 |
| K_d /penconazole | $20.19 + 3.919\text{OM} - 2.743\text{pH}$ | 0.002 | 0.000 | | | | 92.6 |
| K_f /metalaxyl | $-0.556 + 0.474\text{OM} - 0.027\text{clay} + 0.042\text{silt} + 0.016\text{CaCO}_3$ | | 0.027 | 0.114 | 0.062 | 0.051 | 92.8 |
| K_d /metalaxyl | $-0.116 + 0.154\text{OM} + 0.004\text{clay} + 0.002\text{CaCO}_3$ | | 0.000 | 0.076 | | 0.139 | 57.2 |

are necessary and have been carried out by the authors with the view to elucidate the environmental effect of the joint use of SMS and fungicides in soil.

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