

## Research Article

# Effect of Peat Addition on Sorption and Leaching of Triazole Fungicides in Oran Soils

**Kahina Aït Hammi** <sup>1,2</sup>, **Elías Nieto-Latorre**,<sup>3</sup> **María D. Ureña-Amate** <sup>3</sup>,  
**María M. Socías-Viciano**,<sup>3</sup> **Hafida Miloudi**,<sup>1</sup> and **Naoufal Debbagh-Boutarouch**<sup>3</sup>

<sup>1</sup>Department de Chimie, Laboratoire de Chimie des Matériaux, Université Oran1 Ahmed Ben Bella, BP 1524, El-M'naouer, Oran, Algeria

<sup>2</sup>Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques (CRAPC), BP 384, Bou-Ismaïl, RP 42004 Tipaza, Algeria

<sup>3</sup>Department of Chemistry and Physics, Agroalimentary Campus of International Excellence (ceiA3), University of Almeria, La Cañada San Urbano, s/n, 04120, Almeria, Spain

Correspondence should be addressed to Kahina Aït Hammi; [aithamikahina@yahoo.fr](mailto:aithamikahina@yahoo.fr) and María D. Ureña-Amate; [damate@ual.es](mailto:damate@ual.es)

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In this paper, the authors treat the impact of peat amendment on sorption and leaching of fungicides penconazole and flusilazole in two Algerian topsoil samples (Misserghine and Es-Senia). The batch equilibration technique was applied for adsorption experiments, and leaching was tested through soil column simulated experiments under laboratory conditions. Adsorption data fitted well to the Freundlich and linear models, showing the higher adsorption capacity of the Es-Senia soil for both fungicides, the order of sorption being flusilazole > penconazole. Organic amendments increased the adsorption of both fungicides especially for the soil with the lower organic matter (OM) content, obtaining a good correlation of this parameter with  $K_f$ , thus implying that OM is the principal soil parameter governing fungicides adsorption. Results of soil column experiments indicated that peat amendment decreased leaching of both pesticides in the soils studied. So, the use of organic addition might be an effective management practice for controlling potential pollution of penconazole and/or flusilazole to the environment.

## 1. Introduction

Algeria is a country with great environmental challenges, among which we can mention soil erosion, desertification, hydrocarbons spills and toxic sludge from refineries, and fertilizer and pesticide runoff that lead to the pollution of Mediterranean waters [1], forcing this fact to Algeria to cooperate with other nations in protecting the sea from pollution and degradation. It is interesting to note in this point that the use of pesticides, and in particular, of fungicides in this country, has suffered a vertiginous increase in the last years [2].

The protection and recovery of soils and waters contaminated by pesticides have demanded a big effort in the development of techniques of remediation and prevention. A vulnerability study of the soils of the Oran region was carried out by this research group in collaboration with the

University of Oran, and given the results of hydrogeology, agricultural activities, etc., it was proved that soils S1 and E4 were of great interest because they presented a great contamination vulnerability and therefore potential contamination of aquifers in the area. In relation to this, two main aspects have been considered: on one hand, the great environmental problem that affects the soils from the northern zone of Algeria, such as those selected in this study, and on the other hand, the lack of information about the adsorption behavior of the fungicides. Taking into account these considerations, the authors consider that the research carried out in this paper contributes to increase the knowledge about the behavior of pesticides similar to those used in this study in agricultural soils with a potential risk of vulnerability to contamination such as those selected in this paper.

Organic matter amendment is widely recommended as practice offering many benefits to soil [3, 4]. Thus, it has been

a problem of great interest because it has been reported that the interaction of organic matter with pesticides affects the destiny of these compounds in the soil or aquatic systems [5–10].

Triazole fungicides are widely applied on crops protection. Penconazole [1-(2,4-dichloro- $\beta$ -propylphenethyl)-1H-1,2,4-triazole] and flusilazole [bis (4-fluorophenyl)(methyl)(1H-1,2,4-triazol-1-ylmethyl)silane] (exceedingly used in the west area of the Oran region) are two systemic fungicides belonging to the triazole derivatives, utilized for the oversight of a wide spectrum of pathogens. They act by suppressing the biosynthesis of sterols of the cellular membranes, thus stopping the fungus development. However, a possible cause of concern is their long persistence in soil, which may lead to accumulation following repeated application, runoff events, or leaching to groundwater [11, 12]. Knowing that the environment behavior of nonionic pesticides such as sorption, degradation, and migration maybe influenced by the OM amendments, we have considered it useful to investigate the influence of adding different percentages of a commercial peat amendment on the sorption and mobility processes of flusilazole and penconazole in two soils located in the Algerian area, with a high potential risk of contamination, and provide an effective field management practice for preventing potential pollution of these fungicides to environment.

## 2. Materials and Methods

**2.1. Adsorbents.** Fresh soils were collected from two different sampling areas at the west of the region of Oran, that is, Misserghine (35° 36, 706' N latitude and 0° 44, 647' W longitude) for the soil labeled as S1 and Es-Senia (35° 36' 45, 20" N latitude and 0° 40' 41, 20" W longitude) for the soil labeled as E4. Soil samples were collected according to the French standard protocol NF-X31-101 (AFNOR, 1996). So, soil sampling was carried out in several points in an area randomly traversed by using a zigzag sampling method and at 20 cm depth. For each sample, about 20 subsamples per hectares of land were taken and homogeneously mixed in a clean container and collecting about 2 kg of each type of soil. Then, the soil samples were air-dried for seven days, the stones removed, the aggregates broken with a roller, and finally passed through a 2 mm sieve and stored in plastic containers. Physicochemical characteristics of the soils are given in Table 1. Soil pH was measured using 1:2.5 soil-solution ratio [13]; organic matter by the Walkley-Black procedure [14]; particle size analysis by using the Bouyoucos densimeter [15]; carbonate was assessed with a Bernard calcimeter; and a barium acetate method was used for determining CEC and exchange acidity [16]. As can be observed, the CEC for the E4 soil was not possible to determine. The explanation for this is based on the physical characteristics of this soil. So, E4 is an extremely saline soil, and the clay mineralogy analysis showed the presence of a high content of gypsum (15%), absent in the other soil and anhydrite (4%). This fact justifies the impossibility of determining the value of the CEC for E4 soil because in soils with a gypsum content higher than 5%, the calcium ions

released from the gypsum solution compete with the barium ions to occupy the exchange sites [17].

Amended soils used in the experiments were prepared by uniformly mixing original soil samples (S1, E4) with different amounts of a commercial black peat (Pindstrup Mosebrug S.A.E., Spain) previously sieved at 2 mm particle size. The peat percentages obtained for the amendment were 3, 6, and 18 (w/w). Their characteristics are also included in Table 1 together with those of the peat.

**2.2. Adsorbates.** Analytical standard samples of fungicides (99.9 % purity) were purchased from Sigma-Aldrich (Spain). Penconazole water solubility was 0.073 g·L<sup>-1</sup> (20°C), pKa = 1.51, and DT<sub>50</sub> was 117 days. Flusilazole water solubility was 0.045 g·L<sup>-1</sup> (20°C), pKa = 2.5, and DT<sub>50</sub> was 300 days.

**2.3. Adsorption Experiment.** Pesticides adsorption experiment on the soils selected was conducted using a batch equilibrium technique (25°C, 150 rpm) by equilibrating in stoppered conical flasks 0.5 g of each soil sample or peat with 25 mL of the fungicide aqueous solution prepared on 0.01 M CaCl<sub>2</sub> medium at varied initial concentrations (C<sub>0</sub>) ranging between 2 and 35 ppm. In all cases, the values of C<sub>0</sub> were lower than the solubility limit of each pesticide.

Preliminary investigations on the sorption rate indicated that equilibration was completed within 24 h for both fungicides in the S1 soil, whereas 48 h was needed for flusilazole adsorption in the E4 soil sample and also for the sorption of both pesticides in the peat.

Following, the samples were centrifuged at 4000 rpm, the supernatant was filtered and then quantified by HPLC (Dionex, Sunnyvale, USA) with a UV detector and C18 (150 × 4.6 mm id) column, using a mixture of acetonitrile and water as the mobile phase (65:35, V/V). The wavelength used for the detection of penconazole was 200 nm and 195 nm for flusilazole.

Adsorption was carried out in duplicate for each series of experiments.

**2.4. Column Experiment.** Leaching study was performed for fungicides penconazole and flusilazole in the soils used. Downward mobility was compared by using original soils and those amended with 18% of organic matter. The soil columns (250 mm length × 43.5 mm i.d.) were constructed from PVC pipes and fitted with a 60  $\mu$ m nylon membrane. Once the columns were installed, 300 g of soil was added and previous fungicides were applied, and the columns were saturated with 0.01 M CaCl<sub>2</sub> aqueous solution and then left draining for 24 h. The columns were weighed before and after saturation, and pore volume (PV) was determined by using a mass balance.

After that, 50 g of each sample was contaminated with 25 mL of methanol containing 12 mgL<sup>-1</sup> of fungicide. Following this, soils being mixed and air-dried [18]. The contaminated sample was added to the top of each column and covered with glass wool and acid washed sand [19, 20].

Next, the columns were eluted with around 4 times the pore volume determined for each soil sample (650 mL) by

TABLE 1: Physicochemical characteristics of original and amended soils and commercial peat.

Sample	CEC (meq 100 g <sup>-1</sup> )	pH(H <sub>2</sub> O)	Sand (%)	Silt (%)	Clay (%)	CaCO <sub>3</sub> (%)	OM (%)
S1	16.2	8.1	60	28	12	22.5	2.52
S1-3%	17.5	8.2	68	24	8	18.6	2.64
S1-6%	18.1	8.0	74	20	6	14.9	2.67
S1-18%	21.2	7.1	78	20	2	13.8	2.75
E4	Not determined	7.6	54	36	10	18.3	3.81
E4-3%	Not determined	7.4	56	38	6	17.6	4.96
E4-6%	Not determined	7.2	60	36	4	13.1	5.40
E4-18%	Not determined	6.9	70	28	2	11.5	5.52
Peat	66.3	4	—	—	—	—	24.5

using 0.01 M CaCl<sub>2</sub> (constant flow rate equal to 0.8 cm·h<sup>-1</sup>). The concentration at the column outlet after 4 pore volumes of displacement was below the detection limit. After the elution, the soil columns were left to percolate naturally and frozen at -18°C. Finally, columns were cut into 5 cm cores for further analysis.

### 3. Results and Discussion

**3.1. Soil Adsorption Study.** Figures 1 and 2 show the adsorption isotherms of penconazole and flusilazole in both soils, whereas the adsorption in the peat amendment is shown in Figure 3. According to the classification of Giles [21], the isotherm for adsorption of penconazole in S1 original soil (Figure 1(a)) is of the S-type, indicating a low affinity of the pesticide for this soil, so there is a remarkable competition for substrate sites from pesticide. The rest of the isotherms of penconazole in the S1 amended soils (Figure 1(a)) and E4 (Figure 1(b)) and also the isotherms for flusilazole (Figures 2(a) and 2(b)) in both soils are of the L-type, indicating a medium affinity of these pesticides for the soil samples. However, it can be observed in nearly all cases a slight tendency to change to C-type with the increasing peat content. The linearity observed in these cases shows the importance of the nonspecific interactions (H and hydrophobic bonding) and emphasizes the influence of the OM in the phenomena of aqueous phase partition. Similar results have been published related to the adsorption of hydrophobic and nonionic pesticides in soils [22–24]. On the other hand, the isotherms for adsorption of both fungicides in the peat (Figure 3) are of the type L for the adsorption of penconazole, whereas a type C isotherm is obtained for the adsorption of flusilazole, indicating in this case a higher affinity of this pesticide for sorption sites than solvent molecules.

The adsorption isotherms for both fungicides were described by the Freundlich adsorption model:

$$\log X = \log K_f + n \log C_e, \quad (1)$$

where  $X$  is the concentration of fungicide sorbed (mg·g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of the fungicide in solution (mg·L<sup>-1</sup>),  $K_f$  and  $n$  are constants that represent adsorption capacity at low concentration and adsorption intensity, respectively. The  $K_d$  distribution coefficient which reflects the distribution ratio of the fungicide in the sorbed phase was fitted to the experimental adsorption isotherms

( $X = K_d \cdot C_e$ ). Adsorption parameters for both fungicides in the peat and the soils studied are presented in Table 2 together with the coefficients of determination ( $r^2$ ).

As shown in Table 2, the  $K_f$  and  $K_d$  values increased with increasing organic amendment content in soil samples. Thus, the adsorption capacity of selected fungicides on both samples is improved with the organic amendment.

It can also be observed that, in the case of penconazole, the  $K_f$  values obtained for original E4 soil are about 8 times higher than those obtained for original S1 soil, whereas for flusilazole,  $K_f$  values were around 5 times higher. In relation to the  $K_d$  values, these showed the same tendency. In any case, both parameters followed the same variation order:

$$\text{penconazole (S1)} < \text{flusilazole (S1)} < \text{penconazole (E4)} < \text{flusilazole (E4)}.$$

This variation can be justified if we take into account, on one hand, the slightly higher hydrophobicity of flusilazole ( $K_{ow} = 7.41 \cdot 10^3$ ) versus penconazole ( $K_{ow} = 5.25 \cdot 10^3$ ) and, on the other hand, the higher OM content of E4 soil. According to these results, the variation order indicated above shows that, apparently, at the experimental conditions of pH used in this work, the clay fraction present in the soils studied plays an irrelevant role in the adsorption process of these compounds. This fact has been confirmed in other reports where the dominant role is pointed out of the OM against the clay fraction, in particular in horizons of soils with a high OM content [22, 25].

If we take into account that the value of  $K_{OC}$  gives information about the affinity of one molecule for the soil OM content, the  $K_{OC}$  values (Table 2) were determined by normalizing the  $K_d$  parameter to the soils organic carbon content (OC) which was obtained by the Walkley-Black procedure [14]:

$$K_{OC} = \frac{(K_d \cdot 100)}{\% \text{ OC}}. \quad (2)$$

The  $K_{OC}$  parameter (equation (2)) was used to control the soil adsorption ability. The higher the  $K_{OC}$  value, the more strongly the pesticide is sorbed, and therefore, the less mobile it is. In this study, the results obtained confirmed the higher adsorption capacity of the soil E4 for both pesticides.

It can be clearly seen that the  $K_{OC}$  values of S1 amended soils increased with increasing organic amendment content of soil samples, suggesting that organic addition could significantly increase the adsorption capacity and weaken

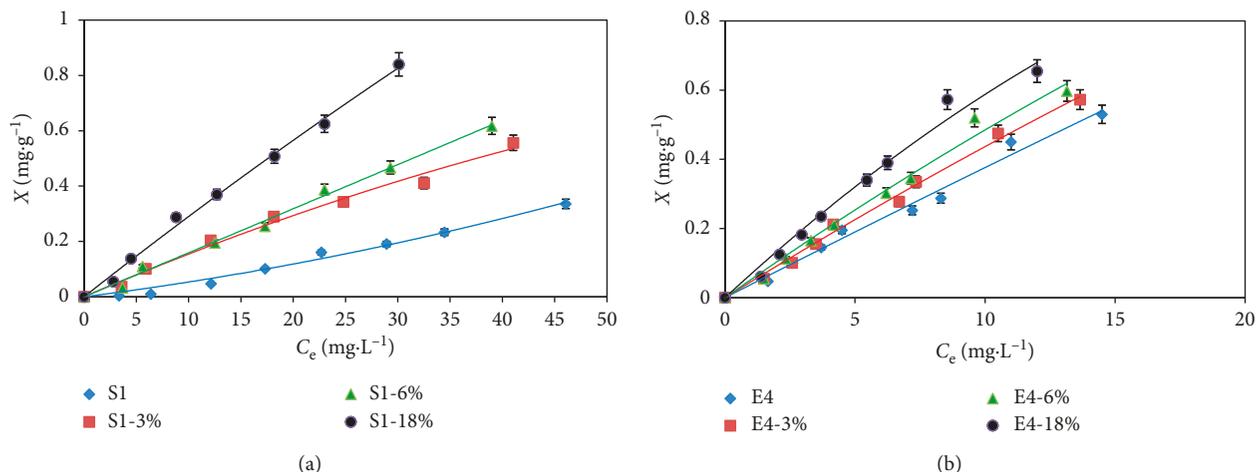


FIGURE 1: Penconazole adsorption isotherms on original and amended S1 (a) and E4 (b) soil samples.

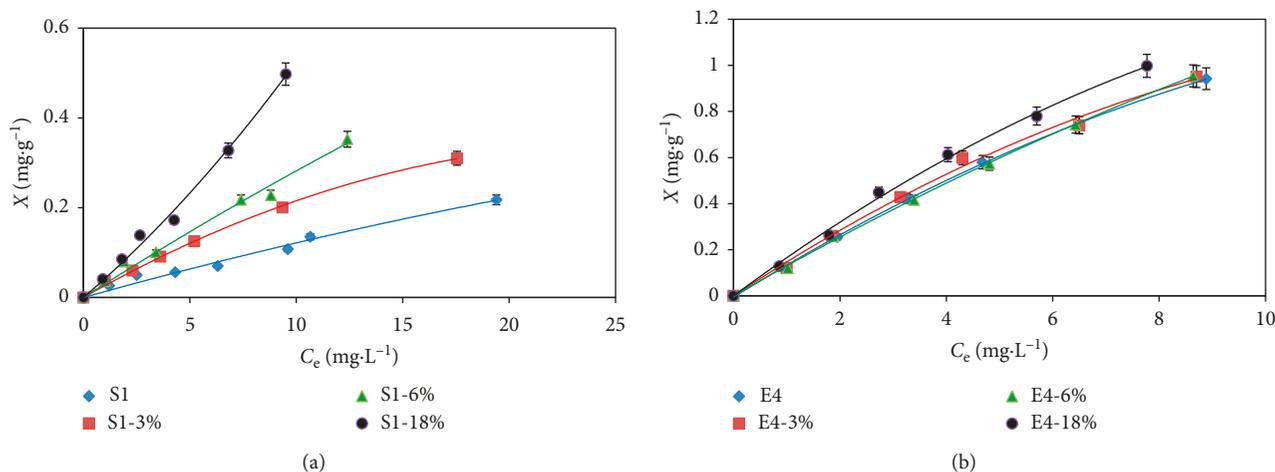


FIGURE 2: Flusilazole adsorption isotherms on original and amended S1 (a) and E4 (b) soil samples.

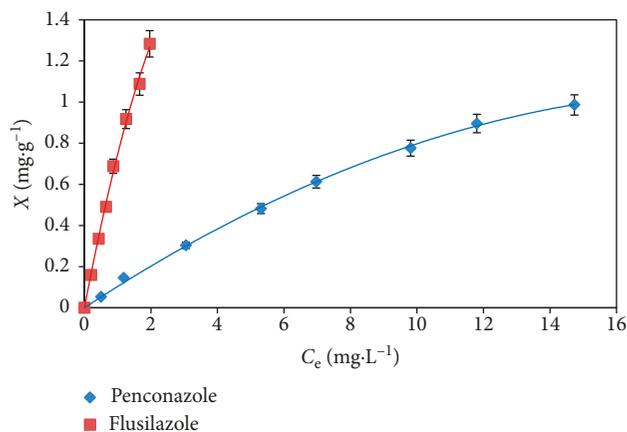


FIGURE 3: Adsorption isotherms of penconazole and flusilazole in peat.

the downward mobility of both fungicides on this soil [26]. On the contrary, there is not a significant difference in the variation trend of  $K_{OC}$  values for original and amended E4

soils (3% and 6%). In this case, the original soil has high organic matter content and the capacity of adsorption of each pesticide is nearly the same for the indicated organic amendments with the exception of that at 18% where the adsorption slightly increases.

To determine the influence of OM on adsorption of penconazole and flusilazole, the linear correlation analyses were conducted between the  $K_f$  and soil OM. The results showed that the correlations between  $K_f$  and OM content were especially significant for the adsorption of both pesticides in S1 amended soils but not for E4 amended samples (not shown), what is expected given its higher OM content. So, the linear regression equation was  $y = 6.9966x + 2.5131$  ( $r = 0.955$ ) for adsorption of penconazole on S1 amended soils and  $y = 9.4051x + 2.3135$  ( $r = 0.997$ ) for adsorption of flusilazole on the same soil samples, respectively.

3.2. Column Experiments. Figures 4 and 5 show the downward movement of the pesticide studies in laboratory soil columns after passing 4 pore volumes of saline solution

TABLE 2: Comparison of the Freundlich isotherm parameters, distribution coefficients, and  $K_{OC}$  values.

Fungicide	Sample	$K_f$	$n$	$r^2$	$K_d$ (L·kg <sup>-1</sup> )	$r^2$	$K_{OC}$
Penconazole	Peat	0.409 ± 0.020*	0.751 ± 0.080*	0.981	216 ± 10*	0.980	1968
	S1	0.005 ± 0.001*	1.082 ± 0.091*	0.978	08 ± 0.7*	0.992	708
	S1-3%	0.013 ± 0.003*	1.030 ± 0.002*	0.962	13 ± 1.0*	0.981	1102
	S1-6%	0.021 ± 0.005*	0.907 ± 0.001*	0.986	16 ± 0.9*	0.992	1345
	S1-18%	0.036 ± 0.006*	0.923 ± 0.007*	0.995	27 ± 1.2*	0.994	2195
	E4	0.041 ± 0.005*	0.956 ± 0.006*	0.983	36 ± 2.1*	0.990	2118
	E4-3%	0.043 ± 0.002*	1.008 ± 0.006*	0.981	43 ± 3.3*	0.990	1937
	E4-6%	0.049 ± 0.003*	0.995 ± 0.004*	0.992	46 ± 2.2*	0.995	1901
Flusilazole	Peat	0.342 ± 0.030*	1.467 ± 0.080*	0.940	654 ± 20*	0.973	5962
	S1	0.022 ± 0.005*	0.733 ± 0.006*	0.965	11 ± 1.3*	0.987	973
	S1-3%	0.034 ± 0.007*	0.773 ± 0.002*	0.996	17 ± 0.9*	0.988	1441
	S1-6%	0.039 ± 0.007*	0.852 ± 0.004*	0.984	26 ± 1.2*	0.988	2185
	S1-18%	0.046 ± 0.006*	1.030 ± 0.005*	0.990	52 ± 4.0*	0.987	4228
	E4	0.108 ± 0.012*	0.895 ± 0.010*	0.999	82 ± 4.5*	0.999	4824
	E4-3%	0.145 ± 0.035*	0.845 ± 0.010*	0.988	86 ± 3.7*	0.991	3874
	E4-6%	0.174 ± 0.015*	0.801 ± 0.020*	0.991	104 ± 5.4*	0.987	4298
E4-18%	0.195 ± 0.012*	0.773 ± 0.021*	0.996	118 ± 5.5*	0.997	4777	

\*These values represent the 95% confidence limits.

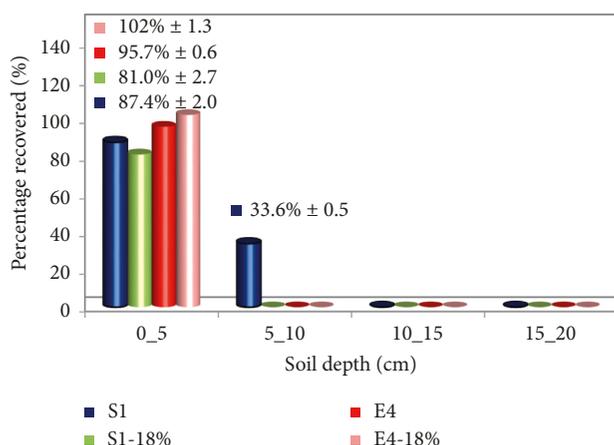


FIGURE 4: Distribution of penconazole in natural and amended soils.

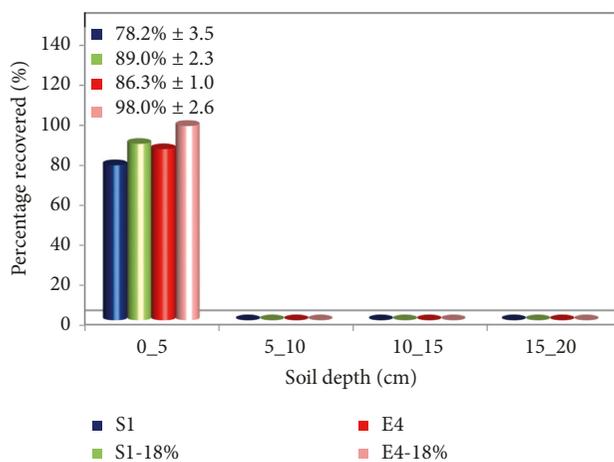


FIGURE 5: Distribution of flusilazole in natural and amended soils.

(CaCl<sub>2</sub>). None of the fungicides were detected in the leachates from amended or original samples.

As can be seen, the distribution of both fungicides along the column indicated that penconazole and flusilazole were mainly maintained in the 0–5 cm layer, showing a low movement on the soils studied. However, penconazole was slightly more mobile than flusilazole in S1 soil as this pesticide leached down to 5–10 cm depth with 33.6 % of the fungicide maintained. This fact could be explained if we take into account that the lower adsorption of penconazole on the S1 sample, which was characterized by the lower OM content, allows the pesticide to leach and reach deeper depths whereas flusilazole, with a lower solubility and higher retention on both soils, would be maintained in the 0–5 cm layer. This fact is in agreement with the sorption finding indicated above. Results as those showed in this paper indicate that the adsorption of pesticides with a low solubility is favored when soils are treated with exogenous organic matter, especially in those with a low content of OM due to the increment of soil sites disposable for adsorption. The total amount recovered of both fungicides was in general <100% for original and amended soils, this amount being slightly lower for S1 compared to E4 soil. The fungicide molecules retained are protected from degradation or dissipation processes that could take place in the soil amended with such a high percentage of peat (18%). Besides this, some recent studies show that the organic matter slows down the degradation of fungicides, so during the contact time that the column study took place (7–10 days), the small amount of fungicides not recovered in the extraction procedure might be mainly due to the bound residues between fungicide and soil as no metabolites of penconazole or flusilazole were seen in leachate samples and soil extracts. Thus, the adsorption of the fungicides by the main soil components (OM and clay) forming strongly bound residues might explain that low total balance [27].

The fact that no fungicide was detected in any of the addition soils beyond the 5–10 cm depth demonstrates that the organic amendment added to soils delayed movement of penconazole and flusilazole and augmented the amount of fungicide maintained. The effect of OM amendment could not only decrease leaching but also make structural changes in the porosity induced by the higher OC content [28].

There are numerous indices for measuring the environmental risks related to the use of pesticides. Gustafson [29] developed an index named GUS (equation (3)) that classifies pesticides in relation to their ability to be transferred to groundwater:

$$\text{GUS} = \log(\text{DT}_{50}) \cdot [4 - \log(K_{\text{OC}})]. \quad (3)$$

From monitoring data, it has been found that the risk of contamination of groundwater is high if the  $\text{GUS} > 2.8$ , while the risk is low when  $\text{GUS} < 1.8$ . Thus, according to the estimated GUS index, penconazole and flusilazole would show a low risk of leaching in E4 soil (1.3 and 1, respectively), whereas both fungicides have a moderate risk of leaching in S1 soil (2.5 and 2.6 for penconazole and flusilazole, respectively). The physical and chemical properties of the fungicide can affect its movement potential through soil and vary the results obtained. Some of these factors include fungicide persistence ( $\text{DT}_{50}$ ) in different settings, solubility in water, sorption potential ( $K_{\text{OC}}$ ), and its ability to become a vapor. Fungicides that have a short  $\text{DT}_{50}$ , low water solubility, and high sorption potential may have less potential to move through soil and vice versa.

#### 4. Conclusions

The results presented in this study showed that adsorption of penconazole and flusilazole on original and amended soils is well described by the Freundlich model. The  $K_f$  values of adsorption of flusilazole were much higher than those for penconazole not only in the original but also in the amended E4 soils, suggesting the higher adsorption capacity of this pesticide on this soil compared with that of the S1 soil. Adsorption of both pesticides on soil was greatly increased by organic amendment, this fact being especially significant for the adsorption in S1 soil, as this soil showed the lower OM content. In addition, the results of soil column experiments showed that penconazole was slightly more mobile than flusilazole in S1 soil because of its lower OM content, allowing the pesticide to leach until 5–10 cm depth. However, results also showed that organic amendments decreased the leaching of both pesticides as no pesticide was detected in leachates and might reduce ground-water contamination risks, an inhibitory effect that is more obvious with increasing the content of organic amendment. This study suggests that the use of peat amendment might be an effective management experiment for monitoring mobility of these fungicides.

The addition of organic matter (OM) to soils is a common practice in arid or semiarid climates. However, a control over the addition of OM is necessary for several reasons. In the short term, if the amendment is made with a high content of organic matter, the pesticides can be retained

in the organic fraction and subsequently leached to the aquifers. On the other hand, in the long term, it must be borne in mind that successive amendments can cause soil acidification problems and cause changes in the microflora and microfauna. For these reasons, it is necessary to carry out follow-up controls, analogous to the one presented in this paper, in soils where the amendment with organic matter is a frequent agricultural practice.

#### Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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