



Use of farming and agro-industrial wastes as versatile barriers in reducing pesticide leaching through soil columns

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ABSTRACT

Increased interest has been recently focused on assessing the influence of the addition of organic wastes related to movement of pesticides in soils of low organic matter (OM) content. This study reports the effect of two different amendments, animal manure (composted sheep manure) and agro-industrial waste (spent coffee grounds) on the mobility of 10 pesticides commonly used for pepper protection on a clay-loam soil (OM = 0.22%). The tested compounds were azoxystrobin, cyprodinil, fludioxonil, hexaconazole, kresoxim-methyl, pyrimethanil, tebuconazole, and triadimenol (fungicides), pirimicarb (insecticide), and propyzamide (herbicide). Breakthrough curves were obtained from disturbed soil columns. Cumulative curves obtained from unamended soil show a leaching of all pesticides although in different proportions (12–65% of the total mass of compound applied), showing triadimenol and pirimicarb the higher leachability. Significant correlation ($r=0.93$, $p<0.01$) was found between the observed and bibliographical values of GUS index. The addition of the amendments used drastically reduced the movement of the studied pesticides. Only two pesticides were found in leachates from amended soils, pyrimethanil (<1%) for both, and pirimicarb (44%) in the soil amended with spent coffee grounds. A decrease in pesticide leaching was observed with the increase in dissolved organic matter (DOM) of leachates. The results obtained point to the interest in the use of organic wastes in reducing the pollution of groundwater by pesticide drainage.

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1. Introduction

The EU Water Framework Directive (WFD, 2000/60/EC1) [1] defines “good ecological and chemical status” in terms of low levels of chemical pollution as well as a healthy ecosystem. The establishment of detailed quality criteria for the assessment of groundwater chemical status in Europe were laid down in the new Groundwater Directive (GWD, 2006/118/EC) [2]. Groundwater quality is increasingly monitored in Europe where various levels of nitrate and pesticide contamination have been demonstrated [3].

Man-made chemicals, mainly pesticides, may reach soil directly via deliberate application or via indirect routes like wastewater, sewage sludge, air or wet/dry deposition. For risk assessment of these chemicals, it is important to estimate their potential for transformation in soil and for movement (leaching) into deeper soil layers and eventually into groundwater. Leaching, the movement of water and dissolved chemicals through the soil, of pesticides into the groundwater from agricultural practices is receiving increasing

attention in European countries because a high percentage of the drinking water is subtracted from groundwater. For this reason, the EU established the individual ($0.1 \mu\text{g L}^{-1}$) and total ($0.5 \mu\text{g L}^{-1}$) concentrations of pesticides in drinking water to safeguard people from harmful effects.

Under certain conditions, some pesticides may leach to groundwater from normal field applications. In this process, the physicochemical properties of the agrochemicals used, as well as soil properties (texture, clay content, organic matter and permeability) play a decisive role [4]. However, among various soil properties, organic carbon content (OC) is the single largest factor that has maximum influence on pesticide adsorption and mobility in soil. The soil organic adsorption coefficient (K_{OC}) values are universally used as measures of the relative potential mobility of pesticides in soils and in fugacity models describing the partitioning of pesticides in soil/water/atmosphere systems [5–7].

Application of organic carbon in the form of manure, sludge, or crop residues is a common soil management practice followed in agriculture. Its addition contributes to enhancement of active humified components, such as humic acid (HA) and fulvic acid (FA) [8]. Generally, addition of organic matter (OM), including soluble (SOM) and insoluble (IOM) fractions, increases the adsorp-

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Table 1
Physical-chemical characteristics of the pesticides used in this study.

Active ingredient ^a	Molecular formula	Molecular weight	log K_{OW}	S_W ^b	Aqueous hydrolysis ^c	Soil sorption log K_{OC}	GUS index ^d
Azoxystrobin ^F	C ₂₂ H ₁₇ N ₃ O ₅	403.4	2.5	7	Stable	2.6	2.5 (M)
Cyprodinil ^F	C ₁₄ H ₁₅ N ₃	225.3	4.0	13	Stable	3.2	1.2 (L)
Fludioxonil ^F	C ₁₂ H ₆ F ₂ N ₂ O ₂	248.2	4.1	2	Stable	4.8	-1.8 (L)
Hexaconazole ^F	C ₁₄ H ₁₇ Cl ₂ N ₃ O	314.2	3.9	18	Stable	3.0	2.0 (M)
Kresoxim-methyl ^F	C ₁₈ H ₁₉ NO ₄	313.4	3.4	2	34	2.5	1.8 (M)
Pirimicarb ^I	C ₁₁ H ₁₈ N ₄ O ₂	238.3	1.7	3100	Stable	1.9	2.7 (M)
Propyzamide ^H	C ₁₂ H ₁₁ Cl ₂ NO	256.1	3.1	9	Stable	3.3	1.8 (M)
Pyrimethanil ^F	C ₁₂ H ₁₃ N ₃	199.3	2.8	121	Stable	2.5	2.6 (M)
Tebuconazole ^F	C ₁₆ H ₂₂ ClN ₃ O	307.8	3.7	36	Stable	2.9	2.0 (M)
Triadimenol ^F	C ₁₄ H ₁₈ ClN ₃ O ₂	295.8	3.2	72	Stable	2.4	3.7 (H)

^a F: fungicide; H: herbicide; I: insecticide.

^b Water solubility (mg L⁻¹).

^c DT₅₀ (days) at 20 °C and pH 7.

^d Groundwater Ubiquity Score (GUS) Index. Leachability in parentheses: (L, low; M, medium; H, high).

tion of pesticides and decreases their subsequent mobility in the soil profile, as the humic substances are the major factor controlling this process [9]. The main benefit from sorption of pesticides to OM is that this generally restricts their leaching. However, decreased leaching may not be only due to the presence of additional OM in amendment soil, but also due to structural changes in the porosity induced by the increment in the OC content [10]. On the other hand, through organic amendment (OA), dissolved organic matter (DOM) is incorporated, which affects the pesticide sorption and movement [11,12]. Competition between pesticides and DOM molecules for sorption sites and pesticide–DOM interactions can both account for enhanced pesticide leaching [13]. The extent and nature of this interaction depends on factors such as molecular weight and polarity of the pesticide [14]. Moreover, the addition of OA to soil normally results in an increase in the microbiological activity. As consequence, OA enhances pesticide biodegradation in polluted soils. Therefore, pesticide behavior in amendment soil has reported different responses, and diverse influences have been recognized. The main results obtained from recent literature can be consulted in the review by Briceño et al. [15].

With this aim, we have compared the influence of two amendments, composted sheep manure (CSP) and spent coffee grounds (SCGs), on the leaching of ten pesticides commonly used during pepper cultivation. The coffee grounds after oil extraction are ideal materials for garden fertilizer, feedstock for ethanol, and as fuel pellets [16]. However, to our knowledge, there is no published information concerning the effect of this important waste in pesticide leaching.

2. Experimental

2.1. Chemicals

Pesticide analytical standards (≥98%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The main physical-chemical properties of the active ingredients are shown in Table 1. Experimental values of octanol/water partition coefficient (K_{OW}), soil/organic partition coefficient (K_{OC}), aqueous solubility (S_W), aqueous hydrolysis, and Groundwater Ubiquity Score (GUS) Index were taken from The Pesticide Properties DataBase [17]. Pesticide grade dichloromethane, ethyl acetate, cyclohexane and *n*-hexane were supplied by Scharlau (Barcelona, Spain).

Stocks solutions (1000 μg mL⁻¹) of each pesticide standard were prepared in ethyl acetate/cyclohexane (1/1, v/v), protected from light and stored at 5 °C. A pesticide intermediate standard solution

Table 2
Chemical characteristics of the amendments (n = 3).

Parameter	CSM Mean (RSD)	SCG Mean (RSD)
pH (H ₂ O, 1:1)	7.1 (2.1)	5.1 (1.8)
Electrical conductivity (dS m ⁻¹)	2.84 (3.5)	1.04 (2.8)
Total organic carbon (g kg ⁻¹)	529.2 (6.2)	413.5 (5.8)
Total N (g kg ⁻¹)	18.5 (3.5)	22.3 (4.8)
Total P (g kg ⁻¹)	1.10 (8.2)	0.01 (7.9)
Total K (g kg ⁻¹)	5.2 (6.5)	0.11 (7.3)
Ratio C/N	28.6	18.5

was prepared by dilution in the same solvent to obtain a concentration of 10 μg mL⁻¹. Several standard solutions, with concentrations of 0.05–2 μg mL⁻¹, were injected to obtain the linearity of detector response and the detection limits (LOD) of the pesticides studied. The correlation coefficient derived from linear regressions were in all cases higher than 0.997, with significant correlation between concentration and area for all pesticides. The LOD obtained at an S/N of 3 for the individual pesticides were lower than 0.09 μg L⁻¹.

2.2. Soil and amendments

The soil chosen for this study was a clay loam soil (bulk density 1.34 g cm⁻³) from the Campo de Cartagena (South-eastern Spain). Soil samples were collected from the surface (top 20 cm), air-dried, and passed through a 2 mm sieve. The composition of the soil was: sand 37%, silt 33%, clay 30%, organic matter 0.22%, pH 8.71.

As amendments, ecological compost (sheep manure, CSM) and coffee (*Coffea arabica*) wastes (spent coffee grounds, SCG) were used. SCG is a waste generated from instant coffee production, one of the largest agricultural products that are mainly used for beverages. Composting of manure was carried out in piles with periodical turning (indore method) over a period of 4 months. After composting, the compost was left untouched in static piles for 3 months to complete the maturation process. On the other hand, spent coffee grounds, were extracted with hot water, air-dried and then refluxed with *n*-hexane to extract the oil from the coffee particles. Finally, the grounds were dried, and sieved through 0.3 mm mesh sieve. Table 2 shows the main chemical characteristics of the amendment used.

2.3. Determination of the soil degradation half-lives ($t_{1/2}$) of the pesticides

For knowledge of the pesticide persistence, soil samples (50 g, as dry weight basis) were placed into each incubation flask (n = 3). Two mL of a methanol/water solution (10 + 90, v/v) containing all

the studied pesticides was applied in order to achieve an initial concentration of about 0.4 mg kg^{-1} of each one, which represents the common agricultural rate of the pesticides. All the flasks were incubated in a growth chamber for 360 days with a 16 h photoperiod a day/night temperature regime of $25/18^\circ\text{C}$ with the soil moisture kept constant for all the experiments at 20% (w/w). Six UV lamps (Performance CLEO 40W, Philips) were used to simulate the photoperiod. The mean values of UVA (315–400 nm), and UVB (280–315 nm) measured during the photoperiod were 9.74 W m^{-2} and 0.27 W m^{-2} , respectively. Throughout the incubation period water losses exceeding 10% of the initial values were compensated by the addition of fresh distilled water every two weeks. Relative humidity was maintained at 70%. After 3, 7, 14, 31, 60, 90, 180, and 360 days of incubation three pots from each treatment were taken and kept at 4°C for 2–3 days until analysis. Dried soil samples (5 g) were extracted with 30 ml of acetonitrile/water (2/1) by sonication. After this, 20 ml of dichloromethane were added and then centrifuged for 10 min at $1900 \times g$. Finally, the organic phase was concentrated, dissolved in ethyl acetate/cyclohexane (1/1, v/v) and analyzed by GC–MS.

The dissipation of all pesticides could be described by pseudo first-order kinetics: $\ln C_t = \ln C_0 - kt$, where C_0 and k denote y-intercept values and the slope of the dissipation lines, respectively, C_t is the concentration of pesticide in soil, and t is the post-application time in days. Hence, their half-lives ($t_{1/2}$) were calculated from the equation $(t_{1/2}) = \ln 2/k$.

2.4. Determination of GUS indices

The leaching potential of the studied pesticides was calculated as Groundwater Ubiquity Score (GUS), according to Gustafson [18], applying the following equation:

$$\text{GUS} = \log(t_{1/2}) \times [4 - \log K_{oc}]$$

2.5. Downward movement of the pesticides through the soil columns

The experiment was performed according to the OECD guidelines [19]. Atrazine, a compound with known leaching behavior was used as reference substance for evaluating the relative mobility of the pesticides. Downward movement of the pesticides was studied in polyvinyl chloride (PVC) columns of 40 cm (length) \times 4 cm (i.d.). There were three sets of columns: (i) soil (200 g), (ii) soil (160 g) plus compost (40 g), and (iii) soil (160 g) plus coffee wastes (40 g). The top 3 cm of the columns were filled with sea sand and the bottom 3 cm with sea sand plus nylon mesh with an effective pore diameter of $60 \mu\text{m}$ to minimize the dead-end volume and prevent losses of soil during the experiment. Before the application of the compound, columns (three replications at room temperature, avoiding direct light) were conditioned with 0.01 M CaCl_2 in distilled water to their maximal water holding capacity and then allowed to drain for 24 h. The pore volume (PV) of the packed columns was estimated by the weight difference of water-saturated columns versus dry columns. The calculated PVs (ml) of the soil columns after saturation were 66 ± 3.1 (soil), 86.2 ± 2.8 (soil + compost) and 108.14 ± 3.5 (soil + coffee wastes). Following this, 2.5 mL of a methanol/water solution (10 + 90, v/v) containing $50 \mu\text{g}$ of each compound (equivalent to 200 g/Ha) were added to the top of each column. Twenty four hours after pesticide application, the compounds were leached with 800 ml of 0.01 M CaCl_2 in order to minimize soil mineral balance disruption during 16 days with a peristaltic pump. The leachates (50 ml/day) were quantitatively collected at the bottom of the columns, filtered through nylon membrane filter ($0.45 \mu\text{m}$) and extracted with 40 ml of *n*-hexane–dichloromethane 1:1 mix-

ture solvent. After this time, the columns were opened and the soil separated in two segments of approximately 10 cm each. Dried soil samples (5 g) were extracted following the same procedure specified in Section 2.3. Recoveries from soil and water ranged from 74 to 112% and limits of quantification (LOQ, signal-to noise ratio 10) varied from 0.4 to $21 \mu\text{g kg}^{-1}$ and 0.01 to $0.3 \mu\text{g L}^{-1}$ in soil and water, respectively. Determination of pesticide residues in leachates and soil extracts was accomplished in both cases by GC/MS.

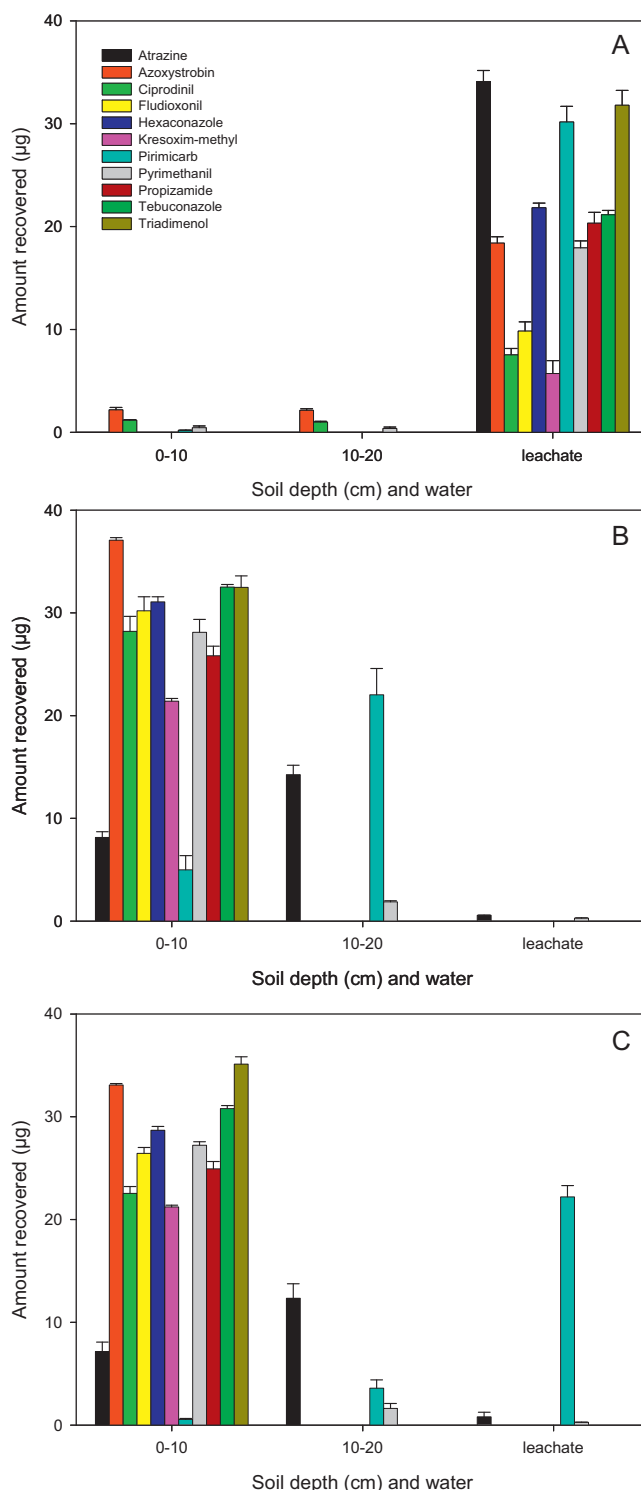


Fig. 1. Distribution of pesticides applied to unamended (A) and amended soil columns with CSM (B) and SCG (C). The error bars denote standard deviation.

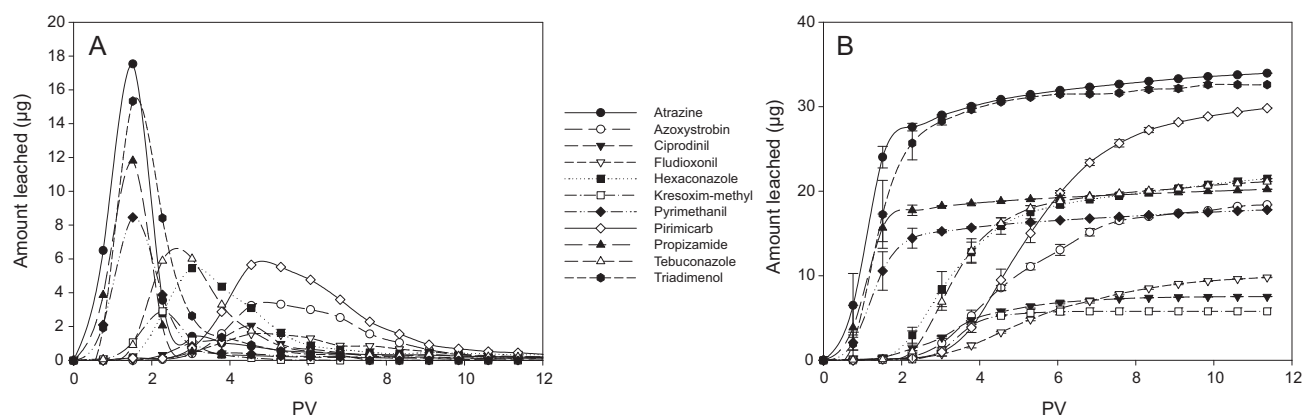


Fig. 2. Relative (A) and cumulative (B) breakthrough curves (BTCs) of pesticides applied to soil (not amended) columns. The error bars have been omitted in the left figure for better observation.

2.6. Analytical determinations

2.6.1. GC/MS analysis

An Agilent (Waldbronn, Germany) HP 6890 gas chromatograph equipped with a 5973N mass spectrometer and automatic split-splitless injector Agilent 7683 was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from m/z 50–500 at 3.21 s per scan. The ion source temperature was 230 °C, and the quadrupole temperature was 150 °C. The electron multiplier voltage (EM voltage) was maintained at 1 300 V, and a solvent delay of 4.5 min was employed. An HP-5MSI fused silica capillary column (30 m × 0.25 mm i.d.) and 0.25 µm film thickness, supplied by Agilent Technologies, was employed. The column temperature was maintained at 70 °C for 2 min and then programmed at 25 °C/min to 150 °C, increased to 200 °C at a rate of 3 °C/min, followed by a final ramp to 280 °C at a rate of 8 °C/min, and held for 10 min. One microliter of samples was injected in splitless mode. Analysis was performed with selected ion monitoring (SIM) mode using primary and secondary ions. The target and qualifier abundances were determined by injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from m/z 50 to 500. Pesticides were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier-to-target ratios. Retention times had to be within 0.1 min of the expected time, and qualifier-to-target ratios had to be within a 10% range for positive confirmation. The concentration of each compound was determined by comparing the peak areas in the sample

to those found for mixtures of pesticide standards of known concentration.

3. Results and discussion

3.1. Leaching and persistence of pesticides on unamended soil

The distribution from soil and water for the pesticides applied to unamended soil columns is shown in Fig. 1A. Total recoveries of pesticides from soil and water were in the range 11–64% for kresoxim-methyl and triadimenol, respectively. The difference between initial and recovered amounts can be attributed to biochemical degradation during the experiment. Atrazine was only used for comparison. All pesticides were found in leachates although in different proportions. Only azoxystrobin (8%), cyprodinil (4%), pirimicarb (2%), and pyrimethanil (1.5%) were recovered from the upper and lower soil layers.

Relative and cumulative breakthrough curves (BTCs) of the pesticides applied to unamended soil columns are shown in Fig. 2. Relative BTCs show that triadimenol, pirimicarb and pyrimethanil behave as atrazine with a rapid leaching (maximum about 1.5 PV). For triazole fungicides (hexaconazole and tebuconazole the maximum amount leached is observed at 3 PV while the rest of the studied pesticides the higher potential leaching is about 5 PV. At the end of the experiment, when 9 PV were leached the shape of the curves with upward tendency indicates a certain interaction with the organic and inorganic soil colloids. Cumulative BTCs show that triadimenol, and pirimicarb behave as “leacher”

Table 3

Parameters obtained ($n=3$) from the first-order kinetics for the studied pesticides.

Pesticide	R^2 ^a	C_0 ^b	K (days ⁻¹) ^c	$S_{V/X}$ ^d	$t_{1/2}$ (days) ^e
Azoxystrobin	0.92 ^{***}	0.32	0.001	0.01	693
Cyprodinil	0.80 ^{**}	0.32	0.001	0.02	693
Fludioxonil	0.93 ^{***}	0.30	0.003	0.02	231
Hexaconazole	0.77 ^{**}	0.30	0.001	0.02	693
Kresoxim-methyl	0.99 ^{***}	0.32	0.005	0.01	139
Pirimicarb	0.97 ^{***}	0.30	0.010	0.02	69
Propyzamide	0.98 ^{***}	0.33	0.006	0.01	115
Pyrimethanil	0.88 ^{***}	0.31	0.001	0.01	693
Tebuconazole	0.79 ^{**}	0.31	0.001	0.02	693
Triadimenol	0.93 ^{***}	0.34	0.001	0.01	693

^a Determination coefficient.

^b Theoretical initial concentration.

^c Rate constant.

^d Standard error of estimation.

^e Half-lives.

^{**} $p < 0.01$.

^{***} $p < 0.001$.

compounds because 60–65% of their initial amount was found in leachates, similar to atrazine (68%), a compound with known leaching behavior while azoxystrobin, tebuconazole, hexaconazole, pyrimethanil and propizamide show medium leachability (about 40% was found in leachates) and they have transient properties (i.e., borderline leacher) according to Groundwater Ubiquity Score Index [18]. Finally, the other compounds (kresoxim-methyl, fludioxonil, and ciprodinil) have low leachability because the amount leached was lower than 20% of the total mass fraction applied to the column. Field studies carried out by us with the same soil and using soil lysimeters (unpublished data) corroborated the presence of the studied pesticides in leaching water. As we previously demonstrated [20], the leachability of some of the studied pesticides was markedly lower in a soil with similar texture but high OM content (1.6%). Like this, for pirimicarb, triadimenol and pyrimethanil, 48%, 41% and 6% of their initial amounts, respectively were recovered from leachates while the amount recovered of azoxystrobin, hexaconazole, kresoxim-methyl, and tebuconazole was lower than 2%.

Bearing in mind the potential leachability of the studied compounds, the evolution of pesticide residues with the time was simultaneously assessed in the same soil to know the GUS index of each compound in our experimental conditions. The initial concentration recovered for all pesticides was in the range $0.34\text{--}0.37\text{ ng g}^{-1}$. The dissipation of all pesticides follows a pseudo first-order kinetics ($R^2 = 0.77\text{--}0.99$). The kinetic parameters obtained can be seen in Table 3. A greater dissipation rate was observed for pirimicarb, propizamide, kresoxim-methyl, and fludioxonil with percentages remaining at the end of the experiment lower than 25% ($t_{1/2} = 69\text{--}139$ days) as can be seen in Fig. 3, where the time-course of herbicide residues is shown. For the other compounds, more than 60% ($t_{1/2} \approx 700$ days) of the initial amount was recovered after 360 days.

Fig. 4 shows the calculated GUS Index from the obtained half-lives and the values of K_{OC} obtained from scientific literature [17]. With the exception of fludioxonil and propizamide, all the other

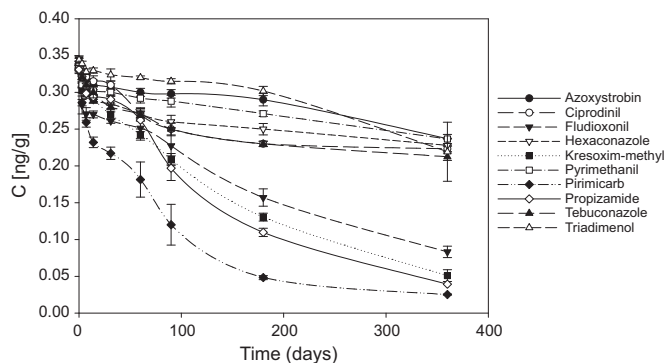


Fig. 3. Evolution of pesticide residues in the soil. The error bars denote standard deviation.

pesticides exhibit higher values one than the obtained from bibliography. The higher leachability of the pesticides in our case is probably due to the low organic matter content of the soil used. The inserted graphic in Fig. 4 shows a good correlation between the observed and bibliographical values of GUS Index ($r = 0.93$). Only propizamide (underestimation of 1.75 units) and pirimicarb (overestimation of 1.45 units) are outside of the 95% confidence interval. For the other pesticides residuals were lower than 0.7 units.

3.2. Effect of amendments on pesticide leaching

The greater water pore volumes in amended soils imply an increase in the water holding capacity as consequence of the decrease in larger pores and the increase in the smallest size pores by amendments. Cox et al. [21] showed a reduction of large conducting pores ($>1\ \mu\text{m}$) upon amendment with solid sewage sludge compared to liquid amendment of the same material. They suggest that nonsoluble OM cements and aggregates together soil particles, blocking large conducting pores.

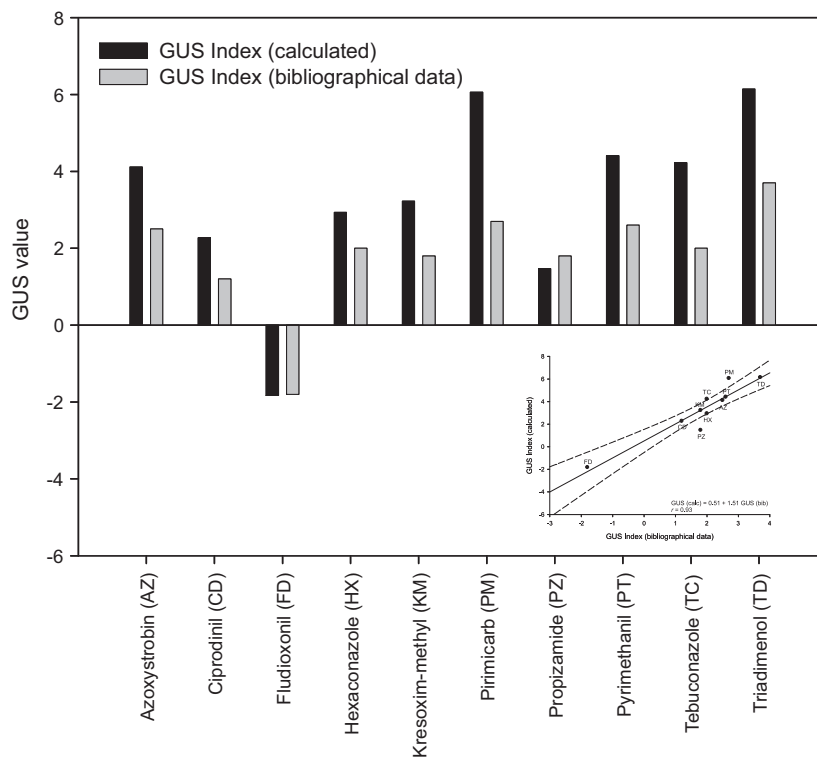


Fig. 4. Comparison between calculated and bibliographical GUS indexes.

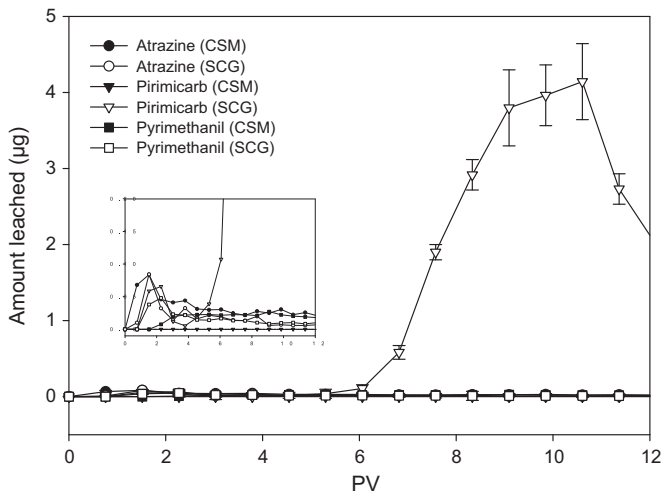


Fig. 5. Relative breakthrough curves (BTCs) of pesticides applied to amended soil (CSM and SCG) columns. The error bars denote standard deviation.

As can be seen in Fig. 1, where the distribution from soil and water of pesticides applied to amended soil columns is shown, the addition of OM drastically reduced their movement. For the soil amended with CSM (Fig. 1B) only atrazine (1%) and pyrimethanil (0.6%) were found in leachates. The amount recovered from the soil ranged from 43% to 74% of the initial mass applied to the columns for kresoxim-methyl and atrazine, respectively. The higher proportions were recovered from the upper layer (0–10 cm) with the exception of pirimicarb where 44% of its initial amount was found in the lower layer (10–20 cm). Similar behavior was observed for the movement of the pesticides in the soil amended with SCG (Fig. 1C) but in this case the major fraction (44%) of pirimicarb was found in leachates. As it is shown in Fig. 5 BTC of pirimicarb in soil columns amended with SCG begin at about 6 PV and reach a maximum at about 10.5 PV. Pirimicarb has the lower log K_{OC} (1.9) and log K_{OW} (1.7) and higher water solubility (3100 mg/L) of the stud-

ied compounds. Therefore, this compound had a high probability to leach. For the other pesticides, the maximum amount leached is lower than 0.1 µg. The decrease in pesticide leaching by use of SCG can be attributed to its high content in lignocellulosic biomass (cellulose, hemicellulose and lignin). Lignocellulosic materials are commonly used as starting material for preparing activated carbon, a compound with high adsorption capacity [22]. A lignocellulosic substrate from the agro-industry was shown good as a low-cost and effective adsorbent for removal pesticides from soil [23] and wastewaters [24].

Many papers contribute relevant information about the influence of different organic wastes (solid, semisolid, and liquid waste) originated by human and productive activity on the movement of pesticides in soils [15]. However, there is no published information about the effect of coffee wastes on pesticide leaching. The OM is reported as a major controller component in the sorption, transformation, and transport of many organic pollutants in soil [25]. Specially, pesticide sorption has shown and increase through organic amendment addition to the soil. However, in this way dissolved organic matter (DOM), is incorporated, which affects the pesticide sorption and movement [21].

The fraction of DOM that absorbs light is referred to as CDOM (colored dissolved organic matter). The absorption of light by organic compounds is dependent on their chemical nature. CDOM absorbs light strongly in the UV and blue region and its absorption decreases with increasing wavelength. When present in high concentrations, CDOM therefore gives water a yellow-brown color. The shape of the adsorption curve is often characterized by an exponential equation. So a degree of the variations in the spectral slope coefficient (S) values observed in the natural environment can be explained by varying relative proportions of humic and fulvic fractions. The amber color of the amended soils leachates is indicative of the presence of DOM, as it is shown in Fig. 6, which shows the absorbance measurements UV (285 nm) and VIS (450 nm). At lower pore volumes applied higher absorbance was observed. After 2–3 PVs an important decrease in the DOM was observed for the amended soils. Amending the soil always induces an increase in DOM [9], and the pesticides would interact with the soluble form

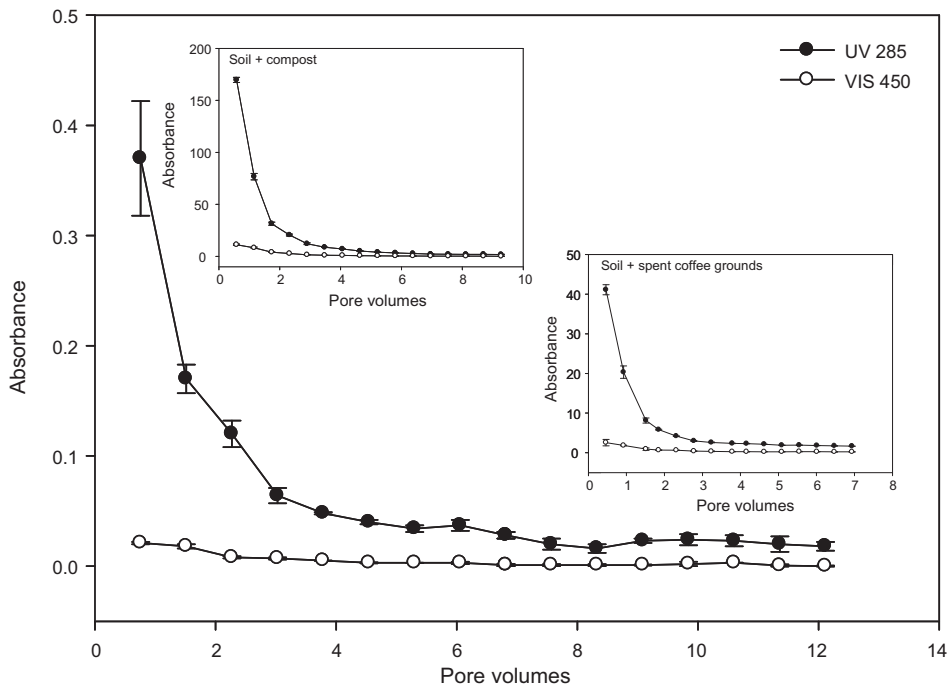


Fig. 6. Absorbance measurements of the leachates obtained from the unamended and amended (inserted graphics) soils. The error bars denote standard deviation.

of OM. In our case, a decrease in pesticide leaching was observed with the increase in DOM of leachates. The environmental effect of the amendment on pesticide transport is ambiguous. On the one hand, it could enhance their retention by increasing soil organic carbon content [25]. The type and capacity of adsorption of humic acids (HAs) from various soil and organic amendment for different classes of pesticides appear to depend more on the molecular structure and chemical reactivity of the pesticide than on the structural and functional properties of the HAs [14,26]. Like this, leaching studies using a soil with low OM content (0.5%) show that OM application drastically reduces the metolachlor leaching losses from 50% to <1% [27]. On the other hand, it has been established that DOM plays an important function in benefit in terms of pesticide movement, reducing the sorption and increasing leaching. Results obtained by Li et al. [28] show that chlorpyrifos sorption to soil (OM = 0.48%) decreased with addition of organic fertilizers; they explained this decrease in K_{OC} value by a possible effect in the reduction of the surface tension with DOM addition, increasing the solubility of the compound. Also, some authors have observed a DOM effect in diuron transport which could be explained by higher DOM leaching increasing diuron–DOM interactions [29].

4. Conclusions

Many soils, mainly in the Mediterranean area, are characterized by low organic matter content. Therefore, the application of organic waste originating from different sources (farming, agro-industrial, urban and industrial by-products) to agricultural soils is a practice that has been carried out for centuries, due to its fertilizer properties and contribution to the physicochemical and biological properties of the soil. Recently, an increasing interest has been focused on assessing the consequences of exogenous sources of organic matter on the behavior of pesticides, especially on their movement through the soil.

As a consequence of phytosanitary treatments during pepper cultivation, an important fraction of pesticides, mainly insecticides and fungicides, can be deposited on soil surface. Some compounds used to control pest and fungal diseases with scarce capacity of soil adsorption and high solubility in water such as pirimicarb, triadimenol and pyrimethanil can be leached along the clay-loam soil profile. In these cases, high pesticide loads are released into restricted areas with the potential to leach to groundwater which not only affects the human health but also can act as a source of contamination for the food chain, when used for irrigation. The results obtained in this work indicate the efficiency of both animal and coffee wastes in decreasing the mobility of the studied pesticides. The reduction in leaching losses can be attributed through increased sorption capability on the amended soils. Therefore, the application of farming or agro-industrial waste such as spent coffee grounds, an available waste at low- or no-cost is a safe practice as far as pesticide leaching is concerned.

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