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Effect of Applying an Organic Amendment on the Persistence of Tebuconazole and Fluopyram in Vineyard Soils

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Abstract: The persistence of fluopyram and tebuconazole has been studied in different crops and agricultural soils. However, the behaviour of these fungicides may be altered when they are applied as a combined formulation in organically amended vineyard soils under field conditions. The purpose of this study is to evaluate the effect of applying spent mushroom substrate (SMS) or this residue re-composted with ophite (SMS + OF) on the adsorption, dissipation, and mobility of the fungicides fluopyram and tebuconazole in vineyard soils. Triplicate 10 m^2 plots per treatment were set up in two different vineyard soils in the eastern La Rioja region: silt loam (ARN1) and sandy loam (ARN2), respectively, with low organic carbon (OC) content. The organic residues SMS and SMS + OF were applied at doses of 25 and 100 Mg ha^{-1}. The adsorption distribution coefficients (K_d) increased when SMS and SMS + OF were applied, especially at the higher dose (100 Mg ha^{-1}). The dissipation curve of both compounds fitted a two-phase kinetic model, with a very fast initial dissipation rate, followed by slower prolonged dissipation during the second phase. The dissipation half-lives (DT_{50}) ranged between 4.7 and 26.3 days for fluopyram and between 2.3 and 6.3 days for tebuconazole in the different soils, increasing for fluopyram in the ARN1 amended with SMS and SMS + OF. The fungicide residues at 15–30 cm depth were lower in the unamended and amended sandy loam soil (ARN2), indicating that fungicides are dissipated mainly in the topsoil. The results indicate different dissipation mechanisms for both fungicides, as the adsorption by soil OC prevented the dissipation of fluopyram but facilitated the dissipation of tebuconazole, probably due to the formation of non-extractable residues.

Keywords: spent mushroom substrate; ophite; agricultural soil; fungicide; persistence; dissipation

Citation: Herrero-Hernández, E.; Andrades, M.S.; Sánchez-Martín, M.J.; Marín-Benito, J.M.; Rodríguez-Cruz, M.S. Effect of Applying an Organic Amendment on the Persistence of Tebuconazole and Fluopyram in Vineyard Soils. *Agronomy* **2023**, *13*, 1270. https://doi.org/10.3390/agronomy13051270

Academic Editor: David Houben

Received: 7 March 2023
Revised: 18 April 2023
Accepted: 27 April 2023
Published: 28 April 2023

1. Introduction

Fungicides are compounds used to control fungal diseases, accounting for more than 40% of total pesticide sales in the European Union, while organic fungicides do so for 60% of total fungicides [1]. These compounds are applied on grains and cereals, fruit and vegetables, with particularly intensive use in viticulture, where they make up 90% of all pesticide applications in wine-growing regions [2]. New fungicidal compounds or a combination of several fungicides with different modes of action are currently being considered strategies of interest for preventing resistances to commonly used fungicides [2,3].

The fungicide fluopyram (N-[2-[3-chloro-5-(trifluoromethyl)-2-pyridyl]ethyl]-α,α,α-trifluoro-ortho-toluamide) is the first compound of a new group of fungicides called pyridinyl ethylbenzamides [4], which have been swiftly developed and launched onto the market because they inhibit the succinate dehydrogenase enzyme [5]. These compounds control several plant disease-causing pathogens (*Botrytis cinerea*, powdery mildew,

Sclerotinia spp. and *Monilinia* spp.) in horticultural, field, and vegetable crops. Fluopyram is highly effective even at low application rates, both on its own and in co-formulations with other fungicides. Tebuconazole, 1-(4-chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-ylmethyl)pentan-3-ol is a broad-spectrum fungicide that inhibits demethylation synthesis in the fungal cell membrane, and its co-formulation with fluopyram could provide several advantages, such as higher efficacy and a lower risk of pathogens developing a resistance to fungicides [3]. The co-formulation of fluopyram and tebuconazole has protective, curative, and eradicative properties against the fungal pathogens of a number of fruit and vegetable crops and has recently been registered for the effective control of powdery mildew and anthracnose in chilli and grape [5,6].

Fluopyram has proven to be moderately-to-highly persistent with DT_{50} values ranging from 21 to 386 days and 24 to 539 days in different types of soil at European and US field sites, respectively [5], or DT_{50} ranging from 117 to 717 days or 93.2 to 144.6 days under laboratory or field conditions, respectively [7]. However, tebuconazole is considered moderately or highly persistent with DT_{50} values in soils of 25.8–91.6 days and >365 days under field or laboratory conditions, respectively [7,8]. In fact, residues of both fungicides have been detected in soils following their application in different crops across numerous countries [6,9]. Despite this high persistence, both fungicides have also been detected in surface water and groundwater when they have been included in different monitoring studies worldwide [10–12]. The presence of both compounds has been detected in groundwater and/or vineyard soils in northeast and northwest Spain [13,14].

According to the groundwater ubiquity score (GUS) leaching potential index, fluopyram is classified as a highly leachable fungicide, while tebuconazole is a transition state, with values of 3.23 and 1.86, respectively [7]. Diffuse or point contaminations could therefore occur due to the extensive use and continuous application of these fungicides in specific crops, especially vineyards, as indicated for other organic fungicides [3].

Adsorption–desorption, leaching, and degradation are the main processes that lead to the final dissipation of organic fungicides [15], depending on the soil and agricultural management practices, and/or the conditions of fungicide application [5]. The dissipation rates of fluopyram and tebuconazole in laboratory and field studies have recorded a wide range of DT_{50} values, which are very high in different types of bare soils [4,5,7]. However, narrower ranges and shorter DT_{50} values have been reported, depending on the concentrations applied, soil type, organic matter (OM), moisture, and environmental conditions [16].

Dissipation studies of fluopyram and tebuconazole following their application as the Luna® Experience (Bayer Crop Science) co-formulation are less frequent, and their residues have been determined in different fruits and vegetables, although only a few studies have addressed the dissipation of both fungicides in soils [6,17,18]. The Luna® Experience formulation is usually applied to crops cultivated over large areas; however, there are no studies on the dissipation of these fungicides applied as a combined formulation in vineyards.

Vine cultivation is very extensive in La Rioja region (NE Spain), where 35.7% of the total agricultural land is dedicated to this crop. The application of both fungicides as a combined formulation is recommended by the authorities [19]. These vineyard soils are characterised by a low OM content and by degradation and erosion issues. They are therefore subjected to different management practices, which could alter the behaviour of fungicides after their application. Current management practices for these soils include the application of organic residues as amendments to maintain appropriate soil aggregate stability and structure [20,21], or organic residues mixed with rock dust as organic-mineral amendments to restore the nutrients extracted from the soil with each harvest [22,23]. Both amendments enhance the fertility and re-mineralisation of soils, and they are applied in vineyard soil in the La Rioja region, Spain [24,25].

Spent mushroom substrate (SMS) is an organic waste generated by the production of edible mushroom [26]. Its use as organic amendment is increasing because global

mushroom farming has spread over the past fifty years [27]. Each ton of mushroom generates up to 3.5 tons of SMS, amounting to 250,000 tons per year [28]. SMS and SMS re-composted with rock dust are recommended as soil amendments for their beneficial effects in soils and for improving a vineyard's nutritional balance and resistance to disease [29].

However, the SMS applied as an amendment may alter the behaviour of pesticides applied to vineyard soils. Previous laboratory and field studies have reported on the influence of sources and doses of SMS on the degradation/dissipation or persistence of different fungicides [30–33]. The OC from SMS enhances the adsorption of fungicides, thus decreasing their dissipation in amended soils, while dissolved organic carbon (DOC) enhances their dissipation and leaching [34]. The results reflect the influence of organic amendment, soil characteristics, and the chemical structure of fungicides on the fate of these compounds in amended soils [35]. There are no studies on the effect that the application of SMS or SMS + rock dust to vineyard soils has on the dissipation of both fungicides applied as a combined formulation, although microbial populations are stimulated during the initial stages of the composting process, which may affect the dissipation rate of fungicides applied simultaneously [36,37].

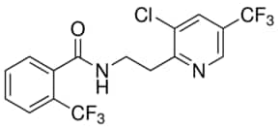
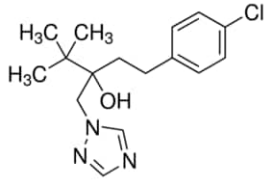
The scientific significance and application value of the simultaneous evaluation of these two fungicides lie in the fact that the processes (adsorption, dissipation, and mobility) controlling the behaviour of these fungicides applied as a combined formulation may be altered in organically amended vineyard soils under field conditions. With a view to improve our understanding of the fate of fungicides in vineyard soils subject to different management practices, the aim here was to study the following: (1) the adsorption and dissipation in topsoil samples (0–15 cm), and mobility in soil samples at a depth of 15–30 cm of fluopyram and tebuconazole in two sites located in eastern La Rioja, and (2) the effect on the persistence of two doses of two organic amendments based on SMS alone or re-composted with rock dust (ophite). The fungicides were applied as a combined commercial formulation (Luna® Experience), and the study was carried out in experimental plots under field conditions.

2. Materials and Methods

2.1. Chemicals

The PESTANAL™ analytical standards of fluopyram (≥98.0% purity) and tebuconazole (99.3% purity) were purchased from Sigma-Aldrich, Madrid, Spain, and the commercial formulation of fluopyram and tebuconazole, Luna® Experience (200 g L^{-1} fluopyram and 200 g L^{-1} tebuconazole *w*/*v*) from Bayer CropScience S.L., Paterna, Spain, was used (Table 1) [7]. HPLC grade methanol was supplied by VWR International Eurolab, S.L.U. (Barcelona, Spain).

Table 1. Characteristics of fluopyram and tebuconazole [7].

Properties	Fluopyram	Tebuconazole
Chemical structure		
Molecular weight (MW)	396.76	307.82
Solubility in water (mg L^{-1})	16 (low)	36 (low)
log Kow	3.3 (high)	3.7 (high)
Kf/Kfoc (mL g^{-1})	4.41/278.9 (moderately mobile)	12.69/769 (slightly mobile)
Field DT_{50} (days)	118.8 (persistent)	47.1 (moderately persistent)
Field DT_{90} (days)	833 (very persistent)	177 (persistent)
GUS index	3.23 (high leachability)	1.86 (transition state)

2.2. Organic and Inorganic Amendments

The SMS organic amendment was produced by *Agaricus bisporus* cultivation. SMS initially consists of a mixture of cereal straw and poultry litter, ammonium nitrate, urea, and minerals (gypsum and/or calcium carbonate). Once the mushrooms have been harvested, the remaining substrate is aerobically re-composted in 2.5 m high piles for three months under aerobic conditions prior to its use as an amendment. SMS is initially mixed with woodchips for aeration, being regularly turned to favour maturation and decomposition, which increase its uniformity and stability [30].

The SMS was also mixed with ophite (OF) at 15%, and the mix (SMS + OF) was re-composted for one month. OF is a sub-volcanic igneous rock composed of manganese, iron, zinc, and copper, among other metals, with a high concentration of magnesium titanite and plagioclase, and a medium-low concentration of epidote, quartz, and montmorillonite–chlorite. It is used to re-mineralise the soil. Both SMS and SMS + OF were kindly supplied by Sustratos de La Rioja S.L. (Pradejón, La Rioja, Spain). The characteristics of SMS, OF, and SMS + OF were determined on a dry weight basis by the usual analysis methods [24,30] (Table 2).

Table 2. Characteristics of the organic and inorganic materials SMS, ophite (OF), and SMS + OF applied as an organic amendment to the soils and those of the unamended soils (ARN1 and ARN2).

Parameters	SMS	OF	SMS + OF	ARN1	ARN2
Texture				Silty loam	Sandy loam
Sand (%)				27.8	56.7
Silt (%)				55.3	27.0
Clay (%)				16.9	16.2
pH	7.60 ± 0.04	8.37 ± 0.34	7.48 ± 0.01	8.10 ± 0.10	8.20 ± 0.02
Electrical conductivity (dS m^{-1})	10.9 ± 0.08	0.25 ± 0.00	10.6 ± 0.27	0.30 ± 0.01	0.17 ± 0.04
$CaCO_3$ (%)	14.6 ± 0.27	2.38 ± 0.14	10.7 ± 0.33	9.85 ± 0.78	12.9 ± 0.28
OM (%)	41.9 ± 0.34	0.09 ± 0.04	31.2 ± 0.68	1.67 ± 0.34	1.53 ± 0.38
OC (%)	24.3 ± 0.20	0.05 ± 0.02	18.1 ± 0.39	0.97 ± 0.20	0.89 ± 0.22
Total N (%)	2.05 ± 0.00	0.02 ± 0.00	1.67 ± 0.03	0.12 ± 0.02	0.10 ± 0.00
C/N	11.9 ± 0.09	3.21 ± 1.55	10.8 ± 0.07	8.08 ± 0.33	8.90 ± 2.90
CEC (cmol + kg^{-1})	42.9 ± 1.01	1.66 ± 0.03	32.9 ± 1.84	7.50 ± 0.90	6.56 ± 0.75

2.3. Experimental Setup

Two vineyard soils (Aridisol, Typic Haplocalcid) [38] were selected in "La Rioja Oriental" (NE Spain) at Arnedo (ARN1 (42°16′23.6″ N, 2°04′0.058″ W) and ARN2 (42°12′0.029″ N 2°04′13.7″ W)). ARN1 and ARN2 have a silty loam and a sandy loam texture, respectively. Both soils have an OM content < 2% (Table 2). The weather conditions (precipitation and air and soil temperature) were monitored over time at a weather station close to the study site.

The dissipation field assay was conducted over 258 days (from March to November 2019). An experimental layout of randomised complete blocks was designed with five treatments and three replicates per treatment (15 plots of 10 m^2) at each site.

Prior to its amendment, the soil was tilled using a field cultivator. ARN1 and ARN2 plots were amended with SMS or SMS + OF at doses of 25 and 100 Mg ha^{-1} (dry weight), corresponding to an application rate of ≈5 and 20 g C kg^{-1} soil, respectively. SMS or SMS + OF was incorporated into the first 25–30 cm of topsoil layer in February 2019, using a rotavator. Five treatments were undertaken at each site: unamended soil (ARN), soil amended with SMS at both doses (ARN + SMS25, ARN + SMS100), and soil amended with SMS + OF at both doses (ARN + SMS + OF25, ARN + SMS + OF100). Five more control plots at each site (one unamended and four amended with a high and low rate of SMS or SMS + OF, respectively) did not receive any fungicide. Untreated soils from these plots were used as controls for adsorption studies of fluopyram and tebuconazole in the laboratory, as indicated below.

Samples of unamended and amended soils (0–15 cm) were taken one month after SMS application (March 2019). The soil samples were air dried and sieved (<2 mm). Tables 2 and 3 and Figure 1 present the principal soil characteristics determined by validated methods [24]. Briefly, soil pH and electrical conductivity (EC) were determined in a soil/water suspension (1/5 w/v ratio). Total OC and N were determined using a LECO CN628 elemental analyzer (LECO Corporation, St. Joseph, MI, USA). OM was calculated from the OC results multiplied by 1.724. DOC was determined in soil extracts (1/2 w/v ratio in deionized water) after soil shaking for 24 h at 20 °C, centrifugation for 20 min at 10,000 rpm, and filtering (Minisart NY 25 filter 0.45 µm, Sartorius Stedim Biotech, Göttingen, Germany), using the LECO CN628 elemental analyzer. Soil particle size distribution was determined using the pipette method. Inorganic carbon was determined as $CaCO_3$ with a Bernard calcimeter. Clay minerals (illite and kaolinite) were qualitatively identified in the soil fraction by the X-ray diffraction technique using a Philips PW-1710 diffractometer (Eindhoven, The Netherlands).

Table 3. Organic carbon content, OC (%), of unamended soils (ARN) and soils amended with SMS (+SMS) or SMS + OF (+SMS + OF) at two doses (25 and 100 Mg ha^{-1}), one month after amendment application (March 2019).

Soil	ARN	+SMS25	+SMS100	+SMS + OF25	+SMS + OF100
ARN1 (0–15 cm)	0.97 ± 0.06	1.76 ± 0.14	3.13 ± 0.26	2.58 ± 0.15	5.43 ± 0.51
ARN1 (15–30 cm)	1.00 ± 0.15	1.20 ± 0.11	1.70 ± 0.13	1.20 ± 0.09	2.50 ± 0.21
ARN2 (0–15 cm)	0.89 ± 0.03	1.53 ± 0.09	2.58 ± 0.40	1.27 ± 0.12	3.94 ± 0.29
ARN2 (15–30 cm)	0.60 ± 0.02	0.96 ± 0.11	2.20 ± 0.32	1.10 ± 0.08	1.40 ± 0.02

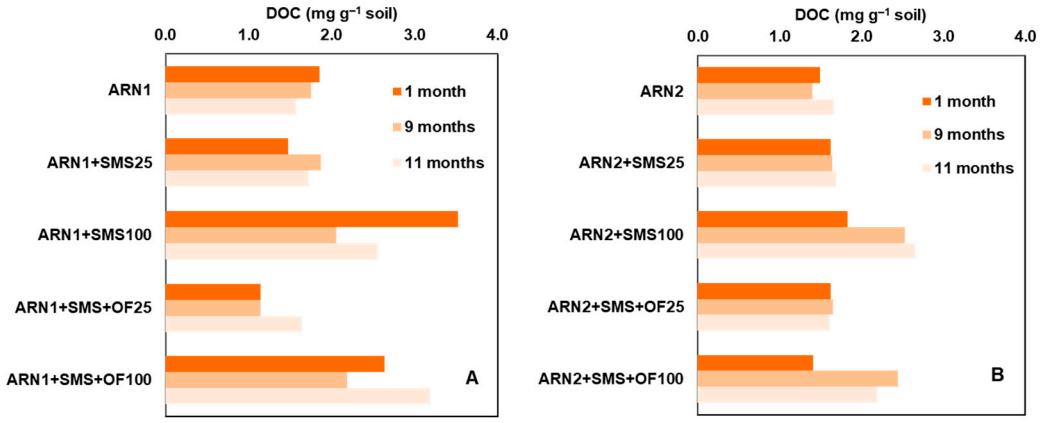


Figure 1. Dissolved organic carbon content, DOC (mg g^{-1} soil), of unamended soils (ARN1 (**A**) and ARN2 (**B**)) and soils amended with SMS or SMS + OF at two doses (25 and 100 Mg ha^{-1}) at 20, 103, and 215 days after fungicide application.

2.4. Fungicide Application and Soil Sampling

One month after the amendment of ARN1 and ARN2, the commercial formulation (20% fluopyram and 20% tebuconazole w/v) was applied manually using a backpack sprayer. The fungicide dose (0.38 L ha^{-1}) at the recommended agronomical rate was applied to the plots in March 2019. Neither fungicide had been applied to these soils during the five previous years.

Soil samples from 0 to 15 cm were collected to determine fungicide dissipation at 0, 2, 6, 14, 20, 30, 45, 60, 103, 133, 215, and 258 days after treatment. Five sub-samples were taken in each plot, mixing them before they were transferred to polypropylene bottles. Additionally, five soil cores were also collected at a depth of 30 cm at 20, 60, 103, 133, 215, and 258 days after fungicide application in each plot to determine fungicide residues and mobility at a depth of 15–30 cm. The cores were then sectioned into two segments of 15 cm each, and composite samples of five cores were transferred to a polypropylene bottle. All

the samples were stored and transported to the laboratory in portable refrigerators. The soil samples were air-dried overnight if necessary and then sieved (<2 mm). The moisture content of the bulk sample was determined by weight difference, measuring the soil sample mass before and after drying at 110 °C for 24 h.

2.5. Fungicides Extraction and Analysis

Both fungicides were extracted from duplicate subsamples of moist soil (6 g) from each plot, which were transferred to a glass tube, with methanol (12 mL). The samples were shaken at 20 °C for 24 h and then centrifuged at 5045 g for 15 min and filtered to remove particles >0.45 μm in a Millex HV filter (Millipore, Bedford, MA, USA). A volume of 7.5 mL was transferred to a clean glass tube and evaporated until dryness at 37 °C under a nitrogen stream using an EVA-EC2-L evaporator (VLM GmbH, Bielefeld, Germany). The residue was dissolved in 1 mL of methanol and transferred to a HPLC glass vial for analysis.

The amounts recovered were determined by spiking three unamended and amended soil samples with analytical grade fluopyram and tebuconazole to a final concentration of 0.100 μg g^{-1} and performing the extraction procedure as described above. The mean recovery values of fluopyram and tebuconazole from spiked unamended and SMS- or SMS + OF-amended soils at both doses ranged between 79% and 98%.

Fluopyram and tebuconazole were analysed by HPLC-MS using a Waters chromatograph (Waters Assoc., Milford, MA, USA), equipped with a model e2695 multisolvent delivery and autosampler system attached to a ZQ mass spectrometer detector (MS), with Empower software as the data acquisition and processing system. A Luna 3 μm PFP2 100 Å (Phenomenex, Torrance, CA, USA) LC column (150 × 4.6 mm) was used at ambient temperature, and the mobile phase was methanol + water + 5 mM ammonium formate (90 + 10%). The flow rate of the mobile phase was 0.25 mL min^{-1} and the sample injection volume was 20 μL. Detection was carried out by HPLC/MS to quantify and confirm the identity of the compounds by monitoring the positive molecular ion (m/z): 397 for fluopyram and 308 for tebuconazole. Under these conditions, the fluopyram and tebuconazole retention times were 5.4 and 6.6 min, respectively. Calibration was performed from 0.01 to 2.5 μg mL^{-1}, and the limit of detection (LOD) and limit of quantification (LOQ) were 0.3 and 1.0 μg L^{-1} for fluopyram and 0.6 and 1.9 μg L^{-1} for tebuconazole, respectively.

2.6. Adsorption Experiments

The batch equilibrium technique was used to assess fluopyram and tebuconazole adsorption by the unamended and amended topsoil samples (0–15 cm) taken from the control plots (without fungicide) after one month of SMS or SMS + OF application. Duplicate soil samples (5 g) were equilibrated with a 0.01 M $CaCl_2$-ultrapure water solution of each fungicide or both fungicides applied jointly (10 mL) at an initial concentration of 10 μg mL^{-1}. The suspensions were shaken at 20 ± 2 °C for 24 h in a thermostated chamber, with intermittent shaking for 2 h at 3 h intervals. Preliminary experiments revealed that contact for 24 h was long enough to reach equilibrium. The suspensions were subsequently centrifuged at 5045 g for 15–30 min, and the equilibrium concentrations of fungicides were determined as previously described. The number of fungicides adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the soil. The calculations were based on the assumption that the fungicide did not degrade during the adsorption studies.

2.7. Data Analysis

The dissipation data for the fungicides were fitted to the single first-order (SFO), first-order multi-compartment (FOMC), and double first-order in parallel (DFOP) kinetic models following the FOCUS work group's guidelines for selecting the best kinetic model. The coefficient of determination (r^2) and the chi-square (χ^2) test were calculated as indicators of the goodness of fit. The dissipation time for 50% (DT_{50}) and 90% (DT_{90}) of the fungicides

applied in the soils was calculated from the kinetic model that best fitted the dissipation data using the Excel Solver add-in package [39].

The adsorption data for the fungicides were used to calculate the distribution coefficient (K_d, mL g^{-1}) with the equation: $K_d = C_s/C_e$, where C_s (µg g^{-1}) is the amount of adsorbed fungicide, and C_e (µg mL^{-1}) is the equilibrium concentration of the fungicide in solution.

Standard deviation (SD) was used to indicate variability among replicates, and the Tukey post hoc test at $p \leq 0.05$ was used to determine significant differences among means. IBM SPSS Statistics v.29.0.0.0 software (2022) was used.

3. Results and Discussion

3.1. Weather Conditions during the Field Experiment

Figure 2 shows the values for precipitation, and air and soil temperature over the experimental period (258 days) recorded by an in situ weather station. The climate at these experimental sites in La Rioja is dry and warm, with a Mediterranean influence. The air and soil temperatures recorded were 42.3 °C and 33.0 °C (maximum) and −3.0 °C and 5.4 °C (minimum) (mean 16.9 °C and 19.0 °C); the maximum daily precipitation recorded was 29.1 mm at 124 days, and the total cumulative precipitation was 313.7 mm.

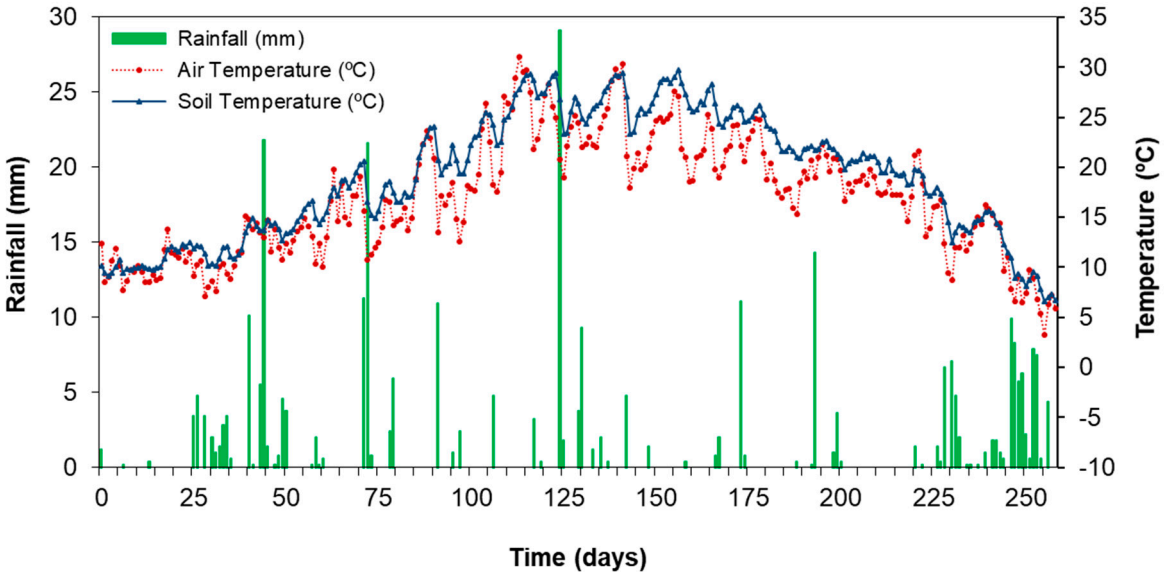


Figure 2. Precipitation and air and soil temperatures from 7 March to 19 November 2019.

The mean values for soil temperature at the different sampling times ranged between 9.6 °C and 20.1 °C, and the cumulative precipitation was 1.2, 1.4, 1.8, 63.6, 76.0, 132.3, 185.9, 229.5, and 313.7 mm at 2, 6, 14, 45, 60, 103, 133, 215, and 258 days.

3.2. Adsorption of Fungicides by Unamended and Amended Soils

The distribution coefficients (K_d) were determined to assess the adsorption capacity of fluopyram and tebuconazole by unamended and amended soils taken from the field plots one month after amendment application (Table 4).

Table 4. Distribution coefficients (K_d) for the sorption of fluopyram and tebuconazole by ARN1 and ARN2 and SMS- or SMS + OF-amended soils and by single amendment SMS and SMS + OF.

	Soils/Amendments	+SMS25	+SMS100	+SMS + OF25	+SMS + OF100
			Fluopyram		
ARN1	1.39 ± 0.22	1.95 ± 0.06	3.59 ± 0.13	3.91 ± 0.33	5.70 ± 0.28
ARN2	0.45 ± 0.13	0.71 ± 0.03	1.61 ± 1.26	1.66 ± 0.37	4.73 ± 0.18
SMS	57.4 ± 6.93				
SMS + OF	104 ± 0.37				
			Tebuconazole		
ARN1	7.26 ± 0.00	8.25 ± 0.27	15.0 ± 0.58	17.8 ± 1.82	27.3 ± 0.73
ARN2	2.21 ± 0.21	3.19 ± 0.20	4.82 ± 1.40	6.42 ± 0.91	16.4 ± 0.80
SMS	239 ± 10.2				
SMS + OF	277 ± 4.64				

The K_d values varied between 0.45 and 1.39 mL g^{-1} and between 2.21 and 7.26 mL g^{-1} for the adsorption of fluopyram and tebuconazole by unamended soils, respectively, and these values increased following the application of the amendments. The K_d values indicate the higher adsorption of tebuconazole than of fluopyram by the unamended and amended soils due to the former's higher hydrophobicity [7]. The adsorption of both fungicides was higher by the silty loam ARN1 than by the sandy loam ARN2 (Table 4). These K_d values were consistent with the Freundlich adsorption constants (K_f) reported for fluopyram and tebuconazole in unamended soils, which range between 2.94 and 6.82 and between 1.52 and 16.39 [4,8]. Fluopyram is strongly bound once adsorbed into the soil [5], with its adsorption depending on soil type, pH, and OM content [40]. Tebuconazole adsorption is influenced mainly by soil CEC, OC, and clay content [41,42]. Škulcová et al. [42] have reported that relatively low K_d values (<10) imply an appreciable risk of runoff and the leaching of tebuconazole from soils, and the application of organic residues could prevent these risks.

There was an increase in K_d values when SMS or SMS + OF were applied, especially at the higher dose (100 Mg ha^{-1}). The K_d coefficients for soils amended with SMS at both doses increased 1.4–3.6 times for fluopyram and 1.1–2.2 times for tebuconazole. When the soils were amended with SMS + OF at both doses, the K_d values increased 2.8–10.5 times for fluopyram and 2.4–7.4 times for tebuconazole. These results indicate a much higher increase in the K_d coefficients for soils amended with SMS + OF (Table 4).

There was a positive and significant correlation between K_d and OC content for fluopyram ($r = 0.924$, $p < 0.001$) and tebuconazole ($r = 0.892$, $p < 0.01$), when considering both unamended and amended soils. Soil DOC may increase or decrease the adsorption of pesticides and other hydrophobic compounds [35,43]. However, in this study, DOC had no significant effect on the adsorption of fluopyram and tebuconazole, and no correlation was found between K_d and DOC content.

An increase in the adsorption of pesticides by SMS-amended soils has already been reported [35,43]. Tebuconazole adsorption increases with the application of different organic amendments [30,44,45]. However, there are no studies on the influence of organic residues on the adsorption of fluopyram by amended soils.

The adsorption of tebuconazole by SMS and SMS + OF amendments was 2.7–4.2 times higher than that of fluopyram. The adsorption K_d values of tebuconazole by cow manure, humic acids, peat, and garden substrates have been reported to range between 41 and 529 mL g^{-1} [42], close to the values recorded here.

3.3. Dissipation of Fungicides in Unamended and Amended Soils

The amounts of dissipated fungicides in the unamended and amended soils were calculated by determining the concentrations in soil extracts. The amount determined in the samples taken the day after the application of the commercial formulation was considered to be 100% of the fungicide applied. The dissipation curves for fluopyram and

tebuconazole followed a biphasic trend (Figure 3), with a very fast initial dissipation rate followed by a slower rate during the second phase, and were best fitted to the FOMC model. According to the EFSA reports [4,8], the dissipation curves of fluopyram and tebuconazole in unamended soils in Europe fit the SFO or DFOP models.

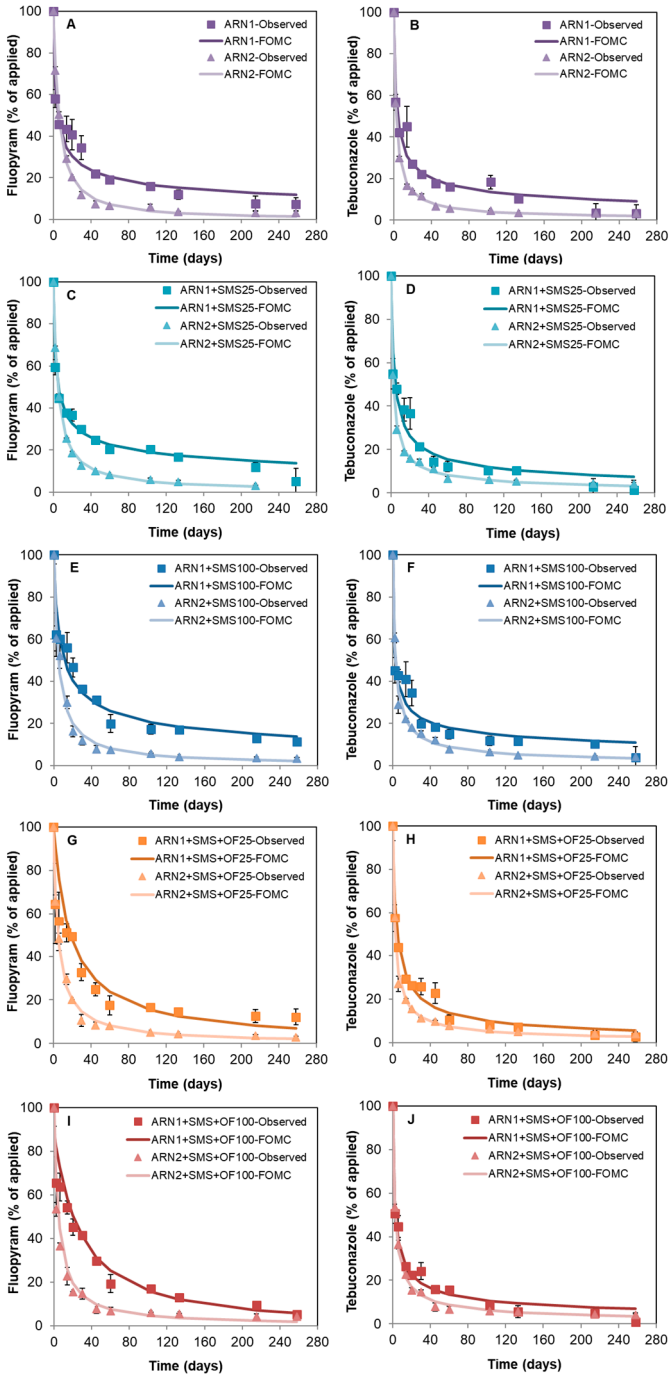


Figure 3. Dissipation kinetic curves of fluopyram (**A**,**C**,**E**,**G**,**I**) and tebuconazole (**B**,**D**,**F**,**H**,**J**) in unamended soils (ARN1 and ARN2) and soils amended with SMS or SMS + OF at rates of 25 and 100 Mg ha^{-1}. The data observed and the curves obtained from fitting the data to the FOMC kinetic model are included in graphs.

The DT_{50} and DT_{90} values, as well as the chi-square—χ^2 and coefficient of determination—r^2 parameters, which indicate the goodness of fit of observed data to the FOMC model, are included in Table 5. Overall, the DT_{50} values were higher for fluopy-

ram than for tebuconazole for all the soil treatments, indicating that the dissipation rate of fluopyram was slower than that of tebuconazole.

Table 5. Dissipation parameters (DT_{50} and DT_{90}, days) of fluopyram and tebuconazole in unamended soils (ARN1 and ARN2) and soils amended with SMS or SMS + OF at rates of 25 and 100 Mg ha^{-1}.

Soils	M0 (%)	α	β	DT_{50} (days)	DT_{90} (days)	χ^2	r^2
Fluopyram							
ARN1	99.0	0.38	0.93	4.9	408.5	13.0	0.984
ARN1 + SMS25	99.2	0.34	0.78	5.2	677.2	13.0	0.982
ARN1 + SMS100	93.8	0.44	3.50	13.1	617.8	13.3	0.970
ARN1 + SMS + OF25	101.4	0.95	16.7	17.9	170.7	10.9	0.987
ARN1 + SMS + OF100	88.1	1.35	39.3	26.3	176.5	15.2	0.971
ARN2	99.2	1.18	7.09	5.7	42.9	5.6	0.998
ARN2 + SMS25	99.9	0.93	4.18	4.7	46.0	3.0	1.000
ARN2 + SMS100	97.6	0.91	4.25	4.8	48.4	13.4	0.991
ARN2 + SMS + OF25	98.7	0.94	4.52	4.9	47.9	7.7	0.997
ARN2 + SMS + OF100	98.5	1.01	5.06	5.0	44.1	9.0	0.996
Tebuconazole							
ARN1	99.1	0.43	1.02	4.1	214.3	15.1	0.981
ARN1 + SMS25	97.9	0.50	1.55	4.7	153.2	16.0	0.979
ARN1 + SMS100	99.4	0.34	0.39	2.6	339.7	16.3	0.975
ARN1 + SMS + OF25	90,6	0.63	3.16	6.3	116.6	6.6	0.984
ARN1 + SMS + OF100	99.3	0.47	0.87	2.9	117.7	13.4	0.989
ARN2	100.2	0.79	1.77	2.5	30.6	3.8	0.999
ARN2 + SMS25	100.2	0.63	1.13	2.3	43.3	4.6	0.999
ARN2 + SMS100	100.4	0.65	1.46	2.8	48.2	7.5	0.997
ARN2 + SMS + OF25	100.4	0.69	1.41	2.4	38.1	6.9	0.998
ARN2 + SMS + OF100	99.7	0.64	1.32	2.6	47.6	5.8	0.998

The dissipation rate of fluopyram in both unamended soils was very similar (4.9 and 5.7 days), whereas the dissipation rate for tebuconazole was higher in ARN2 (2.5 days) than in ARN1 (4.1 days) (Table 5). European field studies have reported that fluopyram records high to very high persistence (DT_{50} = 21–347 days) in unamended soils, depending on soil characteristics and texture [4]. However, the rapid dissipation of fluopyram has been reported in greenhouse experiments, with DT_{50} values of 4.2–5.7 days in a sandy loam soil [46]. Tebuconazole has a moderate to medium persistence, and its DT_{50} values in European field trials range between 19.9 and 91.6 days for unamended soils [8], although it has recorded a limited persistence in the field with DT_{50} values of 1.5–2.5 days in a sandy loam soil (OC = 1.52%) at different application rates [47]. Papadopoulou et al. [47] have reported that the rapid initial dissipation phase of tebuconazole in field studies could be due to the vertical leaching of a large fraction of tebuconazole residues. The slower second dissipation phase could be due to a strongly adsorbed fraction of the pesticide that is less accessible to dissipation processes. Wang et al. [48] have reported DT_{50} values of 5.76–6.26 days for the dissipation of tebuconazole in two black soils (OC = 1.45–1.63%) under field conditions. The formation of non-extractable residues after 100 days in unamended soils is reported to be higher for tebuconazole than for fluopyram. However, the mineralisation of fluopyram after 100 days is higher than that of tebuconazole [4,8]. Furthermore, the main metabolites formed during the degradation of fluopyram and tebuconazole are fluopyram-7-hydroxy and 1,2,4-triazole [4,8]. This suggests that the main processes controlling the dissipation of these fungicides in soils are the degradation and mineralisation of fluopyram and the degradation and formation of recalcitrant residues of tebuconazole over time.

The dissipation of fluopyram and tebuconazole applied to the soil as a combined commercial formulation under field conditions has scarcely been studied. Dong and Hu [17] have reported the rapid dissipation of fluopyram and tebuconazole residues, which in field experiments involving foliar application to watermelon reach the soil with DT_{50}

of 15.8 and 11.2 days in a sandy loam soil (OM = 1.71%) and 24.8 and 14.4 days in a clay loam soil (OM = 3.89%), respectively. Matadha et al. [6,49] have determined dissipation DT_{50} values for fluopyram and tebuconazole in field experiments of 29.7–36.0 days and 26.8–49.5 days in a sandy loam soil (OC = 0.4%). These DT_{50} values are higher than those determined here.

During the first 20 days after fungicide application, a cumulative precipitation of 1.8 mm and a mean soil temperature of 10.2 °C could have contributed to the fast dissipation of the fungicides due to the formation of unextractable residues. Thereafter, during the 60 days following fungicide application (first phase of the dissipation curve), a cumulative precipitation of 76 mm and a mean soil temperature of 12.1 °C (Figure 2) may have increased the dissipation rate of the compounds due to their degradation and/or mobility in the soil profile.

The DT_{50} value in ARN1 + SMS25 (5.2 days) for fluopyram was similar to the unamended soil (4.9 days), although its dissipation rate in ARN1 + SMS100, ARN1 + SMS + OF25, and ARN1 + SMS + OF100 was slower than in ARN1, presenting DT_{50} values up to five times higher than in the unamended soil (Table 5). Fluopyram is a fungicide with low solubility in water that could record a higher retention rate in soils with higher OC content, thus decreasing its availability and dissipation rate. There are no laboratory or field studies on the effect of organic amendments on the dissipation of fluopyram in soils. The degradation of fluopyram in unamended soils is influenced primarily by soil type, OM, fungicide dose, and soil moisture content [16].

The DT_{50} values for tebuconazole in ARN1 + SMS25 (4.7 days) and ARN1 + SMS + OF25 (6.3 days) were similar, while slightly lower in ARN1 + SMS100 (2.6 days) and ARN1 + SMS + OF100 (2.9 days) compared to the unamended soil (4.1 days). The higher OC content in amended soils (Table 3) did not have the same effect on the dissipation rate of tebuconazole (Table 5). There was an apparent dissipation of the fungicide that may be attributed to its higher adsorption by SMS- or SMS + OF-amended soil. The DT_{50} values reported for the dissipation of tebuconazole in a sandy loam vineyard soil, amended with SMS at doses of 40 and 100 Mg ha^{-1}, are slightly higher (8.17–10.9 days) than those calculated here [30]. The DT_{50} values of both fungicides in ARN1 amended with SMS + OF were slightly higher than those of ARN1 amended with SMS, which was due to the higher OC content of the soil amended with SMS + OF (Table 3) and higher K_d values (Table 4). The laboratory dissipation of tebuconazole in vineyard soils amended with SMS at doses of 5% and 50% w/w [33] and in biomixtures of soil and organic residues, such as olive pruning and wet olive cake [45], record higher DT_{50} values (141–592 days) than in this field study. The dissipation of pesticides is generally faster in field studies than in laboratory studies, which could be due to the processes controlling the dissipation of pesticides in the field, such as transport (runoff and leaching), degradation (photodegradation, chemical degradation, and biodegradation), adsorption, the formation of non-extractable residues, immobilisation, and plant uptake [7].

In general, the dissipation of both fungicides in ARN2 with all soil treatments was faster than in ARN1. This was evidenced mainly by the lower DT_{90} values in ARN2 than in ARN1 (Table 5). This result could be related to the lower OC content of ARN2 and its sandy loam texture (Table 3), which would result in a lower retention rate, increasing the degradation and/or mobility of fungicides. The adsorption of fluopyram and tebuconazole was lower in ARN2 (Table 4), and fungicides could be more bioavailable for degradation by microorganisms. During the first phase of dissipation, the DT_{50} values of tebuconazole and fluopyram in ARN1 amended with SMS or SMS + OF were in the same range as those of ARN2; however, the DT_{90} values during the second phase were up to 3.6–14 and 2.5–7 times higher than those of ARN2 for fluopyram and tebuconazole, respectively. In ARN1, the DT_{90} values were higher for the soil amended with SMS than for the soil amended with SMS + OF. This slowing down of the dissipation rate during the second phase could be due to the higher OC content of soils amended with SMS or SMS + OF (Table 3), which could facilitate the formation of bound residues that are less bioavailable for dissipation [33]. These results

are consistent with the highly persistent nature of fluopyram and tebuconazole reported in previous studies [4,5,8,50]. Bošković et al. [51] have reported a decrease in tebuconazole biodegradation in biochar-amended soils due to higher sorption and lower desorption rates, reducing pesticide availability for soil microorganisms. Gámiz et al. [52] have reported an increase in DT_{50} values for the dissipation of tebuconazole in a sandy loam soil amended with biochar from 50 to 58 days.

The results could be explained by the significant correlation between DT_{50} and K_d values for fluopyram in ARN1 ($r = 0.987$, $p < 0.01$), but not in ARN2. A significant correlation was also found between DT_{50} and the OC content of ARN1 ($r = 0.929$, $p < 0.05$), in agreement with the significant correlation found between K_d and OC content ($r = 0.964$, $p < 0.01$). However, no significant correlation was found for ARN2, which has a sandy loam texture. In the case of tebuconazole, a correlation was found between K_d and OC content ($r = 0.960$, $p < 0.01$) for ARN1, but no correlation was found with DT_{50}, which indicates a different dissipation mechanism for both fungicides. Adsorption by the soil OC may prevent the dissipation of fluopyram but may facilitate the dissipation of tebuconazole, probably due to the formation of non-extractable residues, as indicated previously [8,33].

3.4. Mobility of Fungicides at 15–30 cm Depth in Unamended and Amended Soils

The mobility of fluopyram and tebuconazole in unamended and amended soils was studied from the concentrations determined at the 15–30 cm soil depth at different times (20, 60, 103, 133, 215, and 258 days) after fungicide application (Figure 4).

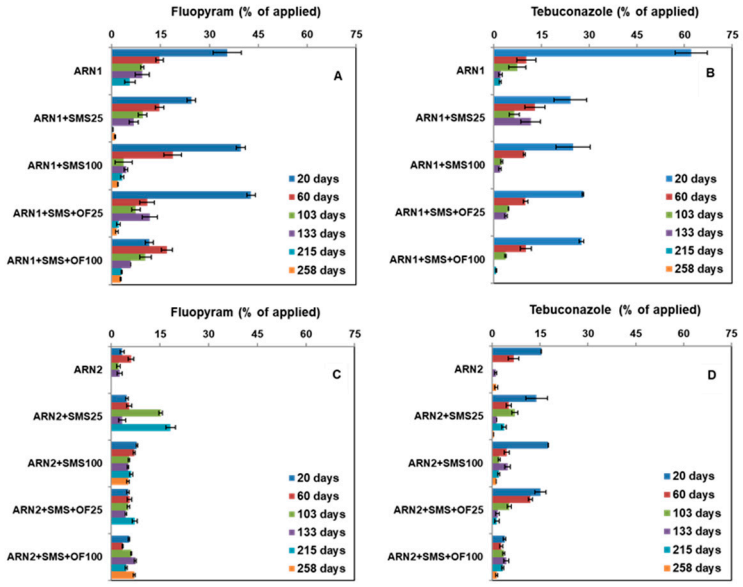


Figure 4. Fluopyram (**A**,**C**) and tebuconazole (**B**,**D**) mobility at 15–30 cm in unamended soils (ARN1 and ARN2) and soils amended with SMS or SMS + OF at rates of 25 and 100 Mg ha^{-1} at different sampling times (20, 60, 103, 133, 215, and 258 days) after fungicide application.

A fluopyram amount of 0.151 μg g^{-1} was determined in the topsoil in ARN1 20 days after its application, which is 45.7% of the fungicide initially applied (Figure 3). The fungicide dissipation rate in the topsoil was similar to that of tebuconazole, but the leached amount was lower (35.5%) according to the residual amount determined (0.117 μg g^{-1} soil) at 15–30 cm. The amounts leached decreased over time to 14.7% after 60 days of treatment, in agreement with the dissipation of fluopyram in the topsoil. Residual amounts were also detected for up to 215 days (0.018 μg g^{-1}, corresponding to 5.59% of the fungicide initially applied) (Figure 4). The moderate soil mobility of fluopyram in soils has been reported, although fungicide residues have been detected at 30–60 and 60–90 cm depths after two years of application in sandy loam soils, being attributed to excessive irrigation [5]. Nevertheless, Zhou et al. [40] have not detected fluopyram in the leached water in a sandy

soil column experiment, with most of the fungicide being found in the top 0–10 cm of a soil column, and only small amounts leached at 10–20 cm or 20–30 cm depth.

Fluopyram dissipation was slower in the amended soil than in the unamended soil, especially in the one amended with the high dose (100 Mg ha^{-1}) of SMS or SMS + OF (Table 5). In general, the amount of fungicide leached at 15–30 cm depth in these amended soils was higher after 20 days, ranging from 24.4% to 42.8% of the compound initially applied. The leached amount was lower only in ARN1 + SMS + OF100 (11.6%). Leached fungicide amounts were generally similar in all the soil treatments after 60 and 103 days, although a lower amount was determined after 133 days in ARN1 amended with the high dose of SMS and/or SMS + OF, although residual amounts (up to 0.080 μg g^{-1}) were detected in the amended soil after 258 days (Figure 4). It is worth noting the higher residual amounts detected in the soil amended with SMS + OF, with a slower dissipation rate and higher DT_{50} values in the topsoil (Table 5), as this could lead to longer fungicide residue leaching. Lohithaswan et al. [16] have reported the reduced downward mobility of fluopyram in soil columns due to the higher soil OC content, although the volume of water for leaching was increased.

The behaviour of fluopyram In ARN2 soil was similar in the unamended and amended soils. Only fungicide leaching was higher in ARN2 + SMS25, with leached amounts after 103 and 215 days of 15.2% and 18.3% of the fungicide initially applied. There were no differences in the dissipation rate of the fungicide, which indicated a faster dissipation of fluopyram than in ARN1, and the presence of residues in the unamended and amended soil is explained by the adsorption constants, which were generally low (Table 4). Fungicide residues up to 0.049 μg g^{-1} were detected after 258 days in ARN2 + SMS + OF100.

The leaching of tebuconazole in the unamended and amended ARN1 and ARN2 followed a similar pattern to that of fluopyram. The analysis of tebuconazole residues in the soil profile indicated mobility of the fungicide in all soil treatments despite this compound having a low leaching potential [8]. A residual amount of 0.146 μg g^{-1} soil was determined in the topsoil (0–15 cm) in ARN1 20 days after fungicide application (Figure 3), which is ≈50% of the amount initially applied. This fungicide is expected to dissipate in the topsoil over time, although simultaneous leaching also occurred according to the residual amount determined at 15–30 cm depth. More than 60% (0.184 μg g^{-1} soil) of the amount initially applied was determined in this soil layer after 20 days (Figure 4). The amount leached decreased over time to 10% at 60 days after fungicide application, in agreement with the dissipation of the compound in the topsoil (Figure 3). Nevertheless, residual amounts at 15–30 cm were detected for up to 215 days (0.010 μg g^{-1}, corresponding to 1.94% of the fungicide initially applied) (Figure 4). The mobility of tebuconazole could explain the presence of this compound in groundwater [13,14], although the limited transport of this fungicide from the topsoil has also been reported [52].

The residual amounts of tebuconazole in ARN1 topsoil amended with SMS or SMS + OF ranged between 0.126 and 0.173 μg g^{-1} after 20 days (34–56% of the fungicide initially applied). These values were higher in ARN1 + SMS + OF, in agreement with the adsorption coefficients determined (Table 4). Tebuconazole leaching in SMS- or SMS + OF-amended soil was also found, although the residual amounts determined in the corresponding topsoils were higher than in the unamended soil. However, leached amounts decreased in these soils compared to the unamended soil. Residual amounts of 0.079–0.102 μg g^{-1} (24.1–28.1% of the fungicide initially applied) were detected at 15–30 cm after 20 days. The fungicide residues found in the amended soils followed a similar pattern to the unamended soil over time, although lower residual amounts were generally determined (Figure 4). No tebuconazole residues were detected after 133 days of its application, and the lowest values were found in ARN1 + SMS100 and ARN1 + SMS + OF100 (<2%) (Figure 4). Residual amounts of tebuconazole were detected (0.0026 μg g^{-1}) in ARN1 + SMS + OF100 after 215 days.

The behaviour of tebuconazole in the sandy loam soil (ARN2) was different to that observed in the silty loam soil (ARN1). The dissipation rate was similar in the unamended

and amended soil, and DT_{50} values were lower than in ARN1, indicating faster dissipation (Table 5). Accordingly, lower residual amounts of tebuconazole between 0.065 and 0.087 μg g^{-1} were detected in the topsoil after 20 days (11.3–15.3% of the fungicide initially applied) (Figure 3). The leached amounts were therefore lower than those determined in ARN1 after 20 days and they were similar in all the samples, ranging between 13.9% and 17.5% of the amount initially applied, with the exception of ARN2 + SMS + OF100 (3.87%). However, over time, the residual amounts of fungicide at 15–30 cm were higher in amended soils than in the unamended one. After 258 days, fungicide residues ranged between 0.49% and 1.46% of the amount initially applied (0.007 and 0.009 μg g^{-1}) (Figure 4). The residual amounts in ARN2 + SMS + OF100 were the same as in ARN1 + SMS + OF100, possibly due to the higher adsorption capacity of this SMS + OF-amended soil. The SMS composted with rock dust such as OF has been reported to stimulate microbial populations [36,37], which could contribute to fungicide degradation. Nevertheless, the fungicide adsorption by the OM provided by the SMS amendment may be more important here than in the biodegradation process.

The results indicate that tebuconazole leaching differs in the two soils. The amounts of tebuconazole leached at 15–30 cm in ARN1 are similar in the soil amended with different doses of SMS, being generally lower than in the unamended soil. The effect of the amendment in ARN2 helped to increase tebuconazole leaching, albeit not initially, but over time. The effect of the OC provided by the amendment could facilitate the retention of tebuconazole in the topsoil and decrease its dissipation and/or leaching. The adsorption coefficients indicate the greater retention of tebuconazole by soils amended with SMS100 or SMS + OF100 than by unamended soils (Table 4). No significant relationships were found between dissipation rates and adsorption coefficients, as stated above. These results indicate a faster dissipation of the compound in amended soils due to other mechanisms, such as the formation of bound residues, as previously indicated [8].

The higher DOC content in the SMS100- or SMS + OF100-amended soils than in the unamended soil or SMS25- or SMS + OF25-amended soils (Figure 1) could facilitate fungicide mobility over time, following an initial increase in tebuconazole retention in the topsoil. This opposite effect of OC and DOC on adsorption could also explain the faster dissipation of tebuconazole in soils amended with the higher dose of SMS. The effect of OC in ARN2 played little part in retaining tebuconazole in the topsoil, as the residual amounts at 15–30 cm are similar. The leaching and/or degradation of tebuconazole in this sandy loam soil may prevail over its adsorption. The effect of DOC in this soil led to higher residual amounts of fungicide in SMS100- or SMS + OF100-amended soils, whose DOC content increased over time (Figure 1). The influence of DOC on the mobility of pesticides has already been reported, as well as its capacity to favour the adsorption or degradation of hydrophobic compounds that can be adsorbed in solution [34]. The interaction of DOC with tebuconazole in solution could facilitate the mobility of the fungicide in ARN2 more than in ARN1, as reported for other pesticides [34,53–55]. A higher initial leaching of tebuconazole in SMS-amended soils than in unamended soils has been reported in a field experiment [30], with higher fungicide concentrations through the soil profile (0–50 cm) in the SMS-amended soil. However, the opposite effect has been reported, indicating an inhibition of tebuconazole leaching in soils amended with other organic residues, such as sheep manure or spent coffee grounds [56].

4. Conclusions

The results highlight the capacity of SMS or SMS + OF amendments to increase the adsorption and decrease the dissipation and mobility of fluopyram and tebuconazole in vineyard soils with a low OC content and different textures. OC content and soil texture determine the adsorption, dissipation rate, and mobility of fluopyram and tebuconazole. The application of SMS or SMS + OF to silty loam soil increases adsorption and slows the dissipation rate of both fungicides. However, the application of organic residues to the sandy loam soil increases the degradation of fluopyram and tebuconazole, and lower

fungicide residues have been found at 15–30 cm, indicating a decrease in fungicide mobility from the topsoil. The results indicate that these organic residues produced locally in the eastern La Rioja region could be used as soil amendments to improve soil quality and decrease its degradation and erosion, while at the same time decreasing fungicide mobility, especially in sandy soils, by increasing the degradation of fluopyram or the immobilisation of tebuconazole. Nevertheless, when using SMS and SMS + OF as organic amendments, the texture and characteristics of the soils where they are applied need to be considered to prevent soil and groundwater contamination.

Author Contributions: Conceptualization, M.S.A., M.J.S.-M. and M.S.R.-C.; methodology, E.H.-H. and J.M.M.-B.; software, M.S.R.-C.; validation, E.H.-H., J.M.M.-B. and M.S.R.-C.; formal analysis, E.H.-H. and J.M.M.-B.; investigation, E.H.-H. and J.M.M.-B.; resources, M.S.A., M.J.S.-M. and M.S.R.-C.; data curation, M.J.S.-M. and M.S.R.-C.; writing—original draft preparation, M.J.S.-M. and M.S.R.-C.; writing—review and editing, M.J.S.-M. and M.S.R.-C.; visualization, M.J.S.-M. and M.S.R.-C.; supervision, M.S.A., M.J.S.-M. and M.S.R.-C.; project administration, M.S.A., M.J.S.-M. and M.S.R.-C.; funding acquisition, M.S.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was co-funded by the European Agricultural Fund for Rural Development (FEADER, European Union), the Council for Agriculture, Livestock and Environment of La Rioja (Spain), and the Spanish Ministry of Agriculture, Fisheries and Food (MAPAMA, Spain) (project 25P/18-VITIREG).

Data Availability Statement: Not applicable.

Acknowledgments: We give thanks to Project TED2021-129962B-C41, funded by MCIN/AEI/10.13039/501100011033/and the European Union (NextGenerationEU/PRTR), and Project CLU-2019-05—IRNASA/CSIC Unit of Excellence,funded by the regional government, the Junta of Castilla y León (Spain), and co-financed by the European Union (FEDER–Europe drives our growth, European Union). E. Herrero-Hernández thanks University of La Rioja, Spain, for his postdoctoral contract. We also thank Vidar Soluciones Agroambientales S.L., Sustratos de La Rioja S.L., and Nuestra Señora de Vico Winery for their technical support.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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