**Effect of olive-mill waste addition to soil on sorption, persistence, and mobility of
herbicides used in Mediterranean olive groves**

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ABSTRACT

Laboratory and field experiments were conducted to evaluate the effect of olive-mill waste (OMW) addition to a Mediterranean olive grove soil on sorption, persistence, and mobility of two herbicides which are simultaneously applied for weed control in olive groves: terbuthylazine (TA) and fluometuron (FM). Laboratory batch sorption experiments showed that OMW addition to the soil at rates of 5 and 10% (w/w) greatly enhanced the sorption of both herbicides, thus suggesting that amendment with OMW could be useful to enhance the retention and reduce the mobility of FM and TA in the soil. Incubation experiments showed that OMW increased the persistence of FM and had little effect on the long persistence of TA in the soil studied. A demonstration field experiment was also conducted in field plots with a slope of about 5%, either unamended or amended with OMW at a rate of 10 kg m⁻², and then treated with a commercial formulation containing a mixture of TA and FM. Extraction of field soil samples, taken from different soil depths (0-5, 5-10, 10-20, and 20-30 cm) at different times after herbicide application, showed that both TA and FM moved deeper in unamended soil than in OMW-amended soil, and that OMW addition affected the persistence of FM in the top layer, increasing its half-life from 24 to 58 days, while having little effect on the persistence of TA. Thus, data obtained under real field conditions were consistent with those obtained under controlled laboratory conditions. Preliminary herbicide runoff data indicated that the total herbicide runoff losses were also reduced upon OMW addition. Addition of OMW could be beneficial in reducing the mobility of TA and FM in olive grove soils, and also in increasing the persistence of FM in soils where this herbicide could be rapidly degraded.

Keywords: Organic amendment; Olive-mill waste; Fluometuron; Terbuthylazine; Leaching; Runoff

1. Introduction

The use of pesticides in agricultural activities has become a matter of concern due to potential adverse effects of pesticides on the environment and human health (Arias-Estévez et al., 2008; Hapeman et al., 2003; Rice et al., 2007). Mediterranean olive groves comprise a high-risk scenario of ground and surface water contamination by herbicides, mainly because most olive grove soils have little capacity for reducing pesticide mobility as a result of their low (< 2%) organic matter content (Albarrán et al., 2003; Celis et al., 2007; Trigo et al., 2009). In addition, pronounced slopes and climatic conditions, i.e. short but heavy rainfall events commonly occurring in seasons when herbicides are applied for weed control, exacerbate the risk of pesticide runoff and leaching (Ramos and Porta, 1994; Trigo et al., 2009). For instance, a long-term monitoring study conducted in the Guadalquivir river basin (southern Spain) revealed important seasonal contamination of ground and surface waters by herbicides commonly applied for weed control in olive growing areas (Hermosín et al., 2009). In this context, it is necessary to develop strategies to reduce the impact caused by pesticides in high-risk scenarios such as Mediterranean olive groves. Some of the currently used strategies include the use of vegetative filter strips (Krutz et al., 2005), a careful selection of the pesticide formulation or the way the pesticide is applied to the soil (Trigo et al., 2009), and the addition of inorganic and organic amendments to enhance the soil sorption capacity for the applied pesticides (Albarrán et al., 2003; Cabrera et al., 2007; Gámiz et al., 2010; Sánchez et al., 2003).

Organic waste addition to agricultural soils is a widely used agricultural practice in Spain and other Mediterranean countries, where soils have, in general, low organic matter contents (Albarrán et al., 2003; Cabrera et al., 2009; Cox et al., 1997; Herrero-Hernández et al., 2011; López-Piñero et al., 2011). This practice can also be considered as an “ecological” way for the disposal of these wastes (Barriuso et al., 2011; Crohn, 1996). The current two-phase

olive processing technology generates in Spain a great amount ($4\,000\,000\text{ Mg yr}^{-1}$) of a solid byproduct known as *alperujo* or olive-mill waste (OMW), which is rich in organic matter and whose disposal without affecting the environment represents a problem for the industry (Alburquerque et al., 2004; López-Piñeiro et al., 2007; Morillo et al., 2009). The main components of the organic fraction of OMW are lignin (32-56%), hemicellulose (27-42%), cellulose (14-25%), fats (8-20%), proteins (4-11%), water-soluble carbohydrates (1-16%), and water-soluble phenols (1-2%) (Alburquerque et al., 2004). An alternative for the disposal of this waste is its application to agricultural soils, which has been shown to improve soil structure, increase soil fertility, and control soil erosion (Alburquerque et al., 2004; Brunetti et al., 2005; Lozano-García et al., 2011). In this regard, soil amendment with OMW could be particularly beneficial since most olive oil producing countries are exposed to desertification. In contrast to other organic residues, OMW has very low concentrations of heavy metals and pathogenic microorganisms (Albarrán et al., 2003; Cabrera et al., 2009), and several studies have shown that, due to its high content in organic matter, OMW has high sorptive capacity for many pesticides, which can reduce the offsite movement of herbicides applied to agricultural soils (Albarrán et al., 2003; Cabrera et al., 2007; Cox et al., 1997; Delgado-Moreno et al., 2007; López-Piñeiro et al., 2011).

Fluometuron (FM) and terbuthylazine (TA) are applied together for preemergence and early postemergence annual weed control in olive tree cultures in Spain. The fate of TA and FM in soils differs due to their different chemical nature. The water solubility of FM (110 mg L^{-1}) is considerably higher than that of TA (8.5 mg L^{-1}), and FM is less sorbed in soils ($K_{oc} = 31\text{-}117\text{ L kg}^{-1}$) than TA ($K_{oc} = 162\text{-}278\text{ L kg}^{-1}$) (Tomlin, 2006). The half-lives of TA and FM in soils have been reported to range between a few days to several months, depending on soil characteristics, previous herbicide applications, and environmental conditions (Gámiz et al., 2010, 2012; López-Piñeiro et al., 2011; Tomlin, 2006).

Several studies have been conducted to assess the persistence and leaching of TA in OMW-amended soils under laboratory and field conditions (Cabrera et al., 2007, 2009; Dolaptsoglou et al., 2010; López-Piñeiro et al., 2011). However, there are no published results on how TA runoff losses are affected by OMW addition to soil or on its environmental fate when applied in combination with the herbicide FM. Information on the effect of OMW addition on the fate of the herbicide FM in soils is very scarce (Cabrera et al., 2011), with lack of data under real field conditions. The objective of this study was to assess the effect of OMW addition to a Mediterranean olive grove soil on the sorption, persistence, and mobility of a commercial formulation containing TA and FM, in the context of indentifying possible environmental benefits from the addition of OMW in reducing the risk of ground and surface water contamination by herbicides used for weed control in olive groves.

2. Materials and methods

2.1. Soil, organic amendment, and herbicides

The soil was a sandy clay loam soil from an olive grove of an experimental farm located in Sevilla (SW Spain). The 0-20 cm soil layer contained $72 \pm 1\%$ sand, $7 \pm 1\%$ silt, $21 \pm 1\%$ clay, $3.5 \pm 0.2\%$ CaCO_3 , $1.0 \pm 0.2\%$ organic carbon, and $\text{pH} = 8.5 \pm 0.1$. The experimental site was a controlled area of 12 m^2 carefully selected for having a uniform slope ($\sim 5\%$), the same management history, and on the basis of laboratory measurements which indicated negligible spatial variability in soil physicochemical characteristics and in sorption behavior with regard to TA and FM. For the laboratory experiments, untreated soil samples taken from the top 0-20 cm layer were air-dried, sieved to pass a 2 mm-aperture mesh, and used within one week after sampling.

A fresh (uncomposted) olive-mill waste (OMW) from an olive-processing factory located in Osuna (Sevilla, Spain) was used to amend the soil. For laboratory experiments, the residue was air-dried and ground to pass a 2 mm-aperture sieve prior to use. For the field experiment, the air-dried residue was manually added to the soil surface as pellets with a size of about 1 cm. The elemental analysis of the OMW revealed a C content of 43.8% and a N content of 1.8%.

The commercial formulation containing TA and FM used in the laboratory and field experiments was Athado Olivo (concentrated suspension, 23 % TA and 23 % FM) purchased from Probelte, S.A. High-purity standards of TA and FM purchased from by Sigma-Aldrich (Spain) were used to prepare the external calibration curves for herbicide analysis.

2.2. Laboratory experiments

Terbuthylazine and fluometuron sorption isotherms on unamended and OMW-amended soil samples were obtained by the batch equilibration procedure using glass centrifuge tubes lined with screw caps. For this purpose, triplicate 4 g of soil samples, either unamended or amended with OMW at rates of 5 and 10% (w/w), were shaken at 20 ± 2 °C for 24 h with 8 mL of commercial TA+FM solutions containing both herbicides at initial concentrations (C_{ini}) ranging between 0.1 and 2 mg L⁻¹. After shaking, the suspensions were centrifuged, filtered, and the supernatant solutions were analyzed by high performance liquid chromatography (HPLC) to determine the apparent (24 h) equilibrium concentration (C_e) for each herbicide. The amount of TA and FM sorbed, C_s (mg kg⁻¹), was calculated from the difference between the initial and the apparent equilibrium concentrations. A Freundlich isotherm ($C_s = K_f C_e^{1/n_f}$) was fitted to the measured sorption data using a log-log linear fit, and the Freundlich coefficients, K_f and $1/n_f$ were calculated.

The persistence of TA and FM in unamended and OMW-amended soil samples under controlled laboratory conditions was determined by incubation experiments in which 100 g of unamended or OMW-amended soil samples (5 and 10% w/w) were spiked with the commercial formulation of TA and FM at a rate of 3 mg of each active ingredient kg⁻¹ soil. The spiked soil samples were incubated in glass jars at 20 ± 2°C for 52 days. The moisture content of the soil was maintained at a constant level (~ 30% or -0.02 MPa) throughout the experiment by adding distilled water as necessary. Once a week, triplicate 3 g-soil aliquots were sampled using a sterilized spatula and frozen immediately until analyzed.

Terbuthylazine and fluometuron residues in the 3 g soil-aliquots were determined by extraction with 8 mL of methanol (24 h shaking), followed by centrifugation and analysis of the supernatant by HPLC. This extraction procedure recovered > 95% of the herbicides freshly applied to the soils. Differences between the amount of TA and FM added to the soil and the amounts extracted with methanol were assumed to be due to degradation and/or formation of strongly-bound herbicide residues (Albarrán et al., 2003). Incubation data were fit to first-order herbicide dissipation kinetics: $\ln C = \ln C_0 - k \cdot t$, where C (mg kg⁻¹) is the herbicide concentration in the soil at time t (days), C_0 (mg kg⁻¹) is the herbicide concentration at time zero, and k (days⁻¹) is the first-order dissipation constant. The half-life ($t_{1/2}$) was calculated as $t_{1/2} = 0.693/k$.

2.3. *Demonstration field experiment*

Two 4 m long × 1 m wide plots separated by a distance of 4 m were defined in the experimental site with 15 cm-high stainless steel frames which were pushed 5 cm into the soil. Prior to the experiment, weeds were removed and the plots were tilled to a 20 cm depth. Then, one of the plots was amended with OMW at a rate of 10 kg m⁻², mixing with the top 0-5 cm soil, whereas the other plot remained unamended and served as a control. For treatment

and sampling, each plot was divided into four 1 x 1 m subplots. The OMW application rate used was within the range of 2-20 kg m⁻² used in previous studies (Albarrán et al., 2003; Cabrera et al., 2007; Delgado-Moreno et al., 2007; López-Piñeiro et al., 2011), and according to its composition, it was calculated that the OMW increased the organic C content of the top 0-5 cm soil layer from 1.0 up to 6.7%. The commercial formulation containing TA and FM was applied to the plots at a rate of 0.3 g active ingredient (a.i.) m⁻² (3 kg a.i. ha⁻¹) dissolved in 4 L of water. Herbicide application was carried out in November 27, 2008. Temperature and natural rainfall were recorded in the course of the experiment. No artificial watering was applied to the plots.

At selected times, i.e. 0, 6, 20, 42, 68 and 102 days from herbicide application, quadruplicate soil samples were taken from each plot. Sampling times were selected on the basis of the rainfall events which occurred during the experiment. Each sample consisted of four subsamples taken at 0-5, 5-10, 10-20 and 20-30 cm depths using a 3 cm-internal diameter spade. Each soil subsample was immediately frozen until extracted in triplicate by shaking 5 g of soil with 10 mL of methanol for 24 h. After shaking, the suspensions were centrifuged, filtered, and the methanolic extracts analyzed by HPLC to determine the concentration (mg kg⁻¹ dry soil) of TA and FM at different soil depths. Triplicate aliquots of 1 g of each soil sample were dried at 100 °C to determine their water content. It was previously confirmed that the soil plots contained no detectable amounts of TA and FM prior to the experiment. Soil extraction data were fitted to first-order herbicide dissipation kinetics: $\ln C = \ln C_0 - k \cdot t$, where C (mg kg⁻¹) was the average herbicide concentration in the top 0-30 cm of soil at time t (days), C_0 (mg kg⁻¹) the herbicide concentration at time zero, and k (days⁻¹) the first-order dissipation constant. The half-life ($t_{1/2}$) of the herbicides in the topsoil (0-30 cm) was calculated as $t_{1/2} = 0.693/k$.

Runoff water was collected using a tank installed at the downslope end of each plot. After each runoff event, the volume of runoff water collected in the tanks was measured, and a representative sample was taken for its immediate analysis. Because the runoff water coming from the four subplots was combined in a sole trap, a statistical comparison between the two treatments could not be made, and thus runoff data should be considered as preliminary. For the analysis, triplicate 25-mL of runoff water aliquots were filtered under vacuum using 0.45 μm membrane filters, and then analyzed by HPLC to determine the solution concentrations of TA and FM. In addition, the particulate matter remaining on the filters was weighed, extracted with 16 mL of methanol, and then the methanolic extract was analyzed by HPLC to determine the amount of TA and FM associated with particles suspended in the runoff water samples.

2.4. Analysis of herbicides

The analysis of TA and FM in methanolic extracts and runoff water was carried out by HPLC using a Waters chromatograph coupled to a Waters 600E System Controller, a Waters 998 Photodiode Array Detector, and a Waters 717 Autosampler injector. The following chromatographic conditions were used: Nova-Pack C18 chromatographic column of 150 mm length $\times$ 3.9 mm internal diameter and 4 μm particle size (Waters), 50 μL injection volume, 50:50 acetonitrile:water isocratic eluent mixture at a flow rate of 1 mL min^{-1} , and UV detection at 220 nm for TA and 243 nm for FM. Five standard solutions containing TA and FM at concentrations ranging between 0.01 and 4 mg L^{-1} were used for quantification. The limits of quantification, calculated as the herbicide concentrations resulting in a signal to noise ratio of 10:1, were 0.005 mg L^{-1} for TA and 0.01 mg L^{-1} for FM.

3. Results and discussion

3.1. Laboratory experiments

Figure 1 shows TA and FM sorption isotherms on unamended and OMW-amended soil samples. Sorption coefficients, K_f and $1/n_f$, resulting from fitting sorption isotherm data to the Freundlich equation are given in Table 1. While there was insignificant preexisting variability in TA and FM sorption on soil samples taken from the two original (untreated) field plots, addition of OMW at rates of 5 and 10% (w/w) greatly enhanced the sorption of both herbicides by the soil and, apparently, also increased the nonlinearity ($1/n_f < 1$) of both TA and FM sorption (Fig. 1, Table 1). The increase in sorption of TA upon amendment of the soil with OMW was similar to that reported in previous laboratory studies, and can be attributed to the high affinity of OMW for this herbicide (Cabrera et al., 2007; Delgado-Moreno et al., 2007; López-Piñeiro et al., 2011). Fluometuron was sorbed to a lesser extent by all unamended and OMW-amended soil samples compared to TA. Normalization of the K_f values to the organic carbon content of the unamended and OMW-amended soil samples yielded K_{foc} values in the range of 140-176 L kg⁻¹ for TA and 30-35 L kg⁻¹ for FM (Table 1), which were consistent with literature values for the sorption of these pesticides in soils (Tomlin, 2006).

Terbuthylazine and fluometuron dissipation curves in unamended and OMW-amended soil samples are given in Fig. 2. Terbuthylazine displayed a long persistence in unamended and OMW-amended soil samples; less than 20% of the herbicide was dissipated after an incubation period of 52 days (Fig. 2). Cabrera et al. (2007) studied the effect of OMW addition to a coarse-textured Mediterranean soil on TA dissipation under laboratory conditions and also found that the dissipation of the herbicide in unamended and OMW-amended soil samples accounted for less than 20% after 30 days. The data in Fig. 2 show that FM dissipated faster than TA in unamended soil ($t_{1/2} = 63 \pm 7$ days); however, the

persistence of FM was greatly enhanced upon OMW addition, resulting in negligible
 dissipation of the herbicide during the 52 day-incubation period (Fig. 2). We noted that the
 decline in FM concentration observed in unamended soil during the incubation experiment
 was accompanied by an increase in the concentration of desmethylfluometuron (DMF), a
 metabolite resulting from the microbial degradation of FM. This indicated that
 biodegradation was a major cause of FM dissipation in unamended soil. Previous work has
 shown that FM in soil is dissipated mainly by microbial degradation, with formation of the
 metabolites DMF, trifluoromethylphenylurea (TFMPU), and trifluoromethylaniline (TFMA)
 (Bozarth and Funderburk, 1971; Gámiz et al., 2010; Lancaster et al., 2008; Locke et al.,
 2007).

3.2. Field experiment

3.2.1. Environmental conditions

Temperature and rainfall data in the course of the field experiment are shown in Fig. 3.
 Temperatures were relatively low as a result of the winter season in which the experiment
 was conducted. The maximum daily temperatures ranged between 7.6 and 24.9 °C with an
 average of 15.2 °C, while the minimum daily temperatures ranged between -3.4 and 13.6 °C
 with an average of 4.9 °C. The total rainfall during the 102 days of experiment was 270 mm
 with peaks of 55 and 36 mm occurring at 66 and 70 days, respectively, from herbicide
 application. Therefore, the most intense rainfall events occurred at relatively long times after
 herbicide application.

3.2.2. Herbicide persistence and leaching

The concentrations of TA and FM (mg kg^{-1} dry soil) in different soil layers of unamended
 and OMW-amended plots as a function of time from herbicide application are shown in Fig.

4 and 5. For both the unamended and OMW-amended plots and for all sampling times, the highest amounts of TA and FM were always found in the top 0-5 cm soil layer. This reflected limited leaching of both herbicides, most likely due to the fact that rainfall was moderate up to long times since the herbicides were applied to the plots. It should also be noted that the concentrations (mg kg^{-1}) of TA and FM in the top 0-5 cm of soil just after herbicide application ($t=0$) for the OMW-amended plot ($\sim 8 \text{ mg kg}^{-1}$) were two-fold greater compared to the unamended plot ($\sim 4 \text{ mg kg}^{-1}$). This was attributed to the low bulk density of OMW ($\sim 0.6 \text{ g cm}^{-3}$) compared to the soil ($\sim 1.3 \text{ g cm}^{-3}$), and to the fact that OMW accumulated within the top 0-5 cm soil layer. The initial herbicide concentration of 4 mg kg^{-1} obtained for TA and FM in the 0-5 cm soil layer of the unamended soil plot is in accordance with the expected value of 4.4 mg kg^{-1} , which can be calculated from the herbicide application rate (3 kg ha^{-1}), the soil bulk density (1.3 g cm^{-3}), and assuming that the herbicide is uniformly distributed within the top 0-5 cm soil layer.

Despite TA and FM accumulating within the 0-5 cm surface layer during the course of the experiment, the amounts of TA and FM present at deeper soil layers (5-10, 10-20, and 20-30 cm depth) indicated both herbicides moved deeper in the untreated soil plot compared to the OMW-treated plot. For instance, while TA was repeatedly detected in the 10-20 and 20-30 cm soil layers of the untreated plot along the experiment, it was rarely detected at those depths in the OMW-treated plot (Fig. 4). A similar behavior was observed for FM (Fig. 5), thus indicating OMW reduced the leaching of TA and FM in the soil, most likely as a result of the enhanced retention of these herbicides in OMW-amended soil (Fig. 1, Table 1). This result is in contrast to data recently reported by Cabrera et al. (2008a) revealing a small effect of OMW on TA sorption and leaching in a Mediterranean olive grove soil. However, it should be noted that the texture of the soil (silty clay soil: 6% sand, 42% silt, 52% clay, 1.07% organic carbon) and the OMW application rate ($\sim 2 \text{ kg m}^{-2}$) used by Cabrera et al.

(2008a) differed from those used in the present study. Other studies have shown that organic matter is a primary sorbent for TA and FM and that organically-amended soils display enhanced sorption of these herbicides both under laboratory and field conditions (Cabrera et al., 2007, 2009; Delgado-Moreno et al., 2007; Dolaptsoglou et al., 2010; Locke et al., 2007; López-Piñeiro et al., 2011; Mueller et al., 1992; Savage and Wauchope, 1974).

Also in agreement with the results of the laboratory experiments (Fig. 2), addition of OMW had distinct effects on the field persistence of TA and FM. Terbutylazine displayed a long persistence both in the unamended and in the OMW-amended soil plots (Fig. 4). At the end of the experiment ($t = 102$ days), 40-50% of the TA extracted at $t = 0$ was still present in both plots (Fig. 4). Applying first-order kinetics to the changes in TA concentration in the top 0-30 cm of soil with time, we obtained half-lives ($t_{1/2}$) of 114 days for the unamended soil and 72 days for the OMW-amended soil, but the fitting of the experimental data to the model was very poor ($R^2 < 0.78$), making the estimate of $t_{1/2}$ values uncertain. The half-lives for TA in soils have been reported to range between a few days and several months depending on soil characteristics, previous herbicide treatments, and environmental conditions (López-Piñeiro et al., 2011; Tomlin, 2006). Longer half-lives for TA have been reported in coarse-textured, Mediterranean soils, similar to that used in this study (Cabrera et al., 2007). The low temperatures occurring during our experiment should have further contributed to prolong the persistence of TA in the present study.

Fluometuron dissipated more rapidly than terbutylazine, with a marked decrease in FM soil concentrations at sampling times ≥ 40 days (Fig. 5). The decrease in the soil concentrations of FM in the unamended soil plot was more pronounced compared to the OMW-amended plot (Fig. 5). This indicated that OMW prolonged the persistence of FM in the topsoil, probably due to enhanced sorption and reduced degradation of the herbicide, as supported by the results of the laboratory experiments (Fig. 1 and 2). Applying first-order

kinetics to the experimental data, we obtained half-lives of 24 days for FM in the top 0-30 cm of the unamended field plot and of 58 days in the OMW-amended plot, with a very good fitting of the experimental data to the model ($R^2 > 0.92$). Faster dissipation of FM under field conditions compared to laboratory conditions (Fig. 2) can be explained taking into account that several dissipation routes, such as leaching, volatilization or runoff, accounted for the dissipation of the herbicide in the field, but not in the laboratory.

Fluometuron is degraded primarily by soil microorganisms (Bozarth and Funderburk, 1971; Lancaster et al., 2008; Locke et al., 2007), and higher organic matter contents are often associated with greater microbial activity (Mueller et al., 1992). Accordingly, previous work has shown greater rates of FM degradation in amended soils (i.e., poultry litter, cornmeal, or ryegrass amendment) or glucose addition compared to unamended soils (Bouchard et al., 1982; Bozarth and Funderburk, 1971; Mueller et al., 1992; Wagner and Zablotowicz, 1997). However, the increase in persistence of FM upon OMW addition found in this work could be also related to the increase in organic matter content, since an increase in carbon substrate availability for microbial biomass and a reduction in herbicide bioavailability by its sorption to OMW would reduce biodegradation and prolong herbicide persistence in the OMW-amended soil (Albarrán et al., 2003; Cabrera et al., 2007, 2008b; López-Piñeiro et al., 2011). In fact, several field experiments on mobility and degradation of FM in agricultural soils have shown prolonged persistence of the herbicide in cases where the amount of organic matter was greater, either by tillage or the presence of cover crops, due to an increase in the sorption phenomenon (Brown et al., 1994; Lancaster et al., 2008; Locke et al., 2007; Zablotowicz et al., 2000).

3.2.3. *Herbicide runoff*

The results of the analysis of runoff water collected from the unamended and OMW-amended plots are summarized in Tables 2-4 and Fig. 6 and 7. The initial runoff events were of low to moderate intensity (Table 2). The most intense runoff events resulted from heavy rain occurring at 66 and 70 days after herbicide treatment (Fig. 3). Nevertheless, the highest concentrations of TA and FM, both in solution and associated with suspended particulate matter, were found in the first runoff events (Tables 3 and 4, Fig. 6), confirming that herbicide runoff becomes particularly relevant when it occurs shortly after herbicide application, before the herbicide degrades and/or moves vertically into the soil profile and becomes less available for runoff (Baughman et al., 2001; Hermosín et al., 2009; Leonard, 1990; Wiese et al., 1980).

In the first runoff events, i.e. those occurring at 6, 20, and 42 days after herbicide application, the solution and particle-associated concentrations of FM in runoff water from the unamended soil plot were greater than those found for TA (Tables 3 and 4, Fig. 6), probably because the runoff losses were dominated by the dissolved concentration of the herbicides in the uppermost centimeters of the soil. Considering the sorption parameters reported in Table 1, the dissolved concentrations of FM were expected to be considerably greater than those of TA. For the last runoff events, at 68 and 71 days after herbicide application, the solution and particle-associated concentrations of TA were similar or even greater than those of FM, most likely reflecting the greater concentrations of TA in the surface (0-5 cm) soil layer compared to FM at such sampling times, as a result of the longer persistence of TA in the field plots (Baughman et al., 2001). An apparent distribution coefficient for the herbicides between the solid and solution phases in the collected runoff water, K_d , was calculated dividing the amount of sorbed herbicide by the solution herbicide concentration (Tables 3 and 4). In all runoff events, TA displayed greater K_d values than FM,

revealing its higher sorptivity and hence its higher tendency to be transported by suspended particulate matter (Potter et al., 2006). In this regard, it should also be noted that the cumulative amount of particulate matter lost in runoff water during our experiment decreased from 14.7 ± 0.5 g for the unamended soil to 12.2 ± 0.4 g for the OMW-amended soil, with the highest soil losses occurring during the two most intense rainfall events at 68 and 71 days of the experiment (Table 2). This result may reflect the protective effect against soil erosion induced by OMW addition to soil, particularly during heavy rainfall events (Lozano-García et al., 2011).

One of the most interesting features of the herbicide runoff data is that for all samples collected, TA and FM solution concentrations in runoff water from the untreated plot were from 5 to 60 times greater than those in runoff water from the OMW-treated-plot (Fig. 6). A similar result was observed for particle-associated herbicide, where sorbed TA and FM concentrations were 2 to 40 times greater for the unamended plot compared to the OMW-amended plot (Tables 3 and 4). The only exception was the sample collected from the OMW-amended plot 71 days after herbicide application, which contained more FM than that collected from the unamended plot. This was because most FM had dissipated in the unamended soil plot at 71 days after application (Fig. 5).

The total amount of TA lost by runoff process during the experiment, calculated as the sum of dissolved and particle-associated herbicide, was $0.16 \pm 0.03\%$ of the applied herbicide for the unamended plot and $0.03 \pm 0.01\%$ for the OMW-amended plot. For FM, the total herbicide losses by runoff were $0.12 \pm 0.02\%$ for the unamended plot and $0.08 \pm 0.01\%$ for the OMW-amended plot (Fig. 7). The general decrease in herbicide runoff losses by treatment with OMW was probably caused by an increase in the retention capacity of the soil after OMW addition (Fig. 1). Apparently, the high concentrations of dissolved organic matter in runoff water collected from the OMW-amended plot, evidenced by the darkness of

the runoff water samples, did not contribute significantly to facilitate the transport of TA and FM by runoff process.

4. Conclusions

Addition of OMW to a Mediterranean olive grove soil increased the sorption of the herbicides terbuthylazine and fluometuron, prolonged the persistence of fluometuron, and had little effect on the persistence of terbuthylazine in the soil under laboratory conditions. Data obtained under real field conditions were consistent with those obtained under controlled laboratory conditions, since they indicated that OMW reduced the vertical movement and runoff of terbuthylazine and fluometuron most likely because the enhanced herbicide sorption resulting from OMW addition to the soil prevented herbicide leaching and runoff. Furthermore, the soil persistence of fluometuron under field conditions was also prolonged by OMW addition, whereas the persistence of terbuthylazine was long and not significantly different in unamended- and OMW-amended soil. Accordingly, the results of this study indicate that soil amendment with OMW could be beneficial in reducing the risk of ground and surface water contamination associated with the use of terbuthylazine and fluometuron in olive groves and similar high-risk scenarios of ground and surface water contamination, as well as to prolong the persistence of fluometuron in soils where its rapid degradation could result in reduced weed control efficacy.

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FIGURE CAPTIONS

Fig. 1. Terbutylazine (TA) and fluometuron (FM) sorption isotherms on unamended and OMW-amended soil samples. Error bars indicate standard errors of triplicate measurements.

Fig. 2. Terbutylazine (TA) and fluometuron (FM) dissipation curves in unamended and OMW-amended soil samples. Error bars indicate standard errors of triplicate measurements.

Fig. 3. Rainfall (bars) and temperatures (lines) during the field experiment. Vertical dotted lines indicate runoff water sampling days.

Fig. 4. Terbutylazine (TA) concentrations (mg kg^{-1}) at different soil depths of unamended and OMW-amended field plots as a function of time after herbicide application. Error bars correspond to the standard errors of quadruplicate soil samples.

Fig. 5. Fluometuron (FM) concentrations (mg kg^{-1}) at different soil depths of the unamended and OMW-amended field plots as a function of time after herbicide application. Error bars correspond to the standard errors of quadruplicate soil samples.

Fig. 6. Terbutylazine (TA) and fluometuron (FM) solution concentrations in runoff water from the unamended and OMW-amended field plots. Error bars correspond to the standard errors of triplicate water samples.

Fig. 7. Cumulative runoff losses of terbutylazine and fluometuron from the unamended and OMW-amended soil plots during the field experiment. Error bars correspond to the standard errors of triplicate water samples.

Table 1

Freundlich coefficients for terbuthylazine (TA) and fluometuron (FM) sorption by unamended and OMW-amended soil samples.

	TA				FM			
	K_f	$1/n_f$	R^2	K_{foc}^a	K_f	$1/n_f$	R^2	K_{foc}
Unamended soil (Plot 1)	1.4 (1.2-1.7) ^b	1.10 ± 0.08^b	0.989	140	0.30 (0.27-0.34)	0.93 ± 0.08	0.985	30
Unamended soil (Plot 2)	1.4 (1.2-1.6)	0.97 ± 0.07	0.989	140	0.35 (0.33-0.37)	0.94 ± 0.03	0.998	35
Soil + OMW (5%)	5.0 (4.6-5.2)	0.77 ± 0.02	0.999	165	1.00 (0.87-1.15)	0.77 ± 0.08	0.981	33
Soil + OMW (10%)	8.6 (6.9-10.8)	0.76 ± 0.07	0.992	176	1.66 (1.60-1.72)	0.74 ± 0.02	0.999	34

^a K_{foc} : Organic carbon-normalized K_f value.

^b Standard errors about the coefficients.

Table 2

Volume and particulate matter concentration of runoff water collected from the unamended and OMW-amended soil plots.

Sampling time (days)	Unamended plot		OMW-amended plot	
	Volume collected (mm)	Particulate matter (g L ⁻¹)	Volume collected (mm)	Particulate matter (g L ⁻¹)
6	0.010	2.78 ± 0.26 ^a	0.025	2.46 ± 0.17
20	0.068	1.89 ± 0.05	0.148	1.78 ± 0.09
42	0.005	0.68 ± 0.02	0.092	0.45 ± 0.02
68	0.812	1.08 ± 0.03	0.650	0.79 ± 0.10
71	6.000	0.44 ± 0.29	1.625	1.33 ± 0.06

^a Mean ± standard error of triplicate water samples.

Table 3

Terbuthylazine (TA) concentration in solution and in suspended particulate matter of runoff water collected from the unamended and OMW-amended soil plots. Apparent distribution coefficients, K_d , for TA adsorption on runoff particulate matter.

Day	Unamended plot			OMW-amended plot		
	TA in solution	TA in particulate matter	K_d	TA in solution	TA in particulate matter	K_d
	(mg L ⁻¹)	(mg kg ⁻¹)	(L kg ⁻¹)	(mg L ⁻¹)	(mg kg ⁻¹)	(L kg ⁻¹)
6	0.32 ± 0.04 ^a	102.4 ± 1.4	320	0.02 ± 0.01	14.1 ± 0.3	705
20	0.58 ± 0.04	120.6 ± 1.6	208	0.01 ± 0.00	6.57 ± 0.8	657
42	0.22 ± 0.02	229.4 ± 1.1	1043	0.01 ± 0.00	23.6 ± 2.5	2360
68	0.10 ± 0.01	46.1 ± 5.0	461	0.01 ± 0.00	- ^b	-
71	0.03 ± 0.01	38.8 ± 8.0	1293	0.03 ± 0.01	12.23 ± 0.2	408

^a Mean ± standard error of triplicate water samples.

^b Not detected.

Table 4

Fluometuron (FM) concentration in solution and in suspended particulate matter of runoff water collected from the unamended and OMW-amended soil plots. Apparent distribution coefficients, K_d , for FM adsorption on runoff particulate matter.

Day	Unamended plot			OMW-amended plot		
	FM in solution (mg L ⁻¹)	FM in particulate matter (mg kg ⁻¹)	K_d (L kg ⁻¹)	FM in solution (mg L ⁻¹)	FM in particulate matter (mg kg ⁻¹)	K_d (L kg ⁻¹)
6	0.81 ± 0.04 ^a	118.1 ± 0.6	146	0.04 ± 0.01	3.2 ± 0.8	80
20	2.26 ± 0.04	169.7 ± 0.3	75	0.05 ± 0.01	8.5 ± 2.6	170
42	1.10 ± 0.02	735.2 ± 2.0	668	0.05 ± 0.01	32.5 ± 5.8	650
68	0.10 ± 0.01	19.6 ± 2.0	196	0.02 ± 0.00	10.3 ± 2.3	515
71	0.01 ± 0.01	- ^b	-	0.10 ± 0.01	13.9 ± 0.3	139

^a Mean ± standard error of triplicate water samples.

^b Not detected.

Fig. 1. Terbutylazine (TA) and fluometuron (FM) sorption isotherms on unamended and OMW-amended soil samples. Error bars indicate standard errors of triplicate measurements.

Fig. 2. Terbutylazine (TA) and fluometuron (FM) dissipation curves in unamended and OMW-amended soil. Error bars indicate standard errors of triplicate measurements.

Fig. 3. Rainfall (bars) and temperatures (lines) during the field experiment. Vertical dotted lines indicate runoff water sampling days.

Figure 4
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Fig. 4. Terbutylazine (TA) concentrations (mg kg⁻¹) at different soil depths of unamended and OMW-amended soil plots as a function of time after herbicide application. Error bars correspond to the standard errors of quadruplicate soil samples.

Fig. 5. Fluometuron (FM) concentrations (mg kg⁻¹) at different soil depths of the unamended and OMW-amended soil plots as a function of time after herbicide application. Error bars correspond to the standard errors of quadruplicate soil samples.

Fig. 6. Terbutylazine (TA) and fluometuron (FM) solution concentrations in runoff water from the unamended and OMW-amended soil plots. Error bars correspond to the standard errors of triplicate water samples.

Fig. 7. Cumulative runoff losses of terbutylazine and fluometuron from the unamended and OMW-amended soil plots during the field experiment. Error bars correspond to the standard errors of triplicate water samples.