Science of the Total Environment 429 (2012) 292–299

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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

B. Gámiz, R. Celis *, L. Cox, M.C. Hermosín, J. Cornejo

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Avenida Reina Mercedes 10, P.O. Box 1052, 41080 Sevilla, Spain

ARTICLE INFO

Article history:
Received 29 February 2012
Received in revised form 12 April 2012
Accepted 12 April 2012
Available online 14 May 2012

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

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 toplayer, 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.

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-Piñeiro 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 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

* Corresponding author. Tel.: +34 954624711; fax: +34 954624002.
E-mail address: rcelis@irnase.csic.es (R. Celis).

0048-9697/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2012.04.038

(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} = 31–117 L kg^{-1}) than TA (K_{oc} = 162–278 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 ± 1% sand, 7 ± 1% silt, 21 ± 1% clay, 3.5 ± 0.2% $CaCO_3$, 1.0 ± 0.2% organic carbon, and pH = 8.5 ± 0.1. The experimental site was a controlled area of 12 m^2 carefully selected for having a uniform slope (~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 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 ($C_s = K_f\, C_e^{1/nf}$) 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 fitted to first-order herbicide dissipation kinetics: $\mathrm{Ln}\, C = \mathrm{Ln}\, C_0 - k \cdot t$, 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 × 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