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De-oiled two-phase olive mill waste may reduce water contamination by metribuzin

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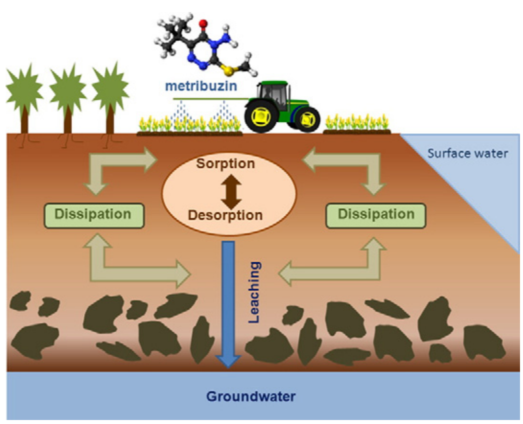
HIGHLIGHTS

- De-oiled two-phase olive mill waste (DW) affected the fate of metribuzin.
- DW amendment significantly increased metribuzin sorption in soils.
- Fresh DW could prolong the persistence of metribuzin but aged DW could reduce it.
- DW amendment reduced metribuzin leaching in soils.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact of de-oiled two-phase olive mill waste (DW) on the behavior of metribuzin in Mediterranean agricultural soils is evaluated, and the effects of the transformation of organic matter from this waste under field conditions are assessed. Four soils were selected and amended in the laboratory with DW at the rates of 2.5% and 5%. One of these soils was also amended in the field with 27 and 54 Mg ha^{-1} of DW for 9 years. Significant increases in metribuzin sorption were observed in all the amended soils. In the laboratory, the 5% DW application rate increased the $t_{1/2}$ values of metribuzin from 22.9, 35.8, 29.1, and 20.0 d for the original soils to 59.2, 51.1, 45.7, and 29.4 d, respectively. This was attributable mainly to the inhibitory effect of the amendment on microbial activity. However, the addition of DW transformed naturally under field conditions decreased the persistence down to 3.93 d at the greater application rate. Both amendments (fresh and field-aged DW) significantly reduced the amount of metribuzin leached. This study showed that DW amendment may be an effective and sustainable management practice for controlling groundwater contamination by metribuzin.

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1. Introduction

Pesticides have been one of the major technological advances that allowed food production to increase spectacularly over the past half-century (Gosme et al., 2010). However, pesticides pose a risk to human and environmental contamination of soil, water, and air (Barceló, 1991; Oluwole and Cheke, 2009). These environmental problems suggest that is necessary to develop effective management practices to control risks of the pesticides and transitions towards sustainable agricultural intensification should be sought (Pretty et al., 2011). Metribuzin [4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one], is a triazine herbicide applied pre- or post-emergence to intensive vegetable crops, including potatoes, tomatoes, and wheat. Its herbicidal efficiency and its relatively low toxicity are such that it is widely used around the world (Oukali-Haouchine et al., 2013). However, it presents very low sorption by soils and a relatively high water solubility (1050 mg L^{-1}), so that it is frequently detected in ground and surface waters (Pot et al., 2011).

Agronomic practices like the addition of organic amendments play an important role in the management of run-off and leaching losses of pesticides from agricultural fields (Singh, 2008). Usually, with the increase in total organic carbon (TOC), the sorption of herbicides onto soil particles also increases, and thus their mobility down the soil profile may be reduced (Si et al., 2011; Singh, 2003). Since alternatives such as animal manure or green covers are usually expensive or impractical, the application of residues rich in organic matter to agricultural soils is increasingly being recommended (Delgado-Moreno and Peña, 2008). Moreover, the other possible destinations of these residues (landfill, or incineration) can cause environmental problems, so that their agricultural re-use as organic amendment represents a sustainable opportunity to obviate such problems (Reis et al., 2014).

In many Mediterranean areas, the soils are generally characterized by low organic matter content. This contributes to their limited fertility and productivity together with problems of erosion and desertification (Nunes et al., 2007; Pleguezuelo et al., 2009). Therefore, the agricultural use of waste as soil amendment can be particularly advantageous in these areas because it not only recycles the waste, lessening problems of pollution, but also improves the physical, chemical, and biotic condition of their soils (Costa et al., 2008).

Currently, the most commonly used procedure in olive oil extraction is a two-phase continuous centrifuge process that generates a liquid phase (olive oil) and an organic slurry known as two-phase olive mill waste (OW). After drying, the OW is generally subjected to extraction with hexane to recover the remaining oil still present, leading to the formation of a solid residue known as de-oiled two-phase olive mill waste (DW). In the Mediterranean countries, more than $30 \cdot 10^6$ m^3 of these two wastes are produced during the harvest season, (Barbera et al., 2013) and thus constitute a major problem for the industry. The use of OW and DW as organic amendments has been proposed as an effective strategy in the control of herbicide leaching in Mediterranean agricultural soils (Cañero et al., 2015; López-Piñeiro et al., 2013; Peña et al., 2013). However, application of raw OW and DW can add a major amount of water soluble organic carbon (WSOC) to the soil which may enhance herbicide mobility down the soil profile (Cabrera et al., 2011; Cox et al., 2007; García-Jaramillo et al., 2014; Peña et al., 2015). Therefore, the effect of the organic amendment on herbicide behavior depends on the type of amendment and the dosage, as well as on the herbicide's properties and on the type of soil (Ahangar et al., 2008; Albarrán et al., 2004). Moreover, the evolution and transformation of organic matter may also modify the further interactions of pesticides with the amended soils (López-Piñeiro et al., 2014), so that it would be of great interest to know the effect of aging, preferably under field conditions, on the herbicide's behavior.

Although metribuzin is widely used and represents a potent source of water pollution, only a very few studies have investigated the effects of organic amendment on its behavior (Majumdar and Singh, 2007; Singh, 2008; Singh et al., 2013), and only one study has investigated the impact of OW on its sorption-desorption, leaching, and persistence in the soil (López-Piñeiro et al., 2013). Also, to the best of our knowledge, there have been no published studies evaluating metribuzin's fate in DW-amended soils. Such information would be useful from the environmental perspective of pesticide management in soils receiving this waste. The objective of this study was to evaluate the effects of de-oiled two-phase olive mill waste on metribuzin's behavior in different Mediterranean agricultural soils, and to assess the effects of the transformation of organic matter from this waste under field conditions. We shall compare the results of the present study with those of a previous study in which the intermediate by-product (OW) was applied to the same soils (López-Piñeiro et al., 2013).

2. Materials and methods

2.1. Herbicide

Metribuzin [4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one, purity 99.5%] was obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany). Its water solubility was 1050 mg L^{-1} at 20 °C.

2.2. Soils and organic amendment

Four typical Mediterranean agricultural soils, with different physicochemical properties, were collected for this study (0–30 cm depth). Three soils were selected from Extremadura (south-western Spain) and the fourth soil was collected from the Alentejo (south-eastern Portugal) Localization, and clay, silt, and sand content of the soils are given in Table SM1 (Supplementary Material). Prior to analyses, the soil samples were air-dried at room temperature, and the fraction that passed through a 2-mm sieve was stored at 4 °C until use.

The organic amendment used in this study (DW) was obtained from the UCASUL oil industry located in Beja (Portugal). It had the following properties: pH 5.30, 516 g kg^{-1} total organic carbon (TOC), 74.3 g kg^{-1} water soluble organic carbon (WSOC), 14.6 g kg^{-1} water soluble phenols (WSP), 5.40% moisture content, and 5.30 dS m^{-1} electrical conductivity (EC). The DW amendment was air-dried and homogenized to <2 mm.

To investigate the effect of DW on metribuzin's behavior, the amendment was added to the original soils in the laboratory at 2.5% and 5% dosages by weight. The samples of the amended soils so obtained were labeled as S1DW2.5 and S1DW5, S2DW2.5 and S2DW5, S3DW2.5 and S3DW5, and S4DW2.5, and S4DW5 (2.5% and 5% of DW for each of the S1, S2, S3, and S4 soils, respectively). To evaluate the "aging" effects of DW organic matter transformation on metribuzin's behavior under field conditions, amended soil samples (0–30 cm) were also collected from a field experiment 15 months after the last DW addition to the same S4 soil mentioned above. The soil had received application of this waste for 9 years. The two amendment treatments selected for this study consisted of 27 Mg DW ha^{-1} yr^{-1} (equivalent to 0.56% yr^{-1}, S4ADW5) and 54 Mg DW ha^{-1} yr^{-1} (equivalent to 1.12% yr^{-1}, S4ADW10), dry weight equivalents. Therefore, after nine years of repeated field DW application, the total amount of DW received by the field-amended soil is similar to the amounts received by the laboratory amended soils. For this reason, the S4 soil was also amended in the laboratory with 10% of DW, labeled as S4DW10, in order to give a similar final total organic matter content as in the S4ADW10 field-amended soil. Selected characteristics of the unamended and amended soils are given in Table 1. Texture was determined by sedimentation using the pipette method after organic carbon destruction with H_2O_2 and chemical dispersion using $Na_4P_2O_7$ (Gee and Or, 2002). The TOC was determined by dichromate oxidation. WSOC was extracted with de-ionized water at 3:1 (water to soil) and 100:1 (water to DW) ratios. Humic and fulvic acids (HA and FA, respectively) were extracted by a solution of 0.1 M $Na_4P_2O_7$ + NaOH using a ratio of extractant to sample