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Long-term effects of olive mill waste amendment on the leaching of herbicides through undisturbed soil columns and mobility under field conditions

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ABSTRACT

Olive mill waste has recently been proposed for use as soil amendment in Mediterranean environments because of its potential for soil carbon sequestration, improving the soil's quality and productivity. MCPA and S-metolachlor are herbicides applied worldwide in agricultural soils. They readily leach down to lower soil depths. The aim of this study was to evaluate the impact of oiled and de-oiled olive mill waste amendments (OW and DW, respectively) on the sorption, leaching through undisturbed soil columns, and movement and persistence of MCPA and S-metolachlor under real field conditions, in a sandy clay loam soil with low organic matter content which had received addition of these wastes for nine years. The soil had been amended with 30 and 60 Mg ha^{-1} yr^{-1} of OW (OW30 and OW60) and 27 and 54 Mg ha^{-1} yr^{-1} of DW (DW27 and DW54). The OW or DW addition resulted in significantly enhanced sorption and sorption irreversibility for both herbicides. Compared with unamended soils, leaching losses of the herbicides were reduced in the undisturbed soil columns by 84 and 97% of the applied MCPA and by 85 and 92% of the applied S-metolachlor for the OW60 and DW54 amended soils, respectively, despite the greater volume of soil macropores in OW and DW-amended soils. Under field conditions, slower vertical movement was observed for MCPA and especially for S-metolachlor in the OW- and DW-amended than in the unamended soil profiles. While the OW and DW addition extended the field persistence of S-metolachlor, increasing its half-life from 53 to 69 and 63 days for unamended, OW60, and DW54 soils, respectively, MCPA dissipation was not significantly affected by these amendments. The results suggest that previous laboratory persistence studies performed in unamended, OW, and DW-amended soils might have underestimated the real half-lives of herbicides in the field. Both OW and DW addition could be beneficial in reducing the mobility of MCPA and S-metolachlor in agricultural soils with low organic matter content, thus, decreasing the risk of groundwater contamination by these herbicides.

1. Introduction

The use of herbicides as a complement or alternative to tillage is a worldwide practice to enhance or protect agricultural productivity. However, excessive or inappropriate use of these chemicals can have detrimental effects on human heath, wildlife, and the environment (Comoretto et al., 2007; Márquez et al., 2005). The herbicides 4-chloro-2-methylphenoxyacetic acid (MCPA) and (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-((1S)-2-methoxy-1-methylethyl) acetamide) (S-metolachlor) are two of the most commonly used herbicides in farming for post-emergence (MCPA) and pre- and post-emergence weed control (S-metolachlor) for a great variety of crops worldwide. Their relatively high water solubility (825 mg L^{-1} and 480 mg L^{-1} for MCPA and S-metolachlor, respectively), low retention potential in soils, and intensive use are responsible for the contamination of ground and surface waters at concentrations frequently above the European threshold for potability, 0.1 $\mu g\,L^{-1}$ (Environment Agency, 2003). Indeed, studies have found MCPA and S-metolachlor to be two of the most important contaminants in terms of frequency of detection in water samples of agricultural areas (e.g., Konstantinou et al., 2006; Silva et al., 2006; Matamoros et al., 2012). It is therefore necessary to develop effective management practices to control water contamination by MCPA

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and S-metolachlor particularly in high-risk environments such as Mediterranean agricultural systems with a climate characterized by very intense, short-lived rain events, and soils which are very poor in organic matter content.

Organic amendments are being promoted to enhance the sustainability of agricultural systems, especially in arid and semi-arid zones where the soils are frequently very poor in organic matter content. The addition of organic amendments leads to significant changes in the biological, chemical, and physical properties of the soil, and these changes may influence the mobility and persistence of herbicides and thus modify their environmental fate. Consequently, this practice is regarded as one of the most efficient strategies for reducing herbicide leaching. Although, increasing organic matter content in a soil generally results in greater herbicide sorption and reduced water contamination (Majumdar and Singh, 2007; Fernández-Bayo et al., 2009; Delgado-Moreno et al., 2010), it could also raise the risk of soil and associated water resource contamination (Cabrera et al., 2008; Kodešová et al., 2012). The continuous centrifuge process used in olive-oil extraction generates a liquid phase (olive oil) and a two-phase olive mill waste (OW). After drying the OW, the remaining oil still present in this waste is usually extracted with hexane, leaving a de-oiled solid residue (DW). Since both OW and DW contain a major proportion of organic matter, and lack pathogenic organisms and heavy metals, their recycling as organic amendments has recently been proposed for Mediterranean environments.

Although, there is a growing evidence that the application of both OW and DW to soils may provide beneficial effects for the soil's properties and crop productivity (López-Piñeiro et al., 2008, 2011a; Altieri et al., 2014), contradictory trends have been recognized in the determination of a herbicide's fate in a specific soil under OW or DW-amendment. This could be due to the quantity and nature of the organic amendment, its effect on microbial activity, and the particular herbicide's characteristics (Barriuso et al., 2011). Furthermore, previous studies have demonstrated that preferential flow through macropores may speed up a herbicide's movement through the soil profile relative to what would be expected from its physicochemical properties (e.g., Elliott et al., 2000). Therefore, the contribution of organic amendments to soil porosity could make the effect of these amendments ambiguous (Cox et al., 1996). Indeed, Mahmoud et al. (2010) found that addition of olive mill wastewater (OWW), a liquid residue, also generated from the olive oil extraction process, created preferential flow pathways which could have increased the risk of groundwater contamination. Cox et al. (1996) reported that modified soil porosity, reducing the total volume of pores by diminishing the volume of the large size pore fraction, decreased the leaching of the herbicide clopyralid. However, Albarrán et al. (2003) found that the amount of simazine herbicide leached also decreased upon OW addition to a soil, despite an increase in soil pore volume.

A review of the literature revealed that most herbicide leaching studies have been limited to disturbed soil column experiments under laboratory conditions, although, there are reports suggesting that undisturbed soil columns maintain most of the soil structure and macropores, and therefore better approximate the field movement of water and solute than columns with repacked, homogenized soils (e.g., Smith et al., 1985; Singh et al., 2002; Landry et al., 2006). The reason for the lack of studies of the mobility and persistence of herbicides in soil profiles under field conditions is their high cost and difficulty, particularly for medium- and long-term studies. Additional research with field experiments therefore ought to be conducted in order to obtain realistic results that take the effects of climate conditions into account. Also, there have been very few studies conducted to assess the persistence and leaching of MCPA and S-metolachlor in OW- and DW-amended soils (Cabrera et al., 2011; López-Piñeiro et al., 2013; Peña et al., 2013). To the best of our knowledge, there are no published results on the leaching of these two herbicides using undisturbed soil columns, or of their persistence and mobility under field conditions in soils affected by the addition of OW or DW, even though this information would be useful for a better understanding of these herbicides' fate in soils receiving these wastes so as to conciliate agricultural and environmental interests. The objectives of the present study were therefore: (i) to determine the effects of OW and DW on the sorption–desorption of the herbicides MCPA and S-metolachlor applied to a Luvisol, a typical Mediterranean agricultural soil, which had received addition of these wastes for nine years; (ii) to evaluate the long-term impacts of OW and DW addition on the leaching of the two herbicides using undisturbed soil columns; and (iii) to assess the long-term effects of OW and DW application on the movement and persistence of the two herbicides under real field conditions.

2. Materials and methods

2.1. Herbicides and organic residues

For the laboratory studies, MCPA ((4-chloro-2-methylphenoxy)-acetic acid) and S-metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-((1S)-2-methoxy-1-methylethyl)acetamide) were obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany). The water solubility at 25 °C is 825 and 480 mg L^{-1} for MCPA and S-metolachlor, respectively. For the field studies, the commercial formulations Hermenon (60% MCPA) and Dual Gold (96% S-metolachlor) were purchased from Sipcam Inagra (Valencia, Spain) and Syngenta Agro (Madrid, Spain), respectively.

Two organic residues, OW and DW, were used in this study. The OW was obtained from a two-phase olive oil industry located in Portalegre (Portugal). The DW was obtained from an oil industry located in Beja (Portugal) which employs chemical means (hexane) to obtain a second-extraction olive-oil. The physicochemical characteristics of both wastes are given in Table 1.

2.2. Soil and experimental design

A field experiment was conducted in a typical Mediterranean agricultural soil using conventional tillage practices. Comparisons of the unamended soil were made with soils amended for 9 years with OW or DW. The soil, classified as Cutanic Luvisol (ISSS-ISRIC-FAO, 1994), contained 19.7% clay, 19.7% silt, 60.6% sand, and was located in Elvas, Portugal (38°53′N; 7°9′W) at a mean altitude of 290 m above sea level. The climate is semi-arid Mediterranean (Papadakis, 1966) with an average annual rainfall of 500 mm occurring mostly in autumn and spring and a mean annual temperature of 16.7 °C. The experimental design consisted of fifteen plots, with amendments made in a complete randomized design with three replicates per treatment (each replicate 15 m × 20 m). The five treatments were: 30 (OW30) and 60 (OW60) Mg ha^{-1} of OW, 27 (DW27) and 54 (DW54) Mg ha^{-1} of DW, both dry weight equivalents, and unamended (US) treatment. Amendments were applied annually in February (from 2001 to 2009), spreading the waste on the soil surface, followed by arable-level homogenization. For the soil characterization and laboratory experiments, soil samples from the unamended and amended plots were collected in 2010 (15 months after the last OW and DW application). Four soil subsamples from each plot were taken randomly at a 25 cm depth. 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.