INFLUENCE OF TWO-PHASE OLIVE MILL WASTE ON THE SORPTION, LEACHING AND DEGRADATION OF MCPA AND S-METOLACHLOR IN A SOIL UNDER INTENSIVE CROPPING

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1 INTRODUCTION

The new technology for olive-oil extraction is a continuous centrifuge two-phase process that generates a liquid phase (olive oil) and organic slurry (two-phase olive mill waste, TPOMW). In Spain alone this new system generates more than 4 000 000 Mg of TPOMW year^{-1} (López-Piñeiro et al., 2008a). Therefore, with the continued generation of TPOMW, the need for proper disposal or utilization strategies is imperative. TPOMW has very high organic matter contents (92%), therefore its recycling as amendment to agricultural soils has been proposed as a solution for its disposal which will enrich soils that are poor in organic matter at the same time (López-Piñeiro et al., 2008b).The low organic matter content of most intensive-crop soils, together with their degradation problems, make it particularly interesting to enrich them, and improve their physical and chemical characteristics. The aim of this work was to determine the influence of the TPOMW, when it was added to soils as organic amendment, on the sorption-desorption, leaching, and degradation of MCPA and s-metolachlor, two herbicides widely used in intensive crop production.

2 MATERIALS AND METHODS

2.1 Herbicides

MCPA ((4-chloro-2-methylphenoxy)-acetic acid), (purity = 99%), and s-metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-[(1*S*)-2-methoxy-1-methylethyl]acetamide), (purity = 99%), both purchased from Dr. Ehrenstorfer GmbH (Augsburg,Germnay), were used to prepare the herbicide solutions in the laboratory test.

2.2 Soil and the organic amendment

A representative soil dedicated to intensive cropping was selected from fertile lowlands of the Guadiana river (Vegas del Guadiana). The TPOMW was obtained from the Olidal oil industry. Unamended soil (ALB0) was amended in the laboratory at a rate of 2.5% (ALB1) and 5% (ALB2) by weight of fresh TPOMW. Characteristics of the TPOMW, unamended and amended soils are given in Table 1.

TABLE 1 **Selected characteristics of the soils and the organic amendment**

Properties	**ALB0**	**ALB1**	**ALB2**	**TPOMW**
Total organic carbon (g kg^{-1})	13.4	29.0	41.5	920.4
Water-soluble organic carbon (g kg^{-1})	0.195	1.87	2.83	42.6
pH (H_2O)	8.15	7.40	6.90	5.7
Sand (g kg^{-1})		433.1		-
Silt (g kg^{-1})		144.4		-
Clay (g kg^{-1})		422.5		-

2.3 Herbicides analysis

MCPA and s-metolachlor were analyzed by HPLC using a Waters 2695 Separations Module coupled to a Waters 2696 diode-array detector. The following conditions were used: Nova –Pack C18 column (150 mm length x 3.9 mm

i.d.); flow rate 1 mL min^{-1}; eluent system for MCPA 60:40 methanol/water with orthophosphoric acid 1N and UV detection at 228nm, and for s-metolachlor 50:50 water/acetonitrile mixture and detection at 202nm.

Total organic carbon content (TOC) was determined by dichromate oxidation. Water-soluble organic carbon (WSOC) was extracted with de-ionized water at a 3:1 (water to soil) and 100:1 (water to TPOMW) ratio. pH was measured in a 1:1 (w/v) soil/water and 1:5 (w/v) TPOMW water mixture using a combination electrode.

2.4 Adsorption–desorption experiment

The isotherms were determined using a batch equilibration method. Triplicate soil samples (5 g) were equilibrated with 10 mL of initial MCPA and S-metolachlor solutions (5–50 μM in 0.01 M $CaCl_2$) by shaking mechanically at 20 ± 2 ºC for 24 h. Equilibrium concentrations in the supernatants were determined by high performance liquid chromatography (HPLC). The herbicide sorption and desorption experiments were fitted to the empirical Freundlich equation, $C_s = K_f \times C_e^{1/nf}$, where C_s is the amount of herbicide sorbed at equilibrium concentration C_e, and K_f and and n_f are the Freundlich constants. The K_d values were calculated from the fit of the experimental sorption isotherms ($C_s = K_d \times C_e$). Desorption was measured immediately after sorption by successive dilution from the 5, 20, and 50 μM initial concentration points. This desorption procedure was repeated three times. Hysteresis coefficients, for the sorption–desorption isotherms were calculated, $H = n_a/n_d$, where n_a and n_d are the Freundlich n constants obtained from the sorption and desorption isotherms, respectively.

2.5 Degradation studies

The soil samples (500 g) were spiked with 8 mL of an ethanol solution of MCPA and S-metolachlor to give a concentration of 1.5 mg MCPA kg^{-1} and 1.5 mg s-metolachlor kg^{-1} respectively, of dry soil. The moisture content was adjusted to 40% field capacity, and then the samples were thoroughly mixed, passing them several times through a 2 mm-sieve. Herbicide-treated soil samples were transferred to 1 L glass jars where they were incubated at 20 ± 2 ºC for 100 days for both herbicides. The soils were sampled periodically, and finally frozen until assay. For the assay, 5 g of soil samples in duplicate were extracted with 10 mL of 60:40 methanol/water with orthophosphoric acid 1N (MCPA) and methanol (s-metolachlor) for 24 h, and the herbicide concentration in the extracts was determined by HPLC. Herbicides dissipation curves in soils were fitted to first-order kinetics and the half-lives ($t_{1/2}$) were calculated.

2.6 Column leaching test

Leaching was studied in 30 cm length x 5 cm internal diameter PVC columns made up of six sections of 5 cm-long sealed with silicon. The soil columns were saturated with 0.01 M $CaCl_2$, allowed to drain for 24 h, and then the amount of both herbicides corresponding to an application rate of 1.5 kg ha^{-1} dissolved in methanol was applied to the top of the columns. The columns were leached with 0.01 M $CaCl_2$ at a rate of 50 mL per day, until no herbicide was detected in the leachates. At the end of the leaching experiment, soil samples (20 g) from the different rings were extracted once with 40 mL of 60:40 methanol/water witch orthophosphoric acid 1N (MCPA) and methanol (s-metolachlor) by shaking mechanically at 20 ± 2 ºC for 24 h. The suspensions were centrifuged, filtered, and assayed by HPLC in order to determine the residual amount of herbicide at the different depths of the soil column.

3 RESULTS AND DISCUSSION

3.1 Soil characteristics

The TPOMW application significantly increased the total organic carbon content in the soil. The increase over the unamended soil was by a factor of 2.2 and 3.1 for ALB1 and ALB2, respectively. Similarly, the soluble organic carbon values were also raised by the TPOMW amendments. However, the pH values decreased after TPOMW amendments (Table 1).

3.2 Sorption-desorption studies

The sorption of MCPA in amended soils was slightly higher than in unamended soil (Table 2). However, the addition of TPOMW increased s-metolachlor sorption by factors of 1.5 and 2.2 for ALB1 and ABL2, respectively (Table 2). This can be attributed in part to the higher affinity of s-metolachlor for organic matter.

For both herbicides, lower hysteresis coefficients (higher reversibility) were observed in the amended than in the unamended soil, which is not coherent with the amended soils's higher sorption capacity (Table 2). According to previous reports, high soluble organic carbon content of some organic materials used as amendment would give rise to higher herbicide reversibility (Albarrán et al., 2003; Cabrera et al., 2007), and this could promote

herbicide desorption and enhance its apparent water solubility through stable interactions in solution between herbicide and soluble organic matter (Graber et al., 2001; Navarro et al., 2003).

TABLE 2 **Effects of the two-phase olive mill waste addition on Freundlich sorption coefficients for MCPA and s-metolachlor**

	MCPA				s-metolachlor			
Soil	n_f	$K_{d\text{-}10\ \mu M}$	R^2 **sorption**	**H (%)**	n_f	$K_{d\text{-}10\ \mu M}$	R^2 **sorption**	**H (%)**
ALB0	0.55	0.29	0.972	4.7	0.88	2.83	0.939	6.9
ALB1	0.78	0.29	0.999	2.8	1.00	4.27	0.884	3.2
ALB2	0.89	0.32	0.992	3.0	1.06	6.06	0.913	3.0

3.3 Degradation studies

The TPOMW addition significantly increased the half-life of MCPA from 5.7 to 16.2 days for ALB0 and ALB2, respectively. Similarly, the s-metolachlor half-life was also increased from 27.0 to 46.8 days for ALB0 and ALB2, respectively (Fig 1). This finding can be attributed to the higher sorption capacity of amended soils or to a toxic effect of the organic amendment on the soil microbial population (Albarrán et al., 2004).

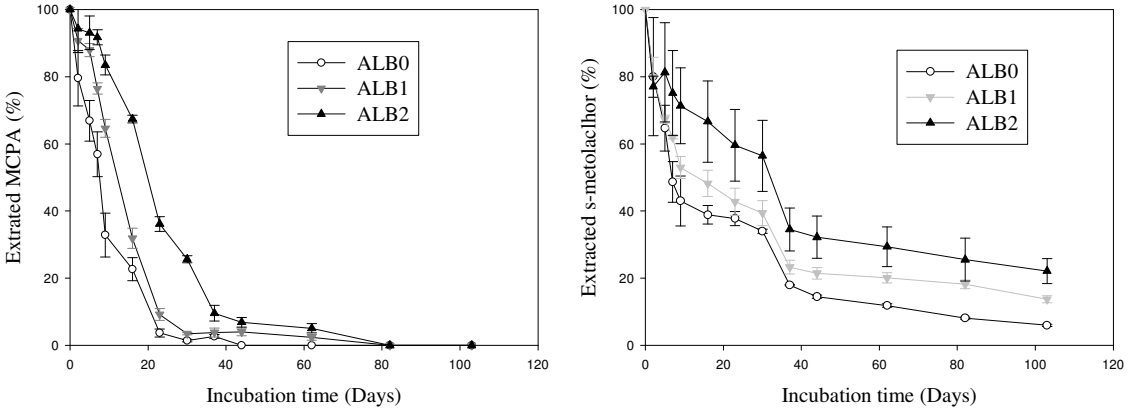

FIGURE 1 **Effects of the two-phase olive mill waste addition on MCPA and s-metolachlor dissipation. Error bars represent one standard error of the mean.**

3.4 Leaching studies

The addition of TPOMW increased the downward movement of MCPA in the columns. Thus, recovery of MCPA in leachate ranged from 79.4% for the unamended soil to 90% for amended soils (Fig. 2a). The observed increase in MCPA concentrations in leachates is consistent with the higher adsorption reversibility also observed in amended soils (Table 2). Therefore, greater percentage of water soluble organic carbon in TPOMW-amended soils could facilitate transport and accelerate the leaching of the herbicide. Contrarily, the addition of TPOMW reduced the downward movement of s-metolachlor in the columns (Fig. 2b). Thus, the amounts of s-metolachlor recovered in the leachates ranged from 54.8% to 48.4 and 38.8% for ALB0, ALB1 and ALB2, respectively (Fig 2b). The decreased movement of s-metolachlor observed in the TPOMW-amended columns suggested that s-metolachlor was mainly bound to the solid phase organic matter.

MCPA and s-metolachlor leached down to 20 cm depth in both the unamended and the TPOMW-amended soil columns. However, the total amount of s-metolachlor recovered was much higher than MCPA in the unamended and amended soil columns (Table 4), which agrees with the results observed previously in the sorption and degradation experiments of this study.

TABLE 3 **Effects of the two-phase olive mill waste addition on percentage extracted from the soil columns for MCPA and S-metolachlor**

Soil	**Extracted MCPA (%)**	**Extracted s-metolachlor (%)**
ALB0	7.48	32.6
ALB1	8.65	37.4
ALB2	8.40	44.4

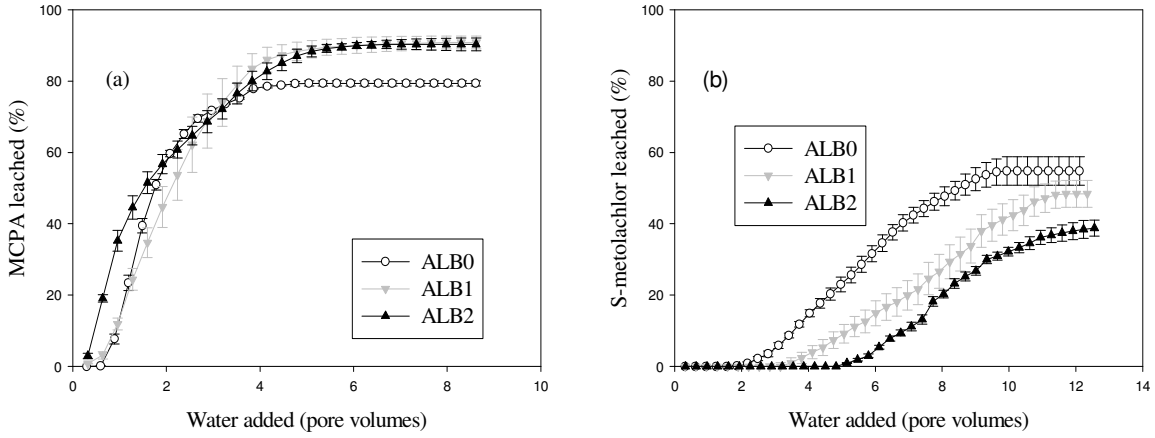

FIGURE 2 **Cumulative breakthrough curves of MCPA (a) and s-metolachlor (b) in unamended and two phase olive mill waste amended soils. Error bars represent one standard error of the mean.**

4 CONCLUSIONS

The application of two-phase olive mill waste to soil influenced the sorption capacity of soil for MCPA and specially s-metolachlor, and subsequently their dissipation and leaching. The TPOMW amendment effectively reduced s-metolachlor leaching losses. However, TPOMW amendment increased the MCPA mobility and leaching losses in soils, also increasing the risk of groundwater contamination, even at the lower TPOMW dose. The greater leaching of MCPA might be due to its lower adsorption and higher solubility to s-metolachlor. Due to non-equilibrium physical transport effects and other equilibrium sorption effects, herbicides transport in field trials should be studied.

ACKNOWLEDGMENTS

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