BEHAVIOUR AND FATE OF S-METOLACHLOR IN TWO INTENSIVE CROP SOILS AMENDED WITH DE-OILED OLIVE MILL WASTE

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1 INTRODUCTION

The process of olive oil extracted generates a residue whit high concentration of organic carbon. In Spain, there are 264 million olive trees. The new technology for olive-oil extraction is a continuous centrifuge two-phase process that generates olive oil and organic waste (OMW). In Spain alone this new system generates approximately 4 000 000 Mg year^{-1} of this waste. After drying the OMW, the remaining oil still present in this waste is usually extracted with hexane, leaving a solid residue - de-oiled two-phase olive mill waste (DOMW). De-oiled two-phase olive mill waste contains large amount of organic matter (>90%), and is free of heavy metals and pathogenic microorganisms, therefore it might be used as amendment to agricultural soils (Lopez-Piñeiro et al., 2008).

Several studies have reported that application of various wastes, either raw or after composting, can affect behaviour of pesticides (e.g. Albarran et al., 2003; Delgado-Moreno and Peña, 2008; López-Piñeiro et al., 2010). Few studies, however, have investigated the beneficial effects of fresh olive mill wastes in restoring crop productivity in degraded soils (López-Piñeio et al., 2008) and even fewer has yet investigated the pesticide´s behaviour in DOMW-amended soils. The aim of this study was to evaluate the impact of DOMW amendment on the sorption-desorption, degradation and leaching of the herbicide s-metolachlor applied to intensive crop soils which are poor in organic matter.

2 MATERIAL AND METHODS

Two representative soils (LB and PB) dedicated to intensive cropping were selected from fertile lowlands of the Guadiana river (Vegas del Guadiana). The DOMW was obtained from the UCASUL oil industry located in Beja (Portugal), which employs chemical and heat treatment to obtain a second-extraction olive-oil. The amendment using the DOMW was performed by thoroughly mixing the original soils with air-dried DOMW at 2.5 and 5% levels. The samples of the unamended and amended soils so obtained were labelled as LB0, LB1 and LB2 (control, 2.5 and 5% of DOMW applied in the soil LB), and PB0, PB1 and PB2 (control, 2.5 and 5% of DOMW applied in the soil PB). Soil samples were collected from the surface (0–30 cm) horizon. Selected characteristics of the soils and the de-oiled two-phase olive mill waste are given in Table 1.

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

Properties	LB0	LB1	LB2	PB0	PB1	PB2	DOMW
Total organic carbon (g kg^{-1})	6.69	19.41	31.31	9.7	21.09	32.88	890
Water soluble organic carbon (g kg^{-1})	0.1	2.64	4.43	0.13	2.13	3.97	74.3
pH (H_2O)	5.7	5.43	5.17	6.8	6.44	6.05	5.3
% Sand		53.2			43.7		
% Silt		32.4			32.4		
% Clay		14.4			23.9		

Total organic carbon (TOC) was determined by dichromate oxidation (Nelson and Sommers, 1996). pH was measured in a 1:1 (w/v) soil/de-ionized water and 1:5 (w/v) DOMW water suspension using a combination electrode. Water-soluble organic carbon (WSOC) was extracted with de-ionized water at a 3:1 (water to soil) and at a 5:1 (water to DOMW) ratio, and determined by wet oxidation with $K_2Cr_2O_7$.

The s-metolachlor sorption isotherms were determined in triplicate using the batch equilibration procedure. Sorption isotherms were fitted to the logarithmic form of the Freundlich equation: $\log Cs = \log K_f + n_f \log Ce$, where Cs ($\mu mol\ kg^{-1}$) is the amount of herbicide sorbed at the equilibrium concentration Ce ($\mu mol\ L^{-1}$), and K_f and n_f are the empirical Freundlich constants. The K_d values have been calculated from the fit of the experimental sorption isotherms ($Cs=K_d \times Ce$). Desorption was measured immediately after sorption by successive dilution from the 5, 20, and 50 µM initial concentration points.

For the degradation studies, the soil samples (500 g) were spiked with 8 mL of an ethanol solution of s-metolachlor to give a concentration of 1.5 mg s-metolachlor kg^{-1} respectively, of dry soil. The moisture content was adjusted to 40% field capacity. Herbicide-treated soil samples were transferred to 1 L glass jars where they were incubated at 20 ± 2 ºC for 100 d. The moisture content was maintained at a constant level throughout the experiment by adding distilled water as necessary followed by vigorous shaking. The soils were sampled periodically, and finally frozen until assay. For the assay, soil samples in duplicate were extracted with methanol for 24 h, and the herbicide concentration in the extracts was determined. Herbicides dissipation curves in soils were fitted to first-order kinetics and the half-lives ($t_{1/2}$) were calculated.

Leaching was studied in methacrylate columns made up of six 5 cm-long sections 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 s-metolachlor corresponding to an application rate of 1.5 kg ha^{-1} was applied to the top of the columns. The columns were leached with 0.01 M $CaCl_2$ until no herbicide was detected in the leachates. At the end of the leaching experiment, soil samples from the different rings were extracted once with methanol by shaking mechanically for 24 h. The suspensions were centrifuged, filtered, and analyzed in order to determine the residual amount of s-metolachlor at the different depths of the soil column. The leaching experiment was also conducted in triplicate.

S-metolachlor assays were performed by HPLC using a Waters 2695 chromatograph coupled to a Waters 2996 diode-array detector.

3 RESULTS AND DISCUSSION

3.1 Sorption studies

The adition of DOMW amendment increased TOC by a factors of 4.7 and 3.4 for LB2 and PB2, respectively (Table 1). Similarly, s-metholachlor sorption increased by factors of 3.0 and 2.2 for LB2 and PB2, respectively (Table 2). These results together with the fact that the variability of the K_d values was greatly reduced after normalization to the organic carbon content ($K_{d\text{-}oc}$ values in Table 2) clearly indicate that the amount of organic matter played a fundamental role in the s-metolachlor retention by these amended soils (Albarrán et al., 2004; Sanda et al. 2005).

TABLE 2 **S-metolachlor sorption-desorption coefficients and half-live ($t_{1/2}$) in dissipation studies.**

	$K_{d\text{-}10\mu M}$	n_f ±(error)	R^2	$K_{d\text{-}OC}$	H (%)	$t_{1/2}$ (error)
LB0	1.25 ± 0.32	0.873 ± 0.053	0.989	186.37	4.38	48.0 ± 0.5
LB1	2.35 ± 0.18	0.984 ± 0.021	0.999	120.87	2.59	78.2 ± 1.3
LB2	3.83 ± 0.48	1.036 ± 0.044	0.995	122.42	2.06	94.8 ± 3.6
PB0	1.85 ± 0.42	0.788 ± 0.040	0.992	190.75	3.26	42.5 ± 1.8
PB1	2.68 ± 0.16	0.957 ± 0.014	0.999	127.15	2.98	76.1 ± 6.0
PB2	4.03 ± 0.30	0.998 ± 0.028	0.998	122.42	2.06	102.9 ± 9.7

The lower hysteresis coefficients (higher reversibility) (Table 2) were observed in the amended than in the unamended soils. This can be attributed to the higher WSOC content observed in the amended soils (Table 2). This is consistent with previous reports indicating that pesticides were able to form stable complexes with WSOC from organic amendment and, therefore, the great affinity of s-metholachlor for the high amount of WSOC present in the amended soils would give rise to a higher reversibility on s-metolachlor sorption in amended soils.

3.2 Degradation studies

Only slight and non-significant differences were observed between unamended (LB0 vs PB0) and amended (LB1 vs PB1 and LB2 vs PB2, respectively) soils. However, the DOMW addition significantly increased the half-life ($t_{1/2}$) of s-metolachlor from 48.0 to 94.8 d for LB0 and LB2, and from 42.5 to 103 d for PB0 and PB2, respectively (Table 2). This finding can be attributed to the amended soils´s higher sorption capacity o or to a toxic effect of the organic amendment on the soil microbial population (Albarrán et al., 2004). There was little difference observed in the herbicide extracted between the unamended and the DOMW-amended soils at short incubation time (Fig. 1). However, a longer incubation times a pronounced decrease in s-metolachlor extractability was observed in the unamended soil, while little change was observed in the amended soils (Fig. 1).

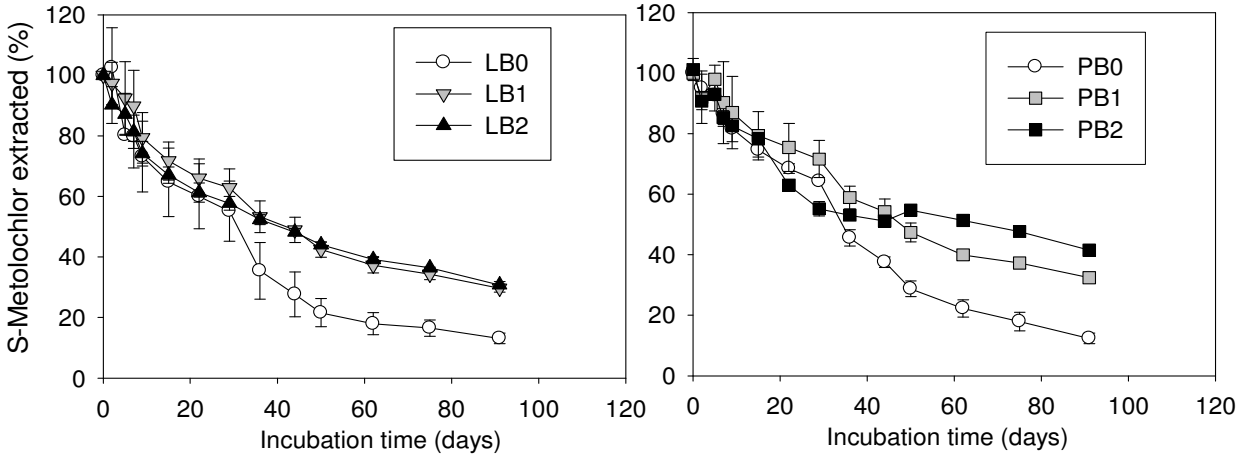

FIGURE 1 **Effects of the DOMW addition on s-metolachlor dissipation. Error bars represent one standard error of the mean.**

3.3 Leaching studies

In unamended soils s-metolachlor breakthrough occurred after passing 2.7 (LB0) and 2.3 (PB0) pore volumes of water, whereas in amended soils breakthrough was delayed, occurring after passing 4.6 and 6.5 volumes of water for LB1 and LB2, and 5.0 and 5.6 volumes of water for PB1 and PB2, respectively (Fig. 2).

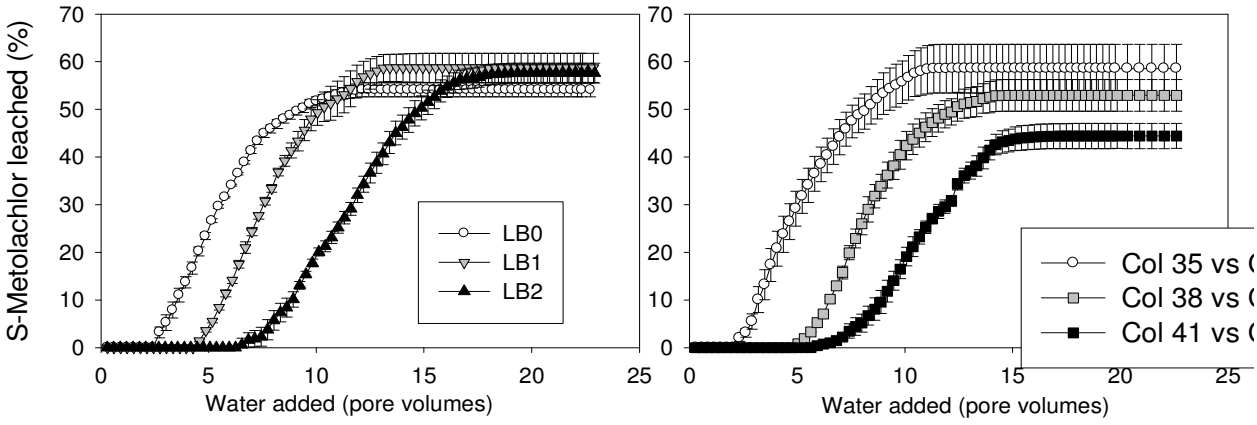

FIGURE 2 **Cumulative breakthrough curves of s-metolachlor in unamended and DOMW-amended soils. Error bars represent one standard error of the mean.**

A significant decrease of s-metolachlor concentrations in the leachates was observed following DOMW addition in PB soil, especially at the greater DOMW rate. However, only slight and non-significant differences were observed in the total amount of s-metolachlor recovered from leachates in unamended and DOMW-amended LB soils.

The amounts of s-metolachlor extracted from the soil columns are given in Table 3. S-metolachor leached down to 20 cm depth in all unamended and DOMW-amended soil columns. However, the total amount of s-metolaclor recovered in the unamended soil columns was less than that recovered in the amended soil columns

(Table 3), which can be attributed to the higher persistence and higher sorption of s-metolaclor in DOMW-amended soils, especially at the greater DOMW rate.

TABLE 3 **Percentage of s-metolachlor extracted from the soil columns after the leaching study.**

Depth columns (cm)	LB0	LB1	LB2	PB0	PB1	PB2
0-5	5.3	7.1	12.2	3.7	4.7	8.8
5-10	3.5	6.2	4.9	3.9	4.7	6.1
10-15	4.8	4.5	4.4	5.5	5.8	6.5
15-20	3.5	5.5	4.9	8.5	6.5	5.7
Total	17.1	23.3	26.4	21.6	21.7	27.1

4 CONCLUSIONS

The incorporation of organic matter to intensive crop soils by de-oiled two-phase olive mill waste addition influenced s-metolachlor sorption capacity, dissipation and leaching behaviour in soils. The DOMW amendment greatly increased sorption and persistence of the herbicide s-metolachlor in DOMW-amended soils. However, the addition of this amendment to soil does not always ensure decreased leaching of the herbicide, especially in the case of DOMW-amended sandy soils.

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