S-Metolachlor sorption in soils amended with olive oil residues: effect of organic waste transformation

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ABSTRACT
Herbicides are the main type of pesticides causing water contamination. The chloroacetanilide herbicide S-metolachlor is frequently detected in ground and surface waters, and represents a potential source of water pollution. The addition of organic residues to soils to reduce losses of organic pollutants constitutes sometimes an efficient method to control contamination. One of the recent technologies used in olive oil extraction is a continuous centrifuge two-phase process that in Spain alone generates huge amount of organic residues. The use of this residue, which contains major proportion of organic matter, can be a low-cost alternative for their disposal and at the same time can help reducing pesticide contamination by increasing its retention. The aim of the present study was to evaluate the effect of two organic residues from olive oil production, fresh and transformed in the soil, on the sorption-desorption of the herbicide S-metolachlor. Measurements on unamended and fresh-amended soils were made and compared with those made after 20 months of the organic wastes maturation in a field which had received addition of these wastes for nine years. These wastes modified the physicochemical properties of the unamended soil, increasing content of TOC, DOC, EC and reducing pH. Amendment increased S-metolachlor sorption and decreased desorption. The aging of the organic matter in the field-amended soils revealed important differences in S-metolachlor behavior in these soils, as referred to the sorption-desorption dynamic, mainly due to the lower DOC content of field amended soils.

Key words: olive oil organic waste, soil, S-metolachlor, sorption, desorption

INTRODUCTION
Worldwide pesticide usage increased dramatically over the last thirty years, coinciding with changes in farming practices. Herbicides are the main type of pesticides causing water contamination, with the group of chloroacetanilides, being one of the most frequently detected in surface and ground waters at concentrations above the European threshold for drinking water, 0.1 µg L⁻¹ (Silva et al., 2012). Metolachlor, a chloroacetanilide herbicide, comprises four stereoisomers, with herbicidal activity deriving mainly from the S-isomer atropisomer pair. It is a growth inhibitor by suppressing synthesis of proteins, fatty acids, lipids, and chlorophyll by plants. This pre-emergent or early post-emergent herbicide has been used for more than 25 years for selective weed control for more than 70 crops worldwide and now is currently being replaced by S-metolachlor, the herbicide enantiomerically enriched with the biologically active (S)-isomers (Xie et al., 2010). Due its very low sorption capacity and high water solubility (488 mg L⁻¹ at 20°C) it is frequently detected in ground and surface waters and represents a potential source of water pollution (Martins et al., 2007).

One of the new technologies used in olive oil extraction is a continuous centrifuge two-phase process that in Spain alone generates more than 4.000.000 t per year of organic slurry (two-phase olive mill waste, OW). The disposal of OW is a major concern for this agri-food industry (Alburquerque et al., 2004). After drying, the OW is generally subjected to a subsequent extraction with hexane to recover the remaining oil still present, leading to the formation of a different solid residue –de-oiled two-phase olive mill waste (DW). The residues OW and DW contain major proportion of organic matter, and lack of heavy metals and pathogenic organisms respect other organic wastes, so their use as organic amendments may represent a low-cost alternative for their disposal. Several studies have found that the application of OW or DW as organic amendments leads to beneficial effects in restoring soils and improving crop yields (López-Piñeiro et al., 2011; Cañero et al., 2012).

The aim of the present study was to evaluate the effect of fresh and transformed OW and DW amendments on the sorption-desorption of the herbicide S-metolachlor applied to a soil. To study the influence of the transformation of OW and DW organic matter under field conditions on S-metolachlor’s sorption behaviour, measurements on unamended and fresh-amended soils were made and compared to those made after 20 months of OW and DW maturation in soils which had received field addition of these wastes for nine years.
MATERIALS AND METHODS

Chemicals, organic amendments and soils
S-metolachlor[2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl] acetamide; purity 99%] was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Two olive oil extraction process residues were used in this study, OW and DW. The former was obtained from the Oldal oil industry located in Portalegre (Portugal) and the last was obtained from the UCASUL oil industry located in Beja (Portugal). Physicochemical properties of OW and DW are shown in the Table 1.

Unamended soil samples (US) were collected (0-30 cm depth). The texture was: 19.7% clay, 19.7% silt, and 60% sand. Each amendment was air dried, homogenized to < 2 mm, and added to the unamended soil at 5% and 10% (w/w) dosages (OW5, OW10, DW5 and DW10, respectively) under laboratory conditions. Amended soil samples (0-30 cm) were also collected from a field experiment 20 months after the last OW and DW addition to the same soil which had received addition of these wastes for nine years. The four amendment treatments selected for this study consisted of 30 t OW ha⁻¹ yr⁻¹ (equivalent to 0.62% yr⁻¹, FDW10), 60 t OW ha⁻¹ yr⁻¹ (equivalent to 1.24% yr⁻¹, FOW10), 27 t DW ha⁻¹ yr⁻¹ (equivalent to 0.56% yr⁻¹, FDW5), and 54 t DW ha⁻¹ yr⁻¹ (equivalent to 1.12% yr⁻¹, FDW10), both wastes as dry weight equivalents. The collected soil samples were air dried, and the fraction that passed through a 2-mm sieve was stored at 4°C until use. Physicochemical properties are shown in the Table 1.

Analysis of OW, DW and the soils
Total organic carbon content (TOC) was determined by dichromate oxidation (Nelson and Sommers, 1996). Water-soluble organic carbon (DOC) was extracted with de-ionized water at 3:1 (water:soil) and 100:1 (water:OW and water:DW) ratios. The DOC and the TOC associated with each fraction of HA (CHA) and FA (CFA) were determined by dichromate oxidation and measurement of the absorbance at 590 nm (Sims and Haby, 1971). The pH was measured in 1:1 (w/v) soil/water and 1:5 (w/v) DW or OW water mixtures using a combination electrode. Electrical conductivity (EC) was measured in a saturation extract for soil (US Salinity Laboratory Staff, 1954) and 1:10 (w/v) DW or OW water mixtures. Lignin was determined using the acid and neutral fibre detergent method (Goering and Van Shoest, 1970). Soil texture was determined by sedimentation using the pipette method.

Adsorption-desorption experiment
The isotherms were determined using a batch equilibration method. Triplicate soil samples (5 g) were equilibrated with 10 mL of initial S-metolachlor solutions (5, 10, 20, 40 and 50 μM) by shaking mechanically at 20±2°C for 24 h. Equilibrium concentrations in the supernatants were determined by high performance liquid chromatography (HPLC). The amount of S-metolachlor sorbed (Cₑ) was calculated as difference between the initial (Cᵢ) and equilibrium (Cₑ) solution concentrations.

Following the adsorption experiment, desorption of the herbicide from the soils to the solution was measured by successive dilutions from the 50 μM solution initial concentration point removing 5 mL of supernatant for sorption analysis, and replaced with the same volume of S-metolachlor-free water. The samples were re-suspended, shaken for 24 hours, and centrifuged, and the equilibrium concentration in the supernatant was determined. All treatments were done in triplicates. The herbicide sorption and desorption results were fitted by the Freundlich model, \( Cₑ = K_f Cᵢ^{1/n_f} \), where \( Cₑ \) (mM kg⁻¹) is the amount of herbicide sorbed at the equilibrium concentration \( Cᵢ \) (mM L⁻¹), and \( K_f \) (mM⁻¹·L·kg⁻¹) is the Freundlich coefficient and linearity parameter, respectively.

Statistical analysis
Statistical analyses were carried out using the SPSS package (11.5) for Windows. The data obtained were subjected to one-way analysis of variance (ANOVA). Pairwise multiple comparisons were performed using the Duncan test. Differences between results were considered statistically significant at a p<0.05 level of probability.

RESULTS AND DISCUSSION

Physicochemical properties of amended soils.
Addition of OW and DW modified the original properties of the soil (Table 1). Total organic carbon (TOC) increased in both OW and DW amended soils. Although the TOC of the wastes were similar (535 g kg⁻¹ for OW and 516 g kg⁻¹ for DW), differences between the two treatments were found in TOC of soils amended in the field: DW amended soils (FDW5, FDW10, DW5 and DW10) had higher TOC than OW amended soils, which can be attributed to higher accumulation of organic matter in DW amended soils due its higher stability, as higher content in lignin was found in DW than OW (Table 1) which is known to limit degradation (Alburquerque et al., 2009). The addition of OW and DW increased DOC and this increase was much higher in the case of soils amended in the laboratory (OW5, OW10, DW5 and DW10). This difference between field and laboratory amended soils can be explained by the loss of DOC in the field soils as a consequence of leaching and runoff processes, and also as a consequence of degradation processes, since DOC...
comprises the easiest available source of energy for soil microorganisms.

The pH and electric conductivity (EC) of soils was also affected by amendment with OW and DW. Soils FOW5, FOW10, FDW5 and FDW10 had similar pH values than unamended soil (US), whereas lower pH was found in soils OW5, OW10, DW5 and DW10. The EC of amended soils was higher than that of US, and this increase is very high in the case of soils amended in the laboratory (Table 1). Differences in the effect of soil amendment with OW and DW, of acidic pH and high EC, between field and lab amended soils on these soil properties, can be also attributed to losses of soluble compounds through transport processes in the 9-year period of amendment in the field and to organic matter degradation processes.

Adsorption-desorption of S-metolachlor

Sorption and sorption-desorption isotherms for S-metolachlor in the US and amended soils are represented in the Figure 1 and Figure 2, respectively, and sorption-desorption coefficients fitted to the Freundlich equation are shown in the Table 2.

Amendment with OW and DW increased S-metolachlor sorption when compared to US. This agrees with studies in the literature reporting organic matter as an important factor determining S-metolachlor sorption (Torrents y Jayasundera, 1997; Weber et al., 2003; Shaner et al., 2006). Increase in residue dose did not enhance sorption capacity in field amended soils, as no significant differences were detected between FOW5 and FOW10 and between FDW5 and FDW10 soils (Table 2). However, the increase in residue dose enhanced the sorption capacity of the soils amended in the laboratory between 1.4 and 2-fold at 10% respect to 5% amended soils. The higher amount of DOC in soils amended with the higher dose can be responsible for this, since DOC can sorb to soil particles and this coating can generate further sorption surfaces. The soils amended with DW in the field (FDW5 and FDW10) and in laboratory at 10% with OW (w/w) (OW10) showed the highest sorption capacity of S-metolachlor (Table 2). These soils presented the highest TOC, describing a positive relation between $K_{fads}$ and TOC values ($r^2$= 0.857) (Table 1). However, no relation was observed between sorption and DOC content ($r^2$=0.0008) as observed in a previous study with the herbicide bentazone (Cañero et al., 2012), which can be attributed to the different chemical properties of the molecules.

Desorption isotherms for S-metolachlor fitted well to Freundlich equation, except for DW10 soil ($R^2$= 0.194) (Table 2). This low fitting coefficient made impossible to predict a clear tendency respect the amendment effect. Except for the DW10 soil, the amended soils revealed lower $n_f$ values than $n_f$ads, what indicates non reversible sorption and hysteresis phenomenon for the herbicide in these soils (Table 2 and Figure 2).

CONCLUSIONS

The addition of OW and DW modified the physicochemical properties of the unamended soil S, increasing content of TOC, DOC, EC and reducing pH. The aging of the organic matter in the field-amended soils revealed important differences in S-metolachlor behavior in these soils, as referred to the sorption-desorption behavior dynamic, mainly due to the lower DOC content of field amended soils.

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### Table 1. Physicochemical properties of organic residues (OW and DW) and physicochemical properties of unamended (US) and amended soils in field with OW at 30 and 60 Mg ha$^{-1}$ (FOW5 and FOW10), at 27 and 54 Mg ha$^{-1}$ (FDW5 and FDW10), and soils amended in laboratory with the residues at 5% and 10% doses (w/w) (OW5, OW10, DW5 and DW10).

<table>
<thead>
<tr>
<th></th>
<th>OW</th>
<th>DW</th>
<th>US</th>
<th>FOW5</th>
<th>FOW10</th>
<th>FDW5</th>
<th>FDW10</th>
<th>OW5</th>
<th>OW10</th>
<th>DW5</th>
<th>DW10</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (g kg$^{-1}$)</td>
<td>535</td>
<td>516</td>
<td>14.6a</td>
<td>30.7b</td>
<td>37.6c</td>
<td>46.1d</td>
<td>63.5f</td>
<td>37.8c</td>
<td>54.8e</td>
<td>34.2bc</td>
<td>54.6e</td>
</tr>
<tr>
<td>DOC (g kg$^{-1}$)</td>
<td>43</td>
<td>74</td>
<td>0.127a</td>
<td>0.542b</td>
<td>0.712c</td>
<td>0.760c</td>
<td>1.51d</td>
<td>3.29e</td>
<td>5.25f</td>
<td>5.54f</td>
<td>8.42g</td>
</tr>
<tr>
<td>CHA (g kg$^{-1}$)</td>
<td>52</td>
<td>31</td>
<td>0.965a</td>
<td>2.07b</td>
<td>2.78c</td>
<td>2.94c</td>
<td>4.14d</td>
<td>3.28c</td>
<td>5.16e</td>
<td>1.84b</td>
<td>3.20c</td>
</tr>
<tr>
<td>CFA (g kg$^{-1}$)</td>
<td>35</td>
<td>62</td>
<td>1.14a</td>
<td>1.94b</td>
<td>2.00b</td>
<td>1.77b</td>
<td>2.29c</td>
<td>2.59c</td>
<td>4.40e</td>
<td>3.68d</td>
<td>8.42f</td>
</tr>
<tr>
<td>pH (H$_2$O)</td>
<td>5.70</td>
<td>5.3</td>
<td>7.95d</td>
<td>7.83d</td>
<td>7.74cd</td>
<td>7.81d</td>
<td>7.59c</td>
<td>6.81b</td>
<td>6.45b</td>
<td>6.56b</td>
<td>6.07a</td>
</tr>
<tr>
<td>EC (dS m$^{-1}$)</td>
<td>0.704</td>
<td>1.21</td>
<td>0.704a</td>
<td>1.21b</td>
<td>1.58c</td>
<td>1.11ab</td>
<td>1.87c</td>
<td>3.10d</td>
<td>4.94e</td>
<td>7.08f</td>
<td>12.39g</td>
</tr>
<tr>
<td>Lignin (g kg$^{-1}$)</td>
<td>19</td>
<td>24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

Table 2. S-metolachlor sorption-desorption coefficients $R^2_{ads}$, $Kf_{ads}$, $n_f_{ads}$ and $R^2_{des}$, $Kf_{des}$, $n_f_{des}$ in unamended (US) and soils amended in (FOW5, FOW10, FDW5 and FDW10), and in the laboratory (OW5, OW10, DW5 and DW10).

<table>
<thead>
<tr>
<th></th>
<th>$R^2_{ads}$</th>
<th>$Kf_{ads}$</th>
<th>$n_f_{ads}$</th>
<th>$R^2_{des}$</th>
<th>$Kf_{des}$</th>
<th>$n_f_{des}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.985</td>
<td>2.79 (1.63/3.95)</td>
<td>1.06±0.078</td>
<td>0.986</td>
<td>3.09 (1.82-4.36)</td>
<td>1.19±0.098</td>
</tr>
<tr>
<td>FOW5</td>
<td>0.994</td>
<td>5.27 (4.18/6.35)</td>
<td>0.999±0.044</td>
<td>0.976</td>
<td>25.1 (24.1/26.2)</td>
<td>0.389±0.043</td>
</tr>
<tr>
<td>FOW10</td>
<td>0.974</td>
<td>6.69 (5.52/7.86)</td>
<td>0.939±0.088</td>
<td>0.966</td>
<td>40.7 (39.7/41.7)</td>
<td>0.344±0.011</td>
</tr>
<tr>
<td>FDW5</td>
<td>0.959</td>
<td>10.4 (9.22/11.6)</td>
<td>0.970±0.116</td>
<td>0.956</td>
<td>39.3 (38.2/40.5)</td>
<td>0.295±0.044</td>
</tr>
<tr>
<td>FDW10</td>
<td>0.990</td>
<td>12.2 (11.1/13.3)</td>
<td>0.968±0.055</td>
<td>0.937</td>
<td>69.5 (68.5/70.5)</td>
<td>0.113±0.021</td>
</tr>
<tr>
<td>OW5</td>
<td>0.984</td>
<td>5.06 (3.91/6.03)</td>
<td>1.06±0.078</td>
<td>0.983</td>
<td>8.96 (7.77/10.1)</td>
<td>0.819±0.075</td>
</tr>
<tr>
<td>OW10</td>
<td>0.996</td>
<td>10.4 (8.37/11.4)</td>
<td>1.03±0.039</td>
<td>0.961</td>
<td>26.0 (24.8/27.2)</td>
<td>0.339±0.076</td>
</tr>
<tr>
<td>DW5</td>
<td>0.994</td>
<td>5.81 (4.73/6.89)</td>
<td>0.971±0.043</td>
<td>0.925</td>
<td>8.49 (7.15/9.83)</td>
<td>0.537±0.108</td>
</tr>
<tr>
<td>DW10</td>
<td>0.998</td>
<td>8.37 (7.37/9.41)</td>
<td>1.05±0.025</td>
<td>0.194</td>
<td>68.4 (67.2/69.6)</td>
<td>0.059±0.086</td>
</tr>
</tbody>
</table>

Figure 1. S-metolachlor sorption isotherms in US and soils amended in the field (FOW5, FOW10, FDW5 and FDW10), and in the laboratory (OW5, OW10, DW5 and DW10).
Figure 2. S-metolachlor sorption-desorption isotherms in US and soils amended in the field (FOW5, FOW10, FDW5 and FDW10), and in the laboratory (OW5, OW10, DW5 and DW10).