# ADSORPTION OF SULFONYLUREA HERBICIDES BY SOIL AMENDED WITH DIFFERENT OLIVE OIL MILL WASTES

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## ABSTRACT

The addition of exogenous material (peat, manure, sewage sludge, compost, etc) to soil has been extensively used in the last years to enhance its fertility and to modify pesticide fate in the environment. The olive culture generates some by-products with potential application in crop management, which can be used without further treatment (wet olive cake) or by modifying them with composting or vermicomposting processes. Adsorption kinetics and isotherms of three sulfonylurea herbicides (chlorsulfuron, bensulfuron-methyl and prosulfuron) have been carried out with the batch equilibration procedure in a soil proceeding from Granada (Spain) amended or not with wet olive cake (CA), with its compost (C) and its vermicompost (V). Analysis of the herbicides was performed by HPLC with diode-array detection. Chlorsulfuron and prosulfuron were only weakly retained by the soil and the adsorption was not significantly enhanced by the presence of the amendments. These results agree with previous reports on ionisable pesticides, for which no relationship between sorption and soil organic matter content has been found, a fact explained by the repulsion between the negative charge of the molecules and the net negative charge of organic matter and clays. Increased sorption was encountered for bensulfuron-methyl which, due to its higher pKa, should be present in a larger percentage in its neutral form at the soil pH.

***Keywords:*** *Sulfonylureas, adsorption, olive by-products, amendment.*

## INTRODUCTION

Soils from the Mediterranean countries are usually poor and subject to erosion processes. The addition of amendments rich in OM is a good alternative to increase soil fertility and to modify some characteristics, such as water retention, hydraulic conductivity or soil porosity (Cox et al., 1997; Abu-Zreig and Al-Widyan, 2002). Recently, these amendments have been also applied to soil in an attempt to increase adsorption of chemicals, such as pesticides and hence, reduce their mobility and increase their degradation (Albarrán et al., 2003, 2004; Sánchez et al., 2003). Agricultural by-products of the olive culture can be used without further treatment (*alperujo* or wet olive cake) or by modifying them with composting or vermicomposting processes (Paredes et al., 1990; Nogales et al., 1998; Benítez et al., 2003).

Olive-mill wastes are being produced in large quantities in South of Spain. Therefore these wastes, very rich in organic matter should have the ability to increase soil OM content or else, modify pesticide behaviour.

## MATERIALS AND METHODS

**Soil and organic amendments**. The soil is a calcareous silt loam (Typic xerofluvent) from the Plain of Granada (SE Spain), sampled from the upper layer (0-25 cm), whose main physicochemical characteristics consisted of 31% sand, 58% silt, 11% clay, 34% $CaCO_3$ and 27 % water holding content (1/3 bar). The amendments used, were obtained from olive residues and consisted in: wet olive cake from a two-stage centrifugation process, which will be called cake (CA), compost of wet olive cake which will be called compost (C) and vermicompost of wet olive cake which will be called vermicompost (V). The cake was obtained from an olive oil industry (Romeroliva, Deifontes, Granada), the compost was supplied by “Sociedad Cooperativa Sierra de Génave” (Puente-Génave, Jaen), from ecologically managed olive groves and the vermicompost was produced at the Estación Experimental del Zaidín. In the latter case, a mixture of cake and residual biosolids (8:1 w:w) was vermicomposted during six months (Benítez et al., 2002), using clitellated and non-clitellated worms of *Eisenia andrei*. Some chemical properties of the soil, the organic amendments and the soil amended with the olive residues, determined following the MAPA methodology (1986), are shown in Table 1

***Table 1***. *Some chemical properties of the soil and the organic amendments*

| | TOC ($g\ kg^{-1}$) | TKN ($g\ kg^{-1}$) | C/N | pH $H_2O$ | pH $CaCl_2$ | CE ($dS\ m^{-1}$) |
|---|---|---|---|---|---|---|
| **Soil** | 14 | 2.1 | 14 | 8.1 | 7.5 | 0.28 |
| **Olive cake (CA)** | 480 | 6.5 | 74 | 5.8 | | 6.28 |
| **Compost (C)** | 243 | 14.5 | 17 | 8.8 | | 1.02 |
| **Vermicompost (V)** | 351 | 14.4 | 24 | 7.8 | | 1.33 |
| **Soil + CA** | 42 | | | 7.3 | 6.9 | |
| **Soil + C** | 25 | | | 8.2 | 7.7 | |
| **Soil + V** | 32 | | | 8.0 | 7.5 | |

*TOC: total organic carbon, TKN: total Kjeldahl nitrogen, CE: conductivity, pH 5/20 proportion*

**Herbicides.** The selected herbicides, which belong to the sulfonylureas, were chlorsulfuron (pKa 3.6) (a gift from DuPont), bensulfuron-methyl and prosulfuron (pKa = 5.2 and 3.76) (Dr. Ehrenstrofer). Their purity was in all cases > 98.5%.

**Adsorption isotherms**. Sorption isotherms were carried out using a batch equilibration method, using non-amended and amended soil, with $CaCl_2$ solutions (0.1 N) of the sulfonylurea herbicides, each at 2, 4, 6, 8 and 10 mg $L^{-1}$, for 24 h. Then, they were centrifuged at 3000 rpm at 18 ºC for 15 min (Eppendorf 5810R). A small volume of the supernatant was poured into an Eppendorf vial, further centrifuged at 15000 rpm for 20 min at 15 ºC (Sigma 2K15, Germany) and analysed as described below. Isotherms were run in duplicate with a control of the herbicides solution without soil, to account for possible herbicide degradation.

**Extraction and analytical procedure.** The supernatants were filtered and the herbicide content was determined by HPLC-DAD (1100 Series, Agilent, USA), with a Zorbax C8 column (5µm, 150 x 2.1 mm) connected to an Eclipse XDB-C8 precolumn (2.1 x 12.5 mm) (Agilent, USA). The mobile phase was a v:v mixture of acetonitrile and trifluoroacetic acid 0.1 N brought to pH 3.0 with triethylamine. The flow was set at 0.2 mL $min^{-1}$, injection volume 20 µL, oven temperature 40 ºC and detector wavelengths 237 nm for bensulfuron and 225 for chlorsulfuron and prosulfuron. Retention times were 6.24, 9.69 and 14.47 min, for chlorsulfuron, bensulfuron-methyl and prosulfuron, respectively.

## RESULTS AND DISCUSSION

Adsorption kinetics showed that equilibrium was reached after 15 h. Therefore, isotherms were run for 24 h. Adsorption for chlorsulfuron and prosulfuron was low in all cases (Table 2, Figure 1). Both herbicides are weak acids with similar pKa of and 3.6 and 3.76, respectively (Tomlin, 1997). According to Green and Karickhoff (1990) weak acids can be considered to be anionic in soils if pKa ≤ pH-3.0. For the soil used, slightly basic due to its calcareous nature

(Table 1), a large proportion of both herbicides would be anionic and hence, not retained on the soil surface because of repulsions with the similarly charged OM and clay. Due to the low change in herbicide concentration, variation in the measurement was high (Table 2) (Green and Yamane, 1970) and adsorption was even slightly negative in some cases, as has been reported previously (Borgaard and Streibig, 1988). In general low adsorption values have been reported for these and other sulfonylureas of similar pKa (Barriuso et al., 1997; Borgaard and Streibig, 1988; Oliveira et al., 2001; Berglöf et al., 2003). $K_{oc}$ values lower than 50 L kg$^{-1}$, can be considered negligible (Barriuso et al., 1997).

***Table 2**. Freundlich coefficients for the three sulfonylurea herbicides on unamended and amended soil.*

| | S[a] | SV | SC | SCA |
|---|---|---|---|---|
| **Chlorsulfuron** | | | | |
| $K_f$ | 0.34 ± 0.11 | 0.47 ± 0.03 | 0.49 ± 0.62 | - |
| 1/n | 0.46 ± 0.19 | 0.81 ± 0.04 | 0.58 ± 0.07 | |
| $R^2$ | 0.959 | 0.991 | 0.888 | |
| $K_{oc}$[b] | 23.6 | 14.7 | 19.6 | |
| **Bensulfuron-methyl** | | | | |
| $K_f$ | 3.79 ± 0.11 | 5.50 ± 0.03 | 3.98 ± 0.25 | 3.62 ± 0.27 |
| 1/n | 0.70 ± 0.05 | 0.64 ± 0.06 | 0.70 ± 0.05 | 0.88 ± 0.06 |
| $R^2$ | 0.420 | 0.959 | 0.964 | 0.965 |
| $K_{oc}$ | 263 | 172 | 159 | 86.2 |
| **Prosulfuron** | | | | |
| $K_f$ | 0.33 ± 0.03 | 0.35 ± 0.15 | 0.46 ± 0.17 | 0.60 ± 0.19 |
| 1/n | 1.35 ± 0.35 | 1.45 ± 0.21 | 1.15 ± 0.23 | 0.97 ± 0.19 |
| $R^2$ | 0.623 | 0.857 | 0.763 | 0.759 |
| $K_{oc}$ | 23.9 | 10.9 | 18.4 | 14.3 |

*[a]Value ± standard error. bKoc = $K_f$/OC x 100*

Bensulfuron-methyl, with higher pKa, presents in all cases higher adsorption coefficients (Figure 1). $K_{oc}$ values, which range from 263 to 86, seem to indicate that organic matter is not playing a dominant role in the adsorption of this herbicide. But, since the Freundlich slope values (1/n) differ markedly among experiments, the corresponding constants $K_f$ and $K_{oc}$, are affected by errors and comparisons of their values may lead to wrong conclusions. Therefore, the values of the adsorbed pesticide X (µg g$^{-1}$) have been compared at one equilibrium concentration. When X values are correlated with the organic C content in different soil samples (Table 1), a linear fit of the two variables with $r^2 = 0.92$ was achieved, ranked in the order S<SC<SV<SCA, which seems to stress that organic C, independently of its nature, is mainly responsible for this adsorption increase.

Bensulfuron-methyl should be present in soil in its neutral form at a larger percentage than chlorsulfuron and prosulfuron, which explains the different behaviour observed for the herbicides. The modification of pesticide behaviour by the addition of olive by-products will therefore depend on the chemical nature of the compound considered.

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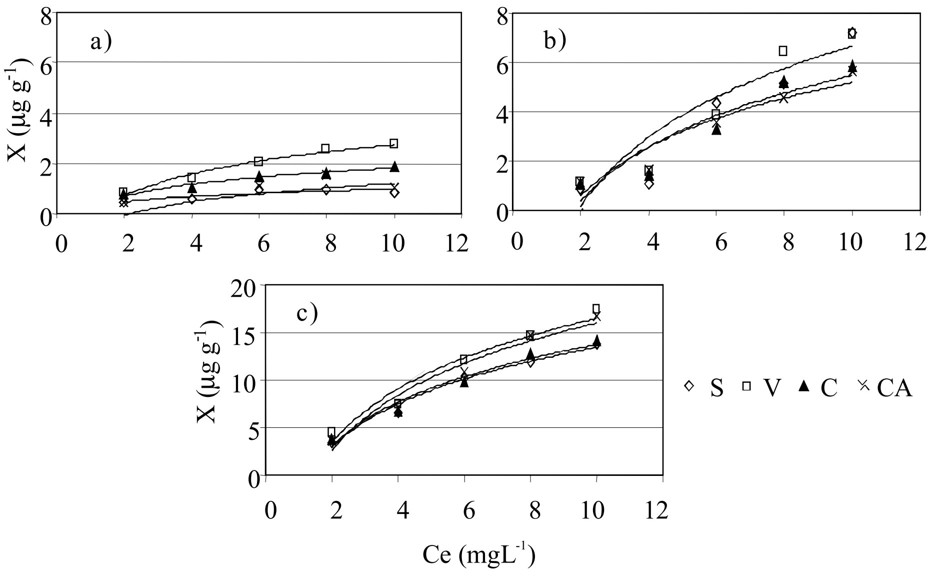


***Figure 1***. *Sorption isotherms of a) chlorsulfuron; b) prosulfuron; c) bensulfuron methyl in soil (S) and soil amended with vermicompost (V), compost (C) and olive cake (CA).*

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