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Influence of Dissolved Organic Matter from Waste Material on the Phytotoxicity and Environmental Fate of Triflurosulfuron Methyl

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Bioassays and chemical analyses were performed to study the effect of hydrophobic dissolved organic matter (HoDOM) extracted from a municipal waste compost (MWC) on the behavior of triflurosulfuron methyl in soil and water. Bioassays with oilseed rape showed that HoDOM in culture solution lowered the effective dose 50 of triflurosulfuron methyl by up to 4.8 times. Equilibrium dialysis experiments showed that in aqueous solution triflurosulfuron methyl was adsorbed to HoDOM (K_{OC} of 446.5 mL g⁻¹). The half-life in water (pH 7.0) was increased from 52 to 76 days in the presence of HoDOM, but this cannot completely explain its phytotoxicity, as bioassays lasted for 21 days only. On the other hand, the addition of HoDOM to soils did not change the degradative behavior of triflurosulfuron methyl. Fluorescein diacetate hydrolysis showed that HoDOM in soil did not significantly influence soil microbial activity, which may explain the above result on degradation in soil. Furthermore, in batch equilibrium experiments on soil, triflurosulfuron methyl was only weakly adsorbed and the presence of HoDOM significantly modified the isotherm form. Results suggest that although the addition of exogenous HoDOM from MWC to soil did not influence the herbicide's persistence, its enhanced mobility could be of environmental concern and may deserve further research.

Introduction

The application of treated organic waste to soil may be considered as an environmentally acceptable practice to increase soil fertility and as an economical waste disposal strategy. Recently, increased interest has been devoted to the investigation of how the application of composted organic refuse may affect the behavior of xenobiotics in soil systems (1–6).

In addition to humic-like substances, composted or stabilized organic waste contains water-soluble organic matter defined as dissolved organic matter (DOM) which can pass through a 0.45 μ m filter (7). DOM consists of a complex mixture of polymeric materials and readily biodegradable organic molecules such as neutral sugars, uronic acids, amino sugars, and amino acids (8).

The influence of DOM originating from different organic waste materials on pesticide sorption–desorption in soil has given rise to considerable interest in recent years. However, very few studies are available in the literature on the influence of DOM on the degradation processes of pesticides. DOM may reduce pesticide sorption through stable DOM–pesticide interactions in solution (9–11) or by competing with pesticide molecules for sorption sites on the soil surface (12). However, it may also enhance pesticide sorption if the DOM sorbed on soil particles provides additional sites for pesticide sorption.

The influence of DOM on pesticide degradation processes is not well-known. In soil, microbial processes are critical to several aspects of soil fertility and are influenced by a number of factors. Amendment may affect soil microbial activity and consequently the degradation rate of pesticides. Generally, amendments rich in stabilized organic matter provide readily biodegradable organic molecules that stimulate microbial activity and thus enhance pesticide degradation (1). In some cases soil amendment has led to a decrease in pesticide degradation possibly due to a preference of microorganisms to utilize fresh organic matter as carbon and energy sources rather than pesticides (2, 4, 6). Triflurosulfuron methyl is a selective sulfonylurea herbicide used at low application rates (20–45 g of ai ha⁻¹; ai = active ingredient) for weed control in sugar beet. Like most sulfonylurea herbicides, triflurosulfuron methyl exhibits low mammalian toxicity; however, because of the high herbicide efficacy of sulfonylureas, concerns have been expressed about its residual effect on soil and on the following crops (13–15).

Although numerous studies have been carried out to evaluate the fate of triflurosulfuron methyl in soil, they usually focused on determination of its retention and degradation as a function of soil characteristics (13–16). However, limited information is available on the effect of amendments on the fate of triflurosulfuron methyl in soil, and no studies have dealt with the influence of exogenous DOM on the bioavailability and environmental fate of this herbicide.

The main objective of this work was to assess the effect of hydrophobic DOM (HoDOM) extracted from a municipal waste compost (MWC) on (i) the phytotoxicity of triflurosulfuron methyl to higher plants by *in vivo* bioassays, (ii) the degradative behavior and sorption of triflurosulfuron methyl in aqueous solution, and (iii) the degradative behavior and overall sorption of triflurosulfuron methyl in a microbially active soil.

Materials and Methods

Chemicals. Triflurosulfuron methyl (methyl-2-[4-(dimethyl-amino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-ylcarbamoxysulfamoyl]-*m*-toluate; purity 99.0%) was supplied by Du Pont de Nemours and used in all experiments with the exception of bioassays, where Safari (triflurosulfuron methyl, 500 g of ai kg⁻¹; Du Pont de Nemours, Wilmington, DE) was used. The active ingredient was quoted to have a pK_a of 4.3 in water (17). It must be noted that all the following experiments were performed under pH conditions above 4.3 and thus the most soluble anionic form of triflurosulfuron methyl was always prevalent. All solvents were of HPLC grade (BDH Ltd., Poole, England) and were used without further purification. All other reagents were of analytical grade (Carlo Erba Reagenti, Milan, Italy).

Soil and Compost. The soil used throughout this work was collected in April from the Ap horizon of a clay-loam soil located in central Italy (Tiber Valley, Umbria). After collection, the soil was air-dried approximately to 10% humidity content,

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crushed to pass through a 2 mm sieve, thoroughly mixed, and stored at 4 °C prior to use. The chemical and physical properties of the soil are sand content 250 g kg⁻¹, silt content 450 g kg⁻¹, clay content 300 g kg⁻¹, bulk density 1.5 g cm⁻³, field capacity 303 g kg⁻¹, pH in water 8.1, total CaCO₃ content 20 g kg⁻¹, total organic C (TOC) content 9 g kg⁻¹, dissolved organic C (DOC) content 0.11 g kg⁻¹, and CEC 15 cmol_e kg⁻¹.

MWC was collected from a composting plant in the North of Italy. The mature compost was produced under aerobic conditions from a mixture of source-separated municipal solid waste and yard trimmings. The main characteristics of the compost are moisture content 520 g kg⁻¹, pH in water 8.2, TOC content 247 g kg⁻¹, total N content 22 g kg⁻¹, DOC content 24.2 g kg⁻¹, and hydrophobic DOC content 12.6 g kg⁻¹. The DOM and HoDOM contents can be estimated by assuming an OM/OC ratio of 1.72. The compost was air-dried, crushed to pass through a 2 mm sieve, and thoroughly mixed prior to use.

Extraction and Fractionation of Compost Dissolved Organic Matter. DOM was extracted from MWC, separated into a hydrophilic and a hydrophobic fraction, and then purified as previously described by Gigliotti et al. (8). Throughout this work only the HoDOM fraction was used. The HoDOM sample was finally freeze-dried and stored in a dry environment to ensure stability over time.

The HoDOM was characterized by means of ¹³C NMR spectroscopy and showed the following C distribution percentages: aliphatic C, 40%; anomeric C, 15%; aromatic C, 27%; carbonyl C, 18%.

Analysis for Triflurosulfuron Methyl. Herbicide concentrations in solution were determined by HPLC using a Perkin-Elmer Series 200 system equipped with a variable-wavelength UV/vis detector set at 235 nm. Chromatographic separation was carried out on a Spherisorb Octacyl reversed-phase column (200 × 4.0 mm, particle size 5 μm) from Sigma-Aldrich (St. Louis, MO). The mobile phase was a 60:40 mixture of acetonitrile and water adjusted to pH 8.1 at a flow rate of 1 mL min⁻¹. Herbicide standard solutions were prepared in acetonitrile from a 100 μg mL⁻¹ stock solution and stored at 4 °C in the dark until use. The standard solutions were prepared weekly, and calibration curves were obtained by injecting 20 μL of solutions at 0.5, 1.0, 2.5, 5.0, and 10.0 μg mL⁻¹.

The limit of quantification, estimated to be 10 times the background noise, was 0.1 μg mL⁻¹.

Short-Term Bioassays in Culture Solution. Short-term bioassays were carried out in a greenhouse with minimum temperatures ranging from 10 to 15 °C and maximum temperatures ranging from 20 to 30 °C. A series of 64 plastic pots were filled with 65 mL of quartz-sand (0.2–2.0 mm mesh size, 35.4% maximum water holding capacity, and 1.24 g cm⁻³ bulk density). The first series of 32 pots were treated by subirrigation with 20 mL of a water solution containing triflurosulfuron methyl + HoDOM, while the second series of 32 pots were treated only with triflurosulfuron methyl. In all the cases, pH was adjusted to 7.0 by using a phosphate buffer. The dose of triflurosulfuron methyl was chosen to prepare eight concentrations and four replicates: 0 (control), 2, 5, 7, 10, 25, 50, and 100 ng of ai mL⁻¹ of sand. These pesticide concentrations chosen after a preliminary bioassay encompass the whole range of response for the test plant and also include the field application rate (45 g of ai ha⁻¹). The concentration of HoDOM used (70 μg mL⁻¹ of sand, equivalent to 227 μg of HoDOM mL⁻¹ of water solution) was calculated considering an amendment of soil with MWC at an application ratio of 30 Mg ha⁻¹, the percentage composition of HoDOM, the moisture content of the compost, and the soil bulk density and field capacity and assuming a soil depth of 300 mm. Pots were put in a greenhouse in a completely randomized design. Nine seeds of oilseed rape

(*Brassica napus* L. ssp. *oleifera* var. Express) were sown in each pot. After emergence, seedlings were thinned out to five plants per pot. The water content of the pots was kept constant at 20 mL by subirrigation with a commercial nutrient solution containing all the necessary macro- and microelements (FLORY 9, AGRIMPORT), and having pH adjusted to 7.0 by a phosphate buffer. The necessary amount of solution was placed in a water reservoir under the pot and absorbed by capillary rise, through a hole in the bottom of the pot.

Three weeks after emergence, plants were harvested and the above-ground fresh biomass per pot was recorded. The biomass data were fitted into a log-logistic dose-response model to estimate ED50 (effective dose 50) levels for triflurosulfuron alone and triflurosulfuron + HoDOM. To homogenize variances, a TBS (transform both sides) technique was adopted by using a power transformation family and setting the transformation parameter to 0.25 (18). The effect of HoDOM was included as a categorical variable in the model, and its significance was assessed by an approximate *F* test. Regression analyses were performed by using an Excel macro add-in (19) following the procedure proposed by Streibig et al. (20). The effect of HoDOM on triflurosulfuron phytotoxicity to oilseed rape was expressed by comparing the ED50 in soil and the ED50 in soil + HoDOM. The bioassay procedure was independently repeated three times.

Hydrolysis Rate of Triflurosulfuron Methyl in Aqueous Solutions. The hydrolysis rate of triflurosulfuron methyl was determined by monitoring the disappearance of pesticide in aqueous solutions in the presence and absence of HoDOM.

Aqueous solutions of triflurosulfuron methyl with an initial concentration of 1 μg mL⁻¹ were prepared in HPLC-grade water, at pH 7.0 using a phosphate buffer. Some of the solutions also contained HoDOM extracted from compost, at a concentration of 116 mg of OC L⁻¹. The solutions were sterilized by filtration through a 0.2 μm membrane filter (Whatman, Springfield Mill, U.K.) to minimize microbial activity, and maintained in the dark at 20 °C. At 0, 1, 4, 10, 20, 30, 50, 70, and 90 days, 1 mL of each test solution was sampled and analyzed directly by HPLC as described previously. The experiment was carried out in triplicate. Residual herbicide concentrations were expressed as a percentage of the concentration before incubation (time zero). The natural logarithms of the herbicide concentrations (as percentages) were regressed against time, and half-lives were derived from the linear regression lines.

Interaction between Triflurosulfuron Methyl and HoDOM in Aqueous Solution. The extent of interaction in solution between triflurosulfuron methyl and HoDOM extracted from MWC was determined by an equilibrium dialysis technique. Spectral/Por 6 dialysis tubing (Spectrum Medical Industries, Houston, TX; 29 mm diameter) with a molecular weight cutoff of 1000 was washed repeatedly in distilled water. Aliquots of a 20 mL aqueous solution containing 3.0 mg of OC mL⁻¹ of HoDOM were transferred to dialysis tubing and placed into flasks containing 80 mL of aqueous solutions of triflurosulfuron methyl having concentrations of 2.5, 5.0, 7.5, and 10.0 μg mL⁻¹. The flasks were equilibrated by shaking in the dark for 24 h at 20 °C. To verify that the dialysis membrane did not constitute a barrier to the passage of the herbicide and to verify that equilibrium was achieved, a water solution with 5 μg mL⁻¹ triflurosulfuron methyl was dialyzed against distilled water. Pesticide concentrations inside and outside the dialysis tubing were determined by HPLC as described previously. The difference between pesticide concentrations inside and outside the dialysis tubing was assumed to be the HoDOM-bound pesticide concentration. Complete dissociation of the pesticide–HoDOM complex in the mobile phase used during HPLC analysis was confirmed by comparing known pesticide concentrations in the absence and presence of HoDOM.

All analyses were carried out in triplicate. Adsorption isotherms were obtained by plotting the amount of bound triflusaluron methyl ($\mu\text{g g}^{-1}$ of OC) against free triflusaluron methyl ($\mu\text{g mL}^{-1}$), and the observed data were fitted into a nonlinear regression adapted for the Freundlich equation.

Degradation of Triflusaluron Methyl in Soil. The degradation study was carried out in chemically inert PVC containers filled with 110 g of air-dried soil sieved at 2 mm. Triflusaluron methyl in HPLC-grade water was added to each container to give an initial pesticide concentration of $60 \mu\text{g of ai kg}^{-1}$ of dry soil, equivalent to a field application rate of $45 \text{ g of ai ha}^{-1}$ considering a soil bulk density of 1.5 g cm^{-3} and assuming a depth of 50 mm.

Half of the containers were used as the unamended controls, while the remaining containers were enriched with a dose of HoDOM (0.206 g kg^{-1} of dry soil) equivalent to 90 Mg ha^{-1} compost according to the percentage composition of HoDOM in the compost. A soil depth of 300 mm and bulk density of 1.5 g cm^{-3} were assumed. Although this compost application rate is greater than that normally used in agronomic practices (30 Mg ha^{-1}), it was chosen after preliminary trials with the normal application rate showed no measurable effect. Soil samples had their moisture content adjusted to 75% of the field capacity by adding distilled water and then incubating in the dark at 20°C . The moisture content was checked daily by weighing and adjusting as necessary. The experiment was performed according to a completely randomized design with three replicates.

The residual triflusaluron methyl during degradation in a 100 g soil subsample was quantified 0, 4, 15, 30, 45, and 60 days after treatment.

Extraction of triflusaluron methyl was carried out by transferring the soil to a 250 mL centrifuge tube, adding 150 mL of methanol, and shaking for 60 min on a reciprocating mechanical shaker at 150 rpm. The suspension was then centrifuged for 20 min at 3500g, the supernatant removed, and the procedure repeated with shaking for 30 min. The supernatants were reunited, and triflusaluron methyl was then extracted twice from the methanolic solution by dichloromethane, adjusting the pH to a value of 2. The extracts were reunited in a round-bottomed flask, and dichloromethane was removed by rotary evaporation. The residue was redissolved in the mobile phase, filtered through a $0.2 \mu\text{m}$ membrane filter, and analyzed by HPLC as previously described. The residual concentration was expressed as a percentage of the initial concentration. The average percentage recovery for this method was $87.8\% \pm 1.8\%$ (mean and standard deviation of three measurements).

Analysis of Fluorescein Diacetate (FDA) Hydrolysis. The microbial activity of soil was indirectly evaluated by the analysis of FDA hydrolysis as reported elsewhere (21). The rate of FDA hydrolysis was estimated according to the Schnurer and Rosswal (22) method, which involves the spectrophotometric determination (wavelength 490 nm) of FDA hydrolyzed by 5 g of soil after 2 h at 25°C . The data are expressed as $\mu\text{g of FDA hydrolyzed h}^{-1} \text{ g}^{-1}$ of soil dry weight.

All determinations were carried out on the same soil samples (soil + herbicide and soil + herbicide + HoDOM) and at the same times (in six sampling times) as in the degradation experiment. The data were subjected to two-way factorial ANOVA, with incubation time and HoDOM presence (with or without HoDOM) as explanatory variables.

Adsorption of Triflusaluron Methyl on Soil. Adsorption isotherms of triflusaluron methyl on soil and on soil + HoDOM were determined using the batch equilibrium method at 20°C . HoDOM was added to the soil as described in the Degradation of Triflusaluron Methyl in Soil subsection.

Triplicate samples of 10 g (dry weight) of soil and soil + HoDOM were equilibrated in polycarbonate centrifuge tubes

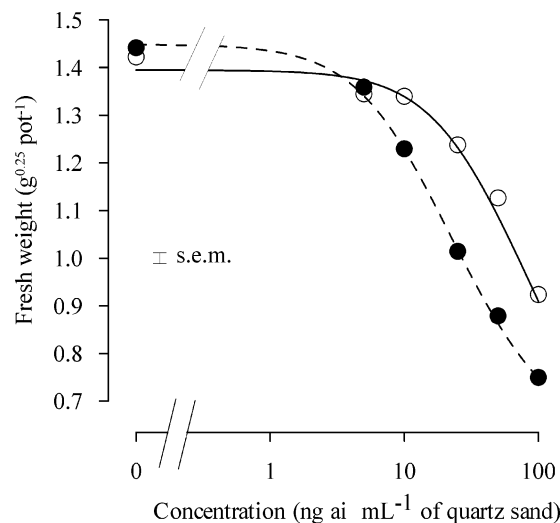


FIGURE 1. Response curve for the fresh weight of oilseed rape to increasing concentrations of triflusaluron methyl in quartz sand, as observed in the first bioassay run. Fresh weight was power transformed to meet basic assumptions for regression analysis. Symbols show the observed data (○, triflusaluron alone; ●, triflusaluron + HoDOM); lines show fitted curves.

with 10 mL of herbicide solutions at concentrations of 1, 2, 3, 4, and $5 \mu\text{g mL}^{-1}$. CaCl_2 (0.005 M) was used as a background electrolyte to minimize ionic strength changes. After equilibration for 24 h on a reciprocating shaker, the soil suspensions were centrifuged at 10000g for 15 min and the supernatants filtered through a cellulose acetate, $0.45 \mu\text{m}$ membrane filter (Whatman). Previously, it was checked that equilibrium was reached within the 24 h period and that no apparent degradation or adsorption to the centrifuge tubes occurred. Equilibrium triflusaluron methyl concentrations were determined in the supernatants by HPLC as described previously. The amounts sorbed were calculated from the difference between the initial and equilibrium concentrations of triflusaluron methyl in solution and expressed on a dry weight basis. Adsorption isotherms were obtained by plotting the amount of adsorbed herbicide against the equilibrium concentration, and the observed data were fitted into the generic Freundlich equation by nonlinear regression analysis.

Results

Short-Term Bioassays in Culture Solution. A significant stimulation of growth at low herbicide rates was observed, as commonly found with sulfonylureas (19); as a consequence, the two lowest doses were masked to improve the fit, as commonly done in herbicide bioassays (18, 20). In all the bioassays, dose-response curves did not show any significant deviation from the log-logistic model proposed by Streibig et al. (20). An example is given in Figure 1, referring to the first bioassay run. The parameters obtained in the three runs are reported in Table 1. It is possible to observe that in two of the three trials the presence of HoDOM slightly but significantly enhanced the development of the test plant when compared to the control (see the *D* parameters) probably due to the fertilizing effect of HoDOM.

The presence of HoDOM did not affect the slope of the response curves (*F* tests at $p < 0.05$), which were parallel in all the cases, thus indicating that HoDOM did not affect the mode of action of triflusaluron methyl (20). However, ED50 levels (*F* tests at $p < 0.05$) were significantly lowered in the presence of HoDOM, indicating that this fraction of DOM enhanced triflusaluron methyl phytotoxicity to the test plant by a factor of 1.4–4.8 with respect to that in the presence of herbicide alone. The lowest difference in ED50 values was

TABLE 1. Parameters of Dose–Response Curves (20) in Three Bioassay Runs with Triflurosulfuron Methyl and Oilseed Rape in Culture Solution with or without HoDOM^a

run	experimental treatment	<i>D</i> (g pot ⁻¹)	<i>C</i> (g pot ⁻¹)	<i>b</i>	ED50 (ng of ai mL ⁻¹)
1	triflurosulfuron	3.80 (0.18)	0.15 (0.1)	1.42 (0.16)	87.4 (8.83)
1	triflurosulfuron + HoDOM	4.38 (0.26)	0.15 (0.1)	1.42 (0.16)	27.3 (3.23)
2	triflurosulfuron	2.52 (0.20)	0	1.57 (0.18)	35.0 (2.29)
2	triflurosulfuron + HoDOM	2.07 (0.15)	0	1.57 (0.18)	25.5 (2.09)
3	triflurosulfuron	3.47 (0.32)	0	1.74 (0.21)	48.7 (8.7)
3	triflurosulfuron + HoDOM	4.13 (0.57)	0	1.74 (0.21)	10.2 (2.2)

^a *D* is the weight of the control test plant without herbicide treatment, *C* is the weight of the test plant at very high herbicide doses (higher and lower asymptotes in Figure 1), *b* is the slope of the curve around the inflection point (see Figure 1), and ED50 is the dose of triflurosulfuron causing 50% weight reduction. Standard errors are in parentheses.

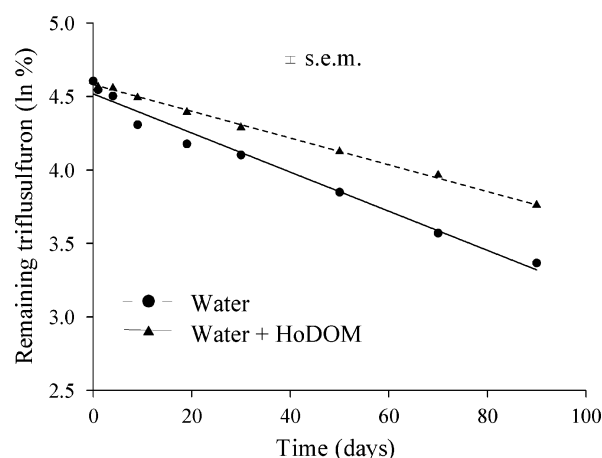


FIGURE 2. Degradation kinetics of triflurosulfuron methyl in aqueous solutions.

observed in the same run in which the treatment with HoDOM did not enhance the development of oilseed rape in the control (run 2).

Hydrolysis Rate of Triflurosulfuron Methyl in Aqueous Solutions. The rate of hydrolytic degradation of triflurosulfuron methyl at 20 °C followed first-order kinetics (Figure 2) as assessed by an *F* test for lack of fit ($p < 0.05$). The rate constant (*k*) was $13.3 \times 10^{-3} \text{ day}^{-1}$ (SE of $0.7 \times 10^{-3} \text{ day}^{-1}$) for the sample without HoDOM and $9.1 \times 10^{-3} \text{ day}^{-1}$ (SE of $0.2 \times 10^{-3} \text{ day}^{-1}$) for the sample with HoDOM in solution, while the r^2 values were 0.997 and 0.981, respectively.

Half-life values were 52 days without HoDOM and 76 days with HoDOM, and these values were statistically different (*F* test at $p < 0.05$). The results obtained for the hydrolytic degradation of triflurosulfuron methyl in solution compare well with values reported in the literature for other sulfonylurea herbicides and confirm the relative stability of this herbicide at neutral pH (23).

Interaction between Pesticide and Dissolved Organic Matter in Aqueous Solution. The adsorption isotherm obtained from the equilibrium dialysis experiment (Figure 3) gave a K_{OC} value of 446.5 (SE = 144.9) mL g⁻¹ and an n_f value of 0.80 (SE = 0.18), thus indicating a great affinity between the pesticide and HoDOM. The n_f sorption coefficient was not statistically different from 1 (see standard error), indicating a linear, C-type sorption isotherm.

Degradation of Triflurosulfuron Methyl in Soil. The kinetics of triflurosulfuron methyl degradation during laboratory incubation in HoDOM-treated and untreated soils are shown in Figure 4. The assumption of first-order kinetics was always correct (*F* test for lack of fit at $p < 0.01$), and the r^2 values were 0.922 and 0.911 for untreated and HoDOM-treated soil, respectively. The rate constant (*k*) was $40.1 \times 10^{-3} \text{ day}^{-1}$ (SE = $6.0 \times 10^{-3} \text{ day}^{-1}$) in untreated soil and $39.4 \times 10^{-3} \text{ day}^{-1}$

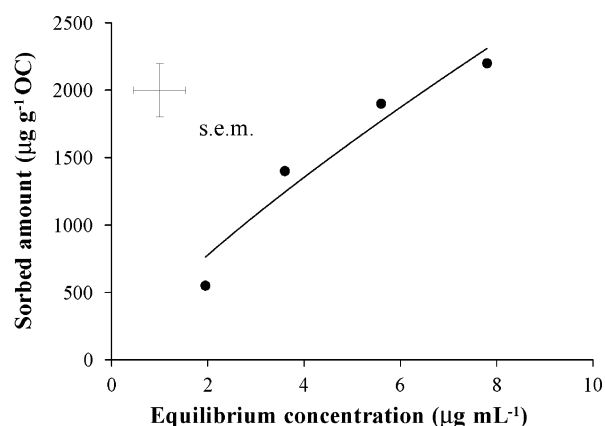


FIGURE 3. Sorption isotherm for triflurosulfuron methyl and HoDOM in water solution. Symbols show the observed data; the solid line shows the fitted curve for the Freundlich equation.

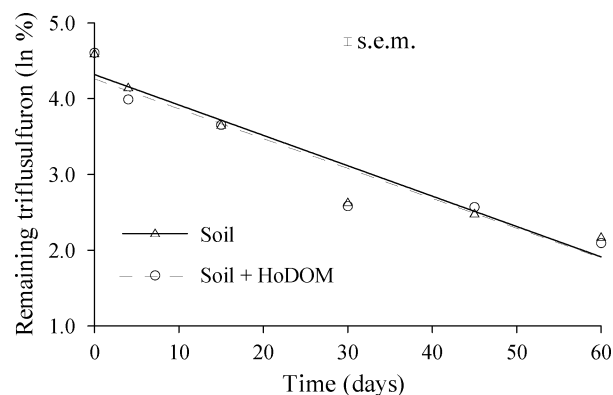


FIGURE 4. Degradation kinetics of triflurosulfuron methyl in HoDOM-treated and untreated soil.

(SE = $6.0 \times 10^{-3} \text{ day}^{-1}$) in HoDOM-treated soil, and the half-life values were 17 and 18 days, respectively. These values were not significantly different from each other.

Analysis of FDA Hydrolysis. Although the addition of biodegradable compounds present in HoDOM to soil was expected to result in an increase in the FDA hydrolysis due to a stimulation of the microbial activity, results obtained show that treatment with HoDOM (main effect and interaction) did not influence this parameter as shown by the ANOVA (Figure 5). In fact, even if significant changes are noticed with time throughout the experiment, these occurred both in the HoDOM-treated and in the untreated soil.

Adsorption Studies with Soils. Triflurosulfuron methyl sorption isotherms on untreated and HoDOM-treated soils were adequately described by the Freundlich equation (Figure 6).

The n_f sorption coefficient for triflurosulfuron methyl in soil without HoDOM (1.19 ± 0.13) was not significantly

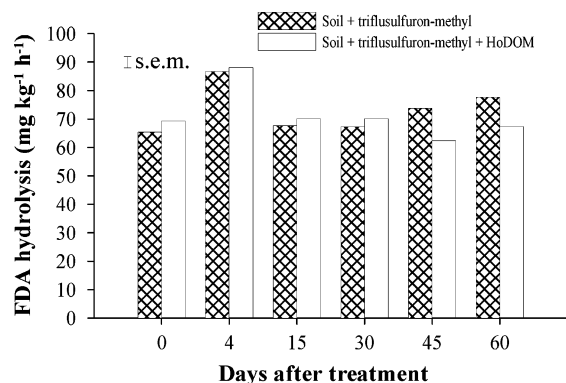


FIGURE 5. Fluorescein diacetate hydrolysis in soils, as observed during the degradation trial (the least significant difference at $p = 0.05$ was 12.1).

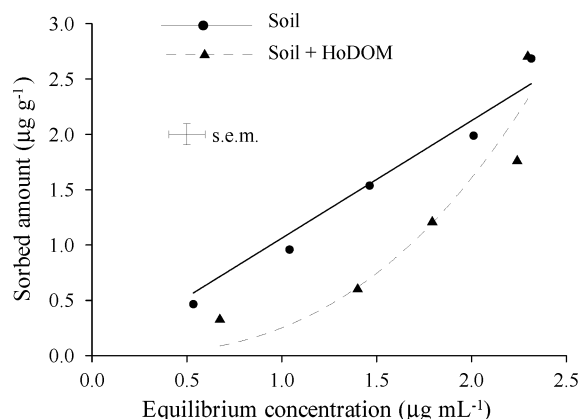


FIGURE 6. Sorption isotherms for triflurosulfuron methyl on HoDOM-treated and untreated soil. Symbols show the observed data; the solid and dotted lines show the fitted curves.

different from 1 ($p < 0.05$), indicating a linear, C-type isotherm. However, when HoDOM was added to the soil, the n_t sorption coefficient was greater than 1 (2.67 ± 0.89), indicating a concentration-dependent herbicide solid–solution distribution. The isotherm suggests that the soil has a moderately higher affinity for the herbicides at higher final concentrations (the beginning of an S-type isotherm). Nonlinear isotherms are also confirmed with changes in the sorption coefficients over the experimental concentration range used (data not shown).

K_f values were $0.93 \pm 0.84 \text{ mL g}^{-1}$ for the untreated soil and $0.25 \pm 0.18 \text{ µg}^{1-n} \text{ mL}^n \text{ g}^{-1}$ for the HoDOM-treated soil. The concentration-dependent sorption coefficients, calculated as described by Chen et al. (24), facilitate comparisons between isotherms having different n_t values and confirm a lower sorption of herbicide in the presence of HoDOM over the concentration range studied.

Discussion

The enhanced phytotoxicity of triflurosulfuron methyl to oilseed rape in the presence of HoDOM from MWC could be explained either by a lower degradation rate of the herbicide in the presence of HoDOM or by an increase in the herbicide uptake by the plant.

Although the rate of hydrolytic degradation of triflurosulfuron methyl was found to decrease in the presence of HoDOM, resulting in a greater persistence, the difference in the concentration of herbicide in the presence and absence of HoDOM during the first 15–20 days of the experiment was very small. This suggests that it is unlikely that the higher phytotoxicity of the herbicide observed in the 21 day, *in vivo*

bioassay in the presence of HoDOM was due to a slower rate of degradation.

On the other hand, the observed fertilizing effect of HoDOM in the absence of triflurosulfuron methyl (Table 1) may have initially stimulated the development of plants treated with sublethal herbicide doses, resulting in higher transpiration rates and root uptake. In fact, the enhancement of phytotoxic effects of triflurosulfuron methyl in the presence of HoDOM was very low and barely significant in the second bioassay run, when the fertilizing effect of HoDOM was absent (Table 1). Any other hypothesis of the uptake of HoDOM-bound herbicide by the test plant certainly requires further research.

The above-mentioned reduction in the degradation rate of triflurosulfuron methyl in the presence of HoDOM in aqueous solution may be due to the high affinity of the herbicide to compost HoDOM, as shown with the results from the interactions between triflurosulfuron methyl and HoDOM. This decrease in the potential for abiotic degradation in the presence of HoDOM has already been observed with other sulfonylureas (23). Those findings are rather important because they may play a role in the environmental behavior of herbicides since such amendment practices with MWC may introduce an appreciable amount of HoDOM into the soil system.

Results clearly show that the biodegradation of triflurosulfuron methyl in a microbiologically active soil was faster than the abiotic hydrolytic degradation in aqueous solution (half-lives of 17 days in soil and 52 days in aqueous solution). Furthermore, the presence of HoDOM did not significantly influence its degradation in soil. This suggests that the microbial degradation of the herbicide in the soil system plays a major role in determining its persistence (25); however, the lack of influence of the added HoDOM on herbicide degradation is in contrast with the effects of amendment on the fate of herbicides normally reported in the literature, where modifications in the rate of pesticide degradation are noticed (1, 2, 4, 6). Moreover, the ^{13}C NMR characterization of HoDOM shows a relatively high content of carbohydrates (15% of C was attributed to anomeric C), suggesting that the addition of this organic fraction to soil could have resulted in an increase in biodegradable compounds and was expected to increase the microbial activity. This was not found to be the case as was confirmed by the FDA hydrolysis measurements that did not show a significant difference between HoDOM-treated and untreated soils.

The relatively high solubility (26) of triflurosulfuron methyl in water (260 mg L^{-1} at pH 7.0), especially at pH > 6 at which its anionic form is predominant, suggests that this herbicide is only weakly adsorbed to soils and may therefore leach down the soil profile. In fact, the low K_f values obtained confirm the low affinity of triflurosulfuron methyl to soil and its preference to remain in solution. Treatment of soil with HoDOM resulted in a decrease in the K_f value and an increase in the n_t sorption coefficient. These results, together with the affinity between herbicide and HoDOM, indicate the important role exogenous HoDOM plays in increasing herbicide mobility, particularly at low herbicide concentrations. However, the nonlinearity of the isotherm obtained for the adsorption of triflurosulfuron methyl to HoDOM-treated soil suggests that at higher herbicide concentrations the solid–solution distribution in the treated soil approaches that of the soil not treated with HoDOM. This behavior could be attributed to the saturation of sorption sites on the HoDOM surface in solution, at higher herbicide concentrations at which adsorption to soil constituents prevails.

The biotic degradation and adsorption behavior of triflurosulfuron methyl in HoDOM-treated and untreated soil shows that the addition of exogenous HoDOM to soil did not influence the herbicide's persistence. However, the enhanced

mobility in the presence of HoDOM from MWC could be of environmental concern and may deserve further research effort.

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