Behavior of clomazone in paddy soil under different management and irrigation techniques: preliminary results.

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***Abstract*—** Agricultural Mediterranean soils are very poor in organic matter and are at a high risk of groundwater contamination from intensive annual pesticide applications. The aim of this study was to evaluate the impact of compost olive mill waste amendment (COW) on the sorption and leaching of clomazone in a paddy soil with different irrigation and tillage systems. The soil had been amended with 80 Mg ha^{-1} with COW. Sorption of clomazone in amended treatments (k_f = 6.71 - 8.52) was greater than unamended treatments (k_f = 2.82 - 3.74). The COW addition significantly reduced the amount of clomazone leached. Therefore, the COW addition could be beneficial in reducing the mobility of clomazone in paddy soils, thus, decreasing the risk of groundwater contamination by this herbicide. More differences results between treatments are expected to be found after long-term implementation of the management techniques (tillage vs. no-tillage, sprinkler vs. flooding irrigation).

***Keywords*—**clomazone, leaching, organic amendment, sorption

I. INTRODUCTION

CLOMAZONE, 2-(2-is 2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one, is widely used on many crops including soybeans, cotton, tobacco, and rice, among others [1,2]. Physicochemical properties indicate that clomazone is relatively water soluble (1100 μg mL^{-1} at 25 ◦C), and not rapidly degraded by environmental fate processes [3]. These physicochemical characteristics and its intensive use are responsible for the contamination of groundwater [4,5]. Clomazone persists in agricultural water at least for 130 days, and was present in 90% of the water samples analyzed [6].

Agronomic practices like the addition of organic amendments play an important role in the management of run-off and leaching losses of pesticides from agricultural fields. Usually, with the increase in total organic carbon (TOC), the sorption of herbicides onto soil particles also increases, and thus their mobility down the soil profile may be reduced.

In many Mediterranean areas, the soils are generally characterized by low organic matter content. This contributes to their limited fertility and productivity together with problems of erosion and desertification [7,8]. Therefore, the agricultural use of waste as soil amendment can be particularly advantageous in these areas because it not only recycles the waste, lessening problems of pollution, but also improves the physical, chemical, and biotic condition of their soils [9].

Currently, the most commonly used procedure in olive oil extraction is a two-phase continuous centrifuge process that generates a liquid phase (olive oil) and an organic slurry known as two-phase olive mill waste (OW), that in Spain alone amounts to more than 4000000 Mg per year. This waste is a slightly acidic semi-solid waste characterized by a high organic matter content, and a lack of heavy metal and pathogenic organism contamination [10].

Although, there is a growing evidence that the application of OW to soils may provide beneficial effects for the soil's properties and crop productivity [11,12], contradictory trends have been recognized in the determination of a herbicide's fate in a specific soil under OW. This could be due to the quantity and nature of the organic amendment, its effect on microbial activity, and the particular herbicide's characteristics [13].

To date, only a few reports have studied the environmental fate of clomazone [2,14,15]. Moreover, although clomazone is widely used to control weeds in many crops and represents a potent source of water pollution, to the best of our knowledge, there have been no published studies evaluating its behavior in OW amended soils. Such information would be useful from the environmental perspective of pesticide management in soils receiving this waste.

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The aim of the present study was therefore to investigate the effect of composted OW (COW) amendment on the sorption-desorption, and leaching of the herbicide clomazone applied to a paddy soil with different irrigation and tillage systems.

II. MATERIALS AND METHODS

A. Herbicide and organic residue

Clomazone (2-(2-is 2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one) was obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany). Its water solubility was 1100 μg mL^{-1} at 25 ◦C. The COW was obtained from a 9:1 mixture of OW and olive leaves which were added as bulking agent. The mixture was composted in a trapezoidal pile with occasional turning, and water was regularly added to maintain appropriate moisture. Its main properties were as follows: pH 7.71, 382 g kg^{-1} organic carbon, 21.7 g kg^{-1} total nitrogen, and 2.32 dS m^{-1} electrical conductivity.

B. Soil and experimental desing

The soil, classified as Hydragic Anthrosol [16] was selected from Extremadura (south-western Spain). This soil had a sandy clay loam texture, which consisted of 20.9% clay, 28.8% silt, and 50.3% sand.

The experimental design consisted of eighteen 18×20 m plots with amendment made in a complete randomized design with three replicates per treatment. The six treatments were: (CTF) applying the techniques that are conventional in the region, i.e., tillage to 30 cm and flooding with continuous water flow, (CTS) conventional tillage and sprinkler irrigation; (NTS) conservation agriculture techniques (no-tillage and seeding by direct drilling) and sprinkler irrigation. In addition, in these treatments mentioned above 80 Mg ha^{-1} of COW, dry weight equivalent, has been applied in March (2015), spreading the waste on the soil surface manually, followed by arable-level homogenization using a mould-board plough, labeled as CTF80, CTS80, and NTS80, respectively.

For the soil characterization and laboratory experiments, soil samples from the unamended and amended plots were collected in May (2 months after the COW application). Four soil subsamples from each plot were taken randomly at a 25 cm depth. Prior to analyses, the soil samples were air-dried at room temperature, and the fraction that passed through a 2-mm sieve was stored at 4 ºC until use. Selected characteristics of the different treatments are given in Table 1.

C. Analysis of the soil and COW

Texture was determined by sedimentation using the pipette method. The TOC was determined by dichromate oxidation [17]. WSOC was extracted with de-ionized water at 3:1 (water to soil) and 500:1 (water to COW) ratios. Humic and fulvic acids (HA and FA, respectively) were extracted by a solution of 0.1 M $Na_4P_2O_7$ + NaOH using a ratio of extractant to sample of 10:1, and to precipitate humic acid the supernatant was acidified to pH 2 with H_2SO_4. The electrical conductivity (EC) was measured in a saturation extract for soil and 1:10 (w/v) COW water mixtures. The pH was measured in 1:1 (w/v) soil/water and 1:5 (w/v) COW water mixtures using a combination electrode.

D. Sorption-desorption experiment

The isotherms were determined using a batch equilibration method. Soil samples (5 g) were treated with 10 mL of clomazone. The initial concentration of clomazone ranged between 5 and 50 μM in 0.01 M $CaCl_2$ and each concentration was replicated three times. Samples were equilibrated by shaking mechanically at 20 ± 2 °C for 24 h. Preliminary kinetic studies were carried out to determine the optimal soil:solution ratio and the equilibration time according to OECD guideline 106 [18]. Equilibrium concentrations in the supernatants were determined by high performance liquid chromatography (HPLC). The amount of clomazone sorbed (Cs) was calculated from the difference between the initial (Ci) and equilibrium (Ce) solution concentrations.

Following the sorption experiment, the desorption of clomazone from the soils was measured by successive dilution from the 50 μM initial concentration points. The 5 mL of supernatant removed for sorption analysis was replaced with 5 mL of 0.01 M $CaCl_2$. The samples were re-suspended, shaken for 24 h, and centrifuged, and the equilibrium concentration in the supernatant was determined. This desorption procedure was repeated three times. All treatments had three replicates. The herbicide sorption and desorption results were fitted by the Freundlich model, $Cs = K_f\ Ce1/^{n}{}_{f}$, where Cs (mM kg^{-1}) is the amount of herbicide sorbed at the equilibrium concentration Ce (mM L^{-1}), and K_f (mM1 - 1/n $kg^{-1\ L1/n}$) and n_f are the Freundlich coefficient and linearity parameter, respectively. The organic carbon soil sorption coefficient (K_{fOC}) was calculated from the K_f values as $K_{fOC} = (K_f)/TOC\%$. The desorption percentage was calculated as $\%D = ((Csa-Csd)/Csa)\times 100$, where Csa is the amount of clomazone sorbed in adsorption process and Csd is the amount of clomazone sorbed in desorption process.

Table1. Selected characteristics of the treatments studied

Treatments	TOC (g kg^{-1})	WSOC (mg kg^{-1})	HA (g kg^{-1})	FA (g kg^{-1})	pH	EC (dS m^{-1})
NTS	12.1	164	1.94	1.16	4.53	6.57
NTS80	31.7	1562	4.48	1.57	5.79	9.06
CTS	11.1	156	2.04	1.09	4.57	4.11
CTS80	28.6	1649	4.27	1.48	5.94	8.88
CTF	13.0	150	2.17	1.09	4.27	5.86
CTF80	28.0	988	4.59	1.59	5.63	9.53

TOC, Total Organic Carbon; WSOC, Water Soluble Organic Carbon; HA, Humic Acid; FA, Fulvic Acid; EC, Electrical Conductivity

E. Column leaching tests

Leaching experiments were carried out using disturbed-soil columns (30 cm length × 5 cm i.d.) constructed of PVC. To minimize losses of soil during the experiment, the top 5 cm of the columns was filled with sea sand and the bottom 5 cm with sea sand plus glass wool. The remaining 20 cm was hand-packed with unamended or amended air-dried soil. The experiment was performed with triplicates of the unamended and amended soil samples. The soil columns were saturated with 0.01 M $CaCl_2$, allowed to drain for 24 h, and then the amount of clomazone corresponding to an application rate of 1.0 kg ha^{-1} dissolved in ethanol was applied to the top of the columns. Each day the columns were leached with 0.01 M $CaCl_2$ at a rate of 50 mL day^{-1} until no herbicide was detected in the leachates. Leachates containing the herbicide were collected daily, filtered, and assayed by HPLC. At the end of the leaching experiment, the columns were sectioned into 5-cm deep portions in order to determine the residual amount of clomazone at the different depths of the soil column.

F. Clomazone extraction

For the assay, 5 g of soil samples from leaching studies were extracted with 10 mL of methanol by shaking mechanically on an end-over-end shaker at 20 ± 2 °C for 24 h followed by centrifugation, and the clomazone concentration in the extracts was determined by HPLC. This extraction procedure recovered ≥ 95% of the clomazone applied to the soils.

G.Herbicide assay

The clomazone was assayed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The following conditions were used: Nova-Pack C18 column (150 mm length × 3.9 mm i.d.), mobile phase of acetonitrile + water (70% + 30% by volume) at a flow rate of 1 mL min^{-1}, 25 mL injection volume, and UV detection at 214 nm.

H.2.8. Statistical analyses

Statistical analyses were carried out using the SPSS package (11.5) for Windows. Pearson's correlation coefficient was used to test for relationships between sorption and leaching parameters and selected soil properties.

III. RESULTS AND DISCUSSION

A. Sorption-desorption studies

The sorption isotherms of clomazone in the unamended and field amended soils are shown in Figure 1. The values of the correlation coefficient (Table 2) for all treatments were very high ($R^2 \geq 0.998$), indicating that the Freundlich sorption equation satisfactorily explained the clomazone sorption results. The values of n_f in the unamended soils ranged from 0.737 to 0.791 (Table 2), indicating an L-type curve [19] which suggests a decrease in specific sorption sites as the concentrations of herbicide in solution increased. The K_f values for herbicide sorption on the original soils ranged between 2.82 for CTS and 3.74 for CTF. These values are consistent with earlier findings by [20] who reported values 3.29 in a silty clay loam soil.

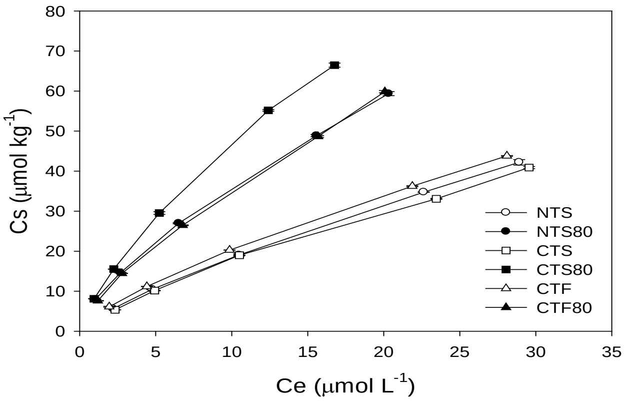

Figure 1. Sorption isotherms of clomazone in the different treatments studied. Vertical bars represent one standard error of the mean which were lower than the symbols in all cases.

The COW amendment had a significant influence on the sorption of clomazone (Table 1). The K_f values of the soils amended were greater than those of unamended soils. Thus, the addition of COW significantly increased the K_f of clomazone from 3.06 in NTS soil to 7.65 in NTS80, from 2.82 in CTS to 8.52 in CTS80, from 3.74 in CTF to 6.71 CTF80 (Table 1). Indeed, K_f was positively and significantly ($p < 0.01$) correlated with TOC ($r^2 = 0.968$). These results indicate the importance of COW in influencing clomazone sorption in agricultural soils. The increases in clomazone sorption due to increases in TOC content of the soils has been observed previously by various workers. For example, [21] reported, in different soils, a positive correlation ($r^2 = 0.62$) between clomazone sorption and soil organic carbon contents. Also, [22] observed that clomazone sorption quantity was significantly correlated with organic carbon ($r^2 = 0.62$) and clay content ($r^2 = 0.67$) in the tested paddy soils. In addition, the variability between K_f values for unamended and amended soils was greatly reduced after normalization to the TOC content (K_{fOC}), showing similar variation for all treatments (Table 2) and indicating therefore that TOC of this waste in soils was mainly responsible for increased clomazone sorption.

Table 2. Sorption and desorption parameters and percentage of Clomazone leached and extracted from the different treatments

Treatments	n_f	K_f	R^2	K_{fOC}	%D^b	Leached (%)	Extracted (%)
NTS	0.780	3.06	0.999	2.55	32.2	39.7	25.5
NTS80	0.676	7.65	0.999	2.41	24.8	9.69	31.1
CTS	0.791	2.82	0.998	2.54	34.6	46.1	19.1
CTS80	0.737	8.52	0.999	2.98	27.8	20.4	20.2
CTF	0.737	3.74	0.999	2.88	43.7	35.5	19.2
CTF80	0.725	6.71	0.999	2.40	25.3	15.7	21.2

[b] Values of percentage of clomazone desorbed after three desorption steps

The desorption percentage (% D) were significantly lower in field-amended soils than unamended (Table 2). Therefore, COW amendment provide more active sites than original matter of the soil; for this reason, the adsorbed clomazone might be easily desorbed in unamended soils. These results are consistent with those of [12] and [23] who suggested that the adsorbed MCPA and metribuzin, respectively, could be easily desorbed in OW-amended soils if the amendment is not composted.

B. Leaching studies

Relative and cumulative breakthrough curves (BTCs) of clomazone applied to soil columns in unamended and amended soils are shown in Figure 2. In the unamended soils, there was no significant difference in the herbicide breakthrough that occurred after passing about 1.0 pore volumes of water, as is typical of highly mobile compounds [24]. However, clomazone breakthrough was delayed in the amended soils (Figure 2).

Mass balance calculations (Table 2) showed that 39.7%, 46.1%, and 35.5% of the initially applied clomazone was recovered from the leachates in the NTS, CTS, and CTF soils, respectively. For all the treatments, the application of COW amendment significantly ($p < 0.05$) decreased the amount of clomazone leached (Figure 2). In particular, the amounts of clomazone in the leachates relative to the unamended soils were reduced by about 4.1, 2.3, and 2.3 times for NTS80, CTS80, and CTF80, respectively. The increase in sorption of clomazone may explain the greater reduction of this herbicide in the leachate of the COW-amended soils (Table 2). The amount of clomazone leached was negatively correlated with K_f (r^2= - 0.916) and with TOC (r^2 = - 0.974) indicating that the clomazone leaching in COW-amended soils depends on the organic matter content. This is consistent with results observed by [25] who found that clomazone show a tendency to be leached, with more pronounced effects in soils with lower organic matter content.

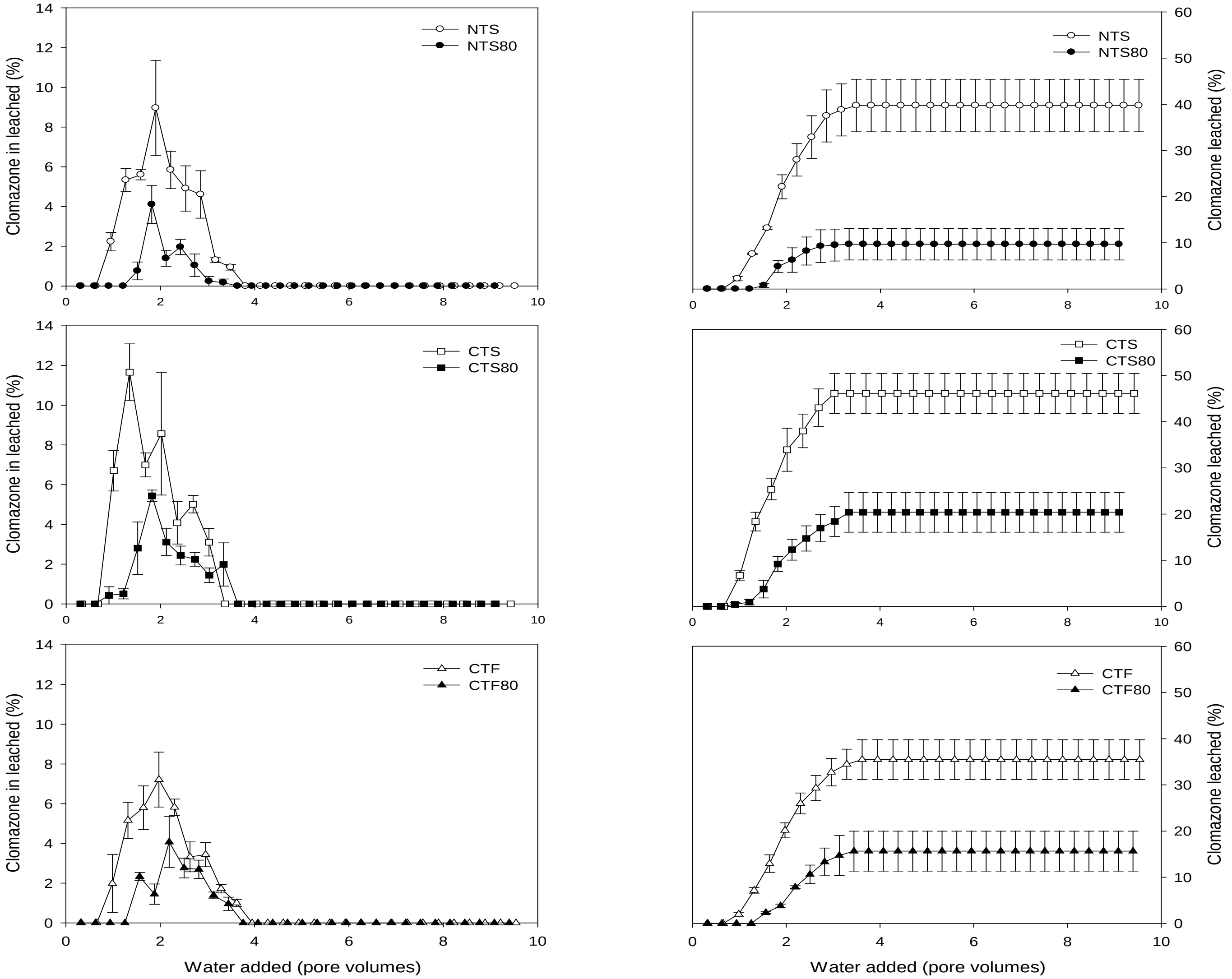

Figure 2. Relative (left) and cumulative (right) breakthrough curves of clomazone in the different treatments studied. Vertical bars represent one standard error of the mean.

The application of COW led to an increase in the amount of clomazone extracted, although this increase was not significant (Table 2), and the clomazone was distributed uniformly in every soil column, confirming the high mobility of clomazone [5].

IV. CONCLUSIONS

The application of COW to Hydragic Anthrosol greatly influenced the behavior of the herbicide clomazone. The amendment led to an increase in the clomazone sorption capacity and a decrease in the amount of herbicide leached. This suggests that application of COW may well be an environmentally and economically good practice, with a positive effect that could be especially significant in Mediterranean areas, whose agricultural soils are very poor in organic matter and are at a high risk of groundwater contamination from intensive annual pesticide applications. More differences results between treatments are expected to be found after long-term implementation of the management techniques (tillage vs. no-tillage, sprinkler vs. flooding irrigation).

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