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# Direct and residual effects on diuron behaviour and persistence following two-phase olive mill waste addition to soil: Field and laboratory experiments

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## ABSTRACT

Two-phase olive mill waste (TPOMW) is a by-product of olive oil extraction, contains up to 90% organic matter, and may be used as a soil amendment. In order to investigate the impact of TPOMW amendments to soil on the sorption-desorption, degradation, leaching, and persistence of the herbicide diuron, field and laboratory experiments were conducted on a representative olive grove soil. The soil was amended in the laboratory with TPOMW at the rates of 5% and 10%, and in the field with 30 and 60 Mg ha<sup>-1</sup> of TPOMW for seven years. Direct and residual effects were evaluated in the last year and two years after the last TPOMW field application (2005 and 2007, respectively). Significant increases in diuron sorption were observed with the greater amount of TPOMW in the laboratory and field-amended soils, mainly promoted by an increase in humic acid content, this process being more reversible in the laboratory than in the field amended soils. The TPOMW soil application only significantly increased the half-life of diuron in the laboratory amended soils, ranging from 8.5 days for the original soil to 32 days at the greater application rate. The TPOMW amendments significantly reduced the downward mobility of diuron, and reduced the amount of herbicide leached in the laboratory and field-amended soils, with a major residual decrease two years after the last waste addition since no herbicide leached through these amended-soil columns. In the field persistence study, TPOMW addition increased diuron retention mainly in the upper 30 cm of the soils, decreasing the herbicide's vertical movement through the amended soils. The residence time of diuron increased with increasing TPOMW rate, especially in the direct year (2005). The results revealed major changes in diuron's behaviour due to the different TPOMW loading rates and the transformation of the amendment during two years of biodegradation in the soil. This study has shown the usefulness of TPOMW for reducing groundwater contamination by pesticides for at least 24 months following its application.

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## 1. Introduction

The olive oil extraction industry is an important activity in Mediterranean countries, and more than 11,000,000 Mg per year of olive mill waste is produced during the process in Mediterranean countries. The new technology for olive-oil extraction is a continuous centrifuge two-phase process that generates a liquid phase (olive oil) and organic slurry (olive-mill watery husk, or two-phase olive mill waste, [TPOMW]). In Spain alone this new system generates approximately 4,000,000 Mg per year of TPOMW, usually from November to January, whose gradual accumulation or improper land disposal may have damaging effects on the environment (Alburquerque et al., 2004; Roig et al., 2006). Since TPOMW has a very high organic matter content with a range from 85 to 97% (Alburquerque et al., 2004), recycling of TPOMW as soil amendment

for agricultural soils has been proposed as a solution for its disposal which will at the same time enrich soils that are poor in organic matter (Abu-Zreig and Al-Widyan, 2002; López-Piñeiro et al., 2008). The low organic matter content (<1.5%) of most Mediterranean soils under intensive continuous cultivation, together with their problems of erosion and desertification (Nunes et al., 2007; Pleguezuelo et al., 2009), make TPOMW addition particularly interesting for enrichment of these soils and to improve their physical and chemical characteristics (Brunetti et al., 2005; López-Piñeiro et al., 2006) and crop yields (López-Piñeiro et al., 2008).

Diuron is a commonly used herbicide in olive groves, in many other agricultural crops, and for pre-emergence weed control that lasts several months in non-crop areas. It is relatively persistent in the soil, with half-lives of from 1 month to 1 year (Field et al., 2003; Cabrera et al., 2007). The intensive use of this herbicide can lead to the contamination of surface and subsurface waters at concentrations higher than the European threshold for drinking water, 0.1 µg L<sup>-1</sup> (European Community Council, 1998; Landry et al., 2006; Dores et al., 2009). For example, Lapworth and Goody (2006) reported that

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diuron was observed in 90% of the groundwater samples analysed in the Cretaceous Chalk aquifer of southeast England at levels from 0.02 to 1.2  $\mu\text{g L}^{-1}$ ; also, according to the French Environmental Institute (IFEN, 2008), in 2005 in France diuron was detected in 34.6% of surface waters and its concentration in low quality sites ranged from 2.1 to 36  $\mu\text{g L}^{-1}$ . It is thus clearly important to implement practices to reduce and avoid water contamination by this pesticide. These environmental problems are particularly expected in a Mediterranean climate characterized by very intense, short-lived rain events, and in soils under olive production which are very often located on slopes steeper than 20% (Fleskens and Stroosnijder, 2007).

There is growing recognition of the advisability of applying organic-matter rich residues such as TPOMW to agricultural soils (Delgado-Moreno and Peña, 2008) because alternatives such as animal manure or green covers can be in some cases expensive or impractical. A strong correlation has usually been observed between soil organic carbon content and diuron sorption (e.g. Yu et al., 2006; Cabrera et al., 2007; Ahangar et al., 2008). Therefore TPOMW soil application as organic amendment could represent an important management strategy for reducing herbicide leaching. However, although it is known that increased organic matter in the soil generally results in greater pesticide sorption and decreased leaching (Albarrán et al., 2003; Majumdar and Singh, 2007), herbicide persistence can also be increased by organic amendment (Albarrán et al., 2003; Cabrera et al., 2007), and consequently the risk of soil and associated water resource contamination could also be raised (Cabrera et al., 2008a,b).

The size, polarity, and molecular configuration of the organic matter determine its effectiveness in interacting with soils and pesticides, with the binding capacity of the humic substances playing an important role in the fate of pesticides in aquatic systems (Thurman, 1986; Celis et al., 1998). Therefore, organic matter transformation following field application may also modify the further interactions of herbicides with the amended soils, so that it is of interest to know the effect of aging on the transformation of the organic amendments added to soils, and on pesticide behaviour (Martinez-Iñigo and Almendros, 1992; Morillo et al., 2002).

Several studies have demonstrated the beneficial effects of TPOMW in restoring crop productivity in degraded soils (López-Piñeiro et al., 2006, 2008), but very few studies have investigated diuron's behaviour in fresh TPOMW-amended soils (Cabrera et al., 2007; Cox et al., 2007), and even fewer have been carried out *in situ* under field conditions, due to the high cost and difficulty (Cabrera et al., 2008a,b, 2009). In addition, to the best of our knowledge, there is no information on the influence of TPOMW organic matter transformation on diuron's fate in soils following repeated applications of this waste also under field conditions, although such information would be useful from the environmental perspective of the management of this herbicide in soils receiving this waste.

The objectives of the present study were therefore: (1) to investigate the medium-term effect of repeated TPOMW addition (seven years) on sorption–desorption, degradation, and leaching of the herbicide diuron applied to a typical olive grove soil when compared to laboratory amendments; (2) to measure the influence of TPOMW on the persistence and distribution of diuron through these field amended soil profiles; and (3) to evaluate the influence of aging on the transformation of the organic matter on diuron's behaviour in the soils two years after the last TPOMW field application (aging effect). Previous studies have shown that two years is long enough for the organic matter of the fresh TPOMW added to the soil undergo humification in the soil itself.

## 2. Materials and methods

### 2.1. Herbicide

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] (purity = 99%), purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany)

was used to prepare the herbicide solutions in the laboratory tests. Diurokey 80 (80% concentrated suspension, Industrial Química Key, S.A., Spain) was used as a reference standard formulation in the field experiment.

Diuron analysis was performed 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  $\times$  3.9 mm i.d.), 60:40 water/acetonitrile eluent mixture at a flow rate of 1 mL  $\text{min}^{-1}$ , 25  $\mu\text{L}$  injection volume, and UV detection at 250 nm. The retention time under these conditions was 4.2 min. External calibration curves with standard diuron solutions were used in the calculations. A blank sample was run between standards and samples and after 10 samples to ensure the system was free from any diuron contamination or carryover. The quantification limit was 0.02  $\text{mg L}^{-1}$ . Recoveries were >90%.

### 2.2. Experimental design

A two-year field experiment was conducted on an olive grove (*Olea europaea* L.) whose soil was amended for seven years with three levels of two-phase olive mill waste. In order to prevent herbicide run-off the slope gradient was about 0.2%. The soil, classified as Cutanic Luvisol (ISSS-ISRIC-FAO 1994), contained 19.7% clay, 19.7% silt, 60.6% sand, and was located in Elvas, Portugal (38°53' N; 7°9' W) at a mean altitude of 290 m above sea level. The climate is semiarid Mediterranean (Papadakis, 1966) with an average annual rainfall of 500 mm occurring mostly in autumn and spring and a mean annual temperature of 16.7 °C. The TPOMW was obtained from the Olidal oil industry located in Portalegre (Portugal), which employs two-phase decanter centrifugation to separate the oil. The TPOMW had the following properties: pH 5.7, 535  $\text{g kg}^{-1}$  organic carbon, 36.5  $\text{g kg}^{-1}$  water soluble organic carbon, 48.2% moisture content, and 5.02  $\text{dS m}^{-1}$  electrical conductivity.

The experimental design consisted of nine 14  $\times$  15 m plots with amendments made in a complete randomized design with three replicates per treatment. The three treatments were: 30 and 60  $\text{Mg ha}^{-1}$  of two-phase olive mill waste, dry weight (DW) equivalent, and unamended treatment. Amendments were applied annually in February (from 1999 to 2005), spreading the waste on the soil surface manually, followed by arable-level homogenization using a mould-board plough.

### 2.3. Physicochemical analysis of the soil and the TPOMW

Total organic carbon content (TOC) was determined by dichromate oxidation (Nelson and Sommers, 1996). Water-soluble organic carbon (WSOC) was extracted with de-ionized water at a 3:1 (water to soil) ratio. Humic and fulvic acids (HA and FA, respectively) were extracted by a solution of 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  + NaOH using a ratio of extractant to sample of 10:1, and to precipitate humic acid the supernatant was acidified to pH 2 with  $\text{H}_2\text{SO}_4$ . The WSOC and the total organic carbon associated with each fraction of HA and FA were determined by dichromate oxidation and absorbance at 590 nm to detect  $\text{Cr}^{3+}$  formation, calibrated against standard solutions of glucose (25–50  $\mu\text{g C mL}^{-1}$ ) (Sims and Haby, 1971). The polymerization grade (PG) was calculated as (CHA/CFA) (Iglesias and Pérez, 1989). The pH was measured in a 1:1 (w/v) soil/water and 1:5 (w/v) TPOMW water mixture using a combination electrode. Electrical conductivity (EC) was measured in a saturation extract (United State Salinity Laboratory Staff, 1954). The moisture content of the TPOMW was calculated from weight loss after oven drying to constant weight at 105 °C. Texture was determined by sedimentation using the pipette method.

### 2.4. Laboratory experiments

For the laboratory experiments, soil samples from the unamended and both amended plots were collected in October 2005 and 2007.

Four soil subsamples from each olive grove plot were taken randomly from 0 to 25-cm depth. Samples were air dried, and the fraction that passed through a 2-mm sieve was stored at 4 until use. The measurements made in 2005 and 2007 represented the “direct” (T0D, T1D, and T2D samples) and “residual” (T0R, T1R, and T2R samples) effects, respectively. In order to compare the field and laboratory results, unamended soil collected in 2005 (T0D) was also amended in the laboratory at a rate of 5% (T5) and 10% (T10) by weight of the same fresh TPOMW applied in the field in 2005. Thus, considering a bulk mean density of 1.5 g/cm<sup>3</sup> and a depth of 25 cm, the amount of TPOMW applied over 7 years represents about 5% and 10%.

#### 2.4.1. Adsorption experiment

Diuron adsorption–desorption in the field and laboratory amended soil samples was determined by the batch equilibration technique. Triplicate soil samples (5 g) were equilibrated with 10 mL of initial diuron solutions (5, 10, 20, 40, and 50 μM in 0.01 M CaCl<sub>2</sub>) by shaking mechanically on a rotator-shaker (125 rpm) at 20 ± 2 °C for 24 h. After shaking, the suspensions were centrifuged, and the equilibrium concentrations in the supernatants were determined by high performance liquid chromatography (HPLC). The amount of diuron sorbed ( $C_s$ ) was calculated from the difference between the initial ( $C_i$ ) and equilibrium ( $C_e$ ) solution concentrations. Preliminary experiments had shown that equilibrium was reached before 24 h and that no measurable degradation occurred during this period.

Desorption was measured immediately after sorption by successive dilution from the highest (50 μM) initial concentration point. After the samples were shaken and centrifuged, 5 mL of supernatant was carefully removed and analysed, and 5 mL of 0.01 M CaCl<sub>2</sub> was added to the centrifuge tubes. The samples were resuspended, shaken for another 24 h, centrifuged, and the equilibrium concentration in the supernatant was determined. This desorption procedure was repeated three times. The herbicide sorption and desorption experiments were fitted to the empirical Freundlich equation,  $C_s = K_f C_e^{1/n_f}$ , where  $C_s$  (μM kg<sup>-1</sup>) is the amount of herbicide sorbed at the equilibrium concentration  $C_e$  (μM L<sup>-1</sup>), and  $K_f$  (μM<sup>1-1/n</sup> kg<sup>-1</sup> L<sup>1/n</sup>) and  $n_f$  are constants that characterize the relative sorption capacity. The organic carbon distribution coefficient ( $K_{oc}$ ) was calculated from the  $K_d$  values for a  $C_e$  value of 10 μM L<sup>-1</sup>,  $K_{oc} = K_d / \%OC \times 100$ .

Hysteresis coefficients,  $H$ , for the sorption–desorption isotherms were calculated,  $H = [(1/n_{fa}) / (1/n_{fd})]$ , where  $1/n_{fa}$  and  $1/n_{fd}$  are the Freundlich constants obtained from the sorption and desorption isotherms, respectively (Cabrera et al., 2007; Delgado-Moreno and Peñá, 2008).

#### 2.4.2. Degradation studies

Triplicates of laboratory and field amended soil samples (500 g) were spiked with 8 mL of an ethanol solution of diuron to give a concentration of 3 mg diuron kg<sup>-1</sup> of dry soil. The moisture content was adjusted to 40% field capacity, and then the samples were thoroughly mixed by passing them several times through a 2 mm-sieve (Albarrán et al., 2003). Herbicide-treated soil samples were transferred to 1 L glass jars where they were incubated at 20 ± 2 °C for 55 days. The moisture content was maintained at a constant level throughout the experiment by adding distilled water as necessary, followed by 5 min vigorous manual shaking. The soils were sampled 2 h and 2 days after preparation, and then at 7-day intervals for 49 days, and finally frozen until assay. For the assay, 5 g of soil samples in duplicate 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 diuron concentration in the extracts was determined by HPLC. Diuron dissipation curves in soils were fitted to first-order kinetics ( $C = C_0 e^{-kt}$ ) and the half-lives ( $t_{1/2}$ ) were calculated. Here  $C$  is the herbicide concentration at time  $t$  (days),  $C_0$  is the initial herbicide concentration, and  $k$  (day<sup>-1</sup>) is the degradation constant.

#### 2.4.3. Column leaching tests

Leaching was studied in 30 cm length × 5 cm internal diameter PVC columns made up of six 5 cm-long sections sealed with silicon. The top ring was filled with sea sand and the bottom ring with sea sand plus glass wool, to minimize losses of soil during the experiment. The other four rings were hand-packed with unamended or amended air-dried soil. The experiment was carried out using triplicate columns. The columns were packed to bulk densities of 1.45 kg L<sup>-1</sup> for T0D and T0R, 1.25 kg L<sup>-1</sup> for T1D, 1.06 kg L<sup>-1</sup> for T2D and T1R, 1.01 kg L<sup>-1</sup> for T2R, 1.29 kg L<sup>-1</sup> for T5, and 1.18 kg L<sup>-1</sup> for T10. The soil columns were saturated with 0.01 M CaCl<sub>2</sub>, and allowed to drain for 24 h. The mean calculated pore volumes of the soil columns after saturation were 0.157, 0.167, and 0.175 L for the T0D, T1D, and T2D treatments, 0.162, 0.177, and 0.189 L for the T0R, T1R, and T2R treatments, and 0.166 and 0.171 L for the T5 and T10 treatments, respectively. The amount of diuron corresponding to an application rate of 3 kg ha<sup>-1</sup> was applied dissolved in methanol to the top of the columns. The columns were leached with 0.01 M CaCl<sub>2</sub> at a rate of 50 mL day<sup>-1</sup> until no herbicide was detected in the leachates. Leachates containing the herbicide were collected daily for 44 days, filtered, and assayed by HPLC. At the end of the leaching experiment, soil samples (20 g) from the different rings were extracted once with 30 mL of methanol by shaking mechanically at 20 ± 2 °C for 24 h. The suspensions were centrifuged, filtered, and assayed by HPLC in order to determine the residual amount of diuron at the different depths of the soil column.

#### 2.5. Field experiment

Diuron was applied at a rate of 3 kg ha<sup>-1</sup> to the unamended and TPOMW-amended plots, as a standard commercial formulation (80% concentrated suspension, Industrial Química Key, S.A., Spain) in November (2005 and 2007). At selected times after the herbicide application (2, 7, 18, 31, 95, and 145 days), each year four soil subsamples were taken randomly from different soil depths (0–5, 5–10, 10–30, and 30–60 cm) using a gouge auger. Samples were extracted twice with methanol at 1:2 soil solution ratio and centrifuged, and the extracts were assayed by HPLC in order to determine the persistence and distribution of diuron through the soil profiles. Measurements made in 2005 (T0D, T1D, and T2D samples) and 2007 (T0R, T1R, and T2R samples) represented the direct and residual effects, respectively. The two years had very similar rainfall over the complete period of the field study, with total amounts of 166.8 and 172.9 mm in the study area for 2005 and 2007, respectively. The mean monthly temperature during the field study ranged from 7.6 to 17.9 °C and from 8.6 to 18.0 °C for 2005 and 2007, respectively.

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

### 3. Results and discussion

Selected chemical properties of the soils are given in Table 1. In the direct and residual years of the experiment, the TPOMW application significantly increased the OC concentration (Table 1) compared with the control. The increase over the unamended soil was by a factor of 3.3 for the direct and residual years at 60 Mg ha<sup>-1</sup> of TPOMW. Similarly, the WSOC, HA, and FA values were also raised by the TPOMW amendments (Table 1). As would be expected, after two years of the TPOMW's natural composting in the soils to which it was applied, organic matter from TPOMW was transformed into humic substances and the HA value was much higher. Thus, compared with the control, the HA increased by a factor of 1.7 and 3.2 for the direct and residual years, respectively, at the higher rate of TPOMW application. Contrarily, the residual year had much lower WSOC

**Table 1**

Selected characteristics of the unamended and two-phase olive mill waste amended soils.

Properties	Unit	T0D	T1D	T2D	T0R	T1R	T2R	T5	T10
Organic Carbon	(g kg <sup>-1</sup> )	11.07a	26.16b	36.42c	10.26a	23.93b	33.83c	30.90c	55.70d
WSOC	(mg kg <sup>-1</sup> )	142a	224b	489c	122a	152a	189ab	1620c	3060d
HA	(g kg <sup>-1</sup> )	1.348a	1.894b	2.353c	1.268a	2.534c	4.027d	4.424d	7.559e
FA	(g kg <sup>-1</sup> )	0.873a	1.522b	1.706c	0.830a	0.826a	1.084a	3.256d	4.729d
HI		12.1b	7.2c	6.4c	12.3b	10.5bc	12.1b	14.3a	13.5ab
PG		1.54a	1.24a	1.37a	1.52a	3.06b	3.71c	1.36a	1.59a
pH		8.00a	7.80a	7.51b	8.03a	8.01a	7.91a	6.59c	6.15c
Field Capacity	(%)	30.1a	35.8b	39.2c	29.5a	33.5b	37.2bc	35.0b	37.1bc

WSOC = water soluble organic carbon; HA = humic acid; FA = fulvic acid; HI = humification index; PG = polymerization grade; TOD = unamended soil, T1D = amended soil at rate of 30 Mg ha<sup>-1</sup> yr<sup>-1</sup>, T2D = amended soil at rate of 60 Mg ha<sup>-1</sup> yr<sup>-1</sup> in the last year of TPOMW application; TOR = unamended soil, T1R = amended soil at rate of 30 Mg ha<sup>-1</sup> yr<sup>-1</sup>, T2R = amended soil at rate of 60 Mg ha<sup>-1</sup> yr<sup>-1</sup> two years after the last TPOMW application. Values with the same letter within a row are not significantly different at  $p < 0.05$  level of probability.

(152 and 189 mg kg<sup>-1</sup>) than the direct year (224 and 489 mg kg<sup>-1</sup>) at 30 and 60 mg ha<sup>-1</sup> of TPOMW application rates, respectively.

### 3.1. Sorption studies

The adsorption and desorption isotherms of diuron in the field and laboratory amended and unamended soils are shown in Fig. 1. The regression coefficients ( $R^2$ ) were in all cases greater than 0.880 (Table 2) and highly significant ( $p < 0.001$ ), thus indicating that the assumption of the Freundlich equation was acceptable.

In the laboratory amended soils, the addition of TPOMW increased diuron sorption compared to the control by factors of 3.1 and 4.6 for T5 and T10, respectively (Table 2). There were very similar increases for the organic carbon content (by factors of 2.8 and 5.0 for T5 and T10, respectively, Table 1). These findings clearly indicate the influence of the organic amendment on diuron sorption. The fact that the variability between  $K_f$  values was reduced after normalization to the organic carbon content ( $K_{OC}$  values in Table 2) also indicates that organic matter played a fundamental role in diuron retention by the soils studied (Hamaker and Thompson, 1972; Albarrán et al., 2003; Ahangar et al., 2008). Indeed, the diuron sorption ( $k_f$ ) values were highly and significantly ( $R^2 = 0.991$ ;  $p < 0.001$ ) correlated with the TOC content. While some workers report significant associations between the  $K_f$  for diuron and TOC content (Liyanaage et al., 2006; Cabrera et al., 2007; Cabrera et al., 2008a,b), other studies have found no such correlation (Oliver et al., 2005; Nkedi-Kizza et al., 2006).

The repeated TPOMW application in the field also significantly increased the diuron sorption values (Table 2), although lower  $K_f$  coefficients were observed in the field-amended than in laboratory-amended soils due, probably, to the much lower TOC content (compared to the highest rate, 34.6% and 39.2% lower for T2D and T2R, respectively) observed in these soils. For both the direct and residual years, higher hysteresis coefficients (lower reversibility) were observed in the field-amended soils than in the control, whereas in the laboratory-amended soil the hysteresis coefficients were markedly reduced, indicating that it is easier to release diuron from fresh TPOMW-amended soils than from the field TPOMW-amended soils (Table 2). This can be attributed to the higher WSOC content observed in the laboratory-amended soil than in the field-amended soils and to the great affinity of diuron for the high amount of WSOC present in the laboratory-amended soils. These results are consistent with previous reports indicating that the high WSOC content of some organic materials used as amendment would give rise to greater pesticide reversibility (Celis et al., 1998; Graber et al., 2001; Albarrán et al., 2003; Navarro et al., 2003; Cabrera et al., 2007).

Although diuron sorption has previously been related to the TOC content of soils (Liyanaage et al., 2006; Yu et al., 2006), the highest  $K_f$  coefficients were obtained in the residual year, despite its slightly lower TOC content, compared with those observed in the direct year. This indicates that the TOC content may not be the only factor determining diuron sorption in TPOMW-amended soils. Thus, the  $K_{OC}$

values of the field-amended soils in the direct year were about 50% lower than those observed in the control and the residual year, indicating that the direct addition of this waste could in part impede the herbicide's sorption. Indeed, a more pronounced residual than direct effect was observed in diuron sorption. Compared with the control,  $K_f$  increased by a factor of 1.9 and 2.7 at the greater rate of TPOMW application in the direct and residual years, respectively. Also, lower hysteresis coefficients were observed in the field-amended soils two years after the last waste addition (2007). This seems to indicate that the nature of the organic matter has to be taken into account, since not all organic matter has the same effectiveness for herbicide sorption (Morillo et al., 2002). Thus, it is important to bear in mind that the quantity and quality of the organic matter are among the most important sources of variability in the sorptive interactions. Indeed,  $K_f$  was correlated positively and highly significantly ( $p < 0.001$ ) with HA and PG ( $r = 0.965, 0.870$ ) and significantly ( $p < 0.05$ ) with TOC ( $r = 0.774$ ), indicating that the HA fraction is involved in diuron sorption-desorption. This is consistent with previous reports indicating that aromatic C was identified as having the highest affinity for diuron (Ahmad et al., 2001; Ahangar et al., 2008).

### 3.2. Degradation studies

In the case of the soils amended in the laboratory, the TPOMW addition significantly increased the half-life of diuron from 8.5 to 32.2 days for T0 and T10, respectively (Table 2), which is coherent with the amended soils' higher sorption capacity because sorption protects the herbicide from biodegradation (Fernandes et al., 2006; Cabrera et al., 2008a,b). There was little difference observed in the amount of diuron extracted between the TPOMW amended soils (T5 and T10) at short incubation times (i.e., <20 days) (Fig. 2). However, at longer incubation times the amount of diuron extracted from the TPOMW-amended soil at the greater rate (T10) was significantly greater than from the TPOMW-amended soil at the lower rate (T5), although by the end of the experiment all soils presented a negligible amount of extractable diuron.

Only slight and non-significant differences were observed in the half-lives of diuron between the unamended and the TPOMW field amended soils in both the direct and the residual years (Table 2). The diuron half-life was significantly shorter in the field TPOMW-amended soils than in the laboratory TPOMW-amended soils, coherent with the latter's higher sorption capacity. In addition, a toxic effect of the organic amendment on the microbial population of the laboratory amended soils (Albarrán et al., 2003) would also explain why the  $t_{1/2}$  was shorter in field amended soils, where the microbial population could have adapted to TPOMW after seven years of repeated field application.

The diuron half-life in all cases, except for treatment T10, was similar to or slightly lower than those reported in previous studies under laboratory conditions (Bernard et al., 2005; Dores et al., 2009).

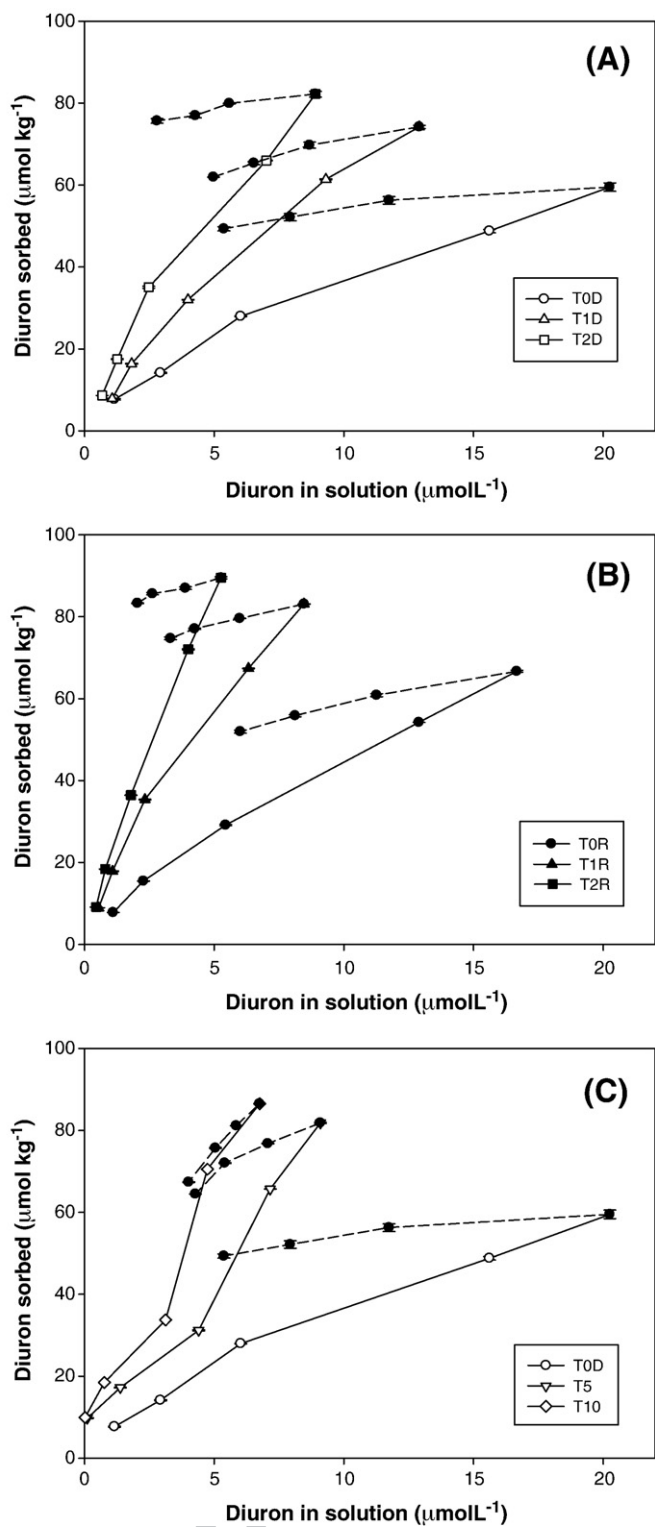


Fig. 1. Diuron sorption-desorption isotherms in the direct-year field amendments (A), residual-year field amendments (B), and laboratory amendments (C). Dashed lines connect desorption points. Error bars represent one standard error of the mean.

228 However, in another study using field and laboratory amended soils  
 229 (Cabrera et al., 2007), the diuron  $t_{1/2}$  of TPOMW-amended soils  
 230 was longer than those found in our study, despite the lower diuron  
 231 sorption capacity observed in those soils. This difference could again  
 232 be attributed to microorganism adaptation which could well  
 233 accelerate diuron degradation in the previously exposed soil (Dores  
 234 et al., 2009). Indeed, this agrees with data reported by Rouchaud et al.

Table 2

Direct and residual effects of the two-phase olive mill waste addition on Freundlich sorption coefficients and half-life ( $t_{1/2}$ ) in dissipation studies for diuron.

Soils	$K_f$	$1/n_f$	$R^2$ sorption	$K_{OC}$	$R^2$ desorption	$H$	$t_{1/2}$ (days)	$R^2$ ( $t_{1/2}$ )
T0D	6.93a ± 0.44	0.719b ± 0.029 <sup>b</sup>	0.995	306b	0.992	4.26b	8.5a ± 0.15	0.897
T1D	8.58b ± 0.95	0.877c ± 0.063	0.985	235a	0.998	4.12b	8.0a ± 0.40	0.871
T2D	13.6c ± 1.24	0.844bc ± 0.062	0.984	253a	0.885	11.11d	8.1a ± 0.05	0.962
T0R	7.63a ± 0.31	0.775b ± 0.024	0.997	420c	0.999	3.09b	8.7a ± 0.09	0.897
T1R	15.8c ± 1.00	0.800bc ± 0.044	0.991	415c	0.993	7.53c	9.5a ± 0.11	0.971
T2R	20.5 cd ± 0.8	0.911d ± 0.039	0.995	501d	0.714	12.13d	8.7a ± 0.07	0.962
T5	21.8d ± 3.7	0.406a ± 0.014	0.886	279a	0.928	1.25a	10.5a ± 0.85	0.863
T10	32.0e ± 4.0	0.341a ± 0.067	0.883	224a	0.995	0.891a	32.2b ± 1.27	0.660

Values of  $K_f$ ,  $n_f$  and  $t_{1/2}$  are presented as mean ± standard deviation.

Values with the same letter within a column are not significantly different at  $p < 0.05$  level of probability.

(2000) who found that degradation of diuron was significantly increased in soils to which it had been applied consecutively for 12 years. In fact, in our study, the soils had been treated with diuron for the past 11 years (soils sampled in 2005) or 13 years (soils sampled in 2007), whereas in the aforementioned study of Cabrera et al. (2007) the diuron had been applied in the field for only 5 years.

### 3.3. Leaching studies

Addition of TPOMW reduced the downward movement of diuron in the columns and affected the breakthrough time of diuron in the leachate (Fig. 3). In the unamended soil (T0D), diuron breakthrough occurred after the passage of 3.4 pore volumes of water, whereas in the laboratory-amended soils breakthrough was delayed, occurring after the passage of 6.3 and 6.7 volumes of water for T5 and T10, respectively. This indicates the major influence of the sorption process on the leaching of diuron, corroborating the sorption studies (Table 2). Retardation of herbicide breakthrough as a result of TPOMW addition to the soil was also reported by Cox et al. (1997) using olive mill wastewater and the herbicide metatrimin, by Majumdar and Singh (2007) using fly ash and the herbicide metribuzin, and by Albarrán et al. (2003) also using TPOMW but the

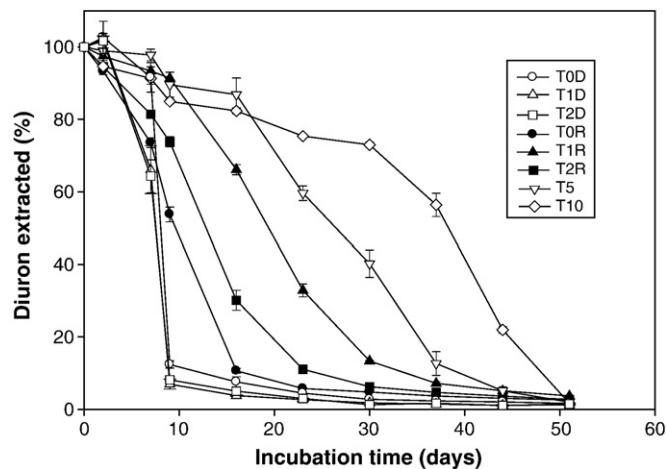


Fig. 2. Direct and residual effects of two-phase olive mill waste addition on diuron dissipation. Error bars represent one standard error of the mean.

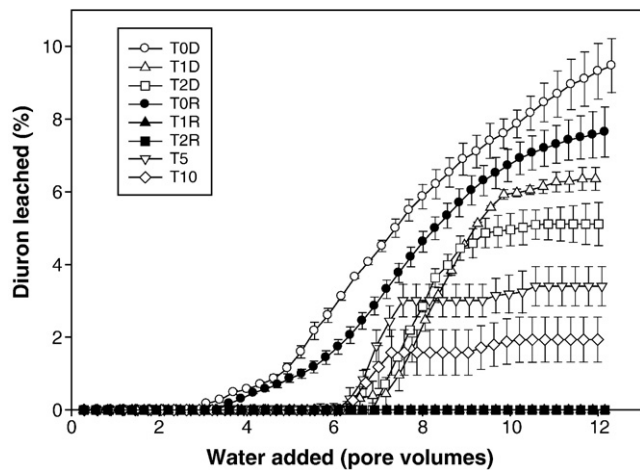


Fig. 3. Cumulative breakthrough curves of diuron in unamended and two-phase olive mill waste amended soils. Error bars represent one standard error of the mean.

herbicide simazine, all indicating that lower sorption will lead to less retardation, and hence earlier breakthrough. A significant ( $p < 0.05$ ) large decrease of diuron concentrations in the leachates was observed following TPOMW addition in the laboratory amended soils (Table 3), which can be attributed to their higher diuron sorption. Thus, the amount of diuron recovered in leachates was 9.5% of the applied herbicide for the unamended soil, but 3.4% and 1.9% for T5 and T10, respectively (Table 3). The observed decrease in diuron concentrations in leachates is consistent with the results of other studies using fresh TPOMW-amended soils but simazine herbicide (Albarrán et al., 2003). Cabrera et al. (2007) found that diuron was not detected in leachates from a laboratory TPOMW-amended soil, although in our study the increase in diuron reversibility found after TPOMW amendment was much greater than that reported by those workers.

Diuron leached down to 20 cm depth in both the unamended and the TPOMW amended soil columns (Fig. 4). However, its distribution pattern in the TPOMW-amended soils was quite different from that in the unamended soil column. Thus, whereas only 3% of diuron retention was observed within the first 10 cm depth in the unamended soil column (T0D), nearly 10% and 32% of the applied herbicide was recovered for the T5 and T10 soil columns, respectively, suggesting that TPOMW increased the diuron retention in the soil column. Also, the total amount of diuron recovered in the unamended soil columns was much less than that recovered in the TPOMW-amended columns (Fig. 4; Table 3), which agrees with the results observed in the sorption and degradation studies (Table 2). Thus, the herbicide-WSOC interaction might be in part responsible for the greater diuron persistence in these amended soils as a consequence of the formation of stable complexes which also protected herbicide molecules from soil microorganisms (Cox et al., 2001).

In the case of columns filled with field TPOMW-amended soils, a major difference in the diuron behaviour was observed between the

direct and the residual years. Thus, whereas diuron was detected in leachates from unamended and TPOMW-amended soil columns in the direct year (T0D, T1D, and T2D), it was only detected in leachates from the unamended soil column in the residual year (T0R) (Table 3), which agrees with the results of the sorption–desorption studies. The transformation of the organic matter of the TPOMW due to humification and maturation processes are likely to be responsible for this behaviour. Thus, the higher WSOC content of T1D and T2D (224 and 489  $\text{mg kg}^{-1}$ , respectively) and their lower polymerization grade (1.24 and 1.27) when compared to the WSOC content of T1R and T2R (152 and 189  $\text{mg kg}^{-1}$  respectively) and PG of T1D and T2D (3.06 and 3.071) (Table 1), can well explain why diuron was not detected two years after the last TPOMW application (Table 3). The application of TPOMW significantly decreased the amount of diuron recovered from the amended soil columns in both the direct and the residual years, and independently of the loading rate of the applied waste, despite the lower, or even null, amount of diuron detected in the leachates from these soils.

The total amounts recovered from TPOMW-amended soil columns in the direct and residual years (T1D, T2D, T1R, and T2R) were much less than those observed in the laboratory amended soils (T5 and T10; Table 3). This indicates that TPOMW addition enhanced the degradation and/or irreversible sorption of diuron in soils that have received this organic amendment consecutively for years. The greater persistence of diuron in the laboratory TPOMW-amended soils compared to the field TPOMW-amended soils (Table 2) may also explain this different leaching behaviour. These results are coherent with those observed in the degradation studies explained on the basis of the duration of the experiments.

### 3.4. Field studies

The total amounts of diuron extracted from unamended and TPOMW-amended plots are shown in Fig. 5. The field dissipation estimated from these data corresponded to the TPOMW addition decreasing the half-lives of diuron from 41 to 35 days and from 39 to 27 days for T0D and T2D and for T0R and T2R, respectively, although the differences were not significant ( $p > 0.05$ ). The field half-lives of diuron are in the range reported by Rouchaud et al. (2000) in a study in which this herbicide was applied for 12 consecutive years.

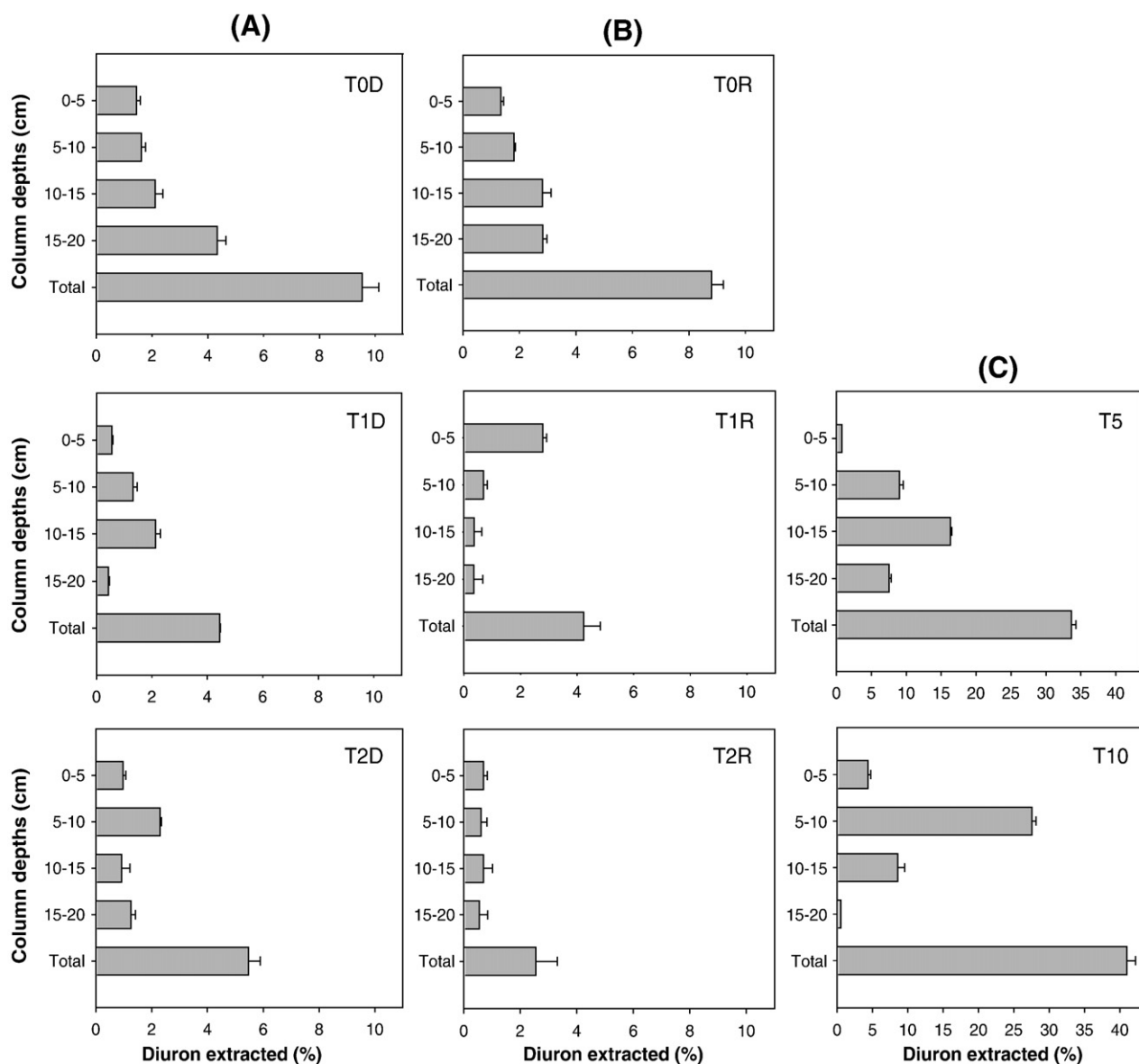
The TPOMW application significantly increased the amount of herbicide recovered in both the direct and the residual years. Thus, at the beginning of the experiment, whereas only about 6% of diuron retention was observed within the first 5 cm depth in unamended plots (T0D and T0R), more than 31% and 58%, and nearly 11% and 17% of applied diuron was recovered for amended plots at the low and high loading rates, and in the direct (T1D and T2D) and the residual years (T1R and T2R), respectively (Fig. 5). The increasing diuron retention with increasing TPOMW rates confirmed the observations of the soils' increased diuron sorption following the TPOMW treatments (Table 2).

Diuron was detected in decreasing concentrations until the end of the study (145 days after diuron application) in all treatments. However, after seven years of repeated TPOMW application, the

Table 3 Direct and residual effects of two-phase olive mill waste addition on the diuron that is leached, extracted from the soil columns, and not recovered during the leaching experiment.

	Soils							
	T0D	T1D	T2D	T0R	T1R	T2R	T5	T10
Leached (%)	9.5e ± 0.7	6.4 cd ± 0.3	5.1c ± 0.6	7.6de ± 0.7	0.0a	0.0a	3.4b ± 0.5	1.9a ± 0.6
Extracted (%)	9.5c ± 0.6	4.4b ± 0.1	5.5b ± 0.4	8.8c ± 0.6	4.3b ± 0.6	2.5a ± 0.7	33.6d ± 0.6	41.0d ± 1.2
Not recovered (%)	81.0	89.2	89.4	83.6	95.7	97.5	62.9	57.0

Values are presented as mean ± standard deviation.



**Fig. 4.** Diuron extracted from different depths of the soil columns at the end of the leaching experiment on the direct-year field amendments (A), residual-year field amendments (B), and laboratory amendments (C). Error bars represent one standard error of the mean.

field plots (T1D and T2D) always contained a greater amount of diuron than those in the residual years (T1R and T2R), despite the higher sorption coefficients observed in these latter soils (Table 2), and independently of the annual applications of amendment received. Considering the amount extractable with methanol as an estimate of the amount of herbicide present in a potentially available form (Albarrán et al., 2003; Cornejo et al., 2008), this result indicates that the availability of diuron in the amended soils is reduced by increasing the humified organic matter fraction. Indeed, compared with the direct year, the PG increased by factors of 2.5 and 2.7 for the low and high application rates after two years of the last TPOMW application, confirming the importance of the quality rather than the quantity of the organic matter in affecting diuron's behaviour. This is consistent with previous reports that herbicides such as ethametsulfuron-methyl (Si et al., 2006) or diuron (Ahangar et al., 2008) are more strongly adsorbed by humic acid.

TPOMW decreased diuron's vertical movement especially in the residual year. Thus, diuron residues were found at depths down to 60 cm in the unamended and direct TPOMW-amended plots. However, a very low mobility of diuron at depth was observed in the residual-amended

plots since herbicide was found no deeper than 30 and 10 cm depth at 30 and 60 Mg ha<sup>-1</sup> of TPOMW loading rates, respectively, suggesting that no leaching of diuron would be found in these soils. These results are consistent with the previous results of the sorption, leaching, and degradation studies for these field TPOMW-amended soils.

#### 4. Conclusions

Fresh laboratory amendment and seven years of field amendment of soils with two-phase olive mill waste (TPOMW) markedly influenced the behaviour, mobility, and persistence of the herbicide diuron. The application of TPOMW resulted in increased sorption and decreased leaching of diuron, with a reduction of downward vertical migration dependent on the TPOMW rate and the grade of organic matter maturity. Indeed, after two years of TPOMW application under field conditions, the soil humic acid content and polymerization grade rose to the seven-year cumulative-amendment levels. Similarly, the sorption coefficients increased and leaching decreased, indicating that fresh and naturally composted TPOMW in the soil *in situ* have significantly different behaviours. Results from the field persistence

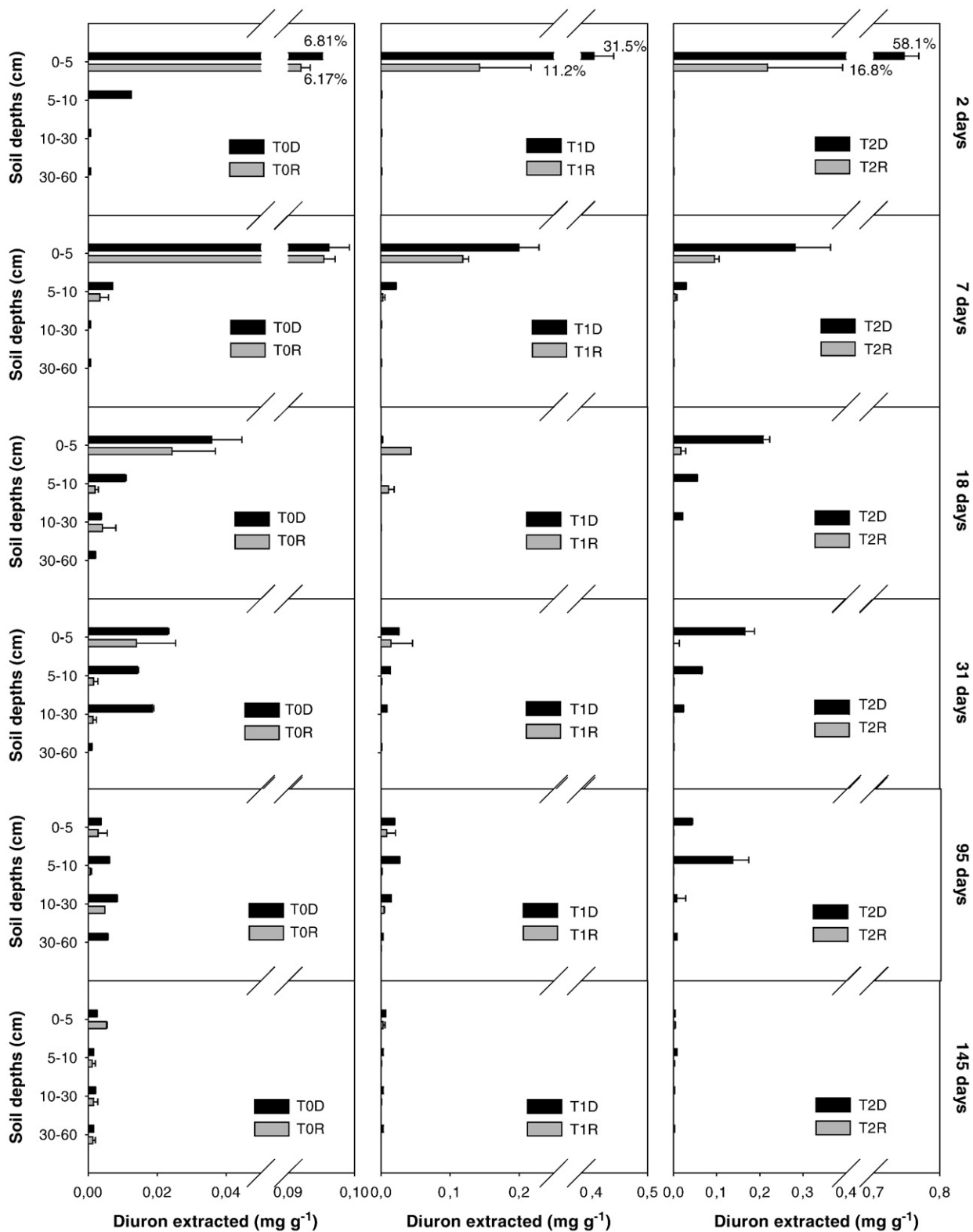


Fig. 5. Direct and residual effects of two-phase olive mill waste (TPOMW) addition on diuron extracted from different depths of field plots after herbicide application: (A) unamended soils, (B) soils amended with  $30 \text{ Mg ha}^{-1} \text{ yr}^{-1}$  of TPOMW, and (C) soils amended with  $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$  of TPOMW. Error bars represent one standard error of the mean.

576 study showed that amendment with TPOMW may be useful to prolong  
 577 residence time in the top-soils. It could allow the farmer to reduce the  
 578 rates and frequency of diuron application while maintaining weed  
 579 control efficacy. In addition, the TPOMW organic matter maturity also  
 580 determined its effectiveness in modifying diuron's downward vertical  
 581 mobility and its persistence in the soil profiles. Thus, our results

indicated that TPOMW amendments effectively reduce diuron leach- 582  
 ing in the soil and may be an effective management practice for 583  
 controlling pesticide leaching. Successive land application of TPOMW 584  
 as organic amendment followed by no TPOMW application for at least 585  
 two years may well be environmentally and economically good 586  
 practice. The positive residual effect of TPOMW could be especially 587



588 significant in semiarid Mediterranean areas, whose agricultural soils  
589 are very poor in organic matter and are at a high risk of groundwater  
590 contamination by intensive annual pesticide applications.

## Q12591 5. Uncited reference

592 [Paredes et al., 2005](#)

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598 Extremadura.

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