JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

J. Agric. Food Chem. XXXX, XXX, 000–000 A
DOI:10.1021/jf102960g

Effect of Soil Wetting and Drying Cycles on Metolachlor Fate in Soil Applied as a Commercial or Controlled-Release Formulation

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A controlled-release formulation (CRF) has been developed for metolachlor, which reduced its leaching in a sandy soil and improved weed control in comparison with the commercial formulation. The current study tested the effect of soil wetting and drying cycles (WDCs) on metolachlor fate (desorption, leaching, and weed control) applied as the CRF and as the commercial formulation. Metolachlor adsorption to a heavy soil (Terra-Rosa) was predominately to the clay minerals and oxides. Metolachlor release from a heavy soil subjected to WDCs was higher than its release from the soil not subjected to WDCs. Consequently, a bioassay in soil columns treated with the commercial formulation indicated enhanced metolachlor leaching in heavy soils under WDCs. In contrast, when metolachlor was applied as the CRF, leaching was suppressed and not affected by WDCs. These results emphasize the advantages of the CRF also in heavy soils subjected to WDCs.

KEYWORDS: Metolachlor; controlled-release formulations; wetting and drying cycles; leaching

INTRODUCTION

Applying herbicides provides substantial agronomic and economic benefits; however, in some cases their use poses environmental issues, due to leaching and surface migration, which cause soil, surface water, and groundwater contamination (*1*−*3*). Furthermore, migration and leaching reduce herbicide concentration at the topsoil, which reduces weed control efficacy. Insufficient weed control brings an increase in herbicide application dose and frequency, which further increase treatment costs and environmental contamination.

Herbicide leaching in the soil is governed by several factors, such as soil structure and characteristics, chemophysical properties of herbicides, and the effects of climatic conditions and tillage methods (*1*, *4*). Among climate conditions the effects of rain and irrigation on herbicide leaching have been widely explored (*5*, *6*). For example, heavy rain intensities and high irrigation frequencies have been found to enhance the migration of metolachlor (MTC) in sandy soil (*5*). In contrast, very little is reported on another important impact of climate, the influence of wetting and drying cycles (WDCs).

The phenomenon of WDCs implies that the soil undergoes frequent changes in water content due to rain events or irrigation accompanied by dry periods. This phenomenon is most pronounced in semiarid areas. WDCs of the soil affect herbicide fate in the soil and in particular their persistence, leaching, migration, sorption to soil particles, and degradation (*7*). A number of studies have shown that microbial degradation of herbicides is inhibited during drying cycles, which enhances their persistence in soil (*8*−*11*). The effect of WDCs on adsorption/desorption of herbicides was less studied and is less understood. Different trends are reported on this effect; for example, imazaquin desorption from the soil increased following WDCs (*9*), whereas diuron (*12*, *13*) and atrazine (*8*) desorption was reduced due to WDCs. The main mechanism suggested was strong adsorption of the herbicide to soil organic matter.

Metolachlor is a selective preplant herbicide that controls a broad spectrum of grass weeds and small-seeded broadleaves in many crops and is widely used worldwide mainly in corn, soybean, sunflower, sugar beet, potato, and cotton. Its adsorption to the soil is considered to be moderate and is positively correlated with soil organic matter and clay content (*14*−*20*). Its water solubility is relatively high (S_w = 488 mg/L, 20 °C); therefore, it is prone to extensive leaching and has been detected in groundwater (*14*, *21*−*25*).

One of the approaches pursued to reduce herbicide migration in soil while maintaining suitable weed control is developing controlled-release formulations (CRFs) (*26*−*30*). We have designed a CRF for metolachlor based on herbicide solubilization in micelles and adsorption of the mixed micelles on clay minerals (*31*). This formulation was tested and found to reduce metolachlor leaching through a sandy soil column and improve weed control in comparison with the commercial formulation. In the current study the effect of WDCs on metolachlor desorption, leaching, and weed control in the soil was investigated.

We hypothesized that the CRF will moderate the negative effects of WDCs on metolachlor behavior, that is, desorption, leaching, and weed control efficiency. Therefore, the CRF's

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properties of improved weed control and reduced leaching are expected to be even more pronounced under WDCs. To test this hypothesis, we first studied the adsorption of metolachlor to different soils and examined the effect of WDCs on the desorption kinetics and at equilibrium of metolachlor. The second stage included comparison of metolachlor release and leaching through a thin layer of heavy soil under WDCs, when applied as the commercial formulation (S-Dual Gold) or as the CRF formulations. Finally, a bioassay was conducted by applying these formulations to Clayey and Loess soil columns subjected to 0−4 WDCs. Metolachlor release from the formulations, leaching through the soil, and weed control were tested.

MATERIALS AND METHODS

Materials. Metolachlor 2-chloro-*N*-(6-ethyl-*o*-tolyl)-*N*-[(1*RS*)-2-methoxy-1-methylethyl]acetamide (Metolachlor) technical (purity = 98.6%) and commercial metolachlor [S-Dual Gold 915 g of active ingredient (ai)/L liquid] were obtained from Agan Chemicals, Ashdod, Israel. The clay used was a Wyoming sodium montmorillonite (SWy-2) obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO). Octadecyltrimethylammonium (ODTMA) was purchased from Sigma-Aldrich (Steinheim, Germany). Acetonitrile and water of HPLC grade were purchased from Merck (Darmstadt, Germany). All soil samples were collected from the top 20 cm and air-dried and sieved through a 2 mm screen. Rehovot sandy soil was collected from the Faculty of Agriculture campus experimental farm (95.5% sand, 3.3% silt, 1.2% clay, and 0.2% organic matter (OM)). A heavy clayey soil, Terra-Rosa (25% sand, 22.5% silt, 52.5% clay, and 11% OM) was collected form the hills of Jerusalem (near the sources of the Sorek stream). Loess Gilat (78.8% sand, 6.2% silt, 15% clay, and 1% OM) was collected from the Gilat experimental farm. The soils were used after sifting to 2 mm particles. The soils were used for analytical release tests and for the soil column plant bioassays. The test plant for the metolachlor bioassay was foxtail millet [*Setaria italica* (L.) P. Beauvois].

Methods. *Metolachlor Adsorption*. Metolachlor adsorption experiments were conducted in batch experiments in Teflon centrifuge tubes. Sodium azide (100 g/L) was added to all metolachlor solutions to inhibit microbial degradation. All measurements were performed in triplicate. The tubes were kept at 25 ± 1 °C under continuous agitation until equilibrium was reached (3 days and 1 day for adsorption on Terra-Rosa and on montmorillonite, respectively). Supernatants were separated by centrifugation at 15000*g* for 20 min. Metolachlor concentrations in the supernatant were measured by HPLC. The adsorbed concentrations were calculated by subtracting the concentration measured in the supernatant from the initial added concentration.

Prior to HPLC analysis supernatants were filtered with acrodisc (polypropylene) filters (Pall Corp.), of 0.45 μm pore diameter. The HPLC (Agilent Technologies 1200 series) was equipped with a diode array detector. The HPLC column was a LiChroCARTR 250-4 PurospherR STAR RP-18 (5 μm), operating at a flow rate of 1.0 mL min^{-1}. Measurements were carried out isocratically. A mobile phase of acetonitrile/water (70:30) was used. The concentrations of metolachlor were measured at a wavelength of 225 nm. The detection limit was 0.01 mg/L, and the presence of ODTMA did not interfere with herbicide detection.

(*a*) *Metolachlor Adsorption on Soils*. Metolachlor adsorption to a sandy soil (Rehovot sandy soil) and to a heavy clayey soil (Terra-Rosa) was studied in batch experiments by adding a metolachlor solution of 350 mg/L (20 mL) to different amounts of soils. The metolachlor solution included sodium azide (100 mg/L), which inhibits microbial degradation. With the addition of 8 g of soil the final soil concentration was 400 g/L (~88 kg of ai/ha calculated for a depth of 10 cm). The adsorption on the heavy soil was also studied at a concentration of 9.6 g/L by adding 0.192 g of soil (~2.1 kg of ai/ha) to reach an equivalent clay concentration to that present in 400 g/L sandy soil. The adsorption of metolachlor to the clayey soil was further studied at concentrations relevant to field application, which ranged between 0.8 and 4.5 kg of ai/ha (*13*) by adding metolachlor (1−20 mg/L) to 500 g/L soil (0.2−4 kg of ai/ha). The dose calculations were based on the weight of a hectare including a depth of 10 cm.

The adsorption of metolachlor (20−300 mg/L) on Terra-Rosa (50 g/L) with and without its OM was measured. The OM was removed by introducing the soil to an oven at 400 °C for 16 h or by mixing the soil with H_2O_2 (30%) and waiting until the reaction finishes and then rinsing the soil three times with distilled water to remove any remaining H_2O_2.

(*b*) *Metolachlor Adsorption on Montmorillonite*. A metolachlor solution of 350 mg/L (20 mL) was added to sodium motmorillonite suspensions of 0.6−15 g/L (10 mL) in centrifuge tubes (final concentrations). The clay concentrations were equivalent to their concentrations in the adsorption experiments on Terra-Rosa (described in the previous section). For example, to add metolachlor to 4.8 g clay/L, the herbicide was added to 400 g of sandy soil/L, 9.6 g of clayey soil/L, and 4.8 g of montmorillonite/L.

WDCs Procedure. The air-dry soil was first weighed and then wetted as described in the different experiments (see below). Drying was achieved by placing the soil samples in an oven at 40 °C for 3−5 days until the soil returned to its original weight. This method simulates the temperature in the summer in hot regions, eliminates photodegradation, and does not require a very long time (drying at room temperature ± 25 °C was also attempted but discontinued as it took several weeks).

Metolachlor Desorption from the Soil Subjected to WDCs. The desorption kinetics and at equilibrium of metolachlor from Terra-Rosa were studied in batch experiments in Teflon centrifuge tubes. The desorption was studied from a soil adsorbed with 4.5 ± 0.3 μg/g (adding 20 mL of 5 mg/L metolachlor to 10 g of soil reaching 500 g/L soil). Each concentration was performed in triplicate. Metolachlor analysis was performed as described for the the adsorption experiments.

(*a*) *Desorption Kinetics*. Distilled water (20 mL) was added to the soil samples (reaching a soil concentration equivalent to that in the adsorption experiment) subjected to 0 or 1 WDC. The tubes were agitated for 1−24 h. After centrifugation, the metolachlor concentration in the supernatant was measured to determine desorption.

(*b*) *Desorption at Equilibrium*. Distilled water (8−20 mL) was added to the soil samples subjected to 0 or 1 WDC. The tubes were agitated for 24 h. After centrifugation, the metolachlor concentration in the supernatant was measured to determine desorption.

Formulation Preparation. The micelle−clay formulations were prepared as described in Ziv and Mishael (*31*). Metolachlor was solubilized in a 2.5 mM ODTMA solution and mixed for 24 h, reaching a metolachlor concentration of 1500 ppm. The mixed micelles (ODTMA and metolachlor) were adsorbed on 2 g/L montmorillonite. The suspensions were centrifuged for 20 min at 15000*g*. Supernatants were removed, and herbicide concentrations were measured by HPLC to determine the percent of active ingredient in the micelle−clay formulation. The herbicide−micelle−clay precipitates were frozen and lyophilized. The percent of active ingredient of the CRF was 34%.

Metolachlor Release and Leaching through Soils under WDCs

(*a*) *Metolachlor Leaching through a Thin Soil Layer Applied as CRF and as the Commercial Formulation under WDCs*. The release of metolachlor from micelle−clay formulations and from the commercial formulations was measured by applying the formulations on a thin layer (2 cm) of Terra-Rosa soil (160 g) deposited on a filter paper in a Buchner funnel (area of 7.85×10^{-3} m^2) as described (*31*). Water (50 mL) was sprayed as a control. The formulations were sprayed (50 mL) on the soil at a rate of 5 mg of ai per funnel, equivalent to 5800 g/ha. Application rates were high due to the HPLC detection limit. Half of the soil samples were subjected to 3 WDCs by placing the funnels in an oven, at 40 °C, for 3 days. Following the WDCs (0 or 3) the funnels were irrigated 10 times (every 15 min) with 5 mm of water (40 mL per funnel), reaching a total irrigation of 50 mm water. The leachates were collected after each irrigation, and herbicide concentrations were measured by HPLC. Each treatment was preformed in triplicate.

(*b*) *Soil Column Bioassay of Metolachlor Applied as the CRF and as the Commercial Formulation under WDCs*. Weed control and metolachlor leaching in soil subjected to WDCs (0 and 4) were studied by applying the CRF and the commercial formulation to soil columns sowed with a test plant. Polyethylene mesh sleeves (pore diameter = 0.6 mm, 50.2×10^{-3} m^2 surface area, and 20 cm long) used as columns were filled with Terra-Rosa or Loess soils. Metolachlor as the CRF and as S-Dual Gold was applied in water on top of the soil columns at rates of 2000 g of ai/ha for Terra-Rosa and 1500 g of ai/ha for Loess. The recommended dosages are between 1000 g of ai/ha for light soil and 2000 g of ai/ha for heavy soils as commercial formulation. Ten milliliters of distilled water was added at the top of the control columns. Each treatment was performed in 7−11

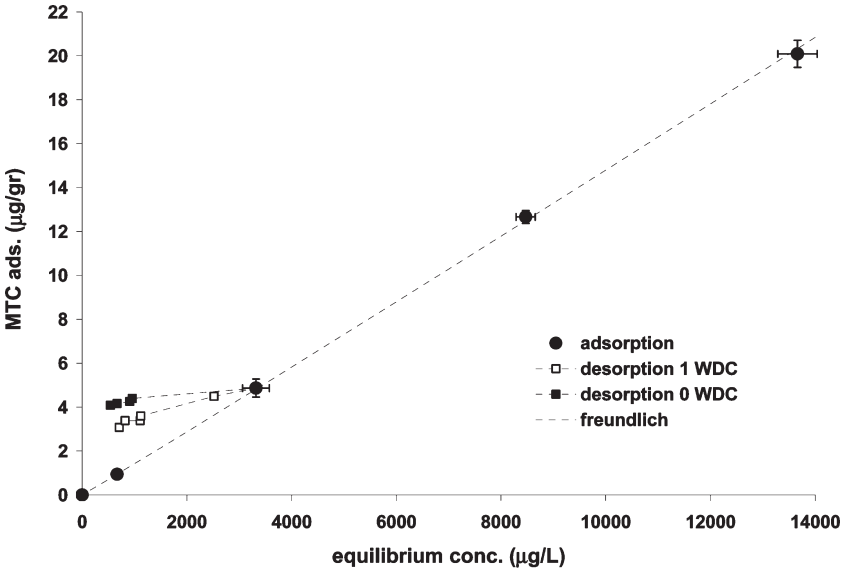

Figure 1. Adsorption isotherm of metolachlor (1−20 mg/L) on Terra-Rosa (500 g/L): desorption of metolachlor from Terra-Rosa adsorbed with 4.5 μg/g and subjected to 0 or 1 WDC. Error bars present the stand deviation.

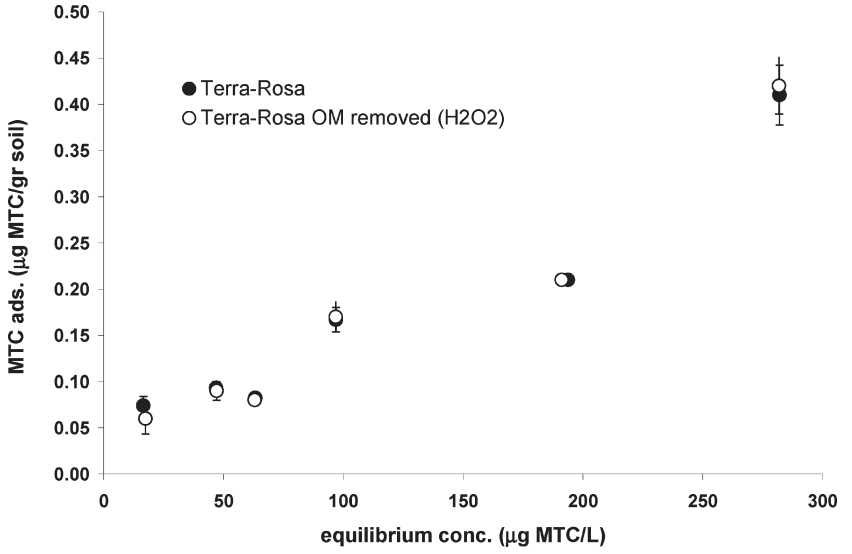

Figure 2. Metolachlor (20−300 mg/L) adsorption to Terra-Rosa (50 g/L) with and without organic matter. Error bars present the standard deviation.

replicates. Following herbicide application the columns were irrigated with water according to their pore volume, 360 and 300 mL for the Terra-Rosa and Loess soils, respectively. A day after irrigation, half of the columns were subjected to 4 WDCs. A drying cycle included putting the soil column in an oven at 40 °C for 3−5 days for the soil to return to its original weight. Following the drying, a wetting cycle was performed; that is, the columns were resaturated with water at a volume equivalent to the pore volume (see above) and left to equilibrate for 24 h. All of the columns, subjected to 0 or 4 WDCs, were laid horizontally, and a 4 cm wide and 20 cm long window of polyethylene mesh sleeve was cut and removed. A single continuous row of foxtail millet seeds was sowed along the soil column (now pots) through the cut window, expanding the whole length of the column. The soil pots were irrigated regularly to enable plant growth. After 14 days, plant height along the columns was measured and plant growth inhibition as a function of soil depth was calculated by comparison to the control treatment.

Data Analysis. The experiment design was three factors in a randomized split plot for each soil type. Two crossed factors (2 × 2) in the whole plots (columns) were herbicides, with two levels (commercial and CRF), and WDCs with two levels (with and without). Nine soil layers of each column (represented depth) were the subplot. Replications (7−11 columns) were done for each formulation and WDC combination. For this design the appropriate ANOVA was made using JMP7 (SAS 2007), and contrast tests were used for testing the interactions within each soil layer.

RESULTS AND DISCUSSION

Metolachlor Adsorption to Soils. Metolachlor (350 mg/L) adsorption to a sandy soil (Rehovot sand) and to a heavy clayey soil (Terra-Rosa) (400 g/L) was studied (~88 kg of ai/ha). Even under these extreme conditions (a very high application rate), no adsorption was attained to the sandy soil, whereas approximately 30% of the added metolachlor adsorbed to the heavy soil. The same percent of metolachlor adsorbed on Terra-Rosa when the concentration was reduced to 9.6 g/L to reach a clay concentration equivalent to that in the sandy soil, suggesting a partitioning adsorption mechanism on the Terra-Rosa soil. Metolachlor adsorption to the clayey soil was further studied at concentrations relevant to field application rates, which range between 0.8 and 4.5 kg of ai/ha (*14*). Metolachlor (1−20 mg/L) was added to 500 g/L soil, which is equivalent to a rate of 0.2−4 kg of ai/ha. The C-shape adsorption isotherm was in good agreement (R^2 = 0.999) with the Freundlich model, where $K_f = 1.25 \times 10^{-3}$ (L/g)

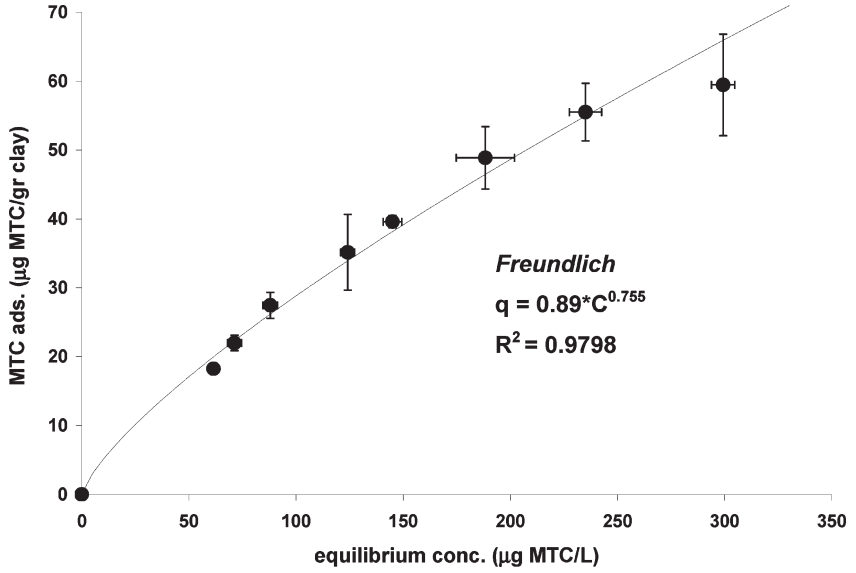

Figure 3. Metolachlor (350 mg/L) adsorption to montmorillonite (0.6−15 g/L). Error bars present the standard deviation.

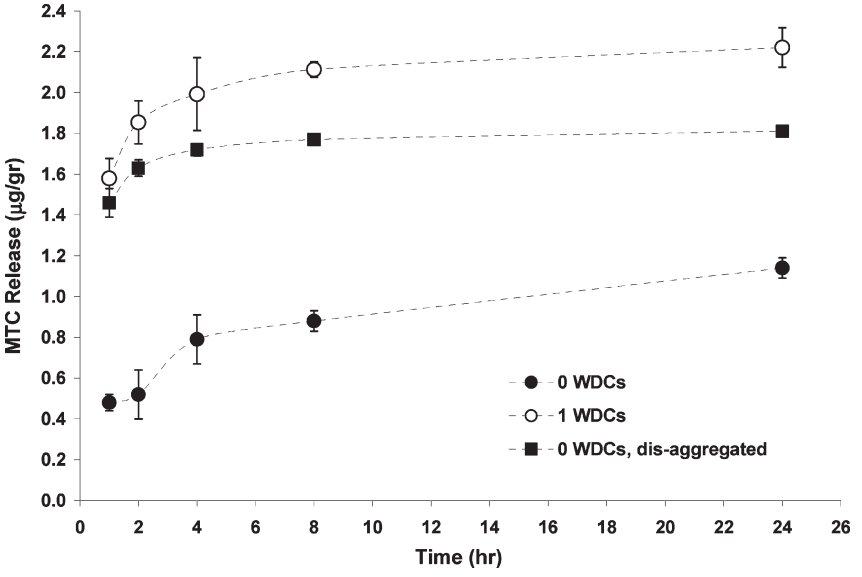

Figure 4. Desorption kinetics of metolachlor from Terra-Rosa soil (4.5 μg/g) subjected to 0 and 3 WDCs: desorption from the soil subjected to 0 WDCs following disaggregation of the soil. Error bars present the standard deviation.

and n = 1.08 (**Figure 1**). Approximately 45% of the added metolachlor adsorbed. The Freundlich coefficient (K_f) obtained is within the range of coefficients (5×10^{-4}−2.7×10^{-2} L/g) reported for the adsorption of metolachlor to soils with various clay and OM concentrations (*15*, *18*, *20*).

To explore which soil fraction, OM or clay, has a larger impact on metolachlor adsorption, the adsorption of metolachlor to Terra-Rosa was studied as is and after removal of the OM fraction (**Figure 2**). The OM was removed by heating the soil to 400 °C (in an oven) or by oxidation with H_2O_2. Metolachlor adsorption to Terra-Rosa was not affected by oxidation of the OM, and it even increased when the OM was removed by heating to 400 °C. A few studies have reported the decrease in herbicide adsorption to the soil due to clay−OM complexation (higher adsorption in the absence of OM) and that the ratio between the two components will determine the degree of adsorption (*32*,*33*). However, they did not report a mechanism explaining the phenomena. We suggest that the increase in metolachlor adsorption upon OM removal may be due to the exposure of oxide surfaces by the high temperatures. Indeed, following the heating process the soil was more reddish, which may indicate the exposure of hematite. These findings, in addition to the observation that metolachlor did not adsorb to the sandy soil, suggest that in the case of Terra-Rosa metolachlor does not adsorb to the OM fraction, which implies that the clay fraction including the clay minerals and oxides is the main adsorbent. To support this suggestion the metolachlor adsorption to one clay mineral present in the soil was examined.

Metolachlor (350 g/L) adsorption to montmorillonite (0.6−15 g/L) was studied. The adsorption isotherm was in good agreement (R^2 = 0.979) with the Freundlich model, where K_f = 0.89 (L/g) and n = 0.755 (**Figure 3**). As expected and reflected by the K_f, which is 3 orders of magnitude larger, metolachlor adsorption to montmorillonite was much higher to the clay than to the sandy or to the Terra-Rosa soil (normalizing the adsorption to the clay content). For example, to add metolachlor to 4.8 g clay/L, the herbicide was added to 400 g of sandy soil/L, 9.6 g of clayey soil/L, and 4.8 g of montmorillonite/L, resulting in

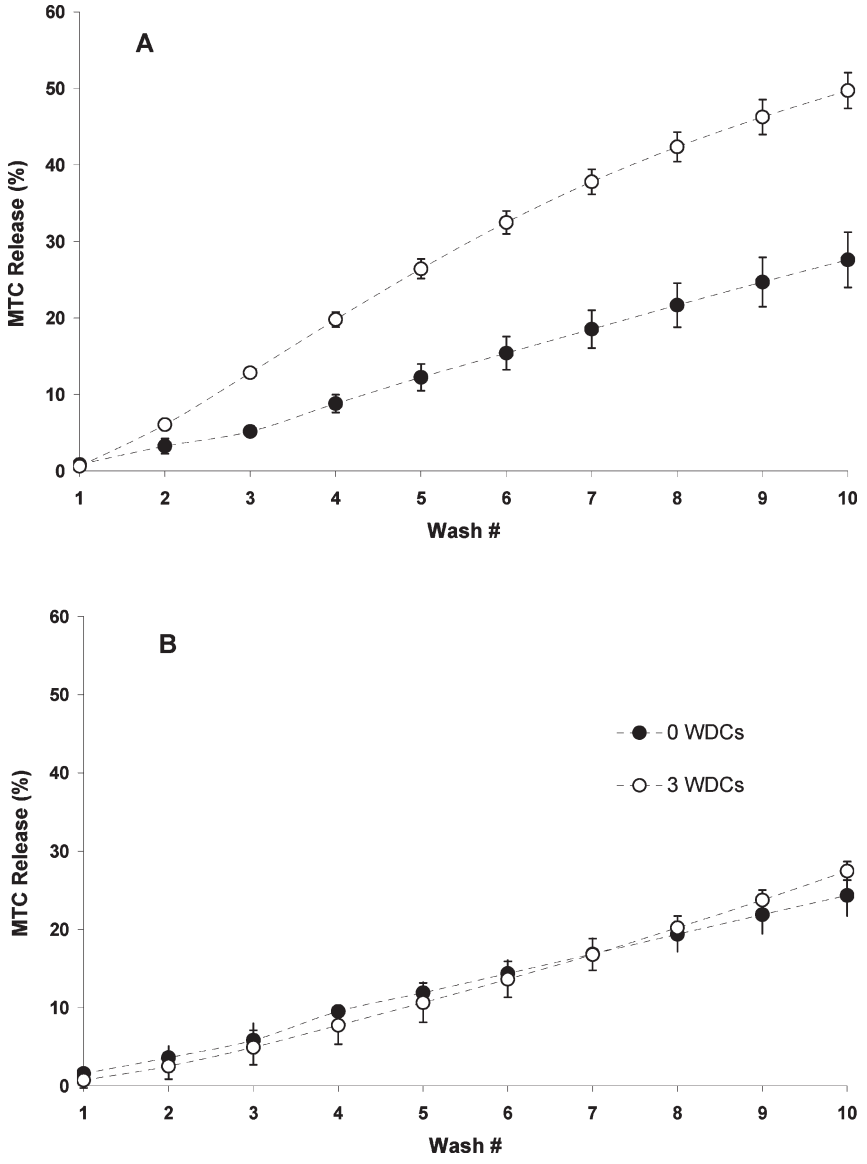

Figure 5. Metolachlor leaching through Terra-Rosa soil layer (5 cm) under WDC (0 and 3) when applied as commercial formulation (**A**) and as micelle−clay formulation (**B**). Error bars present the standard deviation.

0, 30, and 60% adsorption, respectively. The high adsorption of metolachlor to montmorillonite may be explained as follows: (1) the clay fraction in the soil consists of not only montmorillonite, which has a large surface area, but also of kaolinite and Illite, which have much smaller surface areas, and (2) the clay particles are dispersed much better in the clay suspension in comparison to their dispersion in the natural soil suspension, in which the adsorbent is aggregated and surfaces are less accessible. Metolachlor adsorption to montmorillonite has been extensively studied, and several mechanisms have been suggested ranging from weak London interactions to specific interaction of the carbonyl group of the herbicide (*33*, *34*).

The conclusion is that metolachlor adsorption to Terra-Rosa is mainly to the clay fraction of the soil. Following the above metolachlor adsorption studies we examined the effect of WDCs on the rate and degree of metolachlor release from Terra-Rosa soil.

Metolachlor Desorption from the Heavy Soil under Wetting and Drying Cycles. The kinetics of metolachlor desorption from Terra-Rosa preadsorbed with 4.5 μg/g soil and subjected to 0 or 1 WDC was measured between 1 and 24 h (**Figure 4**). For both treatments maximum release was reached within 4 h. Metolachlor release was significantly (almost 2-fold) higher from the soil subjected to a WDC than from the soil samples not subjected to a WDC (45 and 24%, respectively). Massive aggregation was observed for the soil samples not subjected to a WDC, which may result in physical trapping of herbicide molecules and explain the suppressed release. To test this possibility, metolachlor release from the soil samples not subjected to a WDC was studied after mechanically separating the aggregates. Indeed, metolachlor release from these soil samples (0 WDC and disaggregated) increased, reaching 40% of the amount adsorbed. This strengthens our suggestion that the suppressed desorption from the soil samples not subjected to WDCs was due to physical trapping of the herbicide molecules in soil aggregates.

Metolachlor desorption at equilibrium (after 24 h) from the soil adsorbed with 4.5 μg/g subjected to WDCs (0 and 1) was studied by adding various amounts of water (**Figure 1**). Desorption from the soil subjected to a WDC was enhanced as observed in the kinetic study. We hypothesized that the enhanced release of metolachlor from the Terra-Rosa samples subjected to a WDC may result in enhanced leaching in the soil subjected to WDCs.

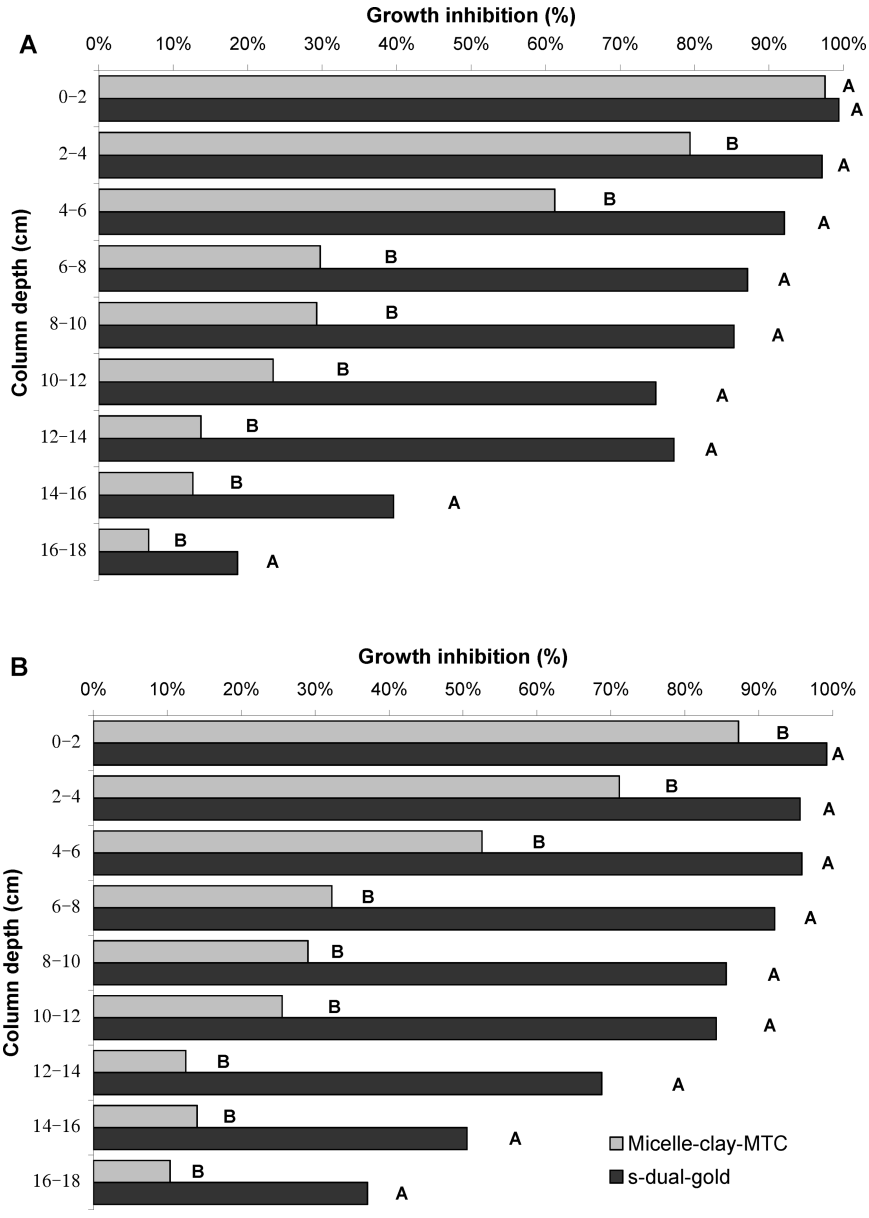

Figure 6. Metolachlor leaching and weed control in Terra-Rosa soil columns treated with metolachlor as the commercial formulation and as a micelle−clay formulation under (**A**) 0 WDCs and (**B**) 4 WDCs. Standard deviation did not exceed 6%.

Metolachlor Leaching through a Thin Soil Layer Applied as CRF and as Commercial Formulation under WDCs. Metolachlor release from the commercial formulation (S-Dual Gold) and leaching through a thin layer (2 cm) of Terra-Rosa under WDCs (0 or 3) was tested by applying the formulation at a rate equivalent to 5800 g of ai/ha, irrigating the soil (50 mm) in 10 portions (5 mm each), and measuring herbicide concentration in the leachates (**Figure 5A**). The cumulative percentage of herbicide released and leached from the soil under 3 WDCs was nearly twice the amount released and leached from the soil that had not been subjected to WDCs (50 and 27%, respectively). Enhanced release and leaching from the soil subjected to WDCs is in agreement with the release results obtained from the batch experiments (**Figures 1** and **4**).

In contrast, metolachlor release and leaching from the CRF (the same leaching study was applied for this formulation) were not higher from the soil subjected to WDCs (**Figure 5B**). These results suggest that the CRF "protects" the herbicide from enhanced release under WDCs. In addition, the release from the CRF was slightly lower than (although not statistically different from) that obtained for the commercial formulation without WDCs (23 vs 27%, respectively). Although the release was not inhibited much when the CRF was applied, the percent of metolachlor released from each irrigation was constant at 2.5%, whereas the release from the commercial formulation was not constant (high for the first irrigation, 6%, and then decreased). The advantage of this CRF was more pronounced when tested in a sandy soil, in which leaching is significant, with metolachlor release from the commercial formulation and from the CRF (after 10 irrigations) reaching 80 and 40%, respectively (*31*).

Soil Column Bioassay of Metolachlor Applied as CRF and as Commercial Formulation under WDCs. The efficiency of metolachlor CRFs to control weeds and to reduce herbicide leaching in soils subjected to WDCs was examined by spraying the CRF, the commercial formulation (S-Dual Gold), and water (control) on soil columns under WDCs (0 and 4) and performing a bioassay test with the test plant foxtail millet (**Figures 6** and **7**). The bioassay was conducted on two soils: Terra-Rosa with high clay (50%) and significant OM content (11%) and Loess with moderate clay content (20%) and negligible OM content.

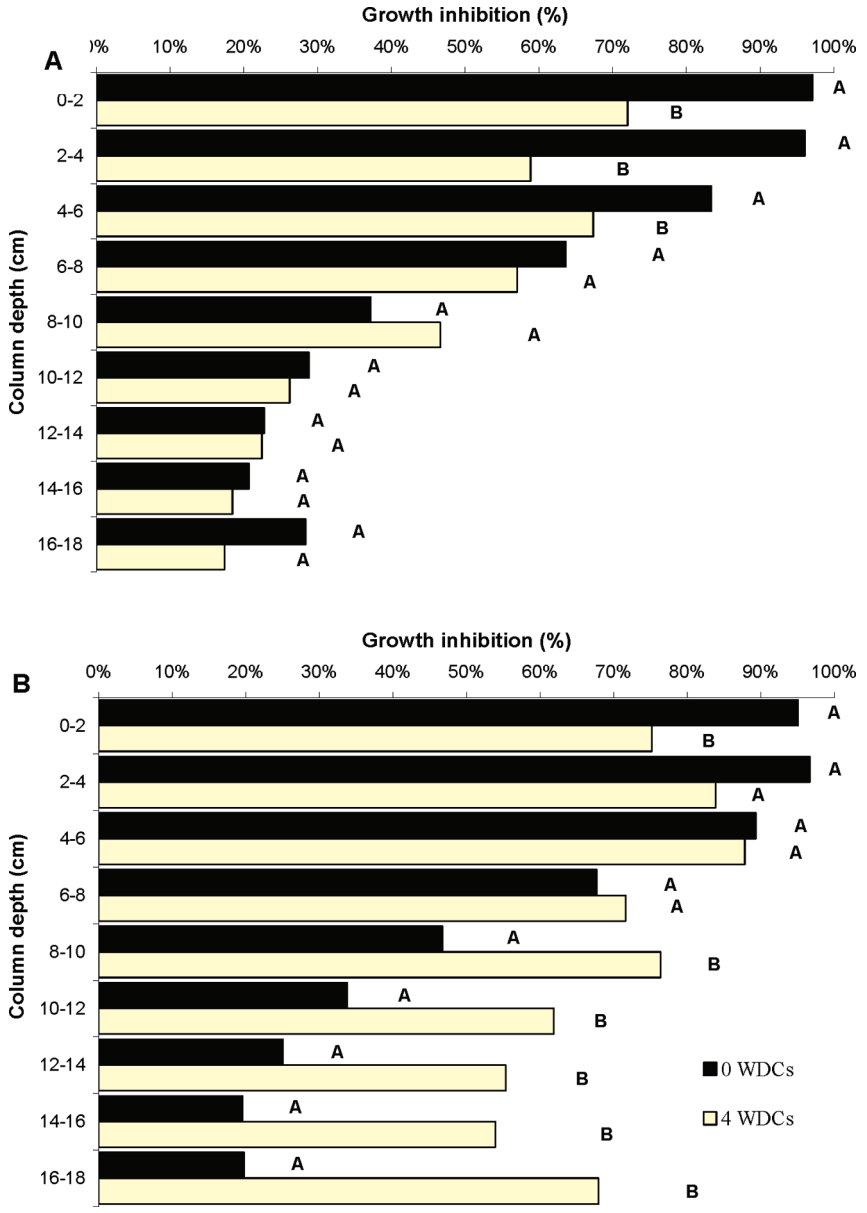

Figure 7. Metolachlor leaching and weed control in Loess soil columns under 0−4 WDCs when applied as (**A**) a controlled-release micelle−clay formulation or (**B**) the commercial formulation. Standard deviation did not exceed 7%.

The Terra-Rosa columns treated with the metolachlor commercial formulation showed sufficient weed control at the top of the columns (0−3 cm), but significant leaching was obtained throughout the columns subjected to WDCs and also in those not treated (**Figure 6**). At depths of 0−6 cm ~100% growth inhibition was obtained, but also at depths of 6−14 cm high inhibition was achieved (70−95%), and at the bottom of the columns inhibition was observed as well (20−50%).

The Terra-Rosa columns treated with the CRF also showed sufficient weed control at the top of the columns (slightly less in the case of 4 WDCs), but in contrast to the columns treated with the commercial formulation, no significant leaching was obtained throughout the columns (**Figure 6**). At depths of 6−14 cm only 10−30% inhibition was obtained in comparison to 70−95% inhibition obtained in the columns sprayed with the commercial formulation. Weed inhibition at the bottom of the columns sprayed with the CRF was ~10%, whereas inhibition at the bottom of the columns sprayed with the commercial formulation reached 20−50%. This bioassay indicated that applying the metolachlor−micelle−clay CRF significantly reduced leaching, in comparison to the commercial formulation, not only in sandy soils (*29*) but also in heavy soils such as Terra-Rosa.

The effect of WDCs of Terra-Rosa on metolachlor leaching from the commercial formulation and consequent weed growth inhibition was statistically significant at the bottom of the columns (14−18 cm). Inhibition was enhanced in the soil columns treated with the commercial formulation and subjected to 4 WDCs from 20% (0 WDCs) to 40%. On the other hand, weed growth inhibition in the columns treated with the CRF was not affected by WDCs and remained 5−10%.

The enhanced metolachlor release from the commercial formulation, but not from the CRF, and extensive leaching in soils subjected to WDCs was more pronounced in the Loess columns (**Figure 7**). Growth inhibition due to application of the CRF or of the commercial formulation as a function of soil depth of Loess and of the soil subjected to 4 WDCs is shown in **Figure 7**, panels **A** and **B**, respectively. Metolachlor leaching in the Loess columns subjected to 4 WDCs and sprayed with the commercial formulation was extremely high, reaching 75% at the bottom of the column. In comparison, the inhibition reached only 20% when

the soil (sprayed with S-Dual Gold) was not subjected to WDCs. However, WDCs did not affect metolachlor leaching from the CRF, which remained low (15−25%). This trend of enhanced metolachlor release and leaching from the soil treated with the commercial formulation subjected to WDCs is in agreement with the release results obtained from the batch experiments (**Figure 4**) and with the thin soil layer tests (**Figure 5**). In both treatments (CRF and commercial formulation) good weed control was obtained at the tops of columns not subjected to WDCs and a slight reduction in control was observed at the tops of columns subjected to WDCs. Specific contrast tests for the interactions between WDC and formulation were found to be not significant for the top layers ($p < 0.15-0.77$) but significant ($p < 0.02$) for the bottom layers (8−20 cm). These results indicate that applying the CRF under WDCs (in comparison to applying the commercial formulation) will significantly reduce leaching without compromising weed control.

One should point out that the CRF was based on the *R*, *S*-metolachlor, and the commercial formulation is composed of *S*-metolachlor. If only the *S*-metolachor was active, this may suggest that the dose of the active ingredient applied in the case of the CRF is somewhat lower. However, the herbicidal activity of both formulations applied to Loess soil columns (not subjected to WDCs) does not differ statistically throughout the column, indicating that in this case the enantiomers had the same effects on growth inhibition (**Figure 7**). Furthermore, even if the dose of the active ingredient applied in the case of the CRF was somewhat lower, the herbicidal activity of the CRF (in most cases) was as good as that of the commercial formulation. Good herbicidal activity at lower application rates may be another benefit of the CRFs.

In the current study we report enhanced metolachlor (technical and commercial) desorption and leaching as a result of WDCs as reported for imazaquine desorption following WDCs (*8*). However, in the literature suppressed leaching is reported as well (*8*, *12*, *13*). The complexities of WDCs were discussed in a recent field study on the persistence, leaching, and bioefficacy of several alachlor formulations (*35*). The impact of WDCs on microbial degradation, which was not examined in the current study, adds to the complexity of effects of WDCs and should be explored. There are also issues concerning the application of CRFs that should be explored, for example, persistence in the soil, which may enable lowering the frequency and rate of application but may also have an effect on the following crop.

To conclude, the results clearly indicate that WDCs increase metolachlor release from soils. We suggest that physical trapping in the soil aggregates not subjected to WDCs suppressed metolachlor release. Increased release from soils under WDCs results in enhanced metolachlor leaching through soil columns under WDCs, as seen from the high growth inhibition rate at the bottom of the soil columns subjected to WDCs. However, when metolachlor was applied as a CRF, WDCs did not enhance metolachlor release from the formulation, and as a result reduced leaching was obtained. According to our findings we suggest that the micelle−clay formulation "protected" the herbicide molecules from the effects of WDCs by controlling its release and therefore may also have the potential to protect the herbicide from microbial and photochemical degradation.

ABBREVIATIONS USED

CRF, controlled-release formulation; ai, active ingredient; WDCs, wetting and drying cycles; MTC, metolachlor; ODTMA, octadecyltrimethyl ammonium.

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Received for review July 29, 2010. Revised manuscript received November 29, 2010. Accepted December 10, 2010. This research was supported by Research Grant Award IS-3656-05 R from BARD, The United States−Israel Binational Agricultural Research and Development Fund and by internal funding for applied sciences of Hebrew University.