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ARTICLE

Reduction in Metolachlor and Degradate Concentrations in Shallow Groundwater through Cover Crop Use

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Pesticide use during crop production has the potential to adversely impact groundwater quality. In southern Florida, climatic and hydrogeologic conditions and agronomic practices indicate that contamination risks are high. In the current study, dissipation of the widely used herbicide, metolachlor, and levels of the compound and selected degradates in shallow groundwater beneath six 0.15-ha plots in sweet corn (*Zea mays*) production were evaluated over a two-year period. During fallow periods (May to October), plots were either left bare or cover cropped with sunn hemp (*Crotalaria juncea* L.). Metolachlor was broadcast applied at label recommended rates prior to planting sweet corn each year. Groundwater monitoring wells hydraulically upgradient and downgradient, and within each plot were sampled biweekly. Results showed that metolachlor dissipation was rapid, as evidenced by the detection of relatively high levels of the metolachlor ethane sulfonic degradate (MESA) in groundwater beneath plots and a rapid metolachlor DT_{50} (9−14 days) in a companion laboratory soil incubation. Other degradates detected included hydroxymetolachlor in soil and in groundwater metolachlor oxanilic acid (MOA) and a product tentatively identified as 2-chloro-*N*-(2-acetyl-6-methylphenyl-*N*-(2-methoxy-1-methylethyl) acetamide, a photo-oxidation product. Metolachlor and MESA levels, up to 16 and 2.4 times higher in groundwater beneath the noncover cropped plots when compared to those of the cover cropped plots, indicate that cover cropping results in more rapid dissipation and/or reduced leaching. The study demonstrated that integration of cover crops into agronomic systems in the region may yield water quality benefits by reducing herbicide inputs to groundwater.

KEYWORDS: Metolachlor; metolachlor ethane sulfonic acid; groundwater; cover cropping; soil dissipation

INTRODUCTION

The USGS-National Water Quality Assessment (NAWQA) program demonstrated that pesticide use during crop production may impair groundwater quality and threaten aquifers that serve as domestic/or municipal water supplies (*1*). More than 30% of the 2000 domestic water sources tested in this program had detectable levels of one or more pesticides (or pesticide degradates). The highest frequencies of detection were associated with areas where agriculture was the predominant land use (*2*).

Contamination risk appears high at the southern tip of peninsular Florida (USA) where crops are grown in a 32-km^2 region that is bordered to the northwest by Big Cypress National Preserve, to the south and west by the Everglades National Park, and to the east by Biscayne National Park. The area overlies the Biscayne−Gray Limestone aquifer system that serves as south Florida's water supply (*3*). Diversions from this aquifer were specified in plans for the Everglades Restoration Project that is focused on increasing water deliveries to Everglades National Park; thus, there are also concerns that impacts on the quality of the water in this aquifer system due to agricultural pesticide use could adversely impact this massive project (*4*).

The aquifer's pesticide contamination risk is linked to several factors. The region's mineral soils are shallow and porous, and the water table is typically within 1−3 m below the soil surface throughout the year (*5*, *6*). Additionally, humid subtropical climatic conditions combined with winters that are often frost free permit intensive tropical fruit and vegetable crop production. Sweet corn is a favored winter crop with about 1000 ha in production in Dade County, FL (Mossler, M., personal communication, 2009). High pest pressures typically result in high rates of pesticide use including the herbicides atrazine (6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide) (*7*).

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Both atrazine and metolachlor are commonly found in surface and groundwater where these products are used (*1*). This includes southern Florida where they were detected in samples collected from surface water and groundwater wells (*8*). Both atrazine and metolachlor have a tendency to form degradates which exhibit relatively high stability and or environmental mobility. Detection of degradates in groundwater is common with their concentration often exceeding that of the parent compounds (*9*). This was observed by Potter et al. in a study that focused on evaluating atrazine levels in groundwater beneath corn fields in southern Florida that were treated annually (*6*). Atrazine's desethyl degradate (DEA) was found at the highest concentration in samples collected over a 3.5-yr period. This was linked to rapid and extensive atrazine degradation in soil and development of an adapted community of atrazine degrading organisms following successive atrazine applications. The study also found that the use of a cover crop during summer fallow periods and turning crop residues into soil prior to planting corn crops contributed to a significant reduction of atrazine and degradate concentration in groundwater.

Here, we describe metolachlor responses at the same study site. Metolachlor was selected for investigation because of detection in the regional aquifer (*8*) and the herbicide's widespread use. Products containing this active ingredient are registered on more than 70 crops worldwide (*10*); many are grown in southern Florida. The primary objective of our study was to assess the potential for metolachlor to contaminate shallow groundwater during crop production in South Florida. We also examined the extent to which the use of a cover crop during summer fallow periods in this subtropical climatic region may reduce the levels of metolachlor and its degradates in groundwater and or impact metolachlor degradation kinetics in soil. The formation and occurrence of numerous metolachlor degradates in both surface and groundwater is well documented (*11*). Findings serve as a case study in the evaluation of farming, soil, and climatic impacts on the fate of metolachlor and transport in an area where groundwater contamination risks appear high.

MATERIALS AND METHODS

Study Site and Management. The study was conducted in a level 4-ha field at the University of Florida Tropical Research and Education Center near Homestead, FL (**Figure 1**). The field soil series is the Krome loamy-skeletal, carbonatic, hyperthermic Lithic Udorthents (*12*). Physical and chemical properties of composite samples collected before planting corn in 1999 were as follows: gravel (> 2 mm diameter), 669 ± 52 g kg^{-1}; sand, 194 ± 6.2 g kg^{-1}; silt, 75 ± 11 g kg^{-1}; clay, 61 ± 8.4 g kg^{-1}; organic carbon, 11 ± 1.0 g kg^{-1}; organic nitrogen, 0.6 ± 0.1 g kg^{-1}; median pH, 8.1 (*6*).

The first sweet corn (variety Attribute, Rodgers Seeds, Boise, ID) crop was planted in November 1999 in a 192×47 m rectangular area positioned diagonally across the field. The planted area was subsequently divided into six plots and with three each randomly selected to represent either noncover cropped or the cover cropped treatments (**Figure 1**). Plot assignments were retained for three following corn crops produced during 2000−2003. Planting was in October−November and harvest in February−March. Prior to planting, cropped areas were tilled and the herbicide Atrazine 4 L broadcast applied at a target rate of 2.2 kg ha^{-1} using a tractor-mounted sprayer. Beginning in 2001, the atrazine was tank mixed with the herbicide Dual II Magnum. The target application rate of the product's active ingredient, metolachlor, was 1.1 kg active ingredient ha^{-1}. Irrigation, fertilizer rates, and pest management followed recommended practices for the region (*13*). After each harvest, corn stover was mowed and tilled into the soil. Sunn hemp (*Crotalaria juncea* L.) was seeded in cover cropped plots during April−June and was mowed after reaching a 1 m height (June−July), and again after reaching a height of 1.5 m (October). Fields were then repeatedly disked to turn crop residue into the soil. The noncover cropped plots and the area adjacent to the planted area in the surrounding field were tilled occasionally to control weeds.

Hydrologic Monitoring and Water Sample Collection. Rainfall and water table elevation data were collected from automated monitoring

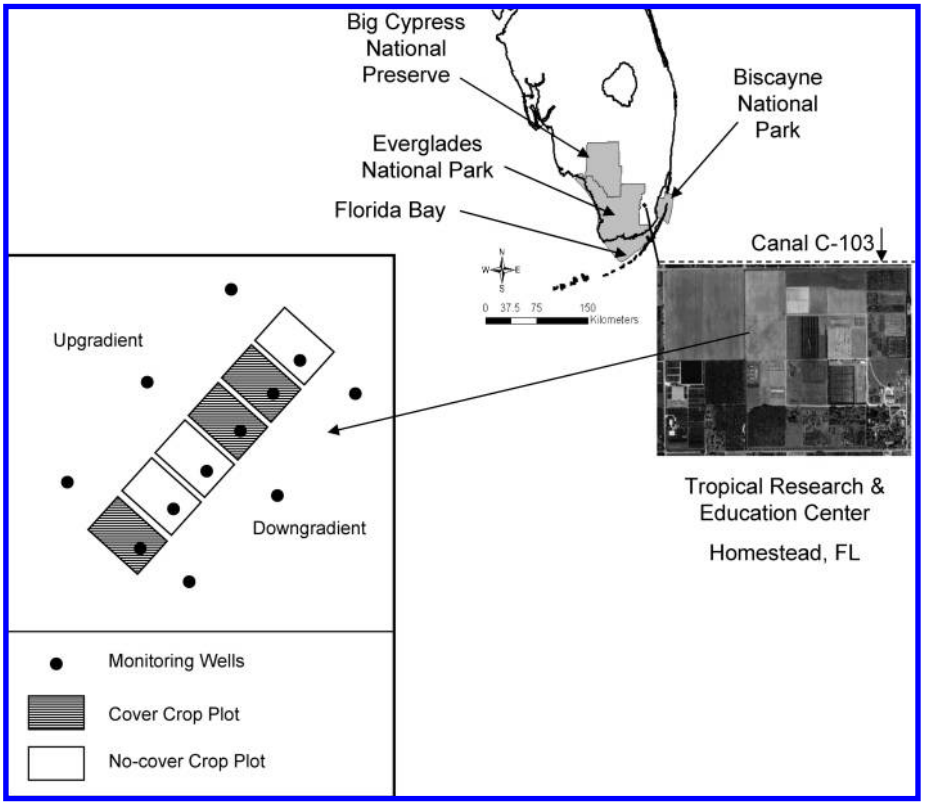

Figure 1. Study site was at the University of Florida Tropical Research and Education Center in Homestead, Florida. The inset shows the location of groundwater wells sampled during the study and the possible impact areas surrounding the agricultural area of south Florida.

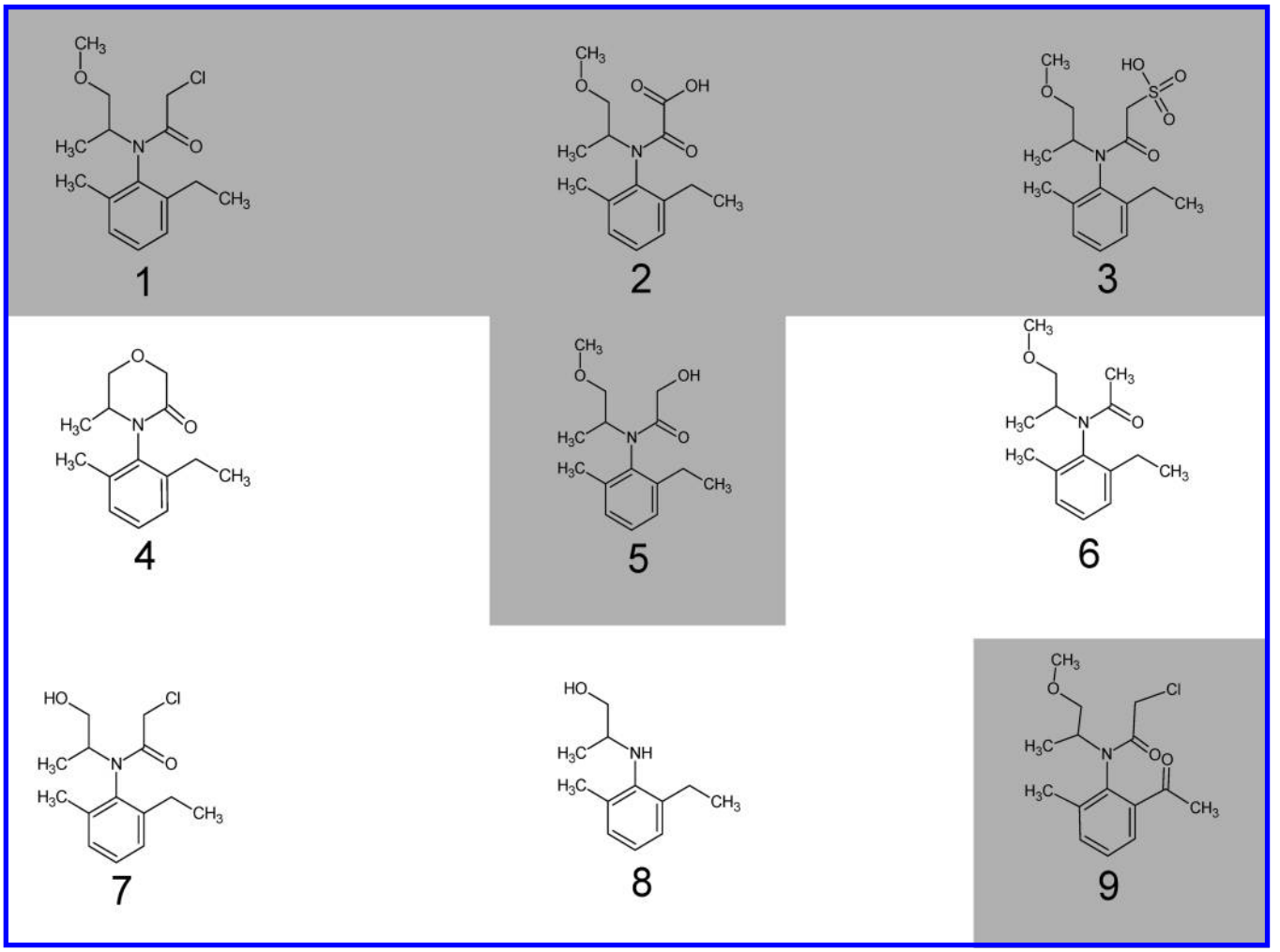

Figure 2. Structures of parent molecule and degradates evaluated in the present study in groundwater and soil incubation samples. Structures include (1) metolachlor, (2) metolachlor oxanilic acid, (3) metolachlor ethane sulfonic acid, (4) metoloachlor morpholinone, (5) hydroxymetolachlor, (6) deschlorometolachlor, (7) desmethyl-metolachlor, (8) deschloroacetyl metolachlor propanol, and (9) phenyl alkyl-substituted metolachlor. Shaded structures indicate the molecules were detected during experiments.

stations located 1 km west of the experimental field (*14*, *15*). Rainfall followed the typical seasonal pattern for the region with a wet season that extended from May to October and a dry season from November to April (*6*). Irrigation (17−25 mm) was applied to the corn plots every 3 to 5 days during the growing season with groundwater extracted from a 25-cm diameter well, 10 m deep and 30 m downgradient of the plots. The potential drawdown in the groundwater table monitoring well closest to the irrigation well was estimated to be <0.3 mm after irrigation (*6*). Rainfall total during the 2002 wet season was 1542 mm. Water table elevation generally fluctuated with rainfall with a range of 0.57 to 1.80 m and a mean of 1.08 m.

Groundwater samples were collected from monitoring wells installed within the corn plots (centers) and three each at hydraulically upgradient and downgradient locations (**Figure 1**). Wells were constructed with 3-m slotted screens that spanned annual fluctuations in the water table. Groundwater flow direction and velocity (3−9 m d^{-1}) were determined using tracer studies in 2002 and 2003 (*6*). All wells were sampled biweekly. Throughout most of the year, water levels in the canal (C-103) located about 0.5 km NW were maintained above the water table surface; thus, subsurface flow from the canal was typically SE toward the research plots (*16*). During 2002, seven additional storm-event samples were collected on the basis of the following criteria: ≥ 2.5 cm rain within a 24-h period at least 2 days before or 7 days after scheduled biweekly samples. For each scheduled and event sample set, a field equipment blank was prepared using distilled−deionized water. Blanks and water samples were analyzed concurrently. Sampling protocol followed that of Potter et al. (*6*).

Soil Incubations. Two composite soil samples, one representing the noncover cropped plots and the other the cover cropped plots, were collected prior to herbicide application for the 2002−2003 corn crop. Twenty-five grams of dry weight equivalent subsamples of soil passing a 2-mm sieve were placed in 250-mL square glass bottles. Soil−water was adjusted to field capacity, 0.18 g H_2O g^{-1}, by adding distilled water and an aqueous solution of metolachlor. Metolachlor was added at a target rate of 0.5 μg g^{-1} dry soil. Fifty milliliters of methanol was immediately added to three bottles from each treatment; bottles were capped, shaken, and stored at −20 °C. The remaining bottles were capped and incubated in the dark at 24 °C. Three bottles representing each treatment group were removed from the incubator after 1, 4, 7, 14, 21, 28, 42, 63, 91, 119, 147, and 175 d, 50 mL of methanol was added to each bottle, and the bottles were placed in a freezer (−20 °C).

Selection of Target Analytes and Source of Reference Standards. Metolachlor and nine degradates were targeted in analyses (**Figure 2**; **Table 1**). Degradates 2−8 were selected on the basis of reported occurrence in surface waters (*11*, *17*) and in groundwater (*18*). Degradate 9 was included after review of full-scan high performance liquid chromatography−atmospheric pressure chemical ionization−mass spectrometry (HPLC-APCI-MS) acquisitions obtained by Potter et al. (*6*) indicated the presence of a peak with $(M + H)^+ = 298$ in some water sample extracts. The sample with the highest level of this peak was sequentially reanalyzed by MS^2, MS^3, and MS^4 with collision-induced dissociation (CID) of product ion spectra base peaks and produced ions $(M + H)^+$ 266, 190, and 172. A 14 mass unit difference between principal ions, m/z = 284−252−176−134 of metolachlor and the degradate,

Table 1. Metolachlor and Degradates Analyzed in Groundwater and Soil Samples[a]

analyte #	compound	retention time (min)	ion product	primary ion (*m*/*z*)	quantification secondary ion (*m*/*z*)
1	metolachlor	8.2	$(M + H)^+$	284	252
2	metolachlor oxanilic acid	2.9	$(M - H)^-$	278	206
3	metolachlor ethane sulfonic acid	2.4	$(M - H)^-$	328	121
4	metolachlor morpholinone	7.0	$(M + H)^+$	234	148
5	hydroxymetolachlor	7.5	$(M + H)^+$	266	234
6	deschlorometolachlor	6.7	$(M + H)^+$	208	148
7	desmethylmetolachlor	7.5	$(M + H)^+$	270	238
8	deschloroacetyl metolachlor propanol	4.7	$(M + H)^+$	194	136
9	phenyl alkyl-substituted metolachlor	7.1	$(M + H)^+$	298	266

[a] Analyte numbers refer to **Figure 2**.

298−266−190−148, was consistently observed, indicating that the degradate was likely formed by oxidation of the ring ethyl group to form an acetyl substituent. Observation of ions produced by neutral loss of 18 (H_2O) from m/z = 298, 266, and 190 supported this conclusion. This loss was not observed from corresponding metolachlor ions. GC-MS analysis of this sample provided further support. The EI-spectrum of one of the compounds detected and the published spectrum of photooxidation product matching this structure closely matched (*19*). Metolachlor, metolachlor ethane sulfonic degradate (MESA) (2), metolachlor oxanilic acid (MOA) (3), and degradate 8 analytical standards were purchased (Chem-Service, West Chester, PA). Reference mixtures containing degradates 4−7, were prepared by acid (2 N HCl) and base (2 N KOH) metolachlor hydrolysis at room temperature for 86 h. After neutralization and dilution in deionized water, products were recovered by liquid−liquid extraction with methylene chloride and following solvent exchange to methanol mixtures were analyzed by HPLC-APCI-MS using a Thermoquest-Finnegan LCQ DECA ion trap system (Thermo-Fisher Scientific, San Jose, CA). Peaks assignments were made on the basis of products described by Carlson et al. (*20*). These mixtures were used to establish retention time and MS-MS conditions for these compounds.

Sample Analysis and Quality Control. Soil incubation bottles were warmed to ambient temperature and shaken for 1 h on a rotary bed shaker. Methanol was decanted and vacuum filtered (70-mm Whatman GF/F filters). The process was repeated twice and extracts combined. Water samples (500 mL) were vacuum filtered (70-mm Whatman GF/F filters) and solid phase extracted on 6-mL (200 mg) Oasis HLB cartridges (Waters, Milford, MA) under vacuum followed by sequential elution with 3 mL of methanol and 3 mL of methylene chloride, which were combined. Soil extracts were concentrated to 10 mL, and water extracts were reduced to 1 mL at 55 °C under N_2 gas. After the addition of the internal standard, 2-chlorolepidine, HPLC-MS for target compounds was completed.

Metolachlor (1) and degradates 4−9 (**Figure 2**), were separated on a Gemini C18 HPLC column (150 × 4.6 mm, 5 μm, 110 Å (Phenomenex, Torrance, CA)) and detected after the production of positive ions using APCI. Twenty microliters of sample was injected onto the HPLC column. Gradient elution was accomplished using 0.1% formic acid (by volume) (A) and methanol (B) at a mass flow rate of 1 mL min^{-1}. After sample injection, the initial mobile phase composition 90% A and 10% B was changed linearly to 10% A and 90% B in 6 min. Conditions were held constant for 5 min and returned to initial conditions in 1 min. MESA and MOA, degradates 2 and 3 (**Figure 2**), were separated on a Zorbax C8 HPLC column (50 × 2.1 mm; 3 μm, 110 Å (Agilent, Santa Clara, CA)), and negative ions formed after their electrospray ionization were used for detection (*21*). Gradient elution at 0.6 mL min^{-1} was with 0.1% formic acid (C) and acetonitrile + 0.1% formic acid (by volume) (D). Initial conditions, 90% C and 10% D, were changed linearly to 10% C and 90% D in 5 min. Conditions were held for 2 min followed by return to initial conditions in 1 min.

Base peaks in full-scan (m/z = 100 to 450) MS spectra were $(M + H)^+$ for metolachlor and degradates 4−9 and $(M - H)^-$ for MESA and MOA (**Table 1**). Corresponding $(M + H)^+$ or $(M - H)^-$ were used as precursors for MS-MS spectra obtained by CID. Prior to each set of analyses, instrument response was optimized for metolachlor $(M + H)^+$, m/z = 284, or MESA $(M - H)^-$, m/z = 328, by infusion of a 10 μg mL^{-1} solution into the HPLC column effluent. Optimal CID conditions, defined as maximum base peak response in product ion spectra, were established during infusions. Base peaks of product ion spectra were used for quantitation (**Table 1**). Analytical standards were not available for degradates 4, 5, 6, 7, and 9. Metolachlor response was used to estimate their concentration. The lowest concentration metolachlor and degradate 8 standards analyzed was 1 ng mL^{-1} and for MESA and MOA, 10 ng mL^{-1}. On the basis of the extraction of 500 mL of water concentration to 1 mL and 100% recovery, the limit of detection (LOD) was 0.002 μg L^{-1} for metolachlor and the degradates 4−9, and 0.02 μg L^{-1} for MESA and MOA. For soil, the computed LODs were 0.0004 μg g^{-1} and 0.004 μg g^{-1}, respectively.

Metolachlor, MESA, MOA, and degradate 8 were added to groundwater and soil and extracted using the protocols listed above. Samples (n = 3) were spiked prior to extraction with the analytes for a final concentration of 0.1 and 0.2 μg mL^{-1} for water and soil, respectively. Another set of samples (n = 3) were spiked postextraction. Percent recovery was calculated as the peak area of pre-extraction spike divided by the peak of the postextraction spike (*22*). The calculation summarizes extraction efficiency as well as matrix impacts on signal intensity. Recovery means (standard deviation) for metolachlor, MESA, MOA, and degradate 8 were 99 (11), 79 (21), 69 (19), and 94 (17) in groundwater, and 110 (17), 45 (17), 35 (14), and 115 (27) in soil, respectively. Recovery studies were not conducted for degradates 4−7 and 9 as standards were not available. Results were expected to be comparable to those of metolachlor. Other studies used the same solid phase extraction approach and reported that recoveries for metolachlor and neutral degradates from seawater samples were 62−107% (*11*). All target analytes were < LOD in field blanks.

Data Analysis and Statistics. Water quality data were grouped into either premetolachlor application samples, dry season (Nov−May), or wet season (June−Oct), and by year. For metolachlor, MESA, MOA, degradate 9, and total metolachlor residues in groundwater data, the detection limit was substituted for no-detection, and medians and 25th and 75th percentiles were calculated in Excel (Microsoft, Redmond, WA). Data sets with > 50% detection were ranked and sample locations compared pairwise by season and analyte using the Wilcoxon nonparametric test in the Proc NPARWAY1 procedure in SAS v. 9.1 (SAS Institute, Cary, NC). Differences between sample locations are indicated by two-side normal approximation probability tests. The area under the curve for metolachlor or the chloroacetanilide sum (metolachor, MESA, MOA, and degradate 9) by sample time was calculated for each well within each treatment using the AREA.XFM transformation in Sigma Plot v. 11.0 (Systat Software, Inc., San Jose, CA). The integrated area for metolachlor and sum chloroacetanilides over time were subjected to an ANOVA using Proc Mixed in SAS, and means were separated by t-tests. Soil incubation data was natural log-transformed before linear trends lines were used to determine the slope or first order decay rate (k). For comparison, a first order nonlinear regression model was also used to predict dissipation rates based on natural log-transformed data (*23*). Model parameters (α, β) were obtained using Proc NLIN in SAS with the GAUSS-NEWTON iterative setting.

RESULTS AND DISCUSSION

Trends in Metolachlor and Degradate Concentration in Groundwater Samples. Prior to the first metolachlor application, low levels of the compound (0.009 to 0.022 μg L^{-1}) were detected in all well samples (**Table 2**). Medians computed by grouping data

according to well locations were not significantly different (**Tables 3** and **4**). Data indicated that metolachlor was distributed uniformly in groundwater at relatively low levels across the study site. Groundwater concentrations were within the range of values (0.001 to 0.086 μg L^{-1}) obtained for samples from the canal located about 0.5 km NW of the field. (*24*). This canal was determined to be hydraulically upgradient of the study site throughout most of the year (*16*). Canal and aquifer water exchange in the area is common because of their design for flood control (*25*); thus, it appears reasonable to conclude that metolachlor enriched canal water infiltrated into the aquifer and contributed to low initial levels present in groundwater. A similar observation was made for atrazine and degradates (*6*).

The first metolachlor application marked the beginning of the first sweet corn growing season during the study and the start of the 2001−2002 dry season. Rain and irrigation totals for the season were 670 mm, with deep drainage estimated to be 475 mm using a numerical simulation model, WAVE (*26*). Some metolachlor leaching was indicated. During this season, median metolachlor concentrations for water samples beneath cover cropped or noncover cropped plots were significantly higher than those obtained up or downgradient; however, the concentration differences were small (**Table 3**). Throughout the season, the medians for the upgradient and downgradient well groups remained low (0.013 to 0.016 μg L^{-1}) and were not significantly different from medians computed for preapplication samples. In the following wet season (May−October), metolachlor concentration in groundwater beneath noncover cropped plots increased substantially. The seasonal median for this well group, 0.088 μg L^{-1}, was 6- to 15-fold greater than the medians for the upgradient and downgradient, cover cropped plot well groups, respectively. Differences were significant. Data indicated that the residual metolachlor in soil on noncover cropped plots was leached to groundwater by the relatively large amount of rainfall (1542 mm) during this season. Metolachlor leaching was also indicated on cover cropped plots since the median was greater than that for the upgradient well group. The difference, however, was relatively small, 2.5-fold, indicating that leaching rates and or residual levels of metolachlor in soil on cover cropped plots were relatively small when compared to those of the noncover cropped treatment. During this wet season, metolachlor concentrations in groundwater were similar for the up and downgradient test wells, with median values of 0.006 and 0.010 μg L^{-1}, respectively. Values were not significantly different. Failure to detect a significant metolachlor increase in the downgradient wells suggested a high rate of dilution as groundwater moved downgradient from the metolachlor treated areas. These values were slightly lower when compared to those of the previous dry cropping season (**Table 3**).

A similar trend for metolachlor concentration in test wells was observed for the next dry season (2002−2003). This followed the second metolachlor application. Notably, metolachlor concentration in wells beneath no cover plots continued to increase, with a median value of 0.221 μg L^{-1}. The continued increase in metolachlor median concentration in groundwater beneath no cover crop plots in each successive season contrasted with atrazine behavior at the site, where the peak seasonal atrazine median was reached in groundwater samples in the wet season following the first atrazine application (*6*). Atrazine was applied at the beginning of the following three dry seasons; however, median concentrations in both wet and dry seasons remained low and not significantly

Table 2. Metolachlor and Degradate Detection Percentages in the Groundwater Wells for 2001−2003

		monitoring well type			
analyte	season	UPGD	NOCOV	COVER	DNGD
		number of samples			
	pre app	6[a], 3[b]	6[a], 3[b]	6[a], 3[b]	6[a], 3[b]
	dry 01−02	42	42	42	42
	wet 02	33	33	33	33
	dry 02−03	33	33	33	33
		% detection			
metolachlor	pre app	100	100	100	100
	dry01−02	97	100	100	100
	wet 02	97	100	100	100
	dry 02−03	97	100	100	100
MESA	pre app	0	0	0	0
	dry 01−02	41	46	21	23
	wet 02	9	96	83	58
	dry 02−03	12	100	77	45
MOA	pre app	0	0	0	0
	dry 01−02	0	0	0	0
	wet 02	0	24	0	0
	dry 02−03	0	40	0	0
degradate 9	pre app	0	0	0	0
	dry 01−02	0	13	3	0
	wet 02	0	66	30	0
	dry 02−03	0	84	13	0

[a] *n* for metolachlor. [b] *n* for MESA, MOA, and phenyl alkyl-substituted metolachlor.

Table 3. Metolachlor and MESA Medians and 25th and 75th Percentiles in Groundwater Samples

	metolachlor											
	pre app (μg L^{-1})			dry 01−02 (μg L^{-1})			wet 02 (μg L^{-1})			dry 02−03 (μg L^{-1})		
	median	25th	75th	median	25th	75th	median	25th	75th	median	25th	75th
UPGD	**0.0085**	0.0071	0.0101	**0.0130**	0.0090	0.0171	**0.0060**	0.0040	0.0120	**0.0050**	0.0030	0.0080
NOCOV	**0.0099**	0.0088	0.0119	**0.0197**	0.0104	0.0389	**0.0878**	0.0435	0.1581	**0.2208**	0.0662	0.4596
COVER	**0.0099**	0.0090	0.0157	**0.0187**	0.0110	0.0354	**0.0151**	0.0083	0.0281	**0.0140**	0.0060	0.0406
DNGD	**0.0217**	0.0103	0.0251	**0.0161**	0.0110	0.0249	**0.0100**	0.0070	0.0110	**0.0100**	0.0060	0.0231
	MESA											
	pre app (μg L^{-1})			dry 01−02 (μg L^{-1})			wet 02 (μg L^{-1})			dry 02−03 (μg L^{-1})		
	median	25th	75th	median	25th	75th	median	25th	75th	median	25th	75th
UPGD												
NOCOV				**0.1137**	0.0200	0.7911	**7.3659**	0.9226	10.0108	**5.2906**	3.2007	8.3535
COVER							**6.4456**	0.8461	10.0888	**2.2020**	0.3676	3.1525
DNGD							**0.3179**	0.0200	1.1554			

Table 4. Metolachlor Nonparametric Pairwise Comparisons Made by Wilcoxon Two-Way Tests[a]

	preapplication				dry 2001−2002				wet 2002				dry 2002−2003			
	UPGD	NOCOV	COVER	DNGD	UPGD	NOCOV	COVER	DNGD	UPGD	NOCOV	COVER	DNGD	UPGD	NOCOV	COVER	DNGD
preapplication																
UPGD	x	0.298	0.5752	0.3785												
NOCOV	0.298	x	0.298	0.4712												
COVER	0.5752	0.298	x	0.6889												
DNGD	0.3785	0.4712	0.6889	x												
dry 2001−2002																
UPGD	0.257	0.228	0.8714	0.1262	x	**0.0064**	**0.0072**	0.0525								
NOCOV	**0.0297**	0.0545	0.1019	0.4612	**0.0064**	x	0.7693	0.2576								
COVER	**0.0185**	**0.027**	0.075	0.602	**0.0072**	0.7693	x	0.3381								
DNGD	**0.0295**	**0.0421**	0.1174	0.957	0.0525	0.2576	0.3381	x								
wet 2002																
UPGD	0.3198	0.1233	0.0896	**0.0225**	**0.0016**	**<0.0001**	**<0.0001**	**<0.0001**	x	**<0.0001**	**<0.0001**	0.0536				
NOCOV	**0.0005**	**0.0005**	**0.0008**	**0.0023**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	x	**<0.0001**	**<0.0001**				
COVER	0.1011	0.1492	0.3181	0.9705	0.0745	0.3012	0.4534	0.9245	**<0.0001**	**<0.0001**	x	**0.002**				
DNGD	0.7121	0.6811	0.4454	0.1221	**0.0318**	**0.0003**	**0.0002**	**0.0004**	0.0536	**<0.0001**	**0.002**	x				
dry 2002−2003																
UPGD	**0.0442**	**0.0131**	**0.0066**	**0.0052**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	0.1493	**<0.0001**	**<0.0001**	0.0002	x	**<0.0001**	**<0.0001**	0.0004
NOCOV	**0.0003**	**0.0002**	**0.0003**	**0.0004**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	0.0009	**<0.0001**	**<0.0001**	**<0.0001**	x	**<0.0001**	0.5115
COVER	0.4932	0.5586	0.96	0.7256	0.5631	0.2088	0.1974	0.5005	**0.0019**	**<0.0001**	0.643	0.1796	**<0.0001**	**<0.0001**	x	**<0.0001**
DNGD	0.5985	0.9533	0.8607	0.4017	0.705	**0.025**	**0.0266**	0.0913	**0.021**	**<0.0001**	0.1425	0.5626	0.0004	**<0.0001**	0.5115	x

[a] Numbers are probability of test > |Z|. Significant values are in bold.

different. Soil incubation studies which quantified atrazine degradation rates indicated that development of enhanced atrazine degradation conditions in the soil following the first atrazine application likely explained these results. Increased rate of atrazine degradation in soil due to microbial community adaptation following one or more initial treatments is widely reported (*6*, *27*−*29*).

The case for adaptation and enhanced dissipation of metolachlor in soil is less certain with mixed results reported in published studies. Soil metolachlor half-life was reported to decrease from 18 to 2.5 days with four successive applications over 8 months (*30*). However, in field studies spanning several years, increases in metolachlor degradation rates due to prior applications were not observed (*28*). Our groundwater data generally agree with the later observations in that levels in groundwater increased after the second application.

None of the metolachlor degradates (2−9) monitored was detected in well samples prior to the first metolachlor application at the beginning of the 2001 dry season. This was the case for the duration of the study for the upgradient wells. During the first dry season, MESA was detected in wells in downgradient, no cover, and cover crop well groups, but at frequencies < 50% and at low levels (**Tables 2** and **3**).

Beginning in the following wet season, MESA was detected at high frequency in groundwater below cover cropped and noncover cropped plots and downgradient (**Table 2**). The ratios of MESA to metolachlor medians were 29 (upgradient), 462 (noncover crop), 115 (cover crop), and 106 (downgradient). The relatively high MESA levels, as compared to that of metolachlor, were similar to other reports for groundwater beneath cropped fields with a range of unsaturated and saturated zone physical properties (*18*, *31*−*34*). MESA water solubility is estimated to be more than 400 times greater than that of metolachlor; thus, a much higher MESA leaching rate is indicated (*35*). MESA concentrations were not significantly different between no cover and cover crop plots with medians of 7.4 and 6.4 μg L^{-1}, respectively ($P > |Z| = 0.4588$). Values were within the range reported for groundwater from an agriculturally impacted unconfined aquifer in Nebraska (*31*).

Sustained high levels of MESA were detected in groundwater below both sets of cropped plots ($P > |Z| = 0.8711$) during the subsequent dry season of 2002−2003. However, the no cover plot median, 5.3 μg L^{-1}, was significantly higher compared to the MESA median (2.2 μg L^{-1}) detected below cover cropped plots ($P > |Z| < 0.0001$) (**Table 3**). The difference between the groups may be explained by lower rates of MESA formation in cover cropped plot soils, higher rate of degradation, and or low deep drainage of irrigation and precipitation on these plots.

MOA was detected at a low frequency (4.6%) when compared to that of MESA (53%) and 21 out of 22 MOA detections were from the noncover cropped plot well samples (**Table 2**). In samples in which both compounds were detected, the ratio of MESA to MOA concentration averaged 13, and in all cases, the concentration of MESA was greater than the concentration of MOA. The observation has been reported elsewhere and can be attributed to MESA's greater persistence (*31*, *33*), a higher cumulative MOA mineralization rate in soil (*36*), or lower rate of MOA formation. MESA and metolachlor were both detected in 51% of samples, and the average MESA to metolachlor ratio was 258, and MESA's concentration was greater than that of metolachlor in 237 out of 241 samples. MOA and metolachlor were detected in 4.7% of groundwater samples with an average ratio of 93. MOA was always detected at a higher concentration than that of metolachlor. A higher rate of detection for metolachlor, as compared to that of MOA, is not typical of groundwater samples from other areas in the U.S. and seems to indicate either that conversion to MOA is not the preferred pathway or that metolachlor is leached rapidly below areas of high microbial activity necessary for MOA formation.

The other degradate detected, degradate 9, was detected at relatively low frequency compared to those of MESA and metolachlor (**Table 2**). The rate of detection for degradate 9, MOA, and MESA increased with time and was highest in the well samples from noncover cropped well samples. The highest detection rate was in the last time period of the study, the 2002−2003 dry season (**Table 2**). Median concentration in this season was 0.006 μg L^{-1}. This value was 39- and 944-fold lower than the metolachlor and MESA medians, respectively. Thus, this degradate was only a minor constituent in water samples. None of the other degradates was detected during this period or at other times during the study.

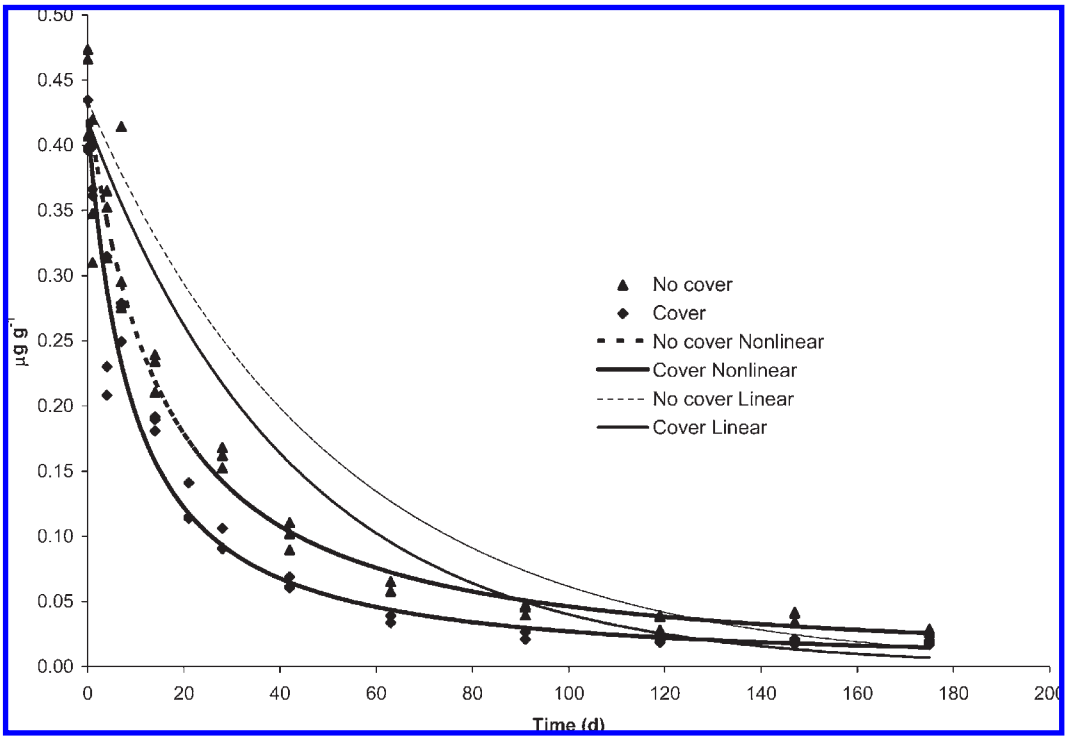

Figure 3. Metolachlor dissipation kinetics during soil incubation. Both nonlinear and linear modeled data are displaced along with actual measured data for cover cropped and noncover cropped soil.

As noted, the structural assignment of this compound was tentative and was based on MS data alone. Data indicated the closest match to that of a photooxidation product (*19*). To our knowledge, the compound has not been reported previously in natural water samples. Its production and leaching to groundwater at our study site was plausible. Solar radiation reported for the period immediately following metolachlor application to 2 weeks after for 2001 (16 Nov 01 to 30 Nov 01) and 2002 (20 Nov 02 to 4 Dec 02) averaged 518 and 445 Wm^{-2} between 10:00 and 14:00 Eastern Standard Time (*37*). Irradiating metolachlor for 30 min using simulated solar radiation at an intensity of 750 Wm^{-2} produced 16 compounds, including degradate 9 (*19*).

Metolachlor Soil Dissipation Kinetics. Metolachlor dissipated in soil with a mean ($n = 3$) calculated DT_{50} using the linear first-order kinetic model of 43 days for noncover cropped and 38 days for cover cropped treatments. These values were within the range of typical values obtained in laboratory incubation studies (*38*). The difference in the means between the soil of the cover cropped and noncover cropped soil was small, but statistically significant ($p = 0.0073$). The linear regression r^2 values were > 0.83 for cover cropped and > 0.89 for noncover cropped soil. Nonlinear regression of the natural log-transformed data was also evaluated. As reported for many dissipation studies, a superior data fit was obtained (*23*) (**Figure 3**). The nonlinear kinetic model improved the modeled data for both cover cropped soil ($r^2 = 0.98$; $DT_{50} = 9$) and noncover cropped soil ($r^2 = 0.98$; $DT_{50} = 14$). The linear regression data overestimated metolachlor levels during the first 90 days of the incubation and underestimated the concentrations later (> 100 days) in the incubation. This led to the lower predicted DT_{50} in the nonlinear model.

Among the degradates, only MESA, MOA, and hydroxymetolachlor were detected in soil extracts. MESA, MOA, and hydroxymetolachlor were detected in 64, 15, and 46% of the samples, respectively, and all three were detected in 11%. When all three were detected, MESA accounted for 36 to 46 mol %, MOA 18 and 28 mol %, and hydroxymetolachlor 27 and 43 mol %. The predominance of MESA during degradation and its high water solubility likely accounted for high rates of detection and relatively high concentrations in groundwater samples. When analyzed statistically by time, metolachlor levels were higher in the soil from noncover cropped treatments at 14, 28, 42, 63, 91, 147, and 175 d (**Figure 4**). At two time points, MESA levels were statistically greater in the noncover cropped soil (14 and 147 days) with the remainder of sample points being similar ($p > 0.05$). Cover cropped soil metolachlor values were never higher than those in noncover crop soil. The low levels of MOA and hydroxymetolachlor observed in the soil samples were not statistically different between noncover cropped and cover cropped plots ($p > 0.2286$ and $p > 0.0694$).

During incubation, the fraction of metolachlor recovered expressed as the molar sum of metolachlor, MESA, MOA, and hydroxymetolachlor declined rapidly in each soil type to a level of approximately 9 mol % at the end of the incubation (**Table 5**). If MESA and MOA data were corrected for 100% recovery, excluding nondetection, the molar sum value increases to about 11 mol %. The rapid decline of recoverable metolachlor residues indicated that up to 90% of the metolachlor applied could be mineralized or irreversibly bound to soil. Metolachlor, MESA, and MOA had DT_{50} of about 28 days in mineralization studies in cultivated or vegetative filter strip soils (*36*). A greater amount of metolachlor residues was recovered in the noncover cropped soil as compared to the cover cropped soil, with means of 40 and 33 mol % respectively. The time $\times$ treatment interaction was not significant ($p = 0.0754$).

Metolachlor dissipation has generally been concluded to be a biological process, with dissipation through multiple pathways accomplished by consortia of soil organisms (*39*). Several researchers have noted the incomplete metabolism and the lack of growth on metolachlor as a sole carbon and nitrogen source as evidence of cometabolism (*40*). At out study site, assuming field crop residue levels for sunn hemp of 5600 kg ha^{-1} (*41*) and 0.45 g carbon g^{-1} residue, carbon levels in soil would have increased by approximately 10% when residues are disked into soil. The increased carbon likely provided a suitable substrate to

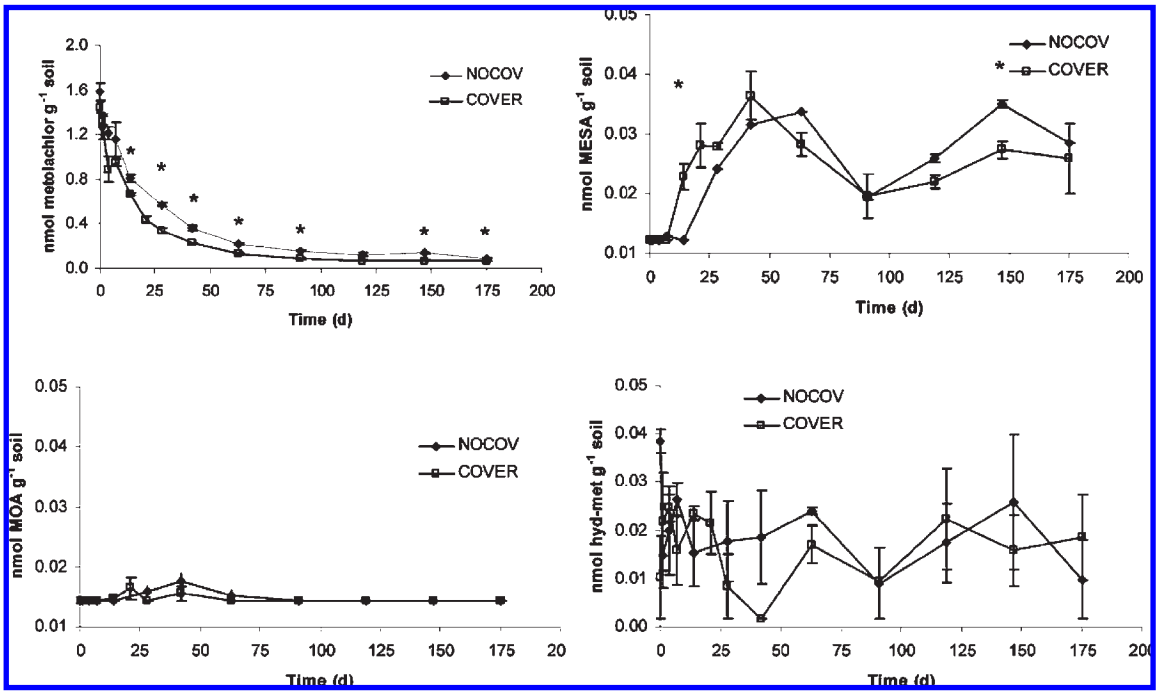

Figure 4. Metolachlor, MESA, MOA, and hydroxymetolachlor levels detected during soil incubation. Points are means ($n = 3$), and lines are ± 1 standard error of the mean. No 21 day samples were taken for the noncover crop soil, and $n = 2$ for the noncover crop soil on time = 63 days. Significant differences ($p < 0.05$) between noncover crop (NOCOV) and cover crop (COVER) samples are indicated with an asterisk.

Table 5. Fraction of Metolachlor Recovered from Noncover Crop and Cover Crop Soils during the Laboratory Incubation[a]

	NOCOV		COVER	
time	mean	SD	mean	SD
0 a[b]	0.938	0.075	0.843	0.052
1 b	0.744	0.114	0.781	0.031
4 c	0.716	0.048	0.533	0.114
7 c	0.689	0.155	0.562	0.040
14 d	0.481	0.038	0.411	0.009
21	nd	nd	0.285	0.038
28 e	0.356	0.026	0.221	0.025
42 f	0.241	0.019	0.158	0.014
63 g	0.165	0.012	0.109	0.011
91 g	0.113	0.013	0.074	0.010
119 g	0.104	0.024	0.073	0.007
147 g	0.121	0.016	0.072	0.010
175 g	0.081	0.012	0.070	0.013

[a] Values reflect the mole sum of metolachlor, MESA, MOA, and hydroxymetolachlor. nd = not determined. [b] Time points followed by the same letter are not different. Time = 21 was not included in the statistical analysis.

facilitate cometabolism as well as increased metolachlor sorption. Thus, more rapid dissipation and low leaching rates were expected in soil from the cover cropped treatment.

Water Quality Implications. Metolachlor was detected in >97% groundwater samples, more frequent than reported for groundwater in the Corn Belt states of Nebraska (<47%) or Iowa (<10%) (*9*, *31*) and likely reflects climatic, soil differences, and/or edge of field effects. Additionally, metolachlor concentration in groundwater below the noncover cropped plots increased with time, indicating persistence (**Tables 3** and **4**).

These data suggest the potential for off-site ecological impacts due to metolachlor leaching. For example, ground and surface water mixing occurs between the surficial aquifer and canals, which drain directly into Biscayne and Florida Bays and into the Everglades. Both atrazine and metolachlor were detected in 90% of canal samples in the area at low concentrations (1−100 ng L^{-1}); however, the large drainage area and high aquifer transmissivity (~28,000 m^2 d^{-1}) could potentially impact ecologically sensitive areas (*24*).

The highest metolachlor level observed in groundwater (7.2 μg L^{-1}) was about 100-fold less than the USEPA human health advisory level of 700 μg L^{-1} (*42*); thus, direct impact on drinking water quality was not indicated. However, the USEPA has listed MESA and MOA on the Contaminant Candidate List (CCL-3) for further evaluation into occurrence and health related impacts (*43*). While the ionic MESA and MOA metabolites are expected to be less toxic to humans, their persistence in the environment may affect aquatic organisms. Levels of MESA observed during the study were highest during the wet season of 2002 and about an order of magnitude greater than the sum of atrazine degradate levels observed for the same site (*6*). High levels of MESA are consistent with other observations that typically reported MESA as the most frequently detected pesticide in groundwater affected by agriculture (*9*, *18*). The observed increase is similar to observations of focused recharge (*31*); however, the drivers are different. In the Nebraska system, residual pesticides concentrate in low areas, and normal irrigation increases the leaching load; in Florida, the levels of pesticides dispersed in the vadose zone are rapidly leached into shallow groundwater by the summer rains.

Cover Crop Impacts. Beginning in the first wet season following metolachlor application, the compound's concentration was significantly lower in groundwater samples taken below cover cropped as opposed to noncover cropped plots (**Tables 3** and **4**). Data suggested that the cover crop reduced metolachlor leaching and groundwater loading. Several factors likely contributed including increased metolachlor sorption and a higher rate of degradation in the soil from cover cropped plots. The cover crop may also have reduced leaching by increasing evapo-transpiration and the water holding capacity of soil. In turn, deep drainage and leaching were presumably lower (*26*). The same processes were presumed responsible for the reduction of atrazine and the

concentration of the degradates DEA and DIA in groundwater that was associated with cover crop use (*6*). In these studies, the principal form of the parent compound detected in water quality samples was the degradate, DEA, and as reported, the cover crop contributed to low levels in groundwater beneath the cropped plots.

As was the case with atrazine, the principal form of metolachlor detected in groundwater was a degradate, which in this case was MESA. Concentration trended lower in groundwater beneath the cover crop plots. Medians, when evaluated on a seasonal basis, were significantly lower in cover versus no cover crop plot well samples. A combination of the factors described above likely contributed to this observation.

Large rainfall events (>2.54 cm) occurred on 6 December, 2001 [20 days after planting (DAP)], 9 February, 2002 (85 DAP), and 28 May, 2002 (193 DAP). By using the nonlinear first order model, calculated noncover cropped to cover cropped metolachlor ratios in soil were 1.5, 1.7, and 1.8 at these times. The residual metolachlor, especially in the noncover cropped plots, would be available for leaching coinciding with the large rainfall events and could explain the elevated metolachlor in groundwater wells below noncover cropped plots. Residual soil metolachlor in May 2002 and 2003 (beginning of the rainy season) would be about 0.028 and 0.016 μg g^{-1} for noncover cropped and cover cropped soils, respectively.

Potential differences in groundwater loading of metolachlor and its degradates between treatments were evaluated by computing the area beneath the concentration over time plots for metolachlor and for the molar sum of metolachlor and degradates. An inherent assumption in this evaluation was that groundwater flow across the study site was uniform. This was also indicated by observations on hydroxyatrazine behavior in a prior study (*6*). For metolachlor, the computed area (average of three plots), i.e., relative load, in groundwater beneath the cover cropped plots, was about 3.2 times lower than that beneath the noncover cropped plots ($p = 0.1229$). When the degradates (MESA, MOA, and degradate 9) were included, the average computed load was 1.7 times lower beneath the cover crop plots ($p = 0.0597$). Overall data indicated that the cover crop contributed to a 68% reduction in metolachlor leaching. The reduction was 41% when metolachlor and degradates were summed.

Conclusions. Metolachlor and several degradates, in particular MESA, were detected at elevated levels in groundwater beneath cropped plots. Data indicated that shallow groundwater contamination is likely during the herbicide's normal agricultural use in the region. Data also showed that metolachlor and degradate concentrations were significantly lower beneath cover cropped plots as compared to those in noncover cropped plots, which reduced the concentration of metolachlor and MESA reaching groundwater. Estimates indicated that groundwater loading with the compounds was reduced by 41% through cover crop use. Several factors including increased sorption and an increased dissipation rate in soil likely explained this result. Use of cover crops during fallow periods in this environment appears to be an effective practice for the protection of shallow groundwater quality from metolachlor and other products during crop production.

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