Solute Transport in Eroded and Rehabilitated Prairie Landforms. 2. Reactive Solute

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The impact of varying soil, landscape, and climate conditions on the off-site transport of pesticides must be determined to develop improved pesticide management practices. This study quantified the rate of *S*-metolachlor dissipation after fall and spring application in eroded and rehabilitated landforms in which topsoil was moved from the lower slope to the upper slope. Fall-applied metolachlor provided no control of annual grasses because ~80% was removed from the root zone during the winter and early spring, presumably by leaching and runoff. *S*-Metolachlor dissipated in the spring with a DT_{50} of 24−29 days. These results suggest that fall-applied metolachlor may not provide economic weed control and presents an increased risk of water contamination. Although landscape position and bulk soil movement within the landform had a large impact on soil properties, no significant differences in metolachlor dissipation between different landscape positions and between eroded and rehabilitated landforms were observed.

KEYWORDS: Frozen soil; leaching; metolachlor; soil-landscape rehabilitation; slope; weed control

INTRODUCTION

Widespread detections of low concentrations of acetanilide herbicides (acetochlor, alachlor, and metolachlor) and their breakdown products in groundwater (*1*) and surface water (*2, 3*) indicate that these herbicides are prone to leaching and runoff under some conditions. Extensive water monitoring has suggested that herbicide transport to surface water shortly after application may be a source of alluvial groundwater contamination (*3*). The temporal transport of herbicides to surface water has been observed to be largely independent of herbicide properties (*4, 5*). Quantifying the impact of varying soil, landscape, and climate conditions on the off-site transport of pesticides is critical to the development of management practices that maintain pest control efficacy while preventing soil, water, and air contamination by pesticides.

Soils in the northern Corn Belt are very productive, but affected by erosion. Soil is redistributed by tillage and water erosion in the hilly landscapes typical of the North American prairies. Long-term (~100 years) cultivation of prairie landforms has resulted in exposed subsoil in eroded upper slope positions, with low organic carbon contents throughout the profile. Net deposition of soil in areas of decreasing slope results in relatively high organic carbon and nutrient concentrations throughout the upper profile and a large depth to the C horizon (*6*). In such landforms, crop yields are spatially variable, corresponding with the variation in soil properties (*6*). Soil-landscape rehabilitation, in which topsoil is moved from areas of net accumulation (lower slope) to areas of net soil loss (upper slope), has been shown to increase crop yields in eroded portions of hilly landscapes (*7*).

The variation in soil properties with landscape position results in spatially variable pesticide sorption and degradation. Herbicide sorption coefficients in surface soil tend to be highest in depressional areas (where topsoil accumulates as a result of erosion and organic carbon contents are high) and lowest in upper slope positions that are low in organic carbon; sorption coefficients in the backslope have been observed to be intermediate between those in upper and lower slope positions (*8−10*). Pesticide degradation rates are also spatially variable in both surface soil and subsurface soil (*9, 11, 12*). The rate of mineralization of several herbicides in surface soil was significantly faster in the upper slope than in the lower slope (*9, 12*).

Estimates of pesticide sorption and degradation determined under static conditions in the laboratory may not be relevant under the dynamic conditions existing in the field. Lennartz (*13*) evaluated pesticide and tracer transport at a constant water flux density in a series of undisturbed soil cores collected from a 1.8 ha field and reported that pesticide mobility was more dependent on unsaturated water flow characteristics than on the soil's sorption capacity for the studied pesticides. Water and sediment fluxes vary with landscape position (*14*). Rapid transport of precipitation to surface water, influenced by topography and other factors, was more important in determining herbicide concentrations in surface water than were variable sorption coefficients and degradation rates (*15*). In eroded landforms, soil chemical and physical properties that influence water relations (infiltration, retention, and runoff) and pesticide fate are highly variable with landscape position (*6, 7*). Sophisticated process-based models exist that are theoretically capable of simulating spatially variable pesticide behavior on a field scale, but information regarding the

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relative importance of soil properties, topography, climatic conditions, and other factors is required to improve and validate transport models and to enable informed risk assessments.

A companion paper (*16*) discusses the dynamics of dissipation of the nonreactive solute bromide in eroded and rehabilitated landforms. Results suggested that water flux removed much of the applied bromide from the root zone by leaching and runoff during the winter and early spring. Bromide results suggested that downward water flux was sufficient to distribute bromide to at least a depth of 1 m during the winter and early spring and that at least part of the overwinter loss of bromide ($\sim$24 kg ha^{-1}) was through leaching beyond 1 m. In contrast, increased evapotranspiration limited downward flux of bromide during crop growth. Soil-landscape rehabilitation produced large changes in soil properties, but had little observable effect on bromide dissipation (*7*, *16*). This study was conducted simultaneously with the bromide evaluation to quantify the dissipation and weed control efficacy of fall- and spring-applied *S*-metolachlor (a reactive solute) as a function of soil properties and landscape position in eroded and rehabilitated landforms typical of the northern Corn Belt.

Metolachlor is one of the most frequently detected agricultural herbicides in groundwater (*1*) and surface water (*17*) in the United States. Metolachlor has been observed to be more highly sorbed (*18*) but more persistent (*19*) than other chloracetanilide herbicides. *S*-Metolachlor (Dual Magnum) is labeled for control of grasses and certain broadleaf weeds in corn, soybean, and other crops. Chloracetanilide herbicides are applied preemergence and inhibit plant growth after germination, such that seedlings are stunted and often do not emerge from the soil (*20*). Despite the recent preponderance of glyphosate use, metolachlor is still frequently used in corn and soybean production. *S*-Metolachlor ranked fourth among all agricultural herbicides (after glyphosate, acetochlor, and atrazine) in the amount of active ingredient sold in Minnesota in recent years, 2001−2007 (*21*). According to the label, *S*-metolachlor may be applied in the fall or spring in Minnesota and its neighboring states; however, there is very little information regarding the fate of fall-applied metolachlor in this region.

MATERIALS AND METHODS

Site. Experiments were conducted in west central Minnesota in a landform including a drained prairie pothole. The site was separated into replicate plots extending from the summit to the toeslope. Each plot was segmented into six landscape positions, which are designated as subplots: summit, shoulder, upper backslope, lower backslope, footslope, and toeslope. Three of the plots were rehabilitated in November 2005 by moving 15−20 cm of soil from the footslope and toeslope and adding 15−20 cm of soil to the summit, shoulder, and upper backslope. Soil-landscape rehabilitation resulted in a large change in soil organic carbon concentrations in the top 20 cm of the soil profile in areas of soil addition (**Figure 1**). Other details regarding the site are given in Papiernik et al. (*16*). The site was cropped to soybean in the growing season preceding this study. Anhydrous ammonia (130 kg of N ha^{-1}) was applied in the fall, and granular fertilizer (240 kg ha^{-1} of 27−70−40) was applied on May 10, 2007. Corn (DeKalb 4492) was planted on May 12, 2007, at a seeding rate of 79000 seeds ha^{-1} with a row spacing of 76 cm. Weather conditions prevailing during the study are given in Papiernik et al. (*16*). Soil temperature was monitored at 1 h intervals using temperature logging devices buried at a depth of 5 cm. Loggers were removed for field operations from April 30 to May 14.

Metolachlor Application. Herbicide solution included metolachlor (formulated as Dual II Magnum), potassium bromide, and an antifoaming agent. Portions of each subplot were treated with *S*-metolachlor according to label instructions in the fall
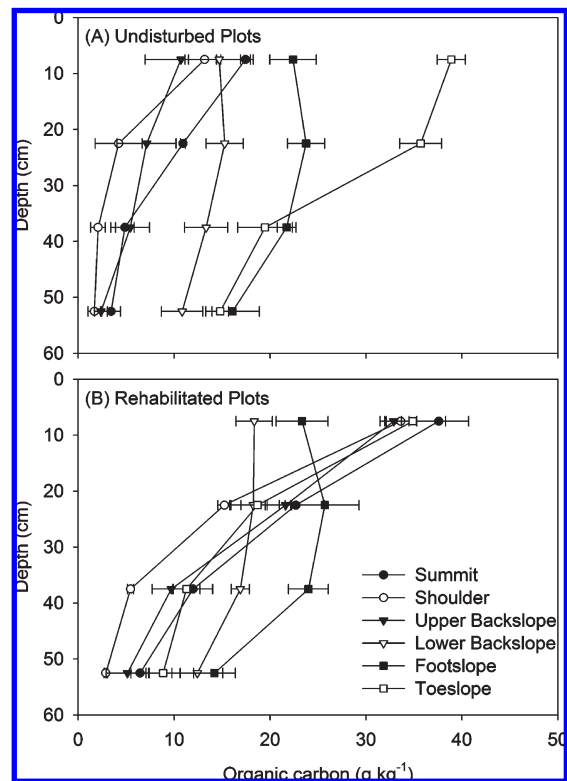
Figure 1. Organic carbon distribution as a function of depth in each landscape position of (**A**) undisturbed plots and (**B**) rehabilitated plots.

(November 7, 2006) at a rate of 1.95 L ha^{-1} (1.8 kg of active ingredient ha^{-1}). Separate portions of each subplot were treated in the spring (preemergence, May 17, 2007) at the same rate. Herbicide and bromide tracer were applied simultaneously (190 L ha^{-1}) using a hooded sprayer with a 3 m wide boom and flat-fan nozzles at 0.21 MPa and not incorporated. Soil temperatures (5 cm depth) during application were 5−7 °C (fall application) and 12−15 °C (spring application). The actual rate of metolachlor applied to each subplot was monitored by collecting spray samples during application. Metolachlor application rates were consistent across landscape positions ($p > 0.05$) for both the fall and spring applications.

Soil Sampling. Soil cores were collected to a depth of 1 m immediately before metolachlor application and throughout the growing season. Soil cores were collected 0, 14, 175, 203, and 226 days after fall application (November 7 and 21, May 1 and 29, and June 21) and 0, 7, 22, and 41 days after spring application (May 17 and 24, June 8 and 27). Samples were segmented into increments of 0−10, 10−20, 20−40, 40−60, and 60−100 cm depths. Details regarding sample collection and sample processing are provided in Papiernik et al. (*16*).

Metolachlor Analysis. A Zymark laboratory robotic system was used to extract metolachlor from soil (*22*). In brief, 10 g of soil, treated with propachlor as a surrogate chemical, was shaken with 20 mL of aqueous methanol (4:1 methanol/water v/v) and then allowed to statically equilibrate overnight. The soil + solution slurry was centrifuged and the supernatant removed. An equal volume of aqueous methanol was added to the soil and reequilibrated. The supernatants were combined, and the methanol was removed by evaporation at 40 °C. The remaining water was passed through preconditioned C18 solid phase extraction cartridges. The metolachlor was then eluted with solvent containing metazachlor as an internal standard and transferred to a vial for analysis.

The samples were analyzed by gas chromatography−mass spectrometry (GC-MS) using an Agilent 5973 mass selective detector coupled to a 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) fitted with a split−splitless injector and

a HP-5MS capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The injection volume was 2 μL. The column was held at 40 °C for 3 min, after which the oven temperature was increased to 250 °C at 20 °C min^{-1} and then held for 5 min. The column was directly connected to the ion source of the mass spectrometer through a heated transfer line maintained at 280 °C. Electron impact (EI) mass spectra were obtained at 70 eV with the instrument scanning from 100 to 300 atomic mass units and the source maintained at 230 °C.

For confirmation and quantification, the GC-MS was operated in selected ion monitoring mode. For confirmation, retention time (RT) and at least two characteristic ions (m/z) were used; metolachlor RT = 13.0 min, m/z 238, 162, and 146; propachlor (surrogate) RT = 11.0 min, m/z 176 and 120; and metazachlor (internal standard) RT = 13.4 min, m/z 209 and 133. Quantification was based on the sum of the abundances of the ions monitored, which were converted to concentrations by external standard calibration. Blanks and standards were analyzed before, during, and after each set of samples. In preliminary studies using soils with OC contents similar to the highest OC content soils in the present study, metolachlor recovery from soils freshly treated with normal metolachlor application rates was > 85%. Soil concentrations were not adjusted for recovery.

Weed Population Monitoring. Weed populations were monitored in each subplot for each herbicide treatment. A 0.25 m^2 quadrat was randomly placed, and the number of weeds present within the quadrat was counted. Weed populations were determined on May 31 and June 14, 2007. Broadleaf weeds were identified to the species level; grassy weeds were not further identified.

Data Analysis. The concentration of metolachlor was determined in fresh soil. The mass of metolachlor in each soil sample was calculated from the metolachlor concentration in field-moist soil, the moisture content of the soil sample, and the mass of dry soil in each sample. Because the diameter of the soil sampler used for the 0−10 cm depth increment was larger than the diameter of the soil probe used for the 10−100 cm increments, the mass of metolachlor per surface area (μg cm^{-2}) was calculated.

The sum of the mass/surface area of metolachlor in each depth increment was used to calculate dissipation rates. The mass/surface area in the top 1 m for each soil core was normalized to the maximum value in each subplot to calculate the proportion of each analyte remaining in the root zone at each sampling time. The maximum mass/surface area was measured on the day of application in most cases; otherwise, the maximum mass/surface area was not significantly different from that on day 0. To determine dissipation rates, a first-order kinetic model was fit to the normalized mass/surface area in the top 1 m. For fall application, the dissipation rate was determined from t = 175 days to t = 226 days to facilitate comparison with the spring application.

Statistical Analyses. Treatments (fall, spring, or no metolachlor application) were imposed on three replicate rehabilitated plots and three replicate undisturbed plots. Landscape position was a blocking factor. ANOVA was used to evaluate the effects of landscape position and soil-landscape rehabilitation on application rates, relative metolachlor concentrations, and weed populations. Treatment differences were evaluated using Tukey's test (α = 0.05). Paired t tests were used to determine differences in normalized mass/surface area values for metolachlor and bromide in the same soil core.

RESULTS AND DISCUSSION

Metolachlor Dissipation from the Root Zone. Herbicide application resulted in surface soil (0−10 cm) metolachlor concentrations of 6.5 ± 0.3 μg g^{-1} (fall application) and 6.7 ± 0.3 μg g^{-1} (spring application). For both the fall and spring applications, relative metolachlor values were the same in all landscape positions, and soil-landscape rehabilitation had no significant effect on relative metolachlor values at each sampling time
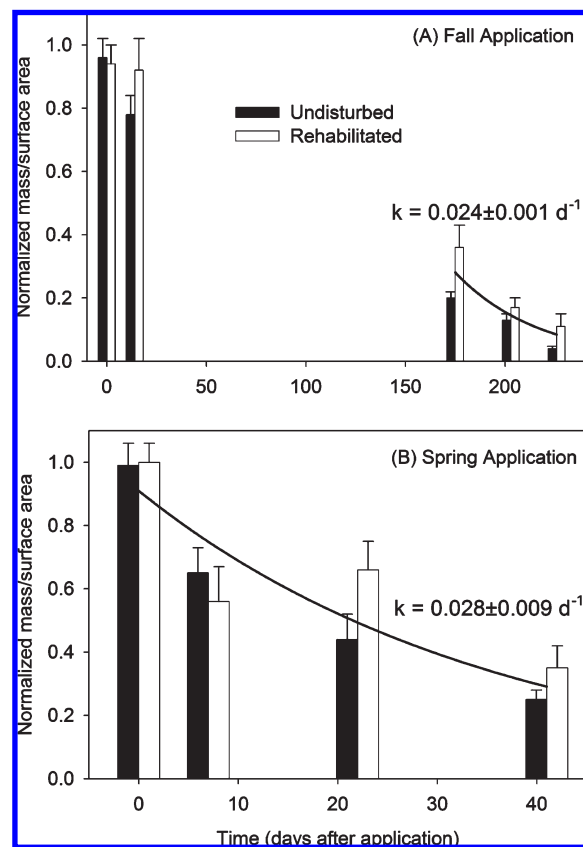
Figure 2. Dissipation of *S*-metolachlor applied in the (**A**) fall and (**B**) spring to undisturbed and rehabilitated landforms. Values are the mean across six landscape positions; error bars indicate standard error. Relative mass/surface area values were not significantly different in undisturbed and rehabilitated plots; lines indicate first-order fit to the mean normalized mass/surface area.

(Figures S1−S4 of the Supporting Information). In the same study, no significant differences were observed for bromide as a function of landscape position and soil-landscape rehabilitation (*16*).

Fall Application. The relative amount of metolachlor remaining 2 weeks after fall application was ∼85% of that applied (**Figure 2A**). Little transport or degradation of metolachlor was expected during this time because soil temperatures were low (average 2 °C) and there was no measurable precipitation (**Table 1**). The average soil temperature (5 cm depth) was < 0 °C each day from November 29 to March 11. Soil temperatures increased steadily throughout the early spring so that the daily average soil temperature was 9 °C on April 30.

Soil samples collected in the spring showed that most of the fall-applied metolachlor and bromide had been depleted from the top 1 m during the winter. The relative mass/surface area of metolachlor remaining in the top 1 m on the first sampling day of the spring (May 1, 175 days after application) was 0.28 ± 0.04 (**Figure 2A**). Paired t tests showed that the relative amounts of metolachlor and bromide remaining in the top 1 m of soil were the same on this (and previous) sampling dates. The overwinter depletion of bromide from the top 1 m was attributed to leaching and runoff (*16*). The similar behavior observed for bromide and metolachlor suggests that the primary route of metolachlor dissipation from November through April was transport out of the root zone rather than degradation; there was no opportunity for plant uptake during this time. The overwinter loss of metolachlor was greater than that observed by Sharratt et al. (*23*) in

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Table 1. Precipitation and Average Soil Temperature (5 cm Depth) between Soil Sampling Episodes[a]

days after application	date range	soil T (°C)	precipitation (mm)
	Fall Application		
0−14	Nov 7−21, 2006	2.1 ± 0.2	0
15−175	Nov 22, 2006−May 1, 2007	−2.0 ± 0.2	212
176−203	May 2−29, 2007	17.7 ± 0.2[b]	41
204−226	May 30−June 21, 2007	21.5 ± 0.2	131
	Spring Application		
0−7	May 17−24, 2007	17.7 ± 0.3	6
8−22	May 25−June 8, 2007	18.2 ± 0.1	108
23−41	June 9−27, 2007	24.4 ± 0.1	24

[a] Temperature values are the mean of two undisturbed and two rehabilitated plots at five landscape positions (summit, shoulder, upper backslope, footslope, and toeslope) ± standard error. [b] Soil temperature loggers were removed for field operations on April 30 and replaced on May 14. Soil temperature values are for May 14−29.

Minnesota, who reported a 25−30% decrease in metolachlor from soil columns placed in the field over the winter. In that study, runoff was limited because the column walls extended above the soil surface; the decrease in metolachlor was attributed to degradation because runoff was restricted and no leaching of metolachlor to depths of >10 cm was observed (*23*).

During the growing season, fall-applied metolachlor was depleted more quickly than bromide from the root zone. On May 29 (203 days after application), the average mass/surface area remaining in the root zone was 15% of the applied metolachlor and 30% of the applied bromide. On June 21, the final sampling date for the fall application, an average of 8% of the applied metolachlor and 24% of the applied bromide remained in the top 1 m of the soil profile. Metolachlor presumably dissipated during the growing season by degradation, transport, and plant uptake. Dissipation of fall-applied metolachlor proceeded in the spring with an approximate DT_{50} of 29 ± 1 days (**Figure 2A**).

Spring Application. As observed for the fall application, landscape position had no effect on relative bromide and relative metolachlor values after spring application (Figures S3 and S4 of the Supporting Information). Rainfall of only 6 mm occurred during the first 7 days after spring application (**Table 1**), and there was no significant decrease in the mass/surface area of bromide in the top 1 m (*16*). In contrast, the mass/surface area of metolachlor decreased by approximately 40% during the first 7 days after application (**Figure 2B**). Unlike the fall application, soil conditions during the spring application were favorable for metolachlor degradation. The average soil temperature (5 cm depth) during the first 7 days after application was 18 °C (**Table 1**) and the average surface soil (0−10 cm depth) moisture was 0.16 g g^{-1} in undisturbed plots and 0.20 g g^{-1} in rehabilitated plots. Volatilization of metolachlor from moist soil may be an important route of dissipation at relatively high soil temperature (*24*), but is not expected to be a major route of dissipation during the first 7 days of this study.

At 22 and 41 days after application, there was no significant difference in relative metolachlor and relative bromide amounts remaining in the root zone. Spring-applied metolachlor dissipated with an approximate DT_{50} of 24 ± 12 days (**Figure 2B**), which is similar to that observed for the dissipation of the fraction of fall-applied metolachlor that remained in the root zone in the spring (DT_{50} of ~29 days, **Figure 2A**). These observed metolachlor dissipation rates are consistent with previous reports (half-lives from 17 to >50 days) for the dissipation of spring-applied

metolachlor determined in field studies under a variety of cropping, soil, and climatic conditions (*4, 19, 22, 25−27*). During the same time frame, bromide dissipated with a DT_{50} of 27 ± 9 days (data not shown). Bromide and metolachlor were depleted from the root zone at the same rate during the first part of the growing season. Solute leaching out of the root zone was minimal after crop establishment, and plant uptake accounted for most of the bromide loss from soil during the spring (*16*). Metolachlor uptake by corn is primarily through the shoot (*28*) and accounted for 55% of the applied ^{14}C-metolachlor within 15 days after emergence in small-pot studies (*29*). Thus, plant uptake may have been a significant route of metolachlor dissipation from the top 10 cm of soil in these experiments. In these studies, metolachlor degradation and plant uptake likely acted together to result in a dissipation rate similar to that for a nonreactive tracer, which was primarily dissipated through plant uptake.

Depth Distribution. Although bromide and metolachlor followed similar trends in their overall dissipation from the top 1 m of soil, they showed markedly different depth distributions. Whereas a significant fraction of the applied bromide leached to depths of >10 cm (*16*), very little metolachlor was detected at depths of >10 cm (Figures S1−S4 of the Supporting Information). Leaching of the parent compound below 10 cm accounted for <10% (fall application) or <4% (spring application) of the applied metolachlor at each sampling time at each landscape position. Low concentrations (≤0.1 μg g^{-1}) of fall-applied metolachlor were detected at depths of >60 cm in the spring, but the highest concentrations were detected in the surface soil (0−10 cm) at all sampling times. These results are consistent with previous reports for fall-applied metolachlor, which was not detected at depths of >10 cm the following spring (*23*).

In this study, we observed very few detections of spring-applied metolachlor at depths of >40 cm. Other researchers have reported no detection of spring-applied metolachlor in soil at depths of >30 cm (*22, 25*), but leaching of spring-applied metolachlor to depths of >60 cm has been reported under a variety of conditions (*27, 30, 31*). In another study in Minnesota, spring-applied metolachlor was not detected at depths of >30 cm but bromide was detected at depths of >1 m (*22*), consistent with the results of this study, which showed more downward movement of bromide than of metolachlor. In this study, only the parent herbicide compound (metolachlor) was analyzed. The primary metabolites of metolachlor, metolachlor OA and metolachlor ESA, were not analyzed in this study, but are more commonly detected in groundwater (*32, 33*) and surface water (*2*) than the parent compound and are considered to be more mobile than the parent compound (*34*).

Landscape Position Effects. Soil processes that affect herbicide dissipation, such as herbicide sorption and transformation rates, have been reported to be dependent on soil properties that vary with landscape position (*8−12*). Large differences in soil properties occur in the studied landform, including soil organic carbon contents that vary by up to a factor of 4 (**Figure 1**), but the rates of metolachlor and bromide dissipation from the top 1 m were essentially the same at all landscape positions. Others have reported that some herbicides, including the chloracetanilide alachlor, dissipated at approximately the same rate in different soil types within the same landform, but soil properties in those studies were generally not as variable as in this study (*9, 27, 35*). There is interest in using spatially variable estimates of sorption and degradation rate in risk assessments (*36*). The results of this research suggest that even when soil properties vary dramatically, other factors may be more important in determining the overall rate of herbicide dissipation. Thus, additional research is required to discern the relative importance of soil properties that affect

pesticide sorption and degradation, soil and topographic effects on soil−water movement, temporal effects of plant uptake, and other factors in determining the fate and transport of herbicides in spatially variable landscapes.

Weed Control Efficacy. Broadleaf weed populations were dominated by lambsquarters (*Chenopodium album*), which metolachlor does not control. There were approximately 15 annual grasses m^{-2} on May 31 (19 days after planting), with no differences between areas treated with metolachlor (fall or spring application) and those with no herbicide application. Populations of grassy weeds in areas treated with spring-applied metolachlor were unchanged at 32 days after planting (June 14), whereas populations increased by approximately a factor of 3 (to 40 annual grasses m^{-2}) in areas treated with fall-applied metolachlor or no herbicide. Weed populations were highly variable 32 days after planting, and no significant differences were observed in herbicide-treated plots between different landscape positions or between undisturbed and rehabilitated plots. There was no significant difference in the number of grassy weeds in plots treated with fall-applied metolachlor and plots receiving no herbicide. In these trials, fall-applied metolachlor dissipated prior to spring planting and provided no control of annual grasses.

ACKNOWLEDGMENT

Supporting Information Available: Mass/surface area and depth distribution of metolachlor remaining in the top 1 m of soil following (a) fall application to undisturbed plots; (b) fall application to rehabilitated plots; (c) spring application to undisturbed plots; and (d) spring application to rehabilitated plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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