

Spatial Variability of Atrazine and Metolachlor Dissipation on Dryland No-tillage Crop Fields in Colorado

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An area of interest in precision farming is variable-rate application of herbicides to optimize herbicide use efficiency and minimize negative off-site and non-target effects. Site-specific weed management based on field scale management zones derived from soil characteristics known to affect soil-applied herbicide efficacy could alleviate challenges posed by post-emergence precision weed management. Two commonly used soil-applied herbicides in dryland corn (*Zea mays* L.) production are atrazine and metolachlor. Accelerated dissipation of atrazine has been discovered recently in irrigated corn fields in eastern Colorado. The objectives of this study were (i) to compare the rates of dissipation of atrazine and metolachlor across different soil zones from three dryland no-tillage fields under laboratory incubation conditions and (ii) to determine if rapid dissipation of atrazine and/or metolachlor occurred in dryland soils. Herbicide dissipation was evaluated at time points between 0 and 35 d after soil treatment using a toluene extraction procedure with GC/MS analysis. Differential rates of atrazine and metolachlor dissipation occurred between two soil zones on two of three fields evaluated. Accelerated atrazine dissipation occurred in soil from all fields of this study, with half-lives ranging from 1.8 to 3.2 d in the laboratory. The rapid atrazine dissipation rates were likely attributed to the history of atrazine use on all fields investigated in this study. Metolachlor dissipation was not considered accelerated and exhibited half-lives ranging from 9.0 to 10.7 d in the laboratory.

SITE-SPECIFIC management of a crop field requires that the variability associated with factors that limit productivity be spatially characterized. If such factors vary across a field at an agronomically significant level, the use of site-specific or precision farming techniques may be beneficial. One area of interest in precision farming is variable-rate application of herbicides to optimize herbicide use efficiency and minimize negative off-site and non-target effects.

The conventional approach to herbicide application is to treat an entire field uniformly. Recent studies have suggested that herbicides might be applied differentially according to spatially varying soil properties (Jaynes et al., 1995; Gaston et al., 2001; Williams et al., 2002). Herbicide bioavailability is affected by soil pH, cation exchange capacity, texture, and organic matter, all of which vary spatially across a crop field (Novak et al., 1997; Gaston et al., 2001; Williams et al., 2002; Liu et al., 2002). For instance, more atrazine is needed with a lower soil pH, increasing organic matter, and finer soil texture due to higher rates of herbicide sorption (Novak et al., 1997). Gaston et al. (2001) recommended that to maintain weed control, higher rates of herbicides should be applied in areas with higher clay and organic C. Liu et al. (2002) illustrated that the efficacy of atrazine and alachlor varied spatially across fields due to differences in sorption, persistence, and degradation depending on soil properties and landscape position. Liu et al. (2002) also reported that the atrazine mineralization rate (i.e., decomposition of the s-triazine ring of atrazine) was spatially positively correlated to weed biomass (Liu et al., 2002). The findings of Gaston et al. (2001) and Liu et al. (2002) suggest that poor herbicide efficacy may explain why some weeds occur in patches.

There have also been studies focused on characterizing the spatial variation of herbicide dissipation (Vischetti et al., 1997; Liu et

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Abbreviations: DAT, days after treatment; DGPS, differential global positioning system; EC_a, apparent electrical conductivity; EC_{4cm}, shallow soil apparent electrical conductivity; GC/MS, gas chromatography/mass spectrometry; ISODATA, iterative self-organized data analysis technique; SOM, soil organic matter.

al., 2002; Muller et al., 2003; Charney et al., 2005; Bending et al., 2006). Liu et al. (2002) and Charney et al. (2005) reported high spatial variability for atrazine mineralization. Vischetti et al. (1997) found the dissipation of chloridazon and metamitron to vary considerably within their study sites, which they attributed to variation in soil properties.

An approach to rapidly and accurately mapping soil properties at the field scale that influence herbicide efficacy is the use of geo-referenced soil apparent electrical conductivity (EC_a) measurements (Johnson et al., 2001). Soil EC_a has been correlated to soil texture (Williams and Hoey, 1987), water content (Kachanoski et al., 1988), soil salinity (Rhoades et al., 1989), and crop yield (Kitchen et al., 1999; Heermann et al., 1999). Furthermore, soil EC_a maps have been correlated to atrazine sorption coefficients (Jaynes et al., 1995). Specifically, the use of shallow soil apparent electrical conductivity (EC_{s-sh}) measurements, which are an average of the soil EC_a from the top 30 cm of the soil profile (Farahani et al., 2003), could accurately describe the variation in topsoil properties that may affect soil applied herbicide efficacy.

Dividing a field into subunits or zones based on soil properties that can be managed variably in terms of productivity potential has been extensively studied on irrigated crop fields in the semiarid Western Great Plains (Fleming et al., 2000; Khosla et al., 2002; Koch et al., 2004; Mzuku et al., 2005; Inman et al., 2005). However, little work has been done to delineate fields into herbicide management zones, especially in dryland environments in this region. Soil EC_a maps are one way to rapidly characterize the soil variability in a field. These maps could be used to delineate zones across a field to which differential rates of herbicide could be applied based on soil properties.

Atrazine (6-chloro-4-(ethylamino)-6-isopropylamino)-s-triazine) is a selective herbicide used in corn (*Zea mays* L.) production to control broad-leaved weeds and some grass species. Atrazine kills plants by inhibiting photosynthesis and is typically applied pre-emergence to the soil for early-season weed control. Producers expect early-season weeds to be controlled by atrazine for approximately 40 d after application to the soil. Metolachlor (2-chloro-*N*-(6-ethyl-*o*-tolyl)-*N*-(2-methoxy-1-methylethyl) acetamide) is also used as a soil-applied herbicide in corn and is commonly tank mixed with atrazine. Metolachlor kills plants by inhibiting very long-chain fatty acid biosynthesis (Matthes et al., 1998) and controls many grasses and small-seeded broad leaf weeds.

A growing concern of producers in the Western Great Plains in the USA is the accelerated degradation of atrazine resulting in the loss of residual weed control. Shaner and Henry (2007) recently reported rapid atrazine dissipation in irrigated corn fields of eastern Colorado, USA. Additionally, there have been several studies showing enhanced degradation of atrazine in other parts of the USA (Stolpe and Shea, 1995; Zablotowicz et al., 2006), Europe (Barriuso and Houot, 1996), Australia (Popov et al., 2005), and New Zealand (Aislabie et al., 2004). In all cases, the authors of these studies attributed the accelerated degradation to adapted microflora selected by repeated atrazine applications. Furthermore, soil

properties such as pH, organic C, and nitrogen availability can influence the behavior of atrazine mineralization in soils with adapted microbial populations (Houot et al., 2000; Abdelhafid et al., 2000a, 2000b). The behavior of metolachlor in soils has been reported to vary with the addition of organic amendments (Moorman et al., 2001) and with repeated exposure (Sanyal and Kulshrestha, 1999).

No work has been performed on the variability of dissipation of atrazine or metolachlor in soil taken from dryland fields in the Western Great Plains region. Moreover, documenting accelerated herbicide dissipation in these dryland environments is of scientific and agronomic importance to producers so they can alter weed management practices by instituting variable-rate herbicide application and by avoiding herbicides that are rapidly degraded. The objectives of this study were to (i) compare the rates of dissipation of atrazine and metolachlor under laboratory conditions from different soil EC_{s-sh}-derived zones and (ii) to determine if rapid dissipation conditions of atrazine and/or metolachlor occurred in soil from dryland fields.

Materials and Methods

Study Fields

This study was conducted on soil collected from three dryland, no-tillage fields in northeastern Colorado. Fields in this study, referred to as Fields 1 through 3, ranged in size from 32.2 to 54.4 ha. The predominant soil type in all study fields was Weld silt loam (USDA, 2006). The Weld soil series is a deep, well drained soil with slopes ranging from 0 to 8%. The official taxonomic class for the Weld series is fine, smectitic, mesic Aridic Argiustolls (Soil Survey Staff, 1986).

Field 1 was under dryland, no-tillage crop production for at least the previous 10 yr before conducting this study. A variety of crops had been rotated on this field, including corn (*Zea mays* L.), winter wheat (*Triticum aestivum* L.), proso millet (*Panicum miliaceum* L.), and confection sunflower (*Helianthus annuus* L.) (R. Lewton, personal communication, 2006). Fields 2 and 3 were in no-till dryland crop production since 1990, and both were in winter wheat-corn-fallow rotations (D. Wagers, personal communication, 2006). Herbicides applied for all fields for the 5 yr before conducting this study are summarized in Table 1.

Soil EC_{s-sh} Zone Delineation

Soil zones based on EC_{s-sh} were derived for each field to delineate areas representing homogeneous surface soil properties. Soil EC_{s-sh} was measured as the average apparent electrical conductivity for the top 30 cm of the soil profile, and geo-referenced data were collected using a Veris 3100 Soil EC Mapping System (Veris Technologies, Salina, KS) in conjunction with a Trimble Ag132 differential global positioning system (DGPS) receiver. The instrument collected over 8000 soil EC_{s-sh} measurements within each field by pulling it behind a vehicle traveling at speeds between 13 and 24 km h⁻¹. The average distance between two swaths of data for all fields in this study was 12 m. Field 1 data were collected in September

Table 1. Herbicide use history for each field in this study from 2001 to 2006.

Year	2001	2002	2003	2004	2005	2006†
Herbicides	prosulfuron	glyphosate; 2,4-D	<u>Field 1</u> glyphosate; 2,4-D w/ 2-ethylhexyl ester	atrazine; s-metolachlor; glyphosate	glyphosate; sulfentrazone	glyphosate; 2,4-D
Herbicides	glyphosate; 2,4-D; atrazine	glyphosate; 2,4-D; dicamba	<u>Field 2</u> metsulfuron methyl or tribenuron methyl; 2,4-D	glyphosate; 2,4-D; atrazine	glyphosate; 2,4-D; dicamba	metsulfuron methyl or tribenuron methyl; 2,4-D
Herbicides	metsulfuron methyl or tribenuron methyl; 2,4-D	glyphosate; 2,4-D; atrazine	<u>Field 3</u> glyphosate; 2,4-D; dicamba	metsulfuron methyl or tribenuron methyl; 2,4-D	glyphosate; 2,4-D; atrazine	glyphosate; 2,4-D; dicamba

† Soil samples of this study were collected before herbicide applications in Field 1 and Field 3. Field 2 was in winter wheat at time of sampling.

2004, Field 2 data were collected in September 2002, and Field 3 data were collected in April 2002. Absolute values of soil EC_e measurements vary depending on moisture content of the soil at time of collection; however, soil EC_e spatial patterns and variability across a crop field are stable over time (Farahani and Buchleiter, 2004).

Soil EC_e zones were defined by first interpolating the soil EC_e data. Modified residual kriging was the geostatistical procedure (Reich and Davis, 2003) used within ESRI Spatial Analyst and Geostatistical Analyst extensions to interpolate the discrete soil EC_e point data for each field. First, a linear polynomial trend surface was fit to each of the soil EC_e data sets for each field. Trend surface residual values represented spatially autocorrelated random variables that underwent ordinary kriging based on exponential semi-variogram models. Kriging models were selected based on a minimized RMSE value during a cross-validation procedure within Geostatistical Analyst. The interpolated residual surfaces for each field were added to their corresponding polynomial trend surface to derive the final interpolated soil EC_e geographic information system data layers.

Interpolated soil EC_e surfaces for each field were divided into zones using the Iterative Self-Organizing Data Analysis Technique (ISODATA) and maximum likelihood classification within Spatial Analyst (ESRI, 2005). The ISODATA clustering algorithm relies on the number of classes (i.e., zones) to be user-defined and then seeks to minimize within-class variance and maximize between-class variation. The algorithm was used to determine three classes of soil EC_e for each field. The ISODATA procedure produced three parametric soil EC_e signatures for each field based on the mean and covariance matrix for each class (ESRI, 2005).

Maximum likelihood classification defined and mapped three soil EC_e zones for each field using the ISODATA signatures. Soil EC_e data for each field were assessed for normality and were determined as meeting the underlying assumptions for maximum likelihood classification. For each soil EC_e value, EC_e zone membership was based on the highest probability of belonging to each of the three zones as determined by the maximum likelihood classifier (ESRI, 2005). Minimal smoothing of the classified maps was imposed to derive soil EC_e zones that were practical for herbicide management for each field (Fig. 1).

Soil Samples

Soil samples for our study were collected from each site in May 2006. The locations of three soil sample replicates were identified within each of the low and high soil EC_e zones of each field and geo-referenced with a Trimble Ag114 DGPS receiver (Fig. 1). Soil samples within each soil EC_e zone were expected to have like properties that would affect herbicide dissipation similarly and, thus, were assumed to be spatially autocorrelated. High and low soil EC_e zones were selected for sampling and experimentation because they were hypothesized to represent soil properties that would respond differently in terms of herbicide dissipation. Based on previous research using soil EC_e to characterize soil properties for productivity or fertility management zones, three zones are preferred by farmers, and the "medium" zone generally represents a combination of the high and low zones (Herning et al., 2004).

There were a total of 18 surface soil samples from the three fields, all of which were carefully collected using a shovel at a uniform depth and volume from the top 13 cm of soil. The time of sampling was before application of any herbicides for Field 1, which was in a summer fallow for the 2006 growing season. Field 2 was sampled before winter wheat harvest. Field 3 was fallow but was sampled before any herbicides were applied. Soil samples were air-dried for approximately 1 h, sieved through a 2-mm sieve, and stored in a laboratory cold room at 4°C for approximately 5 wk before laboratory incubation studies and other associated experiments.

Routine soil analyses were performed on each soil sample by a commercial soil testing laboratory (MDS Harris Laboratories, Lincoln, NE; available at <http://ag.agsource.com/>). Soil properties measured included, but were not limited to, soil pH (Thomas, 1996), NO₃-N (mg kg⁻¹) (Mulvaney, 1996), and organic matter (%) (Nelson and Sommers, 1996). Composite soil samples taken within each soil EC_e zone were analyzed for topsoil texture (Gee and Bauder, 1986). Total aerobic microbial plate counts for each soil sample were measured (Colorado State University's Environmental Quality Laboratory, Fort Collins, CO; available at www.ehs.colostate.edu/WEnviroQual/). Moisture content at field capacity for each soil sample was determined by measuring the gravimetric moisture content of the soil at a pressure of -33 kPa (Cassel and Nielson, 1986).

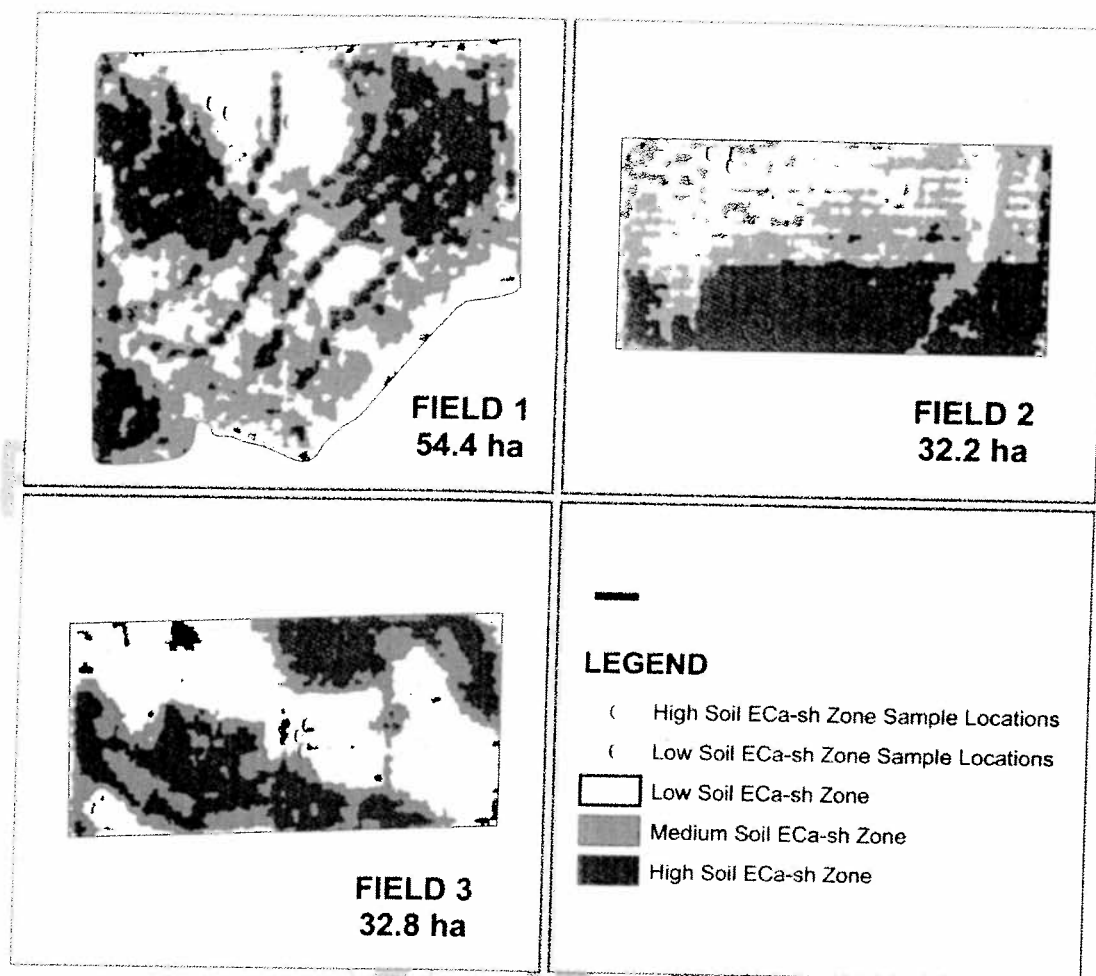


Fig. 1. Shallow soil apparent electrical conductivity (EC_{a-sh}) zones delineated for each field in this study. Locations of where soil samples were taken within each zone are depicted on each map. Maps of all fields are oriented north and are displayed at the same scale.

Incubation Experiment 1

An incubation experiment that involved treating laboratory replications of each field-collected soil sample with atrazine and metolachlor was conducted twice using methods described by Shaner and Henry (2007). Two laboratory replications of field-collected soil samples from each soil EC_{a-sh} zone within each of the study fields were treated with 1.0 µg certified analytical grade atrazine per gram of soil and 1.0 µg certified analytical grade metolachlor per gram of soil. The appropriate amount of distilled water was added to each laboratory replication to bring the soil to a moisture content of ~33 kPa. Laboratory replications were incubated under aerobic conditions at 25°C and sampled at 0, 3, 7, 14, 21, 25, and 35 d after treatment (DAT). Samples were assayed for concentrations of atrazine and metolachlor using a toluene extraction procedure with gas chromatography/mass spectrometry (GC/MS) (GC model 5890; MSD model 5972; Agilent Technologies, Wilmington, DE) analysis (Shaner and Henry, 2007). The limit of quantification for each herbicide was 100 µg kg⁻¹ of soil; however, the mass spectrometer was able to detect peaks corresponding to 25 µg kg⁻¹ of soil. Recovery efficiencies from

the quality control samples for atrazine and metolachlor were between 91 and 100%.

At every time point that soils were analyzed for herbicide concentrations, soil moisture content was measured by sampling 2 to 3 g of soil from each treated laboratory replication and oven-drying at 105°C. Soil masses were determined before and after oven-drying. Residual herbicide concentration calculations were corrected for oven-dried soil mass for each laboratory replication.

Incubation Experiment 2

The sampling protocol in Incubation Experiment 2 was modified to improve the modeling of atrazine dissipation kinetics. After evaluating atrazine concentrations from the first incubation experiment on 0, 3, and 7 DAT, it was determined that there were insufficient data regarding the decline of atrazine concentrations to properly model and evaluate its dissipation. The second experiment addressed all days after treatment between 0 and 7 DAT and at 14 DAT, with the exception of Field 2, which was evaluated at 16 DAT rather than at 14 DAT for logistical reasons.

Herbicide Soil Sorption Experiment

Soil sorption coefficients for each herbicide were determined for each field-collected soil sample using the batch-slurry equilibration technique (Smith et al., 2003). A soil sorption coefficient (K_d) is the ratio of the concentration of pesticide sorbed by the soil to the concentration remaining in soil solution (Weber et al., 2004). Field-collected soil samples were air-dried for 24 h. Four 5-g laboratory replications of each air-dried field-collected soil sample were placed into 50-mL plastic centrifuge tubes and were treated with 1.0 μg of atrazine and metolachlor per gram of soil. Ten milliliters of a 0.02 mol L^{-1} CaCl_2 /0.5 mol L^{-1} HgCl_2 solution were added to each treated sample. Tubes were shaken horizontally for 24 h. The 24-h time period had been determined in preliminary studies (data not shown) as adequate time for treated soil samples to reach equilibrium. Laboratory sample replications were then centrifuged at 10,000 rpm for 25 min. For each laboratory replication, 6.0 mL of the equilibrium solution supernatant were transferred to a 15-mL glass test tube with a Teflon-lined cap. Three milliliters of water-saturated toluene were added to each glass test tube. The tubes were shaken horizontally for 2 h and centrifuged for 15 min at 2000 rpm. The toluene phase was analyzed for atrazine and metolachlor concentrations by GC/MS methods as described previously. Quality control samples were included in each analytical GC/MS run.

The amount of herbicide adsorbed to each of the soils was calculated by the difference between the initial concentration of the herbicide in the soil solution (1.0 $\mu\text{g mL}^{-1}$) and the final concentration after equilibrating with the soil. The herbicide K_d was determined by Eq. [1].

$$K_d = [\text{herbicide sorbed to the soil } (\mu\text{g g}^{-1})] / [\text{herbicide in solution } (\mu\text{g g}^{-1})] \quad [1]$$

Herbicide Dissipation Analysis

Herbicide concentration data from treated laboratory replications resulting from Incubation Experiment 1 were used to model metolachlor dissipation, and such data from Incubation Experiment 2 were used to model the dissipation of atrazine. A first-order exponential decay model with indicator variables (Neter et al., 1985) (Eq. [2]) was fit to all the atrazine data and metolachlor data separately using SPLUS 6.2 statistical software (Insightful Corporation, 2001). Previous research suggests that atrazine and metolachlor degrade according to first-order kinetics (Dinelli et al., 2000; Vanderheyden et al., 1997).

$$Y = A \times \exp(-k \times t - k1 \times I1 \times t - k2 \times I2 \times t - k3 \times I3 \times t - k4 \times I4 \times t - k5 \times I5 \times t) \quad [2]$$

where $I1 = 1$ if Field 1, $I1 = -1$ if Field 3, $I1 = 0$ otherwise; $I2 = 1$ if Field 2, $I2 = -1$ if Field 3, $I2 = 0$ otherwise; $I3 = 1$ if low $\text{EC}_{\text{e-sh}}$ zone from Field 1, $I3 = -1$ if high $\text{EC}_{\text{e-sh}}$ zone from Field 1, $I3 = 0$ otherwise; $I4 = 1$ if low $\text{EC}_{\text{e-sh}}$ zone from Field 2, $I4 = -1$ if high $\text{EC}_{\text{e-sh}}$ zone from Field 2, $I4 = 0$

otherwise; and $I5 = 1$ if low $\text{EC}_{\text{e-sh}}$ zone from Field 3, $I5 = -1$ if high $\text{EC}_{\text{e-sh}}$ zone from Field 3, $I5 = 0$ otherwise. Herbicide concentration (Y) was modeled as being equal to the initial concentration, A , times the exponential of the product of the negative first-order rate constant, k , and time, t . Parameters estimated in this nonlinear regression model were A and k .

Indicator variables were used to simultaneously estimate first-order rate parameters, k , corresponding to each field and each soil $\text{EC}_{\text{e-sh}}$ zone within each field (Eq. [2]). The use of indicator variables allowed us to test for differences in dissipation rates across fields and between zones within fields by assessing the equality of different regression functions. This was an alternative statistical method to administering an ANOVA on independently estimated k parameters for each field and soil $\text{EC}_{\text{e-sh}}$ zones within each field.

The "full model" (Eq. [2]) enabled comparison of the herbicide dissipation among the three fields evaluated in this study. However, soil $\text{EC}_{\text{e-sh}}$ zones were fixed effects nested within fields; therefore, inferences regarding rates of herbicide dissipation were limited to individual fields. A "reduced model" was derived from the "full model" (Eq. [2]) that removed the effects of the fields and was used to derive the initial concentration, A , and first-order rate constants, k , for each soil $\text{EC}_{\text{e-sh}}$ zone within each field.

Differences in herbicide dissipation rates between soil $\text{EC}_{\text{e-sh}}$ zones within each field were evaluated using one-tailed Student's t tests. The null hypothesis was that there was no difference in the rate of dissipation between low and high soil $\text{EC}_{\text{e-sh}}$ zones. The alternative hypothesis was that significantly higher rates of herbicide dissipation would be exhibited in the high soil $\text{EC}_{\text{e-sh}}$ zones within each field. The level of significance used for the hypothesis testing was set at $\alpha = 0.10$.

Half-lives of each herbicide were derived by using the estimated first-order rate constants (k). The equation used to calculate half-lives is presented in Eq. [3].

$$T_{1/2} = \ln 2/k \quad [3]$$

Additional Statistical Analyses

A series of one- and two-tailed Student's t tests was used on selected measured soil properties. The null hypothesis for all tests was no significant difference in the mean value of a soil property between low and high soil $\text{EC}_{\text{e-sh}}$ zones. The alternative hypothesis required a one- or two-tailed t test according to the soil characteristic of interest. The alternative hypotheses formed for each of the variables were derived from results of previously published studies describing the influence of soil properties on herbicide dissipation (Houor et al., 2000; Abdelhafid et al., 2000a, 2000b; Wackett et al., 2002; Moorman et al., 2001; Popov et al., 2005).

Results and Discussion

Shallow soil electrical conductivity values ranged from 0.01 to 0.72 dS m^{-1} , with coefficients of variation spanning between 23.3 and 30.3% across all fields. Variability in soil $\text{EC}_{\text{e-sh}}$ values was less within each delineated soil $\text{EC}_{\text{e-sh}}$ zone

Table 2. Characteristics of measured soil properties for each field site in this study. Mean values based on three soil samples are given with SE in parentheses.

	EC _{a-sh} † zone	Texture class‡	Water-holding capacity (at -33 kPa)	Organic matter	NO ₃ -N	pH	Microbial counts	ATZ K _d §	MOC K _d ¶	EC _{a-sh} #
			%		mg kg ⁻¹		propagules g ⁻¹			mS m ⁻¹
Field 1	low	silt loam	17.43 (0.37)	1.60 (0.06)	14.67 (2.33)	6.37 (0.28)	2.14E + 06 (7.45E + 05)	0.61 (0.05)	1.02 (0.07)	0.16 (0.01)
	high	clay loam	22.13 (1.79)	2.33 (0.19)	11.00 (3.61)	6.53 (0.18)	3.53E + 06 (4.91E + 05)	0.66 (0.03)	1.26 (0.06)	0.29 (0.03)
Field 2	low	silt loam	18.10 (0.12)	2.40 (0.25)	11.00 (3.06)	6.17 (0.20)	8.20E + 06 (1.08E + 06)	0.96 (0.06)	1.73 (0.09)	0.26 (0.02)
	high	clay loam	21.47 (0.41)	2.17 (0.09)	17.00 (6.11)	6.40 (0.12)	7.03E + 06 (5.17E + 05)	0.80 (0.08)	1.50 (0.17)	0.62 (0.01)
Field 3	low	loam	14.17 (0.26)	1.67 (0.12)	22.33 (2.60)	5.93 (0.09)	3.80E + 06 (1.53E + 05)	0.72 (0.05)	1.24 (0.13)	0.22 (0.01)
	high	clay loam	17.20 (0.80)	1.60 (0.06)	9.33 (1.76)	6.23 (0.18)	3.83E + 06 (1.38E + 06)	0.80 (0.03)	1.25 (0.10)	0.41 (0.01)

† ATZ, atrazine; EC_{a-sh}, shallow soil apparent electrical conductivity; MOC, metolachlor.

‡ Textural class based on composite of three soil sample locations.

§ Microbial count based on a total aerobic plate count using Standard Methods Agar.

¶ Mean value based on the average values of herbicide sorption coefficients (K_d) calculated from four replications.

Mean value based on absolute values of shallow soil apparent electrical conductivity for the locations of soil samples estimated from modified residual kriging.

(Table 2) where differential rates of atrazine and metolachlor were also observed.

Characteristics of Soil EC_{a-sh} Zones

There was significantly less variability of soil EC_{a-sh} values within each delineated soil EC_{a-sh} zone (Fig. 1) compared with whole field soil EC_{a-sh} variability. Coefficients of variation (CV) for EC_{a-sh} values within zones, based on an assessment of all soil EC_{a-sh} values measured within each delineated zone, ranged from 8.0 to 16.4%, whereas overall field CV ranged from 23.3 to 30%. In addition, there were differences in topsoil texture as classified by particle size analysis of soil samples between low and high soil EC_{a-sh} zones within each field (Table 2). Likewise, the percent water-holding capacities (-33 kPa) were significantly higher in the soils of the high EC_{a-sh} zones of each field ($P = 0.10$).

The texture and moisture differences in the non-saline soil samples (Williams and Hoey, 1987; Kachanoski et al., 1988) of this study confirm the utility of soil EC_{a-sh} maps to create soil zones within a field. Previous work also supports the use of soil EC_{a-sh} measurements for characterizing soil types across fields (Anderson-Cook et al., 2002; Kitchen et al., 2004).

Atrazine Dissipation

There were differences in the rates of dissipation (k) of atrazine between nested soil EC_{a-sh} zones across all fields ($P < 0.001$). These differences were due to the faster rate of atrazine dissipation in the high soil EC_{a-sh} zones of Fields 2 and 3 relative to their low soil EC_{a-sh} zones (Table 3). Although dissipation rates were not significantly different between the soil EC_{a-sh} zones in Field 1, the trend was similar as seen in the other fields (Table 3). The half-lives of atrazine for soils in our incubation study ranged from 1.75 to 3.22 d (Table 3). The half-lives for atrazine reported in the literature have ranged from 45 to 180 d (Wauchope et al., 1992; Wackett et al., 2002; Johnson et al., 2003; Miller and Westra, 2006). However, Shaner and Henry (2007) found that atrazine had a half-life between 3 and 5 d in irrigated fields in eastern Colorado that had received annual atrazine applications for at least 5 yr

before soil analysis. In laboratory studies, the half-life of atrazine in soils taken from fields that showed enhanced degradation was between 1 and 2 d (Shaner and Henry, 2007). The results of our study were comparable to those of Shaner and Henry (2007), suggesting that soils from fields evaluated in our study were exhibiting accelerated atrazine dissipation. To our knowledge, there have been no reports of accelerated atrazine dissipation in semiarid dryland cropping environments.

Disparities observed in the rates of atrazine dissipation between soil EC_{a-sh} zones nested within fields may be due to different cropping system practices and atrazine applications over the 5 yr before our study (Table 1). Fields 2 and 3 were managed by the same farmer and were under the same crop rotation (Table 1). The highly significant difference in rates of atrazine dissipation between soil EC_{a-sh} zones exhibited on Field 3 ($P < 0.001$) (Table 3) compared with the other fields might have been due to the most recent atrazine application that occurred 1 yr prior (in 2005) to soil collection for our study (Table 1). The other two fields in this study had not been exposed to atrazine since 2004. In addition, Field 1, which showed no significant differences of atrazine dissipation rates between soil EC_{a-sh} zones, had only one application of atrazine in the 5 yr before this study (Table 1).

Atrazine behavior observed among the fields and between soil EC_{a-sh} zones within fields in our study is further evidence that field management history was likely an influential factor in our results. Other studies have found that atrazine management practices influence rates of atrazine dissipation (Vanderheyden et al., 1997; Yassir et al., 1999; Shaner and Henry, 2007). Johnson et al. (2003) reported that study sites never receiving atrazine had half-lives ranging from 45 to 102 d, whereas other studies conducted using soils recently and repeatedly exposed to atrazine had corresponding half-lives ranging from approximately 5 to 20 d (Vanderheyden et al., 1997; Yassir et al., 1999). Barriuso and Houot (1996) were among the first to report accelerated mineralization of the s-triazine ring of atrazine in soils having recent and repeated exposure to this herbicide, and they speculated that the soils examined in their study contained adapted microflora capable

of rapidly decomposing atrazine. There have been several studies attributing adapted microbes as the reason for accelerated atrazine dissipation (Houot et al., 2000; Aislabie et al., 2004; Popov et al., 2005; Zablotowicz et al., 2006). Because of the controlled condition under which our study was performed, microbial degradation was likely the cause of the atrazine dissipation we observed versus losses by leaching or volatilization. Although chemical degradation could have contributed to dissipation, the accelerated rate of atrazine dissipation coupled with the history of atrazine use on all fields in this study suggested microbial decomposition.

Soil samples from one field in our study that exhibited a higher rate of atrazine dissipation in the high soil EC_{e-sh} zone (Table 3) also had lower concentrations of nitrate ($P = 0.01$) in the high soil EC_{e-sh} zone (Table 2). Microbes responsible for the breakdown of atrazine have been reported to be heavily influenced by organic carbon (C) and mineral nitrogen (N) availability in the soil. Yassir et al. (1999) reported that soils deemed adapted to atrazine due to a history of exposure showed the release of a high rate of ¹⁴C-CO₂ from radioactively labeled atrazine, suggesting that soil microbes used atrazine as a carbon source. Atrazine dissipation is negatively correlated to N mineralization, signifying that, in the absence of mineral N, microbes use atrazine as a nitrogen source (Houot et al., 2000; Abdelhafid et al., 2000a).

Aerobic microbial plate counts (propagules per gram) were not significantly different throughout the various soil EC_{e-sh} zones (Table 2); hence, these data suggest that there were similar amounts of microbes throughout the field. This trend was similar to previous findings showing no relationship between atrazine degradation rates and microbial biomass (Yassir et al., 1999; Houot et al., 2000; Aislabie et al., 2004; Zablotowicz et al., 2006). Jayachandran et al. (1998) illustrated that populations of atrazine-degrading microbes are correlated with rates of atrazine mineralization. However, atrazine degraders may only comprise a small portion of the total microbial population (Jayachandran et al., 1998).

It is probable that there were differences in microbial capabilities to degrade atrazine across the crop fields of our study because of variation in soil properties. Microbial activity has been reported to vary with soil properties such as moisture, pH, organic matter, and texture (Issa and Wood, 2005; Beulke et al., 2005). In our study, there were higher field-capacity moisture contents (i.e., water-holding capacity at -33 kPa) in the soil samples corresponding to high soil EC_{e-sh} zones as compared with those of the low soil EC_{e-sh} zones ($P \leq 0.10$). Greater moisture content and finer topsoil texture exhibited in the soils of the high soil EC_{e-sh} zones might explain their higher rates of atrazine dissipation.

Metolachlor Dissipation

There were higher rates of metolachlor dissipation in the high soil EC_{e-sh} zones of two of the three fields evaluated in this study (Table 3). The other field, however, demonstrated the opposite trend, with a higher rate of metolachlor dissipation in the soil samples of the low soil EC_{e-sh} zone (Table 3). Half-lives

Table 3. Estimated decay rate constants (k) and half-lives ($T_{1/2}$) for each shallow soil apparent electrical conductivity (EC_{e-sh}) zone within each field of this study.

	Herbicide	EC _{e-sh} zone	k †	$T_{1/2}$ ‡	ρ Value ¶
			d ⁻¹	d	
Field 1	atrazine	low	0.30 (0.024)	2.31	0.34 (NS) #
		high	0.31 (0.024)	2.23	
	metolachlor	low	0.05 (0.005)	10.35	0.08
Field 2	atrazine	low	0.07 (0.005)	9.12	0.001
		high	0.26 (0.024)	2.63	
	metolachlor	low	0.35 (0.024)	1.99	0.02
Field 3	atrazine	low	0.06 (0.005)	10.66	0.02
		high	0.07 (0.005)	9.00	
	metolachlor	low	0.22 (0.023)	3.22	<0.001
		high	0.40 (0.023)	1.75	
	metolachlor	low	0.08 (0.005)	9.00	0.96 (NS) #
		high	0.07 (0.005)	10.50	

† First-order rate constant with standard errors in parentheses.

‡ Half-lives calculated from dividing the natural log (ln) of 2 by the first-order rate constant.

¶ ρ Values based on a one-tailed Student's t test for where the alternative hypothesis is that first-order rate constants are higher in high EC_{e-sh} zones within each field.

NS, not significant.

for metolachlor varied from 9.0 to 10.7 d (Table 3). This was not considered accelerated dissipation as compared with rates reported from a study by Shaner and Henry (2007).

Metolachlor decomposition is primarily governed by microbial degradation (Liu et al., 1989), as is the case with atrazine. The previous discussion regarding atrazine degradation provided a case for the possible spatial heterogeneity of microbial activity that is also relevant for metolachlor dissipation. It could be spatial variation in microbial communities and activity that explains the higher rates of metolachlor dissipation in the high soil EC_{e-sh} zones of two of the three fields evaluated in our study (Table 3). Moreover, the soil samples from one field exhibiting a significant difference in metolachlor dissipation between the low and high soil EC_{e-sh} zones ($P = 0.08$; Table 3) had a higher total microbial count in the high soil EC_{e-sh} zone ($P = 0.10$; Table 2). This might suggest that the size of the microbial populations was related to metolachlor's dissipation, likely confounded by other soil properties, such as metolachlor's sorption coefficient (K_d), soil moisture content, and percent soil organic matter (Table 2).

Sorption coefficients (K_d) for metolachlor were significantly higher in the soil samples of the high soil EC_{e-sh} zone ($P = 0.03$; Table 2) of Field 1, one of the fields that exhibited differences in metolachlor dissipation rates between soil EC_{e-sh} zones ($P = 0.08$; Table 3). Additionally, the percent soil organic matter (SOM) of the soil samples from Field 1 was higher in the high soil EC_{e-sh} zone ($P = 0.06$; Table 2). This agrees with the results of Weber et al. (2004), who reported a positive correlation between SOM and metolachlor's mean K_d value across various soil types. Likewise, organic amendments, such as crop residues, can increase the rate of metolachlor degradation (Moorman et al., 2001). It could be hypothesized that, in dry-land fields of Colorado, areas of the field with higher soil EC_{e-sh}

values could be spatially coincident with higher-yielding areas contributing more crop residues. Field 2 of our study, which also exhibited a higher metolachlor dissipation rate in the high soil EC_{e-sh} zone ($P = 0.02$; Table 3), had contrasting results of lower percent SOM (not significant; Table 2) and lower metolachlor sorption (not significant; Table 2) in the soil samples of the high soil EC_{e-sh} zone.

The relationship between a soil's exposure to metolachlor and metolachlor dissipation has had conflicting reports in the literature. Frank et al. (1991) illustrated how metolachlor half-lives increased (i.e., dissipation rates decreased) in a field after three successive years of metolachlor applications, whereas Sanyal and Kulshrestha (1999) found accelerated rates of metolachlor degradation after four applications within 8 mo. In a recent study, Shaner and Henry (2007) did not report accelerated metolachlor dissipation on fields despite histories of acetanilide herbicide applications. Of all the fields evaluated in our study, only Field 1 had a history of metolachlor application, occurring in 2005 (Table 1). Perhaps this application of metolachlor on Field 1 contributed to the higher rate of metolachlor dissipation observed in the high soil EC_{e-sh} zone (Table 3). However, this does not help to explain metolachlor's behavior on Field 2, which also showed a faster rate of dissipation in its high soil EC_{e-sh} zone (Table 3). Because metolachlor dissipation behaved similarly on these two fields and only one had a history of metolachlor use, it is possible that certain soil properties characterized by soil EC_{e-sh} and not use history influenced the differential rates of dissipation between soil zones. Perhaps the spatial structure of soil properties affecting microbial activity contributed to the differences in rates and the inconsistent trends in those differences of metolachlor dissipation between soil EC_{e-sh} zones of the fields evaluated in our study.

Conclusions

Accelerated dissipation of atrazine was exhibited on all fields of this study, with half-lives ranging from 1.8 to 3.2 d, as compared with previously reported half-lives for atrazine ranging from 45 to 180 d in the soil (Wauchope et al., 1992; Wackett et al., 2002; Johnson et al., 2003; Miller and Westra, 2006). Our data support results reported by Shaner and Henry (2007) regarding frequent exposure to atrazine, rapid atrazine dissipation, and associated shortened half-lives in Colorado soils. Our study, however, is among the first to report such high rates of atrazine dissipation in soil from semiarid dryland cropping environments. There were significantly higher rates of atrazine and metolachlor dissipation in the soils of the high EC_{e-sh} zones on at least two of the three fields in this study. These results suggest the potential for differential herbicide application based on soil EC_{e-sh} -defined management zones. Although this work identified statistically different rates of dissipation with respect to soil EC_{e-sh} -defined zones, a producer would most likely not manage his herbicide program differently in response to these small differences. Further work under field conditions needs to be performed to confirm the results of this research and to determine the

agronomic significance (i.e., effects on weed control) of the different rates of herbicide dissipation. More studies are also needed to understand the mechanisms contributing to differential rates of herbicide dissipation across crop fields.

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