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Processes Affecting the Dissipation of the Herbicide Isoxaflutole and Its Diketonitrile Metabolite in Agricultural Soils under Field Conditions

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Two-year field dissipation studies were conducted in three soil types in Minnesota to examine the processes affecting the dissipation of the herbicide isoxaflutole and its phytotoxic diketonitrile metabolite (DKN) under relatively cool, wet soil conditions. Plots of cuphea were treated with isoxaflutole and potassium bromide, a nonsorbed, nondegraded tracer. Replicate soil cores were collected six times during the growing season to a depth of 1 m, and the bromide or herbicide concentration was measured in each of five depth increments. The dissipation half-life (DT50) of isoxaflutole + DKN was 8–18 days in each soil. Bromide and herbicide concentrations were low at depths >40 cm throughout the study, and herbicide concentrations in soil 100 days after application were usually undetectable. Simulation modeling using Hydrus-1D for the loam soil suggested that plant uptake was an important mechanism of dissipation.

KEYWORDS: Degradation; herbicide; isoxaflutole; isoxazole; metabolite; plant uptake; soil; terrestrial dissipation

INTRODUCTION

Pesticide dissipation studies are a common assessment of environmental fate, and they have been required for the registration of pesticide uses in the United States since 1982 (*1*). Field dissipation studies typically involve application of the test herbicide to bare or cropped soil, followed by monitoring of soil concentrations as a function of depth and time. These studies provide information about pesticide residues expected to occur in soil under field conditions.

Isoxaflutole (5-cyclopropyl-4-(2-methylsulfonyl-4-trifluoromethylbenzoyl)isoxazole) is a pre-emergence herbicide used in corn and sugar cane production throughout the world. It is the first in a new class of herbicides (isoxazoles) that target 4-hydroxyphenylpyruvate dioxygenase. Isoxaflutole is rapidly converted to a diketonitrile (DKN) metabolite in plants (**Figure 1**), which is the phytotoxic agent; DKN is further metabolized to a nontoxic benzoic acid (BA) metabolite (**Figure 1**). The rate and extent of conversion of DKN to BA impart selectivity (*2*). Abiotic conversion of isoxaflutole to DKN also occurs in soil, the rate of conversion increasing with increasing temperature, soil moisture, and pH (*3*). Plants preferentially take up isoxaflutole rather than DKN (*4*).

In the United States, isoxaflutole is labeled for use on corn in 18 states (*5*). Fifteen states restrict the application of isoxaflutole on sand, sandy loam, or loamy sand soils where the water table is less than 7.6 m below the ground surface (*5*). Use of isoxaflutole is not currently registered in some major corn-producing states, including Minnesota, Michigan, and Wisconsin, due to water quality concerns. Application restrictions are based on the tendency of isoxaflutole and DKN to be in the water phase. Both have generally low sorption and are easily desorbed, making them susceptible to leaching (*6*, *7*) and runoff (*8*). Isoxaflutole and its DKN metabolite have been detected in groundwater (*9*) and surface water (*10*, *11*) in the United States.

Field leaching and runoff studies have indicated that isoxaflutole and its metabolites are relatively mobile. Bare-soil lysimeter experiments (0.5 m deep) indicated that leaching loss accounted for >15% of the applied isoxaflutole in 25 days, with

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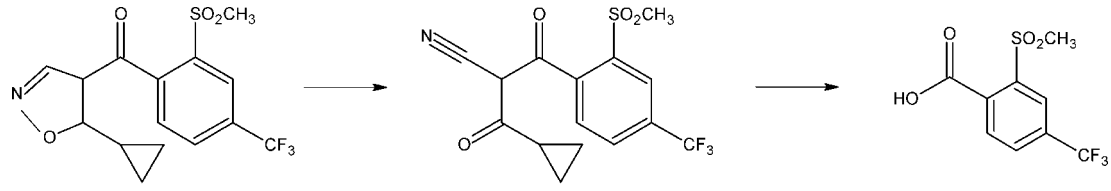

Figure 1. Isoxaflutole and its diketonitrile and benzoic acid metabolites.

Table 1. Selected Properties of Soils Used in These Experiments[a]

depth increment (cm)	organic carbon (%)	inorganic carbon (%)	pH	gravel (%)	sand (%)	silt (%)	clay (%)
			Sverdrup Sandy Loam				
0–10	3.07 ± 0.04	0.11 ± 0.02	7.80 ± 0.04	4.8 ± 0.9	49.6 ± 2.1	30.3 ± 0.8	15.3 ± 1.3
10–20	2.96 ± 0.09	0.15 ± 0.03	7.77 ± 0.04	3.7 ± 0.8	50.3 ± 2.2	29.7 ± 1.7	16.2 ± 1.4
20–40	2.42 ± 0.13	0.45 ± 0.08	7.75 ± 0.05	9.3 ± 1.8	47.0 ± 4.2	29.8 ± 4.0	13.8 ± 2.1
40–60	1.27 ± 0.16	2.48 ± 0.25	8.04 ± 0.07	5.7 ± 1.5	54.7 ± 3.1	25.0 ± 4.7	14.6 ± 1.3
60–100	0.64 ± 0.14	2.58 ± 0.22	8.26 ± 0.08	18.8 ± 2.4	50.0 ± 3.2	20.2 ± 3.7	11.0 ± 2.2
			Barnes Loam				
0–10	3.72 ± 0.03	0.01 ± 0.00	7.44 ± 0.05	1.6 ± 0.4	46.5 ± 0.9	35.1 ± 0.6	16.8 ± 1.7
10–20	3.50 ± 0.05	0.01 ± 0.00	7.39 ± 0.08	2.5 ± 0.3	45.5 ± 0.3	35.2 ± 0.9	16.9 ± 1.2
20–40	1.59 ± 0.10	1.38 ± 0.18	7.65 ± 0.09	3.3 ± 1.3	45.5 ± 2.3	34.2 ± 0.7	17.0 ± 1.5
40–60	0.17 ± 0.05	4.13 ± 0.16	8.10 ± 0.06	6.6 ± 1.6	41.6 ± 2.5	33.0 ± 3.2	18.7 ± 2.2
60–100	0.00 ± 0.06	3.32 ± 0.16	8.32 ± 0.06	11.0 ± 2.8	42.7 ± 2.2	27.7 ± 1.2	18.6 ± 1.3
			Hamerly Clay Loam				
0–10	4.08 ± 0.07	0.23 ± 0.04	7.92 ± 0.03	1.5 ± 0.3	40.6 ± 2.3	36.0 ± 1.6	22.0 ± 1.0
10–20	3.61 ± 0.26	0.54 ± 0.27	7.89 ± 0.05	1.2 ± 0.2	40.8 ± 2.6	36.2 ± 2.1	21.8 ± 1.8
20–40	1.51 ± 0.18	2.34 ± 0.34	8.07 ± 0.08	3.6 ± 2.0	35.5 ± 2.4	36.8 ± 1.8	24.0 ± 1.6
40–60	0.18 ± 0.07	3.85 ± 0.16	8.36 ± 0.06	17.6 ± 3.4	35.6 ± 1.8	32.5 ± 3.2	14.3 ± 4.7
60–100	0.31 ± 0.29	3.18 ± 0.25	8.39 ± 0.04	17.9 ± 6.5	37.0 ± 3.5	35.0 ± 4.0	10.1 ± 4.5

[a] Values are mean (±standard error) of 18 samples (C, N, pH) or 4 samples (particle size) for each soil type.

the bulk of the leached herbicide detected as DKN (*6*). Runoff of isoxaflutole and DKN under natural precipitation conditions totaled <3% of the applied isoxaflutole (*8*).

Differential mobility between isoxaflutole and DKN is affected by properties of the solute and the soil. Isoxaflutole is more strongly sorbed than its DKN and BA metabolites in a variety of soils (*12–14*). Sorption of both isoxaflutole and DKN tends to increase with increasing soil organic matter content (*12–16*). Some studies have indicated that sorption increases with increasing clay content and decreasing soil pH (*13*, *15*). In some soils, DKN appears to become more tightly bound over time (*17*), and DKN can form very stable chelate complexes with residual cations and/or partially coordinated structural cations (*18*).

The environmental fate of isoxaflutole and its DKN metabolite is not extensively reported in the peer-reviewed literature. In these experiments, 2-year dissipation studies were conducted to estimate the degradation rate of isoxaflutole and its DKN metabolite and their tendency to leach under typical field conditions in a moist, cool environment. A simulation model was used to further investigate processes affecting the transport and dissipation of the herbicide and a nonsorbed, nondegraded tracer.

MATERIALS AND METHODS

Chemicals. Isoxaflutole (formulated as Balance Pro) was donated by Bayer CropScience (Kansas City, MO). Potassium bromide (purity >99%) and acetonitrile (pesticide grade) were purchased from Fisher Scientific and were used as received. Purified water (>18.2 MΩ·cm^{-1}) was prepared from reverse-osmosis stock. All labware used for isoxaflutole/DKN samples was either glass or polytetrafluoroethylene (PTFE) and rinsed with methanol before use.

Field Site and Preparation. Field experiments were conducted at the Swan Lake Research Farm near Morris, MN (45°41′14″ N latitude and 95°47′57″ W longitude). Weather conditions monitored at the site included precipitation, air temperature, soil temperature at 5 and 10 cm, barometric pressure, wind speed, and water evaporation from uncovered and covered pans. A variety of soil types are represented at this site. Experiments were conducted in a Sverdrup sandy loam (sandy, mixed, frigid Typic Hapludolls), Barnes loam (fine loamy, mixed, frigid Calcic Hapludolls), and Hamerly clay loam (fine loamy, mixed, frigid Aeric Calciaquolls). Slopes in each plot ranged from 1.5 to 1.9% (Hamerly), 2.4 to 3.1% (Barnes), and 3.4 to 3.7% (Sverdrup).

These experiments were conducted in plots of cuphea (*Cuphea viscosissima* × *C. lanceolata*), a potential new oilseed crop that has been shown to be tolerant to isoxaflutole (*19*). Prior to planting, the soil was tilled using a field cultivator and a rototiller, leaving essentially no residue on the soil surface. Cuphea was planted using a garden seeder at a rate of 240 seeds m^{-1} in rows spaced 56 cm apart. Soil was packed following planting using a roller. Cuphea emerged 10 days after planting (10 days after herbicide application), plant height was ∼15 cm 50 days after planting, and cuphea was flowering 100 days after planting. Weeds were controlled in plots not receiving isoxaflutole application using glyphosate supplemented with hand weeding. One pre-emergence application of glyphosate was used in year 1, and wick application of glyphosate was used in both years.

To compare the movement of isoxaflutole/DKN with that of a nonsorbed, nondegraded tracer (bromide), concurrent leaching experiments were conducted using potassium bromide. Duplicate plots (2 m × 5 m) were used for each of three treatments (herbicide, bromide, and untreated control) within each soil type, and the six plots were randomly located within the study area. The entire experiment was replicated in two consecutive years on plots that had no history of isoxaflutole application. (Plots were in a different location in the second year of the study.)

Herbicide and Bromide Application. Solutions of isoxaflutole and potassium bromide were applied without incorporation immediately after planting. Isoxaflutole was mixed and applied according to label instructions for corn (0.16 L ha^{-1}; 77 g ha^{-1}) with 190 L ha^{-1} water. Sodium bromide was applied with the same amount of water at a rate

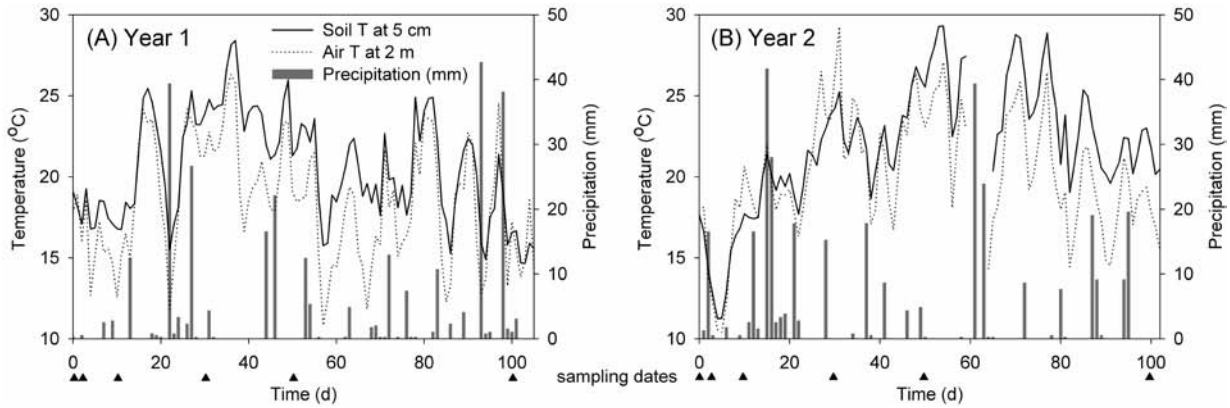

Figure 2. Temperature and precipitation measured during (**A**) year 1 and (**B**) year 2 of the experiment.

of 90 kg ha^{-1}. Both solutions were applied manually using a backpack sprayer with a 1.5 m boom. Application occurred on 14–15 June 2004 and 23 May 2005.

Soil Sampling. Triplicate soil cores were collected to a depth of 1 m approximately −2, 0, 2, 10, 30, 50, and 100 days after application in each plot treated with herbicide or bromide. Samples from the untreated control plots were collected at −2, 0, and 10 days after application. A 5.7 cm diameter Hoffer probe was used to collect a core from 0 to 10 cm. Brass rings were used to retain the opening and to avoid the contamination of soil >10 cm deep with surface soil. A 3.2 cm soil probe with a poly(ethylene terephthalate glycol) (PETG) copolyester liner was used to collect a core from 10 to 100 cm using a tractor-mounted Giddings hydraulic system. Soil samples from 0 to 10 cm were transferred to a plastic bag; soil cores were capped on each end. All samples were stored on dry ice until transport to the laboratory, where they were stored at −10 °C until processing. Each hole was backfilled with soil and the sampling location and marked with a wooden stake to avoid resampling at the same location.

Sample Processing and Analysis. Frozen soil cores (in liners) were sectioned into segments 10–20, 20–40 40–60, and 60–100 cm depth using a miter saw with a carbide blade. Total carbon was determined by combustion using a LECO analyzer (*20*). Inorganic carbon was determined from the pressure increase resulting from CO_2 liberation upon addition of acid (*21*). Soil organic carbon was calculated as the difference between total carbon and inorganic carbon. Soil pH was measured in a 1:1 slurry of 5 g of dry soil in 0.01 M aqueous $CaCl_2$ solution. Physical and chemical properties of each soil are given in **Table 1**.

Samples to be analyzed for bromide determination were dried and sieved to 0.5 mm. The moisture content of the bulk sample was determined gravimetrically. A 2 g aliquot of dry soil was placed in a plastic centrifuge tube and extracted with 20 mL of 0.1 N $NaNO_3$. Samples were agitated on a wrist-action shaker for 30 min and centrifuged at 760*g* for 5 min, and then the supernatant was filtered to remove particles >2.5 μm. Extracts were frozen at −20 °C until analysis using a continuous flow analyzer.

Samples for isoxaflutole/DKN determination were thawed and mixed to homogenize. A ∼10 g subsample was removed for moisture determination. An additional 100 g subsample of moist soil was transferred to a PTFE centrifuge bottle, followed by 100 mL of 50/50 acetonitrile/water. Samples were agitated on a reciprocating shaker for 10 min and then centrifuged at 760*g* and 23 °C for 10 min. A 5 mL glass syringe with Luer-Lok needle was used to draw up 2.0 mL of the supernatant, followed by 2.0 mL of purified deionized water (resistivity 18 MΩ·cm). The syringe was shaken to mix the solution, and the solution was pushed through a 0.45 μm syringe filter. The first 1.0 mL was used to condition the filter; the second 1.0 mL eluted through the filter was collected in an amber glass GC vial and capped. Samples were stored at 4 °C until analysis using a Waters Alliance high performance liquid chromatograph coupled to a mass spectrometer using an electropspray interface. A Zorbax, RX-C8 column with dimensions 2.1 mm i.d. × 150 mm long × 5 μm film thickness was used for separation. The column temperature was maintained at 40 °C. The mobile phase was a gradient starting with 75% water (0.1% formic acid) (A): 25% acetonitrile (B); 75% A at 0 min; 75% A at 3 min; 50% A at 5 min; 50% A at 10 min; 10% A at 13 min; 10% A at 19 min; 75% A at 20 min; and 75% A at 26 min. The mobile-phase flow rate was 0.2 mL min^{-1}. The sample injection volume was 100 μL. Samples were maintained at 8 °C in the autosampler to minimize isoxaflutole decomposition.

Isoxaflutole was analyzed in the positive ion electrospray ionization mode with full scan spectra (100–500 amu) acquired at 2 scans s^{-1}, whereas DKN was analyzed in the negative ion electrospray ionization mode. Isoxaflutole could also be analyzed using the negative ion electrospray ionization mode, but with much less sensitivity. The capillary exit and entrance voltages were selected to optimize formation of fragment ions while keeping the molecular ion at 100% relative abundance. Selected ion monitoring (SIM) was used for analyte confirmation and quantitation, monitoring the ions $m/z = 360$ ($[MH]^+$), 251, and 85.5 for isoxaflutole and $m/z = 358$ ($[MH]^-$), 278, and 79 for DKN.

Identification of isoxaflutole and DKN was based on retention times being ±2% of those of the corresponding standards. The retention times were 9.7 min for DKN and 14.7 min for isoxaflutole. Favorable comparison of three selected ions ($[MH]^+$ isoxaflutole or $[MH]^-$ for DKN and two parent–daughter transitions) and a signal-to-noise ratio (S/N) of >5 in the extracted samples and the known standards provided additional confirmation criteria. Once confirmed, quantitation was based on the peak area of $[MH]^+$ for isoxaflutole and $[MH]^-$ for DKN. No matrix effects (e.g., signal enhancement or suppression) were observed, based on use of matrix-based calibration standards. Under these conditions, the isoxaflutole limit of quantitiation (LOQ) was <10 μg kg^{-1}, the DKN LOQ was <1 μg kg^{-1}, and the method limits of detection were approximately a factor of 10 lower. This method provides extraction efficiencies of >90% for both isoxaflutole and DKN in freshly treated samples.

Concentrations of isoxaflutole + DKN or Br^- in soil were calculated from the concentration in the extract multiplied by the volume of the extractant divided by the mass of soil extracted (dry weight basis). In the case of the herbicide extractions, the volume included the volume of solvent added (100 mL) and the volume of water present in the soil, since moist soil was extracted. At each sampling time, six cores were collected from herbicide-treated and bromide-treated plots for each soil type. The mean (±standard error of the mean) concentration in each depth increment of the six replicate samples was calculated.

Transport Modeling. Hydrus-1D (*22*), a finite element model describing solute transport in one dimension, was used to simulate herbicide (isoxaflutole and DKN) and bromide transport in Barnes loam. Application parameters were set at field values. The soil hydraulic properties were estimated in Hydrus using the van Genuchten model for a loamy soil to provide water retention curve characteristics: the saturated water content (θ_s) was 0.43 cm^3 cm^{-3}, the residual water content (θ_r) was 0.078 cm^3 cm^{-3}, α was 0.036 cm^{-1}, n was 1.56, the saturated hydraulic conductivity (K_s) was 24.96 cm day^{-1}, and the empirical constant (L) was 0.5. The water content at application was set at 0.23 g g^{-1}, consistent with the water contents measured in the field.

Transport of all compounds was assumed to occur only in the dissolved phase (no gas-phase transport). The molecular diffusion

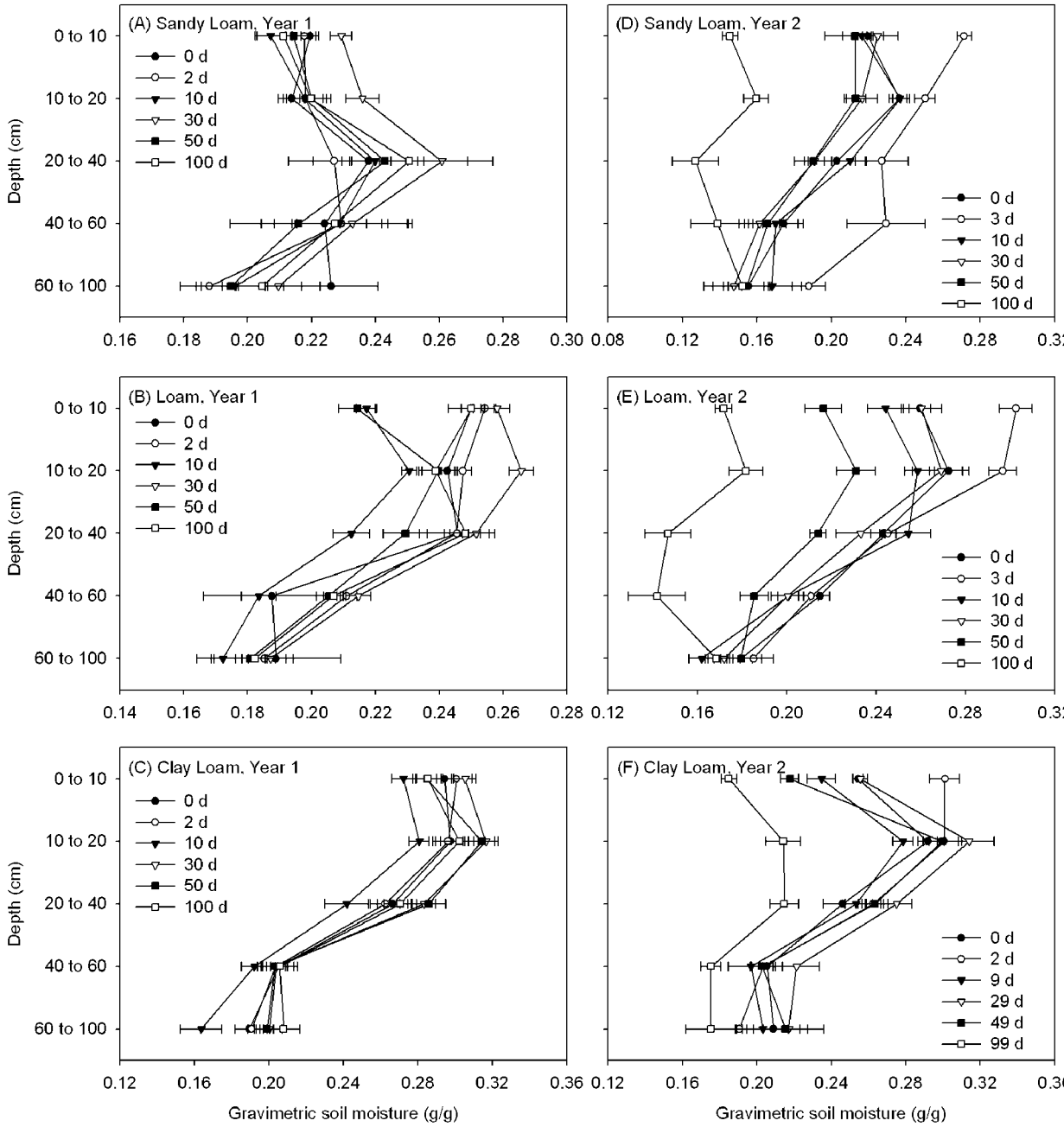

Figure 3. Gravimetric soil moisture at each sampling time in (**A–C**) year 1 and (**D–F**) year 2. Values are mean ± standard error of the mean.

coefficient in water was 3 cm^2 day^{-1} for all simulated compounds. No sorption of bromide was assumed. Sorption coefficient (K_d) values for isoxaflutole and DKN were estimated as 0.92 and 0.25 L kg^{-1}, respectively. These values were calculated using K_{foc} values reported by Rice et al. (*13*) for a soil with properties similar to Barnes loam and were based on a soil organic carbon content of 2% (representative of the upper profile, **Table 1**). The conversion of isoxaflutole to DKN, the first step in a series of sequential reactions, was assumed to follow first-order kinetics with a rate constant of 2.77 day^{-1} (half-life of 6 h, from ref (*3*) for a soil with similar organic carbon content). The rate constant for the conversion of DKN to other, nonmonitored products was 0.04 day^{-1}, giving a half-life of 17 days, which is within the range of DKN half-lives (10–39 days) reported for aerobic soil incubations (*10*).

Modeling of root water uptake relied upon the Hydrus module using alfalfa as the model crop. The root growth submodel was used, assuming a maximum rooting depth of 90 cm. The root growth model assumed that roots were at 50% of the maximum rooting depth halfway through the growing season. This rate of growth is in agreement with observations of above-ground biomass development of cuphea measured at this location (*23*). The root growth model used a "harvest date" of 100 days, which represented about 900–1000 growing degree days (°C days) in these experiments. The predicted root distribution included almost no roots beyond 60 cm at 100 days, consistent with the cuphea root distribution measured at this location (*24*). The maximum solution concentration of both herbicide and bromide taken up by the plant was 100 μg cm^{-3}. If soil solution concentrations were <100 μg cm^{-3}, plants took up the prevailing concentration. Evapotranspiration was estimated by the evaporation of water from covered pans. Covered pan ET values were ~90% of uncovered pan values, the same ratio as reported for ET/ETpan in well-watered corn (*25*). Evapotranspiration was partitioned to 25% evaporation (E) and 75% transpiration (T), and these values were used for the potential E and potential T in Hydrus.

Hydrus provides solute concentrations in the water phase. Total herbicide concentrations in soil were calculated using

$$C_{herb} = (\Theta + \rho_B K_{d,isox}) C_{isox} + (\Theta + \rho_B K_{d,DKN}) C_{DKN} \quad (1)$$

where C_{herb} is the total concentration of isoxaflutole and DKN in soil (M L^{-3}), Θ is the soil–water content (L^3 L^{-3}), ρ_B is the soil bulk density

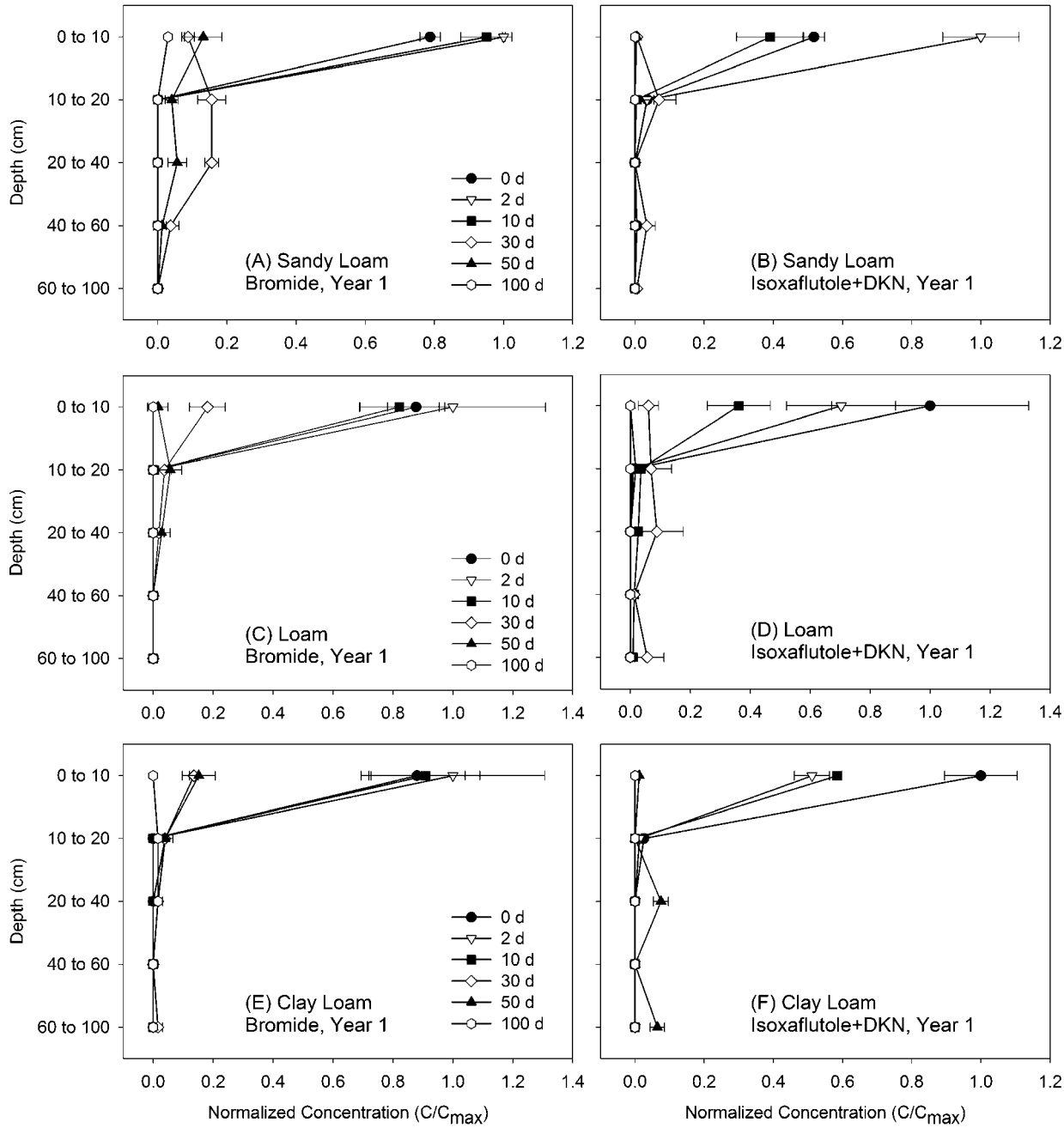

Figure 4. Concentration in each depth increment in Sverdrup sandy loam (**A**) bromide and (**B**) isoxaflutole + DKN; Barnes loam (**C**) bromide and (**D**) isoxaflutole + DKN; Hamerly clay loam (**E**) bromide and (**F**) isoxaflutole + DKN in the first year of the experiment. Concentrations are normalized to the maximum concentration measured in each soil type.

(1.5 g cm^{-3}), $K_{d,isox}$ and $K_{d,DKN}$ are the sorption coefficients for isoxaflutole and DKN, respectively (L^3 M^{-1}), and C_{isox} and C_{DKN} are the liquid-phase concentrations (Hydrus output) of isoxaflutole and DKN, respectively (M L^{-3}). Since bromide is nonsorbed, aqueous concentrations were taken as the total concentration in soil.

RESULTS AND DISCUSSION

Weather and Soil Conditions. Weather conditions prevailing throughout the experiment were typical of the area. The average air temperature (measured at 2 m) was 18 °C, and the average soil temperature (measured at 5 cm depth) was 20 °C during the first year (**Figure 2A**). Air and soil temperatures were slightly higher in the second year of the experiment, averaging 20 °C (air) and 21 °C (soil) (**Figure 2B**). Rainfall totaling >20 mm occurred 22, 27, 46, 93, and 98 days after herbicide application, with frequent low-intensity rains occurring during the first year of the experiment (**Figure 2A**). Cumulative precipitation during the first year was 290 mm. In the second year, frequent rainfalls produced cumulative precipitation of 383 mm, ~90 mm more than in year 1 (**Figure 2B**). Rainfall totaling >20 mm occurred 15, 16, 61, and 63 days after herbicide application in the second year of the experiment (**Figure 2B**).

Surface soil moisture varied in response to precipitation, while soil moisture in the deepest depth increment (60–100 cm) was generally less variable with time (**Figure 3**). In year 1, saturated conditions were observed in the deepest depth increment in the clay loam plots at all sampling times. Soil moisture in most depth increments in loam and clay loam plots decreased from 0 to 10 days after herbicide application (**Figure 3**) due to the lack of rainfall in the first 10 days in year 1. The sandy loam plots did not exhibit a large change in soil moisture during the first 10 days (**Figure 3**). Soil moisture increased from 10 to 30

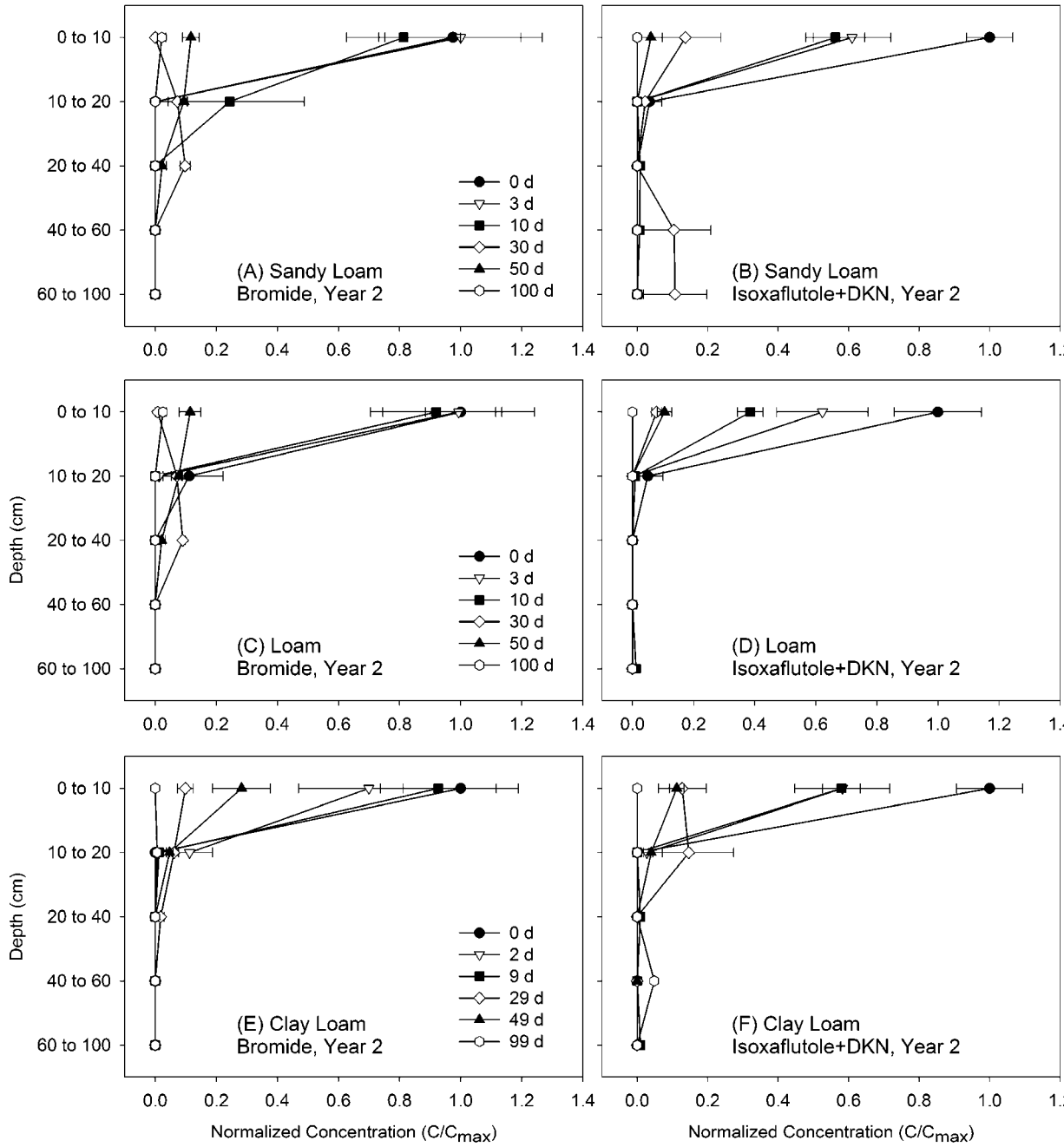

Figure 5. Concentration in each depth increment in Sverdrup sandy loam (**A**) bromide and (**B**) isoxaflutole + DKN; Barnes loam (**C**) bromide and (**D**) isoxaflutole + DKN; Hamerly clay loam (**E**) bromide and (**F**) isoxaflutole + DKN in the second year of the experiment. Concentrations are normalized to the maximum concentration measured in each soil type.

days after herbicide application (**Figure 3**), during which rainfall totaling 87 mm was measured. In year 2, surface soil moisture increased from 0 to 3 days after herbicide application (**Figure 3**), during which rainfall of 18 mm was recorded. Soil moisture measured throughout each profile 100 days after herbicide application in year 2 were the lowest values observed in the 2-year experiment (**Figure 3**).

Measured Concentrations of Herbicide and Bromide in Soil. Samples collected from all monitored depths (0–100 cm) before herbicide application in year 1 contained undetectable amounts of isoxaflutole or DKN, as was expected since this site had never been treated with this herbicide. Plots were shifted in the second year of the study, and preapplication samples again contained no detectable amounts of isoxaflutole or DKN. Background samples also indicated no detectable concentrations of Br^- at all sampled depths in either year of the study.

Surface soil concentrations measured on the day of herbicide application indicated that initial herbicide concentrations were similar in both years: mean surface soil concentrations (0–10 cm depth) were 1.8 μg cm^{-2} in year 1 and 1.6 μg cm^{-2} in year 2. Samples (0–100 cm) collected from untreated plots immediately following and 10 days after herbicide application showed undetectable concentrations of isoxaflutole, DKN, and Br^- in years 1 and 2.

Isoxaflutole can rapidly decompose to the DKN metabolite in soil, with a half-life of $\leq$3 days in moist soil at temperatures $\geq$15 °C (*3*, *4*, *26*). Additional decomposition is possible during sample preparation, extraction, and analysis. Therefore, the concentration of DKN in soil is typically greater than that of the parent compound within days following application of isoxaflutole (*13*, *26*). We observed that on the day of application isoxaflutole concentrations were greater than those of its DKN

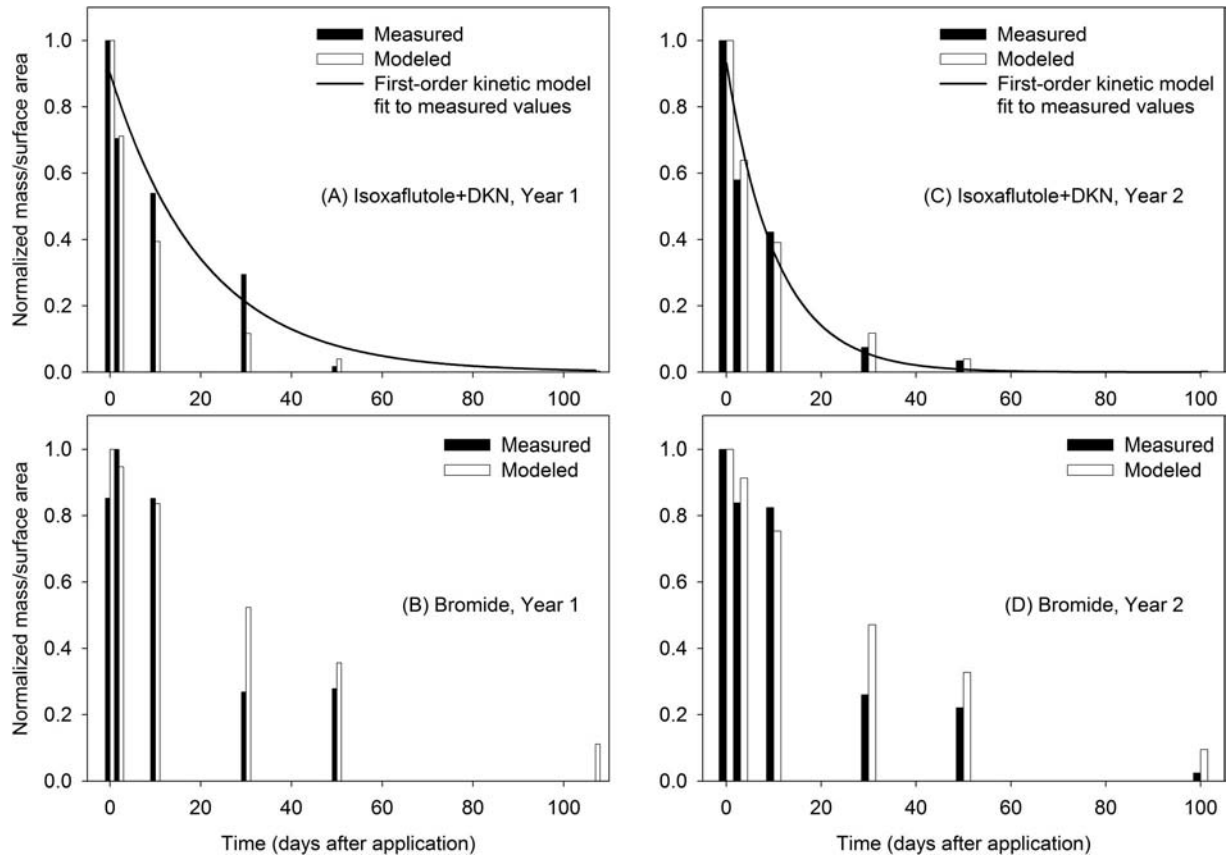

Figure 6. Dissipation of isoxaflutole + DKN in Barnes loam in (**A**) year 1 and (**C**) year 2; lines indicate first-order dissipation model fit to measured data. Bromide remaining in the soil in Barnes loam in (**B**) year 1 and (**D**) year 2. Solid bars are measured values, and open bars are values simulated using Hydrus-1D.

metabolite, but at all subsequent sampling times, concentrations of DKN were greater than those of isoxaflutole. In this study, remaining residue concentrations are reported as isoxaflutole + DKN. It should be noted, however, that all samples collected ≥10 days after isoxaflutole application had nondetectable concentrations of isoxaflutole, so that for these sampling times reported isoxaflutole + DKN concentrations were comprised entirely of DKN.

In all soils, isoxaflutole + DKN concentrations in the surface increment (0–10 cm) declined by about 50% in the first 10 days after application in both years of the study (**Figures 4B**,**D**,**F** and **5B**,**D**,**F**). In year 1, the mean concentration across all soil types declined from 0.047 μg g^{-1} on the day of herbicide application to 0.026 μg g^{-1} at 10 days after application. During this same time period, Br^- concentrations in the surface 10 cm showed no significant change (**Figure 4A**,**C**,**E**) because of the limited rainfall during the first 10 days after application (**Figure 2A**) and limited potential for plant uptake shortly after planting. In year 2, the mean herbicide concentration declined from 0.048 μg g^{-1} at 0 days to 0.024 μg g^{-1} at 10 days after application, while Br^- concentrations in the surface 10 cm decreased by <20% (**Figure 5A**,**C**,**E**). The decrease in herbicide concentration observed in the surface soil during the first 10 days after application may be attributed primarily to nontransport processes, including transformation and bound residue formation. By 100 days after application, bromide and herbicide concentrations were nearly undetectable (**Figures 4** and **5**), accounting for <5% of the applied mass in all cases.

Herbicide Dissipation. Dissipation rates were determined for the mass/surface area of herbicide (isoxaflutole + DKN) in the monitored zone (0–100 cm), which is the sum of the mass/surface area in each depth increment. The mass in each increment was calculated by multiplying the concentration in each depth increment (μg per g of dry soil) by the mass of dry soil in each increment (g). To account for differences in core diameter (5.7 cm for 0–10 cm; 3.2 cm for 10–100 cm), the mass in each depth increment was divided by the surface area of the core for that increment to give the mass/surface area in each depth increment at each sampling time (**Figure 6**). A first-order dissipation model was fit to the herbicide data (**Figure 6**; r^2 = 0.82 to 0.96 for all soil types in both years of the study). Results indicated that isoxaflutole + DKN first-order dissipation half-lives (DT50) in year 1 were 13–14 days (**Table 2**) for each soil type. In year 2, herbicide DT50 ranged from 8 days (loam) to 18 days (clay loam) (**Table 2**). Dissipation rates were approximately the same in both years because the overall soil and climatic conditions were similar. Differences in overall dissipation rates were small, and under these conditions, isoxaflutole dissipation proceeded at approximately the same rate, regardless of soil type (**Table 2**).

Table 2. Dissipation of Isoxaflutole + DKN and Bromide in the Top 1 m of Three Soils[a]

	year 1		year 2	
	k (day^{-1})	DT50 (days)	k (day^{-1})	DT50 (days)
Sverdrup sandy loam	0.05 ± 0.03	13	0.06 ± 0.02	12
Barnes loam	0.05 ± 0.01	14	0.09 ± 0.02	8
Hamerly clay loam	0.05 ± 0.03	13	0.04 ± 0.01	18

[a] Values are regression estimates (±standard error of the estimate) based on the mean mass remaining in the top 1 m of 6 replicate soil cores collected at each of six sampling times for each soil type.

Limited leaching of isoxaflutole + DKN was observed in these studies. In both years, the maximum concentration of

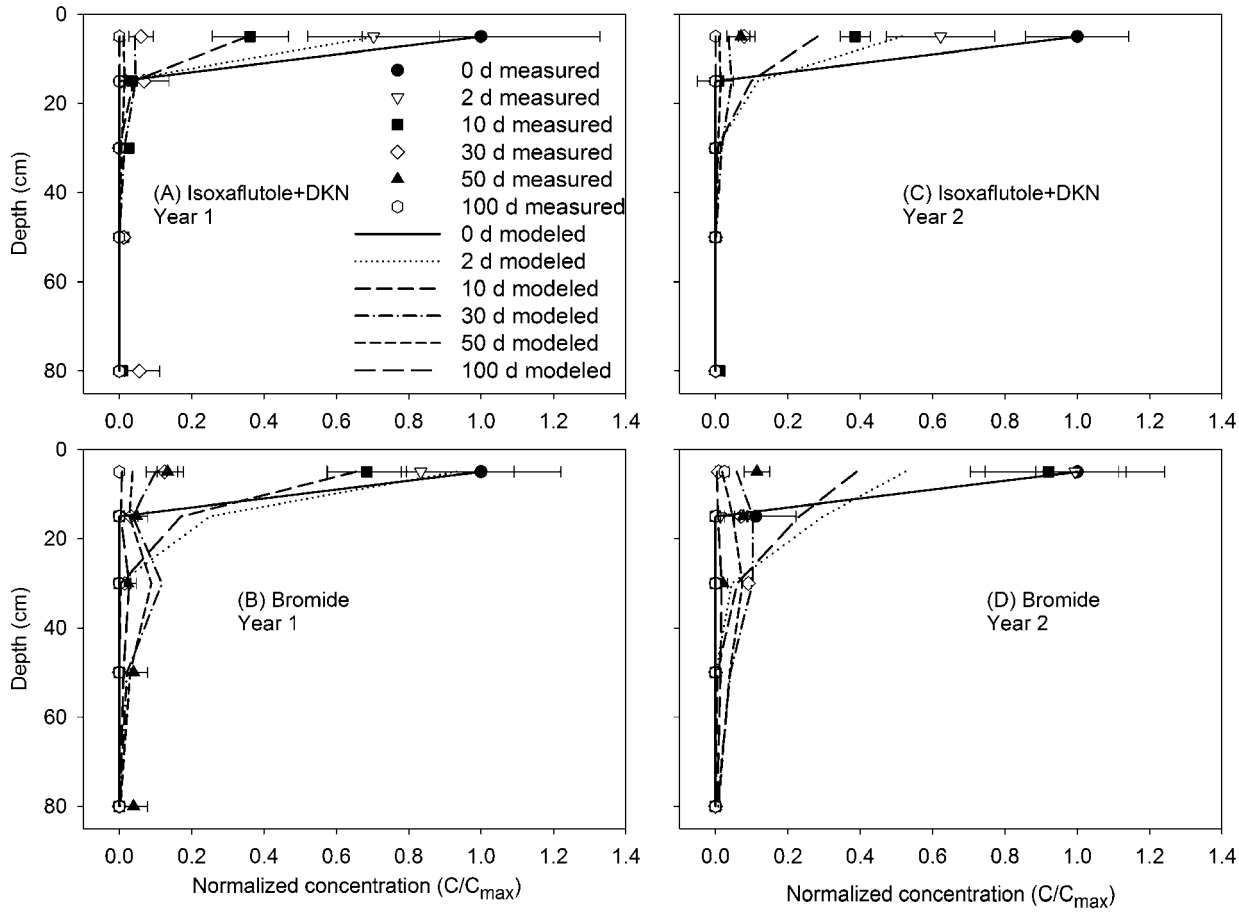

Figure 7. Measured (symbols) and modeled (lines) normalized concentrations of herbicide and bromide in Barnes loam in year 1 (**A** and **B**) and year 2 (**C** and **D**).

isoxaflutole + DKN measured at depths >40 cm was <0.03 μg g^{-1} (**Figures 4** and **5**). In each soil type, the maximum amount of herbicide measured at depths 40–100 cm accounted for ≤16% (year 1) and <5% (year 2) of the applied herbicide. Bromide leaching to depths >40 cm accounted for 10% or less of the applied mass. Leaching was not a major pathway of herbicide or bromide loss in either year of the experiment.

Bromide is assumed to be a conservative (nonsorbed, nondegraded) tracer in this environment, removed from the monitored zone by plant uptake, leaching, and runoff. The faster mass loss of herbicide compared to bromide is attributed to nontransport processes that remove isoxaflutole + DKN from the extractable pool, most notably transformation. However, the decrease in isoxaflutole + DKN residues measured in soil could be due in part to an increase in bound residue formation. Previous research indicated that the recovery of DKN did not decrease during 12 weeks of aging in sandy loam soils at pH < 7, whereas aging did affect DKN extractability (using acidified acetonitrile) in silty clay soil (*17*). We did not conduct studies with different solvent systems to assess the change in the extractability of isoxaflutole + DKN with increased aging in soil. Observations of strong interactions between DKN and organoclays (*18*) suggest that DKN sorption may be at least partially irreversible. Also, laboratory studies have indicated that soil and environmental conditions, including temperature, moisture, pH, and other factors can impact the sorption–desorption and transformation of isoxaflutole and its DKN metabolite (*4*, *12*, *13*, *15*, *16*, *26*). The present studies were conducted to evaluate the overall dissipation of isoxaflutole and its phytotoxic metabolite, and the field methods employed do not allow for an accounting of the dissipation mechanisms. The relative importance of transport and transformation in these experiments was estimated through use of the conservative tracer.

Simulation Modeling. Simulation modeling using Hydrus-1D provided additional information about the processes that may be depleting herbicide and bromide concentrations in soil. Preliminary simulations that included degradation and leaching only (no plant uptake) indicated that nearly all of the applied bromide mass should have been detectable in the top 1 m of soil through at least 50 days. Observations indicated that <30% of the applied bromide was detectable at 50 days after application (**Figure 6**). The water transport module of Hydrus has been verified under a wide range of conditions (*27*). The discrepancy between these preliminary model results and the measured values suggests either that the model inputs did not sufficiently describe this system or that a process other than leaching was impacting bromide concentrations in these experiments.

When plant uptake was included in the model, Hydrus-1D estimates of bromide and herbicide concentrations in soil at each depth were generally in good agreement with measured values (**Figure 7**). The modeled mass/surface area of bromide and herbicide remaining in soil as a function of time was also in good agreement with measured values (**Figure 6**). As parametrized, the simulation model predicted that plant uptake was a large sink for bromide in these studies, accounting for 90% of the applied mass during each 100-day study. Similar results (~95% uptake) have been reported for soils spiked with bromide at concentrations orders of magnitude higher than those used

in this study (*28*). The model predicted negligible leaching (<1% of the applied mass) of bromide below 1 m during these experiments. These results are in agreement with field observations, in which no bromide was detected in the deepest sample increment at any time during the experiment (**Figure 7**). The model predicted that ~10% of the applied bromide would remain in soil 100 days after application, in general agreement with field observations (**Figure 6**).

According to the Hydrus simulation, herbicide leaching below 1 m was negligible, in agreement with field observations of low herbicide concentrations below 60 cm (**Figure 7**). The model predicted that <0.5% of the applied herbicide would remain in soil 100 days after application, in agreement with field observations which showed no herbicide was detectable in soil 100 days after application (**Figure 6**). Simulation modeling suggested that evapotranspiration (which removes water from the root zone, reducing hydraulic conductivity) and plant uptake (which removes solutes from the root zone) may have been major factors preventing herbicide and bromide leaching.

The model predicted that dissipation of isoxaflutole + DKN by degradation and plant uptake were of a similar magnitude and that, together, these two processes accounted for >99% of the applied herbicide in the first 100 days after application. The simulation predicted that plant uptake of the herbicide (isoxaflutole + DKN) accounted for ~50% of the applied mass, or about 40 g ha^{-1}. These model predictions could not be verified because these experiments did not include direct measurements of plant uptake. Few assessments of plant uptake of herbicides from soil under field conditions are available. The simulation modeling suggested that plant uptake may be an important process in the dissipation of low concentrations of reactive and nonreactive solutes under typical field conditions, but additional research is needed to evaluate the role of plant uptake in herbicide dissipation in field soils. Isoxaflutole/DKN is not expected to be conserved within the plant. Both isoxaflutole and DKN are taken up and degraded within plants (*2*, *4*). Isoxaflutole-tolerant plants (like corn and, presumably, cuphea) can detoxify isoxaflutole/DKN within days (*2*). Bromide may be taken up by plants, methylated within the plant, and volatilized as methyl bromide, although this process eliminated only a small proportion of the bromide taken up by the plant (*28*). Other mechanisms, such as bound residue formation, were not included in the model but may also be an important route of herbicide dissipation.

The results of these field studies indicate that concentrations of isoxaflutole and DKN in soil >1 m deep were low under the prevailing conditions. These results will assist in the development of management practices that reduce the threat of water contamination by isoxaflutole and DKN. Additional research is required to further quantify the processes affecting solute dissipation under field conditions. In these experiments, inclusion of the bromide tracer provided critical information about water flow that could not be obtained through monitoring a reactive solute only. Inclusion of nonreactive tracers has been uncommon in pesticide dissipation studies reported in the peer-reviewed literature. The results of this research suggest that plant uptake may be a large sink for solutes. In response to a recent emphasis on determining expected pesticide residues in food and nonfood crops and the recognition that plant uptake is a potential sink for pesticides, plant sampling is now recommended as part of some dissipation studies (*29*). The results of this research support recommendations that plant uptake be accounted for in pesticide dissipation studies. This research suggests that simulation modeling using expected soil, pesticide, and climatic variables may be useful in estimating the importance of plant uptake in pesticide dissipation, providing guidance in planning costly field dissipation studies. These results further suggest that use of a conservative tracer coupled with simulation modeling may be a useful approach to estimate plant uptake for pesticides that undergo dissipation within plants.

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