Effect of Soil Properties on the Degradation of Isoxaflutole and the Sorption–Desorption of Isoxaflutole and Its Diketonitrile Degradate

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The transformation of isoxaflutole (ISOX) to its herbicidally active diketonitrile degradate (DKN) was significantly enhanced in the presence of soil and occurred more rapidly in systems containing soil with a greater soil pH. Sorption–desorption of ISOX and DKN in five soils collected within a field revealed both ISOX and DKN were more readily sorbed to soils with greater organic matter, clay content, and lower soil pH. Sorption of ISOX residues occurred within 2 h, and extracts contained similar concentrations of ISOX and DKN at 24 h, suggesting the 24-h sorption coefficients for ISOX-treated systems were actually for mixed ISOX residues. Freundlich sorption coefficients were 3 and 4 times greater for ISOX than for DKN. On the basis of the Freundlich organic carbon sorption constants, ISOX and DKN can be categorized in the very high and high mobility classes, suggesting their potential to leach in the soils needs to be evaluated.

KEYWORDS: Isoxaflutole; diketonitrile degradate; sorption; desorption

INTRODUCTION

Isoxaflutole [5-cyclopropyl isoxazol-4-yl-2-mesyl-4-trifluoromethylphenyl ketone] (ISOX) (Figure 1) is a pre-emergence isoxazole herbicide used to control grass and broadleaf weeds in corn and sugarcane (1, 2). This recently developed pesticide is readily hydrolyzed in water, soil, and vegetation by the opening of the isoxazole ring to form a diketonitrile degradate [2-cyclopropyl-3-(2-mesyl-4-trifluoromethylphenyl)-3-oxopropanenitrile] (DKN), also herbicidally active, which inhibits 4-hydroxyphenylpyruvate dioxygenase, an enzyme of carotenoid synthesis (1, 3–5). Following foliar or root uptake, ISOX is converted to DKN, which can undergo further degradation to a biologically inactive benzoic acid analogue (2-mesyl-4-trifluoromethyl benzoic acid) (BA). The basis of herbicide selectivity appears to be correlated to the extent of this degradation, being the slowest in susceptible vegetation and the most rapid in tolerant vegetation such as corn and sugarcane. Foliar symptoms of the herbicide in susceptible plants include bleaching of newly developed tissue followed by growth cessation and necrosis (4, 6).

Being a soil-applied herbicide, it is important to understand factors that influence the fate and behavior of ISOX and degradates (i.e., DKN) in soil. Hydrolysis of ISOX to DKN in soil has been shown to be influenced by the soil moisture content, temperature, and pH and primarily the result of chemical processes, whereas further degradation of DKN to BA has been

Figure 1. Structures of isoxaflutole and a diketonitrile degradate.

reported to be primarily the result of biodegradation (7, 8). DKN is more water soluble than isoxaflutole (6.2 mg L⁻¹ ISOX vs 300 mg L⁻¹ DKN), has a greater rate of uptake in plants, and is more mobile in soil than ISOX (6). As a result, the chances of crop injury and groundwater contamination due to leaching may be more likely to occur with DKN as compared to ISOX.

Soils have a remarkable capacity to sorb chemicals; the removal of herbicides from solution by sorption contributes to their availability and controls other processes including mobility/transport, degradability/persistence, and plant uptake/herbicidal activity (9–13). Studies have suggested that only pesticides in solution, or readily desorbable from soil, are available for plant uptake, degradation, or transport. Pesticides that are easily desorbed would be readily available, whereas pesticides that are strongly sorbed and hysteretic during desorption would be slowly available over time or unavailable.

Sorption–desorption processes are affected by the physical and chemical properties of the pesticide and soil. Therefore, it is important to understand the influence of factors such as soil pH, organic matter, and clay content on the strength of sorption of ISOX and DKN to soil. Assessing the hydrolysis of ISOX to DKN and the influence of the variability of soil properties within a field on sorption–desorption of both ISOX and DKN

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Table 1. Mass Balance at 48 h of [^{14}C]isoxaflutole Residues on Three Soils, Collected from the Same Field, with Dissimilar Soil Properties

	soil		
	A	C	D
% clay	12.3	25.4	24.2
% total organic carbon	1.98	1.72	3.72
soil pH	7.42	6.46	6.56
initial extract			
% applied ^{14}C	41.3 $\pm$ 0.38 ^a	40.2 $\pm$ 0.74	33.0 $\pm$ 1.36
% isoxaflutole	3.74 $\pm$ 0.14	4.66 $\pm$ 1.14	4.42 $\pm$ 0.78
% diketonitrile degradate	34.2 $\pm$ 1.52	29.8 $\pm$ 2.02	25.3 $\pm$ 1.95
% unidentified degradates	3.31 $\pm$ 1.28	5.80 $\pm$ 3.90	3.33 $\pm$ 0.19
soil extract			
% extractable ^{14}C ^b	10.1 $\pm$ 0.31	9.82 $\pm$ 0.02	14.3 $\pm$ 2.16
% isoxaflutole	1.83 $\pm$ 0.25	3.65 $\pm$ 0.11	4.27 $\pm$ 0.82
% diketonitrile degradate	6.94 $\pm$ 0.31	4.66 $\pm$ 0.27	7.70 $\pm$ 0.74
% unidentified degradates	1.29 $\pm$ 0.25	1.50 $\pm$ 0.35	2.32 $\pm$ 0.60
bound			
% unextractable ^{14}C ^c	48.7 $\pm$ 0.69	50.0 $\pm$ 0.72	52.7 $\pm$ 0.79

^a Value $\pm$ standard error. ^b Extracted by shaking for 2 h with 1:1 (v/v) acetonitrile/water. ^c Percentage of unextractable ^{14}C = (% applied ^{14}C in the soil phase – % extractable ^{14}C in the soil phase).

will improve the understanding of the potential availability of these compounds for plant uptake, degradation, and/or off-site movement. The specific objectives of the present study were (a) to evaluate the hydrolysis of ISOX, to the diketonitrile degradate, in a CaCl_2 solution without soil and in the presence of different soils and (b) to determine whether the variability of organic matter content, clay content, and soil pH within a field would sufficiently effect the sorption–desorption of ISOX and DKN on soil to significantly change their mobility classification.

MATERIALS AND METHODS

Chemicals. Analytical and radiochemical standards of ISOX and DKN were supplied by Rhone-Poulenc Agriculture Ltd (Essex, U.K.), now Bayer Crop Science (Figure 1). Radiochemical purity and specific activity were, respectively, 99.1% and 1554 MBq mmol⁻¹ (4309 kBq mg⁻¹) for [^{14}C]ISOX and 100% and 909.1 MBq mmol⁻¹ (2521 kBq mg⁻¹) for [^{14}C]DKN. Chemical purity of the analytical standards was 98.6 and 99.9% for ISOX and DKN, respectively.

Soils. Soils (0–15 cm depth) were collected from a field at the Rosemont Agricultural Experiment Station in Dakota County, Minnesota, which consists of different soils according to landscape position (coarse silty, mixed, mesic Typic Hapludoll of the Tallula series on the convex hilltops and upper side slopes; fine silty, mixed, mesic Typic Hapludoll of the Port Byron series on the side slopes; and fine silty, mixed, mesic, Cumulic Haplaquoll of the Colo series in the lower drainage ways and toe slope positions). There was no previous history of isoxazole herbicide application in this area. Collected soils were passed through a 2-mm-diameter sieve and analyzed according to standard protocol to characterize physical and chemical properties. Soil texture was determined according to the hydrometer method (14), whereas the soil organic carbon content was quantified by dichromate oxidation (15). Soil pH was measured in a 1:2 (w/w) soil/deionized water mixture. Five soils were selected on the basis of their percent organic carbon content, clay content, and soil pH (Tables 1–3). Experimental results were compared between pairs of soils that differed in one of the three soil characteristics. Three and five soils were evaluated for the degradation (soils A, C, and D) and sorption studies (ISOX, soils A–E; DKN, soils A and C–F), respectively. Insufficient quantities of soil B required the addition of soil F for the DKN study.

Degradation Kinetics Study. [^{14}C]ISOX was added to a 0.01 M CaCl_2 solution to prepare a stock treatment solution (0.193 $\mu\text{g mL}^{-1}$, 833 Bq mL⁻¹). Ten milliliters of the treatment solution was added to each 35-mL glass centrifuge tube containing 5 g (dry weight) of soil.

The centrifuge tubes were sealed with Teflon-lined lids and agitated on a shaker for 2, 4, 6, 16, 24, and 48 h at 20 ± 2 °C. Two replicate tubes were removed at each time point, and 10 mL of acetonitrile was added to each tube followed by a 2-h agitation to extract ^{14}C residues. Following extraction, replicate tubes were centrifuged at 478g (2000 rpm) for 15 min, and the supernatant was removed. Two 1-mL aliquots of the supernatant were mixed with 5 mL of scintillation cocktail, and ^{14}C was quantified by liquid scintillation spectroscopy (LSS) using a Packard 1500 TRICARB liquid scintillation analyzer. Additional aliquots of the supernatant were analyzed for ISOX and DKN by high-performance liquid chromatography (HPLC) (discussed below). Following the completion of the extraction and centrifugation of the 48-h time point, the remaining soil pellet was resuspended in 10 mL of 1:1 (v/v) acetonitrile/acidified water (0.8% formic acid) and shaken for 2 h. The tubes were removed from the shaker and centrifuged at 478g (2000 rpm) for 15 min. One-milliliter aliquots of the soil extract were added to 5 mL of liquid scintillation cocktail to quantify extractable ^{14}C residues. Additional aliquots of the soil extract were analyzed for ISOX and DKN by HPLC. Three soil-free replicates of the treating solution were also sampled at each time point, and ^{14}C residues were quantified by LSS and characterized by HPLC.

Sorption–Desorption Studies. Batch equilibrium experiments were conducted to determine sorption isotherms of ISOX and its diketonitrile degradate DKN on soils, collected from the same field, with dissimilar organic carbon contents, clay contents, and pH levels. Analytical grade ISOX or DKN was dissolved in acetonitrile and added to 0.01 M CaCl_2 to mimic soil conditions and to obtain four solution concentrations. Final solution concentrations of 0.04, 0.1, 0.4, and 1.1 $\mu\text{g mL}^{-1}$ with solution radioactivity of 83.3 Bq mL⁻¹ were obtained by adding 0.019 $\mu\text{g mL}^{-1}$ [^{14}C]ISOX to the ISOX treatment solutions and 0.033 $\mu\text{g mL}^{-1}$ [^{14}C]DKN to the DKN treatment solutions. Ten milliliters of a treatment solution was added to a 35-mL glass centrifuge tube containing 5 g (dry weight) of soil. Each 2:1 solution/soil system was replicated twice resulting in 80 solution/soil systems (5 soils $\times$ 2 chemicals $\times$ 4 solution concentrations $\times$ 2 replicates). The centrifuge tubes were sealed with Teflon-lined lids, shaken for 24 h at 20 ± 2 °C, and centrifuged for 15 min at 478g (2000 rpm). Five milliliters of the supernatant was removed. Two 1-mL aliquots of the supernatant were each added to 5 mL of Ecolume liquid scintillation cocktail and quantified by LSS. Additional aliquots of the supernatant were analyzed for ISOX and DKN using HPLC.

Immediately following the sorption experiments, desorption was measured from two concentration points of the sorption isotherms (0.04 and 0.4 $\mu\text{g mL}^{-1}$ for ISOX and 0.1 and 1.1 $\mu\text{g mL}^{-1}$ for DKN). Five milliliters of 0.01 M CaCl_2 was added to each centrifuge vial to replace the 5 mL of supernatant removed for the sorption analysis. The vials were mechanically shaken for 24 h at 20 ± 2 °C and centrifuged at 2000 rpm for 15 min, and 5 mL of the supernatant was removed for quantification and characterization of ^{14}C by LSS and HPLC analysis, respectively. Similar desorption cycles were repeated an additional three times.

Instrumental Analysis. All supernatants, described in the previous sections, were analyzed on a 1090 Hewlett-Packard high-performance liquid chromatograph equipped with a diode array detector. ISOX and DKN were separated using a 150 mm $\times$ 21 mm i.d. Zorbax Rx-C8 column operated at room temperature (20 ± 2 °C) with a 68% acidified water (0.8% formic acid)/32% acetonitrile mobile phase at a flow rate of 1 mL min⁻¹. Injection volumes were 100 μL . Pure analytical standards were injected to determine retention times of DKN (1.8 min) and ISOX (10.4 min) at 254 nm. HPLC fractions were collected, mixed with liquid scintillation cocktail, and ^{14}C quantified by LSS.

Calculations. The dissipation of ISOX was calculated on the basis of first-order kinetics using the equation

$$\ln C = \ln C_0 - kt \quad (1)$$

where C_0 is the initial concentration, C is the concentration of ISOX after time t , and k is the first-order rate constant (16). The natural log of the concentrations was plotted against time to give a straight line with a slope proportional to the rate constant. Time for 50% dissipation (DT_{50}) was calculated by the formula

Table 2. [^{14}C]Isoxaflutole Residue Sorption Coefficients on Five Soils, Collected from the Same Field, with Dissimilar Soil Properties

soil	TOC ^a (%)	clay content (%)	soil pH	K_f	K_{loc}	$1/n_f$
A	1.98	12.3	7.42	0.49 (0.49–0.50) ^b	24.8 (24.8–25.3) ^b	0.99 ± 0.01 ^c
B	2.05	22.8	7.10	0.90 (0.79–1.02)	43.9 (38.5–49.8)	0.99 ± 0.06
C	1.72	25.4	6.46	1.20 (1.09–1.33)	70.0 (63.4–77.3)	0.98 ± 0.04
D	3.72	24.2	6.56	1.72 (1.48–2.00)	46.2 (39.8–53.8)	1.05 ± 0.07
E	2.56	23.1	5.69	2.19 (1.94–2.46)	85.3 (75.8–96.1)	1.03 ± 0.05

^a Total organic carbon. ^b Value (standard error range). ^c Value ± standard error ($r^2 = 0.995 \pm 0.003$).

Table 3. [^{14}C]Diketone nitrile Degradate Sorption Coefficients on Five Soils, Collected from the Same Field, with Dissimilar Soil Properties

soil	TOC ^a (%)	clay (%)	soil pH	K_f	K_{loc}	$1/n_f$	$1/n_{\text{d}0.1}$	$1/n_{\text{d}1.1}$	$H_{0.1}$ ^b	$H_{1.1}$
A	1.98	12.3	7.42	0.16 (0.15–0.18) ^c	8.2 (7.6–9.1) ^c	1.04 ± 0.06 ^d	0.77 ± 0.31 ^e	0.64 ± 0.09 ^f	0.74	0.62
C	1.72	25.4	6.46	0.29 (0.26–0.32)	16.7 (15.1–18.6)	1.07 ± 0.05	0.70 ± 0.08	0.67 ± 0.12	0.65	0.63
D	3.72	24.2	6.56	0.47 (0.39–0.56)	12.5 (10.5–15.1)	0.84 ± 0.08	0.65 ± 0.09	0.70 ± 0.05	0.77	0.83
E	2.56	23.1	5.69	0.57 (0.52–0.63)	22.2 (20.3–24.6)	0.92 ± 0.04	0.77 ± 0.04	0.70 ± 0.03	0.84	0.76
F	2.66	23.7	7.48	0.29 (0.26–0.32)	14.1 (12.6–15.6)	1.03 ± 0.05	0.69 ± 0.10	0.71 ± 0.07	0.67	0.69

^a Total organic carbon. ^b $H = (1/n_d)/(1/n_f)$. ^c Value (standard error range). ^d Value ± standard error ($r^2 = 0.993 \pm 0.006$). ^e Value ± standard error ($r^2 = 0.930 \pm 0.088$). ^f Value ± standard error ($r^2 = 0.973 \pm 0.021$).

$$\text{DT}_{50} = 0.693/k \quad (2)$$

The amounts of ISOX and DKN sorbed to the soil in the batch equilibrium sorption–desorption studies were calculated as the difference between the initial solution concentration and the equilibrium solution concentration of the supernatant, considering both the volume of the solution and the quantity of soil. Sorption and desorption isotherms were calculated using the linearized form of the Freundlich equation

$$\log C_s = \log K_f + 1/n_f \log C_e \quad (3)$$

where C_s ($\mu\text{g g}^{-1}$) is the sorbed concentration, C_e ($\mu\text{g L}^{-1}$) is the equilibrium concentration of sorbate in solution, $1/n_f$ is an empirical constant expressing the concentration dependence of sorption, and K_f is the Freundlich coefficient. Both the sorption and desorption data fit the Freundlich isotherm well ($r^2 = 0.930$ – 0.995). Sorption coefficients normalized to organic C, K_{loc} , were calculated by dividing K_f by the percentage of organic carbon of the soil.

$$K_{\text{loc}} = (K_f/\% \text{OC}) \times 100 \quad (4)$$

The distribution coefficient (K_d) was calculated as the ratio between the content of the chemical sorbed on the soil at sorption equilibrium, $C_s(\text{eq})$ ($\mu\text{g g}^{-1}$), and the concentration of the chemical substance in the aqueous phase at sorption equilibrium, $C_e(\text{eq})$ ($\mu\text{g mL}^{-1}$), where

$$K_d = C_s/C_e \quad (5)$$

Hysteresis coefficients, H , were calculated according to

$$H = (1/n_d)/(1/n_f) \quad (6)$$

where $1/n_f$ and $1/n_d$ are the Freundlich slopes for the sorption and desorption isotherms, respectively.

RESULTS AND DISCUSSION

Hydrolysis of Isoxaflutole. In a soil-free system, the quantity of ISOX in 0.01 M CaCl_2 solution decreased from 90.7 ± 1.2 to $82.9 \pm 0.9\%$ of the applied ^{14}C , whereas DKN increased from 7.7 ± 0.8 to $15 \pm 1.2\%$, over a period of 48 h, indicating ~7% hydrolysis. Similar rates of hydrolysis were reported by Taylor-Lovell et al. (17) in soil-free 0.01 M CaCl_2 solutions in which approximately 7% hydrolysis was noted in 48 h at 5 °C and 13% hydrolysis in 24 h at 25 °C. Ratios of ISOX/DKN in

our soil-free systems decreased with time from approximately 11:1 at 2 h to 6:1 at 48 h.

Hydrolysis of ISOX to DKN was enhanced in the presence of soil. Using a rapid, single extraction with acetonitrile to minimize ISOX decomposition during the extraction of ISOX and degradates from the 2:1 solution/soil slurries, the recoveries of applied radioactivity in the initial extracts were 41.4 ± 2.6 and $38.2 \pm 4.5\%$ for the 2- and 48-h samples, respectively. **Figure 2** depicts the percentage of applied ^{14}C identified as ISOX and DKN in the initial extracts. Ratios of ISOX/DKN decreased with time from approximately 9:1 at 2 h to 1:1 at 24 h and to 1:7 at 48 h.

Following the initial extraction, soil from the 48-h samples was subsequently extracted with 1:1 (v/v) acetonitrile/0.01 M CaCl_2 , which recovered an additional $11.4 \pm 2.5\%$ of the applied radioactivity. A mass balance of the applied [^{14}C]isoxaflutole residues at 48 h is presented in **Table 1**. More than 75% of the initial extract was identified as DKN, whereas <15% represented ISOX or unidentified degradates. The percentage of applied radioactivity remaining in the soil after the initial extract was 59–67% of the applied ^{14}C . Soil extracts were essentially half DKN, one-third ISOX, and <17% unidentified degradates. When both the initial extracts and soil extracts were considered, DKN residues were 4–7 times greater than isoxaflutole residues. After 48 h, $36.2 \pm 4.4\%$ of the applied ^{14}C was characterized as DKN in the combined initial and soil extracts, which represents a 21% increase in hydrolysis from the soil-free systems (DKN = $15.0 \pm 1.2\%$ in the soil-free systems at 48 h) and confirms the catalytic effect of soil as previously reported (17).

The mechanisms involved in the increased hydrolysis of ISOX in the presence of soil have not yet been determined. Enhanced hydrolysis of ISOX to DKN was noted in the presence of sterile soil but not in solutions containing soil soluble components (17). Sorption-catalyzed hydrolysis has been reported for several pesticides including atrazine, diazinon, and malathion (18). Carrizosa et al. (19) reported enhanced hydrolysis of ISOX to DKN in aqueous solutions in the presence of organoclays relative to natural clays or soil-free systems. No measurable sorption of applied [^{14}C]ISOX was measured on pure clays, and only 8, 8, 20, and 25% hydrolysis were observed in the soil-free and 0.01 M CaCl_2 /natural clay systems (SA-smectite, SW-

Figure 2. Characterization of isoxaflutole and the diketone nitrile degradate of isoxaflutole in the initial extracts of the 2:1 0.01 M CaCl₂/soil systems.

smectite, and hectorite), respectively. In contrast, the incorporation of large organic cations in the interlayer of the smectites resulted in organoclays that had greater sorption and enhanced hydrolysis of ISOX. The greater hydrolysis of ISOX in the presence of organoclays compared to the lack of ¹⁴C sorption and minimal hydrolysis in the presence of natural clays suggests sorption-catalyzed decomposition (19).

Soil texture, organic carbon content, and pH can affect sorption and therefore influence the availability of pesticides for degradation and sorption-catalyzed decomposition (11–13). The DT₅₀ of ISOX has been reported to range from 12 h to 14 days under laboratory conditions depending on factors such as soil type, pH, temperature, and moisture (6, 20). Rouchaud et al. (21) reported greater field dissipation of ISOX in soil with higher soil pH (i.e., pH 5.5, DT₅₀ = 14.4 days; pH 7.2, DT₅₀ = 12.1 days). Beltran et al. observed that the degradation of ISOX in aqueous solutions (8, 22) and soil (7) occurred more rapidly at higher pH and at higher temperatures, and the conversion of ISOX into DKN followed pseudo-first-order kinetics. The calculated time for 50% dissipation (DT₅₀) of ISOX from the 2:1 CaCl₂/soil slurries revealed similar findings, in which soil A with the greatest pH (7.42) had a DT₅₀ of 13.7 ± 0.2 h, whereas the DT₅₀ values for soil C (pH 6.46) and soil D (pH 6.56) were 17.3 ± 3.2 and 16.3 ± 1.7 h, respectively. The DT₅₀ of ISOX increased with the increasing clay content of the soil (12.3% clay = DT₅₀ of 13.7 ± 0.2 h; 24.2% clay = DT₅₀ of 16.3 ± 1.7 h; 25.4% clay = DT₅₀ of 17.3 ± 3.2 h). Although the DT₅₀ was correlated with soil pH ($r^2 = 0.97$) and clay content ($r^2 = 0.97$), it was not correlated with the soil organic carbon content ($r^2 = 0.02$). Others have reported a correlation between the rate of reaction from ISOX to DKN with soil pH, but not clay or organic carbon content (7). It should be noted that DT₅₀ values presented are calculated on the basis of the initial extraction and are reported for the purpose of comparison between the soils evaluated. Further extractions may have

resulted in greater recovery, which in turn could possibly influence the calculated DT₅₀ values.

Isoxaflutole Sorption. Sorption isotherms of ISOX residues (¹⁴C = [¹⁴C]ISOX and [¹⁴C]ISOX degradates) (Figure 3) were fitted to the Freundlich equation, and sorption coefficients were calculated (Table 2). Paired comparisons were made between soils that differ in one of three soil characteristics to determine the influence of clay content, total organic carbon content (TOC), and soil pH on the sorption of ISOX residues to soil.

Soils with larger clay content had greater sorption of ISOX residues. In paired comparisons with soils of similar pH and TOC, the soil with the larger percentage clay was more sorptive (Table 2, soil A vs soil B, soil A vs soil C). When soil A was compared with soil B, a 1.9 times increase in percent clay (soil A = 12.3%, soil B = 22.8%) resulted in a 1.8 times increase in the sorption coefficient ($K_f = 0.49$ for soil A, $K_f = 0.90$ for soil B). A similar trend was noted for soils A and C in which a 2.1 times increase in percent clay (from 12.3 to 25.4%) resulted in a 2.5 times increase in K_f (from 0.49 to 1.20).

Soils, which were similar in clay content and soil pH, but dissimilar in TOC, were compared to determine effects of organic carbon on sorption. The 2.0% increase in percent OC of soil D, as compared to soil C, resulted in a greater sorption as indicated by the small, but significant increase in the sorption coefficient ($K_f = 1.72$ for soil D, $K_f = 1.20$ for soil C).

For the three soil characteristics evaluated, soil pH appears to have the greatest effect on sorption of ISOX residues. When soils with different pH levels and similar clay and organic carbon contents were compared, the soil with the lower pH had greater isoxaflutole sorption (soil E pH = 5.69, $K_f = 2.19$; soil B pH = 7.10, $K_f = 0.90$). For the five soils studied, there appears to be an inverse relationship between soil pH and sorption even when the clay and TOC content varied. Results in Table 2 show that sorption (K_{foc}) decreased in the order soil pH of 5.69 > 6.46 > 6.56 > 7.10 > 7.42. When soil pairs were compared,

Figure 3. $[^{14}\text{C}]$ isoxaflutole residue sorption-desorption on soil (solid symbols, adsorption; open symbols, desorption).

in which two of the three soil characteristics were similar, a smaller change in pH (20% change from soil B vs soil E) resulted in a greater change in K_f (60% change), compared to TOC (soil C vs soil D: 54% change in TOC, 30% change in K_f) or clay content (soil A vs soil B: 46% change in clay content, 45% change in K_f). The influence of pH being greater than that of TOC or clay content is further illustrated when we compare soil D with soil E. Soil E with the lower pH was more sorptive than soil D, despite both the greater clay content and organic carbon content of soil D.

Sorption was not affected by ISOX residue concentration ($1/n_f = 0.98\text{--}1.05$). Overall trends noted in the paired soil comparisons were an increase in organic matter content and clay content resulted in increased sorption, whereas the reverse was true for soil pH in which a reduced soil pH resulted in greater sorption. For the five soils evaluated in this study, the main soil characteristic influencing the sorption of ISOX residues appears to be the pH of the soil ($r^2 = 0.89$). Little correlation was found between the extent of adsorption and TOC

($r^2 = 0.34$) or clay content ($r^2 = 0.42$). Mitra et al. (23) also observed a strong relationship between soil organic matter and sorption ($r^2 = 0.99$) and, similar to our observations, a correlation between soil pH and sorption ($r^2 = 0.95$) but little correlation between clay content and sorption ($r^2 = 0.45$) (24).

Isoxaflutole Desorption. Supernatants were analyzed by HPLC to characterize the ^{14}C remaining in the solution at the completion of the isoxaflutole sorption experiment. Following the 24-h equilibration, $7.0 \pm 4.0\%$ of the radioactivity detected in the CaCl_2 solution was identified as isoxaflutole, whereas $91.5 \pm 4.3\%$ was identified as the diketonitrile degradate of isoxaflutole. As a result, the subsequent desorption study was limited to a single desorption step because the results of this experiment would not reflect isoxaflutole desorption but rather a mixture of DKN/ISOX. Additional studies evaluating the sorption-desorption of the diketonitrile degradate were initiated.

Isoxaflutole versus Isoxaflutole Residues. K_d values for ISOX residues (measured $^{14}\text{C} = [^{14}\text{C}]\text{ISOX}$ and $[^{14}\text{C}]\text{ISOX}$ degradates) at 48 h were 2.85, 2.97, and 4.06 for soils A, C, and D, respectively. In our hydrolysis study we observed that in the 2:1 $\text{CaCl}_2/\text{soil}$ systems hydrolysis occurred within 2 h, and after 48 h, $<10\%$ of the applied $[^{14}\text{C}]\text{ISOX}$ was extracted from the combined extracts of the solution and soil phases with 30% of the applied ^{14}C identified as $[^{14}\text{C}]\text{DKN}$. Therefore, it is possible that the K_d calculated from the ratio of ^{14}C in the soil and solution phases is actually the K_d for a mixture of ISOX and ISOX degradates. By measurement of the quantity of ISOX in both the initial extract and the sediment extract by HPLC analysis and utilization of these values to recalculate a K_d of ISOX after 48 h, the K_d values overall were reduced to 0.98, 1.57, and 1.93 for soils A, C, and D, respectively. These results illustrate that the use of the distribution of radioactivity to determine the sorption coefficient of readily degradable compounds rather than the extractable quantities of the parent compound may over- or underestimate the sorption coefficient.

DKN Sorption. The diketonitrile sorption isotherms, presented in Table 3 and Figure 4, were fitted to the Freundlich equation ($r^2 = 0.993 \pm 0.006$). Similar to the observations in the ISOX residue sorption study, sorption of DKN was minimally dependent on herbicide concentration ($1/n_f = 0.84\text{--}1.07$). Paired comparisons were made between soils that differ in one of three soil characteristics (percent clay, TOC, and pH) to determine their impact on the sorption of DKN to soil. The following trends were observed.

Soil with the greater clay content was the more sorptive soil of the paired comparison. The 2-fold increase in percentage clay of soil (12.3% soil A and 25.4% soil C) resulted in an almost doubling of the K_f . Similar observations were noted in the comparison of soil A with soil F. For the five soils evaluated, the soil with the smallest clay content, soil A, had the smallest K_f (Table 3).

Soils C and D, which were similar in clay content (25.4 and 24.2%, respectively) and soil pH (6.46 and 6.56, respectively) but dissimilar in TOC, were compared. An increase in percent OC from 1.72 to 3.72% resulted in an increased K_f from 0.29 to 0.47, which suggests greater sorption of DKN in soils with larger organic matter content. Our results are in agreement with those of Mitra et al. (24), who reported sorption of DKN increased with an increase in soil organic matter. Comparable observations were noted in our evaluation of the effect of organic matter on the sorption of isoxaflutole. Previous research has reported similar effects of organic matter on the sorption of

Figure 4. Sorption–desorption of the diketonitrile degradate on soil (solid symbols, adsorption; open, desorption).

isoxaflutole (23), metolachlor (25, 26), and atrazine and atrazine degradates (27).

Soils E and F, soils with similar clay (23.1 and 23.7%, respectively) and TOC (2.56 and 2.66%, respectively) contents, were compared to determine the influence of soil pH (5.69 and 7.48, respectively) on DKN sorption. Soil E with the lower pH had sorption coefficients that were almost twice that of soil F (soil E, $K_f = 0.57$; soil F, $K_f = 0.29$) (Table 3). Sorption (K_{foc}) decreased in the order pH 5.69 > 6.46 > 7.48 > 6.56 > 7.42.

Similar trends were noted in the paired soil comparisons for DKN as with ISOX residues: an increase in organic matter content and clay content resulted in increased sorption, whereas reduced soil pH resulted in greater sorption. For the five soils evaluated little correlation was found between the sorption coefficient of DKN and organic matter ($r^2 = 0.34$), clay content ($r^2 = 0.34$), or soil pH ($r^2 = 0.71$), and DKN was less sorptive than ISOX [K_{foc} of ISOX = 24.8–85.3 (Table 2); K_{foc} of DKN = 8.2–22.2 (Table 3)], which was analogous to the observations of Beltran et al. (28).

DKN Desorption. DKN was more readily desorbed from soils D and E ($H = 0.76$ –.84) than from soil A, C, or F ($H =$

0.62–0.74) at both 0.1 and 1.1 $\mu\text{g mL}^{-1}$ (Table 3). Soils D and E had the largest percent OC with a lower soil pH. When soil pairs in which two of three soil characteristics (TOC, clay content, pH) were similar were compared, DKN was more readily desorbed from soil with a lower soil pH (soil E vs soil F) or greater percent OC (soil D vs soil C). When the five soils were compared, desorption of DKN was not substantially influenced by organic matter ($r^2 = 0.34$), clay content ($r^2 = 0.02$), or soil pH ($r^2 = 0.30$). Mitra et al. (26) also found clay content did not significantly affect DKN desorption; however, increased organic carbon content did result in larger quantities of nondesorbable DKN, and desorption of DKN in soils was found to be influenced primarily by organic matter. Carrizosa et al. (19) reported no measurable sorption of DKN on natural clays, yet incorporation of large organic cations in the interlayer of smectites resulted in organoclays with greater sorptive properties for DKN, and desorption isotherms revealed irreversibility of the sorption–desorption process. Desorption isotherms of DKN, on the five soils evaluated in this study, revealed reversibility of the sorption–desorption process.

ISOX versus DKN. Freundlich sorption coefficients (K_f) were 3 and 4 times greater for ISOX ($K_f = 0.49$ –2.19) than for DKN ($K_f = 0.16$ –0.57). The increased availability of DKN along with its greater biological activity, persistence, and water solubility (ISOX, 6.2 mg L^{-1} ; DKN, 326 mg L^{-1}) suggests DKN is more likely to cause crop injury and leach to groundwater than ISOX. Sorption coefficients normalized for the soil organic carbon content (K_{foc}) ranged from 24.8 to 85.3 for ISOX and from 8.17 to 22.2 for DKN, which classifies ISOX as highly mobile to very highly mobile and DKN as very highly mobile (29). These results correspond to those previously reported (ISOX, $K_{oc} = 134$, high mobility; DKN, $K_{oc} = 17$, very high mobility) (17, 29). Within-field variability of organic matter content, clay content, and soil pH did not influence the mobility classification of ISOX or DKN in soil.

Pesticide degradation and sorption–desorption interactions of pesticides and pesticide degradates with soil affect their availability for plant uptake and transport, which will influence the agronomic and environmental impact of these toxicologically and environmentally significant compounds. Sorption coefficients and half-life values of pesticides are utilized with mathematical models to conduct risk assessments that characterize the availability of pesticides for degradation and transport and estimate leaching potential. The retention or release of pesticides from soil will be influenced by both chemical and physical properties of the pesticide and soil. Therefore, it is important to evaluate pesticide–soil interactions in various soils to determine the influence of soil characteristics on sorption–desorption as well as identify hysteresis effects. A greater understanding of these processes will provide more accurate input to effectively predict pesticide behavior and estimate risk and environmental and agronomic impact.

ABBREVIATIONS USED

DKN, diketonitrile degradate [2-cyclopropyl-3-(2-mesyl-4-trifluoromethylphenyl)-3-oxopropanenitrile]; DT₅₀, time for 50% dissipation; H , hysteresis coefficients; HPLC, high-performance liquid chromatography; ISOX, isoxaflutole [5-cyclopropyl isoxazol-4-yl-2-mesyl-4-trifluoromethylphenyl ketone]; K_d , distribution coefficient; K_f , Freundlich sorption coefficients; K_{foc} , Freundlich organic carbon sorption constants; LSS, liquid scintillation spectroscopy; TOC, total organic carbon content

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