

Hydrolysis and Soil Adsorption of the Labile Herbicide Isoxaflutole

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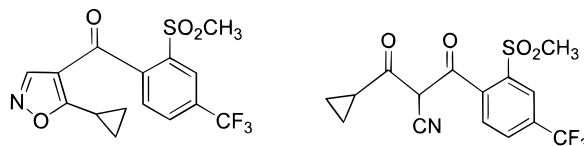
Isoxaflutole (5-cyclopropyl isoxazol-4-yl-2-mesy-4-trifluoromethylphenyl ketone) is a new herbicide marketed for broadleaf and grass weed control in corn, but little information has been published on the soil behavior and environmental fate of the compound. The herbicide exhibits an unusual behavior in which it is functionally reactivated by rainfall events, providing control of small weeds that have emerged. Isoxaflutole is extremely labile in aqueous solution, thus measuring equilibrium sorption is challenging. A qualitative kinetic evaluation was performed to characterize the sorption of isoxaflutole, during rapid hydrolysis to its bioactive product, a diketonitrile derivative (2-cyclopropyl-3-(2-mesy-4-trifluoromethylphenyl)-3-oxopropanenitrile). The transformation was measured over time in a herbicide-treated aqueous solution with or without soil. At 25 °C, 83% of the parent compound remained in solution at 24 h in the soil free system, but only 15% remained in the solution in the presence of soil. The sorbed phase consisted mainly of isoxaflutole, although a small percentage of diketonitrile was also detected in increasing concentrations as the study progressed. Hydrolysis prevented the attainment of sorption equilibrium, thus the apparent K_d of isoxaflutole increased over time, while that of diketonitrile remained close to zero at both 5 and 25 °C. Batch sorption isotherms were conducted with both isoxaflutole and diketonitrile using four Illinois soils of the Drummer, Flanagan, Catlin, and Cisne series ranging in organic carbon (OC) from 1.0 to 2.5%. Freundlich K_d values were 6–12-fold greater for isoxaflutole than diketonitrile, with the greatest difference in the lower organic carbon soils. After removing the hydrolysis effect, sorption of the isoxaflutole and diketonitrile was independent of temperature, suggesting that it was an entropy-driven process. Based on soil OC content, K_{oc} values of 134 and 17 mL g⁻¹ were calculated for isoxaflutole and diketonitrile, respectively. Results suggest that desorption coupled to hydrolysis promotes reactivation of the herbicide's function after rainfall and contributes to the efficacy of the compound by resupplying the soil solution with a bioactive product.

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Isoxaflutole

Diketonitrile

FIGURE 1. Chemical structures for isoxaflutole and its diketonitrile derivative.

Introduction

Isoxaflutole (5-cyclopropyl isoxazol-4-yl-2-mesy-4-trifluoromethylphenyl ketone) (Figure 1) is a new preemergence herbicide for grass and broadleaf weed control in corn, a crop which represents the greatest herbicide market covering 1.3×10^8 ha worldwide (1). This herbicide exhibits a new mode of action, inhibition of 4-hydroxyphenylpyruvate dioxygenase (HPPD) by the diketonitrile derivative of isoxaflutole, which causes bleaching of new leaf tissue in susceptible weeds (2–4). Environmental benefits of isoxaflutole include rapid degradation, low application rate, and favorable toxicology in comparison to conventional herbicides such as atrazine (1, 5, 6). As the only registered herbicide exhibiting this mode of action, there is a great potential for a rapid increase in use. To date, very limited research has been published on the fate of isoxaflutole in soil, so it is important to characterize the sorption and transformation processes of this new compound.

Although it is convenient to assume equilibrium between a chemical in solution and sorbed phases, it is now clear that sorption of certain materials may be limited by chemical reactions such as hydrolysis (7–10). First-order rate models may be used to predict sorption of labile compounds (11), but direct measurement of nonequilibrium sorption requires the use of a kinetic analysis. In many kinetic studies, analysis of the solution phase is used to make inferences about the sorbed phase (12), and analysis of reaction products may be ignored (13). This may not be adequate in the case where significant hydrolysis is occurring during the course of the study, a potential concern with isoxaflutole, which hydrolyzes rapidly in neutral pH conditions. Because sorption is known to affect chemical reactions in the soil (14, 15), a comparison between the rate of the reactions in the presence and absence of soil would provide insight on the effect of sorption on isoxaflutole hydrolysis. For example, Macalady and Wolfe (9) showed that alkaline-catalyzed hydrolysis rates for organophosphorothioate esters were decreased in the sorbed state, while neutral hydrolysis reactions were not affected greatly compared to aqueous hydrolysis. Nonbiological hydrolysis reactions of several pesticides have been shown to occur more rapidly in the soil than an aqueous system due to catalysis by clay surfaces (16).

Hydrolysis of isoxaflutole requires special attention because it is considered to be a proherbicide, or one that becomes active after transformation. In this case, the diketonitrile derivative of isoxaflutole (2-cyclopropyl-3-(2-mesy-4-trifluoromethylphenyl)-3-oxopropanenitrile) (Figure 1) has been proven as an active form of the herbicide (6, 3), making it important to understand what conditions influence hydrolysis to form this product. This active diketonitrile derivative can be formed in the soil prior to plant uptake or after the plant has absorbed isoxaflutole. In both cases, the diketonitrile derivative is known to inhibit the HPPD enzyme, providing herbicidal activity. The sorption of diketonitrile must also be considered in relationship to isoxaflutole, as

TABLE 1. Properties of Four Illinois Soils Used in Batch Equilibrium Isotherms

series name	location	taxonomic class	texture	OC (%)	CEC (mequiv/100 g)	pH	sand (%)	silt (%)	clay (%)
Drummer	Champaign, IL	Typic Endoaquolls	silty clay loam	2.5	21.0	7.0	16	44	40
Flanagan	Champaign, IL	Aquertic Argiudolls	silt loam	2.2	15.1	7.0	15	53	32
Catlin	Champaign, IL	Oxyaquic Argiudolls	silt loam	1.8	13.2	7.3	13	53	34
Cisne	Brownstown, IL	Vertic Albaqualfs	silt loam	1.0	7.3	7.1	25	55	20

the two chemicals are likely to be in the system simultaneously. Sorption not only is useful in retaining a pesticide in the zone where it is most likely to control weeds but it also decreases the bioavailability of the compound, a problem that may be overcome by increasing the dose rate (17). A variety of approaches, such as microencapsulation, have been used to retain a pesticide within a target zone to sustain a bioactive concentration while reducing pesticide transport. Isoxaflutole may represent a model for a new approach in which greater sorption of the parent retains the material in the target zone, and subsequent hydrolysis increases bioavailability, as the product exhibits less sorption.

Isoxaflutole is dependent on adequate moisture for optimum weed control and demonstrates a unique ability to provide "rechargeable activity" following a rainfall event, controlling weeds which had escaped initial control due to dry conditions or poor coverage (18, 19), even after the weeds have emerged. This phenomenon is unique for a soil-applied herbicide and likely results from increased exposure of the weeds to the diketonitrile hydrolysis product with moisture or an increase in the concentration as a result of hydrolysis. The parent compound is not likely to persist in a great concentration in the solution due to rapid hydrolysis, so there must be a mechanism for sequestering isoxaflutole and preventing degradation to provide the residual control demonstrated in the field. The reactivation of herbicidal activity following rainfall implies an interaction between sorption and hydrolysis, making water the limiting factor. Because the solubility of diketonitrile is 50 times greater than that of isoxaflutole ($326 \mu\text{g mL}^{-1}$ versus $6.2 \mu\text{g mL}^{-1}$), it would be expected to occur more readily in the soil solution and exhibit less sorption. By simultaneously quantifying the sorption of both compounds in an aqueous soil system, a more complete understanding of sorption and the mechanisms for the unusual "recharge activity" should result.

The goal of the following research was to determine the effect of isoxaflutole hydrolysis on sorption by analyzing aqueous and sorbed phases over the course of 48 h. Characterization of the sorption of both isoxaflutole and its diketonitrile derivative on a range of Midwest soils was used to better establish the mechanism of soil sorption. The data were used to calculate K_{oc} values for each of the compounds on soils representing the area where the herbicide is likely to be used.

Materials and Methods

Soil. The four Illinois soils used in the sorption isotherms, Drummer, Flanagan, Catlin, and Cisne, are detailed in Table 1. The soils were chosen because they are representative of soils in the major use area for the herbicide; they vary in OC content and have similar pH. Composite samples of moist soil were collected between June and November, 1998 from the top 10 cm (A horizon) of fields which had not previously received an application of isoxaflutole. Soil was sieved through a 2-mm screen and stored at 5 °C in thin-walled polyethylene bags. Prior to conducting sorption studies, the soil was allowed to air-dry for at least 24 h.

Chemicals. In the kinetic and sorption studies, [*phenyl*-(U)- ^{14}C]isoxaflutole with specific activity of 909.1 MBq/mmol (2525 kBq/mg) and 100% radiopurity was used. Radiolabeled isoxaflutole was supplemented with technical grade material

to obtain necessary concentrations for the isoxaflutole equilibrium study. The equilibrium study on the diketonitrile derivative of isoxaflutole employed technical grade diketonitrile and [*phenyl*-(U)- ^{14}C]diketonitrile with the same specific activity and radiopurity of isoxaflutole. The sorption studies were also analyzed for the benzoic acid derivative of diketonitrile (2-*mesyl*-4-*trifluoromethylbenzoic acid*).

Qualitative Kinetic Evaluation. A stock treatment solution was prepared by combining 20.3 μg of [^{14}C]isoxaflutole (51 430 Bq) with 350 mL of 0.01 M CaCl_2 electrolyte solution, giving a concentration of 0.058 $\mu\text{g mL}^{-1}$ of isoxaflutole (147 Bq mL^{-1}). In 50-mL PTFE (Teflon) centrifuge tubes, 10 mL of the treatment solution was added to 5 g of air-dry Drummer soil to give a 1:2 soil-to-solution ratio, providing a total amount of 0.58 μg of [^{14}C]isoxaflutole per tube. Sealed tubes were agitated on a reciprocating shaker for 1, 2, 4, 8, 12, and 24 h at 25 °C and 1, 2, 4, 8, 12, 24, and 48 h at 5 °C. A longer time period was used at 5 °C due to slower reaction kinetics at that temperature. At each sampling time, three replicate tubes were removed and centrifuged at 7800g for 10 min at 5 °C. Following separation of the supernatant, 1 mL of the solution was mixed with 15 mL of scintillation cocktail and analyzed by liquid scintillation spectrometry (LSS). A 5-mL aliquot of the remaining supernatant was adjusted to pH < 3 with the addition of 0.1 N HCl and then partitioned with ethyl acetate to remove isoxaflutole and its products. The aqueous phase was removed, and the ethyl acetate solution containing the radiolabeled compounds was concentrated by evaporation and analyzed by thin-layer chromatography (TLC) on silica gel plates in a mobile phase of 92:5:3 ethyl acetate:methanol:acetic acid. The TLC system had been previously shown to provide separation and quantification of isoxaflutole, the diketonitrile product, and a benzoic acid transformation product of the diketonitrile (3). The latter product did not appear in significant quantities herein. The remaining 4 mL of electrolyte supernatant was discarded, and the soil pellet was resuspended in 2 mL of 0.01 M CaCl_2 , 200 μL of 0.1 N HCl, and 10 mL of ethyl acetate and extracted for 1 h at 5 °C. The tubes were removed from the shaker and centrifuged at 7800g for 10 min at 5 °C. A 1-mL aliquot was removed from the ethyl acetate phase, mixed with 15 mL of scintillation cocktail, and analyzed by LSS. Five milliliters of the remaining ethyl acetate solution were removed, concentrated, and analyzed using TLC. Three replicates of the soil-free solutions were subjected to the same procedures as the supernatant at each sampling time. Samples containing only the soluble components of the soil were obtained by agitating 10 mL of 0.01 M CaCl_2 electrolyte solution with 5 mL soil for 24 h, then centrifuging the samples, and removing the supernatant. The samples containing soluble components of the soil were compared to the soil-free solution after 24 h at 25 °C. To determine the effect of biological activity on hydrolysis, triplicate samples of soil sterilized by autoclaving or treatment with HgCl_2 (1000 mg per kg soil) were compared to nonsterile soil after 24 h at 25 °C. All samples were analyzed as described previously.

Isoxaflutole Batch Isotherm. Batch isotherms were measured at 5 °C for the four soils described in Table 1 and on the Drummer soil at 25 °C for comparison. The 5 °C temperature was chosen for the majority of the isotherms to minimize hydrolysis effects. Using a stock solution of 10 mg

of technical grade isoxaflutole dissolved in 1 mL of acetonitrile, the treatment solutions at concentrations of 0, 0.01, 0.05, 0.1, 0.5, and 1.0 $\mu\text{g mL}^{-1}$ were prepared by adding the appropriate volume in 0.01 M CaCl_2 and diluting as necessary. Fifty milliliter volumes of each stock solution were spiked with 0.65 μg of [^{14}C]isoxaflutole, providing concentrations of 0.013 $\mu\text{g mL}^{-1}$ (33 Bq mL^{-1}) of [^{14}C]isoxaflutole, which were mixed thoroughly. Ten milliliters of each treatment solution was added to three Teflon tubes containing 5 g of air-dry soil and agitated for 24 h at the appropriate temperature. The 24 h time period was chosen because in the kinetic study the apparent K_d appeared to reach a steady state at that time. Extraction techniques and analysis of supernatant and extraction solutions were conducted as described for the kinetic analysis. Samples from each treatment solution were also removed and quantified by LSS.

Diketonitrile Batch Isotherm. The batch isotherms for the diketonitrile derivative of isoxaflutole were conducted on the same four soils at a temperature of 25 °C and on the Dummer soil at 5 °C. Concentrations of 0, 0.01, 0.05, 0.1, 0.5, and 1.0 $\mu\text{g mL}^{-1}$ were prepared with technical grade diketonitrile in 0.01 M CaCl_2 . As with the isoxaflutole isotherm, 0.013 $\mu\text{g mL}^{-1}$ (33 Bq mL^{-1}) of [^{14}C]diketonitrile was added to each treatment solution and mixed thoroughly. Three replicates of each concentration were prepared at a 1:2 soil-to-solution ratio in Teflon tubes. Tubes were agitated for 24 h and then centrifuged for 10 min at 7800g. A 1-mL aliquot of the supernatant was removed, mixed with 15 mL of scintillation cocktail, and analyzed by LSS. Because diketonitrile had been previously shown to be stable during the time course of the study, extraction and TLC analysis were not necessary.

Results and Discussion

Qualitative Kinetic Evaluation. The percentages of isoxaflutole and diketonitrile in each of the aqueous and sorbed phases as a function of time are presented in Figure 2. In the soil-free system, the concentration of isoxaflutole decreased from 0.057 to 0.053 $\mu\text{g mL}^{-1}$ over a period of 48 h at 5 °C and from 0.055 to 0.048 $\mu\text{g mL}^{-1}$ in 24 h at 25 °C, demonstrating approximately 7% and 13% hydrolysis, respectively. The remainder of radioactivity in the solution was determined to be diketonitrile. As with many chemical reactions, the hydrolysis decreased at a lower temperature. In the presence of soil, the solution concentration of isoxaflutole decreased from 0.014 $\mu\text{g mL}^{-1}$ at 1 h to 0.007 $\mu\text{g mL}^{-1}$ at 48 h in the 5 °C system and from 0.017 to 0.004 $\mu\text{g mL}^{-1}$ in only 24 h at 25 °C, much greater differences than those demonstrated in the soil-free system. The hydrolysis could not be determined based on proportions in the solution phase alone, owing to preferential sorption of the parent compound. Analysis of the sorbed phase demonstrated that isoxaflutole was the main component throughout the course of each study. At the final sampling time, the hydrolysis reactions corrected for the sorbed phase were 27 and 60% at 5 °C and 25 °C, respectively, when the concentrations in both solution and sorbed phases were considered. Thus, the rate of the reaction was increased considerably when soil was present in the system. Significant soil enhanced hydrolysis was also demonstrated in sterile soil, indicating the reaction was abiotic (data not shown). The transformation of isoxaflutole to diketonitrile did not differ significantly between the soil-free solution and the solution containing only the soil soluble components, indicating the soluble components in the soil were not responsible for enhancing hydrolysis. Since sorption concentrates isoxaflutole locally on the soil surface, the resulting increased concentration is likely to enhance the rate of hydrolysis.

Abiotic hydrolysis in the sorbed phase is known to occur with some organic compounds (9, 20), but an increase in the

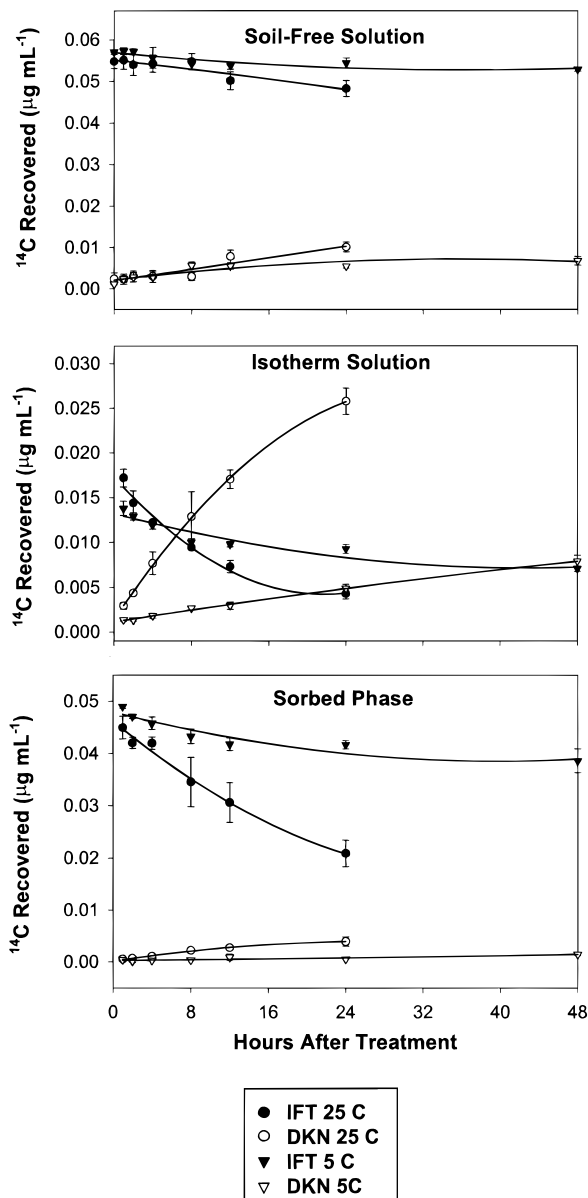


FIGURE 2. Recoveries of isoxaflutole at 25 °C (●) or 5 °C (▼) and diketonitrile at 25 °C (○) or 5 °C (▽) over time in soil-free solution, soil suspension aqueous phase, or soil suspension extractable sorbed phase. Concentrations in the soil suspension are based on 1:2 soil-to-solution ratio and 1:2 extraction solvent-to-soil ratio. Samples at 5 °C were continued through 48 h due to slower kinetics at that temperature. Confidence intervals determined from the three replications are given for $\alpha = 0.05$.

hydrolysis rate is less common. One notable exception is atrazine hydrolysis which was shown to increase in the sorbed state, from a half-life of 209 days in the soil-free system, to 22 days in the presence of soil at the same pH (21). The insecticides diazinon and malathion have also exhibited enhanced hydrolysis in the soil due to sorption catalysis (16). Soil characteristics that may affect sorption include soil texture, metals, organic carbon, and soil pH (20). Clay surfaces are a likely location for catalysis because they are reactive and have been shown to facilitate transformations, such as oxidation of phenolic compounds (22). With atrazine, clay surfaces may contribute to hydrolysis by protonation of the herbicide (23) and catalyzing redox reactions (24).

Although the mechanisms involved in the increased hydrolysis of isoxaflutole have not yet been determined, the consequences of this phenomenon must be considered. For

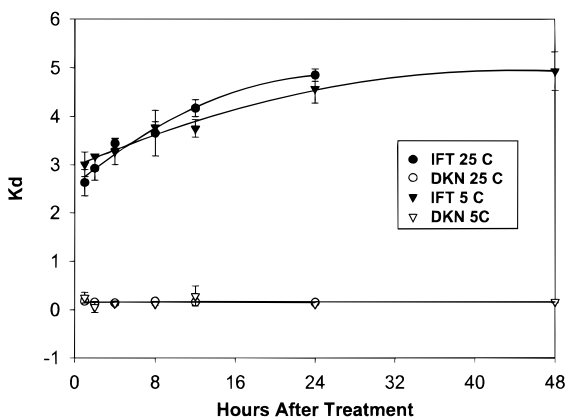


FIGURE 3. Apparent K_d values for isoxaflutole at 25 °C (●) or 5 °C (▼) and diketonitrile at 25 °C (○) or 5 °C (▽) over time in a Drummer soil isotherm. Samples at 5 °C were continued through 48 h due to slower kinetics at that temperature. Confidence intervals determined from the three replications are given for $\alpha = 0.05$.

example, Koskinen et al. (7) demonstrated degradation of 2,4,5-T during the desorption phase of isotherms contributed to hysteresis. In the case of isoxaflutole, hydrolysis occurred so rapidly that even a very short-term adsorption isotherm (<24 h) could not be performed without some transformation. The research provided here suggests a simple and effective approach to the study of nonequilibrium sorption of a labile compound. With the direct measurement of the components, results are likely to be more accurate than with methods that rely on assumptions of degradation behavior or specific relationships between the parent and its products.

The qualitative kinetic analysis was also useful in demonstrating the change in sorption over time (Figure 3). Apparent K_d values were calculated prior to the attainment of equilibrium using the equation $K_d = C_s/C_w$, where K_d is a constant related to sorption, C_s is the amount sorbed by the soil ($\mu\text{g g}^{-1}$), and C_w is the solution concentration ($\mu\text{g mL}^{-1}$) (14). The apparent K_d for isoxaflutole increased from 2.8 to 4.7 mL g^{-1} over a 24 h period, with similar results for both temperatures, even though the percent of isoxaflutole in the extractable phase remained the same or decreased. Apparent K_d values have exhibited nonequilibrium for much longer periods of time with other herbicides such as clomazone (25) and simazine (26). With isoxaflutole, the apparent K_d values appeared to be approaching steady state at 24 or 48 h after initiation of the study, demonstrating a short-term increase in sorption. Diketonitrile K_d values remained close to zero throughout the study and did not show a trend for increase.

Isoxaflutole Batch Isotherm. With the discovery that hydrolysis of isoxaflutole was inevitable during a 24 h period, it became apparent that some method of accounting for hydrolysis must be included in batch isotherms. Several models and methods have been proposed to deal with nonequilibrium during sorption (10, 27–29), but determination of proportions of reactants and products in both the sorbed and solution phases was a simple and obvious approach that proved very effective in determining sorption of isoxaflutole.

Sorption of isoxaflutole in four Illinois soils is depicted by the values given in Table 2. With all soils tested at 5 °C, a near linear relationship was observed, with regression coefficients between 0.994 and 0.997 for the direct relationship between the concentration sorbed and that in solution. The data were then fit to a Freundlich isotherm according to the equation $C_s = K_d C_w^{1/n}$, where $1/n$ is a constant related to the curve direction of the isotherm. While the K_d values are a function of the specific soil used for each isotherm, K_{oc} values

TABLE 2. Sorption of Isoxaflutole (IFT) and Diketonitrile (DKN) on Four Soils

soil	linear K_d	linear R^2	Freundlich K_d	1/n	Freundlich R^2
IFT					
Cisne 5 C	1.24	0.997	1.17	0.926	0.999
Catlin 5 C	2.59	0.994	2.37	0.938	0.999
Flanagan 5 C	3.52	0.997	3.00	0.909	0.999
Drummer 5 C	3.95	0.994	3.30	0.913	0.998
Drummer 25 C	3.59	0.984	3.11	0.949	0.994
DKN					
Cisne 25 C	0.102	0.908	0.098	0.887	0.977
Catlin 25 C	0.236	0.980	0.247	0.958	0.994
Flanagan 25 C	0.384	0.957	0.362	0.979	0.991
Drummer 25 C	0.488	0.948	0.479	0.918	0.991
Drummer 5 C	0.490	0.991	0.491	0.958	0.997

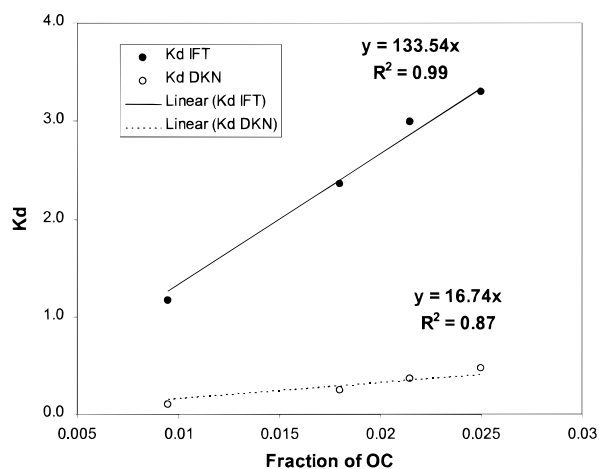


FIGURE 4. K_{oc} determined by regression with four Illinois soils for isoxaflutole (●) and diketonitrile (○).

calculated based on the direct relationship between K_d and the fraction of organic carbon in the soil are thought to represent hydrophobic sorption mechanisms (30) common with organic materials. Figure 4 shows the determination of K_{oc} equal to 134 mL g^{-1} for isoxaflutole based on regression with the four Illinois soils. Little difference in sorption was demonstrated in the isotherm carried out at 25 °C compared to that at 5 °C in the Drummer soil, even though hydrolysis occurred much more rapidly at the higher temperature. This similarity indicates that the sorption reaction is largely an entropy driven process, the result of partitioning of a nonpolar organic onto hydrophobic surfaces of the soil.

Diketonitrile Batch Isotherm. Sorption of diketonitrile was determined by analysis of the solution phase, because preliminary studies showed little degradation of diketonitrile occurred during the 24 h period. As with isoxaflutole, sorption of diketonitrile was nearly linear, with regression coefficients > 0.9 (Table 2). Sorption of diketonitrile was similar at the two temperatures tested on the Drummer soil, suggesting entropy-driven hydrophobic sorption. Although some characteristics of the sorption of diketonitrile and isoxaflutole were similar, the sorption K_d values for isoxaflutole were 6–12 times greater than those for diketonitrile on corresponding soils, a difference that might be expected based on the large differences in solubility of the two compounds. Sorption of diketonitrile alone on the Drummer soil at 5 °C ($K_d = 0.49$) was greater than the sorption of diketonitrile in the qualitative kinetic evaluation at 24 h, in which diketonitrile was produced by hydrolysis of isoxaflutole ($K_d = 0.17$). This phenomenon may be the result of the failure to reach equilibrium in a system where the diketonitrile concentration continued to

increase as isoxaflutole was degraded. Although competition between the two compounds is another possible explanation, nonequilibrium is expected in such a dynamic system and is consistent with the hydrophobic partitioning mechanism as the primary sorption process for both compounds. The herbicidal function of the material in the field may be controlled by the rate of conversion of isoxaflutole to the bioactive available product.

This research may also aid in the understanding of "rechargeable activity", characteristic of isoxaflutole. Under dry soil conditions, isoxaflutole is likely to remain relatively stable and unavailable. A subsequent rainfall event could cause rapid transformation to the bioactive diketone nitrile derivative that exhibits much less soil sorption and thus allows uptake by emerged plants. The greater sorption of isoxaflutole compared to diketone nitrile appears to be a factor in sequestering the herbicide until it is released as a hydrolysis product as adequate moisture is provided. This phenomenon is an environmental benefit if the herbicide is retained in the zone where it is most effective for weed control until a rainfall event occurs, converting the herbicide to the active form in solution where it is bioavailable.

Given the rapid hydrolysis of the proherbicide to its active product, it may be simpler to apply this material as the diketone nitrile derivative. However, the hydrophobic nature of the isoxaflutole enhances soil sorption, which probably explains the functionally advantageous "recharge" behavior and thus may allow lower use rates. Though too little data are available to evaluate the success of such an approach on this particular chemistry, it appears that application of a highly adsorptive and labile pesticide precursor may prove a useful strategy in reducing pesticide inputs as well as movement in the environment.

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