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Report Follows

Progress Report for the United States Geological Survey, Department of Interior

Adsorption of the Isoxaflutole Degradate Diketonitrile to Aluminum and Iron Hydrous Oxides

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Summary

Herbicides used for weed control in agroecosystems are common contaminants in water resources of the United States, and concerns surrounding the presence of herbicides in surface and ground waters are attributable to the toxic and potential carcinogenic effects of these agrichemicals. One agrichemical of concern is the relatively new pre-emergence herbicide isoxaflutole (IXF) used on ~10% of all corn planted in Midwestern states. IXF is rapidly transformed to a diketonitrile degradate (DKN), the active herbicide principle, shortly after field application. Subsequently, DKN is more slowly degraded to a benzoic acid (BA) derivative. Both degradates and very highly mobile compounds that have been detected in soil leachate, surface waters, and aquifers of the Midwest. A principle factor governing pollutant fate and transport in the environment is compound interactions with soil components (i.e., sorption processes). We are investigating IXF degradate adsorption and retention by hydrous aluminum and iron oxides (HAO and HFO, respectively). These variable-charge minerals have high specific surface areas and reactive surface function groups, thus, they function as major "sinks" for an array of environmental pollutants.

The original objectives of this research were to (1) quantify DKN adsorption and retention by HAO and HFO, (2) assess changes in DKN uptake by mineral surfaces as a function of aqueous chemical composition (i.e., pH and initial DKN concentration), and (3) employ infrared spectroscopy to investigate the mechanism(s) through which DKN binds to HAO and HFO surfaces. However, we have modified the objectives to investigate BA in all of our studies as well. Research conducted to date includes (1) development of techniques to synthesize DKN and BA from the parent compound IXF, (2) development of HPLC techniques to analyze concentrations of the compound in solution, (3) synthesis and characterization of HAO and HFO, (4) sorption isotherm experiments investigating DKN to sorption to both metal oxides and BA sorption of HAO. Throughout the remainder of the year we will complete sorption edge experiments to investigate IXF degradate sorption of HAO and HFO as a function of pH and spectroscopic studies to elucidate mechanisms of DKN and BA sorption to the metal oxides.

This research will enhance our understanding of how HAO and HFO in soils and sediments impact the environmental fate and transport of IXF degradates. A thorough understanding of DKN and BA sorption processes will enhance predictive capabilities of pollutant transport models and aid in identifying soil characteristics that reduce DKN migration to water resources.

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Nature, Scope, and Objectives of Research

The development and use of herbicides for controlling weeds and grasses in agroecosystems has resulted in enhanced food production to meet the needs of Earth's growing population [1]. However, solute transport processes in soil can result in migration of these compounds from areas of application to surface and ground waters. Due to potential carcinogenic and endocrinogical effects and toxicity of these compounds to non-target organisms, herbicides and herbicide degradates pose a significant contamination threat to water resources of Missouri [2] and the United States [3-4].

Within soils, sorption (i.e., adsorption and absorption) to organic and mineral components is of primary importance for determining organic pollutant fate and transport in the environment [5]. Organic matter (OM) strongly retains nonpolar herbicides and it is the dominant soil component retaining these compounds in horizons containing > 3% OM (e.g., surface soil horizons). Clay minerals and metal oxides are also important herbicide sorbents when compounds are polar and/or OM content is low [6]. Owing to the fact that much geomedia in the vadose zone contains little OM, studies investigating herbicide and herbicide degradate retention by soil minerals is particularly relevant.

Isoxaflutole, sold under the trade names Balance™, Balance Pro™ and Epic™, is a relatively new herbicide that rapidly hydrolyzes to the degradate DKN after application to soil. Subsequently, DKN is more slowly degraded to form a benzoic acid (BA) derivative. However, information regarding interactions of DKN and BA with specific soil components is lacking. The overarching goal of this research proposal is to investigate DKN sorption and retention by important soil minerals and elucidate how differing chemical reactivities of these components may influence DKN mobility in the pedosphere. However, we have modified our goal to investigate BA sorption as well. We are working to achieve our goals by investigating DKN and BA interactions with highly reactive and variable-charge hydrous aluminum and iron oxides (HAO and HFO, respectively) which are common accessory minerals found in soil. Specific objectives include: (1) assessing the influence of soil mineral chemical composition (HAO and HFO) on DKN and BA sorption and retention; (2) determining the influence of aqueous chemical composition (pH and organic compound concentration) on DKN uptake and sequestration; and (3) elucidating the mechanism(s) of DKN binding to metal hydrous oxide surfaces.

This research will enhance our understanding of how reactive mineral surfaces in soils, sediments, and aquifers may diminish (or enhance) environmental mobility of DKN. Data collected will have utility for modeling DKN transport in geomedia by providing quantitative parameters for use as retardation coefficients in convective-dispersion equations. In addition, this study will provide land managers and regulatory agencies information that can be incorporated into comprehensive plans aimed at minimizing IXF degradate loss from source areas. The proposed research will contribute significantly to the research focus area *Quality of Surface and Groundwater in Missouri*.

Methodology and Principal Findings

Mineral Synthesis and Characterization. HAO was synthesized by gradually neutralizing 0.5 M $AlCl_3$ solution with 0.5 M NaOH to pH 7.0. The suspension was held at room temperature for 48 h to allow time for mineral neosynthesis[7]. HFO was prepared by dissolving ferric nitrate in 0.01 M HCl to create a 0.2 M $Fe(NO_3)_3$ solution. Solution pH was then rapidly increased to pH by titration with 0.1 M NaOH and the suspension was kept at room temperature for 48 h[7]. Synthesized minerals were centrifuged at 5000 rpm for 20 min to concentrate the mineral as a pellet. After centrifugation, the supernatant solution was aspirated and electrical conductivity (E.C.) of the solution was measured and recorded. HFO and HAO were resuspended in Barnstead ultra-pure water, the pellet was resuspended, and suspension was centrifuged again. This process was repeated until no change in E.C. was observed. Minerals were then frozen at -20^{o}C, freeze-dried, and stored in a dessicator.

Powder X- ray diffraction (XRD) analysis was used to confirm the amorphous nature of the synthesized minerals. HAO analysis was conducted on random-oriented, back-filled sample and diffraction patterns were collected on a MiniFlex Desktop XRD using Ni-filtered CuK_{α} radiation at 40 kV and 40 mA. A continuous scan mode was used to collect 2 θ data from 20-80° with a step size of approximately 0.04°. Scan speed was 0.1 degrees per minute and the divergent slit was 0.125°. Following similar procedures, HFO was analyzed using Nicolet I2 diffractometer using Ni-filtered CuK_{α} radiation equipped with single monochromator. Diffraction patterns shown in Fig. 1 confirm that HAO and HFO are amorphous in nature.

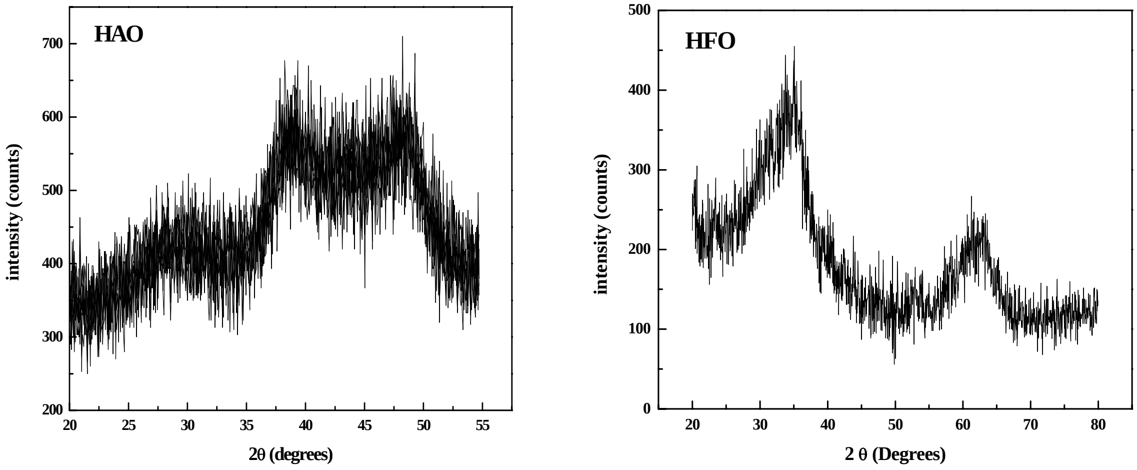

Figure 1. X-ray diffraction (XRD) patterns of HAO and HFO.

Specific surface area (SSA) of the adsorbents was examined using N_2 sorptometry by the Micrometrics Analytical Services (Micrometrics TriStar 3000; Norcross, GA). Samples (1.000 g) were out-gassed prior to analysis, and adsorption-desorption isotherms were measured at 77.3 K. SSA was estimated using multi-point adsorption data from the linear segment of the N_2 adsorption isotherms in the relative pressure range 0.05 – 0.30 using Brunauer-Emmett-Teller (BET) theory. The SSA of HAO and HFO were 201.2 ± 0.38 $m^2 g^{-1}$ and 152.9 ± 5.05 $m^2 g^{-1}$, respectively.

Purification and Analysis of DKN and BA. In order to obtain DKN and BA from IXF, 200 mg of IXF (99.99% purity; Sigma-Aldrich, St. Louis, MO) was dissolved in 1000 ml of ultra pure water. Solution pH was increased to pH 9 via addition of 0.1 M $Ca(OH)_2$ and the solution was heated at 40°C for 7 d to accelerate transformation of IXF to DKN. The BA degradate of IXF was prepared by dissolving 100 mg of $Ca(OCl)_2$ in 250 ml of DKN solution and allowing the sample to react until transformation was complete (~24 h).

Aliquots of the DKN and BA stock solutions were analyzed using high performance liquid chromatography (HPLC) on a temperature controlled (40°C), reverse-phase column (Phenomenex Columbus C_8, 4.6 x 100mm, 5μm particle size; Torrance, CA) attached to a Beckman HPLC system (San Ramon, CA) equipped with UV detector[8-9]. DKN and BA are detected and quantified by UV absorbance at 280 nm (Table 2). The mobile phase consists of 0.1% phosphoric acid (H_3PO_4) buffer (pH 2.2) and 100% acetonitrile (MeCN) solution mixed to give an isocratic mixture of 40% MeCN:60% H_3PO_4 buffer at a flow rate of 1 mL min^{-1}. The retention times for BA and DKN are 3.3 min. and 7.6 min., respectively (Table 1, Fig. 2). Analyte concentrations were determined from standard curves. HPLC calibration standards were prepared from analytical standards obtained from Bayer CropScience (Pittsburgh, PA). Calibration standards (10-100 μg L^{-1}) containing DKN and BA showed good linearity ($r^2 > 0.99$).

Table 1. Summary of UV response and stock concentrations of DKN and BA measured using HPLC.

Wavelength (λ, nm)	Compound	Retention time (min)	Stock Conc. (mg L^{-1})
280	DKN	7.60	81.26
280	BA	3.30	46.80

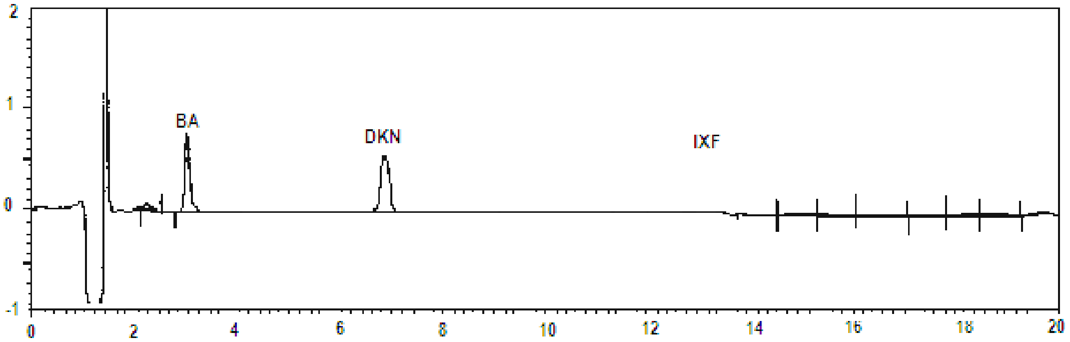

Figure 2. HPLC-UV chromatogram of DKN and BA.

Adsorption and Desorption Experiments. To generate adsorption isotherms, mineral adsorbents (0.500 g) are suspended in 20.00 mL of 0.01 M $CaCl_2$ solution in polypropylene co-polymer (PPCO) centrifuge tubes. Solutions of 0.03 M HCl or 0.01 M $Ca(OH)_2$ are added to yield a final pH of 5.5 after 24 h of reaction. Samples are then spiked with DKN or BA stock solutions to achieve varying concentrations (0, 0.25, 0.5, 1.0, 2.5, 5.0 μmol L^{-1}), and reacted in the dark on end-over-end shakers (7 rpm) at 25°C for 24 hrs. Samples and controls (no mineral) are conducted in triplicate and duplicate, respectively. After reaction, samples and controls are centrifuged at 14,000 g for 30 min at room temperature, supernatant solutions are removed by pipette, and solutions are saved in PPCO bottles for analysis of degradate concentrations and pH. The adsorbed amount of DKN and BA was calculated as:

$$\Gamma_{ads} = \frac{(C_{ads,B})(V_B) - (C_{ads,s})(V_s)}{m_s} \qquad (1)$$

Where Γ_{ads} is the surface excess after the reaction period (µmol kg^{-1}), $C_{ads,\,B}$ and $C_{ads,\,S}$ are the equilibrium DKN (or BA) concentrations (µmol L^{-1}) in blank (*B*) and samples (*S*) after reaction, V_B and V_S are the volume of solution (L) added to samples and blanks, respectively, and m_S is mass of mineral (kg).

Desorption experiments are initiated immediately after the adsorption step by adding a mass of 0.01 M $CaCl_2$ solution, adjusted pH 5.5, equivalent to the mass of supernatant removed. Adsorbate retention was calculated from Eq.(2):

$$\Gamma_{des} = \Gamma_{ads} - \left\{ \frac{(C_{des,s})(V_{des}) - (C_{ads,s})(V_{ent})}{m_s} \right\} \qquad (2)$$

Where Γ_{des} is the surface excess remaining on the surface after the desorption period (µmol kg^{-1}), $C_{des,\,S}$ is the equilibrium DKN (or BA) concentrations in solution after desorption reaction period, V_{des} is the volume of solution in the reaction vessel during desorption phase, and V_{ent} is the volume of entrained solution remaining in the adsorption pellet after aspiration of adsorption phase supernatant.

Adsorption of IXF degradate to metal oxide adsorbents was fit to the Freundlich equation (Eq. 3) to provide a concise set of parameters for comparison of adsorbent affinity.

$$\Gamma_{ads} = AC_{ads,}^{N} \qquad (3)$$

Where parameters *A* and *N* are the intercept and slope, respectively, in a log-log plot of adsorption isotherm data.

Results from the adsorption/desorption experiments are in Figs. 3-6 and Table 2. The data indicate that DKN and BA are adsorbed to the variable-charged minerals HAO and HFO at pH 5.5 (Fig. 3). Thus, validating that these minerals may be important sorbents for IXF degradates. Additionally, DKN was adsorbed more readily to surface functional groups present on HFO than HAO over a wide range of initial concentrations, and BA is sorbed to HAO to a greater extend than DKN at higher initial concentrations but not at low initial concentrations. Hysteresis was not observed between DKN adsorption/desorption isotherms for HFO (Fig. 5), but was observed between the isotherms for HAO (Fig. 4). These data suggest that DKN may interact with surface functional groups on HFO via weak electrostatic interaction and interact with HAO through a stronger mechanism of adsorption (e.g., a ligand exchange mechanism). However, spectroscopic experiments must be conducted to verify hypotheses of adsorption mechanisms. Although these

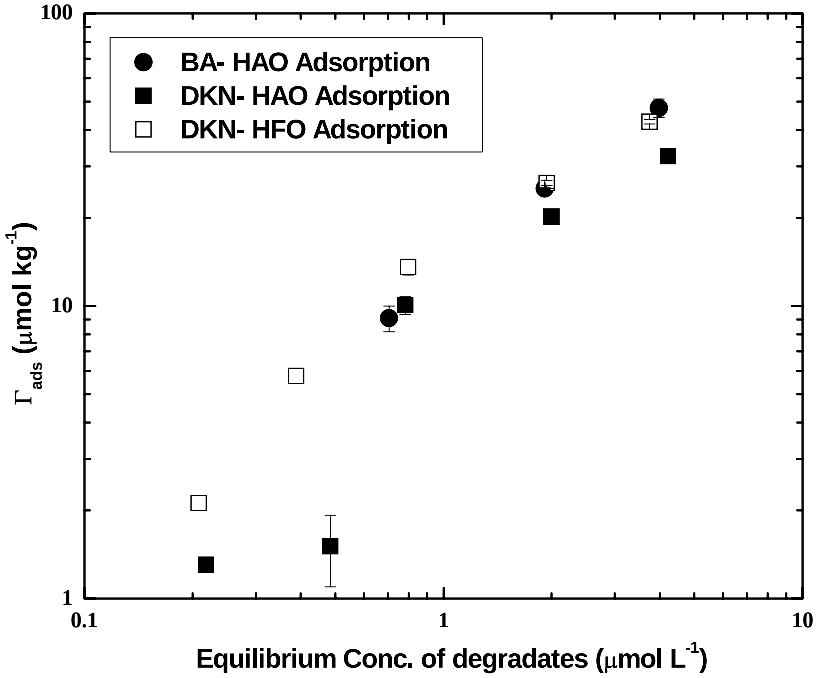

Figure 3. Adsorption of DKN and BA to HAO and HFO at pH 5.5 as a function of initial degradate concentration. Error bars, where observed, represent 95% CI.

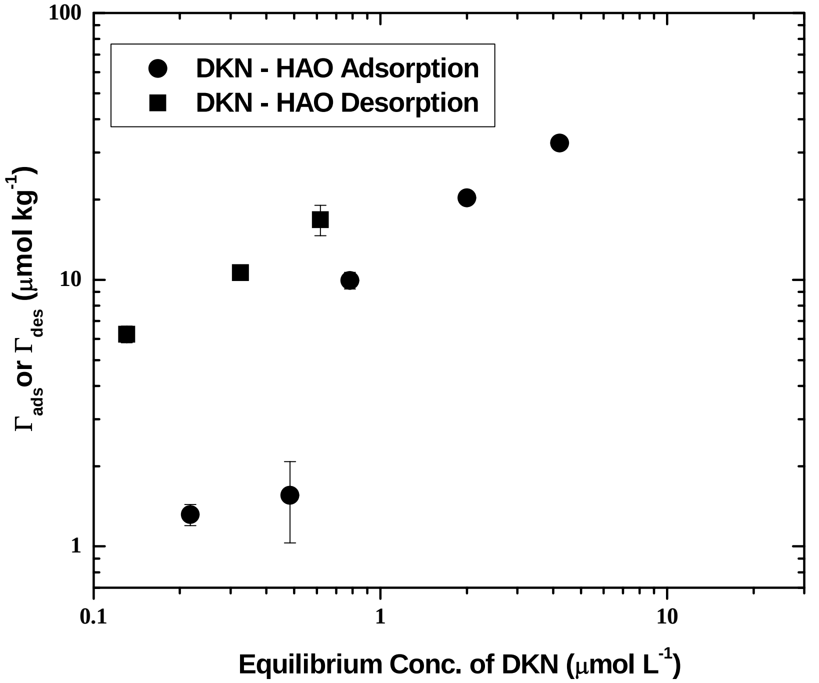

Figure 4. . DKN adsorbed on HAO after adsorption and desorption reactions at pH 5.5. Error bars, where observed, represent 95% CI.

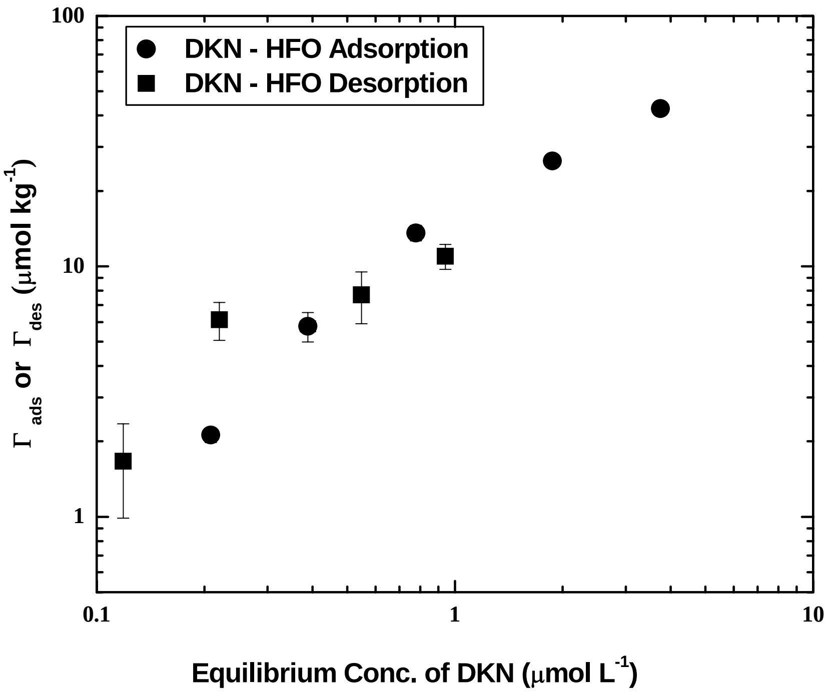

Figure 5. . DKN adsorbed on HFO after adsorption and desorption reactions at pH 5.5. Error bars, where observed, represent 95% CI.

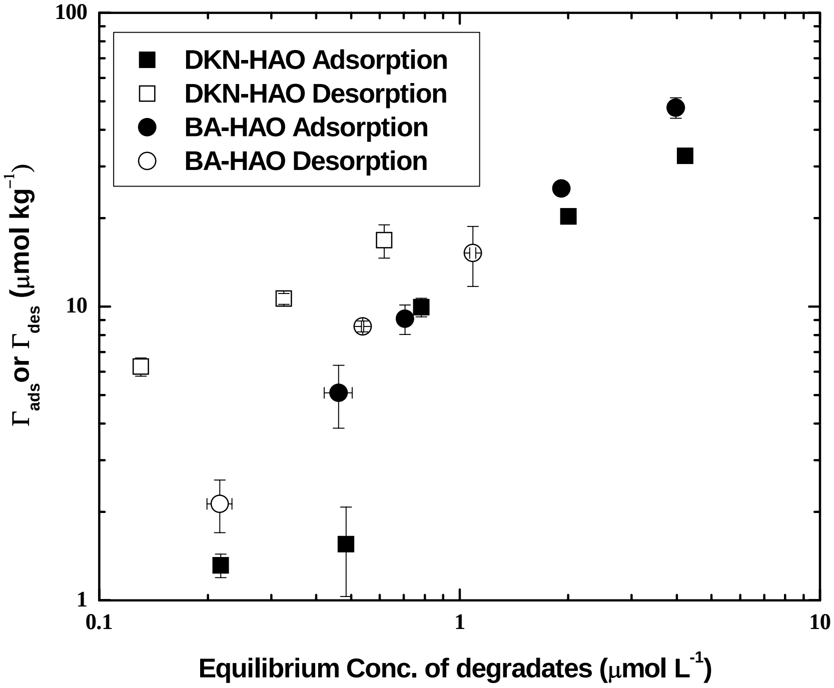

Figure 6. DKN and BA adsorbed on HAO after adsorption and desorption reactions at pH 5.5. Error bars, where observed, represent 95% CI.

Table 2. Freundlich parameters for BA and DKN sorption to HAO and HFO.

Degradate	Adsorbent	log K_f ± 95% CI	N ± 95% CI	r^2 (n)†
DKN	HAO	0.86 ± 0.12 a‡	1.20 ± 0.27 a	0.88 (15)
	HFO	1.13 ± 0.05 b	1.01 ± 0.12 a	0.96 (15)
BA	HAO	1.09 ± 0.03 b	1.01 ± 0.07 a	0.97 (12)

† Where (n) represents the number of data points used in the linear regression analysis.
‡ Mean values within a column followed by the same letter (a, b) are not significantly different ($\alpha = 0.05$).

results may seem contradictory, for example greater sorption to HFO through weaker mechanisms of adsorption, one possible explanation is that the HFO surface may be populated with a greater number of reactive surface functional groups. Measurements of surface charge will need to be conducted to verify this assumption.

Figure 6 demonstrates that BA sorption to HAO is greater at higher initial concentrations than sorption of DKN. Additionally, hysteresis between adsorption and desorption isotherms of BA is not observed, but hysteresis is observed between the DKN isotherms. This suggests that BA is more weakly retained on the mineral surface, relative to DKN. We hypothesize that this may be related to DKN chelating the metal centers on the mineral surface to form a stable 6-member ring structure that is more stable than a monodentate complex that can be formed by BA. Similar results have been observed by Furrer and Stumm[10] with respect to mineral dissolution in the presence of vary types of organic acids.

Significance of Project

Significance of research to Missouri needs, as well as regional and national significance and potential users: Contamination of surface and ground waters by organic agrichemicals used as pesticides continues to degrade water quality in Missouri and surrounding states [2-4]. The DKN degradate of IXF may contribute to this problem via herbicide drift during application or offsite migration after field application. Based on our lack of knowledge regarding interactions of DKN with specific soil components, the proposed research is particularly relevant and timely.

IXF is registered for use in Missouri, however, it may not be applied to soils with loamy sand or sand surface/subsurface horizons having an average OM content in the upper 30 cm of less than 2% by weight [11]. Additional restrictions, imposed by the Missouri Department of Agriculture, prohibit use of this herbicide in the Southeast Missouri Delta because of ground water contamination threats [12]. Statistical data on the usage of this IXF in Missouri are unavailable. However, IXF is used on ~ 10% of total acreage planted to corn in surrounding states with watersheds draining into the Missouri and Mississippi Rivers (Table 3). Thus, IXF and IXF degradation products may pose a significant contamination threat to water resources of Missouri. Detection of these compounds in waters of Nebraska suggests that this is a likely scenario [13].

Table 3. Use of isoxaflutole (IXF) in states surrounding Missouri[†].

State	Acres receiving IXF	Mass applied (kg)
Illinois	672,000	19,955
Indiana	560,000	15,420
Iowa	2,108,000	61,225
Kansas	174,000	2,721
Nebraska	1,134,000	25,397
Ohio	165,000	3,628
South Dakota	440,000	13,605
Total	**5,253,000**	**141,950**

[†] Data obtained from USDA-NASS[14].

The research being conducted will provide quantitative information regarding the interaction of DKN with highly reactive minerals prevalent in soils, particularly subsoils. This will enhance our understanding of DKN sorption and retention within the vadose zone and aqueous chemical conditions that enhance or diminish DKN migration to surface and ground waters. We anticipate that land managers and regulatory agencies will be able to use obtained results as part of an overall evaluation regarding use of IXF on Missouri soils. Results will also have utility in predictive chemical transport models by providing data that can be inserted into convective-dispersion equations as a retardation coefficient.

Student involvement: USGS funds have been used to support one Ph.D. student (Ms. Si Hyun Wu), who has been actively working to complete this project. This research will be used to partially fulfill the requirements of Ms. Wu's graduate degree program.

Additional Funds Garnered and Grants Submitted Based on this Research: The USDA, Agricultural Research Service (ARS) has agreed to provide 1.5 years of additional student support (tuition and stipend) toward completing the proposed research and additional research on DKN and BA interactions in soil. The grant listed below is pending:

> Interactions of Isoxaflutole and Its degradates in the Rhizosphere of Vegetative Buffers: Sorption, Degradation, and Impacts on Microbial Communities. USDA, CSREES, Soil Processes Program. $399,615, 9/01/07 – 8/31/11. K.W. Goyne, R.J. Kremer, R.N. Lerch, C.-H. Lin, and T. Wong.

Abstract and Presentation from International Meeting:

> Wu, Si-Hyun, K.W. Goyne, R. N. Lerch, C.-H Lin, and S. H. Anderson. 2006. Adsorption of isoxaflutole degradates to aluminum and iron hydrous oxides. CD-ROM. Indianapolis, IN. 12-16 Nov. 2006. ASA, CSSA, SSSA International Meetings.

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