

Characterization of Nicosulfuron Availability in Aged Soils

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Sorption–desorption interactions of pesticides with soil determine their availability for transport, plant uptake, and microbial degradation. These interactions are affected by the physical–chemical properties of the pesticide and soil, and for some pesticides, their residence time in the soil. This research evaluated changes in sorption/availability of nicosulfuron (2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-*N,N*-dimethyl-3-pyridinecarboxamide) herbicide with aging in different soils, using a radiolabeled (¹⁴C) tracer. Aging significantly increased sorption. For instance, after the 41-day incubation, calculated $K_{d,app}$ increased by a factor of 2 to 3 in Mollisols from the Midwestern United States and by a factor of 5 to 9 in Oxisols from Brazil and Hawaii, as compared to freshly treated soils. In view of this outcome, potential transport of nicosulfuron would be overpredicted if freshly treated soil K_d values were used to predict transport. The fact that the nicosulfuron solution concentration decreased faster than the soil concentration with time suggested that the increase in sorption was because the rate of degradation in solution and on labile sites was faster than the rate of desorption of the neutral species from the soil particles. It may have also been due to nicosulfuron anion diffusion to less accessible sites with time, leaving the more strongly bound neutral molecules for the sorption characterization. Regardless of the mechanism, these results are further evidence that increases in sorption during pesticide aging should be taken into account during the characterization of the sorption process for mathematical models of pesticide degradation and transport.

KEYWORDS: Nicosulfuron; sorption; availability; aged soils

INTRODUCTION

Nicosulfuron (2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-*N,N*-dimethyl-3-pyridinecarboxamide) (**Figure 1**) is a sulfonylurea herbicide (SU) used for selective postemergence control of annual and perennial grasses in corn. In contrast to traditional herbicides used in corn that are applied at rates >1 kg ha⁻¹, nicosulfuron is typically applied at rates <100 g ha⁻¹ (*I*). Because of the low application rates, it has been thought to have a lower potential for contamination of surface and ground waters than other traditional corn herbicides, as there is less herbicide available for offsite movement.

The information on SU availability for movement is limited. The SUs, which are weak acids, are generally weakly sorbed to soils, with sorption decreasing with increasing pH as the result of increased amounts of anionic molecules in solution (*I*), mainly at pH $> pK_a$ (4.3, for nicosulfuron). Therefore, SU movement in soil is closely related to soil-solution pH (2, 3).

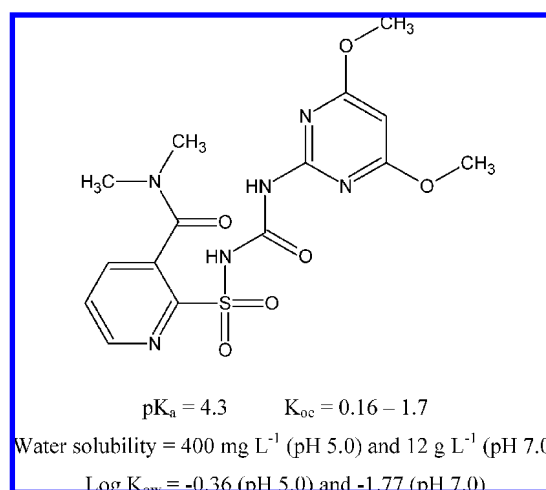


Figure 1. Chemical structure and physical–chemical properties of nicosulfuron.

SUs also generally have low K_{ow} values and relatively high water solubility, which has resulted in suggestions of a high potential for mobility in soils (4–7). Nicosulfuron physical–chemical properties are presented in **Figure 1**.

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Table 1. Physical–Chemical Properties of the Soils

soil	soil properties				
	pH-H ₂ O	%			
		OC	clay	silt	sand
US-S	6.3	0.95	4	3	93
US-SiL	6.3	2.26	19	56	25
US-SiCL	6.5	2.92	39	51	10
BR-SaCL	5.6	0.98	22	11	67
HW-C	5.5	1.43	74	18	8

In spite of the suggested high potential for mobility, there are very few published reports of detections of SUs in general in surface water and ground water, and even fewer for nicosulfuron. Nicosulfuron was reported to reach the surface of a shallow groundwater table 16 days after application, which was followed by frequent rainfall events (8). In a monitoring study of rivers and ground water in the Midwestern United States, nicosulfuron was found in 52% of 130 stream and river samples, with median and maximum concentrations of 0.01 and 0.27 $\mu\text{g L}^{-1}$, respectively, and in 2 out of 25 groundwater samples, with a maximum concentration of 0.02 $\mu\text{g L}^{-1}$ (9). The lack of published reports of detections and the low concentrations observed in surface waters are expected in view of the low application rates and assuming that less than 0.5% of the applied chemical ran off the field (10). The few reports of detections may also be in part due to the lack of analytical instrumentation (i.e., HPLC interfaced to a mass spectrometer) with the necessary sensitivity prior to the mid 1990s.

Sorption is one of the main processes that affects the fate of pesticides in soil and water (11), and sorption–desorption interactions of pesticides with soil determine the availability of the pesticide for plant uptake, microbial degradation, and transport in soil (12). Transport models used to predict the mobility of pesticides in soil typically use equilibrium sorption estimates (K_d and K_{oc} values) to describe pesticide retention by soil (13–15). The accuracy of the sorption estimates can be more important than the choice of transport model in correctly simulating pesticide leaching (15), emphasizing the need to understand the sorption–desorption processes as well as the effects of soil and environmental factors on them.

While sorption–desorption is well characterized for many classes of herbicides, information on SUs, particularly nicosulfuron, in soil is limited and often conflicting. For instance, Freundlich sorption coefficient (K_f) ranged from 3.5 to 8.8 in seven diverse Iowa Mollisols (16), whereas it was an order of magnitude lower, ranging from 0.3 to 0.5, in four Tennessee soils (17). In four Brazilian Oxisols, K_f ranged from 1.0 to 2.2, and it was correlated to OC content of the soils (16). In contrast, K_d ranged from 0.1 to 0.4 L kg^{-1} in a different study with six Brazilian Oxisols, and it was not correlated to OC (18). Also, strong and irreversible sorption of nicosulfuron on negatively charged clay surfaces (Ca^{2+} -montmorillonite and Ca^{2+} -hectorite, mainly) has been reported (19), whereas no sorption was found on hectorite or Arizona and Wyoming montmorillonite (20). In the same study, it was noted that organoclays, formed from the interaction of the same clays with alkylammonium cations, were very effective sorbents for nicosulfuron.

Sorption–desorption processes are affected by the physical and chemical properties of the pesticide and soil, but in many cases, it is a much more complex process and cannot be adequately characterized by a single number (11). For instance, the desorption of many pesticides cannot be predicted from their sorption isotherms; less chemical is desorbed than would be

predicted by the sorption isotherm. Also, it appears that sorption may be affected by the residence time or aging in the soil. Increases in the sorption coefficient (K_d) with incubation time has been observed for a variety of classes of pesticides (21–25). The objective of the present study was to determine the changes in distribution between sorbed and solution phases of nicosulfuron in aged soils in order to characterize availability for offsite transport.

MATERIALS AND METHODS

Soils and Chemicals. Five representative soils from glacial and tropical regions were used in this study: three Mollisols from the North Central United States, a sand (US-S), a silt loam (US-SiL), and a silt clay loam (US-SiCL), and two Oxisols, a sandy clay loam from Brazil (BR-SaCL), and a clay from Hawaii (HW-C). The soils were collected from the surface layer (0–0.2 m depth) and passed through a 2-mm sieve. Part of the soil samples was air-dried to determine soil properties and sorption, whereas the remaining samples were kept moist and stored in the dark at room temperature until used. Soil texture was determined according to the hydrometer method (26). Soil pH was measured using a 1:2 (w/v) soil/deionized water mixture. The organic carbon (OC) content was determined by dichromate oxidation (27). The results of soil analyses are presented in Table 1. [Pyridine-2- ^{14}C]-nicosulfuron (2.33 MBq mg^{-1} , >98% radiochemical purity) was mixed with unlabeled nicosulfuron (97.9% of purity) to prepare solutions for sorption and aging studies. Labeled and unlabeled nicosulfuron were graciously provided by DuPont Crop Protection.

^{14}C -Nicosulfuron Dissipation and Sorption in Aged Soils. Aliquots (0.62 mL) of methanolic ^{14}C -nicosulfuron solution, at concentrations of 40.4 $\mu\text{g mL}^{-1}$ and 4.88 kBq mL^{-1} , were added to 25 g (oven dry basis) of soil samples in 200-mL Erlenmeyer flasks. Soil moisture contents were adjusted to 60% of field capacity (-33 kPa), and the soil samples were thoroughly mixed. Vials containing 1 mL of 1 N NaOH were placed inside the Erlenmeyer flasks by attachment to the inside of stoppers. Soils were incubated in the dark at 25 ± 1 °C, for either 0, 6, 13, 27, or 41 days. To determine the nicosulfuron mineralization rate, trapped $^{14}\text{CO}_2$ in NaOH solutions were replaced and measured weekly, which also aerated the soil samples. One-milliliter aliquots of NaOH solutions were added to 6 mL of EcoLite cocktail and ^{14}C -radioactivity analyzed by liquid scintillation counting (LCS) for 5 min, using a Tri-Carb 1500 Packard instrument. Solutions were kept in the dark overnight prior to measurement.

After each incubation period, duplicate soil samples were first extracted once with 25 mL of 0.01 N CaCl_2 and then twice with 50 mL of the 0.1 mol L^{-1} $(\text{NH}_4)_2\text{CO}_3$ plus methanol mixture (9:1, v:v). The soil slurries were shaken on a horizontal shaker for 20 h and centrifuged at 3000 rpm ($1076 \times g$) for 15 min, and 1-mL aliquots of the supernatants were removed and analyzed for ^{14}C as described above. The $(\text{NH}_4)_2\text{CO}_3$ extracts were rotary evaporated at 35 °C to remove methanol, acidified with 200 μL of 2.0 N HCl, and centrifuged at 12,000 rpm ($23,420 \times g$) for 20 min to remove humic material. Both extracts, aqueous CaCl_2 and $(\text{NH}_4)_2\text{CO}_3$, were partitioned twice with 10 mL of dichloromethane, evaporated to just dryness at 35 °C, and then resuspended in methanol.

The extracts were analyzed by high performance liquid chromatography (HPLC) using a 1090 Hewlett-Packard High Performance Liquid Chromatograph and a 150 mm \times 4.6 mm i.d. Supelco Discovery C18 (5 μm) column, operating at ~ 30 °C. The mobile phase was a gradient of methanol and 0.1% formic acid buffer, and the flow rate was 1.0 mL min^{-1} . Injection volumes were 100 μL . The HPLC fraction corresponding to the retention time of authentic nicosulfuron was collected, mixed with liquid scintillation cocktail, and quantified by LSC. It allowed for the calculation of the percentage of nicosulfuron in both extractors. Fractions that would contain ^{14}C -peaks that were more and less mobile than the parent chemical were also collected and quantified by LSC.

The remaining soil slurries were dried at 40 °C for ~ 36 h and thoroughly mixed, and 0.25 g of subsamples were combusted using a Packard 307 sample oxidizer (Packard Instrument Company, Downers Grove, IL, USA) to determine nonextractable (bound) ^{14}C -nicosulfuron

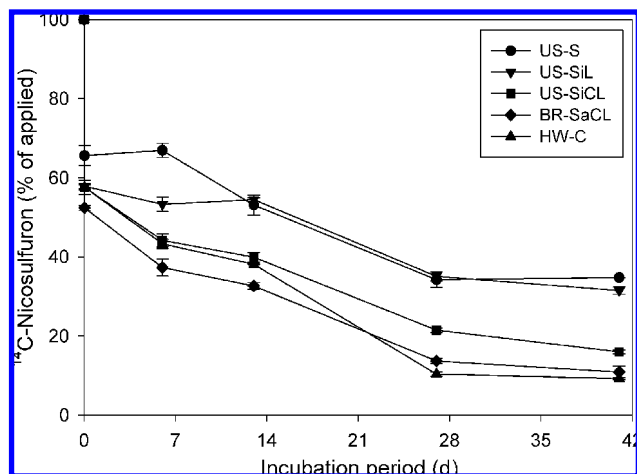


Figure 2. Percentage of nicosulfuron dissipated in five soils during a 41-day incubation.

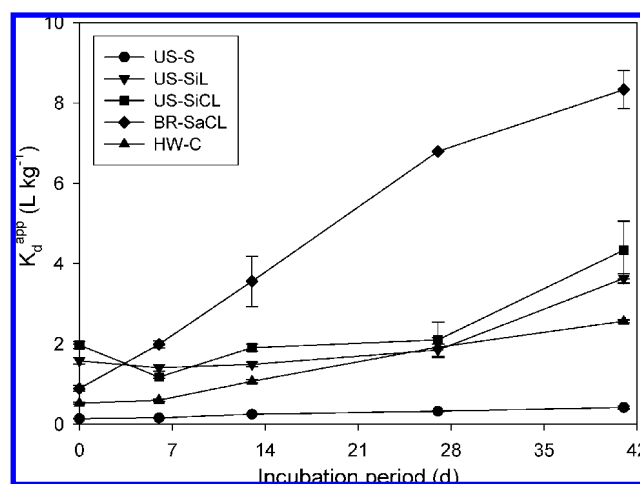


Figure 3. Effect of incubation time (aging) on nicosulfuron sorption as characterized by apparent sorption coefficients ($K_{d,app}$) on five soils.

residues. The resulting $^{14}\text{CO}_2$ was trapped in Carbo-Sorb E mixed with Permafluor V, and the ^{14}C was quantified by LSC. Oxidizer efficiency was calculated prior to combustion of the samples to correct for any possible error in recovery.

To calculate apparent sorption coefficients ($K_{d,app}$) with aging, it was assumed that CaCl_2 and $(\text{NH}_4)_2\text{CO}_3$ extractable fractions of nicosulfuron represented the solution (C_e') and sorbed (S') concentrations, respectively, and that $K_{d,app} = S'/C_e'$. Total recovered nicosulfuron in CaCl_2 and $(\text{NH}_4)_2\text{CO}_3$ extractable fractions for the five soils were used to characterize nicosulfuron dissipation.

Batch Sorption. Aliquots (5 mL) of aqueous ^{14}C -nicosulfuron solution at four different concentrations (0.08, 0.28, 0.98, and 2.98 $\mu\text{g mL}^{-1}$ in 0.01 N CaCl_2 , each having 0.12 kBq mL^{-1}) were added to duplicate 5-g samples of air-dried soils. Soil slurries were horizontally shaken for 24 h at $25 \pm 1^\circ\text{C}$, centrifuged at 3000 rpm ($1076 \times g$) for 15 min, and 0.5-mL aliquots of the supernatants removed and added to 6 mL of EcoLite scintillation cocktail. ^{14}C -radioactivity in the solution (C_e) was measured by LCS, as mentioned before. Sorbed concentrations (S) of nicosulfuron were calculated by the difference between its initial concentration (C_i) and C_e , but results were expressed in terms of soil mass. The data were fit to Freundlich equation: $S = K_f C_e^N$, in which K_f is the Freundlich sorption coefficient and N is the exponential coefficient of the equation. Linear sorption coefficients ($K_d = S/C_e$) were also calculated as an average value for the four initial concentrations, and were normalized to OC content of the soils to give K_{oc} [$K_{oc} = (K_d/\% \text{ OC}) \times 100$].

RESULTS AND DISCUSSION

Nicosulfuron Recovery in Aged Soils. The mass balance for ^{14}C (mineralized, extracted, and bound) in the experiment was excellent for all soils ($>93\%$ of applied), averaging 101% for sampling days 0 to 13; 98% for day 27; and 97% for day 41, which allowed the characterization of nicosulfuron dissipation in the diverse soils. There was little ^{14}C -mineralization during the 41-day incubation of the five soils ($<1.3\%$ of applied ^{14}C , in all cases). There was also little nonextractable ^{14}C (bound), which was $<4.0\%$ for all soils and sampling times, except US-SiCL and HW-C, which were $\sim 6\%$ on day 41 (data not shown). The amount of extractable ^{14}C was high for all soils and sampling times ($>89\%$ of applied ^{14}C) and nearly constant during the incubation period. It corresponded to parent nicosulfuron and unidentified ^{14}C -labeled chemicals (data not shown). These outcomes reinforced that decrease in recovery of nicosulfuron during the incubation was due to degradation. SUs degrade in soil biotically and abiotically (28).

In general, less nicosulfuron was recovered from the Oxisols (BR-SaCL and HW-C), having lower pH values (5.6 and 5.5, respectively) (Figure 2). The faster dissipation on these soils would be expected since SUs are decomposed mainly by chemical hydrolysis and microbial degradation, and hydrolysis is a pH-dependent reaction (29, 30). Environmental conditions including warm, moist soil, and soil pH of 5.7 encouraged rapid nicosulfuron dissipation (29). In general, SU degradation is faster in acidic rather than in neutral or in weakly basic conditions, and at high temperature (30).

Limited soil half-lives have been reported for nicosulfuron, with values ranging from <6 days in laboratory and field studies (29) to 14–49 days in the field (31). The extrapolated half-lives in this laboratory study ranged from 20 to 30 days in the five soils (Figure 2). Although this study was not designed to determine either kinetics or mechanism of degradation, there was, however, sufficient herbicide remaining in the soil at each sampling time ($>10\%$ of applied) to determine the distribution between sorbed and solution phases of the remaining amount of nicosulfuron, thereby allowing the determination of the effect of the aging process on sorption and subsequent potential availability.

Sorption and Aging Effects. Nicosulfuron apparent sorption coefficients ($K_{d,app}$ values), calculated from 0.01 N CaCl_2 and $(\text{NH}_4)_2\text{CO}_3$ extractable amounts without previous incubation (at time zero), were 0.14, 1.58, 1.97, 0.89, and 0.53 L kg^{-1} for US-S, US-SiL, US-SiCL, BR-SaCL, and HW-C, respectively (Figure 3). These values were similar to the average K_d values obtained by batch equilibration with similar initial concentration ranges (Table 2), emphasizing the feasibility of using this extractors to predict nicosulfuron availability and the low sorption potential of nicosulfuron to the soil particles. Sorption, as characterized by $K_{d,app}$ values, increased with incubation time, mainly after 27 days of incubation (Figure 3). In the Mollisols, nicosulfuron sorption increased by a factor of 2 to 3 during the incubation period (41 days). In sand (US-S), the increase (from 0.14 to 0.42 L kg^{-1}) was linear during incubation, whereas sorption on heavier textured soils (US-SiL and US-SiCL) remained relatively constant for the first 27 days and then increased (Figure 3). Sorption on US-SiL increased from 1.58 to 3.63 L kg^{-1} , while sorption on US-SiCL increased from 1.97 to 4.34 L kg^{-1} . The increase in nicosulfuron sorption was greater in the Oxisols as compared to the Mollisols. $K_{d,app}$ values increased by a factor of 9 in BR-SaCL (from 0.89 to 8.33 L kg^{-1}) and 5 in HW-C (from 0.53 to 2.57 L kg^{-1}).

Table 2. Nicosulfuron Sorption on Mollisols (from United States) and Oxisols (from Brazil and Hawaii) as Characterized by Batch Sorption Isotherm Results and Calculated Sorption Coefficients for the Neutral Molecules of Nicosulfuron

soil	K_f^a (mg ^{1-N} kg ⁻¹ L ^N)	N^b	K_d (L kg ⁻¹)	K_{OC} (L kg ⁻¹)	sorbed (%)	K_{d-ns}^c (L kg ⁻¹)	K_{OC-ns}^c (L kg ⁻¹)
US-S	0.14 ± 0.01	0.97 ± 0.02	0.14 ± 0.01	14.7	12.5 ± 0.7	7	753
US-SiL	1.31 ± 0.02	0.94 ± 0.01	1.44 ± 0.13	63.7	58.3 ± 2.3	73	3250
US-SiCL	1.69 ± 0.03	0.96 ± 0.01	1.81 ± 0.12	62.0	63.6 ± 1.5	146	4980
BR-SaCL	0.73 ± 0.03	0.92 ± 0.02	0.81 ± 0.11	82.7	44.5 ± 3.2	9	909
HW-C	0.42 ± 0.01	0.94 ± 0.01	0.45 ± 0.04	31.5	29.9 ± 1.9	4	280

^a Standard error is rounded to the nearest 0.01, and it is not symmetric about the K_f value. ^b For all the isotherms, $r^2 > 0.999$. ^c Calculated value for the neutral molecules.

The mechanism for increased sorption with aging is not known. SU herbicides are weak acids. In most agricultural soils, these herbicides exist predominantly as anions since soil pH values are higher than the molecule pK_a . However, dependent on soil pH, a varying proportion of the SU is the neutral species, which is more strongly sorbed and may not readily desorb using the traditional batch equilibration method (32). In the batch equilibration system, the solution pesticide concentration is measured in the bulk 0.01 M CaCl₂ solution; therefore, the contribution of the anion to the calculation of K_d becomes important. The batch system equilibrium would be as follows.

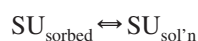


Assuming only neutral species are sorbed and using the batch K_d , the pK_a and the soil pH, we can calculate a predicted batch sorption coefficient for the neutral species (K_{d-ns}) in soils with different pH values, using the following equation:

$$K_{d-\text{batch}} = f_{SU}(K_{d-ns}) + (1 - f_{SU})(K_{d-SU^-})$$

where $K_{d-\text{batch}}$ is the batch sulfonylurea sorption coefficient, f_{SU} is the fraction of the SU in the neutral species ($f_{SU} = 1/(1 + 10^{(pH-pK_a)})$), K_{d-ns} is the sorption coefficient for the SU neutral species, and K_{d-SU^-} is the sorption coefficient for the SU anionic species.

The resultant K_{d-ns} would be independent of solution pH, where the SUs in solution are the neutral species, and the equilibrium being characterized is as follows:



The resultant calculated K_{d-ns} values for the five soils were up 80 times greater than the comparable K_d values (Table 2), indicating that nicosulfuron is able to be sorbed to a much greater extent than would be indicated by the traditional batch sorption coefficients. Similarly, Berglöf et al. (32) found measured K_d values for sorption of the neutral species of metsulfuron methyl in diverse field-moist soils to be ~500 times greater than batch K_d values obtained for the same soils. For imazaquin, also an acidic herbicide, the estimated $K_{OC,n}$ value was on average ~40 times greater than the batch K_{OC} values (33).

Therefore, the observed increase in sorption coefficients for nicosulfuron with incubation time can be attributed to the rate of anionic nicosulfuron decomposition in solution that was faster than the rate of neutral nicosulfuron desorption from soil. The increase in sorption with aging can also be attributed to the diffusion of nicosulfuron anion to less accessible sorption sites, coupled to the decomposition of readily available chemical, leaving relatively a higher proportion of more strongly sorbed neutral molecules of nicosulfuron. It would explain the greater enhancement in sorption potential of the Oxisols with aging since they have higher Fe and Al oxide contents as compared to Mollisols, which serve as specific microsites for anionic and/

or ligand exchange reactions with anionic organic molecules (34, 35), in addition to the fact that these soils exhibited faster degradation rates. It is difficult to distinguish between the two possible mechanisms; the net result is probably a combination of the two mechanisms occurring during incubation. It should be noted that the increase in sorption of nicosulfuron is not a concentration effect, whereby sorption is usually greater at low concentrations as compared to higher concentrations. This effect has been often observed for a variety of pesticides as evidenced by Freundlich isotherm slopes (N) < 1. However, for nicosulfuron sorption on these soils, $N \sim 1$ (Table 2).

Regardless of the mechanism of the increase in sorption, the net effect would be that use of simplistic equilibrium partitioning coefficients based on freshly treated samples under slurry conditions would predict greater movement of nicosulfuron than if we used the sorption coefficients determined on aged residues. In the case of this chemical, the mobility classification would change to less mobile. These results would explain, in part, the lack of observed offsite movement of this chemical.

If we are to improve models describing pesticide availability for transport and biodegradation in soil, we need to better understand the complex interactions of the sorption–desorption and degradation processes, particularly for aged herbicide residues. The use of simplistic equilibrium partitioning coefficients based on freshly treated samples under slurry conditions is inadequate.

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