

SHORT COMMUNICATIONS

Irreversible Sorption of Nicosulfuron on Clay Minerals[†]

Keywords: *Nicosulfuron; adsorption; clay minerals; sulfonylureas*

INTRODUCTION

Nicosulfuron [2-[[[(4,6-dimethoxypyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]-*N,N*-dimethyl-3-pyridine-carboxamide] is an active ingredient of Accent (DuPont), a relatively new postemergence sulfonylurea (SU) herbicide used for corn. Its application rates are very low (50–100 g ha⁻¹), and thus its potential for groundwater contamination is expected to be low compared to that of other corn herbicides with much higher application rates (e.g. 2–5 kg ha⁻¹ for atrazine). Sulfonylureas are weakly acidic herbicides considered to be relatively mobile compounds in soils (Beyer et al., 1988). Their mobility usually increases with increasing pH and decreasing soil organic matter (Blair and Martin, 1988; Beyer et al., 1988).

There are no published studies on sorption and degradation of nicosulfuron. Here we report on the studies conducted to quantify the role of soil minerals in the nicosulfuron adsorption in soils, which led us to discover unexpectedly strong and irreversible adsorption of nicosulfuron on layer silicate clay minerals.

MATERIALS AND METHODS

Adsorbents. Five oxides (ferrihydrate, goethite, silica gel, alumina, and buserite) and five clays (calcium and aluminum montmorillonite, calcium hectorite, biotite, and muscovite) were used as sorbents. Ferrihydrate, goethite, and buserite were synthesized according to published procedures (Schwertmann and Cornell, 1991; Ukrainczyk and McBride, 1993). Chromatographic grade silica gel and alumina were obtained from Aldrich (Milwaukee, WI). The homoionic sodium smectites were prepared from montmorillonite (SWy-2, Clay Minerals Society Repository, Columbia, MO) and hectorite (Baroid Division of NL Industries, Houston, TX) as described previously (Ukrainczyk et al., 1994). Calcium and aluminum exchanged smectites were prepared by exchanging sodium smectites with the appropriate chloride salt. The clays were then dialyzed free of salt and freeze-dried. Biotite and muscovite (<50 μ m fraction) were identical to the samples used by Scott and Smith (1966).

Adsorption and Desorption of Nicosulfuron. Technical grade nicosulfuron (solubility 400 ppm, K_{ow} = 0.44 at pH 5) was obtained from DuPont (Wilmington, DE) and used without further purification. Fresh nicosulfuron stock solutions were prepared for each experiment by dissolving the compound in water and stirring overnight.

The purity of nicosulfuron was 97%, and two additional very small peaks (peak height less than 0.5 milliabsorbance unit) were observed in the chromatographs, most likely corresponding to the hydrolysis products. In adsorption experiments on clay minerals, except hectorite, their peak heights increased by up to twice that of the fresh standard, indicating some degradation of nicosulfuron had occurred.

Adsorption isotherms were constructed by using eight nicosulfuron concentrations (0.25, 0.5, 0.75, 1.0, 2.5, 5.0, 7.5, and 10.0 ppm) and a sorbent/solution ratio of 1:20. Background electrolyte was 0.01 M NaCl (oxides, micas, and aluminum montmorillonite) or 0.01 M CaCl₂ (clay minerals). For each nicosulfuron concentration added, 0.5 g (on an air-dry basis) of an oxide or a clay was placed in a weighed 25 mL Corex glass centrifuge tube, and the pH was adjusted to 6–6.5 by a predetermined amount of dilute HCl. Suspensions were equilibrated for 24 h prior to nicosulfuron addition. The tube was then sealed with a Teflon-lined cap and placed on a reciprocating shaker for 24 h at 25 \pm 1 °C. Each experiment was run in duplicate. After equilibration, the tubes were centrifuged at 5000g for 20 min at constant temperature. The pH of the supernatant was measured, and the supernatant was filtered through a 0.2 μ m Nucleopore nylon membrane filter to remove any particulate materials. Nicosulfuron concentrations in filtrates were determined by high-performance liquid chromatography (HPLC). HPLC analysis was performed on an HP 1050 series quaternary pump (Hewlett-Packard) equipped with an autoinjection system and a variable wavelength detector. Instrumental system control was maintained through HPLC Chem Station, DOS Series (Hewlett-Packard). A reversed-phase ODS C₁₈ column (4.6 \times 150 mm, particle size 5 μ m) was used; injection volume was 100 μ L, and the detector wavelength was set at 254 nm. The mobile phase was a mixture of 35% acetonitrile and 65% 0.1 M acetic acid. The flow rate was 1.5 mL min⁻¹. Calibration was performed by external standards. The amount of nicosulfuron adsorbed was taken as the difference between the amount

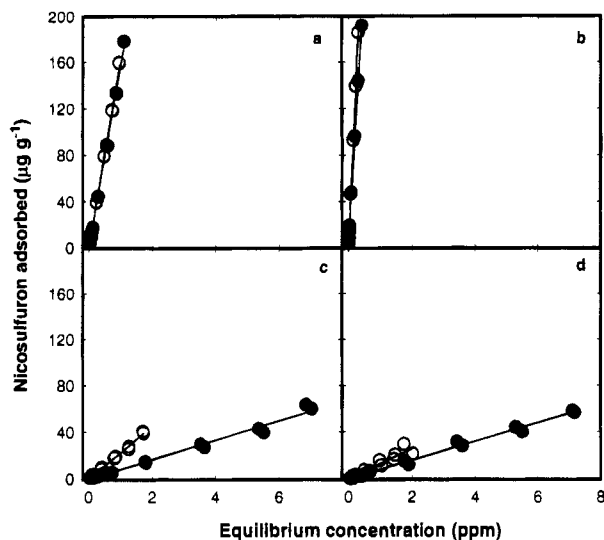


Figure 1. Nicosulfuron adsorption (●) and desorption (○) isotherms on (a) calcium montmorillonite (pH 6.5 ± 0.1), (b) calcium hectorite (pH 6.5 ± 0.1), (c) silica (pH 6.0 ± 0.1), and (d) ferrihydrite (pH 6.0 ± 0.1).

added and that remaining in the solution after equilibration. To check for possible loss of nicosulfuron due to adsorption on filters and degradation by hydrolysis, duplicate blank samples containing 1 and 10 ppm of nicosulfuron solution in 0.01 M background electrolyte without sorbent were run in each experiment and treated in the same way as the other samples. The loss of nicosulfuron from the blanks was less than 2%.

The desorption was performed on the same samples at 1:20 sorbent/solution ratio. Supernatant was decanted after adsorption, and 0.1 M CaCl_2 was added. Tubes were equilibrated for 24 h, and the desorbed nicosulfuron was measured as described above. Because the desorption was very low, desorption was performed twice on the selected samples, again resulting in very low desorption. Several other extracting solutions were tested as desorbents: 0.1 M CaCl_2 (pH 9), 0.1 M NaOH in methanol, and acetonitrile. For calcium montmorillonite 10% nicosulfuron was desorbed by using neutral 0.1 M CaCl_2 and 15% nicosulfuron by using 0.1 M CaCl_2 (pH 9).

Kinetic experiments were performed in serum bottles closed with Teflon-coated rubber septa. Aliquots of the suspension were withdrawn at the desired time intervals and quickly centrifuged and filtered. The concentration of nicosulfuron in the filtrates was determined as described above.

RESULTS AND DISCUSSION

The representative nicosulfuron adsorption and desorption isotherms on calcium montmorillonite, calcium hectorite, silica, and ferrihydrite are presented in Figure 1. The sorption isotherms on all sorbents were linear. The K_d values for all of the systems studied are presented in Table 1 along with some of the properties of the sorbents. The strong adsorption only occurred on layer silicate minerals, while on the oxides the extent of adsorption was much less. The kinetic experiments (Figure 2) indicate that the decrease in the nicosulfuron concentration in solution occurs rapidly. This is consistent with an adsorption process rather than a rapid hydrolysis catalyzed by clay minerals. However, the process obviously requires more than the high surface area or high ion exchange capacity. Silica and busserite (a layered manganese oxide) have a large surface area and a high cation exchange capacity, respectively, but the adsorption of nicosulfuron on those two sorbents is low.

The differences in the K_d values for the two micas (Table 1, biotite and muscovite) demonstrate that the

Table 1. Properties of Minerals Used in This Study and Linear Adsorption and Desorption Partition Coefficients

mineral	surface area ($\text{m}^2 \text{g}^{-1}$)	cmol kg^{-1}		L kg^{-1}			
		CEC ^c	AEC ^c	$K_{d,ads}$	SE ^d	$K_{d,des}$	SE
alumina	164	0.5	6.3	4.92 ^b	0.10	13.69	0.43
silica	524	3.0	0.4	8.26 ^b	0.28	22.39	0.55
ferrihydrite	233	0.8	6.1	7.96 ^b	0.20	12.82	1.03
goethite	36	0.4	7.0	5.40 ^b	0.16	13.43	0.95
buserite	76	109.8	0.3	7.42 ^b	1.37	19.37	1.56
calcium montmorillonite	625	84.9	0.3	157.36 ^c	1.91	163.86	1.58
aluminum montmorillonite	574	81.5	0.4	31.45 ^b	0.97	406.61	17.26
biotite (<50 μm)	nd ^a	3.8	nd	79.00 ^b	8.59	667.22	25.54
muscovite (<50 μm)	nd	3.1	nd	4.17 ^b	0.99	22.88	8.76
calcium hectorite	nd	70.0	nd	456.93 ^c	3.53	589.21	7.22

^a Not determined. ^b Determined at pH 6.0 ± 0.1 . ^c Determined at pH 6.5 ± 0.1 . ^d Standard error.

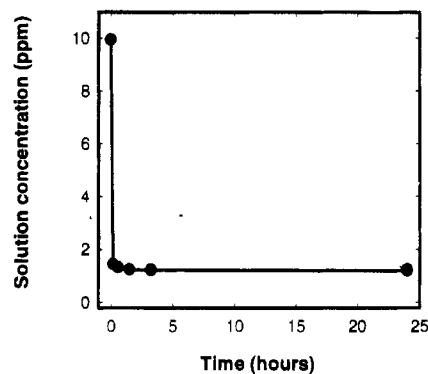


Figure 2. Rate of nicosulfuron sorption at pH 6.5 on calcium montmorillonite. $c_0 = 10$ ppm; clay/solution ratio is 1:20.

interlayer regions of clay minerals are involved in the sorption process. Both biotite and muscovite have their interlayers collapsed with potassium, which is virtually nonexchangeable. However, biotite (a trioctahedral mica) is known to weather and release the interlayer potassium (Scott and Smith, 1966) much more readily than muscovite (a dioctahedral mica). Thus, the higher adsorption K_d on biotite than on muscovite may be a result of the biotite interlayers opening more readily than those of muscovite.

The accessibility of the interlayer region could account for the highest K_d being observed on a low charge density clay hectorite. The distance between exchangeable cations on low charge density clays is greater compared to high charge density clays. Consequently, there is more "free" interlayer space that can be occupied by organic molecules. Layer charge effects on adsorption of organic compounds on calcium smectites (Laird et al., 1992) and quaternary ammonium smectites (Jaynes and Boyd, 1991) have been demonstrated.

The strong and irreversible sorption of nicosulfuron on negatively charged clay surfaces is not expected, given that its reported $\text{p}K_a$ is 4.3, which implies it should be predominantly in the anionic form at pH 6–6.5, where the experiments reported here were performed. Chlorsulfuron ($\text{p}K_a = 3.3$) is the only other sulfonylurea whose adsorption on montmorillonite has been studied. It exhibits low (Brogard and Streibig, 1988) or even negative (Shea, 1986) adsorption on montmorillonite. However, nicosulfuron differs from most other SUs by the presence of the pyridine ring instead of benzene on the left side of the sulfonylurea bridge and by the presence of a carboxamide group on the pyridine ring (Figure 3). One possible explanation for strong nicosulfuron interaction with clay minerals

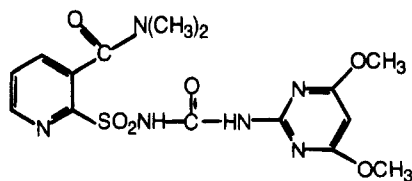


Figure 3. Structure of nicosulfuron.

may be that nicosulfuron is present in solution as a zwitterion, with one of the nitrogens on the molecule being protonated. Spectrophotometric titration (Ukrainczyk, unpublished results) indicates that nicosulfuron has three pK_a values, 2.0, 4.3, and 9.6, but the location of the highest pK_a on the molecule is not known. Adsorption of some other zwitterions, for example amino acids (Theng, 1974), on clays gives linear isotherms at the low concentration range, consistent with isotherms observed for nicosulfuron. Another possible, less likely, explanation is the rapid hydrolysis catalyzed by surface acidity of clay minerals, resulting in the basic products which adsorb strongly on the clays. One of the nicosulfuron hydrolysis products, 2-amino-4,6-bis(dimethoxy)pyrimidine (EPA Pesticide Fact Sheet, 1990), is similar to aniline, which adsorbs strongly on layer silicates (Theng, 1974).

Further studies on the chemistry of nicosulfuron are currently being conducted and should give more insight into nicosulfuron-clay mineral interactions.

SIGNIFICANCE

The strong adsorption of nicosulfuron on clay minerals should decrease its mobility in soils and its potential to leach into groundwater. Sorption on mineral surfaces is especially important in the subsurface horizons and in soils with low organic matter content. The fast kinetics of the adsorption implies that the nicosulfuron moving down the soil profile should be readily and strongly retained on the surfaces of clay minerals.

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Ljerka Ukrainczyk* and Naghmana Rashid

Department of Agronomy, Iowa State University,
Ames, Iowa 50011-1010

JF940704Q

* Author to whom correspondence should be addressed (e-mail l_ukrain@iastate.edu).

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