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INTERACTIONS OF TWO SULFONYLUREA HERBICIDES WITH ORGANOCLAYS

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Abstract—The sorption of two sulfonylurea herbicides (SU), metsulfuron methyl and nicosulfuron, on pure clays and organoclays was investigated. Three clays (Arizona smectite, SAz-1, Wyoming smectite, SWy-2, and hectorite, SHCa-1), were treated with amounts of octadecylammonium (ODA) or dioctadecyldimethylammonium (DODMA) cations equal to ~50 and 100% of the clays' cation exchange capacity (CEC). Sorption isotherms were fitted to the Freundlich equation. While no measurable sorption was found on the pure clays ($K_f = 0$), organoclays prepared using both primary and quaternary amines were effective as SU sorbents. The metsulfuron methyl K_f values ranged between 196 and 1498 $\mu mol^{1-1/n}\ kg^{-1}\ L^{1/n}$, and K_f values for nicosulfuron, which were lower than those of metsulfuron methyl, ranged from 35 to 198 $\mu mol^{1-1/n}\ kg^{-1}\ L^{1/n}$. As shown by sorption coefficients, K_d and K_{OC}, SWy-2 treated with DODMA at ~100% of the CEC was the most effective sorbent for metsulfuron, K_d = 684 L kg^{-1} and K_{OC} = 2138 L kg^{-1}. For nicosulfuron the most effective sorbent was SAz-1 with ODA at ~ 50% of the CEC (K_d = 147 L kg^{-1} and K_{OC} = 1233 L kg^{-1}). In contrast to other weak-acid herbicides, such as phenoxy and picolinic acids, no clear relationships were found between sorption and layer charge, organic carbon content, and basal spacing of the organoclays for both sulfonylurea herbicides. Sorption of both herbicides on organoclays was assumed to involve hydrophobic and polar interactions for which the availability of interlayer room between organocations was a very important factor.

Key Words—Metsulfuron, Nicosulfuron, Organoclays, Sorption, Sulfonylureas.

INTRODUCTION

Sulfonylurea herbicides (SUs) such as metsulfuron methyl (methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-y1)amino]carbonyl]amino]sulfonyl]benzoate), and nicosulfuron (2-[[[[(4,6-dimethoxy-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]-*N,N*-dimethyl-3-pyridinecarboxamide) are used for selective post-emergence control of broadleaf weeds in wheat, and for annual and perennial grasses in corn. The mode of action of these herbicides is inhibition of the production of the acetolactate synthase enzyme, which is responsible for biosynthesis of the branched-chain amino acids isoleucine, leucine and valine.

The SUs, which are weak acids, are generally weakly sorbed to soil, with decreased sorption with increased pH as the result of increased amounts of anionic species in solution (Beyer *et al*., 1988). For acidic herbicides such as SUs, movement in soil is closely related to soil solution pH (Martins and Mermoud, 1999; Hultgren *et al*., 2002). The SUs generally have low octanol/water partitioning coefficients (K_{ow} values) and relatively high water solubilities, resulting in a high potential mobility in soils (Anderson and Dulka, 1985; Mersie and Foy, 1986; Blair and Martin, 1988; Brown, 1990).

The increasing use of pesticides with high potential mobility may pose serious environmental problems through offsite transport, which must be controlled to minimize potential harmful effects. Ultimately, leaching and transport of pesticides may not only result in low efficacy, but also possible groundwater contamination (Koterba *et al*., 1993; Wagner *et al*., 1994; Ritter *et al*., 1996). To decrease the environmental risk, several strategies have been employed to protect and restore soils. Sorption of contaminants on different materials has been used to eliminate them from water or immobilize them in contaminated soils (Yelverton *et al*., 1990; Wagner *et al*., 1994). Different sorbent materials have also been proposed for controlled release formulations (Park *et al*., 1999) to minimize movement.

Clay minerals, especially smectites, as sorbents, are of particular interest because of their large specific surface areas (Cox *et al*., 2000). However, the strong hydration of the natural inorganic exchange cations produces a hydrophilic environment at the clay surface which reduces the sorption capacity for hydrophobic organic compounds (Mortland, 1970; Jaynes and Vance, 1996). An alternative sorbent is a modified clay. When large organic cations occupy the exchange sites of the clay, the surface properties change from hydrophilic to hydrophobic, making them highly effective in the sorption of hydrophobic organic compounds (Boyd *et al*., 1988b; Lee *et al*., 1989; Zhao *et al*., 1996). Recently, there has been increasing interest in organoclays for use as soil containment barriers (Boyd *et al*., 1988a; Lee *et al*., 1989; Burris and Antworth, 1992; Smith and Jaffe, 1994; Gullick and Weber, 2001; Lo, 2001), and as carriers in slow-release formulations (El-Nahhal *et al*.,

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1998, 1999, 2000; Nennemann *et al*., 2001; Celis *et al*., 2002a,b; Carrizosa *et al*., 2003).

There have been many studies dealing with sorption of pesticides on organoclays including: herbicides, such as carboxylic acids (Hermosin and Cornejo, 1992, 1993; Carrizosa *et al*., 2000, 2001), imidazolinones (Celis *et al*., 1999), acetanilides (El Nahhal *et al*., 1999; Pal and Vanjara, 2001), and substituted ureas (Aguer *et al*., 2000); insecticides, such as nitroguanidines (Cox *et al*., 2001); and fungicides, such as triazoles (Celis *et al*., 2000). However, sorption of the weakly acidic sulfonylurea herbicides on organoclays has not received close attention.

The objective of this research was to examine the sorption capacity for two SUs, metsulfuron methyl and nicosulfuron, on organic-saturated (octadecylammonium and dioctadecyldimethylammonium) clays. The selection of smectites with different layer charges, diverse saturating cations (primary and quaternary), and use of two different coverage levels might help to optimize the clay characteristics in order to design the most appropriate sorbent for use as a soil containment barrier.

MATERIAL AND METHODS

Pesticides

Pure analytical-standard grade metsulfuron methyl and nicosulfuron (chemical purities >99% and >90%, respectively), and ^{14}C-labeled metsulfuron methyl (phenyl-^{14}C(4)), and ^{14}C-labeled nicosulfuron (pyridine-2-^{14}C), with radiochemical purities >99%, and specific activities of 38.3 and 62.9 μCi mg^{-1} respectively, were supplied by Dupont Agricultural Products. Metsulfuron methyl (Figure 1) has a pKa value of 3.3, and water solubilities of 270 mg L^{-1} (pH 4.6, 25ºC), 1750 mg L^{-1} (pH 5.4, 25ºC), and 2790 mg L^{-1} (pH 7.0, 25ºC), whereas nicosulfuron (Figure 1) has a pKa value of 4.3, and water solubilities of 400 mg L^{-1} (pH 5.0, 25ºC) and 12000 mg L^{-1} (pH 7.0, 25ºC) (M.J. Duffy, DuPont Agricultural Products, pers. comm.).

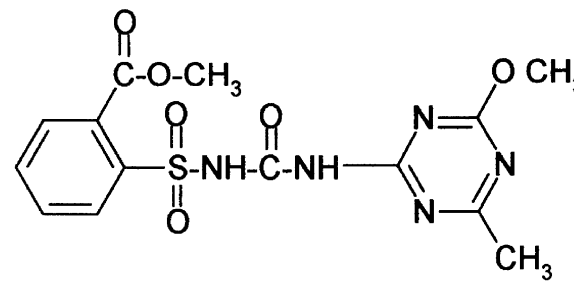
Sorbents

Table 1 summarizes the characteristics of the different sorbents used in this study. The main differences between Arizona montmorillonite (SAz-1), Wyoming montmorillonite (SWy-2), and hectorite (SHCa-1), (supplied by the Source Clays Repository of the Clay Minerals Society, Purdue, IN), are the differences in the octahedral sheet charge, resulting in cation exchange capacities (CEC) of 120 cmol$_c$ kg^{-1}, 76 cmol$_c$ kg^{-1} and 44 cmol$_c$ kg^{-1}, for SAz-1, SW-y-2 and SHCa-1, respectively (van Olphen and Fripiat, 1979). Two different organic cations (octadecylammonium (ODA) and dioctadecyldimethylammonium (DODMA)) and two different organic cation loadings (~50% and ~100% of the CEC of the clays) were used in the synthesis of the organoclays.

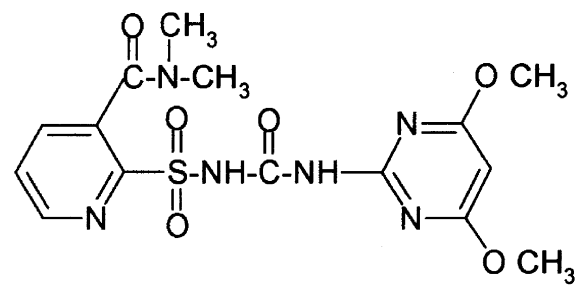
For organoclay synthesis, 100 g of clay were treated with an ethanol:water (50:50) solution containing alkylammonium chloride equivalent to 50% and 100% of the CEC of the clay as described elsewhere (Carrizosa *et al*., 2000, 2001). The suspensions were shaken at 20 ± 2ºC for 24 h, centrifuged, washed with distilled water until Cl free, then freeze dried. The organic carbon (OC) contents of the sorbents were determined using a total elemental carbon analyzer (LECO CHNS932). The percent organocation saturation (%OCtS) was obtained from the OC contents, molecular weight of the alkylammonium cation, and the CEC of the clay (Cox *et al*., 2001). The pH was measured using a combination glass electrode. X-ray diffraction (XRD) patterns were obtained on oriented specimens with a Siemens D-500 diffractometer (Siemens, Stuttgart, Germany) using CuKα radiation.

Sorption studies

Metsulfuron methyl and nicosulfuron sorption isotherms on the different sorbents were obtained using the batch equilibration technique. Metsulfuron methyl solutions were prepared in 0.01 M $CaCl_2$ at concentrations ranging from 5 to 130 μM. Nicosulfuron solutions were also prepared in 0.01 M $CaCl_2$ at concentrations ranging from 2 to 75 μM. Radiolabeled metsulfuron methyl and nicosulfuron were added to non-radioactive solutions to give a final solution radioactivity of ~4000 DPM mL^{-1}. Duplicate 40 mg sorbent samples were equilibrated with 10 mL aliquots of the pesticide solution in 35 mL glass centrifuge tubes sealed with Teflon-lined caps, by



Metsulfuron methyl



Nicosulfuron

Figure 1. Chemical structures of metsulfuron methyl and nicosulfuron.

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Table 1. Surface properties of the clays.

Sorbent	Mineral phase	Interlamellar cation	CEC (meq/100 g)	OC (%)	%OCtS	d_{001} (nm)
SAz-1	SAz-1	–	120	–	–	1.52
SWy-2	SWy-2	–	76	–	–	1.26
SHCa-1	SHCa-1	–	44	–	–	1.11
SA-DODMA$_{50}$	SAz-1	dioctadecyldimethylammonium	120	27	48	3.80
SA-DODMA$_{100}$	SAz-1	dioctadecyldimethylammonium	120	39	70	3.80
SA-ODA$_{50}$	SAz-1	octadecylammonium	120	12	49	1.65^{vb}
SA-ODA$_{100}$	SAz-1	octadecylammonium	120	28	113	3.06
SW-DODMA$_{50}$	SWy-2	dioctadecyldimethylammonium	76	22	62	2.44
SW-DODMA$_{100}$	SWy-2	dioctadecyldimethylammonium	76	32	92	3.42
SW-ODA$_{50}$	SWy-2	octadecylammonium	76	12	51	1.52^{vb}
SW-ODA$_{100}$	SWy-2	octadecylammonium	76	18	93	1.62^{vb}
SH- ODA$_{50}$	SHCa-1	octadecylammonium	44	†	†	1.6 ^{vb}

SAz-1, Arizona smectite; SWy-2, Wyoming smectite; CEC, cation exchange capacity; %OC, organic carbon content; %N, nitrogen content; %OCSt, organic cation saturation calculated from OC and N contents; d_{001}, basal spacing
^{vb} = very broad
†Hectorite (SHCa-1) contains as much as 27% calcite impurity ($CaCO_3$) (van Olphen and Fripiat, 1979)

shaking mechanically at 20±2ºC for 24 h. After equilibration, the suspensions were centrifuged at 2000 rpm for 15 min, and the radioactivity of the supernatant liquid determined by liquid scintillation counting. The amount of pesticide in solution was calculated from the initial specific activity of the pesticide solution.

Sorption data were fitted to the linearized form of the Freundlich equation:

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

where C_s (μmol kg^{-1}) is the concentration of SUs sorbed at the equilibrium concentration C_e (μM), and K_f and $1/n_f$ are the empirical Freundlich constants expressing sorption capacity and sorption intensity, respectively. For comparative purposes, sorption coefficients (K_d) were calculated from the Freundlich sorption coefficients and C_e concentrations within the range of measured solution concentrations, C_e = 50 μM (K_{d50}) for metsulfuron methyl, and 20 μM for nicosulfuron (K_{d20}). Sorption was also normalized to the OC content of the organoclay:

$$K_{OC} = (K_d \times 100)/\%OC \quad (2)$$

RESULTS AND DISCUSSION

Organoclay characterization

The characteristics of the sorbents used in the present work are shown in Table 1 and have been discussed previously (Cox *et al*., 2001). The arrangement of the organic cations on the mineral surface is a function of the cation structure and the mineral charge (Lagaly and Weiss, 1969; Lagaly, 1982; Jaynes and Boyd, 1991). Organocation saturation based on OC content ranged from 48 to 62% for the lower level of saturation (50% of CEC), and from 70 to 113% for the higher level (100% of CEC). The basal spacing values indicate that ODA cations formed mixed monolayer (1.37 nm) and bilayer (1.77 nm) structures in SAz-1 at 50% of CEC, and in SWy-2 at 50% and 100% of CEC. In contrast, ODA formed well-defined paraffin-like complexes in SAz-1 at 100% of CEC level. The basal spacing values indicate that the large DODMA cations formed well-defined paraffin-like complexes with SAz-1 and SWy-2 at both low and high levels of saturation.

Sorption on pure clays and organoclays

Metsulfuron methyl (Figure 2, Table 2) and nicosulfuron (Figure 3, Table 3) did not sorb on the pure clays, SAz-1 and SWy-2. The lack of sorption observed for these pure clays could be due to the acidic nature of both metsulfuron methyl (pKa = 3.3) and nicosulfuron (pKa = 4.3), and the repulsion of the anionic species from the negatively charged hydrophilic clay surfaces, behavior that has been shown before for the acidic herbicide imazamox (Celis *et al*., 1999). In contrast, incorporation of large organic cations in the interlayer of the smectites resulted in organoclays with greater sorptive properties for SUs.

Metsulfuron methyl (Figure 2, Table 2) and nicosulfuron (Figure 3, Table 3) sorption on organoclays fit the Freundlich equation ($r^2 > 0.95$). For metsulfuron methyl, all but one isotherm were L-type according to Giles *et al*. (1960), with $1/n_f$ values <1 (Table 2), indicating concentration dependence of sorption and a potential limit in the sorption capacity. Only SW-ODA$_{100}$, which is the lower layer-charge smectite (SWy-2) with ODA cation at the 100% CEC saturation level was C-type with $1/n_f$ values ≈1, which means an increase in sorption is proportional to an increase in solution concentration. Overall, nicosulfuron sorption isotherms were L-type with values of $1/n_f$ <1 (Table 3). However, it appears that while they are L-type at low concentrations (Figure 3), calculated K_d values are nearly constant at

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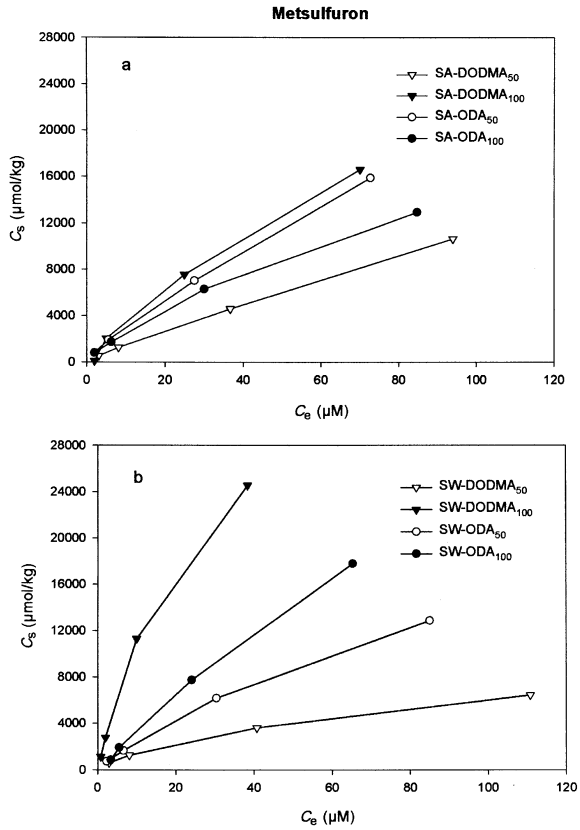


Figure 2. Metsulfuron methyl sorption isotherms on oganoclays: (a) SA-organoclays; (b) SW-organoclays.

higher concentrations, which would produce C-type isotherms.

Because all isotherm slopes ($1/n_f$) were not equal, distribution coefficients (K_d) were calculated from the Freundlich equation at C_e = 50 µM (K_{d50}) for metsulfuron methyl and at C_e = 20 µM (K_{d20}) for nicosulfuron and were normalized to the OC contents of the organoclays (K_{oc50} and K_{oc20}) to compare relative sorptivities of the sorbents. While no measurable sorption of metsulfuron methyl or nicosulfuron was observed for the pure clays, K_{d50} and K_{d20} varied depending on the organoclay used (Table 2 and Table 3). Cations in the organoclay can change the surface properties from hydrophilic to organophilic, making them highly effective in the sorption of pesticide molecules (Mortland *et al*. 1986; Pal and Vanjara, 2001). For DODMA-treated SAz-1 and SWy-2 clays, greater metsulfuron methyl and nicosulfuron sorption was observed with the higher organic cation saturation level as compared to the lower saturation levels (SW-DODMA$_{100}$ > SW-DODMA$_{50}$ and SA-DODMA$_{100}$ > SA-DODMA$_{50}$). This indicates that the higher OC content and the paraffin-like basal spacing (Table 1) favors hydrophobic interactions between SUs and the organoclays (Xu *et al*., 1997). The pH appears to have had little effect on SU sorption on DODMA organoclays. Although, the greater sorption of metsulfuron methyl on SA-DODMA$_{100}$ as compared to SA-DODMA$_{50}$ may have, in part, been due to the decrease in pH, the greater sorption in the other three cases could not be attributed to decreased pH.

For ODA-treated SWy-2 smectites, metsulfuron methyl and nicosulfuron sorption also increased with increased organic cation saturation level, SW-ODA$_{100}$ > SW-ODA$_{50}$. The larger amount of OC together with the higher value of d_{001}, favor the hydrophobic interactions and opening of the silicate interlayer (Hermosin and Cornejo, 1993). It is difficult to determine the magnitude of the effect of the contribution of increased saturation organic cation saturation because of potential effects due to differences in pH levels of the sorbents; metsulfuron methyl-SW-ODA$_{100}$ pH < metsulfuron methyl-SW-ODA$_{50}$ pH, whereas nicosulfuron-SW-ODA$_{50}$ pH < nicosulfuron-SW-ODA$_{100}$ pH.

In contrast to SWy-2, for the high layer-charge smectite (SAz-1), sorption of both SUs decreased with

Table 2. Metsulfuron methyl sorption desorption coefficients on natural clays and organoclays.

Sorbent	r^2	K_f ($\mu mol^{1-1/n}\ kg^{-1}\ L^{1/n}$)	$1/n_f$	K_{d50} ($L\ kg^{-1}$)	K_{oc50} ($L\ kg^{-1}$)	Final pH
SAz-1	–	0	–	–	–	–
SWy-2	–	0	–	–	–	–
SHCa-1	–	0	–	–	–	–
SA-DODMA$_{50}$	0.999	196 ± 3	0.88 ± 0.005	122	452	5.8
SA-DODMA$_{100}$	0.989	402 ± 76	0.90 ± 0.07	271	695	4.9
SA-ODA$_{50}$	0.999	449 ± 10	0.83 ± 0.007	230	1917	3.9
SA-ODA$_{100}$	0.998	452 ± 31	0.76 ± 0.02	176	628	4.7
SW-DODMA$_{50}$	0.998	305 ± 19	0.66 ± 0.02	81	366	5.8
SW-DODMA$_{100}$	0.989	1498 ± 193	0.80 ± 0.06	684	2138	5.6
SW-ODA$_{50}$	0.999	301 ± 65	0.81 ± 0.02	143	1192	4.8
SW-ODA$_{100}$	0.988	367 ± 21	1.00 ± 0.08	366	2033	3.9
SH-ODA$_{50}$	0.956	108 ± 42	0.80 ± 0.12	49	†	4.9

Value ±standard error
* at C_e = 50 µM
† lack of OC value

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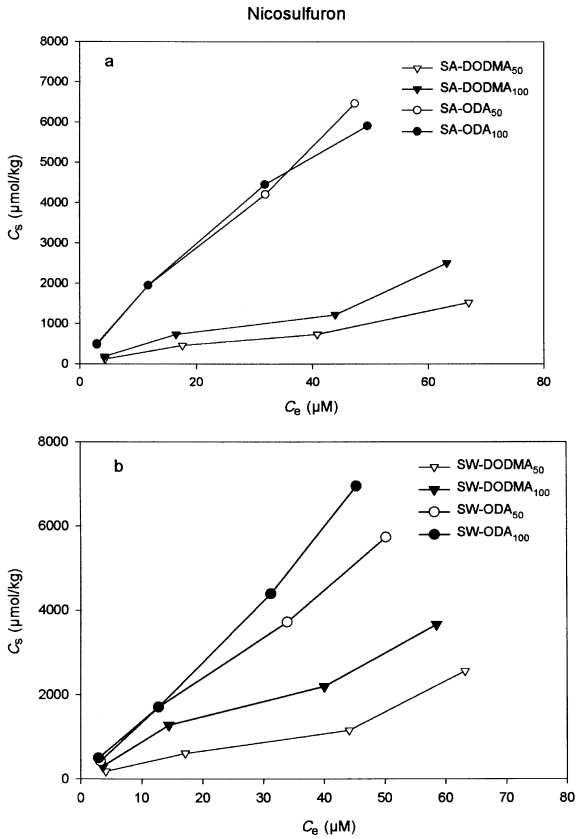


Figure 3. Nicosulfuron sorption isotherms on oganoclays: (a) SA-organoclays; (b) SW-organoclays.

increased saturation level (SA-ODA_{50} > SA-ODA_{100}). In this case, even having a larger basal spacing SA-ODA_{100} (paraffin-like) compared to SA-ODA_{50} (bilayer), the high layer charge favored the packing of ODA in the interlayer and limited the space available for sorption of metsulfuron methyl and nicosulfuron (Serratosa *et al*., 1970). This, in combination with a greater proportion of the SUs being undissociated for SA-ODA_{50} (pH SA-ODA_{50} < pH SA-ODA_{100}), resulted in the greater sorption on SA-ODA_{50} than on SA-ODA_{100}. Similar behavior was previously reported for the nitroguanidine insecticide, imidacloprid (Cox *et al*., 2001).

In general, no clear relationships were found between SU sorption and layer charge, OC content, pH, or d_{001} of the organoclays. The results indicate that sorption of SUs on organoclays is related to maximum polar-free interlayer room, which would be needed to establish polar interactions between SUs and the charged groups of alkylammonium, combined with an hydrophobic environment (Zhao *et al*., 1996; Aguer *et al*., 2000; Cox *et al*., 2001; Carrizosa *et al*., 2001). For instance, metsulfuron methyl K_{oc50} values (Table 2) do not correspond to a particular clay/organic cation combination. In contrast, the higher values of nicosulfuron K_{oc20} for ODA organoclays compared to those corresponding to the hydrophobic DODMA organoclays, also indicates the importance of polar contributions to sorption.

Sorption K_f, K_{d50} and K_{d20} values of metsulfuron methyl and nicosulfuron on hectorite are listed in Table 2 for comparative purposes only. Metsulfuron methyl sorption on hectorite was the lowest of the three smectites; the order was SA-ODA_{50} > SW-ODA_{50} > SH-ODA_{50}. Sorption of nicosulfuron on SH-ODA_{50} was not significantly different from sorption on SA-ODA_{50} and SW-ODA_{50}. It is difficult to ascribe mechanisms to hectorite properties, since it contains as much as 27% calcite (van Olphen and Fripiat, 1979).

We could not determine desorption or d_{001} of metsulfuron methyl and nicosulfuron-saturated clays and organoclays. During the 5 days over which these experiments were conducted, there was significant decomposition of both SUs. Therefore, to determine the sorption-desorption mechanisms of metsulfuron methyl and nicosulfuron on organoclays, more research is required, particularly in controlling the decomposition

Table 3. Nicosulfuron sorption desorption coefficients on natural clays and organoclays.

Sorbent	r^2	K_f ($\mu mol^{1-1/n}\ kg^{-1}\ L^{1/n}$)	$1/n_f$	K_{d20} ($L\ kg^{-1}$)	K_{oc20} ($L\ kg^{-1}$)	Final pH
SAz-1	–	0	–	–	–	–
SWy-2	–	0	–	–	–	–
SHCa-1	–	0	–	–	–	–
SA-$DODMA_{50}$	0.984	35 ± 8	0.88 ± 0.09	21	77	4.7
SA-$DODMA_{100}$	0.973	54 ± 17	0.90 ± 0.10	36	92	4.5
SA-ODA_{50}	0.997	198 ±19	0.90 ± 0.03	147	1223	4.4
SA-ODA_{100}	0.994	168 ± 27	0.89 ± 0.05	111	396	4.8
SW-$DODMA_{50}$	0.969	48 ± 14	0.90 ± 0.12	33	150	4.6
SW-$DODMA_{100}$	0.982	113 ± 28	0.85 ± 0.08	66	206	5.1
SW-ODA_{50}	0.997	148 ± 14	0.92 ± 0.05	107	892	4.1
SW-ODA_{100}	0.994	174 ± 26	0.94 ± 0.05	133	739	4.6
SH-ODA_{50}	0.951	252 ± 88	0.75 ± 0.12	119	†	5.4

Value ±standard error.
* at C_e = 20 µM
† lack of OC value

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process. Preliminary studies showed that some metsulfuron methyl and nicosulfuron decomposed during the sorption experiments (unpublished results), but it did not significantly affect the results. The ^{14}C-metabolites were more polar and less sorbed (more ^{14}C in solution) than the parent, hence the sorption coefficient of the metabolite would be very small. Because we were looking for relative sorption coefficients, the order and magnitude of sorption of metsulfuron methyl nicosulfuron on different organoclays would not be impacted by a small amount of decomposition.

CONCLUSIONS

Results showed that incorporation of large organic cations, particularly ODA, in the interlayer of the pure smectite clays, SAz-1 and SWy-2, resulted in organoclays with high sorptive capacities for the sulfonylurea herbicides, metsulfuron methyl and nicosulfuron. Sorption on the interlayer space of organoclays could be due to a combination of weak hydrophobic interactions with polar contributions. Polar interlayer room between alkylammonium groups in the organoclay and pH are important factors in determining sorption capacity. While metsulfuron methyl and nicosulfuron are representative of the >20 SUs registered for use in various crops, more research in this area is needed. The SUs are complex molecules; they have pyrimidine, triazine, triazole and pyridine heterocycles on one side of the sulfonylurea bridge and phenyl, thiophene, pyridine, and furan groups on the other side, with pKa values ranging from 3.3 to 5.2. Regardless, the selection of the appropriate interlayer cation with a high degree of saturation would be a good strategy to increase the sorptivity of organoclays for a wide range of pesticides, including weak acids. These results showed that organoclays may find an environmental application as sorbents in soil containment barriers, or as carriers in slow-release herbicide formulations.

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