

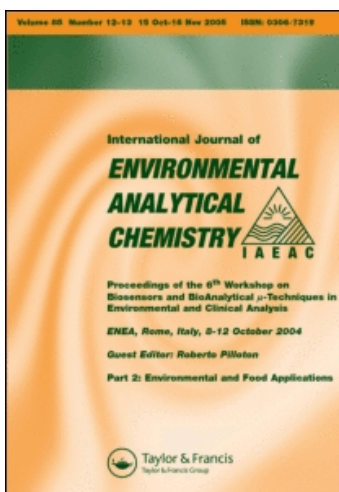
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SORPTION OF TWO NEW SULFONYLAMINOCARBONYLTRIAZOLINONE HERBICIDES AND THEIR METABOLITES ON ORGANIC AND INORGANIC EXCHANGED SMECTITES

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The sorption capacity and possible mechanisms of sorption of two new sulfonylaminocarbonyltriazolinone herbicides, methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1*H*-1,2,4-triazol-1-yl)carbonyl]amino]sulfonyl]benzoate (MKH 6561) and (4,5-dihydro-3-methoxy-4-methyl-5-oxo-*N*-[[2-(trifluoromethoxy)phenyl]sulfonyl]-1*H*-1,2,4-triazole-1-carboxamide) (MKH 6562), and their potential metabolites, 2,4-dihydro-4-methyl-5-propoxy-3*H*-1,2,4-triazol-3-one (triazole) and 2-trifluoromethoxybenzenesulfonamide (phenylsulfonamide) on octadecyl (C18) and dioctadecyldimethylammonium (DOD) saturated and Fe³⁺ and Na⁺ saturated smectites has been investigated. Sorption of MKH 6561 on inorganic clays and C18 organoclays was much higher than for MKH 6562, but was similar on DOD saturated clays. For C18 saturated clays, sorption of both parent compounds increased with decreasing layer charge of the organosmectite. Sorption of triazole metabolite, which was much lower than for its parent compound MKH 6561, was higher on inorganic and C18 saturated clays than on DOD saturated clays or inorganic clays. Phenylsulfonamide metabolic sorption, which was also lower than the corresponding parent compound MKH 6562, was higher on DOD saturated clays than on C18 or inorganic saturated clays. These differences in sorption behaviour are related to the diverse relative contribution of hydrophobic and polar interactions for the various compound-clay systems.

Keywords: Alkylammonium cations; Clay; Metabolites; Organoclay; Smectite; Sorption; Sulfonylaminocarbonyltriazolinone herbicides

INTRODUCTION

Agricultural pesticides are often detected in natural waters, and therefore, are an important group of organic pollutants. Sorption on diverse materials is a method used for their elimination from water or their immobilization in contaminated soils

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[1,2]. Sorption is also a basis for controlled release formulation, which can decrease their contamination potential [3]. Recently, there has been an increasing interest in the use of natural and modified clays as support or carrier to reduce the leaching of soil-applied herbicides or insecticides [4–11].

Natural smectites, due to their high interlayer surface and hydration water of exchangeable cations, are good sorbents for polar organic chemicals [12]. When exchangeable inorganic cations are exchanged by organic cations, smectite, surface properties change from hydrophilic to lipophilic making them highly effective in sorption of organic contaminants [13]. Because of their high water solubilities, polar organic pesticides are among the most frequent contaminants of water and soils, and there are many studies dealing with their sorption on natural smectites [14–18] and modified smectites [10,19–24]. High charge of the clay and quaternary ammonium compounds favour sorption of diverse polar herbicides with medium and high water solubility [21,24]. Low charge clays with primary alkylammonium also have been shown to be efficient sorbents for polar pesticides with a carbonyl group. The combination of the hydrophobic and polar interactions in the latter case makes it very difficult to predict the sorbent characteristics resulting in the best adsorption.

This work deals with two new sulfonylaminocarbonyl triazolinone herbicides, methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1*H*-1,2,4-triazole-1-yl)carbonyl]amino]sulfonyl]benzoate (MKH 6561) and 4,5-dihydro-3-methoxy-4-methyl-5-oxo-*N*-[[2-(trifluoromethoxy)phenyl]sulfonyl]-1*H*-1,2,4-triazole-1-carboxamide (MKH 6562), and potential metabolites, 2,4-dihydro-4-methyl-5-propoxy-3*H*-1,2,4-triazol-3-one (triazole) and 2-trifluoromethoxybenzenesulfonamide (phenylsulfonamide). The objective was to examine the sorption capacity and possible mechanisms of sorption for these herbicides and metabolites on organic (octadecyl and dioctadecyldimethylammonium) saturated and inorganic (Fe and Na) saturated smectites. For this purpose, three smectites with different layer charge (H, W and A) and diverse saturating cations (primary and quaternary) were selected.

EXPERIMENTAL

Chemicals and Smectites

Pure analytical standards (chemical purity > 99%) and radiochemical material (radiochemical purity > 97%) were supplied by Bayer Corporation. Figure 1 shows the structures of the parent compounds MKH-6561 and MKH-6562 and their respective triazole (6561M) and phenylsulfonamide (6562M) metabolites.

The smectites used were SAz-1 and SWy-1 montmorillonites and SH-1 hectorite, which were supplied by The Clay Minerals Repository of the Clay Minerals Society (Columbia, USA). From here, these clays will be labelled as A (SAz-1), W (SWy-1) and H (SH-1) [26].

Preparation of Sorbents

The organoclays were prepared by treating the mineral clays (A, W and H) with an ethanol/water solution of octadecylammonium (C18) and dioctadecyldimethylammonium (DOD) chlorides at 100% of CEC level. W smectite was saturated with Na⁺

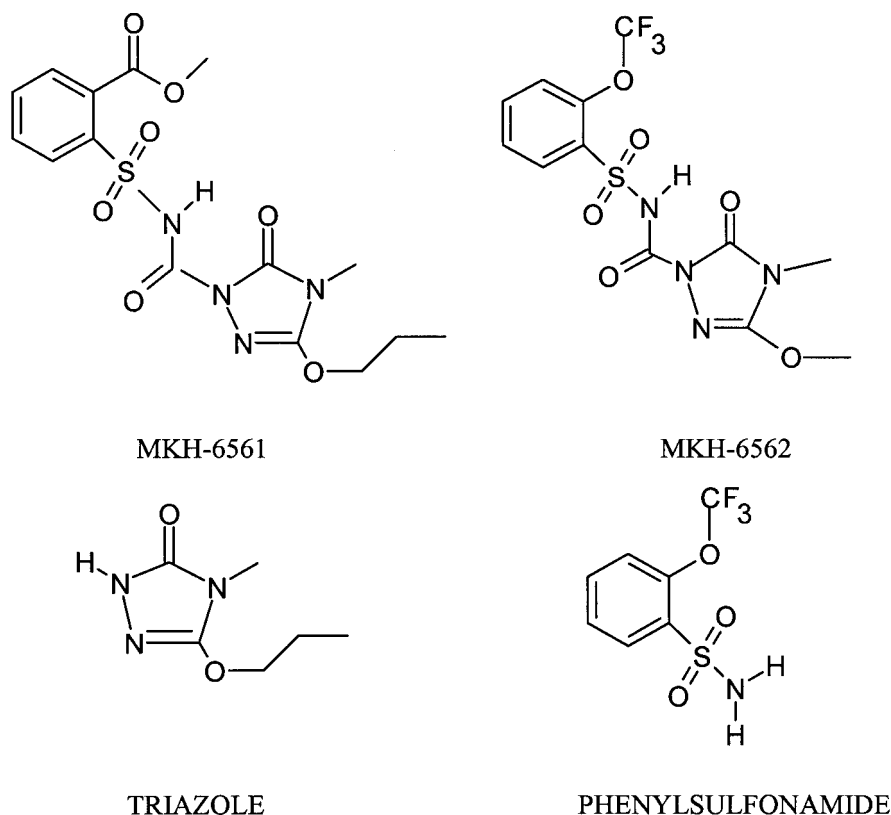


FIGURE 1 Structure of MKH-6561 and MKH-6562, a triazole and a phenylsulfonamide metabolite.

and Fe^{3+} by treating the $< 2 \mu\text{m}$ fraction with 1 M NaCl or FeCl_3 . All samples were washed until Cl^- free and freeze dried. The basal spacings were obtained by X-ray diffraction on oriented specimens. The C and N contents of organoclays were measured in an elemental analyzer LECO CHNS932.

Sorption Studies

Duplicate 0.10 g samples of clay were treated with 3 mL of 0.1 mg L^{-1} solutions of MKH 6561, MKH 6562, 6561M and 6562M. Radiolabelled chemical was added to nonradioactive solutions to give a final solution concentration of 8000 dpm mL^{-1} . Suspensions were shaken at $21 \pm 2^\circ\text{C}$ for 24 h, centrifuged, and 1 mL of supernatant removed for analysis.

Chemical Analyses

One-millilitre clear supernatants were mixed with 6 mL of EcoLite scintillation cocktail, and the amount of radioactivity was determined by liquid scintillation counting for 5 min in a 1500 TRI-CARB Packard Liquid Scintillation Analyzer.

RESULTS AND DISCUSSION

Sorbent Characteristics

Surface properties of the smectites are given in Table I. The saturation of the smectite in alkylammonium compound (% OCTS) was obtained from the N content, nitrogen weight in the molecular form of the corresponding alkylammonium and the CEC of the clay. The OCTS values are all close to the saturation except in the case of A-DOD because of the large and bulky size of this cation allow greater interlayer packing.

Organic carbon (OC) increased with layer charge of the smectite ($A > W > H$), due to the higher CEC (Table I). The basal spacing values indicate that C18 cations formed bilayer structures in H and W smectites, whereas in the high layer charge smectite A, C18 cations formed well defined paraffin-like complexes [27]. Basal spacing values shown in Table I indicate that the large DOD cations formed very well defined paraffin-like complexes with H, W, and A smectites.

Sorption Studies with Parent Compounds MKH-6561 and -6562

Distribution coefficients K_d calculated at $C_i = 0.1 \text{ mg L}^{-1}$ are given in Table II, together with sorption coefficients normalized to OC content of the organoclay

TABLE I Surface properties of the smectites

<i>Smectite</i>	<i>Saturating cation</i>	<i>Layer charge</i> ^a (mol/unit cell)	<i>CEC</i> (meg/100)	<i>OC/N</i> %	<i>OCTS</i> ^b %	<i>d</i> ₀₀₁ (nm)
H-C18	Octadecylammonium	0.31	44	12.6/0.6	94	1.7
W-C18	Octadecylammonium	0.68	76	15.0/1.0	90	1.7
A-C18	Octadecylammonium	1.13	120	25.5/1.8	98	3.2
H-DOD	Diocetyltrimethylammonium	0.31	44	20.0/0.5	89	2.5
W-DOD	Diocetyltrimethylammonium	0.68	76	31.3/1.0	90	3.3
A-DOD	Diocetyltrimethylammonium	1.13	120	38.6/1.3	70	4.0
W-Na	Na	0.68	76	–	–	1.3
W-Fe	Fe	0.68	76	–	–	1.3

^aTotal charge calculated from total chemical analysis [27].

^b%OCTS = saturation level in organic cation calculated from OC content.

TABLE II Sorption coefficients $K_{d,0.1}$ and K_{oc} parent compounds 6561 and 6562

<i>Smectite</i>	6561		6562	
	<i>K</i> _{d,0.1}	<i>K</i> _{oc}	<i>K</i> _{d,0.1}	<i>K</i> _{oc}
H-C18	1147 (± 200) ^a	91	184 (± 2.0)	14
W-C18	471 (± 103)	31	119 (± 12)	8
A-C18	314 (± 73)	12	91 (± 8.2)	4
H-DOD	950 (± 91)	48	662 (± 38)	33
W-DOD	461 (± 47)	15	532 (± 68)	17
A-DOD	539 (± 14)	14	601 (± 54)	15
W-Na	10.4 (± 0.0)	–	0.67 (± 0.54)	–
W-Fe	313 (± 7)	–	14 (± 1.5)	–

^aNumbers in parentheses are standard error about the mean.

($K_{oc} = K_d / \%OC$). While K_d is a measurement of sorption capacity, K_{oc} values indicate the alkylammonium efficiency to adsorb or interact with the chemicals [25,27].

Sorption of MKH-6561 on organoclays increases (Table II) with decreasing charge density (Table I), without significant differences between the two saturating cations (C18 or DOD). The available space for sorption between consecutive alkylammonium cations is limited in high surface charge smectites. The similar sorption of MKH-6561 in H-C18 vs H-DOD, and W-C18 vs W-DOD, indicates that this available space between the organic cation is as important as the hydrophobicity of the interlayer and the basal spacing of the organoclay [10,23,24], both of which are higher in H-DOD and W-DOD clays when compared to H-C18 and W-C18, respectively. High OC content and basal spacing favour hydrophobic interactions and opening of the silicate layer [13,19], whereas the space between saturating cations facilitates polar interactions between the molecular and the charged groups of the alkylammonium and/or the hydrophilic surface of the clay layer [10,23,24]. Consequently, K_{oc} values for MKH-6561, which are higher in C18 saturated clays when compared with the respective DOD-clay (Table II), are not reliable sorption parameters since they largely depend on the clay to which the alkylammonium is associated. Moreover, the higher K_{oc} values for MKH-6561 in C18-clays compared to those corresponding to the very hydrophobic DOD-clays also indicate the contribution of polar interactions in the former clays.

MKH-6561 sorption on inorganic exchanged clay W-Na was very low, whereas sorption on W-Fe was much higher and similar to sorption on some of the organoclays studied (Table II). Due to the high polarizing water associated to Fe(III) and the low pH of the suspension (pH = 3 for W-Fe and pH = 9 for W-Na), protonation of the carboxylic group of MKH-6561 molecule and/or to protonation of the NH group of the sulfonyleurea could take place. Similar results were obtained for the anionic herbicide 2,4-D [18] and for the urea herbicides thiazafluron [17] and fenuron [21]. Protonation on the surface of W-Fe smectite was confirmed in the case of 2,4-D and thiazafluron by FT-IR spectroscopy studies. Protonation of the COOH group would allow weak physical interactions and hydrogen bonding through the carbonyl group of the molecule, and protonation of the NH group, cation exchange sorption.

Sorption of MKH-6562 on C18 organoclays and inorganic clays was lower than on DOD clays, and was much lower than MKH-6561 on C18 and inorganic clays. Similar sorption was measured for both herbicides on DOD saturated clays (Table II). These results indicate that polar interactions, favoured in C18 and inorganic clays and limited in the case of quaternary ammonium, are not as important in the case of this herbicide when compared with MKH-6561. In fact, for diverse acidic herbicides as 2,4-D [14] and dicamba [20], the existence has been shown of H-bonds between hydrogen of the primary alkylammonium and the oxygen atom of the carbonyl group, which enhances adsorption of those organic acids. As for MKH-6561, sorption was higher on lower layer charge smectites, although differences were greater for the C18-clays than for DOD-clays, again revealing the importance of available space for sorption and hydrophobicity. These results with MKH-6561 and -6562 do not agree with previous studies by our research group and other groups. Sorption on organoclays of the anionic herbicide dicamba [20,25], the ionizable herbicide imazamox [22,21] and the urea herbicide fenuron [21] increased with layer charge of the smectite. This difference behaviour can be attributed to the larger size of the MKH-6561 and -6562 molecules.

Sorption of MKH-6562 on inorganic clays W-Na and W-Fe was much lower than on any other organoclay, which also confirms the smaller contribution of polar

interactions when compared with MKH-6561. As in this sulfonylaminocarbonyltrizolinone, sorption was much higher on W-Fe than on W-Na, which can be attributed to protonation of the NH of the sulfonylaminocarbonyltrizolinone group (Fig. 1) and sorption by cation exchange, as described above.

Sorption Studies with Metabolites Triazole (6561M) and Phenylsulfonamide (6562M)

Sorption of 6561M was lower than its parent compound MKH-6561 (Table III), and on C18 clays increased with low layer charge. In contrast to the parent compounds MKH-6561 and -6562, metabolite sorption coefficients, K_d and K_{oc} , were much higher on C18-clays than on DOC-clays, revealing the importance of the polar available space between quaternary ammonium cations and polar interactions in the case of this metabolite. The fact that the highly hydrophobic DOD-clays adsorbed much less 6561M than other organoclays confirms that partition mechanism is not as relevant in sorption of polar organic compounds. Polar bonds between the ring carbonyl group of 6561M and NH group of C18 alkylation [17,19] would explain this high sorption, since these polar interactions would be limited in the case of quaternary ammonium.

The higher sorption of 6561M on W-Na inorganic clay, when compared with DOD-clays, also confirms that sorption of this metabolite takes place mainly through polar interactions. In contrast to its parent compound MKH-6561, sorption was higher on W-Na than on W-Fe smectite, which suggests that protonation of the ring NH group does not take place, and that sorption in the interlamellar space of these montmorillonites could be by substitution of some water molecules hydrating the exchangeable cations, which is facilitated by the small ionic potential ($Na = 9.8$ and $Fe = 40.6 \text{ nm}^{-1}$) of the exchangeable cation [17,28].

As in the case of triazole metabolite, 6561M, sorption of the phenylsulfonamide metabolite, 6562M, was much lower than its parent molecule, MKH-6562. In this case, sorption was much higher on DOD-clays than on C18 or inorganic clays, indicating the importance of hydrophobic interactions in the case of this molecule, as in the case of its parent compound. In contrast to parent compounds, MKH-6561 and -6562, and the triazole metabolite, sorption of phenylsulfonamide metabolite on C18 clays significantly increased with the layer charge of the smectite ($A > W > H$). Due to the small size of the molecule, the available space between organic cations is not as important as hydrophobicity and basal spacing of the organoclay, both higher in high layer charge smectite.

TABLE III Sorption coefficients $K_{d0.1}$ and K_{oc} for 6561 and 6562 metabolites

<i>Smectite</i>	<i>Triazole</i>		<i>Phenylsulfonamide</i>	
	$K_{d0.1}$	K_{oc}	$K_{d0.1}$	K_{oc}
H-C18	91 (± 0.5) ^a	7	4.9 (± 0.00)	0.4
W-C18	33 (± 2.0)	2	9.7 (± 0.41)	0.7
A-C18	8.4 (± 0.3)	0.3	15 (± 0.75)	0.6
H-DOD	5.9 (± 0.5)	0.3	281 (± 13)	14
W-DOD	5.0 (± 1.0)	0.2	217 (± 10)	7
A-DOD	4.3 (± 0.6)	0.1	309 (± 30)	8
W-Na	9.0 (± 1.0)	–	2.6 (± 0.81)	–
W-Fe	0.11 (± 0.01)	–	1.8 (± 0.20)	–

^aNumbers in parentheses are standard error about the mean.

There were no significant differences in sorption of triazole 6561M on W–Na and W–Fe smectites, which indicates that protonation of the molecule on the surface of W–Fe due to the low pH of the suspension does not take place, and also suggests that sorption can take place mainly on hydrophobic microsites of the smectite interlayer [29].

CONCLUSIONS

Sorption of the sulfonylaminocarbonyltriazolinone on the smectites studied was higher than that of the corresponding metabolites. While polar interactions seem to be relevant in the case of MKH-6561 and its triazole metabolite, hydrophobic interactions seem to be more important in the case of MKH-6562 and its phenylsulfonamide metabolite. Results indicate that the sorption space between the exchangeable organocation (greater in low charge smectite and primary alkylation saturation) is as relevant as hydrophobicity and basal spacing of the organoclay (greater in high layer charge smectite and quaternary alkylation saturation), and confirm that partition mechanism is not the only mechanism of sorption of sulfonylaminocarbonyltriazolinone or other polar organic compounds on organoclays. Variation in inorganic and organic cation could be used to increase sorption on smectites and hence their potential use in remediation of contaminated soils and waters [23,30].

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