ADSORPTION AND DEGRADATION OF TRIASULFURON ON HOMOIONIC MONTMORILLONITES

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Abstract—The adsorption and degradation of the herbicide triasulfuron [2-(2-chloroethoxy)-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide] (CMMT) on homoionic Fe^{3+}-, Al^{3+}-, Ca^{2+}-, or Na^+-exchanged montmorillonite in aqueous medium were studied. Ca- and Na-exchanged montmorillonite were ineffective in the adsorption and degradation of triasulfuron. The adsorption on Fe- and Al-exchanged montmorillonite was rapid, and equilibrium was attained after 5 min. Degradation of the herbicide was slow and the type of the degradation products depended on the nature of the exchangeable cations. In the presence of Fe^{3+}-rich montmorillonite, the metabolites 2-(2-chloroethoxy)benzenesulfonamide (CBSA), 2-(2-chloroethoxy)-N-[[(4-hydroxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide (CHMT), and 1-[2-(2-chloroethoxy)benzene-1-sulfonyl]-7-acetyltriuret (CBAT) were the only identified products, whereas 2-amino-4-methoxy-6-methyltriazine (AMMT), CBSA, CHMT, and CBAT were the primary metabolites for the Al^{3+}-rich montmorillonite. A Fourier transform infrared (FT-IR) study of montmorillonite samples after the interaction with triasulfuron in organic solution suggests that the hydrolysis mechanism involves the adsorption of the herbicide on the 2:1 layers.

Key Words—Adsorption, Degradation, Herbicides, Infrared Spectroscopy, Montmorillonite, Triasulfuron.

INTRODUCTION

Triasulfuron is a sulfonylurea herbicide used at very low rates (10–25 g of active ingredient/ha) for selective weed control in cereals (Amrein and Gerber, 1985). Sulfonylureas are a new class of herbicides characterized by low acute and chronic toxicity for mammals and extremely high phytotoxicity against weeds (Brown, 1990). Generally, investigations of the fate of these herbicides in soil and plants have shown that the adsorption processes by soil are of great importance. Several studies have stressed the role of organic matter in the adsorption and inactivation of xenobiotics, whereas little attention is given to inorganic soil colloids. The activity of clay minerals in adsorbing and decomposing pesticides was widely emphasized in several reviews (Mortland, 1986; Ortego *et al.*, 1991; Kowalska *et al.*, 1994). Some sulfonylureas are also strongly adsorbed on clays (Ukrainczyk and Rashid, 1995) and may degrade on smectites (Pantani *et al.*, 1994, 1996; Calamai *et al.*, 1997). Similar to other sulfonylureas (Beyer *et al.*, 1988), triasulfuron is more persistent in neutral or weakly basic media than in acidic media (Braschi *et al.*, 1997). The triasulfuron half life at neutral pH is greater than one year (Braschi *et al.*, 1997); therefore, the herbicide is expected to degrade slowly. Since a large part of inorganic soil colloids is represented by clay minerals that display sorptive and degradative properties towards xenobiotics, an investigation on the interaction between triasulfuron and clay minerals is desirable. This study is focused on the ability of a montmorillonite, saturated by different exchangeable cations, to adsorb and/or degrade triasulfuron.

MATERIALS AND METHODS

Triasulfuron (purity 99.5%) was obtained from Ciba-Geigy, Saronno, Italy. The purity was checked by high performance chromatography (HPLC). The triasulfuron metabolites (Figure 1) AMMT, CBSA, CHMT, CBAT, and 2-amino-4-hydroxy-6-methyltriazine (AHMT) were obtained according to the procedure described by Braschi *et al.* (1997). The structures of triasulfuron and its metabolites are given in Figure 1.

Triasulfuron hydrochloride and methoxytriazine hydrochloride were prepared by bubbling anhydrous HCl into a chloroform solution of triasulfuron and methoxytriazine, respectively. The precipitates were filtered and dried under vacuum. All solvents were of HPLC grade (Carlo Erba Reagenti, Milano, Italy) and were used without further purification.

Montmorillonite No. 26 (bentonite) from Crook County, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, New York, was used. The <2-μm fraction was obtained by sedimentation. The cation-exchange capacity (CEC) of the sodium form, determined by the method of Hendershot and Duquette (1986), was 0.902 eq/kg. Al^{3+}-, Fe^{3+}-, Ca^{2+}-, and Na^+-exchanged samples were prepared by repeated treatments of the clay with 1 N solutions of the respective metal chlorides. The samples were centrifuged, washed repeatedly with deionized water until free of Cl^-, and dried at room temperature.
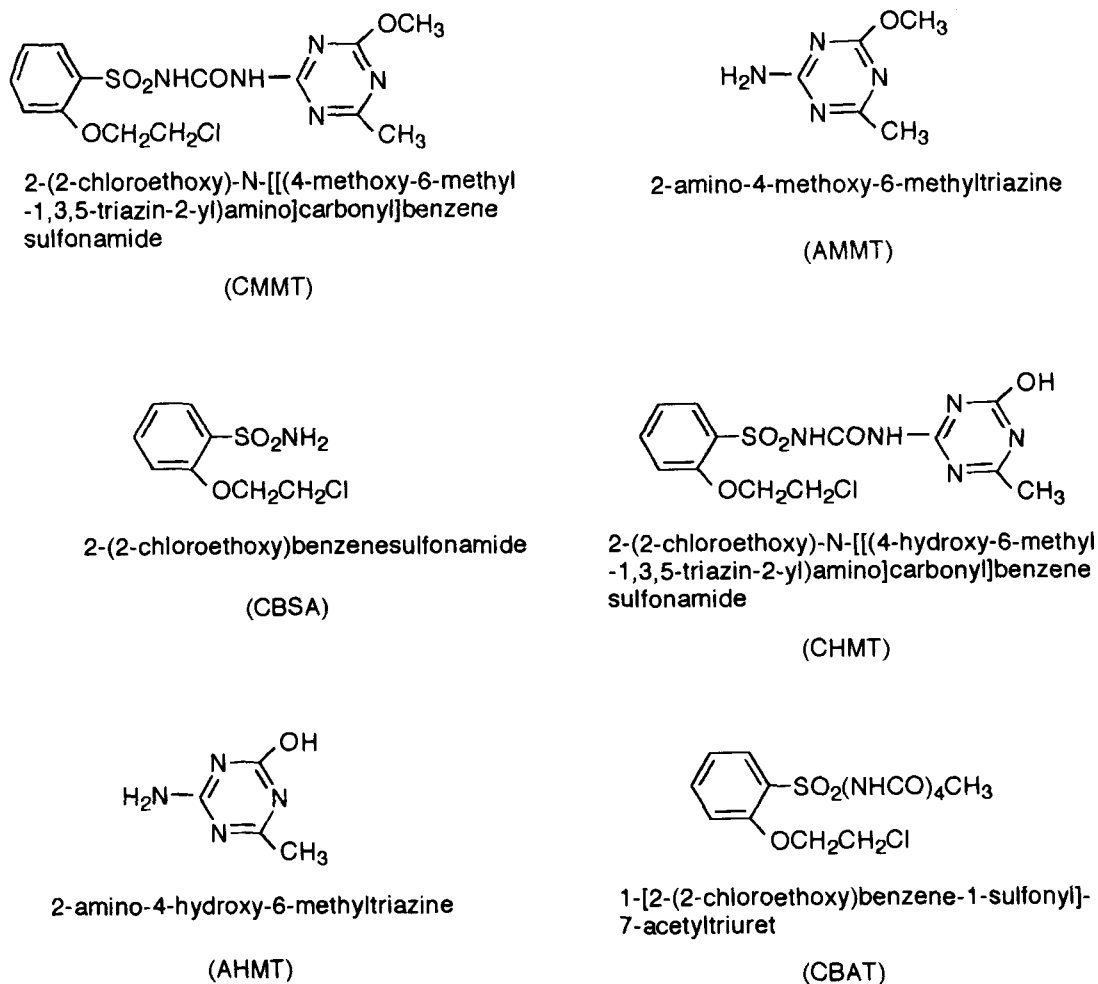
2-(2-chloroethoxy)-N-[[(4-methoxy-6-methyl
-1,3,5-triazin-2-yl)amino]carbonyl]benzene
sulfonamide

(CMMT)

2-amino-4-methoxy-6-methyltriazine

(AMMT)

2-(2-chloroethoxy)benzenesulfonamide

(CBSA)

2-(2-chloroethoxy)-N-[[(4-hydroxy-6-methyl
-1,3,5-triazin-2-yl)amino]carbonyl]benzene
sulfonamide

(CHMT)

2-amino-4-hydroxy-6-methyltriazine

(AHMT)

1-[2-(2-chloroethoxy)benzene-1-sulfonyl]-
7-acetyltriuret

(CBAT)

Figure 1.   Structures of triasulfuron and its metabolites.

Adsorption

Batch distribution isotherms on Al^{3+}- and Fe^{3+}-rich montmorillonite were determined at $25 \pm 2°C$. Triplicate 30-mg samples of air-dried clay were equilibrated in polyallomer centrifuge tubes with 30 mL of aqueous herbicide solution (the range 3.5–39.8 μM was chosen on the basis of solubility). The tubes were stirred using Teflon-coated magnetic stir bars for 30 min. Generally, 95% of adsorption occurred within 5 min on Al^{3+}- and Fe^{3+}-rich montmorillonite. No adsorption was observed on Ca^{2+}- and Na^+-rich montmorillonite, even after 20 d.

After 30 min the suspension was centrifuged, and the supernatant was pipetted and analyzed immediately by HPLC. The amount adsorbed by montmorillonite was calculated from the difference between the initial and final concentrations of triasulfuron in solution. The adsorption studies were performed also in an organic solvent ($CHCl_3$), as described below.

A further adsorption experiment was performed by equilibrating 30 mg of air-dried Fe^{3+}-rich montmorillonite in a centrifuge tube with 30 mL of AMMT aqueous solution (10 μM) for 10 d after which the suspension was centrifuged and the supernatant analysed by HPLC. The percentage adsorbed by clay was 19.8%. The initial concentration of AMMT was the same as that formed after 16 d by triasulfuron degradation in distilled water buffered at a pH value of 4.4 (see below).

Degradation

Degradation experiments for triasulfuron were performed in aqueous clay suspensions. In general, 30-mg samples of Al^{3+}- or Fe^{3+}-rich montmorillonite (~0.03 meq of exchangeable cation), in air-dried form, were suspended in 30 mL of aqueous solution of triasulfuron (36.49 and 35.96 μM for Fe^{3+}- and Al^{3+}-rich montmorillonite, respectively) in glass vials sealed
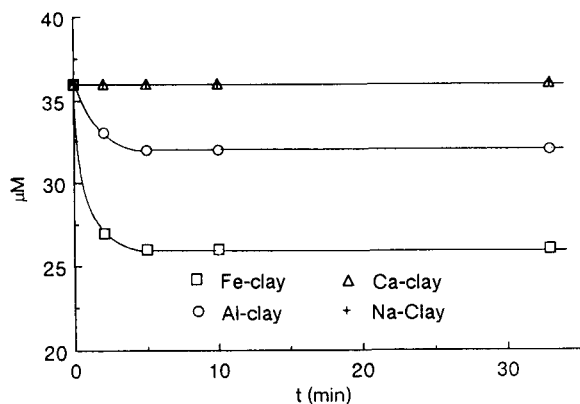
Figure 2.   Time dependence of the adsorption of triasulfuron on montmorillonite.

with Teflon/silicon rubber septa. The suspensions were continuously stirred in a 25°C constant-temperature bath using Teflon-coated magnetic stir bars. After 16 d, the suspensions were ultracentrifuged, and triasulfuron and its hydrolysis products were analyzed in the supernatant by HPLC. The experiments were run in duplicate. Clay-free blanks were examined in distilled water buffered at pH values of 4.4 and 5.2. To study the influence of the cation Fe^{3+} in the salt form, 0.03 meq of $FeCl_3$ was added to 30 mL of aqueous solution of triasulfuron (32.19 μM). The resulting solution had a pH of 2.9. After 16 d at 25°C, the solution was treated as described above.

HPLC analyses

The concentrations of triasulfuron and its degradation products at selected intervals were determined by HPLC. The system was assembled as follows: a Jasco 880-PU Intelligent pump equipped with a Rheodyne 7120 injection valve; a Jasco 875-UV Intelligent UV/ VIS detector at 224 nm; Borwin v 1.21.60. chromatography software; and a Spherisorb C_8 analytical column (5 μm, 4.6 × 250 mm). Acetonitrile plus water (40 + 60 by volume, pH = 2.7) at a flux of 1 mL min^{-1} was the eluant. The quantification of triasulfuron and its degradation products was based on external standards. Calculations were based on the average peak areas of the external standards.

Infrared analysis

Fourier transform infrared (FT-IR) spectra were recorded with a FT-IR Nicolet 205 spectrophotometer over the range 4000–600 cm^{-1}. Spectra of triasulfuron, AMMT, and their hydrochlorides were obtained on KBr disks. Spectra of triasulfuron adsorbed on the Al^{3+}-, Fe^{3+}-, Ca^{2+}-, and Na^+-exchanged montmorillonite were recorded using self-supporting films. Samples for the latter spectra were prepared by evaporating 5 mL of aqueous clay suspension (2% w/v) on a polyethylene sheet at room temperature. The air-dried films

were divided into two portions. One was placed in a 2% herbicide $CHCl_3$ solution for 14 h, then removed and rinsed several times with pure solvent, and airdried. The remaining portion was treated, in a similar way, only with pure solvent. Metabolites were also adsorbed on Fe-rich clay films in the same way as described for triasulfuron. IR spectra were recorded immediately after air-drying. Differential spectra were obtained for herbicide- and metabolite-montmorillonite complexes by subtracting the spectra of the corresponding blank clay film from those of the clay-organic complexes. Only IR absorptions between 2000– 1200 cm^{-1} are discussed here because this region is the most appropriate for providing evidence for adsorption mechanisms in clays. Each adsorption experiment was run in duplicate and repeated three times. All the spectra were the mean of at least 64 scans at 4-cm^{-1} resolution; these conditions are sufficient to produce a good signal to noise ratio.

Data analysis

Data were fit to the logarithmic form of the Freundlich equation, log Cs = log Kf + 1/n log Ce, where Cs (in mmol kg^{-1} units) is the amount of herbicide adsorbed by clay, Ce (in mM units) is the equilibrium concentration in solution, and log Kf and 1/n are empirical constants representing the intercept and the slope of the isotherm, respectively. Fitting was performed by a *least-squares* regression analysis program using the Stat View 512 statistical package (Brain Power, Inc., Calabasas, California) on a Macintosh IIsi computer (Apple Computer, USA).

RESULTS

Adsorption from water

Figure 2 shows the kinetics of triasulfuron adsorption on montmorillonite. The adsorption on Fe- and Al-rich montmorillonite is rapid and a steady state is attained after 5 min. In contrast, Ca- and Na-rich montmorillonite were unable to adsorb the herbicide. The adsorption isotherms of triasulfuron on Fe- and Al-homoionic montmorillonite are shown in Figure 3. The isotherms are the "S" type, according to the classification of Giles *et al.* (1960). This shape indicates that adsorption becomes increasingly favored as concentration increases. This result is usually attributed to a strong competition with the solvent molecules for substrate sites. In certain instances, especially in the adsorption of organic compounds, the "S"-type isotherm may be due to cooperative interactions among adsorbed organic species that stabilize the sorbate and enhance its affinity for the surface (Sposito, 1984). In the presence of Fe-rich montmorillonite the adsorption curve shows a second rise. This curve is defined by Giles *et al.* (1960) as the sub-group 3 (S3) type and is attributed to the development of a fresh surface on
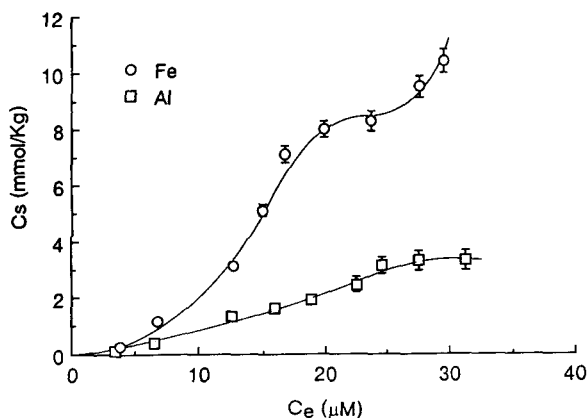
Figure 3. Adsorption isotherms of triasulfuron on Fe- and Al-rich montmorillonite measured after 30 min.

Table 1. Freundlich parameters for the adsorption of triasulfuron on M-exchanged montmorillonite.

M	K_f	$1/n$	r
Fe^{3+}	3.46	1.76	0.986
Al^{3+}	2.23	1.52	0.990

which adsorption can occur. If a second plateau corresponding to the complete saturation of the new surface is not realizable, the curve appears as the S3 type. The empirical Freundlich relationship was used to evaluate the results (r ≥ 0.98). The values of Kf and $1/n$ are given in Table 1. Fe-rich montmorillonite is more effective in promoting triasulfuron adsorption, followed by Al-rich montmorillonite. These results suggest that the different affinity of the homoionic clays for triasulfuron is related to the polarizing power of the exchangeable cation. The lack of adsorption on montmorillonite saturated with Ca and Na ions reflects the lower-polarizing power of these ions, compared with Fe and Al.

Degradation

With elapsing time, degradation products were observed in the herbicide-montmorillonite systems. Table 2 shows the amounts of triasulfuron and its metabolites remaining in suspension after 16 d of contact with Fe- and Al-rich montmorillonite, respectively. In the presence of Fe^{3+}-rich montmorillonite (pH = 4.4), the metabolites CBSA, CHMT, and CBAT were the only products. On the other hand, Al^{3+}-rich montmorillonite (pH = 5.2) yielded the metabolites AMMT, CBSA, CHMT, and CBAT. In the Ca^{2+}- and Na^+-rich montmorillonite systems (pH 6.8 and 7.1, respectively), no significant degradation was observed. The trend may indicate that the pH of the suspension is a critical factor in the decomposition of the herbicide. Experiments performed in clay-free blank solutions, at the same pH as in the clay suspensions, did not show major differences in the amounts of remaining triasulfuron in solution as compared to the corresponding clay systems.

A kinetic study of the reaction was beyond the scope of this work. In fact, the overall process taking place in the clay suspensions is related to several contributions, including adsorption and degradation, both in solution or on the surfaces. Therefore, a simple kinetic law is not expected in the presence of clay, thus preventing a comparison with the clay-free system. The product distribution was remarkably different (Table 2), particularly at pH 4.4, as compared with the Fe^{3+}-rich montmorillonite system. The Fe-rich montmorillonite apparently promotes the formation of metabolite CBAT, and inhibits the pathways yielding metabolites AMMT and AHMT. Free metal ions (as salts) are known to influence both the rate and the pattern of degradation of pesticides (Sànchez-Camazano and Sànchez Martin, 1983; Pusino *et al.,* 1988), and this behavior was observed for sulfonylurea herbicide chlorsulfuron in the presence of Fe^{3+} ions (Sabadie, 1991). A control experiment was performed in a clay-free $FeCl_3$ water solution to establish the effect of the ion in the absence of clay. Note in Table 2, the Fe^{3+} ion increased considerably the degradation of herbicide. After 16 d, only 2% of triasulfuron remained in solution. Most probably, the Fe^{3+} ion in a salt solution reacts more easily with the herbicide and therefore it is more active. The free Fe^{3+} ion favors the formation of triazines AMMT and AHMT by hydrolytic cleavage of the sulfonylurea bridge of triasulfuron and hydroxytriasulfuron, respectively. The hydrolytic breakdown of the triazine ring leading to product CBAT is totally suppressed.

The results substantiate an active role of montmorillonite in the degradation of triasulfuron. The extent and product distribution of the reaction depends on both the pH of the interlayer, that in the case of Fe^{3+} and Al^{3+} is more acidic than in the external solution, and the particular arrangement assumed by a triasulfuron molecule in the interlayer. However, this implies that the adsorption of the herbicide occurs on the clay. Evaluating the mechanisms involved in the adsorption from aqueous solutions is difficult. Herbicide molecules compete with solvent for binding to surfaces. Therefore, because of the low-adsorption level of herbicide from a water solution, no evidence on the adsorption mechanism can be obtained by FT-IR spectra.

Adsorption from organic solvent

The adsorption of triasulfuron on montmorillonite from $CHCl_3$ was also studied. The FT-IR spectra of triasulfuron, in the free, protonated, and Fe clay-complex form, are compared in Figure 4. The spectra indicate that the herbicide undergoes significant changes upon interacting with montmorillonite surfaces. Triasulfuron exhibits an absorption at 1707 cm^{-1} (1730

Table 2. Percentage distribution[1] (mol %) of triasulfuron and its decomposition products in the presence of M-exchanged montmorillonite, in clay-free blanks (B) and in Fe^{3+} solution.

System	CMMT	AMMT	CBSA	CHMT	AHMT	CBAT
Fe-montm.	23.6 ± 1.8	—	45.5 ± 2.1	11.9 ± 0.7	—	19.0 ± 0.7
$B_{pH = 4.4}$	19.8 ± 0.5	25.0 ± 1.2	37.9 ± 2.2	7.7 ± 1.2	3.8 ± 0.3	5.7 ± 0.7
Al-montm.	59.0 ± 1.6	18.1 ± 0.8	14.0 ± 0.8	7.3 ± 1.4	—	1.6 ± 0.2
$B_{pH = 5.2}$	55.0 ± 0.4	15.6 ± 3.0	17.8 ± 1.5	11.5 ± 1.1	—	—
$Fe^{3+}_{pH = 2.9}$	2.0 ± 0.2	29.1 ± 2.1	50.7 ± 1.6	—	18.1 ± 0.9	—

[1] Distribution referred to 16 d. The average value derived as the mean of two samples and the standard deviation are reported.

cm^{-1} in $CHCl_3$ solution, see Pantani *et al.,* 1997) owing to the stretching mode of the carbonyl group of the sulfonamide bridge. The FT-IR spectra of triasulfuron Fe^{3+}- and Al^{3+}-montmorillonite complexes are very similar to each other and show a weak absorption
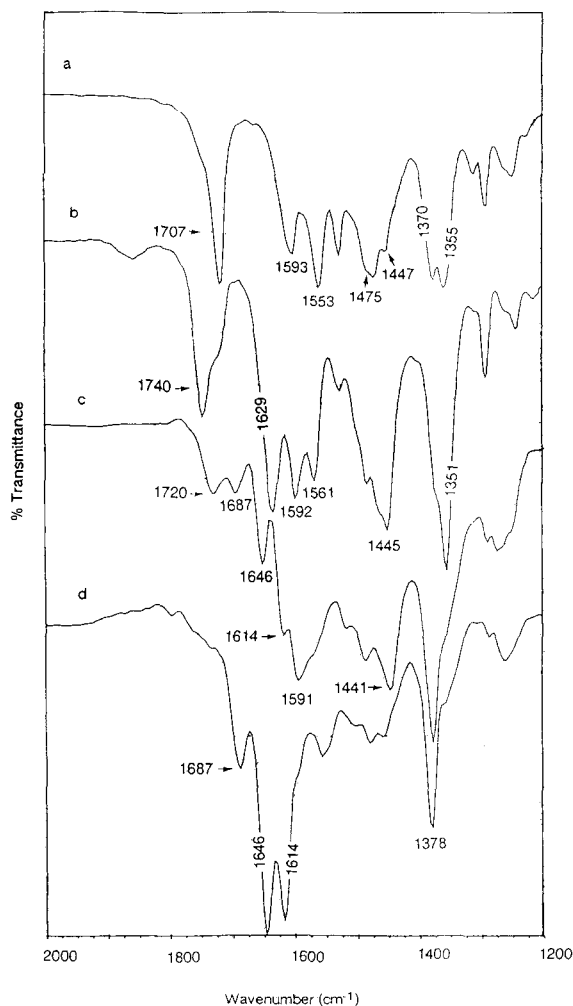

Figure 4. FT-IR spectra of: a) triasulfuron, b) triasulfuron hydrochloride, c) triasulfuron-Fe-rich montmorillonite complex, prepared as described in the experimental part, d) triasulfuron-Fe-rich montmorillonite complex after several washings with $CHCl_3$ (see text).

for the carbonyl group at 1720 cm^{-1}. The displacement to higher wavenumbers suggests an increase in the double-bond character of the C=O group, more likely owing to the electron-withdrawing effect from a protonated neighboring group, or to the loss of intermolecular hydrogen bonding. Further distinguishing features of Fe and Al triasulfuron-montmorillonite complexes are additional absorptions centered at 1614 and 1646 cm^{-1}, respectively, with the latter value typical of the protonated aromatic heterocyclic nitrogen (Cook, 1961; Pouchert, 1975). The above results may be consistent with the triasulfuron form protonated at the triazine moiety. The spectrum of triasulfuron hydrochloride (Figure 4, trace b) shows bands different from those observed for triasulfuron Fe- and Al-montmorillonite complexes. For instance, the absorptions at 1614 and 1646 cm^{-1} of the clay complexes are absent in the spectrum of protonated triasulfuron. The chloroformic supernatant of Fe-rich montmorillonite-triasulfuron suspension was tested for metabolites by HPLC, but only undecomposed triasulfuron and traces of sulfonamide CBSA were found. The clay was washed with chloroform until a chromatogram of the pure solvent was obtained. After the washings, IR analysis of the self-supporting film of Fe-rich montmorillonite-triasulfuron complex produced the spectrum (trace d) in Figure 4. This spectrum has fewer spectral features, which suggests a chemical structure simpler than in triasulfuron, as expected for a breakdown product.

The spectra of each metabolite separately adsorbed on the clay were also comparatively examined. The spectrum observed after washing the montmorillonite-herbicide complex was nearly coincident with that of the metabolite AMMT adsorbed on the Fe-rich montmorillonite (Figure 5, trace b). The IR bands were different from those of AMMT in neutral form (Figure 5, trace a) and close to those of AMMT hydrochloride (Figure 5, trace c). The results suggest that AMMT is adsorbed in the interlayer as the protonated form.

The spectra of Ca^{2+}- and Na^+-rich montmorillonite-triasulfuron complexes (Figure 6) are similar to each other and to that of triasulfuron. Apart from the shift of the carbonyl band from 1707 cm^{-1} in triasulfuron to 1714 cm^{-1} in the Ca- and Na-rich montmorillonite-
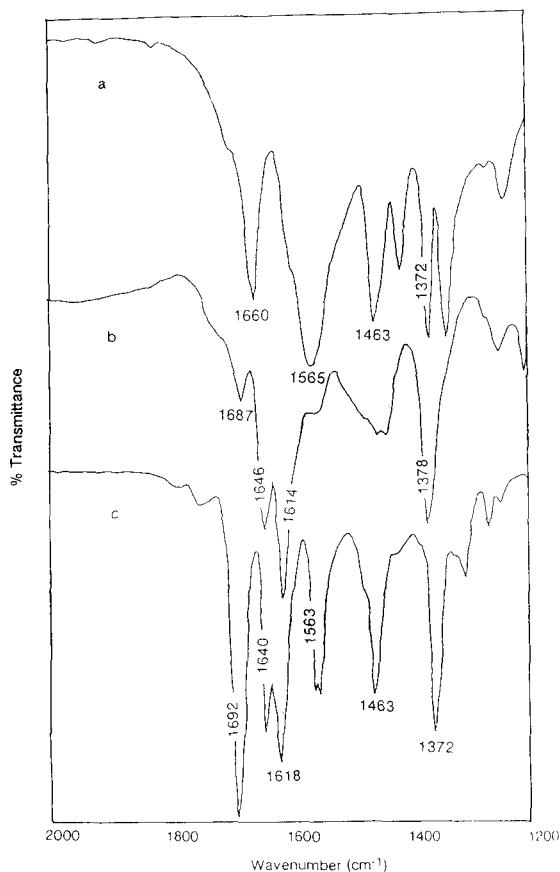
Figure 5. FT-IR spectra of: a) methoxytriazine, b) methoxytriazine-Fe-rich montmorillonite complex, c) methoxytriazine hydrochloride.

Figure 6. FT-IR spectra of (a) Ca- and (b) Na-rich montmorillonite treated with triasulfuron as described in the experimental part.

triasulfuron complexes, the absorption does not undergo any significant change. Therefore, the interaction in these systems seems to be less important, most likely because of the weak forces, *e.g.*, van der Waals, involved.

DISCUSSION

The results indicate that Ca and Na clays are ineffective in adsorbing and degrading triasulfuron from water. Triasulfuron behaves as a weak acid with a pK_a value of 4.5 in water (Worthing and Hance, 1991) owing to the proton dissociation of the NH group within the sulfonamide bridge. At the pH values of the Ca- and Na-rich montmorillonite suspensions (6.8 and 7.1, respectively) the herbicide is in anionic form and therefore has negligible affinity for the negative surfaces of the clay. On the other hand, triasulfuron degrades very slowly ($t_{1/2}$ = 492 d; Braschi *et al.,* 1997) at pH 7. This finding explains the lack of metabolites after 16 d in the Ca- and Na-rich montmorillonite aqueous suspensions.

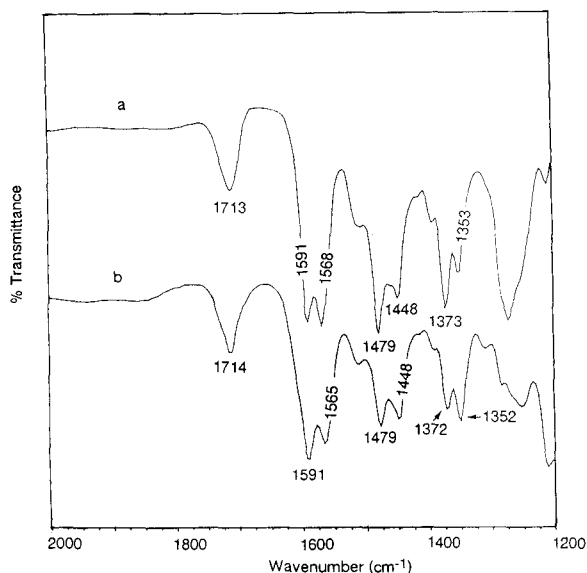The adsorption of triasulfuron by Fe- and Al-rich montmorillonite water suspensions follows the Freundlich equation. With elapsing time, hydrolysis occurs. The metabolites AMMT and AHMT arising from an acid-catalyzed cleavage of the sulfonylurea bridge of triasulfuron and hydroxytriasulfuron CHMT, respectively, are absent in the Fe-rich montmorillonite suspension. The results obtained in the presence of free Fe ions suggest that the absence of these metabolites is not attributable to any peculiar catalytic effect of free Fe ion. The triazines AMMT and AHMT may have been completely removed by Fe-rich montmorillonite, after they are formed in water suspension. Since methoxytriazine AMMT is only partly removed by the Fe-rich montmorillonite from aqueous solution (see experimental section), this hypothesis is ruled out. Alternatively, AMMT and AHMT triazines could be formed in the interlayer and remain adsorbed therein as the protonated species. Triazine, with electron-releasing substituents in the ring, is a weak base, *e.g.,* AHMT has a pK_a value of 3.1 (Hirt *et al.,* 1961). Therefore, the greater acidity of hydrated Fe^{3+} ions, compared with Al^{3+}, may favor adsorption in the interlayer by protonation. This assumption agrees with FT-IR data, which indicate that AMMT remains adsorbed in the clay. Although a similar trend extrapolated to adsorption from water is not shown here, similar behavior is expected in natural environments under dry conditions. The detection of metabolite CBAT, which is formed in the Fe-clay interlayer to a greater extent than in the blank solution, proves the hydrolysis. Product CBAT is the result of an acid-catalyzed hydrolytic breakdown of the triazine ring of triasulfuron.

The organic medium increases the acidity of the residue H_2O molecules surrounding Al^{3+} ions, which may contribute to the greater retention of methoxytriazine. The FT-IR spectra of Fe- and Al-herbicide montmorillonite complexes obtained from organic suspension were very similar. It is unclear if triasulfuron is degraded to triazine AHMT in organic solution also, because the IR bands of this compound may be masked by those of the major compound AMMT. However, the lack of the parent metabolite CHMT in chloroformic equilibrium does not support this hypothesis.

The weak interaction established by triasulfuron with Ca- and Na-rich montmorillonite surfaces in organic medium, as indicated by the minor perturbation of the carbonyl group of triasulfuron, is ineffective in degrading triasulfuron.

In conclusion, despite the complexity and incomplete knowledge of the processes occurring in the montmorillonite, the results indicate that triasulfuron may be removed and degraded by soil containing montmorillonite with loss of herbicidal activity. This may be particularly significant for a slowly degrading herbicide, which may be the cause of injury to sensitive crops long after application.

ACKNOWLEDGMENTS

REFERENCES

Amrein, J. and Gerber, H.R. (1985) CGA 131'036: A new herbicide for broad-leaved weed control in cereals. In *Proceedings of the British Crop Protection Conference on Weeds,* 55–62.

Beyer, E.M., Jr., Duffy, M.J., Hay, J.V., and Schlueter, D.D. (1988) Sulfonylureas. In *Herbicides: Chemistry, Degradation and Mode of Action, Volume 3,* P.C. Kearney and D.D. Kaufman, eds., Dekker, New York, 117–190.

Braschi, I., Calamai, L., Cremonini, M.A., Fusi, P., Gessa, C., Pantani, O., and Pusino, A. (1997) Kinetics and hydrolysis mechanism of triasulfuron. *Journal of Agricultural and Food Chemistry,* **45,** 4495–4499.

Brown, H.M. (1990) Mode of action, crop selectivity and soil relations of the sulfonylurea herbicide. *Pesticide Science,* **29,** 263–281.

Calamai, L., Pantani, O., Pusino, A., Gessa, C., and Fusi, P. (1997) Interaction of rimsulfuron with smectites. *Clays and Clay Minerals,* **45,** 1–5.

Cook, D. (1961) Vibrational spectra of pyridinium salts. *Canadian Journal of Chemistry,* **39,** 2004–2024.

Giles, C.H., Mac Ewan, T.H., Nakhwa, S.N., and Smith, D. (1960) Studies in adsorption: Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society,* **111,** 3973–3993.

Hendershot, W.H. and Duquette M. (1986) A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Science Society of America Journal,* **50,** 605–608.

Hirt, R.C., Schmitt, R.G., Strauss, H.L., and Koren, J.G. (1961) Spectrophotometrically determined ionization constants of derivatives of symmetric triazine. *Journal of Chemical Engineering Data,* **6,** 610–612.

Kowalska, M., Güler, H., and Cocke, D.L. (1994) Interactions of clay minerals with organic pollutants. *Science of the Total Environment,* **141,** 223–240.

Mortland, M.M. (1986) Mechanisms of adsorption of non humic organic species by clays. In *Interactions of Soil Minerals with Natural Organics and Microbes,* P.M. Huang and M. Schnitzer, eds., Soil Science Society of America, Madison, Wisconsin, 59–76.

Ortego, J.D.L., Kowalska, M., and Cocke, D.L. (1991) Interactions of montmorillonite with organic compounds—adsorptive and catalytic properties. *Chemosphere,* **22,** 769–798.

Pantani, O., Calamai, L., and Fusi, P. (1994). Influence of clay minerals on adsorption and degradation of a sulfonylurea herbicide (cinosulfuron). *Applied Clay Science,* **8,** 373–387.

Pantani, O., Pusino, A., Calamai, L., Gessa, C., and Fusi, P. (1996). Adsorption and degradation of rimsulfuron on Al-hectorite. *Journal of Agricultural and Food Chemistry,* **44,** 617–621.

Pantani, O., Calamai, L., Braschi, I., Pusino, A., Fusi, P., and Gessa, C. (1997). Preliminary FT-IR studies on interactions of triasulfuron with smectites at different charge localization. *Agrochimica,* **41,** 130–136.

Pouchert, C.J. (1975) *The Aldrich Library of Infrared Spectra, 2nd edition.* Aldrich Chemical Company, Milwaukee, Wisconsin, 1178.

Pusino, A., Gessa, C., and Kozlowski, H. (1988). Catalytic hydrolysis of quinalphos on homoionic clays. *Pesticide Science,* **24,** 1–8.

Sabadie, J. (1991). Alcoolyse et hydrolyse chimique acide du chlorsulfuron. *Weed Research,* **31,** 309–316.

Sànchez-Camazano, M. and Sànchez Martin, M.J. (1983) Montmorillonite-catalyzed hydrolysis of phosmet. *Soil Science,* **136,** 89–93.

Sposito, G. (1984). *The Surface Chemistry of Soils.* Oxford University Press, New York, 1–46.

Ukrainczyk, L. and Rashid, N. (1995). Irreversible sorption of nicosulfuron on clay minerals. *Journal of Agricultural and Food Chemistry,* **43,** 855–857.

Worthing, C.R. and Hance, R.J. (1991) *The Pesticide Manual, 9th edition.* British Crop Council, Bracknell, UK, 837.

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