

ADSORPTION AND PHOTO-REACTIVITY OF BENSULFURON-METHYL ON HOMOIONIC CLAYS

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Abstract—The adsorption and photolysis of the herbicide bensulfuron-methyl [2-(4, 6-dimethoxypyrimidin-2-carbamoylsulfamoyl)-*o*-toluic acid methyl ester] on homoionic Na⁺-, Ca²⁺- and Fe³⁺-montmorillonite and kaolinite clays were studied. The Freundlich adsorption coefficient, K_f , measured from isotherms on clays followed the order Na⁺ < Ca²⁺ < Fe³⁺. Montmorillonite showed a greater adsorptive capacity than kaolinite. Analysis of Fourier transform infrared spectra of bensulfuron-methyl adsorbed on clay suggested probable bonding interactions between bensulfuron-methyl and homoionic clays. The photolysis rate of herbicide adsorbed on homoionic clay surfaces was quite slow to its free state and decreased in the order Na⁺ > Ca²⁺ > Fe³⁺, indicating that adsorption may have prevented photolysis.

Key Words—Adsorption, Bensulfuron-methyl, Infrared Spectroscopy, Kaolinite, Montmorillonite, Photolysis.

INTRODUCTION

The environmental fate of pesticides depends greatly on the interactions between the pesticides and the solid surface of soil or sediments. The contribution of clay minerals to the adsorption of organic molecules in soil has been the object of several studies (Kowalska *et al.*, 1994; Laird *et al.*, 1994; Ukrainezyk and Rashid, 1995; Cox *et al.*, 1998). Of the various soil-clay constituents, montmorillonite and kaolinite are most important adsorbents of pesticides because they are common components of large groups of soils and are also possible carriers in the practical formulations of pesticides. In most cases, the adsorption of pesticides on clay has been found to relate to their degradation (Pantani *et al.*, 1994, 1996; Calamai *et al.*, 1997; Liu *et al.*, 2000).

Photochemical degradation is an important mechanism of dissipation of pesticide in soils. On dry, sunlight-exposed surfaces, photolysis may dominate other transformation pathways that are favored under conditions found in the bulk soil (Misra *et al.*, 1997). Generally, direct photolysis is assumed to be operative only on or within 0.1–0.5 mm of soil surface, and thus its potential contribution as a dissipation mechanism could be limited once a precipitation event has flushed the pesticide into the soil. However, the upward movement of the pesticides with capillary rise of the water front to the surface can occur in the field under conditions of net negative water balance (Sheppard *et al.*, 1987; Streck, 1998). Indirect photochemical processes can also be an important route for the degradation of the pesticide

because a variety of oxidants are formed on the sunlight-exposed soil surface that can potentially transform pesticides (Hebert and Miller, 1990).

Bensulfuron-methyl [2-(4,6-dimethoxypyrimidin-2-carbamoylsulfamoyl)-*o*-toluic acid methyl ester] is a highly active sulfonylurea herbicide for use on paddy rice. This herbicide is a broad-spectrum product for pre-emergence or early post-emergence control of most broad-leaved grasses and sedges in transplanted or direct-seeded paddy rice (Beyer *et al.*, 1988; Sengnil *et al.*, 1992). Investigation of the fate of bensulfuron-methyl in the environment has shown that the adsorption processes by soil are of great importance (Cavanna *et al.*, 1998). Similar to other sulfonylureas, bensulfuron-methyl is more persistent in neutral or weakly basic media than in acidic media (Nicosia *et al.*, 1991; Langeland and Laroche, 1994). Photodegradation of bensulfuron-methyl on soil surfaces has been reported and the major photolysis processes involve cleavage of the sulfonylurea bridge, scission of the SO₂NH bond, and contraction of the sulfonylurea bridge (Si *et al.*, 2004a). Considering that a large proportion of inorganic soil colloids is represented by clay minerals which display sorptive and degradative properties towards xenobiotics, an investigation on the interaction between bensulfuron-methyl and clay minerals is called for.

In this paper, we investigated the adsorption and photolysis of bensulfuron-methyl on montmorillonite and kaolinite saturated with different exchange cations. This research was aimed at evaluating the probable correlation between adsorption and photolysis, and determining whether adsorption of bensulfuron-methyl onto clay minerals may affect its photolability. Additionally, a spectroscopic study was carried out to elucidate the mechanisms acting in the retention of bensulfuron-methyl by clays.

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MATERIALS AND METHODS

Clay and chemicals

The clays used were montmorillonite (Lujiang county, Anhui Province, China) and kaolinite (Suzhou city, Jiangsu Province, China) supplied by the Institute of Soil Science of the Chinese Academy of Sciences. The surface area of the clay was $645 \text{ m}^2\text{g}^{-1}$ for montmorillonite and $18 \text{ m}^2\text{g}^{-1}$ for kaolinite, and the cation exchange capacity (CEC) values were 0.8 and $0.1 \text{ mol}_c \text{ kg}^{-1}$ for montmorillonite and kaolinite, respectively. The $<2 \mu\text{m}$ fraction was obtained by sedimentation. Na^+ -, Ca^{2+} - and Fe^{3+} -saturated clays were prepared by repetitive treatment of the clay with 0.5 mol L^{-1} NaCl , CaCl_2 and FeCl_3 solutions, respectively. The prepared clay samples were centrifuged, washed repeatedly with deionized water until Cl^- free (determined by titration with AgNO_3), and ground to a fine powder after drying at room temperature.

Technical bensulfuron-methyl (Figure 1, 96.4%) was obtained from Du Pont Inc., Wilmington, USA. Before use, bensulfuron-methyl was further purified to analytical grade by column chromatography using an ethyl acetate/*n*-hexane mixture (1:1, v/v) as an eluent. The purity was determined by high-performance liquid chromatography (HPLC) and found to be greater than 99%. Analytical-grade reagents were purchased locally and purified by distillation before use.

Batch sorption experiment

Adsorption isotherms of bensulfuron-methyl on Na^+ -, Ca^{2+} - and Fe^{3+} -saturated clays were determined at $25 \pm 1^\circ\text{C}$. Triplicate samples of 100 mg of air-dried homoionic clay were equilibrated with 10.0 mL of aqueous herbicide solution in 50 mL flasks. The initial concentration of herbicide ranging from 2.5 to $25 \mu\text{mol L}^{-1}$ was chosen on the basis of solubility. The sample flasks were shaken for 24 h to achieve equilibrium. Preliminary kinetic studies using multiple sampling intervals showed that $>95\%$ of the adsorption took place within the first 6 h. No decomposition product was detected by HPLC analysis during the 24 h equilibration. At equilibrium, the suspension was centrifuged at $30,000 \times g$ for 15 min, and an aliquot was injected into a HPLC device after filtering through a $0.2 \mu\text{m}$ syringe filter. The amount adsorbed on clay was calculated from the difference between the initial and final concentration of herbicide in solution.

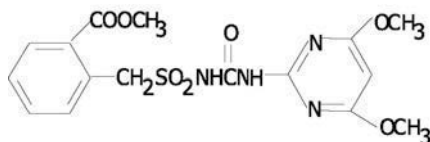


Figure 1. Chemical structure of bensulfuron-methyl.

FTIR analysis of adsorbed herbicide

Adsorption mechanisms of bensulfuron-methyl on clay were investigated using Fourier transform infrared (FTIR) analysis of thin films of herbicide-clay complexes. Self-supporting films of clay were prepared by evaporating 5 mL of homoionic clay suspension in a 5 cm (i.d.) ring on a polyethylene sheet at room temperature. The dried clay films were peeled off the plastic sheet and placed on a sample holder. A manifold controlling air humidity was used to provide moisture-saturated air (100% relative humidity) around the films. After air drying, the thin films were divided into two halves. One half was immersed in 1% herbicide- CH_2Cl_2 solution for 24 h and rinsed several times with clean CH_2Cl_2 after removal. The other half of the film was not treated with herbicide but was similarly washed with CH_2Cl_2 . The FTIR spectra of the treated and untreated films were recorded at room temperature within the range $4000\text{--}400 \text{ cm}^{-1}$ using a Bruker VECTOR-22 infrared spectrophotometer (Bruker Optics Inc., Germany). Differential spectra of adsorbed bensulfuron-methyl were obtained by subtracting the spectra of the herbicide-treated film from that of the herbicide-free film. The spectrum of the pure bensulfuron-methyl was obtained from a KBr disk containing 1 mg of the herbicide. All FTIR spectra of the pure and adsorbed bensulfuron-methyl are reported between 2000 and 1200 cm^{-1} because this region is the most appropriate to provide evidence for the adsorption mechanisms.

Photolysis experiment

The clay containing bensulfuron-methyl was prepared by dropwise addition of aliquots of an aqueous solution of bensulfuron-methyl to the powdered clay. After centrifugation, the flocculated clay was freeze dried and ground to $<50 \mu\text{m}$. The final load of bensulfuron-methyl was $20 \mu\text{mol kg}^{-1}$ clay. 0.5 g of powdered clay was taken and spread homogeneously on the bottom of Petri dishes (5 cm in diameter). To examine the free herbicide, bensulfuron-methyl dissolved in methanol was applied to the Petri dishes and the solvent subsequently evaporated. The samples were exposed to a Xe lamp (500 W) using a Rayonet RPP photochemical reactor (The Southern New England Ultraviolet, CT, USA). The distance between the samples and the light source was adjusted to provide the same light intensity of $\sim 250 \text{ W m}^{-2}$. The temperature at the clay surface was maintained at $25 \pm 1^\circ\text{C}$ by a continuous flow of cooled water below the Petri dishes. The non-irradiated samples were shielded from light by covering with aluminum foil. Samples were taken at 0, 8, 16, 24, 32, 40, 48 and 72 h. At each sampling point, three dishes were removed. The clay was scraped from the Petri dishes and extracted thoroughly with methanol (10 mL), followed by centrifugation at $30,000 \times g$ for 20 min. The supernatant liquid was concentrated and analyzed by HPLC.

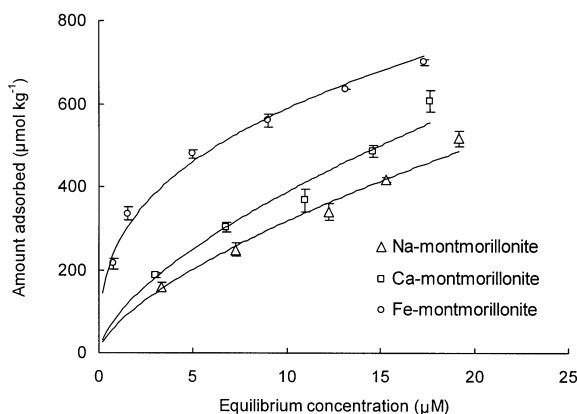


Figure 2. Adsorption isotherms of bensulfuron-methyl on Na^+ , Ca^{2+} - and Fe^{3+} -saturated montmorillonite.

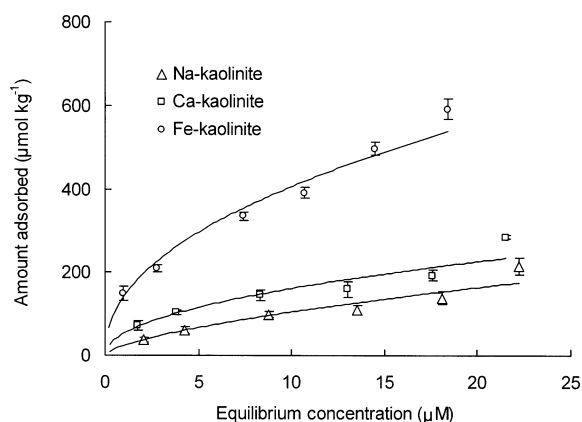


Figure 3. Adsorption isotherms of bensulfuron-methyl on Na^+ , Ca^{2+} - and Fe^{3+} -saturated kaolinite.

The HPLC analysis for bensulfuron-methyl concentration was conducted using an Agilent 1100 HPLC instrument (Agilent Technologies Co. Ltd., USA), equipped with an UV variable wavelength detector set at 254 nm. The column used was a 5 μm Hypersil ODS reversed phase column (C_{18} , 4.6 mm i.d. \times 200 mm; Agilent Technologies Co. Ltd., USA); the mobile phase was methanol + water (85+15 by volume, pH =3.0) at a flow rate of 1.0 mL min^{-1} ; volume injected was 20 μL .

Data analysis

Adsorption data were fitted by the logarithmic form of the Freundlich equation, $\log C_s = \log K_f + 1/n \log C_e$, where C_s ($\mu\text{mol kg}^{-1}$) is the amount of herbicide adsorbed by clay, C_e (μM) is the equilibrium concentration in solution, and $\log K_f$ and $1/n$ are empirical constants representing the intercept and the slope of the isotherm, respectively.

The irradiation studies were subjected to analysis of variance, and the main effects and interactions were tested for significance. Data from the recovery rate of bensulfuron-methyl were analyzed by calculation of the means and standard deviations. *T*-test was also employed to detect differences between means.

RESULTS AND DISCUSSION

Adsorption

Figures 2 and 3 show the adsorption isotherms of bensulfuron-methyl on Na^+ , Ca^{2+} - and Fe^{3+} -montmorillonite and kaolinite clays, respectively. The isotherms were all adequately described by the Freundlich equation, and the correlation coefficient, r , was >0.97 . The values of K_f and $1/n$ are given in Table 1. The estimated Freundlich adsorption coefficient, K_f , was significantly greater for Fe^{3+} -clays than for Na^+ - and Ca^{2+} -clays. The overall order of adsorption follows $\text{Na}^+ < \text{Ca}^{2+} < \text{Fe}^{3+}$. This order coincided with the order of increasing acidity in both the interlayer and the external solution of these homoionic clays. These results suggest

that the different affinity of the homoionic clays for bensulfuron-methyl is related to the polarizing power of the exchangeable cation. The lower adsorption on clays saturated with Na and Ca ions reflects the lower polarizing power of these ions, compared with Fe. Similar results were obtained by Pusino *et al.* for the adsorption of dimepiperate and triasulfuron on homoionic clays (Pusino *et al.*, 1993, 2000).

For a given saturating cation, montmorillonite has a greater adsorptive capacity than kaolinite. The greater adsorption of bensulfuron-methyl by montmorillonite than by kaolinite is related to montmorillonite's larger surface area and CEC.

To gain information on possible bonds formed during adsorption of bensulfuron-methyl, FTIR spectra of the herbicide adsorbed on clay were obtained. The differential spectra of adsorption on Na^+ , Ca^{2+} - and Fe^{3+} -montmorillonite and kaolinite clays are shown in Figures 4 and 5, respectively. The spectra indicate that the herbicide undergoes significant changes upon interaction with clay surfaces. After adsorption, the stretching frequency of the C=O bond on the benzoate ester group was shifted from 1716 cm^{-1} in the free form to 1732 cm^{-1} in the adsorbed form, while stretching frequency of the C=O bond on the sulfonylurea bridge was changed from 1698 cm^{-1} to 1703 cm^{-1} . The shift of the C=O stretch towards higher frequencies suggests an increase in the double-bond character of the C=O group,

Table 1. Freundlich constants (K_f , $1/n$ and correlation coefficients) for the adsorption of bensulfuron-methyl on homoionic clays.

Sorbent	K_f	$1/n$	r
Na-montmorillonite	70.1	0.66	0.994
Ca-montmorillonite	90.6	0.63	0.987
Fe-montmorillonite	261.2	0.35	0.989
Na-kaolinite	23.6	0.65	0.979
Ca-kaolinite	53.1	0.48	0.971
Fe-kaolinite	141.0	0.46	0.989

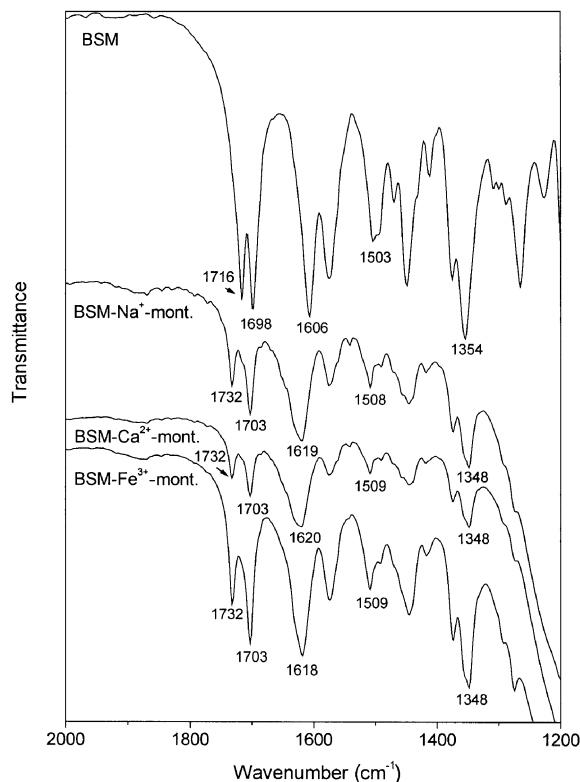


Figure 4. IR spectra of bensulfuron-methyl on montmorillonite saturated with different cations: bensulfuron-methyl (BSM); Na⁺-mont.; Ca²⁺-mont.; Fe³⁺-mont. The spectra were recorded as differential spectra of herbicide-treated and untreated samples.

probably due to the electron-withdrawing effect from a protonated neighboring group, or to the loss of intermolecular hydrogen bonding. Similar shifts were observed for the adsorption of some herbicides on clay minerals (Pantani *et al.*, 1997; Pusino *et al.*, 1995, 2000, 2003). Pusino *et al.* (2000) investigated the adsorption of sulfonylurea herbicide triasulfuron on homoionic montmorillonite and proposed that the upward displacements of the carbonyl group were due to the protonation of aromatic heterocyclic nitrogen.

A further feature of the spectrum is the stretching frequency of the pyrimidine nitrogen (the $\text{C}=\text{N}$ bond) which moved from 1606 to 1620 cm^{-1} , and the bending vibration frequency of the NH bond (mainly secondary amide group on the sulfonylurea bridge) which shifted from 1503 to 1508 cm^{-1} . A change at 1606 cm^{-1} may be attributed to the formation of a coordination bond between the $\text{C}=\text{N}$ group in pyrimidine and the exchangeable cation of clay. The nitrogen of the pyrimidine ring was protonated and underwent co-ordination through direct bonds or, more likely, via hydrogen bonding involving residual water molecules linked to the cations. The protonation of pyrimidine ring nitrogen was confirmed by the shift of the NH-stretching bond (1503 cm^{-1}) towards a higher frequency. Results of

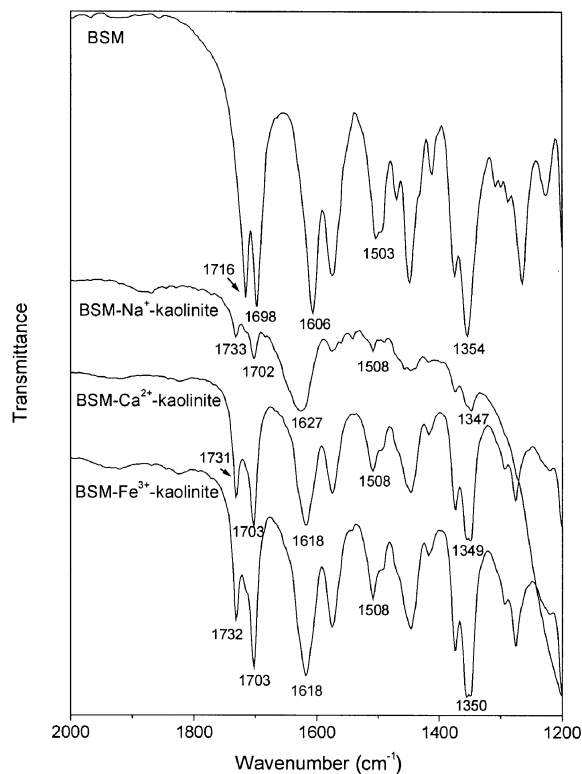


Figure 5. IR spectra of bensulfuron-methyl on kaolinite saturated with different cations: bensulfuron-methyl (BSM); Na⁺-kaolinite; Ca²⁺-kaolinite; Fe³⁺-kaolinite. The spectra were recorded as differential spectra of herbicide-treated and untreated samples.

this type have been reported for several herbicides adsorbed on clays (Pantani *et al.*, 1996; Pusino *et al.*, 1995, 1996, 2000, 2003).

The shift of the SO_2 group stretching band was also observed for the adsorption of some sulfonylurea herbicides on clays. In our case, the asymmetric stretching frequency of the SO_2 groups was shifted from 1354 to 1348 cm^{-1} due to adsorption. Ukrainczyk and Ajwa (1996) reported that primisulfuron adsorption on mineral surfaces involves the two difluoromethoxy substituents on the pyrimidine ring, and the SO_2 group on the sulfonylurea bridge whose high negative partial charges (δ^-) on electronegative F and O atoms may be capable of strong dipole-dipole interactions, particularly hydrogen bonding with clay surfaces.

Photolysis

Adsorption to clay surfaces had a considerable effect on the lability of a herbicide to radiation. Previous results obtained in a photochemical experiment aimed at evaluating different clays as potential photoprotectors of bensulfuron-methyl showed that bensulfuron-methyl could be fast degraded in its free state, whereas the photostabilization of bensulfuron-methyl was achieved when it was adsorbed on clays (Si *et al.*, 2004b). This

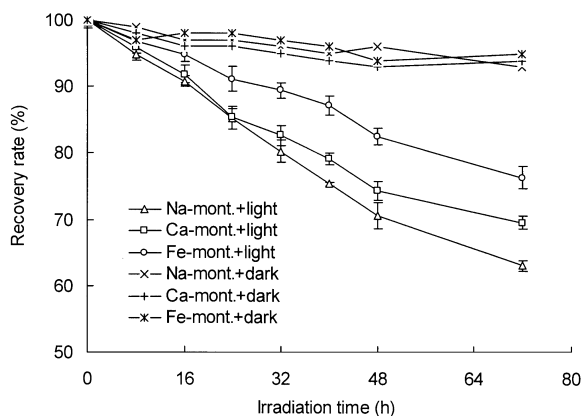


Figure 6. Photolysis of bensulfuron-methyl on Na^+ , Ca^{2+} - and Fe^{3+} -saturated montmorillonite. The error bars denote the standard error.

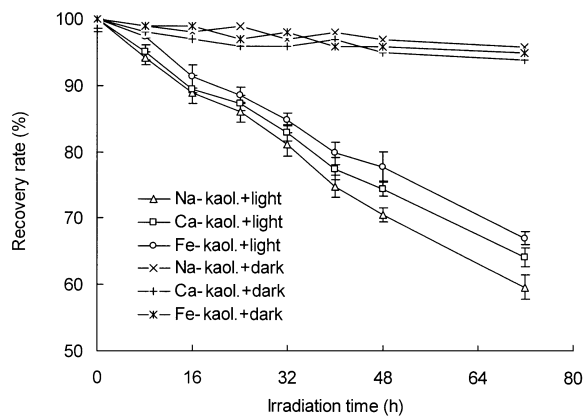


Figure 7. Photolysis of bensulfuron-methyl on Na^+ , Ca^{2+} - and Fe^{3+} -saturated kaolinite. The error bars denote the standard error.

study consistently suggested that adsorption of clays could slow down the photoinactivation of herbicide molecules. The results of photodegradation of bensulfuron-methyl adsorbed on Na^+ , Ca^{2+} - and Fe^{3+} -montmorillonite and kaolinite clays are shown in Figures 6 and 7.

In dark control, bensulfuron-methyl is stable on air-dried clay surfaces. Non-irradiated samples of bensulfuron-methyl adsorbed on montmorillonite or kaolinite gave 95% recovery. After 72 h of irradiation, ~37%, 30% and 25% of bensulfuron-methyl was lost to photolysis on Na^+ , Ca^{2+} - and Fe^{3+} -montmorillonite, respectively; and 40%, 36%, and 33% was lost to photolysis on Na^+ , Ca^{2+} - and Fe^{3+} -kaolinite, respectively. Photodegradation of bensulfuron-methyl on Na^+ , Ca^{2+} - and Fe^{3+} -clay followed pseudo first-order kinetics, and the estimated half-lives of dissipation were 103, 131 and 182 h for Na^+ , Ca^{2+} - and Fe^{3+} -montmorillonite, respectively; and 96, 114 and 124 h for Na^+ , Ca^{2+} - and Fe^{3+} -kaolinite, respectively (Table 2). Photodegradation of bensulfuron-methyl was significantly faster on Na^+ - and Ca^{2+} -clay surfaces than on Fe^{3+} -clay surfaces (Figures 6 and 7). The overall order of herbicide photolysis rate on clay surfaces followed $\text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{3+}$, which reversed with the order of herbicide adsorption on homoionic clays.

Table 2. Rate constant (K) and half-life ($T_{1/2}$) values for photolysis of bensulfuron-methyl on homoionic clays.

	K	$T_{1/2}$ (h)	n^a	r
Na-montmorillonite	0.0067	103	3	0.996
Ca-montmorillonite	0.0053	131	3	0.987
Fe-montmorillonite	0.0038	182	3	0.996
Na-kaolinite	0.0072	96	3	0.998
Ca-kaolinite	0.0061	114	3	0.998
Fe-kaolinite	0.0056	124	3	0.998

^a Number of replicates

From the present results it would appear that intermolecular interactions play a fundamental role in the photo-stabilization mechanisms of bensulfuron-methyl on clay surfaces. Montmorillonite is a 2:1 layer-type structure, where an octahedral aluminate sheet is sandwiched between two tetrahedral silicate sheets; and kaolinite is a 1:1 layer-type structure, where an octahedral aluminate sheet is joined to a tetrahedral silicate sheet. It could be speculated that bensulfuron-methyl was arranged within the interlayer as monolayer bensulfuron-methyl molecules oriented in a perpendicular direction with water molecules between the bensulfuron-methyl and the clay layer surface. As bensulfuron-methyl molecules adsorbed on the clay surface are oriented, their intermolecular distances and orientations might fulfil the requirements for efficient energy dissipation mechanisms such as charge transfer and radiationless energy transfer. In this configuration the photoexcited bensulfuron-methyl molecules could be deactivated before the photodecomposition reaction began. The possibility of energy or charge transfer quenching has recently been suggested as an explanation for the photo-stabilization of some pesticides on the clay surfaces (Margulies *et al.*, 1992, 1993; Rozen and Margulies, 1991; El-Nahhal *et al.*, 2001).

The greater degree of photo-stabilization was obtained with Fe^{3+} -clay as compared with Na^+ - and Ca^{2+} -clays, since Fe acts as a more efficient energy (or charge) acceptor. Banerjee and Dureja (1995) found a slightly lower rate of photo-degradation for quinalphos adsorbed on palygorskite than on kaolinite, in accord with the relatively small structural Fe content in kaolinite.

It is significant that the rate of photolysis was faster when the herbicide was adsorbed onto kaolinite than when adsorbed onto montmorillonite. While this may have been due to its greater adsorption by montmorillonite, it is also possible that it is due to a lower level of radical production in the case of montmorillonite. Katagi

(1990) observed the lower production of hydrogen peroxide from the irradiation of montmorillonite compared with that from kaolinite.

Considering that bensulfuron-methyl can reach the interlayers of montmorillonite whereas kaolinite has only external active surfaces for adsorption, it is therefore likely that the faster reaction onto kaolinite is due to photodegradation on the clay surfaces and the slower reaction onto montmorillonite is due to a reaction in the interlayer spaces, largely independent of irradiation.

CONCLUSIONS

The adsorption of bensulfuron-methyl on homoionic clays was shown to follow the order $\text{Na}^+ < \text{Ca}^{2+} < \text{Fe}^{3+}$ and the different adsorption capacity is related to the polarizing power of the clay cation. The degree of adsorption of bensulfuron-methyl on montmorillonite is greater than that on kaolinite. From shifts in characteristic IR absorption bands of functional groups after sorption, a number of bonding interactions between bensulfuron-methyl and homoionic clays were apparent. The primary interactions were proposed to be the protonation of herbicide molecules and the formation of hydrogen bonds and coordination bonds between bensulfuron-methyl and homoionic clays.

The photolysis of bensulfuron-methyl on homoionic clay surfaces was slow to its free state due to the relative orientation of herbicide molecules. The efficient energy or charge transfer can take place between adsorbed herbicide molecules and clay cations. The overall order of herbicide photolysis rate on clay surfaces is the reverse of that of herbicide adsorption on homoionic clays. The results indicate that the photolysis rate was closely dependent on the adsorption.

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REFERENCES

- Banerjee, K. and Dureja, P. (1995) Photostabilization of quinalphos by crystal violet on the surface of kaolinite and palygorskite. *Pesticide Science*, **43**, 333–337.
- Beyer, E.M., Jr., Duffy, M.J., Hay, J.V. and Schlueter, D.D. (1988) Sulfonyleureas. Pp. 117–190 in: *Herbicides: Chemistry Degradation and Mode of Action*, Vol. 3 (P.C. Kearney and D.D. Kaufman, editors). Dekker, New York.
- Calamai, L., Pantani, O., Pusino, A., Gessa, C. and Fusi, P. (1997) Interaction of rimsulfuron with smectites. *Clays and Clay Minerals*, **45**, 23–27.
- Cavanna, S., Garatti, E., Rastelli, E. and Molinari, G.P. (1998) Adsorption and desorption of bensulfuron-methyl on Italian paddy field soils. *Chemosphere*, **37**, 1547–1555.
- Cox, L., Koskinen, W.C., Celis, R., Yen, P.Y., Hermosin, M.C. and Cornejo, J. (1998) Sorption of imidacloprid on soil clay mineral and organic components. *Soil Science Society of America Journal*, **62**, 911–915.
- El-Nahhal, Y., Undabeytia, T., Polubesova, T., Mishael, Y.G., Nir, S. and Rubin, B. (2001) Organo-clay formulations of pesticides: reduced leaching and photodegradation. *Applied Clay Science*, **18**, 309–326.
- Hebert, V.R. and Miller, G.C. (1990) Depth dependence of direct and indirect photolysis on soil surfaces. *Journal of Agricultural and Food Chemistry*, **38**, 913–918.
- Katagi, T. (1990) Photoinduced oxidation of the organophosphorus fungicide tolclofos-methyl on clay minerals. *Journal of Agricultural and Food Chemistry*, **38**, 1595–1600.
- Kowalska, M., Guler, H. and Cocke, D.L. (1994) Interactions of clay minerals with organic pollutants. *The Science of the Total Environment*, **141**, 223–240.
- Laird, D.A., Yen, P.Y., Koskinen, W.C., Steinheimer, T.R. and Dowdy, R.H. (1994) Sorption of atrazine on soil clay components. *Environmental Science and Technology*, **28**, 1054–1061.
- Langeland, K.A. and Laroche, F.B. (1994) Persistence of bensulfuron-methyl and control of Hydrilla in shallow ponds. *Journal of Aquatic and Plant Management*, **32**, 12–14.
- Liu, W.P., Gan, J.Y., Papiernik, S.K. and Yates, S.R. (2000) Sorption and catalytic hydrolysis of diethyl-ethyl on homoionic clays. *Journal of Agricultural and Food Chemistry*, **48**, 1935–1940.
- Margulies, L., Stern, T., Rubin, B. and Ruzo, L.O. (1992) Photostabilization of trifluralin adsorbed on a clay matrix. *Journal of Agricultural and Food Chemistry*, **40**, 152–155.
- Margulies, L., Rozen, H., Stern, T., Rytwo, G., Rubin, B., Ruzo, L.O., Nir, S. and Cohen, E. (1993) Photostabilization of pesticides by clays and chromophores. *Archives of Insect Biochemistry and Physiology*, **22**, 467–486.
- Misra, B., Graebing, P.W. and Chib, J.S. (1997) Photodegradation of chloramben on a soil surface: a laboratory-controlled study. *Journal of Agricultural and Food Chemistry*, **45**, 1464–1467.
- Nicosia, S., Collison, C. and Lee, P. (1991) Bensulfuron-methyl dissipation in California rice fields and residue levels in agricultural drains and the Sacramento River. *Bulletin of Environmental Contamination and Toxicology*, **47**, 131–137.
- Pantani, O., Calamai, L. and Fusi, P. (1994) Influence of clay minerals on adsorption and degradation of a sulfonyleurea 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., Dousset, S., Schiavon, M. and Fusi, P. (1997) Adsorption of isoproturon on homoionic clays. *Chemosphere*, **35**, 2619–2626.
- Pusino, A., Liu, W. and Gessa, C. (1993) Dimepiperate adsorption and hydrolysis on Al^{3+} , Fe^{3+} , Ca^{2+} , and Na^+ -montmorillonite. *Clays and Clay Minerals*, **41**, 335–340.
- Pusino, A., Gelsomino, A. and Gessa, C. (1995) Adsorption mechanisms of Imazamethabenz-methyl on homoionic montmorillonite. *Clays and Clay Minerals*, **43**, 346–352.
- Pusino, A., Petretto, S. and Gessa, C. (1996) Montmorillonite surface-catalyzed hydrolysis of fenoxaprop-ethyl. *Journal of Agricultural and Food Chemistry*, **44**, 1150–1154.
- Pusino, A., Braschi, I. and Gessa, C. (2000) Adsorption and degradation of triasulfuron on homoionic montmorillonites. *Clays and Clay Minerals*, **48**, 19–25.
- Pusino, A., Gelsomino, A., Fiori, M.G. and Gessa, C. (2003) Adsorption of two quinolinecarboxylic acid herbicides on homoionic montmorillonites. *Clays and Clay Minerals*, **51**, 143–149.
- Rozen, H. and Margulies, L. (1991) Photostabilization of

- tetrahydro-2-(nitromethylene)-2H-1, 3-thiazine adsorbed on clays. *Journal of Agricultural and Food Chemistry*, **39**, 1320–1325.
- Sengnil, K., Usur, K. and Ishizuka, K. (1992) Recovery from growth inhibition and acetolactate synthase activity in rice suspension-cultured cells treated with bensulfuron-methyl. *Weed Research of Japan*, **37**, 28–34.
- Sheppard, M.I., Thibault, D.H. and Mitchell, J.H. (1987) Element leaching and capillary rise in sandy soil cores. *Journal of Environmental Quality*, **16**, 273–284.
- Si, Y.B., Yue, Y.D., Chen, H.M. and Zhou, D.M. (2004a) Photodegradation of bensulfuron-methyl on soil surface. *Pest Management Science*, **60**, 286–290.
- Si, Y.B., Zhou, J., Chen, H.M. and Zhou, D.M. (2004b) Photostabilization of the herbicide bensulfuron-methyl by using organoclays. *Chemosphere*, **54**, 943–950.
- Strek, H.J. (1998) Fate of chlorsulfuron in the environment. 2. Field evaluations. *Pesticide Science*, **53**, 52–70.
- Ukrainzyk, L. and Rashid, N. (1995) Irreversible sorption of nicosulfuron on clay minerals. *Journal of Agricultural and Food Chemistry*, **43**, 855–857.
- Ukrainzyk, L. and Ajwa, H.A. (1996) Primisulfuron sorption on minerals and soils. *Soil Science Society of America Journal*, **60**, 460–467.

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