INTERACTION OF DICLOFOP AND DICLOFOP-METHYL WITH Al^{3+}-, Fe^{3+}-, and Cu^{2+}-SATURATED MONTMORILLONITE

A. Pusino,[1] G. Micera,[2] C. Gessa,[1] AND S. Petretto[1]

[1] Istituto di Chimica Agraria, Università di Sassari
Via E. de Nicola 10, 07100 Sassari, Italy

[2] Dipartimento di Chimica, Università di Sassari
Via Vienna 2, 07100 Sassari, Italy

Abstract—The adsorption from chloroform solution of the herbicide diclofop, (RS)-2-(4-(2,4-dichloro-phenoxy)phenoxy)propionic acid, and its methyl ester diclofop-methyl on Cu^{2+}-, Al^{3+}-, and Fe^{3+}-exchanged bentonite samples was investigated. For comparison, the complexes formed by diclofop were synthesized and studied. Diclofop adsorbed on the clays and formed carboxylate bonds to the interlayer ions. Diclofop-methyl also adsorbed, but its interaction involved the formation of hydrogen bonds with water molecules in the interlayer. Traces of diclofop were observed in both the solution and the clays after adsorption of diclofop-methyl, indicating that some hydrolysis of the ester to the corresponding acid occurred. Thus, pesticides forming neutral complexes with interlayer cations in montmorillonite in soils may be extractable by solvents and therefore released into the environment.

Key Words—Adsorption, Bentonite, Diclofop, Diclofop-methyl, Interlayer cations, Interlayer complexes, Montmorillonite, Pesticide.

INTRODUCTION

Because of the increasing use of herbicides in agriculture, the mechanisms of interaction of these compounds and soil are important. Insofar as the adsorption of organic molecules is concerned, clay minerals are among the most active soil components (Mortland, 1970, 1975; Crosby, 1976). The adsorption of pesticides onto clay minerals is generally disfavored because of the competition with water. Pesticides having complexing properties, however, may interact with the saturating metal ions in the interlayer. The extent of this interaction may strongly affect other processes that contribute to the inactivation of pesticides in soil.

Diclofop-methyl is commonly applied in post-emergence treatments to control wild oats and other annual grasses in a variety of crops. In soil, the hydrolysis of the methyl ester to the corresponding acid, diclofop, the structural formula of which is shown below, is rapid and complete within 9 days after application (Smith *et al.,* 1986).
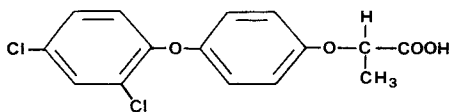
The acid is strongly bound to soil (Karanth *et al.,* 1984), from which it can only be liberated by treatment with hot alkali (Smith, 1977). No attempt has been made to understand the mechanisms through which diclofop and its ester are retained by soil components. The present study was undertaken to gain information about the interaction of diclofop-methyl or diclofop and Fe^{3+}-, Al^{3+}-, and Cu^{2+}-exchanged bentonite.

EXPERIMENTAL

Materials

Montmorillonite 25 (bentonite) from Upton, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, New York, was used in this study. The <2-μm size fraction was obtained by sedimentation. The cation-exchange capacity (CEC) was 90.2 meq/100 g. The Fe^{3+}-, Al^{3+}-, and Cu^{2+}-exchanged samples were prepared by exposing the bentonite to 1 N solutions of the corresponding metal chlorides. The samples were centrifuged, washed repeatedly with deionized water until Cl^--free, and dried at room temperature. Diclofop-methyl ($C_{16}H_{14}Cl_2O_4$) was supplied by Roussel-Hoechst Agrovet S.p.A. (Milan, Italy) as a colorless crystalline solid (m.p. 41°–42°C). The solubility in water was 3 mg/liter and much higher in organic solvents. Diclofop ($C_{15}H_{12}Cl_2O_4$) was prepared by alkaline hydrolysis of diclofop-methyl according to the method described by Smith (1976). The acid was recrystallized from ethanol as white crystals (m.p. 108°–109°C). The compound was soluble in organic solvents, but only sparingly in water.

The Fe^{3+}, Al^{3+}, and Cu^{2+} complexes of diclofop were prepared by mixing equimolar aqueous solutions of the organic acid (1.5×10^{-3} mole) in about 5 ml (pH 6.2) and $Fe(NO_3)_3 \cdot 9H_2O$, $AlCl_3 \cdot 6H_2O$, or $CuCl_2 \cdot 2H_2O$ (1.5×10^{-3} mole) in about 2 ml. The precipitates were filtered and washed with ethanol (99.5%). After recrystallization from absolute ethanol + chloroform (2:1 v:v), the compounds were air-dried.

Adsorption of pesticide

The adsorption of the pesticide onto the clay surfaces was carried out by immersing air-dried self-supporting

Table 1. Analytical data and proposed stoichiometry for the complexes with diclofop acid.[1]

Complex	C (%)	H (%)	H_2O^2 (%)	Residue[3]
$Cu(C_{15}H_{11}Cl_2O_4)_2 \cdot 1.5H_2O$	50.10 (48.50)	3.50 (3.39)	4.0 (3.63)	11.0 (10.71)
$Al(C_{15}H_{11}Cl_2O_4)_2OH \cdot 2H_2O$	49.64 (49.20)	3.82 (3.71)	5.0 (4.91)	7.0 (6.96)
$Fe(C_{15}H_{11}Cl_2O_4)_3 \cdot 3H_2O$	49.66 (49.65)	3.52 (3.61)	5.0 (4.97)	7.5 (7.34)

[1] Calculated values in parentheses.
[2] Thermogravimetric determination.
[3] Binary oxides CuO, Al_2O_3, and Fe_2O_3.

bentonite films in a ~2% solution of diclofop-methyl or diclofop in $CHCl_3$. After 24 hr the films were separated from the solution and washed with $CHCl_3$ to remove excess pesticide. After air-drying, the films were examined by infrared spectroscopy (IR), and the amount of released metal (Fe^{3+}, Al^{3+}, and Cu^{2+}) was determined by analysis of the leachates using colorimetric methods (Bandemer and Schaible, 1944; Chenery, 1948; Nebesar, 1964).

High-performance liquid chromatographic analysis

High-performance liquid chromatography (HPLC) analyses were carried out using a Waters 501 liquid chromatograph equipped with a 125 × 4 mm i.d. Lichrosorb RP 18, 5-μm analytical column, a Waters detector operating at 254 nm, and a Waters 740 data module. The mobile phase (1 ml/min) was composed of acetonitrile + water + acetic acid (70 + 29 + 1, by volume). The retention times were 3.8 and 7.6 min for diclofop and diclofop-methyl, respectively.

Physical measurements

IR spectra were recorded with a Perkin-Elmer 683 spectrophotometer. The spectra for diclofop-methyl, diclofop, and the metal complexes of diclofop were obtained using KBr disks, whereas those for the pesticide-bentonite complexes were recorded as differential spectra using self-supporting films. Electron spin resonance (ESR) measurements at X-band were carried out at room temperature using a Varian E 9 spectrometer. Microanalyses (C and H) were made using a Perkin-Elmer 240 analyzer. Thermogravimetric measurements were made with a Perkin-Elmer TGS 2 apparatus at the heating rate of 5°C/min under a nitrogen flow. The pH of solutions was measured by a Radiometer PHM 84 pH-meter. XRD data were obtained on a Philips PW 1730 instrument equipped with an Olivetti M-20 computer, using CoKα radiation.

RESULTS AND DISCUSSION

Metal complexes of diclofop

The elemental analyses of the Cu and Al complexes of diclofop (Table 1) are consistent with a ligand-to-metal molar ratio of 2:1. The chemical composition of the iron complexes indicates the presence of three deprotonated ligands per metal ion. The ESR spectrum

of the copper complex (g‖ = 2.39, g⊥ = 2.07, and zero-field splitting D = 0.36 cm⁻¹, see Figure 1) is typical of dinuclear complexes in which two metal ions are bridged by four carboxylate groups, as in the well-known compound copper(II) acetate (Brown and Chidambaram, 1973). A similar structure was previously found for the Cu^{2+} complex of fluazifop (Micera et al., 1988). Carboxylate coordination was also found for the Al^{3+} and Fe^{3+} complexes, inasmuch as the 1745-cm⁻¹ absorption band for the undissociated carboxyl group of the free ligand was absent in the IR spectra of all complexes (Figure 2 and Table 2). In its place, two new bands were observed near 1620–1630 cm⁻¹ and 1425–1443 cm⁻¹ and assigned to the ν_{as}(COO) (asymmetric) and ν_{sym}(COO) (symmetric) modes, respectively, of metal-bound carboxylate groups.

Adsorption of diclofop on the bentonite

Only very weak absorptions at 1745 cm⁻¹, assignable to un-ionized carboxyl group, were observed in the IR spectra of Fe^{3+}-, Al^{3+}-, and Cu^{2+}-bentonite samples treated with diclofop (Figure 3 and Table 2). Bands attributable to the ν_{as}(COO) and ν_{sym}(COO) modes of carboxylate groups appeared in the ranges 1603–1572 cm⁻¹ and 1435–1385 cm⁻¹, the former being less intense than the latter. The frequencies of the carboxylate bands, in addition to depending on the metal ion, were different from those of the sodium salt of diclofop (Table 2). Thus, the interaction between diclofop and the bentonite involved the coordination of the pesticide to the exchange cation through the carboxylate group. Note that the IR bands of the carboxylate group in the clay complexes were different from those of the pure com-

Table 2. Infrared absorptions (cm⁻¹) of carboxylate groups for metal and metal-clay complexes of diclofop.[1]

Metal	Metal complexes		Metal-clay complexes	
	ν_{as}	ν_s	ν_{as}	ν_s
Al	1620s	1443w	1603s	1385m
Fe	1625s	1435m	1572s	1432m
Cu	1630s	1425m	1590s	1435w

s = strong; m = medium; w = weak.
[1] ν_{as} and ν_s = carboxylate antisymmetric and symmetric stretches, respectively. Absorptions for the Na-salt = 1615 and 1420 cm⁻¹.
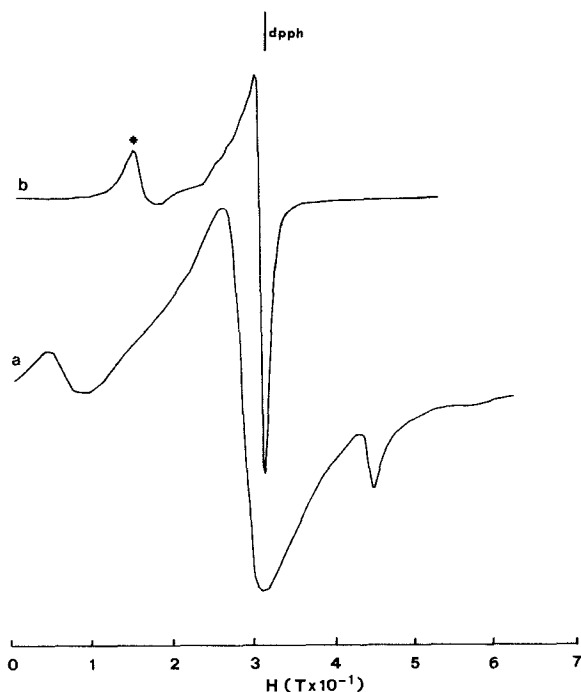
Figure 1. X-band electron spin resonance spectra recorded at room temperature on (a) Cu^{2+} complex of diclofop and (b) Cu^{2+}-bentonite treated with diclofop. Resonance marked by asterisk is that of structural Fe^{3+}. Units for the magnetic field (x-axis) are Tesla $\times$ 10^{-1} (1 Tesla = 10^4 Gauss).

Figure 2. Infrared spectra (KBr disks) of complexes of diclofop with (a) Al^{3+}, (b) Fe^{3+}, and (c) Cu^{2+}.

plexes in the solid state. Although variations of these band-positions were expected due to the presence of water molecules in the interlayer, the observed shifts were rather high, suggesting that they are diagnostic of a coordinating mode of the carboxylates on the clay different from that of the pure complexes in the solid state. Direct evidence for this hypothesis was obtained for Cu^{2+}. Thus, the ESR spectra (Figure 1) indicated that, after adsorption of the pesticide, the Cu^{2+} ions (at least in part) formed monomeric complexes on the clay. No spectral feature was detected to substantiate strong magnetic exchange between metal ions, like that of the copper(II) acetate and related complexes. The spectral parameters ($g\| = 2.330$ and $A\| = 160 \times 10^{-4}$ cm^{-1}) indicate coordination through carboxylate groups. Thus, all the evidence points to the conclusion that in the interlayer, each ligand molecule was bound to a single copper ion through its carboxylate group.

During the equilibration between the clays and diclofop, some of the interlayer cations were released into the $CHCl_3$ solution. Their relative amounts were 24.5, 18.7, and 5.8% of CEC for the Cu^{2+}-, Fe^{3+}-, and Al^{3+}-clays, respectively, treated with an amount of diclofop equivalent to the CEC. The only explanation of this finding was that complexation following the adsorption of pesticide resulted in formation of neutral species that were extractable by $CHCl_3$.
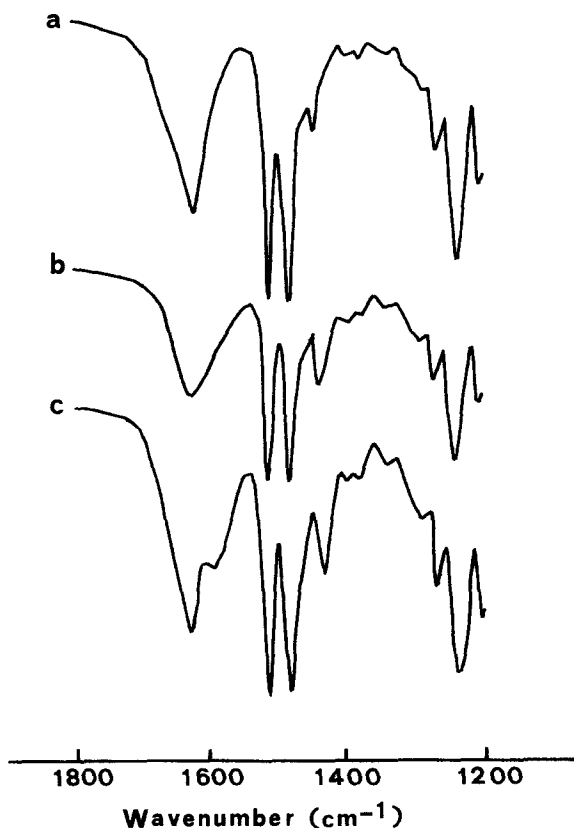
Adsorption of diclofop-methyl on clays

The IR spectra of the air-dried complexes of the Fe^{3+}-, Al^{3+}-, and Cu^{2+}-bentonite samples with diclofop-methyl (Figure 4) were very similar. A common feature was the shift of the 1770-cm^{-1} absorption band of pure diclofop-methyl to 1730 cm^{-1}, demonstrating the perturbation of the CO estereal group. This shift was probably the result of hydrogen bonds between the carbonyl oxygen atom and water molecules surrounding the interlayer cations. A similar behavior has been observed for fluazifop-butyl adsorbed on clays (Gessa *et al.*, 1987). An additional feature was the occurrence of weak IR bands due to ionized carboxyl groups, similar to those observed for absorbed diclofop acid. These observations, of course, indicated that diclofop-methyl partly hydrolyzed on the clay to generate the acid. Traces of diclofop acid were also detected directly in the equilibrium solution by HPLC. The ESR spectra of Cu^{2+}-clay confirmed the absence of direct interaction between metal ions and adsorbed ester, because they showed the signals of the immobilized aqua-ions. These ESR signals were similar to those observed on Cu^{2+}-clays after dehydration at 120°C or after sorption of
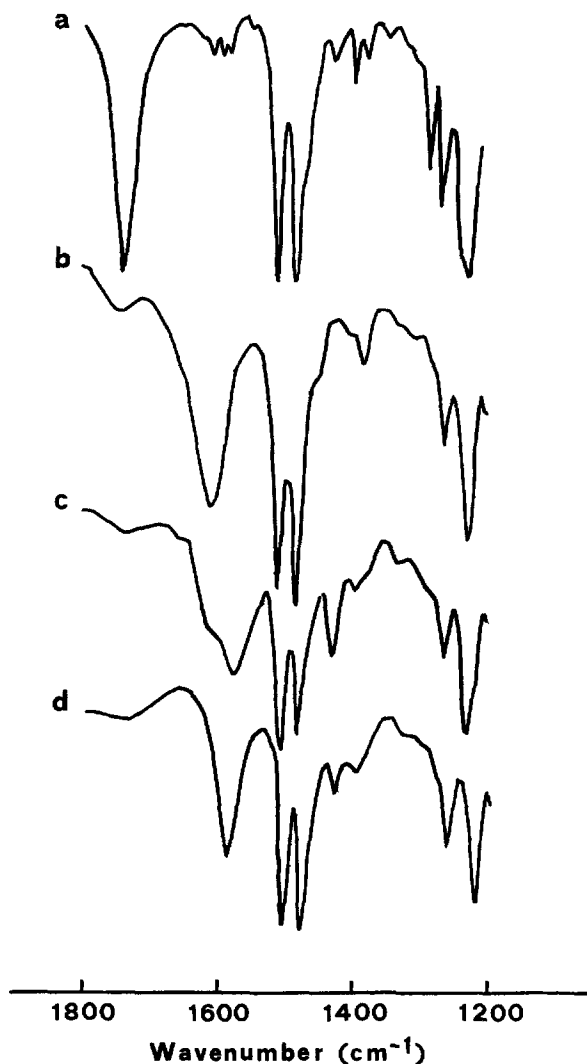
Figure 3. Infrared spectra of (a) diclofop (KBr disk) and homoionic clays treated with diclofop, (b) Al^{3+}, (c) Fe^{3+}, and (d) Cu^{2+}. Spectra of clays were recorded as difference spectra with respect to those of untreated samples.

Figure 4. Infrared spectra of (a) diclofop-methyl (KBr disk) and homoionic clays treated with diclofop-methyl, (b) Al^{3+}, (c) Fe^{3+}, and Cu^{2+}. Spectra of clays were recorded as difference spectra with respect to those of untreated samples.

hydrophobic, non-coordinating compounds, e.g., the butyl ester of fluazifop (Micera *et al.*, 1988).

XRD results

The XRD d(001) values (Table 3) indicated that both the organic acid and ester occupied the interlamellar space of the phyllosilicate, forming monolayers. In particular, d(001) increased for the Cu^{2+}-clay kept at room temperature, but decreased under the same conditions for the Al^{3+}- and Fe^{3+}-clays, probably because of hydrophobic effects produced by the intercalation of the organic molecule. Moreover, the collapse of the interlayer after heating under vacuum was lower than for the corresponding untreated samples. The larger in-
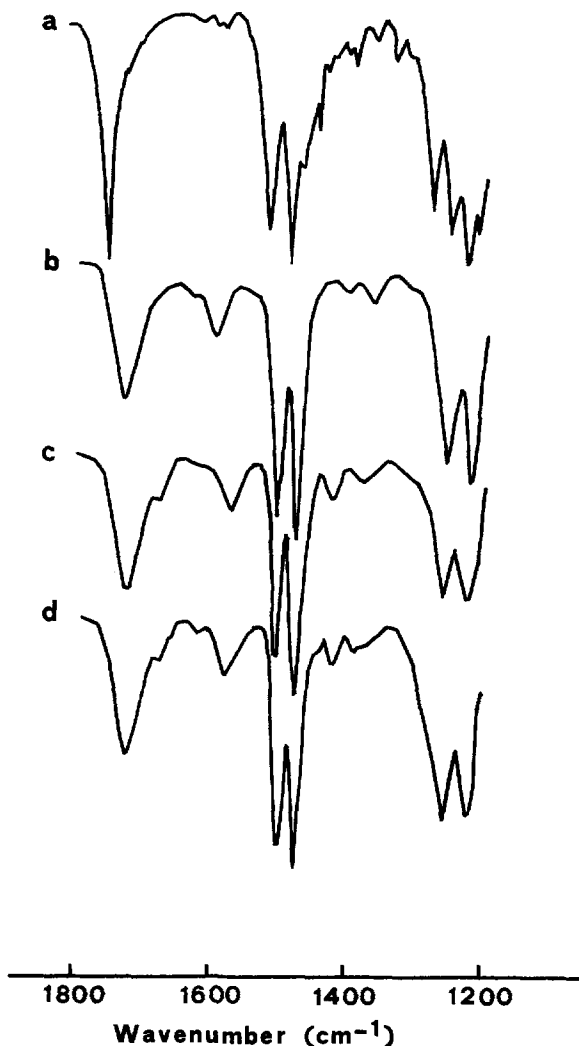
terlayer distance measured for Al^{3+}-clay treated with diclofop may have been due to the lower extent of metal desorption observed for this clay.

SUMMARY AND CONCLUSIONS

Diclofop and diclofop-methyl interacted differently with the Fe^{3+}-, Al^{3+}-, and Cu^{2+}-exchanged bentonite samples. Most of the free acid molecules interacted with the interlayer metal ions and coordinated to at least some of them by forming carboxylate complexes. The methyl ester of diclofop was also adsorbed, but it was engaged in hydrogen bonding with the water molecules rather than being directly coordinated to the metal ions. Some of diclofop-methyl may have hydrolyzed to the free acid, which then coordinated to the

Table 3. d(001) values (Å) for homoionic bentonites untreated and treated with diclofop or diclofop-methyl.

Cation	Untreated		Diclofop-treated		Diclofop-methyl-treated	
	25°C	120°C	25°C	120°C	25°C	120°C
Fe^{3+}	15.0	11.5	13.8	12.8	14.6	14.1
Al^{3+}	15.5	11.9	14.9	14.0	15.0	14.0
Cu^{2+}	12.3	11.3	13.2	12.6	14.6	13.1

metal ion. Metal complex formation may therefore have been an important mechanism here as well.

The d(001) values measured after adsorption are indicative of monolayer intercalation of molecules between the silicate sheets. Also, according to the ESR results for the Cu^{2+} clay, mainly mononuclear complexes are formed in the interlamellar space, conceivably because polynuclear arrangements are favored only in concentrated systems. For example, in dilute aqueous solutions, similar to those in the montmorillonite interlayer, complexes of the Cu^{2+}-acetate type have not been observed.

The present results suggest that pesticides forming neutral complexes with interlayer ions are extractable by solvents. Thus, in a soil they may be released into the environment. Similar behavior was observed by Micera *et al.* (1988) and Pusino *et al.* (1989). Thus, the solubility of metal-pesticide complexes may be one of the factors governing both metal and pesticide cycling in soil.

ACKNOWLEDGMENTS

REFERENCES

Bandemer, S. L. and Schaible, R. J. (1944) Determination of iron. A study of the o-phenanthroline method. *Ind. Eng. Chem. Anal. Ed.* **16**, 317–319.

Brown, G. M. and Chidambaram, R. (1973) Dinuclear copper(II) acetate monohydrate: A redetermination by neutron-diffraction analysis: *Acta Crystallogr.* **B29**, 2393–2403.

Chenery, E. M. (1948) Thioglycollic acid as an inhibitor for iron in the colorimetric determination of Al by means of "aluminon": *Analyst* **73**, 501–502.

Crosby, D. G. (1976) Non biological degradation of herbicides in the soil: in *Herbicides, Vol. 2,* L. J. Andus, ed., Academic Press, London, 65–97.

Gessa, C., Pusino, A., Solinas, V., and Petretto, S. (1987) Interaction of Fluazifop-butyl with homoionic clays: *Soil Sci.* **144**, 420–424.

Karanth, N. G. K., Anderson, J. P. E., and Domsch, K. H. (1984) Degradation of the herbicide diclofop-methyl in soil and influence of pesticide mixture on its persistence: *J. Biosc.* **6**, 829–837.

Micera, G., Pusino, A., Gessa, C., and Petretto, S. (1988) Interaction of Fluazifop with Al-, Fe^{3+}-, and Cu^{2+}-saturated montmorillonite: *Clays & Clay Minerals* **36**, 354–358.

Mortland, M. M. (1970) Clay-organic complexes and interactions: *Adv. Agron.* **22**, 75–119.

Mortland, M. M. (1975) Interactions between clays and organic pollutants: in *Proc. Inter. Clay Conf., Mexico City, 1975,* S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 469–475.

Nebesar, B. (1964) Spectrophotometric determination of Cu in Te and related thermoelectric compounds of the Bi telluride type with 2,9-dimethyl-1,10-phenanthroline: *Anal. Chem.* **36**, 1961–1965.

Pusino, A., Micera, G., Premoli, A., and Gessa, C. (1989) D-Glucosamine sorption on Cu(II)-montmorillonite as the protonated and neutral species: *Clays & Clay Minerals* **37**, 377–380.

Smith, A. E. (1976) Esterification of the hydrolysis product of the herbicide dichlorfop-methyl in methanol: *J. Agric. Food Chem.* **24**, 1077–1078.

Smith, A. E. (1977) Degradation of the herbicide diclofop-methyl in prairie soils: *J. Agric. Food Chem.* **25**, 893–898.

Smith, A. E., Grover, R., Cessna, A. J., Stewchuck, S. R., and Hunter, J. H. (1986) Fate of diclofop-methyl after application to a wheat field: *J. Environ. Qual.* **15**, 234–238.