

Adsorption of herbicide triclopyr on homoionic clays

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Abstract—The adsorption of the herbicide triclopyr on homoionic Fe^{3+} , Al^{3+} , Cu^{2+} , K^+ and Na^+ exchanged montmorillonite samples was investigated and the adsorption isotherm was described by the Freundlich equation. The adsorption capacity decreased in the order Fe^{3+} , Al^{3+} , Cu^{2+} , Ca^{2+} , K^+ and Na^+ clays. The triclopyr adsorption from chloroform solution was also studied by analytical, spectroscopic, and X-ray powder diffraction techniques. IR results suggested that the adsorption involved the formation of hydrogen bonds with water molecules in the interlayer and might have involved both the protonation of the pyridine nitrogen atom, due to a proton transfer from the acid metal-bound water, and also the formation of direct bounds between the carboxylate groups and the exchange cations. The pesticide forming complexes with interlayer cations in montmorillonite in soils might be extractable by solvents and was therefore released into the environment.

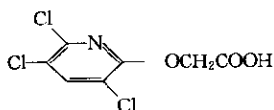
Keywords: adsorption; triclopyr; interlayer cations; montmorillonite; hydrogen bond.

1 Introduction

Because of the increasing use of pesticides in agriculture, studies on the mechanisms of interaction between these compounds and soil become important. Contribution of organic and mineral fractions to the adsorption of organic molecules in soil was the theme of the several studies (e. g. Mortland, 1975; Gessa, 1987; Senesi, 1984; 1992). Evidence was obtained to demonstrate that, depending on the pesticide properties and water content, both these constituents could play an important role in adsorption and retention processes. Under conditions of water saturation, the adsorption of non-ionic organic molecules was generally dominated by its partitioning into soil

organic matter. Conversely, in subsaturated soil and ionic organic molecules, the adsorption onto mineral surfaces was more important. Normally, adsorption by clay minerals is one of the most important factors governing the fate and behavior of pesticides soil (White, 1976).

Triclopyr, 3,5,6 - trichloro - 2 - pyridyloxyacetic acid,



was commonly applied in post-emergence treatment to control wild oats and other annual grasses in a variety of crops (McCall, 1986) because of its wide use. Satisfactory information was available on the bioactivity of this herbicide (Woodburn, 1993), but not on its interaction with the soil components. The aim of this work was to investigate the interaction with triclopyr and clays, therefore adsorption isotherms of herbicide on Fe^{3+} , Al^{3+} , Cu^{2+} , Ca^{2+} , K^+ and Na^+ -saturated montmorillonite from water were studied. To establish the retention mechanisms, the adsorption from chloroform were studied also. It was observed that two different mechanisms were possible.

2 Experimental

2.1 Materials

The $<2\mu\text{m}$ size fraction of bentonite from Upton, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, New York, was used in this study. The sample was obtained by sedimentation. The cation-exchange capacity (CEC), determined by literature methods (Hendershot, 1986), was 90.2 meq/100g. Fe^{3+} , Al^{3+} , Cu^{2+} , Ca^{2+} , K^+ and Na^+ -exchanged samples were prepared by immersing the clay into 1 mol/L or 0.5 mol/L solution of the corresponding metal chlorides. The samples were centrifuged, washed repeatedly with deionized water until Cl^- -free and dried at room temperature; triclopyr ($\text{C}_7\text{H}_4\text{Cl}_3\text{NO}_3$) was supported by DowElanco Company, USA, as a fluffy colorless solid.

2.2 Sorption of herbicide

Batch distribution isotherms on Fe^{3+} , Al^{3+} , Cu^{2+} , Ca^{2+} , K^+ and Na^+ -clay were determined at $25 \pm 1^\circ\text{C}$. In general, duplicate samples of 50 mg of air-dried clay were equilibrated in centrifuge tubes with 5 ml of aqueous herbicide solution. The triclopyr concentrations equilibrium ranged from 25.5 to 450.0 $\mu\text{mol/L}$. The tubes were shaken (end-over-end) for 24hr. After equilibrium was reached, the suspension was centrifuged at 30000 r/min for 20 min using Beckman L5-50B centrifuge. The supernatant was pipetted off and analysed immediately by high performance liquid chromatography (HPLC). The amount adsorbed by clays was calculated from difference between the initial and the final concentrations of triclopyr solution.

The adsorption studies were repeated by immersing air-dried self-supporting clay films into a 2% solution of triclopyr in chloroform. After 24 hr the films were separated from the solution and washed with chloroform to remove excess herbicide. After air-drying, the films were examined by infrared spectroscopy (IR) and X-ray powder diffraction (XRD) analysis, respectively.

2.3 Chromatographic analysis

HPLC analyses were carried out using a Waters 510 liquid chromatography equipped with a 300×4 mm i. d. A 10μ Bondapak^{MT} C₁₈ analytical column, a multiwavelength Waters 490 programmable detector operating at 295 nm and a water baseline 810 chromatography workstation were used. The mobile phase (1ml/min) was composed of acetonitrile and water (70:30 by volume, pH3). Under these conditions the retention time of triclopyr was 4.12 min, and the chromatogram are shown in Fig. 1.

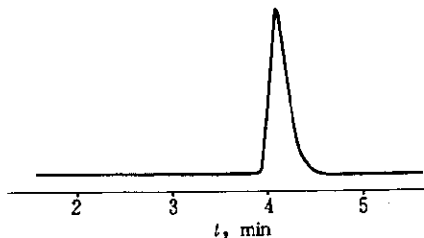


Fig. 1 Chromatogram of triclopyr 300×4 mm, i. d. μ Bondapak^{MT} C₁₈ (10μ m) column; detector wavelength, 295nm; mobile phases, 1 ml/min CH₃CN:H₂O 70:30 (V:V, pH 3)

2.4 Physical measurement

Infrared (IR) spectra were recorded with a Nicolet 205 FT - IR spectrophotometer. Those for triclopyr - clay complexes were obtained as differential spectra using self - supporting films. The IR spectrum of triclopyr was recorded also in a chloroform solution. XRD data were obtained

at 25°C with a Rigaku Corporation D/max - RA diffractometer, using CoK_α radiation.

3 Results and discussion

3.1 Adsorption isotherms

Fig. 2 shows the adsorption isotherms of triclopyr on Fe³⁺, Al³⁺, Cu²⁺, and Ca²⁺-montmorillonite. All the isotherms are of type "S" according to the classification of Giles *et al.* (Giles, 1960). The S - shape of the curve is usually explained as due to competition with the molecules of the solvent for substrate sites. The empirical Freundlich relationship is used to evaluate the results ($\gamma > 0.96$). The linear form of this equation is as follows;

$$\log C_s = \log Kf + 1/n \log C_e,$$

where C_s is the amount ($\mu\text{mol}/100\text{g}$) of pesticide adsorbed, C_e is the herbicide concentration ($\mu\text{mol}/\text{L}$) in the solution at equilibrium, and Kf and n are constant. Kf is the amount of pesticide adsorbed from an unitary equilibrium concentration and $1/n$ reflects the degree of linearity of the adsorption trend. The values of Kf and $1/n$ are given in Table 1. Both the isotherms and values of Kf show that the adsorption capacity decreases in the order Fe³⁺ > Al³⁺ > Cu²⁺ > Ca²⁺ > K⁺-clays and the adsorption by Na⁺-clay from aqueous solution in the experimental concentration range has been found. This result may suggest that the extent of adsorption on clays depends on the saturating cation and, in particular, on its polarizing power. However, because of the rather low adsorption levels of the pesticide from aqueous solution, the results supporting evidence for the adsorption mechanism can be obtained by IR spectra. Moreover, no decomposition product has been found by HPLC analysis of the equilibrium solution

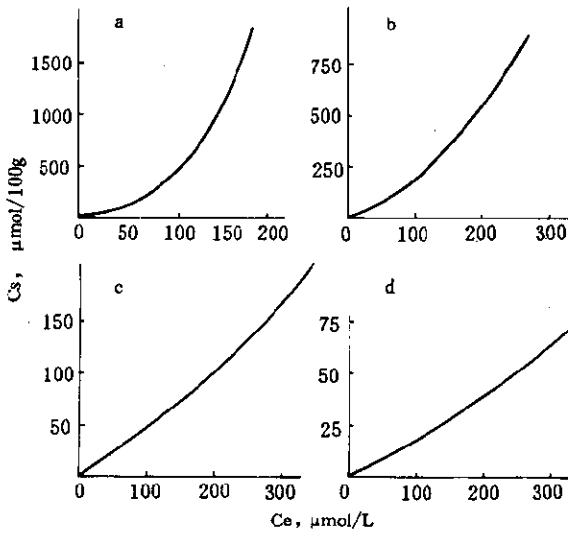


Fig. 2 Adsorption isotherms of triclopyr on montmorillonite

a. Fe^{3+} ; b. Al^{3+} ; c. Cu^{2+} ; d. Ca^{2+} -calys. Ce ($\mu\text{mol/L}$); Cs ($\mu\text{mol}/100\text{g}$)

range $1600\text{--}1620\text{cm}^{-1}$ and $1390\text{--}1420\text{cm}^{-1}$. These bands were assigned to the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ stretches, respectively, indicating metal-bound carboxylate groups. But, the IR adsorption of the free carboxyl group is clear in the latter case, and the range $1600\text{--}1620\text{cm}^{-1}$ is unclear, probably only hydrogen-bonding is existing.

Table 2 Infrared adsorption (cm^{-1}) of carboxylate groups for metal-clay treated with triclopyr

Metal	ν_{as}	ν_{sym}
Fe^{2+}	1610	1417
Al^{3+}	1604	1419
Cu^{2+}	1604	1419
Ca^{2+}	1740	1419
K^+	1740	1418
Na^+	1747	1419
Triclopyr	1736	1395

Over the range of 3000cm^{-1} , the occurrence of a weak adsorption in the N-H stretching region centered at $3065\text{--}3075\text{cm}^{-1}$ due to

Table 1 Freundlich constants (Kf and n) and correlation coefficient (γ^2) for the adsorption of triclopyr on montmorillonite

Sample	Kf	$1/n$	γ^2
Fe^{3+}	0.397	1.501	0.999
Al^{3+}	0.338	1.441	0.983
Cu^{2+}	0.219	1.119	0.936
Ca^{2+}	0.172	1.119	0.994
K^+	0.001	2.056	0.968
Na^+	—	—	—

* did not adsorption

3.2 Adsorption mechanisms

The IR spectra of Fe^{3+} , Al^{3+} , Cu^{2+} , Ca^{2+} , K^+ and Na^+ -clays treated with triclopyr are compared in Fig. 3a, 3b, and Table 2. The frequencies of the carboxylate bands of triclopyr with Fe^{3+} , Al^{3+} , Cu^{2+} clays are different from these with Ca^{2+} , K^+ and Na^+ -clays. In the former case, the 1736cm^{-1} adsorption of the free carboxyl group is absent, and two bands in the

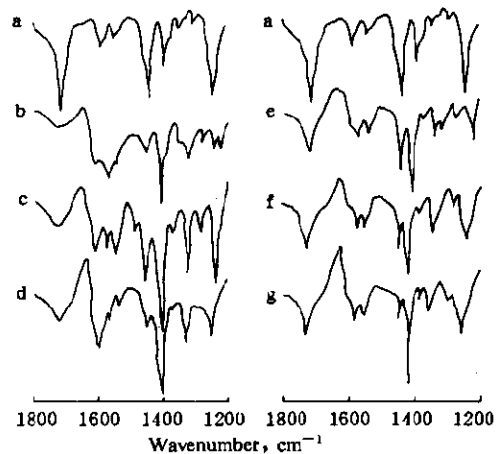


Fig. 3 Infrared spectra of (a) triclopyr (KBr disk) and homoionic clays treated with triclopyr, (b) Fe^{3+} , (c) Al^{3+} , (d) Cu^{2+} , (e) Ca^{2+} , (f) K^+ and (g) Na^+ . Spectra of clays were recorded as differential spectra with respect to those of untreated samples

the protonated pyridinic nitrogen, the shift of the U_{8a} ring vibration from 1572 cm^{-1} (Micera, 1988) to 1580 cm^{-1} , the latter value being typical of pyridinium compound. The mechanisms mentioned above are as follows:



$\text{Me}^{n+} = \text{Fe}^{3+}, \text{Al}^{3+}$ and Cu^{2+}



$\text{Me}^{n+} = \text{Fe}^{3+}, \text{Al}^{3+}, \text{Cu}^{2+}, \text{Ca}^{2+}, \text{K}^+$ and Na^+



$\text{Me}^{n+} = \text{Fe}^{3+}, \text{Al}^{3+}, \text{Cu}^{2+}, \text{Ca}^{2+}, \text{K}^+$ and Na^+



$\text{Me}^{n+} = \text{Fe}^{3+}, \text{Al}^{3+}, \text{Cu}^{2+}, \text{Ca}^{2+}, \text{K}^+$ and Na^+

3.3 XRD results

The XRD $d(001)$ values (Table 3) of untreated clays and those treated with triclopyr in chloroformic solution indicate that the organic acid occupies the interlamellar space of the phyllosilicate, forming monolayers. In particular, $d(001)$ increases for the Cu^{2+} -clay kept at room temperature, but decreases under the same conditions for the Fe^{3+} , Al^{3+} -clays, probably because of hydrophobic effects produced by the intercalation of the organic molecule. Moreover, the collapse of the interlayer heating under vacuum is lower than for the corresponding untreated samples. The larger interlayer distance measured for Al^{3+} -clay treated with triclopyr may have been due to the lower extent of metal desorption observed for this clay.

Table 3 $d(001)$ values for homoionic bentonites untreated and treated with triclopyr (A)

Cation	Untreated		Treated	
	25°C	120°C	25°C	120°C
Fe^{3+}	14.93	12.07	14.32	13.85
Al^{3+}	14.85	12.26	14.76	13.92
Cu^{2+}	13.02	12.01	14.86	13.55
Ca^{2+}	14.45	12.13	14.25	13.42
K^+	12.01	10.38	13.12	13.08
Na^+	12.05	10.28	12.21	12.17

4 Conclusions

The adsorption of triclopyr from water on clays follows Freundlich equation, although water may be competitive enough with the pesticide. The values of Kf show that the adsorption capacity decreases in the order $Fe^{3+} > Al^{3+} > Cu^{2+} > Ca^{2+} > K^+$ -clays and adsorption by Na^+ -clay from aqueous solution has not been found in the experimental concentration range.

The results of this study clearly that the adsorption of triclopyr in interlayer of montmorillonite occurs by means of more than one interaction mechanism. The first mechanism involves the protection of the pyridinic nitrogen atom by the acid water associated with the exchangeable cations. Another adsorption mechanism is connected with coordination of carboxylate groups to the exchange metal ions and also hydro-bonding is possible.

The results demonstrate that triclopyr effectively complex metal ions in montmorillonite. These findings are significant for the soil chemistry of triclopyr, as much as the inactivation following complex formation is responsible for the loss of herbicide activity. Similar behavior was observed by Micera *et al.* (Micera, 1988) for Fluazifop and Pusino *et al.* (Fluazifop, 1989) for Diclofp absorptions on clays. As a consequence of these interactions, relevant soil processes, e. g. , the reversible adsorption of metal ions, may be affected.

Acknowledgements—This research was supported by the foundations of Chinese NEC (File No. 1993. 360) and Italian CNR (special project RAISA), and the authors are also grateful to Mr. S. Petretto and Mr. Q. Wang for technical assistance.

References

- Gessa C, A Pusino, V Solinas, S Petretto. *Soil Sci*, 1987; 144:420
- Giles CH, JH McEwan, SN Nakhwa, D Smith. *J Chem Soc*, 1960;3973
- Hendershot GP, M Duquette. *Soil Sci Soc Amer J*, 1986;50:605
- McCall PJ, PD Gavit. *Environ Toxicol Chem*, 1986;5:879
- Micera G, A Pusino, C Gessa, S Petretto. *Clays & Clay Minerals*, 1988;36:354
- Mortland MM. *Inter clay conf*(Ed by Bailey SW). Mexico City: Applied Publishing, 1991:459
- Pusino A, G Micera, C Gessa. *Clays & Clay Minerals*, 1991;39:50
- Senesi N, C Testini. *Chemosphere*, 1984;13:461
- Senesi N. *The Sci Total Environ*, 1992;123/124:63
- White JL. *Clay - pesticide interactions, in bound and conjugated pesticide residues*, ACS Symp Ser No. 29, Amer Chem Soc, Washington D. C. 1976;208
- Woodburn KB, FR Batzer, FH White, MR Schultz. *Environ Toxicol Chem*, 1993;12:43

(Received March 2, 1994)