CHEMISTRY OF TWO CLAY SYSTEMS AND THREE PHENOXY HERBICIDES*

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Organic pesticides, particularly herbicides, usually find their way into the soil. Phenoxy herbicides when added to soil may react with the soil clay minerals. This study concerns such reactions. Results obtained indicate these organic molecules are strongly sorbed by kaolinitic and montmorillonitic clay minerals to an extent of the cation-exchange-capacity (C.E.C.) of the clay mineral. X-ray diffraction study showed that the phenoxy herbicides were not sorbed on the interlayer surfaces of the clay minerals, since the basal spacings were unaltered; they were probably bound at the edges of the particles at charged sites.

INTRODUCTION

Herbicides are applied to soils in an attempt to control undesirable plants. Although the user intends the herbicide to react with the plant, ultimately most of the chemical enters the soil. Some herbicides react with soil clay in a predictable manner; however, many are nonpolar or weakly polar compounds and, therefore, do not interact with soil clays in a straightforward manner.

Mineral soils are complex heterogeneous mixtures of inorganic silicates, silica (quartz), water, traces of soluble salts, organic matter, and pore space. The reactive portion of the soil, in a chemical sense, is the clay and soil organic matter. The clay present in the soil resembles the clay minerals often found in quite pure geological (mineral) deposits. These minerals may be used as experimental materials in an attempt to approximate conditions which may be encountered in soils (1). That is, soils which contain major quantities of a particular type of clay mineral may be compared to some so-called "pure clay minerals" in a general way.

The objective of this study was to determine the mode of sorption of organic herbicides by clay minerals. The term "sorption" used in this report refers both to adsorption and absorption.

MATERIALS AND METHODS

The three phenoxy herbicides used in this study are 2,4,5-trichlorophenoxyacetic acid (2,4,5-TA),2-(2,4,5-trichlorophenoxy) - propionic acid (2,4,5-TP), and 2,4-dichlorophenoxyacetic acid (2,4-D).

Clay minerals selected for this study were fine Georgia kaolinite <0.2 μm, coarse Georgia kaolinite 2-0.2 μm, and fine (< 0.2 μm) Camargo bentonite from northwestern Oklahoma (1). All were partitioned with the supercentrifuge and saturated with Mg^{++} (2).

Cation exchange capacity determination.

Cation-exchange capacity (C.E.C.) was determined for each clay mineral by treating 10 ml of a clay mineral suspension with 30 ml of 1*N* $CaCl_2$ in three successive 10-ml washings. The excess salt was removed by washing the clays seven times with deionized water until excess $CaCl_2$ was removed, as indicated by a negative $AgNO_3$ test for chloride in the last three washings. The Ca was replaced by four washings with 10-ml portions of 1*N* NaCl. The extract solution thus produced was brought to a final volume of 100 ml with distilled water and its Ca content measured by Versene titration as described by Jackson (2) and as follows.

Fifty milliliters of each sample were transferred to 100 ml pyrex beakers. Ten milliliters of a NH_4Cl-NH_4OH buffer was added to bring the solution to pH 10. Five drops of Eriochrome Black T indicator solution were added to the solution and it was titrated with EDTA (Versene) to a blue endpoint. The C.E.C. in milliequivalents was calculated (3) as

$$\text{meq/100g} = \text{ml Versene} \times N \text{ X } 100/\text{sample wt. in g.}$$

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Herbicide determination.

The herbicide solutions were prepared by adding 0.001 mole of each one to 95% ethanol and bringing the volume to 100 ml.

2,4,5-TA	0.255 g/100 ml
2,4,5-TP	0.269 g/100 ml
2,4-D	0.221 g/100 ml

Standard curves were prepared by diluting the stock solutions 1:10 with 95% ethanol and then with more ethanol to make further dilutions of 1:2, 1:4, 1:6, and 1:8, and measuring absorption of samples on a Perkin-Elmer Model 202 ultraviolet-visible spectrophotometer, with 95% ethanol as a reference. The standard peaks were obtained at 290 nm, 293 nm, and 291 nm for 2,4,5-TA, 2,4,5-TP, and 2,4-D, respectively.

Enough stock solution of each herbicide was added to 10 ml of each clay suspension to supply one, two, and three millimoles of herbicide per milliequivalent of the previously determined C.E.C. The mixtures were shaken on a reciprocal shaker for eight hours and then centrifuged for twenty minutes at 10,000 RPM to give clear supernatant solutions. The concentrations of unsorbed herbicide were determined by taking an aliquot from the supernatant solution and determining the herbicide with the spectrophotometer.

Clay mineral samples were mounted on ceramic slides and examined by the X-ray diffraction technique (1,3) to determine basal or interlayering sorption of herbicide molecules on the clay particle.

RESULTS AND DISCUSSION

The cation exchange capacity of the clay minerals is shown in Table 1.

TABLE 1. *Cation exchange capacity of clay minerals used.*

Clay mineral	Capacity (milliequivalents/100 g)
Georgia kaolinite 2-0.2 μm	21.38
Georgia kaolinite <0.2 μm	25.83
Camargo bentonite <0.2 μm	111.65

Sorption of herbicides by Georgia kaolinite.

Georgia kaolinite is a nonexpanding-type clay mineral. The organic herbicides were probably sorbed on the edges of the clay particles rather than in the interior of the structure (4). This sorption is probably due to the ionic charges of the clay.

The extent of sorption of the organic herbicides by Georgia kaolinite 2-0.2 μm is shown in Table 2. As this shows, variation in levels of organic herbicides applied had no effect on percent sorption; in all cases the organic herbicides were sorbed in amounts close to the C.E.C. of the clay.

TABLE 2. *Sorption of herbicides by Georgia kaolinite 2-0.2 μm.*

Herbicide applied (mmol/meq C.E.C.)	Herbicide sorbed (mmol/meq C.E.C.) 2,4,5-TA	2,4,5-TP	2,4-D
1.00	0.993	0.986	0.991
2.00	0.992	0.970	0.992
3.00	0.993	0.968	0.991

The results for Georgia kaolinite <0.2 μm also showed that organic herbicides were sorbed efficiently to the extent of close to one millimole per milliequivalent of C.E.C. of the clay. Percent sorption of organic herbicides by this clay sample is shown in Table 3. Again the use of different levels had no effect on the extent of sorption.

TABLE 3. *Sorption of herbicides by Georgia kaolinite < 0.2 μm.*

Herbicide applied (mmol/meq C.E.C.)	Herbicide sorbed (mmole/meq C.E.C.) 2,4,5-TA	2,4,5-TP	2,4-D
1.00	0.984	0.945	0.978
2.00	0.990	0.958	0.969
3.00	0.987	0.971	0.969

Sorption of herbicides by Camargo bentonite <0.2 μm.

The Camargo bentonite had a high cation exchange capacity and a high sorptive capacity due to internal charge deficits. The degree of sorption of 2,4,5-TA, 2,4,5-TP, and 2,4-D by this bentonite is shown in Table 4. As this shows, the herbicides applied were sorbed to the same extent as on the kaolinite in terms of C.E.C.

TABLE 4. *Sorption of herbicides by Camargo bentonite.*

Herbicide applied (mmol/meq C.E.C.)	Herbicide sorbed (mmole/meq C.E.C.) 2,4,5-TA	2,4,5-TP	2,4-D
1.00	0.992	0.954	0.992
2.00	0.966	0.956	0.995
3.00	0.980	0.947	0.967

X-Ray diffraction spacing of Georgia kaolinite.

Treatment of Georgia kaolinite 2-0.2 μm with 2,4,5-TA, 2,4,5-TP, and 2,4-D had no effect on the X-ray basal spacings. Results are shown in Table 5. This shows the d-spacing to be the same as the d-spacing of untreated kaolinite.

Since kaolinite is a nonexpanding type of clay mineral, organic herbicides were sorbed around the edges of the clay particle, owing to broken-bond charges there, and did not increase or decrease the 2θ value or the d-spacing value.

Treatment of Georgia kaolinite <0.2 μm fraction with 2,5,5-TA, 2,4,5-TP, and 2,4-D had no effect on the X-ray basal spacing as shown in Table 6. This again shows that the d-spacing (basal) of the untreated clay was the same as that obtained with different amounts of organic herbicides.

X-Ray diffraction pattern of Carnargo bentonite.

The X-ray diffraction spacings of Camargo bentonite <0.2 μm are shown in Table 7. The results show that the d-spacing of the untreated bentonite was the same as the d-spacings obtained after treatment with different amounts of herbicides, whereas glycerol treatment produced the known increase in spacing. The herbicides were probably sorbed on the edges of the clay particles rather than within the interlayer structure (6). This indicates that practically none of the interlayer free water in the structure was displayed by the herbicide.

TABLE 5. *X-Ray diffraction basal spacings of Georgia kaolinite 2-0.2 μm treated with herbicides.*

Herbicide	Diffraction spacings (Å) after herbicide application (mmole/meq C.E.C.)			
	0 (untreated)	1	2	3
2,4,5-TA	7.3	8.0	7.2	7.3
2,4,5-TP	7.3	7.3	7.3	7.3
2,4-D	7.3	7.3	7.3	7.2

TABLE 6. *X-Ray diffraction basal spacings of Georgia kaolinite <0.2μ m treated with herbicides.*

Herbicide	Diffraction spacings (Å) after herbicide application (mmole/meq C.E.C.)			
	0 (untreated)	1	2	3
2,4,5-TA	7.3	7.3	7.3	7.3
2,4,5-TP	7.3	7.2	7.3	7.2
2,4-D	7.3	7.3	7.3	7.2

TABLE 7. *X-Ray diffraction spacings of Camargo bentonite treated with herbicides.*

Herbicide	Diffraction spacings (Å) after herbicide treatment (mmole/meq C.E.C.)			
	0 (untreated)[a]	1	2	3
2,4,5-TA	16.0	16.0	16.0	16.0
2,4,5-TP	16.0	16.0	15.8	16.0
2,4-D	16.0	16.0	16.0	16.3

[a] In comparison, glycerol-treated Camargo bentonite showed diffraction spacing of 17.7 Å.

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