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pH-Dependent Adsorption Isotherms of Glyphosate

James S. McConnell[*1] and Lloyd R. Hossner

The relationship of system pH to glyphosate adsorption was investigated in Al^{3+}, Ca^{2+}, and Na$^+$ saturations of two smectites (montmorillonite and nontronite), NaCl-washed kaolinite, hematite, and goethite. Batch equilibria techniques were used to elucidate adsorption isotherms for these minerals at four specific pH values. Glyphosate adsorption generally decreased as the system pH was increased, although there were exceptions. The exchangeable cation of the smectites influenced glyphosate adsorption capacities; Al^{3+}-saturated smectite adsorbed more glyphosate than Ca^{2+} followed by Na$^+$. Nontronite was found to adsorb more glyphosate than montmorillonite for the same saturating cation and pH. Glyphosate adsorption characteristics of kaolinite, hematite, and goethite were dependent on the pH of the clay–glyphosate system. The amount of glyphosate adsorbed was determined by the charge of the mineral surface and the ionic state of the glyphosate. The increased negative charge of glyphosate and the mineral surfaces with increasing pH resulted in decreased adsorption.

INTRODUCTION

Glyphosate is the active ingredient of the herbicide Roundup (Mullison et al., 1979). This chemical is a nonselective herbicide that is readily translocated to meristematic regions of plants. The ability to translocate and kill the growing points gives glyphosate tremendous potential in the control of such rhizome-producing weeds as johnsongrass and quackgrass (Crawford and Rogers, 1973; Claus and Behrens, 1976).

No-till production systems have employed a glyphosate solution to kill all plants in a field before planting. Planting can begin as soon as the kill has taken place with no crop damage (Peters and Dest, 1975). The lack of damage to crops planted immediately after such a treatment is apparently due to the rapid inactivation of the herbicide in the soil. Two reasons for the inactivation of soil-applied glyphosate have been postulated: (1) decomposition by soil microbes and (2) sorption of the whole molecule to soil components (Sprankle et al., 1975). Adsorption, at least initially, would seem to better account for the behavior of glyphosate where deactivation is immediate.

Adsorption has characteristically been one of the most important factors influencing the behavior of herbicides in soil systems (Hensley et al., 1978). Glyphosate adsorption has been studied on whole soils and individual

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Table I. Surface Area, Cation-Exchange Capacity, and Zero Point of Charge for Montmorillonite, Nontronite, Kaolinite, Hematite, and Goethite

	cation-exch capacity, cmol kg^{-1}	surface area, m^2 g^{-1}	zero pt of charge: pH
montmorillonite	98	813	
nontronite	142	908	
kaolinite	16.2	37.2	3.7
hematite	0.7	11.1	7.9
goethite	6.9	50.7	8.4

minerals by bioassay or radioisotope techniques (Hance, 1976; Sprankle et al., 1975; Nomura and Hilton, 1977; Damanakis, 1976). These reports on glyphosate adsorption vary because of the range in chemical and physical properties of soils employed, the differences in dosage rates, and the contrasting analytical methods.

The purpose of this study was to quantify the adsorption of the four different ionic species of glyphosate onto several soil minerals of the clay size fraction. This would help in understanding the mechanism of glyphosate deactivation as well as allow estimation of the adsorption capacities of the minerals for glyphosate.

EXPERIMENTAL SECTION

Clay Minerals. Clays selected for this study were Oklahoma montmorillonite, Washington nontronite, Georgia Kaolinite, and synthetic hematite and goethite. The smectites were dispersed by agitation in deionized water and then sedimented to separate the clay-sized fractions (less than 2 μm in diameter). These clays were then divided into approximately equal samples and treated

with the chloride salts of Al^{3+}, Ca^{2+}, and Na^+ to produce homoionic saturated smectites. Kaolinite was suspended in pH 10 water and sedimented to obtain the clay fraction. All minerals were then freeze-dried to ensure their preservation.

Cation-exchange capacity (CEC) (Jackson, 1979) and surface area (SA) (Carter et al., 1962) were determined for the clay fractions of all the minerals. Zero point of net charge (ZPNC) and zero point of charge (ZPC) were determined for the clay-sized kaolinite and for hematite and goethite, respectively (Table I) (van Raij and Peech, 1972).

Procedures for Adsorption Isotherms. Three 50-mg samples of clay were used for each isotherm point. Glyphosate solutions were prepared in 0, 10, 25, 50, 75, and 100 ppm concentrations. These solutions were treated with dilute NaOH and HCl to buffer their pH at 2.0, 4.5, 7.0, and 11.5, thereby allowing the Na^+ salt of glyphosate to act as the buffer. Due to the buffering capacity of some of the clays, the pH of all clay–glyphosate slurries was rechecked and readjusted as necessary with HCl or NaOH. The samples were then equilibrated 16 h on a reciprocal shaker. Immediately after the equilibration period, the samples were centrifuged and the supernatant liquid was analyzed for glyphosate content.

An aliquot of the clear supernatant was injected into a Beckman HPLC equipped with a Perkin-Elmer LC75 detector set at 254 μm. The column was an Alltech C-18. The mobile phase was LC-grade water at a rate of 1 mL/min. The equilibrium concentration of glyphosate (C_E) was determined by integrating the area under the peak and comparing with the peak areas of standard glyphosate solutions. The difference between C_E and the initial glyphosate concentration gave the amount of glyphosate adsorbed by the 50 mg of clay. The number was subsequently converted to micrograms of glyphosate adsorbed per gram of clay (x/m).

The Freundlich constants (K and $1/n$) were estimated from the log form of the Freundlich equation ($\log (x/m) = \log K + (1/n) \log C_E$). If either the $\log K$ or $1/n$ values of two compared isotherms was found to be significantly different ($\alpha = 0.05$), then the isotherms were concluded to be different.

The adsorption maximum reported is an experimentally determined value from the isotherm and may not represent the total glyphosate adsorbing capacity of the mineral. The largest x/m value for each isotherm was reported as the experimental adsorption maximum for the particular mineral and pH. This was necessary because the Freundlich equation has no provision for calculating an adsorption maximum.

RESULTS AND DISCUSSION

Adsorption of Glyphosate by Smectites. The adsorption characteristics of neutral glyphosate (pH 2.0) by smectites showed little difference due to the saturating cations. The controlling parameter for these isotherms is the mineral type. The tetrahedrally charged nontronite has a significantly higher capacity for adsorbing neutral glyphosate than octahedrally charged montmorillonite ($\alpha = 0.05$) (Table II). Saturation integrity of the smectites was probably not maintained because of octahedral cation shuttling at such a low pH (Buol et al., 1980). This is probably the reason for the similarities of the adsorption isotherms of montmorillonite and for the isotherms of nontronite.

Some dissolution of the smectites will occur at pH 2.0 (Kittrick, 1977). The first step in the dissolution of smectites is the release of octahedral layer cations. During the dissolution of nontronite Fe^{3+} is released while

Table II. $1/n$ Values, K values, Correlation Coefficients, and Adsorption Maxima of the pH 2.0 Smectite Isotherms

mineral	init satn		K	$1/n$	correln coeff	ads max, mmol kg^{-1}
montmorillonite	Al^{3+}	A[a]	516.3	0.359	0.58	15.2
	Ca^{2+}	A	64.3	0.972	0.89	28.2
	Na^+	A	151.5	0.585	0.74	12.3
nontronite	Al^{3+}	B	738.4	0.766	0.94	100.6
	Ca^{2+}	B	286.6	0.946	0.95	86.1
	Na^+	B	236.4	1.017	0.97	91.5

[a] Isotherms of minerals followed by the same letter do not have significantly different $10n$ or $\log K$ values at the 0.05 level.

Table III. $1/n$ Values, K Values, Correlation Coefficients, and Adsorption Maxima for the pH 4.5 Smectite Isotherms

mineral	init satn		K	$1/n$	correln coeff	ads max, mmol kg^{-1}
montmorillonite	Al^{3+}	A[a]	1155.6	0.595	0.93	72.3
	Ca^{2+}	D	112.8	0.857	0.84	29.6
	Na^+	D	100.7	0.852	0.66	26.6
nontronite	Al^{3+}	B	1621.1	0.442	0.93	55.0
	Ca^{2+}	C	236.8	0.813	0.85	43.0
	Na^+	D	95.6	0.949	0.71	34.3

[a] Isotherms of minerals followed by the same letter do not have significantly different $1/n$ or $\log K$ values at the 0.05 level.

montmorillonite would first release Al^{3+} (Novak and Cicel, 1978). The complexes of Al^{3+}–glyphosate have been shown to be more soluble than Fe^{3+}–glyphosate complexes (Hensley et al., 1978). It is postulated that precipitation of glyphosate as a complex with iron from nontronite is the reason for the radical difference between the nontronite and montmorillonite isotherms at pH 2.0.

Glyphosate assumes a net charge of 1– at pH 4.5. The adsorption of glyphosate by the saturations of montmorillonite increased while that of nontronite decreased compared to the pH 2.0 isotherms. For this set of isotherms, two trends become evident. The first trend is that Al^{3+}-saturated montmorillonite adsorbed more glyphosate than Ca^{2+} and Na^+ ($\alpha = 0.05$). The Ca^{2+}- and Na^+-saturated montmorillonite did not adsorb significantly different amounts of glyphosate. The same series (Al^{3+} greater than Ca^{2+} and Na^+) was also evidenced in the nontronite isotherms, but Ca^{2+}–nontronite adsorbed significantly more glyphosate than Na^+–nontronite ($\alpha = 0.05$) (Table III). This result was not totally unexpected as Sprankle et al. (1975) obtained similar results although their system pH was uncontrolled. The second trend observed was that nontronite adsorbed more glyphosate than montmorillonite for the same saturating cation, except for Al^{3+}. The Na^+ smectites are not significantly different although nontronite adsorbs more glyphosate than montmorillonite (Table III). This supports data from the pH 2.0 isotherms that the difference between smectites is an important criteria in glyphosate adsorption. The difference between isotherms of the same initial saturating cation is not nearly as great at pH 4.5 as at pH 2.0. This indicates the integrity of the homoionic saturations of the smectites is better maintained at pH 4.5 than at pH 2.0.

When glyphosate solutions are buffered at pH 7.0 the glyphosate molecules carry a net charge of 2–. A general decrease in glyphosate adsorption was observed compared to the pH 4.5 isotherms. The general decrease in adsorption is due to the greater net negative charge of the glyphosate resulting in less interaction between the mineral surface and glyphosate.
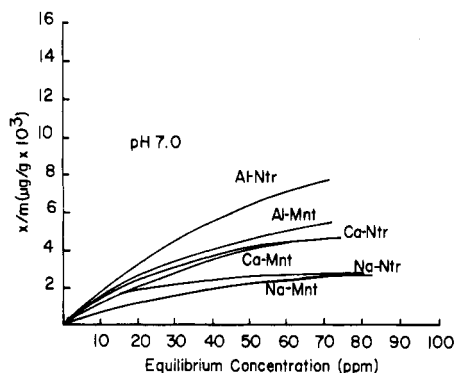
Adsorption Isotherms of Glyphosate

J. Agric. Food Chem., Vol. 33, No. 6, 1985 **1077**

Figure 1. Adsorption isotherms of glyphosate on montmorillonite and nontronite at pH 7.0.

Table IV. 1/n Values, K Values, Correlation Coefficients, and Adsorption Maxima for the pH 7.0 Smectite Isotherms

mineral	init satn		K	$1/n$	correln coeff	ads max, mmol kg^{-1}
montmorillonite	Al^{3+}	A[a]	290.0	0.686	0.87	32.5
	Ca^{2+}	C	360.7	0.605	0.79	28.4
	Na$^+$	D	196.7	0.600	0.73	16.0
nontronite	Al^{3+}	B	421.3	0.683	0.89	46.2
	Ca^{2+}	C	778.4	0.407	0.69	28.4
	Na$^+$	E	831.2	0.265	0.61	17.8

[a] Isotherms of minerals followed by the same letter do not have significantly different $1/n$ or log K values at the 0.05 level.

Table V. 1/n Values, K Values, Correlation Coefficients, and Adsorption Maxima of the pH 11.5 Isotherms of the Smectites

mineral	init satn		K	$1/n$	correln coeff	ads max, mmol kg^{-1}
montmorillonite	Al^{3+}	A[a]	197.5	0.895	0.72	45.6
	Ca^{2+}	C	198.5	0.605	0.95	15.4
	Na$^+$	C	234.5	0.565	0.65	15.4
nontronite	Al^{3+}	B	643.9	0.698	0.85	58.6
	Ca^{2+}	C	244.1	0.654	0.73	24.3
	Na$^+$	C	344.1	0.449	0.79	15.4

[a] Isotherms of minerals followed by the same letter do not have significantly different $1/n$ or log K values at the 0.05 level.

Trends observed for the pH 4.5 smectite isotherms were also observed at pH 7.0 (Figure 1). Nontronite adsorbed more glyphosate than montmorillonite for a given saturating cation although the Ca^{2+} smectites were not significantly different at the 0.05 level (Table IV). The relationship between saturating cations and glyphosate adsorption, Al^{3+} > Ca^{2+} > Na$^+$, for montmorillonite and for nontronite was evident.

At pH 11.5 the charge of the glyphosate is 3−. The Ca^{2+}- and Na$^+$-saturated smectites underwent a drastic decrease in glyphosate adsorption. The isotherms were also very compressed possibly due to the replacement of Ca^{2+} by Na$^+$ and adsorbed much less glyphosate than their pH 7.0 equivalents (Table V). The increase in anion exclusion forces appears to be at work again. The Al^{3+} smectites had greater glyphosate adsorption capacities at pH 11.5 than at pH 7.0. This increase is probably related to the formation of aluminum hydroxy polymers on the interlayer of the smectites. The polymers form at moderately high pH values (>7.5), reduce the net negative charge on the clay, and can provide extra sites for anion adsorption (Barnhisel, 1977).

Conditions that maximized glyphosate adsorption by the smectities were low pH, except montmorillonite at pH 2.0, and highly charged, exchangeable cations. Other excep-
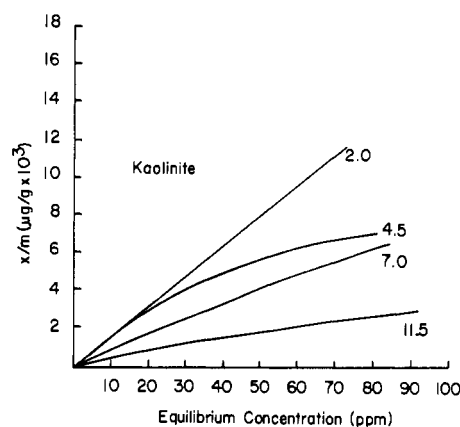

Figure 2. Adsorption isotherms of glyphosate on kaolinite at pH 2.0, 4.5, 7.0, and 11.5.

Table VI. 1/n and K Values, Correlation Coefficients, and Maxima of Adsorption of Kaolinite at Four pH Values

pH		K	$1/n$	correln coeff	max x/m, mmol kg^{-1}
2.0	A[a]	100.0	1.115	0.91	66.9
4.5	B	519.3	0.607	0.94	40.8
7.0	C	66.3	1.036	0.88	37.3
11.0	D	68.8	0.829	0.84	17.2

[a] Isotherms of kaolinite followed by the same letter do not have significantly different $1/n$ or log K values at the 0.05 level.

tions occurred when the clays became resaturated with Na$^+$ at pH 11.5. The general relationship observed between the charge of the saturating cation and the quantity of glyphosate adsorbed (Al^{3+} > Ca^{2+} > Na$^+$) indicates that the primary adsorption mechanism is complexation of the glyphosate to the exchangeable cations. Low pH tended to increase the attraction of glyphosate to the clay by suppressing the ionization of the acid. The glyphosate became more anionic as the pH was increased. The increased negative charge of the glyphosate resulted in decreased electrostatic attraction between the clay and glyphosate. The adsorption of glyphosate by the smectites consequently decreased as the pH was raised.

Other factors of glyphosate adsorption were the saturating cation, source and amount of charge, and surface area. These other factors were most important at pH 4.5, 7.0, and 11.0. The surface areas of nontronite and montmorillonite were found to be 908 and 813 m^2 g^{-1}, respectively. It was originally suspected that the difference in source of charge was the reason for the difference in glyphosate adsorption isotherms of montmorillonite and nontronite with the same saturating cation at the same pH. The close agreement between isotherm maxima of smectites of the same initial saturation and at the same pH, computed as mmol m^{-2}, suggests that surface area is of greater importance. Aluminum-saturated smectites at pH 4.5 exhibited the largest difference in adsorption maxima (2.86 × 10^{-5} mmol m^{-2}). The minimum difference (8 × 10^{-8} mmol m^{-2}) occurred between Na$^+$ smectites at pH 7.0.

Adsorption by Kaolinite, Hematite, and Goethite. Glyphosate adsorption by kaolinite was dictated by pH. The isotherms show that as the system pH was increased, the adsorption capacity of the clay decreased (Figure 2). A study of the kaolinite showed that this sample had a ZPNC at pH 3.7. Below pH 3.7 the mineral surface was net positively charged while above pH 3.7 the surface is net negatively charged although positively charged sites remain. The effect of increasing pH is similar for both glyphosate and the kaolinite surfaces. Glyphosate and kaolinite lose their exchangeable protons as pH is raised.

1078 *J. Agric. Food Chem.*, Vol. 33, No. 6, 1985

McConnell and Hossner

Table VII. 1/n Values, K Values, Correlation Coefficients, and Adsorption Maxima of Hematite and Geothite

mineral	pH		K	1/n	correl coeff	max x/m, mmol kg^{-1}	max x/m, mmol m^{-2} × 10^3
hematite	2.0	A[a]	459.3	0.773	0.93	51.5	4.64
	4.5	B	946.3	0.509	0.97	37.3	3.36
	7.0	C	921.7	0.536	0.99	46.7	4.21
	11.5	D	183.4	0.756	0.62	29.6	2.67
goethite	2.0	E	410.0	1.089	0.88	134.5	2.65
	4.5	F	1825.6	0.574	0.69	96.4	1.90
	7.0	F	1358.3	0.750	0.97	127.8	2.52
	11.5	D	102.3	0.805	0.80	21.8	0.43

[a] Isotherms of hematite and goethite followed by the same letter do not have significantly different $1/n$ or log K values at the 0.05 level.

This results in both the adsorbate and adsorbent becoming increasingly anionic. Less interaction due to increasing charge repulsion resulted in less glyphosate adsorption (Table VI).

Goethite and hematite have similar hydrated surface properties; therefore, the similarities in their isotherms were expected. System pH was the factor controlling glyphosate adsorption for these two minerals (Table VII). The ZPC values of the iron oxides were found to be 7.9 and 8.4 for hematite and goethite, respectively. The ZPC indicates that at pH 2.0, 4.5, and 7.0 the mineral surfaces are positively charged while the glyphosate is anionic or zwitterionic. The attraction caused by opposite charges enhances glyphosate adsorption. Iron oxide surfaces are highly protonated at pH 2.0 and attract the negative moiety of glyphosate, allowing for the greatest adsorption. When the pH is increased to 4.5 and 7.0, protonation of the mineral surfaces decreases and adsorption of glyphosate decreases. The low pH isotherms (2.0, 4.5, 7.0) are in the same proximity compared to the pH 11.5 isotherms. At pH 11.5, the glyphosate ions adopt a net charge of 3– and the iron oxide surfaces also become negative. The repelling forces between glyphosate and the mineral surfaces drastically reduced adsorption.

The empirical difference between the goethite and hematite isotherms probably lies in the more reactive goethite surface and in the greater surface area of goethite (Table I). Both of these factors would tend to enhance the adsorption of glyphosate by goethite compared to that of hematite at the lower pH values. The data indicate that kaolinite, hematite, and goethite adsorb glyphosate through the electrostatic attraction of the negative moieties of glyphosate to positively charged sites on the mineral surface.

CONCLUSIONS

The adsorption of glyphosate by the clays varied with changes in pH and for the smectites with changes in saturating cations. Generally, as pH increased, the adsorption of glyphosate decreased. This effect is due to decreased interaction as both the clay and glyphosate became more negatively charged. Exceptions to this may occur if aluminum polymers form in smectite interlayers, which lower the negative charge of the clay and provide extra sites for anion adsorption, or if dissolution of the smectite occurs.

Nontronite adsorbed larger amounts of glyphosate than montmorillonite. It is postulated that precipitation of iron–glyphosate complexes accounts for most of the great difference between montmorillonite and nontronite at low pH (pH 2.0). At higher pH values the difference in glyphosate adsorption between the two smectite minerals narrows. The difference between nontronite and montmorillonite (same saturating cation and pH) is related to the surface area of nontronite (908 m^2 g^{-1}) and montmo-

rillonite (813 m^2 g^{-1}). The greater surface area of nontronite accounts for the greater adsorption in most cases.

The influence of saturating cation of the smectites on glyphosate adsorption was related to the charge of the cation. Even though some of the isotherms were not statistically different, the trends show that Al^{3+}–montmorillonite adsorbed more glyphosate than Ca^{2+}–montmorillonite, which was greater than Na^+–montmorillonite. The same trend was observed for nontronite. The relationship of the saturating cation of the smectite to glyphosate adsorption indicated that glyphosate was bound to the exchangeable cations and that higher charged cations are capable of complexing more glyphosate than lower charged cations.

Kaolinite, hematite, and goethite adsorption of glyphosate is pH dependent. The system pH determines the charge of both the glyphosate molecules and the mineral surface. Adsorption is maximized when electrostatic attraction and interaction are maximized.

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