AN ABSTRACT OF THE THESIS OF

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Title: REACTIONS OF PICLORAM AND 2,4-D WITH

MONTMORILLONITE CLAYS AND SOILS

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Mobility and adsorption of carboxyl-^{14}C labeled 4-amino-3,5,6-trichloropicolinic acid (picloram) and (2,4-dichlorophenoxy)acetic acid (2,4-D) on 43 western soils, measured with soil thin-layer radiochromatography and batch equilibrium techniques, correlated with soil pH, organic matter content, and aluminum extracted with ammonium acetate at pH 4.8. Multiple linear regression models were developed by computer to relate mobility and adsorption of picloram and 2,4-D to soil parameters. Average deviations of mobility predictions were 0.06 and 0.10 R_F units for picloram and 2,4-D, respectively, for the soils tested. The predicted adsorption of picloram and 2,4-D on soils deviated 6.1% and 7.3%, respectively, from measured adsorption values. For agricultural soils with pH < 7, the mobility and adsorption of picloram and 2,4-D could be predicted from soil pH, organic matter, and extractable aluminum. The predictive

equations for mobility of picloram and 2, 4-D were less applicable to soils with pH > 7.

In KCl or $CaCl_2$ solutions with concentrations less than 0.5 $\underline{N}$, the picloram solubility was higher than in water. Upon increasing the salt concentration to 0.5 $\underline{N}$ or higher, the picloram solubility decreased to 446 and 499 ppm from 597 ppm at the 2.5 $\underline{N}$ KCl and $CaCl_2$ solution, respectively. The greater effect on the salting-out of picloram by increasing KCl concentration was explained by water molecule orientation around K^+ as compared with Ca^{++}.

After 1 or 10% activated charcoal was added to the Molokai and Lookout soils, picloram mobility was drastically retarded as measured by soil thin-layer radiochromatography. The mobility of picloram and 2, 4-D in Minam, Woodcock, and Kinney soils was reduced by addition of HCl. Elution of HCl-treated soils with 2 $\underline{N}$ KCl solution as compared to water, did not increase mobility of picloram and 2, 4-D.

The adsorption of picloram by H-montmorillonite increased from less than 10% to over 90% at 5, 25, and 125 ppm initial picloram concentrations as the suspension pH decreased from 2.6 to 0. With an increase in acidity the picloram was hydrogen bonded to the clay colloid surface. Adsorbed picloram was quantitatively recovered from H-montmorillonite with repeated water wash treatments with the picloram recovery directly related to the increase in suspension pH.

The adsorption of picloram by acid H-montmorillonite paralleled the picloram dissociation curve and the Freundlich isotherm. The measured adsorption values were less than would be suggested by the picloram dissociation curve because of the presence of a proton sink in the H-montmorillonite system. The kd values for the Freundlich isotherm ranged from 2.9 at pH 2.6 to 7586 at pH 0. The slopes of Freundlich isotherms decreased from 1.96 to 1.20 as the suspension pH increased from 0 to 2.6.

Acidified picloram, a derivative of 4-amino-pyridine, did not differ in absorption spectrum from its parent compound after acid treatments, thus indicating an absence of protonation. The picloram molecule could not accept an extra proton due to its dipolar nature, low basicity, and the presence of strong electron withdrawing chloro and carboxylate functional groups. The 4-amino-pyridine accepted a proton on the annular nitrogen in an acid environment (3.6 $\underline{N}$ HCl), as shown by the new absorption bands appearing at 1036 and 1660 cm^{-1} after the acid treatment.

The reaction of picloram with H-montmorillonite adjusted to pH 1.6 increased the carbonyl stretching frequency of picloram from 1705 to 1724 cm^{-1} and NH_2 deformation bands from 1540 and 1602 to 1566 and 1632 cm^{-1}. The increase in carbonyl stretching frequency indicated a preferential interaction between the annular nitrogen rather than the carbonyl oxygen of the picloram molecule with

H-montmorillonite. The infrared spectrum of the Al-montmorillonite-picloram system adjusted to pH 1.6 was similar to the one for picloram-H-montmorillonite at pH 1.6, indicating the association of annular nitrogen of picloram with the aluminum ions through a bridging effect of coordinated water. At pH 3, the infrared spectrum of Al-montmorillonite-picloram system displayed distinct shifts for $\nu C=0$, $\nu C=C$, and $\delta COOH$ bands implying a coordination bond formation between Al and the annular nitrogen atom of the picloram molecule.

The Reactions of Picloram and 2, 4-D with
Montmorillonite Clays and Soils

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DEDICATED TO JUI-IN （瑞吟）

Because of her moral support and unselfish devotion

throughout my many years of graduate studies

I dedicate this thesis

to my wife,

Jui-In

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THE REACTIONS OF PICLORAM AND 2,4-D WITH MONTMORILLONITE CLAYS AND SOILS

INTRODUCTION

Herbicides play an exceedingly important role in agriculture today. Since the herbicidal effect of 2,4-D was reported in 1944 by Marth and Mitchell of the USDA, Beltsville, Maryland, herbicides have been used successfully by the agricultural industry to control the widespread distribution of weeds. Although weeds have been literally described by Emerson as "Plants whose virtues have not yet been discovered" (Appleby, 1967), scientists have been trying in various ways to control them because of their competition with crops for air, water, sunlight, and nutrients.

The acidic herbicides, picloram and 2,4-D, have been used quite extensively in agriculture. With the use of these herbicides weed competition was reduced and the crop yield per acre of land increased. The long-term use of herbicides year after year, however, may result in damage to subsequent crops due to residual herbicidal activity or in the potential contamination of soil water. Therefore, scientists have recently strived to find better ways by which the contamination of the human environment can be reduced.

The movement and adsorption of herbicides are two of the important reactions of herbicides in the soil environment which

contribute to the residual life of herbicides in surface soils. The soil physicochemical properties, the pesticide properties, and environmental factors such as rainfall, temperature and wind determine the extent of movement and adsorption of herbicides in soils. Therefore, it is the primary objective of this thesis to develop information to predict the residual activity of herbicides in surface soils from the existing knowledge about the soil and environmental parameters.

The addition of soil amendments such as liming materials, organic composts, and acid-forming adjuvents, to improve soil tilth has been a practice in agricultural soils. These soil amendments greatly change the physicochemical properties of surface soils. Because the residual activities of herbicides are dependent upon the extent of their adsorption by surface soil constituents and movement through soil profiles, any change in physicochemical properties of surface soils would change the persistence of herbicides in surface soils. The second phase of this thesis was thus primarily devoted to the studies of the effects of soil amendments on the solubility and movement of herbicides in soils.

Montmorillonite clays play an important role in the soil chemistry of many soils. Studies of the reaction between herbicides and montmorillonite clays would provide certain criteria about soil-pesticide relationships. The acidity of soil solution governs the surface properties of the inorganic soil constituents and the ionization

of many acidic compounds. It is important to know how the adsorption-desorption of herbicides is affected by the changes in acidity of soil solution because it is related to movement of herbicides. The third phase of this study was, thus, based upon the studies of how solution acidity affects the adsorption-desorption of herbicides by montmorillonite clays.

The nature of bonding between organic chemicals and model clays has been investigated quite extensively in recent years. Infrared spectrophotometry has been proved to be one of the frequently used techniques for exploration of bonding mechanisms between herbicides and various adsorbents including model clay minerals. The final section of this thesis was devoted to the use of infrared techniques to follow the changes in picloram adsorption characteristics and determine bond formations with pH changes of picloram-montmorillonite systems.

MOBILITY AND ADSORPTION OF PICLORAM AND
2,4-D IN WESTERN SOILS

Introduction

The residual life of herbicides within a given location depends

upon soil parameters, herbicide properties, microbiological degrada-

tion, and external environmental considerations. The plant nutrient

level of a soil has been related successfully to predicted crop

responses, but very few practical results have been obtained to

quantitatively relate the disposition of a given herbicide in a given

soil.

Phytotoxicity and water contamination by herbicides may be

related to adsorption of the chemical by the soil. Picloram and

2,4-D adsorption by soils increased with a decrease in soil pH

(Hamaker, Goring and Youngson, 1966; Weaver, 1947), with an increase

in soil organic matter (Grover, 1968; Hamaker et al., 1966; Upchurch

and Mason, 1962) and metal oxides (Frissel and Bolt, 1962), and with

an increase in clay content (Hamaker et al., 1966).

The influence of pH on adsorption increased markedly as the pK

values of 2,4-D (2.8) and picloram (3.4) were approached. When the

pH >> pK, 2,4-D and picloram, both weak carboxylic acid compounds

were primarily present in the anionic forms while the molecular forms

of 2,4-D and picloram dominate when the pH << pK. Frissel and Bolt

(1962) reported the existence of both positive and negative adsorption of 2,4-D on montmorillonite and illite as a function of pH. Montmorillonite negatively adsorbed 2,4-D at pH values above 3 while illite exhibited negative adsorption only above pH 7. The adsorption isotherms of 2,4-D on montmorillonite and illite showed a marked slope change at a pH of about 4, caused by the transition of 2,4-D anions to 2,4-D molecules. Whether 2,4-D and picloram are present in the molecular or the anionic form can affect the extent of adsorption and the strength by which they are held since the energy of adsorption may be greatly different between dissociated and associated forms (Bailey and White, 1970).

Closely related to chemical adsorption is chemical movement, either through various diffusion pathways or with mass water migration. Several investigators (Goring, Youngson and Hamaker, 1965; Hamaker et al., 1966; Harris and Warren, 1964; Herr, Stroube and Ray, 1966; Ogle and Warren, 1954; Phillips and Feltner, 1972) have correlated increased 2,4-D and picloram movement with lighter textured soils and with low organic matter levels. Harris and Warren (1964) have reported more desorption of 2,4-D from bentonite than from muck soils, in agreement with observed leaching measurements. The movement of 2,4-D and picloram has been related to adsorptive capacity of the soil, water flux, temperature, and soil properties (Helling, 1971c).

One of the primary goals from adsorption-desorption, movement, degradation, and volatilization studies with herbicides is to predict the disposition of a herbicide upon application to the soil. Because of the rather involved techniques associated with column leaching studies, Helling and Turner (1968) and Helling (1971b) have utilized soil thin layer chromatography (TLC) to categorize agricultural chemicals and soils. Soil TLC plates do not provide results directly transposable to conventional field studies because of synthetic conditions created during soil sample preparation (Helling, 1971a); nevertheless this technique is useful to relate soil properties to chemical mobility. Helling (1971a) has observed that picloram and 2,4-D movement was insensitive to removal of coarse and medium sand fractions, thin layer thickness, temperature, and sample size; whereas mobility decreased with decrease in soil pH. Increased water flux tended to relate directly to picloram and 2,4-D mobility (Helling, 1971a).

To predict the movement or adsorption of herbicides based on a single soil property has only limited application. The objective of this research was to determine the combination of soil parameters useful to predict the movement and adsorption of 2,4-D and picloram in western soils.

Materials and Methods

Chemical Characterization of Soils

Soils from Oregon, Washington, Hawaii, and New Mexico were characterized by routine chemical analysis (Appendix Table 1). Soil pH was measured in a 1:1 soil:water system and soil organic matter content was determined by the modified Walkley-Black procedure (Walkley and Black, 1934). Cation exchange capacity was determined by saturation with 0.5 N $CaCl_2$ and subsequent replacement of Ca by 0.5 N $MgCl_2$. Extractable Al was obtained by four extractions with pH 4.8 N ammonium acetate (NH_4OAc). Exchangeable Ca, Mg, and K were determined on pH 7 N NH_4OAc extracts. The cations, Ca, Mg, K, and Al, were assayed by atomic absorption.

Adsorption of Picloram and 2,4-D

Duplicate 5-g air-dry soil samples (sieved at 500 μ) were equilibrated with 10 ml of 10 ppm ^{14}C-labeled picloram (specific activity = 0.142 μC/mg) or 2,4-D solution (specific activity = 0.127 μC/mg) at 25°C in a constant temperature water bath for 24 hr. The supernatant solution was separated by centrifugation of the systems at 15,000 rpm for 5 minutes. A 1-ml aliquot of the supernatant was pipetted into a 10 ml fluor which contained 5.5 g/L 2,5-diphenyloxazole (PPO), 0.1 g/L 1,4-di-[2-(5-phenyloxazolyl)] benzene

(POPOP), in 2:1 (v/v) toluene:Triton X-100. The ^{14}C activity was radioassayed with a liquid scintillation counter. Adsorption of the chemicals was calculated from the difference in herbicide concentration in the original and equilibrium solution.

Soil Thin-Layer Radiochromatography

Coarse sands (> 500 μ) were removed from the soils by dry sieving. A soil slurry was prepared by mixing the sieved soil with water until moderately fluid (Helling and Turner, 1968). Duplicate thin-layer soil plates (20 cm by 5 cm) were prepared by distributing the soil slurry on the glass surface with a glass rod taped on the ends to provide appropriate soil thickness. Upon air-drying, the soil thin-layer plate was spotted with ^{14}C-labeled herbicide (2. 45 μg ^{14}C-picloram in 5 μl ethanol; 1. 15 μg ^{14}C-2, 4-D in 30 μl ethanol) at 4 cm above the base. The specific activities of ^{14}C-picloram and ^{14}C-2, 4-D were 4 μC/mg, and 11 μC/mg, respectively. After evaporation of ethanol, the plate was placed vertically in a closed glass chamber containing 2 cm of water. The plate was removed when the water front reached 10 cm above the origin. The time elapsed to reach 10 cm was recorded and the average water flux (cm/hr) calculated. The soil plate was oven-dried immediately and the ^{14}C activity on the plate was assayed with a radiochromatogram scanner system.

R_F values for the mobility of 2, 4-D and picloram on the soil

TLC plate were calculated:

$$R_F = \frac{\text{Distance between the origin and the point of maximum } ^{14}\text{C activity}}{\text{Distance between the origin and the water front}}$$

Multiple Linear Regression Analysis

Simple correlation coefficients were calculated and multiple linear regression equations were prepared to relate the mobility and adsorption of the herbicides to the soil parameters. After the multiple regression equations were obtained, 11 randomly selected soils were characterized for soil pH, soil organic matter content, and pH 4.8 $\underline{N}$ NH_4OAc extractable Al. Movement and adsorption of 2,4-D and picloram were measured on the 11 soils and correlation coefficients calculated to test the reliability of the equations developed to predict the mobility and adsorption of herbicides.

Results and Discussion

Development of Multiple Linear Regression Models

Adsorption of picloram and 2,4-D increased with organic matter and extractable Al content of soils (Figure 2-1B, C, E, and F). A decrease in soil pH caused a marked increase in adsorptive capacity of soils for picloram and 2,4-D (Figure 2-1A and D). Omission of the
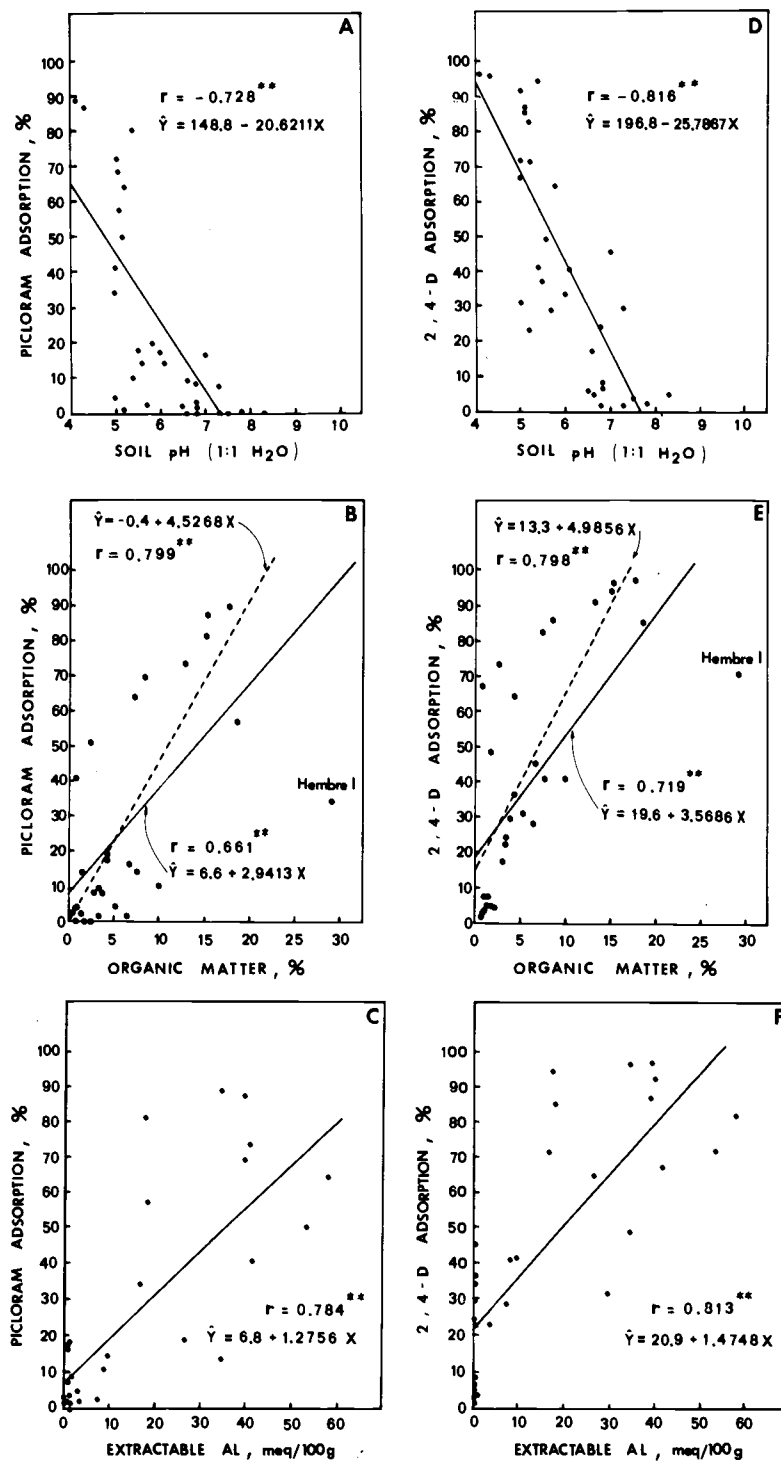
Figure 2-1. Correlation between adsorption of picloram and 2, 4-D with pH, organic matter, and extractable Al for 32 western soils. Hembre 1 soil not included in Figure B and E -----.

Hembre 1 soil, which contained 29% organic matter, from the regres-
sion analysis improved the correlation of adsorption of picloram and
2, 4-D with organic matter. Simple correlation coefficients increased
from 0. 661** to 0. 799** for picloram and from 0. 719** to 0. 798** for
2, 4-D, respectively. The importance of Al, pH, and organic matter
on the reaction of picloram with soils has been pointed out by Hamaker
et al. (1966). Aside from the three parameters described above,
exchangeable Ca, Mg, and total bases also were significantly corre-
lated with adsorption of picloram and 2, 4-D (Table 2-1); however, these
parameters did not exhibit as good a correlation with adsorption of
picloram and 2, 4-D as reflected by the scatter of data points about the
regression lines. Even for the pH, organic matter, and extractable
Al content of the soil, one can see considerable point scatter, reflect-
ing the need for consideration of several soil parameters in relation
to herbicide adsorption.

Mobility of picloram and 2, 4-D in terms of R_F values also
correlated significantly with soil pH, extractable Al, organic matter
content, exchangeable bases (Ca, Mg), and water flux (Table 2-1 and
Figure 2-2). The Hembre 1 soil again affected the slopes of regression
lines relating mobility of picloram and 2, 4-D to organic matter (Figure
2-2B and E). Upon omission of this soil from regression analysis, the
negative correlation coefficients increased to 0. 637** and 0. 692**
from 0. 527** and 0. 630** for mobility of picloram and 2, 4-D, respec-
tively.

Table 2-1. Simple regression correlation coefficients (r) between mobility or adsorption of picloram and 2, 4-D and soil parameters for 32 western soils.

| Soil parameter | Correlation coefficients[a] | | | |
| | Mobility | | Adsorption | |
	Picloram	2, 4-D	Picloram	2, 4-D
Cation exchange capacity	0. 173	0. 040	-0. 190	-0. 076
Exchangeable bases	0. 571**	0. 511**	-0. 507**	-0. 541**
Exchangeable Ca	0. 527**	0. 455**	-0. 475**	-0. 492**
Exchangeable Mg	0. 565**	0. 647**	-0. 492**	-0. 647**
Exchangeable K	0. 238	0. 058	-0. 161	-0. 037
Water flux	-0. 520**	-0. 439*	--	--

[a]* significant at 5%; **significant at 1% probability level
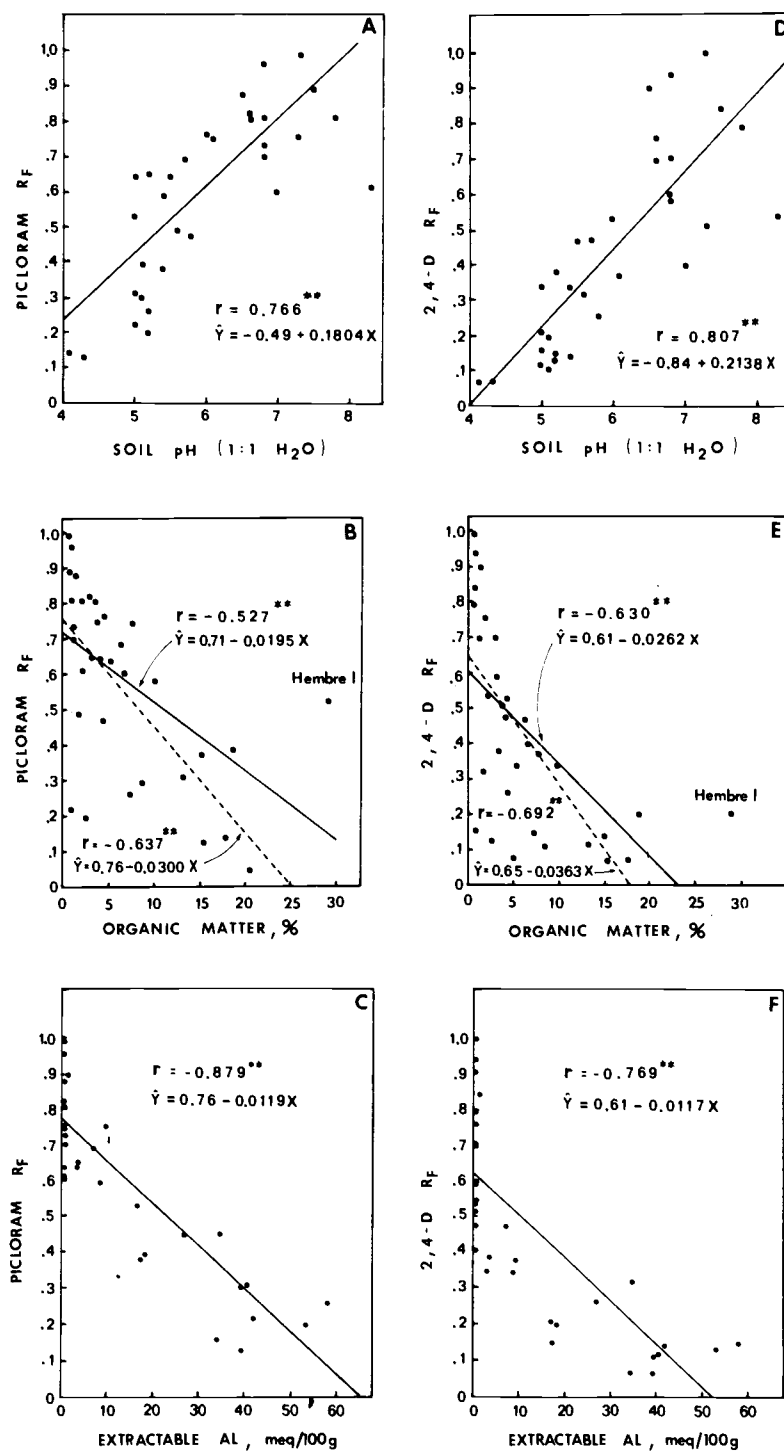
Figure 2-2.   Correlation between mobility of picloram and 2, 4-D with pH, organic matter, and extractable Al for 32 western soils.   Hembre 1 soil not included in Figure B and E ------.

The water flux negatively correlated with mobility of both

chemicals (Appendix Figure 1). There was, however, considerable

point scatter about the regression line. Helling (1971c) observed a

direct relationship between mobility of picloram and 2, 4-D with water

flux. Although the correlation was significant at the 5% level, Helling

did indicate some uncertainty in the relationship between water flux

and mobility of chemicals.

Since movement of chemicals is subject to interaction with soil

components through physical or chemical forces, adsorption-

desorption kinetics of chemicals by active soil components is often

thought to govern the mass transport of chemicals in soil-water

systems. It is, therefore, logical to consider the adsorption of

picloram and 2, 4-D by soils as the best predictor for their mobility in

soils. This was supported by a high correlation coefficient obtained

between mobility and adsorption of picloram and 2, 4-D (Figure 2-3).

Picloram mobility negatively correlated with the adsorption of 2, 4-D

($r = -0.909**$) and picloram ($r = -0.873**$). Negative correlation

coefficients between 2, 4-D mobility and adsorption of picloram and

2, 4-D were $-0.797**$ and $-0.924**$, respectively. The correlations

between picloram and 2, 4-D adsorption and mobility relate to their

chemical similarities.

Although mobility and adsorption of picloram and 2, 4-D were

significantly correlated with individual soil parameters (Figures 2-1, -2,
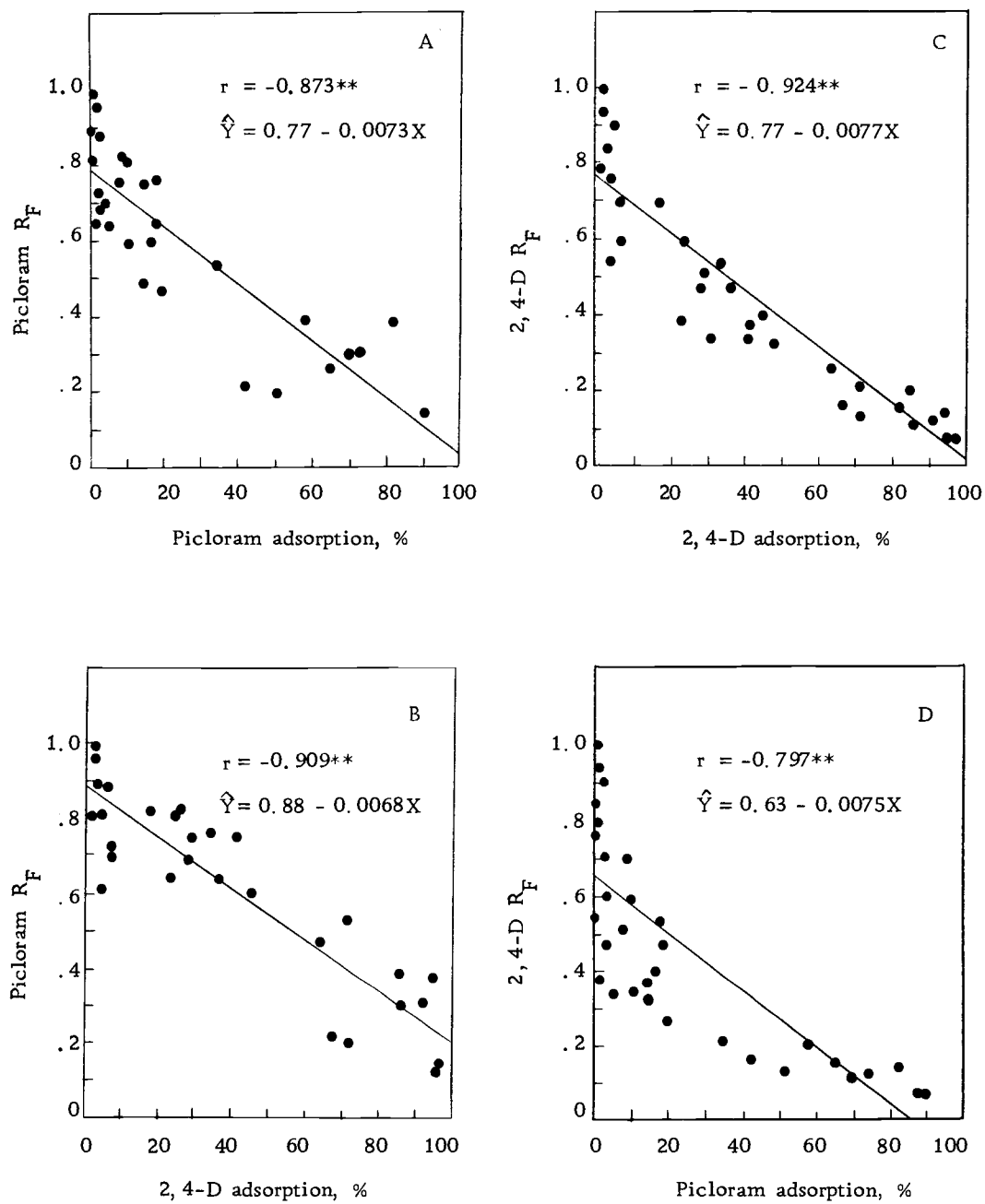
Figure 2-3. Correlation between mobility and adsorption of picloram and 2,4-D on 32 western soils.

-3, and Table 2-1), the point scatter in the correlations exceeded that desirable for good predictive capacity. Stepwise multiple linear regression analyses were, therefore, employed to develop regression models by which the mobility and adsorption of picloram and 2,4-D could be predicted from the soil parameters (Appendix Tables 2, 3, and 4).

Extractable Al, organic matter, exchangeable K, pH, and exchangeable bases accounted for 89.2% of soil-to-soil variability in picloram mobility (Table 2-2). Exchangeable K was not significantly correlated with picloram mobility (Table 2-1); however, the inclusion of this variable into the regression model reduced substantially the residual variability for predicting picloram mobility. Soil pH, extractable Al, organic matter, and exchangeable Ca accounted for 82.1% of variance in predicting 2,4-D mobility (Table 2-2). The inclusion of exchangeable Ca instead of K for predicting 2,4-D mobility also reduced the residual variability.

Regression models for adsorption of picloram contained extractable Al, organic matter, CEC, exchangeable Ca, and exchangeable K parameters which accounted for 91.6% of variance. The fraction of variance in prediction of 2,4-D adsorption accounted for by the extractable Al, organic matter, pH, CEC, and exchangeable Ca was 93.8% (Table 2-2).

As mentioned earlier, adsorption of picloram and 2,4-D was

Table 2-2. Summary of multiple regression coefficients relating mobility and adsorption of picloram and 2, 4-D to soil parameters for 32 western soils.

Dependent Variable	Constant of Regression	2,4-D Ads.	Picloram Ads.	Independent variable[a]							R^2	Standard Error (%)	Average Deviation (%)
				pH	Extractable Al	O. M.	CEC	Exch. Bases	Exch. Ca	Exch. K			
Picloram R_F	0.84	-0.0046***	---	---	-0.0058***	---	---	-0.0030	---	0.0836**	0.922	7.0	6.0
Picloram R_F	0.26	---	---	0.0870**	-0.0100***	-0.0051	---	-0.0079*	---	0.0876***	0.892	9.0	6.0
2,4-D R_F	0.80	-0.0129**	0.0062***	---	---	---	---	---	---	0.0462	0.900	9.0	6.0
2,4-D R_F	-0.10	---	---	0.1298**	-0.0076***	-0.0103*	---	---	-0.0089*	---	0.821	10.3	9.0
Picloram Ads.	6.0	---	---	---	0.9493***	3.3576***	-1.2681***	---	1.2671**	-9.1808*	0.916	9.4	6.4
2,4-D Ads.	62.2	---	---	-8.2881**	0.9801***	2.7023***	-0.6230**	---	1.0303**	---	0.938	8.9	6.7

[a] *significant at 5%; ** significant at 1%; *** significant at 0.1%; rest significant at 10% probability level

significantly correlated with their mobility in soils. Inclusion of

adsorption data as independent variables caused the adsorption of

2, 4-D to enter the regression models preferentially to simple soil

parameters. The R^2 increased from 0.892 to 0.922 for picloram

mobility and from 0.821 to 0.900 for 2, 4-D mobility (Table 2-2).

Exclusion of adsorption data as independent variables showed that pH,

extractable Al, and organic matter were the three most important

predictors for either mobility or adsorption of 2, 4-D and picloram

mobility. Soil pH was not included in the regression model for pre-

dicting picloram adsorption. This could be due to a high correlation

inherently existing between pH and extractable Al (r = -0.679**).

Helling (1971c) developed a regression model (R^2 = 0.828) which

contained CEC and chlorpropham adsorption to predict picloram

mobility. The use of chlorpropham adsorption as a predictor was

somewhat unexpected because of the dissimilarities in chemical

structures of picloram and chlorpropham. For 2, 4-D mobility,

Helling (1971c) obtained a regression model (R^2 = 0.864) which

included chlorpropham adsorption, pH, simazine adsorption, and

water flux. Again, inclusion of adsorption of chlorpropham and

simazine into the model was not expected because the acidic 2, 4-D

should behave in a different manner than non-ionic chlorpropham or

simazine. Bailey, White and Rothberg (1968) had proposed possible

adsorption mechanisms for many organic chemicals in which 2, 4-D,

chlorpropham, and triazine compounds were shown to behave quite differently from one another.

Test of Regression Models

Multiple linear regression equations were developed to predict the mobility or adsorption of picloram and 2, 4-D from pH, extractable Al, and organic matter. Eleven soils were characterized (Table 2-3) for these three properties and the mobility and adsorption of picloram and 2, 4-D were measured and predicted from the regression model equations (Figure 2-4). The average deviations of predicted values from measured values for picloram R_F and 2, 4-D R_F were 0.06 and 0.10, respectively, which were within the standard errors of the regression equations. The respective average deviations of adsorption values were 6.1% for picloram and 7.3% for 2, 4-D.

Because high-pH agricultural soils (pH $\geq$ 7) were not normally found in western Oregon, the 43 soils were subdivided into two groups according to their pH values (Table 2-4). Thirty-one soils had a pH < 6.9 while 12 soils had a pH $\geq$ 7.0. Because of the high water flux and low adsorptive capacity for picloram and 2, 4-D, Ephrata sl (0-15; 15-36 cm) soils were omitted from the category of pH < 6.9. Boyce 1 and Stearns 1 soils were similarly omitted from the category of pH $\geq$ 7.0. The improvement in predicting mobility of picloram and 2, 4-D upon grouping soils into pH < 6.9 was shown by the increase of R^2

Table 2-3. Properties of soils used to test the multiple regression models.

Soil series	pH (1:1 H_2O)	O. M (%)	Extractable Al (meq/100 g)	Water flux (cm/hr)
Parkdale sil	6. 6	1. 2	12. 4	30. 3
Glendale s cl 1	7. 4	1. 4	0. 6	3. 6
Dayton sil	4. 8	3. 1	1. 7	4. 3
Stearns 1	8. 6	3. 4	0. 2	7. 6
Coker c	6. 7	3. 4	0. 5	2. 2
Cloquato sil	5. 8	1. 1	0. 7	5. 1
Amity sil	6. 0	4. 4	1. 1	2. 4
La Grande sil	8. 1	4. 0	0. 2	1. 9
Deschutes sl	7. 0	1. 0	0. 2	8. 8
Crooked sil	7. 7	3. 5	0. 2	2. 1
Quincy sl	7. 5	0. 8	0. 4	7. 9
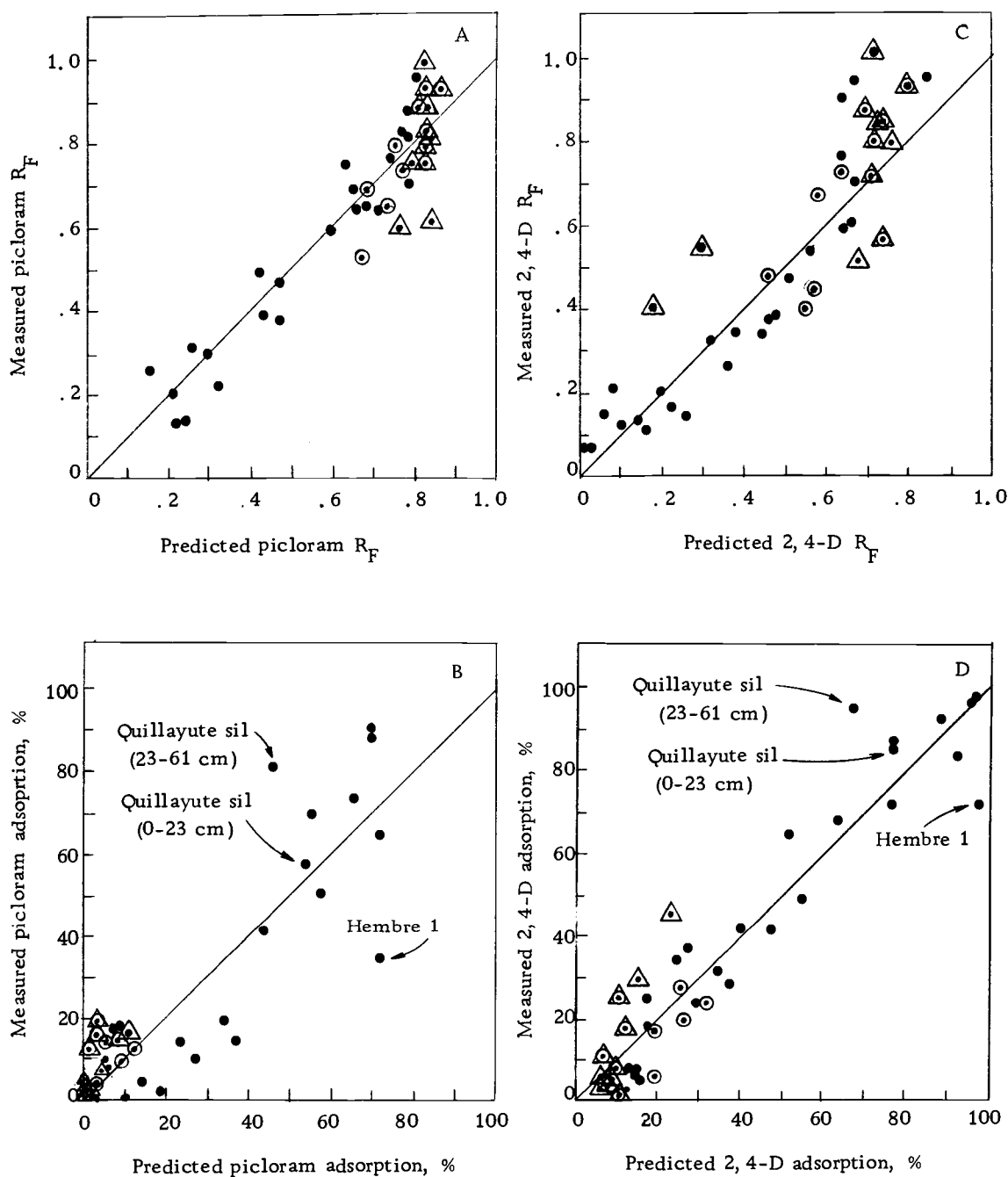
Figure 2-4. Relationships between the measured and predicted values for mobility and adsorption of picloram and 2, 4-D on 43 western soils. The solid lines indicated the 1:1 correlation. ⊙ = soils used for testing regression models; ● = soils with pH < 6.9; ⬠ and △ = soils with pH ≥ 7.0.

Table **2-4**. Multiple regression coefficients among herbicide R_F values, herbicide adsorption capacity and soil parameters for soils grouped by pH values.

Model No.	No. of Soil Samples	Soil pH Range	Dependent Variable	Constant of Regression	Multiple regression coefficients for the independent variable [c]			R^2	Standard Error (%)	Average Deviation (%)
					Extractable Al	pH	Organic Matter			
1	32	4.1-8.3	R_F picloram	0.51	-0.0094***	0.0434	-0.0067	0.846	10.0	8.0
2	29[a]	<6.9	R_F picloram	0.29	-0.0088***	0.0738	-0.0032	0.893	8.0	6.0
3	12	≥7.0	R_F picloram	0.89	-0.1337	0.0134	-0.0500	0.454	10.0	7.0
4	10[b]	≥7.0	R_F picloram	0.70	-0.0298	-0.0320	-0.0458	0.677	8.0	4.0
5	32	4.1-8.3	R_F 2,4-D	0.09	-0.0069***	0.0878*	-0.0115*	0.788	13.0	10.0
6	29[a]	<6.9	R_F 2,4-D	-0.09	-0.0062***	0.1103***	-0.0072*	0.876	8.0	6.0
7	12	≥7.0	R_F 2,4-D	0.70	-0.1627	0.0405	-0.0857**	0.588	14.0	10.0
8	10[b]	≥7.0	R_F 2,4-D	1.16	-0.0473	-0.0283	-0.0842**	0.782	10.0	6.0
9	32	4.1-8.3	Picloram Ads.	10.2	0.9747***	-1.8121	1.8686**	0.795	14.1	9.5
10	29[a]	<6.9	Picloram Ads.	22.7	0.9370***	-3.7925	1.7697**	0.766	15.0	10.6
11	12	≥7.0	Picloram Ads.	-9.4	-6.0904	1.6129	2.8233**	0.790	3.9	2.5
12	10[b]	≥7.0	Picloram Ads.	-41.9	-3.3730	5.7872	3.0702**	0.858	3.5	2.0
13	32	4.1-8.3	2,4-D Ads.	51.3	0.9818***	-6.0715	2.0799***	0.898	11.1	8.1
14	29[a]	<6.9	2,4-D Ads.	50.2	1.0237***	-6.1064	2.0324***	0.899	10.4	7.4
15	12	≥7.0	2,4-D Ads.	43.9	2.9064	-6.5774*	-7.2919***	0.949	3.7	2.5
16	10[b]	≥7.0	2,4-D Ads.	3.1	4.1813	-1.1877	7.5341***	0.972	3.1	1.8

[a] Exclusion of two Ephrata sl soils

[b] Exclusion of Boyce 1 and Stearns 1 soils

[c] *significant at 5%; **significant at 1%; ***significant at 0.1%; rest significant at 10% probability level

from 0.846 to 0.893 for picloram mobility and from 0.788 to 0.876

for 2,4-D mobility (Table 2-4). However, the prediction of adsorption

of picloram and 2,4-D was not improved upon grouping soils into pH <

6.9.

On the other hand, the prediction of mobility of picloram and

2,4-D became worse when the soils of pH $\geq$ 7.0 were grouped. Group-

ing of soils of pH $\geq$ 7.0 did improve the prediction for adsorption of

picloram and 2,4-D. The R^2 of the equations relating mobility of

picloram and 2,4-D to pH, extractable Al, and organic matter for the

12 soils of pH $\geq$ 7.0 were 0.454 and 0.588, respectively. Since only

45.4% and 58.8% of the soil-to-soil variation in predicting mobility of

picloram and 2,4-D in soils of pH $\geq$ 7.0 were attributed by pH,

extractable Al, and organic matter, one might conclude that parameters

other than these three accounted for the variation in chemical mobility.

In fact, the salt content in high pH soils (pH $\geq$ 7.0) could be a better

predictor for mobility of picloram and 2,4-D. Helling (1971a)

observed a drastic decrease in 2,4-D mobility on Norfolk sil TLC

plate after NaCl concentration in soil exceeded 0.1 $\underline{M}$.

Based upon the multiple regression equations developed for the

43 soils (Table 2-4), the individual deviations of the predicted value

from the measured value of 2,4-D and picloram movement and adsorp-

tion was calculated (Figure 2-4). Among the 43 soils, Minam sil

(61 to 84 cm), Quillayute sil (23 to 61 cm), Ephrata sl (0 to 15; 15 to

36; 36 to 53 cm) and Hembre 1 soils deviated to the greatest extent

(R_F deviation > 0.10; adsorption deviation > 15%). The measured

mobilities for these soils were always greater than predicted ones.

Water flux and adsorption data of these soils showed that the Minam

sil and Ephrata sl soils have very small picloram and 2, 4-D adsorp-

tive capacity and have a high water flux (> 8 cm/hr). For the Minam

sil (0 to 23 cm) and Boyce 1 soils, the measured mobilities were less

than predicted values. This could be caused by the low water flux

which allowed the chemicals to react with soil components for a longer

time. The direct relationship between the adsorption of 2, 4-D by

anion-exchange resin and time of reaction (0 to 96 hr) was indicated

by Weber, Perry and Upchurch (1965). The adsorption of picloram

and 2, 4-D by Quillayute sil (23 to 61 cm) as predicted from pH, O.M.,

and extractable Al deviated to a greater extent as compared with the

surface horizon (0 to 23 cm) (Figure 2-4). The two horizons of

Quillayute sil soils are similar in pH, O.M., and extractable Al con-

tent. The difference in the active fraction of organic functional groups

for this allophanic soil may account for a greater deviation in pre-

dicted adsorption values in the lower horizon soil.

Summary and Conclusions

Among the nine chemical properties of soils characterized by

routine chemical analyses, soil pH, organic matter, and extractable

Al were the three most important parameters which determined the adsorption and movement of picloram and 2, 4-D in 43 western soils. The models developed by stepwise multiple linear regression analyses successfully predicted the adsorption and movement of picloram and 2, 4-D from soil pH, organic matter and extractable Al parameters. More than 78% of soil-to-soil variation in prediction could be accounted for by these three parameters.

When the soils of pH < 6. 9 were grouped, the prediction of mobility of picloram and 2, 4-D was improved while the prediction for adsorption was not improved. The prediction of mobility of picloram and 2, 4-D decreased when the soils of pH $\geq$ 7. 0 were grouped.

For the soils with low adsorptive capacity for chemicals and high water flux, the measured mobility values were greater than predicted ones. For the soils with low water flux, the measured mobilities were less than predicted values because chemicals reacted with soil components for longer time periods.

PICLORAM SOLUBILITY IN SALT SOLUTIONS

Introduction

Herbicide solubility relates closely to herbicide movement, residual activity, and resultant phytotoxicity. Upon application of a herbicide to soils, the compound may be adsorbed and consequently desorbed as the moisture conditions change. In addition to the solvent phase in the soil, considerable quantities of cations and anions may occur as a solute. Thus the solubility of organic chemicals in salt solutions becomes important as one relates the partition of the chemical between the solid and liquid phase to its observed phytotoxicity.

The extent of herbicide toxicity has been related to its adsorption on surfaces present in soils. Within a family of some herbicides, it appears that increased water solubility may correlate with decreased adsorption and therefore, increased mobility. Leopold, Schaik and Neal (1960) reported an increase in the extent of chloro-substitution of the aromatic ring of phenoxyacetic acids reduced their water solubility and increased adsorption on soils. In a study of the adsorption of 52 structurally related N-phenylcarbamates, acetanilides, and anilines onto three model organic adsorbents, nylon, cellulose triacetate, and cellulose, Ward and Upchurch (1965) reported an inverse relationship between water solubility and adsorption accounted for 60% of the total variation in adsorption.

On the other hand, herbicide adsorption has also been observed to increase with increase in water solubility. Bailey et al. (1968) compared the extent of adsorption of a wide variety of basic herbicides onto Na- and H-montmorillonite utilizing the Freundlich K value as a criterion of adsorption and concluded that the adsorption of both the s-triazines on Na-montmorillonite and substituted ureas on H-montmorillonite increased with an increase in water solubility. For a particular family of adsorbates, the surface acidity and the relative polarity of the adsorbent interact to determine the relationship between water solubility and adsorption (Bailey and White, 1970).

The chemical adsorption and water solubility of a chemical have been considered as approximate indicators of its leachability in soil-water systems. Gray and Weierich (1968) observed a direct correlation between mobility of six thiocarbamate herbicides in soils with water solubility. However, Rodgers (1968) found the leaching of seven triazines in sandy loam correlated rather poorly with water solubility.

Although the correlations between water solubility and adsorption of chemicals have been studied quite extensively, studies of the effects of salt concentration on solubility of herbicides are rather limited. Salts in a solvent do affect the solubility of chemicals and thus may likely affect herbicide adsorption by soils. Fluometuron adsorption was reduced and prometryne adsorption enhanced on soils when $CaCl_2$ concentrations in equilibrium solutions increased from

0. 01 to 0. 5 $\underline{N}$ (Abernathy and Davidson, 1971). However, differences

in $CaCl_2$ concentration did not appear to influence the mobility of

fluometuron and prometryne in soils.

The objective of this study was to determine the effects of KCl

and $CaCl_2$ concentration on the solubility of 4-amino-3, 5, 6-

trichloropicolinic acid (picloram).

Materials and Methods

Effect of Equilibration Time and KCl Concentration on Picloram Solubility

Aqueous KCl solutions with concentrations ranging from 0,

0. 01, 0. 05, 0. 1, 0. 5, 1. 0, to 2. 5 $\underline{N}$ were adjusted to pH 7 with 0. 01

$\underline{N}$ KOH. The picloram acid salt (0. 1 g) was weighed into 100 ml of

each solution. Each system was equilibrated in a constant temperature

($25^\circ C$) dark room with continuous shaking on a wrist action shaker.

After equilibration times of 88. 5, 113, 185, 256. 5, and 304. 5 hr,

10-ml samples were filtered through Whatman No. 50 filter paper.

The pH of the filtrate solution was measured with a Corning model 7

pH meter equipped with a combination electrode.

Picloram in solution was assayed colorimetrically (Cheng, 1969).

Two ml of the filtrate solution were diluted to 10 ml with water from

which 1 ml was further reacted with 4. 8 ml of 6 $\underline{N}$ H_2SO_4 and 1 ml of

0. 1 $\underline{M}$ $NaNO_2$. The KCl concentration in the final solution was adjusted

to approximately 0.07 $\underline{N}$ with a 2.5 $\underline{N}$ KCl solution. The percent transmittance of the resultant yellow color due to diazotization was read in a room irradiated with yellow light after 10 minutes at 405 mμ with a Spectronic 20 spectrophotometer. The picloram concentration in solution was calculated by comparison to a standard curve ranging from 0, 1, 2.5, 5, 10, 15, to 20 ppm picloram.

Effect of CaCl$_2$ Concentration on Picloram Solubility

Aqueous CaCl$_2$ solutions with concentrations ranging from 0, 0.01, 0.05, 0.164, 0.5, 1.0, and 2.5 $\underline{N}$ were adjusted to pH 7 with 0.01 $\underline{N}$ Ca(OH)$_2$. The picloram solubility in these solutions after equilibration for 192 hr was determined as indicated previously.

Results and Discussion

KCl and Picloram Solubility

The solubility of picloram in the KCl solutions attained a maximum after equilibration between 185 and 256.5 hr (Table 3-1). The solubility of the picloram increased from 597 to 665 ppm as the KCl concentration increased from 0 to 0.1 $\underline{N}$ presumably because of the formation of the more soluble potassium salt of picloram (Herbicide Handbook of the Weed Society of America, 1967). The pH of the equilibrium solution for each system decreased to approximately 3

Table 3-1. Solubility of picloram as a function of equilibration time and KCl and $CaCl_2$ concentration.

Salt	Concentration	Ionic Strength	Picloram Solubility, ppm						$CaCl_2$
			KCl						
			Equilibration Time, hr						
								Average after 185, 256, &	
	$\underline{N}$	μ	88.5	113	185	256.5	304.5	304.5 hr	192
H_2O	0	0	560	578	595	595	602	597	597
KCl	0.010	0.010	571	588	599	620	571	597	--
$CaCl_2$	0.010	0.015	--	--	--	--	--	--	595
KCl	0.050	0.050	606	620	634	655	655	648	--
$CaCl_2$	0.050	0.075	--	--	--	--	--	--	623
KCl	0.100	0.100	613	655	665	655	676	665	--
$CaCl_2$	0.164	0.246	--	--	--	--	--	--	641
KCl	0.500	0.500	637	634	641	655	655	650	--
$CaCl_2$	0.500	0.750	--	--	--	--	--	--	669
KCl	1.000	1.000	595	606	637	655	641	644	--
$CaCl_2$	1.000	1.500	--	--	--	--	--	--	637
KCl	2.500	2.500	410	427	427	452	459	446	--
$CaCl_2$	2.500	3.750	--	--	--	--	--	--	499

after equilibration (Table 3-2). As the picloram reacted with K^+ to form the soluble potassium salt of picloram the H^+ displaced combined with the chloride ion to form hydrochloric acid and reduce the pH of the solution. The solubility of picloram (597 ppm) in water was higher than that obtained by Ramsey (1964); however, no detailed procedure was presented for his water solubility data (430 ppm). As the KCl concentration increased from 0.1 to 1.0 $\underline{N}$, the solubility of picloram decreased. However, the solubility of picloram in $\underline{N}$ KCl was still higher than that in water (Table 3-1). The picloram solubility dropped abruptly to 446 ppm in the 2.5 $\underline{N}$ KCl solution.

$CaCl_2$ and Picloram Solubility

The solubility of picloram in the $CaCl_2$ solution followed the same trend as in the KCl solution except the picloram reached its maximum solubility in a 0.5 $\underline{N}$ $CaCl_2$ solution (Table 3-1). In a 2.5 $\underline{N}$ $CaCl_2$ solution, the solubility of picloram decreased to 499 ppm which was less than the picloram solubility in water (Table 3-1). The equilibrium pH of the picloram-$CaCl_2$ system decreased from 2.97 to 2.49 as the $CaCl_2$ concentration increased from 0 to 2.5 $\underline{N}$ (Table 3-2).

In KCl or $CaCl_2$ solutions with concentrations less than 0.5 $\underline{N}$, the picloram solubility was higher in KCl than in $CaCl_2$ solution (Figure 3-1). Upon increasing the salt concentration to 0.5 $\underline{N}$ or higher, the picloram was more soluble in the $CaCl_2$ solution than in

Table 3-2. pH of picloram solution as a function of KCl and CaCl$_2$ concentration.

Concentration	Solution pH					
	KCl					CaCl$_2$
	Equilibration Time, hr					
$\underline{N}$	88.5	113	185	256.5	304.5	192
0.00	2.94	2.95	2.98	2.97	2.97	2.97
0.01	2.88	2.90	2.94	2.92	2.94	2.85
0.05	2.90	2.87	2.92	2.92	2.90	2.82
0.10	2.85	2.87	2.90	2.90	2.89	--
0.164	--	--	--	--	--	2.77
0.50	2.83	2.82	2.85	2.85	2.82	2.73
1.00	2.82	2.83	2.85	2.85	2.84	2.63
2.50	2.85	2.90	2.90	2.90	2.89	2.49
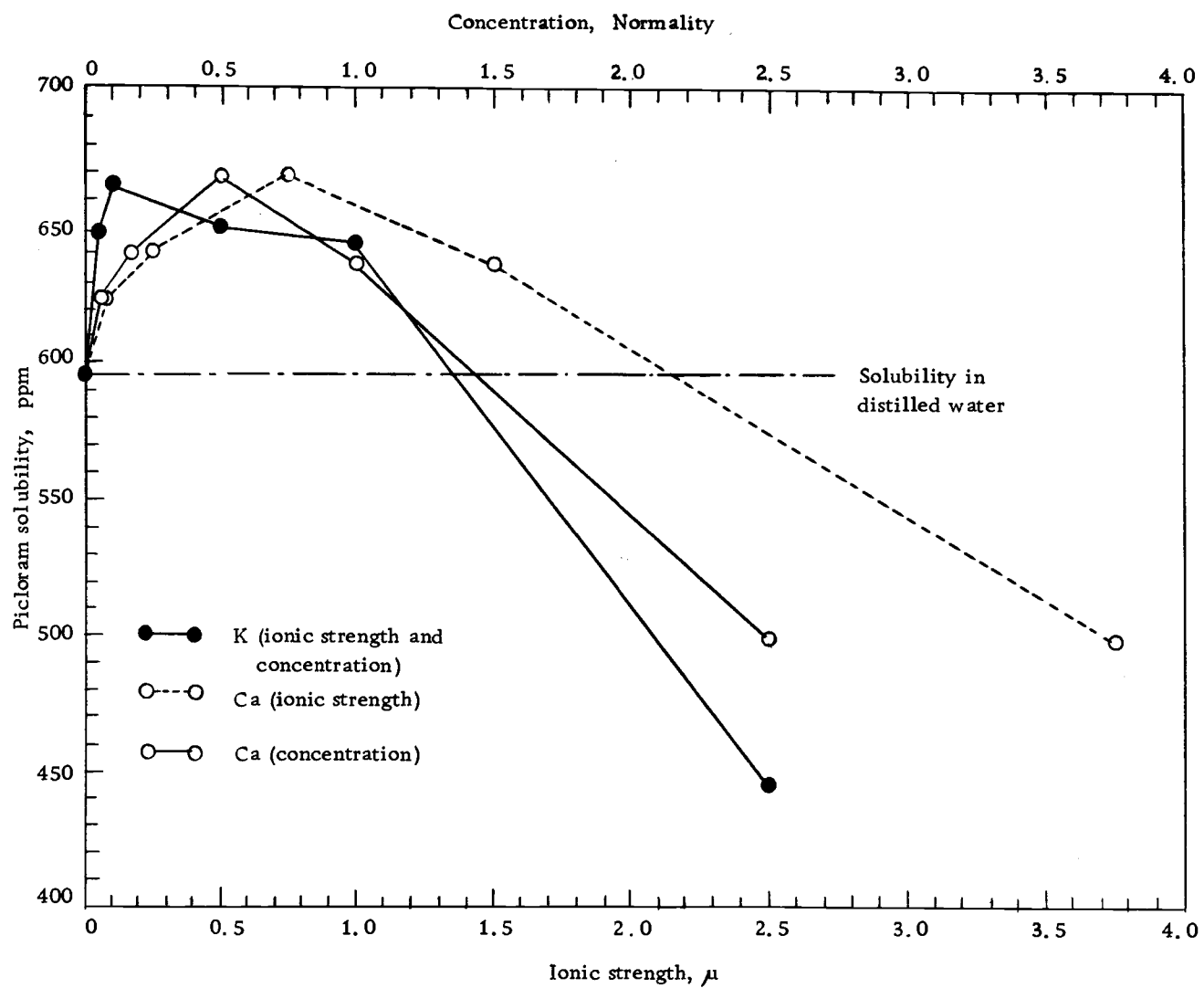
Figure 3-1. Effect of ionic strength and concentration of K and Ca on
picloram solubility.

the KCl solution. The picloram solubility-$CaCl_2$ concentration curve

shifted upon conversion of the concentration figures into ionic strength

(Figure 3-1). At an ionic strength of 0.5 or below, the picloram was

slightly more soluble in the KCl solution than in the $CaCl_2$ solution.

However, the picloram was much more soluble in the $CaCl_2$ solution

than in the KCl solution at an ionic strength above 0.5. The greater

effect on the salting-out of picloram by increasing KCl concentration

can be partially explained by the difference in the hydration energy of

Ca^{++} and K^+ cations. The hydration energy of Ca^{++} and K^+ are 389

and 81 KCal/mole, respectively (Pauling, 1970). Thus, more water

dipoles would tend to orient themselves around Ca^{++} ion as compared

to K^+ ion. This favors the orientation of hydrated Ca^{++} around the

picloram molecule thereby reducing the salting-out effect.

When the solvent system consisted of KCl or $CaCl_2$ with concen-

tration below ca. 1.5 N (Figure 3-1), the concentration of picloram

in the salt solution was greater than in the pure water system (salting-

in effect). The slight increase of picloram solubility in dilute KCl or

$CaCl_2$ solution was caused by the formation of more soluble potassium

or calcium salts of picloram which would enhance the dissociation of

picloram molecule.

Because the total soluble salt concentration normally observed

in soil solution does not exceed 1.5 N, the picloram would be more

soluble in the soil solution than in the pure water system. A higher

chemical solubility in soil solution indicates a greater chemical availability to the percolation water in the soil pores. The salting-in of picloram in the soil solution with low salt concentration would enhance picloram movement through the soil profile thereby reducing the potential accumulation of picloram residue on surface soils.

In high rainfall area, the picloram solubility within the limit of salt concentration encountered in the field may not be sufficiently different to create any effect. However, the salt concentration in the surface soil during dry season could be sufficiently high to cause the salting-out of chemicals.

Summary and Conclusions

The solubility of picloram in water (597 ppm) was affected by addition of KCl and $CaCl_2$ salts. Picloram was more soluble in salt solutions at or below 1.5 $\underline{N}$ than in deionized water. This salting-in effect was caused by the formation of more soluble Ca or K salts of picloram. When the salt concentration increased to 2.5 $\underline{N}$, picloram solubility decreased to 446 ppm in KCl and to 499 ppm in $CaCl_2$ solution. The greater effect on the salting-out of picloram by increasing KCl concentration was explained on the basis of less water dipole orientation around K^+ as compared with Ca^{++}.

EFFECTS OF SOIL AND SOLVENT AMENDMENTS ON MOBILITY
AND ADSORPTION OF PICLORAM AND 2,4-D

Introduction

The movement of herbicides in soils is a complex phenomenon which partially determines the efficacy of soil-applied herbicides. The principal variables which affect the movement of organic chemicals include: (1) soil chemical and physical properties, such as clay, organic matter content, and pH, (2) properties of the pesticide molecule, such as water solubility, molecular weight, polarity, and biodegradability, and (3) environmental factors, such as rainfall, temperature, and wind. The mobility pattern of a pesticide in the soil-water system is thus quite complicated. The residual activity of herbicides on surface soils depends upon their mobility, adsorption-desorption, and degradation in soil-water systems.

Research to control or to remove the residual activity of herbicides has been conducted in recent years. Probably the most promising additive to find commercial acceptance has been activated charcoal (LeBaron, 1970). Activated charcoal adsorbs herbicides and reduces herbicide residual damage. Gast (1962) estimated that 50 to 200 parts of activated charcoal were necessary for complete detoxification of one part of simazine. Research showed that 56 kg/ hec of charcoal deactivated most of the atrazine applied at a rate of

3.6 kg/hec but was less effective at the 5.4 kg/hec application rate (LeBaron, 1970). Under greenhouse conditions, activated carbon, applied as a slurry at the time of seeding, protected Italian ryegrass seedlings from diuron toxicity (Burr, Lee and Appleby, 1972). A mixture of activated carbon and vermiculite was used by Kratky and Warren (1971) to reduce simazine damage to direct-seeded cucumbers and tomatoes in field and greenhouse tests. The increasing concerns over pesticide contamination in ground water warrants the study of the effects of charcoal on mobility of herbicides in soils.

The salts and pH of soil solution also affects herbicide mobility. Previous soil column studies in this laboratory have shown that the mobility of picloram and 2,4-D was significantly reduced with a decrease in soil pH. The presence of Fe, Al, or Cu-saturated homoionic soil also decreased the rate of 2,4-D movement in Lookout sil soil (Kuo, 1970). The mobility of prometryne in Eufaula loamy fine sand and Norge loam soils was decreased by an increase in $CaCl_2$ concentration (0.1-0.5 $\underline{N}$)(Abernathy and Davidson, 1971).

The objective of this study was to investigate the effects of cation distribution, soil pH, and soil amendments on mobility of 4-amino-3,5,6-trichloropicolinic acid (picloram) and 2,4-dichlorophenoxyacetic acid (2,4-D) in selected soils.

Materials and Methods

Chemical Characterization of Soils

Soils were characterized by routine chemical analysis (Appendix Table 1). Soil pH was measured in a soil:water (1:1) system and soil organic matter content was determined by the modified Walkley-Black procedure (Walkley and Black, 1934). Cation exchange capacity was determined by saturation with $0.5 \underline{N}$ $CaCl_2$ and subsequent replacement of Ca by $0.5 \underline{N}$ $MgCl_2$. Extractable Al was obtained by four extractions with pH $4.8 \underline{N}$ ammonium acetate (NH_4OAc). Exchangeable Ca, Mg, and K were determined on pH $7 \underline{N}$ NH_4OAc extracts. The cations, Ca, Mg, K, and Al, were assayed by atomic absorption.

Activated Charcoal and Picloram Mobility

Coarse sands (>500 μ) were removed from the Lookout soil (0-10 cm) of Oregon and Molokai soil (61-79 cm) of Hawaii after which activated charcoal (0.1-10% w/w) was added. A soil-charcoal slurry was prepared by mixing with water until moderately fluid. Duplicate thin-layer soil plates (20 cm by 5 cm) were prepared by distributing the soil slurry on a glass surface with a glass rod taped on the ends to provide appropriate soil thickness. Upon air-drying, the soil thin-layer plate was spotted with ^{14}C-labeled picloram (2.45 μg in 5 μl ethanol) at 4 cm above the base. The specific activity of ^{14}C-picloram

was 4 µC/mg. After evaporation of ethanol, the plate was placed

vertically in a closed glass chamber containing 2 cm of water. The

plate was removed when the water front reached 10 cm above the

origin. The time elapsed to reach 10 cm was recorded and the

average water flux (cm/hr) calculated. The soil plate was oven-dried

immediately and the ^{14}C activity on the plate was assayed with a

radiochromatogram scanner system.

R_F values for the mobility of picloram on the soil TLC plate

were calculated:

$$R_F = \frac{\text{Distance between the origin and the point of maximum } ^{14}C \text{ activity}}{\text{Distance between the origin and the water front}}$$

KCl (pH 7) Solution and
Picloram Mobility

Soil TLC plates were prepared as described previously for the

Oregon soils: Woodcock (0-10, 36-51; 69-111 cm), Kinney (23-46;

46-74 cm), Hembre, Dayton (0-23 cm) and a Washington soil,

Palouse (0-25; 25-46 cm). The R_F values of ^{14}C-picloram on these

soil TLC plates were obtained by radiochromatogram techniques using

either water or $\underline{N}$ KCl (pH 7) as the mobile phase. The R_F values of

^{14}C-picloram on TLC plates of Palouse (25-46 cm) were also obtained

using KCl of various concentrations as a mobile phase. The

concentration of the KCl (pH 7) elution solution ranged from 0, 0.01,

0.05, 0.1, 0.5, 1.0, to 2.5 $\underline{N}$.

HCl and KCl (2 $\underline{N}$)and Mobility of Picloram and 2,4-D

Minam (0-23; 23-33; 61-84 cm), Woodcock (0-10, 35-51; 69-111

cm), and Kinney (23-38; 23-46; 46-74 cm) soils were mixed with 10 ml

of $\underline{N}$ HCl solution and the resultant soil slurries were distributed

uniformly onto soil TLC plates. Water was used as the mobile phase.

The ^{14}C activity was measured after the water front had moved 10 cm.

The ^{14}C-picloram and ^{14}C-2,4-D (1.15 µg in 30 µl ethanol; specific

activity = 11 µC/mg) movement was calculated after measurement of

^{14}C activity with a radiochromatogram scanner. After the soil TLC

plates were scanned for ^{14}C activity, they were again immersed in a

closed glass chamber which contained 2 cm of 2 $\underline{N}$ KCl (pH 7) solution.

The mobility of picloram using 2 $\underline{N}$ KCl as mobile phase was obtained

by the techniques as described earlier.

KCl Concentration and Picloram Adsorption

Solutions of 5, 25, 125 ppm of ^{14}C-carboxyl labeled picloram

were prepared in 0, 0.01, 0.05, 0.1, 0.5, 1, or 2.5 $\underline{N}$ KCl. The

specific activity of ^{14}C-picloram was 0.025 µC/mg in each solution.

Duplicate 5-g air-dry soil samples were equilibrated with 10 ml of

each picloram-KCl solution at 25°C in a constant temperature water

bath for 24 hr. The supernatant solution was separated by centrifuga-

tion of the systems at 15,000 rpm for 5 minutes. A 1-ml aliquot of

the supernatant was pipetted into a 10-ml fluor which contained 5.5

g/L 2,5-diphenyloxazole (PPO), 0.1 g/L 1,4-di-(2-(5-phenyloxazolyl))

benzene (POPOP), in 2:1 (v/v) toluene: Triton X-100. For the system

in 2.5 $\underline{N}$ KCl, 10 ml of thixotropic gel was used as the fluor. The

thixotropic gel contained 3 g PPO, 50 mg of POPOP, 5 ml of glycerol,

4 ml of tween span, and 20 g of thixin per 500 ml of toluene. The ^{14}C

activity was radioassayed with a liquid scintillation counter. Adsorp-

tion of the chemicals was calculated from the difference in herbicide

concentration in the original and equilibrium solution. The pH of the

picloram-KCl solutions and the picloram-KCl-soil systems were

measured by a Corning Model 7 pH meter equipped with a combination

electrode.

Results and Discussion

Activated Charcoal and
Picloram Mobility

Addition of 0.1% activated charcoal to the Molokai soil resulted

in reduced picloram mobility (Table 4-1). Additions of activated

charcoal at the 1% and 10% level caused complete adsorption of

picloram at the origin where the picloarm was initially applied. In

Table 4-1. Effect of activated charcoal on picloram R_F for Lookout and Molokai soils.

Soil	Depth	Activated Charcoal Added	Picloram R_F	Water Flux
	(cm)	(%)		(cm/hr)
Lookout sil	0-10	0.0	0.81	6.7
		0.1	0.81	7.6
		1.0	0.08	8.4
		10.0	0.03	5.5
Molokai c	61-79	0.0	0.70	7.2
		0.1	0.47	6.6
		1.0	0.00	5.6
		10.0	0.00	8.3

contrast picloram mobility in the Lookout soil was not affected by 0. 1% activated charcoal.

The Molokai soil adsorbed more picloram than did Lookout soil although the difference was very small (Appendix Table 1). Picloram adsorption by the untreated Molokai soil was less than 5%. Addition of the charcoal (0. 1%) increased the water flux in the Lookout soil and decreased the water flux in the Molokai soil (Table 4-1). Increased picloram adsorption and a slower water flux explain the reduced picloram mobility in the Molokai soil as compared to the Lookout soil after addition of 0. 1% activated charcoal.

Further increase of activated charcoal to 1% or 10% reduced picloram mobility from 0. 81 to 0. 08 and 0. 03, respectively for the Lookout soil (Table 4-1). The water flux for the soils did not exhibit a significant change with charcoal treatment (Table 4-1). It thus appears possible to prevent picloram movement into ground water through incorporation of activated charcoal into soils.

HCl and KCl Solutions and Mobility
of Picloram and 2,4-D

Upon treatment with 10 meq. of HCl, the Minam, Woodcock, and Kinney soils retarded drastically the movement of picloram and 2,4-D (Table 4-2). The reduced movement was caused by increased adsorption of both chemicals by acidified soils. Hamaker et al. (1966) adjusted an organic soil (O. M. = 32.2%) to pH 2 and 9 with HNO_3 and

Table 4-2. Mobility of picloram and 2, 4-D in selected Oregon soils as determined by soil thin-layer radiochromatography.

Soil	Depth	Before HCl Treatment Water as Eluting Solution				After HCl Treatment[a] Water as Eluting Solution				After HCl Treatment[b] 2N KCl (pH7) as Eluting Solution			
		Picloram R_F	2, 4-D R_F	pH of Soil	Water Flux	Picloram R_F	2, 4-D R_F	pH of Soil	Water Flux	Picloram R_F	2, 4-D R_F	pH of Soil	Water Flux
	(cm)				(cm/hr)				(cm/hr)				(cm/hr)
Minam	0-23	0.60	0.40	7.0	5.4	0.04	0.01	1.1	6.7	0.04	0.02	2.8	9.8
Minam	23-33	0.75	0.51	7.3	9.8	0.03	0.01	0.8	9.2	0.04	0.01	3.1	13.4
Minam	61-84	0.89	0.84	7.5	14.1	0.12	0.04	0.8	6.6	0.12	0.06	3.3	9.7
Woodcock	0-10	0.75	0.37	6.1	13.5	0.06	0.02	1.5	2.6	0.07	0.03	3.6	2.9
Woodcock	36-51	0.47	0.26	5.8	26.7	0.08	0.03	2.0	4.0	0.18	0.04	3.7	4.2
Woodcock	69-111	0.49	0.32	5.6	33.1	0.11	0.04	2.4	5.8	0.28	0.06	3.7	3.6
Kinney	23-38	0.26	0.15	5.2	9.4	0.06	0.01	2.5	1.2	0.06	0.03	3.6	1.5
Kinney	23-46	0.20	0.13	5.2	7.7	0.07	0.03	1.7	1.1	0.15	0.03	3.6	1.4
Kinney	46-74	0.22	0.16	5.0	13.3	0.05	0.07	1.2	1.8	0.07	0.07	3.7	2.1

[a] Ten ml of $\underline{N}$ HCl solution was added to the soil

[b] Soil TLC plates were eluted with water to 10 cm, oven-dried, followed by elution with 2 $\underline{N}$ KCl

NaOH and obtained 98% adsorption at pH 2 and 33% adsorption at pH 9, respectively.

The water flux was reduced appreciably upon addition of HCl to the soil (Table 4-2). The soils were sufficiently flocculated by addition of hydronium ions to increase the number of macro pores. Because the water flux was measured with ascending chromatography, increases in macro pores would reduce the capillary force of the soil thereby decreasing the water flux.

Elution of HCl-treated soil thin-layer plates with a 2 $\underline{N}$ KCl (pH 7) solution did not cause enhanced mobility for picloram or 2,4-D (Table 4-2). Failure to neutralize the soil acidity allowed no further chemical movement. Cheng (1971) showed that 2 $\underline{N}$ KCl was an effective extracting solution for picloram from soils which were adjusted to pH 7.

KCl (pH 7) and Picloram Mobility

Since $\underline{N}$ KCl (pH 7) has been suggested as an extraction reagent for picloram, one could surmise that picloram mobility would be increased when using this salt as a mobile phase in an elution experiment. However, except for Kinney soils, the use of $\underline{N}$ KCl solution as a mobile phase reduced picloram mobility on the soils tested (Table 4-3). Woodcock (0-10 cm), Hembre, and Palouse (0-25; 25-46 cm) soils showed a large decline in picloram mobility when a $\underline{N}$ KCl

Table 4-3. Effect of $\underline{N}$ KCl (pH 7) as the mobile phase on the picloram R_F of soils.

Soil	Depth	Mobile Phase			
		H$_2$O		$\underline{N}$ KCl (pH 7)	
		Picloram R_F	Water Flux	Picloram R_F	Water Flux
	(cm)		(cm/hr)		(cm/hr)
Woodcock	0-10	0.75	13.5	0.32	13.3
Woodcock	36-51	0.47	26.7	0.39	21.5
Woodcock	69-111	0.49	33.1	0.42	25.0
Kinney	23-46	0.20	7.7	0.23	4.1
Kinney	46-74	0.22	13.3	0.34	10.0
Hembre	---	0.53	12.1	0.19	9.6
Dayton	0-23	0.69	4.3	0.40	3.6
Palouse	0-25	0.64	3.2	0.38	3.6
Palouse	25-46	0.76	6.3	0.34	2.1

Table 4-4. Effect of KCl concentration (pH 7) on picloram R_F for Palouse (25-46 cm) soil.

Concentration of KCl	pH of Solution[a]	Picloram R_F	Water Flux
($\underline{N}$)			(cm/hr)
0.00	7	0.76	6.3
0.01	7	0.76	3.2
0.05	7	0.75	3.0
0.10	7	0.80	2.1
0.50	7	0.66	1.9
1.00	7	0.34	2.1
2.50	7	0.37	1.5

[a]Adjusted with KOH solution

solution was used as the mobile elution phase. The water flux before and after elution with the N KCl solution did not differ significantly (Table 4-3).

Because of the reduced picloram mobility in 1 N KCl the picloram mobility as a function of salt and pH was studied. The mobility of picloram in Palouse (25-46 cm) soil did not change as the concentration of KCl in the mobile phase increased from 0.01 to 0.1 N (Table 4-4); however, the water flux was reduced. An increase in KCl concentration from 0.1 to 1.0 N caused a large decrease in picloram mobility (Table 4-4). It was initially thought that the reduction in picloram solubility in KCl solutions retarded picloram movement. However, a previous study showed that the water solubility of picloram in KCl solutions was not reduced until the KCl concentration exceeded 1.5 N.

A second hypothesis by which the reduced picloram mobility in the KCl solution could be explained related to picloram solubility in $CaCl_2$ solutions. Calcium ions could be replaced on the exchange sites by potassium during the elution process. The Palouse (25-46 cm) soil contained 12 meq. Ca per 100 g. The average soil weight on one soil thin-layer plate was determined to be 1.37 g. Therefore, the average weight of soil in this 1-cm section of soil was determined to be 0.137 g. The water content in this 1-cm section of soil was determined to be 0.1 cc after elution with water. Assuming all the exchangeable Ca were replaced by K in the N KCl phase, the final Ca concentration in the 1-cm section was calculated to be approximately

0. 164 $\underline{N}$. The solubility of picloram in 0. 164 $\underline{N}$ $CaCl_2$ has been

determined previously to be 641 ppm (Table 3-1, page 30) which still

exceeded the solubility in water (597 ppm). Therefore, the reduced

picloram mobility in the presence of $\underline{N}$ KCl could not be explained by

the reduced picloram solubility due to the exchange of K^+ for Ca^{++} on

the soil exchange sites.

Because of the failure of the aforementioned hypotheses to

explain the reduced picloram movement, an experiment was conducted

to study the effect of KCl concentration on picloram adsorption by

Palouse soil at three picloram concentrations.

The pH of the picloram-KCl-soil systems dropped from 6. 1 to

ca. 5. 3 when the KCl concentration increased from 0 to 2. 5 $\underline{N}$

(Figure 4-1). An increase in KCl concentration from 0 to 0. 1 $\underline{N}$

caused a rapid decrease in the pH of the picloram-KCl-soil system.

Further increase in KCl concentration from 0. 5 to 2. 5 $\underline{N}$ caused only

a 0. 3 pH unit decrease. Picloram adsorption increased with a

decrease in soil pH (Figure 4-2); however, the increased picloram

adsorption was relatively small until KCl concentrations greater than

0. 1 $\underline{N}$ were obtained. The picloram adsorption increased markedly

when the KCl concentration exceeded 0. 1 $\underline{N}$ although the pH change with

increased KCl ($>$ 0. 1 $\underline{N}$) was relatively small (Figure 4-1). Accord-

ing to a dissociation curve of picloram a small pH change may

significantly affect picloram ionization at the critical pH area.
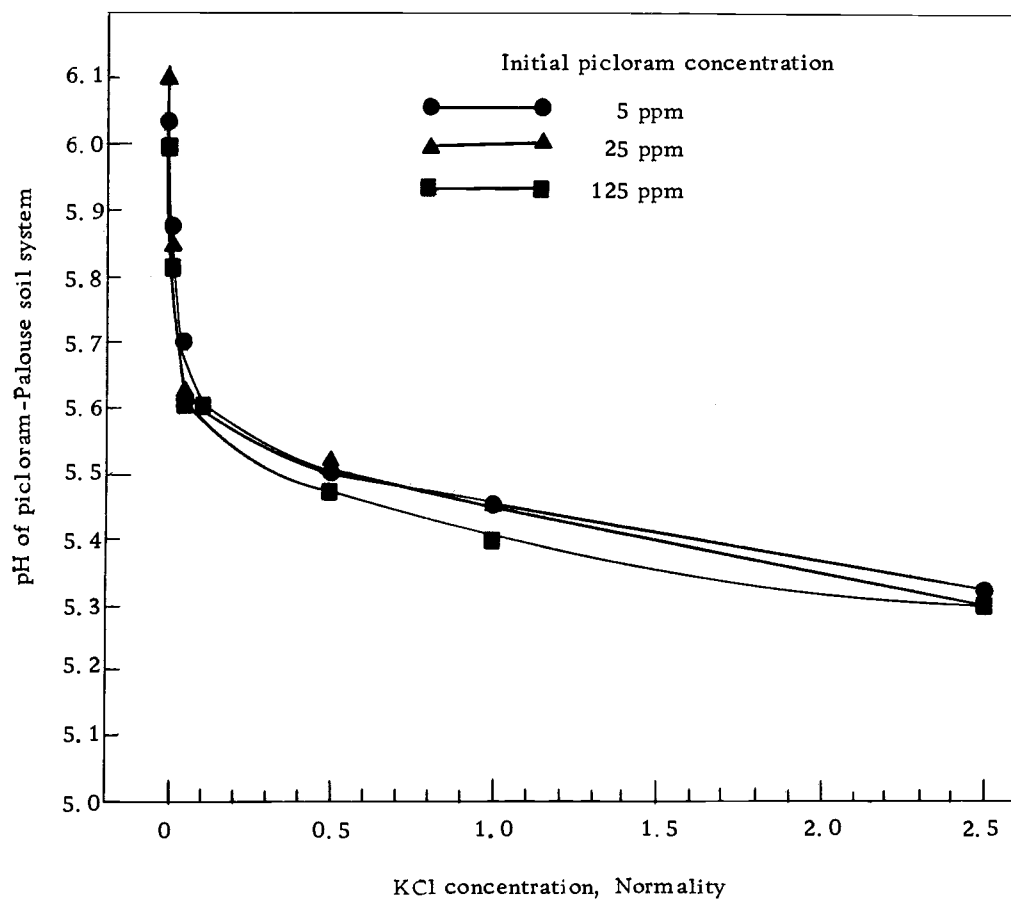
Figure 4-1. Changes in solution pH of picloram-Palouse soil systems as a function
of KCl concentration after equilibration for 24 hr.
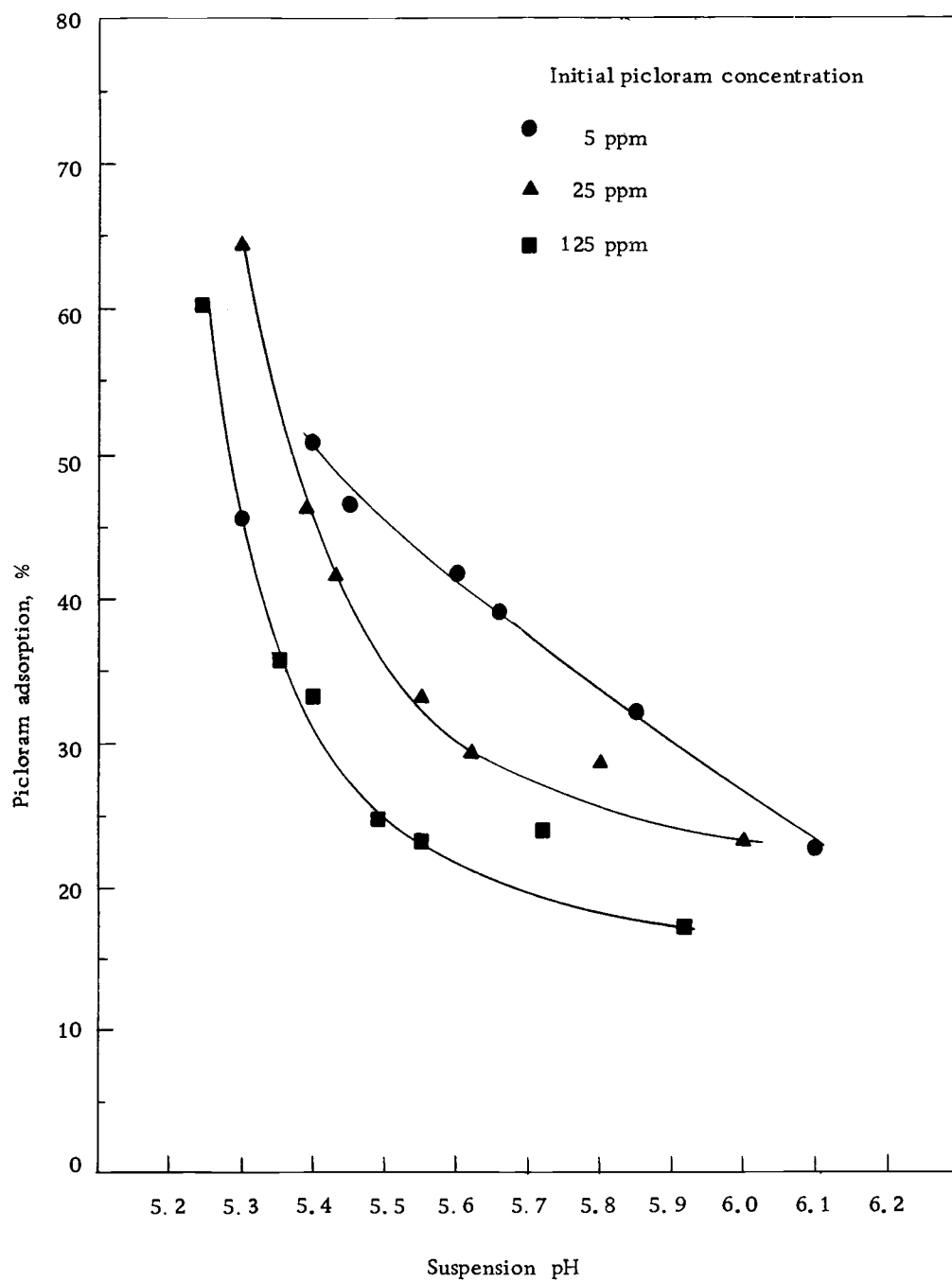
Figure 4-2. Adsorption of picloram by Palouse soil as a function of initial pH of KCl-picloram-Palouse soil suspension.

The addition of KCl salts into the soil replaced the acidic hydronium and aluminum ions from the soil clays. The association of anionic picloram with hydronium ions increased the fraction of molecular picloram in soils. Because the molecular picloram was preferentially adsorbed over its anionic analogue by soils (Cheng, 1971), the adsorption of picloram by Palouse soil was intensified as a result of increased molecular picloram by addition of KCl salts.

In a recent report by Duseja, Evans and Miller (1972), the adsorption of picloram by soils increased with a progressive increase in $CaCl_2$ concentration (0-0.5 $\underline{N}$). Helling (1971a) indicated a reduced mobility of 2,4-D and atrazine when the concentration of NaCl exceeded 0.1 $\underline{N}$. He also suggested that the reduced movement resulted from an increased adsorption of 2,4-D or atrazine at high salt concentration.

The adsorption of picloram on the Palouse soil followed Freundlich adsorption isotherms across the KCl concentrations used. As a consequence of the pH decrease upon increasing the KCl concentration from 0 to 2.5 $\underline{N}$ (Figure 4-1), a three-fold increase in the adsorption of picloram by Palouse soil was observed at the three initial picloram concentrations (Figure 4-3). In contrast to the Palouse soil, no picloram adsorption occurred above pH 3 in an acid montmorillonite clay system which contained no organic materials (Chapter 5). The presence of 4.2% organic matter in Palouse soil (Appendix Table 1)
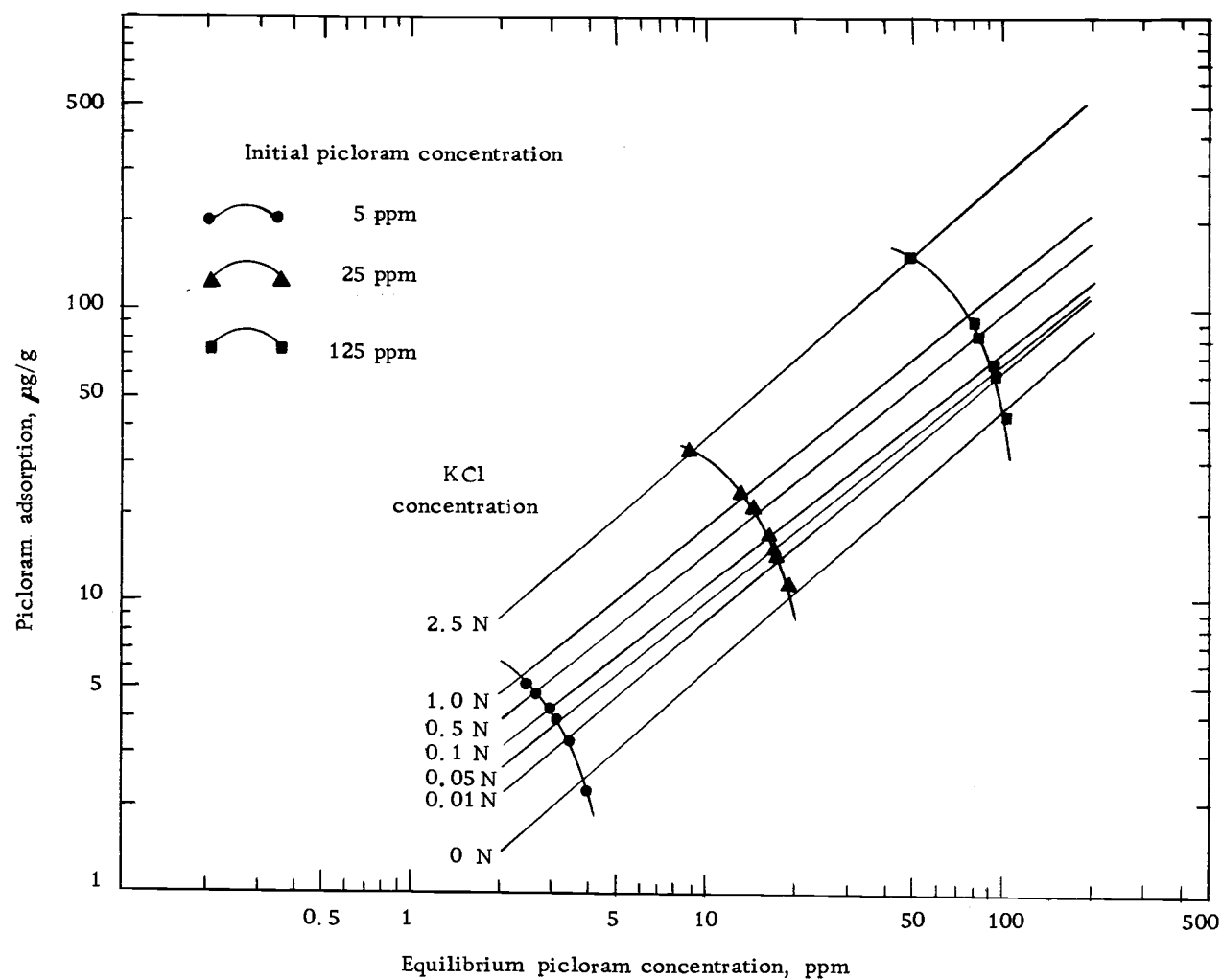
Figure 4-3. Freundlich adsorption isotherms (25°C) for picloram adsorption on Palouse soil as a function of KCl concentration.

and the decrease in soil pH with increased salt concentration caused

the enhanced picloram adsorption.

Summary and Conclusions

Mobility of picloram in Molokai c and Lookout sil soils was

retarded after addition of activated charcoal. Because the Molokai

soil had a higher adsorption for picloram and a faster water flux, the

picloram R_F decreased in Molokai soil but not in the Lookout soil

after 0. 1% activated charcoal was added. Complete immobilization

of picloram occurred on both the Molokai and Lookout soil TLC plates

after 1% or 10% activated charcoal was added to the soils.

The mobility of picloram and 2, 4-D in Minam, Woodcock, and

Kinney soils was drastically retarded after the soils were treated

with 10 meq. of HCl. The reduced movement was caused by enhanced

adsorption of both chemicals by acidified soils. Further elution of

HCl-treated soil thin-layer plates with 2 $\underline{N}$ KCl (pH 7) solution did not

cause increased mobility for picloram and 2, 4-D because of the failure

of KCl solution to neutralize soil acidity.

The mobility of picloram on Palouse (25-46 cm) TLC plates was

not affected by KCl concentrations < 0. 1 $\underline{N}$; however, picloram R_F

values decreased when the KCl concentration in soil solution exceeded

0. 1 $\underline{N}$. Reduced picloram mobility did not result from reduced piclo-

ram solubility in salt solutions. Increased picloram adsorption with

an increase in KCl concentration did explain the reduced picloram

mobility. The enhanced picloram adsorption with increasing KCl

concentration related to an increase in soil acidity in the bulk solution.

ADSORPTION AND DESORPTION OF PICLORAM BY ACID H-MONTMORILLONITE

Introduction

Montmorillonitic clays play an important role in the soil chemistry of many soils. Because of their large surface area and large exchange capacity, montmorillonite clays may serve as sites for chemical and physical adsorption reactions. Pesticide movement and resultant residual activity is strongly affected by the adsorption-desorption reactions which occur within the soil.

Adsorption of picloram to surfaces has been postulated to result from both physical bonding and chemical bonding (Bailey et al. , 1968). Since picloram exists as an uncharged molecule below pH 3. 4, and as an anion at higher pH values, one would logically expect some pH effect on the adsorption reaction. Hamaker et al. (1966) observed increased picloram adsorption on organic matter, hydrated oxides, and clay minerals with a decrease in pH. No adsorption of picloram was detected on montmorillonite (pH 9. 8) and kaolinite (pH 6. 4) clays, cation exchange resins (pH 6. 7), wheat straw (pH 6. 5), or cellulose powder (pH 4. 9), suggesting a total lack of attraction of picloram for hydrophilic surfaces at pH values where anionic picloram exists (Grover, 1971). The order of picloram adsorption by exchange resins was shown by McCall et al. (1972) to be anionic > nonionic > cationic; however, the effect of system pH on picloram adsorption was not studied.

In picloram extraction studies, Cheng (1969) found that recovery of added picloram by a 2 $\underline{N}$ KCl solution decreased as soil pH decreased in the acid range. Upon adjustment of the systems to pH 7, the recovery of the added picloram from soils ranged from 94 to 100% (Cheng, 1971). Therefore, Cheng claimed little or no adsorption of anionic picloram by soils in accordance with that reported by Grover (1971). Based on the dependency of picloram adsorption on soil pH and reversibility of the adsorption process, Cheng (1971) concluded that picloram adsorption was a general surface phenomenon involving no specific sites.

Desorption studies of McCall et al. (1972) employing H_2O, 3 $\underline{N}$ NaCl, and 60% ethyl alcohol indicated that picloram was adsorbed by exchange resins mainly in the anionic form through electrostatic forces and to a lesser degree through weak van der Waals forces.

The adsorption isotherms of picloram on soil colloids and various adsorbents followed a Freundlich equation which implied a logarithmic relationship between the quantity of chemical adsorbed and the equilibrium concentration of chemical (Grover, 1971). The kd values (μg chemical adsorbed per g adsorbent at 1 ppm equilibrium concentration) for the Canadian prairie soils which were studied ranged from 0.09 to 0.75 and were correlated only with soil organic matter. The kd values for wheat straw, montmorillonite, kaolinite, cellulose, and cation exchange resin were zero while activated

charcoal, anion exchange resin and peat moss had kd values of 232, 79, and 4, respectively.

The residual activity of picloram in soils depends upon its adsorption-desorption kinetics with active soil components. The hysteresis effects of adsorption-desorption often determine the mobility pattern of picloram in soil-water systems. Therefore, it is important to consider both adsorption-desorption processes when assessing chemical contamination problems in the environment.

The objective of this research was to elucidate the adsorption-desorption of picloram in a montmorillonite-water system as a function of suspension pH.

Materials and Methods

Preparation of ^{14}C-Picloram Solutions

Stock solutions of ^{14}C-carboxyl-labeled or nonradioactive picloram with concentrations of 10, 50, and 250 ppm were prepared. The purity of ^{14}C-labeled picloram was ascertained through the use of paper chromatography and radiochromatogram scanning systems. The developing solvent contained 200 parts of ethanol, 10 parts of NH_3, and 40 parts of H_2O. The specific activities for 10, 50, and 250 ppm ^{14}C-labeled picloram solutions were 1.48 x 10^{-4}, 2.88 x 10^{-5}, and 5.88 x 10^{-6} $\mu C/\mu g$, respectively.

Preparation of H-Montmorillonite
Clay Suspension

The $< 2\ \mu$ fraction of montmorillonite clay (Wards National

Science Establishment, Inc., Rochester, New York) was obtained by

centrifugation of a montmorillonite sample dispersed in distilled water

by vigorous stirring in a Hamilton Beach stirrer.

The $< 2\ \mu$ montmorillonite suspension was H-saturated by treat-

ment with 10 symmetries of H-exchange resin (Rexyn 101 H, 16-32

mesh, Fisher Scientific Company) for one-half hour. The clay was

filtered through a layer of nylon cloth and re-treated similarly with

the H-resin. The pH of the H-montmorillonite suspension was

measured with a Corning Model 7 pH meter. The cation exchange

capacity of the H-montmorillonite was determined by a potentiometric

titration with a standard NaOH solution.

Adsorption of Picloram

A 10-ml aliquot of the aqueous ^{14}C-labeled picloram was added

to a centrifuge tube containing a 5-ml montmorillonite suspension

with a density of 0.0332 g/ml. The pH of the system was adjusted with

HCl to 0, 0.4, 0.8, 1.2, 1.6, 1.8, 2.0, 2.2, 2.4, and 2.6. Pre-

liminary studies showed no adsorption of picloram by montmorillonite

at pH above 3.0. The volume of the clay-picloram-water system was

adjusted to 20 ml with distilled water so that the final picloram

concentrations were 5, 25, and 125 ppm,respectively. The centrifuge
tubes were sealed with waterproof plastic tape and equilibrated in a
constant temperature water bath at $25^{\circ}C$ for 17 hr. The pH of the clay
suspension was measured after equilibration. Following centrifuga-
tion at 15,000 rpm for 5 minutes, the equilibrium solution was decanted
into a vial and the volume determined. All samples were run in
duplicate.

The picloram concentration in the equilibrium solution was
measured by adding a 1-ml aliquot of equilibrium solution to a 10-ml
fluor containing 4 g/L PPO, 0.1 g/L POPOP, in 2:1 (v/v) toluene:
Triton X-100 and counting in a Packard Tricarb Model 3375 liquid
scintillation counter. Adsorption of Picloram was calculated as a
difference between the initial and equilibrium picloram concentrations.

Desorption of Picloram

Immediately following removal of the equilibrium solution, a
20-ml aliquot of distilled water was added to the centrifuge tube which
contained the clay sediment. The centrifuge tube was shaken on a
horizontal reciprocal shaker with a speed of 230 cycles per minute
for 2 hr after which the pH was measured and the suspension centri-
fuged. The picloram concentration in the supernatant solution was
determined as noted previously. The picloram which remained in the
residual solution after each desorption was considered in the

desorption calculations. Water wash treatments were continued until no ^{14}C activity could be detected in the extractant solution.

KCl Concentration and Picloram Adsorption

The ^{14}C-carboxyl labeled picloram solutions (25 ppm) were prepared in 0, 0.01, 0.1, 1, and 2 N KCl. The specific activity of ^{14}C-picloram was 0.025 μC/mg in each solution.

A 10-ml aliquot of the ^{14}C-labeled picloram solution was added to a centrifuge tube containing a 5-ml H-montmorillonite suspension which contained 0.0645 g of clay. The pH of the system was adjusted with either HCl or NaOH to 1.06, 2.20, 6.40, 6.44, and 10.65 (Table 5-2). The volume of the clay-picloram-water system was adjusted to 20 ml with distilled water so that the final picloram concentration was 12.5 ppm, and KCl concentrations were 0, 0.005, 0.05, 0.5 and 1 N. The centrifuge tubes which contained the clay-picloram solutions were equilibrated in a constant temperature water bath at 25°C for 17 hr. The pH of the suspension was measured after equilibration. Following centrifugation at 15,000 rpm for 5 minutes, the equilibrium solution was decanted into a vial and the pH measured. The picloram concentration in the equilibrium solution was assayed by liquid scintillation and picloram adsorption calculated as a difference between the initial and equilibrium picloram concentration.

Results and Discussion

Adsorption

As the suspension pH of H-montmorillonite-picloram system decreased from 2.6 to 0, picloram adsorption increased from less than 10% to over 90% at 5, 25, and 125 ppm initial picloram concentrations (Figure 5-1). At a given suspension pH, a higher percentage of picloram was adsorbed by the H-montmorillonite (CEC = 108 meq/100 g) with a higher initial picloram concentration (Figure 5-1). The three picloram adsorption curves fall to the left of the picloram dissociation curve (based upon pK_a = 3.4, Appendix Figure 2) to indicate less molecular picloram adsorption than would be predicted from the simple picloram dissociation curve. No picloram was adsorbed by the H-montmorillonite until the suspension pH decreased below 2.6. The H-montmorillonite appeared to serve as a sink for protons thus inhibiting the formation of molecular picloram. The adsorption of picloram by H-montmorillonite (pH 3.0) increased rapidly as H^+ ion was added to the solution (Figure 5-2). The added H^+ ion in the system eventually saturated the sink so that the fraction of molecular picloram and hence the adsorption of picloram increased as the suspension pH decreased. In other words, the H^+ ion activity in the bulk solution determined the fraction of molecular species of picloram present in the equilibrium solution. This is in accordance with that reported by
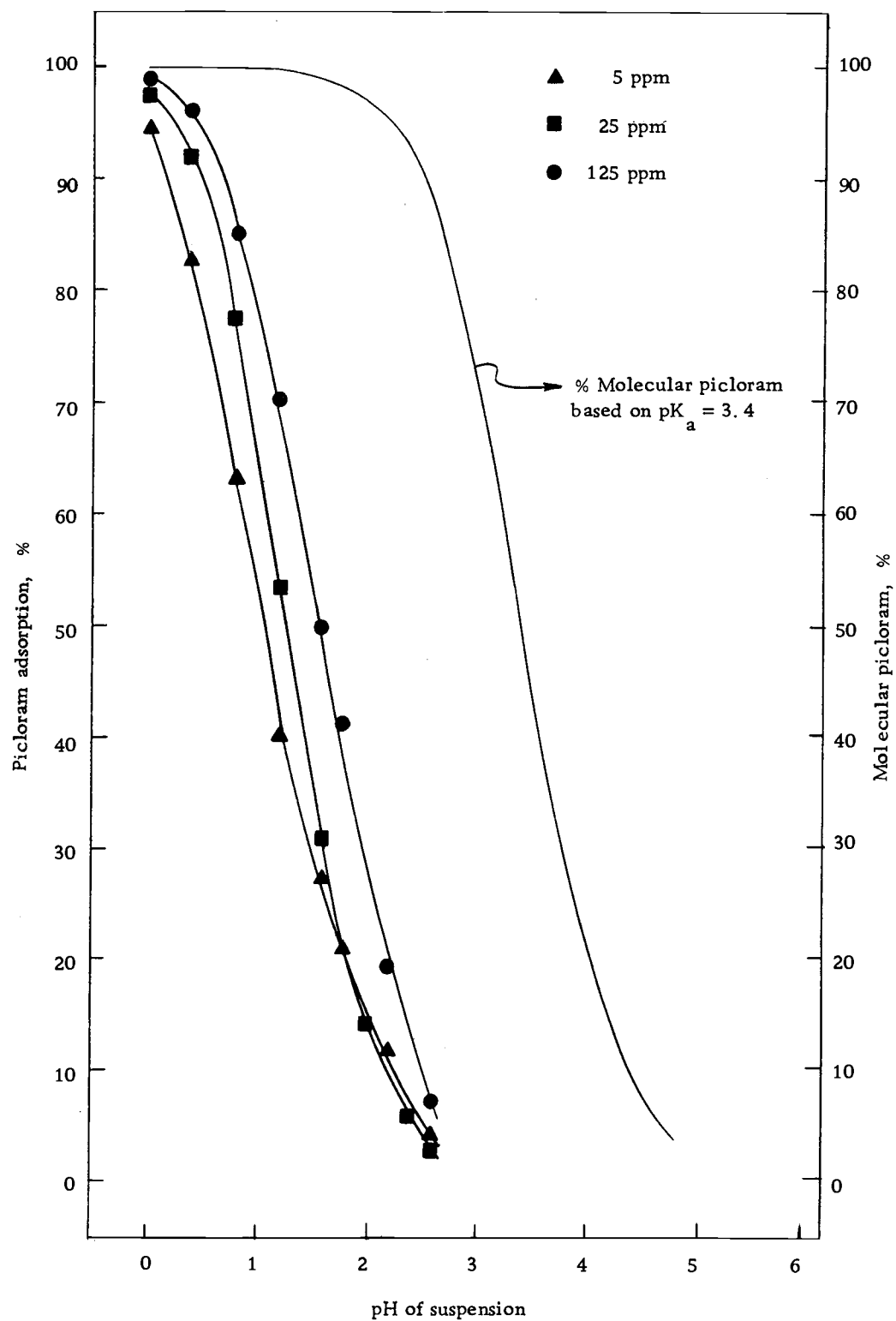
Figure 5-1. Adsorption of picloram by acid H-montmorillonite at three concentrations.
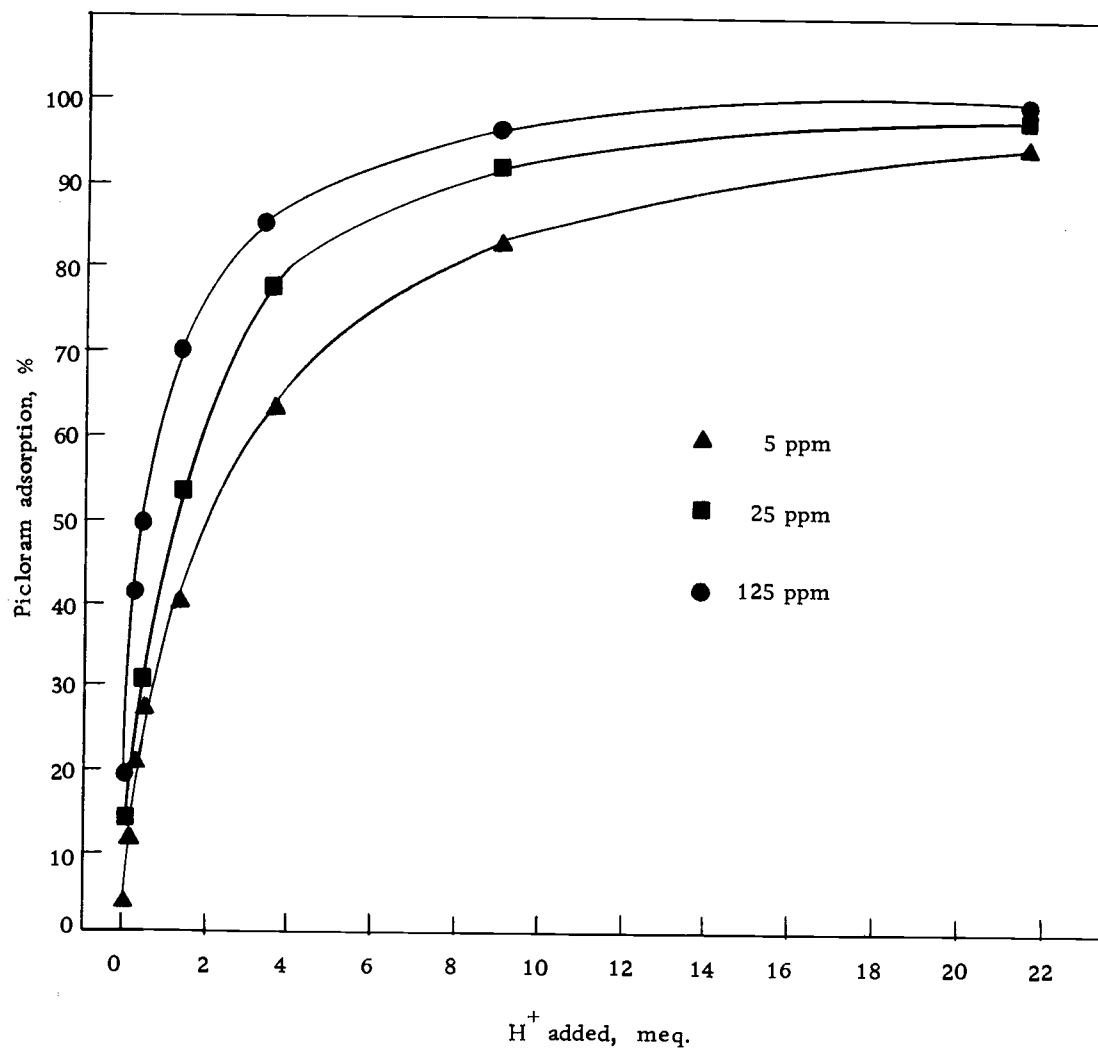
Figure 5-2. Picloram adsorption in relation to added H^+ in the H-montmorillonite clay suspensions.

Bailey et al. (1968) which stated the pH of the bulk solution rather than the surface acidity determined the positive adsorption of 2, 4-D.

To explain the unique adsorption phenomenon for picloram-montmorillonite system, the chemical properties of picloram are reviewed. Although Bailey et al. (1968) had proposed a protonation scheme as one of the possible adsorption mechanisms for picloram, infrared evidence (Chapter 7) showed that the probability of protonating the picloram molecule in an acid environment was extremely small due to the low basicity of the picloram molecule. The electronegativity of the carbonyl oxygen and annular nitrogen is higher than its anionic analogue in molecular picloram. Therefore, it is suggested that hydrogen bonding between the oxygen of the carbonyl group or annular nitrogen of the picloram molecule and the exchangeable H or Al on the montmorillonite clay could account for the pH effect on picloram adsorption. Since hydrogen bonding is formed preferentially between the hydrogen atom and the more electronegative atom (Pauling, 1960), more picloram molecules should react with H-montmorillonite via hydrogen bonding when the acidity of the system increases.

Although the change in exchangeable aluminum content of the H-montmorillonite was not measured, an appreciable increase in aluminum on exchange sites as a result of aging the H-montmorillonite would be expected. At least some of the increase in adsorption of picloram could result from this increase in active aluminum fraction.

Hamaker et al. (1966) found that 46% and 83% of picloram was adsorbed

by gibbsite (pH 1.2) and amorphous Al_2O_3 (pH 1.5) at the adsorbent:

solution ratio of 1:4.

The picloram adsorption data conformed to Freundlich isotherms

at pH ranges employed in this study (Table 5-1 and Figure 5-3).

Conformation to the Freundlich adsorption isotherm suggested no

limitation in adsorption layers for picloram. It is possible for the

molecular picloram to be associated with the adsorbed analogue via

hydrogen bonding or van der Waals force (McCall et al., 1972) and form

a pseudodimer. Similar pseudodimer formation mechanism was

suggested for 2, 4-D by Harter and Ahlrichs (1969). Conformation to

the Freundlich adsorption isotherm also suggested the involvement of

physical forces in the picloram adsorption process. This has been

pointed out by Cheng (1971) and suggested by Bailey et al. (1968).

Desorption

The picloram (25 ppm) initially adsorbed was quantitatively

recovered by the water wash treatments as the suspension pH

increased (Figures 5-4 and 5-5). The suspension pH equilibrated at a

pH value between 3.5 and 3.8 after the eighth water wash (Figure 5-4,

and Appendix Figures 3 and 4). The picloram recovery from the 5 and

125 ppm systems showed similar trends as the 25 ppm picloram

system (Appendix Figures 5 and 6). An increasing number of water

Table 5-1. Freundlich constants for picloram adsorption on acidic H-montmorillonite at 25°C.

Suspension pH	Slope, 1/n	Intercept, Kd[a]
0.00	1.96	7586.0
0.40	1.93	676.1
0.80	1.52	147.9
1.20	1.49	41.7
1.60	1.33	25.7
1.80	1.34	18.6
2.20	1.19	11.8
2.60	1.20	2.9

[a]Kd = μg picloram adsorbed per g H-montmorillonite at 1 ppm equilibrium concentration
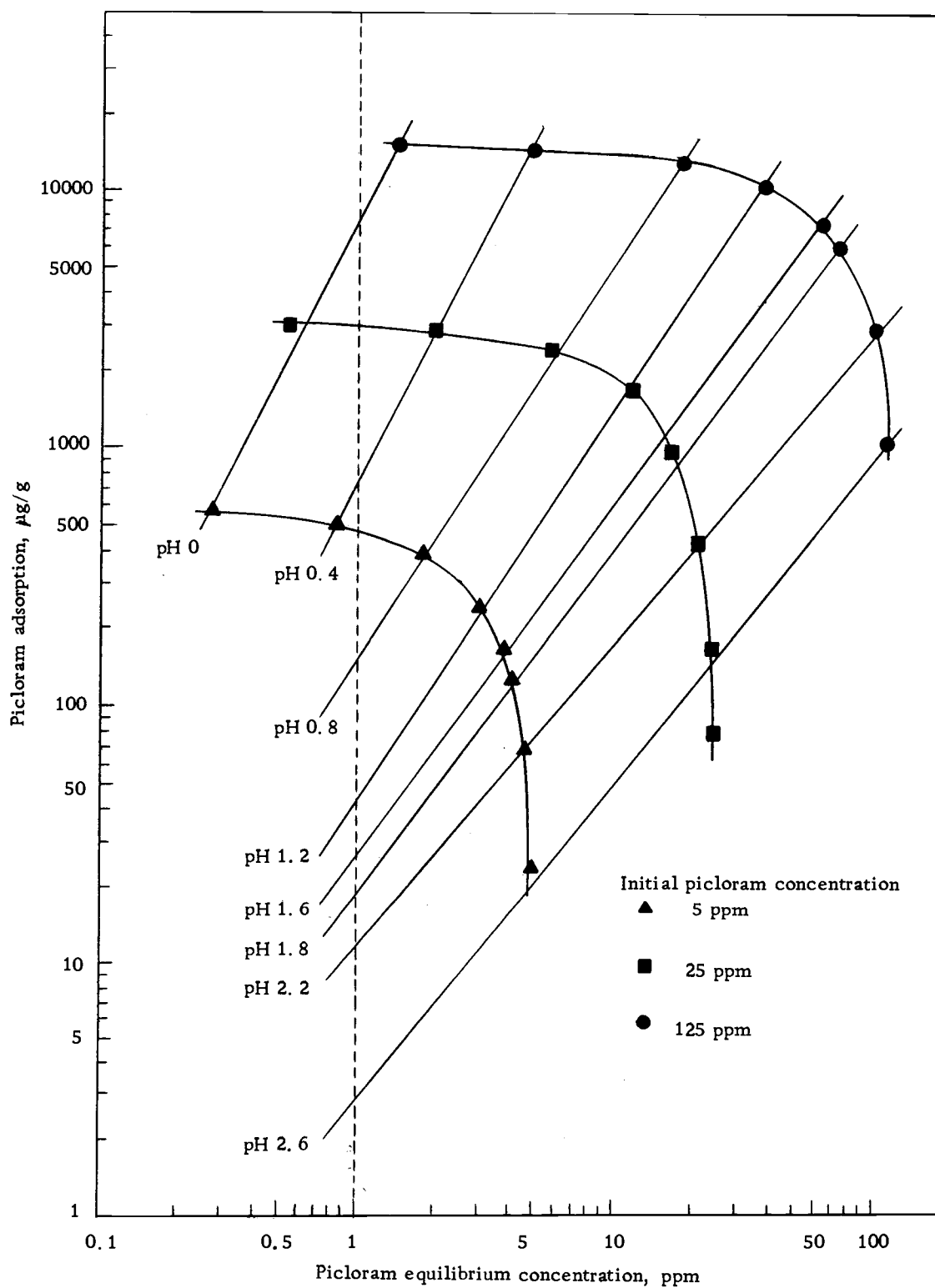
Figure 5-3. Freundlich adsorption isotherms (25°C) for picloram adsorption on acid H-montmorillonite at three concentrations.
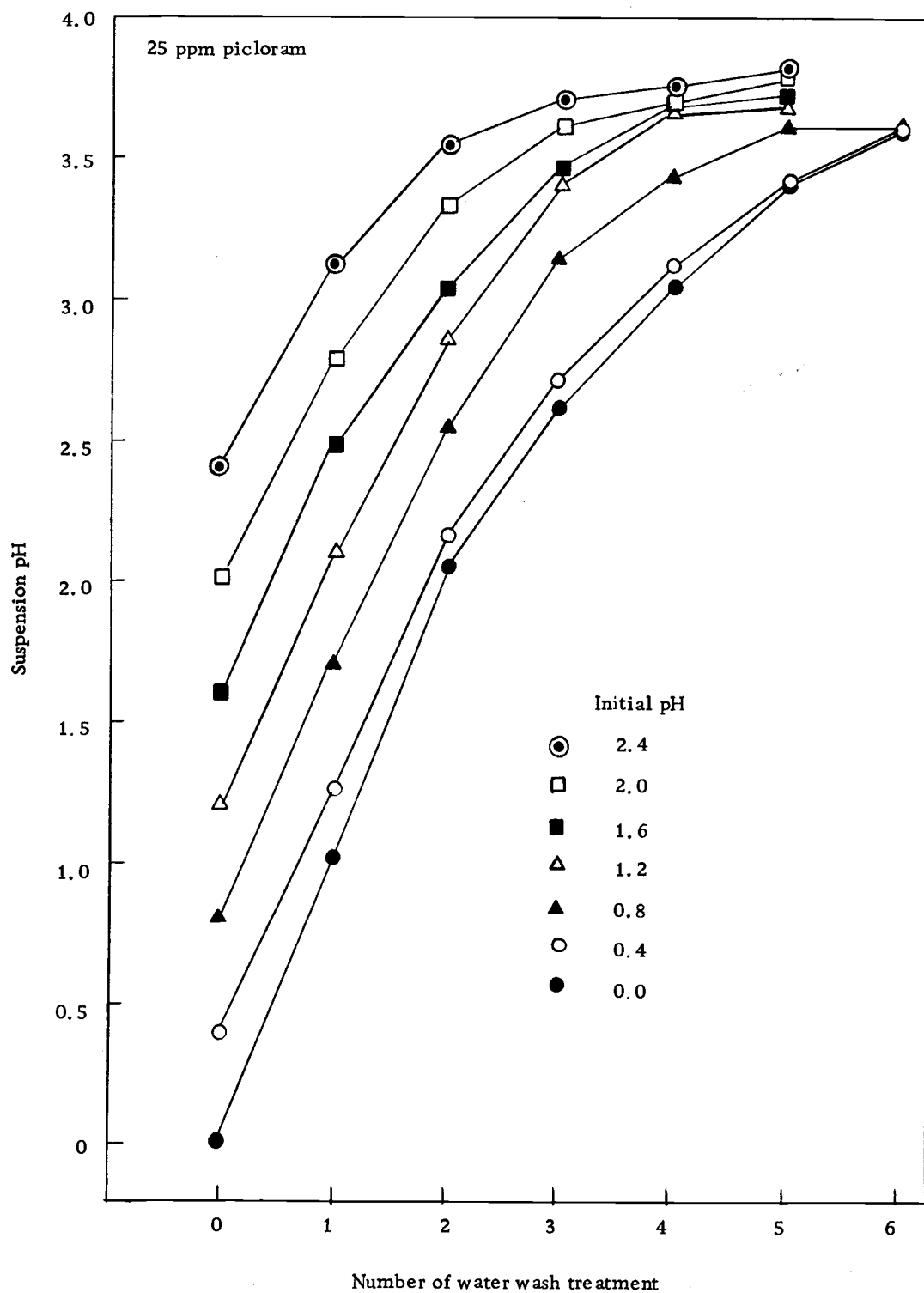
Figure 5-4. Changes in suspension pH of picloram-montmorillonite systems after
water washes at an initial concentration of 25 ppm.
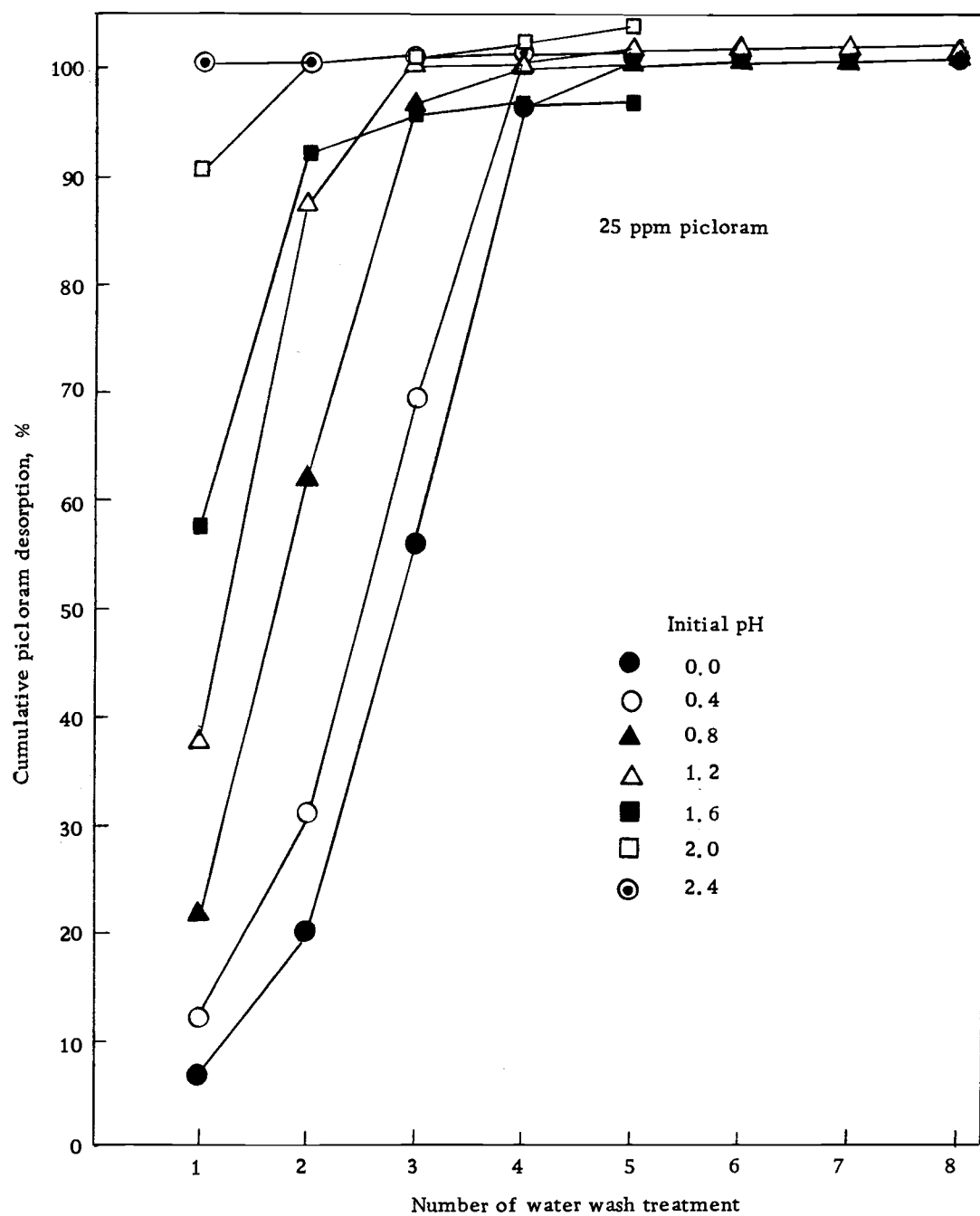
Figure 5-5.   Desorption of picloram from acid H-montmorillonite by water washes at an initial
concentration of 25 ppm.

wash treatments were required for quantitative recovery of picloram from the systems as pH decreased from 2. 6 to 0 (Appendix Figures 7, 8, and 9). The recovery of picloram was directly related to the increase in suspension pH (Figure 5-6).

The quantitative picloram recovery from acid H-montmorillonite by water wash treatments again suggested the importance of pH in picloram adsorption and desorption. Extraction of montmorillonite with a solution of pH similar to the equilibrium solution, such that no pH change would occur, would reduce picloram desorption from H-montmorillonite. In a study of picloram desorption from soils, Cheng (1971) demonstrated an increase of picloram desorption from soils by increasing the pH of the extractant solution.

KCl Concentration and Picloram Adsorption

As the concentration of KCl in the H-montmorillonite-picloram system increased, the changes in the suspension and supernatant pH were not distinct for the systems with initial pH of 1. 06 and 2. 20 (Table 5-2). Theoretically, 0. 36 meq. of hydronium ions was required to cause a drop of 0. 1 pH unit in the pH 1. 06 system. In the 0. 005 $\underline{N}$ KCl solution, the added K^+ ions (0. 1 meq.) probably did not completely displace the exchangeable H^+ from the clay surface. The H-montmorillonite had a total exchange capacity of 0. 0645 meq. in each system. When the KCl concentration reached 1 $\underline{N}$ the suspension pH
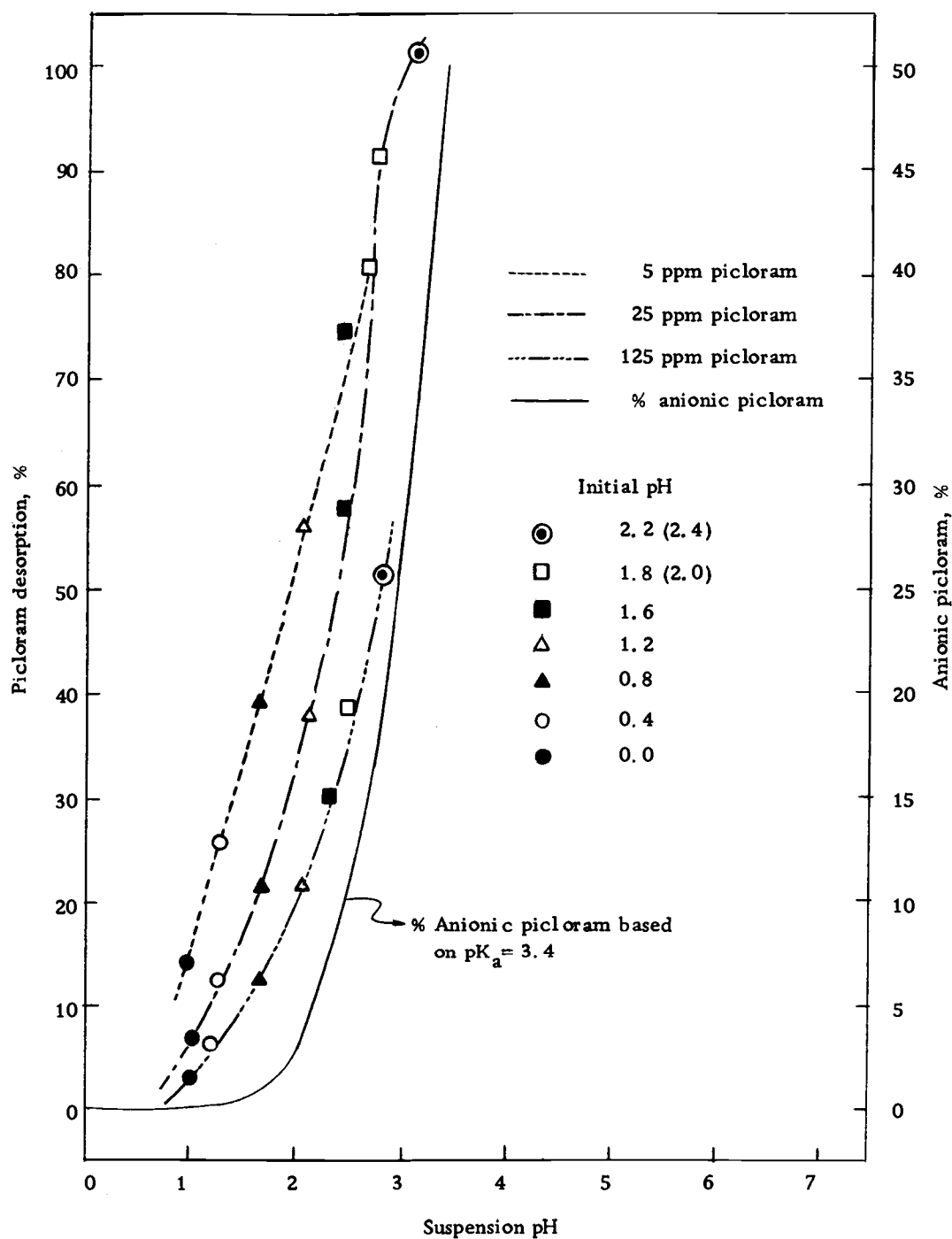
Figure 5-6. Desorption of picloram from acidic H-montmorillonite by first water wash
at three concentrations.

Table 5-2. pH changes of picloram-H-montmorillonite systems as a function of KCl concentration.

KCl concentration	pH									
N	Suspension					Supernatant				
0	1.06[a]	2.20[b]	6.40[c]	6.44[d]	10.65[e]	1.06[a]	2.25[b]	6.50[c]	6.45[d]	10.75[e]
0.005	1.05	2.20	4.98	5.20	10.55	1.07	2.20	4.98	5.25	10.75
0.05	1.05	2.20	4.25	4.40	10.53	1.08	2.21	4.30	4.35	10.63
0.5[f]	1.00	2.00	2.50	2.50	2.80	1.04	2.00	2.50	2.50	2.80
1.0	0.97	2.15	4.10	4.10	10.25	0.97	2.15	4.24	4.45	10.45

[a] 2.5 meq of HCl added

[b] 0.14 meq of HCl added

[c] 0.025 meq of NaOH added

[d] 0.05 meq of NaOH added

[e] 0.1 meq of NaOH added

[f] picloram stock solution contaminated by acid

decreased significantly. A drop of more than one pH unit was noted on
the system with an initial pH higher than 6 as the KCl concentration
increased from 0 to 0.005 $\underline{N}$ (Table 5-2). An increase of KCl concen-
tration to 0.05 $\underline{N}$ caused the pH of the clay-picloram solution to drop
two pH units. No drastic pH change was observed after the KCl
concentration increased from 0.05 to 1.0 $\underline{N}$. The considerable pH
drop at higher initial pH values was easily understood because to
reduce the suspension pH from 6.4 to 4.1 only 0.0016 meq. of
hydronium ions were required. These could be easily obtained by
displacement with excess K^+ ions.

The adsorption of picloram by H-montmorillonite increased
considerably as the KCl concentration increased from 0 to 0.005 $\underline{N}$
(Figure 5-7), especially for the system with initial pH 2.2. No
picloram adsorption was noted by the system with initial pH values
higher than 6. Increase of KCl concentration in these systems did not
enhance picloram adsorption (Table 5-3). The percentage of picloram
adsorbed by H-montmorillonite in the 1 $\underline{N}$ KCl matrix solution for the
systems with an initial pH of 1.06 and 2.20 approached the fraction of
molecular picloram which were predicted from the pK_a (3.4) of
picloram in aqueous solution (Figure 5-1). Apparently, the K^+ ions
replaced the hydronium ions from the proton sink of the H-
montmorillonite clay. The released hydronium ions associated with
anionic picloram to increase the fraction of molecular picloram in the
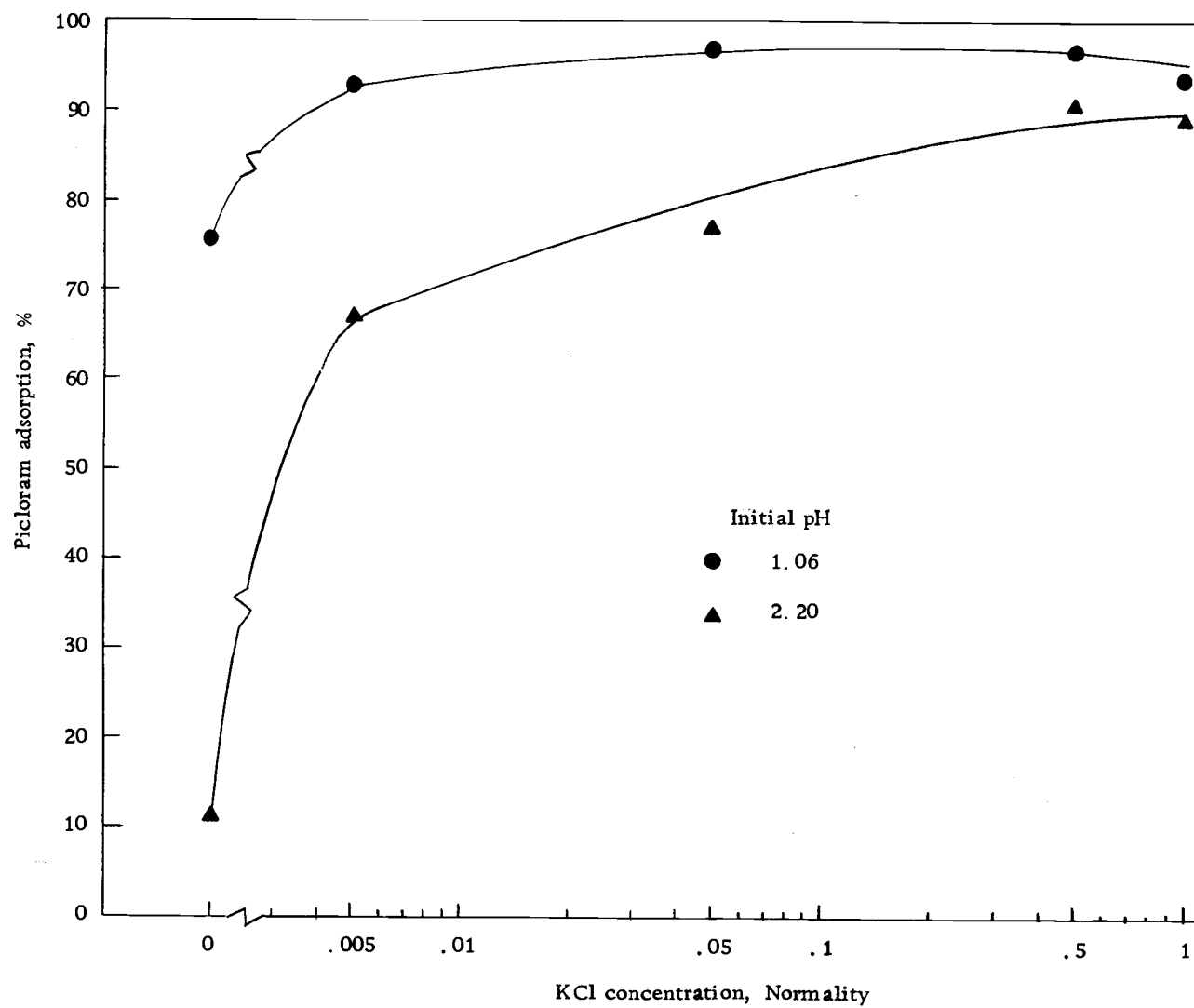
Figure 5-7. Adsorption of picloram by H-montmorillonite as a function of KCl concentration.

Table 5-3. Adsorption of picloram by H-montmorillonite as a function of KCl concentration and initial solution pH.

Initial pH[a]		Picloram adsorbed, %				
		KCl concentration, N				
Suspension	Supernatant	0	0.005	.0.05	0.5[b]	1.0
1.06	1.06	76	93	97	97	94
2.20	2.25	11	67	77	91	89
6.40	6.50	0	1	3	72	0
6.44	6.45	0	1	2	74	0
10.65	10.75	0	1	2	45	0

[a] after equilibration at 25°C for 17 hr

[b] picloram stock solution contaminated by acid

solution. Because it has been postulated that molecular picloram is preferentially adsorbed by H-montmorillonite clay, the increase in the fraction of molecular picloram as induced by increasing KCl concentration would enhance the adsorption of picloram by H-montmorillonite clay.

Summary and Conclusions

The adsorption of picloram by H-montmorillonite bears a close relationship with the picloram dissociation curve. Picloram adsorption increased from less than 10% to over 90% at 5, 25, and 125 ppm initial picloram concentrations as the pH decreased from 2.6 to 0. However, picloram adsorption was less than would be suggested by the picloram dissociation curve. The discrepancy was explained on the basis of the presence of a proton sink in the H-montmorillonite system. With increase in acidity the picloram was hydrogen bonded to the clay colloid surface.

The picloram adsorption data conformed to Freundlich isotherms suggesting a physical adsorption mechanism. The slopes of Freundlich isotherms for picloram decreased as the suspension pH increased.

Quantitative recovery of picloram from H-montmorillonite was obtained with repeated water wash treatments. At lower initial suspension pH, more water wash treatments were required to completely extract the adsorbed picloram.

An increase in KCl concentration in the picloram-H-montmorillonite suspensions greatly enhanced picloram adsorption. In the suspension with initial pH 1.06, picloram adsorption increased from 76 to 93% as the KCl concentration increased from 0 to 0.005 $\underline{N}$ while a five-fold increase in picloram adsorption was observed for the suspension with initial pH 2.20. As the KCl concentration in the suspensions with initial pH of 1.06 and 2.20 increased to 1 $\underline{N}$, the percentage of picloram adsorbed by H-montmorillonite approached the fraction of molecular picloram as would be predicted from the dissociation of picloram in aqueous solution. The enhanced picloram adsorption by H-montmorillonite with an increase in KCl concentration was caused by an increase in the hydronium ions in the bulk solution and hence the fraction of molecular picloram in the outer solution was increased.

PROTONATION OF PYRIDINE AND 4-AMINO-PYRIDINE

Introduction

Picloram, 4-amino-3, 5, 6-trichloropicolinic acid, may be sorbed to soil surfaces through both physical and chemical bonding mechanisms (Bailey et al., 1968). Previous studies (Chapter 5) have shown adsorption characteristics which relate closely to the pK_a of the picloram molecule. Bailey et al. (1968) have suggested the possibility of picloram protonation and a resultant coulombic attraction between the positively charged molecule and a negatively charged soil colloid.

Using pyridine as a basic structural unit, picloram is formed through incorporation of an amino group to the para-carbon atom, a carboxylate and chloro groups to the ortho-carbon atoms, and two chloro groups to the meta-carbons with respect to the annular nitrogen of the pyridine molecule (Figure 6-1). Investigation of the protonation feasibility of compounds such as pyridine and 4-amino-pyridine (Figure 6-1) structurally similar to picloram may aid in the understanding of the bonding mechanism of picloram.

Liquid pyridine has been characterized by C-H and N-H stretching bands from 3500 to 1650 cm^{-1}, nuclear vibrations from 1650 to 1400 cm^{-1}, in-plane hydrogen deformation frequencies from 1400 to 1020 cm^{-1}, and ring-breathing and bending modes as well as out-of-plane hydrogen deformation vibrations from 1020 to 700 cm^{-1}
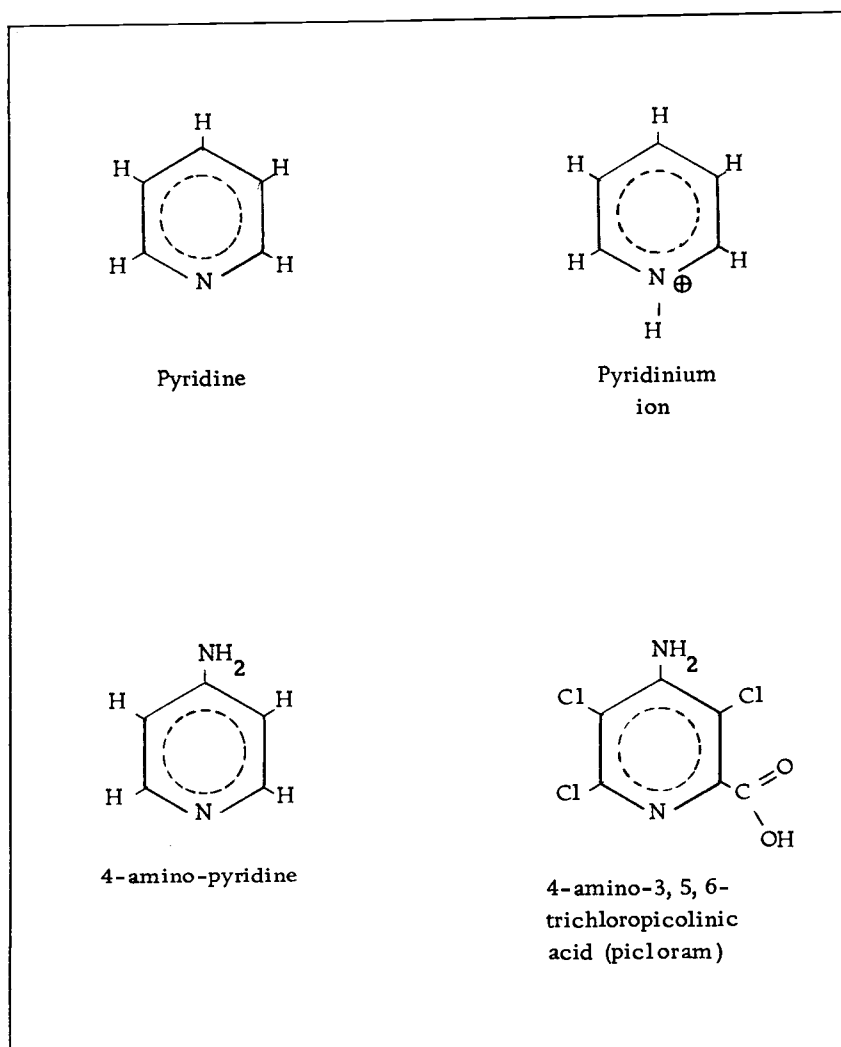
Figure 6-1. Chemical structures of pyridine, pyridinium ion, 4-amino-pyridine, and 4-amino-3, 5, 6-trichloro-picolinic acid (picloram).

(Table 6-1; Cook, 1961). The pyridine molecule forms salts with many

mineral and organic acids (Cook, 1961), and complexes with many

metals (Gill et al., 1961). In the pyridine salts, it is believed that a

proton is transferred from the acid to the pyridine molecule, to form

the pyridinium cation (Figure 6-1) and an anion (Cook, 1961; Green-

wood and Wade, 1960; Spinner, 1960).

Infrared absorption bands have been used to differentiate between

pyridine and its HCl-treated analogue (Table 6-1). Because the

pyridinium ion has an extra proton not present in pyridine, the pro-

tonated species should have three additional fundamental frequencies

in the spectrum. Therefore, the pyridinium ion should have 27 infra-

red active fundamentals because it has C_{2v} symmetry (pyridinium ion

possesses not only a proper axis C_2, but two vertical planes σ_v) (Cook,

1961). The three extra bands locate at 1540, 1620, and 2450 cm^{-1},

respectively. The exact frequencies of these three bands depend upon

the anionic species associated with the pyridinium cations. Cook (1961)

obtained a very broad, intense N-H stretching vibration (ν_{7a}) band at

2439 cm^{-1} for the pyridinium chloride salt; however, Greenwood and

Wade (1960) detected the ν_{7a} vibration band at 2740 cm^{-1}.

Infrared spectroscopy also provides a means to determine the

manner in which molecules are adsorbed by clay surfaces. Upon

exposure of montmorillonite clay films to pyridine at low vapor

pressures (2 mm Hg), Swoboda and Kunze (1965) were able to detect

Table 6-1. Infrared absorption bands of pyridine and pyridinium chloride.

Compound	Form	Wave number of absorption bands, [a] cm^{-1}																						Reference
pyridine	liquid	700 (11)	747 (4)	942 (5)	991 (1)	1031 (12)	1067 (18a)	1145 (15)	1217 (9a)	1350 (6a+10b)	1372 (14)	1436 (19b)	1478 (19a)	1570 (8b)	1578 (8a)	1593 (1+6a)	1627 (1+6b or (6a+12))							Gill et al. (1961)
pyridine	liquid	700	749	886 / 942	981 / 992	1030	1068 / 1085	1148	1218		1375	1439	1482	1572	1583									Wilmshurst and Bernstein (1957)
pyridine	liquid	700	743	810 / 883 / 942	990	1031	1068	1145	1216	1292 / 1355	1374	1439	1486		1582	1603	1637			2933	3030		3077		API project 44 (1945)
pyridine	liquid	704	749	799 / 811 / 837 / 880 / 941	991 / 997	1031	1051 / 1069	1148	1218			1438	1483		1582	1598				3005	3032	3056	3079		Ham et al. (1952)
pyridine	liquid				985	1023	1053	1137	1202			1438		1574									3076		Spense (1914)
pyridine	liquid	710	750		989	1027	1070																		Zingaro and Tolberg (1959)
pyridine	vapor	710 (10b)	744 (10a)	881 (18a) / 936 (5)		1037 (18b, 12, 1)		1136 (9a, 15)	1202 (3)		1376 (14)	1445 (19b)	1481 (19a) / 1510 (19a)			1605							3070 (20a, 20b)		Turkevich and Stevenson (1943)
pyridinium chloride	mull	680 (11)	750 (4)	945 (10b) / 1005 (5)	995 (1)	1030 (18a)	1060 (18b)	1162 (15)	1200 (9a) / 1244 (9b)	1318 (3)			1488 (19a) / 1532 (19b)	1610 (8b)	1634 (8a)			2375 / 2439 (7a)		3042				3130	Cook (1961)
pyridinium chloride	mull	684 (11)	759 (4)	940 (5)	1003 (1)	1059 (12)	1168 (18a)	1198 (15)		1252 (3)		1481 (19b)	1530 (19a)	1603 (8b)	1631 (8a)			2740 (7a)	2840						Greenwood and Wade (1960)
pyridinium chloride	mull	682 (11)	749 (4)	1012 (5)	997 (1)	1027 (18a)	1053 (18b)	1155 (15)	1189 (9a)	1245 (9b) / 1332 (3)		1428 (19b)	1479 (19a)	1604 (8b)	1630 (8a)										Spinner (1960)

[a] Numbers in parenthesis indicate the fundamental band assignments, based upon the work of Wilmshurst and Bernstein (1957) using the notation of Kline and Turkevich (1944)

pyridinium ions at 1538 cm^{-1}, characteristic of the $\overset{\oplus}{=}\underset{|}{N}$-H vibration.

When the vapor pressure was increased to 21 mm Hg, both chemisorbed and physically adsorbed pyridine was detected. The band at 1437 cm^{-1} was assigned to physically adsorbed molecules and the 1490, 1538, and 1634 cm^{-1} frequencies were assigned to chemisorbed pyridinium ions.

Using pyridine as a model compound for certain basic organic substances, Farmer and Mortland (1966) concluded from an infrared study that pyridine molecules formed strong hydrogen bonds with pyridinium ions in the interlayer space of montmorillonite. Their conclusion was based on the replacement of the N-H stretching vibration of the pyridinium ion in the 3300 to 2800 cm^{-1} region by two diffuse bands extending from 3300 to 2350 cm^{-1}, and from 2250 down to about 1900 cm^{-1} in the spectrum of the pyridine-pyridinium-montmorillonite complex.

To differentiate between Lewis (aprotonic) and Bronsted (protonic) acidity on the surface of acidic solids, Parry (1963) used infrared techniques to study the adsorption of pyridine by silica and alumina. He used the ring vibration bands at 1540 cm^{-1}, indicative of the pyridinium ion, along with the band near 1640 cm^{-1} and the very intense band at 1485 cm^{-1} to indicate Bronsted acidity, while a band in the 1440 to 1465 cm^{-1} region indicated Lewis acidity. The coordinated or hydrogen-bonded pyridine has a characteristic band in the

1440 to 1465 cm^{-1} region. It was shown that a Cab-O-Sil silica

hydrogen-bonded pyridine only on the basis of the presence of 1447

and 1599 cm^{-1} bands while an eta alumina (Bayerite) had considerable

strong Lewis acidity. After evacuation of the pyridine-Bayerite

system at successive high temperatures, the low frequency of a doublet

(1453 and 1457 cm^{-1}) disappeared first with evacuation which indicated

that there were at least two groups of Lewis sites on the surface of

the dehydrated alumina differing in acid strength. Based upon the

similarities of the absorption bands of pyridine-Bayerite to those of

coordinated or hydrogen-bonded pyridine, Parry (1963) concluded that

there were no Bronsted sites on the Bayerite surface strong enough to

react with pyridine.

In summary, from the above discussion, it is apparent that the

pyridine molecule can be protonated at the annular nitrogen atom by

reaction with inorganic or organic acids to form pyridinium salts.

The reaction of pyridine with metal chloride salts results in the

formation of coordination compounds. The surface of the montmoril-

lonite clay reacts chemically with pyridine at low vapor pressure while

it physically and chemically adsorbs pyridine at high vapor pressure.

The pyridine is hydrogen-bonded to the silica surface while it can be

coordination-bonded to an alumina surface.

Addition of an amino group to the para position (with respect to

annular nitrogen) of the pyridine molecule forms 4-amino-pyridine

(Figure 6-1). Because 4-amino-pyridine is similar in chemical structure to the picloram molecule, a survey of the chemical properties of 4-amino-pyridine will help understand the chemistry of picloram.

Ramiah and Puranik (1961) did not observe any experimental evidence for the presence of imino forms (Figure 6-2) in either 2-amino- or 4-amino-pyridine in accordance with Angyal and Angyal's studies (1952) which showed the ratio of amino- to imino- form of N-heterocyclic compounds was greater than 10^3:1. A relatively strong solid-solution shift (22 cm^{-1}) of the N-H deformation with increasing dilution occurred with the 4-amino-pyridine to indicate a relatively strong intermolecular association as shown in Figure 6-2 (Ramiah and Puranik, 1961).

The 4-amino-pyridine molecule could also exist in dimeric, tautomeric, and canonical form as illustrated in Figure 6-2.

Because of its dipolar nature, the reactivity of the annular nitrogen atom of 4-amino-pyridine toward a proton source increases while that of the amino group decreases (Katritzky and Lagowski, 1967). This suggests the possibility of protonating the annular nitrogen of 4-amino-pyridine molecule in an acid environment. With this concept in mind a study was initiated to investigate through infrared spectroscopy the protonation of 4-amino-pyridine.
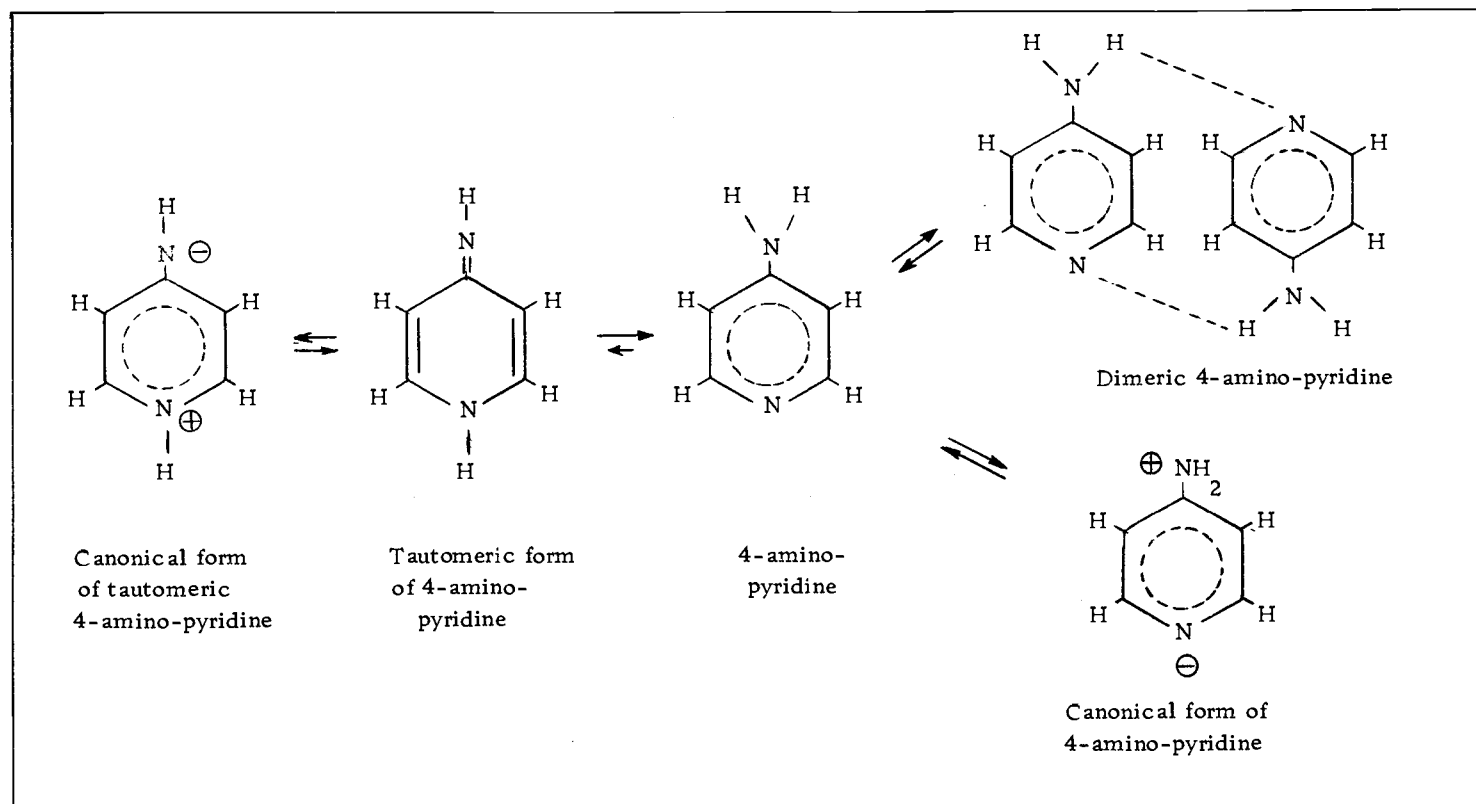
Figure 6-2. Equilibrium between different forms of 4-amino-pyridine.

Materials and Methods

A chemically pure sample of 4-amino-pyridine (0.25 g), recrystallized from 100% ethanol, was dissolved in 10 ml of distilled water. The solution was equilibrated with 4.25 ml of concentrated HCl at room temperature for 4 hr after which the system was oven-dried at 65°C. The infrared spectra of the 4-amino-pyridine and its HCl-treated derivative were obtained with a Beckman IR-7 infrared spectrophotometer.

Results and Discussion

Infrared Absorption Bands of 4-Amino-Pyridine

The 4-amino-pyridine contains 3N-6 infrared fundamental modes of vibration, where N represents the number of uncombined atoms free to move in three dimensions. Theoretically 3N-6 = 33 normal modes of vibration exist for the 4-amino-pyridine molecule. In practice, some of the 33 theoretically possible modes are degenerate and do not appear in the spectrum. The infrared absorption bands of 4-amino-pyridine recorded in this study displayed some minor variations from that recorded by Ramiah and Puranik (1961) (Figure 6-3 and Table 6-2). There were 22 distinct bands appearing between 700 and 4000 cm^{-1}.

The deviations for ν_4, ν_{18a}, ν_5, ν_1, ν_{9a}, ν_3, ν_{14}, ν_{19a}, ν_{8b},
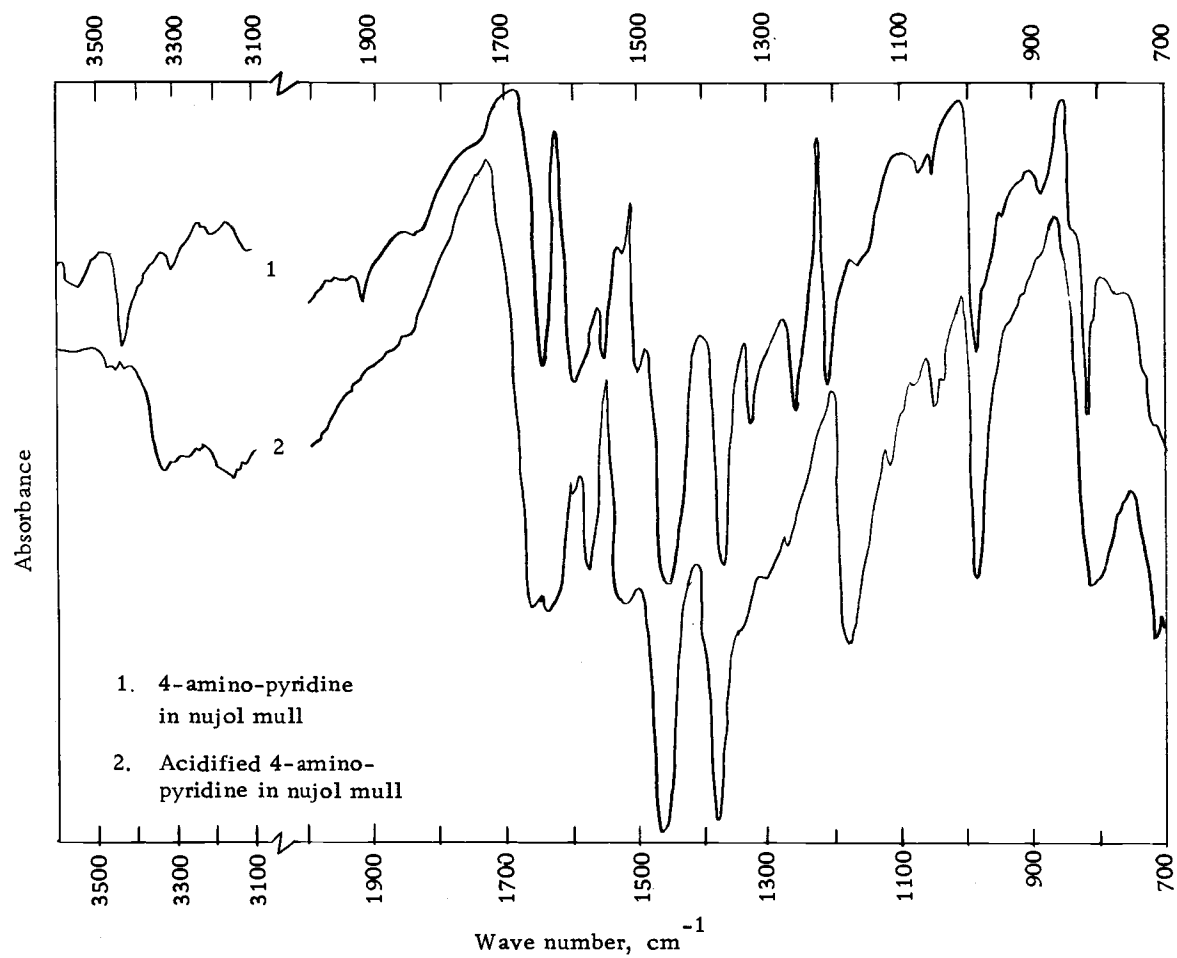
Figure 6-3.   Infrared spectra of 4-amino-pyridine and its HCl-treated analogue.

1. 4-amino-pyridine
   in nujol mull

2. Acidified 4-amino-
   pyridine in nujol mull

Table 6-2. Infrared absorption bands of 4-amino-pyridine and its HCl-treated analogue.

| Band assignment[a] | Infrared absorption bands, cm^{-1} | | 4-amino-pyridine[c] | Acidified 4-amino-pyridine[d] |
| | 4-amino-pyridine[b] | | | |
	Solid nujol mull	In CHCl$_3$	Solid nujol mull	Solid nujol mull
11			720	720
4	738(w)[e]		730	
18a	816(w)	820	810	809
10a, 10b	825 (vs)			
5	843 (ms)	843		
			890	890
			947	947
1	994 (vs)	994	985	988
				1036
18a	1053 (vw)	1053	1050	1050
			1073	1080
			1168	1115
9a(νCN)	1220(s)	1209	1212	1177
3	1271 (ms)	1264	1264	1270
3	1335 (ms)	1314	1330	1307
14	1353 (w)	1361	1350	1340
			1372	1374
19b	1438 (m)	1438	1460	1460
19a	1506 (m)	1499	1500	
			1520	1520
8b	1560 (sh)	1572	1550	1575
8a	1597 (vs)	1604	1600	1600
		1623		
δNH	1645 (s)	1645	1645	1640
				1660
		1840		
		1925		
20a	3040	2940		
20b	3090	3085		
νNH	3185	3175	3200	3155
νNH	3320	3320	3310	3330
νNH	3435	3420	3435	
		3510	3550	

[a] See Table 6-1

[b] Ramiah and Puranik (1961)

[c] This study

[d] This study

[e] vs = very strong; s = strong; ms = medium strong; m = medium, w = weak; vw = very weak, sh = shoulder

and ν_{8a} were less than 10 cm^{-1} while that of ν_{19b} exceeded 20 cm^{-1}.

Infrared Absorption Bands of HCl-
Treated 4-Amino-Pyridine

Upon treatment with 3.6 $\underline{N}$ HCl, new absorption bands appeared at 1036 cm^{-1} and 1660 cm^{-1} (Figure 6-3). The 1660 cm^{-1} band suggested the existence of an $\oplus \overset{\shortparallel}{\underset{\shortmid}{N}}$-H deformation frequency while the 1036 cm^{-1} was due to the ring symmetrical vibration mode. The ν CN band shifted from 1212 to 1177 cm^{-1} because of the bond formation between the annular nitrogen and HCl. The reaction of proton with a molecule would be favored if the molecule is a stronger proton-acceptor. The electron density located at the annular nitrogen of 4-amino-pyridine molecule is much higher than that at the amino-nitrogen due to the dipolar nature of 4-amino-pyridine. Therefore, the reactivity of the annular nitrogen toward a proton source is stronger than that of the amino-nitrogen. The bond formation between the annular nitrogen and HCl lowered the force constant of the C-N bond, so that some low frequency shift of absorption bands which involved the annular nitrogen would be expected. The ν_3 and ν_{14} appearing at 1330 and 1350 cm^{-1}, and the band at 1168 cm^{-1} similarly shifted to 1307, 1340, and 1115 cm^{-1}, respectively.

In addition to the low frequency shifts of the bands from C-N

functional groups, the ring vibrations ν_{19a} at 1500 cm^{-1}, and ν_{8b} at 1550 cm^{-1} shifted to 1520, and 1575 cm^{-1}, respectively. The high frequency shifts of ν_{8b} and ν_{19a} were caused by the increase in force constants of ring vibration due to the perturbation of ring system.

Summary and Conclusions

The 4-amino-pyridine accepted a proton on the annular nitrogen in an acid environment (3.6 $\underline{N}$ HCl). New absorption bands appeared at 1036 and 1660 cm^{-1} after the acid treatment indicating the existence of a ring symmetrical vibration mode and an $=\overset{\oplus}{\underset{|}{N}}$ -H deformation frequency. Four bands at 1168, 1212 (ν CN), 1330 (ν_3), and 1350 (ν_{14}) cm^{-1} showed distinct low frequency shifts indicative of a bond formation between the annular nitrogen and HCl. Two bands at 1500 (ν_{19a}) and 1550 (ν_{8b}) cm^{-1} shifted to 1520 and 1575 cm^{-1} after the acid treatment because of the perturbation of ring system. Because the 4-amino-pyridine has structural similarities with picloram, the information obtained from acidification of 4-amino-pyridine can be used to assess the possibility of protonating picloram in an acid environment and the effects of carboxylate and chloro functional groups on the infrared absorption spectra of picloram.

PROTONATION OF PICLORAM

Introduction

The nature and strength of adsorption of pesticides by soils directly relates to the fate and behavior of pesticides in soil systems. It is, therefore, of significance to explore the nature of bonding between pesticide molecules and soil colloids.

Picloram, 4-amino-3,5,6-trichloropicolinic acid, is uniquely effective against many perennial weeds, poisonous plants, shrubs, and other woody species. Combination sprays with 2,4-D or 2,4,5-T have been very effective for general brush control.

The adsorption of picloram by various adsorbents including montmorillonite clays has been shown to be pH-dependent (Hamaker et al., 1966). The relationship between the picloram adsorbed by montmorillonite clay and the suspension pH relates to the portion of picloram in molecular form (Chapter 5). When the suspension pH exceeds the pK_a of picloram (3.4), picloram occurs primarily in the anionic form while the molecular picloram predominates when the suspension pH falls below the pK_a of picloram. Therefore, the molecular picloram is considered to be preferentially adsorbed by the montmorillonite at pH $<<$ pK_a. To explain this adsorption phenomenon, Bailey et al. (1968) proposed the formation of protonated picloram at pH $\leq$ pK_a + 2.

The pH of a colloidal surface is lower than that in the bulk

solution (Bernstein, 1960; Harter and Ahlrichs, 1967). A consequence

of lower pH at or in close proximity to the colloidal surface suggests

that there may be protonation of compounds by surface acidity of clays

where hydrogen, aluminum, and transition elements are the predomi-

nant exchangeable cations. By means of infrared spectrophotometry,

the changes in charge distribution of pesticide molecules as the result

of protonation can be identified qualitatively.

The picloram molecule consists of a pyridine ring with carboxy-

late and chloro functional groups located at the ortho-carbon atoms

(with respect to annular nitrogen), an amino group at the para-

carbon, and two chloro groups at meta-carbon atoms. The infrared

spectrum of picloram in KBr (Ramsey, 1964; Saha and Gadallah, 1967)

has shown the presence of an $=\overset{\oplus}{\underset{|}{N}}$-H group which suggests the existence

of picloram as a dipolar (or zwitterionic) molecule (Figure 7-1).

Although picloram can also be in equilibrium with its tautomeric form,

the ratio of amino to imino-form of picloram, as for most of the α-

and γ-amino-N-heterocyclic compounds (Angyal and Angyal, 1952), is

so great that picloram molecules exist predominatly in the amino

form (Figure 7-1).

Depending on the pH of the system, picloram can exist either in

the anionic or molecular form (Figure 7-1). In an extremely acid

environment, however, it is of significance to know whether picloram
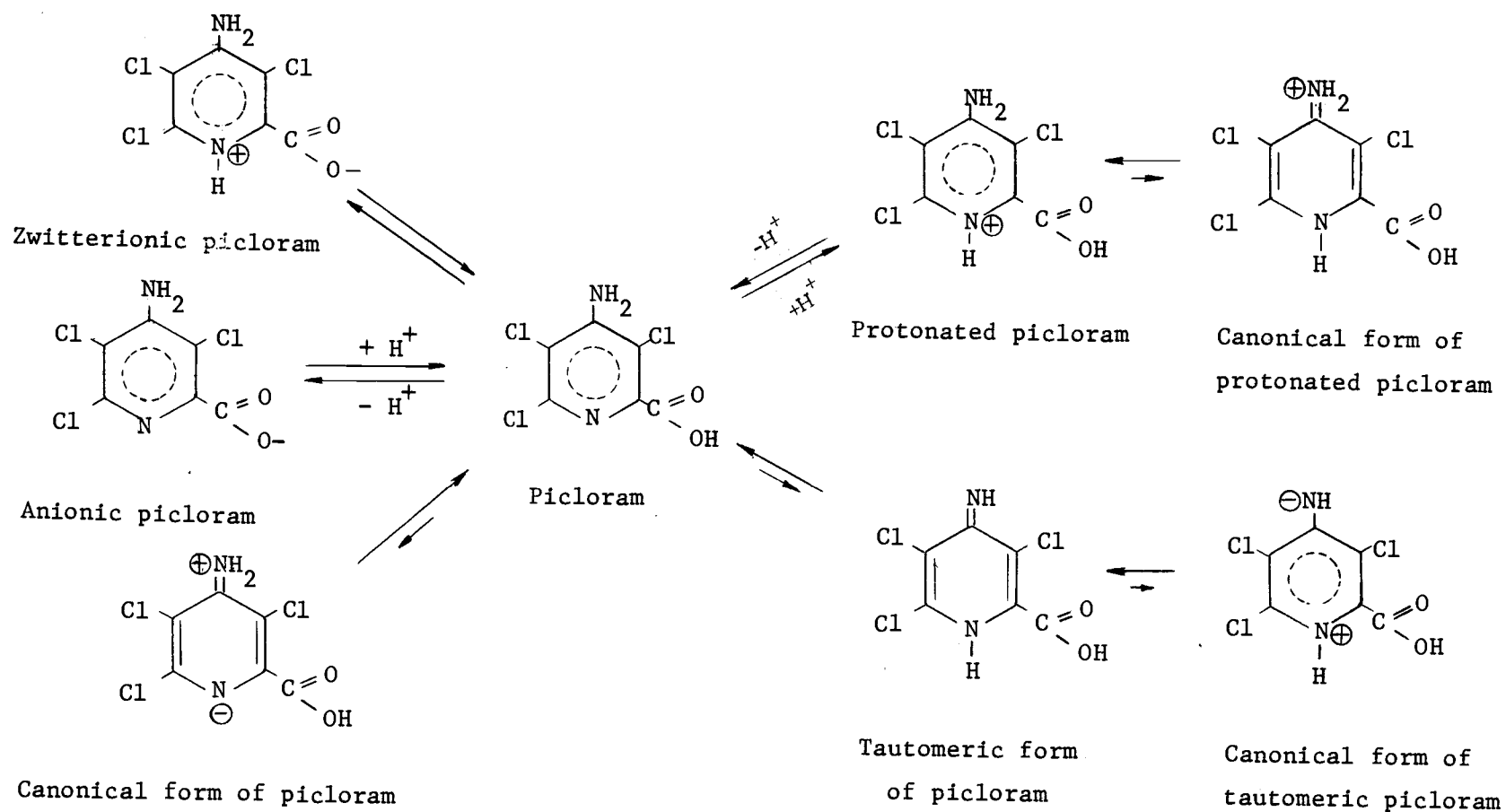
Figure 7-1. The canonical and tautomeric forms of picloram and its protonated analogue.

can be protonated. Bailey et al. (1968) have proposed the protonation of picloram to be one of the possible adsorption mechanisms by H-montmorillonite. From the structure of picloram, it is apparent that both the annular and amino nitrogen atoms possess a lone pair of electrons which may serve as strong proton-acceptors. However, the canonical form of picloram (Figure 7-1) increases the reactivity of the annular nitrogen atom towards the electrophilic reagents (e. g. , protons) but decreases that of the amino group (Katritzky and Lagowski, 1967). Consequently, protons can preferentially react at the annular nitrogen atom of picloram. This suggests the possibility of protonating the annular nitrogen of the picloram molecule if the pH $<<$ pK$_a$ of picloram.

The objective of this research was, thus, to investigate through infrared spectrophotometry the possibility of picloram protonation under acid conditions.

Materials and Methods

Acidification of Picloram

Analytical grade picloram (0. 25 g; 99% pure) was equilibrated in an Erlenmeyer flask with 500 ml of distilled water on a wrist action shaker at room temperature for three days. The flask was wrapped with an aluminum foil to prevent photodecomposition of picloram

by ultraviolet light during equilibration period. One hundred ml of the

saturated picloram solution (597 ppm) was equilibrated with 30 ml of

12 $\underline{N}$ HCl at room temperature for 4 hr after which the system was

oven-dried at $65^{\circ}C$. An additional 100 ml of the saturated picloram

solution, as a check, was treated with 30 ml of distilled water and

dried at $65^{\circ}C$.

After the acid treatment, the picloram crystals (0.03 g) were

ground in a mortar with 5 drops of nujol oil and the mull placed

between two Irtran-II discs. The infrared spectrum from 700 cm^{-1}

to 4000 cm^{-1} was obtained with a Beckman IR-7 infrared spectro-

photometer.

An additional 0.03 g of picloram was reacted with 0.124 ml of

6 $\underline{N}$ HCl or distilled water, transferred to Irtran-II discs, and infra-

red spectra obtained.

Deuteration of Picloram

Picloram (0.03 g) was added to 50 ml of deuterated water and

equilibrated for 192 hr on a wrist action shaker. The solution was

filtered through Whatman No. 50 filter paper and the filtrate oven-

dried at $65^{\circ}C$. The resultant partially deuterated picloram sample

was scanned on an infrared spectrophotometer by the nujol mull

technique described previously.

Results and Discussion

Infrared Absorption Bands of H-Picloram,
and Partially Deuterated Picloram

The absorption bands of acid picloram at 3372 cm^{-1} and 3472 cm^{-1} were assigned to the symmetrical and asymmetrical νNH stretching vibrations of the NH$_2$ group (Table 7-1 and Figure 7-2). Upon partial deuteration of the picloram sample, the symmetrical and asymmetrical νND$_2$ appeared at 2372 and 2470 cm^{-1} with νND$_2$/νNH$_2$ ratios being 0.7034 and 0.7114, respectively. The symmetrical and asymmetrical δNH$_2$ bending vibrations caused frequencies at 1540 and 1602 cm^{-1} (Cross and Jones, 1969; Saha and Gadallah, 1967). These frequencies shifted to 1083 and 1170 cm^{-1} after deuteration with δND$_2$/δNH$_2$ ratios being 0.7032 and 0.7303, respectively. Saha and Gadallah (1967) suggested the band at around 2600 cm^{-1} to be the positively charged immonium ($=\overset{\oplus}{\underset{|}{N}}$-H) stretching vibration. The band at 1705 cm^{-1} is the characteristic νC = 0 vibration (Flett, 1951; Ramsey, 1964).

The two δCOOH frequencies of acid picloram appeared at 1280 and 1377.5 cm^{-1}, respectively (Cross and Jones, 1969; Flett, 1951) and shifted to 965 and 1050 cm^{-1} for δCOOD group (D/H ratios being 0.7539 and 0.7623, respectively). The band at 1240 cm^{-1} was assigned to the νCN vibration (Dyer, 1965). The bands at 887.5 cm^{-1}

Table 7-1. Infrared absorption bands of picloram, and partially deuterated picloram.

Structural group[a]	Wave number of absorption bands of picloram, cm^{-1}	Structural group[a]	Wave number of absorption bands of deuterated picloram, cm^{-1}	D/H ratio	Reference
νCCl	720				Dyer (1965)
νCCl	728				Dyer (1965)
νCCl	759				Dyer (1965)
		X-sensitive (D)	796	0.7439	
δ OH (op)	887.5	δOH (op)	885		Cross and Jones (1969); Flett (1951)
δ OH (op)	910	δOH (op)	915		Cross and Jones (1969); Flett (1951)
		δCOOD	965	0.7539	
ring vibration	992.5				
		δCOOD	1050	0.7623	
X-sensitive (H)	1070				
		δND$_2$ (sym)	1083	0.7032	
X-sensitive (H)	1107	X-sensitive	1097		
		δND$_2$ (asym)	1170	0.7303	
νCN	1240	νCN	1247		Dyer (1965)
δ COOH	1280	δCOOH	1285		Cross and Jones (1969); Flett (1951)
νC=C (ip)	1306	νC=C (ip)	1314		
δ COOH	1377.5	δ COOH	1375		Cross and Jones (1969); Flett (1951)
νC=C	1437				Flett (1951)
νC=C (ip)	1458	νC=C (ip)	1462		
δ NH$_2$ (sym)	1540	δNH$_2$ (sym)	1555		Cross and Jones (1969); Saha and Gadallah (1967)
δ NH$_2$ (asym)	1602	δNH$_2$ (asym)	1603		Cross and Jones (1969); Saha and Gadallah (1967)
νC=O	1705	νC=O	1700		Flett (1951); Ramsey (1964)
		νND$_2$ (sym)	2372	0.7034	
		νND$_2$ (asym)	2470	0.7114	
ν=N-H (sym)	2598				Cross and Jones (1969); Rao (1963); Saha and Gadallah (1967)
ν=N-H (asym)	2653	ν=N-H	2600		Cross and Jones (1969); Rao (1963); Saha and Gadallah (1967)
νNH$_2$ (sym)	3372	νNH$_2$ (sym)	3362		Ramsey (1964); Saha and Gadallah (1967); Swoboda and Kunze (1968)
νNH$_2$ (asym)	3472	νNH$_2$ (asym)	3478		Ramsey (1964); Saha and Gadallah (1967); Swoboda and Kunze (1968)

[a] ν = stretching; δ = bending; op = out-of-plane; ip = in-plane; sym = symmetric; asym = asymmetric
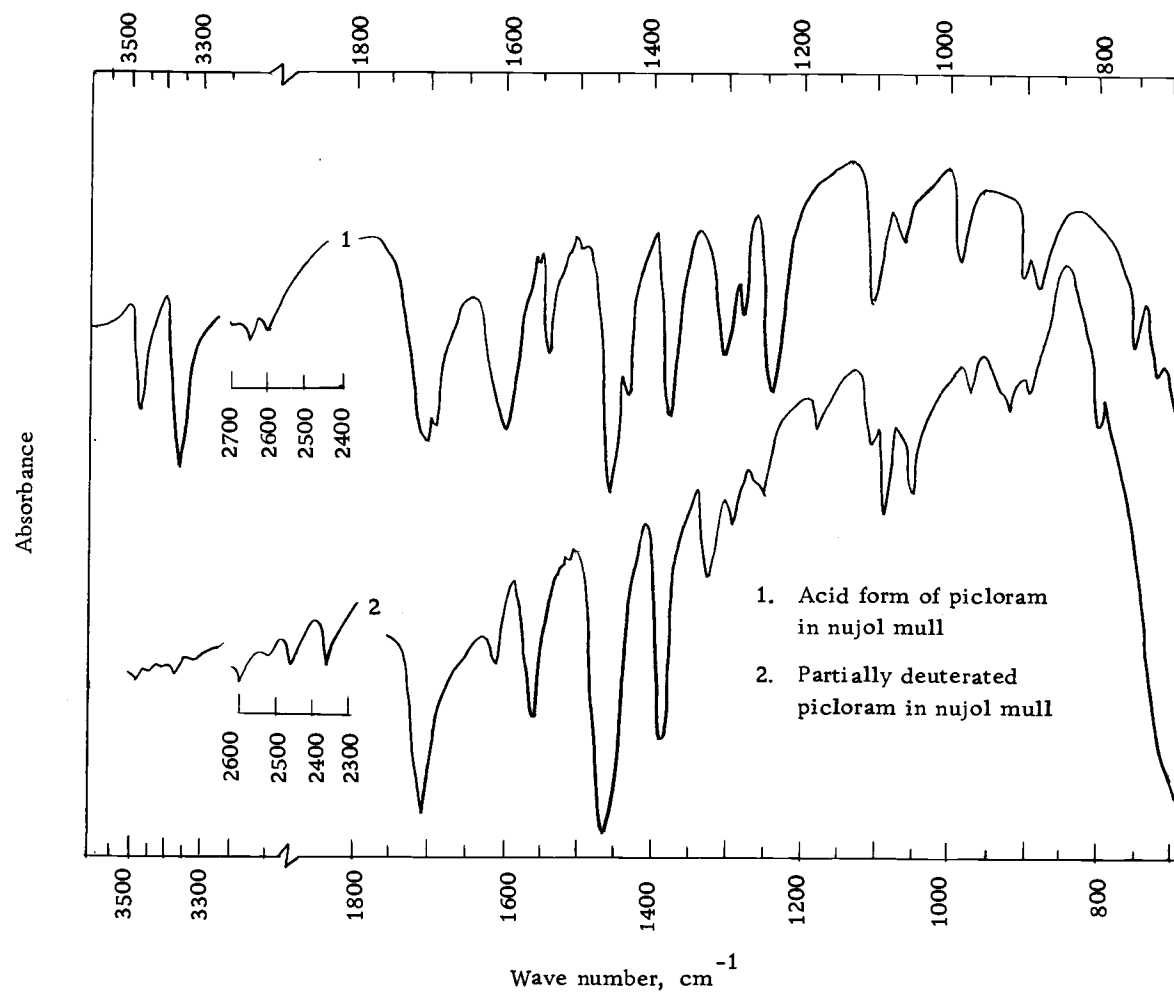
Figure 7-2. Infrared spectra of acid picloram and its partially deuterated analogue.

and 910 cm^{-1} were due to out-of-plane δOH vibration. Other band

assignments for the structural groups are shown in Table 7-1.

Picloram Acidification

The absorption bands of acid picloram (spectrum 1, Figure 7-3)

were not affected by the heat treatment at 65°C (spectrum 2, Figure

7-3). After reaction of acid picloram with the 3.6 $\underline{N}$ HCl solution

and subsequent heat treatment, the absorption bands of picloram did

not show any significant shifts (spectrum 3, Figure 7-3). It was

initially thought that the heat treatment might have inhibited the

acidification of picloram or induced picloram volatilization. An

intimate mixture of picloram with 6 $\underline{N}$ HCl was, therefore, ground in a

mortar, transferred to Irtran-II discs, and infrared spectrum obtained.

The picloram spectrum thus obtained (spectrum 4, Figure 7-3) was

essentially similar to that of the parent picloram compound; however,

the presence of water when the picloram was not dried caused con-

siderable broadness in the 1602, 1705, 3372, and 3472 cm^{-1} bands

(Table 7-2 and Figure 7-3). The resolution of the 1437.5 and 1454

cm^{-1} bands was improved for picloram after acid treatment (spectrum

4, Figure 7-3) because no nujol oil was added to the sample. The

addition of nujol oil to the above system caused the broadening of

1437.5 and 1454 cm^{-1} bands as shown by the spectrum 5 of Figure 7-3.

In aqueous picloram (spectrum 6, Figure 7-3), the resolution of 1437.5

and 1454 cm^{-1} was again improved.
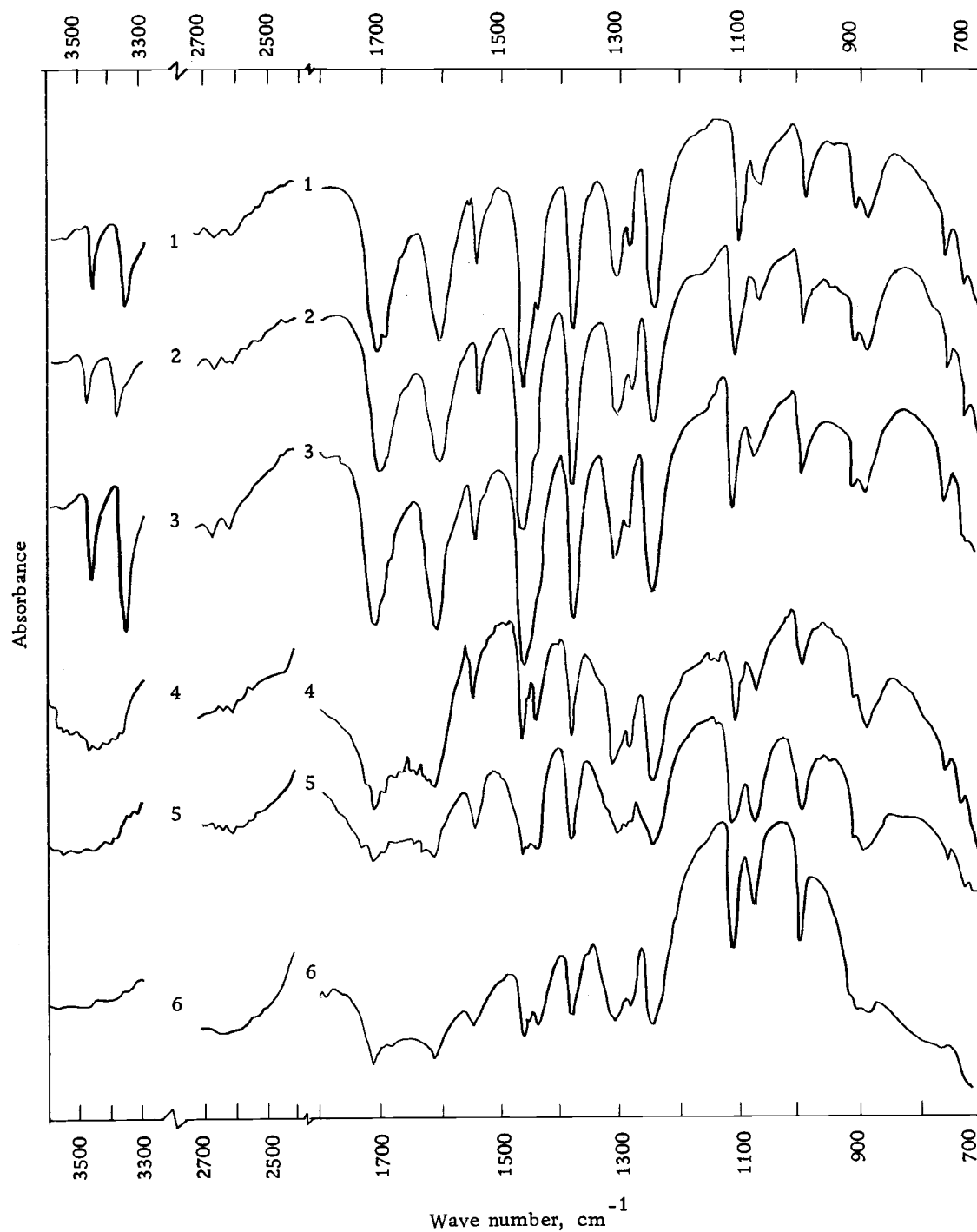
Figure 7-3.   Infrared absorption spectra of picloram and HCl-treated analogues.   Spectrum (1) = 0. 03 g picloram in nujol ; (2) = 0. 03 g picloram aqueous solution, dried at 65°C for 3 days, in nujol; (3) = 0. 03 g picloram in 3. 6 $\underline{N}$ HCl solution, dried at 65°C for 3 days, in nujol; (4) 0. 03 g picloram + 0. 124 ml 6 $\underline{N}$ HCl; (5) 0. 03 g picloram + 0. 124 ml 6 $\underline{N}$ HCl, in nujol; (6) 0. 03 g picloram + 0. 124 ml H_2O.

Table 7-2. Infrared absorption bands of pilcloram and its HCl-treated analogues.

Band Assignment[a]	Intensity[b]	Wave Number, cm^{-1} Systems[c]					
		1	2	3	4	5	6
νCCl	vw	720.0	718.0	720.0	--	720.0	--
νCCl	vw	728.0	728.0	728.0	730.0	727.5	--
νCCl	w	759.0	758.0	760.0	760.0	760.0	760.0
δOH (op)	ms	887.5	888.0	892.0	888.0	888.0	884.0
δOH (op)	ms	910.0	909.0	910.0	910.0	910.0	912.0
ring vibration	ms	992.5	992.5	993.0	995.0	995.0	995.0
X-sensitive	w	1070.0	1067.0	1069.0	1072.5	1074.0	1072.0
X-sensitive	s	1107.0	1105.0	1107.0	1107.5	1110.0	1107.5
νCN	vs	1240.0	1242.0	1242.5	1243.0	1243.0	1245.0
δCOOH	ms	1280.0	1280.0	1282.0	1282.5	1282.5	1284.0
δC=C (ip)	s	1306.0	1304.0	1305.0	1310.0	1308.0	1307.5
δCOOH	vs	1377.5	1377.0	1377.0	1382.0	1382.5	1381.0
νC=C (ip)	sh	1437.0	1437.0	1437.0	1437.5	1442.0	1437.5
δC=C (ip)	vs	1458.0	1459.0	1459.0	1454.0	1454.0	1453.0
δNH$_2$(sym)	vs	1540.0	1540.0	1540.0	1544.0	1543.0	1544.0
δNH$_2$ (asym)	vs	1602.0	1604.0	1604.0	*	*	*
νC=O	vs	1705.0	1704.0	1705.0	1708.0	1710.0	1708.0
ν=N-H (sym)	vw	2598.0	2598.0	2599.0	2600.0	2600.0	--
ν=N-H (asym)	vw	2653.0	2655.0	2653.0	2650.0	2650.0	--
νNH$_2$(sym)	ms	3372.0	3372.5	3374.0	*	*	*
νNH$_2$ (asym)	ms	3472.0	3472.0	3474.0	*	*	*

[a] ν = stretching, δ = bending, op = out-of-plane, ip = in-plane, sym = symmetric, asym = asymmetric

[b] vs = very strong, s = strong, ms = medium strong, w = weak, vw = very weak

[c] Systems   1 = 0.03 g pilcloram in nujol

   2 = 0.03 g pilcloram (aqueous solution dried at 65°C for 3 days) in nujol

   3 = 0.03 g pilcloram (3.6 $\underline{N}$ HCl solution dried at 65°C for 3 days) in nujol

   4 = 0.03 g pilcloram + 0.124 ml 6 $\underline{N}$ HCl

   5 = 0.03 g pilcloram + 0.124 ml 6 $\underline{N}$ HCl + 5 drops nujol

   6 = 0.03 g pilcloram + 0.124 ml H$_2$O

*Overlapped by strong water bands

The infrared absorption spectra of protonated pyridine or 4-amino-pyridine were quite different from those of the parent compounds (Chapter 6). These differences were caused by the increase in fundamental vibration modes and the accompanying band shifts resultant from the proton addition to pyridine or 4-amino-pyridine molecule. It is, therefore, logical to expect a different spectrum for protonated picloram as compared to the acid parent picloram.

The absorption spectrum of the acidified picloram did not differ from its parent compound (Figure 7-3 and Table 7-2). Therefore, it appears impossible to protonate the picloram molecule under the experimental conditions described in this study. The lack of protonation could result from the following:

(1)   The dipolar nature of picloram molecule reduced the basicity of the annular nitrogen of pyridine ring as shown in the following diagram:
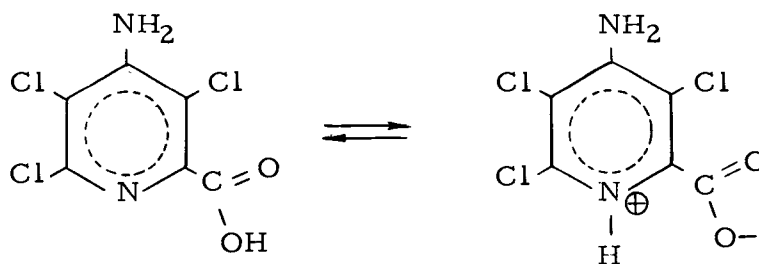
(2)   The electron-withdrawing groups such as the chlorine and carboxylic acid further reduced the basicity of the amino nitrogen of the picloram molecule as reflected by a single pK_a of 3. 4 (Appendix Figure 2).

Summary and Conclusions

Infrared absorption bands for picloram between 700 and 4000 cm^{-1} were assigned and confirmed by deuteration techniques. The positively charged immonium ($=\overset{\oplus}{\underset{|}{N}}$-H) stretching vibration and the characteristic ν C=O vibration appeared at 2600 and 1705 cm^{-1}, respectively. The $=\overset{\oplus}{\underset{|}{N}}$-H stretching vibration did not increase in intensity in an acid environment, nor did the acidified picloram differ in absorption spectrum from its parent compound, thus indicating an absence of picloram protonation. Due to the dipolar nature of the picloram molecule and the electron-withdrawing effects of functional groups, no or very little protonated picloram occurred.

BONDING MECHANISMS BETWEEN PICLORAM AND
ACID MONTMORILLONITE CLAYS

Introduction

Picloram adsorption increases with a decrease in soil pH. The

formation of protonated picloram has been indicated as the mechanism

by which picloram is adsorbed by H-saturated montmorillonite

(Bailey et al., 1968). However, the possibility of picloram protona-

tion under acid (3.6 N) conditions has been discounted in aqueous

systems (Chapter 7). The other possible mechanisms of adsorption of

acid compounds including picloram as suggested by Bailey et al. (1968)

included: (1) physical adsorption; (2) coordination through the

carbonyl functional group; (3) association of the carbonyl by bridging

to coordinated water on the exchange ions; and (4) hydrogen bonding

from the carboxyl group to the clay surface.

Infrared spectroscopy plays a unique role in the characterization

of the reaction between organic chemicals and soil constituents. Infra-

red techniques enable the qualitative interpretation of bond formation

between a chemical and an adsorbent surface. The objective of this

research was to clarify the bonding mechanism between picloram and

acid montmorillonite clays.

Materials and Methods

Picloram-Montmorillonite Interaction

A < 2 μ suspension of montmorillonite clay was equilibrated with ten symmetries of H- and/or Al-exchange resin (Rexyn 101 H, Fisher Scientific Company) for one-half hour after which the clay was filtered through a nylon cloth. The H- or Al-saturation treatment was repeated twice. The pH of the resultant H- and Al-montmorillonite was 2.35 and 4.00 respectively, as measured with a Corning Model 7 pH meter equipped with a combination electrode.

A 15-ml aliquot of 30% ethanol solution containing 0.014 g picloram was pipetted into an Erlenmeyer flask containing approximately 0.16 g of the H- or Al-montmorillonite clay. The pH of the systems were adjusted with HCl or NaOH to 1.6, 3.0, 5.5, 12.0, and 12.6. The volume of the clay slurry was adjusted to 20 ml with distilled water so that the picloram concentration in the final solution was 700 ppm. The systems were equilibrated on a wrist action shaker at room temperature for 24 hr after which 2 ml of each system was pipetted onto Irtran-II discs. Upon drying, the samples were analyzed with a Beckman IR-7 infrared spectrophotometer.

Formation of Na Salt of Picloram

A saturated aqueous picloram solution was titrated with 0.2 $\underline{N}$

NaOH solution to pH 12 and oven-dried at 65°C. The infrared spectrum

of the resultant sodium salt of picloram was obtained by the nujol

mull technique.

Results and Discussion

Picloram and H-Montmorillonite

The skeletal ring vibration of picloram increased from 1458 cm^{-1}

in the parent compound to 1493 cm^{-1} upon its interaction with H-

montmorillonite at pH 1.6 (Table 8-1 and Figure 8-1). This con-

siderable increase in skeletal vibration frequency indicates the per-

turbation of ring vibration. The δCOOH band appearing at 1377.5

cm^{-1} for the parent picloram also shifted to 1389 cm^{-1} (Table 8-1 and

Figure 8-1). Infrared absorption bands which represent structural

Si-O and Al-O below 1100 cm^{-1} and H_2O and clay hydroxyl groups

below 3100 cm^{-1} restrict observations of picloram frequencies in

these regions (Skipper, 1970).

After interaction of picloram with H-montmorillonite in an acid

environment (pH 1.6), the carbonyl stretching frequency of picloram

increased slightly from 1705 to 1724 cm^{-1} (Table 8-1 and Figure 8-1).

One of the NH_2 deformation bands increased from 1540 to 1566 cm^{-1}

while the other probably shifted from 1602 to 1632 cm^{-1} (Table 8-1 and

Figure 8-1). The uncertainty in the latter band shift arises from the

Table 8-1. Infrared absorption bands of reaction products of picloram with H- and Al-montmorillonite as a function of suspension pH.

System	State	Suspension pH	Wave number of absorption bands, cm^{-1}								
Picloram	Nujol mull	--	1705	1602	1540	1458	1437	1377.5	1306	1280	1240
Picloram + HCl + H-montmorillonite	Clay film	1.60	1724	1632	1566	1493	1438	1389	1311	--	--
Picloram + H-montmorillonite	Clay film	2.75	1727.5	1632.5	1564	1492	1435	1400	--	--	--
Picloram + NaOH + H-montmorillonite	Clay film	5.50	--	1622	1545	1458	1424	1358	1312.5	--	--
Picloram + NaOH + H-montmorillonite	Clay film	12.60	--	1637.5	--	1450	--	--	--	--	--
Picloram + HCl + Al-montmorillonite	Clay film	1.60	1724	1634	1567	1493	1441	1388	1312	--	--
Picloram + Al-montmorillonite	Clay film	3.00	1678	1625	1558	1507.5	1482	1404	1337	1275	--
Picloram + NaOH + Al-montmorillonite	Clay film	5.50	1678	1625	1558	1507.5	1482	1404	1337	1275	--
Picloram + NaOH + Al-montmorillonite	Clay film	12.00	--	1618	1537	--	1435	1365	1292	--	--
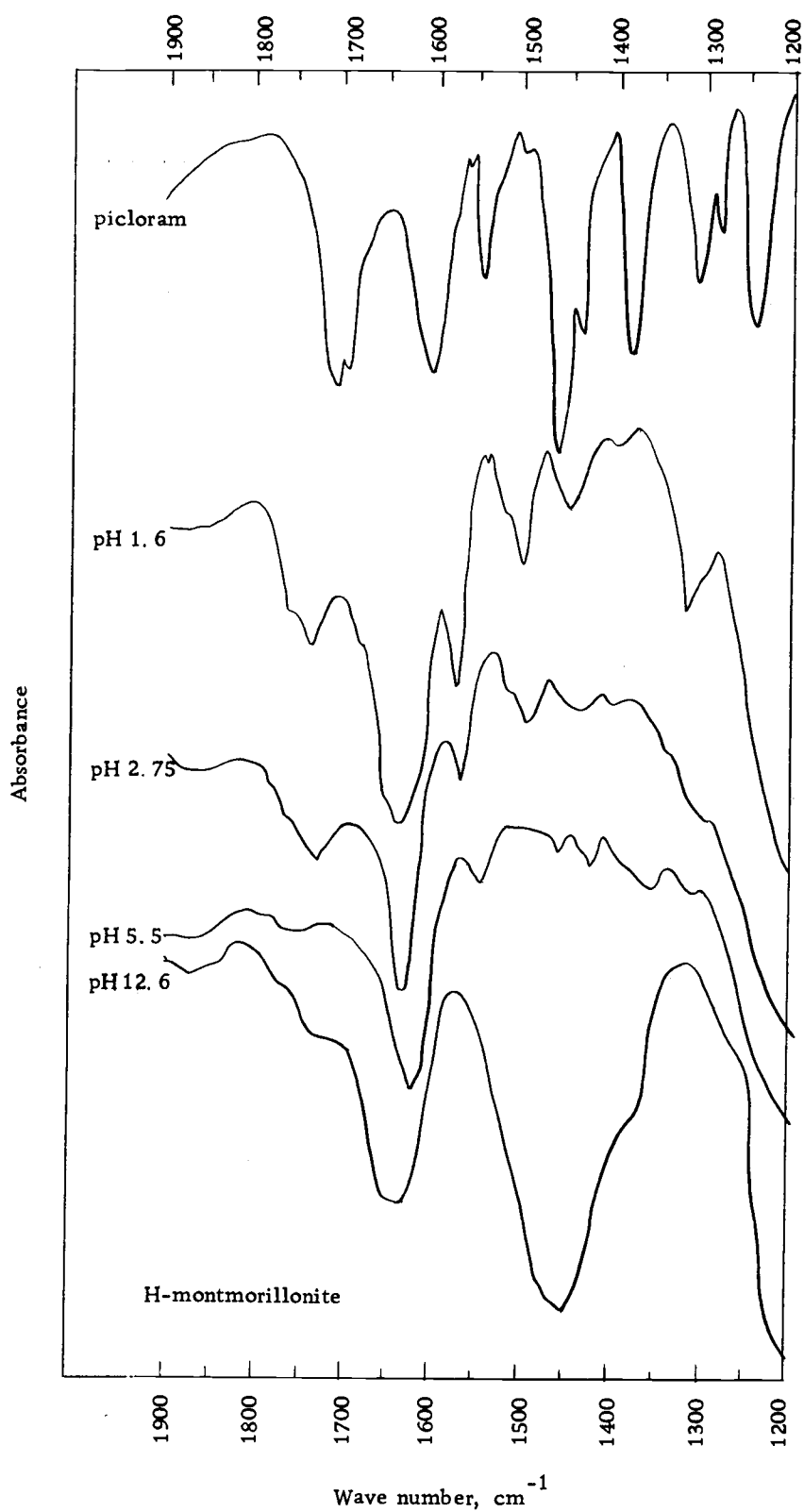
Figure 8-1. Infrared spectra of reaction products of picloram and H-montmorillonite as a function of suspension pH.

fact that the residual water has a very strong absorption band centering around 1632 cm^{-1}. The increase in the carbonyl stretching frequency and NH$_2$ deformation bands seemed to indicate a preferential inter-action between the annular nitrogen rather than the carbonyl oxygen of the picloram molecule with H-montmorillonite. The direct interaction between annular nitrogen and exchangeable hydrogen on the clay surface reduced the force constant of the CN and hence decreased the νCN frequency; however, the change in νCN could not be ascer-tained because the strong absorption band below 1250 cm^{-1}, a result of the clay hydroxyl groups, restricted observations of picloram fre-quencies in this region. The increase in νC=O and skeletal vibrations resulted from changes in molecular symmetry which were caused by a decrease in CN bond energy due to sharing of its electrons with the exchangeable H through a hydrogen bond (Harter and Ahlrichs, 1969; Mortland and Meggitt, 1966).

It was previously proposed that the electronegativity of the carbonyl oxygen and annular nitrogen is higher than its anionic analogue in molecular picloram (Chapter 5). Also, the possibility of picloram protonation in an acid environment has been eliminated in studies on aqueous acidic picloram solutions (Chapter 7). A complete recovery of adsorbed picloram from acid montmorillonite by consecutive water wash treatments provides evidence of a physical adsorption mechanism (Chapter 5). Therefore, it is logical to conclude

that a hydrogen bond formation between the annular nitrogen of the

picloram molecule and the exchangeable H^+ of acid montmorillonite

accounted for increased picloram adsorption at low pH values.

The infrared absorption bands for the picloram-montmorillonite

system at pH 2.75 were similar to those at pH 1.6. This is under-

standable if we consider the acidity of the picloram-montmorillonite

system. Upon air-drying, the pH of the picloram-montmorillonite

system could drop from 1.6 and 2.75 to 0 or below. Previous studies

showed complete adsorption of picloram by H-montmorillonite at pH 0

or below (Chapter 5). It is, therefore, not surprising to obtain simi-

lar infrared spectra for the picloram-montmorillonite system at pH

1.6 or 2.75.

After adjusting the suspension pH of the picloram-

montmorillonite system to 5.5, the montmorillonite clay became Na-

saturated and the picloram could have been partially converted to the

Na-salt. Therefore, the infrared absorption bands displayed at pH

5.5 would reflect the combination of parent picloram and the Na salt

form. At pH 5.5, one of the NH_2 deformation bands appeared at 1545

cm^{-1}, while the other NH_2 deformation band was overlapped by a

strong water band centering around 1622 cm^{-1} (Table 8-1 and Figure

8-1). The NH_2 deformation bands of parent picloram compound

appeared at 1540 and 1602 cm^{-1}, respectively. One of the skeletal

ring vibrations remained at 1458 cm^{-1} while the bands at 1437,

1377.5, and 1306 cm^{-1} for parent picloram shifted to 1424,

1358, and 1312.5 cm^{-1}, respectively. The positions of the latter three

bands did not coincide with those obtained for Na-picloram (Table 8-2

and Figure 8-2).

The formation of the Na-salt of picloram caused a shift of the

νC=O frequency of parent picloram compound from 1705 to 1620 cm^{-1}.

Replacement of Na for H lowers the force constant of the C=O and

thus decreases the frequency. The νNH$_2$ bands were affected only

slightly. The νNH$_2$ bands increased from 3372 and 3472 to 3380 and

3500 cm^{-1}, respectively. The νCN increased from 1240 to 1260

cm^{-1} as expected because the annular nitrogen was affected to a

larger extent by the change in the carboxylate group.

The presence of excess NaOH in the Na-picloram sample did

not interfere with any of the absorption bands. Busing (1955) observed

only one νOH band at 3637.4 cm^{-1} for NaOH in the infrared region

employed in this study, i.e., from 700 to 4000 cm^{-1}.

Upon adjustment of the picloram-montmorillonite suspension pH

to 12.6, two strong, broad bands appeared at 1637.5 cm^{-1} and 1450

cm^{-1}. The presence of these two bands restricted observation of

picloram frequencies. However, at pH 12.6 one would expect no

picloram adsorption and the spectrum obtained should reflect that of

Na-picloram.

Table 8-2. Infrared absorption bands of Na salt of picloram.

Structural group [a]	Wave number of absorption band, cm^{-1}
νCCl	715
νCCl	730
νCCl	780
$\delta ONa(op)$	818
$\delta ONa(op)$	906
ring vibration	1005
X-sensitive	1050
--	1080
X-sensitive	1098
νCN	1260
$\delta COONa$	1375
$\nu C=C$ (ip)	1458
$\delta NH_2(sym)$	1534
$\delta NH_2(asym)$	1595
$\nu C=O$	1620
$\nu NH_2(sym)$	3380
$\nu NH_2(asym)$	3500

[a]See Table 7-1 for abbreviations
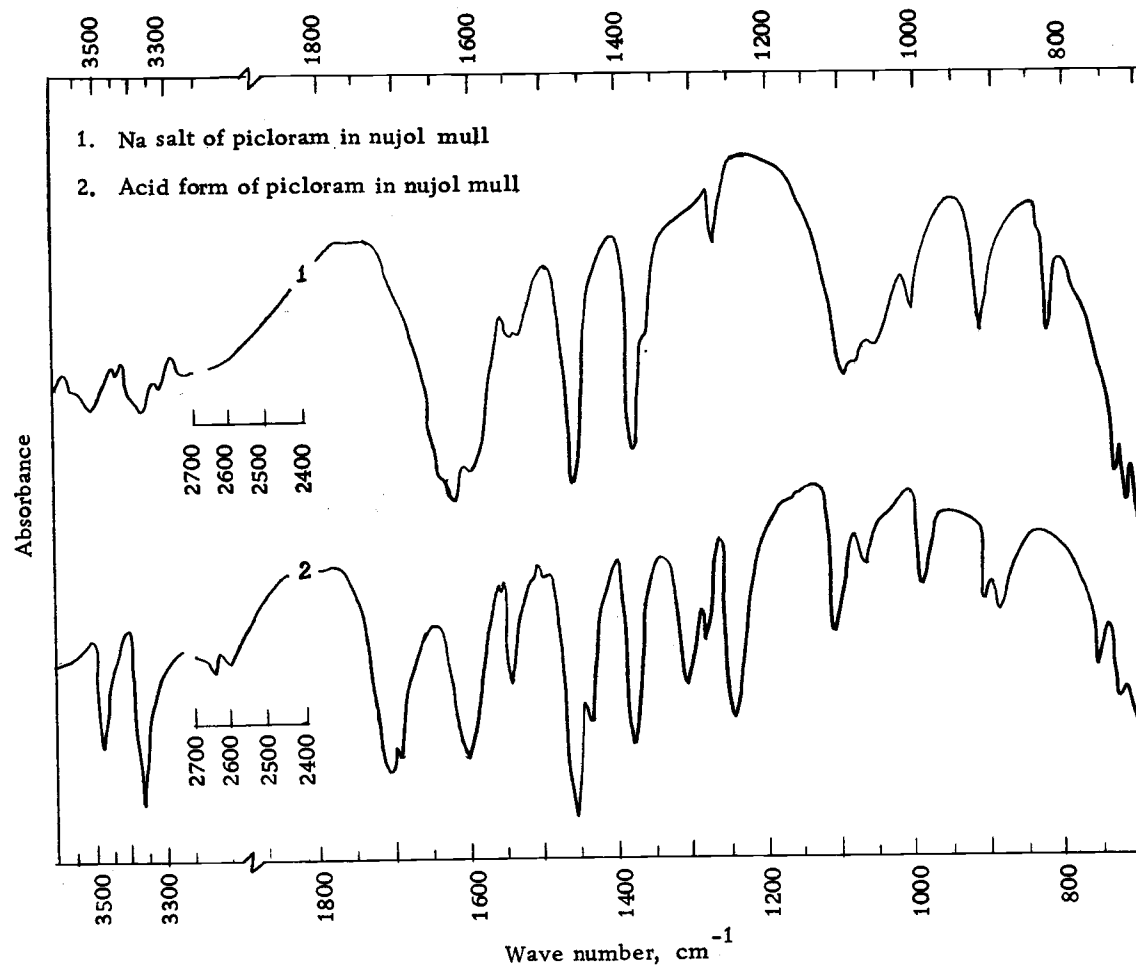
Figure 8-2. Infrared spectra of acid picloram and its sodium salt.

Picloram and Al-Montmorillonite

For the Al-montmorillonite and picloram system adjusted to pH 1.6 the infrared spectrum was similar to the one for picloram-H-montmorillonite at pH 1.6 (Table 8-1 and Figure 8-3). The similarity suggests a possibility that the annular nitrogen of the picloram is associated with the aluminum ions through a bridging effect of coordinated water (Figure 8-4). Farmer and Mortland (1966) have suggested the same mechanism for certain pyridine-metal-clay complexes.

After interaction of picloram with Al-montmorillonite at pH 3.0, a strong water band appeared at 1625 cm^{-1} which restricted the observation of the carbonyl stretching frequency. A shoulder at 1700 cm^{-1} did appear, probably indicating a carbonyl stretching frequency. The symmetrical NH_2 deformation band appearing at 1540 cm^{-1} for parent picloram shifted to 1558 cm^{-1}, while the asymmetrical NH_2 deformation frequency probably shifted from 1602 cm^{-1} to 1625 cm^{-1}. The 1625 cm^{-1} absorption band was overshadowed by the presence of a strong water absorption band (Table 8-1 and Figure 8-3). At pH 3.0, the increase in the NH_2 symmetrical deformation frequency was less than that at pH 1.6. The in-plane skeletal ring vibrations appearing at 1458, 1437, and 1306 cm^{-1} for parent picloram shifted to 1507.5, 1482, and 1337 cm^{-1} upon interaction of picloram with montmorillonite previously saturated with exchangeable Al (suspension pH = 3.0).
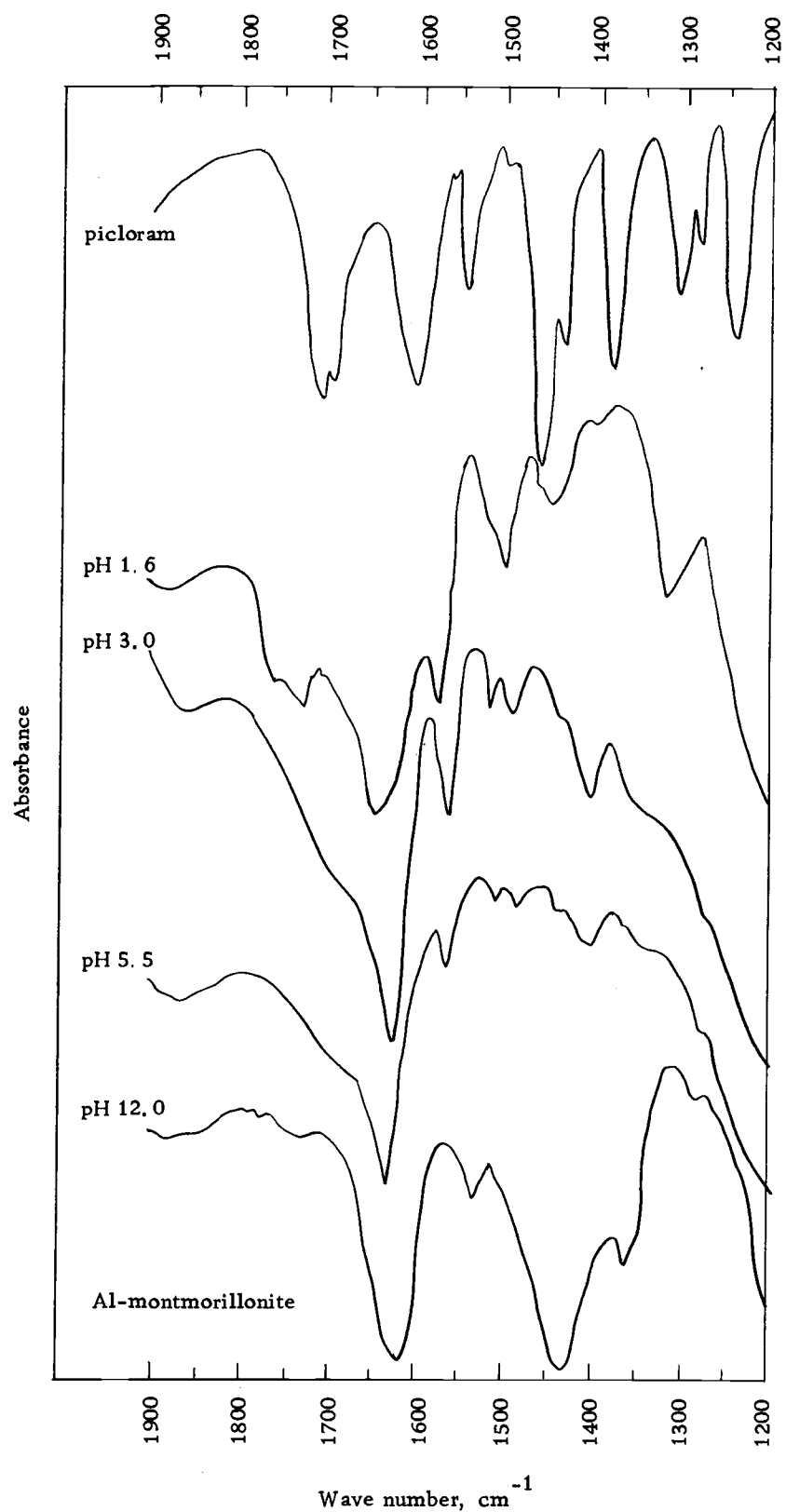
Figure 8-3. Infrared spectra of reaction products of picloram and Al-montmorillonite as a function of suspension pH.

(a) Hydrogen bonding through water bridge

(b) Coordination bond through annular nitrogen
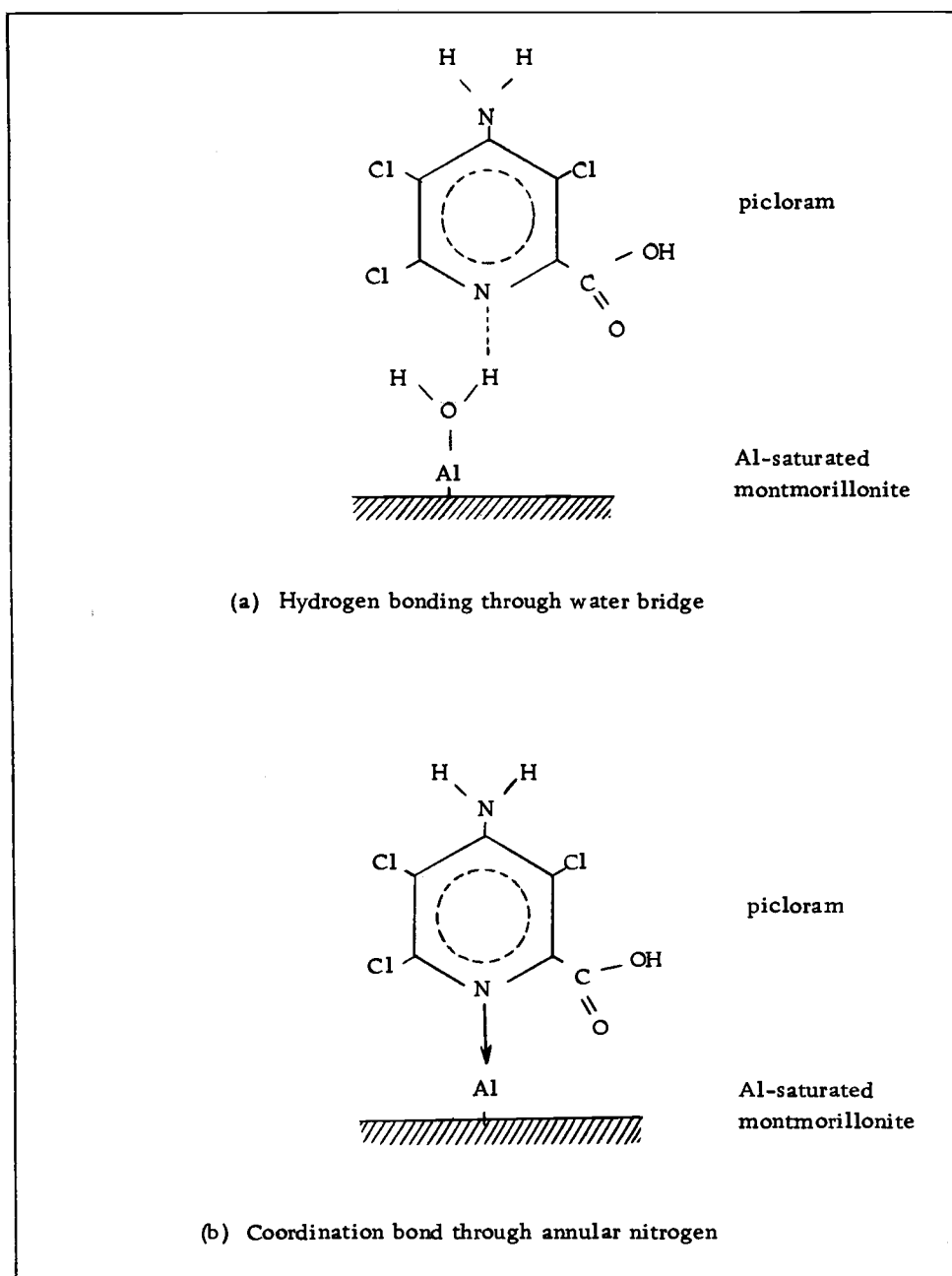
Figure 8-4. Bonding mechanisms between picloram and
Al-saturated montmorillonite clay.

Similarly, the δCOOH shifted from 1377.5 to 1404 cm^{-1} while the 1280 cm^{-1} band did not change. The changes in skeletal ring vibrations of picloram upon reaction with Al-montmorillonite were much greater than those with H-montmorillonite, implying a different mechanism for the picloram-Al-montmorillonite system.

At pH 5.5, the infrared spectrum of picloram and Al-montmorillonite in the presence of NaOH, showed a complete identity with that at pH 3.0. This indicates the montmorillonite system is predominantly saturated with exchangeable Al even at pH 5.5. Adjustment of the picloram and Al-montmorillonite system to pH 12.0 generated two strong bands which restricted the observation of picloram frequencies.

Based upon the high frequency shifts of νC=C ring vibration and δCOOH, the bonding mechanisms between picloram and Al-montmorillonite clay are proposed and illustrated in Figure 8-4. Mechanism (a) of Figure 8-4 was suggested only recently with the advent of detailed infrared absorption studies of clay-organic complexes (Mortland, 1970). Bonding of the annular nitrogen of the picloram molecule to the hydrogen of the polarized water which is coordination-bonded to an aluminum or hydrogen ion on the clay surface provides a mechanism to explain the infrared band shifts observed in both the H- and Al-saturated clay system. This kind of bond has been demonstrated for montmorillonite complexes with

pyridine (Farmer and Mortland, 1966), and ketones (Parfitt and Mortland, 1968). In the case of picloram and the Al-montmorillonite complex, hydrogen bonding through a water bridge would decrease the νCN frequency while the frequency of the skeletal νC=C vibrations would increase.

Mechanism (b) involves a direct coordination of exchangeable Al on the clay to the annular nitrogen of picloram molecules. This reaction would cause a decrease in νCN and a greater increase in both skeletal ring vibration and carbonyl stretching frequencies as compared to those caused by H-bonding. In the spectrum of the Al-montmorillonite-picloram system, the increase in carbonyl stretching frequency was observed only at pH 1.6. Slight decrease in carbonyl stretching frequency was observed on Al-montmorillonite-picloram system at pH 3. However, much greater skeletal vibration shifts were detected at pH 3 than at pH 1.6 for the same system implying a stronger coordination bond formation between picloram and Al-montmorillonite.

Summary and Conclusions

The increase in carbonyl stretching frequency from 1705 to 1724 cm^{-1} and NH_2 deformation bands from 1540 and 1602 cm^{-1} to 1566 and 1632 cm^{-1} indicated a preferential interaction between the annular nitrogen rather than the carbonyl oxygen of the picloram

molecule with H-montmorillonite at pH 1.6. After adjusting the suspension pH of the picloram-montmorillonite system to 5.5, the infrared spectrum displayed combination modes of picloram and its Na salt.

The infrared spectrum of the Al-montmorillonite-picloram system adjusted to pH 1.6 was similar to the one for picloram-H-montmorillonite at pH 1.6 indicating the association of annular nitrogen of picloram with the aluminum ions through a bridging effect of coordinated water. At pH 3, the infrared spectrum of Al-montmorillonite-picloram system displayed distinct shifts for $\nu C=O$, $\nu C=C$ and $\delta COOH$ bands implying a coordination bond formation between Al and the annular nitrogen atom. The infrared spectrum of Al-montmorillonite-picloram system at pH 5.5 was identical to that at pH 3.0 indicating a predominant saturation of montmorillonite with Al ions even at pH 5.5.

Hydrogen bonding through a water bridge and a coordination bond through the annular nitrogen of the picloram molecule were proposed as the possible adsorption mechanisms for the reaction of Al-montmorillonite with picloram.

SUMMARY AND CONCLUSIONS

The mobility and adsorption of picloram and 2, 4-D in western soils were determined by soil thin-layer radiochromatography and batch equilibrium techniques. Stepwise multiple regression analyses were then performed to relate the mobility and adsorption of picloram and 2, 4-D to nine chemical properties of soils. It was shown that soil pH, organic matter and extractable Al were the three most important parameters which successfully predicted either mobility or adsorption of picloram and 2, 4-D in western soils. The average deviations of predicted from measured values for the mobility of picloram and 2, 4-D were 0. 06 and 0. 10 R_F units, respectively. The respective deviations of adsorption values were 6. 1% for picloram and 7. 3% for 2, 4-D. When soils of pH < 6. 9 were grouped the predictive capacity of pH, organic matter, and Al for the mobility of picloram and 2, 4-D increased for chemical movement; however, the prediction of adsorption of picloram and 2, 4-D was not improved. Only 45% and 59% of the soil-to-soil variation in prediction of mobility of picloram and 2, 4-D in soils of pH $\geq$ 7. 0 were attributed to pH, organic matter, and Al. In general, for the soils with a low chemical adsorptive capacity and a high water flux, the measured mobility values were greater than predicted ones. For soils with a low water flux the measured mobilities were less than the predicted values.

Since the salt content in high pH soils may control picloram mobility through its effect on solubility and adsorption, the solubility of picloram was determined. The concentration of picloram in KCl or CaCl$_2$ solutions less than 1.5 $\underline{N}$ was greater than in an aqueous system. The slight increase of picloram solubility in dilute KCl or CaCl$_2$ solution was probably caused by the formation of the more soluble potassium or calcium salt of picloram. When the salt concentration increased to 2.5 $\underline{N}$, picloram solubility decreased from 597 ppm in water to 446 ppm in KCl and to 499 ppm in CaCl$_2$ solutions. The reduced solubility of picloram in the KCl solutions was explained on the basis of more oriented water dipoles around Ca^{++} as compared with K$^+$.

Activated charcoal, soil acidity, and the KCl concentration in the percolation water decreased the mobility of picloram or 2,4-D in soils. Complete immobilization of picloram occurred on both the Molokai and Lookout soil TLC plates after 1% or 10% activated charcoal was added to the soils. The drastically reduced picloram and 2,4-D movement in Minam, Woodcock, and Kinney soils after treatment with HCl was caused by enhanced adsorption of both chemicals by acidified soils. The picloram mobility in Palouse soil decreased as the KCl concentration in the percolating solution exceeded 0.1 $\underline{N}$. Increased picloram adsorption with an increase in KCl concentration was related to an increase in soil acidity in the bulk solution.

Picloram adsorption by H-montmorillonite conformed to a Freundlich isotherm and the picloram dissociation curve. However, the measured adsorption values were less than would be suggested by the picloram dissociation curve because of the presence of a proton sink in the H-montmorillonite system. Repeated water wash treatments quantitatively recovered the adsorbed picloram from H-montmorillonite.

Picloram adsorption was greatly enhanced as the KCl concentration in picloram-H-montmorillonite suspensions increased. As the KCl concentration in the suspensions increased to 1 $\underline{N}$, the measured picloram adsorption approached that predicted from the picloram dissociation curve. The enhanced picloram adsorption by H-montmorillonite with an increase in KCl concentration was caused by the increase of acidity in bulk solution as induced by increasing KCl concentration.

Both pyridine and 4-amino-pyridine, organic molecules with structural configuration similar to picloram, could be protonated in an acid environment as shown by the literature and detailed infrared studies. After a 3.6 $\underline{N}$ HCl treatment of 4-amino-pyridine, new absorption bands appeared at 1036 and 1660 cm^{-1} indicating the existence of a ring symmetrical vibration mode and an $=\overset{\oplus}{\underset{|}{N}}-H$ deformation frequency. The low frequency shifts of the 1168, 1212, 1330, and 1350 cm^{-1} bands and high frequency shifts of the 1500 and 1550 cm^{-1}

bands suggested protonation of the annular nitrogen in the ring structure. The infrared absorption spectra of protonated pyridine or 4-amino-pyridine were quite different from those of the parent compounds. These differences were caused by the increased fundamental vibration modes and the accompanying band shifts resultant from the proton addition to pyridine or 4-amino-pyridine molecule. The absorption spectra of acidified picloram, however, did not differ from its parent compound. The failure for picloram to protonate was due to its dipolar nature and the electron-withdrawing effects of the carboxylate and chloro functional groups.

Upon interaction of picloram with H-montmorillonite at pH 1.6, the carbonyl stretching frequency increased from 1705 to 1724 cm^{-1} and NH_2 deformation bands from 1540 and 1602 cm^{-1} to 1566 and 1632 cm^{-1} indicating a preferential interaction between the annular nitrogen rather than the carbonyl oxygen with exchangeable H on the clay colloid. The infrared spectrum of the Al-montmorillonite-picloram system adjusted to pH 1.6 was identical to the one for picloram-H-montmorillonite at pH 1.6 suggesting the association of annular nitrogen of picloram with aluminum ions through a bridging effect of coordinated water. At pH 3, the infrared spectrum of Al-montmorillonite-picloram system displayed distinct shifts for ν C=O, ν C=C, and δCOOH bands implying a coordination bond formation between Al and the annular nitrogen of the picloram molecule.

In summary, the mobility and adsorption of picloram and 2, 4-D relate closely to the pH, organic matter and extractable Al content of soils. Addition of the KCl or $CaCl_2$ salts to unbuffered soils increased picloram adsorption and retarded picloram movement. The hydrogen or coordination bonding of picloram to the exchangeable H or Al on the clay surface accounted for the enhanced adsorption or reduced mobility of picloram in acid, montmorillonitic soils.

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APPENDIX

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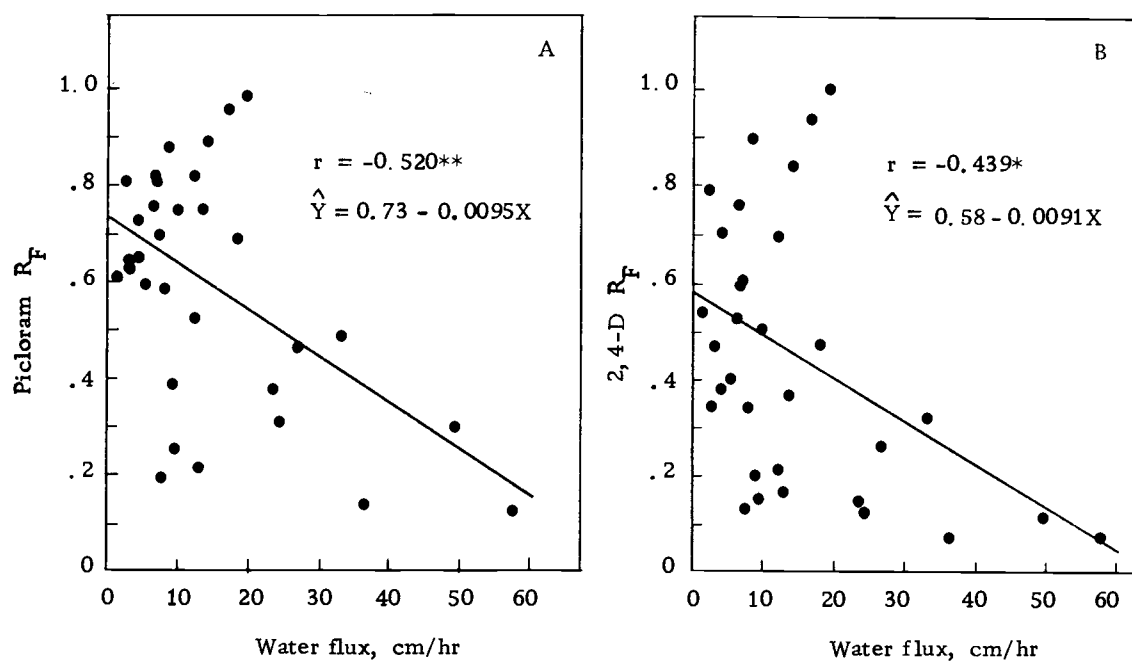
Appendix Figure 1. Correlation between mobility of picloram and 2, 4-D and water flux
on 32 western soils.
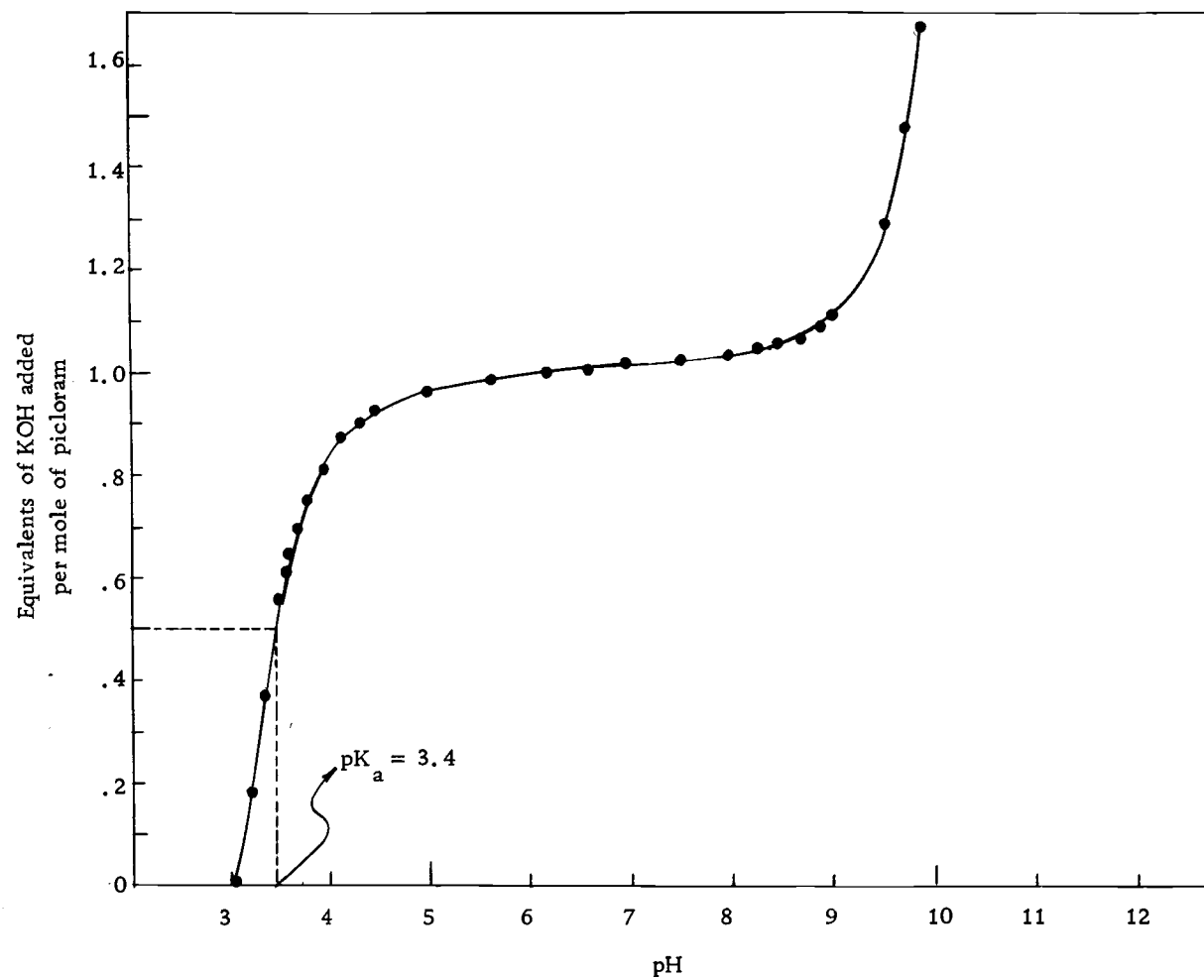
Appendix Figure 2.   Titration of 0. 0015 $\underline{M}$ picloram with 0. 00139 $\underline{N}$ potassium hydroxide at 25°C.
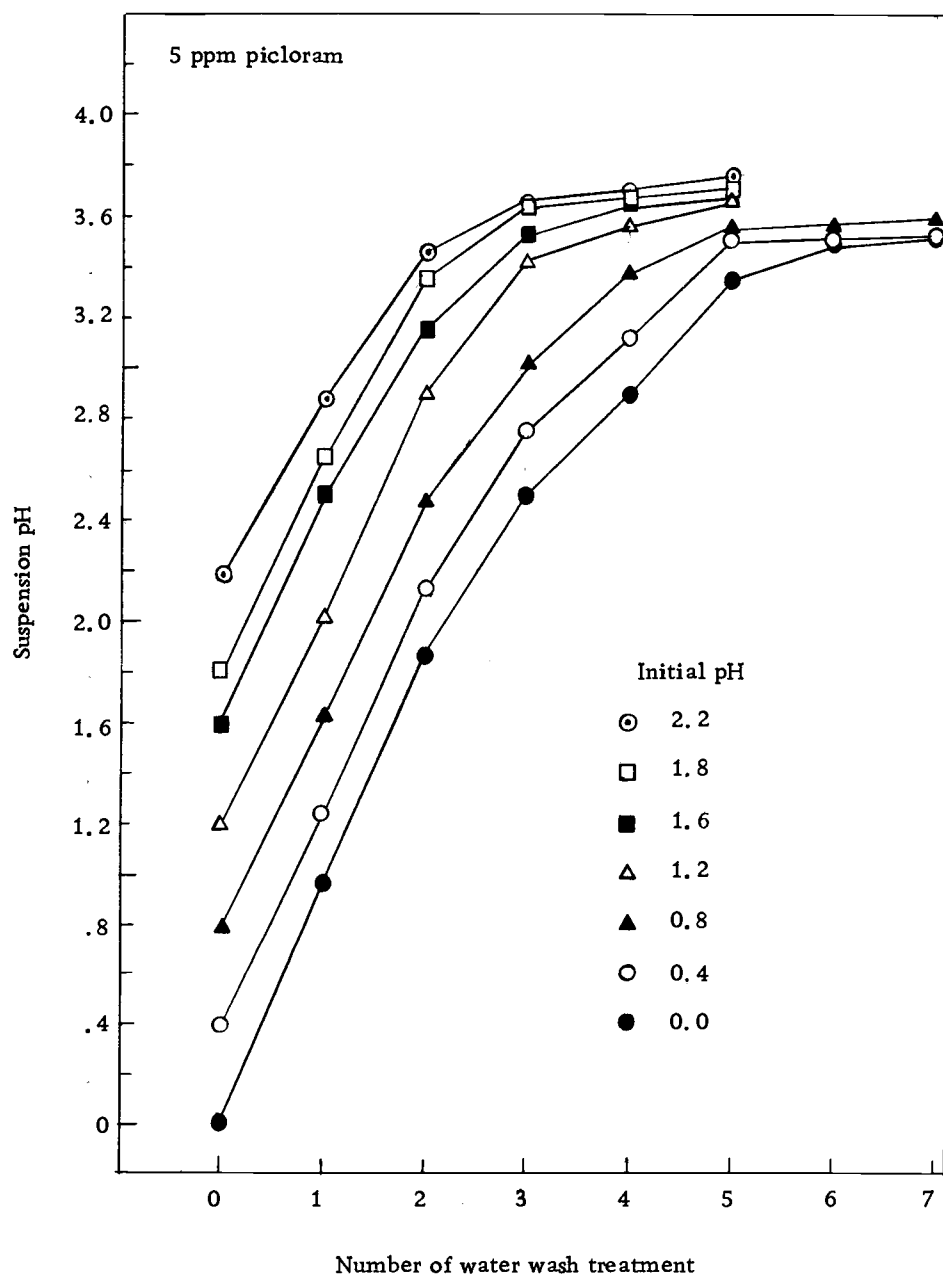
Appendix Figure 3. Changes in suspension pH of picloram-montmorillonite systems
after water wash treatments at an initial picloram concentration
of 5 ppm.
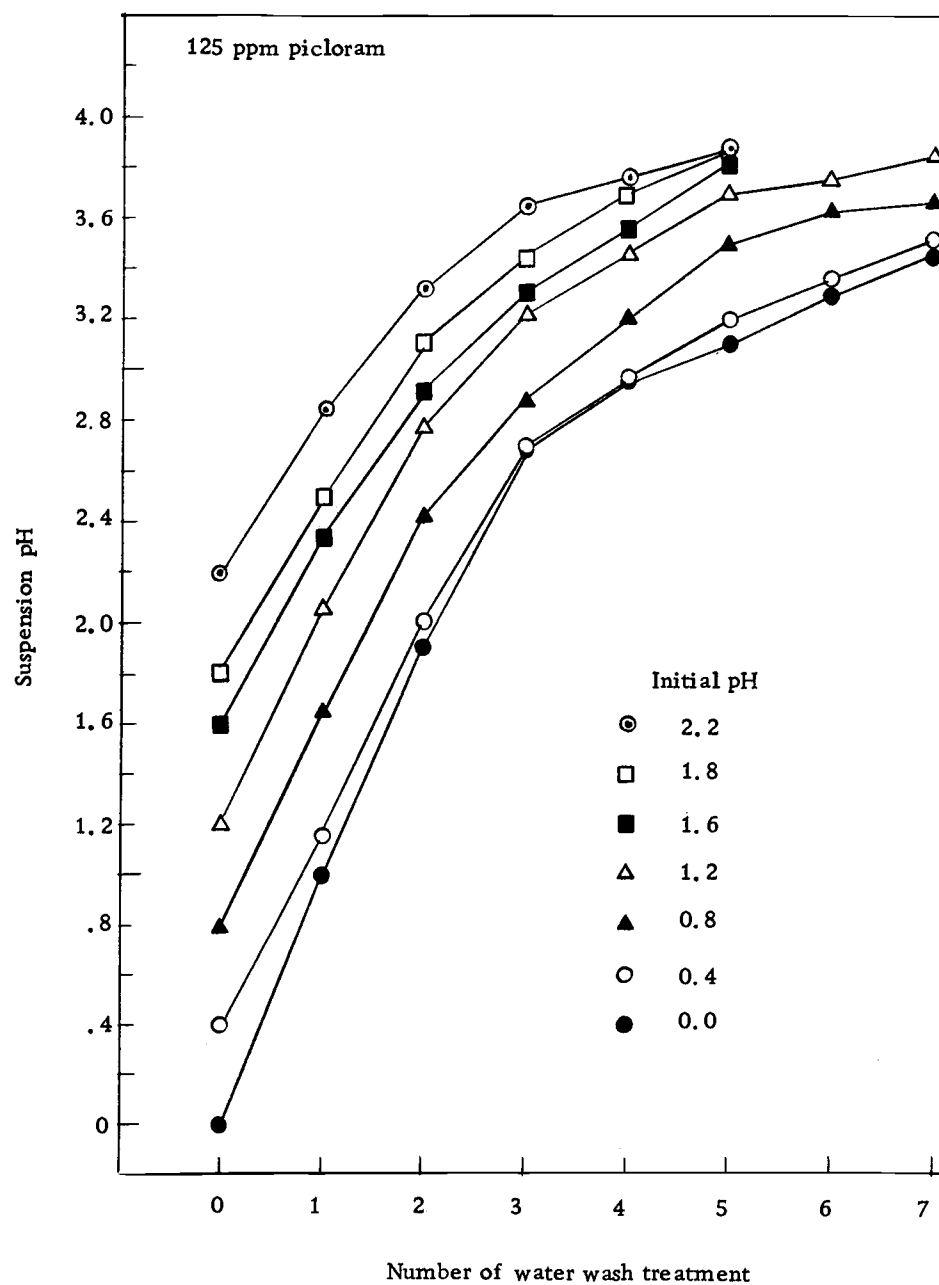
Appendix Figure 4. Changes in suspension pH of picloram-montmorillonite systems after water wash treatments at an initial picloram concentration of 125 ppm.
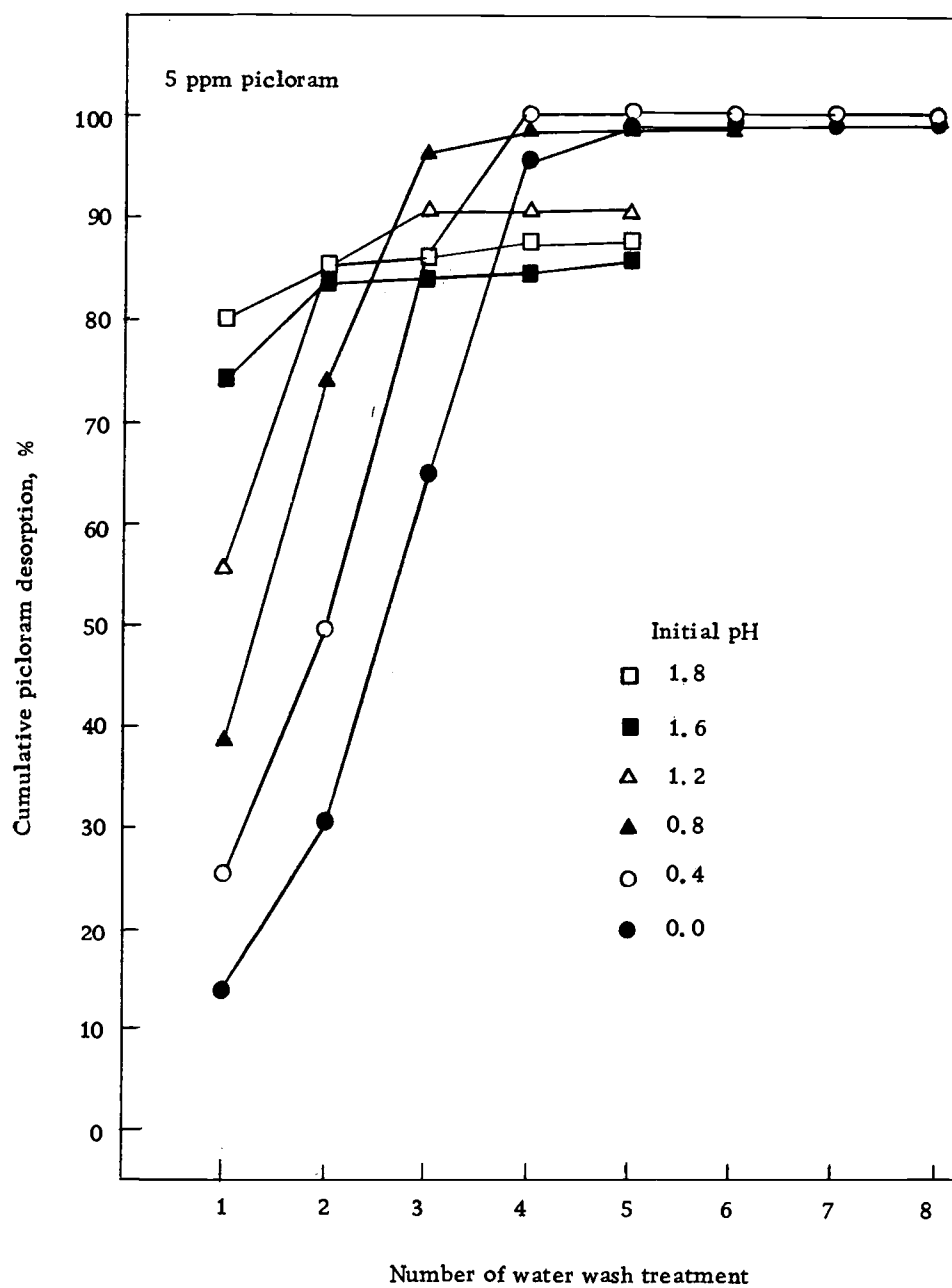
Appendix Figure 5. Desorption of picloram from acidic H-montmorillonite by water wash treatments at an initial concentration of 5 ppm.
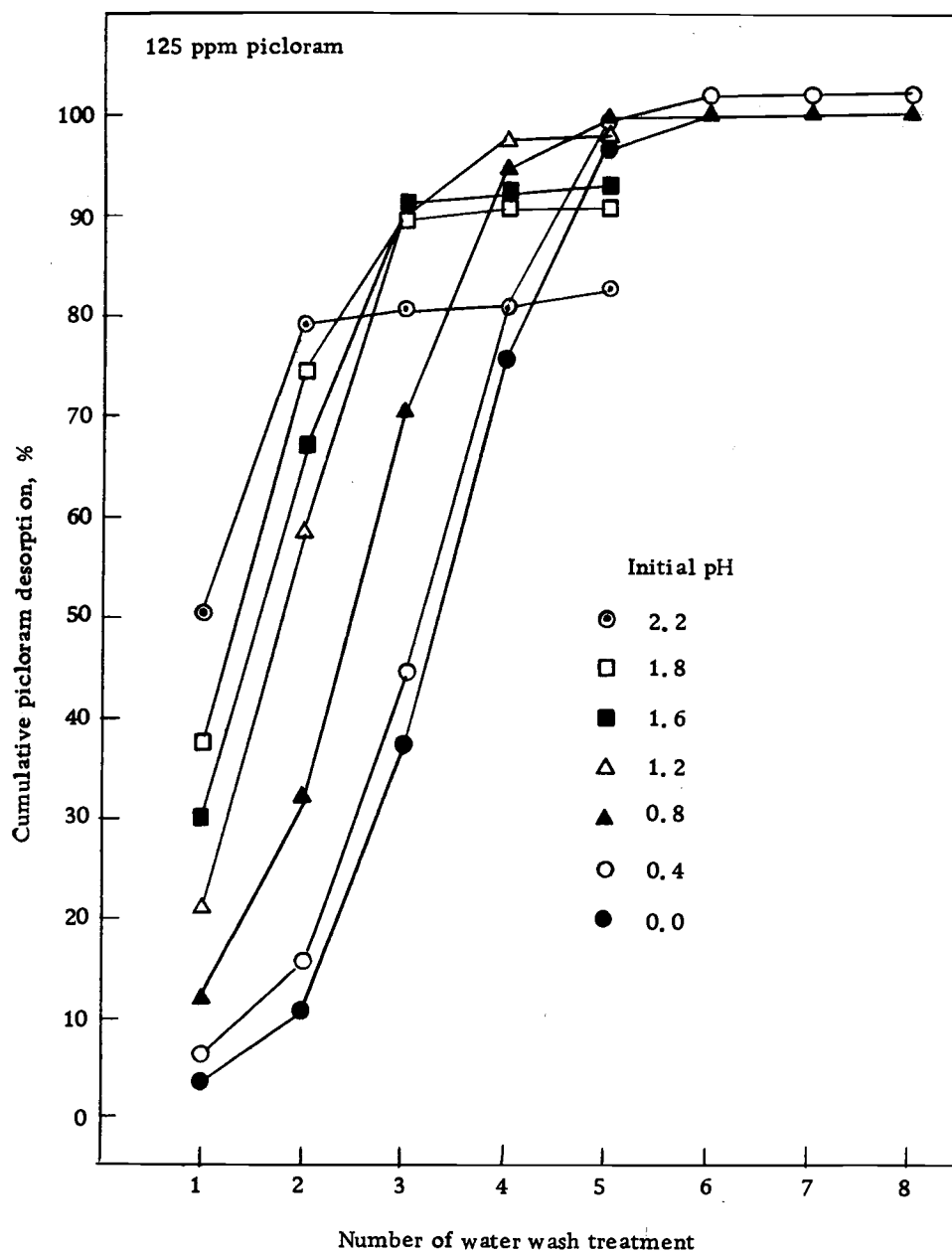
Appendix Figure 6. Desorption of picloram from acidic H-montmorillonite by water wash treatments at an initial concentration of 125 ppm.
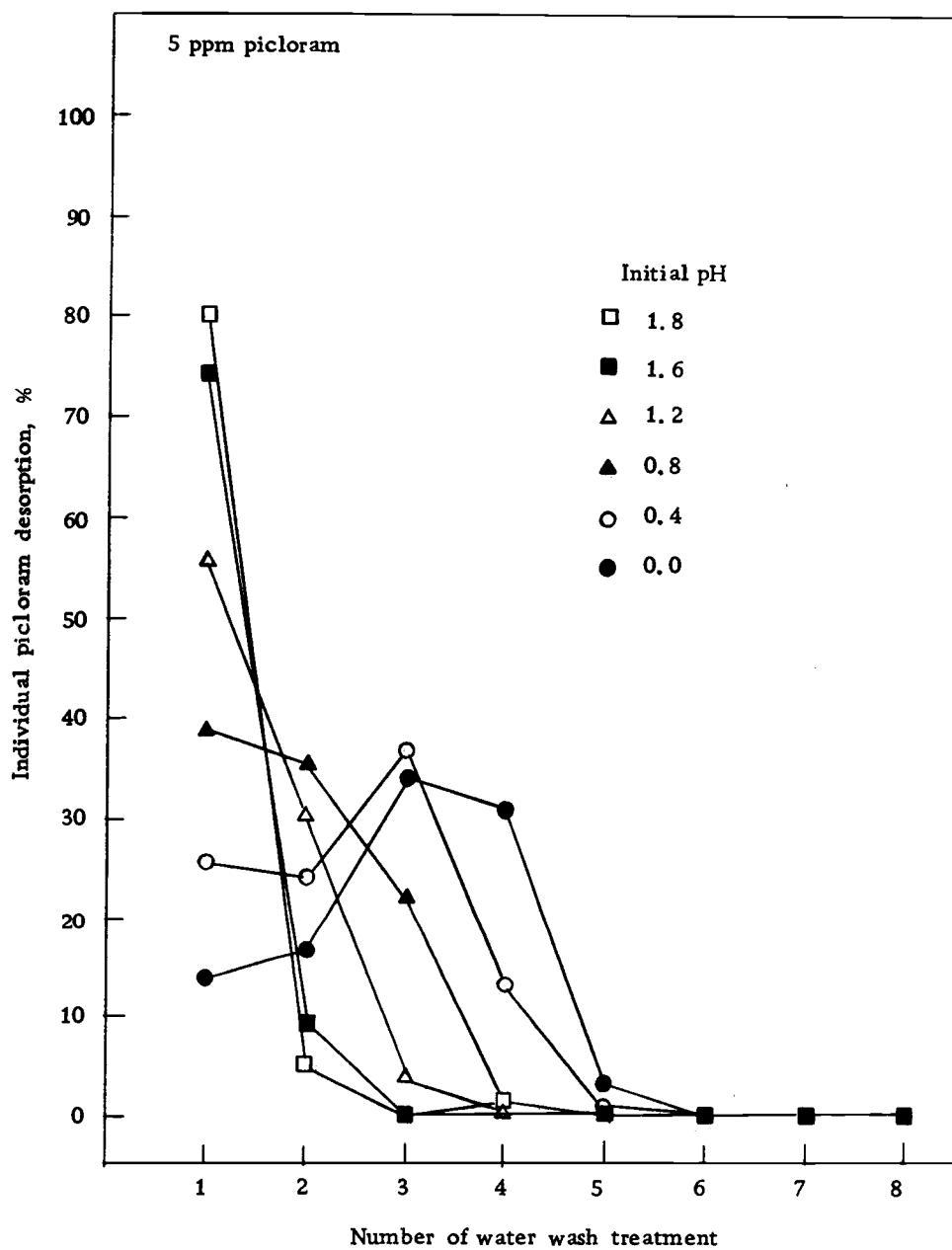
Appendix Figure 7. Desorption of picloram from acidic H-montmorillonite by individual water wash treatment at an initial concentration of 5 ppm.
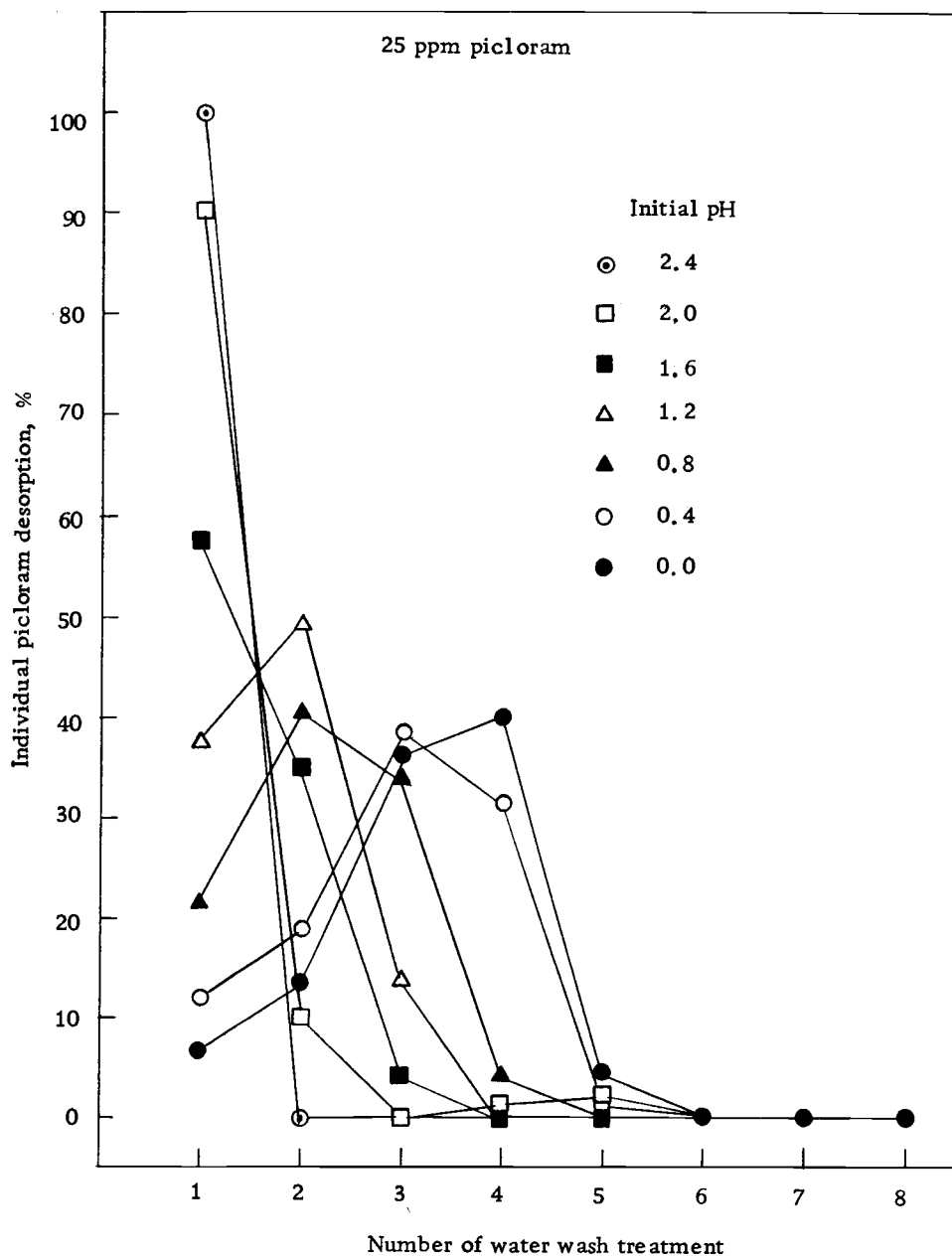
Appendix Figure 8. Desorption of picloram from acidic H-montmorillonite by individual water wash treatment at an initial concentration of 25 ppm.
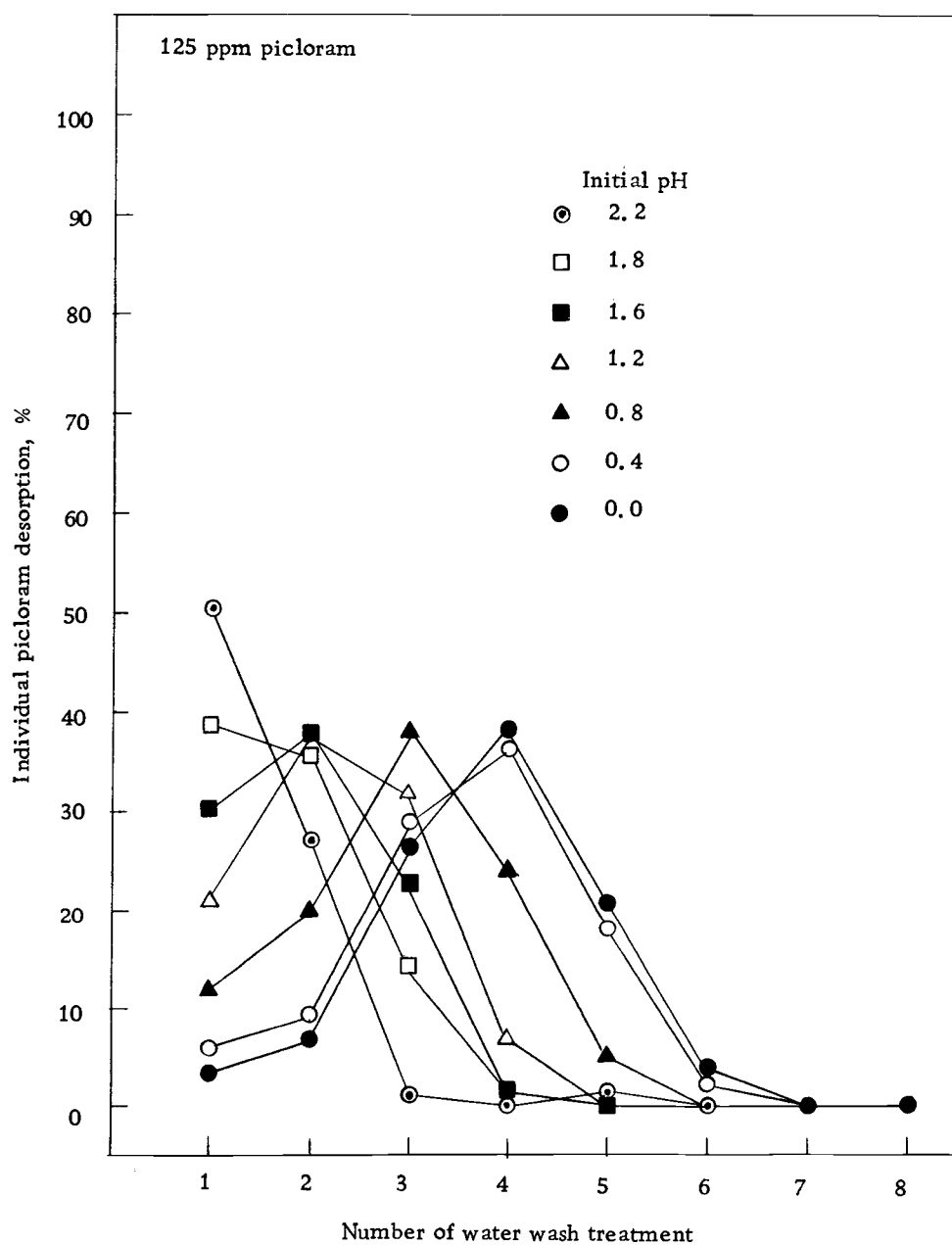
Appendix Figure 9. Desorption of picloram from acidic H-montmorillonite by
individual water wash treatment at an initial concentration
of 125 ppm.

Appendix Figure 10.   Freundlich desorption isotherms (25°C) for picloram after
first water wash of picloram-montmorillonite systems at
three concentrations.

Appendix Table 1. Mobility of picloram and 2, 4-D acid on 32 western soils, using soil thin-layer chromatography.

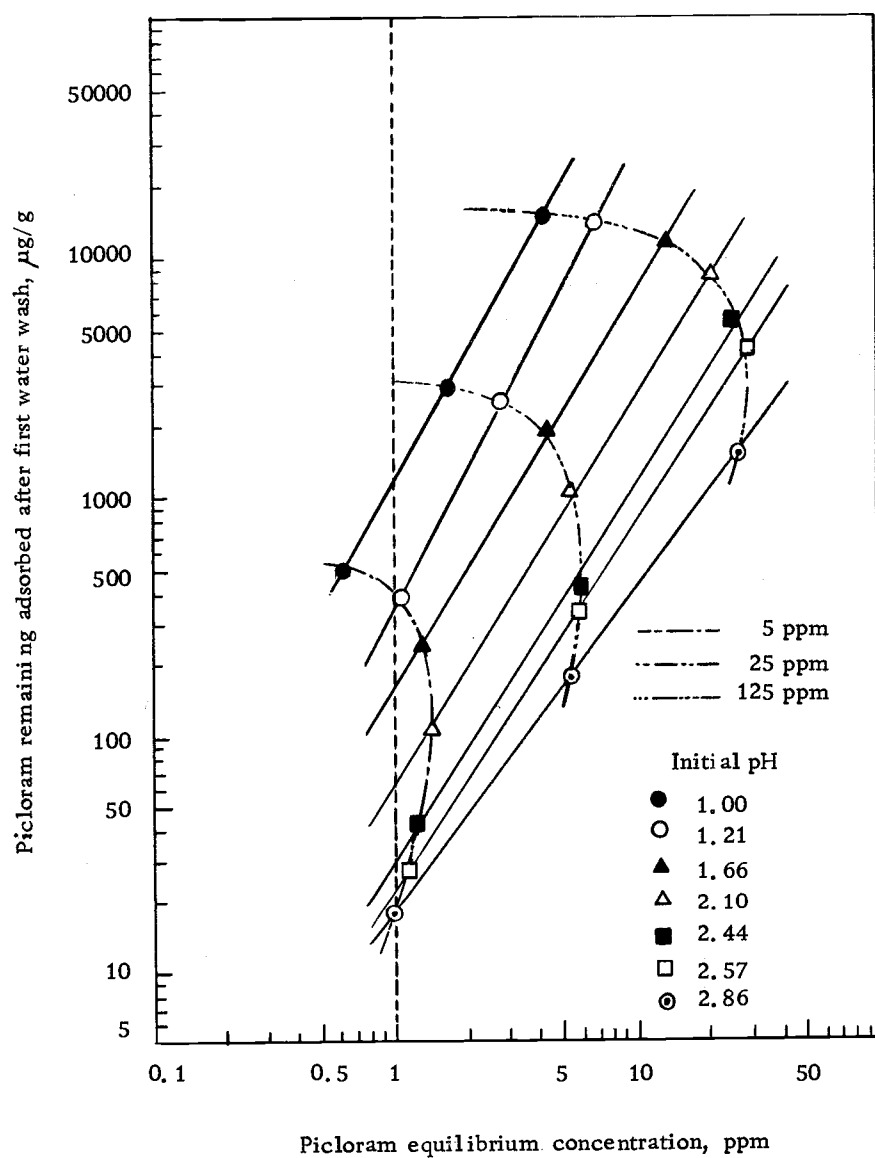| Soil[a]	Soil Depth cm	R_F Picloram	R_F 2, 4-D Acid	Adsorption Picloram	Adsorption 2, 4-D Acid	pH (1:1 H_2O)	O. M. %	CEC (Ca/Mg)	Exchangeable Ca	Mg	K	Bases	Extractable Al	Water Flux (cm/hr)
				------%-------				------------------(Meq/100 gm)-------------------						
Minam	0-23	.60	.40	1.68	45.1	7.0	6.6	28.3	28.9	2.3	1.3	32.5	.3	5.4
Minam	23-33	.75	.51	7.8	29.2	7.3	3.8	24.4	26.2	2.2	1.2	29.6	.3	9.8
Minam	61-84	.89	.84	.0	3.6	7.5	.7	23.8	24.4	4.7	1.0	30.1	1.3	14.1
Woodcock	0-10	.75	.37	14.5	41.5	6.1	7.7	12.9	14.3	1.2	3.1	18.6	9.9	13.5
Woodcock	36-51	.47	.26	19.5	64.0	5.8	4.3	3.6	1.2	.9	1.7	3.8	26.8	26.7
Woodcock	69-111	.49	.32	14.4	48.8	5.6	1.7	3.2	1.1	.8	1.3	3.2	34.6	33.1
Kinney	23-38	.26	.15	64.2	82.2	5.2	7.4	6.5	1.0	.6	.4	2.0	58.0	9.4
Kinney	23-46	.20	.13	50.6	71.8	5.2	2.5	8.9	.5	.4	.2	1.1	53.2	7.7
Kinney	46-74	.22	.16	41.6	67.0	5.0	.8	16.1	.6	.3	.1	1.0	41.9	13.3
Molokai	0-30	.81	.59	9.7	24.2	6.8	3.4	14.4	9.3	4.4	.4	14.1	.6	7.0
Molokai	30-46	.73	.70	2.5	7.9	6.8	1.3	4.5	3.3	2.0	.1	5.4	.8	4.3
Molokai	61-79	.70	.60	3.2	7.6	6.8	1.1	3.2	3.0	2.2	.1	5.3	.9	7.2
Ephrata	0-15	.88	.90	2.5	5.8	6.5	1.4	10.5	5.9	3.2	.7	9.8	.4	8.7
Ephrata	15-36	.96	.94	1.6	2.7	6.8	.9	8.5	6.2	2.9	.8	9.9	.4	17.1
Ephrata	36-53	.99	1.00	.7	2.8	7.3	.6	11.8	7.5	2.9	.5	10.9	.6	19.6
Palouse	0-25	.64	.47	18.0	36.9	5.5	4.2	15.2	11.7	2.2	1.1	15.0	.5	3.2
Palouse	25-46	.76	.53	17.9	34.1	6.0	4.2	16.7	12.7	2.3	1.0	16.0	.4	6.3
Palouse	46-76	.82	.70	8.6	17.8	6.6	2.9	16.0	12.4	2.4	.7	15.5	.6	12.4
Panoche	---	.81	.79	.3	1.9	7.8	.8	17.9	14.1	5.4	.7	20.2	.4	2.5
Hembre A	---	.53	.21	34.5	71.8	5.0	29.0	57.0	1.5	2.3	.6	4.4	16.8	12.1
Boyce	---	.61	.54	.0	4.6	8.3	2.2	20.0	16.7	7.4	.0	24.1	.8	1.4
Lookout	0-10	.81	.76	.0	4.9	6.6	2.0	16.0	9.3	4.3	1.1	14.7	.5	6.7
Woodburn	0-18	.64	.34	5.0	31.4	5.0	5.1	8.0	6.2	1.3	.6	8.1	3.0	2.9
Woodburn	18-33	.65	.38	1.2	23.1	5.2	3.2	8.8	7.4	1.6	.6	9.6	3.3	4.3
Nehalem	0-20	.59	.34	10.5	41.2	5.4	10.0	29.3	1.0	.2	.0	1.2	8.6	8.0
Nehalem	20-38	.69	.47	2.5	28.5	5.7	6.4	30.2	.8	.1	.0	.9	7.1	18.2
Quillayute	0-23	.39	.20	57.9	85.1	5.1	18.7	12.4	1.9	1.2	.3	3.4	18.1	9.3
Quillayute	23-61	.38	.14	81.4	94.6	5.4	15.1	7.2	.8	1.0	.4	2.2	17.6	23.6
Hembre B	0-18	.14	.07	89.8	96.8	4.1	17.7	11.0	1.0	1.3	.1	2.4	34.4	36.5
Hembre B	18-51	.13	.07	87.8	96.1	4.3	15.3	8.3	1.0	1.3	.1	2.4	39.3	57.7
Knappa	---	.31	.12	73.0	91.8	5.0	13.2	9.4	3.2	1.2	1.5	5.9	40.3	24.4
Knappa	---	.30	.11	69.5	86.1	5.1	8.5	6.4	1.0	.4	.7	2.1	39.7	49.6

[a] Chemical properties for Minam, Woodcock, and Kinney were characterized by Gaynor (1971). Chemical properties for Hembre A were characterized by Schreiber (1969).

Appendix Table 2. Multiple regression coefficients among adsorption of herbicides and soil parameters for 32 western soils.

Dependent Variable	Constant of Regression	Multiple regression coefficients								R^2	Standard Error
		pH	O. M.	CEC	Exch. Bases	Extractable Al	Exch. Ca	Exch. Mg	Exch. K		(%)
% Picloram adsorption	6.8	---	---	---	---	1.2756	---	---	---	0.615	--
"	-2.2	---	1.9916	---	---	1.0303	---	---	---	0.793	--
"	9.2	---	2.8157	-0.8923	---	0.7881	---	---	---	0.860	--
"	2.4	---	3.1619	-1.1024	---	0.9127	0.7946	---	---	0.886	--
"	6.0	---	3.3576	-1.2681	---	0.9493	1.2671	---	-9.1808	0.916	--
"	22.0	-2.5499	3.1840	-1.2438	---	0.9051	1.3914	---	-9.5305	0.918	--
"	22.5	-2.6605	3.1778	-1.2423	0.0817	0.9056	1.3069	---	-9.5752	0.918	--
% 2, 4-D adsorption	196.8	-25.7867	---	---	---	---	---	---	---	0.666	19.4
"	122.5	-15.4885	---	---	---	0.8705	---	---	---	0.790	15.7
"	51.3	-6.0715	2.0799	---	---	0.9818	---	---	---	0.898	11.1
"	67.5	-9.8178	1.9788	---	---	1.0495	0.7990	---	---	0.916	10.3
"	62.2	-8.2881	2.7023	-0.6230	---	0.9801	1.0303	---	---	0.938	8.9
"	44.2	-4.0251	2.9791	-0.7137	-3.3379	0.9635	4.5885	---	---	0.949	8.4
"	42.3	-3.7203	2.9816	-0.7038	-2.6361	0.9615	3.8478	-0.8471	---	0.949	8.5

Appendix Table 3. Multiple regression coefficients among herbicide R_F and soil parameters for 32 western soils.[a]

Dependent Variable	Constant of Regression	Multiple regression coefficients											R^2	Standard Error (R_F)	Average Deviation (R_F)
		Picloram Ads.	2, 4-D Ads.	pH	O. M.	CEC	Exch. Base	Extractable Al	Exch. Ca	Exch. Mg	Exch. K	Water Flux			
Picloram R_F	0.88	--	-0.0068	--	--	--	--	--	--	--	--	--	0.826	0.11	0.08
"	0.85	--	-0.0043	--	--	--	--	-0.0056	--	--	--	--	0.884	0.09	0.07
"	0.80	--	-0.0044	--	--	--	--	-0.0051	--	--	0.0681	--	0.915	0.08	0.06
"	0.84	--	-0.0046	--	--	--	-0.0030	-0.0058	--	--	0.0836	--	0.922	0.07	0.06
"	0.61	--	-0.0038	0.0372	--	--	-0.0052	-0.0062	--	--	0.0894	--	0.926	0.07	0.05
"	0.60	--	-0.0050	0.0372	0.0047	--	-0.0048	-0.0048	--	--	0.0928	--	0.931	0.07	0.05
"	0.55	--	-0.0056	0.0516	0.0067	--	-0.0216	-0.0042	0.0182	--	0.1014	--	0.935	0.07	0.05
"	0.58	0.0021	-0.0078	0.0529	0.0078	--	-0.0307	-0.0042	0.0276	--	0.1209	--	0.940	0.07	0.05
"	0.58	0.0020	-0.0077	0.0525	0.0078	--	-0.0303	-0.0042	0.0273	--	0.1190	0.0003	0.941	0.07	0.05
"	0.59	0.0020	-0.0077	0.0511	0.0086	-0.0005	-0.0296	-0.0043	0.0269	--	0.1157	0.0004	0.941	0.07	0.05
2, 4-D R_F	0.77	--	-0.0077	--	--	--	--	--	--	--	--	--	0.853	0.11	0.08
"	0.82	0.0052	-0.0121	--	--	--	--	--	--	--	--	--	0.890	0.10	0.07
"	0.80	0.0062	-0.0129	--	--	--	--	--	--	--	0.0462	--	0.900	0.09	0.06
"	0.80	0.0064	-0.0136	--	0.0042	--	--	--	--	--	0.0495	--	0.905	0.09	0.06
"	0.78	0.0057	-0.0136	--	0.0045	--	--	--	--	--	0.0449	0.0016	0.909	0.09	0.06
"	0.83	0.0065	-0 0147	--	0.0054	--	--	--	--	-0.0121	0.0492	0.0014	0.911	0.09	0.06
"	0.52	0.0067	-0.0143	0.0537	0.0071	--	--	--	--	-0.0292	0.0410	0.0014	0.919	0.09	0.06
"	0.44	0.0067	-0.0141	0.0678	0.0072	--	--	--	-0.0030	-0.0266	0.0538	0.0011	0.922	0.09	0.06

[a] Inclusion of herbicide adsorption as an independent variable

Appendix Table 4. Multiple regression coefficients among herbicide R_F and soil parameters for 32 western soils.[a]

Dependent Variable	Constant of Regression	Multiple regression coefficients									R^2	Standard Error (R_F)	Average Deviation (R_F)
		pH	O. M.	CEC	Exch. Bases	Extractable Al	Exch. Ca	Exch. Mg	Exch. K	Water Flux			
Picloram R_F	0.76	--	--	--	--	-0.0119	--	--	--	--	0.774	0.12	--
"	0.81	--	-0.0096	--	--	-0.0107	--	--	--	--	0.834	0.10	--
"	0.76	--	-0.0093	--	--	-0.0106	--	--	0.0534	--	0.850	0.10	--
"	0.49	0.0404	-0.0066	--	--	-0.0093	--	--	0.0509	--	0.864	0.10	--
"	0.26	0.0870	-0.0051	--	-0.0079	-0.0100	--	--	0.0876	--	0.892	0.09	--
"	0.27	0.0812	-0.0094	0.0038	-0.0097	-0.0096	--	--	0.0998	--	0.906	0.08	--
"	0.32	0.0719	-0.0099	0.0040	-0.0102	-0.0096	--	0.0081	0.1050	--	0.907	0.08	--
"	0.31	0.0714	-0.0106	0.0043	-0.0103	-0.0098	--	0.0084	0.1043	0.0007	0.908	0.09	--
2,4-D R_F	-0.84	0.2138	--	--	--	--	--	--	--	--	0.650	0.17	0.13
"	-0.31	0.1397	--	--	--	-0.0063	--	--	--	--	0.742	0.15	0.10
"	0.09	0.0878	-0.0115	--	--	-0.0069	--	--	--	--	0.788	0.13	0.09
"	-0.10	0.1298	-0.0103	--	--	-0.0076	-0.0089	--	--	--	0.821	0.13	0.09
"	0.02	0.1033	-0.0115	--	0.0219	-0.0076	-0.0321	--	--	--	0.827	0.13	0.08
"	-0.02	0.1063	-0.0120	--	0.0208	-0.0082	-0.0308	--	--	0.0019	0.833	0.13	0.08

[a] Exclusion of adsorption of picloram and 2, 4-D as independent variables

Appendix Table 5. Freundlich constants for picloram desorption from acidic H-montmorillonite by first water wash at 25°C.

Suspension pH	Slope, 1/n	Intercept, K[a]
1.00	1.78	1148.00
1.21	1.89	331.10
1.66	1.65	147.90
2.10	1.57	67.61
2.44	1.62	25.12
2.57	1.56	18.62
2.86	1.34	17.78

[a]K = μg picloram remaining adsorbed per g H-montmorillonite at 1 ppm equilibrium concentration