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Adsorption-Desorption and Movement of Picloram (4-Amino-3,5,6-Trichloropicoloionic Acid) in Soils

Desh Raj Duseja
Utah State University

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ADSORPTION-DESORPTION AND MOVEMENT OF PICLORAM
(4-AMINO-3,5,6-TRICHLOROPICOLINIC ACID) IN SOILS

by

Desh Raj Duseja

A dissertation submitted in partial fulfillment
of the requirements for the degree
of
DOCTOR OF PHILOSOPHY
in
Soil Science and Biometeorology

UTAH STATE UNIVERSITY
Logan, Utah
1972
This work is dedicated to loving memory of: my father Sh. Deviditta Mal Duseja; my mother Shmti. Laxmi Bai Duseja; and my sister Shmti. Vidya Bai Kumar, who are no longer among us.
ACKNOWLEDGEMENT

I take this opportunity to express my indebtedness to Dr. R. W. Miller, my major professor, and Dr. J. O. Evans, my thesis director, for their guidance and help and for the financial support. Thanks are also due to Dr. R. L. Smith for serving on my graduate committee and for acting as my major professor in the absence of Dr. Miller. His financial help is also appreciated.

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Mrs. G. J. Watumull of the Watumull Foundation, Honolulu was kind enough to extend generous financial support in the last days of this project. I am very grateful to her and to the Foundation.

My brothers, Messrs. Bishan Das and Verinder Kumar Duseja, sacrificed a lot to make possible the completion of these studies. Their assistance is unforgettable.

Last, but not the least, to my wife Lata whose patience has been unbelievable, I extend a husband's gratitude.

Desh Raj Duseja
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>NOTATION</td>
<td>xi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xiii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>REVIEW OF LITERATURE</td>
<td>3</td>
</tr>
<tr>
<td>Adsorption-desorption of Pesticides in General</td>
<td>4</td>
</tr>
<tr>
<td>Factors affecting adsorption-desorption</td>
<td>4</td>
</tr>
<tr>
<td>Effect of inorganic salts on adsorption-desorption</td>
<td>6</td>
</tr>
<tr>
<td>Movement in columns and application of chromatographic theory</td>
<td>8</td>
</tr>
<tr>
<td>Adsorption-desorption of Picloram</td>
<td>10</td>
</tr>
<tr>
<td>Factors affecting adsorption-desorption</td>
<td>10</td>
</tr>
<tr>
<td>Field studies and movement in different media</td>
<td>12</td>
</tr>
<tr>
<td>Photolytic, Chemical, and Microbial Degradation of Picloram</td>
<td>12</td>
</tr>
<tr>
<td>THEORETICAL DEVELOPMENT</td>
<td>15</td>
</tr>
<tr>
<td>Adsorption Isotherm Models</td>
<td>15</td>
</tr>
<tr>
<td>Freundlich adsorption isotherm</td>
<td>15</td>
</tr>
<tr>
<td>Other models</td>
<td>16</td>
</tr>
<tr>
<td>Adsorption Mechanisms</td>
<td>17</td>
</tr>
<tr>
<td>Adsorption mechanisms for organic molecules</td>
<td>17</td>
</tr>
<tr>
<td>Adsorption mechanisms for picloram</td>
<td>21</td>
</tr>
<tr>
<td>Mathematical Treatment (Ion Exchange Chromatography)</td>
<td>22</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Materials and Methods</th>
<th>RESULTS AND DISCUSSION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation of Stock Solutions and Calibration Curves</td>
<td>Nature of Adsorbate</td>
</tr>
<tr>
<td>Laboratory Procedures</td>
<td>Degradation of Picloram</td>
</tr>
<tr>
<td>Degradation of Picloram</td>
<td>Effect of Time on the Adsorption and Desorption of Picloram</td>
</tr>
<tr>
<td>Factors affecting soil adsorption-desorption of picloram (batch studies)</td>
<td>Adsorption</td>
</tr>
<tr>
<td>Column Studies</td>
<td>Desorption</td>
</tr>
<tr>
<td></td>
<td>Effect of Soil Type and Organic Matter on Adsorption and Desorption of Picloram</td>
</tr>
<tr>
<td></td>
<td>Adsorption</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
</tr>
<tr>
<td></td>
<td>Effect of Herbicide Concentration</td>
</tr>
<tr>
<td></td>
<td>Adsorption</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
</tr>
<tr>
<td></td>
<td>Effect of Temperature</td>
</tr>
<tr>
<td></td>
<td>Adsorption</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
</tr>
<tr>
<td></td>
<td>Effect of pH on Adsorption</td>
</tr>
<tr>
<td></td>
<td>Effect of Inorganic Salts on Adsorption of Picloram</td>
</tr>
<tr>
<td></td>
<td>Influence of various salts on picloram adsorption by Providence silt loam soil</td>
</tr>
<tr>
<td></td>
<td>Effect of CaCl₂ in solution on picloram adsorption</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Column Studies</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millville silt loam soil</td>
<td>78</td>
</tr>
<tr>
<td>Aiken clay soil</td>
<td>84</td>
</tr>
<tr>
<td>Test of mathematical model for picloram movement in natural and Ca-saturated Millville and Aiken soils</td>
<td>84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SUMMARY AND CONCLUSIONS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BIBLIOGRAPHY</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>APPENDICES</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>106</td>
</tr>
</tbody>
</table>

Appendix 1. Some Physical and Chemical Properties of Picloram (4-amino-3,5,6-trichloropicolinic acid) 107
Appendix 2. Alphabetical List of Common and Chemical Names of Herbicides Used in the Text 108
Appendix 3. Structure of some s-Triazine and Phenyl-alkanoic Acid Herbicides Referred to in the Literature Section 110

<table>
<thead>
<tr>
<th>VITA</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>112</td>
</tr>
<tr>
<td>Table</td>
<td>Effect of soli:solution ratio on the equilibrium adsorption of picloram by Providence silt loam soil from aqueous solutions of 1 ppm concentration</td>
</tr>
<tr>
<td>-------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>13</td>
<td>Effect of temperature on the equilibrium adsorption of picloram by Providence silt loam, Chance loam, and Aiken clay soils from 1.0 ppm concentration</td>
</tr>
<tr>
<td>14</td>
<td>Effect of pH on the adsorption of picloram by Chance loam and Providence silt loam soils at 25 C (initial picloram concentration 1 ppm)</td>
</tr>
<tr>
<td>15</td>
<td>Influence of various salts on the adsorption of picloram by Providence silt loam soil. Initial picloram concentration was 1.0 ppm</td>
</tr>
<tr>
<td>16</td>
<td>Cationic composition of the exchange complex of various soils</td>
</tr>
<tr>
<td>17</td>
<td>Physical data for picloram displacement through Millville silt loam and Aiken clay soils</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>A typical Cl\textsuperscript{-} breakthrough curve (BTC) used for calculating dispersion coefficient</td>
<td>34</td>
</tr>
<tr>
<td>2.</td>
<td>Effect of time on adsorption of picloram by four soils at 1 ppm initial concentration at 25 °C</td>
<td>39</td>
</tr>
<tr>
<td>3.</td>
<td>Effect of organic matter content of three soils and the removal of organic matter on adsorption of picloram</td>
<td>44</td>
</tr>
<tr>
<td>4.</td>
<td>Effect of concentration of picloram in solution on its adsorption by two soils</td>
<td>50</td>
</tr>
<tr>
<td>5.</td>
<td>Freundlich plot for adsorption of picloram by Providence and Chance loam soils at 25 °C</td>
<td>52</td>
</tr>
<tr>
<td>6.</td>
<td>Adsorption of picloram by Providence silt loam and Chance loam soils, and percent of picloram undissociated in response to changes in soil pH</td>
<td>59</td>
</tr>
<tr>
<td>7.</td>
<td>Logarithm of picloram adsorption by Chance loam and Providence silt loam soils as influenced by the pH of soil suspension</td>
<td>60</td>
</tr>
<tr>
<td>8.</td>
<td>Effect of CaCl\textsubscript{2} on the adsorption of picloram by Nibley silty clay loam soil. ○ Natural soil. ▲ Ca-saturated soil. The numbers near the data points denote equilibrium pH for natural soil and Ca-saturated soil, respectively</td>
<td>70</td>
</tr>
<tr>
<td>9.</td>
<td>Effect of CaCl\textsubscript{2} on the adsorption of picloram by Millville silt loam soil. ○ Natural soil. ▲ Ca-saturated soil. The numbers near the data points denote equilibrium pH for natural and Ca-saturated soils, respectively</td>
<td>72</td>
</tr>
<tr>
<td>10.</td>
<td>Effect of CaCl\textsubscript{2} on the adsorption of picloram by Chance loam soil. ○ Natural soil. ▲ Ca-saturated soil. The numbers near the data points denote equilibrium pH. Curve C (○) represents adsorption on Chance loam soil adjusted for pH changes by CaCl\textsubscript{2}</td>
<td>73</td>
</tr>
<tr>
<td>11.</td>
<td>Effect of CaCl\textsubscript{2} on the adsorption of picloram by Aiken clay soil. ○ Natural soil. (▲) Ca-saturated soil. The numbers near the data point denote equilibrium pH</td>
<td>75</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>12.</td>
<td>Relative concentration distribution (C/Co) of picloram in Millville silt loam soil column as affected by amount of picloram solution added on top of the soil column</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>Effect of two rates of picloram applications on the relative concentration distribution (C/Cl) of picloram in Millville silt loam soil column</td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>Effect of Ca-saturation on the relative concentration distribution (C/Co) of picloram in Millville silt loam soil column</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>Relative concentration distribution of picloram in Aiken clay soil, (1) as a function of two application rates (2) as affected by Ca-saturation of the soil</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>Experimental (o) and calculated relative picloram concentration curve from Millville silt loam soil. Solid curve was calculated from retardation factor (K') from batch studies and dashed curve from 'adjusted' K' (See Table 17)</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>Relative concentration distribution (C/Co) of picloram in two columns of Millville silt loam soil of different length</td>
<td></td>
</tr>
<tr>
<td>18.</td>
<td>Experimental (o) and calculated relative picloram concentration distributions from Ca-saturated Millville silt loam soil. Solid curve was calculated from retardation factor (K') from batch studies and dashed curve from 'adjusted' K' (See Table 17)</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>Experimental (data points) and theoretical relative picloram concentration distributions from natural (o), and Ca-saturated (Δ) Aiken clay soil. Solid lines were calculated from retardation factor (K') from batch studies and dashed curve from 'adjusted' K' (See Table 17)</td>
<td></td>
</tr>
</tbody>
</table>
NOTATION

B  base (opposite of acid)
C  concentration in general
Ce  equilibrium concentration
Co  total concentration
erfc  complementary error function
exp  exponential
Do  fluid dispersion coefficient (cm$^2$/hr)
DPM  disintegrations per minute
f  functional symbol
F  functional symbol
$\bar{F}$  average free energy
$\Delta H$  heat of adsorption
$K_a$  dissociation constant
K  equilibrium constant
$K'$  retardation factor = 1 + $\frac{\rho K}{\theta}$
$k_1, k_2$  rate constants
L  column length (cms)
M  symbol for metal cation
n  valence
p  negative logarithm
$q_1$  solute concentration per unit length of exchanger phase
q \quad \text{solute concentration per unit weight of exchanger}

R \quad \text{gas constant} = 1.9872 \text{ cal}/\text{deg}/\text{mole}
\quad = 0.082 \text{ atm}/\text{deg}/\text{mole}; \text{ also symbol for side group}

S \quad \text{surface site}

T \quad \text{temperature (°K)}

t \quad \text{time (hr)}

V \quad \text{volume of input solution or volume of effluent solution at time } t \text{ (ml)}

V_0 \quad \text{pore volume or effluent volume when } C/Co = 0.5 \text{ (ml)}

\nu_0 \quad \text{average interstitial flow velocity (cm/hr)}

X \quad \text{amount of solute on the exchanger phase in general}

X(z,t) \quad \text{relative solute concentration function in the exchanger phase}

z \quad \text{depth of the column (cm)}

\Delta z \quad \text{depth increment (cm)}

\alpha \quad \text{pore fraction}

\theta \quad \text{volumetric water content (cm}^3/\text{cm}^3); \text{ also fraction of sites covered (dimensionless)}
ABSTRACT

Adsorption-Desorption and Movement of Picloram
(4-Amino-3,5,6-Trichloropicolinic Acid) in Soils

by

Desh Raj Duseja, Doctor of Philosophy

Utah State University, 1972

Major Professor: Dr. R. W. Miller
Department: Soils and Biometeorology

Adsorption and desorption of picloram (4-amino-3,5,6-trichloropicolinic acid) in soils was studied utilizing both batch technique and soil columns. The five soils from the states of Utah and California ranged from 0.6 to 18.7 percent in organic matter content, 5 to 21 percent in sesquioxides and 6.45 to 7.55 in pH. In batch studies, the factors affecting picloram adsorption-desorption included time, soil type, organic matter, herbicide concentration, temperature, pH, and inorganic electrolytes. The soils adsorbed 10.8 to 58.2 percent of the added picloram from 0.05 to 10.0 ppm of picloram aqueous solutions. Adsorption was highly correlated with organic matter ($r = 0.99$), pH ($r = -0.98$), and sesquioxides content ($r = 0.96$) of the soils. Adsorption was significantly correlated with cation exchange capacity of the soils at the 0.05 level. Equilibration time ranged from 4 to 120 hours. An increase in the temperature from 17.7 C to 25 C caused increased adsorption; raising the temperature further resulted in a decrease in adsorption. The adsorption followed the Freundlich model, but not the Langmuir, Tempkin, or B.E.T. models. Adsorption was inversely related to induced pH changes from pH 3.6 to pH 9.2.
From 41.0 to 71.8 percent of the initially adsorbed picloram could be eluted with two successive extractions of deionized water from the three soils at 25°C. The desorption thereafter was slow.

No evidence was found of picloram precipitation with the addition of inorganic electrolytes in aqueous solutions without soil. Divalent inorganic cations were, generally, more effective in increasing adsorption than monovalent cations. Studies of the effect of CaCl₂ concentrations (from 5 to 500 mg/l) on picloram adsorption by four soils suggested an exchange type reaction, picloram acting as a cation. These interpretations were not conclusive.

Column studies with two of the soils, at 1.0 and 10.0 ppm picloram concentrations and in the natural state as well as after calcium saturation, corroborated the findings of batch studies; inorganic salts did impede picloram movement in soils, presumably by increasing picloram adsorption.

Applicability of a mathematical model, based on chromatographic theory, to predict picloram movement in two soils was tested. The model overestimated adsorption. However, when a lower retardation factor was used, the prediction was reasonable on the adsorption side of the herbicide distribution curve, but not the desorption side. This suggested that a distribution coefficient, based on its change with soil depth, may improve the predictability of the model.
INTRODUCTION

Picloram\(^1\) (4-amino-3,5,6-trichloropicolinic acid) is a systemic herbicide which is readily absorbed through the leaves and roots of plants. Most woody plants are susceptible to picloram at 0.5 to 2 lb/A when applied as a foliar spray. Several perennial herbaceous broadleaved weeds are killed with 1 to 4 lb/A applied to the foliage as a spray. Similarly, some seedling broadleaved weeds are susceptible to dosages as small as 0.5 to 2 oz/A. Most established grass species are relatively tolerant to foliage applications at the rate needed to control broadleaved weeds, but pre-emergence application controls many seedling grasses.

Picloram is applied to the soil mostly in the form of potassium salt, in beads or pellets (120 to 200 lb/A having an active ingredient of 2 to 3 percent) or mixed with 2,4-D or other herbicides.

Some of the chemical and physical properties of the herbicide are given in Appendix 1. Full chemical names are given in Appendix 2.

Interest in picloram stems from three factors. Although it is highly soluble in water (solubility 430 ppm at 25 C), it is highly residual in soils. As much as 10 times the normal usage rates are often applied along ditch banks for perennial weed control. These two factors, together, can be a source of contamination of canal waters, causing damage to other crop plants that use these waters. Thirdly, the eroded colloids from treated soils can reach and contaminate reservoirs or other fields.

\(^1\)The trademark of Dow Chemical Company for picloram is Tordon.
Most researchers agree that all organic pesticides applied to the soil are detoxified, sooner or later, by one or more of the following factors: photodecomposition, volatilization, chemical alteration, removal by plant, microbial degradation, leaching or adsorption. Previous research indicates that soil adsorption is a primary factor influencing the longevity of picloram in the soils (Bailey and White, 1970). Therefore, the purpose of this study was to determine the effect of several factors on soil adsorption and desorption of picloram.

In this study several behavioral factors of picloram in soils have been investigated. Effect of time, soil type, organic matter, clay, pH, temperature, and inorganic salts on the adsorption and desorption of picloram are some of the aspects of this work.

A mathematical model, based on chromatographic theory and material balance equation, was tested as to its suitability for prediction of picloram movement in soil columns.
REVIEW OF LITERATURE

Work reported in the literature, on the adsorption-desorption and movement of picloram in soils, is similar to the work done on triazines and other herbicides. Also, picloram being an anion at the pH's of this study, some literature has been included on the interactions in soil of inorganic anions like phosphates, borates, and sulfates. The following scheme has been used.

1. Adsorption-desorption of pesticides in general:
   A. Factors affecting adsorption-desorption
      a. s-Triazine compounds
      b. Phenyl alkanoic acids
   B. Effect of inorganic salts on adsorption-desorption
      a. Adsorption-desorption of pesticides
      b. Adsorption of inorganic anions
   C. Movement in columns and application of chromatographic theory

2. Adsorption-desorption of picloram
   A. Factors affecting adsorption-desorption
      a. Soils
      b. Exchange resins, clay minerals, etc.
   B. Field studies and movement in different media

3. Photolytic, microbial and chemical degradation of picloram.
Adsorption-desorption of Pesticides in General

Factors affecting adsorption-desorption

s-Triazine compounds. The structure of atrazine, a common member of this family, is shown in Appendix 3. The pKa of this compound is about 1.68 and solubility in water of 70 ppm at 27 C (Bailey and White, 1965). It should, then, behave as a molecular species at pH's above \( \approx 3.68 \).

Harris and Warren (1964) reported atrazine to be adsorbed by both anion and cation exchangers, to be slightly adsorbed by muck soil, and to be greatly adsorbed by bentonite. Desorption occurred more readily from bentonite than from muck. Talbert and Fletchall (1965) found montmorillonite to be very adsorptive of atrazine, while no herbicide was adsorbed on kaolinite. Organic materials were more adsorptive than clays.

Hilton and Yuen (1963) found atrazine to be quite readily adsorbed on several Hawaiian soils but could not correlate adsorption with any soil property. Harris (1966) found atrazine to be adsorbed in greater quantities by fine textured soils than by coarse textured soils.

To further understand the behavior of atrazine in soils, a nitrogen containing ring compound, the effect of pH and temperature on its adsorption-desorption was examined by Harris and Warren (1964). They found that atrazine adsorption on muck was temperature independent, while adsorption on bentonite was temperature dependent. Talbert and Fletchall (1965) reported that increases in temperature decreased atrazine adsorption on montmorillonite, kaolinite, and organic materials. McGlamery and Slife (1966) reported very slight changes in adsorption
atrazine by a Drummer clay loam soil with temperatures in the range of 0.5 C to 40.0 C. Desorption was increased by increases in temperature in the same range. However, adsorption of atrazine by humic acid was found by these authors to increase with increases in temperature. Desorption from humic acid was very slight. These workers proposed van der Waal's forces as the binding agent in adsorption on clays and ionic bonding in humic acid.

Concerning the effect of pH, Talbert and Fletchall (1965) reported that adsorption of atrazine by montmorillonite, kaolinite, and organic materials was decreased by an increase in pH in the range of 5.0 to 7.0. McGlamery and Slife (1966) also found similar results in the pH range of 3.9 to 8.0, during atrazine adsorption on Drummer clay loam soil and humic acid. Desorption of atrazine from the same soil was increased by increases in pH. Desorption from humic acid was very slight.

Another compound, of the s-Triazine family, prometone, has a pKa of 4.30. Its chemical structure appears in Appendix 3. Prometone exists in molecular form in a neutral aqueous environment and associates strongly with hydrogen as the pH is lowered. Weber, Perry, and Upchurch (1965) found that prometone was not adsorbed by kaolinite, but gave s-shaped curves on sodium and/or aluminum montmorillonite, and the adsorption was inversely related to pH and temperature.

Phenyl alkanoic acids. General structure of this family of compounds appears in Appendix 3.

Weber, Perry, and Upchurch (1965) found that 2,4-D (pKa = 2.80) was negatively adsorbed by clay minerals. Frissel and Bolt (1962)
also obtained similar results. However, Haque et al. (1968) found positive adsorption of 2,4-D on clay mineral illite, kaolinite, and montmorillonite, although adsorption on kaolinite was minimum. Temperature had little effect on the amount adsorbed.

Bailey, White, and Rothberg (1968), studying the effect of pH on 2,4-D and 2,4,5-T (pKa = 3.14) adsorption by montmorillonite, found that the magnitude of adsorption of these compounds is governed by the surface acidity and not by the pH of suspension.

**Effect of inorganic salts on adsorption-desorption**

Adsorption-desorption of pesticides. The paper of Frissel and Bolt (1962) was the earliest report found concerning the effect of inorganic salts on pesticide adsorption. These authors, working with clay minerals, found that the main variables in the adsorption of a number of organic acidic and basic herbicides, were pH and electrolyte concentration of the system. They explained the salt effect on the basis of "salting out."

Nearpass (1967) studied the effects of the predominating cation (Ca, Mg, K, or Na) on the adsorption of simazine (pK1 = 1.65, pK2 = 0) and atrazine (pKa = 1.68) by Bayboro clay soil. He found that adsorption of these herbicides decreased with increasing degree of saturation with these cations. The decrease appeared to be a result of the occupation of adsorption sites by cation, rather than a specific effect of cation species on the adsorption of the herbicide. He also studied the exchange adsorption of 3-amino-1,2,4-triazole (amitrole, pKa = 4.14) by montmorillonite, including the effect of CaCl2 and NaCl on the latter's adsorption (Nearpass, 1970). A decrease in
amitrole adsorption was observed with an increase in salt concentration, which he attributed to occupation of adsorption sites with metal cations. He concluded that adsorption of amitrole by neutral or alkaline soils may be due to molecular adsorption by organic matter.

The importance of exchange type reactions in the adsorption-desorption of charged herbicides is indicated by the work of Weber and Weed (1968). They found that diquat and paraquat (completely ionised) cations were adsorbed by montmorillonitic and kaolinitic clay minerals to the extent of their cation exchange capacity. About 80 percent of each of the herbicides was displaced from kaolinitic clay with Ba$^{+2}$ ions, whereas only 5 percent was removed from montmorillonite. The herbicides were found to exchange for one another. Prometone, a neutral herbicide, was adsorbed by montmorillonite but only slightly by kaolinite. It was released from both minerals more readily with de-ionised water than with Ba$^{+2}$ ions (1M BaCl$_2$).

MacNamara and Toth (1970) studied the effect of weak electrolyte solutions on the adsorption of linuron and malathion by soils and clay minerals and found that, in general, electrolytes appeared to suppress or have little effect on pesticide release.

Hance (1971) made measurements of the effect of exchangeable cations on the adsorption of linuron and atrazine by cation-exchange resin, cellulose phosphate powder, bentonite, and a peat soil. The cations studied were Ca$^{+2}$, Ni$^{+2}$, Cu$^{+2}$, Fe$^{+3}$, and Ce$^{+4}$. The results with linuron are consistent with the hypothesis that complex formation with exchangeable cations is a possible mechanism of adsorption. This was not true with atrazine.
Abernathy and Davidson (1971) studied the effect of CaCl$_2$, at 0.01 and 0.5N concentrations, on the adsorption of prometryne (pKa = 3.05) and fluometuron (a neutral species) in soil. In batch equilibrium studies, fluometuron adsorption was decreased and prometryne adsorption increased by increasing the CaCl$_2$ concentration from 0.01 to 0.5N. The mobility of prometryne decreased in the two soils by increasing the CaCl$_2$ concentration. Fluometuron mobility was unchanged by the two CaCl$_2$ concentrations in one soil, but increased in another soil (Norge loam) at the high CaCl$_2$ concentration.

Adsorption of inorganic anions. Hadas and Hagin (1972) studied boron adsorption by soils as influenced by potassium (K). Potassium-saturated soils adsorbed more boron than the untreated soils, and Langmuir equations indicated a greater strength of adsorption by the K-treated soils. They concluded that potassium influenced the adsorption of boron probably by creating more favorable conditions for boron adsorption in soil.

Barrow (1972) studied the influence of solution concentration of Ca$^{+2}$ on the adsorption of phosphate, sulfate, and molybdate by soils. He showed that adsorption of all three anions increased as the Ca concentration in soil increased. It was shown that simultaneous increase in exchangeable Ca also occurred.

Movement in columns and application of chromatographic theory

Elrick, Erh, and Krupp (1966) devised an apparatus to study miscible displacement processes in soils. The usefulness of this technique was illustrated by a brief description of (1) the mixing of
Cl⁻ in a glass bead medium; (2) the movement and adsorption of atrazine in soil; and (3) the movement and microbiological nitrification of \( \text{NH}_4^+ \) to \( \text{NO}_3^- \). Non-conformity of the mathematical model of movements to the actual movement of atrazine in soil columns was attributed to intra-aggregate adsorption and dead-end pores.

Lindstrom et al. (1967) developed an equation based on chromatographic theory to predict the theoretical curves for pesticide movement for two different boundary conditions in saturated soil for various water velocities in the pores and diffusion coefficients. They did not test their model experimentally.

Davidson and Santelmann (1968), while moving solutions containing fluometuron (a neutral species) and diuron (pKa=1 to -2) through saturated beds of 250-μ glass beads and through Norge loam soil columns at two water flow rates, found that (1) more diuron was adsorbed by a glass bead system than fluometuron, (2) the shape of fluometuron distribution curves at two flow rates were distinctly different, and (3) fluometuron was as mobile as the chloride ion at both high and low flow rates.

Davidson, Riek, and Santelmann (1968) found that the rate at which fluometuron and diuron (two substituted urea herbicides) move through a water-saturated glass bead column and uniformly packed soil column depends upon water flux. Experimental and calculated effluent concentration distribution (calculated one based on a model similar to the one used in this dissertation) did not agree when fluometuron was retained by the porous material (soil).
Davidson and Chang (1972) applied the chromatographic theory of pesticide movement to picloram movement in soils. They demonstrated that average pore water velocity influenced picloram movement more significantly than variations in bulk density or largest aggregate size at a given flow rate. The model based on chromatographic theory failed to predict picloram movement, which they attributed to complexities of the adsorption process including the influence of pore size distribution.

King and McCarty (1968) employed an equation describing the chromatographic movement of pesticides under non-continuous flow conditions. Experimental and theoretical curves agreed fairly well for the leaching of organic phosphorus insecticides in soil columns.

Adsorption-Desorption of Picloram

Factors affecting adsorption-desorption

Soils. Grover (1968) investigated the relationship between the amount of picloram needed to reduce fresh weight of sunflowers by 50 percent (ED$_{50}$) and clay content, organic matter, and cation exchange capacity of seven Saskatchewan soils maintained under controlled environmental conditions. There were no significant correlations between ED$_{50}$ values of picloram and soil clay content or cation exchange capacity. ED$_{50}$ values were highly correlated with soil organic matter content, and increased as the soil pH was lowered or raised from pH 6.5.

Hamaker, Goring, and Youngson (1966) found the greatest adsorption of picloram, 2,4-D and 2,4,5-T in soils containing a high percentage of organic matter, in soils rich in Fe and Al components
(red soils) and in acidic soils. Adsorption occurred rapidly by red soils but slowly by highly organic soils. The data suggest that adsorption of picloram is primarily caused by organic matter and hydrated metal oxides, with clays probably playing a minor role. Adsorption of unionised picloram and its anion was involved.

Herr, Stroube, and Ray (1966) and Keys and Friesen (1968) found that resistance to leaching of picloram in soils was correlated with adsorption. Herr, Stroube, and Ray (1966) also observed that picloram adsorption in soils was inversely related to pH and directly related to organic matter of the soil.

Exchange resins, clay minerals, etc.. Bailey, White, and Rothberg (1968) reported conformity to Freundlich adsorption equation for picloram, when its aqueous solution was incubated with samples of 1 to 0.2 μ (micron) montmorillonite clays adjusted to pH values of 3.35 and 6.80. They concluded that adsorption occurred to the greatest extent on the acid H-montmorillonite compared to the nearly neutral Na-montmorillonite. Negative adsorption occurred when the adsorbent was Na-montmorillonite. There appeared to be slightly more of a driving force (molar free energy) for adsorption of picloram than for phenoxyacetic acid, although the difference in average free energy (\(\bar{F}\)) values for the hydrogen system was not great.

Grover (1971) studied the adsorption of picloram by various soils, activated charcoal, anion and exchange resin, kaolinite and montmorillonite, wheat straw, cellulose powder, cellulose triacetate, and peat moss. He concluded that adsorption of the molecular form probably would involve hydrogen bonding with hydrophobic surfaces, e.g. those
on cellulose triacetate and peat moss. The absence of adsorption on clay minerals and cellulose powder suggested a total lack of attraction of both forms of picloram for hydrophilic surfaces.

**Field studies and movement in different media**

Herr, Stroube, and Ray (1966) found that the region of highest concentration of picloram in heavy and medium-textured soils, when sampled 9 and 15 months after application, was near the surface.

Merkle, Bovey, and Davis (1967) investigated the effect of soil type, temperature, and moisture on the persistence of picloram. Detectable quantities of picloram were present in Houston clay, Axtell sandy loam, and commercial sand after incubation for one year, at 4, 20, and 38°C and moisture levels of both field capacity and 0.1 field capacity, from rates as low as 0.25 μg per gram soil (0.5 lb/A). Movement studies indicated that leaching was an important means of dissipating the herbicide in light soils; picloram moved more completely through the surface 2 feet of soil; the greatest herbicide concentrations generally were found at the deepest sampling depth. Goring, Youngson, and Hamaker (1965) also reported the highest concentrations of picloram in soil samples from four states to be in the top 12 inches.

**Photolytic, Chemical, and Microbial Degradation of Picloram**

Youngson et al. (1967) studied factors influencing decomposition of picloram in soil, including organic matter content, moisture, and
temperature. Decomposition was found to be incidental to breakdown of soil organic matter.

Goring et al. (1967) showed no important effects of picloram herbicide in soils at 100 ppm, on CO$_2$ evolution, urea hydrolysis, population counts of bacteria and fungi, nitrification of ammonium to nitrite or of nitrite to nitrate. Redemann et al. (1968) concluded that biochemical transformations imposed on picloram, whether by means of microorganisms in soil or plants, did not result in complex degradation products closely related to the herbicide but, rather, to a spectrum of simpler compounds more nearly related to materials which are normal to a living system.

Hance (1967) noted very little decomposition of picloram by non-biological chemical processes even at high temperatures. Merkle, Bovey, and Davis (1967) found that picloram was decomposed by ultraviolet radiation and by sunlight even in the presence of soil. Corbin and Upchurch (1965) were not able to detect any detoxification after incubating picloram in soils at various levels of pH for 8 weeks. Dowler, Forestiner, and Tschirley (1968) reported that appreciable picloram remained in Puerto Rican forest soils for 1 year after treatment. Goring, Youngson, and Hamaker (1965) estimated the half-life of picloram in various soils in the United States varying from 1 to 13 months.

The literature contains conflicting reports concerning the kinetics of degradation of picloram. Grover (1967) noted that following a lag period, the degradation of picloram occurred as a first order reaction. However, Hamaker, Youngson, and Goring (1967, 1968) concluded that
half-order and Michaelis-Menton were the kinetic expressions that most satisfactorily described the detoxification of picloram in the soil.

Evans (1972)\(^1\) found that picloram, in the absence of soil, was very sensitive to degradation by sunlight. They were able to detect the following products: decarboxylated picloram \((R_f = 0.60)\), unknown A \((R_f = 0.14)\), unknown B \((R_f = 0.21)\). Unknown A and B correspond to picloram with one chlorine and two chlorine atoms lost respectively.

\(^1\)Evans, J. O. 1972. Personal communication, Assistant Professor, Department of Plant Science, Utah State University, Logan.
THEORETICAL DEVELOPMENT

Adsorption Isotherm Models

Various adsorption models are available in the literature. Conformity to a model may enable us to evaluate any adsorbent with regard to its energy of adsorption, and adsorption capacity. However, it should be remembered that conformity to a particular model is not proof that assumptions of that model are being met.

Freundlich adsorption isotherm

The Empirical Freundlich isotherm is of the form:

\[ Y = b C_e^n \]  \hspace{1cm} [1]

where: \( Y = \mu \text{gms of solute adsorbed/kgm soil} \)

\( C_e = \text{equilibrium concentration in ppm} \)

\( b \) and \( n \) = constants for a given adsorbent and adsorbate.

A linear plot conforming to equation

\[ \log Y = \log b + n \log C_e \]  \hspace{1cm} [2]

should result if \( \log Y \) is plotted against \( \log C_e \), and providing the data fit the Freundlich equation. This equation implies that the distribution function of energy sites is exponential (Adamson, 1967).

However, the derivation of the Freundlich equation is an empirical one. If the data fit the equation, it is probable, but not proven, that the surface is heterogeneous.
Other models

In heterogeneous systems, such as soil, conformity to models like Langmuir model are not anticipated. However, these models are discussed here briefly for comparison.

**Langmuir model.** The Langmuir model is based on the assumption that (1) heat of adsorption is the same for all adsorption sites and does not depend upon the fraction of sites (θ) covered, (2) there is no interaction between molecules on different sites, and that (3) each site can hold one molecule. In the linear form, this equation is written as

$$\frac{c_e}{X/m} = \frac{C_e}{X_m} + \frac{1}{X_m b'} \tag{3}$$

where $C_e$ is the equilibrium concentration of solution phase; $X_m$ is the amount of solute adsorbed per unit weight of adsorbent; $X_m$ is the adsorption maximum; and $b'$ is a constant at a given temperature. If the data fit this model, a plot of $\frac{c_e}{X/m}$ vs $C_e$ should be a straight line.

**B.E.T. model.** This model is an extension of Langmuir model to include multilayer (multimolecular) adsorption. One form of B.E.T. equation is

$$\frac{C}{X(Co-C)} = \frac{1}{X_m A} + \frac{A-1}{X_m A} \cdot \frac{C}{Co} \tag{4}$$

where $C$ is the equilibrium concentration at which an amount, $X$, of a solute is adsorbed; $Co$ is the solubility of the solute in question, $X_m$ is the amount of solute adsorbed when the entire surface is covered with a complete monolayer, and $A$ is a constant related to the heat of
adsorption. This equation is valid when a straight line is obtained upon plotting

$$\frac{C}{X(Co-C)} \propto \frac{C}{Co}.$$  

This equation has been used for studying adsorption of pesticides with reasonably high vapor pressures (Jurinak and Volman, 1957).

**Tempkin model.** This model applies to adsorption where distribution of adsorption sites is linearly related to each other. The equation is written as

$$\theta = -\frac{RT}{B\Delta H} \ln A C$$  \hspace{1cm} [5]  

where $\theta$ is the fraction of surface covered, $\Delta H$ is the heat of adsorption, $A$ and $B$ are constants and $C$ is the equilibrium concentration. This model may be tested by plotting amount adsorbed against $\ln C$ (Gregg, 1961).

**Adsorption Mechanisms**

A number of adsorption mechanisms are proposed in the literature describing the binding of organic molecules with organic matter, clay minerals and amorphous materials in the soil (Grim, 1968; Bailey, White, and Rothberg, 1968; Mortland, 1970). Adsorption mechanisms for organic molecules in general and picloram in particular will be described here.

**Adsorption mechanisms for organic molecules**

According to Mortland (1970), many compounds may become cationic after adsorption on a surface. The source of protons for such a reaction and the other mechanisms given by him are discussed below,
modified where functional groups on organic matter and on amorphous material are involved.

**Exchange with H⁺ occupying cation exchange sites.**

\[ \theta\text{-NH}_2 + H^+ - S \rightarrow \theta\text{NH}_3^+ S \]

or

\[ P_{c^-} - O^- + H^+ - S \rightarrow P_{cOH-S} \]

where

\[ \theta = \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{N} \\
\text{C} = 0 \\
0^- \\
\text{S = Surface site} \\
\text{Pc} = \begin{array}{c}
\text{NH}_2 \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{C} = 0
\end{array}
\]

This reaction goes to completion because it is essentially between a strong acid and a relatively strong base to give a salt. Where the hydrogen is part of a hydroxyl group at the edges of clay minerals or on amorphous material, the ability to protonate organic bases would be strongly pH dependent. This reaction is characterized by high heats of adsorption and a high degree of irreversibility.
Water associated with metal cations at the exchange sites. Water is not likely to be acidic enough to protonate many organic molecules. However, when water is associated with metal cations, hydrolysis of this complex can produce protons, depending upon the properties of the metal ion involved.

\[
\left[ M \left( H_2O \right)_x \right]^{+n} \rightarrow \left[ MOH \left( H_2O \right)_{x-1} \right]^{+n-1} + H^+
\]

where \( M \) is the exchangeable metal cation. The overall reaction involved when an organic molecule is protonated by such a process is:

\[
\left[ M \left( H_2O \right)_x \right]^{+n} + B \rightarrow \left[ MOH \left( H_2O \right)_{x-1} \right]^{+n-1} + BH^+
\]

where \( B \) is the base in question. It would be expected that the ability of a clay surface to protonate compounds would be dependent upon the nature of metal cations on the exchange sites. It has been observed by these workers (Mortland, 1970) that acidity of the clay surface is greater than would be expected from pH measurements of the clay in water.

Proton transfer from protonated species already present on the surface is another mechanism discussed by Mortland (1970). The general reaction is:

\[
AH^+ + B \rightarrow BH^+ + A
\]

where \( AH^+ \) represents the protonated species (proton donor) on the surface (for example \( NH_4^+ \)), and \( B \) represents the base (proton acceptor) such as a picloram anion.
Hemi-salt formation. When the amount of adsorbed base (B) on a surface exceeds the number of protons available for cation formation, two molecules compete for the proton on an equal basis, forming a strong symmetrical hydrogen bond and a cation of the \([B_2 - H]^+\) type. This has been observed by Mortland (1970) in the case of ethyl ammonium-ethylamine complex. However, this complex was found stable only in vacuum, and broke up in water.

Hydrogen bonding is still another mechanism by which organic molecules are bonded to surfaces.

Water-bridge. Involves the linking of a polar organic molecule to an exchangeable metal cation through a water molecule:

\[
\begin{array}{c}
M^{+n} \quad O - H - \quad 0 = C \\
\end{array}
\]

This kind of bond has been demonstrated for montmorillonite complexes with pyridine (Mortland, 1970).

Clay mineral oxygens and hydroxyls. Interaction of molecules capable of hydrogen bonding with oxygens or hydroxyls of the clay mineral surface has been considered to be the primary mode of interaction and the basis for many models of adsorption in the past. For the adsorption of neutral but polar organic molecules by metal saturated clays, ion-dipole interactions are overriding in their effect.

van der Waal's forces. It is generally concluded (Mortland, 1970) that van der Waal's forces become quite significant in clay-organic complexes particularly for organic compounds of large molecular weight.
While clay-organic systems have been described above, it is reasonable to expect that similar mechanisms still operate in other systems such as organic molecules and organic matter, rendering those sites no longer electropositive.

**Adsorption mechanisms for picloram**

According to Bailey, White, and Rothberg (1968), the following mechanisms for bonding of the picloram molecule to soil and to organic matter constituents are possible:

1. Physical adsorption. According to Bailey, White, and Rothberg (1968) this adsorption mechanism is applicable for picloram when acidity of the system is such that \( \text{pH} \leq \text{pKa} + 2 \).

2. R-N-H -- - - 0 - clay. This mechanism is applicable when pH of the system was \( > \text{pKa} + 2 \).

3. \( > \text{C} = \text{O} -- - \text{M}^{Z^+} - \text{clay} \) (where \( \text{M}^{Z^+} \) is a metal cation of \( Z^+ \) charge). It was applicable when \( \text{pH} > \text{pKa} + 2 \).

4. \( > \text{C} = \text{O} \begin{array}{c} \text{H} \\ \text{H} \end{array} - - - \text{M}^{Z^+} - \text{clay} \). This mechanism was applicable irrespective of whether \( \text{pH} \) was greater or less than \( \text{pKa} + 2 \).

5. \( \text{C} - \text{OH} -- - 0 - \text{clay} \). This was applicable when \( \text{pH} \) was less than \( \text{pKa} + 2 \).

6. \( \text{B} + [\text{H}^+ - \text{clay}] \rightarrow \text{HB}^+ - \text{clay} \). This type of mechanism was also applicable when \( \text{pH} \leq \text{pKa} + 2 \). B here signifies organic base.
7. \( \text{M}^{2+} (\text{H}_2\text{O}) - \text{clay} + \text{B} \rightarrow \left[ \text{M}^{2+} (\text{OH}) - \text{clay} \right] + (\text{HB}^+ - \text{clay}) \). It was applicable when pH was \( > \text{pKa} + 2 \).

The above authors worked with clay minerals only. It is reasonable to assume, however, that many of the above mechanisms will be operative in picloram-organic matter interactions. For example, hydrogen for the bonding of picloram through the carbonyl oxygen can be supplied by \(-\text{NH}\) and \(-\text{OH}\) groups of organic matter.

Mathematical Treatment
(Ion Exchange Chromatography)

The concept of ion exchange chromatography is based on the concept of material conservation. In other words, the change in the material flux within a section of column \( \Delta z \) (\( z \) refers to depth) is equal to the sum of the rate of change of concentration of the solution phase and the rate of change of concentration of the exchanger phase within the section.

Three different approaches can be identified in the literature according to the treatment of the rate of ion exchange. The model developed by Thomas (1944) was based on the condition of the conservation of the exchanging ions. It required that within a finite section of column, the change in solute flux must be accounted for by the rate of change of the solution concentration of the exchange phase. This is more clearly depicted by Equation [6] which is written in terms of the notation defined in this paper.

\[
\nu_0 \frac{2C}{\partial \tau} + \frac{3C}{\partial t} + \frac{q}{\partial t} \frac{2q}{\partial \tau} = 0 \quad [6]
\]

where \( C \) is the concentration of solute in solution, \( q \) is the amount
of ion adsorbed per unit weight of adsorbent, \( z \) is the depth of the column, \( t \) is time, \( \nu_0 \) is interstitial flow velocity, \( \rho \) is bulk density of soil column. The characteristic of Thomas' study is the treatment of the reaction rate of solute exchange.

The model developed by DeVault (1963) for single solute chromatography was also based on the same conditions of solute conservation in the column process and is described by an equation similar to that of Equation [6]

\[
\frac{\partial C}{\partial z} + \frac{\partial C}{\partial \nu_0} + \frac{\partial q_1}{\partial \nu_0} = 0
\]  

[7]

where \( q_1 \) is the solute adsorbed per unit length of exchanger. A characteristic of this model is that it assumes an instantaneous equilibrium between the solute and the exchanger.

Neither of the two models mentioned, which considered kinetic and equilibrium approaches respectively, included the fluid dispersion effect. Fluid dispersion is another factor that can cause the spreading of the fluid from the idealized piston flow in a column. Lapidus and Amundson (1952) developed a model which takes into account the dispersion in addition to the mass flow in the flux term of the material balance equation. The equation is written as

\[
D_0 \frac{\partial^2 C}{\partial z^2} + C \frac{\partial C}{\partial z} + \rho \frac{\partial q_1}{\partial t} = \nu_0 \frac{\partial C}{\partial t}
\]  

[8]

where \( D_0 \) is the fluid dispersion coefficient.

This is the model that most closely resembles herbicide movement through porous materials and has been used for this purpose by
various workers with varying success (Davidson, Rieck, and Santelmann, 1968; Elrick, Erh, and Krupp, 1966; Abernathy and Davidson, 1971; and Davidson and Chang, 1972). Conversion of this equation into a working equation is given below.

Assuming an equilibrium between solution and exchanger phases,

\[ q = f(C). \]  

[9]

By using chain rule,

\[ \frac{\partial q}{\partial t} = f(C) \cdot \frac{\partial C}{\partial t} \]

or \[ \frac{\partial q}{\partial t} = K \cdot \frac{\partial C}{\partial t} \]  

[10]

where \( K \) is the slope of the exchange isotherm. Substituting Equation [10] into Equation [8] gives

\[ \frac{D \partial^2 C}{\partial z^2} = \nu_0 \frac{\partial C}{\partial z} + \left( 1 + \frac{\partial K}{\partial t} \right) \frac{\partial C}{\partial t} \]  

[11]

\( K \), the slope of the exchange isotherm, has also been called the distribution coefficient. It is obtained by assuming the following linear relationship between the quantity in solution and that retained.

\[ Y = KC_e \]  

[12]

where \( Y \) is the quantity of solute retained per unit weight of adsorbent and \( C_e \) is concentration of solute per unit volume of soil water. The distribution coefficient is assumed concentration independent over the herbicide concentration range in question.

A problem of interest to agriculture is the uniform application of a herbicide solution to the surface of a semi-infinite body of soil.
At a predesignated time, $T$, a herbicide free solution is applied and the herbicide slug (solution) of width $v_o T$ displaced through the soil profile. The initial and boundary conditions, describing the herbicide application and subsequent displacement are

(a) $C(z, 0) = 0$

(b) $v_o C_0 = v_o C - D_0 \frac{3C}{3z}$ (for $z = 0$ $0 < t < T$)

(c) $v_o C(0, t) = 0$ (for $z = 0$ $t > T$) [13]

where $C_0$ represents the concentration of the incoming solution. The above boundary conditions at $z = 0$ are an improvement over those used by Lapidus and Amundson (1952) in their solution of Equation [8]. For example, the boundary conditions at the inlet or soil surface requires only a constant flux of concentration $C_0$ at $z = 0$ and not $C = C_0$ at $z = 0$ for times greater than zero but less than $T$. The latter constraint may be difficult to achieve for small water fluxes and solutes or adsorbents with large distribution coefficients.

The solution to Equation [11], subject to initial and boundary conditions given in Equation [13], is given by Davidson, Rieck, and Santelmann (1968) as follows:

\[
\frac{C}{C_0} = \frac{1}{2} \left\{ \text{erfc} \left( \frac{z - vt}{\sqrt{4Dt}} \right) - \text{erfc} \left( \frac{z - v(t - T)}{\sqrt{4D(t - T)}} \right) \right\} \\
+ 2v \sqrt{\frac{t}{D}} \exp \left( \frac{z - vt}{\sqrt{4Dt}} \right) \\
- 2v \sqrt{\frac{(t - T)}{D}} \exp \left( \frac{z - v(t - T)}{\sqrt{4D(t - T)}} \right) \\
- \frac{v}{D} \left[ \frac{D}{v} + vt + z \right] \exp \left( \frac{zv}{D} \right) \text{erf} \left( \frac{z + vt}{\sqrt{4Dt}} \right) \\
+ \frac{v}{D} \left[ \frac{D}{v} + v(t - T) + z \right] \exp \left( \frac{zv}{D} \right) \text{erfc} \left( \frac{z + v(t - T)}{\sqrt{4D(t - T)}} \right) \} [14]
\]
where

\[ D = \frac{D_0}{1 + \rho K/\theta} \quad \text{and} \quad \nu = \frac{\nu_0}{1 + \rho K/\theta} \quad [15] \]

This equation, then, gives the concentration of picloram in the effluent from the soil column, relative to the initial or input concentration of picloram, as a function of time in hours. With a relatively constant flow velocity of water, amount of water passed through a body of soil should be proportional to time. Therefore, if the concentration for kill or reduction in plant growth is known, then ideally, a calculation of the amount of water necessary for this concentration to be at a specific depth can be made from previously measured parameters.
MATERIALS AND METHODS

Preparation of Stock Solutions and Calibration Curves

Stock solutions containing 0.05 to 10 ppm of acid-labelled picloram (specific activity 4.13 μC/mg) were prepared in deionized water. The solutions were then subjected to scintillation counting on a Packard TriCarb liquid scintillation counter according to the method of Yaron, Swoboda, and Thomas (1967). One ml aqueous sample was added to 19.0 ml of liquid scintillator, dissolved by slight shaking and counted for at least three 10-minute periods. Radioactivity was usually high and the counting efficiency was approximately 65 percent or better. The counting error was ±3 percent.

Laboratory Procedures

Degradation of picloram

A preliminary 30-day experiment utilizing 25 to 50 ml stock solution of 0.05 to 1 ppm picloram was performed to check any adsorption on glass walls, polypropylene centrifuge tube walls, rubber corks, or degradation by sunlight. As a precautionary measure, the experiments were conducted in a dark room, because the actual handling of samples may be subjected to different light conditions from one experiment to another.

To check for degradation of picloram during the course of an experiment, a thin layer chromatography (TLC) technique was used.
A 100 \( \lambda \) sample (column effluent in case of column studies) was applied to the TLC plate in quadruplicate. The TLC plate (purchased commercially) had a coating, 250 \( \mu \) thick, of Silic AR TLC - 7GF, a neutral sorbent produced by Mallinckrodt, which contained approximately 84 percent Silicic acid, 10 percent CaSO\(_4\), and 6 percent Phosphor.

The developing solvent was benzene: Acetic acid (152:48). TLC plates were viewed under UV light. Portions of adsorbent containing the spot were scrapped with a clean spatula into a scintillation vial, scintillation fluid added, and counted, along with samples of known radioactivity. Portions of TLC plates, with their \( R_f \) values corresponding to known degradation products of picloram, were also counted. Samples were applied to TLC plates immediately after elution from the column, along with samples of known radioactivity.

**Factors affecting soil adsorption-desorption of picloram (batch studies)**

A series of experiments were conducted to determine the influence of incubation time, soil type, organic matter, herbicide concentration, pH, and inorganic salts on the soil adsorption and release of picloram. A slurry technique (Hance, 1965) was used throughout the series and quantitative determinations of the herbicide were made primarily by using radio-labelled picloram. The following procedures were common to all experiments unless otherwise noted.

Ten grams of air-dried (5 grams for Chance and Aiken soils) 60-mesh soil were weighed into a polypropylene tube and 10 ml of herbicide solution added. The tubes were stoppered and placed on a mechanical shaker in a constant temperature bath until equilibrium
was reached or for the indicated time. After shaking, the slurry was centrifuged at 1500 RPM for 10 minutes. A 1 ml aliquot of the supernatant was taken at various intervals and counted. The herbicide adsorbed was determined by subtracting the concentration found in the supernatant from the initial concentration. The temperature fluctuation in the water bath was ±0.3 C. All determinations were made in duplicate, and the experiment was repeated if necessary.

Five soils were used for these experiments. Important characteristics of these soils are described in Table 1.

Effect of time on adsorption-desorption of picloram was investigated by the above mentioned slurry technique by taking aliquots after each 24-hour interval, except in Aiken soil where samples were taken at 1/2-hour intervals. When no change in the picloram concentration of the supernatant was observed, it was assumed that equilibrium had been reached. Similar procedures were followed for desorption, except the time interval for sampling was generally four hours.

One experiment was designed to determine the influence of soil type and organic matter on soil adsorption of picloram. Organic matter was removed from the soil by heating to 350 C for 24 hours in an electric furnace. Adsorption of picloram was determined by the five soils after removing the organic material by using the slurry technique.

Desorption of picloram was studied utilizing the following technique. Adsorption equilibrium was allowed to take place and 1 ml sample of the supernatant was taken after centrifuging the sample. Ten ml water was then added and the system was allowed to re-equilibrate; the tubes were centrifuged and a 1 ml aliquot was again
Table 1. Properties of soils used in the studies

<table>
<thead>
<tr>
<th>Soil type</th>
<th>pH</th>
<th>Organic matter</th>
<th>Air dry moisture</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>Sesqui-oxides</th>
<th>CaCO₃ equiv.</th>
<th>Cation exchange capacity</th>
<th>Picloram dissociated in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nibley silty clay loam</td>
<td>7.35</td>
<td>2.53</td>
<td>2.62</td>
<td>3.4</td>
<td>59.6</td>
<td>37.0</td>
<td>6.9</td>
<td>2.1</td>
<td>25.7</td>
<td>99.94</td>
</tr>
<tr>
<td>Millville silt loam</td>
<td>7.55</td>
<td>1.90</td>
<td>1.14</td>
<td>14.9</td>
<td>65.7</td>
<td>14.9</td>
<td>5.2</td>
<td>28.0</td>
<td>15.6</td>
<td>99.96</td>
</tr>
<tr>
<td>Chance loam</td>
<td>6.50</td>
<td>18.70</td>
<td>4.76</td>
<td>34.6</td>
<td>53.3</td>
<td>19.1</td>
<td>5.1</td>
<td>0.09</td>
<td>37.0</td>
<td>99.60</td>
</tr>
<tr>
<td>Aiken clay</td>
<td>6.45</td>
<td>0.60</td>
<td>4.48</td>
<td>27.2</td>
<td>32.6</td>
<td>40.2</td>
<td>21.7</td>
<td>0</td>
<td>16.3</td>
<td>99.56</td>
</tr>
<tr>
<td>Providence silt loam</td>
<td>7.05</td>
<td>3.59</td>
<td>1.92</td>
<td>31.6</td>
<td>53.1</td>
<td>15.3</td>
<td>5.2</td>
<td>0</td>
<td>30.5</td>
<td>99.89</td>
</tr>
</tbody>
</table>

\( ^a \) includes 2 to 0.05 mm fraction

\( ^b \) based on a pKa of 4.1 (Hamaker, Goring, and Youngson, 1966) for the dissociation of H⁺ from the carboxylic group
taken from the supernatant for analysis. To study the effect of dilution on desorption of picloram, the soil-solution was diluted with additional water after adsorption equilibrium. They were allowed to re-equilibrate for 24 hours and 1 ml samples were withdrawn from the supernatant for counting.

The influence of herbicide concentrations on adsorption of picloram was studied using picloram concentrations ranging from .05 to 10 ppm and following the procedure outlined above.

Four different temperatures (17.7°C, 25°C, 28.2°C, 24.7°C) were used with Providence and Chance soils and three temperatures (17.7°C, 25°C, and 34.7°C) were used with Aiken soil to study the effect of temperature on adsorption and desorption of picloram.

Another experiment was designed to determine the effect of pH on adsorption of picloram by Providence and Chance soils. The pH change was induced by adding either KOH or HCl. Twenty-four hours were allowed for equilibration. The pH effects above pH 9.2 in Providence soil and above pH 8.5 in Chance loam could not be studied because of solubilization of organic matter by the high alkalinity and consequent interference during scintillation counting.

The influence of several salts on adsorption of picloram onto the Providence soil was investigated. Dilute solutions (1 to 5 meq/l) of KCl, K₂SO₄, CaSO₄, and CaCl₂ were used, and their influence on picloram adsorption was studied using the slurry technique. A preliminary test using concentrations of 66 meq/l and 660 meq/l BaCl₂ was performed. The effect of CaCl₂ concentrations on the adsorption of picloram by the other four soils was examined at 0, 5, 10, 25, 50, and 500 meq/l.
Mechanical analysis (particle size distribution) and organic matter analysis were done by the Utah State University Soil Testing Laboratory. The former was based on a method adapted from Kilmer and Alexander (1949). The latter was adapted from the Walkley-Black wet digestion method (Allison, 1965).

Cation Exchange Capacity (C.E.C.) was determined by the method of Chapman (1965) by the Utah State University Soil Testing Laboratory.

Column studies

Columns used in this study were made of pyrex glass, 2 cm in diameter, with fitted glass bottoms. There was a narrow outlet at the center of the bottom of each column. Soil was packed into the column to depths of about 9 cm to 14.5 cm. Soil in the column was saturated with deionized water to eliminate air in the column by gradually immersing the column into water in a graduated cylinder and leaving it until free water appeared on the top of the soil column. Deionized water was then passed through the soil from the top for 24 hours before the herbicide was added. The soil column contained glass beads to a depth of about 0.5 cm at the top of the soil to prevent the soil from puddling.

After the soil had been washed free of herbicide at the end of the experiment, the same column was used to determine the dispersion coefficient (Do). A solution of 0.1N CaCl₂ was used to obtain the Cl⁻ breakthrough curve (BTC). The dispersion coefficient was calculated from the Cl⁻ BTC according to the Equation [16].

$$\frac{\partial C}{\partial t} = -\nu_0 \frac{\partial C}{\partial z} + D_o \frac{\partial^2 C}{\partial z^2}$$  [16]
The solution of this equation was given, for a non-reacting solute (Cl\(^-\)), by Rifai, Kaufmann, and Todd (1956) as

\[
\frac{C}{C_0} = \frac{1}{2} \left[ 1 \pm \text{erf} \frac{z - \nu_0 t}{\sqrt{2} \sqrt{Dt}} \right]
\]

[17]

where the sign is "+" for \( z < \nu_0 t \) and "-" for \( z > \nu_0 t \).

The dispersion coefficient is calculated from Equation [17] by determining the value of \( C/C_0 \) on the BTC of Cl\(^-\) when \( z = L \), where \( L \) is the length of the column. A typical BTC for Millville soil is shown in Figure 1.

The chloride concentration was determined by the potentiometric titration with 0.01N AgNO\(_3\). A Corning Model 12 pH meter with an expanded scale was used; the electrodes used were a double junction electrode as a reference and a silver billet electrode as the indicator electrode.

A Heath Recording Electrometer Model Eu-20-11 was used to monitor flow rates from the column. The average interstitial flow velocity (\( \nu_0 \)) was obtained by averaging the flow rates for the column effluent fractions (3 ml each). As expected, there was a slight decrease in flow rate over the period of a particular experiment.
Figure 1. A typical Cl\(^-\) breakthrough curve (BTC) used for calculating dispersion coefficient.
RESULTS AND DISCUSSION

Nature of Adsorbate

Hamaker (1972)\(^1\) and Volk (1970)\(^2\) have observed that ionization process for picloram involves only the carboxylic group.

\[
\begin{align*}
\text{NH}_2 & \quad \text{Cl} & \quad \text{C} = 0 \\
\text{Cl} & \quad \text{N} & \quad \text{OH} \\
\end{align*}
\]

\[\text{pKa} = 4.1\]

The basicity of amino-nitrogen and ring nitrogen is low and no amphoteric behavior is observed in aqueous solution; apparently the picloram molecule is sufficiently chlorinated to suppress the basicity of the nitrogen.

The \(\text{pKa}\) for the ionization process given in Equation [18] has been reported in the literature to be between 3.6 and 4.1. The value of 4.1 (Hamaker, Goring, and Youngson, 1966) was taken for this study. Consequently, at the equilibrium pH's of concern in this work, namely 6.45 to 7.55, more than 99 percent of the picloram species will be in anionic form as given on the right side of Equation [18].

\(^1\)Hamaker, J. W. 1972. Personal communication, Dow Chemical Company, Midland, Michigan.

Degradation of Picloram

Various aqueous solutions of picloram (0.05 to 1 ppm) were left in Erlenmeyer flasks for up to 12 days in the laboratory, receiving normal amounts of sunlight. No indication of degradation was noted, as determined by liquid scintillation counting.

The microbial regime in the soil may be different from that found in the solutions; therefore, microbial breakdown could still be a possibility in the presence of soil. However, an experiment by Corbin and Upchurch (1965) which included several diverse soils, different temperatures and pH and varying periods of incubation provided evidence that microbial or photolytic decomposition of the herbicide under the conditions used in our experiments would be negligible. For this reason, no attempt was made to extract the chemical quantitatively from the soil. However, all experiments were performed in a dark room, so that conditions of the experiments conformed as closely as possible to those of Corbin and Upchurch (1965).

Because of the time involved in adsorption studies (up to 5 days) and due to the possibility of the microbial regime in our soils being different from that of Corbin and Upchurch (1965), degradation of picloram was tested. Thin layer chromatography (TLC) was applied to random samples from column studies, in two of the soils used. Results reported in Table 2 for Millville and Aiken soils are typical of other results.

Since the picloram was carboxyl-labelled, its decarboxylation would reduce the radioactivity of picloram spots eluted on TLC plates.
Table 2. Radioactivity recovered from picloram spots ($R_f = 0.46$) of thin layer plates after application of given radioactivity from the soil column effluent containing $^{14}C$-labelled picloram

<table>
<thead>
<tr>
<th>Soil</th>
<th>Radioactivity (DPM) applied</th>
<th>Radioactivity (DPM) recovered</th>
<th>Replicates</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Millville $^a$</td>
<td>4760</td>
<td>4680</td>
<td>4530</td>
<td>4660</td>
</tr>
<tr>
<td>Aiken $^b$</td>
<td>4707</td>
<td>4390</td>
<td>5100</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$L.S.D. (1 percent) = 406

$^b$L.S.D. (1 percent) = 1892

However, it is apparent from Table 2 that no decarboxylation of picloram took place in the random water samples taken from the column effluent of the two soils.

Portions of the TLC plates, after application of the effluent samples and development, were eluted and counted at the spots with $R_f$ values close to those expected for known degradation products of picloram (Evans, 1972)$^1$. No radioactivity was detected.

An alternate check on picloram decarboxylation was made on a set of samples of effluent from Millville and Aiken soil columns being eluted with $^{14}C$-labelled picloram. Dry ice (solid CO$_2$) was added to these samples immediately after elution from the column, subsequently an aliquot was drawn for counting. The objective was to drive out any $^{14}CO_2$ that might be present as a result of picloram decarboxylation.

Dry ice was added in small pieces and samples thoroughly shaken. The radioactivity detected before and after addition of dry ice shows that

---

$^1$Evans, J. O. 1972. Personal communication, Assistant Professor, Department of Plant Science, Utah State University, Logan.
decarboxylation of picloram did not take place in the course of the experiment (Table 3). The differences in radioactivity before and after addition of dry ice were not significantly different.

Table 3. Radioactivity detected in random samples of column effluent from Millville and Aiken soils eluted with 14C-labelled picloram

<table>
<thead>
<tr>
<th>Soil</th>
<th>Sample</th>
<th>Radioactivity (DPM) before addition of dry ice</th>
<th>Radioactivity (DPM) after addition of dry ice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millville</td>
<td>1</td>
<td>13960</td>
<td>13764</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>17917</td>
<td>17338</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>14273</td>
<td>14911</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10944</td>
<td>11412</td>
</tr>
<tr>
<td>Aiken</td>
<td>1</td>
<td>2080</td>
<td>2140</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3040</td>
<td>3150</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4500</td>
<td>4400</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5510</td>
<td>5860</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6970</td>
<td>7040</td>
</tr>
</tbody>
</table>

a L.S.D. (1 percent) = 1292

b L.S.D. (1 percent) = 272

Effect of Time on the Adsorption and Desorption of Picloram

Adsorption

As shown in Figure 2, adsorption equilibrium for picloram was essentially attained by Millville, Nibley, and Providence soils in...
Figure 2. Effect of time on adsorption of picloram by four soils at 1 ppm initial concentration at 25C.
5 days (120 hours). Aiken soil attained equilibrium within 4 hours (not given in Figure 2). Chance loam soil was still adsorbing after 5 days.

The adsorption kinetics of soils in Figure 2 shows soils with higher organic matter took longer to reach equilibrium. Although the soils differed in many soil properties (Table 1), organic matter accounted for a major portion of adsorption on these soils.

Talbert and Fletchall (1965) attributed small increases in adsorption of herbicides by soil with time after 1 hour to (1) a delay in the wetting of small interior capillaries, (2) the slow diffusion of the herbicide into these interior surfaces, (3) a slow, irreversible fixation due to chemical forces, (4) the mechanical breakage of soil particles, or (5) the formation of complexes. In the present studies, the use of 60 mesh soil reduced the slowing effects of mechanical breakage of soil particles.

Slow diffusion of picloram into the interior smaller capillaries, as suggested above, may have occurred in these studies. Hamaker, Goring, and Youngson (1966) attributed the slow rate of adsorption of picloram on some soils to diffusion into the lipid-like phase of organic matter. They found aqueous NaOH to be more efficient than water in eluting sorbed picloram, which may be due partly to the ability of NaOH to break up and emulsify lipid systems.

Desorption

Table 4 shows the release of picloram from Providence silt loam soil at various time intervals when the soil was maintained at different temperatures. The major portion of adsorbed herbicide is
Table 4. The release of picloram from Providence silt loam soil at several time intervals when the soil was maintained at 25.0, 28.2, and 31.5°C

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Time hrs.</th>
<th>Picloram desorbed μgm/kgm soil</th>
<th>% initially adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>2</td>
<td>49</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>64</td>
<td>17.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>67</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>72</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>91</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>96</td>
<td>25.9</td>
</tr>
<tr>
<td>28.2</td>
<td>4</td>
<td>80</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>118</td>
<td>31.8</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>126</td>
<td>34.0</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>168</td>
<td>45.3</td>
</tr>
<tr>
<td>31.5</td>
<td>4</td>
<td>85</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>115</td>
<td>31.0</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>131</td>
<td>35.3</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>142</td>
<td>38.3</td>
</tr>
</tbody>
</table>

*average standard deviation = 7.57

desorbed in a few hours. The release thereafter is slow. However, it was established that desorption equilibrium was attained within 24 hours for all soil.

Effect of Soil Type and Organic Matter on Adsorption and Desorption of Picloram

Adsorption

The relation of soil type, organic matter and adsorption of picloram at two concentrations is given in Table 5. Chance loam soil had the largest adsorptive capacity, with adsorptions of 1042 and 582 μg picloram/kgm of soil at the two concentrations used. In decreasing order of adsorption were Providence silt loam, Aiken clay, Nibley clay loam, and the Millville silt loam.
Table 5. Adsorption of picloram by five soils, in their natural state and after removal of organic matter. Incubations were made at 25 °C and picloram concentrations of 0.5 and 1.0 ppm.

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Organic matter</th>
<th>With organic matter</th>
<th>Without organic matter</th>
<th>Reduction in adsorption</th>
<th>Picloram adsorbed on organic matter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>high rate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>low rate&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>µgms /kgm</td>
<td>µgms /kgm</td>
<td>% total adsorbed</td>
<td></td>
</tr>
<tr>
<td>Chance loam</td>
<td>6.50</td>
<td>18.7</td>
<td>1042 52.1</td>
<td>582 58.2</td>
<td>144 7.2</td>
<td>898 85.6</td>
</tr>
<tr>
<td>Providence silt loam</td>
<td>7.05</td>
<td>3.6</td>
<td>371 37.1</td>
<td>175 35.0</td>
<td>49 4.9</td>
<td>322 88.0</td>
</tr>
<tr>
<td>Nibley silt loam</td>
<td>7.35</td>
<td>2.5</td>
<td>236 23.6</td>
<td>- -</td>
<td>18 1.8</td>
<td>218 91.0</td>
</tr>
<tr>
<td>Millville silt loam</td>
<td>7.55</td>
<td>1.9</td>
<td>108 10.8</td>
<td>- -</td>
<td>29 2.9</td>
<td>79 70.0</td>
</tr>
<tr>
<td>Aiken clay</td>
<td>6.45</td>
<td>0.6</td>
<td>268 13.4</td>
<td>135 13.5</td>
<td>240 12</td>
<td>28 10.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>High rate corresponds to 1 ppm of picloram in solution.

<sup>b</sup>Low rate corresponds to 0.5 ppm of picloram in solution.

<sup>c</sup>At high rate.
soils, adsorbing 371, 268, 236, and 108 μgm picloram kgm of soil, respectively from the 1.0 ppm solution. If the Aiken clay is excluded sorption by soils parallels the organic matter content of soils.

The linear regression analysis between organic matter content of the three soils at similar pH levels (Providence, Millville, and Nibley) and adsorption indicates that adsorption increases with an increase in the soil organic matter content (Figure 3). Included in Figure 3 is the linear regression line for the reduction of adsorption with reduction in organic matter for the three soils. The Aiken and Chance soils were excluded from this analysis.

Regression analysis for reduction in adsorption as related to reduction in organic matter content shows a correlation coefficient of 0.98 compared with 0.99 for adsorption vs organic matter content (Table 5). This shows that the amount of picloram adsorption attributable to the organic matter fraction is large. These results agree generally with those of Grover (1968), who found a change in $E_{D50}$ value of about 0.043 ppm picloram (43 μgms/kgm) for each 1 percent increase in organic matter content of five Saskatchewan soils.

Table 5 also shows a reduction in adsorption of up to 91 percent among the five soils when adsorption was attempted after the organic matter was removed. Some of the change in adsorption could be due to disruption of the clay-mineral structures. However, Grover (1971) found a negative adsorption of picloram on kaolinite as well as montmorillonite. Therefore, contribution of clay minerals to picloram adsorption is considered negligible.

In an attempt to relate the soil characteristics affecting adsorption of picloram, correlation coefficients were determined
Figure 3. Effect of organic matter content of three soils and the removal of organic matter on adsorption of picloram.
(Table 6). Adsorption of picloram was most closely related to organic matter content, pH and sesquioxides (Fe and Al oxides).

Table 6. Correlation coefficients (r) between soil properties and adsorption of picloram by five soils

<table>
<thead>
<tr>
<th>Soil property</th>
<th>Correlation coefficientb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic mattera</td>
<td>0.99</td>
</tr>
<tr>
<td>Cation exchange capacity</td>
<td>0.84</td>
</tr>
<tr>
<td>Sand</td>
<td>0.64</td>
</tr>
<tr>
<td>Silt</td>
<td>-0.10</td>
</tr>
<tr>
<td>Clay</td>
<td>-0.25</td>
</tr>
<tr>
<td>Sesquioxides (Fe2O3,Al2O3)</td>
<td>+0.96</td>
</tr>
<tr>
<td>pH</td>
<td>-0.98</td>
</tr>
<tr>
<td>Reduction in organic mattera</td>
<td>0.98</td>
</tr>
</tbody>
</table>

a Chance and Aiken soils excluded

b A correlation coefficient of 0.80 at 5 percent level and 0.90 at 1 percent level is required for significance

Correlation between adsorption and cation exchange capacity was significant at the 0.05 level. Correlation was very poor with clay and silt content. Cation exchange capacity and organic matter are closely associated with each other (Table 7). The pH was negatively correlated with adsorption.

The positive correlation of organic matter with sorption is consistent with the results of Sheets, Crafts, and Drever (1962), who reported that organic matter was the best single predictor of
Table 7. Correlation coefficients\(^a\) (r) of various soil properties among themselves

<table>
<thead>
<tr>
<th>Soil property</th>
<th>CEC</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>R_{2O3}^b</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>O.M.</td>
<td>.81</td>
<td>.52</td>
<td>.1</td>
<td>-.36</td>
<td>-.40</td>
<td>-.48</td>
</tr>
<tr>
<td>C.E.C.</td>
<td>.45</td>
<td>.15</td>
<td>-.34</td>
<td>-.54</td>
<td>-.32</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td></td>
<td>-.49</td>
<td>-.38</td>
<td>.12</td>
<td>-.74</td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td></td>
<td></td>
<td>-.59</td>
<td>-.90</td>
<td>.83</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td></td>
<td></td>
<td></td>
<td>.74</td>
<td>-.30</td>
<td></td>
</tr>
<tr>
<td>Sesquioxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-.56</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) A correlation coefficient of 0.81 at .05 level and 0.92 at .01 level is required for significance.

\(^b\) Sesquioxides

Herbicide sorption among the four factors of organic matter, clay content, soil pH, and cation exchange capacity.

The role of hydrated Fe and Al oxides as sorption agents was illustrated by the work of Hamaker, Goring, and Younson (1966), who found that organic matter and hydrated metal oxides are principally responsible for the adsorption of picloram on the 10 soils they studied. They found the percentage of sorption of \(^{14}\)C-labelled picloram to be 21 percent and 34 percent in one hour from 1 ppm solution on Fe\(_2O_3\) (amorphous) and Fe\(_2O_3\) (partially crystalline), respectively.

In this study, the linear regression analysis between the sesquioxide (Fe\(_2O_3 + Al_2O_3\)) content of the five soils and adsorption, had a correlation coefficient of + 0.96 (Table 6).
Desorption

Table 8 shows the release of adsorbed picloram from three soils. Leaching was with 10 ml portions of deionized water (two elutions).

Table 8. Effect of soil type and organic matter on the release of picloram with 10 ml extractions of deionized water at 25°C

<table>
<thead>
<tr>
<th>Soil</th>
<th>Organic matter</th>
<th>Picloram initially adsorbed</th>
<th>Extraction number</th>
<th>Picloram desorbed</th>
<th>% initially adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>µgms/kgm soil</td>
<td>µgms/kgm soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Millville</td>
<td>1.9</td>
<td>108</td>
<td>1</td>
<td>69.3</td>
<td>64.2</td>
</tr>
<tr>
<td>silt loam</td>
<td></td>
<td></td>
<td>2</td>
<td>8.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Total desorbed</td>
<td></td>
<td></td>
<td></td>
<td>77.5</td>
<td>71.8</td>
</tr>
<tr>
<td>Nibley</td>
<td>2.53</td>
<td>236</td>
<td>1</td>
<td>63.4</td>
<td>26.9</td>
</tr>
<tr>
<td>silty clay</td>
<td></td>
<td></td>
<td>2</td>
<td>58.9</td>
<td>25.0</td>
</tr>
<tr>
<td>loam</td>
<td></td>
<td></td>
<td></td>
<td>122.3</td>
<td>51.9</td>
</tr>
<tr>
<td>Total desorbed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Providence</td>
<td>3.59</td>
<td>371</td>
<td>1</td>
<td>96.0</td>
<td>25.9</td>
</tr>
<tr>
<td>silt loam</td>
<td></td>
<td></td>
<td>2</td>
<td>56.0</td>
<td>15.1</td>
</tr>
<tr>
<td>Total desorbed</td>
<td></td>
<td></td>
<td></td>
<td>152.0</td>
<td>41.0</td>
</tr>
</tbody>
</table>

^average standard deviation = 0.49

The amount of picloram released varied directly with organic matter content. This demonstrates the importance of organic matter in soils on the retention or release of picloram. The total picloram eluted with two extractions with deionized water amounted to 41 to 72 percent of
the initially sorbed picloram. Picloram is not easily removed in successive extractions of water (5.6 and 2.8 percent in the third and fourth extractions, respectively) as shown in Table 9 for Providence soil.

**Effect of Herbicide Concentration**

**Adsorption**

The amount of picloram adsorbed at various herbicide concentrations by Providence silt loam and Chance loam soils is shown in Figure 4 and Table 10. Table 10 shows adsorption values for Aiken soils at two herbicide concentrations. As picloram concentrations in solution were increased from 50 ppb to 10 ppm, the amount adsorbed increased (Table 10).

These data were evaluated in more theoretical terms, using the empirical Freundlich isotherm described earlier (see Equations [1] and [2]).

As shown in Figure 5, the sorption data follow the Freundlich equation (correlation coefficient 0.999). The values of "b" and "n" are the \( y \) intercept and slope, respectively, and were found to be 538.3 \( \mu \text{gmg/kgm} \) and 0.972, respectively for Providence silt loam and for Chance loam soil it was 2009 \( \mu \text{gmg/kgm} \) and 0.837, respectively. The \( n \) value indicates the degree of linearity of the adsorption isotherm, with a value of 1 being linear. The value of "b" can be interpreted to be equal to the concentration of picloram adsorbed by the adsorbent in equilibrium with a unit concentration of the herbicide (in this case 1 ppm).
Table 9. Release of picloram from Providence silt loam soil with four successive 10 ml extractions of deionized water at 25 C. The soil contained 371 μgms picloram/kgm soil initially

<table>
<thead>
<tr>
<th>Extraction number</th>
<th>Herbicide released Replicate</th>
<th>Average</th>
<th>Herbicide released Replicate</th>
<th>Average</th>
<th>Average pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>88.2</td>
<td>96.4</td>
<td>84.0</td>
<td>89.5</td>
<td>21.7</td>
</tr>
<tr>
<td>2</td>
<td>99.1</td>
<td>--</td>
<td>44.0</td>
<td>71.6</td>
<td>26.0</td>
</tr>
<tr>
<td>3</td>
<td>22.0</td>
<td>19.6</td>
<td>20.0</td>
<td>20.5</td>
<td>5.4</td>
</tr>
<tr>
<td>4</td>
<td>14.4</td>
<td>--</td>
<td>7.0</td>
<td>10.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Total desorbed</td>
<td>192.3</td>
<td></td>
<td></td>
<td></td>
<td>52.7</td>
</tr>
</tbody>
</table>

^a^ samples lost during extraction
Figure 4. Effect of concentration of picloram in solution on its adsorption by two soils.
Table 10. Effect of picloram concentration on its adsorption by Providence, Chance, and Aiken soils at 25°C

<table>
<thead>
<tr>
<th>Soil</th>
<th>Initial concentration ppm</th>
<th>Equilibrium concentration ppm</th>
<th>Amount adsorbed μgms/kgm soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Providence</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>silt loam</td>
<td>.05</td>
<td>.032</td>
<td>18.6</td>
</tr>
<tr>
<td></td>
<td>.10</td>
<td>.064</td>
<td>36.3</td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>.325</td>
<td>175.0</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>.652</td>
<td>347.7</td>
</tr>
<tr>
<td></td>
<td>2.015</td>
<td>1.168</td>
<td>863.0</td>
</tr>
<tr>
<td></td>
<td>4.033</td>
<td>2.524</td>
<td>1515.0</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>5.184</td>
<td>2790.0</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>6.436</td>
<td>3611.0</td>
</tr>
<tr>
<td>Chance loam</td>
<td>0.5</td>
<td>.209</td>
<td>582</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>.479</td>
<td>1042</td>
</tr>
<tr>
<td></td>
<td>2.016</td>
<td>1.0502</td>
<td>1930</td>
</tr>
<tr>
<td></td>
<td>4.033</td>
<td>2.13</td>
<td>3806</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>4.435</td>
<td>7130</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>5.6134</td>
<td>8773</td>
</tr>
<tr>
<td>Aiken clay</td>
<td>0.5</td>
<td>0.433</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.867</td>
<td>268</td>
</tr>
</tbody>
</table>
Figure 5. Freundlich plot for adsorption of picloram by Providence and Chance loam soils at 25°C.
Conformity to Tempkin, B.E.T., and Langmuir plots, as described earlier, was also tested. The B.E.T. adsorption isotherm describes the multi-layer adsorption. The Tempkin adsorption isotherm was derived to test for linear distribution of energy sites. No conformity to any of the three models was found.

Desorption

To study the release of picloram with additional elutions of water, 1 ppm solutions of picloram were allowed to equilibrate with soil at 25°C. The bulk solution, which was in equilibrium with the adsorbed picloram, was diluted with deionized water to create different concentration gradients. The system was then allowed to reach equilibrium. The results are presented in Table 11 for the Providence silt loam soil. Dilutions of equilibrated bulk solution from 1.5 to 3.22 were used.

Table 11. Effect of increasing dilution with deionized water on the release of Picloram from Providence silt loam soil at 25°C

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Picloram desorbed (µgms/kgm soil)</th>
<th>Equilibrium concentration (ppm)</th>
<th>Picloram remaining adsorbed after desorption (µgms/kgm soil)</th>
<th>Theoretical amount expected to be adsorbed (µgms/kgm soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>96.4</td>
<td>0.480</td>
<td>262</td>
<td>260</td>
</tr>
<tr>
<td>2.11</td>
<td>142.5</td>
<td>0.390</td>
<td>229</td>
<td>217</td>
</tr>
<tr>
<td>3.22</td>
<td>193.4</td>
<td>0.271</td>
<td>177</td>
<td>150</td>
</tr>
</tbody>
</table>

a extrapolated from the adsorption isotherm (see Figure 4)
The data show the amount of picloram remaining after the first wash, the equilibrium concentration of the bulk solution and the theoretical amount of picloram expected to be adsorbed at the three equilibrium concentrations as extrapolated from the adsorption isotherm (Figure 4). The reversibility of adsorption at lower dilution (1.5) is evident. However, at higher dilutions, the adsorption is not completely reversible. The effect of the soil:solution ratio was studied by an experiment (Table 12) in which soil:solution ratios ranging from 1:5 to 1:0.5 were used. It was found that soil:solution ratios between 1:5 and 1:2.5 did not have any measurable influence on adsorption per unit weight of soil. In this study, the maximum dilution obtained was 1:2.9.

Table 12. Effect of soil:solution ratio on the equilibrium adsorption of picloram by Providence silt loam soil from aqueous solutions of 1 ppm concentration

<table>
<thead>
<tr>
<th>Soil:solution ratio</th>
<th>Amount of picloram adsorbed µgm/kgm soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5.0</td>
<td>345</td>
</tr>
<tr>
<td>1:2.5</td>
<td>338</td>
</tr>
<tr>
<td>1:1.66</td>
<td>316</td>
</tr>
<tr>
<td>1:1.25</td>
<td>350</td>
</tr>
<tr>
<td>1:1.00</td>
<td>342</td>
</tr>
<tr>
<td>1:0.66</td>
<td>307</td>
</tr>
<tr>
<td>1:0.50</td>
<td>268</td>
</tr>
</tbody>
</table>
Effect of Temperature

Adsorption

The effect of temperature (17.7, 25.0, 28.2, and 34.7 °C) on the adsorption of picloram by the Chance loam, Providence silt loam, and Aiken clay soils is given in Table 13. An increase in temperature from 17.7 to 25.0 °C resulted in an increase in adsorption. A decrease in adsorption occurred as the temperature increased to 28.2 °C and 34.7 °C. This suggested that two mechanisms are operative in adsorption.

Table 13. Effect of temperature on the equilibrium adsorption of picloram by Providence silt loam, Chance loam, and Aiken clay soils from 1.0 ppm concentration

<table>
<thead>
<tr>
<th>Soil</th>
<th>Temperature °C</th>
<th>Adsorption µgm/kgm soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Providence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>silt loam</td>
<td>17.7</td>
<td>339</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>371</td>
</tr>
<tr>
<td></td>
<td>28.2</td>
<td>412</td>
</tr>
<tr>
<td></td>
<td>34.7</td>
<td>313</td>
</tr>
<tr>
<td>Chance loam</td>
<td>17.7</td>
<td>968</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>1042</td>
</tr>
<tr>
<td></td>
<td>28.2</td>
<td>1020</td>
</tr>
<tr>
<td></td>
<td>34.7</td>
<td>1006</td>
</tr>
<tr>
<td>Aiken clay</td>
<td>17.7</td>
<td>268</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>34.7</td>
<td>254</td>
</tr>
</tbody>
</table>
Haque et al. (1968) found little effect of temperature on adsorption of 2,4-D on clays at 20, 25, and 40 °C, whereas Talbert and Fletchall (1965) found a decrease in adsorption with increased temperatures for simazine-14C and atrazine-14C by Marshall silty clay loam.

Apparently the two mechanisms of adsorption of picloram, which have opposite temperature coefficients, increase or decrease adsorption depending on temperature. In earlier studies (Hamaker, Goring, and Youngston, 1966) diffusion of picloram was found to be a dominant factor in adsorption. Diffusion is an endothermic process, and is enhanced by increases in temperature. An apparent decrease, after an initial increase in adsorption suggests physical adsorption, or a weak bonding, at the pH levels of these soils.

**Desorption**

Desorption of picloram from Providence silt loam soil is given in Table 4 for the three temperatures 25.0, 28.2, and 31.5 °C. Increasing the temperature helps to remove the adsorbed picloram for the temperatures studied. This agrees with the results obtained in adsorption studies (Table 13) where temperatures above 25 °C decreased adsorption for both Providence and Chance soils.

More studies on adsorption near 0 °C would have better clarified the exothermic or endothermic nature of the adsorption process. This study has shown, however, that picloram retention by soils is affected by temperature variations even within the narrow range (17 °C to 34.7 °C) investigated.
Effect of pH on Adsorption

The relationship between the adsorption of picloram and the pH of the soil suspension is given in Table 14 and Figures 6 and 7 for Providence silt loam and Chance loam soils; pH was adjusted by adding 0.1N KOH or 0.1N HCl to the soils. There was a sharp increase in adsorption as pH decreased. In Table 14 and Figure 6 the percentage of dissolved free acid, calculated using a pKa of 4.1 for the carboxylic group is shown. Adsorption appears to increase as the unionized acid form increases with decreasing pH. Hamaker, Goring, and Youngson (1966) have recently shown a sharp increase in adsorption of picloram as the soil slurry pH is lowered from 6.5 to 4.0.

The adsorption of picloram was influenced by the pH of the soil suspension. The following regression equations shown this relationship for Chance loam and Providence silt loam, respectively (Figure 6).

\[
\log_{10} (\text{ugm adsorbed/kgm soil}) = 3.654 - 0.107 \text{ pH} \quad [19]
\]

and

\[
\log_{10} (\text{ugm adsorbed/kgm soil}) = 3.460 - 0.125 \text{ pH} \quad [20]
\]

The correlation coefficients (0.993 for Chance loam soil and 0.985 for Providence silt loam soil) indicate that adsorption of picloram by soil is governed, to a large extent, by the hydrogen-ion activity relationships which occur between the solution and solid phase of soil.

Although adsorption of picloram is affected by solution pH, it is evident that ionization of picloram is not the only factor. Even
Table 14. Effect of pH on the adsorption of picloram by Chance loam and Providence silt loam soils at 25°C (initial picloram concentration 1 ppm)

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Picloram adsorbed</th>
<th>Picloram undissociated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>µgm/kgm soil</td>
<td>%</td>
</tr>
<tr>
<td>Chance loam</td>
<td>3.40</td>
<td>1832</td>
<td>83.4</td>
</tr>
<tr>
<td></td>
<td>4.35</td>
<td>1584</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>5.15</td>
<td>1278</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>5.75</td>
<td>1132</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>6.20</td>
<td>962</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>6.55</td>
<td>850</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>6.90</td>
<td>868</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>7.05</td>
<td>780</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>7.25</td>
<td>764</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>7.55</td>
<td>730</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>612</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>8.50</td>
<td>522</td>
<td>0.004</td>
</tr>
<tr>
<td>Providence silt loam</td>
<td>3.60</td>
<td>916</td>
<td>76.0</td>
</tr>
<tr>
<td></td>
<td>4.50</td>
<td>806</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>697</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>5.95</td>
<td>594</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>7.10</td>
<td>251</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>7.45</td>
<td>297</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>303</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>8.60</td>
<td>251</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>9.20</td>
<td>200</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

*a undissociated picloram corresponds to the moiety:
Figure 6. Adsorption of picloram by Providence silt loam and Chance loam soils, and per cent of picloram undissociated in response to changes in soil pH.
Figure 7. Logarithm of picloram adsorption by Chance loam and Providence silt loam soils as influenced by the pH of soil suspension.
above pH's at which picloram was essentially ionized (Table 14 and Figure 6), there was a continued decrease in adsorption with increases in pH. In a later study it will be shown that the addition of $K^+$ ions should enhance adsorption, rather than decrease it, as was obtained here. However, the added KOH in the above experiment resulted in a pH change which apparently has greater influence than $K^+$ alone.

Bailey, White, and Rothberg (1968) have suggested hydrogen bonding to clay minerals as a possible mechanism for picloram adsorption. It appears that the proton involved in hydrogen bonding at lower pH values came from the carboxylic group of picloram. A sharp increase in adsorption with decreased pH parallels the sharp increase in unionized species of picloram (Figure 6). Whether or not protons associated with soil constituents play any part in unclear. However, at pH values where the adsorbate is completely ionized or completely unionized, adsorption changes with pH. Picloram is completely unionized below pH 2.1; and completely ionized above pH 6.1. Measurements were not made below pH 3.4 in either of the soils. At lower pH values, other complications occur because of solubilization of clay lattice Fe and Al. However, adsorption of picloram above pH 6.1, when the picloram is 100 percent in ionic form, can be considered.

A number of adsorption mechanisms were discussed earlier for the bonding of picloram at pH values higher than 6.1 ($pK_a + 2$). The hydrogen bonding through the amino group, through the carboxylic acid group, or bridging through metal cations (by coordination with water), are likely to be influenced by addition of $OH^-$. Bailey, White, and Rothberg (1968) concluded that surface acidity of montmorillonite is
3 to 4 pH units lower than the pH of the bulk solution. It is conceivable, then, that with the addition of more hydroxyls, protons from weak hydroxyls on clay mineral edges will continue to react. Consequently, any bonding of picloram anions through these protons will be reduced at pH values that seem to be above the pH range affecting picloram ionization. The replaced protons are incapable of reacting with the carboxylic group of picloram in solution due to its acidity (pKa = 4.1).

The same applies to replacement of protons from -NH$_2$ and -OH groups of organic matter and -OH groups of hydroxy oxides in the soil.

The above seems to be the most feasible explanation for the reduced adsorption at pH values above $\approx 6.1$. However, the increased adsorption at pH below 6 can have an explanation other than the result of increased hydrogen bonding through carboxyl hydrogen. At pH values below $\approx 5.0$, there exists a possibility of releasing lattice Fe$^{+3}$ and Al$^{+3}$ due to hydronium (H$_3$O$^+$) ions action on the clay lattice. The released Fe$^{+3}$ and Al$^{+3}$ ions are capable of complex formation with picloram. Increased adsorption can occur as a result of this complex formation.

In summary, the adsorption of picloram by Providence and Chance loam soils is negatively but strongly correlated with pH of the soil suspension. The mechanism of adsorption at pH values lower than about 6 ($\text{pH} < \text{pKa} + 2$) is probably by hydrogen bonding. The hydrogen atom on the carboxylic group would be the most likely part of picloram to be involved in such a bond. Another possibility at much lower pH
values \((pH < 5)\) is the complexation with \(Fe^{3+}\) and \(Al^{3+}\), which would be released as a result of hydronium ion attack on the clay lattice. The adsorption mechanism at higher pH values \((pH > pKa + 2)\) appears to be hydrogen bonding through carbonyl group of picloram to the weakly acidic protons on the various functional groups on the organic matter and clays of the soil. Bailey, White, and Rothberg (1968) referred to physical adsorption as another possible mechanism at \(pH > pKa + 2\). The above investigators also indicated the possibility of metal-cation-picloram complex directly, or through coordination with water, at \(pH > pKa + 2\).

**Effect of Inorganic Salts on Adsorption of Picloram**

In preliminary studies on the adsorption of picloram by soils, small amounts of inorganic salts increased picloram adsorption considerably. Due to differences in the water quality used for irrigation, differences in salt content of soils and water, and variations in salt concentrations as the moisture is depleted from soils, the effect of these inorganic salts on picloram adsorption is of interest. No literature, in this respect, has appeared concerning picloram.

**Influence of various salts on picloram adsorption by Providence silt loam soil**

Picloram adsorption from 1.0 ppm initial picloram concentration by Providence silt loam soil is given in Table 15. The salts investigated were \(BaCl_2\), \(KCl\), \(K_2SO_4\), \(CaCl_2\), and \(MgCl_2\). Concentration of each electrolyte was 5 me/l of solution, except \(BaCl_2\) and \(KCl\) also had concentrations up to 666.0 me/l and 130.43 me/l, respectively.
Table 15. Influence of various salts on the adsorption of picloram by Providence silt loam soil. Initial picloram concentration was 1.0 ppm

<table>
<thead>
<tr>
<th>Salt</th>
<th>Salt concentration me/l</th>
<th>Equilibrium pH</th>
<th>Adsorption μgms/kgm soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCl₂</td>
<td>0</td>
<td>7.10</td>
<td>356</td>
</tr>
<tr>
<td></td>
<td>1.16</td>
<td>7.40</td>
<td>356</td>
</tr>
<tr>
<td></td>
<td>2.84</td>
<td>7.30</td>
<td>402</td>
</tr>
<tr>
<td></td>
<td>5.53</td>
<td>7.15</td>
<td>442</td>
</tr>
<tr>
<td></td>
<td>62.10</td>
<td>6.41</td>
<td>643</td>
</tr>
<tr>
<td></td>
<td>666.00</td>
<td>5.90</td>
<td>752</td>
</tr>
<tr>
<td>KCl</td>
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<td>7.05</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>6.95</td>
<td>388</td>
</tr>
<tr>
<td></td>
<td>74.10</td>
<td>6.66</td>
<td>531</td>
</tr>
<tr>
<td></td>
<td>130.43</td>
<td>6.45</td>
<td>555</td>
</tr>
<tr>
<td>K₂SO₄</td>
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<td>7.05</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>6.94</td>
<td>344</td>
</tr>
<tr>
<td>CaCl₂</td>
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<td>7.05</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>6.79</td>
<td>411</td>
</tr>
<tr>
<td>MgCl₂</td>
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<td>7.05</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>6.81</td>
<td>387</td>
</tr>
</tbody>
</table>

There was, generally, a drop in soil suspension pH with the addition of salts. However, the enhanced picloram adsorption could not be accounted for by the theoretical increase in molecular picloram as a result of drop in pH. Miller (1972)¹ has observed significant adsorption changes as a direct effect of pH change occurring within

¹Miller, R. W. 1972. Personal communication, Professor of Soils, Utah State University, Logan, Utah.
± 3 pH units of the pKa value of the various phenols or 2,4-D sorbed to an organo-clay. The pH changes below pH 7 would be within this range since the pKa of picloram is about 4.1. Perhaps the apparent salt effect is largely a pH effect.

The drop in pH was expected on the basis of replacement of exchangeable H⁺ from the exchange complex of soil by the metallic cations. However, at higher BaCl₂ and KCl concentrations, replacement of protons from the weak hydroxyls of exposed layers of clay minerals, hydroxy oxides, and organic matter -NH₂ and -OH groups is also a possibility (Buckman and Brady, 1967). An unexplainable slight increase in pH was obtained with the addition of small amounts of BaCl₂. Increased salt concentrations induced some increases in picloram adsorption independent of changes in pH; therefore, the pH effect is not likely to be the sole cause of increased adsorption.

Another alternative was considered. The disappearance of picloram from solution with the addition of inorganic electrolytes may have been a result of herbicide precipitation rather than soil adsorption. Such precipitation commonly occurs where salts are added to an aqueous solution containing neutral organic molecules (Abernathy and Davidson, 1971). Picloram precipitation was investigated by centrifuging solutions of picloram-BaCl₂, and picloram-CaCl₂ concentrations from 5.0 to 500 me/l. Picloram concentrations before and after centrifuging were not significantly different, indicating that precipitation did not occur.

Comparison of picloram adsorption (Table 15) at 5.0 me/l of KCl, CaCl₂, and MgCl₂ revealed that divalent cations, generally, were more
effective in increasing adsorption on Providence soil than are monovalent cations. Although the replaced protons did not react with picloram anion in solution to form the molecular form at the pH's obtained at 5.0 me/l concentrations, the divalent ions did often result in more acid pH than did monovalent ions. The increase in picloram adsorption at higher salt concentrations could not be accounted for by theoretical increase in molecular picloram, but the metal cations may serve as a bond between the exchange site and the herbicide. This was suggested by Mortland (1970) for organic molecules and clay minerals, and by Hance (1971) for linuron adsorbed to several adsorbents saturated with metal cations. Hance (1971) concluded that atrazine did not complex this way.

The carboxyl of picloram is the most likely group to be involved in complex formation with the metal cations. However, Providence soil is 74 percent base-saturated in the natural state, and about 85 percent of these bases are the divalent cations, Ca and Mg (Table 16). Therefore, the continued increase in picloram adsorption with increasing \( \text{BaCl}_2 \) and KCl concentrations cannot be the result of picloram complexing with additional \( \text{Ba}^{+2} \) (or \( \text{K}^+ \)) ions adsorbed on the soil. The picloram adsorption occurring at 130.43 me/l KCl and 666.0 me/l \( \text{BaCl}_2 \) concentrations (Table 15) was much higher than expected on this basis.

It is conceivable that the picloram anion in solution will undergo the following reactions with added metal cations in solution:

\[
M^{+2} + P^- \xrightleftharpoons[I]{} [MP]^+ \xrightleftharpoons[II]{} [MP_2]^0
\]  

[21]
\[
M^+ + P^- \rightarrow [MP]^\circ \tag{22}
\]

\[
[MP_2]^\circ + M^{+2} + P^- \rightarrow [MP]^+ + [MP_2]^\circ \tag{23}
\]

where \( P^- \) is picloram anion, \( M \) is a metal cation, and I, II, and III refer to species numbers. The most likely constituent of picloram to be involved in the formation of species I and II would be the carboxyl group (Bailey, White, and Rothberg, 1968).

Table 16. Cationic composition of the exchange complex of various soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Cation exchange capacity</th>
<th>Base(^a) saturation</th>
<th>Ca + Mg % of exchangeable bases(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nibley silty clay loam</td>
<td>25.7</td>
<td>( \approx 100 )</td>
<td>91.2</td>
</tr>
<tr>
<td>Millville silt loam</td>
<td>15.6</td>
<td>( \approx 100 )</td>
<td>83.7</td>
</tr>
<tr>
<td>Chance loam</td>
<td>37.0</td>
<td>95.7</td>
<td>87.6</td>
</tr>
<tr>
<td>Aiken clay</td>
<td>16.3</td>
<td>49.9</td>
<td>87.1</td>
</tr>
<tr>
<td>Providence silt loam</td>
<td>30.5</td>
<td>74.0</td>
<td>84.8</td>
</tr>
</tbody>
</table>

\(^a\) bases denote Na + K + Ca + Mg

The species \([MP]^+\) may be involved in cation exchange with inorganic cations on the exchange complex of the soil. This possibility was suggested by Dekking (1964) for the adsorption of polystyrene by kaolinite and montmorillonite. A quantitative estimate of the extent
of \([MP]^+\) as a function of \(M^{+2}\) concentration in solution is not available, although it would increase with increasing \(M^{+2}\) ions.

A number of other possibilities exist for the increased picloram adsorption with enhanced salt concentrations. Salts would change the thickness of the double layer of ions, which could result in increased metal ion-picloram complexation. Hemi-salt formation, which occurs when the amount of adsorbed base on a surface exceeds the number of protons available for cation formation, is also possible. According to Mortland (1970), in hemi-salt formation, the already protonated molecule at the surface of clay retains its proton against attraction by the non-protonated molecule, and a cation of \([B_2 - H]^+\) type results. It is possible that additional salts contribute to \([B_2 - H]^+\) formation by making more base (picloram anions) available for bonding. The exact mechanism by which this occurs is not clear.

The increase in picloram adsorption with increasing monovalent cations (\(K^+\), for example, in Table 15) is unexplained. However, from Equation [22], the species \([MP]^0\), the result of monovalent cation and picloram anion interaction, is neutral. It is conceivable that a neutral species will have a greater tendency to adsorb by physical forces (Bailey, White, and Rothberg, 1968) than an anionic species, which will be repelled by the negative charges on the soil. McCall et al. (1972) found that picloram was adsorbed by cationic resin (H - form), non-ionic resin and anionic resin (Cl - form) to the extent of 2.3, 4.0, and 375 mgms/gm of oven dry resin, respectively. They concluded that picloram was adsorbed mainly in the anionic form by coulombic forces (electrostatic) and to a lesser degree by weak physical bonding (van der Waal's forces).
Effect of CaCl₂ in solution on picloram adsorption

Some properties of the four soils used are given in Table 1. Initial concentration of picloram was 0.5 ppm in all the cases.

Nibley silty clay loam soil. Figure 8 shows the amount of picloram adsorbed by Nibley silty clay loam soil as a function of CaCl₂ concentration in solution. The adsorption on Ca-saturated Nibley soil as affected by CaCl₂ concentrations in solution is also shown. The numbers near the data points denote equilibrium pH for natural and Ca-saturated soils, respectively.

Picloram adsorption is greatly increased by increasing CaCl₂ concentration in solution to 500 me/l. The extent of adsorption remains the same whether soil was Ca-saturated or not. Ca-saturation of the soil did not affect the suspension pH at any of the CaCl₂ concentrations. This was expected because the soil was 100 percent base-saturated in the natural state (Table 16).

The above results are mostly consistent with the theory of complex formation between picloram anions and metal ions on the exchange complex. Nibley soil is 100 percent base-saturated, as shown in Table 16 and the divalent cations, Ca + Mg, constitute about 91 percent of the total cations. If the mechanism of picloram adsorption to the soil surface site is by bonding through the metal cations, saturation of the soil with Ca⁺² ions (a divalent ion) should not alter adsorption characteristics of the soil.

However, increased picloram adsorption with increasing CaCl₂ in solution both in natural and Ca-saturated soil is more difficult to explain (Figure 8). In order to result in higher adsorption of
Figure 8. Effect of CaCl$_2$ on the adsorption of picloram by Nibley silty clay loam soil. ○ Natural soil. △ Ca-saturated soil. The numbers near the data points denote equilibrium pH for natural soil and Ca-saturated soil respectively.
picloram, the increase in $[\text{CaP}_2]^0$ or $[\text{CaP}]^+$ species in solution according to Equation [21] would need replacement (exchange) of adsorbed $\text{Ca}^{++}$ cations by $[\text{CaP}]^+$ species of picloram.

**Millville silt loam soil.** The behavior of this soil (Figure 9) is similar to the Nibley soil. At lower $\text{CaCl}_2$ concentrations (up to 50 me/1), picloram adsorption was the same for natural and Ca-saturated soils. Reduced adsorption by Ca-saturation of the soil at 500 me/1 $\text{CaCl}_2$ concentration was noted but unexplained.

Millville soil is ~ 100 percent base saturated (Table 16), and $\text{Ca} + \text{Mg}$ constitute 83.7 percent of the total exchangeable bases. Therefore, equal adsorption of picloram by natural and Ca-saturated Millville soil was expected.

The trends of adsorption by this soil are consistent with the hypothesis of cation exchange of picloram-calcium cation with adsorbed metal ions.

**Chance loam soil.** Data obtained for Chance loam soil and for Ca-saturated Chance loam soil are given in Figure 10 (Curves A and B, respectively). Increases in picloram adsorption with increasing $\text{CaCl}_2$ concentrations were exponential for both the natural and Ca-saturated soils. The drop in pH obtained in both cases, as $\text{CaCl}_2$ concentration increased, was significant. This drop in pH was probably due to the replacement of protons from the surface of natural soil by $\text{Ca}^{+2}$ ions. However, the pH declined considerably even with Ca-saturated Chance soil. This is largely unexplained although the soil was leached to remove excess salts; possibly the limited number of adsorbed protons from the leaching process are
Figure 9. Effect of CaCl₂ on the adsorption of picloram by Millville silt loam soil. O Natural soil △ Ca-saturated soil. The numbers near the data points denote equilibrium pH for natural and Ca-saturated soils, respectively.
Figure 10. Effect of CaCl₂ on the adsorption of picloram by Chance loam soil. O Natural soil
D Ca-saturated soil. The numbers near the data points denote equilibrium pH. Curve C
(△) represents adsorption on Chance loam soil adjusted for pH changes by CaCl₂.
displaced by Ca\(^{+2}\) ions in the herbicide experiment to produce a
decrease in pH. Chapman (1965) discusses this possibility in the
leaching of NH\(_4\)-saturated soils, to remove excess salt.

Curve C in Figure 10 is a theoretical curve of picloram adsorption
on Chance loam soil based on adjustment of pH changes at various CaCl\(_2\)
concentrations. This was done on the basis of Figure 7 and Equation
[19]. A comparison of Curves A, B, and C in Figure 10, suggests that
the increase in adsorption cannot be accounted for by a decrease in
soil pH alone.

The replacement of adsorbed cations (or Ca\(^{+2}\) in the case of Ca-
saturated soil) by picloram cations (CaP\(^{+}\)) is a likely possibility
for the increase in picloram adsorption by Chance loam soil with in-
creasing CaCl\(_2\) in solution. Chance soil was highly (95.7 percent)
base saturated, with Ca + Mg constituting 87.6 percent of the exchangea-
ble bases (Table 16).

**Aiken clay soil.** Aiken clay soils due to its different exchange
character, provided an alternate method of checking the mechanism by
which inorganic salts enhance picloram adsorption. The picloram
adsorption by Aiken clay soil as influenced by increasing CaCl\(_2\) in
solution is reported in Figure 11. After an initial increase in
adsorption (Curve A in Figure 11) at 5 me/1 of CaCl\(_2\) concentration,
there was a gradual drop in the adsorption curve with higher concen-
trations up to 500 me/1. The initial increase in adsorption parallels
the considerable drop in pH of the soil from 6.28 to 5.57. This
probably resulted in an increase in molecular picloram.

Further additions of CaCl\(_2\) produced a slight drop in pH in each
case and completely reversed the pattern of pH-adsorption observed
Figure 11. Effect of CaCl₂ on the adsorption of picloram by Aiken clay soil. (○) Natural soil, (△) Ca-saturated soil. The numbers near the data points denote equilibrium pH.
with the other soils. This demonstrates the importance of functional
groups on the soil, in addition to functional groups on the picloram
molecule, as discussed in the pH studies. Table 1 showed this soil
was entirely different from the three soils discussed above. The
most obvious difference was the predominance of hydroxy oxides
(sesquioxides) of Fe and Al— and almost a complete absence of organic
matter.

If the adsorption process in this soil was coulombic attraction
between picloram anions and positive charges on Fe$_2$O$_3$ and Al$_2$O$_3$, as
suggested by Hamaker, Goring, and Youngson (1966), then as the molecular
form of picloram predominates as a result of drop in pH, its attraction
for positive charges on the soil would be lessened compared to the
attraction of a picloram anion. This is consistent with the drop in
adsorption obtained with increases in CaCl$_2$. However, an initial
increase in adsorption with the addition of 5 me/l of CaCl$_2$ is unclear.

The initial rise in adsorption could be due to adsorption of
molecular picloram by clay minerals and organic matter in the soil
through bonding by the carboxyl hydrogen. It is apparent that cation
exchange capacity of the Aiken soil (16.3 me/100 gm, Table 1) is not
satisfied at this stage (addition of 5 me/l CaCl$_2$). Only about 3.27
percent of picloram, however, is in molecular form at pH 5.57 obtained
by adding 5 me/l CaCl$_2$.

Another possible cause of the initial rise in picloram adsorption
is the bonding of anionic picloram to adsorbed Ca$^{+2}$ ions through
metallic complexes as discussed above. Approximately 50 percent of the
exchange complex of Aiken soil is base saturated as shown in Table 16.
The presence of Ca\(^{+2}\) ions in solution allows their adsorption by the soil-complexing of picloram anions.

A decline of picloram adsorption by natural Aiken soil with further additions of CaCl\(_2\) shows that the proportion of molecular picloram increases due to the drop in pH. Molecular picloram is not capable of forming metal-complexes as shown by Curve B (Figure 11). Picloram adsorption by Ca-saturated Aiken soil is a function of CaCl\(_2\) concentration in solution. Ca-saturation of the soil more than doubled the picloram adsorption. This demonstrated the importance of exchangeable Ca\(^{+2}\) in complexing picloram at the exchange sites; the pH of the soil did not change significantly by adding CaCl\(_2\). Further decrease in picloram adsorption by both natural and Ca-saturated soils (Figure 11) with higher CaCl\(_2\) concentrations, is not understood. The reason for the decline in pH was discussed previously.

The hypothesis of [MP]\(^+\) exchange with adsorbed metal cations was tested by a quantitative measurement of the replaced calcium ions during picloram adsorption on Ca-saturated Millville silt loam, Chance loam, and Aiken clay soils. The results were not consistent with the hypothesis that the exchange of [MP]\(^+\) and the Ca\(^{+2}\) occurs. However, the disagreement was expected because according to Equation [21], all the added calcium does not result in the formation of [MP]\(^+\). It is suggested that a quantitative determination of [MP]\(^+\), as a function of Ca\(^{+2}\) in solution, would be helpful to test the theory.

In summary, the enhanced picloram adsorption by soils, as a result of an increase in inorganic electrolytes, is considered to be primarily through a mechanism involving exchange of [MP]\(^+\) cation with the exchangeable inorganic metal cations. The validity of this
mechanism was reinforced by the increase in adsorption obtained with a Ca-saturated soil by increasing \( \text{CaCl}_2 \) concentrations. However, one soil, Aiken, did not follow this pattern. The complete mechanism is more complex or there are various mechanisms possible as soil characteristics change.

**Column Studies**

Columns simulate the field conditions more closely than batch studies, and allow better control of variables. The influence of herbicide dosage level and Ca-saturation of the soil were studied in the two soils, Millville silt loam and Aiken clay. The columns were also used to test the predictability of a mathematical model based on the chromatographic theory of herbicide movement, a theory often used to predict behavior of herbicides in the soil.

**Millville silt loam soil**

Characteristic properties of this soil are given in Table 1 (see page 29).

**Back-diffusion effects.** Due to the small amount of sample used for column studies, the relative concentration \( \frac{C}{C_0} \) peaks in Figure 12, may not be the true herbicide peaks. To evaluate back-diffusion effects 1.0 ppm solutions of picloram were eluted through an 8.9 cm column of Millville soil. The volume of picloram solution added varied from 3.52 ml in one case to 5.0 ml in another. The elution curves, for nearly the same pore water flow velocity \( (v_0) \) are essentially the same for the two volumes as shown in Figure 12. A lower peak height for 3.52 ml sample would have indicated a back-diffusion effect. The left side (adsorption phase) of 5.0 ml sample
3.52 ml of 1.0 ppm picloram, \( \nu_0 = 4.0967 \text{ cm Hr}^{-1} \)

5.00 ml of 1.0 ppm picloram, \( \nu_0 = 4.4923 \text{ cm Hr}^{-1} \)

Figure 12. Relative concentration distribution \((C/Co)\) of picloram in Millville silt loam soil column as affected by amount of picloram solution added on top of the soil column.
curve is shifted to the left of 3.52 ml sample because of slightly higher pore water flow velocity of the 5.0 ml sample. The higher velocity is also responsible for the earlier appearance of picloram in the effluent of 5.0 ml sample.

**Effect of application rate of picloram.** The distribution of picloram eluted from 8.9 cm column of Millville silt loam soil at two concentrations of picloram is shown in Figure 13. The two curves are essentially identical, except for a slightly higher peak and slightly higher C/Co points on the desorption side of the elution curve, for the 1.0 lb/A rate. The slightly lower flow velocity (vo) for the 1.0 lb/A dosage resulted in a higher peak height than expected compared to the lower dosage. The higher peak demonstrates that the adsorption isotherm tends to flatten as the concentration of herbicide is increased. Although essentially a linear isotherm was obtained (Figure 4) for the adsorption of picloram, it is expected that the curve in Figure 4 would flatten as we approached the adsorption-capacity of the soil. The tendency for less adsorption would result in higher peaks as observed in Figure 13.

The adsorption isotherm of picloram on Millville silt loam soil is essentially linear at room temperature from 1.0 ppm (0.1 lb/A) to 10.0 ppm (1.0 lb/A) picloram concentrations.

The appearance of picloram in the effluent (at 0.5 pore volume) much before one pore volume of liquid at both concentrations of picloram indicates molecular diffusion is significant during picloram movement in this soil. One limitation to mathematical prediction of solute movement in porous media, is the inability to adequately characterize
Figure 13. Effect of two rates of picloram application on the relative concentration distribution (C/Co) of picloram in Millville silt loam soil column.
diffusion. The dispersion coefficient, $D_0$, derived from Equation [8] described above is a combination of mixing by diffusion, $D_1$, and hydrodynamic dispersion, $D_2$:

$$D_0 = D_1 + D_2$$  \[24\]

$D_2$ is linearly related to pore water velocity, $v_o$ (Erick, Erh, and Krupp, 1966). Nielson and Bigger (1963) have reported that $D_2$ increases as $v_o$ decreases; therefore, the diffusion effects noted in this experiment may be related to the $v_o$'s used in these studies.

Effect of calcium saturation of the soil. In Figure 14, the movement of 0.1 lb/A dosage picloram as related to calcium saturation of Millville silt loam is given. Calcium saturation of the 8.9 cm column of soil did not appreciably affect the amount of adsorption as shown by the peak heights of the curves. The slightly lower peak for the Ca-saturated soil is consistent with a lower flow velocity of water (0.5882 cm hr$^{-1}$) for this soil. This is consistent with results from batch studies (Figure 9) showing that Ca-saturation did not appreciably affect picloram adsorption by this soil.

The shift of the desorption side of the curve for Ca-saturated soil to the left is probably due to picloram being held more tightly on the calcium saturated soil as discussed previously. Three pore volumes ($V_o$'s) were required to elute picloram from each of the two columns. The arrival of picloram in the effluent before one pore volume is probably due to diffusion of the herbicide within the column.
Figure 14. Effect of Ca-saturation on the relative concentration distribution ($C/Co$) of picloram in Millville silt loam soil column.
Aiken clay soil

Some properties of the Aiken clay soil are listed in Table 1. Movement of picloram in a soil column (12.3 cm long) was studied as related to herbicide concentration and calcium saturation of the soil. Applicability of Equation [14] to picloram movement was also tested.

Effect of application rate of picloram. The distribution curve for 1.0 lb/A dosage is shifted slightly to the right of 0.10 lb/A curve (Figure 15), indicating greater soil adsorption at the higher concentration. The tendency of greater adsorption of the higher dosages is also evident from the later appearance of picloram in the effluent.

Both dosages of picloram started to appear in the effluent of the Aiken soil after about one pore volume of liquid had passed through the column, and all picloram was eluted after 2.25 to 2.5 pore volumes had passed.

Calcium saturation of the Aiken soil increased the herbicide adsorption capacity almost two-fold. The picloram did not appear in the effluent until about 2.25 pore volumes had passed through the salt saturated soil even when the flow velocities were nearly equal. About four pore volumes of displacing liquid were required to elute all of the herbicide. This is consistent with observations from batch adsorption studies with Ca-saturated Aiken soil.

Test of mathematical model for picloram movement in natural and Ca-saturated Millville and Aiken soils

The model of Davidson, Riek, and Santelmann (1968) was used to predict picloram movement in two soils. The choice of soils was
Figure 15. Relative concentration distribution of picloram in Aiken clay soil, (1) as a function of two application rates (2) as affected by Ca-saturation of the soil.
arbitrary, dictated by their availability. They did, however, represent soils of diverse properties in organic matter, clay and sesquioxides contents; properties found in batch studies to be important in picloram adsorption.

**Millville silt loam soil.** Some properties of this soil are listed in Table 1.

The relative distribution concentration \((C/Cl)\) as a function of pore volume \((V/Vo)\), i.e., the number of pore volumes passed through the column, is presented in Figure 16. The theoretical distribution curve (solid line) for the same pore water velocity \((Vo)\) and distribution coefficient \((K)\) calculated from batch studies (Table 5), is also given. The experimental curve is the same as the one given in Figure 13, with picloram applied at 0.10 lb/A and with \(Vo\) of 2.0183 cm hr\(^{-1}\).

The model (solid line) predicts quite well the concentration of picloram in the effluent at the start of the leaching, near the end of leaching and estimates peak height reasonably well. However, the model overestimates adsorption over most of the leaching process as evidenced by the shift of the theoretical curve to the right. The occurrence of peak height of the theoretical curve at a pore volume greater than was shown experimentally is also indicative of overestimation of adsorption by the model.

Some investigators (Davidson, Riek, and Santelmann, 1968; Cargill and Davidson, 1969; and Davidson and Chang, 1972) have encountered similar problems in predicting picloram to movement in soils. The term \(1 + \frac{\Delta K}{V}\) (Equation [15]) represents the apparent increase in pore volume due to the linear retention process. This term is called the 'retardation
Figure 16.Experimental (o) and calculated relative picloram concentration curve from Millville silt loam soil. Solid curve was calculated from retardation factor ($K'$) from batch studies and dashed curve from 'adjusted' $K'$ (See Table 17).
factor' by some and supposedly corrects the overestimation of adsorption. The dashed line in Figure 16 is the theoretical curve based on this lower retardation factor (Table 17). This model adequately describes the left hand (adsorption) side of the elution curve, as well as the position of the peak.

If a lack of equilibrium between the soil and flowing system was the reason for the failure of calculated curves (Figure 16) to describe the data, then the left hand portion of each concentration distribution curve obtained for different soil lengths would be separate and distinct from each other (Cargill and Davidson, 1969). The concentration distributions for 8.9 and 14.5 cm columns of Millville silt loam soil, at about the same \( V_0 \), are shown in Figure 17. The picloram concentration in the effluent for each of the two column lengths are similar in the left hand

<table>
<thead>
<tr>
<th>Soil</th>
<th>Average pore water velocity ( V_0 )</th>
<th>Retardation factor ( K' )</th>
<th>Adjusted retardation factor ( K'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millville silt loam</td>
<td>2.0183</td>
<td>1.2289</td>
<td>0.971</td>
</tr>
<tr>
<td>Ca-saturated Millville silt loam</td>
<td>0.5882</td>
<td>1.2365</td>
<td>0.696</td>
</tr>
<tr>
<td>Aiken clay</td>
<td>2.9601</td>
<td>1.6395</td>
<td>0.926</td>
</tr>
<tr>
<td>Ca-saturated Aiken clay</td>
<td>2.6595</td>
<td>3.4649</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 17. Relative concentration distribution \( C/C_0 \) of picloram in two columns of Millville silt loam soil of different length.
portions of the curve. The lower quantity of picloram recovered from
the larger column resulted from adsorption of picloram onto the addi­
tional soil; the amount of picloram added to each column was the same.
The data in Figure 17 show that an equilibrium does exist between the
liquid phase and the soil. In conclusion, the amount of picloram
adsorbed by Millville silt loam soil in a transient system was less
than that determined with the adsorption isotherm procedure (Figure 4).

Ca-saturated Millville silt loam soil. The dotted line in Figure
18 shows the influence of calcium saturation on the movement of picloram
through a Millville silt loam soil column. The solid line curve in
Figure 18 represents the theoretical curve based on Equation [14]. The
results obtained with the Ca-saturation are similar to those obtained
with natural Millville soil (Figure 16). Again, the model overestimated
adsorption as indicted by the shift of the theoretical curve to the
right of the experimental curve. A lower peak height and slightly more
tailing of the theoretical curve on the desorption side was evident.
The model was tested using the lower retardation factor and described
the data quite well (Figure 18). In order to obtain a fit to the
experimental data, the retardation factor used for Ca-saturated
Millville soil was 0.696 compared to the value of 0.971 used for
natural Millville soil (Table 17). Experimental data (Table 17) sug­
gests that the retardation factor for picloram for the Ca-saturated
Millville soil should not be very different from natural Millville
soil. This is another inadequacy of the model and will be discussed
after considering Aiken soil.
Figure 18. Experimental (o) and calculated relative picloram concentration distributions from Ca-saturated Millville silt loam soil. Solid curve was calculated from retardation factor ($K'$) from batch studies and dashed curve from 'adjusted' $K'$ (See Table 17).
Aiiken clay soil. Figure 19 gives the relative concentration distribution \((C/Co)\) of picloram in the effluent as a function of pore volumes \((V/Vo)\) of solution passing through columns of Aiiken clay and Ca-saturated Aiiken clay soil. The solid curve in Figure 19 is the theoretical curve for Aiiken clay soil based on Equation [14] and the retardation factor of picloram obtained from batch adsorption studies (Table 17). Inadequacy of the model to describe the experimental data is evident. The model overestimated adsorption on this soil as shown by the predicted late arrival of picloram in the effluent and the reduced peak. By selecting a lower retardation factor for this soil the model described the left hand portion of the curve but was inadequate in other respects.

Ca-saturated Aiiken clay soil. In Figure 19, the theoretical curve for Ca-saturated Aiiken soil (Curve 2) is shown based on the retardation factor of picloram calculated from the batch studies. The model poorly describes picloram movement in this soil. In this case, however, the model actually underestimated adsorption, as evidenced by shift of the theoretical curve to the left of the experimental points, rather than to the right of the experimental points as obtained in the earlier cases (Figures 16, 17, and 18).

From the discussion above, it appears that part of the failure of the model to describe the movement of picloram in soil columns is related to frequent overestimation of the picloram retardation factor based on the distribution coefficient calculated from batch studies. Although it was established, for the Millville soil (Figure 17), that picloram in liquid flowing through a column was in equilibrium with
Figure 19. Experimental (data points) and theoretical relative picloram concentration distributions from natural (○), and Ca-saturated (△) Aiken clay soil. Solid lines were calculated from retardation factor (K') from batch studies and dashed curve from 'adjusted' K' (See Table 17).
that in the soil, it seems that the distribution coefficient for picloram changes as the solution moves through the column. When the herbicide first enters the soil column at a concentration $C_0$, some of it is retained; the solution containing the remaining herbicide moves forward at a lower concentration to be retained and so on, until it travels the complete length of the soil column. This allows a large quantity of herbicide to be retained at the start, but a smaller amount at the effluent end. It offers a possible explanation for the early arrival of picloram observed compared to that calculated using the retention isotherm. A knowledge of the distribution of adsorbed phase with soil depth would assist in solving this problem.

Few reports were encountered which attempted to determine distributions of adsorbed herbicides at various depths in soil columns undergoing leaching with herbicides. Lai (1970) did this type of study with Ca→Mg, Na→Ca, and Na→Mg exchange in soil columns undergoing miscible displacement with considerable success. Such an approach may be fruitful in the study of herbicides.

A lower retardation factor helped to predict picloram movement only for the left hand portion of the distribution curve. However, the lower retardation factor applied to every effluent from the column. An approach that is suggested, similar to the one used by Lai (1970), would utilize a gradation of retardation factors as a function of soil depth.

Davidson, Riek, and Santelmann (1968) and Cargill and Davidson (1969) worked with fluometuron (a urea derivative herbicide) movement and Davidson and Chang (1972) worked with picloram movement in soil
columns and used the model to predict herbicide movement. They also reported a failure of the model to predict herbicide movement in soil columns and that the prediction was improved by assuming a lower retardation factor. They suggested that mixing processes in the column, a consequence of different size pores in the column, could be a complicating factor in prediction. The distribution of the solute as a function of soil depth should help account for differences as a result of differential adsorption with movement of solution through different size pores in the soil at different velocities (mixing).
SUMMARY AND CONCLUSIONS

Equilibrium studies on five soils, Chance loam, Providence silt loam, Nibley silty clay loam, Millville silt loam, and Aiken clay, with varying organic matter contents, were conducted to study the influence of various soil variables on the adsorption and desorption of picloram (4-amino-3,5,6-trichloropicolnic acid). Comparison of the adsorption of these soils before and after removal of organic matter (at 350°C) revealed that up to 91 percent of the adsorption could be accounted for by organic matter.

The five soils adsorbed from 10.8 to 58.2 percent of the added picloram in the picloram concentration range of 0.05 to 10 ppm. The adsorption was highly significantly correlated with organic matter \( (r = 0.991) \), pH \( (r = -0.98) \) and sesquioxides content \( (r = 0.96) \) of the soils. It was significantly correlated with C.E.C. \( (r = 0.84) \) at the 0.05 level. However, C.E.C. and organic matter were also correlated with each other. Correlation between adsorption and clay content of the soils was poor.

Kinetic studies on the five soils revealed that soils with higher amounts of organic matter take longer to reach equilibrium, (up to 120 hours). Studies of the effect of temperatures from 17.7°C to 34.7°C on picloram adsorption by three of the five soils revealed that the picloram adsorption within this temperature range is endothermic. A further increase in temperature to 34.7°C decreased picloram adsorption.
Adsorption by two of the soils, Chance loam and Providence silt loam, was linear at 25°C from 0.05 to 10 ppm initial picloram concentrations. The Freundlich isotherm was obeyed; no conformity to the Langmuir, B.E.T., or Tempkin adsorption models was observed.

In studies of the effect of induced pH on picloram adsorption by Chance loam and Providence silt loam soils, it was found that adsorption was inversely related to pH of soil suspension from pH 3.6 to pH 9.2. The regression equations relating the adsorption with pH were:

Chance loam soil:

\[
\log_{10} \left( \frac{\mu\text{gms adsorbed/kgm soil}}{\text{kgm soil}} \right) = 3.654 - 0.107 \cdot \text{pH} \\
\]

\[r = 0.993\]

Providence silt loam soil:

\[
\log_{10} \left( \frac{\mu\text{gms adsorbed/kgm soil}}{\text{kgm soil}} \right) = 3.460 - 0.125 \cdot \text{pH} \\
\]

\[r = 0.985\]

In studies on desorption from the three soils, Providence silt loam, Nibley clay loam, and Millville silt loam, with two successive water extractions, it was shown that 41.0 to 71.8 percent of the initially adsorbed picloram could be eluted at 25°C with the first two extractions. The elution thereafter was very slow.

Contrary to reports in the literature concerning precipitation of herbicides with the addition of inorganic electrolytes, no evidence was found of this occurring in picloram solutions without soil. The disappearance of picloram from solution, with inorganic electrolyte addition, seems to be characteristic adsorption on soils. The inorganic salts tested were BaCl₂, KCl, K₂SO₄, CaCl₂, and MgCl₂. The divalent cations
appeared to be more effective than monovalent cations in increasing picloram adsorption. The results, in this respect, however, were not conclusive. The magnitude of picloram adsorption by Nibley, Millville, and Chance soils was generally the same whether natural soils or Ca-saturated soils were used. These observations suggested an exchange type reaction of picloram with soil, picloram acting as a cation.

Work with Aiken soil, high in hydroxy oxides of Fe and Al and low in bases, provided further evidence that another mechanism for picloram adsorption is through hydrogen bonding. Ca-saturation of this soil resulted in increased picloram adsorption by two-fold, suggesting that cation-complex formation with the soil surface is also a mechanism of picloram adsorption.

Column studies of picloram with Millville and Aiken soils corroborated the observation that picloram adsorption is essentially linear between 1.00 ppm and 10.00 ppm concentration. Ca-saturation of these soils did not appreciably affect picloram movement in Millville soil, but considerably reduced it in Aiken soil. This is in agreement with data obtained in batch studies and showed that batch work is reliable in estimating picloram movement in soils.

Applicability of a mathematical model to picloram movement in soils columns was tested. After adjusting the retardation factor, prediction of picloram concentration in the column effluent improved. However, the prediction was not good after the peak concentration was attained. This was probably due to changing distribution coefficients of picloram with soil depth. An equation used by Lai (1970), giving distribution coefficients of ions at various depths is suggested to improve the predictability of the model.
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Appendix 1

Some Physical and Chemical Properties of Picloram
(4-amino-3,5,6-trichloropicolinic acid)

Structural formula:

\[ \text{C}_6\text{H}_3\text{Cl}_3\text{N}_2\text{O}_2 \]

Molecular formula:

\[ \text{C}_6\text{H}_3\text{Cl}_3\text{N}_2\text{O}_2 \]

Molecular weight: 241.5

Melting point: Decomposes before melting

Decomposition temperature: Approximately 215°C

Vapor pressure: 6.16 \times 10^{-7} \text{ mm Hg at 35°C}
1.07 \times 10^{-6} \text{ mm Hg at 45°C}

Solubility at 25°C: ppm

Water: 430
Acetone: 19,800
Benzene: 200

Solubility of K-salt: 400,000 ppm

pK\text{a} 4.10

---

### Appendix 2

**Alphabetical List of Common and Chemical Names of Herbicides Used in the Text**

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>ametryne</td>
<td>2-(ethylamino)-4-(isopropylamino)-6-(methylthio-s-triazine)</td>
</tr>
<tr>
<td>amitrole</td>
<td>3-amino-s-triazole</td>
</tr>
<tr>
<td>atrazine</td>
<td>2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine</td>
</tr>
<tr>
<td>barban</td>
<td>4-chloro-2-butynyl m-chlorocarbanilate</td>
</tr>
<tr>
<td>bromacil</td>
<td>5-bromo-3-sec-butyl-6-methyluracil</td>
</tr>
<tr>
<td>chloramben</td>
<td>3-amino-2,5-dichlorobenzoic acid</td>
</tr>
<tr>
<td>chlorazine</td>
<td>2-chloro-4,6bis(diethylamino)-s-triazine</td>
</tr>
<tr>
<td>chlorpropham</td>
<td>Isopropyl-m-chlorocarbanilate</td>
</tr>
<tr>
<td>CIPC</td>
<td>Isopropyl-m-chlorocarbanilate</td>
</tr>
<tr>
<td>dalapon</td>
<td>2,2-dichloropropionic acid</td>
</tr>
<tr>
<td>DCPA</td>
<td>dimethyl tetrachloroterephthalate</td>
</tr>
<tr>
<td>dicamba</td>
<td>3,6-dichloro-o-anisic acid</td>
</tr>
<tr>
<td>dinoseb</td>
<td>2-sec-butyl-4-6dinitrophenol</td>
</tr>
<tr>
<td>diphenamind</td>
<td>N,N-dimethyl-2-2-diphenylacetamide</td>
</tr>
<tr>
<td>diquat</td>
<td>6,7-dihydrodipyrido [1,2-a:2'1'-c] pyrazinediium ion</td>
</tr>
<tr>
<td>diuron</td>
<td>3-(3,4-dichlorophenyl)-1,1-dimethylurea</td>
</tr>
<tr>
<td>DNC and DNOC</td>
<td>4,6-dinitro-o-cresol</td>
</tr>
<tr>
<td>endothall</td>
<td>7-oxabicyclo[2.2.1]heptave-2,3-dicarboxylic acid</td>
</tr>
<tr>
<td>EPTC</td>
<td>S-ethyl dipropylthlocarbamate</td>
</tr>
<tr>
<td>erbon</td>
<td>2-(2,4,5-trichlorophenoxy)ethyl 2,2-dichloropropionate</td>
</tr>
<tr>
<td>fenac</td>
<td>(2,3,6-trichlorophenyl)acetic acid</td>
</tr>
<tr>
<td>fenuron</td>
<td>1,1-dimethyl-3-phenylurea</td>
</tr>
<tr>
<td>fenuron TCA</td>
<td>1,1-dimethyl-3-phenylurea mono(trichloroacetate)</td>
</tr>
<tr>
<td>fluometuron</td>
<td>1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea</td>
</tr>
<tr>
<td>ipazine</td>
<td>2-chloro-4-(diethylamino)-6-(isopropylamino)-s-triazine</td>
</tr>
<tr>
<td>isocil</td>
<td>5-bromo-3-isopropyl-6-methyluracil</td>
</tr>
</tbody>
</table>
linuron 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
MCPA [(4-chloro-o-tolyl)osylacetic acid
monuron 3-(p-chlorophenyl)-1,1-dimethylurea
monuron TCA 3-(p-chlorophenyl)-1,1-dimethylurea
neburon 1-butyl-3-(3,4-dichlorophenyl)-1-methylurea
paraquat 1,1'-dimethyl-4,4'-bipyridinium ion
picloram 4-amino-3,5,6-trichloropicolinic acid
prometone 2,4-bis(isopropylamino)-6-methoxy-6-s-triazine
prometryne 2,4-bis-isoptopylamino)-6-(methylthio)-s-triazine
propazine 2-chloro-4,6-bis(isopropylamino)-6-triazine
pyrazon 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinione
sivex 2-(2,4,5-trichlorophenoxy)propionic acid
simazine 2-chloro,4,6-bis(ethylamino)-s-triazine
simetone 2,4-bis(ethylamino)-6-methoxy-s-triazine
simetryne 2,4-bis(ethylamino)-6-(methylthio)-s-triazine
TCA trichloroacetic acid
tricamba 3,5,6-trichloro-0-anisic acid
trifluralin α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine
$2,3,6$-TBA 2,3,6-trichlorobenzoic acid
$2,4$-D (2,4-dichlorophenoxy)acetic acid
$2,4,5$-T (2,4,5-dichlorophenoxy) acetic acid
Appendix 3

Structure of some s-Triazine and Phenyl-alkanoic Acid Herbicides Referred to in the Literature Section

Triazines

General structure:

\[
\begin{array}{c}
N \quad N \\
\mid \quad \mid \\
R_1 \quad R_2 \\
\mid \quad \mid \\
N - C - N \quad N - C - N \\
R_3 \quad R_4 \quad R_5
\end{array}
\]

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Specific Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_1 )</td>
</tr>
<tr>
<td>Atrazine</td>
<td>H</td>
</tr>
<tr>
<td>Prometone</td>
<td>H</td>
</tr>
<tr>
<td>Simazine</td>
<td>H</td>
</tr>
</tbody>
</table>

Phenyl alkanoic acids

General structure:

\[
\begin{array}{c}
O \quad R \\
\mid \\
6 \quad 5 \\
\mid \\
2 \quad 3 \\
\mid \\
\quad 4
\end{array}
\]
2,4-D.

2,4,5-T.
VITA

Desh Raj Duseja

Candidate for the Degree of

Doctor of Philosophy

Dissertation: Adsorption-desorption and Movement of Picloram
(4-amino-3,5,6-trichloropicolinic acid) in Soils

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