



The leaching, adsorption and residual properties of chlorsulfuron
by Daniel C Burkhart

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Agronomy
Montana State University
© Copyright by Daniel C Burkhart (1985)

Abstract:

The leaching properties of chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]benzenesulfon-amide) were determined using soil columns containing intact field soil cores. Gravitational water leached the herbicide throughout the soil columns. Nearly all of the herbicide moved back to the top of the columns when water was permitted to move upward via capillary action. Adsorption of chlorsulfuron was compared in six soils using the Freundlich equation. Adsorption was low on all soils tested but increased as soil pH decreased.

Silica gel thin layer chromatography analysis of the supernatant from the adsorption study showed that approximately 60% of the radioactivity remained at the origin, apparently bound to a water soluble organic fraction from the soil. Twenty five percent of the radioactivity had an R_f equal to chlorsulfuron. The remaining 15% was apparently a metabolite of the parent compound. The radioactivity was not removed from the water soluble organic material by extraction with chloroform or petroleum ether.

Chlorsulfuron was applied at rates of 4, 8, 16, 35, and 70 g/ha in the spring of 1983 to plots located in Bozeman, Kalispell, Huntley, Havre, and Glasgow, Montana. Twelve crops were planted into the chlorsulfuron soil residues in the spring of 1984 and 1985. Percent crop injury varied in both years by crop, rate, and location. Multiple regression analysis showed that percent injury by location decreases with decreasing soil pH and increasing precipitation. Precipitation was below normal levels at all locations in 1985 and as a result chlorsulfuron did not significantly dissipate from 1984 to 1985 except at the two highest rates of application, 35 and 70 g/ha and at the Huntley location, which was irrigated. A model was developed to predict when various crops, which range from very sensitive to relatively tolerant to chlorsulfuron residues, can be planted without a yield reduction.

**THE LEACHING, ADSORPTION AND RESIDUAL PROPERTIES
OF CHLORSULFURON**

by

Daniel C Burkhart

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Agronomy

**MONTANA STATE UNIVERSITY
Bozeman, Montana**

December 1985

MAIN LIB.
N378
B9183
Cop. 2

ii

APPROVAL

of a thesis submitted by

Daniel C. Burkhart

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Dec 23, 1985

Date

Pat K Foy

Chairperson, Graduate Committee

Approval for the Major Department

Dec 23, 1985

Date

Dwane H Miller

Head, Major Department

Approval for the College of Graduate Studies

Jan. 22, 1986

Date

Henry L Parsons

Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Director of Libraries when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature Daniel C. Burkheit

Date Dec 22 1985

ACKNOWLEDGEMENTS

I thank my advisor, Dr. Pete Fay, for the help and encouragement he provided during my education.

I also appreciate the assistance and direction given by my committee, Mike Foley, Ralph Olson, Vern Stewart and Greg Carlson.

I would also like to thank the people in the weeds group, Cel Lacey, Scott Nissen, Bruce Maxwell, Tim Chicoine, Gary Fellows, Lee Coble and Mark Stannard, for their help, support and friendship.

TABLE OF CONTENTS

Chapter		Page
	VITA	iv
	ACKNOWLEDGMENTS	v
	TABLE OF CONTENTS	vi
	LIST OF TABLES	viii
	LIST OF FIGURES	xiii
	ABSTRACT	xv
1	LITERATURE REVIEW	1
	Introduction	1
	Mechanisms of Adsorption	2
	Characteristics of the Adsorbate	5
	Solvent Effects and Soil Reaction	9
	Adsorption Models and Equations	11
	Movement of Herbicides in Soil	14
	Methods of Studying Herbicide Movement	18
	Adsorption of Leaching of Chlorsulfuron	20
	Herbicide Persistence in Soil	22
2	THE LEACHING AND SOIL ADSORPTION PROPERTIES OF CHLORSULFURON	26
	Abstract	26
	Introduction	26
	Materials and Methods	28
	Thin Layer Chromatography Study	32
	Results and Discussion	34
	Conclusion	42

Chapter		Page
3	SOIL RESIDUAL ASPECTS OF CHLORSULFURON . .	43
	Abstract	43
	Introduction	44
	Methods and Materials	45
	Results and Discussion	48
	Comparison of Crop Injury in 1984 and 1985	58
	Huntley	59
	Bozeman	59
	Kalispell	61
	Glasgow	61
	All Locations Combined	65
	The Predictive Model	65
	Summary	70
	REFERENCES CITED	71
	APPENDICES	82
	Appendix A - Tables 14 - 16. Tables showing the results of chlorsulfuron leaching and adsorption studies	83
	Appendix B - Tables 17 - 26. Tables showing the results of chlorsulfuron plantback studies at five locations for two years in Montana	89

LIST OF TABLES

Table	Page
1. Selected properties of soils used in chlorsulfuron adsorption studies	33
2. Freundlich K values for adsorption of chlor- sulfuron in six Montana soils	37
3. Simple correlation coefficients (r) between Freundlich K values and selected soil properties and among soil properties of soils used in chlorsulfuron adsorption studies . .	39
4. Soil characteristics of chlorsulfuron plantback locations	45
5. Planting and harvest dates of chlorsulfuron plantback locations in 1984 and 1985	46
6. The combined average percent injury to 12 crops from 6 rates of chlorsulfuron soil residues at 5 locations in 1984 and 4 locations in 1985 . . .	49
7. Average percent injury of 12 crops from 6 rates of chlorsulfuron 16 months after application at 5 locations	50
8. Percent injury to 12 crops planted in soil which received 6 rates of chlorsulfuron, estimated percent injury from multiple regression analy- sis, soil pH, and total precipitation from the time of herbicide application until har- vest for 5 locations for the 1984 cropping season	51
9. Average percent injury to 12 crops planted in soil treated with 6 rates of chlorsulfuron 28 months before seeding at 4 locations in 1985 . . .	53

Table	Page
10. Actual percent crop injury of 12 crops planted in soil treated with 6 rates of chlorsulfuron, estimated percent crop injury from multiple regression analysis, soil pH, and total precipitation from harvest in 1984 until harvest in 1985 at 4 locations for the 1985 cropping season	54
11. Crop growth of 11 crops seeded in soil treated with 5 rates of chlorsulfuron 28 months before planting, expressed as a percentage of crop growth in untreated plots at Havre	56
12. The percent water by weight in the 70 g/ha and the control plots at the Havre chlorsulfuron plantback location after harvest in 1985	57
13. Crop safety ratings for 12 crops, 12 and 24 months after application of 5 rates of chlorsulfuron, for three pH-precipitation regimes	69
14. The soil weight, total DPM/g of soil, total DPM/2.5 cm depth, and percent of radioactivity recovered at each of 12 depths in 2.5 cm increments in soil leaching columns after leaching downward with 150 ml of water and allowing 150 ml of water to move upwards in the columns via capillary action	83
15. The soil weight, total DPM/g of soil, total DPM/2.5 cm depth, and percent of radioactivity recovered at each of 12 depths in 2.5 cm increments in soil leaching columns after leaching downward with 150 ml of water	84
16. The total DPM found in the supernatant before and after equilibration, the chlorsulfuron concentration (ng/ml) in the supernatant and the soil after equilibration and the log of the chlorsulfuron concentration in the supernatant and the soil after equilibration for the adsorption studies of chlorsulfuron in six soils	85

Table

Page

17.	The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1984, 12 months after application of 5 rates of chlorsulfuron at Bozeman, MT.	89
18.	The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1985, 24 months after application of 5 rates of chlorsulfuron at Bozeman, MT.	91
19.	The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1984, 12 months after application of 5 rates of chlorsulfuron at Kalispell, MT.	93
20.	The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1985, 24 months after application of 5 rates of chlorsulfuron at Kalispell, MT.	95

Table

Page

21. The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1984, 12 months after application of 5 rates of chlorsulfuron at Huntley, MT. 97

22. The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1985, 24 months after application of 5 rates of chlorsulfuron at Huntley, MT. 99

23. The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1984, 12 months after application of 5 rates of chlorsulfuron at Glasgow, MT. 101

24. The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1985, 24 months after application of 5 rates of chlorsulfuron at Glasgow, MT. 103

Table

Page

25.	The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1984, 12 months after application of 5 rates of chlorsulfuron at Havre, MT.	105
26.	The dry weight (grams) of the biomass of 1 meter of 1 row of 11 crops and the grain yield (kg/ha) of barley and the dry weight of 11 crops and the grain yield of barley expressed as a percentage of crop growth in the untreated plots averaged from 4 replications of each crop planted in 1985, 24 months after application of 5 rates of chlorsulfuron at Havre, MT.	107

LIST OF FIGURES

Figure	Page
1. Classification of adsorption isotherms where the S curve indicates cooperative adsorption, the L curve indicates a high affinity between solute and adsorbent at lower concentrations, the C curve indicates new sites becoming available as adsorption proceeds and the H curve indicates a high affinity between the solute and the adsorbent	12
2. The structure of the chlorsulfuron molecule showing the position of the radio-labeled carbon atoms	29
3. Percent of applied ¹⁴ C in 2.5 cm segments of soil from soil leaching columns after leaching downward or leaching downward followed by leaching upward	35
4. The log form of the Freundlich equation for adsorption of ¹⁴ C labeled chlorsulfuron by six Montana soils at eight chlorsulfuron concentrations	38
5. Percent of applied radioactivity from the supernatant of the chlorsulfuron soil adsorption studies, the supernatant after washing with petroleum ether, the petroleum ether fraction which was used to wash the supernatant, and stock chlorsulfuron detected at various R _f values after thin layer chromatography on silica gel plates	40

Figure	Page
6. Nomogram showing the results of multiple regression analysis between percent crop injury from 5 rates of chlorsulfuron soil residues at 5 locations versus soil pH and precipitation from time of herbicide application in 1983 until time of crop harvest in 1984	52
7. Nomogram showing the results of multiple regression analysis between percent crop injury from 5 rates of chlorsulfuron soil residues at 4 locations versus soil pH and precipitation from time of crop harvest in 1984 until time of crop harvest in 1985	55
8. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Huntley, Montana	60
9. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Bozeman, Montana	62
10. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Kalispell, Montana	63
11. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Glasgow, Montana	64
12. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron. These are the combined results of 5 locations in 1984 and 4 locations in 1985	66
13. Nomogram showing the pH-precipitation categories resulting from various combinations of soil pH and precipitation from time of chlorsulfuron application to 12 months after application and precipitation from 12 months after application until 24 months after application	68

ABSTRACT

The leaching properties of chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]benzenesulfon-amide) were determined using soil columns containing intact field soil cores. Gravitational water leached the herbicide throughout the soil columns. Nearly all of the herbicide moved back to the top of the columns when water was permitted to move upward via capillary action. Adsorption of chlorsulfuron was compared in six soils using the Freundlich equation. Adsorption was low on all soils tested but increased as soil pH decreased.

Silica gel thin layer chromatography analysis of the supernatant from the adsorption study showed that approximately 60% of the radioactivity remained at the origin, apparently bound to a water soluble organic fraction from the soil. Twenty five percent of the radioactivity had an R_f equal to chlorsulfuron. The remaining 15% was apparently a metabolite of the parent compound. The radioactivity was not removed from the water soluble organic material by extraction with chloroform or petroleum ether.

Chlorsulfuron was applied at rates of 4, 8, 16, 35, and 70 g/ha in the spring of 1983 to plots located in Bozeman, Kalispell, Huntley, Havre, and Glasgow, Montana. Twelve crops were planted into the chlorsulfuron soil residues in the spring of 1984 and 1985. Percent crop injury varied in both years by crop, rate, and location. Multiple regression analysis showed that percent injury by location decreases with decreasing soil pH and increasing precipitation. Precipitation was below normal levels at all locations in 1985 and as a result chlorsulfuron did not significantly dissipate from 1984 to 1985 except at the two highest rates of application, 35 and 70 g/ha and at the Huntley location, which was irrigated. A model was developed to predict when various crops, which range from very sensitive to relatively tolerant to chlorsulfuron residues, can be planted without a yield reduction.

CHAPTER 1

LITERATURE REVIEW

Introduction

Chlorsulfuron [2-chloro-N-((4-methoxy-6-methyl-1,3,5 triazin-2-yl) amino carbonyl)benzenesulfonamide] is a selective herbicide for broad-leaf weed control in small grains (Miller and Nalawaja, 1979; Palm et al, 1980; O'Sullivan, 1982). It has foliar as well as soil activity (O'Sullivan, 1982). Wheat (Triticum aestivum L.) has excellent tolerance to chlorsulfuron (Nalewaja, 1980; Palm et al, 1980; Brewster and Appleby, 1983) because it rapidly metabolizes the herbicide into non-toxic compounds (Sweetser et al, 1982).

Chlorsulfuron inhibits the enzyme acetolactate synthase which catalyzes the first step in the biosynthesis of valine and isoleucine (Ray, 1984). Sensitive weeds are controlled by rates as low as 10 to 20 gm/ha chlorsulfuron.

Chlorsulfuron is degraded biologically by soil microbes (Joshi, 1984) and chemically by acid hydrolysis (Palm et al, 1980). Microbial degradation in soil occurs more rapidly when moisture, temperature, pH, and nitrogen and carbon content are optimal for microbial growth (Joshi, 1984). Acid hydrolysis proceeds more rapidly at high soil temperature, high soil moisture and low soil pH (Palm et al, 1980).

The fate of pesticides in soil systems is affected by adsorption, movement, chemical and microbial decomposition, volatilization, and plant or organism uptake (Bailey and White, 1970). Adsorption either directly or indirectly influences the magnitude of the effect of the other six factors and therefore, appears to be one of the major factors affecting interactions between pesticides and soil colloids.

Mechanisms of Adsorption

Van der Waals forces. Van der Waals forces arise from the motion of electrons in atoms and molecules which creates instantaneous dipoles. The dipoles create an attraction between the atoms of molecules which are in close proximity to each other (Sienko and Plane, 1966). The magnitude of van der Waals forces depends on the size of the atom or molecule, and temperature. Large molecules or atoms are more easily polarized and are therefore subject to stronger van der Waals forces. A rise in temperature reduces van der Waals forces by increasing the motion and state of disorder in atoms or molecules (Allinger et al, 1971).

The contribution of van der Waals forces to adsorption of chemicals in soil is greatest for those molecules which are in intimate contact with the surface of soil colloids (Bailey and White, 1970). Van der Waals forces have been demonstrated in the adsorption of a variety of neutral, polar, and non-polar organic compounds onto montmorillonite clay (Bradley, 1945; Greene-Kelly, 1955; MacEwan, 1958).

Ion exchange. An important property of soil colloids is their ability to exchange and retain positively charged ions. The exchange capacity of soil is related to the organic matter content, and to the predominant clay mineral. Soils with high organic matter content and a high percentage of 2:1 expanding clay minerals will have a higher exchange capacity than a soil with low organic matter content and a high percentage of 1:1 non-expanding clay minerals (Bohn et al, 1979). The persistence and behavior of pesticides which are adsorbed by ion exchange depends to a large degree on the exchange capacity of the soil, and the stoichiometry of the exchange reaction (Bailey and White, 1970).

There are reports of adsorption of organic cations by ion exchange well in excess of the exchange capacity of the clay particles (Grim et al, 1947; Cowan and White, 1958; Tahoun and Mortland, 1966; Bailey et al, 1968; Bodenheimer and Heller, 1968). The adsorption of ethylamine (Farmer and Mortland, 1965), urea (Mortland, 1966) and amides (Tahoun and Mortland, 1966) by montmorillinite in excess of the exchange capacity is caused by the formation of "hemi" salts where two basic molecules share a single proton. It has also been shown that large organic cations are adsorbed by ion exchange in amounts less than the exchange capacity (Hendricks, 1941; Kinter and Diamond, 1963). The explanation for this phenomenon is that the large cations cover more than one adsorption site.

The nature of the exchangeable ion appears to have an effect on the ease and stoichiometry of ion exchange reactions. An amine salt

and a quaternary ammonium salt replaced sodium stoichiometrically from montmorillonite, but a greater than stoichiometric amount was required to replace calcium and magnesium (McAtee, 1962). Diquat (6,7-dihydro-dipyrido[1,2-a:2',1'-c]pyrazinedium ion {9,10-dihydro-8a,10a-diazoniaphenanthrene-2A}) and paraquat (1,1'-dimethyl-4,4'-bipyridinium ion) are two herbicides that are applied as cations. They are adsorbed by soil via ion exchange exclusively and are adsorbed until the total cation exchange capacity of soil is reached (Weber and Weed, 1968).

Hydrogen Bonding and Protonation. Hydrogen bonding occurs on the clay surface where surface oxygen atoms bind to protons of adsorbed water. The water molecule then forms a bridge between the clay particle and a polar organic molecule (Low, 1961). Molecules with terminal -OH, -COOH and -NH₂ groups can bind directly through the terminal H atom to negatively charged sites on the clay particle (Brindley and Thompson, 1966).

Certain pesticides may require protonation before adsorption can occur. Once a molecule is protonated it can be adsorbed by ion exchange as described above or by hydrogen bonding (Bailey and White, 1970). Protonation is dependant upon the pH of the soil system and the chemical character of the organic molecule.

Coordination. Coordination compounds, or metal complexes, are compounds that contain a central atom or ion, usually a metal surrounded by a cluster of ions or molecules. The number of atoms or ligands that can surround the central ion is a function of the coordination

number of the metal ion. The complex is formed by the donation of electron pairs by the surrounding compounds and acceptance of these electrons by the central metal ion (Bailey and White, 1970). In order for a pesticide to replace one of the ligands and be adsorbed, the pesticide must have stronger chelating properties than the compound or ion it is replacing (Hamaker and Thompson, 1972). Ashton (1963) using chromatography showed that amitrole (3-amino-s-triazole[3-amino-1,2,4-triazole]) forms complexes with nickel, cobalt and copper ions, but does not react with magnesium, manganese, ferric or ferrous ion. Mortland (1966) showed evidence that urea is held onto copper-, manganese-, and nickel-montmorillinite by means of a coordinate covalent bond. Bonding occurs through the carbonyl group rather than the amino group. Farmer and Mortland (1965) calculated that in a pyridine-Cu-montmorillinite complex there were four pyridine molecules surrounding each copper ion.

Characteristics of the Adsorbate

The physical and chemical properties of a given pesticide strongly influence the adsorption process. These properties include: (1) chemical character, shape, and configuration of the molecule, (2) dissociation constant (pKa or pKb), (3) water solubility, (4) charge distribution on the organic cation, (5) polarity and polarizability, and (6) size of the molecule (Greenland, 1965; Bailey et al 1968). Each property will be discussed separately but it should be

understood that more than one of these factors can be operating simultaneously.

Chemical Character, Shape, and Configuration. The nature of the functional group of a molecule determines the molecule's acidity or alkalinity; its potential for hydrogen bonding, or its ability to be adsorbed by ion exchange (Bailey and White, 1970). Weber (1966) showed that the amount of adsorption for 4,6-bis (isopropylamino-s-triazine) herbicides was dependent on the functional group found in the 2-position of the triazine ring. The order of adsorption was $-SCH_3 > -OCH_3 > OH > Cl$. The variation in adsorption of these compounds was attributed to differences in water solubility, electronegativity, and steric differences of the molecules.

Molecular configuration and shape determine the ease of orientation of the molecule on an adsorbing surface. Hayes et al (1972) found that paraquat is adsorbed preferentially to diquat because paraquat's molecular configuration permits internal rotation. They theorized that energy may be required to "flatten" diquat before it can be adsorbed.

Dissociation Constant. The pKa of a compound expresses the degree of ionization the compound exhibits with respect to water. A low pKa indicates a high degree of ionization when the compound is in solution (Allinger et al, 1971). The ratio of dissociated to undissociated forms of the compound decreases as the pH approaches the pKa of the compound. This reduces the negative charge of the compound which

increases the chances of becoming adsorbed by hydrogen bonding or ion exchange (Weber, 1970).

Frissel (1961) noted that negative adsorption of 2,4-D ([2,4-dichloro-phenoxy]acetic acid) and 2,4,5-T ([2,4,5-tri-chlorophenoxy]acetic acid) occurred until the pH of the system approached the pKa of the particular compound. Positive adsorption commenced when the pH reached the pKa and increased as the pH was lowered. Talbert and Fletchall (1965) studied the adsorption of five s-triazines and found that the pKa influenced adsorption. Colbert et al (1975) found that as soil pH was raised from pH 5 to pH 8 adsorption of atrazine (2-chloro-4-ethylamino-6-iso-propylamino-5-triazine) decreased. Hermosin et al (1982) reported almost complete adsorption of atrazine on a cation exchange column at pH 3.7. Weber et al (1969) reported that maximum adsorption of the triazine herbicides occurs at the pKa of each individual compound.

Water Solubility. There is a relationship between soil adsorbance and water solubility within a chemical family (Bailey et al, 1968). Wolf and Ward (1958) found that water solubility was inversely related to the degree of adsorption of four substituted ureas. Monuron (3-[p-chlorophenyl]-1,1-dimethylurea mono [trichloro-acetate]), which is five times more water soluble than diuron (3-[3,4-dichlorophenyl]-1,1-dimethylurea) was adsorbed to a greater degree than diuron on several soils (Yuen and Hilton, 1962; Hilton and Yuen, 1963). However, Bailey and White (1970) point out that care should be taken before

assuming that direct correlations exist between solubility and adsorbance because additional factors may be interacting in addition to water solubility and adsorbance within a particular herbicide family.

Charge Distribution. The electrostatic charge distribution on an organic cation has a major influence on its adsorbance. Paraquat is adsorbed to a greater degree than diquat by montmorillinite, kaolinite and the external surface of vermiculite because there is a wider charge center in paraquat than in diquat (Philen, 1968). This more effectively counters the charge on an adsorbent with a low charge density. Weed and Weber (1968) showed that the wide charge spacing permits paraquat to displace diquat more easily than diquat displaces paraquat from montmorillinite. In addition, desorption studies showed that $BaCl_2$ displaced more paraquat than diquat from vermiculite indicating that diquat is adsorbed to a greater degree on the inner surface of vermiculite. The internal surface of vermiculite, and the expanding micas preferentially adsorb more diquat than paraquat because there is a high charge density on these surfaces. The shorter charge center of diquat covers these adsorption sites more effectively than paraquat (Weber and Weed, 1968).

Polarity and Polarizability. Polarity of a molecule arises when electrons are unequally shared by two or more atoms in the molecule. The unequal sharing of electrons creates positively and negatively charged ends on the molecule which influence the degree of dissolution in solution (Sienko and Plane, 1966). Dipolarity also influences

the amount of energy expenditure required for adsorption to occur. A non-polar molecule exhibits greater preference for an adsorbent that is less polar than the solvent, while a polar molecule has more affinity for an adsorbent that is more polar than the solvent (Sienko and Plane, 1966).

Polarizability is a measure of the ease by which the positive and negative charges of a molecule can be displaced with respect to each other in the presence of an electric field. Molecules containing oxygen and nitrogen are more polarizable than molecules containing just hydrogen and carbon. While molecules containing sulfur or bromine are even more polarizable (Allinger et al, 1971).

Molecular Size. Large molecules often cover more than one available adsorption site which reduces adsorption capacity. Large alkaloid molecules such as brucine and codeine neutralized less of the adsorption sites on montmorillonite than smaller molecules such as aniline or benzidine (Hendricks, 1941). Large molecules are also barred from adsorption on the inner surfaces of expanding clay minerals. Molecules greater than 5 Å cannot be adsorbed on the inner surface of vermiculite (Bailey and White, 1970).

Solvent Effects and Soil Reaction

The kind and the amount of the solvent affects the amount of adsorption that can occur from a given solution (Weber, 1970). The

solvent in a natural soil system is always water, therefore the properties of water effect pesticide adsorption.

Water molecules do not exist individually, rather the hydrogen in one water molecule connects to an oxygen of another water molecule, which results in a hexagonal lattice structure of many tightly bound molecules (Kosower, 1968). Water is an excellent solvent because it exists as a dipole. The negative pole of water orients itself with the positive pole of the solute and the positive pole of water contacts the negative pole of the solute. A compound is soluble in water when its molecules have more affinity for water than to itself (Sienko and Plane, 1966). Water adsorbed on clay particles assumes an "ice-like" or crystalline structure which is more orderly than the molecular arrangement of liquid water. (Low, 1961). Nuclear Magnetic Resonance studies by Ducros and Dupont (1962) have shown that water adsorbed by montmorillinite is at least 1000 times more dissociated than liquid water and is so tightly bound that it is impossible to completely dehydrate montmorillinite without destroying its structure (Fripiat et al, 1960).

When water molecules are located near the clay surface the pH at or near the surface is 3 to 4 pH units lower than that of the bulk solution. Possibly the most important single property of soil that affects the extent of adsorption of organic compounds is the pH at clay surfaces (Bailey and White, 1970).

Adsorption Models and Equations

Adsorption isotherms describe the adsorption of solutes by solids in quantitative terms and are developed using "slurry" techniques. This involves shaking a known amount of soil in an aqueous solution containing a known concentration of pesticide. The difference between the initial pesticide concentration in solution and the final concentration is assumed to be the amount of pesticide adsorbed by the soil (Morrill et al, 1982).

Giles et al (1960) studied the adsorption of a variety of solutes from various aqueous solutions and classified the adsorption isotherms into four categories based on the shape of the curve obtained when adsorption was plotted against equilibrium concentration (Figure 1).

The S-type isotherm indicates cooperative adsorption where adsorption of one molecule of the solute encourages further adsorption of the solute. This occurs when molecules of the solute have a strong attraction to each other.

The L-type curve, called the Langmuir curve, is the most common type of adsorption by pesticides. It occurs when the affinity between the solid and the solute is relatively high at lower concentrations of the solute, but as the solute concentration increases adsorption sites are saturated and adsorption approaches a plateau.

The C-type curve is common when new sites become available as the solute is adsorbed. Adsorption is always proportional to solution concentration. The C-type curve is found mainly with textile fibers, where the adsorbate penetrates the fibers as the solute concentration

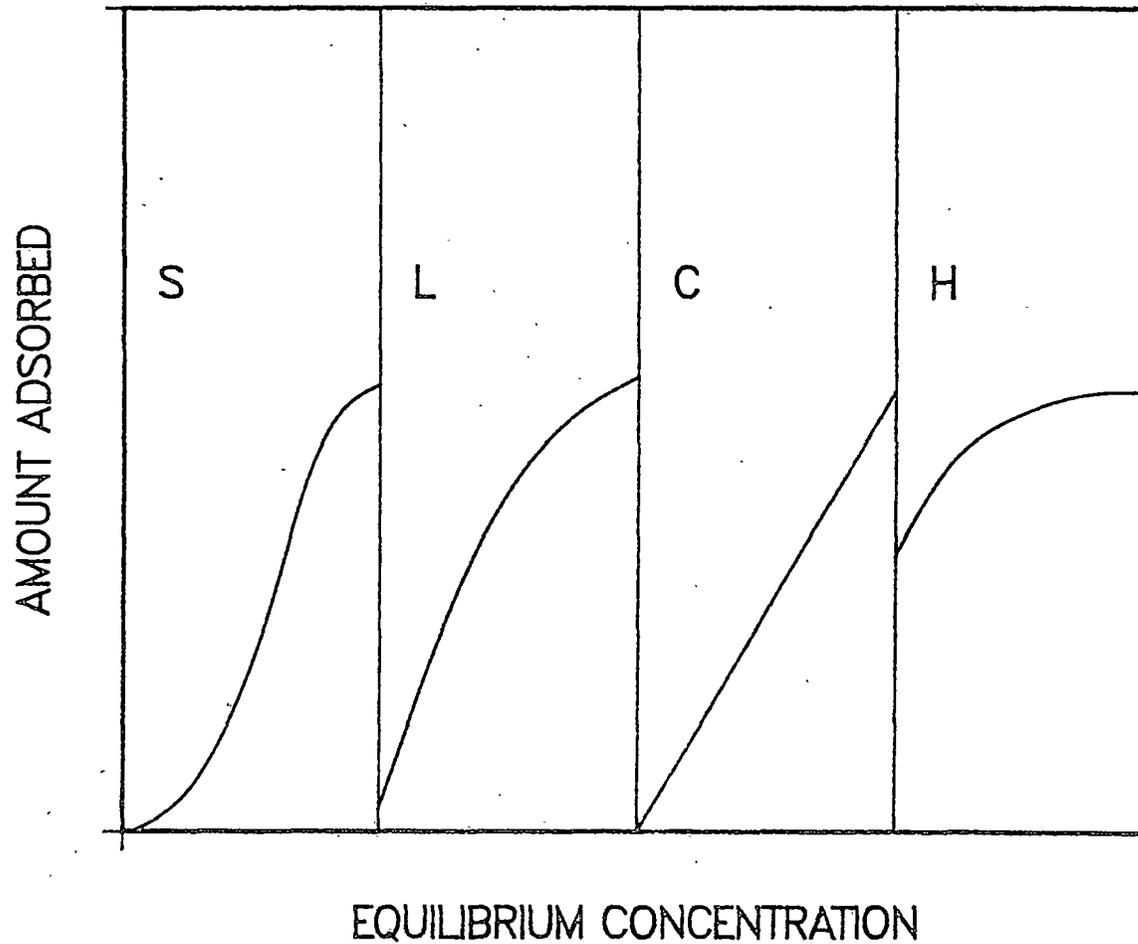


Figure 1. Classification of adsorption isotherms where the S curve indicates cooperative adsorption, the L curve indicates a high affinity between solute and adsorbent at lower concentrations, the C curve indicates new sites becoming available as adsorption proceeds and the H curve indicates a high affinity between the solute and the adsorbent.

increases. The H-type curve is obtained in systems where an exceptionally high affinity exists between the solute and the solid. This relationship is quite uncommon.

Many equations have been developed to mathematically describe adsorption isotherms. Only those relating to soil adsorption of pesticides will be discussed.

Freundlich Equation. The Freundlich equation is expressed as $X/M = KC^n$. X is the amount of solute adsorbed, M is the weight of the soil, C is the equilibrium concentration and K and n are constants. When the data is converted to the log form and the equilibrium concentration is plotted as the independent variable against the amount of solute adsorbed as the dependent variable, a linear relationship is established (Freundlich, 1926). The constant K is derived from the Y intercept and the constant n is derived from the slope of the line formed. The Freundlich equation is limited in that it cannot predict a maximum adsorption capacity, therefore data should not be extrapolated beyond the experimental ranges tested (Bohn et al, 1979). In spite of this, the Freundlich equation is the most common adsorption equation being used for predicting pesticide adsorption and behavior in soil (Tan, 1982).

Langmuir Equation The Langmuir equation was developed for adsorption of gases onto solids using the following assumptions:

1. The energy of adsorption is constant and independent of surface coverage.

2. Adsorption occurs on localized sites and there is no interaction between adsorbate molecules.
3. The maximum adsorption possible is that of a complete monolayer.

The Langmuir equation is expressed as $X/M = KCb/l + KC$. X is the amount of solute adsorbed, M is the weight of the soil, C is the equilibrium concentration, K is a constant relating to the binding strength and b is the maximum amount of adsorbate that can be adsorbed. The Langmuir equation can be converted into the linear form $C/X/M = 1/Kb + C/b$. A plot of $C/X/M$ versus C yields a straight line with slope $1/b$ and intercept $1/Kb$ (Langmuir, 1918). An advantage of the Langmuir equation is that a finite adsorption capacity is defined. This capability has been used to estimate the total adsorption capacity of particular soils for individual pesticides (Bohn et al, 1979).

Movement of Herbicides in Soil

Adsorption greatly influences the nature and extent of herbicide movement in soil, however, the relationship between adsorption and movement is not fully understood. Upchurch and Pierce (1957) found that two factors are involved in the leachability of a herbicide: (1) solubility of the compound in water and (2) degree of adsorption of the compound to soil particles. The pesticide can enter the soil solution either from dissolution of the particulate form or from

desorption of the compound from soil particles. The factors which affect overall movement are adsorption, water solubility, water amount and flow rate, and physical properties of the soil (Hartley, 1960).

Adsorption. Adsorption is the most significant factor affecting herbicide mobility in soil (Helling, 1970). Abernathy and Wax (1973) showed that bentazon (3-isopropyl-1H-2,1,3-benzothiadiazin-4[3H]-one 2,2-dioxide) was not adsorbed by any of twelve soils tested, and moved with the water front on both soil thin-layer plates, and in soil columns. Rodgers (1968) found that the mobility of seven s-triazine herbicides decreased in order as adsorption increased. The mobility of amitrole decreased as the adsorption capacity of quartz sand and three soils increased (Day et al 1961). Freed (1961) studied the leaching potential of nine herbicides and concluded that the stronger the adsorption properties the more resistance there was to leaching. Wu et al (1975) found the movement of napropamide [2-(*a*-naph-thoxy)-N,N-diethyl propionamide] in five soil types increased as adsorption decreased. Harris (1966) reported that the movement of several urea and triazine herbicides was inversely correlated to the extent of adsorption of these herbicides on four soils.

Water Solubility. The influence of water solubility on movement of herbicides in soil has not been precisely defined. The correlation between mobility and solubility is variable and seems to be strongly dependant upon the family of herbicides being studied. Swanson and Dutt (1973) included water solubility as one of the parameters that is

needed to predict the mobility of atrazine in soil. Wiese and Davis (1963) found a general relationship between the depth of movement into soil columns, and solubility of the herbicides 2,3,6-TBA (2,3,6-trichlorobenzoic acid), PBA (poly-chlorobenzoic acid), fenac (2,3,6-trichloro-phenylacetic acid), fenuron (3-phenyl-1,1-dimethylurea), silvex [2-(2,4,5-trichloro-phenoxy) propionic acid], monuron, 2,4-D, and 2,4,5-T. Nicholls et al (1983) developed a computer model for the movement of simazine in soil. They found that they could most accurately simulate simazine behavior in soil when the water solubility of simazine was incorporated into the model.

Gray and Weierich (1967) reported the depth of leaching of five thiocarbamate herbicides in soil was directly correlated to their solubility in water. In contrast, Bailey et al (1968) found that the leaching properties of seven s-triazine herbicides in a sandy loam soil correlated poorly with water solubility. Rodgers (1968) reported that the degree of adsorption of seven s-triazines herbicides was a better predictor of mobility than water solubility.

Water Amount and Flow Rate. Movement of immobile herbicides is not increased by application of additional water, but to a herbicide that exhibits some movement, increasing the amount of water applied will increase the depth to which the herbicide will move (Helling, 1970). Water flow rate is an important factor in herbicide mobility and is influenced by a variety of physical characteristics of the soil (Fuller and Korte, 1976; Alesii et al, 1980).

Rogers (1968) found that increasing the amount of water used in soil leaching columns increased the depth to which seven s-triazine herbicides travelled. In addition, he showed that a given volume of water caused more leaching when applied in a shorter period of time. Weber and Whitacre (1982) reported a thirty fold increase in movement of tebuthiuron {N-[5-(1,1-di-methyl ethyl) -1,3,4-thiadiazol-2-yl]-N,N-dimethyl urea} through soil columns under saturated rather than under unsaturated flow conditions. Under unsaturated conditions it took 30 days for 2.7 L of water to flow through soil columns. It took 40 days for 3.4 L of water, to move through soil columns under saturated conditions. He showed that when more water moved at a slower rate, the movement of tebuthiuron through soil was increased. Wiese and Davis (1963) showed that increasing the amount of water used to leach various herbicides in soil columns increased the depth to which the herbicides moved. No mention was made of flow rate. Friesen (1965) found that slow leaching with more water increased the mobility of dicamba (3,6-dichloro-o-anisic acid). He stated that slower water movement allowed greater capillary movement through small pores which permitted increased desorption of the herbicide from soil particles.

Physical Properties of the Soil. The physical properties of soil influence the degree of adsorption of a herbicide, the flow rate of water, and amount of water that can move through soil (Alesii, 1980). Herbicides are leached to a greater degree in light-textured soils than in heavier-textured soils (Rodgers, 1962; Donaldson and Foy,

1965; Harris, 1966; Keys and Friesen, 1968). Soil texture changes generally affect a change in soil structure. Pore size and pore size distribution affect the rate at which water enters and moves through the soil (Bailey and White, 1970). As discussed previously the amount and flow rate of water are factors which determine the leachability of herbicides. Pore size also determines the air space content of soil which is a pathway for movement of volatile pesticides. This pattern of movement is only important for highly volatile pesticides such as soil fumigants (Goring, 1957) because it takes several years for just one percent of most herbicides to move two feet by gaseous diffusion (Hartley, 1961).

Other physical properties such as percent organic matter, percent and type of clay, pH, and type of predominating cation can be so closely correlated to herbicide adsorption that relating these properties to leachability is redundant.

Methods of Studying Herbicide Movement

Herbicide mobility has been studied using soil leaching columns, soil thin-layer chromatography and field observations. The most satisfactory method for evaluating the relative mobility of herbicides in soil are those which most closely approximate actual field conditions (Weber and Whitacre, 1982).

Soil Leaching Columns. Ogle and Warren (1954) first reported the use of soil columns to study the movement of herbicides in soil. They

