



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
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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.

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OF CHLORSULFURON**

by

Daniel C Burkhardt

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of the requirements for the degree**

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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.

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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 montmorillonite 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 (pK_a or pK_b), (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 codiene neutralized less of the adsorption sites on montmorillinite 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

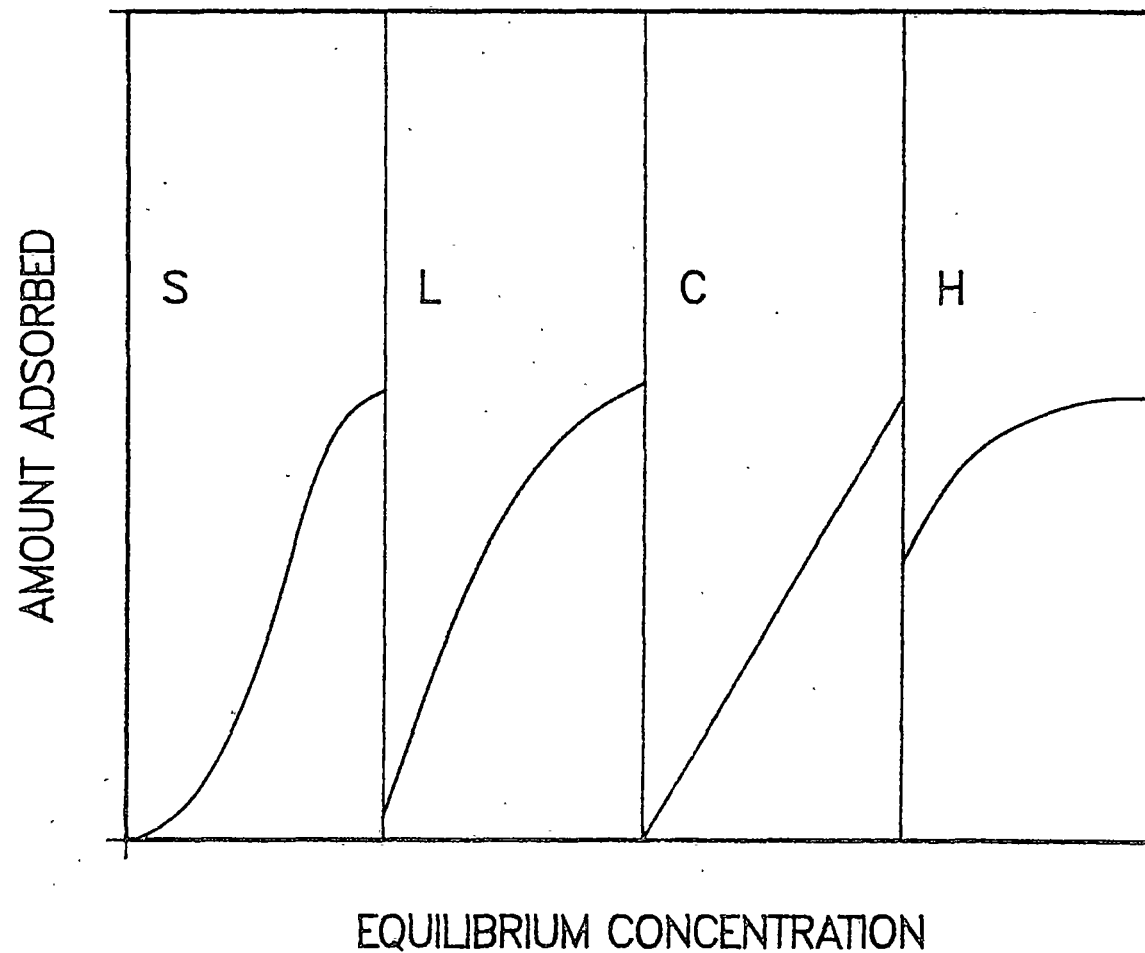


Figure 1. Classification of adsorption isotherms where the S curve indicates cooperative adsorption, the L curve indicates a high affinity between solute and adsorbent at lower concentrations, the C curve indicates new sites becoming available as adsorption proceeds and the H curve indicates a high affinity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

used vertical columns filled either with a homogenous soil, or an intact field soil core. Herbicides are applied to the surface of the column and water is percolated downward by gravity flow or upward via capillary flow. After leaching, the columns are sectioned and each section is analyzed for herbicide concentration (Helling, 1970). Herbicide analysis techniques include the use of radio-labelled compounds, plant bioassays, or chemical analysis of the herbicide after extraction from the soil.

Water movement via capillary flow in subirrigated columns is relatively uniform; however, water added to the tops of columns generally moves faster near the column walls than at the center of the column (McNeal and Reeve, 1964). This problem can be avoided by using silicon ridges, or wax layers on the inner surface of the column (Weber and Peeper, 1977).

Soil Thin-Layer Chromatography. This method, first reported by Helling and Turner (1968), employs thin-layer chromatography techniques. Soil is used as the stationary phase and distilled water is the mobile phase. Chromatography plates are constructed by spreading a slurry of soil and water on glass plates. Radioactive herbicide is applied to the dry soil near the bottom of the plate. The plates are then placed in a chromatography tank and water ascends the thin layer of soil by capillary action. Herbicide movement can be visualized by auto-radiography, or quantified by scraping the soil from the plates in sections and analyzing by scintillation spectrometry (Helling and Turner, 1968).

Helling (1971) has described the mobility of many herbicides using conventional Rf values. His results correlated well with observations from other studies of herbicide mobility. Absolute movement on thin-layer plates cannot be directly correlated to field or soil column experiments because the soil structure and texture on thin-layer plates are much more homogeneous than under field conditions (Helling, 1970).

Field Observations. The mobility of herbicides in field soil is commonly determined by analyzing soil for the herbicide at various time intervals and soil depths. Laboratory sampling and extraction techniques are very important since field soils are much more heterogeneous than soil thin-layer plates or soil columns. Animal burrows, soil cracks, slopes and swails all add variation to herbicide movement. In addition other variables such as water application, temperature, and rates of microbial degradation are difficult to control under field conditions (Helling, 1970).

Adsorption and Leaching of Chlorsulfuron

Soil adsorption of chlorsulfuron is low. Palm et al (1980) reported increased activity of chlorsulfuron on sandy-gravelly soils with less than 1% organic matter indicating that adsorption increases with increasing organic matter and clay content. Freundlich K values obtained on a Flanagan silt loam soil (5% OM, pH 5.0) and a Keyport silt loam (2.1% OM, pH 5.8) were 0.69 and 0.40 respectively (Dupont,

1980). Thirunarayanan et al (1985) reported Freundlich K values of 0.22 to 0.28 at 8C and 0.08 to 0.24 at 30C. Although there was not a strong relationship, chlorsulfuron adsorption did increase as the pH was lowered. Shea (1982) reported low adsorption on natural soils, but also found that adsorption increased as soil pH decreased. Mersie and Foy (1985) reported a definite increase in adsorption of chlorsulfuron as soil pH decreased.

Chlorsulfuron is weakly acidic with a pKa of 3.8. The negatively charged, dissociated species is the predominate form under normal field conditions. As the pH is lowered the molecule becomes protonated and could be adsorbed by hydrogen bonding or ion exchange. The two -NH₂ groups on the urea portion of the molecule are possible sites of protonation as are the nitrogen moieties in the triazine ring (Shea, 1982).

Water solubility of chlorsulfuron is pH dependent. At pH 5 water solubility is 300 ppm while at pH 7 solubility increases to 2800 ppm (Herbicide Handbook, Fifth Ed.). The relatively high water solubility of chlorsulfuron at pH 7 is an important factor which influences the low soil adsorption properties of chlorsulfuron.

Chlorsulfuron has potential to be extremely mobile in soil as a result of its low adsorption properties and high water solubility. Hageman and Behrens (1979) found that chlorsulfuron is quite mobile in a silty clay soil with 2.8% organic matter. Field experiments conducted by Nilsson (1982) showed that chlorsulfuron moved in a downward and lateral direction. O'Sullivan (1982) reported that chlorsulfuron

was mobile in a silt loam soil (13.7% OM, pH 6.8) in soil columns made of polyvinyl chloride (PVC) pipe. He detected chlorsulfuron, using a bioassay, at 11 cm and 17 cm following applications of water equivalent to 38 and 75 mm of rainfall respectively. Dyer (1984) using soil thin-layer chromatography, showed that chlorsulfuron moves in a concentrated band with the water front. In soil leaching columns filled with Bozeman silt loam (1.3% OM, pH 7.6), Dyer (1984) found chlorsulfuron distributed throughout the soil columns however approximately 40 % of the recovered chlorsulfuron was recovered in the top 5 cm.

Herbicide Persistence in Soil

While phytotoxic residues of herbicides in soil are often undesirable, residual herbicide activity does eliminate frequent applications of less persistent herbicides. One concern, however, is that the residual period will extend longer than desired and damage rotational crops. Another concern is that repeated use of a persistent herbicide will result in a buildup in concentration to undesirable levels of that herbicide in cropland (Sheets, 1970).

The s-triazine herbicides exhibit varying degrees of persistence in soil (Sheets, 1970; Esser et al, 1975). Those with a methoxy substituent in the two position of the ring are more persistent than those containing chloro or methylthio substituents (Sheets et al, 1962; Holly and Roberts, 1963; Sheets and Shaw, 1963). Burnside et al (1969) reported that successive applications of atrazine over a three

year period on several loam soils resulted in a buildup of atrazine concentrations. Khan and Marriage (1977) reported that residues of atrazine persisted in a peach orchard soil for several years.

The persistence of analogs of the substituted urea herbicides also varies (Khan, 1980). Persistence increases with increased ring chlorination and N-alkylation (Kearney, 1966). Approximately one year is required for detoxification of 1 to 2 lb/acre of diuron (Upchurch et al, 1969). Dawson et al (1969) found phytotoxic levels of monuron in a vineyard soil one year after application.

Residual problems with 2,6-dinitroanilines have been minimal (Wiese et al, 1969). Savage (1973) found the half-life of some dinitroanilines to range from 29 to 124 days in moist soils. Parks and Tepe (1969) reported that about 90% of the trifluralin (a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) applied under field conditions is degraded within five months. In contrast, Hamilton and Arle (1972) reported significant trifluralin injury to sugar beet (Beta vulgaris L.) in non-irrigated desert soils 24 months after herbicide application.

The uracil herbicides persist in the soil for more than 1 year (Gardiner et al, 1969). Terbacil (3-tert-butyl-5-chlor-6-methyluracil) residues from two annual applications of 1.5 lb/acre injured sensitive crops two years after treatment (Swan, 1972). Jenson and Kimball (1981) reported injury to raspberries one year after application of 3 kg/ha of terbacil.

Weather and climate affect persistence through their effects on volatilization, leaching, and chemical and biological degradation. Although volatilization and herbicide movement reduce herbicide residues in soil, persistence is not altered since the herbicide still exists somewhere in the soil environment (Sheets, 1970). Microbial and chemical decomposition both depend on warm, moist conditions for optimal activity (Harris, 1967). Dissipation of the triazine herbicides has been shown to occur more rapidly during the warm, summer months than during the cold, winter months (Burnside et al, 1961; Buchanan and Rogers, 1963).

The rate of degradation of phenoxy herbicides in soil is effected by soil moisture and temperature. The half-life of 2,4,5-T at 35 C and 34% soil moisture is four days, but extends to 60 days at 10 C and 20% soil moisture (Walker and Smith, 1979).

The rate of degradation of three dinitroaniline herbicides is accelerated under warm, moist soil conditions (Zimdahl and Gwynn, 1977). Hamilton (1979) observed sorghum (*Sorghum bicolor* L.) injury when it was planted one year after trifluralin application in years of low rainfall.

Salazer and Appleby (1982) reported that glyphosate [N-(phosphonomethyl) glycine] reduced the germination and growth of alfalfa (*Medicago sativa* L. "Vernal") and red clover (*Trifolium pratense* L. "Kenstar") for up to 24 hours after application.

Several research workers have reported injury to succeeding crops from chlorsulfuron residues in soil. Hageman and Behrens (1979)

reported injury to sugar beet and sunflower (*Helianthus annuus*) one year after application of 125 and 250 g/ha. Van Himme et al (1981) reported 100% injury to sugar beet, spinach (*Spinacia oleracea*), onion (*Alium cepa*) and red clover (*Trifolium incarnatum*) seven months after application of chlorsulfuron at 25 g/ha. Norris et al (1981) observed injury to sugar beet, onion, alfalfa and carrot (*Daucus carota*) 10 months after applications of 17, 35, and 70 g/ha of chlorsulfuron. Brewster and Appleby (1983) reported chlorsulfuron injury to sugar beet 18 months after application of 35 g/ha. Zimdahl and Fithian (1984) reported injury to sugar beet, sunflower, dry beans (*Phaseolus vulgaris*), and corn (*Zea mays*) from chlorsulfuron applied 2 years previously.

Junnila (1983) found that the residual activity of chlorsulfuron in Finland varied with climatic conditions. Injury to sugar beet two years after application was less when rainfall and temperature were above normal. Kurtz and Jordan (1983) reported less injury to soybeans from chlorsulfuron residues following a wet spring. Peterson and Arnold (1983) observed that injury to several crops at two locations two years after application of 17, 34, and 68 g/ha was less at the location with a lower soil pH and higher organic matter content. Walker and Brown (1981) developed a computer model to simulate the rate of dissipation of several herbicides. The predicted rates of degradation of chlorsulfuron were similar to results of field studies reported by Palm et al (1980), in that soil moisture and soil temperature were the two most important parameters affecting the rate of chlorsulfuron dissipation.

CHAPTER 2

THE LEACHING AND SOIL ADSORPTION PROPERTIES OF CHLORSULFURON

Abstract

The leaching behavior of chlorsulfuron was 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. The supernatant from the adsorption study was analyzed using silica gel thin layer chromatography. Approximately 60% of the total radioactivity recovered remained at the origin, apparently bound to a water soluble organic fraction from the soil. Twenty five percent of the radioactivity had the same R_f as 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.

Introduction

The leaching and adsorption characteristics of a herbicide are important factors affecting soil activity of the herbicide. Leaching

potential is regulated by the water solubility and soil adsorption characteristics of the herbicide (Swanson and Dutt, 1973). A herbicide with high water solubility which is only slightly adsorbed to soil particles is more likely to leach than a herbicide which is insoluble in water and tightly adsorbed to soil (Swanson and Dutt, 1973). The leaching potential of chlorsulfuron in Montana may be high because it is not tightly adsorbed to soil particles (Shea, 1982; Mersie and Foy, 1985; Thirunaryanan et al, 1985) and is very water soluble (Herbicide Handbook, Fifth Ed.).

Many methods have been used in laboratory studies to characterize herbicide movement in soil. Weber and Whitacre, (1982) stated that methods used to evaluate herbicide mobility in soil must approximate actual field conditions. Columns that contain an intact soil field core are much better approximations of field conditions than are hand packed columns or soil thin-layer plates. Soil structure, soil texture and soil bulk density vary throughout the soil profile and intact soil cores reflect these changes. A hand-packed column contains a homogeneous soil mixture while an intact soil core will be as heterogeneous as the original soil profile it is taken from. McMahon and Thomas (1974) showed that solute movement differed appreciably between undisturbed soil columns and soil that had been sieved and air dried. They stated that sieving of the soil altered the structural organization and porosity which affected solute movement.

Soil adsorption of a herbicide is affected by the chemical and physical characteristics of both the soil and the herbicide.

Chlorsulfuron is weakly acidic with a pka of 3.8 and exists in the anionic form in most soil systems (Shea, 1982). This negatively charged, dissociated form of chlorsulfuron has a low affinity for negatively charged clay particles. However, as the soil pH decreases chlorsulfuron molecules revert to the molecular form which could be adsorbed via hydrogen bonding (Weber, 1972).

The objectives of this study were to determine the leaching and adsorption properties of chlorsulfuron in Montana soils.

Materials and Methods

Leaching Studies. Leaching columns constructed from 4 cm diameter by 30 cm long poly vinyl chloride (PVC) pipe were driven into a soil profile at the Post Research Farm, Bozeman, MT. The soil was a Bozeman silt loam (pachic cyroboroll, fine, mixed, 1.8% OM, pH 6.6). The columns containing an intact soil core were removed from the soil and stored at -5 C until ready for use. Eighteen micrograms of ^{14}C -phenyl-labeled chlorsulfuron (6.01 uCi per mg) (Figure 2) was dissolved in 1 ml of acetone uniformly applied to the surface of the soil columns with a 100 microliter syringe. The columns were placed on a platform rotating at 1 rpm and leached with enough water (150 ml) to bring the soil throughout the columns to field capacity. Water was applied to the columns at a rate of 30 ml per hour using a 650067 flat

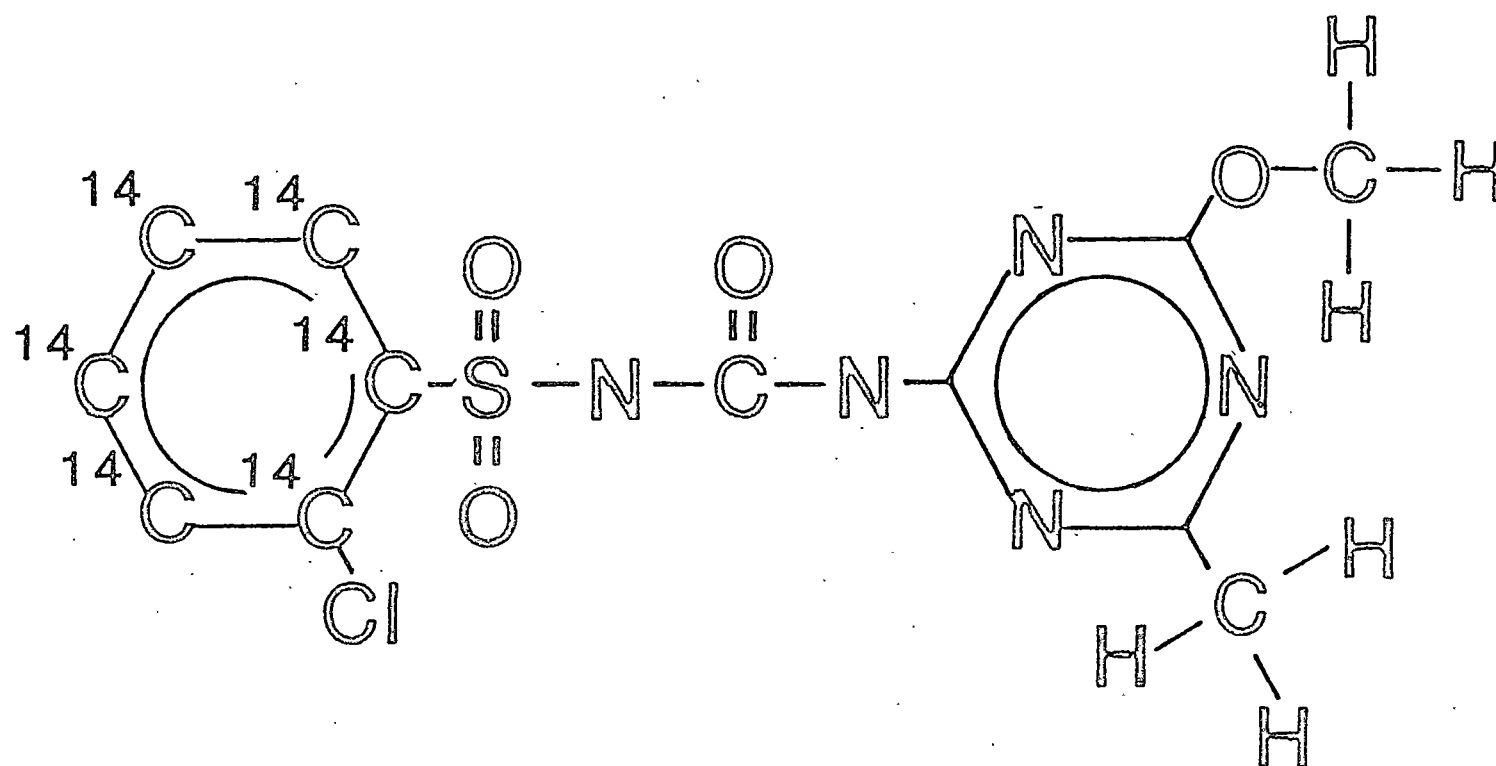


Figure 2. The structure of the chlorsulfuron molecule showing the position of the radio-labeled carbon atoms.

fan nozzle in a sprayer, attached to a water faucet maintained at 30 psi.¹

Some of the columns were frozen and cut with a bandsaw into 2.5 cm sections. The soil from each section was oven dried at 105 C for 24 hours and weighed. One g subsamples were taken from each section, combusted in a biological material oxidizer² and the evolved $^{14}\text{CO}_2$ was trapped in 15 ml of scintillation fluid³. The radioactivity was measured in a scintillation counter⁴. Counting efficiency was determined by treating 1 g of soil from each 2.5 cm depth in the soil profile with a radioactive standard. The soil was then combusted and analyzed for $^{14}\text{CO}_2$ as above.

Other columns were placed in 500 ml glass beakers containing 150 ml water which was allowed to move upward in the columns for 15 days via capillary action. The columns were frozen, sectioned and analyzed for radioactivity as described above. All treatments were replicated four times. The experiment was conducted twice and the data from both experiments were combined.

Adsorption Studies. Sites were selected for adsorption studies from six locations in Montana. The soil at these sites was collected by

¹ Spraying Systems Co., Wheaton, IL.

² Model OX 300. R.J. Harvey Instrument Co. Hillsdale NJ.

³ Carbon-14 Cocktail. R.J. Harvey Instrument Co. Hillsdale NJ.

⁴ Tri-Carb Model 2002, Packard Instruments Co. Downers Grove IL.

mixing approximately 3 kg of soil taken from the top 10 cm of the soil profile from eight locations in a 0.2 hectare area. The soil was air dried, and ground to pass through a 2 mm mesh sieve. All of the soils were analyzed by a commercial soil testing laboratory⁵. Organic matter content was determined by the Walkley-Black method. Soil pH was determined with a glass electrode from a mixture of 5 g of soil and 5 ml of water. Cation exchange capacity was determined from the sum of the exchangeable cations extracted by 1N ammonium acetate. All other tests were conducted according to published procedures.⁶ Selected characteristics of these soils are listed in (Table 1). Adsorption isotherms were calculated for these soils by adding ¹⁴C-labeled chlorsulfuron, as described above, at concentrations of 0.8, 1.6, 2.4, 3.2, 4.0, 4.8, 5.6, and 6.4 ng per ml to 7.5 gm of soil in 75 ml of deionized water. The mixtures were equilibrated at room temperature for 24 hours on a mechanical shaker and then centrifuged⁷ at 4000 rpm for 30 minutes. Five ml aliquots of the supernatant were added to 15 ml of scintillation fluid⁸ and counted in the scintillation counter as

⁵ Harris Laboratories, Inc., 624 Peach St P.O. Box 80837, Lincoln, Nebraska

⁶ Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Publication. No. 221 (Revised). Oct, 1980. W.C. Dahnke (Ed.).

⁷ Model J-6 centrifuge. Beckman Instruments Inc. Palo Alto CA.

⁸ Scinti Verse E. Fisher Scientific Co. Fair Lawn NJ.

described above. Counting efficiency was determined by adding a radioactive standard to 5 ml of the supernatant of a soil-water mixture that had not been treated with ^{14}C -chlorsulfuron. The amount of the herbicide adsorbed by the soil was calculated using the difference in concentration in the supernatant before and after equilibration. Adsorption of chlorsulfuron was described using the Freundlich equation $X / M = KC^{1/n}$ where X equals the amount of herbicide adsorbed, M equals the weight of soil, C equals the equilibrium concentration of the soil solution and K and n are constants (Bohn et al, 1979). The log form of the Freundlich equation is $\log X/M = \log K + n \log C$. The adsorption data was converted into log form and the equilibrium supernatant concentration, C , was plotted as the independent variable against the amount of herbicide adsorbed by the soil, X/M , as the dependant variable. The slope of this line is the constant n in the Freundlich equation and the Y intercept is the constant K . The Y intercept is converted back from the log form which results in the Freundlich K value. All treatments were replicated three times in a completely randomized design.

Thin Layer Chromatography Study

The supernatant of all treatments from the Bozeman soil was combined, filtered, and evaporated at 30C under reduced pressure in a flash evaporator to a volume of 50 ml. The pH was adjusted to 9.8 with 0.1N NaOH and washed 3 times with 50 ml of chloroform. The

aqueous fraction was separated from the chloroform in a separatory funnel and the pH of the aqueous fraction was adjusted to 3.8 with 0.1 N H_2SO_4 . The chloroform contained no radioactivity and was discarded. The aqueous solution at pH 3.8 was washed 3 times with 50 ml of petroleum ether and then separated from the petroleum ether fraction in a separatory funnel. The petroleum ether used for washing was evaporated to approximately 40 ml and brought to a volume of 50 ml with stock petroleum ether. One hundred microliter aliquots of the aqueous fraction and the petroleum ether fraction were then spotted on

Table 1. Selected properties of soils used in chlorsulfuron adsorption studies.

Soil	pH	% OM	CEC meq/100g	% Clay	Ca ppm	Na ppm	Mg ppm	K ppm
Joplin Sandy Clay Loam	6.6	1.1	12.6	25.28	1498	13	497	360
Bozeman Silt Loam	6.6	1.8	16.2	39.28	2290	16	449	357
Pierre Clay Loam	7.3	2.2	31.9	55.28	3656	421	1210	666
Vananda Clay Loam	7.4	2.4	29.1	39.28	4387	54	686	485
Judith- Danvers Loam	7.3	3.1	27.6	21.28	4947	16	209	413
Kalispell Silt Loam	7.8	4.4	32.2	17.28	5379	26	544	259

silica gel thin layer chromatography plates. An aliquot of the chlor-sulfuron standard was also spotted on the same thin layer plate to serve as a reference standard. The plates were developed to a distance of 18 cm with a solution of methylene chloride:methanol:9N NH_4OH , 72:25:3 (v/v/v). The silica gel was then scraped from the plates in sections 2 cm wide which were added to 15 ml of scintillation fluid⁹ and analyzed for radioactivity as described above.

Results and Discussion

Leaching Studies. Radioactivity was detected throughout the soil columns after column leaching. Thirty seven percent of the recovered ^{14}C moved 10 to 15 cm, 33% moved 17.5 to 22.5 cm, approximately 12% moved below 25 cm and 9% remained in the top 5 cm (Figure 3).

When the direction of water movement was reversed, 55% of the radioactivity recovered was found in the top 2.5 cm of the columns. Only 13% was detected below 15 cm while 31% remained between 5 and 15 cm (Figure 3). The radioactivity remaining in the 5 to 15 cm depths indicates that soil adsorption had occurred and was strong enough for the ^{14}C labeled compound to resist leaching. The majority of the ^{14}C applied in these columns moved freely with capillary water. The total radioactivity recovered was approximately 90% of the total radioactivity applied for both experiments.

⁹ Hydro-Count. J.T. Baker Chemical Co. Philipsburg NJ.

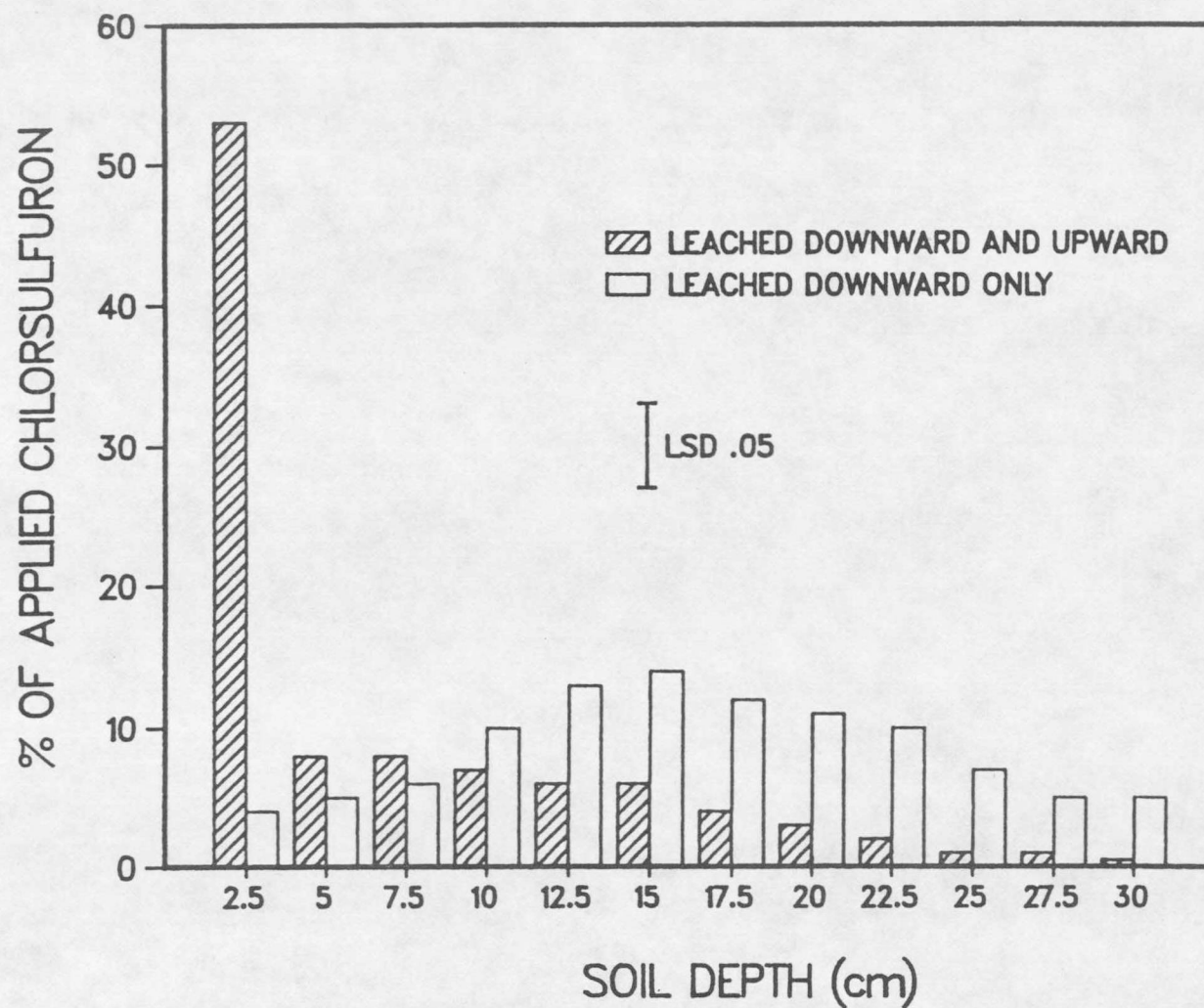


Figure 3. Percent of applied ^{14}C in 2.5 cm segments of soil from soil leaching columns after leaching downward, or leaching downward followed by leaching upward.

The difference in herbicide movement in the columns that were leached downward and those that were released upward may be due to the difference in the rate of water movement. Leaching the columns downward with 150 ml of water took only 18 hours. It took 12 days for 150 ml to move upward. The most important aspect of water and chemical movement in soil may be the amount of water entering the soil as a function of time (McMahon and Thomas, 1974).

Water movement by capillary flow in subirrigated columns is relatively uniform and is analagous to movement on soil thin layer plates. Conversely water added to the tops of soil columns generally moves downward faster near the column walls than at the center of the column as a result of the influence of boundary flow (McNeal and Reeve 1964; Weber and Whitacre, 1982). Methods such as soil thin layer plates and subirrigated column may be the best methods to approximate the actual movement of chlorsulfuron under field conditions.

Adsorption Study. Soil adsorption was low on all soils tested, as the Freundlich K values ranged from 0.65 to 2.49 (Table 2). Adsorption increased with chlorsulfuron concentration, which is typical behavior for acidic organic molecules (Grover, 1968; Cheng, 1971) (Figure 4).

The correlation of chlorsulfuron adsorption with soil calcium, soil pH and percent organic matter was -0.96 , -0.89 , and -0.85 , respectively (Table 3). Soil calcium was also highly correlated to soil pH ($R^2 = 0.94$). As the calcium content of a soil increases the pH of that soil also increases (Bohn et al, 1979), therefore the correlation between chlorsulfuron adsorption and calcium is probably due to the

Table 2. Freundlich K values for adsorption of chlorsulfuron in six Montana soils.

Soil	Freundlich K value	S.E.	Soil	Freundlich K value	S.E.
Joplin	2.49	1.15	Vananda	0.83	1.22
Bozeman	2.28	1.11	Judith-Danvers	0.76	1.20
Pierre	1.86	1.15	Kalispell	0.65	1.24

strong relationship between soil calcium and soil pH. Soil pH can have a profound effect on herbicide adsorption (Bailey and White, 1970). For acidic herbicides, adsorption is generally high at lower pH values, and decreases as pH increases (Bailey and White, 1968). Adsorption of chlorsulfuron has been shown to follow a similar pattern (Shea, 1982; Mersie and Foy, 1985; Thirunarayanan et al, 1985).

The correlation between chlorsulfuron adsorption and percent clay was not significant ($R^2 = .27$). Since chlorsulfuron is weakly acidic with a pKa of 3.8, the anionic form normally exists in soil (Shea, 1982). A negatively charged, dissociated species like chlorsulfuron has a very low affinity for negatively charged clay particles. Palm et al (1980), and Mersie and Foy (1985) also reported that adsorption of chlorsulfuron on clay was low. However, as the pH of the soil decreases, the majority of the chlorsulfuron molecules will occur in a non-ionic form which could then be adsorbed via hydrogen bonding (Weber, 1972). Our results indicate that as soil pH decreases chlorsulfuron adsorption increases.

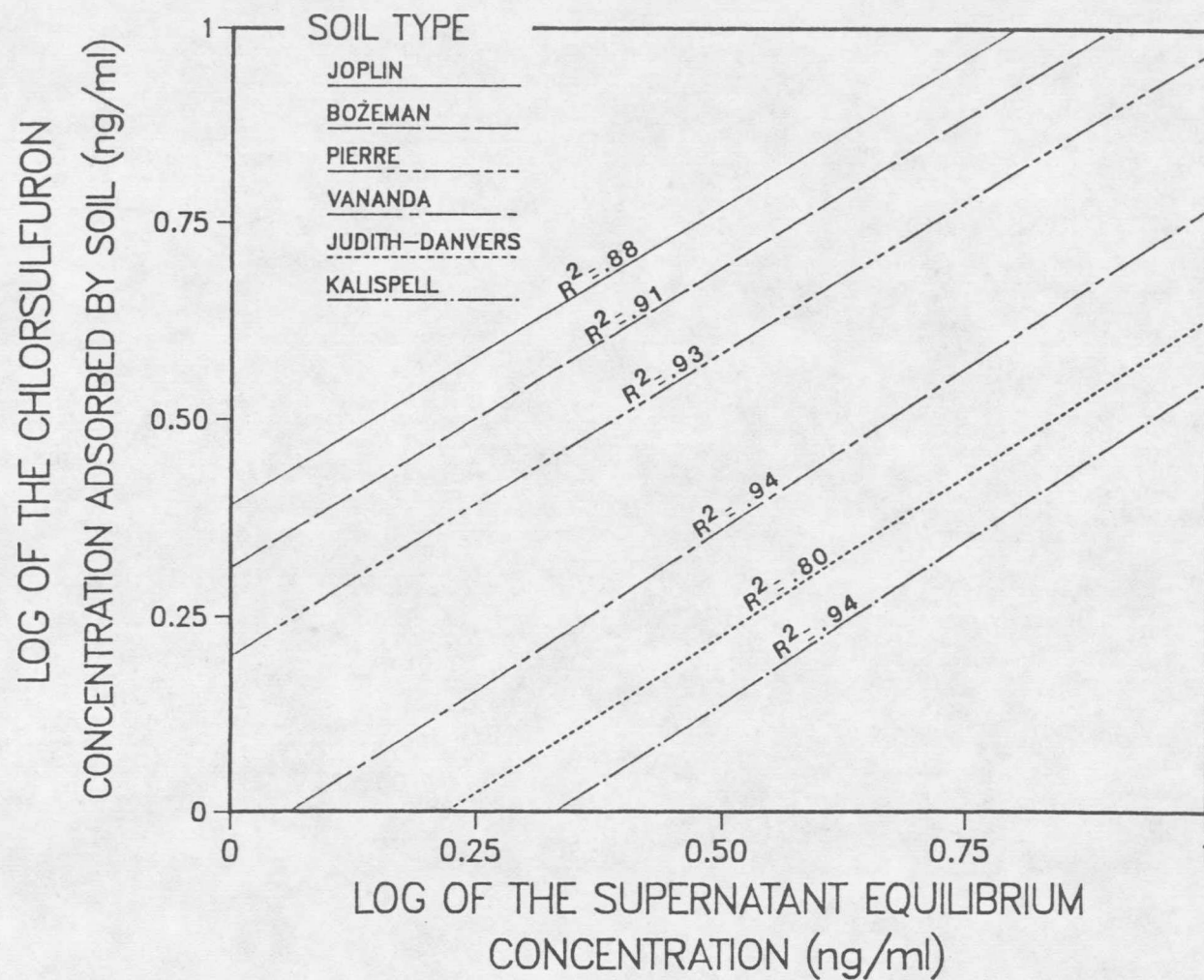


Figure 4. The log form of the Freundlich equation for adsorption of ^{14}C labeled chlorsulfuron by six Montana soils at eight chlorsulfuron concentrations.

Table 3. Simple correlation coefficients (r) between Freundlich K values and selected soil properties and among soil properties of soils used in chlorsulfuron adsorption studies.

	K Value	Ca	pH	OM	CEC	Clay	Mg	Na	K
Ca	-.96								
pH	-.89	.94							
%OM	-.85	.91	.89						
CEC	-.79	.89	.94	.75					
% Clay	.27	-.15	-.03	-.39	.27				
Mg	.34	-.13	.10	-.13	.31	.76			
Na	.17	.03	.18	-.11	.45	.86	.93		
K	.14	.02	.44	.33	.35	.94	.67	.87	

Normally, the organic fraction of soil is the most important factor regulating herbicide adsorption (Sheets et al, 1962; Bailey et al, 1968). Our results show that chlorsulfuron adsorption decreased as percent organic matter increased. This unexpected relationship may be caused by the fact that the soils tested with higher organic matter also had a high soil pH ($R = .89$). Soil pH may be more important than organic matter content in regards to chlorsulfuron adsorption.

Thin Layer Chromatography. The R_f value of 90% of the radiolabeled chlorsulfuron was 0.89 on silica gel thin layer chromatography plates. Approximately 6% of the radioactivity had an R_f value of 0.67 and the remaining 4% of the radioactivity was distributed in small quantities on the remainder of the plate (Figure 5).

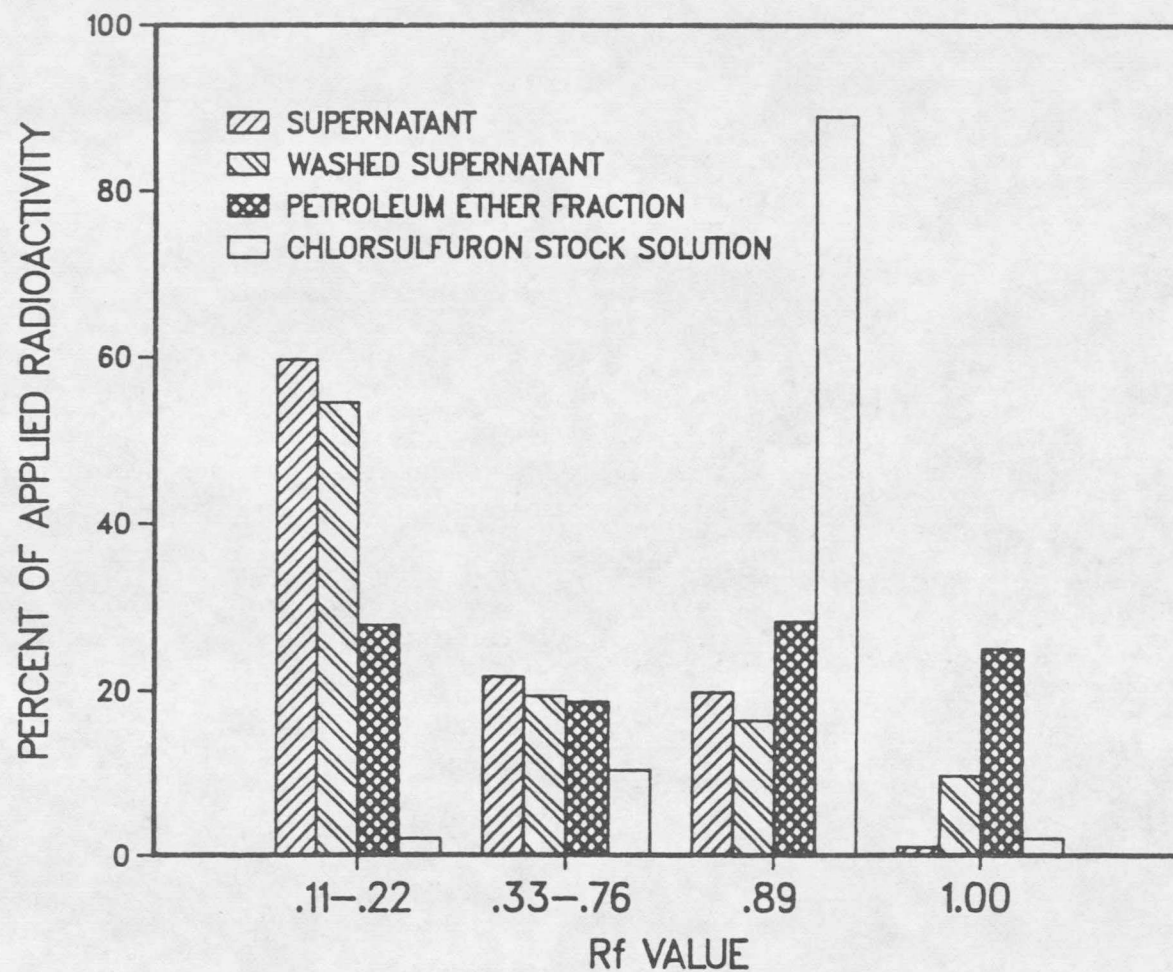


Figure 5. Percent of applied radioactivity from the supernatant of the chlorsulfuron soil adsorption studies, the supernatant after washing with petroleum ether, the petroleum ether fraction which was used to wash the supernatant and the stock chlorsulfuron detected at various Rf values after thin layer chromatography on silica gel thin layer plates.

When an aliquot of the evaporated supernatant solution from the adsorption study was chromatographed, nearly 60% of the radioactivity applied remained at the origin. It was apparently bound to a yellow, water soluble, organic fraction from the soil. Approximately 20% of the radioactivity in the unwashed supernatant had an Rf of 0.89. The remaining 20% of the radioactivity was distributed between Rf 0.33 and Rf 0.76 (Figure 5).

Chloroform and petroleum ether failed to extract the radioactivity from the organic material. A 100 ul aliquot taken from 50 ml of washed supernatant solution was chromatographed. Approximately 55% of the radioactivity remained at the origin of the silica gel thin layer plates. Sixteen percent of the radioactivity of this solution had an Rf of 0.89, and 21% was distributed between Rf 0.33 and Rf 0.76 (Figure 5).

The chloroform fraction was not chromatographed since it contained no radioactivity. However 28% of the total radioactivity found in the petroleum ether fraction had an Rf of 0.89. Approximately 25% of the radioactivity in the petroleum ether fraction remained at the origin. The yellow color was not detectable in the petroleum ether solutions. Twenty five percent of the radioactivity had an Rf of 1.00 and the remaining 20% was distributed from Rf 0.33 to Rf 0.78 (Figure 5).

The soluble, organic material present in the supernatant from the adsorption studies has traditionally been ignored. It has been assumed that any herbicide bound to this material is intact herbicide

which remains phytotoxic (Strek, 1985). We have not tested this assumption, but if it is made for our adsorption experiments then approximately 85% of the radioactivity in the unwashed supernatant is intact chlorsulfuron.

Conclusion

The typical A horizon of agricultural soils in Montana is shallow, followed by a B horizon that becomes increasingly calcareous with depth (Montagne et al, 1980). While some chlorsulfuron is adsorbed in the A horizon, little or no adsorption will occur in the B horizon. Chlorsulfuron will move freely with gravitational and capillary water, once it reaches the B horizon.

Precipitation generally ranges from 35 to 45 cm/yr in Montana, therefore the downward water movement from precipitation is normally offset by upward water movement via capillary action and evapotranspiration. While the potential for movement of chlorsulfuron into groundwater in semi-arid Montana is remote, deep leaching may pose a problem in areas with higher precipitation.

CHAPTER 3

SOIL RESIDUAL ASPECTS OF CHLORSULFURON

Abstract

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 injury was determined by comparing the dry weight of crops in the treated plots to the dry weight of crops in the control plots. Percent crop injury varied in both years by crop, rate, and location. Multiple regression analysis showed that percent injury decreased as soil pH decreased and precipitation increased. Precipitation was below normal levels at all locations in 1985 and as a result chlorsulfuron did not significantly dissipate from August, 1984 to August, 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 yield reduction.

Introduction

Chlorsulfuron is widely used in Montana for broadleaf weed control in wheat. While chlorsulfuron is persistent in soil, the length of the residual period varies (Junnala, 1984; Brewster and Appleby, 1983; Walker and Brown, 1983; Sampson et al, 1982). Determination of the rate of degradation of chlorsulfuron is important because it injures sensitive rotational crops and has the potential to leach into groundwater.

Chlorsulfuron is degraded in soil by chemical hydrolysis (Palm et al, 1980) and microbiological activity (Joshi et al, 1984). Acid hydrolysis of chlorsulfuron occurs rapidly when soil moisture and soil temperature are high and soil pH is low (Walker and Brown, 1983; Palm et al, 1980). The rate of microbiological degradation of chlorsulfuron is rapid when soil temperatures are high (Joshi et al, 1984). Chlorsulfuron is degraded rapidly in Alabama where soil temperatures are warm for extended periods of time, rainfall is abundant, and the soil pH is generally low (Wetje, 1985). The opposite conditions exist in some northern regions such as Montana, where rainfall and mean annual soil temperatures are low, and soil pH is normally alkaline.

The objectives of this experiment were to determine the sensitivity of twelve common rotational crops grown in Montana to soil residues of chlorsulfuron, to determine the rate of degradation of chlorsulfuron in Montana soils and to develop a model to predict

when various rotational crops can be safely planted after chlorsulfuron use.

Methods and Materials

Field experiments were established in the spring of 1983 at Bozeman, Kalispell, Huntley, Havre and Glasgow, Montana. Soil characteristics of each location are given in Table 4. Spring wheat was planted and chlorsulfuron was applied at rates of 4, 8, 16, 35 and 70 g/ha. There were four replications arranged in a randomized complete block design at each location. The grain was combined and the stubble disced in the fall of 1983.

Table 4. Soil characteristics of chlorsulfuron plantback locations

Location	Soil Type	pH	CEC	%OM	%Sand	%Silt	%Clay
Bozeman	Silt Loam	6.6	16.2	1.8	16.4	53.6	30.0
Kalispell	Loam	7.8	32.2	4.4	46.2	36.6	17.3
Huntley	Clay Loam	7.4	29.1	2.4	24.2	36.6	39.3
Glasgow	Clay	7.3	31.9	2.2	18.2	26.6	55.3
Havre	Sandy Clay Loam	6.6	12.6	1.1	48.2	26.6	25.3

In the Spring of 1984 the plots were fertilized with 65 kg/ha nitrogen, 65 kg/ha phosphorous, 65 kg/ha potassium, roto-tilled and

culti-packed. The following crops were then seeded into the plots: 'Clark' barley, 'Chilean' lentils, 'Apollo II' alfalfa, 'Betaseed 1433' sugar beet, 'Culbert' flax, 'UI 111' pinto bean, 'Acuperle' faba bean, 'UC-5' garbanzo bean, 'Greenway G-X 33' corn, 'IS984' sunflower, 'S-108' safflower, and 'Russet' potato. Date of planting for each location is given in Table 5. Prior to planting, EPTC (S-ethyl dipropyl thiocarbamate) was applied and incorporated at 3.5 kg/ha in the plot area where sugar beet, safflower, potato, pinto bean, faba bean, garbanzo bean, flax, alfalfa, and sunflower were to be planted. Oryzalin (3,5-dinitro N,N-dipropylsulfanilamide) was applied and incorporated at 1.0 kg/ha in the plot area where safflower, faba bean, pinto bean, garbanzo bean, and sunflower were to be planted. Weeds that were not controlled by these herbicides or the chlorsulfuron residue were controlled by hand throughout the season.

Table 5. Planting and harvest dates of chlorsulfuron plantback locations in 1984 and 1985.

Location	Planting Date		Harvest Date	
	1984	1985	1984	1985
Bozeman	June 6	June 7	Sept 11	Sept 11
Kalispell	May 8	April 26	Aug 28	Aug 14
Huntley	April 16	April 18	Aug 9	Aug 12
Havre	April 29	May 6	July 26	July 25
Glasgow	April 28	April 27	July 27	July 26

The plots were harvested in the fall by taking 10 plants per crop per plot. Harvest dates for each location are shown in Table 5. The plants were dried at 30 C for 5 days and weighed. The entire plot area containing barley was harvested with a small plot combine and grain yields were determined at all locations except Havre and Glasgow. At Havre and Glasgow 2 m of one barley row per plot was harvested, dried and weighed. All of the plots were disced following harvest. Harvest data for all crops from treated plots, except where barley grain yield was determined, was expressed as a percentage of the dry weight of 10 plants from the control plot. Barley grain yield in the treated plots was expressed as a percentage of barley grain yield in the control plots. The percentage was subtracted from 100 and all results were reported as percent injury.

In the spring of 1985 the plots were again fertilized as in 1984, disced and culti-packed. Eradicane, a commercially formulated mixture of EPTC and R-25788, was applied and incorporated at 3.5 kg/ha to the entire plot area except where barley and lentils were to be planted. The same crops that were planted in 1984 were then planted in a completely randomized design. Planting date for each location is given in Table 5. The crops were harvested by taking 2 m of one row per plot for all crops except barley and potato. The entire plot area containing barley was threshed and grain yields determined. Potato tuber yields were determined from 10 plants per plot at Bozeman, Kalispell and Huntley. The dry weight of 10 entire potato plants was determined at Havre and Glasgow. Pinto bean, and garbanzo bean grain

yields and sugar beet root yields were determined from 2 m of one row per plot at Bozeman. Harvest dates for 1985 are given in Table 5. The harvest data was analyzed, as in 1984, as a percentage of the control plots and reported as percent injury.

Soil samples were taken after harvest in 1985 at Havre from depths of 15 cm, 30 cm, 60 cm, 90 cm, and 120 cm in the control plots and the 70 g/ha plots. There were six replications per plot. The soil samples were weighed, dried at 105 C for 24 hours, reweighed and percent moisture by weight was determined.

Results and Discussion

Crop Sensitivity. The tolerance of twelve crops to chlorsulfuron soil residues varies. The relative sensitivity of each crop was determined by averaging the percent injury of each crop for each rate and location (Table 6).

Barley and safflower, the least sensitive crops, are not injured or only slightly injured at the higher rates while lentils, alfalfa, sugar beets and corn are sensitive to lower levels of chlorsulfuron.

Sweetser et al, (1982) showed that small grain crops are able to rapidly metabolize the herbicide into non-toxic compounds. The most sensitive crops apparently do not metabolize chlorsulfuron rapidly enough to escape injury.

Effect of Rate and Location. In 1984 crop injury from chlorsulfuron soil residues varied by rate and location. There is no reliable single

Table 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.

Crop	Percent Injury ¹	
	1984	1985
	<u>Most Tolerant</u>	
Barley	8 a	0 a
Safflower	15 ab	9 b
	<u>Intermediate Tolerance</u>	
Pinto Bean	21 bc	19 cd
Potato	26 cd	17 c
Faba Bean	30 cd	25 cde
	<u>Intermediate Sensitivity</u>	
Flax	36 d	25 de
Sunflower	34 ed	29 ef
Garbanzo Bean	45 ef	30 ef
	<u>Sensitive</u>	
Corn	48 f	37 fg
Sugar Beet	51 f	38 gh
Alfalfa	47 f	45 hi
	<u>Most Sensitive</u>	
Lentil	62 g	50 i

¹ percentages in columns followed by the same letter are not significantly different at the .5% level using the LSD test.

plant species bioassay for chlorsulfuron soil residues, therefore a single numerical estimate of the relative chlorsulfuron injury at each rate and each location was derived by averaging the percent injury of all crops at each rate and each location. Since the twelve crops range from very sensitive to relatively tolerant the numerical estimate implies nothing about injury to individual crops.

Percent crop injury in the plots originally treated with 4 g/ha was not significant at any location except Huntley. At Bozeman, injury was not significant in plots treated with 8 g/ha, but was significant in the plots treated with 16, 35 and 70 g/ha. Crop injury at all other locations was significant in the 8, 16, 35, and 70 g/ha plots (Table 7).

Table 7. Average percent injury to 12 crops planted in soil treated with chlorsulfuron 12 months before seeding 5 locations.

	Location				
	Bozeman	Kalispell	Huntley	Havre	Glasgow
Chlorsulfuron Rate g/ha	% Crop Injury ¹				
0	0.0 a	0.0 a	0.0 a	0.0 a	0.0 a
4	0.7 a	6.5 ab	21.3 b	12.3 a	7.0 a
8	1.6 a	17.4 bc	24.9 b	30.8 b	37.6 b
16	14.1 b	23.4 c	41.1 c	54.1 c	48.9 b
35	26.9 b	69.1 d	58.5 d	88.1 d	67.1 c
70	64.4 c	75.2 d	82.6 e	83.4 d	87.9 d

¹ Percentages in columns followed by the same letter are not significantly different at the 5% level using the LSD test.

Crop injury from chlorsulfuron soil residues varied by location in 1984 (Table 7). The percent injury of all crops at all rates was combined and averaged for each location to obtain a single numerical estimate of the relative amount of chlorsulfuron injury at each location. Correlations between percent injury at each location and several

environmental factors and soil properties showed that no single factor significantly accounted for the variation between locations. Multiple regression analysis revealed a highly significant correlation ($R^2 =$ received from the time of herbicide application until the time of harvest. Chlorsulfuron injury increased as soil pH increased and precipitation decreased (Figure 6). Actual percent injury, estimated injury from regression analysis, soil pH and total precipitation from herbicide application until harvest for each location are given in Table 8.

Table 8. Percent injury to 12 crops planted in soil which received 6 rates of chlorsulfuron, estimated percent injury from multiple regression analysis, soil pH, and total precipitation from the time of herbicide application until harvest for 5 locations for the 1984 cropping season.

Location	Soil pH	Total Precipitation for 16 month period (cm)	Actual Crop Injury (%)	Estimated Crop Injury (%)
Bozeman	6.6	73.9	16.1	16.6
Kalispell	7.8	72.8	31.9	30.7
Huntley	7.3	45.8 ¹	38.1	41.9
Havre	6.6	30.9	41.7	41.1
Glasgow	7.4	39.4	46.4	44.2

¹ Includes 10.2 cm irrigation

The results in 1985 were similar to those in 1984. While crop injury generally decreased, evidence of chlorsulfuron activity was

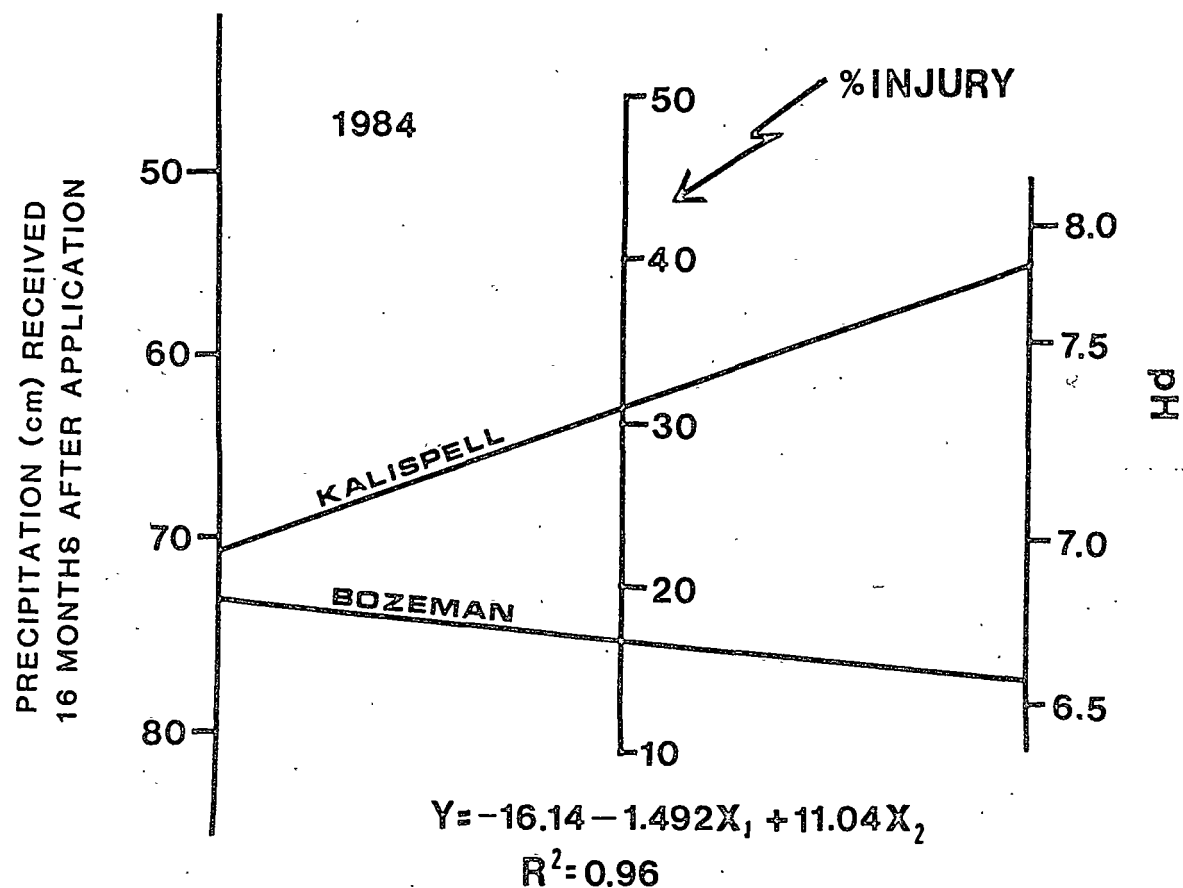


Figure 6. Nomogram showing the results of multiple regression analysis between percent crop injury from 5 rates of chlorsulfuron soil residues at 5 locations versus soil pH and precipitation from time of herbicide application in 1983 until time of crop harvest in 1984.

still obvious. Chlorsulfuron injury at each rate and location was analyzed in the same manner as in 1984. At Huntley and Glasgow there was significant injury in all plots treated with chlorsulfuron. At Kalispell injury was significant at all rates except 4 g/ha. Injury at Bozeman was significant only in the plots treated with 16, 35 and 70 g/ha chlorsulfuron (Table 9). Injury at Havre was confounded by drought conditions so it will be discussed separately.

Table 9. Average percent injury to 12 crops planted in soil treated with 6 rates of chlorsulfuron 24 months before seeding at 4 locations.

Chlorsulfuron Rate g/ha	Location			
	Bozeman	Kalispell	Huntley	Glasgow
	% Crop Injury ¹			
0	0.0 a	0.0 a	0.0 a	0.0 a
4	3.9 a	2.8 a	12.3 b	25.7 b
8	9.7 ab	19.3 b	10.4 bc	35.2 c
16	17.0 bc	26.3 b	20.8 cd	47.4 d
35	23.3 cd	57.4 c	26.6 d	68.3 e
70	32.7 d	69.6 c	39.8 e	81.6 f

¹ Percentages in columns followed by the same letter are not significantly different at the 5% level using the LSD test.

Chlorsulfuron injury varied by location again in 1985. Multiple correlation analysis of crop injury in 1985 by location versus soil pH and total precipitation from harvest in 1984 until harvest in 1985

(12 months) totally accounted for the variation between locations ($R^2=.99$)(Figure 7). As in 1984, crop injury decreased as soil pH decreased and precipitation increased. Actual percent injury, estimated injury from regression analysis, soil pH and total precipitation from harvest in 1984 until harvest in 1985 at each location in 1985 are shown in Table 10.

Table 10. Actual percent crop injury to 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.

Location	Soil pH	Total Precipitation for 12 month period (cm)	Actual Crop Injury (%)	Estimated Crop Injury (%)
Bozeman	6.6	50.4 ¹	14.4	15.2
Kalispell	7.8	44.6	29.3	30.4
Huntley	7.3	58.8 ²	18.3	16.9
Glasgow	7.4	16.0	43.1	42.6

¹ Includes 15.3 cm of irrigation

² Includes 30.5 cm of irrigation

The results recorded at Havre were confounded by extreme drought conditions in 1985. Midway through the season, crop growth in the chlorsulfuron treated plots appeared to be equal or greater than crop growth in the control plots in the first, second and third replications. There was no visual difference in crop growth in any of the plots in the fourth replication.

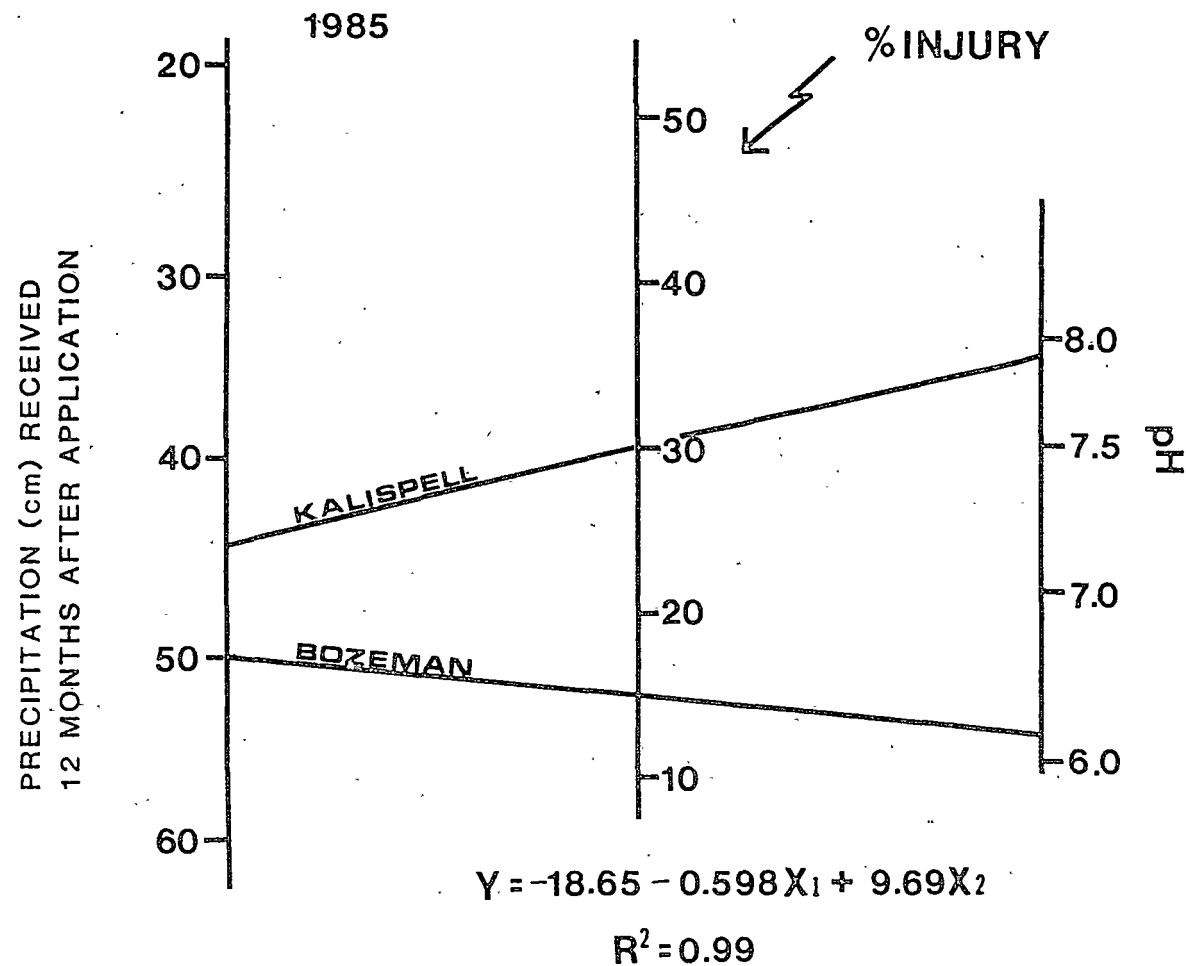


Figure 7. Nomogram showing the results of multiple regression analysis between percent crop injury from 5 rates of chlorsulfuron soil residues at 4 locations versus soil pH and precipitation from time of crop harvest in 1984 until time of crop harvest in 1985.

Harvest results showed a trend for crop growth in all chlorsulfuron treated plots, except plots treated with 70 g/ha, to be greater than crop growth in the control plots. However, differences in crop growth were not significantly different in any of the plots (Table 11).

Table 11. Crop growth of 11¹ crops seeded in soil treated with 5 rates of chlorsulfuron 24 months before planting, expressed as a percentage of crop growth in untreated plots at Havre.

Chlorsulfuron Rate (g/ha)	Crop Growth as a percent of Control
0	100 a ²
4	122 a
8	132 a
16	122 a
35	134 a
70	94 a

¹ Garbanzo beans were not harvested at Havre in 1985 due to browsing by rabbits.

² Percentages in columns followed by the same letter are not significantly different at the 5% level using the LSD test.

Soil samples were taken at 5 depths in control plots and plots treated with 70 g/ha. There was a higher percentage of water by weight in the 70 g/ha plots than in the control plots in the first three replications. The water content in the plots treated with 70 g/ha in the fourth replication (plot 405) was not different from

the control plot (plot 403) or the control plots in the first three replications (Table 12).

Table 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.

Chlorsulfuron Rate (g/ha)	Plot	% Water by Weight
0	104	9.1 a ¹
0	202	8.8 a
0	304	9.0 a
0	403	8.2 a
70	105	11.4 b
70	206	11.5 b
70	302	11.1 b
70	405	8.2 a

¹ Percentages in columns followed by the same letter are not significantly different at the 5% level using the LSD test.

The average percent crop injury in the 70 g/ha plot at Havre in 1984 was 93.4% (Table 7). Many of the sensitive crops, such as lentils, alfalfa, corn and sugar beets, germinated in 1984 but died within two or three weeks. The crops with intermediate sensitivity were severely stunted and the most tolerant crops, barley and safflower, occupied only one-sixth of the total plot area. This left the plots treated with 70 g/ha in a nearly fallow condition in 1984. In 1985 the control plots were occupied by the third consecutive crop while moisture in the 70 g/ha plots had been at least partially

recharged in 1984. It is therefore reasonable to conclude that the dry soil conditions in the control plots were more detrimental to the crops than chlorsulfuron residues in the treated plots.

Comparison of Crop Injury in 1984 and 1985

Percent crop injury was generally less in 1985 than in 1984, however the decrease in injury varied by location. In many cases injury was only significant in plots treated with 35 and 70 g/ha of chlorsulfuron. Since crop injury is correlated to precipitation and soil pH, soil water is an important component which regulates the rate of dissipation of chlorsulfuron. While the soil pH at each location did not change, the precipitation for the twelve month period following harvest in 1984 was below normal at all locations.

Dissipation of chlorsulfuron occurs through leaching, and through chemical and microbial decomposition. The reduced precipitation levels in 1985 could have decreased chlorsulfuron dissipation since chlorsulfuron was not diluted throughout the soil profile by downward leaching. Instead it was concentrated near the surface via capillary water movement upward. Secondly the rate of chemical and microbial decomposition was decreased because water was limiting.

Different concentrations of herbicides do not necessarily decompose at the same rate. Concentration affects the rate of decomposition by determining how often collisions occur between the herbicide and an activator. An activator is defined as a factor that

initiates or controls the rate of chemical or biological reactions. Activators in soil include soil water, soil enzymes, and microorganisms. The activator and the herbicide concentrations can both limit breakdown rates (Hamaker and Thompson, 1972). In the case of chlorsulfuron, water is an important activator. When water is not limiting, decomposition of a wide range of chlorsulfuron concentrations will occur at similar rates. However, when water is limiting, the decomposition rate changes as chlorsulfuron concentrations change.

Huntley

Crop injury was significantly lower at Huntley in 1985 than in 1984 (Figure 8.). While rainfall was below normal at Huntley, it was supplemented with 30.5 cm of irrigation water. Therefore, the rate of chemical and microbial decomposition was never limited by a lack of soil moisture. In addition net water movement was downward which diluted chlorsulfuron throughout the soil profile. Chlorsulfuron dissipation at Huntley from 1984 to 1985 may have been as close to "normal" as is possible in Montana.

Bozeman

Crop injury at Bozeman was not significantly lower in 1985 than in 1984 on plots treated with 4 and 8 g/ha chlorsulfuron. Apparently these rates had dissipated to non-injurious levels by the end of the 1984 season and therefore, had no effect in 1985. There was signifi-

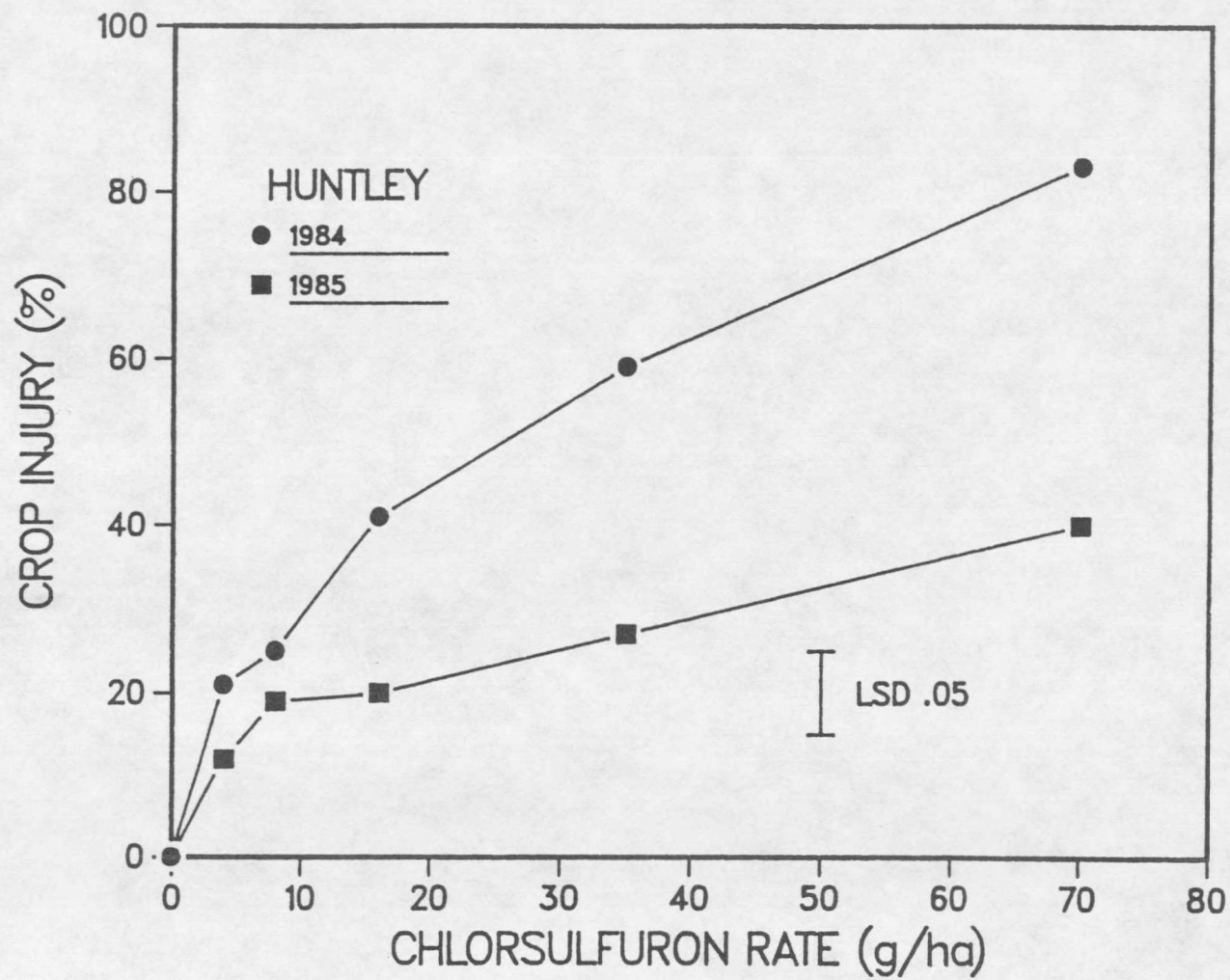


Figure 8. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Huntley, Montana.

cant injury in the 16, 35, and 70 g/ha plots in both 1984 and 1985, but the reduction in injury from 1984 to 1985 was significant only in plots treated with 70 g/ha (Figure 9). Precipitation was 20% below normal at Bozeman in 1985 and although the plots received 15.2 cm of supplemental irrigation, lack of water probably limited plant growth. There was no net water movement downward and significant degradation of chlorsulfuron was limited to plots with the highest herbicide concentration.

Kalispell

Crop injury from soil residues of chlorsulfuron did not change from 1984 to 1985 in any of the treated plots at Kalispell (Figure 10). Precipitation in 1985 was approximately 10 cm less in 1985 than in 1984, a 15% reduction, and was not supplemented with irrigation. Dry soil conditions combined with a high soil pH (7.8) resulted in essentially no chlorsulfuron dissipation from 1984 to 1985.

Glasgow

Crop injury was significantly different in 1985 from 1984 only on the plots which received 4 and 35 g/ha chlorsulfuron. At the 4 g/ha rate crop injury increased and at 35 g/ha injury decreased. The percent crop injury had not changed in 1985 from 1984 in plots treated with 8, 16 and 70 g/ha (Figure 11). The location at Glasgow has received only 55.4 cm of precipitation since chlorsulfuron was applied

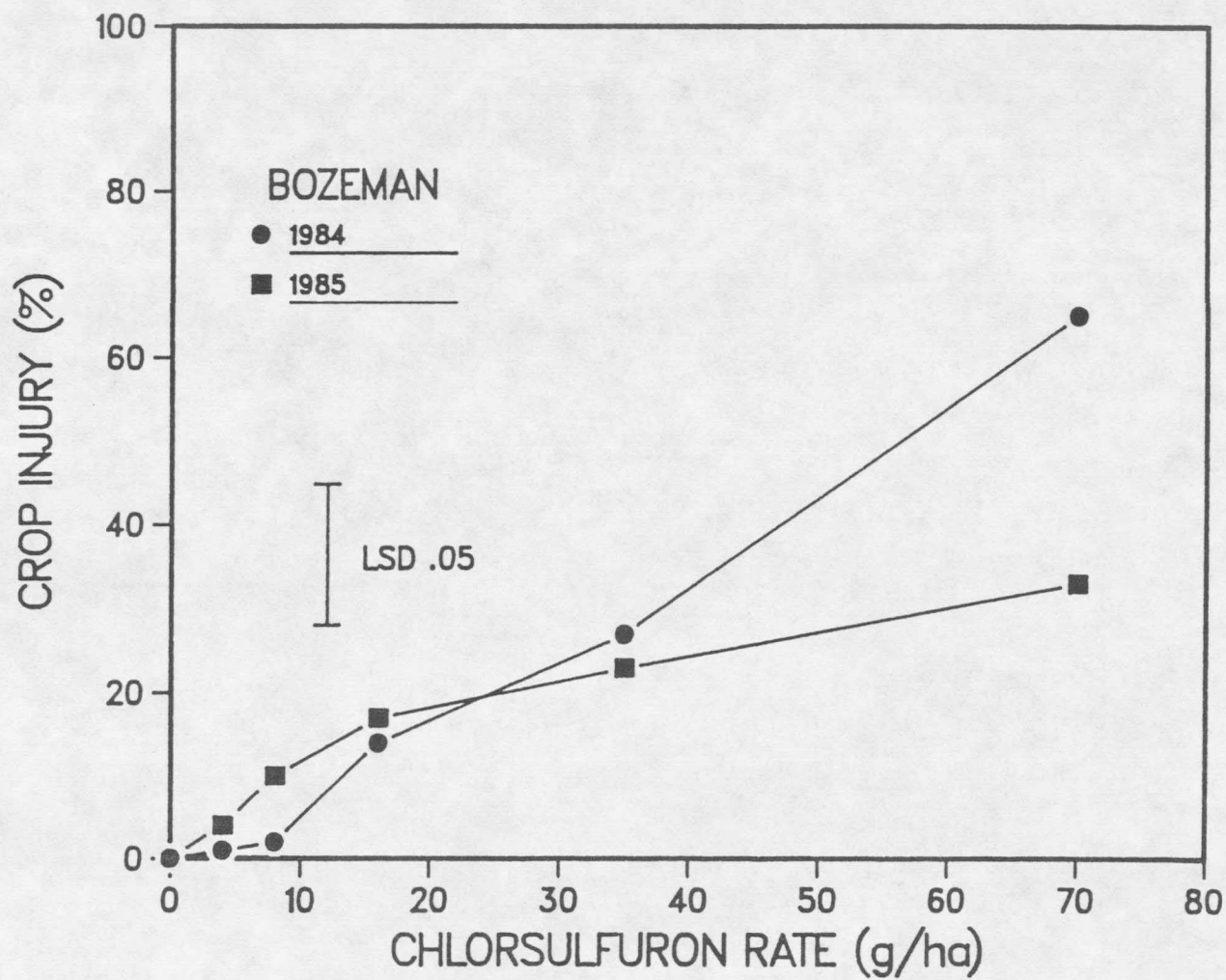


Figure 9. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Bozeman, Montana.

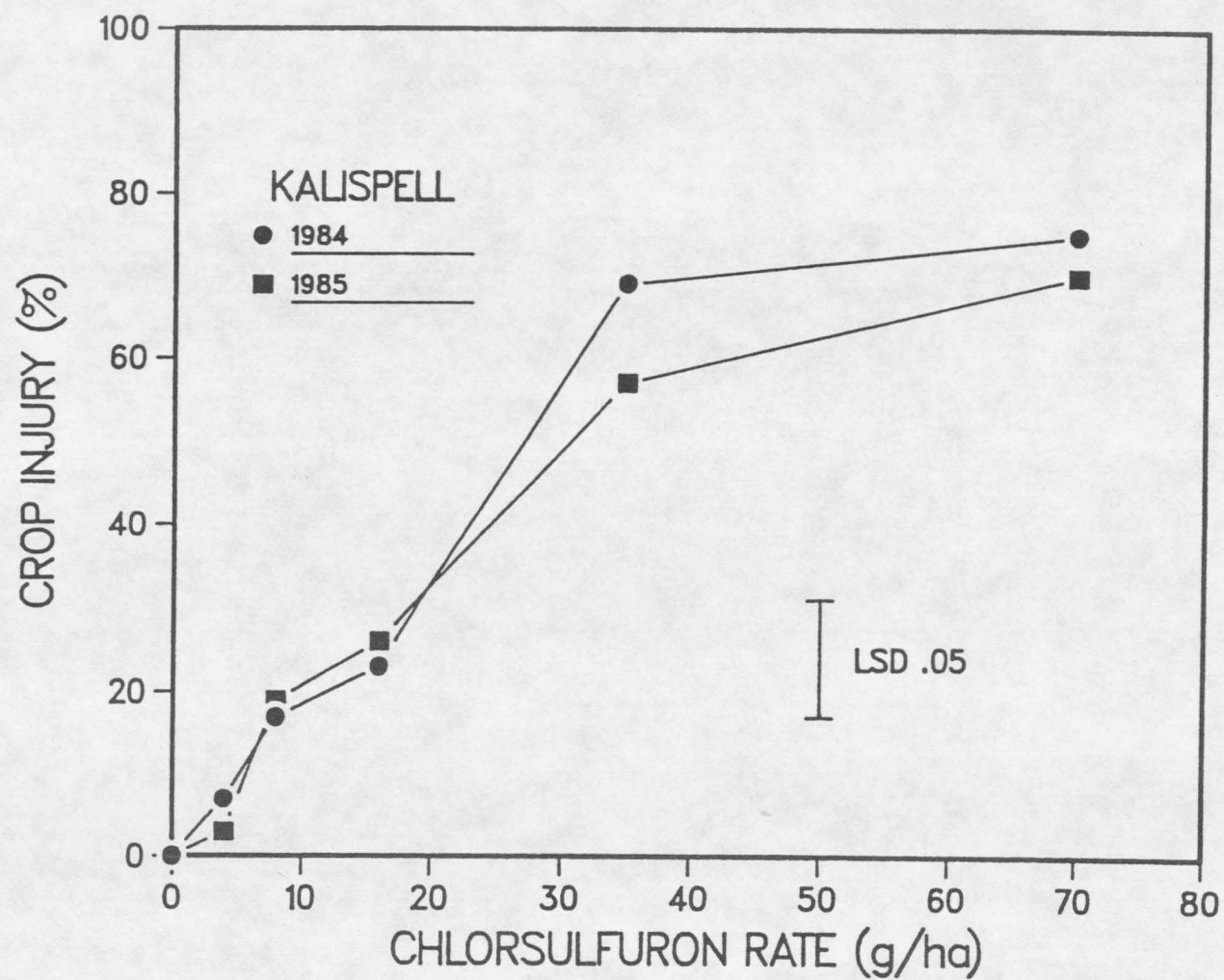


Figure 10. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Kalispell, Montana.

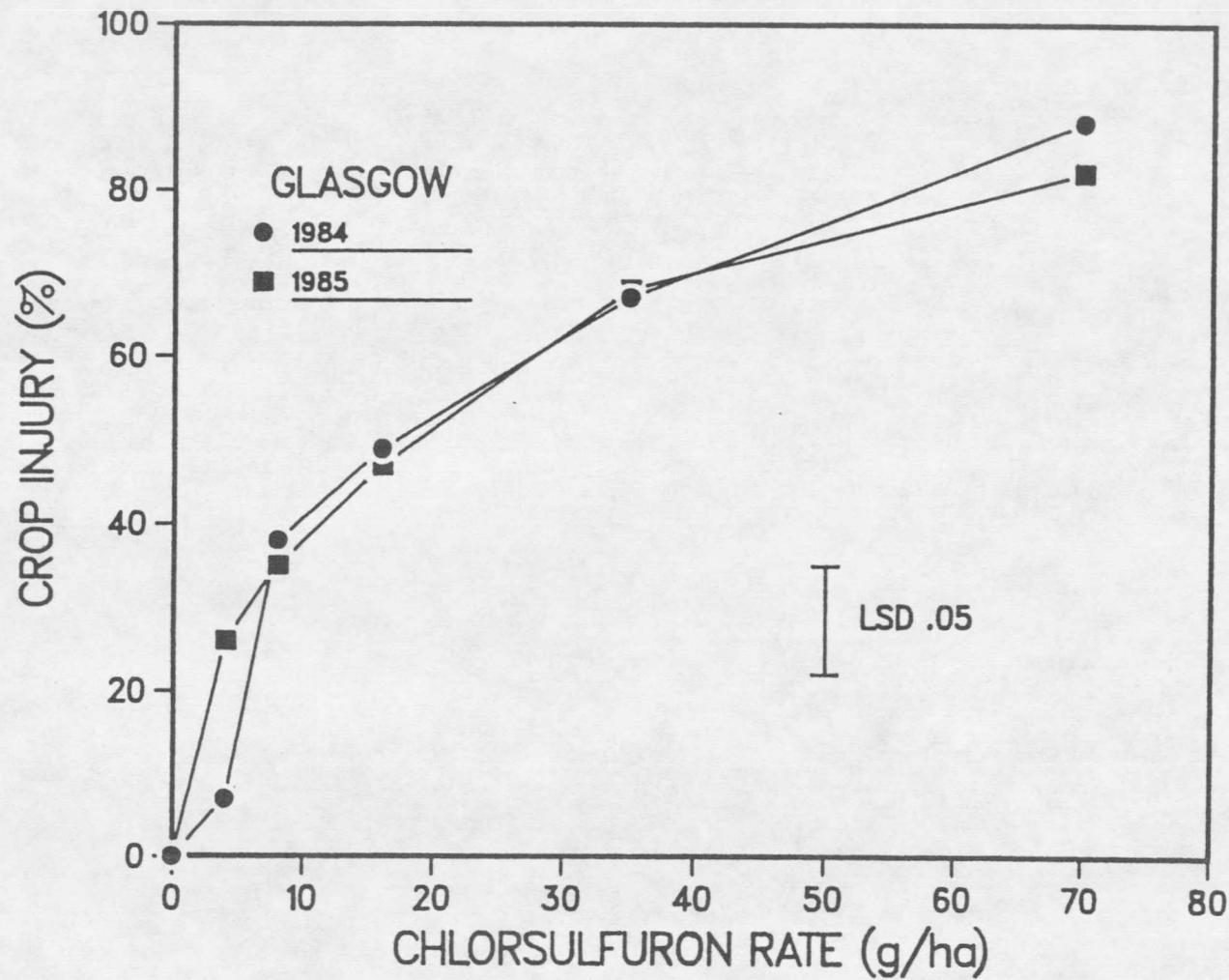


Figure 11. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron at Glasgow, Montana.

in 1983. This is approximately 40% of the amount recieved at Bozeman or Kalispell in the same period of time. Chlorsulfuron dissipates very slowly in dry environments.

All Locations Combined

The combination of all rates and all locations showed that crop injury decreased significantly from 1984 to 1985 only at the two highest rates of application (35 and 70 g/ha) (Figure 12). Crop injury decreased approximately 30% on plots treated with 35 and 70 g/ha. While the decrease in crop injury was not significant at 8 and 16 g/ha, percent crop injury declined 2% and 16%, respectively, at these rates. There was no decrease in crop injury at 4 g/ha. These results indicate that chlorsulfuron dissipation is minimal under dry conditions, and the rate of dissipation depends upon herbicide concentration.

The Predictive Model

One major objective of this study was to develop a simple model that can be used under field conditions to predict the rate of degradation of chlorsulfuron. An effective model would permit farmers to plan crop rotations without crop injury. Soil pH and annual precipitation are simple parameters that are readily available to farmers. These two parameters, which regulate chlorsulfuron dissipation, are all that is needed for the following model.

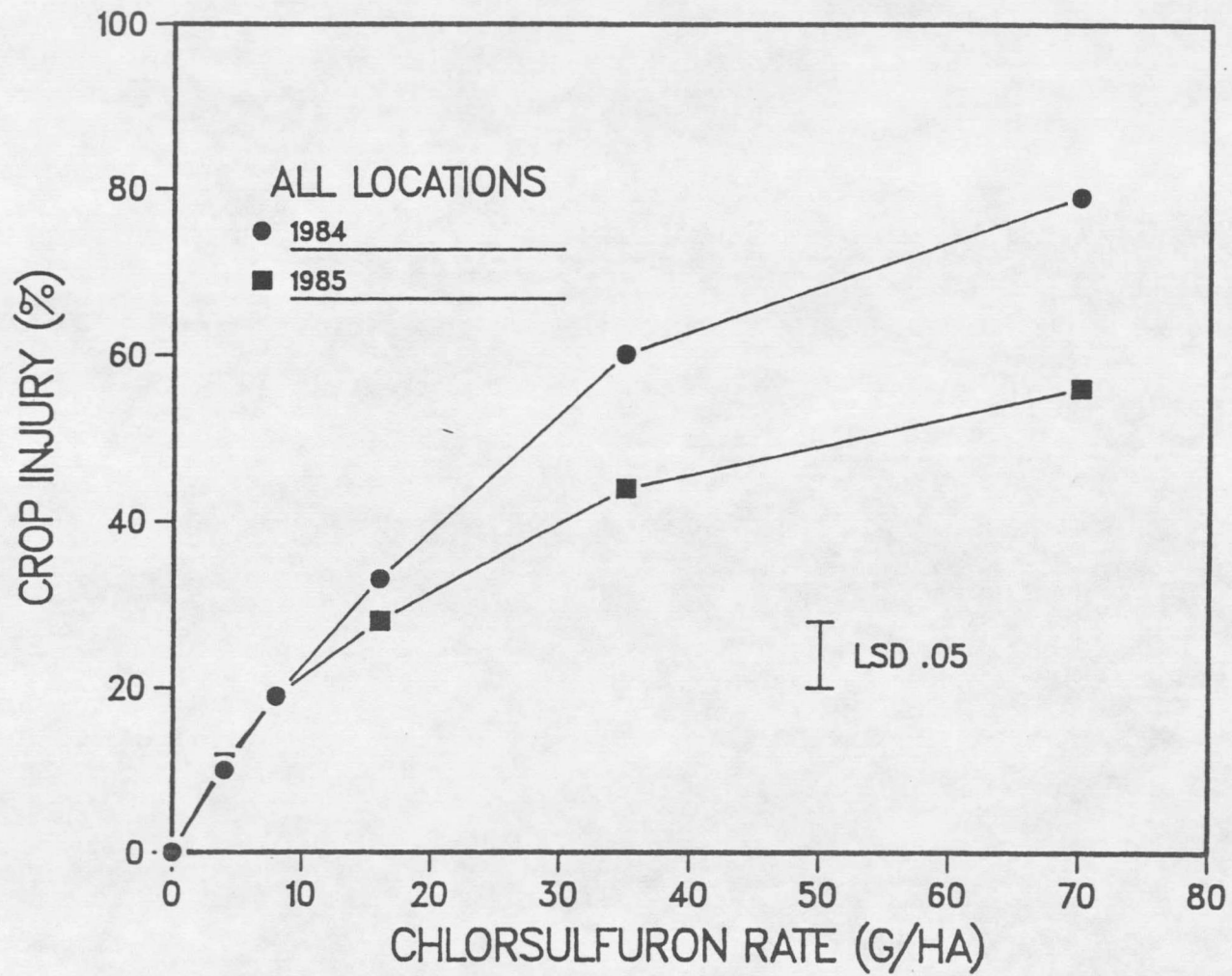


Figure 12. Percent injury to 12 crops in 1984 and 1985. The crops were planted 12 and 24 months after application of 5 rates of chlorsulfuron. These are the combined results of 5 locations in 1984 and 4 locations in 1985.

The model is based on percent crop injury measured at the four locations. It is divided into three categories based on soil pH and precipitation regimes. Category I is characterized by high precipitation levels and low soil pH. Category II has intermediate precipitation levels and intermediate soil pH, and category III contains low precipitation amounts coupled with high soil pH.

The potential for injury to the twelve crops used in this study 12 months after herbicide application is determined by finding the point on the X-1 axis of Figure 13 that corresponds to the pH of the field where the herbicide was applied. A line is then drawn from that point to the point on the X-2 axis corresponding to the precipitation received from the date of application of chlorsulfuron to the approximate planting date 12 months later. The line intersects the Y axis in the pH-precipitation category which corresponds to the field in question. Predictions of crop safety are provided for all crops in Table 13.

The potential for crop injury 24 months after herbicide application is determined by drawing a line from the X-1 axis to a point on the X-3 axis that corresponds to the amount of precipitation received during the 12 month period from 12 months after herbicide application until 24 months after herbicide application. The line intersects the pH-precipitation category that the field now corresponds to 24 months after herbicide application.

The model indicates that the rate of chlorsulfuron dissipation is slow, especially at lower rates of application. Crop safety ratings

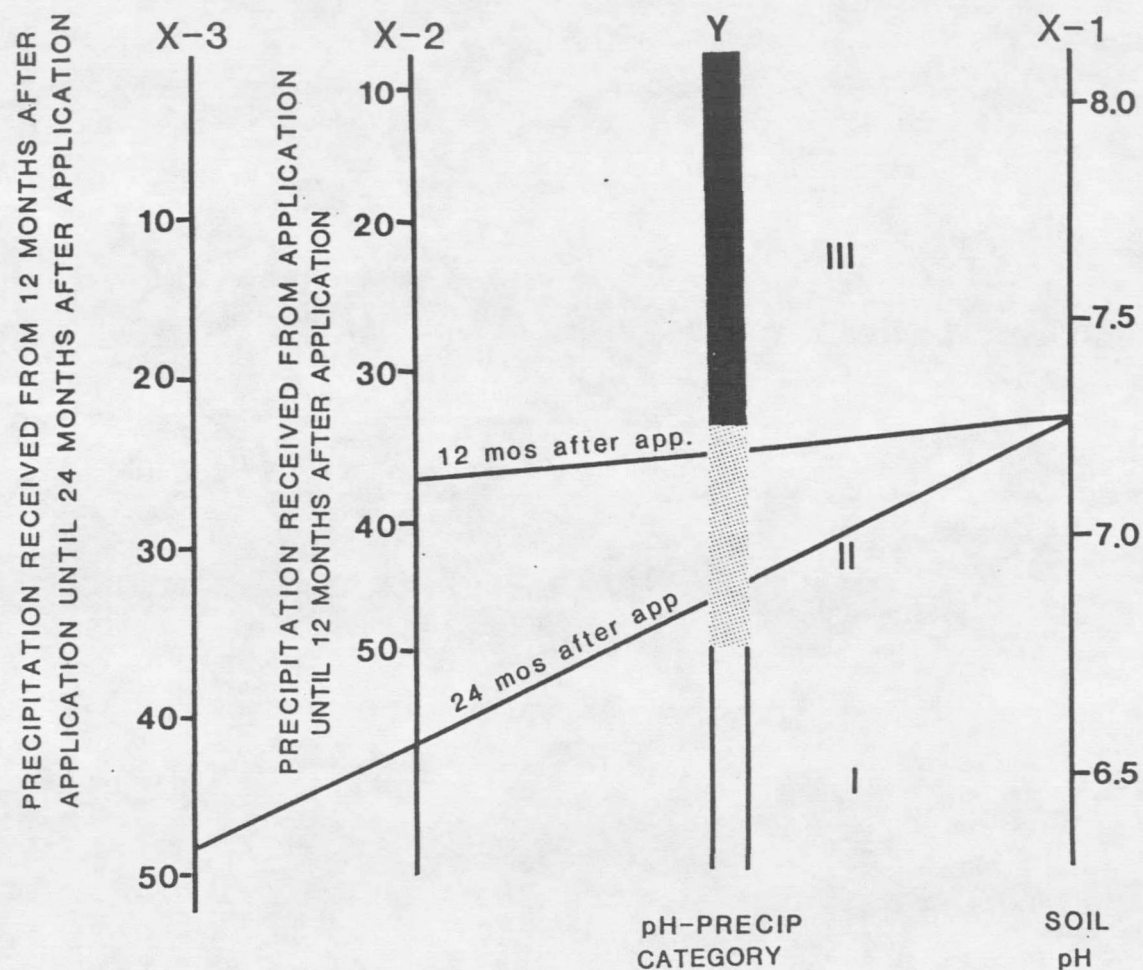


Figure 13. Nomogram showing the pH-precipitation categories resulting from various combinations of soil pH and precipitation from time of chlorsulfuron application to 12 months after application and precipitation from 12 months after application until 24 months after application.

Table 13. Crop safety ratings for 12 crops, 12 and 24 months after application of 5 rates of chlorsulfuron, for three pH-precipitation regimes.

		Soil-Precipitation Category														
		I					II					III				
Crop	Months After Application	Chlorsulfuron Rate (g/ha)														
		4	8	16	35	70	4	8	16	35	70	4	8	16	35	70
Barley	12	S	S	S	S	S	S	S	S	S	M	S	S	S	M	U
	24	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Safflower	12	S	S	S	S	S	S	S	S	M	U	S	S	M	U	U
	24	S	S	S	S	S	S	S	S	S	S	S	S	S	M	U
Potato	12	S	S	S	M	M	S	S	M	U	U	S	M	U	U	U
	24	S	S	S	S	M	S	S	S	M	M	S	S	M	U	U
Pinto	12	S	S	S	M	M	S	S	M	U	U	S	M	U	U	U
	24	S	S	S	S	M	S	S	S	M	M	S	S	M	U	U
Faba	12	S	S	M	M	U	M	M	U	U	U	M	U	U	U	U
	24	S	S	S	M	M	S	S	M	M	U	S	M	M	U	U
Sunflower	12	S	S	M	U	U	S	M	U	U	U	M	U	U	U	U
	24	S	S	S	M	M	S	S	S	M	U	S	M	U	U	U
Flax	12	S	S	M	M	U	S	M	U	U	U	M	U	U	U	U
	24	S	S	S	M	M	S	S	M	U	U	S	M	U	U	U
Garbanzo	12	S	S	M	M	U	M	U	U	U	U	M	U	U	U	U
	24	S	S	S	M	M	S	S	M	U	U	S	M	U	U	U
Corn	12	S	M	U	U	U	M	U	U	U	U	U	U	U	U	U
	24	S	S	M	M	U	S	M	U	U	U	M	M	U	U	U
SugarBeet	12	S	M	U	U	U	M	U	U	U	U	U	U	U	U	U
	24	S	M	M	M	U	S	M	U	U	U	M	U	U	U	U
Alfalfa	12	S	M	U	U	U	U	U	U	U	U	U	U	U	U	U
	24	M	M	M	U	U	M	M	U	U	U	M	U	U	U	U
Lentil	12	M	M	U	U	U	M	U	U	U	U	U	U	U	U	U
	24	M	M	M	U	U	M	M	U	U	U	M	U	U	U	U

S = No yield reduction M = High probability of yield reduction
 U = Crop will be severely damaged.

did not change very much from 1984 to 1985, particularly at 16 g/ha which is the recommended use rate in Montana. The model shows how dependent dissipation is upon soil pH and precipitation since crop safety ratings for category I are very different from those of category III.

Summary

Dissipation of chlorsulfuron in soil is dependent upon soil pH and precipitation. Dissipation occurs more rapidly at low soil pH and high precipitation than it does at high soil pH and low precipitation.

Crop rotation options after chlorsulfuron use in Montana depend upon the crop to be planted, the rate of chlorsulfuron originally applied, soil pH and precipitation. Several crop rotation options exist both 12 and 24 months following chlorsulfuron application in Montana.

In most of the major agricultural areas in Montana, soil pH is high and precipitation is low. Under these conditions soil residues of chlorsulfuron will persist for several years which will limit crop rotations. However the crop rotation of much of the area where chlorsulfuron is used is a wheat-summer fallow rotational system. Wheat is not injured by chlorsulfuron soil residues, therefore the herbicide residue is beneficial since the extended period of control lasts well into the fallow season.

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APPENDICES

APPENDIX A

**TABLES SHOWING THE RESULTS OF CHLORSULFURON
LEACHING AND ADSORPTION STUDIES**

Table 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.

SOIL DEPTH (cm.)	SOIL WEIGHT	DPM/GM SOIL	TOTAL DPM PER 2.5 CM	PERCENT OF RADIOACTIVITY RECOVERED
2.5	37.47	3299.16	45395.75	52.58
5.0	41.68	468.47	19582.25	8.48
7.5	45.60	421.72	19057.75	8.25
10.0	46.65	366.12	16946.00	7.36
12.5	49.60	302.35	14674.12	6.37
15.0	52.64	249.78	12813.87	5.53
17.5	52.36	177.26	9041.87	3.88
20.0	53.87	130.47	6947.37	2.97
22.5	53.73	75.13	3878.87	1.62
25.0	49.66	47.30	2190.00	0.91
27.5	50.65	42.53	1972.75	0.78
30.0	38.13	40.28	1381.50	0.55

Table 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.

SOIL DEPTH (cm)	SOIL WEIGHT	DPM/GM SOIL	TOTAL DPM PER 2.5 CM	PERCENT OF RADIOACTIVITY RECOVERED
2.5	33.32	263.12	8753.50	3.85
5.0	42.46	275.91	11550.75	5.06
7.5	46.58	310.60	13752.25	6.02
10.0	42.70	541.77	23254.25	0.29
12.5	44.84	656.42	29032.37	2.76
15.0	48.09	665.06	31553.37	3.78
17.5	49.07	623.13	31060.12	3.55
20.0	50.19	484.73	24138.50	0.52
22.5	50.43	417.01	20784.87	9.08
25.0	49.63	311.65	15041.00	6.57
27.5	52.80	202.28	10886.87	4.78
30.0	48.05	203.51	10246.50	4.51

Table 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.

Soil Type	DPM in Supernatant before Equilibration	DPM in Supernatant after Equilibration	Chlorsulfuron Concentration in Supernatant after Equilibration ng/ml	Chlorsulfuron Concentration in Soil after Equilibration ng/ml	Log Chlorsulfuron Concentration in Supernatant after Equilibration	Log Chlorsulfuron Concentration in Soil after Equilibration
Bozeman SiL	787.40	683.26	0.68	1.04	-.11	0.00
	1575.29	1183.85	1.19	3.94	0.07	0.58
	2362.69	1833.20	1.84	5.33	0.26	0.70
	3150.60	2296.05	2.31	8.60	0.36	0.93
	3937.95	2962.86	2.98	9.85	0.47	0.97
	4914.85	3500.86	3.52	14.24	0.54	1.13
	5702.25	4209.35	4.24	15.04	0.62	1.15
	6490.14	4771.73	4.80	17.31	0.67	1.22
Pierre Cl	831.25	714.81	0.72	1.17	-.14	-.21
	1662.44	1348.36	1.35	3.16	0.13	0.49
	2493.69	2139.83	2.15	3.56	0.33	0.54
	3110.94	2607.50	2.62	5.07	0.41	0.69
	3942.20	3278.98	3.30	6.67	0.51	0.81
	2419.44	3858.00	3.88	9.21	0.58	0.95
	5604.64	4412.61	4.44	2.00	0.64	1.07
	6435.89	5091.51	5.12	3.53	0.70	1.13

Table 16 (con't)

Soil Type	DPM in Supernatant before Equilibration	DPM in Supernatant after Equilibration	Chlorsulfuron Concentration in Supernatant after Equilibration ng/ml	Chlorsulfuron Concentration in Soil after Equilibration ng/ml	Log Chlorsulfuron Concentration in Supernatant after Equilibration	Log Chlorsulfuron Concentration in Soil after Equilibration
Joplin SiCL	669.85	551.85	0.55	1.18	-.27	0.04
	1612.19	1278.48	1.28	3.36	0.10	0.50
	2271.30	1762.29	1.77	5.12	0.24	0.67
	2941.14	2226.36	2.24	7.19	0.35	0.83
	3611.00	2884.78	2.90	7.31	0.46	0.84
	4543.10	3645.70	3.67	9.03	0.56	0.93
	5223.64	4321.50	4.35	9.08	0.63	0.94
	5893.50	4832.63	4.86	0.68	0.68	1.01
Vananda CL	698.85	313.53	0.66	0.49	-.17	-.39
	1713.19	926.25	1.57	1.46	0.19	0.12
	2412.10	1202.43	2.12	3.01	0.32	0.41
	3110.95	1526.71	2.67	4.60	0.42	0.61
	3809.79	1807.11	3.27	5.63	0.51	0.70
	4508.64	2071.98	3.85	6.82	0.58	0.81
	5523.04	2592.98	4.73	8.34	0.67	0.91
	6221.89	2957.06	5.32	9.47	0.72	0.96

Table 16 (con't)

Soil Type	DPM in Supernatant before Equilibration	DPM in Supernatant after Equilibration	Chlorsulfuron Concentration in Supernatant after Equilibration ng/ml	Chlorsulfuron Concentration in Soil after Equilibration ng/ml	Log Chlorsulfuron Concentration in Supernatant after Equilibration	Log Chlorsulfuron Concentration in Soil after Equilibration
Kalispell SiL	814.60	790.16	0.79	0.48	-.09	-.40
	1629.70	1480.01	1.49	1.50	0.17	0.12
	2239.30	1977.80	1.99	2.63	0.29	0.38
	3054.39	2628.11	2.64	4.29	0.41	0.60
	3869.00	3351.68	3.37	5.21	0.52	0.70
	4478.10	3721.30	3.74	7.61	0.57	0.85
	5292.70	4553.78	4.58	7.44	0.66	0.83
	6107.80	5149.00	5.18	9.65	0.71	0.97
Judith- Danvers L	852.35	807.80	0.81	0.56	-.09	-.26
	1704.70	1566.88	1.57	1.38	0.19	-.02
	2340.70	2206.01	2.20	1.35	0.34	-.28
	3120.75	2887.56	2.90	2.34	0.46	0.31
	3882.75	3496.63	3.52	3.89	0.54	0.53
	4644.75	3903.80	3.90	7.46	0.59	0.85
	5460.94	4799.95	4.83	6.65	0.68	0.81
	6223.44	5391.13	5.43	8.38	0.73	0.91

APPENDIX B

TABLES SHOWING THE RESULTS OF CHLORSULFURON PLANTBACK
STUDIES AT FIVE LOCATIONS FOR TWO YEARS IN MONTANA

Table 17. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	2859.	3110.	2412.	2199.	2534.	2921.
% of CHECK	97.00	106.0	82.02	74.00	85.80	100.0
LENTILS						
DRY WT	41.50	20.75	11.00	.0000	.0000	32.25
% OF CHECK	137.4	60.05	47.95	.0000	.0000	100.0
ALFALFA						
DRY WT	28.75	26.50	14.75	9.250	.0000	35.75
% OF CHECK	96.32	92.85	51.45	47.70	.0000	100.0
SUGAR BEET						
DRY WT	52.00	65.50	52.25	14.75	.0000	78.00
% OF CHECK	82.22	72.80	68.57	23.50	.0000	100.0
FLAX						
DRY WT	27.50	28.00	23.75	23.00	8.750	29.00
% OF CHECK	93.92	101.0	67.97	116.8	54.58	100.0
POTATO						
DRY WT	324.0	283.0	219.7	170.0	109.3	253.0
% OF CHECK	140.1	118.2	95.85	76.93	52.67	100.0
SAFFLOWER						
DRY WT	164.0	185.0	245.2	236.7	172.0	188.8
% OF CHECK	88.85	100.7	129.0	135.0	95.95	100.0
FABA BEAN						
DRY WT	85.00	78.50	61.00	38.00	29.50	86.75
% OF CHECK	102.1	95.72	70.50	51.27	30.77	100.0
GARBANZO BEAN						
DRY WT	174.0	165.2	186.7	148.0	39.50	182.5
% OF CHECK	94.15	100.0	92.90	90.60	23.88	100.0

Table 17 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTOBEAN						
DRY WT	75.00	103.5	58.50	105.8	23.00	84.75
% OF CHECK	89.97	126.4	65.92	124.6	29.98	100.0
SUNFLOWER						
DRY WT	820.5	783.0	869.0	355.5	.0000	751.5
% OF CHECK	117.8	106.9	117.7	48.93	.0000	100.0
CORN						
DRY WT	147.8	194.5	142.0	154.0	28.00	209.5
% OF CHECK	49.77	99.85	141.6	87.68	53.85	100.0

* Grain yield value in kg/ha

Table 18. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CHLORSULFURON RATE (g/ha)						
CROP	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	1204	1295	1357	1215	1198	1258
% OF CHECK	100.8	110.4	110.8	102.3	102.6	100.0
LENTILS						
DRY WT	251.5	148.7	160.5	127.0	76.75	302.0
% OF CHECK	89.45	47.20	44.62	30.52	18.65	100.0
ALFALFA						
DRY WT	140.5	123.0	96.25	88.50	72.25	179.8
% OF CHECK	84.85	73.32	59.27	54.27	42.67	100.0
SUGAR BEET						
DRY WT	1423.	1420.	969.7	816.0	528.3	1443.
% OF CHECK	104.7	97.40	71.63	56.65	36.85	100.0
FLAX						
DRY WT	346.5	388.3	348.5	380.2	341.5	357.6
% OF CHECK	99.47	116.3	110.9	113.2	108.2	100.0
POTATO						
DRY WT	6172.	6873.	5708.	6678.	5308.	6410.
% OF CHECK	97.12	109.9	91.12	105.6	83.62	100.0
SAFFLOWER						
DRY WT	320.8	254.8	266.0	266.5	309.2	244.2
% OF CHECK	135.1	107.7	108.2	107.2	123.9	100.0
FABA BEAN						
DRY WT	225.5	306.0	236.0	208.5	190.8	272.5
% OF CHECK	85.77	107.5	85.22	80.17	67.17	100.0
GARBANZO BEAN						
DRY WT	93.75	103.0	105.5	84.00	62.50	129.5
% OF CHECK	77.63	72.52	72.40	47.85	43.50	100.0

Table 18 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	153.8	141.5	128.2	130.2	79.00	181.7
% OF CHECK	95.15	83.27	77.85	82.40	41.58	100.0
SUNFLOWER						
DRY WT	4603.	3905.	4236.	3692.	3329.	4924.
% OF CHECK	96.05	83.77	91.07	79.87	70.7	100.0
CORN						
DRY WT	1378.	1442.	1263.	1200.	1173.	2014.
% OF CHECK	86.32	74.50	72.70	61.02	68.30	100.0

* Grain yield value in kg/ha

Table 19. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	4939.	4274.	4655.	3600.	3603.	4232.
% OF CHECK	117.7	100.9	109.9	84.90	85.22	100.0
LENTILS						
DRY WT	27.25	23.75	9.750	.0000	.0000	63.75
% OF CHECK	44.45	54.52	28.77	.0000	.0000	100.0
ALFALFA						
DRY WT	70.00	77.25	27.75	8.500	.0000	106.5
% OF CHECK	70.47	85.62	35.72	11.18	.0000	100.0
SUGAR BEET						
DRY WT	45.00	33.50	14.50	.0000	.0000	66.50
% OF CHECK	78.50	49.65	15.58	.0000	.0000	100.0
FLAX						
DRY WT	39.75	25.25	17.75	.0000	.0000	40.25
% OF CHECK	98.40	66.75	42.15	.0000	.0000	100.0
POTATO						
DRY WT	200.2	169.2	260.8	63.50	26.25	230.0
% OF CHECK	87.05	76.20	112.3	29.13	10.27	100.0
SAFFLOWER						
DRY WT	243.7	211.7	297.7	193.3	182.2	264.8
% OF CHECK	95.10	84.50	118.6	74.77	68.30	100.0
FABA BEAN						
DRY WT	209.2	163.0	194.2	125.3	81.75	306.0
% OF CHECK	104.0	93.30	121.0	70.70	45.90	100.0
GARBANZO BEAN						
DRY WT	293.0	269.2	171.5	62.50	27.00	341.5
% OF CHECK	88.22	81.15	52.08	15.97	5.975	100.0

Table 19 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	294.5	185.2	265.8	198.5	170.5	265.5
% OF CHECK	127.0	86.77	125.8	85.07	81.60	100.0
SUNFLOWER						
DRY WT	993.7	1001.	842.0	.0000	.0000	724.2
% OF CHECK	138.2	137.0	123.0	.0000	.0000	100.0
CORN						
DRY WT	659.5	631.0	325.5	.0000	.0000	927.5
% OF CHECK	72.67	74.62	34.33	.0000	.0000	100.0

* Grain yield value in kg/ha

Table 20. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	1563.	1452.	1716.	1721.	1643.	1469.
% OF CHECK	106.1	99.32	117.2	118.0	114.6	100.0
LENTILS						
DRY WT	50.25	7.000	7.750	.0000	.0000	81.50
% OF CHECK	65.42	7.975	16.58	.0000	.0000	100.0
ALFALFA						
DRY WT	155.2	101.3	28.25	.0000	.0000	204.2
% OF CHECK	100.9	56.58	38.50	.0000	.0000	100.0
SUGAR BEET						
DRY WT	320.5	177.3	185.2	.0000	.0000	315.2
% OF CHECK	101.4	55.15	56.75	.0000	.0000	100.0
FLAX						
DRY WT	394.5	258.7	221.2	6.750	1.000	387.3
% OF CHECK	102.3	66.63	54.45	1.625	.2500	100.0
POTATO						
DRY WT	4779.	4658.	4100.	3277.	2858.	4674.
% OF CHECK	103.5	98.97	88.05	68.42	58.10	100.0
SAFFLOWER						
DRY WT	552.3	772.2	533.0	604.8	421.0	625.2
% OF CHECK	81.02	131.2	86.15	101.4	65.52	100.0
FABA BEAN						
DRY WT	107.7	83.75	86.25	62.50	23.00	129.5
% OF CHECK	97.93	66.50	82.27	47.33	20.30	100.0
GARBANZO BEAN						
DRY WT	46.00	54.00	52.00	13.25	3.250	59.75
% OF CHECK	83.90	92.63	105.9	40.40	4.950	100.0

Table 20 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	153.0	115.7	148.0	99.50	85.50	145.0
% OF CHECK	105.8	92.90	108.0	80.17	64.67	100.0
SUNFLOWER						
DRY WT	626.0	451.7	284.2	.0000	19.25	516.5
% OF CHECK	127.5	103.6	53.20	.0000	3.225	100.0
CORN						
DRY WT	1144.		976.5	687.3	401.0	1253.
% OF CHECK	90.50	96.70	77.07	53.75	32.58	100.0

* Grain yield value in kg/ha

Table 21. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	5485.	5472.	5347.	5455.	4961.	5729.
% OF CHECK	98.32	98.12	97.65	97.53	88.72	100.0
LENTILS						
DRY WT	47.00	52.00	37.25	.0000	.0000	91.00
% OF CHECK	63.22	67.25	38.95	.0000	.0000	100.0
ALFALFA						
DRY WT	54.25	55.00	80.00	9.750	.0000	74.50
% OF CHECK	86.17	80.17	91.30	21.87	.0000	100.0
SUGAR BEET						
DRY WT	391.0	290.5	247.5	171.0	.0000	501.0
% OF CHECK	91.62	66.63	57.80	36.77	.0000	100.0
FLAX						
DRY WT	48.25	47.50	24.50	22.75	.0000	56.00
% OF CHECK	85.22	82.10	42.92	39.85	.0000	100.0
POTATO						
DRY WT	187.3	163.0	129.8	121.0	114.8	272.0
% OF CHECK	78.67	69.27	55.85	50.52	46.75	100.0
SAFFLOWER						
DRY WT	439.5	470.2	429.5	275.2	185.2	558.7
% OF CHECK	78.57	81.95	77.05	50.08	33.25	100.0
FABA BEAN						
DRY WT	148.5	177.0	127.5	90.75	13.75	255.5
% OF CHECK	59.20	68.95	52.10	34.45	6.050	100.0
GARBANZO BEAN						
DRY WT	446.7	337.3	240.0	143.3	.0000	598.7
% OF CHECK	75.17	56.55	40.77	24.47	.0000	100.0

Table 21 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	160.5	143.0	107.0	105.5	47.75	181.2
% OF CHECK	91.07	81.82	61.05	59.68	26.50	100.0
SUNFLOWER						
DRY WT	838.8	865.0	781.7	513.0	.0000	1273.
% OF CHECK	77.85	87.50	59.13	48.43	.0000	100.0
CORN						
DRY WT	588.8	575.0	347.0	380.0	62.00	1059.
% OF CHECK	59.53	60.70	31.87	33.90	7.775	100.0

* Grain yield value in kg/ha

Table 22. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	4602.	3927.	4409.	4985.	5690.	4009.
% OF CHECK	121.3	99.42	116.3	128.2	151.9	100.0
LENTILS						
DRY WT	257.0	249.2	159.3	150.0	158.5	264.2
% OF CHECK	97.22	95.32	59.80	56.60	61.38	100.0
ALFALFA						
DRY WT	199.8	182.5	165.5	138.0	94.75	249.2
% OF CHECK	80.80	74.02	66.45	56.48	39.13	100.0
SUGAR BEET						
DRY WT	231.7	249.0	211.7	172.7	119.7	281.2
% OF CHECK	82.85	87.60	74.85	63.15	42.83	100.0
FLAX						
DRY WT	204.8	202.7	160.5	148.5	101.5	225.2
% OF CHECK	91.37	91.40	72.55	66.52	44.98	100.0
POTATO						
DRY WT	4918.	5751.	3820.	3238.	2322.	5228.
% OF CHECK	100.4	113.1	74.52	66.35	40.58	100.0
SAFFLOWER						
DRY WT	324.5	417.5	293.5	321.0	256.2	401.0
% OF CHECK	82.60	114.7	78.12	89.65	71.30	100.0
FABA BEAN						
DRY WT	401.5	444.5	406.0	361.5	321.2	476.7
% OF CHECK	81.30	95.97	88.20	77.88	70.45	100.0
GARBANZO BEAN						
DRY WT	385.8	421.2	477.0	386.5	309.2	516.0
% OF CHECK	77.42	81.95	91.32	76.07	60.55	100.0

Table 22 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	190.2	213.5	203.5	224.5	165.2	294.5
% OF CHECK	66.35	75.45	69.97	77.12	54.15	100.0
SUNFLOWER						
DRY WT	3697.	2982.	3520.	2720.	1572.	4121.
% OF CHECK	92.40	77.45	90.02	65.10	40.18	100.0
CORN						
DRY WT	1444.	1253.	1207.	1036.	828.0	1847.
% OF CHECK	80.25	69.30	68.60	58.00	45.08	100.0

* Grain yield value in kg/ha

Table 23. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	84.75	66.25	75.75	43.25	29.50	72.50
% OF CHECK	123.1	103.8	128.1	66.85	54.65	100.0
LENTILS						
DRY WT	.5000	.0000	.0000	.5000	.0000	5.750
% OF CHECK	14.82	.0000	.0000	9.100	.0000	100.0
ALFALFA						
DRY WT	3.750	2.750	.0000	.0000	.0000	3.500
% OF CHECK	104.5	110.1	.0000	.0000	.0000	100.0
SUGAR BEET						
DRY WT	18.25	10.25	8.000	.0000	.5000	23.50
% OF CHECK	128.9	63.18	52.45	.0000	2.650	100.0
FLAX						
DRY WT	5.750	5.750	6.750	.0000	.0000	7.500
% OF CHECK	72.52	83.88	69.05	.0000	.0000	100.0
POTATO						
DRY WT	156.7	116.0	48.50	26.75	25.00	207.2
% OF CHECK	101.2	68.65	28.12	14.40	13.53	100.0
SAFFLOWER						
DRY WT	41.50	37.00	28.75	10.50	2.500	34.00
% OF CHECK	125.5	111.6	90.72	29.52	8.400	100.0
FABA BEAN						
DRY WT	28.75	23.50	12.75	6.500	.0000	36.75
% OF CHECK	88.07	68.65	41.25	18.22	.0000	100.0
GARBANZO BEAN						
DRY WT	38.25	24.50	3.250	.0000	.0000	52.50
% OF CHECK	76.65	47.27	6.225	.0000	.0000	100.0

Table 23 (con't.)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	16.75	11.50	4.000	1.500	.0000	19.00
% OF CHECK	93.50	51.83	36.05	5.200	.0000	100.0
SUNFLOWER						
DRY WT	193.3	173.5	133.0	.0000	.0000	196.2
% OF CHECK	102.7	95.07	69.02	.0000	.0000	100.0
CORN						
DRY WT	9.750	14.75	16.25	.0000	.0000	53.75
% OF CHECK	20.62	26.83	29.72	.0000	.0000	100.0

* Grain yield value in kg/ha

Table 24. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	704.0	822.5	860.1	932.3	652.2	739.2
% OF CHECK	101.0	112.0	118.1	129.3	92.02	100.0
LENTILS						
DRY WT	11.50	8.000	3.600	.5500	.0000	23.20
% OF CHECK	52.77	38.77	16.45	2.250	.0000	100.0
ALFALFA						
DRY WT	8.325	6.750	1.800	.0000	.0000	19.25
% OF CHECK	44.47	37.02	11.90	.0000	.0000	100.0
SUGAR BEET						
DRY WT	54.77	42.12	16.43	.0000	.0000	78.00
% OF CHECK	71.55	57.05	19.37	.0000	.0000	100.0
FLAX						
DRY WT	36.08	30.17	25.75	5.175	.0000	37.73
% OF CHECK	95.13	78.02	65.27	13.15	.0000	100.0
POTATO						
DRY WT	67.77	46.23	58.12	38.92	28.25	86.92
% OF CHECK	82.63	54.08	71.47	44.52	36.30	100.0
SAFFLOWER						
DRY WT	167.9	184.6	149.6	74.27	32.92	198.5
% OF CHECK	91.90	88.28	78.37	38.08	16.17	100.0
FABA BEAN						
DRY WT	104.4	93.80	85.10	61.48	33.55	144.1
% OF CHECK	72.65	64.82	58.93	42.12	22.83	100.0
GARBANZO BEAN						
DRY WT	42.37	42.50	37.00	12.57	2.350	53.60
% OF CHECK	78.37	77.65	69.42	23.05	4.400	100.0

Table 24 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN	17.52	15.45	14.45	12.00	8.225	21.45
DRY WT	79.85	73.75	67.17	54.90	40.60	100.0
% OF CHECK						
SUNFLOWER	260.2	228.9	158.1	113.8	31.55	352.3
DRY WT	71.12	65.55	45.70	29.45	8.450	100.0
% OF CHECK						
CORN	25.40	14.40	5.050	2.075	.0000	51.10
DRY WT	49.83	30.70	8.650	3.275	.0000	100.0
% OF CHECK						

* Grain yield value in kg/ha

Table 25. The dry weight (grams) of the biomass of 1 meter of 1 row of 12 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	27.08	22.85	20.39	19.58	12.91	28.86
% of CHECK	95.70	81.70	77.05	73.70	42.65	100.0
LENTILS						
DRY WT	.9200	.8400	.9375	.0200	.0000	9.977
% OF CHECK	13.62	22.55	33.12	.3000	.0000	100.0
ALFALFA						
DRY WT	3.340	1.045	.0000	1.503	.0000	6.712
% OF CHECK	53.30	16.95	.0000	25.18	.0000	100.0
SUGAR BEET						
DRY WT	8.135	3.432	.0000	.0000	.0000	12.88
% OF CHECK	59.67	26.08	.0000	.0000	.0000	100.0
FLAX						
DRY WT	8.847	5.500	4.137	3.320	.0000	8.185
% OF CHECK	130.3	111.1	36.23	36.87	.0000	100.0
POTATO						
DRY WT	148.3	131.8	116.4	65.72	49.54	165.1
% OF CHECK	103.1	79.40	97.72	61.12	48.43	100.0
SAFFLOWER						
DRY WT	29.30	23.63	28.94	26.81	8.060	32.71
% OF CHECK	96.10	77.72	84.35	88.65	23.18	100.0
FABA BEAN						
DRY WT	24.63	14.82	17.71	6.450	1.740	17.63
% OF CHECK	139.8	83.65	101.4	36.95	10.70	100.0
GARBANZO BEAN						
DRY WT	54.05	24.12	19.54	3.087	.0000	58.98
% OF CHECK	94.10	44.08	36.77	7.050	.0000	100.0

Table 25 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	35.43	18.99	20.73	9.485	3.285	21.88
% OF CHECK	157.4	87.17	101.3	51.58	14.80	100.0
SUNFLOWER						
DRY WT	90.24	48.27	8.205	.0000	.0000	115.8
% OF CHECK	91.75	54.70	6.650	.0000	.0000	100.0
CORN						
DRY WT	53.92	45.56	27.58	9.655	2.430	78.21
% OF CHECK	70.97	63.80	38.02	13.00	4.475	100.0

* Grain yield value in kg/ha

Table 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.

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
BARLEY						
GRAIN YIELD*	85.77	105.9	230.8	270.0	247.3	362.0
% of CHECK	100.0	176.9	446.7	515.4	681.6	453.1
LENTILS						
DRY WT	8.450	12.65	11.67	4.750	5.500	2.150
% OF CHECK	100.0	219.7	181.8	100.5	74.13	49.15
ALFALFA						
DRY WT	6.650	5.825	4.925	2.550	3.525	3.050
% OF CHECK	100.0	89.22	86.82	48.83	64.15	48.27
SUGAR BEET						
DRY WT	54.62	39.75	26.45	20.70	22.37	5.875
% OF CHECK	100.0	73.32	47.70	37.05	39.95	10.20
FLAX						
DRY WT	17.80	22.92	18.73	14.60	15.50	15.58
% OF CHECK	100.0	129.7	106.4	85.95	88.67	88.42
POTATO						
DRY WT	99.20	100.8	85.72	90.32	73.22	42.18
% OF CHECK	100.0	100.2	83.55	91.00	75.95	43.58
SAFFLOWER						
DRY WT	43.00	35.20	39.65	31.25	30.48	31.95
% OF CHECK	100.0	90.12	98.45	78.85	75.82	81.20
FABA BEAN						
DRY WT	14.72	24.55	17.48	17.90	13.73	13.07
% OF CHECK	100.0	178.8	120.3	131.4	98.82	112.7
GARBANZO BEAN	(NOT HARVESTED IN 1985)					
DRY WT						
% OF CHECK						

Table 26 (con't)

CROP	CHLORSULFURON RATE (g/ha)					
	4	8	16	35	70	CK
PINTO BEAN						
DRY WT	32.95	38.98	36.08	23.90	35.30	19.10
% OF CHECK	100.0	123.7	112.9	79.75	110.5	64.30
SUNFLOWER						
DRY WT	118.1	85.57	77.60	66.27	77.42	39.15
% OF CHECK	100.0	73.92	64.42	56.08	63.15	32.05
CORN						
DRY WT	59.85	47.95	60.92	68.27	56.48	23.25
% OF CHECK	100.0	89.55	106.6	123.3	101.7	50.52

* Grain yield value in kg/ha

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