DISSIPATION OF [¹⁴C]AMIDOSULFURON (HOE 075032) IN PRAIRIE SOILS

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by

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ABSTRACT

DISSIPATION OF [^{14}C]AMIDOSULFURON (HOE 075032) IN PRAIRIE SOILS

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The degradation of the herbicide [^{14}C]amidosulfuron (HOE 075032) was studied in two Saskatchewan (SK) and one Manitoba (MB) soil. The half-life of [^{14}C] amidosulfuron, calculated at the 0-5 cm soil depth, when applied at 97 g/ha ranged from 256 ± 9 days (mean $\pm$ standard deviation) in the fine-loamy soil from Minto, MB to 13 ± 1 days in the fine-silty soil from Swift Current, SK. In the coarse-loamy soil from Bradwell, SK, the half-life of [^{14}C]amidosulfuron was 29 ± 1 days. Herbicide degradation followed first-order dissipation kinetics in all three soils. There was less movement of [^{14}C] amidosulfuron in the soil from Manitoba compared to both soils from Saskatchewan. The higher pH of the Minto, MB soil, and the drier, cooler climatic conditions, may account for the longer half-life of amidosulfuron in this soil.

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1.0 GENERAL INTRODUCTION

The sulfonylureas were discovered in 1975 by Dr. George Levitt of Du Pont (Beyer *et al.*, 1987). They were reported to give unprecedented herbicidal activity (2 to 8 g/ha) when compared to traditional herbicide chemistry of that era (1 to 4 kg/ha). At present, 20 sulfonylureas are commercialized worldwide and more are being developed for use in the near future (Dinelli *et al.*, 1997). The sulfonylureas have been adapted for use in a wide range of agricultural crops (Table 1.1) from Canadian dryland barley to tropical paddy rice to intensively managed wheat/sugarbeet rotations in Europe. In 1994 it was estimated that more than 57 million hectares were treated with sulfonylurea herbicides (Brown *et al.*, 1995). They have provided excellent control of difficult to control weeds (*Stellaria media*, *Veronica* sp., *Polygonum aviculare*, *Galium aparine*, *Matricaria inodorum* and *Chenopodium album*) (Table 1.2) in a number of major crops.

Table 1.1 Use and application rate of sulfonylurea herbicides (Adapted from Beyer *et al.*, 1988).

Sulfonylurea	Use	Rate (g ai/ha)
Chlorsulfuron	Cereals	4- 26
Chlorsulfuron	Noncrop	13-158
Sulfometuron methyl	Noncrop	70-840
Metsulfuron methyl	Cereals	2- 8
Metsulfuron methyl	Noncrop	3-126
Chlorimuron ethyl	Soybeans	8- 13
Bensulfuron methyl	Rice	20- 75
DPX-M6316	Cereals	9- 53

The sulfonylureas have moderate to rapid dissipation rates in the field. One of specific criteria used to select new sulfonylurea herbicides has been selection for shorter soil dissipation half-lives. Most sulfonylureas are classified as having either high or very high mobility in soil. The pka for most herbicidal sulfonylureas range from 3 to 5 (Hay,

1990). Sorption to soil (K_{oc}) varies as a function of pH, with those sulfonylureas with pyrimidin heterocycles (chlorimuron ethyl and bensulfuron methyl) having higher K_{oc} than those with a triazine heterocycle. Sulfonylureas with low K_{oc} values, and hence low soil sorption, (i.e., $K_{oc}=50-100$) leach excessively and contaminate ground water primarily if they have long half-lives in soil (Brown *et al.*, 1995).

Table 1.2 Sulfonylurea herbicides for weed control in wheat and barley crops (Adapted from Brown *et al.*, 1995).

Active ingredient/ Application rate	First sales	Key uses
Chlorsulfuron 9-25 g ai/ha	1982	Residual broad spectrum broadleaf and select grass weeds, esp. in low rainfall cropping systems
Metsulfuron methyl 3-7.5 g ai/ha	1984	Moderate residual broad spectrum broadleaf weeds in low rainfall and intensive production
Thifensulfuron methyl 15-20 g ai/ha	1987	Broad spectrum broadleaf weeds in intensive cropping systems
Tribenuron methyl 9-18 g ai/ha	1987	Broad spectrum broadleaf weeds in low rainfall and extensively rotated systems
Triasulfuron 10-30 g ai/ha	1987	Residual broad spectrum broadleaf and select grass weeds, esp. in low rainfall cropping systems
Amidosulfuron 30-60 g ai/ha	1991	Select broadleaf weeds (esp. <i>Galium aparine</i>) in intensive cropping systems

1.1 Sulfonylurea Mobility and Degradation in Soil

The use of synthetic organic herbicides in agriculture over the past six decades has lead to concern about their fate and persistence in the environment. Specific concerns regarding the behavior of pesticides in soil include: persistence, transformation or accumulation in environmental compartments, formation of toxic degradation products, carry-over of residues that could injure subsequent crops, and effects on microbial biochemical processes in soil (Frehse and Anderson, 1983).

It is important to understand the factors influencing persistence of herbicide residues in soil to assess the potential of injury to subsequent crops by herbicide carry-

over. Soil persistence is dependent on factors such as herbicide chemical structure, herbicide physical properties (i.e. water solubility and volatility), soil adsorptive properties, soil temperature and moisture conditions, soil composition, and soil microbial content (Smith, 1982). The degradation of sulfonylurea herbicides in soil is primarily dependent on chemical and biological degradation, which is influenced by temperature, pH, and moisture content (Beyer *et al.*, 1987, 1988).

Some sulfonylurea herbicides have herbicidal activity at concentrations as low as 1 g/ha (Hay, 1990) with as little as 0.5 g/ha of residual herbicide severely reducing the yield of some sensitive rotation crops (Walker and Brown, 1983). The sulfonylurea herbicides degrade slowly in cold, dry, heavy soils that have a high pH (>7.5) thus causing potential injury problems in broadleaf crops planted the following season (Walker and Brown, 1982; Beyer *et al.*, 1988). Carry-over is of particular concern in western Canada due to the long, cold winters, and hot dry summers which are not conducive to continuous, steady breakdown of herbicides (Smith, 1994).

Once a herbicide is applied, there are eight possible routes that may affect its dissipation: 1. adsorption to clay and organic matter, 2. leaching with the downward percolation of water, 3. volatilization to the atmosphere, 4. uptake by plants and/or soil organisms, 5. movement with runoff water or eroded soil, 6. microbial degradation, 7. chemical degradation, and 8. photolysis (McEwen and Stephenson, 1979). These processes are affected by the adsorption of a herbicide to soil colloids and soil organic matter. The greater the adsorption of a herbicide to a particular soil, the less the losses from leaching and volatilization (Smith, 1982). Depending on the chemical nature of the herbicide the importance of each of these routes can be quite different.

1.1.1 Adsorption by Soil

Adsorption and desorption affect the ease by which herbicides move through the soil profile. These processes also influence availability to plants, microbial degradation and persistence (Mersie and Foy, 1986). Organic pesticides adsorb onto both organic and inorganic surfaces depending upon the chemical properties of the adsorbents and adsorbate involved (Weber, 1972). Organic matter and clay content appear to be positively and highly correlated with pesticide adsorption or reduction in bioavailability (Green and Obien, 1969; Briggs, 1976; Brady, 1984) although acidic pesticides, such as the sulfonylureas, are adsorbed in moderate amounts on organic matter and in relatively low amounts on clay minerals (Carringer *et al.*, 1975).

Adsorption to soil can be physical (van der Wäals and hydrogen bonding) or due to chemisorption (co-ordination complexes, ion exchange, and protonation or charge-transfer). Possible mechanisms for adsorption of acidic compounds include: physical adsorption, coordination through the carbonyl carbon, association of the carbonyl carbon by bridging to coordinated water on the exchange ion and hydrogen bonding from the carboxyl group to the clay surface. All of these mechanisms are influenced by the various properties of the soil including soil type, organic matter, clay content, pH, moisture and temperature and by the chemical properties of the herbicide.

1.1.1.1 Soil Type. Soil type is determined by the amount of sand, silt and clay present in the top layer of the soil surface. The percentage of each of these three components of the soil determines pore size distribution within the soil structure. Herbicide mobility and leaching is increased in coarse textured soils containing large amounts of sand (Hance, 1983) because water conductivity is greater than in fine-

textured soils (Kohnke, 1968). Coarse textured soils with low organic matter and clay content also tend to have low microorganism populations thereby reducing herbicide microbial degradation (Nash, 1988). Fine textured soils containing large amounts of clay have higher water holding capacities and cation exchange capacity (C.E.C) than coarse textured soils thereby slowing herbicide movement in soil solution (Nash, 1988).

1.1.1.2 Soil Organic Matter. Of the four soil properties, organic matter, total clay, C.E.C and pH, organic matter content is often considered to be the best single predictor of herbicide adsorption (Hartley, 1976). Organic matter can increase herbicide persistence by direct chemical attachment of the residues to reactive sites on colloidal organic surfaces and incorporation into the structure of newly formed humic and fulvic acids during the humification process. Nash (1988) suggested that organic matter may affect herbicide dissipation in two ways. First, as herbicide adsorption to organic matter increases, its rate of degradation decreases. Second, if microbial degradation is a major dissipation pathway of the herbicide, enhanced microbial activity associated with higher organic matter content may increase the rate of dissipation.

Organic matter is composed of nonhumic (carbohydrates, proteins, fats, waxes, and resins) and humic (humic and fulvic acids) substances. Humic acid is defined as material extracted from soil by alkaline solutions that precipitates upon acidification. Fulvic acid is the material remaining in solution. Fulvic acids are soluble in both acid and alkali. Humic material represents the most reactive component of organic matter and consists of a series of highly acidic polyelectrolytes containing a high content of oxygen functional groups (COOH, phenolic, aliphatic and enolic-OH and C=O structures). Amino, heterocyclic amino, imino and sulfhydryl groups may be present. Humic acids

can combine with herbicides by electrostatic bonding (attraction of a positively charged organic cation to an ionized COOH or phenolic OH group), H-bonding, and ligand exchange (formation of covalent bond with an attached metal ion). Humic acids contain high concentrations of stable free radicals, which can bind herbicides and act as transporting agents for pesticides in soils. The high acidity of humic acids may catalyze the chemical decomposition of certain pesticides and nonbiological transformations of herbicides.

Unlike clay, organic colloids have a strongly pH-dependent charge (Stevenson, 1975). The relative contribution of organic matter to C.E.C. and subsequent retention of cations will be higher in neutral and slightly alkaline soils than in acidic ones. For each unit change in pH, the change in C.E.C. for organic matter is several times greater than for clay. Relative affinities of pesticides for organic matter are listed in an approximate order: cationic herbicides (diquat) are most strongly bound, followed by those weakly basic types (capable of being protonated under moderate acidic conditions), then those having very low pKa values but which contain one or more polar groups suitable for H bonding. Anionic pesticides may or may not be adsorbed depending on soil pH (Stevenson, 1975). Adsorption to organic matter is greatest for nonionizable hydrophobic herbicides and least for ionizable, highly water-soluble chemicals, though all herbicides have some affinity for organic matter.

Since organic matter is mostly negatively charged, it adsorbs weak acid herbicides when they are in their molecular state. Weak acids such as the sulfonylureas, are more likely to leach when in the anionic form at pH levels above their pKa (Fig. 1.2). In general, acidic pesticides are adsorbed in moderate amounts on organic matter and in low

amounts on clay minerals (Carringer *et al.*, 1975). The mobility of the sulfonylurea herbicides decreases as organic matter content increases (Smith, 1982, Beyer *et al.*, 1988, Harvey *et al.*, 1985; Mersie and Foy, 1985; Mersie and Foy, 1986) but the relationship between organic matter and sorption is complex. A positive correlation between chlorsulfuron (Mersie and Foy, 1985; Walker *et al.*, 1989; Vicari *et al.*, 1996; Miller *et al.*, 1997), sulfometuron methyl (Harvey *et al.*, 1985), primisulfuron (Werkheiser and Anderson, 1996), and rimsulfuron (Zimdahl *et al.*, 1996) sorption and soil organic matter in soils of varying pH has been found. Phytotoxicity to corn in a laboratory bioassay study was highest in soils with high organic matter content and low soil pH indicating increased soil adsorption (Mersie and Foy, 1985).

1.1.1.3 Soil Clay Content. Clay and organic matter are intimately bound (clay-metal-organic complex) and function as a unit. The amount of organic matter that coats the clay particles will vary from one soil to another and will depend on the amount of clay present. When soils have similar clay and organic matter contents, the contribution of organic matter will be lowest when the predominant clay mineral is kaolinite and highest when montmorillonite is the main clay mineral (Stevenson, 1975). Bailey *et al.* (1968) demonstrated that the adsorption capacity of clays increased when the components of the soil contained montmorillonite>illite>kaolinite. Swelling of montmorillonite provides a very large surface area for interactions with pesticide molecules (White, 1975) while interactions in kaolinite are limited to the outer edges. Pesticides can become either biologically inactive (i.e. tightly bound by montmorillonite soil) or still active (i.e. when bound only by outer surfaces in kaolinite soils).

Clay minerals have a permanent negative charge and a variable charge associated with it that is pH dependent. As soil pH increases, hydrogen ions are lost from clay colloids and they become negatively charged. Many soil minerals will still have some positive charge up to a soil pH of 7 and above depending on their zero point of charge (zpc) which can be as high as 7.8 to 9.5 for soils containing aluminum oxyhydroxide (Hingston *et al.*, 1972). This acidity may be important in adsorption of basic pesticides as well as in degradation and detoxification of other pesticides. Cations on clay surfaces can compete for adsorption sites with positively charged organic molecules i.e.: paraquat (Weber *et al.*, 1969; Hayes, 1970) and by acting directly as adsorption sites through the formation of coordination bonds. Cations can act indirectly via hydrated water molecules (Mortland *et al.*, 1968; Calvet, 1980) and can form hydroxides on clay surfaces, which can increase the adsorption capacity of the mineral (Terce and Calvet, 1977). Clay mineral surfaces and associated cations have very strong attraction for water molecules and competition between pesticide and water molecules for adsorption sites on mineral surfaces may determine the degree of adsorption, volatility, biological activity, etc. During drought conditions adsorbed molecules are not available for exchange while under hydrated conditions they are spatially distributed in the soil solution, this increases the potential for exchange to occur. Low adsorption on some soils could be due to inaccessibility of clay interlayers in soils caused by either aggregation, Al-hydroxy interlayers or by the presence of other organic compounds in soil that are blocking adsorption sites on clay minerals.

Due to their anionic nature, sulfonylureas generally exhibit very low adsorption on clay minerals especially at a pH above their pKa, as more of the herbicide is anionic

and repelled by the negatively charged soil colloids. However, there have been some instances of binding of sulfonylurea herbicides to clay. Soils containing amorphous iron oxides have a capacity for adsorption of sulfonylureas although the forces are relatively weak (Borggarrd and Streibig, 1988). Goetz *et al.* (1989) found that iron and aluminum oxyhydroxides could provide adsorptive sites for chlorsulfuron. Shea (1986) reported adsorption of chlorsulfuron on aluminum oxide anionotropic resins, which indicates potential for interaction with soil aluminum or iron oxides. Some binding of chlorsulfuron to bentonite clay saturated with calcium at pH 8.2 was also found, possibly due to binding to metal oxides on the clay surfaces or ligand exchange between the sulfone or carbonyl functional groups on chlorsulfuron and water molecules hydrating the cations at the exchange surface of the clay. Rimsulfuron adsorption was positively correlated with soil organic matter and clay content (Schneiders *et al.*, 1993). It is possible that surface acidity could be lower than the measured suspension pH (Bailey *et al.*, 1968) in which case more of a sulfonylurea herbicide may be in the molecular state and therefore more likely to be bound to the soil. Also, force fields emanating from the surface of clays and or the presence of protons may induce a significant change in the pKa of a herbicide when it comes into close proximity to clay molecules (Bailey *et al.*, 1968). Anionic exchange is greatest in soils containing kaolinite and/or hydrous oxides of iron and aluminum but is usually limited as pH increases.

1.1.1.4 Soil pH. Soil pH determines whether an ionizable herbicide is present in the molecular, cationic or ionic form. Herbicides that are weak bases will be protonated (cationic) at a pH below their pKa and molecular at a pH above their pKa. Weak acids will be in the molecular state at a pH below their pKa and in the anionic state at a pH

above their pKa. At pH levels common to many agricultural soils, weak acid herbicides such as the sulfonylureas will be mostly anionic and less likely to be adsorbed to soil. As soil pH increases more of the herbicide will be in the water-soluble, ionized form, moving more of compound from the bound fraction to the soil water phase where it is free to travel with net soil water movement (Nicholls and Evans, 1987; Shea, 1986, Beyer *et al.*, 1987) especially under conditions of high rainfall (Nicholls *et al.*, 1987).

Walker and Welch (1989) found that relative extent of adsorption of three sulfonylurea herbicides by different soils was metsulfuron-methyl < chlorsulfuron < triasulfuron which follows the same order as their acid dissociation constants (3.3, 3.8, 4.5) indicating the importance of soil pH on adsorption. Shea (1986) tested numerous adsorbents and chlorsulfuron exhibited only limited affinity for a fine sandy loam (pH 8.7). Soil pH was the only soil property that correlated with the amount of chlorsulfuron adsorbed from solution. Decreasing a high pH soil to 4.6 with H₂SO₄ increased adsorption while increasing pH to 8.5 with CaCO₃ depressed adsorption. The adsorption of chlorsulfuron and metsulfuron-methyl (Walker *et al.*, 1989; Mersie and Foy, 1986; Blacklow and Pheloung, 1992), sulfometuron methyl (Harvey *et al.*, 1985), and primisulfuron (Werkheiser and Anderson, 1996) was negatively correlated with soil pH and positively correlated with soil organic matter.

1.1.1.5 Soil Moisture and Temperature. Climatic conditions determine local precipitation and temperature. These conditions directly effect soil moisture and temperature, which play a large role in determining the environmental fate of many pesticides. The effect that climatic conditions have on the rate of herbicide degradation is

predictable since many chemical reactions are temperature and moisture dependent (Walker, 1987).

Herbicides are more soluble at higher temperatures as the kinetic energy of absorbed molecules increases and electrostatic attraction decreases allowing more molecules to be in soil solution. As solubility increases adsorption decreases. Solubility differences are often used to predict relative adsorption of similar pesticides within a chemical family but are not useful as a predictor between pesticides from different chemical families. As weak acids, the sulfonylureas are water-soluble and, therefore, mobile in most agricultural soils. Temperature affected the amount of chlorsulfuron adsorbed to soil with most being adsorbed at 8 °C compared to 30 °C (Thirunarayanan, 1985).

Soil moisture influences concentration of pesticide in the soil solution as well as amount adsorbed and processes that influence biological activity (McEwen and Stephenson, 1979). With increases in soil solution, herbicide adsorption to clay particles and organic matter may decrease due to competition with soil water for binding sites. Therefore, under moist conditions, less herbicide binds to soil compared to dry conditions leaving the compound available for microbial degradation and desorption. Many soil surfaces adsorb water more readily than non-polar compounds but can adsorb the latter if water is absent. As soil dries new adsorptive sites become available and volatility losses decrease. Adsorption does not increase markedly with weakly adsorbed compounds until the water content is less than that needed to form a monomolecular layer. Sulfonylurea herbicides are water soluble in most agricultural soils and, therefore, under conditions of high soil moisture (high rainfall) could leach through the soil profile.

The concentration of herbicide in soil solution (C_w) as described by Green and Obien, 1969 is defined by:

$$C_w = \frac{Q}{m(W_e + K)}$$

Where C_w is the concentration of herbicide in the soil solution, Q is the μg of herbicide applied in soil solution, m is the total soil weight (g), W_e is the available moisture per total moisture in soil (g/g) and K is the distribution coefficient. The total herbicide available to plants $C_w \times W_e$.

1.1.1.6 Chemical Structure. The chemical structure of a herbicide can influence its affinity to clay and/or organic matter. It also can influence its solubility in the soil solution. Certain functional groups exhibit specific affinities for adsorption to soil i.e. OH, NH_2 , NHR , CONH_2 , COOR and R_3N^+ . Generally, sulfonylureas have moderate melting points, low octanol-water partition coefficients at neutral pH, very low vapor pressure, and low to moderate water solubilities at neutral pH (Table 1.3). The water solubility and partition coefficient of weak acids are greatly affected by pH. As pH increases the proportion of water-soluble anion increases. For example, the water solubility of chlorsulfuron increases from 60 ppm at pH 5 to 7000 ppm at pH 7. In soils of low pH, sulfonylureas will be primarily in the molecular form and more will be adsorbed to soil than at higher soil pH. The degree of adsorption will be affected by soil composition (i.e. organic matter, clay content) as well as moisture and temperature. In general, sulfonylureas with a triazine heterocycle such as chlorsulfuron are more water-

soluble than those with a pyrimidine heterocycle such as sulfometuron methyl (Beyer *et al.*, 1988).

Some possible mechanisms of adsorption of sulfonylureas to soil include: physical adsorption, co-ordination through the carbonyl carbon, association of the carbonyl carbon by bridging to the co-ordinated water on the exchange ions, hydrogen bonding from carboxyl group to clay surfaces, proton association (anionic) and van der Waals type adsorption if in molecular state (Bailey *et al.*, 1968).

Table 1.3 Physical and chemical properties of sulfonylurea herbicides (Adapted from Beyer *et al.*, 1988).

	Melting point (°C)	Molecular weight	Dissociation constant (pKa)	Partition coefficient (octanol-water at 25°C)		Vapor pressure (mm Hg at 25°C)	Water solubility (ppm at 25°C)	
				pH 5	pH 7		pH 5	pH 7
Chlorsulfuron	174-178	357.78	3.6	6	0.046	2.3×10^{-11}	60	7000
Sulfometuron methyl	203-205	364.39	5.2	15	0.31	5.5×10^{-16}	8	70
Metsulfuron methyl	158	381.37	3.3	1	0.014	2.5×10^{-12}	1100	9500
Chlorimuron ethyl	186	414.83	4.2	320	2.3	3.7×10^{-12}	11	1200
Bensulfuron methyl	185-188	410.40	5.2	155	4.1	2.1×10^{-14}	3	120
Thifensulfuron	186	387.40	4.0	3	0.027	1.3×10^{-10}	260	2400 ^a

^aAt pH 6.

1.1.2 Movement in Soil

1.1.2.1 Adsorption Isotherms. The movement of a herbicide in soil is inversely proportional to its adsorption. Factors that influence adsorption will also affect movement. Movement can be downward (leaching) or upward (volatilization), or laterally (run-off water or eroded soil). Adsorption of herbicides to soil directly affects their likelihood of persistence and mobility. Adsorption isotherms are often used to classify herbicides as either mobile or immobile.

Adsorption is due to attraction of a herbicide to the soil surface, generally by physical and/or chemical forces. The strength with which the herbicide is bound is known as the energy of adsorption. The relationship between the amount of solute adsorbed at constant temperature and its concentration in solution is defined as the adsorption isotherm (Hance, 1983). Adsorption and desorption coefficients help determine movement through soil profiles, plant availability, microbial degradability and, therefore, persistence of a pesticide (Mersie and Foy, 1986).

Adsorption isotherms have five general applications: comparison of adsorption of one pesticide to several soils, of several pesticides to one soil, of one pesticide to one soil at several temperatures, of one pesticide to one soil at several soil to water ratios and investigation of binding mechanisms between soil and pesticide (Frehse and Anderson, 1983). Both the Freundlich and Langmuir's adsorption equations are used to calculate adsorption isotherms.

The Freundlich equation is defined by: $x/m = KC_{eq}^{1/n}$ where x/m is the concentration of the herbicide adsorbed on the soil (μg herbicide/g of soil), C_{eq} is the concentration of herbicide in soil solution at equilibrium, K is an equilibrium constant (measure of the degree or strength of adsorption) and $1/n$ is an exponent (often less than one) which is indicative of the nonlinearity between solution concentration and adsorption. The non-linear nature of soil sorption processes explains the phenomenon that as concentration of a solute in solution increases, sorption sites begin to become saturated. Therefore, as solution concentration increases the amount of chemical sorbed is not necessarily linearly proportional (McCall *et al.*, 1980). At lower concentrations the

value of $1/n$ becomes unity and the isotherm becomes linear. If the equilibrium solution phase is kept below 10^{-5} M this linearity holds.

The equation can be expressed in logarithmic form to give a linear relationship: $\log x/m = \log K + 1/n \log C_{eq}$. $\log K$ is the x intercept and when $n=1$ there is a linear relationship between C and x/m and, therefore, no need for log transformation. Usually n is between 1 and 2 but can be less than 1. The slope of the line is described by the rate at which the concentration of a compound on soil particles changes with an increase in concentration of the pesticide in solution. Adsorption also can be correlated to organic carbon content in the soils, and is often expressed as amount of herbicide adsorbed in relation to organic carbon content as per the following equation: $K_{oc} = K_d / \% \text{ organic carbon} \times 100$, where $\% \text{ organic carbon} = \% \text{ organic matter} / 1.72$. As the K_{oc} value increases the adsorption of solute to soil also increases (Figure 1.1).

The Langmuir equation is less used. It is considered applicable when a straight-line plot is generated and when multilayer adsorption does not occur. Much of the experimental data does not obey the Langmuir isotherm but does obey Freundlich's isotherm. The Langmuir equation was first developed for the adsorption of gases onto solids assuming that energy of adsorption is constant and independent of surface coverage, adsorption is on localized sites and there is no interaction between adsorbate molecules, and the maximum adsorption possible is that of a complete monolayer. The equation is defined by: $x/m = KC_{eq}$.

Both equations assume that at equilibrium, the ratio of amount sorbed to that in solution is equal to the partition coefficient. Continuous adsorption/desorption of a herbicide in soil as a result of continuous changes in moisture content may result in

equilibrium never being obtained. Partition coefficients are often a fairly good index of relative sorption of a herbicide but cannot accurately describe the fluctuations in sorption that occur with time in the field (Hutson and Wagenet, 1989).

Figure 1.1 Relative mobility of sulfonylurea and other herbicides in soil (Adapted Russell *et al.*, 1995).

Another problem encountered with the use of partition coefficients is the method of determination. Repeated shaking and centrifugation is required which may alter the physical and chemical characteristics of the soil resulting in changes in binding site properties. Partitioning of pesticides between soil particles and soil solutions may not be the same in field-moist soils as in batch slurry systems in the laboratory (Hance, 1983). Berglof *et al.* (1997) found that K_d values under unsaturated conditions were a hundred times greater than those found using the batch slurry technique and could result in pesticide mobility being incorrectly categorized.

1.1.2.2 Leaching. Leaching is determined by both the adsorption of a herbicide to soil colloids and the water solubility of a herbicide (Smith, 1984). Soil characteristics

such as organic matter, pH, soil type and porosity as well as environmental factors such as time of year of application, rainfall and temperature affect adsorption (Beyer *et al.*, 1988) and, therefore, leaching potential.

Movement of a herbicide through a soil occurs as a result of a combination of processes listed in order of their importance: convection (mass flow) of the chemical dissolved in moving soil water, convection of the volatile chemical in the vapor phase, diffusion of a volatile chemical in soil air, and diffusion in the liquid phase (Hutson and Wagenet, 1989). Mass flow is the mechanism primarily responsible for bulk pesticide transport since diffusion occurs slowly over several months (Lavy, 1970). Rate of water flow through the soil is controlled by pore size. Within pores, flow rate increases concomitantly with distance from the wall (laminar flow). Liestra (1980) found that strong adsorption reduces availability of herbicide and restricts its penetration into the soil even with sufficient rainfall. If considerable time lapses between application of a herbicide to the soil and commencement of leaching, the herbicide is available for both greater penetration into small pores and for adsorption onto the solid surfaces. Under droughty conditions, soils high in clay content may form large cracks and during intense rainfall part of the water may percolate rapidly via the cracks before the top layer is completely moistened. This water may rapidly carry a small amount of the herbicide downward but the main fraction will remain in the structural elements of the soil. Herbicide remaining in the small pores of fine-textured soils may be unavailable for microbial degradation.

During periods (summer) of net upward flow of soil water, a relatively mobile compound (e.g. chlorsulfuron) may re-enter root zones from deeper in the soil profile

where it had penetrated during earlier periods (spring) of net downward water flow. Movement to deeper soil layers may lead to persistence since microbial activity is often less than in the plough layer (Nicholls *et al.*, 1987).

1.1.2.3 Movement with Runoff Water or Eroded Soil. In soils where adsorption of herbicides is usually high (i.e. high organic matter and clay, low moisture content), herbicides can move with eroded soil. Furthermore, as soil moisture increases herbicides can desorb and move with soil water

Sulfonylureas are considered to be, for the most part, mobile, as they are water-soluble and exist as anions in most agricultural soils and, therefore, will not usually be subject to movement in runoff water or eroded soil. Smith and Hsiao (1985) considered losses of chlorsulfuron on prairie soils due to erosion (wind and rain) to be negligible.

1.1.2.4 Volatilization. Four factors determine how much herbicide is lost due to volatilization: vapor density of the herbicide, atmospheric conditions at application, time before incorporation by leaching or cultivation of the herbicide into the soil, (Hutson and Wagenet, 1989) and soil moisture conditions. For significant losses from volatilization to occur, chemical vapor pressures of greater than 10^{-4} mm of mercury are required (Smith, 1984). Once incorporated in the soil, herbicide volatilization rapidly decreases.

The transfer of vapor occurs by diffusion (random molecular motion from high to low concentration). Temperature, adsorption, and soil water content control vapor phase diffusion in soils. Soil porosity, bulk density, tortuosity of soil pores and number of blocked pores affect soil moisture content. Soil moisture content gives a measure of air space available for vapor diffusion. The greater the soil water content, the more herbicide that may be lost to volatilization since water competes for adsorption sites on

soil colloids by displacing the adsorbed herbicide molecules or preventing adsorption. Increased adsorption of a herbicide to soil colloids results in less herbicide lost to volatilization.

The octanol/water partition coefficient (K_{ow}) of a herbicide may have a relationship with vapor pressure (Chiou and Freed, 1977). The K_{ow} is related to the lipophilicity of a compound. Herbicides with a high coefficient are less water soluble and more likely to be volatilized. In general, sulfonylurea herbicides have low vapor pressures (Table 1.2) and low K_{ows} and, therefore, losses due to volatilization are insignificant.

Table 1.4 Vapor pressures of selected sulfonylurea herbicides
(Adapted from Brown *et al.*, 1995).

Active ingredient	Vapor pressure @ 25°C (mm Hg)
Azimsulfuron	3.0×10^{-11}
Bensulfuron methyl	2.1×10^{-14}
Chlorimuron ethyl	3.7×10^{-12}
Chlorsulfuron	2.3×10^{-11}
DPX-DE459	1.0×10^{-11}
Ethametsulfuron methyl	5.8×10^{-15}
Metsulfuron methyl	2.5×10^{-12}
Nicosulfuron	1.2×10^{-16}
Rimsulfuron	$< 1 \times 10^{-7}$
Sulfometuron methyl	5.4×10^{-16}
Thifensulfuron methyl	1.3×10^{-10}
Tribenuron methyl	4.0×10^{-10}
Triflurosulfuron	6.7×10^{-9}

1.1.2.5 Photodegradation. The importance of photodegradation to overall dissipation of a herbicide is limited to those residues that are very close to the soil surface. Immobile herbicides that require rainfall for penetration into soil, such as

simazine, are more likely to photodegrade. Typically, mobile herbicides such as sulfonylureas are less likely to be photodegraded.

1.1.3. Degradation in Soil

1.1.3.1 Microbial Degradation. Frehse and Anderson (1983) suggest that the rate of microbial metabolism of pesticides in soil is a function of the following: availability of chemicals to microorganisms or enzyme systems, which can degrade them; quantity of these microorganisms or enzyme systems; and, their activity level. Soil moisture, temperature, aeration, pH and nutrient status can influence both the availability of a pesticide to soil microbes and the ability of soil microbes to degrade a pesticide.

If a pesticide is readily degraded by soil microbes (i.e., it is a good substrate for enzymatic attack) and if it is available to soil organisms and if the organisms are metabolically active, then in general, a high correlation between microbial biomass and degradation rates can be expected. If only a small proportion of the biomass can attack the compound (i.e., it is a poor substrate for enzymatic attack) its degradation and dissipation will be more dependent on external physical forces such as light, and the chemical and physical properties of both the chemical and the soil. Sulfonylurea herbicides are degraded both chemically and biologically, with both types of degradation being promoted by high soil temperatures and moisture (Thirunarayanan *et al.*, 1985, Beyer *et al.*, 1988, Smith and Aubin, 1992).

Availability of a pesticide for degradation is determined by the extent of its adsorption and its ease of desorption from soil solids (Briggs, 1976; Anderson, 1981; Burkhard and Guth, 1981; Soulas, 1982). The quantity of herbicide available for

degradation is approximately equivalent to the amount dissolved in the soil solution. Increasing the ratio of water to soil solids increases the total amount of herbicide in solution resulting in an increase in both the metabolic rate and quantity of microflora in the soil (Anderson, 1981). Adsorption of most herbicides increases with an increase in soil organic matter. Consequently adsorption reduces the amount of herbicide available in the soil solution thereby reducing herbicide degradation (Hurle and Walker, 1980). Hamaker (1972) suggested that an increase in organic matter content may increase the rate of degradation in mineral soils up to a limiting value above which the rate of loss would be retarded. Results are conflicting and it is clear that adsorption does not always protect a chemical from degradation, (Burns, 1973) or does it always lead to increased rates of loss.

In most cases, sulfonylurea herbicides are subject to microbial degradation. Chlorsulfuron dissipated more rapidly in non-sterile soils than in sterilized soils (Joshi *et al.*, 1985, Oppong and Sagar, 1992a) with differences between degradation in sterile and non-sterile soil being more pronounced in higher pH soils (Table 1.5) where chemical hydrolysis is often limited. Half-lives of 2 to 3 weeks in non-sterile versus 7 weeks in sterile soils were reported for [^{14}C]-primisulfuron (Werkheiser and Anderson, 1996; Miller *et al.*, 1997). Similar half-lives were calculated for soils treated with azimsulfuron (Barefoot *et al.*, 1995a).

Fredrickson and Shea (1986) found that soil microbes accounted for 25% of initial degradation of chlorsulfuron in soil and that re-inoculation of sterile soil with a microbial suspension from the non-sterile soil restored degradation of chlorsulfuron. Several groups of microorganisms including actinomyces, fungi, and bacteria have been shown to

actively metabolize chlorsulfuron, metsulfuron-methyl and chlorimuron-ethyl (Beyer *et al.*, 1988). *Streptomyces griseolus* (actinomycete) metabolized chlorsulfuron via hydroxylation of a methyl group. *Aspergillus niger* and *Pencillium* sp. (soil fungi) catalyzed hydrolysis of the sulfonyl bridge and resulted in hydroxylation of the methoxy substituent on the heterocycle of chlorsulfuron (Beyer *et al.*, 1988). Biological degradation products of sulfonylurea herbicides are often more complex than those produced by chemical hydrolysis.

Table 1.5 The effect of temperature on the half-life (weeks) of chlorsulfuron under laboratory conditions (Adapted from Beyer *et al.*, 1988)

Temperature (°C)	Rochelle, IL silt loam (pH=5.7, 4.9% OM)		Fargo, ND silt loam (pH=7.5, 5.7% OM)	
	Sterile	Nonsterile	Sterile	Nonsterile
40	1.0	0.40	8.0	1.1
35	2.4	0.65	14.0	2.0
30	4.3	1.2	33.0	7.8
20	14.0	4.0	69.0	32.0

1.1.3.2 Enhanced Microbial Degradation. Although microbes normally occupy a volume of less than 1 % of the soil, their populations can be as high as 10^9 organisms per gram of soil and they can degrade many types of chemicals. Under normal conditions, herbicide microbial degradation consists of three phases. After application, microbial degradation begins with a lag phase when breakdown is relatively slow presumably because the microbes or enzymes are adapting to the recently applied herbicide. This phase is followed by a phase when microbial degradation is rapid and rates increase logarithmically. The final phase is the plateau when degradation returns to a slower rate due to depletion of the herbicide present in the soil or an accumulation of toxic metabolites that reduce the rate of degradation.

Enhanced degradation refers to an increase in the rate of microbial degradation that occurs after repeated use of the thiocarbamate, phenoxy, aliphatic acid, and phenylcarbamate herbicides. These soils are referred to as “history soils” because the phenomenon occurs only after repeated application over a number of years to the same soil.

Roeth (1986) explained that microbes are able to adapt to degrade herbicides after the herbicide is first applied to the soil. The same microbes are capable of degrading subsequent applications of the same or similar compounds more rapidly. Enhanced degradation influences the sigmoid degradation pattern that normally occurs with microbial degradation. The initial lag phase disappears with the log phase appearing immediately after application. The decrease in the lag phase often results in the herbicide being degraded before its herbicidal activity can be exerted.

There are two types of enhanced degradation. Bean *et al.* (1988) describes the first type as self-enhancement, which occurs when the same compound is applied repeatedly to the same soil. The second type is cross enhancement, which occurs when a particular herbicide is repeatedly applied to an area. Subsequently, when a herbicide from the same chemical family is applied to that soil it undergoes enhanced degradation. The degradation rate of a herbicide is usually slower with cross-enhancement than self-enhancement.

Addition of a herbicide to the soil can change the microbe population and can alter its ability to degrade the chemical. The increased carbon source from the herbicide may lead to an increase in microbe populations due to the additional energy source.

Within the microbes themselves, production of enzymes capable of herbicide degradation may be increased.

The ability of a microbe to survive and degrade herbicides is dependent on its ability to exchange genetic material allowing it to adjust to a wide range of environmental conditions (Skipper *et al.*, 1986). Clarke (1984) hypothesized that degradative plasmids help microbes degrade herbicides into a form that may be used as a source of energy. Several degradative plasmids are common among microbes. The ability of a microbe to transmit these plasmids amongst themselves plays an important role in determining the rate of herbicide degradation (Skipper *et al.*, 1986).

1.1.3.3 Chemical Degradation. Many herbicides are degraded both microbially and chemically. In most agricultural soils (pH 6.7 and below) chemical hydrolysis is more important to the rate of dissipation of sulfonylurea herbicides than is microbial degradation (Joshi *et al.*, 1985; Thirunarayanan, *et al.*, 1985; Beyer *et al.*, 1988; Blair and Martin, 1988; Walker *et al.*, 1989; Hay, 1990; Makita *et al.*, 1996). As weak acids (pKa 3.3-5.2), sulfonylureas obtain equilibrium between ionized and molecular forms at a pH equal to the pKa. Only the molecular form of the sulfonylureas can be hydrolyzed as the sulfonylurea bridge is at least 250 to 1000 times more sensitive to hydrolysis than the anionic form (Brown, 1990). When in the molecular state the carbonyl carbon is subject to nucleophilic attack by water molecules and is released as CO₂ with the cleaving of the sulfonylurea. The anionic bridge form is markedly deactivated toward hydrolysis since the negative charge is distributed throughout the bridge, reducing the electrophilic nature of the carbonyl carbon (Figure 1.2).

Figure 1.2 Effect of pH on hydrolysis of amidosulfuron (Adapted from Beyer *et al.*, 1988).

Degradation rates of chlorsulfuron and metsulfuron-methyl decreased with soil depth and were positively correlated with soil microbial biomass and negatively correlated with soil pH (Walker, 1987). Half-lives of chlorsulfuron of 38.1, 62.0, 82.0, and 99 days were found for soils at pH 6.2, 7.1, 7.7, and 8.1, respectively (Thirunarayanan, *et al.*, 1985). A similar trend was noted with chlorsulfuron degradation as pH increased from 5.6 to 8.2 across a wide range of soil types (Table 1.6). Smith (1994) also reported that metsulfuron-methyl degradation followed first order kinetics and reported half-lives of 70, 102 and 178 days in soils with pH 5.2, 6.8, and 7.5, respectively. Kotoula-syka *et al.* (1993) found that phytotoxicity of four sulfonylureas was not affected by soil texture but increased with increasing herbicide concentration and

pH as determined by bioassay tests with sensitive species (Mersie and Foy, 1985; Gunther *et al.*, 1989; Walker *et al.*, 1989). Joshi *et al.* (1986) found that the half-lives of chlorsulfuron in soil ranged from 3 (pH 5.9) to 45 weeks (pH 8) while Fredrickson and Shea (1986) found similar trends with half-lives ranging from 1.5 (pH 5.6) to 9 weeks (pH 7.5) in soils amended with calcium carbonate.

Although pH is the predominant factor affecting degradation of sulfonylurea herbicides, with many of these herbicides having shorter half-lives in lower pH soils (Walker and Brown, 1983; Walker and Welch, 1989; Walker *et al.*, 1989; Dinelli *et al.*, 1997), other factors such as soil moisture (Anderson and Barrett, 1985; Anderson and Dulka, 1985; Smith and Aubin, 1992) and temperature (Anderson and Barrett, 1985; Thirunarayanan, *et al.*, 1985; Smith and Aubin, 1992; Dinelli *et al.*, 1997) also affect dissipation rates.

In general, herbicide degradation increases as soil temperatures increase (Nash, 1988). Since herbicide adsorption is an exothermic process, higher soil temperature causes some of the hydrogen and ionic bonds formed to break during desorption. Chemical reactions, chemical volatility, microbial/enzyme activity all increase as soil temperatures increase contributing to greater degradation (Bailey and White, 1964). Generally, herbicide degradation ceases at temperatures at or below the freezing level. Therefore, herbicide degradation is much slower on the Canadian prairies where the soil is frozen for several months each year compared to more southerly agricultural locations (Nash, 1988). Increased degradation of sulfonylurea herbicides at higher temperatures has been reported (Smith and Aubin, 1992; Zimdahl *et al.*, 1996)

The dependence of degradation on temperature can be characterized using the Arrhenius equation:

$$\log H_1 - \log H_2 = \frac{E_a}{2.30R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

H_1 and H_2 are half-lives at absolute temperatures of T_1 and T_2 , respectively, E_a (Jmol^{-1}) is the Arrhenius activation energy, and R is the molar gas constant. When time zero data in half-life calculations are included, the E_a is often higher suggesting that degradation is temperature dependent. However, when half-life calculations exclude time zero data E_a values are often lower which may mean that shortly after application, degradation is predominantly by chemical hydrolysis in acidic soil whereas the enzymatic processes, especially in alkaline soils, assume a greater role at later.

Degradation rates of herbicides are often assumed to follow first order reaction kinetics and are often expressed in terms of half-lives. Sulfonylureas often have biexponential degradation kinetics in field and laboratory studies held at constant temperature and moisture (Brown and Kearny, 1991) with half-life values being rated as rapid to moderate (Figure 1.3). Often there is an initial rapid loss of herbicide followed by a more gradual rate of decline in soil residues. With many sulfonylurea herbicides, the transition to the slower breakdown phase occurs 2 to 4 weeks after application (Thirunarayanan *et al.*, 1985; Duffy *et al.*, 1987). This two-stage degradation may be explained by a two-compartment model (Duffy *et al.*, 1987). The herbicide is first in a “available compartment” where it undergoes both chemical and microbial degradation (Figure 1.4). Over time the herbicide may move into a “protected compartment” where it is unavailable to soil microbes but still subject to chemical hydrolysis. Even though the

microbial degradation component is 5 to 10 times more than the hydrolysis rate, especially in alkaline soils, it can not affect the herbicide in the protected compartment. Eventually decomposition will proceed at a rate that is determined by movement of the herbicide out of the “protected compartment” where it is once again degraded both microbially and chemically .

Table 1.6 Half-life of chlorsulfuron under field conditions (Adapted from Beyer *et al.*, 1988).

Location	Soil type	pH	Organic matter (%)	Half-life (weeks)
Clay Center, NE	Silt loam	5.6	3.8	4
Newark, DE	Silt loam	6.0	1.4	4
Swift Current, Sask.	Silt loam	6.1	1.0	2
Saskatoon, Sask.	Silty clay loam	6.2	3.4	4
Versailles, France	Loam	6.4	1.9	3
Carrington, ND	Loam	6.6	4.4	3
Rochelle, IL	Silt loam	6.7	7.4	3
Akron, CO (site 1)	Silt loam	6.9	1.0	5
Stettler, Alberta	Sandy loam	6.9	4.4	12
Rosetown, Sask.	Clay loam	7.3	2.3	7
Fargo, ND	Silty clay loam	7.6	5.3	8
Fisher Branch, Manitoba	Silty clay loam	7.8	6.4	9
Kimberely, ID	Silt loam	8.0	1.3	13
Akron, CO (site 2)	Silt loam	8.2	1.2	11

The degradation rate of sulfonylurea herbicides is generally faster in moist than dry soils. Zimdahl *et al.*(1996) found that increasing soil moisture from 25 to 75% of the soil water holding capacity decreased half-life values of primisulfuron from 32.7 weeks to 8.9 weeks. Degradation of [¹⁴C]-thiameturon (Smith *et al.*, 1990) and [¹⁴C]amidosulfuron (Smith and Aubin 1992) were both moisture dependent. Vicari *et al.*

(1994) calculated the half-life of chlorsulfuron when applied to four soils in Italy to be 149, 70, 59, and 51 days. The highest value was attributed to low rainfall (250-mm) at that site compared to the other three sites (508, 700, and 1224 mm). Vicari *et al.* (1994) speculated that decreased rainfall left the soil dry for a longer time, impeding chemical hydrolysis and microbial activity. Several authors also state that moisture may be the most important factor in the dissipation of chlorsulfuron (Anderson and Dulka, 1985; Oppong and Sagar, 1992b). The increase in herbicide degradation rate as soil moisture increases is due primarily to decreased adsorption making the herbicide more available for both chemical and microbial degradation (Beyer and Duffy, 1988). Degradation products suggest that chemical hydrolysis is primary mode of degradation in dry soil whereas both chemical hydrolysis and microbial degradation are contributing factors in moist soils.

As the sulfonylurea herbicides are degraded both chemically and microbially, different degradation pathways can be expected. Cleavage of the triazine ring, conversion of the methoxy to a hydroxyl group and hydrolysis of the carboxylic acid occur under both acid or alkaline conditions (Sabadie, 1990, 1992, Bastide, *et al.*, 1994) whereas the rate of cleavage of the sulfonylurea bridge is pH specific (Berger, 1996). The postulated primary degradation mechanisms in soil for four sulfonylureas are shown in Table 1.7. These degradation mechanisms render the herbicide inactive and include microbial metabolism and hydrolysis of the sulfonylurea bridge, accelerated bridge hydrolysis (afforded by the N-methyl modification as in tribenuron methyl), rapid deesterification of thifensulfuron methyl and IPSO bridge contraction of rimsulfuron and DPX-KE459

where the urea nitrogen proximal to the pyrimidine ring attacks the pyridine ring at the bridge carbon cleaving the sulfonylurea bridge (Brown *et al.*, 1995).

Figure 1.3 Field dissipation rates of sulfonylurea herbicides. (Adapted from Russell *et al.*, 1995).

Figure 1.4 The two-compartment model of soil degradation (Adapted from Duffy *et al.*, 1987).

Table 1.7 Soil dissipation rates and primary degradation mechanisms of representative sulfonylurea herbicides (Adapted from Brown *et al.*, 1995).

Active Ingredient	DT ₅₀ (days)	Mechanisms
Metsulfuron methyl	14.7	Microbial metabolism and pH dependent bridge hydrolysis
Tribenuron methyl	2.1	Accelerated pH-dependent bridge hydrolysis
Thifensulfuron methyl	2.2	Microbially-catalyzed deesterification
Rimsulfuron	3- 7	IPSO bridge contraction
DPX-KE459	8-25	IPSO bridge contraction

1.2 Methodology for Soil Mobility and Degradation Studies

1.2.1 Field and Laboratory Studies

Movement and persistence studies may be conducted in either the field and/or laboratory. Field studies provide a more realistic scenario in a typical agricultural setting but variables such as climactic conditions and soil variations may be difficult to control. Under laboratory conditions the researcher may control the environment but information may not correlate well with more variable field situations. However, data from laboratory studies may be used to compare the relative persistence and mobility of different sulfonylureas.

Most field studies involve the application of the herbicide, often radiolabelled, to a field site and subsequent sampling at various times and soil depths. Micro-plots are sampled by pushing large stainless steel tubes (approximately 10 cm in diameter) into the ground and removing samples from within the perimeter of the tube.

Laboratory studies to determine the mobility and persistence of a herbicide are determined by removing soil from the field at various depths and incubating them with a herbicide in a controlled environment. Variables such as soil moisture, temperature, and

pH can be altered to determine their effect on herbicide dissipation. Adsorption of a herbicide is often measured and correlated to mobility (see section 1.1.2.1.).

The mobility and persistence of the sulfonylurea herbicides as described in the literature has most often been conducted in the laboratory and correlated to soil characteristics such as organic matter, clay content, pH, moisture and/or temperature.

1.2.2 Soil Thin-Layer Chromatography

Helling and Turner (1968) first described the use of soil thin-layer chromatography

(TLC) for the determination of herbicide mobility. This method offers several advantages compared to soil columns, including simplicity, good reproducibility of soil layer characteristics and pesticide mobility, lack of plugging, continuous leaching profile analysis, comparison of 6-9 chemicals simultaneously, R_f value calculation (Table 1.8), and good interlaboratory standardization (Helling and Dragun, 1980). Mobility of pesticides using soil TLC is generally not affected by soil layer thickness, movement distance, and temperature or sample size. A survey of the literature shows that data obtained by soil TLC on pesticide mobility correlate well with mobility trends predicted from field data (Helling, 1971a). Disadvantages of this method include difficulty in modifying soil-water flux, inadaptability to volatile herbicides, loss of natural soil aggregates, difficulty in equating pesticide application with field rates, and inability to maintain long-term incubation/leaching studies (Helling and Dragun, 1980).

Soil TLC plates are prepared after soil has been sieved through a fine mesh screen (Wu and Santelmann, 1975). Radiolabelled herbicide may be spotted a few cm from the

bottom of the plate (Helling, 1971a). The bottom of the plate is placed in water contained in a TLC tank and removed from the tank after the waterfront has moved up the plate. The plates are allowed to dry and placed in contact with X-ray film (Helling, 1971b, Wu and Santelmann, 1975), scraped and combusted or extracted, or scanned with a radionuclide scanner (Helling, 1971b). Autoradiography provides a qualitative measurement of movement and shows diffusion and tailing of the herbicide, and calculation of the R_f value. Although several days to weeks are required to expose the film sufficiently it is relatively simple method. Soil removed from the plate can be extracted and extracts assayed for radioactivity by liquid scintillation spectroscopy (LSS), and/or combusted and analyzed by LSS. Plates treated with non-radioactive samples can be extracted and assayed by conventional analysis (e.g. gas chromatography). Bioassays can also be conducted on the TLC plate by covering the plate with algae or seeds to determine the location of the herbicide (Helling, 1971a).

Immobile herbicides are strongly adsorbed and do not ascend the plate. Mobile herbicides ascend up the plate and separate according the principles of ascending chromatography. Movement of water on TLC plates is controlled by capillary action and herbicides are under saturated flow conditions. Generally, herbicides will move faster under saturated than unsaturated conditions (Weber and Whitacre, 1982). Mobility of sulfonylureas increases with increasing pH and decreasing soil organic matter (Beyer *et al.*, 1988). A positive correlation between soil pH and soil TLC mobility and a negative correlation between soil organic matter and soil TLC mobility of chlorsulfuron have been reported (Mersie and Foy, 1986, Nicholls and Evans, 1987). A positive correlation

between soil pH and soil TLC mobility was reported for chlorimuron (Goetz *et al.*, 1989) and sulfometuron methyl (Harvey *et al.*, 1985).

1.2.3 Soil Thick-Layer Chromatography

Soils for thick layer chromatography are sieved through a coarse screen and placed in metal trays. The herbicide is applied and mixed with a small amount of air-dried soil which is placed at one end of the soil layer. The tray is elevated at a 5° angle and placed in a humidified chamber containing water that wets the bottom of the tray. Once water has moved the length of the soil layer the herbicide application zone is removed and the remaining soil may be assayed as described above for TLC. Bioassays also can be conducted using seeds of species susceptible to the herbicide. Seeds are uniformly planted along soil surface and covered with quartz sand to prevent desiccation and movement. Trays are placed in a growth chamber with controlled temperatures and moisture (Helling and Dragun, 1980). Soil thick-layer chromatography can be used for the soils that are not suitable for thin-layer chromatography, those that are high in organic matter, clay, and/or silt and when radioactive herbicides are not available.

1.2.4 Soil Columns

There are many variations in the use of columns to study the mobility and dissipation of herbicides in soil. Column dimensions, column materials, soil status (intact versus disturbed soil cores), method of herbicide application, water status during leaching, amount and frequency of water additions, duration of experiment and method of analysis can be varied. Factors that increase hydraulic conductivity will increase water

percolation and therefore, increase the potential for leaching. Coarse textured soils are typically more permeable as are soils low in organic matter (Helling and Dragun, 1980).

Some advantages of using soil columns include; flexibility in choice of herbicide application method, ability to study volatile compounds, use of intact soil cores that more accurately represent field conditions, and ability to study long term leaching and degradation (Helling and Dragun, 1980). Furthermore, herbicide mobility under saturated and unsaturated flow conditions as well as conventional tilled versus reduced tilled soils can be compared. Herbicide degradation product mobility through herbicide treated, aged soil columns also can be measured (Weber *et al.*, 1986).

Table 1.8 Mobility of sulfonylurea herbicides (Adapted from Beyer *et al.*, 1988).

Compound	Soil thin-layer chromatography R _f value ^a			
	Woodstown sandy loam	Cecil Sandy loam	Flanagan silt loam	Keyport Silt loam
Chlorsulfuron	0.90 (5) ^b	0.64 (4)	0.59 (3)	0.52 (3)
Metsulfuron methyl	0.88 (4)	0.74 (4)	0.70 (4)	0.58 (3)
Sulfometuron methyl	0.84 (4)	0.59 (3)	0.26 (2)	0.21 (2)
Chlorimuron ethyl	0.71 (4)	0.59 (3)	0.41 (3)	0.18 (2)
Bensulfuron methyl	0.46 (3)	0.30 (2)	0.06 (1)	0.05 (1)
DPX-M6316	0.92 (5)	0.73 (4)	0.44 (3)	0.49 (3)

^aThe R_f value is the ratio of the migration of the compound relative to the water solvent front.

^b Mobility descriptor	Range of R _f values	U.S. EPA mobility classification
Immobile	0.0 - 0.09	1
Low mobility	0.10-0.34	2
Intermediate mobility	0.35-0.64	3
Mobile	0.65-0.89	4
Very mobile	0.90-1.00	5

Disadvantages of using soil columns to study herbicide mobility and persistence include disruption of soil physical and chemical properties associated with sieving and air-drying and difficulty in recovery of soil segments (Topp *et al.*, 1994). Variable

results can occur due to unhomogeneously packing of columns. Although much of the natural soil structure remains, macropore structure is lost. These macropores are present in structured field soils due to worms, cracks or root channels and allow for flow of water and solutes.

At various times after application of the herbicide to the column, leachate is collected from columns and assayed for radioactivity by LSS or conventional methods such as gas chromatography (GC) if non-radiolabel is used. Soil from columns can be combusted or extracted with solvent and assayed for radioactivity by LSS. When non-radiobelled herbicides are used, soil can be assayed using bioassays.

Soil columns have been used to test the mobility of the sulfonylurea herbicides in soils of varying pH, organic matter, and clay content. Soil mobility of both ethametsulfuron and chlorsulfuron (Beckie and McKercher, 1990) and sulfometuron methyl (Harvey *et al.*, 1985) was positively correlated to soil pH and inversely correlated to soil organic matter.

1.2.5 Lysimeters

Lysimeters can provide realistic data on movement and persistence of herbicides in soil under field conditions. Experimental conditions closely mimic agricultural situations and general soil structure (macro- and micro-pores, fissures and channels) and allow monitoring of soil temperature and soil moisture throughout the soil profile. As well, mass balance estimations of the fate of herbicides in soil-water-plant-air complex can be made including information on volatilization of the herbicide from plant and/or soil surfaces (Hance and Fuhr, 1990).

Other advantages of using lysimeters include generation of sufficient soil material to carry out extensive analytical investigations (Hance and Fuhr, 1990) and complete collection of leachate (Leake, 1991). Limitations to the use of lysimeters include inability to evaluate movement due to slopes or horizontal dissipation (Hellpointer *et al.*, 1990), range of soil types that can be used are limited to soils without high clay and/or stones and environmental factors cannot always be controlled and often do not reflect field variability. Water content in lysimeters did not correlate well with field situations (Putz *et al.*, 1990) due to lack of continuity of the lysimeter with the deeper soil layers resulting in drier soil since replenishment of soil water during hot dry conditions cannot occur. Similarly, in conditions of high precipitation and little evapotranspiration, soils in lysimeters are unable to store water to the same extent, as can natural field soils.

Soil cores can be removed by sampling and holes refilled with untreated soil. For a long term lysimeter study (e.g. 2 years) soil core removal is restricted to the tillage layer, as refilled soil cores can act as soil pores for water and herbicide movement (Traub-Eberhard *et al.*, 1990). At completion of the study, the monolith is lifted out of the outer container and the inner container is removed. The monolith is sectioned and detailed information about the occurrence of macropores, stones, earthworm channels etc. is recorded. Soil samples are obtained from each segment and analyzed as described in sections 1.2.6 and 1.2.7.

Lysimeters have been used for the determination of both mobility and degradation of sulfonylurea herbicides in soils of varying pH, organic matter content, clay content, and moisture. For example, [^{14}C]amidosulfuron degradation was not

correlated to soil pH when incubated in lysimeters with soil that had been adjusted to various pH levels (Fent *et al.*, 1993).

1.2.6 Soil Bioassays

Soil bioassays are important for predicting the effect of residual levels of a herbicide on a rotational crop. In the past it has been a challenge to find a method for detecting extremely small quantities of herbicide residues in soil and correlating these quantities of herbicides to an effect on a wide range of crop species. Different analytical methods such as high pressure liquid chromatography have been used to detect herbicide residue levels as low as 0.2 ppb (Duffy *et al.*, 1987) but routine analysis is difficult due to the extensive sample preparation required to detect these low levels.

Bioassays are often extremely sensitive depending on the indicator species chosen and require no expensive instrumentation. Only biologically available herbicide is measured so correlation to subsequent crop damage can be more meaningful. As well, samples can be analyzed with very little preparation. Unfortunately, only limited dose-response ranges can be determined for a particular indicator species, therefore, several species are often required to analyze a broad concentration range. Separate calibration curves are usually required for each herbicide and plant species. Preparation of calibration curves and data analysis of samples can take several weeks depending on the response time of a particular indicator species to a herbicide (Beyer *et al.*, 1988). Different indicator species can show different sensitivities. For example, sugarbeet was found to be the most sensitive crop to four sulfonylurea herbicides while sunflower was the least sensitive and lentil showed intermediate sensitivity (Kotoula-Syka, 1993).

Bioassays are be particularly useful for detecting residues of sulfonylurea herbicides (Table 1.9) especially if the residues are unavailable for microbial degradation but available for uptake by rotational crops. Often more than 99.6% of the applied sulfonylurea herbicide must be degraded before sensitive crops can be safely replanted. Chlorimuron ethyl must be degraded from 35 ppb (based on 35 g/ha) to 0.1 ppb before sorghum or rice can be replanted (Brown and Kearney, 1991). Beyer *et al.* (1988) reported that sugarbeet can be damaged by chlorsulfuron residues as low as 0.1 – 1 ppb and may cause damage 53 weeks after application of 10 g/ha. Legumes, potatoes, flax, and sugarbeet appear to be susceptible to damage by chlorsulfuron residues of 0.01 ppb or less in soil (Moyer *et al.*, 1990). These detection limits are difficult to obtain using conventional chromatography methods. Laboratory bioassays are often cost effective, easy to conduct and provide a direct measure of the activity of a pesticide on a plant species without the need for chemical analysis and interpretation (Santelmann, 1977).

1.2.7 High Pressure Liquid Chromatography and Enzyme Linked Immunosorbent Assay

High-pressure liquid chromatography (HPLC), liquid chromatography/mass spectrometry (LC/MS), and enzyme-linked immunosorbent assay (ELISA) are often used for detecting herbicide residues in soil. Of the conventional detection methods, often HPLC provides the most sensitive and easy to perform analysis for determination of the sulfonylurea herbicides although extensive cleanup is often required (Shalaby *et al.*, 1992). Extensive cleanup is often required for analysis by ELISA as well. Detection limits in soil samples employing HPLC have been reported from 0.1 to 1 ppb for chlorsulfuron (Barefoot, 1995b) and 0.2 ppb for sulfometuron-methyl (Blair and Martin,

1988). Detection limits for chlorsulfuron in soil samples have been reported from 0.4 to 1.2 ppb (Kelley *et al.*, 1985) employing ELISA.

Table 1.9 Relative sensitivity of common rotational crops to chlorsulfuron soil residues (Adapted from Beyer *et al.*, 1988).

Tolerant	Moderately Sensitive	Sensitive	Very Sensitive
Wheat (winter/spring Durum Rye Oats Triticale Barley (winter/spring)	Sorghum Soybeans Peas Safflower Millet (proso/pearl) Dry beans Ryegrass Bluegrass Guar Mungbeans Cotton	Flax Corn Sunflower Mustard Rape Potatoes Alfalfa Millet (setaria)	Lentils Sugarbeets Onions

Thermospray LC/MS involves a simple extraction procedure and requires no specific sample cleanup prior to analysis. Nicosulfuron and rimiduron extracted from soils have been detected at 0.02 ppm using this method (Shalaby *et al.*, 1992). Gas chromatography is not used for the detection of the sulfonylurea herbicides due to their low volatility and thermal instability (Beyer *et al.*, 1988).

1.3 Amidosulfuron

1.3.1 Discovery and Uses

Amidosulfuron, also known as HOE 075032 (Figure 2.1, R=CH₃, 3-(4,6-dimethoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl) aminosulfonylurea), is a sulfonylurea herbicide being tested in Canada at doses up to 45 g/ha for postemergence

control of broadleaf weeds in cereals and other crops (Smith and Aubin, 1992). It is currently being used in Europe in cereal crops for control of a variety of weeds including cleavers, which is considered to be the most competitive dicot weed in cereals. The solubility of amidosulfuron is pH dependent. In aqueous media, at 20°C, it was 3.3, 9.0, and 13,500 mg/L at pH values of 3, 5.8, and 10, respectively (*Technical Information HOE 075032 Experimental Herbicide*, 1990). The octanol/water coefficient (K_{ow}) of amidosulfuron is also pH dependent but decreases with increasing pH. Amidosulfuron is non-volatile (vapor pressure 1.3×10^{-5} Pa at 20°C), with a pKa of 3.58, and is 99% anionic at pH 5.6. It undergoes microbial and chemical degradation to the demethylated breakdown product known as HOE 101630 (Figure 2.1, R=H; 3-(6-hydroxy-4-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl) aminosulfonylurea).

Figure 2.1 Structure of amidosulfuron. The asterisk indicates the position of the ^{14}C label.

1.3.2. Uptake and Translocation

Uptake of amidosulfuron is primarily through the leaf tissue and as a weak acid it is transported in the symplast which can be explained by the unified mathematical model (Beyer *et al.*, 1987). Normal plant cells maintain a pH gradient across the plasmalemma with an external pH of 4.5-5 and an internal pH of 7. In the external environment, the ratio of dissociated to undissociated molecules of amidosulfuron will be greater at the more basic internal pH. The undissociated molecular species is more lipophilic than the

dissociated anionic molecule, and more diffuses across the plasmalemma compared to the anion. When the molecular species diffuses out of the cell membrane and reaches the more basic internal environment, it dissociates; the anion becoming trapped in the cell. The rate of uptake into the cell is directly dependent on the lipophilicity of the molecular species. Once trapped in the symplast, amidosulfuron moves in the phloem accumulating in the growing points and affecting the branched chain amino acid pathway that functions primarily in the meristematic tissues (growing point).

Absorption through the root tissue is a passive process that is dependent on the pH of the external solution and the lipophilicity of the herbicide. Availability of the herbicide to the plant is complicated due to the interaction with the soil. The concentration in the soil solution is dependent on the pH of the soil. As pH decreases, the binding to the soil increases and the availability to the plant decreases (Beyer *et al.*, 1987).

1.3.3 Mode of Action

As a sulfonylurea herbicide, amidosulfuron is a potent inhibitor of plant growth while seed germination is not usually affected. Root and shoot growth is severely inhibited in sensitive species with visual symptoms appearing within 1 to 2 days after application. Phytotoxicity is first apparent in the meristematic tissues where growth ceases soon after treatment (Hawkes *et al.*, 1989). There are a variety of secondary plant responses including enhanced anthocyanin production, abscission, vein discoloration, terminal bud death, chlorosis and necrosis (Beyer *et al.*, 1988). Amidosulfuron inhibits acetolactate synthase (ALS), also known as acetohydroxyacid synthase (AHAS), a key

enzyme in the branched-chain amino acid biosynthetic pathway responsible for the production of isoleucine, leucine and valine. The precise mechanism of plant death is not clear. However, it is quite understandable that it is indirectly due to lack of the branched-chain amino acids. Another hypothesis is that toxic intermediates such as α -ketobutyrate and α -aminobutyrate accumulate when branched-chained amino acid synthesis is inhibited.

1.3.4 Environmental Dissipation

Under laboratory conditions half-life of amidosulfuron ranged from 14 days in a sandy loam soil incubated at 30°C to 231 days in a clay soil maintained at 10°C (Smith and Aubin, 1992). Degradation was both temperature and moisture dependent and followed first order kinetics. Smith and Aubin (1993) investigated the hydrolysis of [14 C]amidosulfuron in buffered aqueous solution with pH values of 5, 7 and 9 at 10, 20, 30, 40, and 50°C. Hydrolysis was both temperature and pH dependent following first-order kinetics. The half-life ranged from 1.1 days in buffer at pH 5 and 50°C to >500 days in solution of pH 9 at 10°C. Regardless of the pH and temperature, [14 C]-2-amino-4, 6-dimethoxypyrimidine (formed as a result of cleavage of the sulfonylurea bridge) was the major degradation product. Smith and Aubin also incubated [14 C]amidosulfuron in a silt loam (pH 5.2) at 20°C and 85% field capacity (21% moisture) and calculated a half live of 36 ± 6 days. The half-life of [14 C]amidosulfuron when incubated at 20°C and 85% field capacity in a loamy sand soil (pH 7.3) in a previous study (Smith and Aubin, 1992) was 26 ± 3 days. From these studies it was concluded that although degradation in

aqueous buffers was strongly pH dependent, factors other than pH dependent chemical hydrolysis were responsible for degradation in soil.

Fent *et al.* (1993) found a rapid loss of radioactivity in lysimeters within 3 to 5 months after application. Most of the remaining radioactivity (30% of applied) was unextractable. Intact amidosulfuron was recovered in trace amounts and only in the 0-10 cm layer of soil. For their study the half-life of [^{14}C]amidosulfuron was 14 days and no damage occurred to canola the next year. Climatic conditions in this study are not comparable to those of western Canada. Fent *et al.* (1993) suggested that microbial degradation rather than chemical (pH) hydrolysis was the major mechanism of degradation.

1.4. Research Objectives

The objective of this study was to determine the dissipation rate of [^{14}C]amidosulfuron and its degradation products under field conditions from three different locations in western Canadian dryland soils with different pHs, textures, moistures, and temperatures. The treated areas were cultivated using typical agronomic practices for western Canada. Based on half-life data the expected carry-over and susceptibility of subsequent crops to soil residues of amidosulfuron were determined.

At the onset of this study, my hypothesis was that degradation of amidosulfuron would be slower at the Minto, Manitoba site than at the two Saskatchewan sites as the soil pH and organic matter were all higher in the soil from the Minto site.

2.0 MATERIALS AND METHODS

2.1 Chemicals

3-(4,6-dimethoxypyrimidin-[2-¹⁴C]-yl)-1-(N-methyl-N-methylsulfonyl)amino-sulfonylurea was obtained from Hoechst Aktiengesellschaft (Frankfurt am Main, Germany) with a specific activity of 2,267 MBq/g and a radiochemical purity of >99%. Analytical samples of non-radioactive amidosulfuron (HOE 075032, R=CH₃, 98.5% pure) and the soil degradation product 3-(6-hydroxy-4-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl)aminosulfonylurea (HOE 101630, R=H, 97.2% pure) were provided by Hoechst Aktiengesellschaft. For HPLC analysis, a solution of non-radioactive amidosulfuron was prepared in acetonitrile (1 mg/mL), while HOE 101630 (1 mg/mL) was prepared using a mixture of water and acetonitrile (3:1 v/v).

2.1 Soils

2.2.1 Soil Type

Three types of soils were used in the study: a Bradwell soil (Typic Haploboroll, coarse-loamy, mixed) from Saskatchewan (SK), a Ryerson soil (Udic Haploboroll, fine loamy, mixed) from Minto, Manitoba (MB), and a Swinton soil (Typic Haploboroll, fine silty, mixed) from Swift Current, Saskatchewan (SK). Physical characteristics of each soil are summarized in Table 2.1.

2.2.2 Soil Preparation

At the three different sites, Bradwell, Saskatchewan, Minto, Manitoba and Swift Current Saskatchewan, an 8-m x 7-m area was cultivated and leveled using a rake. A 1.2-

Table 2.1 Composition and physical characteristics of soils.

Soil Depth (cm)	soil type	% composition			Physical characteristics					
		Sand	Silt	Clay	CEC ^a	pH ^b	EC ^c	OM ^d	IC ^e	FC ^f
	coarse-loamy	Bradwell, SK								
0-10		53	26	21	17.2	6.4	0.1	3.3	0.06	18.6
10-20		60	21	19	12.5	6.8	0.1	1.7	0.04	16.8
20-30		58	22	20	12.3	7.1	0.1	1.2	nd ^g	14
	fine-loamy	Minto, MB								
0-10		28	39	33	31.5	7.9	0.6	6.6	0.18	34.8
10-20		22	42	36	30.1	8.2	0.6	4.8	0.32	33.3
20-30		22	42	36	24.6	8.1	1.9	3	0.77	39.9
	fine-silty	Swift Current, SK								
0-5		33	42	25	20.7	6.2	0.1	1.8	0.14	18.1
5-10		31	44	25	21.2	6.4	0.1	1.8	0.02	20.0
10-15		28	45	27	21.4	6.5	0.1	1.5	0.03	24.7
15-30		25	47	28	22.7	7.2	0.1	1.4	0.02	24.9

^aCation exchange capacity (meq/100g). ^b1:2 soil to water. ^cElectrical conductivity (mS/cm). ^d% organic matter. ^e% inorganic carbon. ^fField moisture capacity (1/3 bar). ^gNot determined.

m high plastic snow fence was erected to surround the entire treatment area. Thirty micro-plots (5 rows of 6 micro-plots) were positioned within the 8-m x 7-m area. Each micro-plot area was delineated with four flat, wooden stakes positioned in the ground forming a 10-cm x 10-cm area. These stakes were used as a guide when adding the treated soil as well as to identify the treated areas for subsequent sampling. Each micro-plot was located no closer than 1 m from any adjacent micro-plot or the site perimeter. The fenced-in areas were kept weed-free during the monitoring period.

2.2.3 Treatment Preparation

Soil from the 0-5 cm depth at all locations was collected several weeks prior to the application of [^{14}C]amidosulfuron. The soil was air dried and screened through a 2-mm sieve. Thirty scintillation vials, containing 10 g of soil, were prepared for each site. A stock solution of [^{14}C]amidosulfuron was prepared in a 1:1 v/v (95% ethanol:acetone). Liquid scintillation spectroscopy was used for quantitative detection of radiolabelled amidosulfuron. Analysis confirmed that the solution contained 1.46 MBq/mL.

The soil contained in each vial was spiked with 0.22 MBq (97 μg of herbicide) of [^{14}C]amidosulfuron stock. The solvent was allowed to evaporate and the vials were shaken by hand for 15 seconds.

2.2.4 Treatment Application

The Bradwell, Minto, and Swift Current sites were treated on July 3, 1992 (Bradwell), July 8, 1992 (Minto), and June 11, 1993 (Swift Current), respectively. During the application, a wooden form (10x10x5 cm) was positioned around flat, wooden

stakes to minimize wind interference. Spiked soil (described above) from each scintillation vial was carefully poured through a glass funnel onto the surface of each micro-plot (10x10cm). A small volume of acetone was used to rinse the vial and the rinsate was added to the micro-plot as part of the application. Immediately following each application, the surface area of each micro-plot was covered with fresh sieved soil and lightly tamped with a flat-bottomed instrument. Since the treatment area in the micro-plot was 100 cm², applying 97 µg of [¹⁴C]amidosulfuron to this area was equivalent to an application rate of 97 g/ha.

2.2.5 Soil Sampling

At all sites, soil samples were collected from three micro-plots in a random fashion at 13 different times ranging from 0 to 66 weeks after treatment (WAT). Soil samples were excavated incrementally from the 0-5, 5-10, 10-15 and 15-30 cm depths using a stainless steel form that was designed to sample a 100 cm² area 5-cm deep. Prior to the removal of the 0-5 cm depth, a Back-Saver soil probe (3.18-cm diameter) was used to collect soil from the buffer area outside the metal form. A single, solid core was removed to a 30-cm depth along all four sides of the metal form. Soil samples from the buffer area around each micro-plot were analyzed to determine if any radioactivity moved laterally. Cores from all four sides of the micro-plot were subdivided into the four depths mentioned above and combined. Soil from the buffer area and lower depths within the micro-plots were not collected 0 WAT.

Once buffer samples were collected, the treated area was excavated. Soil surrounding the stainless steel form was removed to a specified depth (e.g. 5-cm) to allow a hacksaw blade to cut across the bottom of the metal form. This technique minimized the

amount of disturbance to the sampling profile and provided a uniform soil volume. The entire sample within the steel form was removed and transferred to a labeled, foil-lined bag. The metal form was then repositioned and pressed down another 5-cm depth. All excavated holes were repacked with untreated soil and leveled.

Untreated soil samples were collected 0, 4 and 16 WAT. Triplicate sites were selected at random along the inside perimeter of the fence. Untreated soil was taken prior to collection of treated soil to avoid contamination of the metal form and hence the untreated soil samples.

All collected samples were transported in coolers packed with dry ice or in a portable freezer equipped with a gas-powered generator. Samples were stored frozen prior to analysis. The moisture content of the soil was determined by weighing duplicate sub-samples before and after drying at 105°C for 24 hours.

AgrEvo Canada Inc. and Ag-Quest Inc conducted soil and treatment preparation, treatment application and, soil sampling.

2.2.6 Recovery Studies

Laboratory studies were conducted to assess the extractability of [^{14}C]amidosulfuron from the soils. Soil samples from all four depths (0-5, 5-10, 10-15 and 15-30 cm) were weighed and subsequently air dried overnight. Soil (40 g) from each experimental site was spiked with 0.011 MBq [^{14}C]amidosulfuron (0.12 μg of herbicide/g of soil) dissolved in ethanol. The samples were incubated for 36 hours in sealed glass jars that were kept in the dark and extracted as described by Smith and Aubin (1992). The soil samples (40 g) were shaken with 100 mL of aqueous acetonitrile [(acetonitrile:water:glacial acetic acid (80:20:2.5 v/v/v)], centrifuged, and the

radioactivity in an aliquot of the supernatant was determined. A 25-mL aliquot of the supernatant (equivalent to 10 g of moist soil) was evaporated to near dryness under reduced pressure at 40°C using a rotary evaporator. The remaining residue was brought up to 2 mL in water:acetonitrile (1:1 v/v) and filtered through a 0.22 µm nylon filter before being injected into the HPLC. After solvent extraction, the soil (ca. 40-g) was collected by vacuum filtration, successively washed to remove all solvent-extractable radioactivity, and dried. Triplicate samples (1 g) of each soil were assayed for radioactivity by combustion analysis to determine bound radioactivity. Following extraction, [¹⁴C]amidosulfuron was determined by HPLC to be the only radioactive species present in the spiked soil samples.

2.2.7 Soil Extraction

Extraction of radioactive amidosulfuron from field samples was accomplished in two steps. First, frozen soil samples from the three [¹⁴C]amidosulfuron treated field sites were thawed at 20°C and mixed using a rotary blender. Triplicate samples of 1 g were taken randomly throughout the mixture and combusted to quantitate radioactivity. Samples that contained high radioactivity (>25Bq/1g soil) were taken through the extraction process. The extraction and analysis methods were identical to those described for the radioactivity recovery study. Soil samples (50 g) were shaken with 100-mL aqueous acetonitrile. The amount of solvent added was corrected to account for the moisture content of each soil sample. Soil particles were separated from the aqueous solution by centrifugation. Radioactivity remaining in the soil was determined by combustion. Radioactivity in the aqueous solutions was measured by liquid scintillation spectroscopy.

Figure 2.2 Rainfall recorded at each location from July – Oct., 1992-1993 Bradwell, Minto; June – Oct., 1993-1994 Swift Current). The number after the month denotes the year (i.e. -1 is year of application, -2 is year after application, data was not collected from Oct-April).

Figure 2.3 Mean temperatures recorded at each location from July – Oct., 1992-1993 Bradwell, Minto; June – Oct., 1993-1994 Swift Current). The number after the month denotes the year (i.e. -1 is year of application, -2 is year after application, data was not collected from Oct-April).

2.2.8 Measurement of Radioactivity

Radioactivity in the various solutions was measured using a Beckman LS6K-SC scintillation counter (Beckman Instruments Inc., Fullerton, California, USA). Ecolite (+) (ICN Biomedicals Inc., Irvine, California, USA) scintillation cocktail was used. Unextracted radioactivity was quantified by oxidizing the extracted soil material in a model OX-300 biological oxidizer (R.J. Harvey Instrument Corp., Hillsdale, NJ, USA).

The resulting $^{14}\text{CO}_2$ was trapped in Carbon-14 cocktail (R.J. Harvey Instrument Corp.) and quantified by liquid scintillation counting as described above. The efficiency of $^{14}\text{CO}_2$ recovery, as determined by combusting [^{14}C]Spec Chec (Packard, Downers Grove, IL) calibration standards, was greater than 95 %.

2.2.9 High Pressure Liquid Chromatography Analysis

Filtered extracts were analyzed on a Shimadzu Model LC-6A liquid chromatography system (Shimadzu Scientific Instruments Inc., Columbia, Maryland, USA), equipped with a Spherex column (10 x 250 mm, 5 μm particle size; reverse phase (C_{18}); Phenomenex, Torrance, California, USA). Chromatographic conditions generally consisted of a mobile phase of A= H_2O + (0.1 % v/v) sulfuric acid (pH 2.5), B=acetonitrile and a linear gradient from 0 to 90% B over 70 minutes; flow rate 2.0 mL/min.; ambient temperature 22°C. For the Bradwell samples, from day 308 onward, the same chromatographic conditions were used except a concave (#2) gradient was employed to help separate the parent from degradation products. For all Swift Current and Minto soils (308 to 448 days), a linear gradient and a flow rate of 1.0 mL $\cdot\text{min}^{-1}$ were used to improve the resolution of the chromatograms. Radiolabeled residues were detected and quantified by a Radiomatic FL-ONE\Beta A-200 radioactivity flow detector (Radiomatic Instruments and Chemical Co. Inc., Tampa, Florida, USA). The column eluant was automatically augmented with 4 mL $\cdot\text{min}^{-1}$ of Ecolite liquid scintillation solution before reaching the detector. The retention time of amidosulfuron was compared to the authentic radiolabeled standard. The retention time of amidosulfuron and HOE 101630

also was compared to a non-labeled standard using a Shimadzu model SPD-M6A photodiode array UV-VIS detector at a wavelength of 238 nm.

3.0 RESULTS

The mean recovery of radioactivity from the three air-dried soil types (40 g) from each soil depth, spiked with [^{14}C]amidosulfuron (0.12 μg) 36 h prior to extraction, was 94 ± 4 % of the applied radioactivity. All of the radioactivity was [^{14}C]amidosulfuron as determined by HPLC, indicating that the conditions used for extraction and chromatography did not cause degradation of the parent compound.

As time after application of amidosulfuron increased, there was a gradual loss of applied radioactivity from all three soils. Losses ranged from 55% after 462 days in the Bradwell, SK soil, 73% after 462 days in the Swift Current, SK soil, and 54% after 448 days in the Minto, MB soil (Table 2.2). These losses can be attributed to unrecovered $^{14}\text{CO}_2$ being produced by degradation of [^{14}C]amidosulfuron and its [^{14}C] degradation products (Smith and Aubin, 1992), and/or leaching of [^{14}C] compounds through the soil profile.

3.1 Mobility in Soil

Amidosulfuron was more mobile in soils from the Bradwell and Swift Current sites (Table 2.2). Seven days after application of [^{14}C]amidosulfuron, these soils had detectable radioactivity in the 5-10 cm soil horizon. From day 28 to 462, detectable radioactivity was found at all soil depths of the Swift Current soil. In the Bradwell soil, radioactivity was found at all soil depths from day 112 onward. In contrast, there was little movement of radioactivity in the Minto. For example, 308 days after

Table 2.2 Radioactivity recovered from soils treated with [^{14}C]amidosulfuron

Soil depth (cm)	% of applied radioactivity (days after application) ^a											
	7 d	14 d	28 d	56 d	105 d	112 d	308 d	364 d	371 d	420 d	448 d	462 d
Bradwell, SK												
0-5	103±5	92±5	85±2	101±6		57±2	61±7		37±1			35 ^b
5-10	1±0	6±0	4±0	7±0		18±2	15±2		14±1			6
10-15	nd ^c	nd	nd	nd		4±0	4±0		4±0			3
15-30	nd	nd	nd	nd		3±1	3±0		4±1			1
Total	104±5	98±3	89±3	108±5		82±4	83±6		59±3			45
Minto, MB												
0-5	98±9	88±3	99±4	107±3	97±4		84±2	58±9			36±2	
5-10	nd	nd	nd	nd	nd		2±1	5±1			10±3	
Total	98±9	88±3	99±4	107±3	97±4		86±2	63±7			46±3	
Swift Current, SK												
0-5	86±3	69±8	28±2	28±2		18±4			13±7	10±2		13±1
5-10	5±0	38±0	17±1	13±1		9±1			6±1	5±0		7±1
10-15	nd	nd	12±1	7±0		7±1			3±1	4±1		4±1
15-30	nd	nd	14±2	9±3		6±0			4±0	3±0		3±1
Total	91±3	107±6	71±2	57±3		40±3			26±5	22±2		27±1

^aData are expressed as a % of radioactivity recovered at day 0; mean and standard error from three replicates. ^bDetermined from one replicate. ^cNot detectable.

[¹⁴C]amidosulfuron was applied, only 2% of the applied radioactivity was below the 0-5 cm soil profile (Table 2.2). No radioactivity was detected below the 5-10 cm profile at the Minto site. Regardless of soil type, there was little (<3.34 Bq/g of soil) or no radioactivity detected in soil from the buffer strips indicating that there was little lateral movement of the herbicide.

3.2 Degradation in Soil

Breakdown of amidosulfuron was found to be greater in the 0-5 cm depth of the Bradwell and Swift Current soils than in the Minto soil. Half-lives (from soils at the 0-5 cm depth) were calculated assuming first order kinetics (Figure 2.4) and were 13±1, 29±1, and 256±9 days for the Swift Current, Bradwell, and Minto soils, respectively (Table 2.3). A degradation product, hereafter known as metabolite A, co-migrated with the authentic standard of HOE 101630 as determined by HPLC (Figure 2.5). This metabolite was found in the Bradwell soil from day 7 to 56 (0-5 cm) with a maximum amount of 11% (of applied radioactivity) occurring at day 28. Three other degradation products were found in the Bradwell soil, hereafter known as metabolite B, C, and D., Metabolite B was found from day 7 to 56, metabolite C from day 14 to 56 and metabolite D from day 28 to 56 (Table 2.5). In the Minto soil (0-5 cm), metabolite A was found from day 7 to 448 and metabolite B from day 28 to 448 (Table 2.5). In the Swift Current soil, metabolite A and metabolite B were found from day 7 to 56 (0-5 cm) (Table 2.5). Most of the [¹⁴C] degradation products were polar, and their proposed structures are indicated in Figure 2.6. No attempts were made to identify these degradation products. Regardless of the soil type or depth, less than 25% of the recovered radioactivity was bound (not extracted with solvent).

Table 2.3 Half-life values for the breakdown of [¹⁴C]amidosulfuron at the 0-5 cm soil depth.

Soil Type	Half-Life ^a , days
Bradwell sandy loam	29±1
Minto clay loam	256±9
Swift Current loam	13±1

^aMean and standard deviation from three replicates.

Evaluation of an amidosulfuron re-cropping trial was conducted at the Minto site. Several rotational crops were evaluated after emergence for plant number, plant height, and injury (Table 2.4). Amidosulfuron had no effect on emergence of the crops. However, lentil, sugar beet and sunflower were severely injured by the herbicide one-year after application. There was no injury to canola, peas, flax, or oat. There were no significant differences in plant height or numbers for any of the crops tested (data not shown).

Table 2.4 Effect of amidosulfuron on rotation crops one year after application to the Minto, MB site.

Weed/Crop	Canola	Lentils	Peas	Sunflower	Flax	Oats	Sugar Beets
Rating Unit	0-9	0-9	0-9	0-9	0-9	0-9	0-9
ECW ^a							
Untreated	9.0a	9.0a	9.0a	9.0a	9.0a	9.0a	9.0a
Treated	9.0a	5.7b	8.3a	5.3b	8.7a	9.0a	5.3b

^aMeans followed by the same letter are not significantly different ($P \leq 0.5$) as determined by a Duncan's Multiple Range Test. Means are based on a 0-9 visual damage evaluation system recommended by the Expert Committee on Weed (ECW), Canada.

4.0 DISCUSSION

4.1 Mobility in Soil

In general, soil pH and organic matter are the main factors affecting the mobility of the sulfonylurea herbicides, with mobility being reduced as organic matter content and pH increase (Smith, 1982; Beyer *et al.*, 1988). In the Minto soils, amidosulfuron may be

expected to leach more than in the lower pH Bradwell and Swift Current soils since more of the herbicide would be in the anionic form. However, the high organic matter and clay content in the Minto soil as well as low precipitation may explain why amidosulfuron did not move beyond the 0-5 cm horizon until 308 days after application (Table 2.3). Conversely, increased mobility in the two Saskatchewan soils, especially at the Swift Current site, may be attributed to more rainfall (Figure 2.2), as well as lower soil organic matter and clay content.

4.2 Degradation in Soil

Degradation of amidosulfuron in soil results from both biological and chemical mechanisms, which are influenced by temperature, pH and moisture content. Chemical hydrolysis of sulfonylurea herbicides is the predominant means of degradation in acidic soils (Joshi *et al.*, 1985; Duffy *et al.*, 1987; Beyer *et al.*, 1988; Blair and Martin, 1988; Walker *et al.*, 1989; Hay, 1990). At a pH above the pKa, the sulfonylurea bridge exists as an anion and is not subject to hydrolysis while at a pH near or below the pKa, the bridge is protonated and readily undergoes hydrolysis. Microbial breakdown also contributes to the degradation of sulfonylureas in soils, although it is usually less significant than chemical hydrolysis. Furthermore, higher soil temperatures and moisture content promote both faster microbial degradation and chemical hydrolysis of sulfonylurea herbicides (Thirunarayanan *et al.*, 1985; Beyer *et al.*, 1988) although microbial degradation can be reduced when soil pH is greater than 7-7.5 (Thirunarayanan, 1985). In alkaline soils, it was thought that microbial action was the rate-limiting step in the breakdown of sulfometuron methyl (Anderson and Dulka, 1985). Thus, the slower degradation of

Table 2.5 Quantification of [^{14}C] degradation products found at the 0-5 cm depth in soils treated with [^{14}C]amidosulfuron

^{14}C extracted from soil	% of applied radioactivity (days after application) ^a										
	7 d	14 d	28 d	56 d	105 d	112 d	308 d	364 d	371 d	448 d	462 d
Bradwell, SK											
solvent extractable	95±8	80±6	68±2	76±8		38±7	37±7		22±2		15 ^b
Amidosulfuron	87±8	62±4	42±1	31±3		13±1	8±1		4±1		2
Metabolite A	4±0	9±1	11±0	10±2		nd	nd		nd		nd
Metabolite B	3±0	5±1	5±0	11±1		nd	nd		nd		nd
Metabolite C	nd ^c	3±0	8±2	20±3		nd	nd		nd		nd
Metabolite D	Nd	nd	1±1	3±1		nd	nd		nd		nd
Other	1±0	1±0	1±0	1±1		25±1	29±6		18±1		13
Soil associated ^d	8±1	12±1	17±0	25±2		19±1	24±5		15±3		20
Total recovered ^{14}C	103±5	92±5	85±2	101±6		57±2	61±7		37±1		35
Minto, MB											
Solvent extractable	89±7	80±5	84±8	94±4	84±6		67±1	44±14		24±2	
Amidosulfuron	85±7	78±5	81±9	90±4	79±6		60±1	37±12		13±2	
Metabolite A	2±2	1±0	1±1	2±1	2±0		3±0	3±1		2±1	
Metabolite B	Nd	nd	1±1	1±1	2±1		2±1	1±1		1±1	
Other	2±1	1±1	1±0	1±0	1±1		2±0	3±1		8±1	
Soil associated	9±3	8±2	15±3	13±1	13±1		17±0	14±4		12±2	
Total ^{14}C recovered	98±9	88±3	99±4	107±3	97±4		84±2	58±9		36±2	
Swift Current, SK											
Solvent extractable	81±6	59±8	22±2	21±2		11±4					
Amidosulfuron	74±6	49±7	16±2	11±1		4±2					
Metabolite A	2±1	3±1	1±0	1±0		nd					
Metabolite B	2±1	4±1	2±1	2±0		nd					
Other	3±1	3±1	3±1	7±1		7±2					
Soil associated	5±0	10±2	6±2	7±1		7±3					
Total ^{14}C recovered	86±3	69±8	28±2	28±2		18±4					

^aData are expressed as a % of radioactivity recovered at day 0; mean and standard error from three replicates. ^bDetermined from one replicate. ^cNot detectable. ^dDetermined by combustion of the solvent-extracted soils.

amidosulfuron in the Manitoba soil may be attributed mainly to the higher pH of the soil, and the drier environmental conditions during the growing season (106 mm of precipitation in 1992) compared to Bradwell (185 mm of precipitation in 1992) and Swift Current (395 mm of precipitation in 1993) soils (Figure 2.2). A 100-year average for precipitation, during the growing season, at the Minto site is 246 mm while a 30-year average at the Swift Current site is 201 mm. There was no historical record for precipitation at the Bradwell site. The faster degradation in the two Saskatchewan soils may also be attributed to slightly higher mean temperatures in 1992 at the Bradwell and in 1994 at the Current locations (Figure 2.3).

Although the degradation products were not identified in this study, it is presumed that some of the amidosulfuron was degraded to HOE 101630, a product of demethylation. Other degradation products may have resulted from the cleavage of the sulfonylurea bridge. Smith (1993) determined that [^{14}C]amidosulfuron underwent hydrolysis to [^{14}C]-2-amino-4,6-dimethoxypyrimidine (2-ADMP) when incubated in aqueous buffers. This degradation product is a result of cleavage of the sulfonylurea bridge. At pH 7 and 9, the entire radioactivity was identified (by TLC analysis) as either [^{14}C] amidosulfuron or [^{14}C] -2-ADMP. At pH 5 there was a ^{14}C polar product whose concentration increased with time before being hydrolyzed, presumably to 2-AMDP. Smith (1993) did not find either of these breakdown products in soils treated with [^{14}C]amidosulfuron. It is possible that 2-ADMP was formed transiently before undergoing biological modification to demethylated hydroxypyrimidines. In earlier studies, Smith and Aubin (1992) found that a considerable amount of radioactivity applied as [^{14}C] amidosulfuron was converted to polar, water-soluble products, which

were probably modified pyrimidines. Based on degradation products, it is clear that bridge cleavage, ring cleavage, alkaline hydrolysis, and ester hydrolysis can all occur (Figure 2.6). However, when different sulfonylureas were studied under aqueous conditions, especially at low pH values (Sabadie 1990, 1991; Berger and Wolfe, 1996), bridge cleavage was the most common degradation reaction.

Although calculations of the half-life for amidosulfuron were based on the extractable radioactivity, if the unextracted portion or the bound residue is unaltered amidosulfuron, it may have a significant impact on subsequent rotational crops. Bound residue formation is promoted by fast microbial degradation (Lichtenstein, 1980) and once the herbicide is incorporated into humic substances, the extent to which degradation occurs may be limited (Kaufman, 1976). Both physical and chemical binding of the herbicide or its metabolites may result in bound residues that remain after chemical extraction (Khan, 1991). At the Minto, MB site, bound residues reached a maximum value of 17% at 308 days after treatment compared to 25% at 56 days after treatment at the Bradwell, SK site (Table 2.5).

The chemical nature of bound herbicide residue is not always known. Consequently their significance, in terms of toxicity and availability, is hard to predict. Bound residues of some herbicides have been shown to be released from the soil and taken up by plants although uptake was mostly below 1% of the amount bound in soil (Helling and Krivonak, 1978; Fuhr and Middelstaedt, 1980; Khan, 1980). Bioassays are good indicators of whether these bound residues are biologically available and phytotoxic. In laboratory bioassay experiments amidosulfuron had an ED₅₀ of 6.75 ppb and 6.59 ppb for foliar freshweight reduction in sugarbeet and witloof chicory,

respectively (Bulcke and Callens, 1995). Five weeks after spring application of amidosulfuron at 30 g/ha, both witloof chicory and sugarbeet exhibited severe foliar injury and subsequent yield reductions greater than 85%. The soil persistence of amidosulfuron in the Minto soil is confirmed by the damage to sensitive rotational crops one-year after application (Table 2.4), whereas, there was no damage to rotational crops at the two Saskatchewan sites (data not shown).

Figure 2.4 Non-linear regression of [^{14}C]amidosulfuron degradation.

Figure 2.5 HPLC chromatogram indicating retention times of [^{14}C]amidosulfuron and degradation products.

Figure 2.6 Proposed degradation pathway of amidosulfuron in soil.

5.0 CONCLUSIONS

The mobility and degradation of amidosulfuron in prairie soils is highly dependent on soil pH, organic matter content, and climatic conditions. The movement and degradation of [^{14}C]amidosulfuron was greater in low pH, low organic matter content soils such as the Bradwell and Swift Current, Saskatchewan soils in this study. Conversely, applications of amidosulfuron to alkaline (>pH 7.5) soils like the Minto, Manitoba soil result in carry-over residues that can damage sensitive broadleaf crops planted the year after application. The 10 to 20 fold increase in the half life of amidosulfuron in the Minto, Manitoba soil is unprecedented and indicates the importance of understanding all of the factors contributing to degradation. Future research to understand the degradation of amidosulfuron in soil should include controlled factorial experiments in order to determine which of the factors, soil pH, organic matter, clay content, temperature and moisture, are most important.

Both short and long-term studies of persistence are important for agronomic and environmental reasons. More quantitative interpretation of soil residue data is required to allow better use of information generated. Extensive data for many herbicides remain specific to the sites and seasons of collection. The compilation of data from different sites and seasons together with soil characteristics and weather records may allow development of predictive regression equations (modeling).

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