



Soil movement and residual aspects of chlorsulfuron and its control of Canada thistle (*Cirsium arvense* (L.) Scop.)

by William Edward Dyer

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Agronomy

Montana State University

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Abstract:

Chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl] benzenesulfonamide) is a new, residual herbicide used for the control of broadleaf weeds in small grains. Chlorsulfuron controls several 2,4-D [(2,4-dichlorophenoxy)acetic acid] resistant weeds and Canada thistle [*Cirsium arvense* (L.) Scop.]. Suggested use rates, which depend upon soil pH, range from 9 to 26 g a.i./ha. Chlorsulfuron is mobile in the soil, and has a high potential for leaching. Degradation of chlorsulfuron, which is accomplished through chemical hydrolysis, is slower in alkaline soils.

The movement of chlorsulfuron was measured in soil columns. Bioassays using foxtail millet [*Setaria italica* (L.) Beauv. 'Golden German'] indicated that chlorsulfuron was present to the bottom of 22.5 cm soil columns, after leaching the soil to field capacity. Under similar leaching conditions, <sup>14</sup>C-labeled chlorsulfuron was found in decreasing amounts with increasing depth in soil columns. Delays after herbicide application and before leaching with water had little effect on the degree of chlorsulfuron movement. <sup>14</sup>C-labeled chlorsulfuron moved as a concentrated front on soil thin-layer chromatography (TLC) plates. Increased movement on soil TLC plates was attributed to the high herbicide:soil ratio used.

The effect of soil residues of chlorsulfuron on 11 rotational crops grown in Montana was measured. Weed control and crop injury ratings, and crop dry weights were taken for 3 successive years after applications of 35, 70, and 140 g a.i./ha. Dry weight was reduced for all crops tested by all rates of application except wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), and oats (*Avena sativa*) 36 months after herbicide application. The rate of degradation of chlorsulfuron in two Montana soils appeared to be consistent with a reported half-life of 60 days.

The effect of chlorsulfuron on Canada thistle regrowth was measured. Chlorsulfuron, applied at 18, 35, and 70 g a.i./ha, reduced Canada thistle stems/m<sup>2</sup> 1 year after application. Applications at the 5 leaf stage of Canada thistle appeared to be slightly more effective than treatments applied at the bud stage. There was no reduction of Canada thistle stems/m<sup>2</sup> by any rate 2 years after application. Treatments applied in 2 successive years at lower rates provided more control of Canada thistle regrowth after 2 years than single applications at higher rates.

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William Edward Dyer

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## ABSTRACT

Chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]benzenesulforamide) is a new, residual herbicide used for the control of broadleaf weeds in small grains. Chlorsulfuron controls several 2,4-D [(2,4-dichlorophenoxy)acetic acid] resistant weeds and Canada thistle [*Cirsium arvense* (L.) Scop.]. Suggested use rates, which depend upon soil pH, range from 9 to 26 g a.i./ha. Chlorsulfuron is mobile in the soil, and has a high potential for leaching. Degradation of chlorsulfuron, which is accomplished through chemical hydrolysis, is slower in alkaline soils.

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The effect of chlorsulfuron on Canada thistle regrowth was measured. Chlorsulfuron, applied at 18, 35, and 70 g a.i./ha, reduced Canada thistle stems/m<sup>2</sup> 1 year after application. Applications at the 5 leaf stage of Canada thistle appeared to be slightly more effective than treatments applied at the bud stage. There was no reduction of Canada thistle stems/m<sup>2</sup> by any rate 2 years after application. Treatments applied in 2 successive years at lower rates provided more control of Canada thistle regrowth after 2 years than single applications at higher rates.

## CHAPTER 1

## LITERATURE REVIEW

Movement of Chlorsulfuron in Soil

Movement of herbicides in soil is affected by (1) adsorption, (2) physical properties of the soil, and (3) climatic conditions (Bailey and White, 1970). Each of these factors must be considered before a discussion of chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl] benzenesulfonamide) and its behavior in the soil can progress.

Adsorption

The relationship between adsorption and herbicide movement is not fully understood. Upchurch and Pierce (1957, 1958) proposed that two steps are involved in the leachability of a herbicide: (1) entrance of the molecule into solution and (2) adsorption of the molecule to soil colloids. Entrance of a herbicide into the soil solution can take place either from the dissolution of the herbicide particle or from desorption from a colloidal surface. Once the herbicide molecule is present in the soil solution, factors including the soil or colloid type, the chemical nature of the herbicide molecule, soil reaction (pH), temperature, and the nature of the herbicide formulation will influence its adsorption onto soil colloids. Each of these factors will be discussed as they apply to the adsorption and leaching potential of chlorsulfuron.

Soil colloids are generally divided into the mineral and organic fractions. The expanding 2:1 clay minerals, such as montmorillonite (which is the predominant clay in Montana) (Anon., 1975), have a high cation exchange capacity and large surface area. These proper-

ties impart a high adsorption capacity. However, because chlorsulfuron is weakly acidic (Shea, 1982), it would tend to be negatively adsorbed to clay colloid surfaces (Carringer et al., 1975). Further, clay surfaces in natural soils are usually coated with organic matter, which reduces the number of clay sites available for adsorption (Hance, 1969). If this is the case, chlorsulfuron is not adsorbed to a significant degree by clay colloids.

Adsorption of herbicides to organic matter is strongly correlated to retention against leaching (Helling et al., 1971). Goring (1967) cited 41 references attesting to the importance of organic matter in soil adsorption of pesticides. Chlorsulfuron, which is classified as a sulfonylurea herbicide, is related to the triazine and urea families of herbicides (Figure 1). There are several reports (Williams, 1968; Walker and Crawford, 1970; Wu and Santelmann, 1975; Lambert et al., 1965) which showed that triazine herbicides were adsorbed more and leached less in heavy, high organic matter soils than in light, sandy soils. The substituted urea herbicides have been shown to behave in a similar manner (Harris and Warren, 1964; Hilton and Yuen, 1963; Upchurch and Pierce, 1958; Sherburne et al., 1956; Grover, 1975; Yuen and Williams, 1962; Rhodes et al., 1970). There should therefore be more adsorption and less leaching potential for chlorsulfuron on high organic matter soils, as has been reported by Palm et al. (1980).

The chemical nature of a herbicide molecule has a direct influence on its capacity to be adsorbed. Adsorption is increased by the presence of such functional groups as  $R_3N^+$ ,  $-CONH_2$ ,  $-OH$ ,  $-NHCOR$ ,  $-NH_2$ ,  $-OCOR$ , and  $-NHR$  on the adsorbate molecule (Helling et al., 1971). Amino groups may become protonated and be adsorbed as cations. Carbonyl and amino groups may participate in hydrogen bonding. Chlorsulfuron, which contains two amino groups, should be adsorbed. However, polarity and polarizability (a measure of the ease by which the positive and negative charges in a molecule can be displaced with respect to each other in the presence of an electric field) are also important forces in

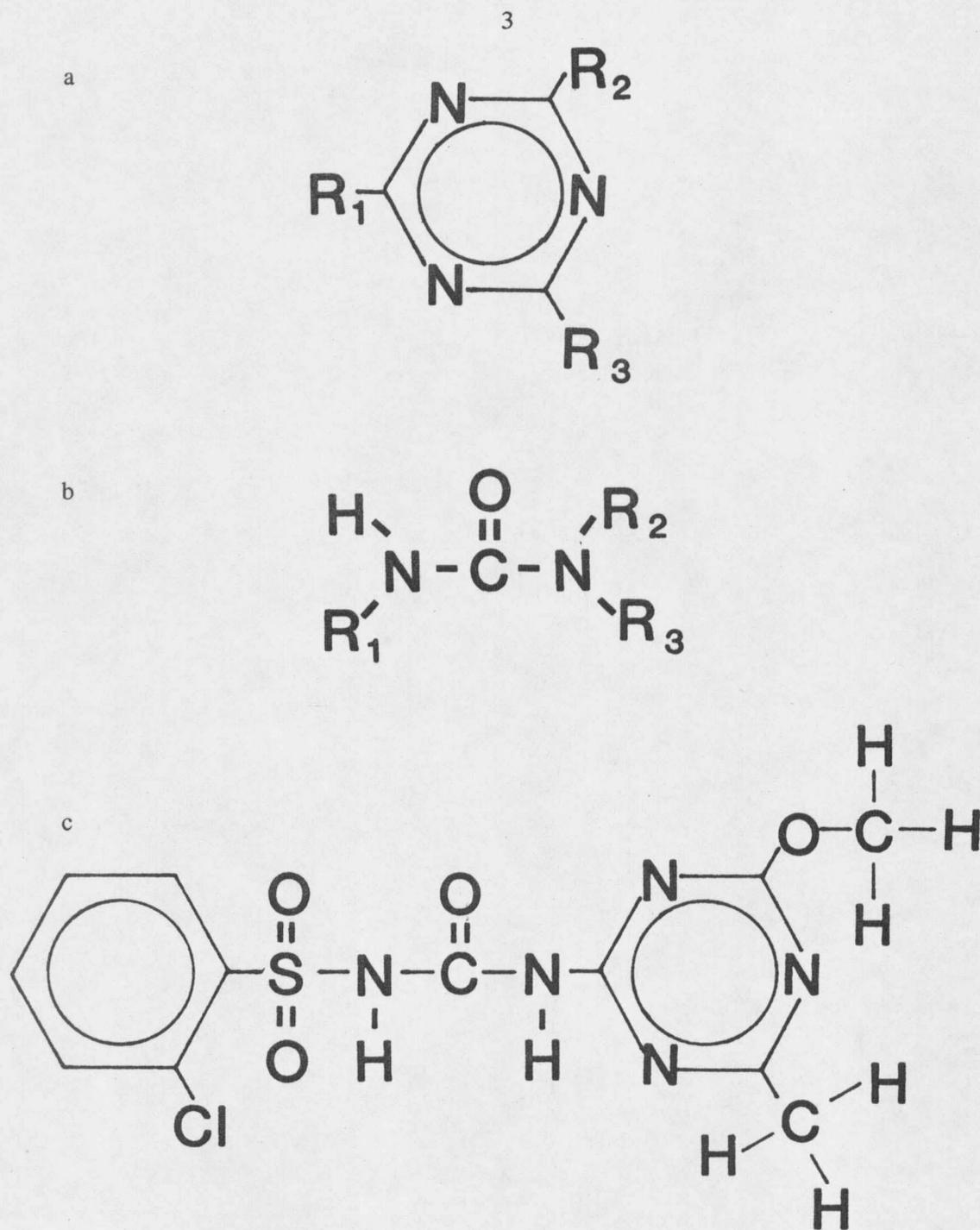


Figure 1. Chemical structures of the *s*-triazine (a) and urea (b) herbicide families, and the structure of chlorsulfuron (c).

adsorption (Bailey and White, 1970). The chlorsulfuron molecule appears to be highly polar, and at the same time, somewhat polarizable (Shea, 1982) (Figure 2).

The polar nature of the molecule would increase the degree to which it is solvated in the soil solution, which, in turn would increase the overall energy required for adsorption to occur. Water molecules can effectively compete with polar herbicide molecules for adsorption sites on clay, which would reduce adsorption.

The polarizability, or delocalization of charges, of the chlorsulfuron molecule suggests that it can participate in hydrophobic or charge transfer bonds (Shea, 1982), which are significant in acidic or neutral environments (Bailey and White, 1970). These types of bonding reactions would be less significant in alkaline soils which predominate in Montana.

Molecular size or parachor has been used as a measure for adsorption of herbicides on soil (Lambert, 1967). This relationship, however, assumes that organic matter is the primary adsorbing medium in the soil and that the adsorbate or solute is an uncharged molecule. The attempt to relate the molecular weight of the polar chlorsulfuron molecule (GMW. 358) to adsorption potential would thus be questionable, using Lambert's method.

The dissociation constant ( $pK_a$  or  $pK_b$ ) of a herbicide molecule is an important factor in determining the extent of adsorption and the ease of desorption by colloidal systems. The dissociation constant is reported to be the major factor controlling the magnitude of adsorption for the *s*-triazine and substituted urea herbicides (Bailey et al., 1968). The  $pK_a$  of chlorsulfuron is 3.8 (Shea, 1982). Frissel (1961) noted that negative adsorption for such herbicide acids as 2,4-D [(2,4-dichlorophenoxy)acetic acid] and 2,4,5-T [2-(2,4,5-trichlorophenoxy)propanoic acid] occurred as the pH of a clay-water system approached the  $pK_a$  of the particular compound (starting from neutral). As the pH continued to decrease, positive adsorption commenced and increased gradually. Bailey et al. (1968) reported that positive adsorption of acidic compounds did not begin until the pH of the bulk solution was 1 to 1.5 pH units above the  $pK_a$  of the acid. Thus chlorsulfuron, which is



























































































































































