

Sulfonylurea Herbicides' Fate in Soil: Dissipation, Mobility, and Other Processes

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Sulfonylurea herbicides used in turfgrass—including chlorsulfuron, flazasulfuron, foramsulfuron, halosulfuron, metsulfuron, rimsulfuron, sulfometuron, sulfosulfuron, and trifloxysulfuron—are all weak acids, with dissociation constants ranging from 3.3 to 5.2. Sulfonylureas are used at low rates ranging from 4 to 280 g ha⁻¹. Although these use rates put their soil concentration in parts per billion, they still have residual activity with variable persistence. They have limited susceptibility to soil leaching with weak adsorption to soil clay minerals. Sulfonylurea herbicides used in turfgrass have variable soil organic matter adsorption, which is soil dependent. The persistence and activity of these sulfonylureas are affected by soil pH. At soil pH of 7.0 and greater, some of these sulfonylurea herbicides tend to persist for longer periods with half-lives extending into years rather than days. In normal use patterns with soil pH of 7.0 and less, dissipation occurs via chemical hydrolysis and microbial degradation with half-lives ranging from days to months. Overall, sulfonylurea herbicide adsorption is negatively correlated to increasing pH (increased persistence) and positively correlated to increased organic matter (decreased activity).

Nomenclature: Chlorsulfuron, flazasulfuron, foramsulfuron, halosulfuron, metsulfuron, rimsulfuron, sulfometuron, sulfosulfuron, trifloxysulfuron.

Key words: Exponential decay equation, half-life, herbicide dissipation, herbicide persistence.

Los herbicidas sulfonylurea usados en céspedes, incluyendo chlorsulfuron, flazasulfuron, foramsulfuron, halosulfuron, metsulfuron, rimsulfuron, sulfometuron, sulfosulfuron, y trifloxysulfuron, son todos ácidos débiles, con pK_as que varían de 3.3 a 5.2. Los herbicidas sulfonylurea son usados a bajas dosis variando de 4 a 280 g ha⁻¹. Mientras estas dosis ponen su concentración en el suelo en ppb, aún así tienen actividad residual con persistencia variable. Además, tienen susceptibilidad limitada a la lixiviación dentro del suelo con débil adsorción a los minerales de las arcillas. Los herbicidas usados en céspedes tienen adsorción variable a la materia orgánica del suelo, la cual depende del suelo mismo. La persistencia y la actividad de éstos herbicidas sulfonylurea se ven afectadas por el pH del suelo. A un pH de 7.0 o mayor, algunos de estos herbicidas sulfonylurea tienden a persistir por períodos más largos, con vidas medias que pueden extenderse por años en vez de días. En patrones de uso normal con pH del suelo de 7 o menor, la disipación ocurre vía hidrólisis química y degradación microbiana con vidas medias que varían de días a meses. En general, la adsorción del herbicida sulfonylurea está negativamente correlacionada al incremento del pH (incremento en persistencia) y positivamente correlacionada con un incremento de la materia orgánica (actividad disminuida).

The use of herbicides for turfgrass weed control has become an important aspect of managing golf courses, home lawns, and sod production. Sulfonylurea (SU) herbicides were first synthesized by E. I. DuPont Corp. in the mid 1950s and screened for pesticidal properties, but first attempts revealed no significant biological activity (Bhardwaj 2007). It was not until the 1970s that the analogs of SUs began to be synthesized and their herbicidal activity evaluated. Prior to this there was no precedence for high potency and extremely low use rates (in the grams per hectare range) for weed control. One example, described by Bhardwaj (2007) was that university researchers would move the decimal two places as they could not believe that herbicides could be effectively applied at grams per hectare, rather than kilograms per hectare. The result was that weeds would not grow in treated test plots after 2 yr, despite half-lives of 6 to 8 wk. Thus, the potency of the SUs was recognized and

their use in plant production systems, including turfgrass, was quickly established.

The key components of SUs are two moieties (R₁ and R₂) on either side of a sulfonylurea bridge. Generally, the moieties are composed of an aryl group, a pyrimidine ring, or a triazine ring (Maheswari and Ramesh 2007; Sarmah and Sabadie 2002). Variation in herbicidal activity occurs by substitutions made to branches on these rings. Chlorsulfuron was the first SU herbicide released by E. I. Du Pont for weed control in small grains, but it was also noted for other potential uses (Ray 1982). LaRossa and Schloss (1984) reported that sulfometuron-methyl was a potent acetolactate synthase (ALS) isozyme II inhibitor by testing of *Salmonella typhimurium*. Since then all SUs have been identified as ALS inhibitors (Senseman 2007).

Maloy and Christians (1986) evaluated chlorsulfuron on seven cool-season grasses at high rates (141 and 282 g ha⁻¹) finding variable tolerance and weed control which indicated its potential turfgrass uses. Low use rates for chlorsulfuron weed control and cool-season turfgrass tolerance were later established (Gaul and Christians 1988). There are currently several SUs used in multiple turfgrass weed control scenarios including golf courses, home and industrial sites, and sod

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production. These SUs include chlorsulfuron, flazasulfuron, foramsulfuron, halosulfuron-methyl, metsulfuron-methyl, rimsulfuron, sulfometuron-methyl, sulfosulfuron, and trifloxysulfuron-sodium. Usage rates vary, but fall primarily within a range of 4 to 280 g ai ha⁻¹ (McCullough 2011). On a soil hectare furrow-slice basis (2.2 × 10⁶ kg ha⁻¹), these rates fall within a range of 2 to 125 µg g⁻¹.

Although herbicides can be grouped with respect to many general properties, most are evaluated independently for fate in the environment by independent researchers. However, there have been extensive studies for multiple SUs that will be discussed by factors that influence their environmental fate.

pH Effect

These SUs have similar characteristics pertaining to overall chemical properties. They are all weakly acidic with disassociation constants (pKa) ranging from 3.3 to 5.2 (Senseman 2007). Consequently, these herbicides should be predominantly neutral at pH values below the herbicide's pKa and anionic when the pH is above the pKa. Because these pKa values are within the range of pH values typically encountered in most soils, neutral and anionic forms of these sulfonylureas should predominate. In the anionic form, an OH⁻ replaces an H⁺ on one of the Ns in the sulfonylurea bridge; this deprotonation results in a net negative charge (Beyer et al. 1987; Sarmah et al. 1998). Another characteristic that is similar for these SUs is increasing solubility with increasing pH. For example, foramsulfuron's water solubility increases from 37 mg L⁻¹ at pH 5 to 945,800 mg L⁻¹ at pH 8 (Senseman 2007), a 25,562 fold increase in solubility. Although this is an extreme example, chlorsulfuron, flazasulfuron, foramsulfuron, halosulfuron, metsulfuron, and sulfosulfuron are between 50 to 100 times more water-soluble when pH increases from 5 to 7 (Senseman 2007). Overall persistence and activity increases for SUs at pH values above 7.0 primarily due to increased anionic forms resulting in decreased microbial degradation and dissipation, which can result in potential carryover and injury issues.

Chemical Degradation

Overall degradation of SUs begins with chemical hydrolysis of the sulfonylurea bridge resulting in loss of herbicidal activity (Sarmah et al. 1998). In analytical studies, metsulfuron and chlorsulfuron hydrolysis at pH 7 and 10 was slow (Berger and Wolfe 1996). Although this can be good for weed control, it can lead to increased injury to somewhat sensitive turfgrass species when trying to reestablish turf by seed (Lycan and Hart 2005; McCullough and Nutt 2010). Chemical degradation tends to be temperature-dependent for SUs with half-life (DT₅₀) decreasing with increasing temperature (Sarmah and Babadie 2002). For example, at pH 4 and 20 C, chlorsulfuron in aqueous solutions had a DT₅₀ value of 5.59 d, but this decreased to 0.08 d at 55 C, indicating rapid dissipation. Trifloxysulfuron dissipation followed first-order kinetics with rapid hydrolysis, with DT₅₀s of 13, 36, and 35 d for deionized water spray solutions with pH levels adjusted to 5, 7, and 9, respectively (Matocha and Senseman 2007).

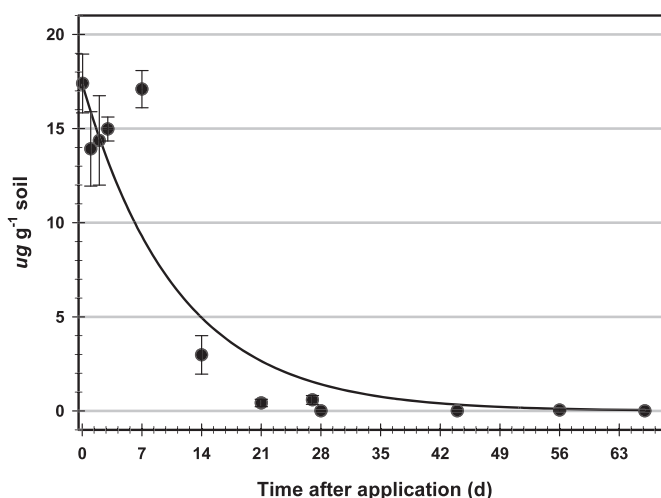


Figure 1. Halosulfuron dissipation for Tifton loamy sand soil in Georgia using the exponential decay equation. The line represents the first-order regression equation. Data points are the means of multiple replications with bars indicating the standard error of the mean: $y = 17.4e^{-0.0004(x)}$, $DT_{50} = 9$ d, $R^2 = 0.66$.

Sulfosulfuron hydrolysis at pH 4 had a DT₅₀ value of 9 d vs. 41 d at pH 7 (Saha and Kulshrestha 2002).

Soil Dissipation

SU herbicide dissipation is an intricate process involving soil pH, soil texture, and organic matter. Sarmah et al. (1998) noted that several researchers reported a negative relationship between sorption and soil pH, with decreased sorption with increased soil pH. Halosulfuron soil dissipation was rapid in a Tifton loamy sand soil with average pH of 6.5, following first-order rate constants with DT₅₀ of 9 d (Figure 1) (Grey et al. 2007). Dermiyati and Yamamoto (1997a,b) indicated that halosulfuron degradation increases with increasing temperature and lower soil pH but varied with soil moisture content and soil texture, with half-lives of 7 to 98 d. Halosulfuron degradation is primarily through chemical hydrolysis. Sulfosulfuron dissipation has been reported to be slower in an Inceptisol soil with pH 7.2 as compared to an Alfisol soil with pH 4.0 with both soils exhibiting first-order rate kinetics and sulfosulfuron hysteresis (Maheswari and Ramesh 2007).

Soils with low pH and high organic matter content strongly adsorb SUs (Beyer et al. 1988). Moyer and Hamman (2001) noted increased sorption of sulfosulfuron with increased organic matter, with similar reports for chlorsulfuron (Beckie and McKercher 1990) and metsulfuron (Berisford et al. 2006). SU herbicides are degraded slowly in alkaline and low-organic-matter soils (Maheswari and Ramesh 2007).

Leaching of SUs can be demonstrated in soil laboratory experiments, with increasing retardation factor values with increasing soil pH (Beyer et al. 1988). However, field experiments with metsulfuron (Berisford et al. 2009) and chlorsulfuron (Beckie and McKercher 1990) have indicated limited mobility in the microgram per gram range to soil depths beyond 36 cm.

Microbial Degradation

At pH values above the pK_a when SUs are in the anionic form, microbial degradation generally decreases and DT₅₀ increases (Sarmah et al. 1998). However, there are differences reported in the literature; metsulfuron-methyl's primary dissipation mechanism at pH less than 6 was via chemical hydrolysis, but at pH greater than 6, microbial dissipation predominated (Sarmah and Babadie 2002). Other reports have noted the opposite effect (Senseman 2007). Regardless of SU herbicide, most microbial degradation properties are influenced by soil characteristics, pH, temperature, and organic matter content. One reason few microbial breakdown studies have been conducted for SUs is that metabolite identification and detection can be difficult (Chen et al. 2000).

In conclusion, based on data from previous research, the SUs utilized in turfgrass—chlorsulfuron, flazasulfuron, foramsulfuron, halosulfuron, metsulfuron, rimsulfuron, sulfometuron, sulfosulfuron, and trifloxysulfuron—will likely have increasing persistence with increasing soil pH (soil alkalinity). Increasing soil temperatures should increase dissipation via hydrolysis. As soil organic matter increases, SU herbicide sorption also increases, with limited soil mobility. Given these factors and limited information about SU herbicide soil dissipation in turfgrass soils, there is an opportunity for future analytical research.

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