Technical Note

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Sulfonylureas

INTRODUCTION

Sulfonylurea herbicides have been registered for use in New Zealand since 1986 when Dupont registered their 'Escort' herbicide, containing the active ingredient metsulfuron-methyl. They can be applied both ‘pre’ and ‘post’ emergence of the crop and have to date proven very effective in the control of a wide range of annual and perennial grasses, as well as broad leaf weeds. Sulfonylureas are one of the largest classes of herbicides, with 27 different sulfonylurea compounds currently registered worldwide.

ABOUT SULFONYLUREA HERBICIDES

Chemical Structure

All sulfonylureas share the same basic structure, containing an aryl ring linked to a heterocycle (triazine or pyrimidine) through the herbicidally active sulfonylurea (SU) ‘bridge’. To increase herbicidal activity, the aryl ring is usually substituted ‘ortho’ to the sulfonylurea bridge, with the substituent typically a carboxylic acid ester (eg. metsulfuron-methyl) or halogen (eg. chlorsulfuron). Substituents on the heterocycle are typically alkyl or alkoxy, and can be partially halogenated. Certain sulfonylureas possess a thienyl (eg thifensulfuron-methyl) or pyridinyl (eg nicosulfuron and rimsulfuron) moiety rather than the analogous aryl ring. The basic structure is presented in Figure 1.

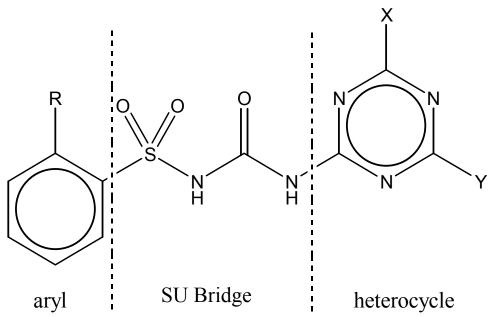

Figure 1 Basic Structure of a Sulfonylurea

HOW THEY WORK

Sulfonylurea herbicides have a simple but effective mode of action. They target the ‘acetolactate synthase’ or ALS enzyme, which is found in plants. The enzyme is key in the first step of the biosynthesis of branched chain amino acids in bacteria, fungi and plants[1]. Inhibition of this enzyme leads to rapid termination of plant cell division and growth[2]. Once sulfonylureas are absorbed by plant foliage and roots, they are rapidly translocated to the meristematic tissues of the plant (new growth), where cell division occurs[3]. This high selectivity for the ALS enzyme, allows application rates of the g/ha level compared to the kg/ha level for conventional herbicides. Some typical application rates for various sulfonylurea herbicides are presented in Table 1. (Adapted and reproduced with permission from Brown and Cotterman, 1994. Copyright (1994) Springer)[7].

Sulfonylurea Herbicide	Crop	Application Rate (g/ha)
Chlorsulfuron	cereals	9-25
Triasulfuron	cereals	10-30
Tribenuron-methyl	cereals	9-18
Amidosulfuron	cereals	30-60
Thifensulfuron-methyl	cereals / corn	15-20 / 5-10
Metsulfuron-methyl	cereals / rice	4-8 / 2-6
Bensulfuron-methyl	rice	20-75
Pyrazosulfuron-ethyl	rice	20
Cinosulfuron	rice	20-40
Primisulfuron-methyl	corn	20-40
Nicosulfuron	corn	35-70
Rimsulfuron	Corn / potatoes	5-15 / 8-35
Chlorimuron-ethyl	soybeans / peanuts	8-13 / 35-70
Sulfometuron-methyl	non-crop	70-680

Table 1. Typical application rates for various sulfonylurea herbicides

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Low application rates help mimimise handling, application and container disposal issues, while simultaneously reducing the amount of chemical being applied to the environment[2]. An example of this is the Dupont herbicide 'Ally®', which is applied at 5-7g/ha for control of broadleaf weeds. This compares with the herbicide '2,4-D', applied at 1-2 kg/ha for a similar purpose.

TOXICITY

Most sulfonylurea herbicides are selective for a particular crop. This is to say, they kill weeds but do not harm the crop. This selectivity is based mainly on the ability of tolerant crops to rapidly metabolise the sulfonylurea compound to non-phytotoxic products before the herbicide molecules reach the ALS enyzyme[5]. Because of a lack of ability to synthesise branched chain amino acids, animals do not possess the target ALS site[2]. For this reason the very specific herbicidal mode of action makes sulfonylureas extremely non-toxic to animals. The acute oral LD_{50} for sulfonylureas in rats is greater than that for table salt (>4000mg/kg cf 3000mg/kg)[4].

DEGRADATION AND METABOLISM

In contrast to most herbicides which degrade by a single mechanism, sulfonylureas degrade as a result of two main processes, (a) chemical hydrolysis and (b) microbial breakdown, both yielding non-toxic biproducts[6]. The balance of these two processes is a function of the compounds structure, soil properties, environmental conditions and residence time in the soil[9]. An example of this is presented in Figure 2 below for the case of chlorsulfuron degradation in sterile and non-sterile soils at alkaline and acidic pH.

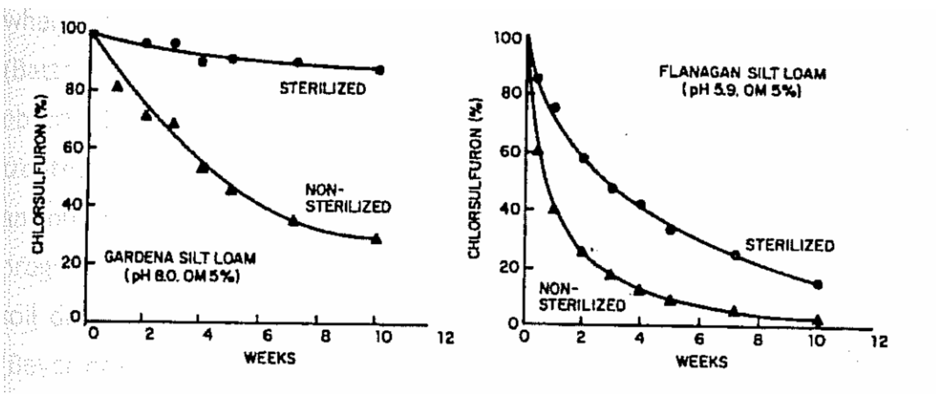

Figure 2 Degradation of chlorsulfuron under sterile versus non-sterile conditions at varying pH

The left-hand graph shows how chlorsulfuron degration was aided by microbes in the fairly alkaline soil (pH 8.0 in this case), compared with little degration in sterile soil. The right-hand graph shows the degrading effects of soil microbes too, but also shows how degradation is even more pronounced in acid soils (pH 5.9 in this case.)

(Reproduced with permission from Joshi et al., 1985. Copyright (1985) Weed Science)[8].

Degradation typically occurs through hydrolysis of the aryl (or pyridyl or thienyl) ring, facilitating a cleavage of the sulfonylurea bridge. This results in formation of an aryl (or pyridyl or thienyl) sulfonamide and 'heterocyclic amine' with a nett loss of CO_2, as portrayed in Figure 3 below. *(Reproduced with permission from Brown, 1990. Copyright (1990) Society of Chemical Industry, permission is granted by John Wiley & Sons on behalf of the Society of Chemical Industry)[2].*

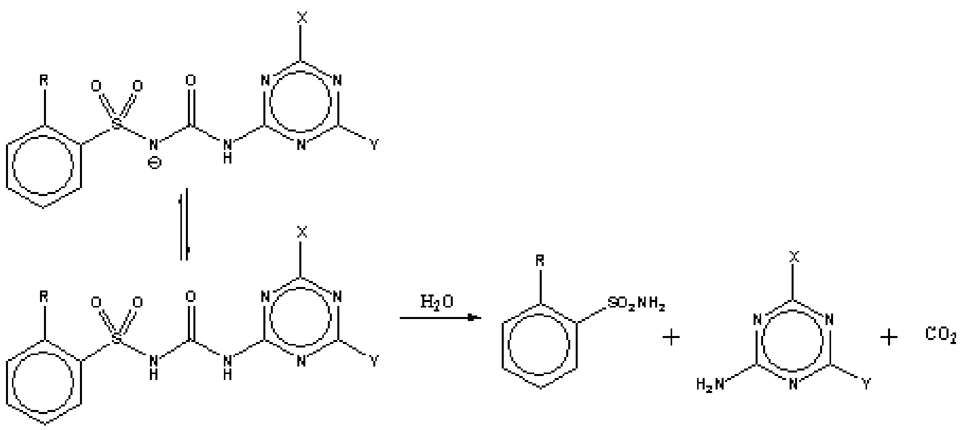

Figure 3 Typical hydrolysis of a sulfonlurea

Note: All substituents on the aryl (or pyridyl or thienyl) ring and the heterocycle are typically retained in the reaction. Therefore there is potential for the monitoring of these ***'SU-specific'*** *biproducts to indicate sulfonylurea usage in the past, long after the herbicide itself has degraded.*

Under field conditions the degradation rate of sulfonylureas is similar to and often faster than other conventional herbicides. Significant progress has been made to modify sulfonylurea chemistry to accelerate soil degradation, thus reducing the residence time in soils[4]. This is an important factor in the planting of rotational crops. An example of this is the comparison between 'metsulfuron-methyl' and its very closely analogous 'tribenuron-methyl', as exhibited in Figure 4 below. The subtle inclusion of a 'N-methyl' substituent on the sulfonylurea bridge in the latter, incurrs a 10-25 times increase in the rate of chemical hydrolysis[2].

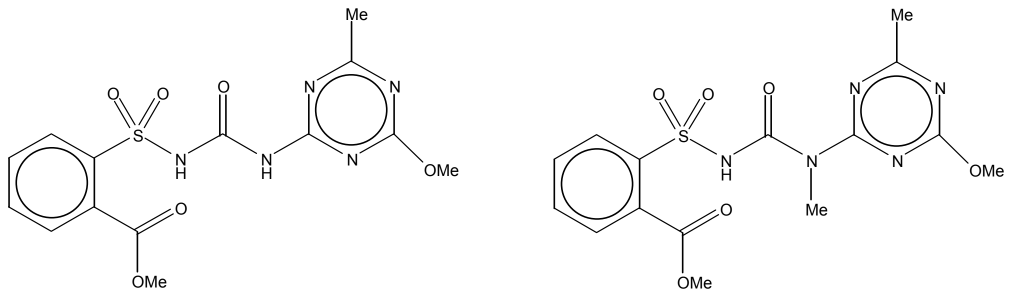

Figure 4 The structure of metsulfuron-methyl (left) versus tribenuron-methyl (right)

ENVIRONMENTAL FATE

Recropping Intervals

Sulfonylureas can cause the reduction of yields of some rotational crops, even when <1% of the originally applied herbicide remains[10]. This residual activity is due to the extreme sensitivity of particular crops and not to an inherently slow rate of breakdown[4]. Therefore, this selectivity and the ability to affect the growth of rotational crops and non-target plants, requires sulfonlyureas to be detected to environmentally significant concentrations[11].

Spray Drift

It has been indicated that spray drift containing less than 1% of the recommended application rate may adversely impact fruit trees. However in saying this, studies have shown that the activity of sulfonylureas on non-target crops, is no different from that of conventional herbicides, when expressed as a fraction of their usage rates[9].

Accidental Residual Effects

The corollary of low application rates for sulfonylureas is that it only requires a minute trace for accidental damage to crops, from events such as spray drift or watershed run-off. One of our clients – a viticulturalist – recently had experience of grapevines being accidently damaged by a sulfonylurea herbicide. A block of land some kilometres away had been sprayed with this herbicide, and shortly afterwards heavy rain caused residues of the spray to enter the irrigation canal that the vineyard drew its water from. In spite of being heavily diluted from the original application rate, and only being present for a short time, the residues were sufficient to cause significant damage to the irrigated grape vines.

HILL LABORATORIES TESTING CAPABILITIES

Currently in New Zealand there are 9 sulfonylurea compounds registered.

Due to their low application rates, sulfonylurea herbicide detection is much more difficult when compared to that of traditional herbicides. Soil analyses typically require detection limits **<0.001mg/kg (<1ppb)**. Due to the high mobility of sulfonylureas in the soil column, analyses in groundwater and that used for irrigation purposes typically require detection limits of **<0.00002g.m^{-3} (<20ppt).**

Hill Laboratories are able to achieve these detection limts and is using LC-MS-MS capabilities towards achieving detection limits routinely 10 times lower. An indication of the benefits of LC-MS-MS capability is exhibited in the chromatogram of a leachate fortified with 0.00002g.m^{-3} of 16 sulfonylureas (Figure 5). The leachate was found to contain 0.000015g.m^{-3} metsulfuron-methyl (Figure 6), whereas laboratories that use LCMS alone would not have been able to detect this substance in such a ‘dirty’ sample.

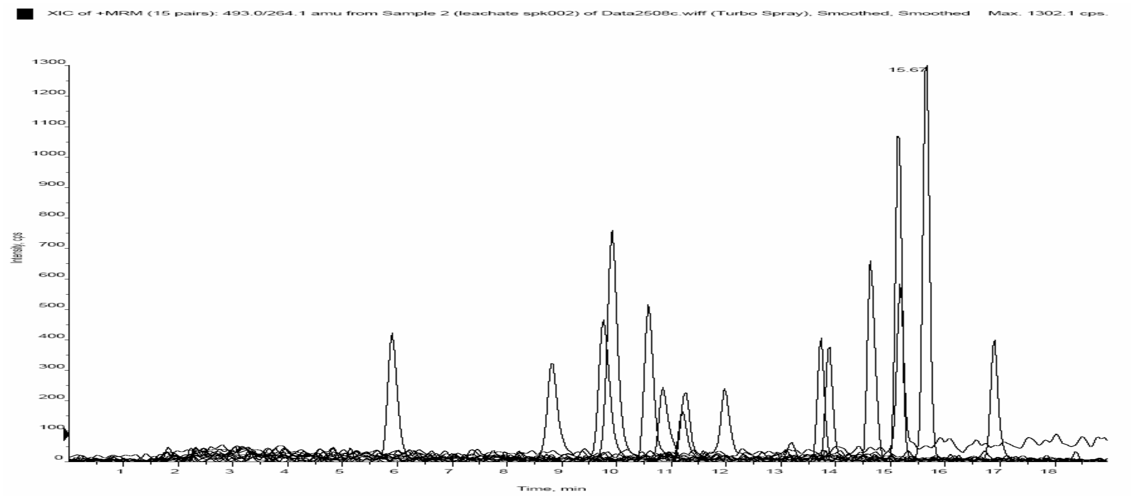

Figure 5 A typical chromatogram of a leachate fortified with 0.00002g.m^{-3} of 16 sulfonylureas

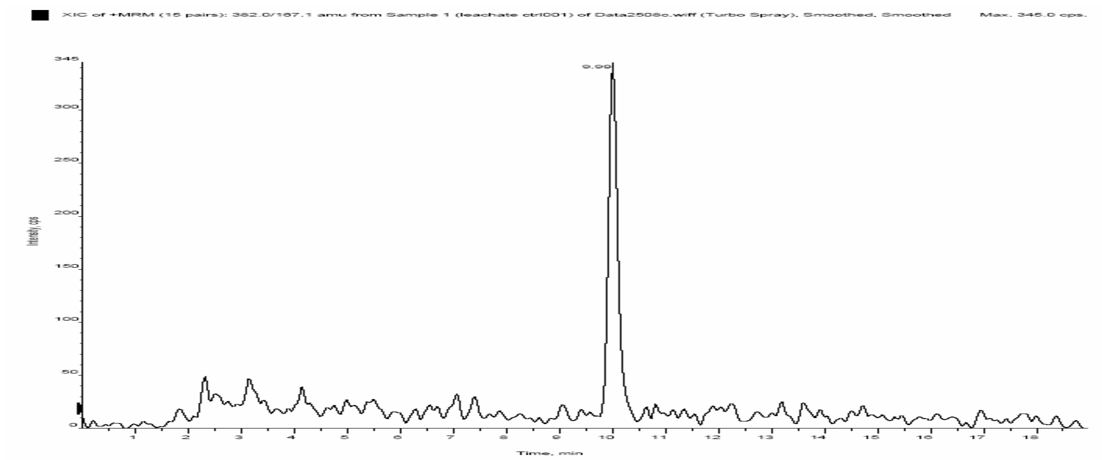

Figure 6 A chromatogram of the unfortified leachate from Figure 5.
The leachate was found to contain 0.000015g.m^{-3} metsulfuron-methyl.

LIST OF ACTIVES

Sulfonylurea actives currently able to be tested by Hill Laboratories are listed below, with those registered for use in New Zealand in bold type.

Amidosulfuron	Bensulfuron-methyl	**Chlorsulfuron***
Cinosulfuron	**Iodosulfuron-methyl***	**Metsulfuron-methyl***
Nicosulfuron*	**Primisulfuron-methyl***	Prosulfuron
Pyrazosulfuron-ethyl	Rimsulfuron	Sulfometuron-methyl
Thifensulfuron-methyl*	**Triasulfuron**	**Tribenuron-methyl***

Testing for the following sulfonylurea actives will soon be offered:

Chlorimuron-ethyl* (Classic)	**Halosulfuron-methyl (Sempra)**
Flazasulfuron* (Kantana)	Oxasulfuron
Flupyrsulfuron-methyl	

**Registered for use in New Zealand by the Agricultural Compounds and Veterinary Medicines Group of New Zealand Food Safety Authority as at 1 August 2004*

DETECTION LIMITS

Hill Laboratories offers sulfonylurea analysis in environmental soil and waters, along with residue analysis in food and crops. Detection limits offered in the various matrices are detailed as follows

Sulfonylurea Active	Brand Example (s)	Water ($g.m^{-3}$)	Soil (mg/kg dry weight)	Food & Crops (mg/kg as received)
Thifensulfuron-methyl	'Harmony'	0.000005	0.0001	0.001
Tribenuron-methyl	'Granstar'	0.00001	0.0002	0.002
Chlorsulfuron	'Glean', 'Tackle'	0.000005	0.0001	0.001
Primisulfuron-methyl	'Beacon'	0.000005	0.0001	0.001
Metsulfuron-methyl	'Escort', 'Mustang', 'Ultimate', 'Matrix', 'Answer', 'Xact', 'Zeal'	0.000005	0.0001	0.001
Nicosulfuron	'Amaze'	0.000005	0.0001	0.001
Amidosulfuron		0.000005	0.0001	0.001
Bensulfuron-methyl		0.000005	0.0001	0.001
Cinosulfuron		0.000005	0.0001	0.001
Iodosulfuron-methyl		0.000005	0.0001	0.001
Prosulfuron		0.000005	0.0001	0.001
Pyrazosulfuron-ethyl		0.000005	0.0001	0.001
Rimsulfuron		0.00001	0.0002	0.002
Sulfometuron-methyl		0.000005	0.0001	0.001
Triasulfuron		0.000005	0.0001	0.001
Triflusulfuron-methyl		0.00001	0.0002	0.002

SAMPLING REQUIREMENTS

The following are recommended procedures for taking samples for sulfonylurea analysis.

Crop Samples

Collect From: If crop damage is the key issue then sample the new growth, as the active ingredient accumulates in meristematic tissue. If residues on crop are a concern, then sample the crop as per the appropriate* protocol for pesticide residues in that crop.

Quantity per Sample: At least 50 gm.

Temperature: Samples should be transported to the laboratory chilled (at <4°C), and delivered lab as quickly as possible to avoid degradation

Soil Samples

Quantity per Sample: At least 200 gm.

Temperature: Samples should be transported to the laboratory chilled (at <4°C), and delivered lab as quickly as possible to avoid degradation

Water Samples

Quantity per Sample: At least 100mL , and if possible duplicate samples should be provided.

Temperature: Samples should be transported to the laboratory chilled (at <4°C), and delivered lab as quickly as possible to avoid degradation.

pH: The sample ideally should be of neutral to slightly alkaline pH (6.5-8.5) to minimise chemical hydrolysis during transport to the laboratory. This is particularly important for 'labile' compounds such as Tribenuron-methyl, Rimsulfuron and Triflusulfuron-methyl.

**Refer to Hill Labs Food & Crop sampling guidelines*

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