

METSULFURON IN SURFACE GROUNDWATER OF A NORTH FLORIDA FLATWOODS. J.L. Michael, D.G. Neary, J. Fischer, and H. Gibbs. USDA-FS, Auburn, AL, 36849; and Gainesville, FL, 32611.

ABSTRACT

A 4 ha Florida flatwoods pine site was monitored for surface groundwater contamination following application of 0.084 kg ai/ha (1.2 oz metsulfuron/ac) in 140 liters of water carrier per hectare. Treatment was applied in November 1989. An HPLC analytical procedure is presented which has a detection limit of 1 mg m⁻³ (1 ppb). A total of 24 shallow groundwater wells were used to monitor for surficial water table contamination, and surface water contamination was monitored in runoff and from water collected from surface depressions. One well sample of 207 collected in the 2 month period between application and 5 January 1990 contained detectable metsulfuron (2.3 mg m⁻³). Two surface depression water samples collected December 9 and 13, 1989 contained 8 mg m⁻³ of metsulfuron. Other samples did not contain detectable amounts of metsulfuron. Lightning strikes disabled the automatic water sampler during the first major storm after application preventing collection of runoff samples. Because the first runoff producing storm occurred at about the second hydrolytic half-life for this herbicide, it is unlikely significant amounts moved off site in storm runoff. The results are similar to those reported for sulfometuron on similar sites.

INTRODUCTION

Metsulfuron is used in forestry for control of many forms of weedy competition(1,4,5,6,9). It is also useful in tank mixtures with other herbicides to increase both the scope of plants affected and to increase activity on specific weed problems (2,3,7,9).

Metsulfuron is a weak acid (pKa = 3.3). Solubility in water is greater for the ionized than the unionized form and increases from approximately 0.064 g L⁻¹ at pH 3 to 9.5 g L⁻¹ at pH 7. Hydrolysis is also a function of pH. The neutral form of metsulfuron is hydrolyzed much more rapidly than the negatively charged form. The hydrolytic half-life therefore increases with pH and ranges from 15 hours at pH 2 and 25° C to 800 hours at pH 5. A related compound, sulfometuron, has a hydrolytic half-life under similar conditions of 475 hours at pH 5. Most soils in the southern pinery have an acid pH ranging from around 4 to 5.5 so the persistence of metsulfuron should be nearly twice as long as that observed for sulfometuron. Further, sorption of metsulfuron (Kd value for soil with 1% organic matter, 0.4) to soil is much less than that of sulfometuron (Kd, 2.9) for similar soils and so metsulfuron should be more mobile than sulfometuron.

There are no published reports concerning the fate of metsulfuron in forest ecosystems, but the closely related sulfometuron has been shown to dissipate rapidly from vegetation, litter, and soil and not to move off-site

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to any appreciable extent in Mississippi and Florida (8). Small amounts of sulfometuron ($< 4 \text{ mg m}^{-3}$) were detected moving off-site in surface runoff from 4 ha watersheds treated with $0.42 \text{ kg ai ha}^{-1}$ (11), but sulfometuron did not contaminate surficial groundwater beneath North Florida flatwoods. Because of the extremely high phytotoxicity of this compound, even small amounts of movement off-site could impact adjacent ecosystems.

The objectives of the study reported here were to:

1. Evaluate metsulfuron methyl movement in surface runoff
2. Measure potential groundwater contamination.

METHODS

The study site, located on the Bradford Experimental Watersheds near Starke, Florida is a typical flatwoods slash pine (*Pinus elliottii* var. *elliottii*) forest site (10) characterized by somewhat poorly drained loamy sands (Typic Haplaquods) with approximately 1 m (3 feet) of elevational relief on 4 ha (10 acre) artificial watersheds (WS). The study site is equipped with standard and recording rain gauges, long throated-flumes, water level recorders, and Isco automatic water samplers. Thirty shallow (1.5 m to 3.0 m deep) groundwater wells were also installed (24 in treated WS 4, and 6 in the control WS 5). The groundwater resource monitored in this study is the surficial water table usually lying within the upper 2 m of the soil. The regional aquifer used for municipal and individual water supplies is much deeper ($>30 \text{ m}$), and in this part of Florida is capped with an impervious mudstone formation named the Hawthorne.

Herbicide was applied by a ground sprayer system mounted on a tractor. WS 4 was treated with the dry-flowable formulation at 0.084 kg ai/ha ($1.2 \text{ oz metsulfuron/ac}$) in 140 liters of water carrier per hectare. Treatment was applied in November 1989. All samples collected in this study were returned to the laboratory and stored at -20° C until analyzed.

Sulfonyl urea herbicides are known to be hydrolytically unstable in acid solution. Pretreatment samples of surface water taken from the treatment site had a pH value of 4.2. In order to determine the stability of metsulfuron in field water samples of varying pH, a set of distilled water samples was buffered with 0.1 M potassium phosphate to pH 4.0, 5.0, and 6.0, then spiked with known amounts of metsulfuron and stored at 35° C . Five replicate samples at each pH level were periodically analyzed to monitor the percent of the original spike remaining. Hydrolysis was rapid at pH 4.0 and pH 5.0 and appreciable even at pH 6.0. It was therefore deemed necessary to add buffer to the sample containers in the field to stabilize the water samples as they are collected. Accordingly, a mixture of 0.04 M KH_2PO_4 and 0.06 M K_2HPO_4 , which produces a pH of 7.0, was added in dry form to each 1 liter field container.

Water samples were taken during and following each storm event and correlated with stream stage. Additional water samples (Grab samples) were collected as a function of time following application. Water samples were collected by Isco automatic samplers installed on the treatment perimeter. Grab samples were taken at the automatic sampler location on each date of servicing for the automatic sampler. Buffer (pH 7) was added to each empty sample bottle at the time of sampler servicing. Each sampler was serviced at least weekly during the study.

A solid phase extraction (SPE) and HPLC analytical method was developed for the metsulfuron analysis. In this method a dilute solution of the metsulfuron is passed through a column of adsorbent particles whose surface has a higher affinity for metsulfuron than does the solvent. Metsulfuron is immobilized on the adsorbent, then released again by elution with a small volume of buffer. The eluate, brought to a known volume, is then subjected to analysis by HPLC using a Supelco LC8-DB column (150 mm x 4.6 mm I.D., 5 micron diameter spherical porous particles), a mobile phase of acetonitrile/0.1 M H₃PO₄ (30:70 vol/vol) pumped at 1.0 ml per minute at 25° C, and UV absorbance detection at 224 nm wavelength. The method is as follows:

1) Precondition an SPE C18-derivatized silica gel adsorbent column (Baker #7020-7) with 5 ml of methanol followed by 10 ml of 0.1 M potassium phosphate buffer and pass 500 ml of the field sample through the column.

2) Elute the column with 5.0 ml 30:70 (v/v) acetonitrile/H₂O (pH 7.0 w/0.1 M potassium phosphate buffer). Make the eluate up to exactly 5.0 ml with buffer. Mix thoroughly.

3) Transfer the sample to an autosampler vial, filtering through a Millipore Millex-SR membrane filter if cloudy.

4) Inject 10 ul on the HPLC. Quantitate with external standards injected after every fourth sample.

No sample clean-up except filtration was necessary and the detection limit for this method was about 1 microgram per liter of water.

RESULTS AND DISCUSSION

The long-term rainfall average in this part of North Florida is about 132.1 cm/yr. Low rainfall months are usually April/May and October/November. The heaviest rainfall usually occurs from June through September when monthly rainfall can total 20 cm, but in recent y- this period has become drier. Rainfall in 1989 was 93.7 cm, only 71 % of normal. This deficit of precipitation contributed to a lack of surface runoff in the late autumn and early winter. Two major storms occurred during the period of the study. The first on November 23 produced 19.8 mm and the second on December 8-9 produced 35 mm. Several small precipitation events in December produced an additional 41 mm.

Groundwater on both WS 4 and WS 5 had a considerable range in pH but averaged near pH 5 (Table 1). The pH range was greatest on WS 4 (2.59 units). At a pH of 5.0, metsulfuron has a hydrolytic half-life of 800 hours. This half-life would be somewhat shorter in some of the more acid wells.

Application of metsulfuron did not result in significant surface groundwater contamination (Table 2). Only one sample on November 17, 1989 contained a quantifiable level of metsulfuron (2.3 mg m⁻³). This positive residue level in Well 20 was not repeated on the subsequent sampling date (November 24). None of the other samples contained residues of metsulfuron. Lack of groundwater contamination was consistent with the low application rate, lack of large amounts of precipitation, and pH of the surface groundwater. Hydrolysis of metsulfuron in the acid surface waters

(pH 3.6-6.4) played a substantial role in preventing significant and persistent groundwater contamination. Based on the 800 hour hydrolytic half-life of metsulfuron at pH 5.0 and the pH range of the soils and surface groundwater on the Bradford site, the first half-life point was December 14, 1989, and the second was January 16, 1990. By the latter date only 25 % of the original herbicide would have been left on-site.

Surface runoff was minimal during the period of late October 1989, through early January 1990, due to previously mentioned low rainfall. Between October 26 and December 20 there was no flow from either watershed. The first measurable surface runoff was in a 10 day period of December 20-29 when flow for one 30 hour period was about $0.00028 \text{ m}^3 \text{ sec}^{-1}$. Total flow during this period was about 22.4 m^3 . During this first runoff event most flow originated from the boundary ditch near the flumes. The first significant runoff event occurred on January 6-8, 1990, when flow peaked at $0.0026 \text{ m}^3 \text{ sec}^{-1}$.

Surface water collected in a drainage depression in WS 4 near Well 9 on December 9 contained 8.1 mg m^{-3} metsulfuron. On December 13 the same surface water contained a residue of 8.0 mg m^{-3} . In early December there was no flow in this ditch and insufficient rainfall occurred to produce flow between this depression and the watershed boundary ditches. Throughout this period Well 9, which had water levels very close to the surface or at the surface, did not contain detectable levels of metsulfuron.

Lightning during the third major storm event (January 8, 1990), the first to produce significant runoff, resulted in a malfunction in the ISCO sampler on the treated watershed. Thus the most important storm event after application of metsulfuron was not sampled. This storm event occurred near the second half-life point when nearly 75 % of the metsulfuron may already have been hydrolyzed. Because of the long time period after application, and acid conditions of the Typic Haplaquod soils and surface waters it is unlikely that significant amounts of metsulfuron moved off-site. However, a decision was made to halt the sampling because of this catastrophic event and repeat the study on the same site after a suitable delay period (1 year).

SUMMARY AND CONCLUSIONS

A method of chemical analysis for metsulfuron in environmental Water samples is presented. This method permits analysis to the 1 microgram/L (part per billion) level using conventional HPLC equipment and solid phase extraction techniques.

Metsulfuron did not produce significant or persistent groundwater contamination in 24 wells within a 4 ha treated watershed. This was consistent with the low application rate of the herbicide, the low pH of both mineral soil and surface groundwater, the prevailing climatic conditions, and with reports of behavior of the very similar herbicide sulfometuron on similar sites (8,11).

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Table 1. Surface groundwater pH in the Typic Haplaquod Soils of WS 4 and 5, Bradford Watersheds, Florida.

Date	Control (WS5)		Treatment (WS4)	
	Mean	Range	Mean	Range
08 NOV	*	*	5.43	5.32-6.16
13 DEC	5.63	5.00-6.42	4.84	3.69-5.20
22 DEC	*	*	5.72	3.81-6.40
05 JAN	5.75	4.08-5.97	5.16	3.68-6.00
09 JAN	5.35	4.23-6.44	4.87	3.85-5.71

* No data for this date.

Table 2. Metsulfuron residues in surface groundwater from Bradford Watershed WS 4 in Florida.

Date	Treatment (WS4)			Control (WS5)		
	Mean	Range	Samples	Mean	Range	Samples
mg m ⁻³mg m ⁻³		
			#			#
08 NOV	ND	ND-ND*	24	ND	ND-ND	5
10 NOV	ND	ND-ND	24	ND	ND-ND	6
17 NOV	NE	ND-2.3	17	ND	ND-ND	2
24 NOV	ND	NC-ND	24	ND	ND-ND	4
01 DEC	ND	ND-ND	23	ND	ND-ND	3
09 DEC	NE	ND-ND	24	ND	ND-ND	3
13 DEC	ND	ND-ND	24	NE	NE-NE	1
14 DEC	ND	ND-ND	23	ND	NC-ND	1
15 DEC	NE	ND-ND	24	ND	NE-ND	3
05 JAN	ND	ND-ND	24	ND	ND-ND	5

* ND indicates non detectable at a level of 1 mg m⁻³.