Analysis of Metsulfuron-methyl in Soil by Liquid Chromatography/Tandem Mass Spectrometry. Application to a Field Dissipation Study

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An analytical method is described for the extraction of metsulfuron-methyl from soil at sub-parts per billion levels (LOQ = 0.2 μg kg^{-1}). The herbicide was quantitatively determined and identified by ESI LC/MS/MS. The method has been applied to a field dissipation study in which metsulfuron-methyl was applied to spring barley at three dosage rates: 4, 8, and 16 g of active ingredient ha^{-1}. The results of 2 years are presented. The dissipation rate of metsulfuron-methyl in topsoil was very rapid, with a calculated half-life of 6.5 days. Laboratory mineralization studies with native soils in contrast to autoclaved soils indicated that microbial degradation of ^{14}C-labeled metsulfuron-methyl and ^{14}C-labeled 2-amino-4-methoxy-6-methyl-1,3,5-triazine in soil microcosms is an important factor for the complete degradation of metsulfuron-methyl in the field. However, the mineralization rate of the sulfonamide was much higher.

Keywords: *Metsulfuron-methyl; triazine amine; ESI LC/MS/MS; field dissipation; microbial degradation; mineralization*

INTRODUCTION

Metsulfuron-methyl, the active ingredient of Ally (DuPont, Wilmington, DE), is a sulfonylurea herbicide widely used for broad-leaf weed control in cereals. Due to its high herbicidal activity, the recommended rate of application is typically in the range of 4−12 g of active ingredient (ai) ha^{-1}.

The chemical and microbial degradations of metsulfuron-methyl have been investigated under laboratory conditions (Bastide et al., 1994; Sabadie, 1990, 1993; Vega et al., 1992; Hemmamda, 1994). The most important pathway of degradation in soil is the chemical hydrolysis of the sulfonylurea bridge, which leads to formation of a sulfonamide and an *s*-triazine ring. This reaction is highly dependent on soil pH, being faster at low pH values.

Because the pK_a of metsulfuron-methyl is 3.3, this compound is mainly present in its anionic form in soils of normal agricultural pH. Consequently, metsulfuron-methyl is only weakly adsorbed (Walker et al., 1989) and has a potential to leach under conditions of high rainfall. The field dissipation of metsulfuron-methyl is therefore a combination of chemical and microbial degradation and leaching into the subsoil.

The persistence and mobility of metsulfuron-methyl under field conditions have been described in a few studies (Nord-Christenson and Bergström, 1989; Vicari et al., 1994; Walker et al., 1989; Wadd and Drennan, 1989). In all except the first of these works, the residues of metsulfuron-methyl in soil were quantitatively determined by plant bioassay, which is based on phytotoxicity of the residual herbicide on sensitive plants.

Plant bioassay will give only an estimate of the plant-available portion of the residual herbicide, not necessarily the total amount residing in the soil (Streibig et al., 1995), and will not in any case respond to the presence of degradation products without herbicidal effect. Further degradation such as cleavage of the sulfonamide and *s*-triazine ring is believed to be mainly attributed to microbial activity.

Field residues of metsulfuron-methyl have also been quantitatively analyzed by ELISA (Nord-Christenson et al., 1989) with a detection limit of 0.05 μg kg^{-1}.

In the past 10 years several analytical methods have been proposed for the determination of sulfonylurea herbicides in soil (Font et al., 1998; Powley et al., 1998; Bernal et al., 1998; Marek and Koskinen, 1996; Li et al., 1996; Galletti et al., 1995; Zahnow, 1985; Klaffenbach and Holland, 1993; Dinelli et al., 1995). Because sulfonylurea herbicides are polar and thermally unstable, the most used chromatographic method is liquid chromatography (LC) coupled to ultraviolet (UV) detection or mass spectrometry (MS) detection.

To detect the low residual concentrations of sulfonylurea herbicides in complex matrices such as soil, an analytical method that can unequivocally identify these compounds is required.

Tandem LC/MS with electrospray ionization (ESI) interface provides the necessary specificity and sensitivity for the analysis of sulfonylurea herbicides in soil (Li et al., 1996).

Extraction with an alkaline aqueous solvent or a mixture of alkaline aqueous/organic solvent followed by

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10.1021/jf981280t CCC: $18.00
Published on Web 09/14/1999

solid-phase extraction (SPE) is the most common approach for determination of sulfonylurea herbicides in soil. Other methods such as microwave-assisted solvent extraction (MASE) (Font et al., 1998) or supercritical fluid extraction (SFE) (Bernal et al., 1998; Berdeaux et al., 1994) have also been applied to the extraction of sulfonylurea herbicides from soil.

However, the MASE method was developed at concentrations >5 μg kg^{-1}, whereas the SFE method was developed at concentrations >60 μg kg^{-1}.

Because sulfonylurea herbicides may have a residual herbicidal activity at concentrations <1 μg kg^{-1} (Beyer et al., 1988), an extraction method for these compounds should be capable of reaching at least a detection limit of 1 μg kg^{-1}. Moreover, if the method has to be applied to monitor for herbicide concentration in soil during a field experiment, many samples have to be processed. This requires a relatively simple, sensitive, and reliable method.

This paper reports a method for the extraction and LC/MS/MS analysis of metsulfuron-methyl. The method has been applied to the analysis of residues of metsulfuron-methyl after field application. The objective of this study was to determine the dissipation rate of metsulfuron-methyl under field conditions in Denmark, to investigate the degree of involvement of microorganisms in this process, and, at the same time, to demonstrate the applicability of the analytical method to real samples.

MATERIALS AND METHODS

Chemicals. Analytical standard (99% purity) of metsulfuron-methyl was purchased from Riedel De Haën (Seelze, Germany). All solvents were of HPLC grade from Merck (Darmstadt, Germany) and Rathburn (Walkerburn, U.K.). The water used for standard dilution and LC mobile phase was purified with a Millipore Super Q apparatus (Millipore, Bedford, MA). Phosphate-buffered saline (PBS) solution (0.01 M phosphate buffer, 2.7 mM potassium chloride, and 138 mM sodium chloride, pH 7.4) from Sigma Chemical (St. Louis, MO) was used as extraction solvent for soil. SPE cartridges were Porapack RDX (500 mg/6 cm^3) from Waters (Milford, MA).

[*phenyl*-U-^{14}C]Metsulfuron-methyl (radiopurity = 99%; specific activity = 38.280 μCi/mg) and [2-^{14}C]-2-amino-4-methoxy-6-methyl-1,3,5-triazine (radiopurity = 99%; specific activity = 18.300 μCi/mg), used for laboratory investigations, were a gift from DuPont (Wilmington, DE).

Field Experiment. A split-plot experiment was performed in 1997 on plots sown with spring barley and on fallow plots. The soil type was a silt loam (coarse sand, 22.6%; fine sand, 42.4%; silt, 16.3%; clay, 15.3%; organic matter, 3.4%; pH 6.4). When the barley had reached the three-leaf stage, the plots were sprayed to four replicate plots with either metsulfuron-methyl (Ally 20DF) in doses of 4, 8, or 16 g of ai/ha or water (untreated plots), giving a total of 32 plots. The experiment was repeated in 1998 on an adjacent field to obtain similar site characteristics but avoiding carry-over effects from any residual metsulfuron-methyl. Soil samples (0−3 cm) were collected prior to spraying and at intervals after spraying. In the first year the samples were collected weekly in the first month (June) and every two weeks in July. On the basis of the dissipation rate obtained for the first year, in the second year the samples were collected every third week until the middle of August. During the growing season the pH was measured in the cultivated and the fallow plots used for mineralization experiments (see below). Soil pH measured in 0.01 M $CaCl_2$ in the fallow soil was 5.90 and in the cultivated soil, 6.35.

Soil Extraction Method. A portion (100 g) of the collected sample was thawed at 20 °C, air-dried in a fume cupboard, homogenized, and screened through a 2 mm sieve. For the extraction of metsulfuron-methyl a 10 g portion was used. Duplicate samples were randomly taken for double determination.

Soil from the field experiment site was collected for recovery experiments before metsulfuron-methyl application and spiked to concentrations of 0.5, 1, 5, 10, and 20 μg kg^{-1}. Portions of 50 g of soil were thoroughly mixed with 10 mL of an acetonitrile solution containing metsulfuron-methyl. The soil slurry was shaken for 1 h, and the solvent was allowed to evaporate in a fume cupboard at 20 °C.

Method validation was performed on freshly spiked samples. The soil sample was extracted with 2 × 20 mL aliquots of PBS solution by mixing for 30 min. The soil slurry was centrifuged at 3200 rpm for 20 min on a Sorvall H-400 centrifuge (DuPont, Wilmington, DE), and the supernatant was decanted into a glass bottle.

The aqueous extract was acidified to pH 3.5 with diluted orthophosphoric acid (1:10) and extracted by SPE using the method proposed by Young (1998). The cartridge was preconditioned with 10 mL of dichloromethane followed by 10 mL of methanol and washed with 20 mL of Millipore water. After sample concentration, the analyte was eluted with 10 mL of dichloromethane. The solvent was reduced to dryness under a stream of N_2, and the sample was reconstituted in 1 mL of Millipore water/methanol 90:10.

LC/MS/MS Analysis. A Finnigan TSQ 700 (Finnigan MAT, San Jose, CA) triple quadrupole equipped with a standard ESI Finnigan MAT source was used for LC/MS/MS analyses. Data were collected with a Digital DEC station 5000/125 (Maynard, MA). The instrument was operated in positive ion mode by applying to the capillary a voltage of 5 kV and an interface temperature of 250 °C. Sheat gas (nitrogen) pressure was 65 psi, and auxiliary gas (nitrogen) flow rate was ∼5 units (∼2 L/min).

Mass spectra were collected in SIM mode by monitoring the ion m/z 382 $(M + 1)^+$ in the first quadrupole. For MS/MS analysis the product ion m/z 167 was monitored in SRM mode while the first quadrupole was locked on m/z 382. Argon was used as collision gas at a pressure of 1 mTorr. A collision offset voltage of −20 V was applied to the collision chamber.

The LC system consisted of a Waters 600 MS solvent delivery system, a Waters 717 autosampler, and a Hypersil BDS C18 column (250 × 2 mm, 5 μm particle size; Shandon, Cheshire, U.K.).

Two solvents (solvent A, 10 mM acetic acid/methanol, 90:10; solvent B, 10 mM acetic acid/methanol 10:90) were employed to run a linear gradient from 100 to 50% A in 3 min and to 100% B in 30 min. The mobile phase flow rate was 0.2 mL/min and the injection volume 50 μL.

The standards used for quantification were prepared by diluting a stock solution of metsulfuron-methyl in acetonitrile (1 mg/mL) with Millipore water/methanol 90:10.

The linearity of the system was calculated in the range 1−200 ng/mL, and $r^2 > 0.999$ was obtained.

Mineralization of Metsulfuron-methyl and 2-Amino-4-methoxy-6-methyl-1,3,5-triazine under Laboratory Conditions. Soil samples were collected on July 4, 1998, from the upper 30 cm of the two kinds of plot (cultivated or fallow plots) from the fields that had been sprayed with 2 times the normal dose. The soil was immediately passed though a 4 mm sieve without drying and carefully mixed. Soil [10 g, dry weight basis (dw)] was added to 100 mL glass bottles with airtight glass stoppers and incubated at the actual field moisture contents (15% water of soil, dw). Soil microcosms used to check for nonbiological degradation were heat-sterilized by autoclaving three times with 24 h in between. ^{14}C-labeled metsulfuron-methyl or triazine amine was added as a phosphate buffer solution (0.01 M; pH 7.4). The application rate corresponded to a concentration of 24 μg kg^{-1}. Incubation temperatures were 10 or 20 °C. $^{14}CO_2$ evolved during mineralization of the two compounds was trapped in a glass test tube containing 2 mL of 0.5 M NaOH. NaOH in the tubes was changed at days 3 and 7 and then at approximately one week intervals. Liquid scintillation counting was performed after addition of 10 mL of scintillation fluid (OpTiPhase HiSafe 3, Wallack, Finland)

Table 1. Average Recovery Percent of Metsulfuron-methyl from Soil at Indicated Fortification Levels

	fortification level				
	0.5 μg kg^{-1} (n = 8)	1 μg kg^{-1} (n = 5)	5 μg kg^{-1} (n = 5)	10 μg kg^{-1} (n = 5)	20 μg kg^{-1} (n = 5)
% recovery	86 (12.1)	85 (6.3)	79 (3.3)	77 (7.7)	81 (3.9)

using a Wallack 1409 liquid scintillation system. Counting data (means of triplicates) from heat-sterilized microcosms were subtracted counting data (means of triplicates) from native microcosms to adjust for nonbiological activity.

To test for biological potential, aliquots of 1 g of soil were taken from each bottle and suspended in 9.5 mL of 0.01 M phosphate buffer. Ten-fold dilution series were prepared, and 100 μL of these solutions were plated in triplicates. Bacterial counts were done on three different types of media. Gould S1 agar plates selecting for the genus *Pseudomonas* (Gould et al., 1985) were read after 3 days, $^1/_{10}$ strength tryptic soy broth (Difco, Detroit, MI) solidified with 1.5% BiTek agar (Difco) were read after 7 days, and H_2O−agar, prepared by Milli Q water and 1.5% Bitek agar plates (Difco) were read after 21 days.

RESULTS AND DISCUSSION

Extraction of Metsulfuron-methyl from Soil. Initial recovery experiments were performed with a 0.1 M ammonium carbonate buffer at pH 9.7. The color of the extract was dark yellow, due to the presence of significant amounts of colored natural organic compounds. The SPE method previously used for soil water (Bossi et al., 1998) was also applied to preconcentration and cleanup of the aqueous extract from soil. This method employed acidified ethyl acetate as eluting solution after preconcentration on the C18 column. The acidic organic compounds that interfered in the LC/MS analysis had to be removed by an additional cleanup step on silica.

The use of PBS solution as extraction solvent significantly reduced the amount of yellow compounds without decreasing the efficiency of metsulfuron-methyl recovery. The presence of interfering compounds in the final extract was further reduced by applying the SPE method proposed by Young (1998). In this method the elution of the SPE cartridge is performed with dichloromethane, which is less polar than ethyl acetate. The presence of interfering compounds was almost eliminated. At this point the cleanup step on silica was not necessary, resulting in a more rapid extraction method.

In some of the proposed extraction methods for sulfonylurea herbicides the liquid/solid extraction of the soil sample is performed with a mixture of organic solvent/buffer (Powley et al., 1998) or acetonitrile/water (Li et al., 1996).

The use of an organic solvent could be justified by a better efficiency in the extraction of residues bound to the organic matter. To verify this assumption, two aged field samples from two different plots were extracted in triplicate, respectively, with PBS solution and a mixture of PBS/acetone 80:20 (v/v).

The average calculated residues of metsulfuron-methyl (2.7 μg kg^{-1} for PBS extraction and 2.2 μg kg^{-1} for PBS/acetone extraction) did not significantly differ between the two methods, demonstrating that the addition of an organic solvent was not necessary even with field-aged samples.

The results of recovery experiments at five different fortification levels are shown in Table 1. The recovery

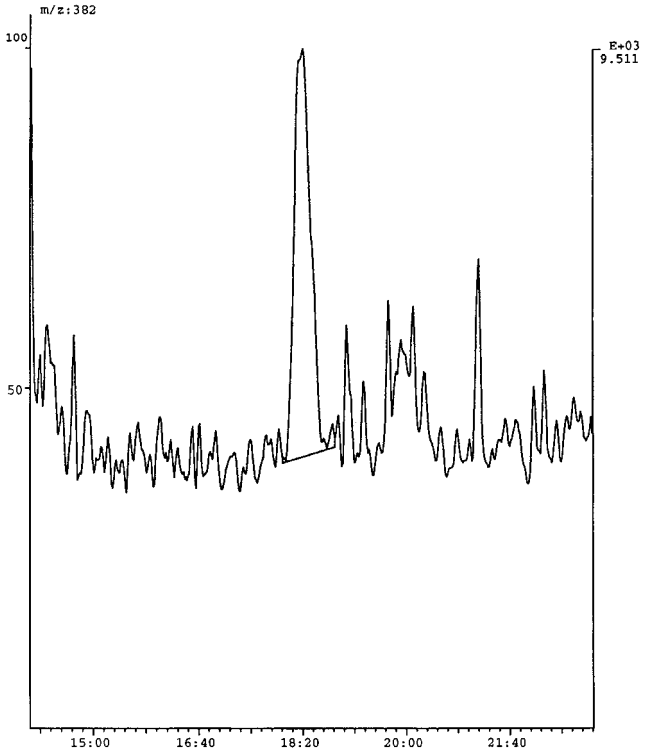

Figure 1. SIM ion chromatogram of a soil sample from a plot treated with metsulfuron-methyl. Concentration = 0.2 μg kg^{-1}.

of metsulfuron-methyl ranged from 77 to 85%, and the precision (RSD%) was between 3.3 and 12.1%.

The limit of quantitation (LOQ) for the method was 0.2 μg kg^{-1}, estimated as 10 times the signal-to-noise ratio for the analyte peak of a soil spiked to a concentration of 0.5 μg kg^{-1}.

The extraction method was applied to soil samples from the field dissipation study. The SIM ion chromatograms resulting from the analysis of, respectively, a treated plot and an untreated plot are shown in Figures 1 and 2. The concentration of metsulfuron-methyl in the sample was 0.2 μg kg^{-1}. The MS/MS ion chromatogram of the same sample obtained by monitoring in SRM mode the ion m/z 167 is shown in Figure 3. It is here demonstrated that with the proposed method it was possible to analyze and confirm metsulfuron-methyl in real samples at concentrations <1 μg kg^{-1}.

Effects of Temperature and Plant Cover on Mineralization in Microcosms. Autoclaved soil microcosms did not show any mineralization above normal background activity (data not shown). The number of total culturable bacteria on the three media did not significantly differ between samples from fallow and cultivated plots (data not shown).

As can be seen from Figures 4 and 5, complete accumulated mineralization of [*phenyl*-U-^{14}C]metsulfuron-methyl and [2-^{14}C]-2-amino-4-methoxy-6-methyl-1,3,5-triazine to $^{14}CO_2$ was higher at 20 °C than at 10 °C. The data suggest that the mineralization of metsulfuron-methyl at 20 °C follows first-order kinetics, whereas at 10 °C it is linear.

The mineralization of the triazine amine seems initially to be rapid, but considering the radiochemical purity of 99% the rapid mineralization of the first 1−2% can possibly be explained by the presence of impurities. Hereafter the mineralization at both temperatures is linear.

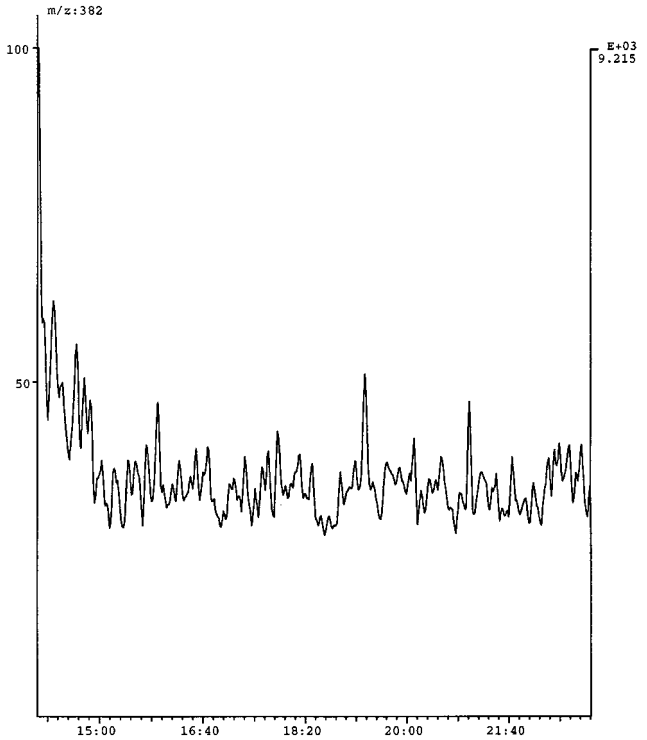

Figure 2. SIM ion chromatogram of a soil sample from an untreated plot.

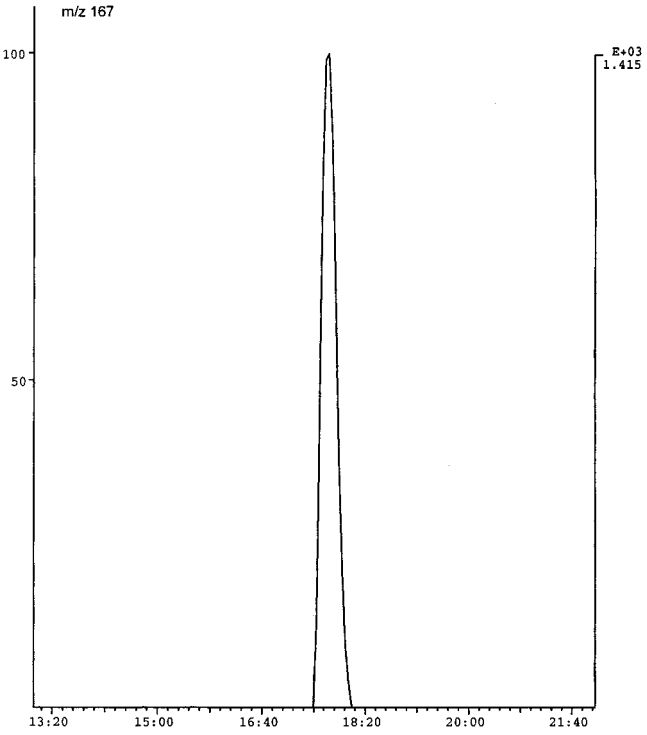

Figure 3. SRM ion chromatogram of a soil sample from a plot treated with metsulfuron-methyl. Concentration = 0.2 μg kg^{-1}.

Mineralization of metsulfuron-methyl was higher in fallow plots, whereas the triazine amine shows the opposite pattern, although less apparent. Metsulfuron-methyl is labeled in the sulfonamide ring, and full mineralization of this ring demands cleavage of the sulfonylurea bridge (Bastide et al., 1994). The difference of a half log unit in the pH of the two soils could explain why metsulfuron-methyl was mineralized more rapidly in the fallow soil (pH 5.90) than in the cultivated soil

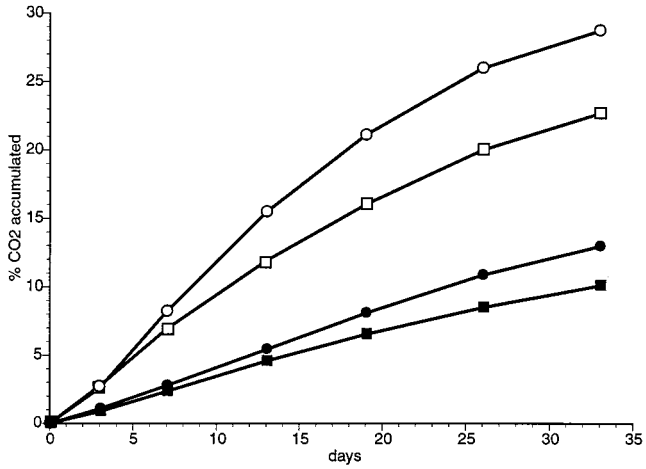

Figure 4. Mineralization curve for [*phenyl*-U-^{14}C]metsulfuron-methyl: (■) 10 °C, cultivated; (●) 10 °C, fallow; (■) 20 °C, cultivated; (○) 20 °C, fallow. Each point is the result of triplicates. Standard deviations are smaller than symbols.

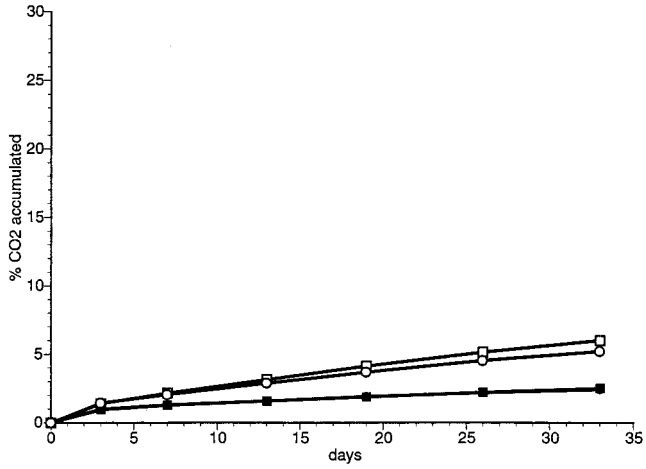

Figure 5. Mineralization curve for [2-^{14}C]-2-amino-4-methoxy-6-methyl-1,3,5-triazine: (■) 10 °C, cultivated; (●) 10 °C, fallow; (■) 20 °C, cultivated; (○) 20 °C, fallow. Each point is the result of triplicates. Standard deviations are smaller than symbols.

(pH 6.35), as it is known that hydrolysis occurs more rapidly at low pH (Berger and Wolfe, 1996; Hemmamda et al., 1994). The mineralization data (Figure 4) show that in the beginning the mineralization rates were almost the same in the two types of plots, indicating that the hydrolysis was not yet started. From day 7 the mineralization was faster in the fallow plot. The effect of pH on the mineralization of the triazine amine is not clear, and the data presented in this work do not solve this question. However, in another study (unpublished results) we did not find clear differences in the mineralization rates of the triazine amine at pH 4.0 and 6.0.

Often, one would expect a higher metabolism in soil with plant roots/organic compounds, stimulating the metabolism of the microflora. Plant roots leach low molecular weight, easily degradable compounds, which will serve as substrate for a cometabolic process leading to increased degradation of more recalcitrant molecules. However, large differences exist among the degradation of herbicides in soil and the effect of cometabolic activity. In a study comparing the degradation of 2,4-D with atrazine Willems et al. (1996) found that, whereas atrazine degradation was stimulated by a high general microbial activity, easily degradable compounds such as

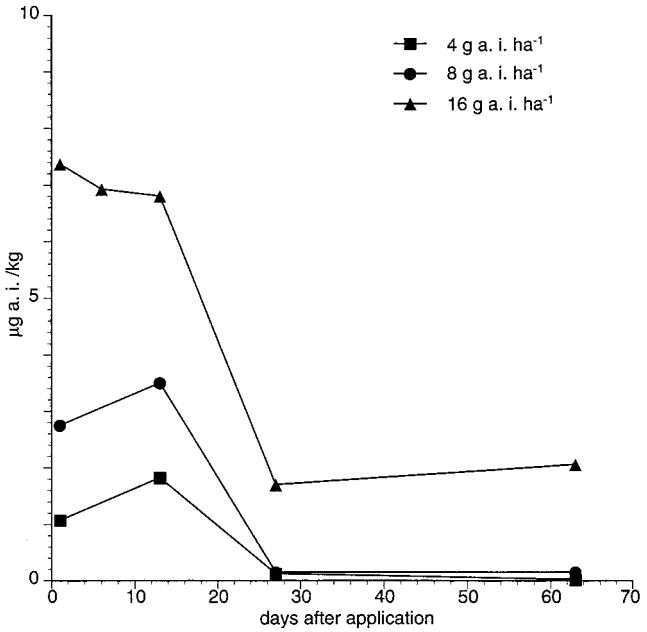

Figure 6. Dissipation of metsulfuron-methyl in fallow plots, 1997.

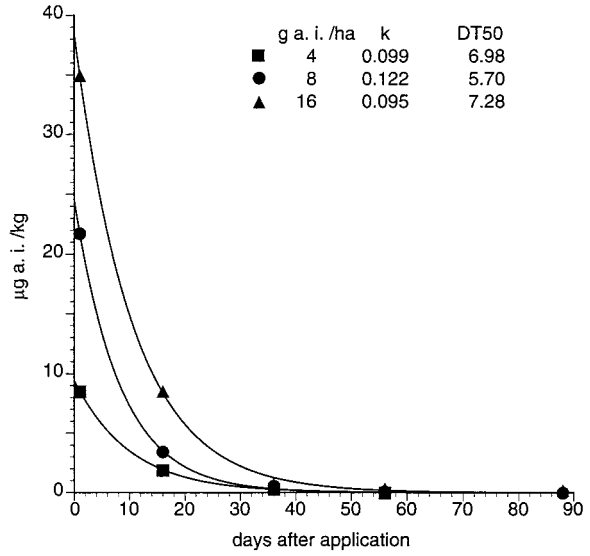

Figure 7. Dissipation of metsulfuron-methyl in fallow plots, 1998. First-order degradation curves are fitted to the data, with DT_{50} and k shown in the inset.

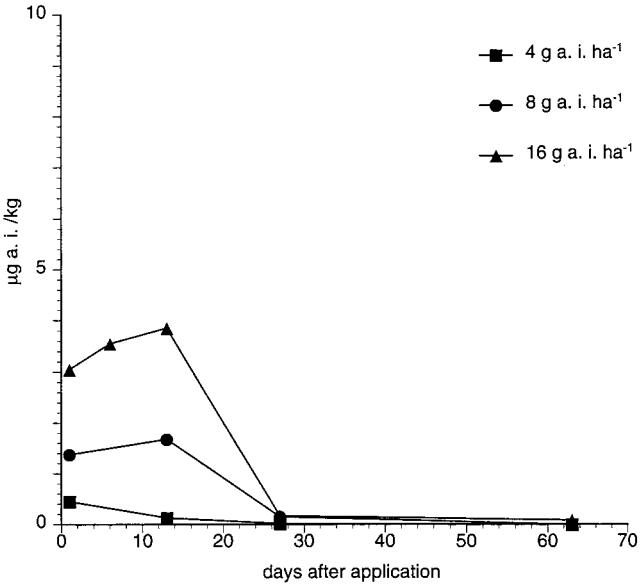

Figure 8. Dissipation of metsulfuron-methyl in cultivated plots, 1997.

2,4-D were degraded irrespective of the general microbial activity in the soil.

The mineralization of the sulfonamide and the triazine amine part of metsulfuron-methyl might reflect such two different structures. The sulfonamide belongs to aromatic benzenes, of which many have been shown to be degradable without the addition of excess carbon source; that is, this class of compounds can serve as carbon and energy sources for specific degraders. The triazine amine, on the other hand, belongs to methoxylated and methylated triazines. Microbial degraders of other triazines (e.g., atrazine, melamine, and simazine) have been found (Cook and Hutter, 1981; Mandelbaum et al., 1995; Radosevich et al., 1995). However, the degradation of the triazine ring normally requires the addition of excess carbon. It might be that the degradation of the triazine amine is enhanced in the cultivated plots where excess carbon is present. Our data show that the mineralization of the two main hydrolysis products of metsulfuron-methyl occurs, but at very different rates.

To our knowledge, no one has found degraders capable of degrading triazine amines from sulfonylureas, and the published data on mineralization in soil are few (Strek, 1998). Degradation of the triazines depends on ring cleavage of the compound, and for the triazine amines in sulfonylurea, chemical ring cleavage has been found only at or below pH 5 (Berger and Wolfe, 1996; Bray et al., 1997; Cambon and Bastide, 1997). This indicates, along with our mineralization data, that microbial degradation of the triazine part (as with the sulfonamide part) is the main mechanism of degradation of the hydrolysis products of metsulfuron-methyl.

Field Dissipation. The field dissipation trial was designed to evaluate the degradation of metsulfuron-methyl in the topsoil. However, soil cores were taken when the degradation of metsulfuron-methyl in the topsoil was completed, to measure a possible leaching of the compound to the subsoil.

The residue levels of metsulfuron-methyl in fallow soil are shown in Figures 6 and 7, reported as the average of four replicate plots. The concentrations of metsulfuron-methyl measured in 1997 just after spraying were lower than the calculated dose rate per unit area. In 1997 heavy rainfall (15 mm over 48 h) occurred immediately before spraying time. This might have caused leaching of the herbicide to the subsoil. Moreover, various factors influence the water flow in the root zone, making it difficult to predict pesticide distribution in the topsoil (Robinson and Dunham, 1982).

In 1998 no rainfall occurred before and 10 days after spraying time, and the soil was very dry. Therefore, the measured concentrations of metsulfuron-methyl at the first sampling corresponded to the calculated dose rates per unit area. Even though we could not do that in 1997, the ratio between measured concentrations corresponded to the ratio between applied doses.

The degradation of metsulfuron-methyl in cultivated plots in 1997 is shown in Figure 8. The dissipation rate in topsoil was not significantly different in cropped and fallow plots, and no consistent effect of metsulfuron-methyl application rate upon its persistence in soil was

observed. These results are in agreement with those obtained by Wadd et al. (1989).

A calculation of dissipation rate for the investigated soil layer gave a DT_{50} at 6.5 days. The dissipation adhered to first-order kinetics with a rate constant of 0.10−0.12, independent of application rates (Figure 8). This value differs from those reported by Walker and Welch (1989) for laboratory degradation of metsulfuron-methyl in topsoil. These authors reported half-lives varying between 23 and 79 days. However, the initial concentration of metsulfuron-methyl was 100 times the normal applied dose rate. At this concentration sulfonylurea herbicides may have a toxic effect on soil microorganisms (Boldt et al., 1998).

The time for a complete dissipation of metsulfuron-methyl was 60 days for the plots sprayed with 4 and 8 g of ai ha^{-1}, whereas low concentrations were still measured after 80 days in plots sprayed with 16 g of ai ha^{-1}.

The analysis of the soil cores taken three months after spraying did not show any residual herbicide. A possible explanation is that the herbicide had leached further down and/or had been degraded in the subsoil.

In conclusion, it has been observed that the rate of dissipation of metsulfuron-methyl in topsoil under Danish conditions is rapid after spring application, particularly in conditions of high soil moisture. The dissipation rate measured in field is more rapid than those reported for laboratory experiments, which, to a certain extent, is due to the very high initial concentration of the compound.

The experiments performed with ^{14}C-labeled metsulfuron-methyl indicated that microbial degradation was an important factor for field dissipation of the sulfonamide part, which is the ^{14}C-labeled part in metsulfuron-methyl. The triazine amine does not have the same mineralization rate as the sulfonamide. Whether this will give rise to accumulation in soil or groundwater remains to be solved.

ACKNOWLEDGMENT

We thank Du Pont de Nemours (Wilmington, DE) for kindly donating the ^{14}C-labeled chemicals. We also thank Mary A. Chrillesen, Annegrete Ljungqvist, Anita Løve Nielsen, Sue Dix, and Keld Skov Nielsen for helpful technical support.

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Received for review November 23, 1998. Revised manuscript received July 6, 1999. Accepted July 19, 1999. Financial support was provided by The Danish Interministry Research Program on Pesticides.

JF981280T