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PESTICIDES AND TOXIC  
SUBSTANCES

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MEMORANDUM

SUBJECT: Environmental Fate Science Chapter for Registration of  
Sulfentrazone (also known as F6285; Methanesulfonamide)

FROM: Larry Liu, Ph.D., Environmental Scientist *LL*  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C)

TO: Joanne Miller, PM 23  
Registration Division (H7505C)

THRU: Mah Shamim, Ph.D., Section Chief *M. Shamim* 3/22/96  
Chemistry Section #2  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C)

Henry M. Jacoby, Branch Chief *Henry Jacoby* 3/25/96  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C)

Attached is the Environmental Fate Science Chapter for registration of Sulfentrazone (a new herbicides for soybeans). This chemical is also known as F6285 and Methanesulfonamide. The Chapter is divided into eight sections--Abstract, Chemical/Physical Properties, Use Pattern/Background, Environmental Fate Assessment, Summary of Submitted Environmental Fate Studies, Recommendations, Bibliography, and Data Evaluation Records for Environmental Fate Studies.

Acceptable information from environmental fate studies with respect to the persistence and mobility of sulfentrazone under laboratory and field conditions has been reviewed. Based on the current environmental fate data base, sulfentrazone has the following characteristics: 1) moderately soluble, 2) not susceptible to hydrolysis, 3) extremely susceptible to direct photolysis in water, 4) very stable to photolysis on soil, 5) very persistent to aerobic

soil metabolism, 5) extremely persistent to anaerobic aquatic metabolism, 6) very mobile in soil, and 7) not volatile from soils and water. With these properties, it appears that sulfentrazone is highly mobile and persistent, and has a strong potential to leach into groundwater and move offsite to surface water. The primary routes of dissipation are through direct aqueous photolysis and leaching. Since sulfentrazone is stable to hydrolysis and biodegradation, the direct photolysis would be the only effective dissipation pathway in clear shallow waters. Low soil/water partition indicates that most sulfentrazone runoff is via dissolution in runoff water, as opposed to adsorption to eroding soil. It also indicates that most sulfentrazone will be partitioned in the water column instead of in the suspended and bottom sediments.

Although significant mobility of sulfentrazone and its major degradate (i.e., 3-carboxylic acid sulfentrazone) was not observed in three field dissipation studies conducted in Iowa, Illinois, and Arkansas, results from a combined field dissipation and small-scale prospective groundwater monitoring study conducted in North Carolina showed that sulfentrazone residues were mobile and they were detected in the shallow groundwater. Based on the environmental fate assessment for sulfentrazone with consideration of the product formulations and application rates, EFGWB believes the use of sulfentrazone is likely to result in the contamination of groundwater and surface water. This was the reason why EFGWB recommended that the labels submitted with EUP be modified to include the ground-water and surface water advisories. The proposed labels have included these advisories.

With the exception of the Small-Scale Prospective Groundwater Monitoring data requirement, the other Environmental Fate data requirements for registration of sulfentrazone have been satisfied (no additional data are required for these data requirements at this time).

No decision has been made at this time regarding what additional measures might be necessary to mitigate any potential for sulfentrazone use to contaminate ground water. Recommendations will be made upon completion of the Agency's review of the final report for the small-scale prospective ground-water monitoring study submitted by the registrant.

Environmental Fate Science Chapter for  
Sulfentrazone (PC Code 129081)

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## A. Abstract

Sulfentrazone (also known as methanesulfonamide and F6285) is a herbicide currently being developed by FMC Corporation for control of annual grass, and annual and perennial broadleaf weeds on soybeans. It can be preplant soil-incorporated to a depth of 1-3 inches, or preemergence surface-applied at a rate of 0.25-0.5 lbs a.i. per acre.

Following review of acceptable and supplemental information in the environmental fate data base, sulfentrazone appears to be persistent and mobile, and has a strong potential to leach into groundwater and move offsite to surface water. This chemical has the following characteristics: (1) moderately soluble in water (water solubility=400 ppm), (2) not susceptible to hydrolysis at acidic, neutral, and alkaline pHs, (3) extremely susceptible to direct photolysis in water, (4) stable to photodegradation on soil, (5) very persistent in sandy loam and silty clay loam soils under aerobic conditions with a half-life of 1.5 years, (6) extremely persistent to anaerobic aquatic metabolism, (7) is expected to be very mobile in soil ( $K_{ads} < 1$ ; or  $K_{oc} = 43$ ), (8) non-volatile in water and soil (vapor pressure =  $< 10^{-12}$  mmHg; Henry's Law constant =  $10^{-12}$  atm m<sup>3</sup>/mol), and (9) does not accumulate in fish ( $K_{ow} = 10$ ).

The major routes of dissipation in the environment appear to be direct aqueous photodegradation and leaching. Since sulfentrazone is stable to hydrolysis and biodegradation, the direct photolysis is the only effective dissipation pathway in clear shallow waters. Low soil/water partition indicates that most sulfentrazone runoff is via dissolution in runoff water, as opposed to adsorption to eroding soil. It also indicates that most sulfentrazone will be partitioned in the water column instead of in the suspended and bottom sediments.

Results from each of four field dissipation studies showed that sulfentrazone was very persistent (dissipation half-lives ranged from 4 to 24 months). Downward movement was not confirmed from analysis of soil samples (detection limit=1 ppb) at the lowest depths at three of the four study sites in Illinois (clay loam), Arkansas (silty clay loam), and in Iowa (silty clay loam). Based on the residues detected in the 0-6 inch soil at the above three study sites, half-lives were estimated to be 1-2 years. Results from the interim report for the fourth field dissipation study (a loamy sand in North Carolina) showed that sulfentrazone was mobile and it was detected in the deeper soil zones (i.e., 6-12, 12-18, 18-24, 24-30, 30-36, 36-42, 42-48 inches) as well as in the shallow groundwater. Based on sulfentrazone detected in the entire 48-inch soil column at the North Carolina site, the dissipation half-life was estimated to be 121 days.

Based on the environmental fate assessment for sulfentrazone with consideration of the product formulations and application rates, EFGWB believes that use of sulfentrazone is likely to result in contamination of groundwater and surface water. In a previous review, EFGWB recommended that the proposed labels be modified to include the ground-water and surface water advisories. The submitted labels have included these advisories. No decision has been made at this time regarding what additional measures might be necessary to mitigate any potential for sulfentrazone use to contaminate ground water. Recommendations will be made upon completion of the Agency's review of the final report for the small-scale prospective ground-water monitoring study submitted by the registrant.

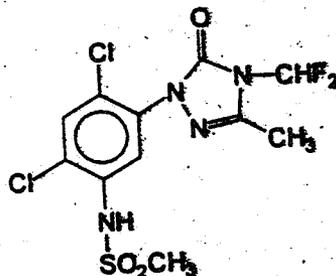
## B. Chemical and Physical Properties

Chemical name: 1-(2,4-dichloro-5-methylsulfonylamino-phenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one

Molecular formula:  $C_{11}H_{10}Cl_2F_2N_4O_3S$

Molecular weight: 387.19

Chemical structure:



Formulations:

4F (4 pounds of active ingredient per gallon)  
75DF (0.75 pound of active ingredient per pound of formulated product)

Physical state:

Solid

Color:

Tan

Odor:

Faint sulfur-like odor

Melting point:

126.5 C.

Boiling point:

unknown

Vapor pressure (25 C):

$8 \times 10^{-10}$  mm Hg

Water solubility (25 C):

400 ppm

Octanol/water partition coefficient ( $K_{ow}$ ):

31.1 (pH 5)

10 (pH 7)

0.3 (pH 9)

### C. Use Pattern/Background

Sulfentrazone (also known as methanesulfonamide; F6285) is a herbicide currently being developed by FMC Corporation for control of annual grass, and annual and perennial broadleaf weeds on soybeans. It can be preplant soil-incorporated applied, or preemergence surface applied at a rate of 0.25-0.5 lbs a.i. per acre. If treatments are to be incorporated, incorporate to a depth of 1-3 inches. Only one application per season is allowed.

The registrant has submitted studies to support the following Environmental Fate data requirements:

161-1	Hydrolysis
161-2	Photolysis in water
161-3	Photolysis on soil
162-1	Aerobic soil metabolism
162-2/3	Anaerobic soil/aquatic metabolism
163-1	Leaching-Adsorption/Desorption
164-1	Field dissipation
165-1	Accumulation in fish
166-1	Small-scale prospective groundwater monitoring

### D. Environmental Fate Assessment

Following review of acceptable and supplemental information in the environmental fate data base, sulfentrazone appears to be persistent and mobile, and has a strong potential to move offsite to surface water and leach into groundwater. The major routes of dissipation in the environment appear to be direct aqueous photodegradation and leaching. Since sulfentrazone is stable to hydrolysis and biodegradation, the direct photolysis would be the only effective dissipation pathway in clear shallow waters.

Sulfentrazone has a moderate water solubility of 400 ppm. It is not susceptible to hydrolysis at pH's 5, 7, and 9. This chemical is readily photodegradable in water (with half-lives of 12, 1, and 1 hours in aqueous pH 5, 7, and 9 solutions, respectively). Results from an aqueous photodegradation study show that sulfentrazone is rapidly dechlorinated and hydroxylated into 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone. These two photodegradation products are short-lived; the chemical bond between the phenyl and the triazole rings is subsequently cleaved, resulting in methyl triazole, 1,3-dihydroxybenzene, and methyl triazole oxidation products. Figure 1 shows the pathway for the photolytic degradation of sulfentrazone in water.

In contrast to the rapid direct photolysis in water, sulfentrazone was relatively stable to photodegradation on sand and sandy loam soils (half-life=129 days). Only one minor degradate, 3-hydroxymethyl sulfentrazone, was identified on the irradiated soils. This degradate was not detected in the aqueous photolysis study, but it was detected at low level (less than 2% of the recovered residues) in soil under aerobic conditions.

Sulfentrazone is very persistent in soil under aerobic conditions (with a half-life of 1.5 years). Four degradates were identified (3-carboxylic acid sulfentrazone, 5'-desmethylsulfonyl sulfentrazone, 3-hydroxymethyl sulfentrazone, and 3-desmethyl sulfentrazone). The major accumulating degradate was 3-carboxylic acid sulfentrazone which continuously increased with time (i.e., from 1.7% of the recovered residues at 7 days to 7.6% at 60 days, then to 10.1% at 181 days) and reached a maximum of 11% at 365 days. 5'-Desmethylsulfonyl sulfentrazone also continuously increased with time and reached a maximum level of 2.9% of the recovered residues at 368 days. Less than 2% of the recovered residues were identified as 3-hydroxymethyl sulfentrazone or 3-desmethyl sulfentrazone at any sampling period during the study.

Based on the findings, the registrant proposed two metabolic pathways for the degradation of sulfentrazone in soil under aerobic conditions (Figure 2). The major metabolic pathway for sulfentrazone in soil under aerobic conditions is the oxidation of the methyl group on the triazolinone ring of the parent compound to form 3-hydroxymethyl sulfentrazone. The hydroxymethyl group is further oxidized to carboxylic acid, forming 3-carboxylic acid sulfentrazone. Subsequently, the carboxylic acid group on 3-carboxylic acid sulfentrazone was decarboxylated, resulting in 3-desmethyl sulfentrazone. The minor metabolic pathway for sulfentrazone in soil under aerobic conditions is the cleavage of the sulfonamide group on sulfentrazone, forming 5'-desmethylsulfonyl sulfentrazone.

The chemical is very persistent in the aquatic environment under anaerobic conditions (with a half-life of 9 years). 5'-Desmethylsulfonyl sulfentrazone was the only degradate detected in the study. This degradate was first detected in water and sediment 14 days posttreatment. The total amounts of 5'-desmethylsulfonyl sulfentrazone detected in the water and sediment samples collected between 14 and 365 days ranged from 0.2-2.9% of the applied.

Sulfentrazone and its two degradates, 3-hydroxymethyl sulfentrazone and 3-carboxylic acid sulfentrazone, are expected to be very mobile in the environment. The soil adsorption coefficients for the parent compound are very low in sandy loam, silt loam, silty clay loam, and sand soils ( $K_{oc}$ =0.2-0.8; or  $K_{oc}$ =26-77). Results from a column leaching study showed that

aged sulfentrazone residues were very mobile. At the end of the column leaching study, 26-31% of the applied radioactivity remained in the aged soil layer, 2-6% was in each 2-inch column segment, and 38-44% was in the column leachates. The two degradates, 3-hydroxymethyl sulfentrazone and 3-carboxylic acid sulfentrazone, were found to be very mobile. Nearly 72% of the applied 3-hydroxymethyl sulfentrazone were detected in the leachate at the end of the study whereas 35% of the applied 3-carboxylic acid sulfentrazone were found.

Taking into account its low vapor pressure and Henry's Law constant ( $8 \times 10^{-10}$  mm Hg at 25C), moderate water solubility (400 ppm), and low organic carbon adsorption coefficient ( $K_{oc}=43$  mL/g), it appears that the volatilization of sulfentrazone from soils and water will not be an important dissipation route<sup>1</sup>. The low octanol/water partition coefficient ( $K_{ow}=10$ ) suggests that the chemical will have a low tendency to accumulate in fish<sup>2</sup>. A fish bioaccumulation study confirmed that sulfentrazone does not accumulate in fish at a significant level upon exposure (bioconcentration factors were <1x, 1.8-2.4x, and 1.1-2.0x for edible tissue, nonedible tissue, and whole fish, respectively). Trace amounts of 3-hydroxymethyl sulfentrazone were identified in the viscera.

Results from three field dissipation studies conducted in Illinois, Iowa, and Arkansas showed that sulfentrazone was very persistent (dissipation half-lives ranged from 1-2 years). It is not fully understood why majority of the residues (including sulfentrazone and 3-carboxylic acid sulfentrazone) remained in the 0-6 inch top soil. Downward movement to lower soil layers could not be confirmed from soil analyses. This was in contrast to the laboratory data which indicate that sulfentrazone and its degradates are highly mobile with sulfentrazone's  $K_{oc}$  in the range of 26-77. The following table summarized some important properties for each of the field dissipation study sites.

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<sup>1</sup>. Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1990. Handbook of Chemical Property Estimation Methods. Chapter 15: Volatilization from Water; Chapter 16: Volatilization from Soil. American Chemical Society.

<sup>2</sup>. Lyman, W. J., W.F. Reehl, and D.H. Rosenblatt. 1990. Handbook of Chemical Property Estimation Methods. Chapter 5: Bioconcentration Factor in Aquatic organisms. American Chemical Society.

Type of Study	field dissip.	field dissip.	field dissip.	field dissip./ small-scale groundwater monitoring
Location	Illinois	Iowa	Arkansas	North Carolina
Soil Texture (0-6")	clay loam	silty clay loam	silty clay loam	loamy sand/sand
Sand Content (%)	20-45	0-20	0-20	>70
Organic Matter (%)	3.4	3.5	1.4	1.2
Depth of Soil Incorp.	unknown	2"	2-3"	4-6"
Rain/Irrig.* (total in.)	103/0 (103)	66/16 (82)	81/10 (91)	62/5 (67)
from	5/1/92	5/1/93	6/1/93	5/15/92
to	11/1/93	11/1/94	12/1/94	7/14/93
Half-Lives (Soil Zone)	1 year (0-6")	2 years (0-6")	1.5 years (0-6")	121 days (0-48")

\* total precipitations (including rainfall and irrigation) received at the study sites were all above the average rainfall.

Results from the interim report for the combined field dissipation/small-scale prospective groundwater monitoring study do confirm the laboratory findings. The study showed that sulfentrazone residues (including the parent and 3-carboxylic acid sulfentrazone) were both persistent and mobile at the study site in North Carolina and readily moved to ground water. The parent compound was detected in the soil to a depth of 48 inches, with maximum concentrations of 37 ppb in the 6-12 inch depth, 11 ppb in the 12-18 inch depth, 7 ppb in the 18-24 inch depth, 5 ppb in the 24-30 inch depth, 11 ppb in the 30-36 inch depth, 3 ppb in the 36-42 inch depth, and 1 ppb in the 42-48 inch depth. Based on sulfentrazone detected in the entire 48-inch soil column at the North Carolina site, the dissipation half-life was estimated to be 121 days. It appears that the major route of dissipation for sulfentrazone at the North Carolina site is leaching than microbial degradation.

According to the reports, although some monthly rainfall at the study sites in Illinois, Arkansas, and Iowa was below the 30 year average, these below normal months along with irrigation did not

result in a lower than average yearly rainfall. For the study site in North Carolina, rainfall plus irrigation was constantly about 25% above average rainfall. Apparently, rainfall did not contribute as significantly as soil properties to the different mobility of sulfentrazone observed at the four study sites. Based on the overall review of these four field dissipation studies, the major factors attributed to the greater mobility of sulfentrazone residues at the North Carolina site than other three sites appear to be: (1) the higher content of sand in the soil at the North Carolina site (see the above table); (2) the lower organic matter content in the soil at the North Carolina site; and (3) sulfentrazone was incorporated deeper at the North Carolina site.

Sulfentrazone has the physical/chemical characteristics in common with those pesticides that are known to leach to groundwater. Results from the interim report for the combined field dissipation/small-scale prospective groundwater monitoring study showed that sulfentrazone residues (including the parent and 3-carboxylic acid sulfentrazone) were mobile at the North Carolina study site and readily moved to ground water. By the last sampling date analyzed so far (365 days after application), sulfentrazone residues (including the parent and 3-carboxylic acid sulfentrazone) averaged about 10 ppb in soil-pore water from all three depths (3, 5, and 7 feet). A similar pattern occurred in ground water with the peak concentrations (30 or 40 ppb) of sulfentrazone residues occurring about 4-5 months after application.

A full assessment has not yet been made of the significance of the data collected in a single small-scale prospective groundwater monitoring study. EFGWB received the final report for this study on March 7, 1996. This study is currently under review. Data from three other field dissipation studies in fine-textured, high-to-medium organic matter soils failed to confirm extensive leaching of sulfentrazone, but did show that sulfentrazone persisted for years at these sites (implying that there will be other sites and other conditions under which extensive leaching of sulfentrazone could occur). Based on our preliminary assessment of the ground-water study results and the environmental fate data base, it appears that the potential for sulfentrazone to leach into groundwater varies with different soil types along with other environmental conditions.

Because of the persistence and mobility, sulfentrazone has a strong potential to move offsite to surface water. Low soil/water partition indicates that most sulfentrazone runoff is via dissolution in runoff water, as opposed to adsorption to eroding soil. It also indicates that most sulfentrazone will be partitioned in the water column instead of in the suspended and bottom sediments.

Based on the environmental fate assessment for sulfentrazone with consideration of the product formulations and application rates, EFGWB believes the use of sulfentrazone is likely to result in the contamination of groundwater and surface water. In a previous review, EFGWB recommended the labels be modified to include the ground-water and surface water advisories. The labels submitted by the registrant have included these advisories:

Ground-water label advisory: this chemical has a potential to leach through soil into ground water under certain conditions as a result of agricultural use. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination.

Surface water advisory: substantial surface water contamination may occur in areas with poorly draining soils and little or no buffers or in areas where drainage systems flow directly to surface water.

No decision has been made at this time regarding what additional measures might be necessary to mitigate any potential for sulfentrazone use to contaminate ground water. Recommendations will be made upon completion of the Agency's review of the final report for the small-scale prospective ground-water monitoring study submitted by the registrant.

## **E. Summary of Submitted Environmental Fate Studies**

### **E-1. Degradation**

#### **161-1 Hydrolysis**

The submitted study (Kabler, K. and K. Williamson. 1991; MRID 41928202) on the hydrolysis of sulfentrazone was determined unacceptable in the 10/28/91 review because of the discrepancy of the mass spectra between the test substance in the 30-day sample and the reference standard. In order to upgrade the hydrolysis study, the registrant reanalyzed the Day 30 pH 7 sample and submitted its mass spectrum for review. Since the mass spectrum of the additional sample correlated with F6285 standard at m/z 307 and 386, the identity of the major compound in the hydrolysis study has been confirmed. Therefore, the study is acceptable and the Hydrolysis (161-1) data requirement is fulfilled.

Results from this study are summarized below:

"Uniformly phenyl ring-labeled [<sup>14</sup>C]sulfentrazone was

relatively stable to hydrolysis with half-lives of 143 days at pH 5, 207-375 days at pH 7, and 348 days at pH 9 in sterile aqueous buffered solutions that were incubated at 25 C in the dark for 30 days. Identification of the only compound, present in the buffered solutions at all sampling intervals, as parent sulfentrazone was based on TLC, HPLC, and MS. During the study, material balances ranged from 73.4-107%."

#### 161-2 Photodegradation in Water

Two studies (Schocken, M.J. 1994a; MRID 43345424 and Willut, J.M. 1995. MRID 43588601) were submitted to satisfy the Aqueous Photolysis data requirement. The first study cannot be used to fulfill data requirements because: (1) the experiment was terminated before the formation and decline of the major degradation products could be defined; and (2) the intensity of the artificial light source was only 12% that of natural sunlight (70 and 558 watts/m<sup>2</sup>, respectively). The second study is acceptable and can be used to fulfill data requirements.

Results from the second study are summarized below:

"Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]sulfentrazone photodegraded with half-lives of 12, 1, and 1 hours in sterile, aqueous pH 5, 7, and 9 buffer solutions, respectively, that were continuously irradiated at 25± C for up to 10 days with a UV-filtered xenon arc lamp. The artificial light source had an emission spectrum between 300 and 800 nm, and the intensity ranged from 522-536 watts/m<sup>2</sup>. The intensity of artificial light was very close to that of natural sunlight. In contrast, [<sup>14</sup>C]sulfentrazone was relatively stable in the dark at all three pH levels for the duration of the exposure period. In the irradiated solutions, sulfentrazone was rapidly dechlorinated and hydroxylated into 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone. However, these two degradates were short-lived; the chemical bond between the phenyl and the triazole rings was subsequently cleaved, resulting methyl triazole, 1,3-dihydroxybenzene, and methyl triazole oxidation product.

In the pH 5 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]sulfentrazone, sulfentrazone degraded with a half-life of 12 hours. Sulfentrazone was 95.2% of the applied immediately posttreatment, 87.4 at 2 hours, 70.7 at 6 hours, 51.3 at 11.4 hours, and 5.7% at 96 hours. Although two photodegradation products (i.e., 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy

sulfentrazone) were detected, none of them reached 10% of the applied. Methyl triazole and methyl triazole oxidation product were the major degradation products, reaching 42.4% and 11.2%, respectively, of the applied at the end of 10 days of exposure.

In the pH 7 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]sulfentrazone, sulfentrazone degraded with a half-life of 1 hour. Sulfentrazone was 55.9% of the applied at 1 hour posttreatment, 32.6% at 2 hours, 11.1% at 4 hours, and 0.6% at 12 hours. Although more than 10 degradation products were detected, only des-dichloromonohydroxy sulfentrazone and 2,4-dihydroxy sulfentrazone exceeded 10% of the applied during the course of the study. Des-dichloromonohydroxy sulfentrazone increased from 4.0% to a maximum 12.8% of the applied at 4 hours posttreatment. 2,4-Dihydroxy sulfentrazone increased from 5.4% to a maximum 11.7% of the applied at 4 hours posttreatment. Methyl triazole was the major degradation product, reaching 25.7% of the applied at the end of 10 days of exposure.

In the pH 9 irradiated EFGWB believes that solutions treated with carbonyl-labeled [<sup>14</sup>C]sulfentrazone, sulfentrazone degraded with a half-life of 1 hour. Sulfentrazone was 95.6% of the applied immediately posttreatment, 54.6% at 1 hour, 23.4% at 2 hours, and 2.8% at 6 hours posttreatment. 2,4-Dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone reached maximums of 11.2 and 8.3% of the applied, respectively, at 4 hours posttreatment; both degradates were no longer detectable following 24 hours of exposure. Methyl triazole and methyl triazole oxidation product were the major degradation products, reaching 49% and 17.1%, respectively of the applied at the end of 10 days of exposure.

In the pH 9 irradiated solutions treated with phenyl ring-labeled [<sup>14</sup>C]sulfentrazone, sulfentrazone degraded with a registrant-calculated half-life of 1 hours. sulfentrazone was 93.5% of the applied immediately posttreatment, 54.5% at 1.1 hours, 8.6% at 4 hours, and 6.4% at 5.9 hours posttreatment. 2,4-Dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone were maximums of 17.8 and 9.3% of the applied, respectively, at 6 hours posttreatment. 1,3-Dihydroxybenzene increased continuously from "non-detectable" to a maximum 21.5% of the applied at 10 days posttreatment.

The submitted study (Schocken, M.J. 1994b; MRID 43345425) on the photolysis of sulfentrazone on soil is acceptable. The Photodegradation on Soil (161-3) data requirement is fulfilled.

Results from this study are summarized below:

"Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]sulfentrazone degraded very slowly on sand and sandy loam soils that were irradiated at 14-34 C for 12 hours/day for 33 days using a xenon arc lamp. One degradate, 3-hydroxymethyl F6285, was identified in the irradiated soils.

In the irradiated sand soil treated with phenyl ring-labeled [<sup>14</sup>C]sulfentrazone, sulfentrazone was 98.5-102% of the applied radioactivity immediately posttreatment, 95.0-96.0% at 21 days, and 82.1-84.6% at 33 days. The half-life was estimated to be 98 days for the irradiated sand soil treated with the phenyl label. 3-Hydroxymethyl F6285 was isolated from the soil at a maximum average of 1.3% of the applied at 7 days posttreatment.

In the irradiated sandy loam soil treated with carbonyl-labeled [<sup>14</sup>C]sulfentrazone, sulfentrazone was 102-103% of the applied immediately posttreatment, 94.1-96.2% at 20 days, and 84.8-90.5% at 33 days. The half-life was estimated to be 161 days for the sandy loam soil treated with the carbonyl label. 3-Hydroxymethyl F6285 averaged a maximum 3.9% of the applied at 14 days posttreatment

## **E-2. Metabolism**

### **162-1 Aerobic Soil Metabolism**

Two studies (Singer, S.S. and M.J. Schocken. 1991; MRID 41928203 and Curry, S. 1993; MRID 42932117) were submitted to satisfy the Aerobic Soil Metabolism data requirement. The first study was determined unacceptable in the 10/28/91 review because: (1) the study was not conducted beyond 195-days posttreatment or until the pattern or decline of parent, and formation and decline of metabolites was established; and (2) the mass spectra of isolated samples (parent compound and metabolites) were not adequately addressed. In response, the registrant submitted additional data to upgrade the first study and committed to conduct a new aerobic soil metabolism study which would be carried out for a longer period of time (possibly up to one year). After reviewing additional data, EFGWB concluded that: (1) the first study is acceptable to satisfy the Aerobic soil Metabolism data requirement for EUP; and (2) when the second

aerobic soil metabolism study is completed, the registrant must submit it for full registration. The second study is acceptable and can be used to fulfill data requirements.

Results from this study are summarized below:

"Uniformly phenyl ring-labeled [<sup>14</sup>C]sulfentrazone or carbonyl-labeled [5-<sup>14</sup>C]sulfentrazone degraded with half-lives of 535-555 days (approximately 1.5 years) in sandy loam soil and 534-541 days (approximately 1.5 years) in silty clay loam soil that were incubated in the dark at 25C and 75% of 0.33 bar moisture. Nonvolatile degradates identified were 3-carboxylic acid F6285, 5'-desmethylsulfonyl F6285, 3-hydroxymethyl F6285, and 3-desmethyl F6285. The major accumulating degradate was 3-carboxylic acid F6285 which reached a maximum of 10.8% of the recovered residues at the end of the course of the study. 5'-desmethylsulfonyl F6285 reached a maximum level of 5.9% of the recovered at 90 days. Less than 2% of the recovered was identified as 3-hydroxymethyl F6285 or 3-desmethyl F6285. Material balance ranged from 93-107%.

The major metabolic pathway for sulfentrazone in soil under aerobic conditions is the oxidation of the methyl group on the triazolinone ring of the parent compound to form 3-hydroxymethyl F6285. The hydroxymethyl group was further oxidized to carboxylic acid, forming 3-carboxylic acid F6285. Subsequently, the carboxylic acid on 3-carboxylic acid F6285 was decarboxylated, resulting in 3-desmethyl F6285. The minor metabolic pathway is the cleavage of the sulfonamide group on F6285, forming 5'-desmethylsulfonyl F6285."

#### 162-2/3 Anaerobic Soil/Aquatic Metabolism

The registrant submitted an anaerobic aquatic metabolism study (Blumhorst, M.R. 1994; MRID 43345426) to support both the Anaerobic Soil and the Anaerobic Aquatic Metabolism data requirements. This study is acceptable and can be used to fulfill the Anaerobic Soil and the Anaerobic Aquatic Metabolism data requirements.

Results from this study are summarized below:

"Uniformly phenyl ring-labeled [<sup>14</sup>C]sulfentrazone or carbonyl-labeled [5-<sup>14</sup>C]sulfentrazone degraded very slowly (<10% degradation) in flooded loamy sand sediment (1:5, w:v) that was incubated in the dark under a static nitrogen atmosphere at 23-27 C for 12 months. The half-life was estimated to be 9 years. One degradate (5'-desmethylsulfonyl sulfentrazone) was

identified in both water and sediment samples. The levels of 5'-desmethylsulfonyl sulfentrazone detected in both water and sediment samples were <3% of the applied. Material balances ranged from 96.7-102.1% of the applied throughout the study."

### **E-3. Mobility/Leachability**

#### **163-1 Leaching-Adsorption/Desorption**

Two studies (Dykes, J. 1990; MRID 41911604 and Saxena, A.M. et. al. 1993; MRID 43355903) were submitted to satisfy the Leaching-Adsorption/Desorption data requirement. The first study was determined unacceptable in the 10/28/91 review because the complete characterization of the test soils was not carried out (such as data on cation exchange capacity and field moisture capacity was missing). The registrant did not explain why sodium azide was chosen to sterilize the soils. Since sulfentrazone is very persistent in the soil and aquatic environment under aerobic and anaerobic conditions, the use of a metabolic inhibitor in the batch equilibrium adsorption/desorption study is not necessary. EFGWB has concerns about the use of metabolic inhibitors for sterilization of soils. Researchers have reported that physical or chemical sterilization procedures may subtly alter the soil chemistry, thus complicating the interpretation of the results obtained in the batch equilibrium study. For example, the addition of azide resulted in the rise of soil pH and CO<sub>2</sub> evolution (Rozycki, M. and R. Bartha. 1981)<sup>3</sup>. If necessary, mercuric chloride should be used to prevent microbial degradation in studies to evaluate adsorption/desorption of organic chemicals by soil (Wolf, et. al., 1989)<sup>4</sup>.

In response, the registrant submitted additional data to upgrade the first study. Since results from the column leaching study along with the batch equilibrium study have clearly demonstrated the potential for sulfentrazone to leach in the environment, EFGWB concluded that the first and the second studies are acceptable to satisfy Leaching-Adsorption/Desorption data requirement. No additional information on the mobility of sulfentrazone and its degradation products in soil is needed at this time.

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<sup>3</sup>. Rozycki, M., and R. Bartha. 1981. Problems associated with the use of azide as an inhibitor of microbial activity in soil. Appl. Environ. Microbiol. p. 833-836.

<sup>4</sup>. Wolf, D.C., T.H. Dao, H.D. Scott, and T.L. Lavy. 1989. Influence of sterilization methods on selected soil microbiological, physical, and chemical properties. J. Environ. Qual. 18:39-44.

Results from these studies are summarized below:

"Based on batch equilibrium studies, uniformly phenyl-labeled [<sup>14</sup>C]sulfentrazone at 0.1, 2, 5, 7, and 10 ppm, was determined to be very mobile in sodium azide-sterilized sandy loam, silt loam, silty clay loam, and sand soil:calcium chloride solution slurries (1:5) that were equilibrated for 24 hours at 25 ± 1 C. Freundlich  $K_{ads}$  values were 0.2 for the sand soil, 0.6 for the sandy loam soil, 0.8 for the silt loam soil, and 0.8 for the silty clay loam soil; respective  $K_{oc}$  values were 77, 29, 26, and 40.  $K_{des}$  values were 1.23-1.44 for the four soils. Because their exponent values (1/n) were very close to 1 (1.03 for adsorption; 0.93 for desorption), the adsorption and desorption isotherms were linear. Material balances ranged from 96.6 to 104.7% of the applied."

"Sulfentrazone residues were mobile in columns (12-inch length) of sandy loam soil that were treated with aged (30 days) [<sup>14</sup>C]sulfentrazone residues and leached with approximately 20 inches of a 0.01 M calcium chloride solution. Prior to leaching, the columns had been topped with sandy loam soil that had been treated with phenyl ring- or carbonyl-labeled [<sup>14</sup>C]sulfentrazone and incubated in the dark at 25 C and 75% of field moisture capacity for 30 days. In the soil columns, 25.8-31.3% of the radioactivity applied to the column remained in the aged soil layer, 2.5-6.5% was in each 2-inch column segment, and 37.6-44.4% was in the column leachates. Two degradates were identified in the soil and leachate: 3-hydroxymethyl F6285 and 3-carboxylic acid F6285. Both degradation products are very mobile. It appears that 3-hydroxymethyl F6285 is more mobile than 3-carboxylic acid F6285. Nearly 72% of the applied 3-hydroxymethyl F6285 were detected in the leachate at the end of the study whereas 35% of the applied 3-carboxylic acid F6285 were found."

#### **E-4. Bioaccumulation**

##### **165-4 Accumulation in Fish**

The submitted study (Dionne, E. 1993; MRID 43345433) on the accumulation of sulfentrazone in fish is acceptable. The Accumulation in Fish data requirement is fulfilled.

Results from this study are summarized below:

"Sulfentrazone residues did not accumulate in the edible tissue (muscle) and accumulated only slightly in the nonedible tissue (viscera and carcass) of juvenile

bluegill sunfish exposed to sulfentrazone at 0.94 mg/L for 28 days under flow-through conditions. Average bioconcentration factors throughout steady state were <1x, 1.8-2.4x, and 1.1-2.0x for edible tissue, nonedible tissue, and whole fish, respectively. The degradate, 3-hydroxymethyl F6285, was identified in the viscera. The  $K_{ow}$  for sulfentrazone is 10."

#### **E-5. Fate of Sulfentrazone in the Field**

##### **164-1 Field Dissipation**

Four studies (Culligan, J.F. 1994; MRID 43345427, Culligan, F.F. 1995; MRID 43651009, Nagel, W.D. and J.F. Dulligan. 1995; MRID 43651008, and Becker, J.M. 1994; MRID 43345434) were submitted to satisfy the Field Dissipation data requirement. All four studies are acceptable and can be used to support the Field Dissipation data requirement.

Results from these studies are summarized below:

Iowa study - sulfentrazone (F6285 75DF; 75% a.i. formulated into a dry flowable powder), at 0.375 lb ai/A, dissipated with an observed half-life of approximately 2 years in the 0-to 6-inch depth of a plot of bareground silty clay loam soil in Iowa. The herbicide was applied to the soil on 5/26/93, and was incorporated into the soil to a depth of 2 inches after application.

In the 0- to 6-inch soil depth, sulfentrazone averaged 94-206 ppb through 29 days posttreatment, 78-176 ppb at 57 through 365 days, 104-108 ppb at 455 and 531 days. Trace amounts of sulfentrazone were detected in the 12-18 inch depth soil at 21, 57, 91, 120, and 180 days. For the samples collected at the depth of 30-36 inches, the parent compound was detected only at days 180. The degradate (3-carboxylic acid F6285), which was converted to 3-desmethyl F6285 prior to analysis, was detected in all samples collected in the 0-6 inch soil zone (with a range of 4-10 ppb). This degradate was not detected in the 6-12 inch soil zone during the first month after application; trace amounts were detected at later dates (1 ppb at days 57, 4 ppb at days 120, 1 ppb at days 180, 4 ppb at days 295, 3 ppb at days 365, and 4 ppb at days 531). For the samples collected at the depth of 12-18 inches, 3-carboxylic acid F6285 was only detected (1 ppb) at days 120, and was not detected (<1 ppb) in soil collected from depths below 18 inches.

Illinois study - sulfentrazone (F6285 4F; 4 lb ai/gallon flowable concentrate), at 0.5 lb ai/A, dissipated with an observed half-life of approximately 1 year in the 0- to 6-

inch depth of a plot of bareground clay loam soil in Illinois. The herbicide was applied to the soil in late May 1992, and was incorporated into the soil immediately after application.

In the 0- to 6-inch soil depth, sulfentrazone averaged 154-279 ppb through 31 days posttreatment, 134-184 ppb at 61 through 186 days, 105 ppb at 305 days, and 68-82 ppb at 362 through 531 days. Sulfentrazone was detected in the 6- to 12-inch soil depth at an average 13 ppb at 31 days posttreatment, 4-9 ppb at 61 through 451 days, and 20 ppb at 531 days; at all sampling intervals, sulfentrazone averaged  $\leq 4$  ppb in soil collected from depths below 12 inches. The degradate, 3-carboxylic acid F6285, which was converted to 3-desmethyl F6285 prior to analysis, averaged  $\leq 11$  ppb in soil from the 0- to 6-inch depth and  $\leq 2$  ppb in soil collected from depths below 6 inches at all sampling intervals.

Arkansas study - sulfentrazone (F6285 75DF; 75% a.i. formulated into a dry flowable powder), at 0.375 lb ai/A, dissipated with an observed half-life of approximately 1.5 years in the 0- to 6-inch depth of a plot of bareground silty clay loam soil in Arkansas. The herbicide was applied to the soil on 6/2/93, and was incorporated into the soil to a depth of 2-3 inches after application.

In the 0- to 6-inch soil depth, sulfentrazone averaged 68-165 ppb through 30 days posttreatment, 53-186 ppb at 61 through 276 days, 60 ppb at 360 days, and 67-95 ppb at 453 through 554 days. Trace amounts of sulfentrazone were detected in the 6- to 12-inch soil depth: 3 ppb on day 1, 2 ppb on days 6, 1 ppb on days 90 and 128. The degradate (3-carboxylic acid F6285), which was converted to 3-desmethyl F6285 prior to analysis, was detected in all the 0-6 inch soil samples collected from days 3 to days 554 with a concentration ranging from 3-13 ppb.

North Carolina study - sulfentrazone (F6285 4F; 4 lb ai/gallon flowable concentrate), at 0.5 lb ai/A, dissipated with an estimated half-life of 121 days in the entire 48-inch soil column of a plot of loamy sand soil in North Carolina. The herbicide was applied to the soil in mid-May 1992, and was incorporated into the soil at a depth of 4-6 inches immediately after application; the site was planted to soybeans at 6 days posttreatment. In the 0- to 6-inch soil depth, sulfentrazone averaged 330 ppb immediately posttreatment, 146 ppb at 32 days, 56.7 ppb at 61 days, and 13.4-22 ppb at 103 through 368 days. Sulfentrazone was detected in the soil to a depth of 48 inches, with maximum average concentrations of 36.7 ppb in the 6- to 12-inch depth, 10.9 ppb in the 12- to 18-inch depth, 6.6 ppb in the

18- to 24-inch depth, 5.2 ppb in the 24- to 30-inch depth, 10.8 ppb in the 30- to 36-inch depth, 3 ppb in the 36- to 42-inch depth, and 1 ppb in the 42-to 48-inch depth.

The degradate, 3-carboxylic acid F6285, which was converted to 3-desmethyl F6285 prior to analysis, averaged  $\leq 11.5$  ppb in soil from the 0- to 6-inch depth and  $\leq 7.3$  ppb in soil collected from depths below 6 inches at all sampling intervals.

166-1 Small-Scale Prospective Groundwater Monitor

The registrant submitted an interim report for a combined field dissipation/small-scale prospective groundwater monitor study (Becker, J.M. 1994; MRID 43345434) to support the Small-Scale Prospective Groundwater Monitoring data requirement. This report was reviewed by the Groundwater Technology Section in EFGWB on 6/27/95. Because important information was missing, EFGWB asked the registrant to submit additional data to upgrade this study. In response, the registrant submitted new data to upgrade the study. A final report for this study was received on March 7, 1996. A full assessment has not yet been made of the significance of the data collected in a single small-scale prospective ground-water monitoring study.

**F. Recommendations**

1. Inform the registrant that the following studies are acceptable and can be used to satisfy their respective Environmental Fate data requirements (no additional data are needed for these requirements):

Guideline Number and Title	MRID
161-1 Hydrolysis	41928202
161-2 Photolysis in water	43345424
	43588601
161-3 Photolysis on soil	43345425
162-1 Aerobic soil metabolism	42932117
	41928203
162-2/3 Anaerobic soil/aquatic metabolism	43345426
163-1 Leaching-adsorption/desorption	41911604
	43353903
164-1 Field dissipation	43345427
	43651009
	43651008
	43345434
165-1 Accumulation in fish	43345433

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2. No decision has been made at this time regarding what additional measures might be necessary to mitigate any potential for sulfentrazone use to contaminate ground water. Recommendations will be made upon completion of the Agency's review of the final report for the small-scale prospective ground-water monitoring study (MRID 43926814). This study was received by EFGWB on 3/7/96.

#### G. Bibliography

Barrett, G.P. 1993. Cold storage of FMC 97285 and FMC 129427 in/on laboratory-fortified soil and groundwater. Study Number: 162CSS92R1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (43345418)

Barrett, G.P. 1994. Cold storage of FMC 97285 and FMC 129427 in/on laboratory-fortified soil. Study Number: 162CSS92R2. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (43345420)

Becker, J.M. 1994. A combined soil dissipation and small scale prospective groundwater monitoring study with F6285 4F herbicide. Blasland, Bouck, and Lee, Inc. Study No.: 376.03. FMC Study No.: 162E6692E1. Unpublished study performed by Blasland, Bouck, and Lee, Inc., Durham, NC, and FMC Corporation, Princeton, NJ, and submitted by FMC Corporation, Princeton, NJ. (43345434)

Blumhorst, M.R. 1994. Anaerobic aquatic metabolism of F6285. EPL-BAS Project ID: 141-002. FMC Project ID: 162E2291E1. Unpublished study performed by EPL Bio-Analytical Services, Inc., Harristown, IL, and submitted by FMC Corporation, Princeton, NJ. (43345426)

Curry, S.J. 1993. Aerobic soil metabolism of F6285. Laboratory Project ID: 162E2191E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (42932117)

Culligan, J.F. 1994. F6285 4F herbicide - terrestrial field dissipation. FMC Study No.: 162E4192E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (43345427)

Culligan, J.F. 1995. Terrestrial field dissipation - F6285 75DF herbicide. FMC Study No.: 162E4193E2. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (43651009)

Dionne, E. 1993. F6285 - Bioconcentration and elimination of <sup>14</sup>C-residues by bluegill sunfish (*Lepomis macrochirus*).

SLI Study No.: 282.1091.6112.140. SLI Report No.: 92-7-4315. FMC Protocol/Project No.: 162E5491E1. FMC Report No.: PC-0186. Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA, and submitted by FMC Corporation, Princeton, NJ. (43345433)

Dykes, J. 1990. Soil adsorption/desorption with <sup>14</sup>C-F6285. ABC Laboratory Project ID: ABC Final Report No. 383611; FMC Study No. 162E3289E1; FMC Report No. PC-0138. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by FMC Corporation, Princeton, NJ. (41911604)

Kabler, K. and K. Williamson. 1991. Hydrolysis as a function of pH at 25 C of <sup>14</sup>C-F6285. ABC Final Report No. 38404. FMC Report No. PC-0151. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by FMC Corporation, Princeton, NJ. (41928202)

Nagel W.D. and J.F. Culligan. 1995. Terrestrial field dissipation F6285 75DF herbicide. FMC Study No.: 162E4193E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (43651008)

Schocken, M.J. 1994a. F6285 - Aqueous photolysis study following FIFRA guideline 161-2 and TSCA guideline 796.3700 (for quantum yield determination). SLI Study No.: 282.1192.6113.720. SLI Report No.: 93-7-4849. FMC Study No.: 162E1293E1. Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA, and submitted by FMC Corporation, Princeton, NJ. (43345424)

Schocken, M.J. 1994b. F6285 - Soil photolysis study following FIFRA guideline 161-3. SLI Study No.: 282.1192.6114.721. SLI Report No.: 94-3-5186. FMC Study No.: 162E1393E1. Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA, and submitted by FMC Corporation, Princeton, NJ. (43345425)

Saxena, A.M., J.R. Marengo, and T.C. Zwick. 1993. The leaching potential of <sup>14</sup>C-F6285 and degradates in a sandy loam soil. Laboratory Study No.: SC910200. FMC Study No.: 162E3191E1. FMC Report No.: PC-0178. Unpublished study performed by Battelle Memorial Institute, Columbus, OH, and submitted by FMC Corporation, Princeton, NJ. (43355903)

Singer, S.S. and M.J. Schocken. 1991. Degradation studies: Aerobic soil metabolism of F6285, a new herbicide. Laboratory Project ID: 162E21RF1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (41928203)

Wang, W.W. 1991. Aerobic soil metabolism of <sup>14</sup>C-RH-651. XenoBiotic Report No. RPT0045. Rohm and Haas Report No. 34-91-03. Unpublished study performed by XenoBiotic Laboratories, Inc., Princeton, NJ, and submitted by Rohm and Haas Company, Spring House, PA. (MRID 42086901)

Willut, J.M. 1995. Formation and decline of major <sup>14</sup>C-sulfentrazone photoproducts in buffered aqueous solution by simulated sunlight. FMC Study No.: 162E1294E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (MRID 43588601)

#### H. Data Evaluation Records for Environmental Fate Studies

1. Hydrolysis - sulfentrazone (Kabler, K. and K. Williamson. 1991. MRID 41928202)
2. Photolysis in Water - sulfentrazone (Schocken, M.J. 1994a. MRID 43345424; and Willut, J.M. 1995. MRID 43588601)
3. Photolysis on Soil - sulfentrazone (Schocken, M.J. 1994b; MRID 43345425)
4. Aerobic Soil Metabolism - sulfentrazone (Singer, S.S. and M.J. Schocken. 1991. MRID 41928203)
5. Aerobic Soil Metabolism - sulfentrazone (Curry, S. 1993. MRID 42932117)
6. Anaerobic Soil/Aquatic Metabolism - sulfentrazone (Blumhorst, M.R. 1994. MRID 43345426)
7. Leaching-Adsorption/Desorption - sulfentrazone (Dykes, J. 1990. MRID 41911604)
8. Leaching-Column - sulfentrazone (Saxena, A.M. et. al. 1993. MRID 43355903)
9. Field Dissipation of Sulfentrazone in Illinois (Culligan, J.F. 1994. MRID 43345427)
10. Field Dissipation of Sulfentrazone in Iowa (Culligan, F.F. 1995. MRID 43651009)
11. Field Dissipation of Sulfentrazone in Arkansas (Nagel, W.D. and J.F. Dulligan. 1995. MRID 43651008)
12. Field Dissipation of Sulfentrazone in North Carolina (Becker, J.M. 1994. MRID 43345434)

13. Accumulation in Fish - Sulfentrazone (Dionne, E. 1993. MRID 43345433)
14. Small-Scale Prospective Groundwater Monitoring - Sulfentrazone (Becker J.M. 1994. MRID 43345434). Because some important information were missing, the submitted interim report was considered incomplete by the Ground Water Technology Section in EFGWB (see attached review for details). On 3/7/96, EFGWB received the final report (MRID 43926814) which is currently under review.

Self-Examination Review

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Pages 25 through 26 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
- 

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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## Hydrolysis (161-1)

Kabler, K. and K. Williamson. 1991. Hydrolysis as a function of pH at 25 C of <sup>14</sup>C-F6285. ABC Final Report No. 38404. FMC Report No. PC-0151. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by FMC Corporation, Princeton, NJ. (41928202)

The submitted study (Kabler, K. and K. Williamson. 1991; MRID 41928202) on the hydrolysis of sulfentrazone was determined unacceptable in the 10/28/91 review because of the discrepancy of the mass spectra between the test substance in the 30-day sample and the reference standard. In order to upgrade the hydrolysis study, the registrant reanalyzed the Day 30 pH 7 sample and submitted its mass spectrum for review.

Since the mass spectrum of the additional sample correlated with sulfentrazone standard at m/z 307 and 386, the identity of the major compound detected in the hydrolysis study was confirmed. EFGWB concluded that this study is acceptable and can be used to fulfill the Hydrolysis (161-1) data requirement. Details can be found in the EFGWB review dated 12/21/92.

Results from this study are summarized below:

"Uniformly phenyl ring-labeled [<sup>14</sup>C]sulfentrazone was relatively stable to hydrolysis with half-lives of 143 days at pH 5, 207-375 days at pH 7, and 348 days at pH 9 in sterile aqueous buffered solutions that were incubated at 25 C in the dark for 30 days. At 30 days, sulfentrazone comprised 80.2% of the initial (time 0) parent recovered from the pH 5 solution, 86% of the initial parent recovered from the pH 7 HEPES-buffered solution, 89.7% of the initial parent recovered from TRIS-buffered solution, and 89.3% of the initial parent recovered from the pH 9 solution. Identification of the only compound, present in the buffered solutions at all sampling intervals, as parent sulfentrazone was based on TLC, HPLC, and MS. During the study, material balances ranged from 73.4-107%."



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

DP Barcode : 181232; 182374  
PC Code No. : 129081  
EFGWB No. : 92-1241/1342

*sulfentrazone  
methanesulfonamide*

MEMORANDUM

SUBJECT: Review of EUP for F6285 Herbicide

FROM: Larry Liu, Ph.D., Environmental Scientist  
Chemistry Review Section #2  
Environmental Fate and Groundwater Branch  
Environmental Fate and Effects Division (H7507C) *file 12-1-92*

TO: Joanne Miller, Product Manager (PM 23)  
Registration Division (H7505C)

THRU: Emil Regelman, Supervisory Chemist  
Chemistry Review Section #2  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C) *Q 12/15/92*  
Henry M. Jacoby, Chief  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C) *12/7/92*

Conclusion :

- (1). EFGWB concurs with the EUP for F6285 because:
  - (A). the following data requirements are fulfilled:

- Hydrolysis (161-1)
- Aerobic Soil Metabolism (162-1)\*
- Leaching-Adsorption/Desorption (163-1)

\* since the submitted study has demonstrated the pattern of decline of the parent compound and identified two major degradation products, the Aerobic Soil Metabolism (162-1) data requirement is fulfilled for the EUP. When available, the aerobic soil metabolism study, currently in progress, should be submitted for review.

(B). the following data requirements are waived:

**Confined Rotational Crop (165-1)  
Bioaccumulation in Fish (165-4)**

\* the proposed labels will be revised to exclude the use of rotational crops.

\*\* waived due to its low  $K_{ow}$ . According to the registrant, the  $K_{ow}$  data have been validated by EPA. EFGWB concurs with this waiver request for the EUP on condition that the PM can verify these  $K_{ow}$  values.

(2). Based on the preliminary data submitted to support a requested EUP, this chemical appears to display some of the characteristics for those chemicals known to leach to groundwater (such as high mobility and persistence). EFGWB recommends that the registration be advised to implement this EUP in such a way to minimize the potential impact on groundwater supplies from the experimental use.

#### Background :

##### A. Introduction

F6285 is a herbicide currently being developed by FMC Corporation for control of annual grass, and annual and perennial broadleaf weeds on soybeans.

##### B. Directions for Use

F6285 can be preplant-soil-incorporated, or preemergence surface applied at a rate of 0.25-0.5 lbs a.i. per acre. If treatments are to be incorporated, incorporate to a depth of 1-2 inches. Do not apply more than once per season.

##### C. Environmental Fate Data

F6285 has been found very persistent in water ( $t_{1/2}$  = 143-375 days at pH 5, 7, and 9), and in aerobic soil ( $t_{1/2}$  = 114-122 days). According to the adsorption/desorption study, F6285 is very mobile with a range of  $K_d$  values of 0.2-0.8 (or  $K_{oc}$  = 26-77).

The major metabolite of F6285 is F6285-3-carboxylic acid which accounted for 24% of the recovered radioactivity for the carbonyl label and 12% of the recovered radioactivity for the phenyl label 90 days after application in an aerobic soil metabolism study.

discussed 10/28/91

**Discussions :**

The registrant, FMC Corporation, has submitted additional information to upgrade three studies [Hydrolysis (161-1); Aerobic Soil Metabolism (162-1); and Leaching-Adsorption/Desorption (163-1)]. These three studies were previously determined unacceptable (see EFGWB reviews of 91-0741 and 92-0100 for details). The registrant has also submitted waiver requests for the Confined Rotational Crop (165-1) and Bioaccumulation in Fish (165-4) data requirements (for the EUP only). The registrant's justifications for the above issues and EFGWB's correspondences are presented below:

**A. Hydrolysis (161-1)**

- a. In response to the comments raised by EFGWB on the difference in the mass spectra of the parent compound (F6285) in the 30-day sample and the reference standard, the registrant reanalyzed a sample extract which was retained after the completion of the study and submitted its mass spectrum.

**Comments by EFGWB:**

Since this new mass spectrum of the Day 30 pH 7 TRIS Replicate II sample (see attachment #1) correlates with F6285 standard at m/z 307 and 386, its identity has been confirmed by mass spectrometer.

- b. The registrant claimed that the fluctuations in the concentrations during the study was due to minor quenching or a binding to glass or other materials used during aliquoting.

**Comments by EFGWB:**

The justifications provided by the registrant are not sufficient to explain why the total radioactivities in the Day 14 and 21 samples were significantly higher than that in the Days 7 samples at all pH's. However, this deficiency is not significant enough to affect the understanding of the fate of F6285 in water. Therefore, the Hydrolysis (161-1) data requirement is fulfilled.

**B. Aerobic Soil Metabolism (162-1)**

The registrant claimed that: (1) two major degradation products (F6285 3-carboxylic acid, and F6285 3-hydroxymethyl) were adequately separated and identified by TLC/HPLC, and further confirmed by mass spectrometer; and (2) efforts were made to purify the samples by GC equipped with a capillary column prior to MS, but with no success.

The registrant is conducting a new study which will be carried out for a longer period of time (possibly up to one year) to define the fate of F6285 in the aerobic soil. In the new study, the registrant will attempt to develop GC/MS methods for spectral characterization of significant metabolites of F6285.

Comments by EFGWB:

1. Based on the additional information submitted by the registrant, EFGWB believes that the identity of two degradation products (F6285 3-carboxylic acid, and F6285 3-hydroxymethyl) have been confirmed. Reasons are given below:

\* F6285 3-carboxylic acid was identified by the following methods:

- a. using one-dimensional TLC;
- b. this chemical was treated with acid to form the desmethyl derivative which was further identified chromatographically;
- c. using mass spectrometry in either EI (Electron Impact) or CI (Chemical Ionization) mode. The EI mass spectra for the TLC-purified F6285 3-carboxylic acid gave a base peak at 293 and 295, and an M-45 (decarboxylated molecule) cluster of ions at 372, 374, and 376 (due to the presence of two chlorine atoms at the phenyl ring). The 373 ion peak for the protonated decarboxylated derivative (M-45) was also found in the CI mode. These spectral data are consistent with those of the reference standard.

\*\* F6285 3-hydroxymethyl was identified by the following methods:

- a. using TLC and HPLC;
- b. using mass spectrometry in either EI (Electron Impact) or CI (Chemical Ionization) mode. This chemical was isolated by TLC prior to MS analysis. The EI spectral data indicates the presence of a base peak at 323 (due to fragmentation) and a molecular ion cluster at 402, 404, and 406 (due to two chlorine atoms at the phenyl ring). Its chemical identity was further confirmed by the CI mode. In that mass spectrum, a

molecular ion cluster at 403, 405, and 407 for M+1 was obtained. These mass spectra are corresponding to those of the reference standard.

2. When available, the aerobic soil metabolism study, currently in progress, should be submitted for review. This new study would probably provide additional data on the formation and decline of degradation products of F6285 and their identification.
3. Since the submitted study has demonstrated the pattern of decline of the parent compound, and identified two major degradation products, the Aerobic Soil Metabolism (162-1) data requirement is fulfilled for the EUP.

C. Leaching and Adsorption/Desorption

The Leaching-Adsorption/Desorption (163-1) data requirement is fulfilled because the registrant has submitted the following data for the test soils.

Soil Type	CEC, meq/100 g	Field Moisture Cap., %
#45 Sandy Loam	7.6	15.77
#46 Silt Loam	14.5	32.5
#47 Silty Clay Loam	14.1	26.8
#49 Sand	0.6	1.37

D. Confined Rotational Crop

The registrant has request a waiver of the Confined Rotational Crop (165-1) data requirement for the EUP. They intend to amend the labels to show a rotational crop restriction indicating that the rotational crop must be destroyed.

Comments by EFGWB:

EFGWB concurs with this waiver request for the EUP.

E. Bioaccumulation in Fish

Based on the low octanol/water partition coefficients for F6285 ( $K_{ow}$  = 31, 10, and 0.3 at pH 5, 7, and 9 respectively), the registrant has requested a waiver of the Bioaccumulation in Fish (165-4) data requirement.

Comments by EFGWB:

According to the registrant, the  $K_{ow}$  data have been validated by the EPA Product Chemistry reviewer. EFGWB concurs with this waiver request for the EUP on condition that the PM can verify these  $K_{ow}$  values.

Substantive Review

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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DATA EVALUATION RECORD

STUDY 1

CHEM 129001

F6285

0161-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41928202

Kabler, K. and K. Williamson. 1991. Hydrolysis as a function of pH at 25 C of <sup>14</sup>C-F6285. ABC Final Report No. 38404. FMC Report No. PC-0151. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MD, and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME - 0

REVIEWED BY: L. Bfnart

TITLE: Staff Scientist

EDITED BY: C. Cooke  
W. Martin

TITLE: Staff Scientist  
Staff Scientist

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation  
Rockville, MD  
TEL: 301-417-9800

APPROVED BY: Mah Shamim

TITLE: Chemist

ORG: EFGWB/EFED/OPP

TEL: 703-557-2025

SIGNATURE:

CONCLUSIONS:

Degradation - Hydrolysis

1. This study is unacceptable and cannot be used to fulfill data requirements at this time.
2. F6285 was reported to be relatively stable to hydrolysis with half-lives of 143 days at pH 5, 207-375 days at pH 7, and 348 days at pH 9 in sterile aqueous buffered solutions that were incubated at 25 C in the dark for 30 days. Identification of the only compound, present in the buffer solutions at all sampling intervals, as parent F6285 was based on TLC and HPLC analysis.

3. This study does not meet Subdivision N guidelines for the following reasons:

the mass spectrum of test substance in 30-day, PH 7 hydrolysis sample and F6285 reference standard appeared to be different; the base peak in the mass spectrum of F6285 reference was m/z 307 compared to m/z 129 in the test substance; also the fragment ions observed in the mass spectrum of reference standard were not present in the mass spectrum of test substance making the chemical identity of hydrolysis product questionable;

recoveries of initial (time 0) radioactivity in all test solutions steadily decreased from the 0- to 7-day samples, then increased in the 14-day samples to an equal or greater concentration of that detected in the 0-day samples, and again steadily decreased from the 14- to 30-day samples.

4. In order for this study to be used to fulfill the hydrolysis data requirement, the registrant must address the differences in the mass spectra of F6285 reference and test substance in the 30-day, PH 7 hydrolysis sample; provide mass spectra of test substance for 0-day and 30-day, PH 5, 7, and 9 hydrolysis samples; provide mass spectral analysis of hydrolysis samples by GC-MS rather than direct probe and if the samples are not positively identified by mass spectrometry, employ other analytical methods such as NMR or IR to characterize the hydrolysis product.

The registrant must address what factors may have caused the decreases and increases in total radioactivity recovered from the test solutions during the study.

#### METHODOLOGY:

Uniformly phenyl ring-labeled [<sup>14</sup>C]F6285 (radiochemical purity 98.5%, specific activity 20.1 mCi/mMol, FMC Corporation), plus unlabeled F6285 (purity 99.8%, FMC), dissolved in methanol, were added to four flasks and the methanol was evaporated under nitrogen. The test substance was redissolved using sonication in filter-sterilized (0.22 u) aqueous buffered solutions adjusted to pH 5 (acetate), pH 7 (one each of TRIS and HEPES), and pH 9 (borate); the nominal concentration of [<sup>14</sup>C]F6285 in solution was 10 ppm. Aliquots of the test solutions were transferred to autoclaved amber borosilicate glass culture tubes, the tubes were sealed with Teflon-lined caps, and the samples were incubated in the dark in an environmental chamber maintained at 25 ± 1 C. Duplicate tubes of each solution were removed for analysis at 0, 3.1, 5.1, 7, 14, 21, and 30 days posttreatment.

Duplicate aliquots (100 uL) of each test solution were analyzed for total radioactivity using LSC. The remaining portion of each sample was partitioned three times with ethyl acetate; the pH 9 test

TRIS - Hydroxymethyl aminomethane  
HEPES - N-2-Hydroxyethylpiperazine - N'-2-ethanesulfonic acid

solutions were neutralized with 1 N hydrochloric acid prior to partitioning. The organic phases were combined, and aliquots of the organic and aqueous phases were analyzed for radioactivity using LSC. Aliquots of the pooled organic phase were also analyzed using one-dimensional TLC on silica gel plates developed with methylene chloride:methanol:concentrated ammonium hydroxide (85:15:1, v:v:v). Radioactive areas were detected using radio-scanning and autoradiography. The radioactive areas were identified by comparison with a reference standard of [<sup>14</sup>C]F6285 cochromatographed with the samples. The radioactive areas on the plates from the 0- and 30-day samples were quantified by scraping the plates, eluting the residues in methanol, and analyzing the eluate by LSC. Additional aliquots of the 30-day samples were analyzed using HPLC on an ODS-2 column with water:acetonitrile (65:35, v:v) as the mobile phase and UV detection (220 nm). Fractions were collected from the column at 1-minute intervals and analyzed for radioactivity using LSC. Identification of the peaks was made by comparison with an unlabeled reference standard of F6285 cochromatographed with the samples. The identity of parent F6285 was confirmed in samples of 30-day pH 7 (TRIS) test solution using MS.

#### DATA SUMMARY:

Uniformly phenyl-ring labeled [<sup>14</sup>C]F6285 (radiochemical purity 98.5%), at 8.60-11.02 ppm, degraded with registrant-calculated half-lives of 143 days at pH 5, 207 and 375 days at pH 7, and 348 days at pH 9 in sterile aqueous buffered solutions that were incubated in the dark at 25 ± 1 C for 30 days (Tables II-V). [<sup>14</sup>C]F6285 was the only compound identified in the buffered solutions at all sampling intervals. At 30 days posttreatment, [<sup>14</sup>C]F6285 comprised 80.2% of the initial (time 0) parent recovered (73.2% of the initial radioactivity) from the pH 5 solution, 86.0% of initial parent recovered (79.4% of initial radioactivity) from the pH 7 HEPES-buffered solution, 89.7% of initial parent recovered (82.1% of initial radioactivity) from the pH 7 TRIS-buffered solution, and 89.3% of initial parent recovered (83.8% of initial radioactivity) from the pH 9 solution (Tables II-V). Following TLC analysis of organic extracts from the test solutions, approximately 6-15% of the organosoluble radioactivity was unaccounted for. Aqueous soluble radioactivity was ≤1.6% of the initial radioactivity (0.02-0.18 ppm) in the test solutions at any sampling interval. During the study, material balances prior to TLC analysis of organic phases ranged from 86.6% to 107% of the initial radioactivity (Tables VI-IX); following TLC, material balances ranged from 73.4% to 96.6% of the initial radioactivity.

At the final sampling interval (30 days posttreatment), the pH of the test solutions were 5.20-5.47, 7.06-7.10 (HEPES buffer), 7.28-7.29 (TRIS buffer), and 8.81-8.85 (Table X).

**COMMENTS:**

1. EFGMB prefers that [<sup>14</sup>C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory methods such as MS in addition to comparison with the R<sub>f</sub> of reference standards.

In this study the [<sup>14</sup>C]residues in hydrolysis samples were identified as parent F6285 by one dimensional TLC and reverse phase HPLC. Mass spectra of the F6285 reference and test substance in the 30-day, PH 7 hydrolysis sample were also provided to confirm the structure of the hydrolysis product. Although the two samples cochromatographed on TLC and HPLC their mass spectral distribution appeared to be different; the base peak in the mass spectrum of F6285 reference was m/z 307 compared to m/z 129 in the test substance; also the fragment ions observed in the mass spectrum of F6285 reference were not present in the mass spectrum of test substance. This indicates that the hydrolysis product is not identical to the parent F6285 but may be closely related in structure and, therefore, remained unresolved on HPLC or TLC. On the other hand additional fragment ions that appeared in the mass spectrum of test substance could be the result of impurities; if this is the case mass spectral analysis of the samples by GC/MS instead of solid probe would prove helpful in resolving this problem.

2. In all four test solutions, recovery of initial radioactivity steadily decreased from the 0- to 7-day samples. However, in the 14-day samples, the concentration of recovered radioactivity abruptly increased to an equal or greater concentration than that of the 0-day samples, then recoveries again steadily decreased from the 14- to 30-day samples. This anomaly was not addressed by the study authors.
3. The study authors reported that HPLC analysis of 30-day samples of the test solutions found parent F6285 comprised 99-108% of the initial dose (Table XI). It could not be determined if this meant percent of the initial (time 0) radioactivity detected in each test solution, the percent of initial parent F6285 detected in each test solution, or the percent of radioactivity applied to the HPLC. If the results are expressed as percent of initial radioactivity, the study authors need to address the discrepancy between the concentrations of F6285 detected using HPLC as compared to TLC; using TLC, F6285 comprised 87-95% of the initial (time 0) radioactivity in the 30-day ethyl acetate fractions.
4. Three preliminary studies were conducted using pH 5, 7 (TRIS and HEPES buffers), and 9 buffer solutions containing 10 ppm [<sup>14</sup>C]F6285. A preliminary 7-day hydrolysis study was conducted at 25 C to estimate rate constants and half-lives; at 7 days posttreatment, parent F6285 comprised 90.7-93.4% the total radioactivity (Figure 3). A second study determined that F6285 did not adsorb to nonsilanized

glassware during a 7-day incubation (Table I). A stability study was conducted at 4 C and -20 C and samples of the test solutions were collected after 0, 3, and 7 days of storage. It was reported that total radioactivity in the test solutions remained "relatively unchanged" at both temperatures, but the data were not provided for review. It could not readily be determined from the raw data how long the test solutions were stored prior to LSC analysis and extraction, or how long extracts were stored prior to LSC and TLC analysis.

5. The statistical estimations of the hydrolytic half-lives of F6285 in the pH 5, 7, and 9 test solutions that were reported are of limited value because the calculations involve extrapolation beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

Substantive Review

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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DATA EVALUATION RECORD

STUDY 2

CHEM 129081

Methanesulfonamide  
(F6285)

S161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY 1: Schocken, M.J. 1994a. F6285 - Aqueous photolysis study following FIFRA guideline 161-2 and TSCA guideline 796.3700 (for quantum yield determination). SLI Study No.: 282.1192.6113.720. SLI Report No.: 93-7-4849. FMC Study No.: 162E1293E1. Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA, and submitted by FMC Corporation, Princeton, NJ. (MRID 43345424)

STUDY 2: Willut, J.M. 1995. Formation and decline of major <sup>14</sup>C-sulfentrazone photoproducts in buffered aqueous solution by simulated sunlight. FMC Study No.: 162E1294E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (MRID 43588601)

DIRECT REVIEW TIME = 34

REVIEWED BY: Larry Liu  
TITLE: Environmental Scientist  
ORG: EFGWB/EFED/OPP  
TEL: 703-305-5372



SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation in Water

1. Two studies were submitted to satisfy the Aqueous Photolysis data requirement. Because the first aqueous photolysis study was terminated before the formation and decline of the degradation products could be defined, the registrant conducted another study in which the period of light exposure was extended to 10 days.
2. The first study cannot be used to fulfill data requirements because: (1) the experiment was terminated before the formation and decline of the major degradation products could be defined; and (2) the intensity of the artificial light source was only 12% that of natural sunlight (70 and 558 watts/m<sup>2</sup>, respectively).
3. The second study can be used to fulfill data requirements. Results from the second study are summarized below:

"Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285] photodegraded with half-lives of 12, 1, and 1 hours in sterile, aqueous pH 5, 7, and 9 buffer solutions, respectively, that were continuously irradiated at 25± C for up to 10 days with a UV-filtered xenon arc lamp. The artificial light source had an emission spectrum between 300 and 800 nm, and the intensity ranged from 521.9-536.4 watts/m<sup>2</sup>. The intensity of artificial light was very close to that of natural sunlight. In contrast, [<sup>14</sup>C]methanesulfonamide was relatively stable in the dark at all three pH levels for the duration of the exposure period. In the irradiated solutions, sulfentrazone was rapidly dechlorinated and hydroxylated into 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone. These two degradates were short-lived; the chemical bond between the phenyl and the triazole rings was subsequently cleaved, resulting methyl triazole, 1,3-dihydroxybenzene, and methyl triazole oxidation product.

In the pH 5 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a half-life of 12 hours. [<sup>14</sup>C]Methanesulfonamide was 95.2% of the applied immediately posttreatment, 87.4 at 2 hours, 70.7 at 6 hours, 51.3 at 11.4 hours, and 5.7% at 96 hours. Although two photodegradation products (i.e., 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone) were detected, none of them reached 10% of the applied. Methyl triazole and methyl triazole oxidation product were the major degradation products, reaching 42.4% and 11.2%, respectively, of the applied at the end of 10 days of exposure.

In the pH 7 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a half-life of 1 hour. [<sup>14</sup>C]Methanesulfonamide was 55.9% of the applied at 1 hour posttreatment, 32.6% at 2 hours, 11.1% at 4 hours, and 0.6% at 12 hours. Although more than 10 degradation products were detected, only des-dichloromonohydroxy sulfentrazone and 2,4-dihydroxy sulfentrazone exceeded 10% of the applied during the course of the study. Des-dichloromonohydroxy sulfentrazone increased from 4.0% to a maximum 12.8% of the applied at 4 hours posttreatment. 2,4-dihydroxy sulfentrazone increased from 5.4% to a maximum 11.7% of the applied at 4 hours posttreatment. Methyl triazole was the major degradation product, reaching 25.7% of the applied at the end of 10 days of exposure.

In the pH 9 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a half-life of 1 hour. [<sup>14</sup>C]Methanesulfonamide was 95.6% of the applied immediately posttreatment, 54.6% at 1 hour, 23.4% at 2 hours, and 2.8% at 6 hours posttreatment. 2,4-dihydroxy sulfentrazone and desdichloromonohydroxy sulfentrazone reached maximums of 11.2 and 8.3% of the applied, respectively, at 4 hours posttreatment; both degradates were no longer detectable following 24 hours of exposure.

Methyl triazole and methyl triazole oxidation product were the major degradation products, reaching 49% and 17.1%, respectively of the applied at the end of 10 days of exposure.

In the pH 9 irradiated solutions treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 1 hours. [<sup>14</sup>C]Methanesulfonamide was 93.5% of the applied immediately posttreatment, 54.5% at 1.1 hours, 8.6% at 4 hours, and 6.4% at 5.9 hours posttreatment. 2,4-dihydroxy sulfentrazone and desdichloromonohydroxy sulfentrazone were maximums of 17.8 and 9.3% of the applied, respectively, at 6 hours posttreatment. 1,3-dihydroxybenzene increased continuously from "non-detectable" to a maximum 21.5% of the applied at 10 days posttreatment.

5. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide] in sterile aqueous buffered solutions at pH 5, 7, and 9.
6. No additional information on the photodegradation of [<sup>14</sup>C]methanesulfonamide in water is required at this time.

#### METHODOLOGY:

##### First Aqueous Photolysis Study

Phenyl ring-labeled [U-<sup>14</sup>C]methanesulfonamide or carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285; radiochemical purities  $\geq 98.6\%$ , specific activities 17.2 and 21.8 mCi/mMol, respectively, Du Pont], dissolved in acetonitrile, was added at approximately 15 mg/L to sterilized (autoclaved) pH 5 (0.01 M acetate), 7 (0.005 M HEPES) or 9 (0.005 M borate) buffer solutions; the concentration of the acetonitrile cosolvent in the final solutions did not exceed 1% by volume. Duplicate aliquots of each treated buffer solution were collected immediately after treatment for analysis. Additional aliquots of the test solutions were transferred to quartz or borosilicate glass tubes (12 x 100 mm). The tubes were filled completely (approximately 12 mL), leaving no headspace; 28 tubes were prepared for each treatment combination. Additional tubes were filled with para-nitroanisole (PNA), an actinometer which would be used to determine quantum yield. The tubes were sealed with Teflon-lined caps, and the borosilicate glass tubes (both buffer and PNA solutions) were wrapped in aluminum foil to serve as dark controls.

All of the filled tubes were placed on black, nonreflective stainless steel racks that were positioned 45° to the horizontal within a

Heraeus Suntest Accelerated Exposure Unit (Figure 4). The solutions were irradiated with a xenon arc lamp filtered to remove wavelengths <300 nm. The lamp had an emission spectrum between 300 and 850 nm, and an intensity that was approximately 12% that of natural sunlight (69.6 watts/m<sup>2</sup> compared to 558.0 watts/m<sup>2</sup> for the lamp and sunlight, respectively; Figures 5 and 6). The light intensity of the xenon arc lamp was measured with a hand-held radiometer/photometer. The photolysis chamber was maintained at 25-28 C by circulating a refrigerated mixture of water:ethylene glycol through coils within the sample racks; the temperature of the solutions was measured with a thermometer placed in a tube of water located on the sample rack. Duplicate tubes of the irradiated and dark control solutions were collected for analysis at 1.5, 3, 6, and 8 hours posttreatment. The samples were analyzed on the day sampled, or were stored refrigerated in an amber vial. The pH of the test solutions was monitored at each sampling interval.

Because 8 hours proved to be insufficient to establish the half-life of methanesulfonamide in the pH 5 solution, the experiment was repeated using nonradioabeled methanesulfonamide (purity 95%). Methanesulfonamide, dissolved in acetonitrile, was added at approximately 15 mg/L to a pH 5 (0.01 M acetate) buffer solution. Aliquots of the treated solution were transferred to individual tubes, then incubated as previously described. Duplicate tubes of the irradiated and dark control solutions were collected for analysis at 0, 2, 4, 8, 12, and 22.5 hours posttreatment.

In order to generate sufficient quantities of degradates for identification and characterization, phenyl or carbonyl ring-labeled [<sup>14</sup>C]methanesulfonamide was added at 100 mg/L to pH 7 and pH 9 buffer solutions. The pH 7 solutions were irradiated for 8 hours on day 1 and an additional 6 hours on day 2; the pH 9 solutions were irradiated intermittently for a total of 19 hours over 3 consecutive days. Also, phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide was added at 15 mg/L to pH 9 buffer solution, then the solutions were irradiated for 8 hours. Following irradiation, the solutions were stored frozen in amber bottles until analysis.

Aliquots of each solution were analyzed for total radioactivity using LSC. Additional aliquots of the test solutions were analyzed by HPLC using a Phenomenex Ultramex C-18 column eluted with acetonitrile:water:phosphoric acid (45:55:1 for parent; 20:80:0.1 to 80:20:0.1 to 20:80:0.1 for degradates); the column was equipped with UV (230 nm) and radiometric detection. [<sup>14</sup>C]Compounds were identified by comparison of the retention times with those of nonlabeled reference standards of methanesulfonamide, 3-hydroxymethyl F6285, 3-carboxylic acid F6285, 3-desmethyl F6285, 5'-nitro F6285, 4-desdifluoromethyl F6285, 5'-desmethylsulfonyl F6285, 3-desmethyl-4-desdifluoromethyl F6285, 4-N-methyl-3-difluoromethyl triazolinone, and desdichloro F6285. The limit of quantification was 0.206 mg/L. Aliquots of some duplicate samples were combined, then concentrated by solid-phase extraction or partitioning with ethyl acetate prior to

HPLC analysis. The identities of the [<sup>14</sup>C]compounds were confirmed using LC/MS or GC/MS.

### Second Aqueous Photolysis Study

Because the first aqueous photolysis study was terminated before the formation and decline of the degradation products could be defined, after consulting with EFGWB staff, the registrant decided to conduct another study in which the period of light exposure was extended to 10 days. Samples were analyzed at 0, 1, 2, 4, 6, 12, 24 hours, 2, 4, 7, and 10 days posttreatment. Since the methods used in the second study were very similar to the first study, refer to the first study for details.

The test solutions were continuously irradiated at 25± C with a UV-filtered xenon arc lamp. In order to determine the light intensity and spectrum at the beginning and the end of exposure, a Li-Cor Li-1800 (Li-Cor Inc., Lincoln, NE) spectroradiometer was used. The artificial light source had an emission spectrum between 300 and 800 nm, and the intensity ranged from 521.9-536.4 watts/m<sup>2</sup>. The intensity of artificial light at the beginning of the study was compared with that of natural sunlight on a clear day at 12:13 PM in Princeton, NJ (Figure 1).

In addition to the TLC, HPLC, GC/MS, and LC/MS used in the first study, additional instruments were used in the second study to identify unknown compounds and CO<sub>2</sub>/CO. The confirmation of the identities of <sup>14</sup>CO<sub>2</sub> and <sup>14</sup>CO as photodegradation products was accomplished by using a Kratos Concept IH mass spectrometer. The instrument was turned with nitrogen and oxygen, and with CF<sub>3</sub>. Nuclear Magnetic Resonance (NMR) spectrum analyses were conducted using a Bruker AMX2-500. The samples for NMR analysis were evaporated to dryness under a stream of nitrogen gas and reconstituted in MeOD (an isotope of MeOH).

### DATA SUMMARY:

#### First Aqueous Photolysis Study

Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide (N-[2,4-dichloro-5[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl]methanesulfonamide; F6285; radiochemical purities ≥98.6%), at 15 mg/L, photodegraded with registrant-calculated half-lives of 8.39-9.56, 2.22-3.05, and 2.45-3.09 hours in sterile, aqueous pH 5, 7, and 9 buffer solutions, respectively, that were continuously irradiated at 25-28 C for up to 22 hours with a UV-filtered xenon arc lamp. The artificial light source had an emission spectrum between 300 and 850 nm, and an intensity that was approximately 12% that of natural sunlight (69.6 and 558.0 watts/m<sup>2</sup>, respectively). In contrast, [<sup>14</sup>C]methanesulfonamide was relatively stable in the corresponding dark control solutions during 8 hours of

incubation. Five degradates were identified in the irradiated solutions:

- 2-hydroxy-4-chloro F6285 ("Photodegradata 16"),
- 3-desmethyl-4-desdifluoromethyl F6285 ("Photodegradata 9"),
- desdichloromonohydroxy F6285 ("Photodegradata 10"),
- 2-chloro-4-hydroxy F6285 ("Photodegradata 12"), and
- a compound resulting from the cleavage of the triazolinone ring ("Photodegradata 4C").

In the pH 5 irradiated solutions treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide. [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 9.56 hours (Table V). [<sup>14</sup>C]Methanesulfonamide was 98.3% of the applied immediately posttreatment, 67.2-67.3% at 3 and 6 hours, and 56.6% at 8 hours (Table XIX). When the study was repeated under similar conditions, methanesulfonamide was 98.7% of the applied immediately posttreatment, 55.3% at 8 hours, 43.1% at 12 hours, and 20.9% at 22.5 hours (reviewer-calculated from Table XVII). The major degradate, 2-hydroxy-4-chloro F6285, was a maximum of 10% of the applied at 6 hours posttreatment, and was 8.3% at 8 hours (Table XIX). Desdichloromonohydroxy F6285 and 2-chloro-4-hydroxy F6285 were maximums of 4.9 and 8.7% of the applied, respectively, at 8 hours posttreatment. Six additional [<sup>14</sup>C]compounds were isolated, each at ≤6.6% of the applied, but were not identified. In the dark control solutions, no degradation of [<sup>14</sup>C]methanesulfonamide was noted (Table VI). At 8 hours posttreatment, the material balances of the irradiated and dark control solutions were 94.8 and 95.3% of the applied, respectively (Table XIV).

In the pH 7 irradiated solutions treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide. [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 2.22 hours (Table V). [<sup>14</sup>C]Methanesulfonamide was 98.1-98.3% of the applied immediately posttreatment, 44.3-46.5% at 3 hours, 24.3-41.5% at 6 hours, and 14.5-17.1% at 8 hours (Table XIX). 3-Desmethyl-4-desdifluoromethyl F6285 increased to 15.2-21.3% of the applied at 6 and 8 hours posttreatment. Desdichloromonohydroxy F6285 was a maximum 13.9-17.9% of the applied at 3 and 6 hours posttreatment, and was 12.1-16.1% at 8 hours. 2-Hydroxy-4-chloro F6285 increased to 6.0-7.9% of the applied at 8 hours posttreatment, and 2-chloro-4-hydroxy F6285 was a maximum 5.3-5.6% at 1.5 hours. Thirteen additional [<sup>14</sup>C]compounds were isolated, each at ≤7.4% of the applied, but were not identified. In the dark control solutions, no degradation of [<sup>14</sup>C]methanesulfonamide was noted (Table VII). At 8 hours posttreatment, the material balances of the irradiated and dark control solutions were 94.5 and 96.5% of the applied, respectively (Table XV).

In the pH 9 irradiated solutions treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 3.09 hours (Table V). [<sup>14</sup>C]Methanesulfonamide was 98.4% of the applied immediately posttreatment, 74.6% at 3 hours, 16.2% at 6 hours, and 20.9% at 8 hours posttreatment (Table XIX). 3-Desmethyl-4-desdifluoromethyl F6285 and desdichloromonohydroxy F6285 were maximums of 19.5 and 12.1% of the applied, respectively, at 8 hours posttreatment; 2-chloro-4-hydroxy F6285 was a maximum 4.0% at 3 hours; and 2-hydroxy-4-chloro F6285 was isolated, but not in sufficient concentrations to quantify. "Photodegradate 1" and "Photodegradate 2", which totaled 12.8 and 8.3% of the applied at 8 hours posttreatment, were determined to consist of several compounds, none present at >10% of the applied [pages 53-55]. Nine additional [<sup>14</sup>C]compounds were isolated, each at ≤9.3% of the applied, but were not identified. In the dark control solutions, [<sup>14</sup>C]methanesulfonamide was 95.3% of the applied immediately posttreatment and 94.0% at 8 hours (reviewer-calculated from Table VIII). At 8 hours posttreatment, the material balances of the irradiated and dark control solutions were 99.8 and 96.7% of the applied, respectively (Table XVI).

In the pH 5 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 8.39 hours (Table V). [<sup>14</sup>C]Methanesulfonamide was 100% of the applied immediately posttreatment, 81.1% of the applied at 6 hours, and 60% at 8 hours (Table XX). 2-Hydroxy-4-chloro F6285, desdichloromonohydroxy F6285, 2-chloro-4-hydroxy F6285, and "Photodegradate 4C" were maximums of 5.0, 3.1, 9.5, and 8.3% of the applied, respectively, at 8 hours posttreatment. Six additional [<sup>14</sup>C]compounds were isolated, each at ≤5.3% of the applied, but were not identified. In the dark control solutions, [<sup>14</sup>C]methanesulfonamide was 94.6% of the applied immediately posttreatment and 92.0% at 8 hours (reviewer-calculated from Table VI). At 8 hours posttreatment, the material balances of the irradiated and dark control solutions were 96.0 and 96.7% of the applied, respectively (Table XIV).

In the pH 7 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 3.05 hours (Table V). [<sup>14</sup>C]Methanesulfonamide was 100% of the applied immediately posttreatment, 42.0-78.9% at 3 hours, 17.6-43.5% at 6 hours, and 25.4-27.4% at 8 hours posttreatment (Table XX). 3-Desmethyl-4-desdifluoromethyl F6285 and desdichloromonohydroxy F6285 were maximums of 13.2-19.7 and 11.6-14.6% of the applied, respectively, at 6 and 8 hours posttreatment. 2-Hydroxy-4-chloro F6285 was 2.8-3.8% of the applied at 3 through 8 hours posttreatment; 2-chloro-4-hydroxy F6285 was 3.3-6.9% at 3 through 8 hours; and "Photodegradate 4C" was 7.6-12.6% at 6 and 8 hours. Eleven additional [<sup>14</sup>C]compounds were isolated, each at ≤7.4% of the applied, but were not identified. In the dark control solutions, [<sup>14</sup>C]methanesulfonamide was 94.0% of the applied immediately posttreatment and 92.0% at 8 hours (reviewer-

calculated from Table VII). At 8 hours posttreatment, the material balances of the irradiated and dark control solutions were 96.7 and 95.4% of the applied, respectively (Table XV).

In the pH 9 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 2.45 hours (Table V).

[<sup>14</sup>C]Methanesulfonamide was 100% of the applied immediately posttreatment, 73.7% at 1.5 hours, 52.7% at 3 hours, 13.9% at 6 hours, and 5.8% at 8 hours posttreatment (Table XX). "Photodegradate 4C" increased to a maximum 31.3% of the applied at 8 hours posttreatment. 3-Desmethyl-4-desdifluoromethyl F6285 and desdichloromonohydroxy F6285 were maximums of 21.2 and 9.9% of the applied, respectively, at 6 hours posttreatment; and 2-chloro-4-hydroxy F6285 was a maximum 5.9% at 3 hours. "Photodegradate 1" and "Photodegradate 2", which totaled 6.2 and 10.7% of the applied at 8 hours posttreatment, were determined to consist of several compounds, none present at >10% of the applied [pages 53-55]. 2-Hydroxy 4-chloro F6285 was isolated, but not in sufficient concentrations to quantify. Five additional [<sup>14</sup>C]compounds were isolated, each at ≤9.0% of the applied, but were not identified. In the dark control solutions, [<sup>14</sup>C]methanesulfonamide was 94.7% of the applied immediately posttreatment and 88.0% at 8 hours (reviewer-calculated from Table VIII). At 8 hours posttreatment, the material balances of the irradiated and dark control solutions were 99.0 and 98.1% of the applied, respectively (Table XVI).

### Second Aqueous Photolysis Study

Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285] photodegraded with half-lives of 12, 1, and 1 hours in sterile, aqueous pH 5, 7, and 9 buffer solutions, respectively, that were continuously irradiated at 25 C for up to 10 days with a UV-filtered xenon arc lamp. The artificial light source had an emission spectrum between 300 and 800 nm, and the intensity ranged from 521.9-536.4 watts/m<sup>2</sup>. The intensity of the artificial light was very close to that of natural sunlight. In contrast, [<sup>14</sup>C]methanesulfonamide was relatively stable in the dark at all three pH levels for the duration of the exposure period. 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone were detected in the irradiated solutions; however, they were short-lived. The major degradates detected in the irradiated solutions were methyl triazole, methyl triazole oxidation product, and 2,4-dihydroxybenzene. The chemical structures for these degradation products can be found in Figure 17.

In the pH 5 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 12 hours (Table 16).

[<sup>14</sup>C]Methanesulfonamide was 95.2% of the applied immediately posttreatment, 87.4 at 2 hours, 70.7 at 6 hours, 51.3 at 11.4 hours,

and 5.7% at 96 hours (Table 16, Figure 37). Although two photodegradation products (i.e., 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone) were detected, none of them reached 10% of the applied. Methyl triazole and methyl triazole oxidation product were the major degradation products, reaching 42.4% and 11.2%, respectively, of the applied at the end of 10 days of exposure. In the dark control solutions, no degradation of [<sup>14</sup>C]methanesulfonamide was noted. At 10 days posttreatment, the material balances of the irradiated and dark control solutions were 86.8 and 102.9% of the applied, respectively.

In the pH 7 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 1 hour (Table 13). [<sup>14</sup>C]Methanesulfonamide was 55.9% of the applied at 1 hour posttreatment, 32.6% at 2 hours, 11.1% at 4 hours, and 0.6% at 12 hours (Table 13, Figure 34). Although more than 10 degradation products were detected, only des-dichloromonohydroxy sulfentrazone and 2,4-dihydroxy sulfentrazone exceeded 10% of the applied during the course of the study. Des-dichloromonohydroxy sulfentrazone increased from 4.0% to a maximum 12.8% of the applied at 4 hours posttreatment. 2,4-dihydroxy sulfentrazone increased from 5.4% to a maximum 11.7% of the applied at 4 hours posttreatment. In the dark control solutions, no degradation of [<sup>14</sup>C]methanesulfonamide was noted. At 10 days posttreatment, the material balances of the irradiated and dark control solutions were 93.3 and 98% of the applied, respectively.

In the pH 9 irradiated solutions treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 1 hour (Table 14). [<sup>14</sup>C]Methanesulfonamide was 95.6% of the applied immediately posttreatment, 54.6% at 1 hour, 23.4% at 2 hours, and 2.8% at 6 hours posttreatment (Table 14, Figure 35). 2,4-dihydroxy sulfentrazone and des-dichloromonohydroxy sulfentrazone reached maximums of 11.2 and 8.3% of the applied, respectively, at 4 hours posttreatment; both degradates were no longer detectable following 24 hours of exposure. Methyl triazole and methyl triazole oxidation product were the major degradation products, reaching 49% and 17.1%, respectively of the applied at the end of 10 days of exposure. In the dark control solutions, no degradation of [<sup>14</sup>C]methanesulfonamide was noted. At 10 days posttreatment, the material balances of the irradiated and dark control solutions were 84.5 and 103.5% of the applied, respectively.

In the pH 9 irradiated solutions treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide degraded with a registrant-calculated half-life of 1 hours (Table 15). [<sup>14</sup>C]Methanesulfonamide was 93.5% of the applied immediately posttreatment, 54.5% at 1.1 hours, 8.6% at 4 hours, and 6.4% at 5.9 hours posttreatment (Table 15). 2,4-dihydroxy sulfentrazone and desdichloromonohydroxy sulfentrazone were maximums of 17.8 and 9.3%

of the applied, respectively, at 6 hours posttreatment. 1,3-dihydroxybenzene increased continuously from "non-detectable" to a maximum 21.5% of the applied at 10 days posttreatment. In the dark control solutions, [<sup>14</sup>C]methanesulfonamide was stable. At 10 days posttreatment, the material balances of the irradiated and dark control solutions were 100.7 and 84.1% of the applied, respectively.

The test solutions were continuously irradiated at 25± C for up to 10 days with a UV-filtered xenon arc lamp. The artificial light source had an emission spectrum between 300 and 800 nm, and the intensity ranged from 521.9-536.4 watts/m<sup>2</sup>. The intensity of artificial light was very close to that of natural sunlight (Figure 1).

The confirmation of the identities of the parent compound and its degradates was accomplished by using TLC, HPLC, GC/MS, LC/MS, and NMR. The HPLC-purified photodegradation products were subject to chemical ionization (CI) and/or electron impact (EI) direct probe mass spectral analysis. The direct probe MS spectrum of standard [<sup>14</sup>C[carbonyl]sulfentrazone demonstrated a parent ion (<sup>14</sup>C M+2) with m/e 388 and a major fragment peak at m/e 353 due to the loss of chlorine (figure 25). As a comparison, the direct probe EI MS spectrum of the [<sup>14</sup>C-[carbonyl]sulfentrazone isolated from the pH 5 buffer exposed for 1 hour is given in Figure 24.

The identity of 2,4-dihydroxy-sulfentrazone (a short-lived degradate) which was isolated at 26 minutes by HPLC from the [<sup>14</sup>C]carbonyl-labeled sulfentrazone treated pH 7 sample after 4 hours of exposure (Figure 9) was further confirmed by direct probe EI MS analysis. An ion (M-H) with m/e at 349 matched with the loss of both chlorine and replacement with two hydroxyl groups from the parent compound (Figure 18). The first major fragment peak at 335 was likely due to the loss of the methyl group.

Another short-lived degradate (des-dichloro-monohydroxy sulfentrazone) was detected at 31 minutes by HPLC (Figure 9). The identity of this compound was further confirmed by LC/MS. An ion (M-H) at m/e 333 was found, which was consistent with the loss of both chlorine atoms and replacement of a single hydroxyl group (Figure 20). A peak of 335 for <sup>14</sup>C M+2 was also observed. Although the position of the hydroxyl group on the ring could not be confirmed, the author stated that it could be located at the 2 or 4 position.

Methyl triazole was the major accumulating photodegradation products formed from [<sup>14</sup>C[carbonyl]sulfentrazone at pH 5, 7, and 9 solutions. Results from the analysis of the HPLC-isolated methyl triazole (retention time=19 minutes) by direct probe MS showed the (MH)<sup>+</sup> peak at m/e 150 and the <sup>14</sup>C M+2 peak at m/e 152 (Figure 26). The major fragment had a peak at m/e 99 due to the loss of the CF<sub>2</sub>H group.

A major compound was detected at 13.7 minutes by HPLC; however, no definite confirmation could be made by MS analysis. Based on the presence of a mass of 149 and a fragmentation pattern similar methyl

triazole during the direct probe MS analysis on a HPLC-purified sample (Figure 29), the author suggested that the compound is structurally related to methyl triazole. Due to the short HPLC retention time, the author concluded that the compound might be the result of the oxidation of the methyl group to alcohol or acid. Therefore, the author called the compound as methyl triazole oxidation product.

Results from the direct probe MS analysis of the HPLC-isolated photodegradation product with 14-15 minute retention time in MeOD showed multiple peaks from m/e 109-114 (Figure 30). The presence of multiple peaks was due to deuterium exchange. The compound was identified as dihydroxybenzene which had an (M-H) of 109. The first set of fragment peaks (with the largest peak at 95) was due to the loss of the first hydroxy group. The second set of fragment peaks (the largest peak was at 79) was caused by the loss of the second hydroxyl group. Based on the retention times of three dihydroxybenzene isomers (i.e., 2,3-dihydroxybenzene, 2,4-dihydroxybenzene, 2,5-dihydroxybenzene), this compound was further identified as 2,4-dihydroxybenzene (also known as resorcinol).

#### COMMENTS:

1. The two most polar HPLC peaks, designated, "Photodegradate 1" (retention time 3.0-3.4 minutes) and "Photodegradate 2" (retention time 4.0-4.3 minutes), comprised >10% of the applied in the irradiated pH 9 buffer solutions. Further analysis of additional samples established that both compounds consisted of several compounds, none exceeding 10% of the radioactivity. Attempts to identify the isolated fractions using LC/MS were unsuccessful due to their complexity and polar nature.
2. The sampling intervals and duration of the photodegradation experiments were determined on the basis of the results of a preliminary study in which pH 7 buffer solution treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide was irradiated continuously with the xenon arc lamp for 8 hours.
3. For the solutions treated with the phenyl ring label, the pHs were 5.05-5.10 for pH 5, 7.32-7.39 for pH 7, and 9.06-9.09 for pH 9. For the solutions treated with the carbonyl label, the pHs were 4.96-4.99 for pH 5, 6.99-7.04 for pH 7, and 9.00-9.04 for pH 9.
4. The samples were stored refrigerated or frozen prior to HPLC analysis. Storage stability was studied in a preliminary experiment in which chromatographic profiles were obtained for a 12-hour irradiated sample (phenyl label, pH 7) and the same sample analyzed after 2 weeks of refrigeration. The similarity between the profiles confirmed the stability of [<sup>14</sup>C]compounds following refrigerator storage (Figures 51 and 52).

5. Results from the first aqueous photolysis study indicated that methanesulfonamide degraded rapidly under light conditions that were only 12% that of natural sunlight in the wavelength range of 300 to 850 nm. Thus, more rapid degradation of methanesulfonamide would be expected under higher intensity sunlight conditions. Results from the second aqueous photolysis study proved that the parent compound photodegraded faster when the intensity of the artificial light was greater.
6. In the first aqueous photolysis study, the solubility of methanesulfonamide in water at pH 7 was reported to be 780 mg/L at 25C. In the second aqueous photolysis study, the water solubility was reported to be 490 ppm at pH 6 and 2,000 ppm at pH 7.5 at room temperature (page 19).
7. The UV-Vis adsorption spectrum for methanesulfonamide in water at 15 mg/L is provided in Figure 7. Absorbance for methanesulfonamide in the buffer solutions is provided in Tables II through IV.
8. The proposed pathway for the photolytic degradation of methanesulfonamide, which includes dechlorination, phenyl-ring hydroxylation, loss of the difluoromethyl and methyl substitutes from the triazolinone ring, and cleavage between the phenyl and triazolinone rings, is presented in Figure 50.
9. The study author calculated quantum yields (number of molecules that photoreact with number of photons absorbed) of [<sup>14</sup>C]methanesulfonamide for both radiolabels at each pH through the use of the actinometer, para-nitroanisole (PNA). The quantum yields of phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide were determined to be 2.34, 0.253, and 0.128 at pH 5, 7, and 9, respectively. The quantum yields of carbonyl-labeled [<sup>14</sup>C]methanesulfonamide were determined to be 1.94, 0.134, and 0.118 at pH 5, 7, and 9, respectively. As stated by the study author, these values indicate that methanesulfonamide (F6285) is "apparently very efficient in undergoing photoreactions after photon capture. In particular, F6285 in solution at pH 5 apparently undergoes secondary chain reaction after absorption of a single photon, resulting in a quantum yield greater than unity [page 46]."
10. The chemical name for the degradate 3-desmethyl-4-desdifluoromethyl F6285 was provided as N-[2,4-dichloro-5-(4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]methanesulfonamide; chemical names for the remainder of degradates identified in the irradiated solutions were not provided.
11. Results from the first aqueous photolysis study are summarized below:  
Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285] photodegraded with half-lives of 9.0, 2.6, and 2.8 hours in sterile, aqueous pH 5, 7,

and 9 buffer solutions, respectively, that were continuously irradiated at 25-28 C for up to 22 hours with a UV-filtered xenon arc lamp. The artificial light source had an emission spectrum between 300 and 850 nm, and an intensity that was approximately 12% that of natural sunlight (70 and 558 watts/m<sup>2</sup>, respectively). In contrast, [<sup>14</sup>C]methanesulfonamide was relatively stable in the corresponding dark control solutions during 8 hours of incubation. Five degradates were identified in the irradiated solutions: 2-hydroxy-4-chloro F6285, 3-desmethyl-4-desdifluoromethyl F6285, desdichloromonohydroxy F6285, 2-chloro-4-hydroxy F6285, and a compound resulting from the cleavage of the triazolinone ring ("Photodegrade 4C").

Substantive Review

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  - Identity of product impurities.
  - Description of the product manufacturing process.
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  - The product confidential statement of formula.
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DATA EVALUATION RECORD

STUDY 2

CHEM 129081

Methanesulfonamide  
(F6285)

\$161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 43345425

Schocken, M.J. 1994b. F6285 - Soil photolysis study following FIFRA guideline 161-3. SLI Study No.: 282.1192.6114.721. SLI Report No.: 94-3-5186. FMC Study No.: 162E1393E1. Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA, and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 30

REVIEWED BY: J. Harlin

TITLE: Staff Scientist

EDITED BY: K. Ferguson  
C. Padova

TITLE: Task Leader  
Staff Scientist

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation  
Rockville, MD  
TEL: 301-417-9800

APPROVED BY: Larry Liu  
TITLE: Environmental Scientist  
ORG: EFGWB/EFED/OPP  
TEL: 703-305-5372



SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study can be used to fulfill data requirements.
2. Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285] degraded very slowly on sand and sandy loam soils that were irradiated at 14-34 C for 12 hours/day for 33 days using a xenon arc lamp. One degradate, N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-

1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-hydroxymethyl F6285), was identified in the irradiated soils.

In the irradiated sand soil treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide was 98.5-102% of the applied radioactivity immediately posttreatment, 95.0-96.0% at 21 days, and 82.1-84.6% at 33 days. The half-life was estimated to be 98 days for the irradiated sand soil treated with the phenyl label. 3-Hydroxymethyl F6285 was isolated from the soil at a maximum average of 1.3% of the applied at 7 days posttreatment.

In the irradiated sandy loam soil treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide was 102-103% of the applied immediately posttreatment, 94.1-96.2% at 20 days, and 84.8-90.5% at 33 days. The half-life was estimated to be 161 days for the sandy loam soil treated with the carbonyl label. 3-Hydroxymethyl F6285 averaged a maximum 3.9% of the applied at 14 days posttreatment.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide] on sand and sandy loam soils.
4. No additional information on the photodegradation of [<sup>14</sup>C]methanesulfonamide on soil is required at this time.

#### METHODOLOGY:

Sieved (2 mm) sand soil (92% sand, 6% silt, 2% clay, 0.16% organic matter, pH 5.7, CEC 1.30 meq/100 g) was weighed (8.87 g dry weight) into individual Petri dishes (60-mm id) and slurried with water. The soil was air-dried overnight, then treated dropwise with approximately 10 ug/g of phenyl ring-labeled [U-<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285; radiochemical purity 99.1%, specific activity 17.2 mCi/mMol, Du Pont], dissolved in acetonitrile. The acetonitrile was allowed to evaporate for 1 hour at room temperature, then the soil was moistened to 85% of field moisture capacity. Two dishes of treated soil were collected as immediate posttreatment samples. Half of the dishes of treated soil were placed inside a stainless steel "soil photolysis module", and the module was sealed tightly with a quartz glass cover (Figures 5 and 6).

Additional samples were prepared as described using sandy loam soil (73.2% sand, 14.8% silt, 12.0% clay, 1.43% organic matter, pH 6.8, CEC 5.22 meq/100 g) that was treated at 2.7 ug/g with carbonyl-

labeled [<sup>14</sup>C]methanesulfonamide (radiochemical purity 99.6%, specific activity 21.8 mCi/mMol, Du Pont).

Both the phenyl ring- and carbonyl-labeled samples were irradiated for 12 hours/day using a xenon arc lamp (Heraeus Suntest) filtered to eliminate wavelengths <300 nm. The lamp had an emission spectrum of 300-850 nm, and a total light intensity of 105.7 and 141.1 watts/m<sup>2</sup> prior to and after the completion of the study, respectively; sunlight intensities outside the analytical laboratory (Wareham, MA; 42°N) during the two portions of the study were 321.8 and 490.40 watts/m<sup>2</sup> (Figures 7 and 8). Sterile, humidified, CO<sub>2</sub>-free air was drawn through the sample chamber for approximately 30-115 minutes/day; the vented air was drawn through single tubes ethylene glycol, 0.5 N sulfuric acid, and 1 N NaOH trapping solutions. The photolysis chamber was maintained 14-34 C by circulating a refrigerated mixture of water:ethylene glycol through the chamber underneath the samples; the temperature of the soils was measured with a thermometer probe placed in a dish of untreated soil located in the chamber with the treated samples. The soils were remoistened every 2-3 days in an attempt to maintain the soil moisture content at 85% of field moisture capacity. The dishes of treated soil that were not irradiated were placed in a "dark control module" that was sealed with borosilicate glass and placed in an incubator or environmental chamber, covered with a black drape, and maintained at 25 ± 1 C. During incubation, volatiles were trapped and the soils were kept moist as described for the irradiated samples.

For the soils treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, duplicate irradiated soil samples were collected at 7, 14, 21, 30, and 33 days posttreatment; duplicate dark control samples were collected at 7, 14, 21, and 28 days; and the trapping solutions were collected for analysis and replaced at each sampling interval. For the soils treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, duplicate samples of the irradiated and dark control soil were collected at 7, 14, 20, and 33 days posttreatment; the trapping solutions were collected for analysis and replaced at each sampling interval.

The soil was extracted three times with acetonitrile:water (7:3, v:v) by vortexing for 3 minutes followed by manual shaking for 3 minutes per extraction; after each extraction, the samples were centrifuged and the supernatant decanted. The extracts were combined, and aliquots of the combined extracted were analyzed for total radioactivity using LSC. If it was believed that the extracted soil still contained >10% of the applied radioactivity, the soil was further extracted with acetonitrile:water (7:3, v:v), acetonitrile:0.1 N HCl (1:1, v:v), and/or methanol:2 N HCl (1:1, v:v) until unextracted [<sup>14</sup>C]residues were <10% of the applied. Aliquots of each soil extract were analyzed for methanesulfonamide by HPLC using a Phenomenex Ultremex C-18 column eluted with acetonitrile:water:phosphoric acid (45:55:0.1, v:v:v); the column was equipped with radioactive flow detection. Because degradation was

noted only in the dark control samples for the phenyl label, an aliquot of the extract from one of the 7-day dark control samples was analyzed by reverse-phase HPLC using a Phenomex Ultremex C-18 column eluted with acetonitrile:water:phosphoric acid (20:80:0.1 to 80:20:0.1 to 20:80:0.1, v:v:v); the column was equipped with UV (230 nm) and radioactive flow detection. [<sup>14</sup>C]Compounds were identified by comparison of the retention times with those of nonlabeled reference standards of methanesulfonamide (F6285), 3-hydroxymethyl F6285, F6285-3-carboxylic acid, 3-desmethyl F6285, 5'-nitro F6285, 4-desdifluoromethyl F6285, 5'-desmethylsulfonyl F6285, and 3-desmethyl-4-desdifluoromethyl F6285. The identification of methanesulfonamide and 3-hydroxymethyl F6285 was confirmed using LC/MS. Portions of the extracted soils that were believed to contain >10% of the applied radioactivity were analyzed for unextracted radioactivity using LSC following combustion.

Aliquots of the trapping solutions were analyzed for total radioactivity using LSC.

#### DATA SUMMARY:

Phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285; radiochemical purities ≥98.6%], at approximately 10 and 2.7 ug/g, respectively, degraded very slowly on sand and sandy loam soils that were irradiated at 14-34 C for 12 hours/day for 33 days using a xenon arc lamp. The lamp had an emission spectrum of 300-850 nm, and a total light intensity of 105.7 and 141.1 watts/m<sup>2</sup> prior to and after the completion of the study, respectively; sunlight intensities outside the analytical laboratory (Wareham, MA; 42°N) during the two portions of the study were 321.8 and 490.40 watts/m<sup>2</sup> (Figures 7 and 8).

[<sup>14</sup>C]Methanesulfonamide also degraded very slowly in the dark control for the sandy loam soil treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide. In contrast, [<sup>14</sup>C]methanesulfonamide degraded rapidly in the phenyl-ring labeled sand soil dark controls, with an observed half-life of <14 days. One degradate,

N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-hydroxymethyl F6285)

was isolated from the irradiated and dark control soils.

In the irradiated sand soil treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide was 98.5-102% of the applied radioactivity immediately posttreatment, 95.0-96.0% at 21 days, and 82.1-84.6% at 33 days (Table VII). 3-Hydroxymethyl F6285 was isolated from the soil at a maximum average of 1.3% of the applied at 7 days posttreatment; three additional [<sup>14</sup>C]compounds were each <2% at all sampling intervals. At 33 days posttreatment,

unextracted soil [<sup>14</sup>C]residues were 0.56-0.65% of the applied, and [<sup>14</sup>C]volatiles totaled <0.1% (Table IX). The material balances were 94.1-107% of the applied through 21 days, 69.3-92.1% at 30 days, and 86.7-89.4% at 33 days. In the dark control soil (Table VII), [<sup>14</sup>C]methanesulfonamide decreased from 98.5-102% of the applied immediately posttreatment to 93.6-102% at 7 days, 25.3-33.7% at 14 days, and 22.4-26.1% at 28 days. 3-Hydroxymethyl F6285 was 46.1-68.4% of the applied with no pattern of formation or decline at 14 through 28 days posttreatment; two additional [<sup>14</sup>C]compounds were each ≤4.6% throughout the study. At 33 days posttreatment, unextracted soil [<sup>14</sup>C]residues were <10% of the applied, and [<sup>14</sup>C]volatiles totaled <0.1% (Table IX). The material balances were 99.7-112% of the applied through 7 days posttreatment, and 92.0-95.3% at 14 through 28 days.

In the irradiated sandy loam soil treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide was 102-103% of the applied immediately posttreatment, 94.1-96.2% at 20 days, and 84.8-90.5% at 33 days (Table XII). 3-Hydroxymethyl F6285 averaged a maximum 3.9% of the applied at 14 days posttreatment; two other [<sup>14</sup>C]compounds each averaged ≤3.3% at all sampling intervals. At 33 days posttreatment, unextracted soil [<sup>14</sup>C]residues were 10.0-11.2% of the applied, and [<sup>14</sup>C]volatiles totaled <0.1% (Table XIII). The material balances were 93.1-110% of the applied throughout the study, with no discernible pattern of decline. In the dark control soil, [<sup>14</sup>C]methanesulfonamide decreased from 102-103% of the applied immediately posttreatment to 93.3-95.9% at 20 days, and 89.4-93.7% at 33 days (Table XII). 3-Hydroxymethyl F6285 averaged a maximum 4.3% of the applied at 14 days posttreatment; two other [<sup>14</sup>C]compounds each averaged ≤3.4% at all sampling intervals. At 33 days posttreatment, unextracted soil [<sup>14</sup>C]residues were 11.4-12.0% of the applied, and [<sup>14</sup>C]volatiles totaled <0.1% (Table XIII). The material balances were 93.4-117% of the applied throughout the study, with no discernible pattern of decline.

#### COMMENTS:

1. The study author stated that the degradation of methanesulfonamide in the dark control but not irradiated samples "is thought to be related to a more rapid evaporation of water in the light-exposed samples (in spite of frequent remoisturizations) which would have resulted in a substantial decrease in the overall microbial activity in the dehydrated soil...The difference in degradation in the two soils [sand and sandy loam dark control samples] apparently had to do with the presence (or absence) of microbial species with the requisite degradative enzymes [page 11]."

Usually the dark control soils were more moist than their irradiated counterparts. Despite remoisturization of the soils every 2-3 days, the irradiated soil lost substantially more water than the dark controls; approximately 85% of the water added to the irradiated

samples was lost by the next remoisturization, but only about 40% of that lost from the dark control samples was lost [pages 36-37]. Also, the study author attributed the lack of degradation in the 15-day preliminary study to the less frequent remoisturization of the preliminary soil samples.

However, the only evidence the study author offers to support the contention that the observed degradation was microbial was that there was "a visually-apparent relatively thick white mycelial mat" covering 28-day dark control sample that was not observed in the irradiated samples. In the dark control sand soil treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide decreased from 93.6-102% of the applied at 7 days posttreatment to 25.3-33.7% at 14 days, a loss of almost 70% of the applied radioactivity in a 7-day period. In an aerobic soil metabolism experiment (MRID 42932117) conducted using sandy loam and silty clay loam soils treated with either phenyl ring- or carbaryl-labeled [<sup>14</sup>C]methanesulfonamide at 2.5 ppm and incubated at a constant 75% of field capacity, [<sup>14</sup>C]methanesulfonamide degraded with a calculated half-life of 534-555 days; 3-carboxylic acid F6285 was the only major degradate. There was no attempt to confirm the study author's theory that an organism that is capable of rapidly degrading methanesulfonamide was present in the sand soil but not in the sandy loam soil obtained from an adjacent site.

It should also be noted that the study author stated that methanesulfonamide is not photolytic in nature; however, in a photodegradation in water experiment (MRID 43345424), methanesulfonamide photodegraded with half-lives of 8.39-9.56, 2.22-3.05, and 2.45-3.09 hours in sterile, aqueous pH 5, 7, and 9 buffer solutions, respectively, that were continuously irradiated at 25-28 C for up to 22 hours with a UV-filtered xenon arc lamp. The artificial light source had an emission spectrum between 300 and 850 nm, and an intensity that was approximately 12% that of natural sunlight (69.6 and 558.0 watts/m<sup>2</sup>, respectively). In contrast, [<sup>14</sup>C]methanesulfonamide was relatively stable in the corresponding dark control solutions during 8 hours of incubation. Five degradates were identified in the irradiated solutions: 2-hydroxy-4-chloro F6285; 3-desmethyl-4-desdifluoromethyl F6285; desdichloromonohydroxy F6285; 2-chloro-4-hydroxy F6285; and a compound resulting from the cleavage of the triazolinone ring ("Photodegradate 4C"). In another photolysis in water study (MRID 43588600), methanesulfonamide was found to be readily degradable in water under light.

2. In the irradiated sand soil treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide was 63.5 and 92.1% of the applied in duplicate samples at 30 days posttreatment. Samples were collected at 33 days posttreatment, at which time [<sup>14</sup>C]methanesulfonamide was 82.1 and 84.6% of the applied.

3. The temperature of the irradiated soil was not kept constant, but ranged from 21.3 to 28.2 C for the phenyl ring-labeled samples and from 13.7 to 34.2 C for carbonyl-labeled samples. In the study protocol, the study author stated that it was difficult to maintain the soil temperatures at  $25 \pm 1$  C, particularly under alternating light and dark periods, but that the temperatures approximate the temperature range expected in a typical temperate climate in spring or summer [page 93].
4. The microbial biomass of the sand and sandy loam soils was determined prior to and after the completion of the studies. Portions of the soil were extracted with water, and the water extract was plated on nutrient agar using pour plate techniques. The concentration of organisms in the sand soil averaged  $1.3 \times 10^6$  cpu/g prior to the initiation of the study,  $3.0 \times 10^6$  cpu/g following 30 days of dark incubation, and  $37 \times 10^6$  cpu/g following 30 days of irradiation. The concentration of organisms in the sandy loam soil was  $3.2 \times 10^6$  to  $3.5 \times 10^6$  cpu/g prior to and after completion of the study.
5. The method detection limits for the HPLC analyses were not reported.
6. The sampling intervals and duration of the photodegradation experiments were determined on the basis of the results of a preliminary study in which sand soil was treated with phenyl ring-labeled [U- $^{14}$ C]methanesulfonamide at 10.0 ug/g and irradiated with the xenon arc lamp on a 12-hour photoperiod for 15 days.
7. The application rate was decreased to 2.7 ppm in the second portion of the study because it is equivalent to the maximum field application rate of 0.375 lb ai/A at a 1-cm soil depth.
8. The registrant-calculated half-lives were 97.5 days for the irradiated sand soil treated with the phenyl label, 161 days for the sandy loam soil treated with the carbonyl label, and 213 days for the carbonyl-labeled dark control. These statistical estimations are of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study.
9. The lamp had an emission spectrum of 300-850 nm, and a total light intensity of 105.7 and 141.1 watts/m<sup>2</sup> prior to and after the completion of the study, respectively; sunlight intensities outside the analytical laboratory (Wareham, MA; 42°N) on clear days of 7/14/93 and 9/5/93 were 321.8 and 490.4 watts/m<sup>2</sup>. The light intensities over the wavelength range of 300-850 nm for the artificial light source prior to and after the completion of the study were 33% and 29% of natural light, respectively. The authors did not explain why the light intensity generated from the xenon arc lamp (Heraeus Suntest) equipped with a sunlight filter (300 nm cutoff) was much lower than that of the natural light.

Different light intensities have been reported in other methanesulfonamide studies. The xenon lamp used in the photolysis in

water study (MRID 43588600) generated a light intensity of 533 watts/m<sup>2</sup>, which is 4-5x higher than that generated from the xenon lamp used in the photolysis on soil study. However, lower light intensity was reported in the photolysis in water study (MRID 43345424), in which the xenon lamp generated only 70 watts/m<sup>2</sup> over the wavelength range of 300 to 850 nm.

Substantive Review

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Pages 129 through 147 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
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  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
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Substantive Review

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  - Description of the product manufacturing process.
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Aerobic Soil Metabolism (162-1)

Singer, S.S. and M.J. Schocken. 1991. Degradation studies: Aerobic soil metabolism of F6285, a new herbicide. Laboratory Project ID: 162E21RF1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ. (41928203)

The submitted study (Singer, S.S. and M.J. Schocken. 1991; MRID 41928203) on the degradation of sulfentrazone in aerobic soil was determined unacceptable in the 10/28/91 review because: (1) the study was not conducted beyond 195-days posttreatment or until the pattern or decline of parent, and formation and decline of metabolites was established; and (2) the mass spectra of isolated samples (parent compound and metabolites) were not adequately addressed. In response, the registrant submitted additional data to upgrade the study and committed to conduct a new aerobic soil metabolism study which would be carried out for a longer period of time (possibly up to one year). After reviewing additional data, EFGWB concluded that: (1) the first study is acceptable to satisfy the Aerobic Soil Metabolism (162-1) data requirement for EUP; and (2) when the second aerobic soil metabolism study is completed, the registrant must submit it for full registration.

Results from this study are summarized below:

"Uniformly phenyl ring-labeled [<sup>14</sup>C]sulfentrazone and carbonyl-labeled [5-<sup>14</sup>C]sulfentrazone, at 3.3 ppm, degraded with half-lives of 122 and 114 days, respectively, in sandy loam soil that was incubated in the dark at 24 C and 75-80% of 0.33 bar moisture for up to 195 days. For both label positions, nonvolatile degradates included 3-carboxylic acid sulfentrazone and 3-hydroxymethyl sulfentrazone; three additional degradates, 3-desmethyl sulfentrazone, sulfentrazone free amine, and 3-aldehyde sulfentrazone, were tentatively identified."

Note: because this study was terminated too early, results from this study should be considered as informational. Refer to the second aerobic soil metabolism study for definite findings.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

DP Barcode : 181232/182374  
PC Code No. : 125081  
EFGWB No. : 92-1241/1342

*sulfentrazone  
methanesulfonamide*

MEMORANDUM

SUBJECT: Review of EUP for F6285 Herbicide

FROM: Larry Liu, Ph.D., Environmental Scientist  
Chemistry Review Section #2  
Environmental Fate and Groundwater Branch  
Environmental Fate and Effects Division (H7507C)

TO: Joanne Miller, Product Manager (PM 23)  
Registration Division (H7505C)

THRU: Emil Regelman, Supervisory Chemist  
Chemistry Review Section #2  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C)

Henry M. Jacoby, Chief  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C)

*file 12-1-92*

*Q 12/15/92*

*12/21/92*

Conclusion :

- (1). EFGWB concurs with the EUP for F6285 because:
  - (A). the following data requirements are fulfilled:

- Hydrolysis (161-1)
- Aerobic Soil Metabolism (162-1)
- Leaching-Adsorption/Desorption (163-1)

\* since the submitted study has demonstrated the pattern of decline of the parent compound and identified two major degradation products, the Aerobic Soil Metabolism (162-1) data requirement is fulfilled for the EUP. When available, the aerobic soil metabolism study, currently in progress, should be submitted for review.

(B). the following data requirements are waived:

Confined Rotational Crop (165-1)  
Bioaccumulation in Fish (165-4)

\* the proposed labels will be revised to exclude the use of rotational crops.

\*\* waived due to its low  $K_{ow}$ . According to the registrant, the  $K_{ow}$  data have been validated by EPA. EFGWB concurs with this waiver request for the EUP on condition that the PM can verify these  $K_{ow}$  values.

(2). Based on the preliminary data submitted to support a requested EUP, this chemical appears to display some of the characteristics for those chemicals known to leach to groundwater (such as high mobility and persistence). EFGWB recommends that the registration be advised to implement this EUP in such a way to minimize the potential impact on groundwater supplies from the experimental use.

#### Background :

##### A. Introduction

F6285 is a herbicide currently being developed by FMC Corporation for control of annual grass, and annual and perennial broadleaf weeds on soybeans.

##### B. Directions for Use

F6285 can be preplant-soil-incorporated, or preemergence surface applied at a rate of 0.25-0.5 lbs a.i. per acre. If treatments are to be incorporated, incorporate to a depth of 1-3 inches. Do not apply more than once per season.

##### C. Environmental Fate Data

F6285 has been found very persistent in water ( $t_{1/2}$  = 143-375 days at pH 5, 7, and 9), and in aerobic soil ( $t_{1/2}$  = 114-122 days). According to the adsorption/desorption study, F6285 is very mobile with a range of  $K_d$  values of 0.2-0.8 (or  $K_{oc}$  = 26-77).

The major metabolite of F6285 is F6285-3-carboxylic acid which accounted for 24% of the recovered radioactivity for the carbonyl label and 12% of the recovered radioactivity for the phenyl label 90 days after application in an aerobic soil metabolism study.

**Discussions :**

The registrant, FMC Corporation, has submitted additional information to upgrade three studies [Hydrolysis (161-1); Aerobic Soil Metabolism (162-1); and Leaching-Adsorption/Desorption (163-1)]. These three studies were previously determined unacceptable (see EFGWB reviews of 91-0741 and 92-0100 for details). The registrant has also submitted waiver requests for the Confined Rotational Crop (165-1) and Bioaccumulation in Fish (165-4) data requirements (for the EUP only). The registrant's justifications for the above issues and EFGWB's correspondences are presented below:

**A. Hydrolysis (161-1)**

- a. In response to the comments raised by EFGWB on the difference in the mass spectra of the parent compound (F6285) in the 30-day sample and the reference standard, the registrant reanalyzed a sample extract which was retained after the completion of the study and submitted its mass spectrum.

**Comments by EFGWB:**

Since this new mass spectrum of the Day 30 pH 7 TRIS Replicate II sample (see attachment #1) correlates with F6285 standard at m/z 307 and 386, its identity has been confirmed by mass spectrometer.

- b. The registrant claimed that the fluctuations in the concentrations during the study was due to minor quenching or a binding to glass or other materials used during aliquoting.

**Comments by EFGWB:**

The justifications provided by the registrant are not sufficient to explain why the total radioactivities in the Day 14 and 21 samples were significantly higher than that in the Days 7 samples at all pH's. However, this deficiency is not significant enough to affect the understanding of the fate of F6285 in water. Therefore, the Hydrolysis (161-1) data requirement is fulfilled.

**B. Aerobic Soil Metabolism (162-1)**

The registrant claimed that: (1) two major degradation products (F6285 3-carboxylic acid, and F6285 3-hydroxymethyl) were adequately separated and identified by TLC/HPLC, and further confirmed by mass spectrometer; and (2) efforts were made to purify the samples by GC equipped with a capillary column prior to MS, but with no success.

The registrant is conducting a new study which will be carried out for a longer period of time (possibly up to one year) to define the fate of F6285 in the aerobic soil. In the new study, the registrant will attempt to develop GC/MS methods for spectral characterization of significant metabolites of F6285.

Comments by EFGWB:

1. Based on the additional information submitted by the registrant, EFGWB believes that the identity of two degradation products (F6285 3-carboxylic acid, and F6285 3-hydroxymethyl) have been confirmed. Reasons are given below:

\* F6285 3-carboxylic acid was identified by the following methods:

- a. using one-dimensional TLC;
- b. this chemical was treated with acid to form the desmethyl derivative which was further identified chromatographically;
- c. using mass spectrometry in either EI (Electron Impact) or CI (Chemical Ionization) mode. The EI mass spectra for the TLC-purified F6285 3-carboxylic acid gave a base peak at 293 and 295, and an M-45 (decarboxylated molecule) cluster of ions at 372, 374, and 374 (due to the presence of two chlorine atoms at the phenyl ring). The 373 ion peak for the protonated decarboxylated derivative (M-45) was also found in the CI mode. These spectral data are consistent with those of the reference standard.

\*\* F6285 3-hydroxymethyl was identified by the following methods:

- a. using TLC and HPLC;
- b. using mass spectrometry in either EI (Electron Impact) or CI (Chemical Ionization) mode. This chemical was isolated by TLC prior to MS analysis. The EI spectral data indicates the presence of a base peak at 323 (due to fragmentation) and a molecular ion cluster at 402, 404, and 406 (due to two chlorine atoms at the phenyl ring). Its chemical identify was further confirmed by the CI mode. In that mass spectrum, a

molecular ion cluster at 403, 405, and 407 for M+1 was obtained. These mass spectra are corresponding to those of the reference standard.

2. When available, the aerobic soil metabolism study, currently in progress, should be submitted for review. This new study would probably provide additional data on the formation and decline of degradation products of F6285 and their identification.
3. Since the submitted study has demonstrated the pattern of decline of the parent compound, and identified two major degradation products, the Aerobic Soil Metabolism (162-1) data requirement is fulfilled for the EUP.

C. Leaching and Adsorption/Desorption

The Leaching-Adsorption/Desorption (163-1) data requirement is fulfilled because the registrant has submitted the following data for the test soils.

Soil Type	CEC, meq/100 g	Field Moisture Cap., %
#45 Sandy Loam	7.6	15.77
#46 Silt Loam	14.5	32.5
#47 Silty Clay Loam	14.1	26.8
#49 Sand	0.6	1.37

D. Confined Rotational Crop

The registrant has request a waiver of the Confined Rotational Crop (165-1) data requirement for the EUP. They intend to amend the labels to show a rotational crop restriction indicating that the rotational crop must be destroyed.

Comments by EFGWB:

EFGWB concurs with this waiver request for the EUP.

E. Bioaccumulation in Fish

Based on the low octanol/water partition coefficients for F6285 ( $K_{ow}$  = 31, 10, and 0.3 at pH 5, 7, and 9 respectively), the registrant has requested a waiver of the Bioaccumulation in Fish (165-4) data requirement.

Comments by EFGWB:

According to the registrant, the  $K_{ow}$  data have been validated by the EPA Product Chemistry reviewer. EFGWB concurs with this waiver request for the SUP on condition that the PM can verify these  $K_{ow}$  values.

Substantive Review

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- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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DATA EVALUATION RECORD

STUDY 2

CHEM 129081

F6285

5162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41928203

Singer, S.S. and M.J. Schocken. 1991. Degradation studies: Aerobic soil metabolism of F6285, a new herbicide. Laboratory Project ID: 162E21RF1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME - 8

REVIEWED BY: L. Binari

TITLE: Staff Scientist

EDITED BY: C. Cooke  
W. Martin

TITLE: Staff Scientist  
Staff Scientist

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation  
Rockville, MD

TEL: 301-417-9800

APPROVED BY: Mah Shamim

TITLE: Chemist

ORG: EFGWB/EFED/OPP

TEL: 703-557-2025

SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study cannot be used to fulfill data requirements at this time.
2. F6285 degraded with half-lives of 114-122 days in sandy loam soil that was incubated in the dark at 24 C and 75-80% of 0.33 bar moisture. Nonvolatile degradates identified were F6285 3-carboxylic acid and F6285 3-hydroxymethyl; tentatively identified minor degradates included F6285 3-desmethyl, F6285 free amine, and F6285 3-aldehyde.
3. This study does not meet Subdivision N guidelines for the following reasons:

at final sampling interval (195-days posttreatment), the concentration of parent was still declining while that of the metabolites was increasing. According to the subdivision N guidelines, the study must be conducted for one year or until the pattern of decline of parent or pattern of formation and decline of all degradates in the soil are established;

major discrepancies in the mass spectra of standards and isolated samples (parent, metabolites) were not adequately addressed.

4. In order for this study to fulfill the aerobic soil metabolism data requirement, the registrant must provide additional information on the formation and decline of parent and metabolites beyond the 195-day sampling interval. The study should be conducted for a longer time period or up to a year if necessary.

The registrant must address the discrepancies in the mass spectra of standards and isolated samples (parent and metabolites); additional fragment ions that appear in the mass spectra of metabolites could be the result of impurities (isomers and other metabolites) that probably remained unresolved on TLC and HPLC and perhaps could be eliminated by use of GC/MS rather than solid probe.

#### METHODOLOGY:

Samples of sieved (2 mm) sandy loam soil (68% sand, 13% silt, 19% clay, 1.1% organic matter, pH 7.1, CEC 6.8 meq/100 g) were weighed (50 g) into biometer flasks and treated with either uniformly phenyl ring-labeled [ $^{14}$ C]F6285 or carbonyl-labeled [5- $^{14}$ C]F6285 (radiochemical purities >95%; specific activities 20.1 and 24.0 mCi/mMol, respectively; New England Nuclear) dissolved in ethanol, at a nominal concentration of 3.3 ppm. The soil samples were adjusted to 75-80% of 0.33 bar moisture and the side well of each biometer flask was filled with a 0.1 M potassium hydroxide trapping solution. The flasks were incubated in the dark at  $24 \pm 1$  C. Duplicate flasks of soil and the corresponding trapping solutions were sampled at 0, 7, 33, 61, 90, 141, and 195 days posttreatment.

The soil samples were extracted twice with acetonitrile:water (70:30, v:v) at "room temperature" using a magnetic stirrer followed by vacuum filtration and a 1-hour reflux in the acetonitrile:water solution. Extracts were filtered, combined, and concentrated by rotary evaporation (<35 C). The concentrated extracts were partitioned three times with ethyl acetate. Aliquots of the organic and aqueous phases were analyzed for radioactivity using LSC. Aqueous phases from the 33- to 195-day soil samples were acidified to pH 1, then repartitioned three times with ethyl acetate. All organic phases were combined, dried over anhydrous sodium sulfate, and concentrated by rotary evaporation (temperature not specified). The concentrated extracts were analyzed using one-dimensional TLC on

silica gel plates developed with methylene chloride:methanol:ammonium hydroxide (75:25:1, v:v:v or 85:15:1, v:v:v). Radioactive areas were detected using autoradiography; the radioactive areas were scraped from the plates, eluted with methanol and quantified by LSC. Unlabeled reference standards of F6285 and possible degradates were detected under UV light; it could not be determined if the reference standards were cochromatographed with the samples. Selected organic phases were also analyzed by reverse HPLC with UV (280 nm) detection using Zorbax ODS or Zorbax C-8 columns eluted with acetonitrile:water:acetic acid gradients. Identities of degradates were confirmed using electron impact MS and chemical ionization MS. The extracted soil was analyzed by LSC following combustion. The potassium hydroxide trapping solutions were analyzed for total radioactivity using LSC.

In order to characterize unextractable [ $^{14}\text{C}$ ]residues, the previously extracted 141-day soil samples treated with phenyl ring-labeled [ $^{14}\text{C}$ ]F6285 were further extracted with hexane and methylene chloride, then fractionated into humin, humic acid, and fulvic acid (Figure 4). Subsamples of the extracted soil were air-dried, refluxed with 0.25 N hydrochloric acid for 1 hour, then centrifuged. The supernatant was partitioned three times with ethyl acetate; the organic and aqueous phases were analyzed by LSC. The remaining soil pellet was stirred with 0.5 N sodium hydroxide for 24 hours and the extract was decanted. Soil solids (humin fraction) were air-dried and analyzed for radioactivity by LSC following combustion. The extract was analyzed for radioactivity by LSC, acidified to pH 1 with concentrated hydrochloric acid to precipitate the humic acid fraction, and centrifuged. The supernatant (fulvic acid fraction) was analyzed by LSC, and the precipitate (humic acid fraction) was redissolved in 0.5 N sodium hydroxide for LSC analysis.

Four additional flasks of soil were autoclaved on three consecutive days (121 C for 1 hour) prior to treatment with phenyl ring-labeled [ $^{14}\text{C}$ ]F6285 and incubated as described above. Duplicate flasks of the sterile soil were sampled at 67 and 170 days posttreatment and analyzed as previously described.

#### DATA SUMMARY:

Uniformly phenyl ring-labeled [ $^{14}\text{C}$ ]F6285 and carbonyl-labeled [ $^{14}\text{C}$ ]F6285 (radiochemical purities >95%), at 3.3 ppm, degraded with calculated half-lives of 122 and 114 days, respectively, in sandy loam soil that was incubated in the dark at  $24 \pm 1$  C and 75-80% of 0.33 bar moisture for up to 195 days. For both label positions, nonvolatile degradates included F6285 3-carboxylic acid and F6285 3-hydroxymethyl; three additional degradates, F6285 3-desmethyl, F6285 free amine, and F6285 3-aldehyde, were tentatively identified.

For both label positions, [ $^{14}\text{C}$ ]F6285 decreased from 94.4-97.2% of the recovered radioactivity at day 0 to 39.7-49.5% at 90 days and 28.9-

31.9% at 195 days (Tables 1 and 2). Five degradates were isolated from the soil:

F6285 3-carboxylic acid (metabolite #1),

at a maximum 11.8-23.9% of the recovered at 90 days;

F6285 3-hydroxymethyl (metabolite #2),

at a maximum 2.3% at 61 days for the carbonyl-label and 6.3% at 33 days for the phenyl ring-label;

F6285 3-desmethyl (metabolite #3),

at a maximum 2.0% at 195 days for the carbonyl-label and 2.7% at 7 days for the phenyl ring-label;

F6285 free amine (metabolite #4),

at a maximum 4.5-4.8% at 195 days; and

F6285 3-aldehyde (metabolite #5),

at a maximum 3.2% at 7 days for the carbonyl-label and 2.4% at 141 and 195 days for the phenyl ring-label.

At 195 days posttreatment, unextracted [<sup>14</sup>C]residues had increased to 39.6-42.6% of the recovered radioactivity and evolved <sup>14</sup>CO<sub>2</sub> totaled <5% of the recovered.

Analysis of the [<sup>14</sup>C]residues from the extracted 141-day soil samples treated with phenyl ring-labeled [<sup>14</sup>C]F6285 determined that 3.7% of the recovered radioactivity was associated with the humin fraction, 12.8% with the humic acid fraction, and 5.7% with the fulvic acid fraction (Table 5).

In sterilized sandy loam soil treated with phenyl ring-labeled [<sup>14</sup>C]F6285, F6285 comprised 92.1 and 89.5% of the recovered radioactivity at 67 and 170 days posttreatment, respectively (Table 4).

Material balances ranged from 86.1 to 105.3% of the applied radioactivity.

#### COMMENTS:

1. At 195 days posttreatment (final sampling interval), the concentrations of metabolite #3 (tentatively identified as F6285 3-desmethyl) in soil treated with carbonyl-labeled [<sup>14</sup>C]F6285 and metabolite #4 (tentatively identified as F6285 free amine) in soil treated with both labels were still increasing. Subdivision N

guidelines specify that the study must be conducted either until the pattern of degradation of the parent and the patterns of formation and decline of all degradates in the soil are established or for 1 year, whichever comes first. Additional information concerning the patterns of formation and decline of metabolites #3 and #4 beyond the 195-day sampling interval is required; the registrant should submit the results from the analysis of soil beyond the 195-day sampling period and up to a year if necessary.

2. EFGWB prefers that [ $^{14}\text{C}$ ]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory methods such as MS in addition to comparison with the  $R_f$  of reference standards.

In this study, the organic extracts were analyzed using one-dimensional TLC with one solvent system; it could not be determined which reference standards other than parent F6285 were cochromatographed with the samples. It was also reported that selected organic phases were analyzed using reverse HPLC; however, it was not specified which samples were analyzed by HPLC, no quantitative data were provided, and only one chromatogram tracing was provided (Appendix B10).

Mass Spectrometry was used to confirm the identities of isolated parent F6285, metabolite #1 (F6285 3-carboxylic acid), and metabolite #2 (F6285 3-hydroxymethyl). Metabolites #3, 4, and 5 were only tentatively identified as F6285 3-desmethyl, F6285 free amine, and F6285 3-aldehyde, respectively. Mass spectra of most of these metabolites seemed to have a high background level which could be due to the presence of impurities that probably remained unresolved by TLC and HPLC. Use of GC/MS instead of solid probe is highly recommended; however, if the mass spectrum of the GC trace still showed these additional fragment ions it would either mean that the isolated peak does not have the same identity as that of the standard or is a mixture of isomers or other metabolites that are not resolved by GC.

3. It was reported that the treated soils were aerobically incubated, but it was not specified how the biometer flasks were sealed after the soil was treated and the trapping solution was placed in the side arm. It was not specified if the moisture content of the soil samples was monitored or maintained during the study.
4. The description of additional extractions of the previously extracted 141-day phenyl ring-labeled [ $^{14}\text{C}$ ]F6285-treated soil samples provided in the methodology section of the study (V. TEST METHOD/C. Analysis of Bound Residues) was not consistent with the fractionation scheme provided in Figure 4 and the results provided in Table 5. Since the fractionation scheme provided in Figure 4 and the data in Table 5

appeared to coincide, the fractionation scheme in Figure 4 was summarized in this review.

5. Results were presented in terms of percent of recovered radioactivity. Results from TLC analysis of ethyl acetate extracts were normalized to 100%. Recoveries of radioactivity applied to the TLC plates were only reported for two replicate samples of 195-day carbonyl-labeled [<sup>14</sup>C]F6285-treated sandy loam soil and were approximately 101% of the applied; TLC plate recoveries were not reported for any other samples.
6. In an additional experiment, samples of silt loam and silty clay loam soil were treated with phenyl ring-labeled [<sup>14</sup>C]F6285 and incubated as described above; soil subsamples were collected at 77, 103, and 145 days posttreatment. At the first sampling interval (77 days posttreatment), F6285 comprised 66.6% and 73.6% of the recovered radioactivity in the silt loam and silty clay loam soils, respectively (Table 3). Results from these experiments were not reviewed; the first sampling interval occurred too late after treatment to confirm the application rate. The study authors did not explain the purpose of conducting these soil incubations with the limited number of sampling intervals. These experiments provide supplemental data and are not needed to fulfill the data requirements.
7. It was reported that bulk soil incubations were conducted to generate additional material for degradate identification. Samples of soil (50 g) were treated with phenyl ring-labeled [<sup>14</sup>C]F6285 and incubated as described above; samples were collected at 62, 74, 111, and 133 days posttreatment. Soil samples were extracted and the extracts were analyzed by preparative TLC or preparative HPLC. The soil used was not described (sandy loam, silt loam, or silty clay loam), and the preparative TLC and HPLC techniques were not described.

Substantive Review

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Pages 207 through 237 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
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DATA EVALUATION RECORD

STUDY

CHEM 129081

F6285

\$162-1

FORMULATION--00--ACTIVE INGREDIENT

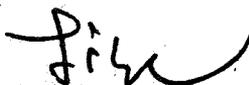
STUDY ID 42932117

Curry, S. 1993. Aerobic soil metabolism of F6285. Laboratory Project ID: 162E219E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 8

REVIEWED BY: Larry Liu  
TITLE: Environmental Scientist  
ORG: EFGWB/EFED/OPP  
TEL: 703-305-5372

SIGNATURE:



CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study can be used to fulfill data requirements.
2. F6285 degraded with half-lives of 535-555 days (approximately 1.5 years) in sandy loam soil and 534-541 days (approximately 1.5 years) in silty clay loam soil that were incubated in the dark at 25C and 75% of 0.33 bar moisture. Nonvolatile degradates identified were F6285 3-carboxylic acid, F6285 5'-desmethylsulfonyl, F6285 3-hydroxymethyl, and F6285 3-desmethyl. The major accumulating degradate was F6285 3-carboxylic acid which reached a maximum of 10.8% of the recovered residues at the end of the course of the study. F6285 5'-desmethylsulfonyl reached a maximum level of 5.9% of the recovered at 90 days. Less than 2% of the recovered was identified as F6285 3-hydroxymethyl or F6285 3-desmethyl. Material balance ranged from 93-107%.

The major metabolic pathway is the oxidation of the methyl group on the triazolinone ring of the parent compound to form F6285 3-hydroxymethyl. The hydroxymethyl group was further oxidized to carboxylic acid, forming F6285 3-carboxylic acid. Subsequently, the carboxylic acid on F6285 3-carboxylic acid was decarboxylated, resulting in F6285 3-desmethyl. The minor metabolic pathway is the cleavage of the sulfonamide group on F6285, forming F6285 5'-desmethylsulfonyl.

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3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the metabolism of phenyl ring- and carbonyl-labeled [ $^{14}\text{C}$ ]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide] under aerobic soil conditions.
4. No additional information on the metabolism of [ $^{14}\text{C}$ ]methanesulfonamide under aerobic soil conditions is required at this time.

#### METHODOLOGY:

Samples of sieved (2 mm) sandy loam soil (source: Wisconsin; 70% sand, 18% silt, 12% clay, 1.6% organic matter, pH 6.7, CEC 5.8 meq/100 g) were weighed (54 g) into biometer flasks (250 mL) and treated with either uniformly phenyl ring-labeled [ $^{14}\text{C}$ ]F6285 or carbonyl-labeled [5- $^{14}\text{C}$ ]F6285 (radiochemical purities >97%; specific activities 20.1 and 24.0 mCi/mMol, respectively; New England Nuclear) dissolved in ethanol, at a nominal concentration of 2.5 ppm. The soil was stored for 22 months at about 4C prior to use. The soil samples were adjusted to 75% of 0.33 bar moisture and the side well of each biometer flask was filled with a 0.1 M potassium hydroxide trapping solution. The flasks were incubated in the dark at 25C. Duplicate flasks of soil were sampled at 0, 7, 14, 21, 29, 60, 90, 120, 181, 272, and 368 days posttreatment. The trapping solutions were sampled and replaced with fresh solutions at 1, 5, 7, 14, 29, 60, 90, 120, 181, 272, and 368 days for sandy loam.

Samples of sieved (2 mm) silty clay loam soil (source: Illinois; 7.6% sand, 56% silt, 36% clay, 4.2% organic matter, pH 6.6, CEC 18.5 meq/100 g) were weighed (61 g) into biometer flasks (250 mL) and treated with either uniformly phenyl ring-labeled [ $^{14}\text{C}$ ]F6285 or carbonyl-labeled [5- $^{14}\text{C}$ ]F6285 (radiochemical purities >95%; specific activities 20.1 and 24.0 mCi/mMol, respectively; New England Nuclear) dissolved in ethanol, at a nominal concentration of 2.5 ppm. The soil was stored for 2 months at about 4C prior to use. The soil samples were adjusted to 75% of 0.33 bar moisture and the side well of each biometer flask was filled with a 0.1 M potassium hydroxide trapping solution. The flasks were incubated in the dark at 25 C. Duplicate flasks of soil were sampled at 0, 7, 14, 21, 30, 63, 90, 120, 181, 272, and 368 days posttreatment. The trapping solutions were sampled and replaced with fresh solution at 1, 2, 5, 7, 14, 30, 63, 90, 120, 181, 272, and 365 days for silty clay loam.

At each KOH change two specially-equipped flasks for each label were purged with  $\text{CO}_2$ -free air and the resulting air was passed sequentially through 0.1 N  $\text{H}_2\text{SO}_4$  solution and ethylene glycol. Aliquots of each trapping solution were collected in duplicate for radioassay.

The soil samples were extracted twice with acetonitrile:water (70:30, v:v) at "room temperature" using a Waring commercial blender followed

by vacuum filtration and a 1-hour reflux in the acetonitrile:water solution (Figure 1). Extracts were filtered, combined, and concentrated by rotary evaporation (<35C). The concentrated extracts were partitioned three times with ethyl acetate. Aliquots of the organic and aqueous phases were analyzed for radioactivity using LSC. Aqueous phases from soil samples were acidified to pH 1, then partitioned three times with ethyl acetate. All organic phases were combined, dried over anhydrous sodium sulfate, and concentrated by rotary evaporation. Each concentrated extract was analyzed using one-dimensional TLC on silica gel plates developed with methylene chloride:methanol:ammonium hydroxide (85:15:1, v:v:v). Selected samples were also analyzed using one-dimensional TLC on silica gel plates developed with methylene chloride:methanol:ammonium hydroxide (75:25:1, v:v:v) or methanol/0.5 N NaCl buffer (60:40). Radioactive areas were detected using autoradiography; the radioactive areas were scraped from the plates, eluted with methanol and quantified by LSC. Unlabeled reference standards of F6285 and possible degradates (Table 7) were included to confirm R<sub>f</sub> values and structural assignments. The standards were visualized under short UV light (254 nm). Selected TLC plates were also analyzed using a Bioscan imaging scanner.

Selected organic phases were also analyzed by HPLC with UV (214 or 230 nm) detection using Beckman Ultrasphere C-18 column eluted with acetonitrile:water:acetic acid gradients. Eluates from the column were collected in one minute intervals for radioassay. Retention times for standards of F6285 and its degradates were compared with unknowns (Table 7). Identities of degradates were further confirmed using a HP-5890 GC/Kratos Concept magnetic sector MS or a Varian model 3400 GC/Finnigan MAT TSQ-70B triple quadrupole MS system.

The extracted soil was analyzed by LSC following combustion. The potassium hydroxide trapping solutions were analyzed for total radioactivity using LSC. To verify the presence of CO<sub>2</sub> in trapping solutions, selected KOH samples were tested: (1) a one mL aliquot from each replicate was neutralized with HCl, saturated with non-radioactive CO<sub>2</sub>, and radioassayed; (2) another one mL aliquot was treated with a 0.4 N BaCl<sub>2</sub> and 0.5 N NH<sub>4</sub>Cl. The resulting precipitate and supernatant were separated by centrifugation and were radioassayed.

In order to characterize unextractable [<sup>14</sup>C]residues, the previously extracted 181-day soil samples treated with phenyl-labeled F6285 were further extracted with hexane and methylene chloride, then fractionated into humin, humic acid, and fulvic acid (Figure 4). Subsamples of the extracted soil were air-dried, refluxed with 0.25 N hydrochloric acid for 1 hour, then centrifuged. The supernatant was partitioned with ethyl acetate; the organic and aqueous phases were analyzed by LSC. The remaining soil pellet was stirred with 0.5 N sodium hydroxide for 24 hours and the extract was decanted. Soil solids (humin fraction) were air-dried and analyzed for radioactivity by LSC following combustion. The extract was analyzed for radioactivity by LSC, acidified to pH 1 with concentrated hydrochloric acid to precipitate the humic acid fraction, and

centrifuged. The supernatant (fulvic acid fraction) was analyzed by LSC, and the precipitate (humic acid fraction) was redissolved in 0.5 N sodium hydroxide for LSC analysis.

Extracts were stored at 4C for short periods during analysis and at -16C for longer term storage. Soil samples prior to extraction and soil-bound residues were stored at -21C. Soil samples were stored for no longer than a month prior to extraction.

#### DATA SUMMARY:

Uniformly phenyl ring-labeled [<sup>14</sup>C]F6285 and carbonyl-labeled [5-<sup>14</sup>C]F6285 (radiochemical purities >97%), at 2.5 ppm, degraded with calculated half-lives of 555 and 535 days, respectively, in sandy loam soil that was incubated in the dark at 25C and 75% of 0.33 bar moisture for up to 368 days. For both label positions, nonvolatile degradates included F6285 3-carboxylic acid, F6285 5'-desmethylsulfonyl, F6285 3-hydroxymethyl, and F6285 3-desmethyl.

For the degradation of carbonyl-labeled F6285 in the sandy loam soil, [<sup>14</sup>C]F6285 decreased from 99.1-99.3% of the recovered radioactivity at day 0 to 85.5-86.5% at 90 days, and to 75.7-75.7% at 368 days (Table 8). Four degradates were isolated from the soil: F6285 3-carboxylic acid, F6285 5'-desmethylsulfonyl, F6285 3-hydroxymethyl, and F6285 3-desmethyl. The major accumulating degradate was F6285 3-carboxylic acid which continuously increased with time and reached a maximum of 10.8-10.9% of the recovered residues at the end of the study. F6285 5'-desmethylsulfonyl reached a maximum level of 2.7-3.1% of the recovered at the end of the study. Less than 2% of the recovered was identified as F6285 3-hydroxymethyl or F6285 3-desmethyl. Bound residues increased throughout the course of the study to a maximum of 21.2% of the recovered (Table 3). On Days 368, approximately 1.1% of the recovered was evolved as CO<sub>2</sub>. Material balances ranged from 99.1-104.7%.

For the degradation of phenyl-labeled F6285 in the sandy loam soil, [<sup>14</sup>C]F6285 decreased from 95.8-95.9% of the recovered radioactivity at day 0 to 58.9-67.9% at 90 days, and to 52.6-53.5% at 368 days (Table 9). Four degradates were isolated from the soil: F6285 3-carboxylic acid, F6285 5'-desmethylsulfonyl, F6285 3-hydroxymethyl, and F6285 3-desmethyl. The major accumulating degradate was F6285 3-carboxylic acid which continuously increased with time and reached a maximum of 9.5-10.2% of the recovered residues at the end of the study. F6285 5'-desmethylsulfonyl reached a maximum level of 4.8-6.9% of the recovered at 90 days, then decreased slightly to 3.0-4.5% at the end of the study. Less than 2% of the recovered was identified as F6285 3-hydroxymethyl or F6285 3-desmethyl. Bound residues increased throughout the course of the study to a maximum of 24.8% of the recovered (Table 4). On Days 368, approximately 1.8% of the recovered was evolved as CO<sub>2</sub>. Material balances ranged from 97.3-102.7%.

Uniformly phenyl ring-labeled [ $^{14}\text{C}$ ]F6285 and carbonyl-labeled [ $5\text{-}^{14}\text{C}$ ]F6285 (radiochemical purities  $>97\%$ ), at 2.5 ppm, degraded with calculated half-lives of 534 and 541 days, respectively, in silty clay loam soil that was incubated in the dark at 25C and 75% of 0.33 bar moisture for up to 368 days. The most significant degradates identified in the aerobic soil metabolism study were F6285 3-carboxylic acid and F6285 5'-desmethylsulfonyl. Two relatively minor degradates identified were F6285 3-hydroxymethyl and F6285 3-desmethyl.

For the degradation of carbonyl-labeled F6285 in the silty clay loam soil, [ $^{14}\text{C}$ ]F6285 decreased from 96.4-96.8% of the recovered radioactivity at day 0 to 71.7-74.1% at 90 days, and to 57.6-60% at 368 days (Table 10). Four degradates were isolated from the soil: F6285 3-carboxylic acid, F6285 5'-desmethylsulfonyl, F6285 3-hydroxymethyl, and F6285 3-desmethyl. The major accumulating degradate was F6285 3-carboxylic acid which continuously increased with time and reached a maximum of 5.0-5.2% of the recovered residues at 90 days. F6285 5'-desmethylsulfonyl reached a maximum level of 3.7-4.1% of the recovered at the end of the study. Less than 2% of the recovered was identified as F6285 3-hydroxymethyl or F6285 3-desmethyl. Bound residues increased throughout the course of the study to a maximum of 22.0% of the recovered (Table 5). On Days 365, the evolved  $\text{CO}_2$  totaled 5.1% of the recovered. Material balances ranged from 95.8-104.7%.

For the degradation of phenyl-labeled F6285 in the silty clay loam soil, [ $^{14}\text{C}$ ]F6285 decreased from 94.3-95.6% of the recovered radioactivity at day 0 to 72-72.5% at 90 days, and to 56.9-57.6% at 368 days (Table 11). Four degradates were isolated from the soil: F6285 3-carboxylic acid, F6285 5'-desmethylsulfonyl, F6285 3-hydroxymethyl, and F6285 3-desmethyl. F6285 3-carboxylic acid and F6285 5'-desmethylsulfonyl were the major degradates whereas F6285 3-hydroxymethyl and F6285 3-desmethyl were the minor degradates. F6285 3-carboxylic acid increased continuously with time and reached a maximum of 5.3-5.4% of the recovered residues at 90 days, then decreased slightly to 4.5-5.0% at the end of the study. F6285 5'-desmethylsulfonyl reached a maximum level of 5.4-6.0% of the recovered at the end of the study. Less than 2% of the recovered was identified as F6285 3-hydroxymethyl or F6285 3-desmethyl. Bound residues increased throughout the course of the study to a maximum of 24.4% of the recovered (Table 6). On Days 365, the evolved  $\text{CO}_2$  totaled 2.2% of the recovered. Material balances ranged from 94.4-104.8%.

Analysis of the [ $^{14}\text{C}$ ]residues from the extracted 181-day soil samples treated with phenyl ring-labeled [ $^{14}\text{C}$ ]F6285 determined that 4.1% of the recovered radioactivity was associated with the humin fraction, 4.9% with the humic acid fraction, and 3.1% with the fulvic acid fraction.

No significant amounts of radioactivities were detected in the ethylene glycol or sulfuric acid traps for either label.

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The identity of F6285 and its degradates was confirmed by TLC (three solvent systems were used) and HPLC. Table 7 listed the  $R_f$  values for F6285 and its degradates for TLC and the retention times for HPLC.

F6285 and its degradates were further confirmed by GC/MS. Figure 23 showed the molecular ions and the fragment ions for F6285, F6285 5'-desmethylsulfonyl, and F6285 3-carboxylic acid. The molecular F6285 ion ( $M$ )<sup>+</sup> peak was observed at 386 while its <sup>37</sup>Cl-isotope ( $M+2$ )<sup>+</sup> peak was observed at 388. Four fragment ions were produced due to the loss of Cl from the parent (m/e 351), the loss of SO<sub>2</sub>CH<sub>3</sub> (m/e 307), the loss of both Cl and SO<sub>2</sub>CH<sub>3</sub> (m/e 273), and the cleavage and rearrangement (forming isocyanate; m/e 280). The F6285 5'-desmethylsulfonyl compound had molecular ions at m/e 308 and 310. The essential fragment ions included monophenylenediamine (m/e 139) and dichlorophenylenediamine (m/e 174). Although F6285 3-carboxylic acid has a molecular weight of 417, the molecular ion was not found. This was likely due to the rapid decarboxylation of F6285 3-carboxylic acid in the mass spectrometer. The spectrum showed the ( $M-44$ )<sup>+</sup> (loss of CO<sub>2</sub>) peaks of m/e 372 and 374. The major fragment ions were: m/e 337 (due to the loss of Cl), m/e 293 (due to the loss of SO<sub>2</sub>CH<sub>3</sub>), m/e 257 (due to the loss of both Cl and SO<sub>2</sub>CH<sub>3</sub>). The GC/MS EI (Electron Impact) spectrum of isolated F6285 and degradates and the spectrum of the standards are shown in Figures 15-20.

In both soils, the formation of F6285 3-carboxylic acid (the most abundant degradate) was faster in the initial 60 days than the remaining 300 days (Figures 8 and 13). More F6285 3-carboxylic acid was formed in the sandy loam soil (10.8% and 9.8% of the recovered residues in the carbonyl-labeled and the phenyl-labeled treatments, respectively) than the silty clay loam (4.5% and 4.8% of the recovered residues in the carbonyl-labeled and the phenyl-labeled treatments, respectively) (Tables 8-11).

The second most abundant degradate (F6285 5'-desmethylsulfonyl), accumulated steadily during the course of the study in both soils except for the sandy loam soil dosed with phenyl-labeled F6285 (the formation of the compound reached its maximum at 90 days) (Figures 8 and 13). Approximately 2.9-3.8% and 3.9-5.7% of the recovered residues were quantified as F6285 5'-desmethylsulfonyl at the end of the course of the study in the sandy loam and the sandy clay loam soils, respectively (Tables 8-11).

#### COMMENTS:

1. Based on the degradates detected in the aerobic soil metabolism study, the author proposed a metabolic pathway for F6285 in the sandy loam and the silty clay loam soils (Figure 24). The author concluded that the primary site for metabolic degradation of F6285 was the "exocyclic allylic methyl group" on the triazolinone ring. Oxidation of this methyl group on the molecule resulted in the formation of F6285 3-hydroxymethyl. The hydroxymethyl group was further oxidized to carboxylic acid, forming F6285 3-carboxylic acid. Subsequently,

the carboxylic acid on F6285 3-carboxylic acid was decarboxylated, resulting in F6285 3-desmethyl. A separate metabolic pathway was also reported: the sulfonamide group on F6285 was cleaved, forming F6285 5'-desmethylsulfonyl.

2. The author reported that the metabolism of F6285 in soil is similar to the metabolism in soybeans and animals. The major metabolic pathway in soybean and rat, goat, and hen is also the oxidation of the methyl group to form F6285 3-hydroxymethyl, followed by the oxidation to F6285 3-carboxylic acid and the decarboxylation to F6285 3-desmethylsulfonyl. The cleavage of the sulfonamide from the methanesulfonamide on the phenyl ring was also reported in the soybean metabolism study, the resulting metabolite was F6285 5'-desmethylsulfonyl.
3. The report stated that the high background noise observed in the spectra of the F6285 desmethylsulfonyl isolated by HPLC was probably caused by the small amount of sample injected into the system.
4. It was reported that the treated soils were aerobically incubated, but it was not specified how the biometer flasks were sealed after the soil was treated and the trapping solution was placed in the side arm.
5. The moisture content of the soil samples was monitored or maintained at 75% of field capacity during the study; however, no details were given.
6. The flasks were incubated in the dark at a constant temperature, ranging from 24.7-25.7C.
7. Results were presented in terms of percent of recovered radioactivity rather than percent of applied radioactivity, which is preferred. Results from TLC analysis of ethyl acetate extracts were normalized to 100%.
8. Results from the determination of the microbial populations and the aerobic conditions in the study soils indicated that the soils were vital and the aerobic conditions were maintained.

Substantive Review

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Pages 245 through 249 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
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5(4H)-one (desmethyl sulfonyl-F6285), was identified in the samples at  $\leq 2.9\%$  of the applied.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the metabolism of phenyl ring- and carbonyl-labeled [ $^{14}\text{C}$ ]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide] under anaerobic aquatic conditions.
4. No additional information on the metabolism of [ $^{14}\text{C}$ ]methanesulfonamide under anaerobic aquatic conditions is required at this time.

#### METHODOLOGY:

Sieved (2 mm) loamy sand sediment (82.5% sand, 7.5% silt, 10% clay, 0.7% organic matter, pH 8.0, CEC 12.6 meq/100 g) obtained from a pond in Macon County, Illinois, was weighed (50 g dry weight) into 500-mL Erlenmeyer flasks and flooded with pond water (250 mL; pH 8.5, hardness 323 mg/L as  $\text{CaCO}_3$ , conductivity 165.2  $\mu\text{mhos}$ ) that had been purged with nitrogen gas. The flasks were then sealed with a two-way (inlet and outlet) adaptor and flushed with nitrogen. The nitrogen was drawn through each sample flask and exhausted through a polyurethane plug and a 1 M NaOH trapping solution; the valve between the sample flask and the trapping solution was kept open throughout the pre-incubation period. The samples were incubated for approximately 60 days (light and temperature not specified) prior to treatment with [ $^{14}\text{C}$ ]methanesulfonamide; during the pre-incubation period, the samples were flushed with nitrogen again after approximately 30 days of incubation, and were flushed with nitrogen and treated with 2 mL of a 10% sucrose solution after approximately 50 days.

Following the pre-incubation period, the samples were treated at 2.4-2.6 ppm (based on a 300-g sample) with either phenyl ring-labeled [U- $^{14}\text{C}$ ]methanesulfonamide or carbonyl-labeled [ $^{14}\text{C}$ ]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285; radiochemical purities >98%, specific activities 17.2 and 19.0 mCi/mMol, respectively, FMC], dissolved in "degassed" ethanol. The flasks were resealed and incubated as described in the dark at 23-27 C. At 203 days posttreatment, the samples were amended with 2 mL of a 10% glucose solution plus 2 mL of a 0.25 g/L cysteine solution [page 93]. Duplicate flasks of flooded sediment were collected for analysis at 0, 1, 3, 7, 14, 30, 59, 120, 182, 287, and 365 days posttreatment. Prior to each sampling and at monthly intervals, the samples were flushed with nitrogen, and the polyurethane foam plugs and the NaOH trapping solutions were sampled and replaced.

Immediately after collection, the pH, "mixed" redox potential (Eh), and dissolved oxygen content (beginning at 59 days posttreatment) of each sample was measured. The water and sediment fractions were separated by filtration and extracted as outlined in Figure 2. The water was diluted with 6 N HCl and acetonitrile (5 and 25 mL, respectively), then extracted twice with methylene chloride. The methylene chloride extracts were combined, and aliquots of the combined extracts and extracted aqueous solutions were analyzed for total radioactivity using LSC. Aqueous extracts containing >1% of the applied radioactivity were concentrated by rotary evaporation (35 C), and the concentrate was stored frozen (-15 C) until further analysis. All methylene chloride extracts were concentrated by rotary evaporation, diluted with acetonitrile, and stored frozen until further analysis.

The entirety of each sediment sample was extracted twice with acetonitrile:1 N HCl (9:1, v:v); after each extraction, the extracts were removed from the sample by filtration. The extracts were combined and partitioned twice with methylene chloride. The methylene chloride extracts were combined, and aliquots of the combined extracts and extracted acetonitrile solutions were analyzed for total radioactivity using LSC. The acetonitrile solutions contained <1% of the applied radioactivity and were not further analyzed. The methylene chloride extracts were concentrated by rotary evaporation, diluted with acetonitrile, and stored frozen until further analysis. The extracted soil was then Soxhlet-extracted with acetonitrile:water (7:3, v:v) for 18 hours. Acetonitrile was removed from the extract using rotary evaporation; the remaining aqueous solution was partitioned twice with ethyl acetate. The ethyl acetate extracts were combined, and aliquots of the combined extracts and extracted aqueous solutions were analyzed for total radioactivity using LSC. The aqueous solutions contained <1% of the applied radioactivity and were not further analyzed. The ethyl acetate extracts were concentrated by rotary evaporation followed by a gentle stream of nitrogen. Portions of the Soxhlet-extracted sediments were air-dried and analyzed for total unextracted radioactivity using LSC following combustion.

Within 2 weeks of collection, aliquots of the concentrated aqueous and organic solutions that contained >1% of the applied radioactivity were analyzed by HPLC using a Spherisorb ODS-2 column eluted with acetonitrile:acidified (1% acetic acid) water (10:90 to 50:50, v:v); the column was equipped with UV (280 nm) and radioactive flow detection. [<sup>14</sup>C]Compounds were identified by comparison to the retention time of unlabeled reference standards of methanesulfonamide (F6285); N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-hydroxymethyl F6285); 1-(2,4-dichloro-5-[N-(methylsulfonyl)amino]phenyl)-4-difluoromethyl-4,5-dihydro-5-oxo-1H-1,2,4-triazole-3-carboxylic acid (3-carboxylic acid F6285); and 1-(2,4-dichloro-5-aminophenyl)-4-difluoromethyl-3-methyl-1H-1,2,4-triazol-5(4H)-one (desmethyl sulfonyl-F6285). Recoveries of

methanesulfonamide, 3-hydroxymethyl F6285, and 3-carboxylic acid F6285 from water fortified at 2 ppm averaged 86.1-102.2% of the applied, and from sediment fortified at 10 ppm averaged 89.8-93.8%. The limit of detection was reported to be 0.3% of the applied.

Also, aliquots of the ethyl acetate extracts from the sediment and selected extracts from the 287-day samples were analyzed using one-dimensional TLC on normal-phase silica gel plates developed in methylene chloride:methanol:ammonium hydroxide (85:15:1, v:v:v). [<sup>14</sup>C]Compounds on the plates were located using an imaging scanner, and were identified by comparison to unlabeled reference standards of methanesulfonamide, 3-hydroxymethyl F6285, 3-carboxylic acid F6285, and desmethyl sulfonyl-F6285, which had been cochromatographed with the samples and visualized using UV light (254 nm).

The foam plugs were Soxhlet-extracted with methanol for 4 hours, and the methanol extracts were analyzed for total radioactivity using LSC. Aliquots of the NaOH trapping solutions were analyzed for total radioactivity using LSC, and the presence of <sup>14</sup>CO<sub>2</sub> in the solutions was confirmed by precipitation with barium chloride.

In an attempt to identify "Compound 3" in the sample extracts, extracts containing this compound were sent to the laboratory of the registrant (FMC), where the extracts were analyzed by HPLC using an Ultrasphere ODS column eluted with 0.01 N acetic acid:acetonitrile (100:0 to 0:100 to 100:0, v:v). The retention time of "Compound 3" was compared to the retention times of unlabeled reference standards of N-(2,4-dichloro-5-[4-(difluoromethyl)4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-desmethyl-F6285) and N-[2,4-dichloro-5-(4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]methanesulfonamide (3-desmethyl-4-desdifluoromethyl-F6285).

#### DATA SUMMARY:

Phenyl ring-labeled and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285; radiochemical purities >98%], at 2.4-2.6 ppm (based on 300-g sample; 13x the maximum application rate), degraded very slowly (<10% degradation) in flooded loamy sand sediment (1:5, w:v) that was incubated in the dark under a static nitrogen atmosphere at 23-27 C for 12 months. One degrade.

1-(2,4-dichloro-5-aminophenyl)-4-difluoromethyl-3-methyl-1H-1,2,4-triazol-5(4H)-one (desmethyl sulfonyl-F6285),

was identified in both sets of samples at ≤2.9% of the applied (Tables V-VIII).

In the flooded sediment treated with phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide averaged 101.3% of

the applied immediately posttreatment, ranged from 96.2 to 102.9% between 1 and 182 days, and was 95.8% at 287 days and 92.4% at 365 days (Table V). Desmethyl sulfonyl-F6285 averaged a maximum 2.9% of the applied at 14 days posttreatment, and was 0.6% at 365 days (Table VII). At 12 months posttreatment, unextracted sediment [<sup>14</sup>C]residues were 1.3-2.5% of the applied and <sup>14</sup>CO<sub>2</sub> totaled 0.5-1.3%; no other [<sup>14</sup>C]volatiles were detected (Table III). The ratio of total [<sup>14</sup>C]residues in the water and sediment was approximately 11:1 immediately posttreatment and 5:1 at 12 months (reviewer-calculated from Tables III, V, and VII). Material balances ranged from 99.6 to 105.4% of the applied through 287 days posttreatment, and were 96.7-98.6% at 365 days (Table III).

In the flooded sediment treated with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, [<sup>14</sup>C]methanesulfonamide averaged 101.2% of the applied immediately posttreatment, ranged from 98.1 to 100.6% between 1 and 182 days, and was 91.7% at 287 days and 93.2% at 365 days (Table VI). Desmethyl sulfonyl-F6285 was not detected until 287 days posttreatment, and averaged a maximum 0.9% of the applied at 365 days (Table VIII). A second [<sup>14</sup>C]degradate, designated "Compound 3", averaged 3.4 and 3.0% at 287 and 365 days, respectively. At 12 months posttreatment, unextracted sediment [<sup>14</sup>C]residues were 0.4-2.1% of the applied and <sup>14</sup>CO<sub>2</sub> totaled ≤0.1%; no other [<sup>14</sup>C]volatiles were detected (Table IV). The ratio of total [<sup>14</sup>C]residues in the water and sediment was approximately 10:1 immediately posttreatment and 4:1 at 12 months (reviewer-calculated from Tables IV, VI, and VIII). Material balances ranged from 98.7 to 102.1% of the applied throughout the study (Table IV).

#### COMMENTS:

1. "Compound 3", isolated from the flooded sediment treated with the carbonyl label, was not identified; this [<sup>14</sup>C]degradate was isolated at up to a maximum average of 3.4% of the applied (0.09 ppm) from the static samples treated with the carbonyl label. The study author stated that Compound 3 did not cochromatograph with any HPLC reference standards, and could not be recovered in sufficient quantities to allow MS analysis [page 33]. It was also stated that Compound 3 had "the same retention time as that of a minor component present in the aqueous polar fraction of the crop rotation extracts [page 219]." The study author stated that "no further attempts were made to identify [Compound 3] due to the low and inconsistent levels detected". Although Compound 3 was isolated at 5.2 and 9.0% of the applied (0.13 and 0.23 ppm, respectively) from the two samples converted from static to flow-through conditions (refer to Comment 2), Compound 3 was not isolated from the samples maintained under flow-through conditions for the entire experiment (Table VIII).
2. To supplement data from the treated samples incubated under static conditions, additional flasks of flooded sediment (three per treatment label; sample codes '116, '216, and '316) were treated with

[<sup>14</sup>C]methanesulfonamide and incubated as described, except that the flow of nitrogen through the flasks was continuous. Volatiles were trapped as described; a single flask of flooded sediment from each treatment was collected at 189 days posttreatment, and duplicate flasks of each treatment were collected at 365 days. Also, static samples (two per treatment; sample codes '114 and '214) were converted from static to flow-through conditions at 295 or 296 days posttreatment; these samples were collected at 365 days posttreatment.

3. In the static samples during the study, the pH of the samples increased from a low of 5.8 at 7-14 days to 9.0-9.1 at 365 days, the dissolved oxygen content increased from  $\leq 0.2$  ppm at 59 days to 0.8-3.2 ppm at 365 days, and the redox potential of the water ranged from -236.3 to 252.4 mV [pages 91-92].
4. Although microorganism populations in the water layer were measured at 189 and 365 days posttreatment, no interpretations were provided.
5. The study author calculated half-lives of 3345 and 3250 days for the phenyl ring-labeled and carbonyl-labeled forms of [<sup>14</sup>C]methanesulfonamide, respectively (half-life is about 9 years). This information is of limited value because the data have been extrapolated far beyond the duration of the experiment.
6. The application rate in this study, 2.5 ppm, was 13x the reported maximum field application rate of 0.375 lb ai/A (based on a 6-inch soil depth).
7. The water solubility of methanesulfonamide was reported to be 780 ug/g at pH 7.0, and the vapor pressure was reported to be  $\leq 10^{-9}$  mmHg at 25 C.
8. According to the study author, portions of the Soxhlet-extracted sediments from the 4-, 9-, and 12-month sampling intervals were extracted with 0.5 N NaOH at room temperature for 12 hours, then centrifuged; the remaining sediment was again extracted with 0.5 N NaOH, this time for 1 hour. A portion of the combined NaOH extracts was acidified to pH 1 using concentrated HCl, and [<sup>14</sup>C]residues in the resulting solution and precipitate were classified as fulvic and humic acids, respectively. The extracted sediment was air-dried and analyzed using LSC following combustion; [<sup>14</sup>C]residues remaining in the sediment following the NaOH extraction were classified as humin. No data were reported for these analyses.

Self-Inspection Review

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
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Adsorption/Desorption (163-1)

Dykes, J. 1990. Soil adsorption/desorption with  $^{14}\text{C}$ -F6285. ABC Laboratory Project ID: ABC Final Report No. 383611; FMC Study No. 162E3289E1; FMC Report No. PC-0138. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by FMC Corporation, Princeton, NJ. (41911604)

This study was determined unacceptable in the 10/28/91 review because the complete characterization of the test soils was not carried out (such as data on cation exchange capacity and field moisture capacity was missing). In response, the registrant submitted additional data to upgrade this study. After reviewing the additional data, EFGWB concluded that this study is acceptable (see EFGWB review dated 12/21/92). The registrant did not explain why sodium azide was chosen to sterilize the soils. EFGWB has concerns about the use of chemicals for sterilization of soils. EFGWB believes that physical or chemical sterilization may subtly alter the soil chemistry, thus complicating the interpretation of the results obtained in the batch equilibrium study. However, since results from the column leaching study along with the batch equilibrium study have clearly demonstrated the potential for sulfentrazone to leach in the environment, no additional information on the mobility of sulfentrazone and its degradation products in soil is needed at this time. The Leaching-Adsorption/Desorption data requirement has been satisfied.

Results from this study are summarized below:

"Based on batch equilibrium studies, uniformly phenyl-labeled [ $^{14}\text{C}$ ]sulfentrazone at 0.1, 2, 5, 7, and 10 ppm, was determined to be very mobile in sodium azide-sterilized sandy loam, silt loam, silty clay loam, and sand soil:calcium chloride solution slurries (1:5) that were equilibrated for 24 hours at  $25 \pm 1$  C. Freundlich  $K_{ads}$  values were 0.2 for the sand soil, 0.6 for the sandy loam soil, 0.8 for the silt loam soil, and 0.8 for the silty clay loam soil; respective  $K_{oc}$  values were 77, 29, 26, and 40. Exponent (1/n) for  $K_{ads}$  was 1.03, indicating that the adsorption was a linear isotherm.  $K_{des}$  values were 1.23-1.44 for the four soils. Exponent (1/n) for  $K_{des}$  was 0.93, indicating that the adsorption was also a linear isotherm. Material balances ranged from 96.6 to 104.7% of the applied."



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

DP Barcode : 181232; 182374  
PC Code No. : 129081  
EFGWB No. : 92-1241/1342

*sulfentrazone  
methanesulfonamide*

MEMORANDUM

SUBJECT: Review of EUP for F6285 Herbicide

FROM: Larry Liu, Ph.D., Environmental Scientist  
Chemistry Review Section #2  
Environmental Fate and Groundwater Branch  
Environmental Fate and Effects Division (H7507C) *file 12-1-92*

TO: Joanne Miller, Product Manager (PM 23)  
Registration Division (H7505C)

THRU: Emil Regelman, Supervisory Chemist  
Chemistry Review Section #2  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C) *Q 12/15/92*

Henry M. Jacoby, Chief  
Environmental Fate and Ground Water Branch  
Environmental Fate and Effects Division (H7507C) *12/21/92*

Conclusion :

- (1). EFGWB concurs with the EUP for F6285 because:
  - (A). the following data requirements are fulfilled:

Hydrolysis (161-1)  
Aerobic Soil Metabolism (162-1)\*  
Leaching-Adsorption/Desorption (163-1)

\* since the submitted study has demonstrated the pattern of decline of the parent compound and identified two major degradation products, the Aerobic Soil Metabolism (162-1) data requirement is fulfilled for the EUP. When available, the aerobic soil metabolism study, currently in progress, should be submitted for review.

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(B). the following data requirements are waived:

Confined Rotational Crop (165-1)  
Bioaccumulation in Fish (165-4)

\* the proposed labels will be revised to exclude the use of rotational crops.

\*\* waived due to its low  $K_{ow}$ . According to the registrant, the  $K_{ow}$  data have been validated by EPA. EFGWB concurs with this waiver request for the EUP on condition that the PM can verify these  $K_{ow}$  values.

(2). Based on the preliminary data submitted to support a requested EUP, this chemical appears to display some of the characteristics for those chemicals known to leach to groundwater (such as high mobility and persistence). EFGWB recommends that the registration be advised to implement this EUP in such a way to minimize the potential impact on groundwater supplies from the experimental use.

#### Background :

##### A. Introduction

F6285 is a herbicide currently being developed by FMC Corporation for control of annual grass, and annual and perennial broadleaf weeds on soybeans.

##### B. Directions for Use

F6285 can be preplant-soil-incorporated, or preemergence surface applied at a rate of 0.25-0.5 lbs a.i. per acre. If treatments are to be incorporated, incorporate to a depth of 1-3 inches. Do not apply more than once per season.

##### C. Environmental Fate Data

F6285 has been found very persistent in water ( $t_{1/2}$  = 143-375 days at pH 5, 7, and 9), and in aerobic soil ( $t_{1/2}$  = 114-122 days). According to the adsorption/desorption study, F6285 is very mobile with a range of  $K_d$  values of 0.2-0.8 (or  $K_{oc}$  = 26-77).

The major metabolite of F6285 is F6285\_3-carboxylic acid which accounted for 24% of the recovered radioactivity for the carbonyl label and 12% of the recovered radioactivity for the phenyl label 90 days after application in an aerobic soil metabolism study.

discuss. 10/1/91

**Discussions :**

The registrant, FMC Corporation, has submitted additional information to upgrade three studies [Hydrolysis (161-1); Aerobic Soil Metabolism (162-1); and Leaching-Adsorption/Desorption (163-1)]. These three studies were previously determined unacceptable (see EFGWB reviews of 91-0741 and 92-0100 for details). The registrant has also submitted waiver requests for the Confined Rotational Crop (165-1) and Bioaccumulation-in Fish (165-4) data requirements (for the EUP only). The registrant's justifications for the above issues and EFGWB's correspondences are presented below:

**A. Hydrolysis (161-1)**

- a. In response to the comments raised by EFGWB on the difference in the mass spectra of the parent compound (F6285) in the 30-day sample and the reference standard, the registrant reanalyzed a sample extract which was retained after the completion of the study and submitted its mass spectrum.

**Comments by EFGWB:**

Since this new mass spectrum of the Day 30 pH 7 TRIS Replicate II sample (see attachment #1) correlates with F6285 standard at m/z 307 and 386, its identity has been confirmed by mass spectrometer.

- b. The registrant claimed that the fluctuations in the concentrations during the study was due to minor quenching or a binding to glass or other materials used during aliquoting.

**Comments by EFGWB:**

The justifications provided by the registrant are not sufficient to explain why the total radioactivities in the Day 14 and 21 samples were significantly higher than that in the Days 7 samples at all pH's. However, this deficiency is not significant enough to affect the understanding of the fate of F6285 in water. Therefore, the Hydrolysis (161-1) data requirement is fulfilled.

**B. Aerobic Soil Metabolism (162-1)**

The registrant claimed that: (1) two major degradation products (F6285 3-carboxylic acid, and F6285 3-hydroxymethyl) were adequately separated and identified by TLC/HPLC, and further confirmed by mass spectrometer; and (2) efforts were made to purify the samples by GC equipped with a capillary column prior to MS, but with no success.

The registrant is conducting a new study which will be carried out for a longer period of time (possibly up to one year) to define the fate of F6285 in the aerobic soil. In the new study, the registrant will attempt to develop GC/MS methods for spectral characterization of significant metabolites of F6285.

Comments by EFGWB:

1. Based on the additional information submitted by the registrant, EFGWB believes that the identity of two degradation products (F6285 3-carboxylic acid, and F6285 3-hydroxymethyl) have been confirmed. Reasons are given below:

\* F6285 3-carboxylic acid was identified by the following methods:

- a. using one-dimensional TLC;
- b. this chemical was treated with acid to form the desmethyl derivative which was further identified chromatographically;
- c. using mass spectrometry in either EI (Electron Impact) or CI (Chemical Ionization) mode. The EI mass spectra for the TLC-purified F6285 3-carboxylic acid gave a base peak at 293 and 295, and an M-45 (decarboxylated molecule) cluster of ions at 372, 374, and 374 (due to the presence of two chlorine atoms at the phenyl ring). The 373 ion peak for the protonated decarboxylated derivative (M-45) was also found in the CI mode. These spectral data are consistent with those of the reference standard.

\*\* F6285 3-hydroxymethyl was identified by the following methods:

- a. using TLC and HPLC;
- b. using mass spectrometry in either EI (Electron Impact) or CI (Chemical Ionization) mode. This chemical was isolated by TLC prior to MS analysis. The EI spectral data indicates the presence of a base peak at 323 (due to fragmentation) and a molecular ion cluster at 402, 404, and 406 (due to two chlorine atoms at the phenyl ring). Its chemical identity was further confirmed by the CI mode. In that mass spectrum, a

molecular ion cluster at 403, 405, and 407 for M+1 was obtained. These mass spectra are corresponding to those of the reference standard.

2. When available, the aerobic soil metabolism study, currently in progress, should be submitted for review. This new study would probably provide additional data on the formation and decline of degradation products of F6285 and their identification.
3. Since the submitted study has demonstrated the pattern of decline of the parent compound, and identified two major degradation products, the Aerobic Soil Metabolism (162-1) data requirement is fulfilled for the EUP.

C. Leaching and Adsorption/Desorption

The Leaching-Adsorption/Desorption (163-1) data requirement is fulfilled because the registrant has submitted the following data for the test soils.

Soil Type	CEC, meq/100 g	Field Moisture Cap., %
#45 Sandy Loam	7.6	15.77
#46 Silt Loam	14.5	32.5
#47 Silty Clay Loam	14.1	26.8
#49 Sand	0.6	1.37

D. Confined Rotational Crop

The registrant has request a waiver of the Confined Rotational Crop (165-1) data requirement for the EUP. They intend to amend the labels to show a rotational crop restriction indicating that the rotational crop must be destroyed.

Comments by EFGWB:

EFGWB concurs with this waiver request for the EUP.

E. Bioaccumulation in Fish

Based on the low octanol/water partition coefficients for F6285 ( $K_{ow}$  = 31, 10, and 0.3 at pH 5, 7, and 9 respectively), the registrant has requested a waiver of the Bioaccumulation in Fish (165-4) data requirement.

Comments by EFGWB:

According to the registrant, the  $K_{ow}$  data have been validated by the EPA Product Chemistry reviewer. EFGWB concurs with this waiver request for the EUP on condition that the PM can verify these  $K_{ow}$  values.

Supplemental Review

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
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  - The document is not responsive to the request.
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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DATA EVALUATION RECORD

STUDY 3

CHEM 129081

F6285

§163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41911604

Dykes, J. 1990. Soil adsorption/desorption with <sup>14</sup>C-F6285. ABC Laboratory Project ID: ABC Final Report No. 383611; FMC Study No. 162E3289E1; FMC Report No. PC-0138. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 4

REVIEWED BY: L. Binari

TITLE: Staff Scientist

EDITED BY: C. Cooke  
W. Martin

TITLE: Staff Scientist  
Staff Scientist

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation  
Rockville, MD

TEL: 301-417-9800

APPROVED BY: M. Shamim

TITLE: Chemist

ORG: EFGWB/EFED/OPP

TEL: 703-557-2025

SIGNATURE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study cannot be used to fulfill data requirements at this time.
2. F6285 is very mobile in sodium azide-sterilized sandy loam, silt loam, silty clay loam, and sand soils. Adsorption increased with increasing soil organic matter content and clay content.
3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reason:

complete characterization of the test soils was not carried out; data on cation exchange capacity (CEC) and field moisture capacity was missing.

4. In order for this study to fulfill the data requirements for mobility of unaged F6285 in soil, the registrant must completely characterize the soils with information on field moisture capacity and cation exchange capacity.

#### METHODOLOGY:

Sandy loam, silt loam, silty clay loam, and sand soils (Table I) were air-dried, sieved (2 mm), and sterilized with the addition of 1% sodium azide (w:w). Filter-sterilized (0.22  $\mu$ ) deionized water was used to prepare the 0.01 M calcium chloride solution. Based on preliminary experiments to define test parameters, an equilibration time of 24 hours and a 1:5 soil:solution ratio were selected for the definitive experiment.

For the adsorption studies, 1 g samples of soil and 5 mL of a 0.01 M calcium chloride solution containing 0.1, 2, 5, 7, or 10 ppm of uniformly phenyl-labeled [ $^{14}$ C]F6285 (radiochemical purity 100%, specific activity 20.1 mCi/mMol, FMC) were transferred to sterilized (autoclaved) culture tubes. The tubes were sealed with Teflon-lined caps; wrapped in foil, and the soil:solutions slurries were shaken in the dark at  $25 \pm 1$  C for 24 hours. After shaking, the slurries were centrifuged and the supernatant was decanted. Aliquots of the supernatants were analyzed using LSC.

Desorption of F6285 was determined by replacing the supernatant removed from the soil after adsorption with an equal volume of pesticide-free calcium chloride solution. The soil:solution slurries were shaken in darkness at  $25 \pm 1$  C for 24 hours. After shaking, the slurries were centrifuged and supernatants were analyzed by LSC. The [ $^{14}$ C]F6285 remaining adsorbed to the soil after desorption was determined by LSC following combustion.

#### DATA SUMMARY:

Based on batch equilibrium studies, uniformly phenyl-labeled [ $^{14}$ C]F6285 (radiochemical purity 100%), at 0.1, 2, 5, 7, and 10 ppm, was determined to be very mobile in sodium azide-sterilized sandy loam, silt loam, silty clay loam, and sand soil:calcium chloride solution slurries (1:5) that were equilibrated for 24 hours at  $25 \pm 1$  C. Freundlich  $K_{ads}$  values were 0.153 for the sand soil, 0.551 for the sandy loam soil, 0.767 for the silt loam soil, and 0.773 for the silty clay loam soil; respective  $K_{oc}$  values were 77, 29, 26, and 40 (Table XVI). Adsorption increased with increasing soil organic matter content and clay content.  $K_{des}$  values were 1.23-1.44 for the

four soils. Material balances ranged from 96.6 to 104.7% of the applied radioactivity (Tables XVII-XX).

COMMENTS:

1. The test soils were not completely characterized; data on cation exchange capacity (CEC) and field moisture capacity was not provided for the soils.
2. The soils were sterilized by the addition of 1% sodium azide (w:w). It is suspected that sterilization of soils by sodium azide alters the soil in such a way that it changes the mobility of pesticides in soil. The registrants should address this issue.
3. It was reported that the test substance was determined to be stable under the test conditions used for this study, but quantitative data were not provided for review.
4. The study author reported that a 20-80% adsorption range was not achieved with an initial 1:5 soil:solution ratio; however, the ratio was not changed for the definitive study because the correlation for the  $K_d$  determination was high ( $r^2 > 0.98$ ). It was also determined that adsorption of the test substance to glass surfaces was insignificant after 24 hours. Quantitative data from the preliminary experiments performed to determine the equilibration time, soil:solution ratio, and if the test substance adsorbed to glassware were not provided for review.

Substantive Review

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  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
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  - The product confidential statement of formula.
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1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285] and incubated in the dark at 25 C and 75% of field moisture capacity for 30 days. In the soil columns, 25.8-31.3% of the radioactivity applied to the column remained in the aged soil layer, 2.5-6.5% was in each 2-inch column segment, and 37.6-44.4% was in the column leachates. Two degradates were identified in the soil and leachate: N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-hydroxymethyl F6285); and N-(2,4-dichloro-5-[N-(methylsulfonyl)amino]phenyl)-4-difluoromethyl-4,5-dihydro-5-oxo-1H-1,2,4-triazol-3-carboxylic acid (3-carboxylic acid F6285). Both degradation products (3-hydroxymethyl F6285 and 3-carboxylic acid F6285) are very mobile. It appears that 3-hydroxymethyl F6285 is more mobile than 3-carboxylic acid F6285. Nearly 72% of the applied 3-hydroxymethyl F6285 were detected in the leachate at the end of the study whereas 35% of the applied 3-carboxylic acid were found.

3. This study is acceptable and partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility (column leaching) of aged (30 days) phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide] residues in sandy loam soil.
4. No additional information of the mobility of aged [<sup>14</sup>C]methanesulfonamide residues in sandy loam soil is required at this time. For complete fulfillment of the data requirement, acceptable data on the mobility of unaged methanesulfonamide is required.

#### METHODOLOGY:

Moist sandy loam soil (72.6% sand, 19.0% silt, 8.4% clay, 1.5% organic matter, pH 6.9, CEC 4.72 meq/100 g) was weighed (50 g dry weight) in 250-mL Erlenmeyer flasks and treated at approximately 5 ppm (250 ug/flask) with either phenyl ring-labeled [U-<sup>14</sup>C]methanesulfonamide or carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; radiochemical purities >98.1%, specific activity 17.2 and 19.0 mCi/mMol, respectively, Du Pont], dissolved in acetonitrile. The treated soil was agitated "gently" by hand, then moistened to 75% of 0.33 bar. The flasks for each label were connected in series to a volatile trapping system; humidified, carbon dioxide-free air was continuously drawn (flow rate unspecified) through the sample flasks, then exhausted sequentially through ethylene glycol (two tubes) and 1 N NaOH (three tubes) trapping solutions. The samples were incubated in the dark at 25 ± 1 C. Duplicate flasks of soil for each label position were removed for analysis at 0, 7, 14, 21, and 30 days posttreatment; the trapping solutions were collected for analysis and replaced at each sampling interval. The soils were "periodically" remoistened to 75% of 0.33

bar. At 30 days posttreatment, the soil in the four remaining flasks for each label was combined, air-dried, and homogenized. Portions of the combined soil were analyzed for total radioactivity using LSC following combustion; additional portions were extracted and analyzed by HPLC and TLC as described below. The remainder of soil was used in the column leaching experiment.

Air-dried sandy loam soil was poured into Lucite columns (18-inch length; 3-inch id) to a depth of 12 inches; two columns were prepared for each label position. The author did not explain what "Lucite" means; based on the information in the report, the column appears to be made of plastics. The columns were wetted with approximately "one pore volume" (571-598 mL) of a 0.01 M calcium chloride solution. Approximately 50 g of the aged soil, equivalent to approximately 250 ug [<sup>14</sup>C]methanesulfonamide residues, were transferred to the top of each column. A layer of glass wool was placed over the aged soil, then each column was leached with 2334-2374 mL (approximately 20 inches) of a 0.01 M calcium chloride solution; column leachates were collected continuously. Leaching was completed in approximately 2 days. Following leaching, the soil columns were divided into 2-inch segments and the soil was air-dried; portions of each soil segment were analyzed for total radioactivity using LSC following combustion.

Aliquots of the leachates were analyzed for total radioactivity using LSC. The initial 25% of the leachates collected, which contained <1% of the applied radioactivity, were not analyzed further; the remainder was partitioned twice against ethyl acetate. The extracted aqueous fraction was acidified, then again partitioned twice against ethyl acetate. The four ethyl acetate fractions for each sample were combined and dried under vacuum; the resulting residues were dissolved in acetonitrile. Aliquots were analyzed by HPLC using a Zorbax ODS column eluted with acidified (0.4% acetic acid) water:acetonitrile (75:25 to 40:60 to 75:25, v:v); the column was equipped with UV (254 nm) and radioactive flow detectors, and eluate fractions were collected. Additional aliquots of the leachate extracts were analyzed by one-dimensional TLC on silica gel plates developed in methylene chloride:methanol:ammonium hydroxide (75:25:1, v:v:v). Radioactive areas on the plates were located and quantified using a linear scanner; unlabeled standards of methanesulfonamide, 3-hydroxymethyl F6285, and 3-carboxylic acid F6285 were cochromatographed with the extracts and visualized under UV (254 nm) light.

Portions of the soil collected during aerobic aging, portions of the aged soil collected prior to leaching, and portions of the soil from each segment of one column for each label position following leaching were extracted twice with acetonitrile:water (7:3, v:v) for 30 minutes per extraction using a wrist-action shaker; after each extraction, the samples were centrifuged and the extracts were decanted and filtered. The extracted soil was then refluxed with acetonitrile:water (7:3, v:v) for 1 hour; after cooling, the samples were filtered. Aliquots of the soil extracts and refluxates were

analyzed for total radioactivity using LSC. The extracts and refluxates were combined, and aliquots of the combined extracts from the 7- through 30-day sampling intervals were concentrated under vacuum to remove the acetonitrile; the day 0 sample was not concentrated before additional processing. Aliquots of the concentrates (and day 0 extracts) were partitioned twice against ethyl acetate. The extracted aqueous fraction was acidified, then again partitioned twice against ethyl acetate. The four ethyl acetate extracts from each sample were combined, dried over anhydrous sodium sulfate, filtered, and dried under vacuum. The resulting residues were dissolved in acetonitrile, and aliquots were analyzed by LSC, HPLC, and TLC as previously described. The extracted soil was air-dried, and subsamples were analyzed for unextracted radioactivity using LSC following combustion.

Aliquots of the ethylene glycol and NaOH trapping solutions were analyzed using LSC.

#### DATA SUMMARY:

[<sup>14</sup>C]Methanesulfonamide residues were mobile in columns (12-inch length) of sandy loam soil that were treated at approximately 250 ug with aged (30 days) [<sup>14</sup>C]methanesulfonamide residues and leached with 2334-2374 mL (approximately 20 inches) of a 0.01 M calcium chloride solution. Prior to leaching, the columns had been topped with approximately 50 g of sandy loam soil that had been treated at 4.82 ppm with phenyl ring-labeled [U-<sup>14</sup>C]methanesulfonamide or at 4.97 ppm with carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; radiochemical purities ≥98.1%] and incubated in the dark at 25 ± 1 C and 75% of field moisture capacity for 30 days. In the soil columns, 25.8-31.3% of the radioactivity applied to the column remained in the aged soil layer, and 2.5-6.5% was in each 2-inch column segment; the column leachates contained 37.6-44.4% (Tables IX, X, XI, and XII). The material balances following leaching were 95.3-99.9% of the radioactivity applied to the column (Table XIII). Two degradates were identified in the soil and leachate:

N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-hydroxymethyl F6285; HOCH<sub>2</sub>-F6285); and

N-(2,4-dichloro-5-[N-(methylsulfonyl)amino]phenyl)-4-difluoromethyl-4,5-dihydro-5-oxo-1H-1,2,4-triazol-3-carboxylic acid (3-carboxylic acid F6285; HOOC-F6285).

In both the columns treated with phenyl ring- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, parent methanesulfonamide was 14.9-17.9% of the radioactivity applied to the column in the aged soil segment,

2.1-2.9% in the 0- to 2-inch segment, increasing to 4.4-5.2% in the 10- to 12-inch segment, and 34.4-39.3% in the leachate (Tables XV and XVII). 3-Hydroxymethyl-F6285 was 0.5-0.6% of the radioactivity applied to the column in the aged soil segment, 0.1-0.2% in the remaining soil segments, and 2.2-3.2% in the leachate. 3-Carboxylic acid F6285 was  $\leq$ 0.5% of the radioactivity applied to the column in the soil segments, and 0.3-0.5% in the leachate. The material balance after leaching was 96.3-99.9% of the radioactivity applied to the column.

Prior to leaching in the aged (30 days) soil treated with phenyl ring- or carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, methanesulfonamide was 78.6-85.4% of the applied radioactivity, 3-hydroxymethyl-F6285 was 2.4-5.5%, and 3-carboxylic acid F6285 was 1.1-1.2%; volatile radioactivity totalled <0.1% of the applied; and unextracted radioactivity was 5.6-6.3% (Tables II, III, VI, and VII). At 30 days, material balances were 90.6-92.2% of the applied for the soil treated with the phenyl ring label, and 96.7-97.6% for the soil treated with the carbonyl label.

Both degradation products (3-hydroxymethyl F6285 and 3-carboxylic acid F6285) are very mobile. Based on the information in Tables VI, VII, XV, and XVII, the reviewer summarized the data to depict the mobility of the degradates detected in the soil at the end of 30-day incubation under aerobic conditions and in the leachate at the end of the column leaching study. The following table shows that 3-hydroxymethyl F6285 is more mobile than 3-carboxylic acid F6285. Nearly 72% (the average recovery of phenyl-labeled and carbonyl-labeled F6285 tests) of the applied 3-hydroxymethyl F6285 were detected in the leachate whereas 35% of the applied 3-carboxylic acid were found in the leachate at the end of the column leaching study.

	% of applied		
	Residues in soil	Residues in leachate	Recovery %
<u>Phenyl label</u>			
3-hydroxymethyl F6285	2.5	3.2	>100
3-carboxylic acid F6285	1.1	0.5	45
<u>Carbonyl label</u>			
3-hydroxymethyl F6285	4.9	1.2	45
3-carboxylic acid F6285	2.2	0.3	25

COMMENTS:

1. The study authors stated that the soil was not sieved because it was free of plant remains and "coarse materials."
2. The solubility of methanesulfonamide in water (pH 7) is 780 ppm. The solubilities of 3-hydroxymethyl F6285 and 3-carboxylic acid F6285 were not reported.
3. The study authors stated that aliquots of all intermediate extracts generated in the soil extraction procedure were analyzed by LSC. The results of the final acetonitrile extract were used in the determination of the material balance [page 21].
4. Based on the total radioactivities detected in the soil and in the leachate at the end of the column leaching study, the average  $K_d$  was reported to be 1.2 for phenyl-labeled F6285 and 1.5 for carbonyl-labeled F6285.

Substantive Review

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posttreatment, 134-184 ppb at 61 through 186 days, 105 ppb at 305 days, and 68-82 ppb at 362 through 531 days. Methanesulfonamide was detected in the 6- to 12-inch soil depth at an average 13 ppb at 31 days posttreatment, 4-9 ppb at 61 through 451 days, and 20 ppb at 531 days; at all sampling intervals, methanesulfonamide averaged  $\leq 4$  ppb in soil collected from depths below 12 inches. The degradate N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamido-3-carboxylic acid (3-carboxylic acid F6285), which was converted to N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-desmethyl F6285) prior to analysis, averaged  $\leq 11$  ppb in soil from the 0- to 6-inch depth and  $\leq 2$  ppb in soil collected from depths below 6 inches at all sampling intervals.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the field dissipation of sulfentrazone 4F.
4. No additional information on the field dissipation of sulfentrazone 4F is required at this time.

#### METHODOLOGY:

Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 4F; 4 lb ai/gallon flowable concentrate, FMC] was broadcast once, at 0.5 lb ai/A, onto an unvegetated plot (100 x 60 feet) of clay loam soil (0- to 12-inch depth: 3.4% organic matter, pH 6.1; soil not further characterized) that was located in Champaign, Illinois. The application was made on May 29, 1992, using a tractor-mounted field sprayer; the herbicide was incorporated (depth not reported) into the soil immediately after treatment. An untreated bareground plot (100 x 60 feet) located "near" the treated plot was used as a control. During the study, the site was kept free of "dense weed growth", and was not irrigated.

For sampling purposes, the treated and control plots were divided into five subplots, and each subplot was divided into 1-m<sup>2</sup> sub-subplots. Fifteen soil samples were collected from the treated plot prior to and immediately after application, and at 1, 3, 7, 14, 21, 31, 61, 89, 119, 186, 305, 362, 451, and 531 days posttreatment. Samples were collected from the 0- to 6-inch depth using a probe (2.25-inch diameter). Samples were then collected from the entire 6- to 36-inch depth through the existing sample hole using a probe (1.5-inch diameter) equipped with an acetate liner, and the cores were divided into 6-inch segments. The soil cores collected prior to treatment were combined according to sample depth to create a single composite sample. The cores from the treated plot, except for the 0- to 6-inch segment of the 1-day posttreatment samples, were combined according to sampling interval and sample depth to create three composite samples (five cores per composite sample). For the control

plot, fifteen soil samples were collected prior to and immediately after application, and at 7, 31, 89, 186, 305, 362, and 531 days posttreatment as described; the cores were divided into 6-inch segments, then combined to create a single composite sample. Samples collected on and prior to 186 days posttreatment were frozen within 8 hours of collection, and were shipped frozen to the analytical laboratory; later samples were shipped overnight at "ambient" temperatures to the analytical laboratory. All samples were stored frozen (-18 C) at the analytical laboratory for 1 to 9 months prior to extraction.

Subsamples of each composite sample were extracted with acetonitrile:0.25 N HCl (70:30, v:v) by refluxing for 1 hour; during the reflux procedure, the 3-carboxylic acid F6285 was decarboxylated into 3-desmethyl F6285. The mixture was cooled, and an aliquot of the extract was concentrated under nitrogen. The concentrate was diluted with 5% NaCl, then partitioned three times with hexane:ethyl acetate (80:20, v:v). The hexane:ethyl acetate fractions were combined and evaporated to dryness; the resulting residues were dissolved in hexane:ethyl acetate (80:20, v:v) and filtered through a silica gel solid-phase extraction cartridge. Residues were eluted from the cartridge with hexane:ethyl acetate (70:30, v:v), and the eluate was evaporated to dryness. The dried residues were dissolved in acetonitrile, and the acetonitrile solution was analyzed for methanesulfonamide and 3-desmethyl F6285 using GC with electron-capture detection. The limit of detection was 1 ppb, and the limit of quantitation was 5 ppb. Recovery of methanesulfonamide and 3-carboxylic acid F6285 from soil fortified with both compounds at 5-550 ppb ranged from 101 to 120% of the applied (average  $110 \pm 6\%$ ) for methanesulfonamide, and from 70 to 106% (average  $87 \pm 10\%$ ) for 3-carboxylic acid F6285.

#### DATA SUMMARY:

Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 4F; 4 lb ai/gallon flowable concentrate], at 0.5 lb ai/A, dissipated with an observed half-life of approximately 1 year in the 0- to 6-inch depth of a bareground plot of clay loam soil located in Champaign, Illinois. The herbicide was applied to the soil in late May 1992, and was incorporated into the soil immediately after application. In the 0- to 6-inch soil depth, methanesulfonamide averaged 154-279 ppb through 31 days posttreatment (raw data 55.4-506.0 ppb); 134-184 ppb at 61 through 186 days (83.3-273.7 ppb), 105 ppb at 305 days (100.2-107.7 ppb), and 68-82 ppb at 362 through 531 days (48.5-95.8 ppb; Tables 1a and 10-24). Methanesulfonamide was detected in the 6- to 12-inch soil depth at an average 13 ppb at 31 days posttreatment, 4-9 ppb at 61 through 451 days, and 20 ppb at 531 days; methanesulfonamide averaged  $\leq 4$  ppb in soil collected from the 12- to 18-inch depth, and  $\leq 2$  ppb in soil collected from depths below 18 inches (Table 1a). The degradate

N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamido-3-carboxylic acid (3-carboxylic acid F6285).

which was converted to N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-desmethyl F6285) prior to analysis, averaged a maximum 11 ppb at 14 and 21 days posttreatment (raw data 5.7-14.4 ppb), and  $\leq 9$  ppb at all other sampling intervals (Tables 1b, 14, and 15) in the 0- to 6-inch depth. 3-Carboxylic acid F6285 averaged  $\leq 2$  ppb in soil collected from the 6- to 12- inch depth, and was not detected ( $< 1$  ppb) in soil from collected from depths below 12 inches (Table 1b).

During the study, air temperatures ranged from -9 to 95 F; soil temperatures were not provided [page 93]. Monthly precipitation totaled 3.43 inches during June 1992, 13.75 inches during July, 1.35 inches during August, and 16.25 inches between September and December; precipitation totaled 53.09 inches between January and November 1993. Because the site received above average rainfall and good soil moisture was present, irrigation was not deemed necessary.

#### COMMENTS:

1. The study author stated that the stability of methanesulfonamide and 3-carboxylic acid F6285 in a clay loam soil stored at -18 C for 12 months has been established. The data were reported separately (MRID 433454420, Barrett, G.P. Cold storage stability of FMC 97285 and FMC 129427 in/on laboratory fortified soil, February 1994, Study Number: 162CSS92R2, FMC Corporation). All soil samples collected in this study were analyzed within 9 months from the date of sampling.
2. No clear pattern of dissipation emerged during the first 6 months of the study because the concentrations of methanesulfonamide in the soil, both measured and averaged, were extremely variable. The most extreme example of the variability of the raw data was at 1 day posttreatment, when the concentration of methanesulfonamide in the 0- to 6-inch soil depth ranged from 55.4 to 506.0 ppb. The average concentration of methanesulfonamide rose from 154 ppb immediately posttreatment to a maximum 279 ppb at 31 days, and varied from 134 to 184 ppb between 61 and 186 days, and decreased to 105 ppb at 305 days and 68-82 ppb at 362 through 531 days. Using first-order linear regression equations, the study author calculated a half-life of 302 days ( $r^2 = 0.804$ ) for methanesulfonamide in the bareground clay loam soil; the observed half-life (based on the theoretical application rate of 250 ppb) ranges from 61 to 305 days. The perception of variability is heightened because the data are expressed in terms of "ppb" rather than "ppm" (i.e., values ranging from 0.13 to 0.28 ppm seem more similar than values ranging from 134 to 279 ppb).
3. Prior to analysis, 3-carboxylic acid F6285 in the soil was converted to 3-desmethyl F6285, which is also a degradate of

methanesulfonamide. The soil was then analyzed for methanesulfonamide and 3-desmethyl F6285. The study author stated that 3-carboxylic acid F6285 was the only degradate of significance in field soil.

In an aerobic soil metabolism experiment (MRID 42932117) conducted using sandy loam and silty clay loam soils treated with either phenyl ring- or carbonyl-labeled [<sup>14</sup>C]methanesulfonamide at 2.5 ppm and incubated at 25 C and 75% of field moisture capacity, 3-carboxylic acid F6285 was the only degradate isolated from the soil at >10% of the applied; other degradates identified were 3-hydroxymethyl-F6285, 3-desmethyl-F6285, and 5'-desmethylsulfonyl-F6285 at maximums of 3.9, 1.1, and 4.8% of the applied, respectively (according to HPLC analysis). [<sup>14</sup>C]Methanesulfonamide degraded with a calculated half-life of 534-555 days.

4. The current proposed maximum field application rate is 0.375 lb ai/A; the application rate in this study, 0.5 lb ai/A, was 1.3x the maximum proposed application rate. Based on a theoretical application of 0.5 lb ai/A, the concentration of methanesulfonamide in the 0- to 6-inch soil depth would be expected to be 250 ppb, which is very close to the average concentration of 220-279 ppb measured at 14 through 31 days.
5. The site description was incomplete. Soil characteristics, such as particle size distribution and CEC, the slope of the test plots, and the depth to the water table were not reported; these values are important considering the heavy, frequent rains the site received in the months following treatment. Also, the depth to which methanesulfonamide was incorporated into the soil was not reported; which is a serious omission because methanesulfonamide degrades rapidly in sunlight (refer to MRIDs 43345424 and 43345425; Studies 1 and 2, respectively, of this submission).
6. Daily precipitation amounts were not reported; the study author stated that rainfall during some months was "above average". During this period, parts of the Midwest received record rainfalls and flooding was widespread. Because of these atypical meteorological conditions, the study author should have provided more specific information about rainfall at the site and the moisture status of the soil. It is important to note that methanesulfonamide remained relatively stable, significant leaching did not occur, and methanesulfonamide was not carried away in runoff during the periods of record rainfall.

Also, precipitation amounts were collected at the site from May through October 1992, and during other months were collected at the Illinois Water Survey Research Center in Champaign, Illinois.

7. Samples collected on and before 186 days posttreatment were shipped frozen to the analytical laboratory, while those collected on and after 305 days were shipped at "ambient" temperatures overnight. At

the analytical laboratory, all samples were stored frozen prior to analysis.

8. In 1987, the test plots had been planted to soybeans and treated with trifluralin/metribuzin; in 1988, the test plots had been part of a field trial for clomazone; in 1989, the test plots had been planted to soybeans and treated with alachlor plus metribuzin; in 1990, the test plots had been planted to field corn and treated with alachlor; and in 1991, the test plots had been planted to soybeans and treated with chlorimuron-ethyl plus thifensulfuron-methyl. During the study, the test plots were treated with glyphosate for vegetation control.

Substantive Review

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Page \_\_\_\_\_ is not included in this copy.

Pages 356 through 374 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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DATA EVALUATION RECORD

STUDY

CHEM 129081

Methanesulfonamide  
(F6285)

S164-1

FORMULATION---DRY FLOWABLE POWDER. (DF)

STUDY ID 43651009

Culligan, J.F. 1995. Terrestrial field dissipation - F6285 75DF herbicide. FMC Study No.: 162E4193E2. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 15

REVIEWED BY: Larry Liu  
TITLE: Environmental Scientist  
ORG: EFGWB/EFED/OPP  
TEL: 703-305-5372



SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study can be used towards the fulfillment of data requirements.
2. Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285-75DF: 75% a.i. formulated into a dry flowable powder], at 0.375 lb ai/A, dissipated with an observed half-life of approximately 2 years in the 0- to 6-inch depth of a plot of bareground silty clay loam soil in Iowa. The herbicide was applied to the soil on 5/26/93, and was incorporated into the soil to a depth of 2 inches after application.

In the 0- to 6-inch soil depth, methanesulfonamide averaged 94-206 ppb through 29 days posttreatment, 78-176 ppb at 57 through 365 days, 104-108 ppb at 455 and 531 days. Trace amounts of methanesulfonamide were detected in the 12-18 inch depth soil at 21, 57, 91, 120, and 180 days. For the samples collected at the depth of 30-36 inches, the parent compound was detected only at days 180. The degradate (3-carboxylic acid F6285), which was converted to 3-desmethyl F6285 prior to analysis, was detected in all samples collected in the 0-6 inch soil zone (with a range of 4-10 ppb). This degradate was not detected in the 6-12 inch soil zone during the first month after application; trace amounts were detected at later dates (1 ppb at days 57, 4 ppb at days 120, 1 ppb at days 180, 4 ppb at days 295, 3 ppb at days 365, and 4 ppb at days 531). For the samples collected

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at the depth of 12-18 inches, 3-carboxylic acid F6285 was only detected (1 ppb) at days 120, and was not detected (<1 ppb) in soil collected from depths below 18 inches.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the field dissipation of sulfentrazone 75DF.
4. No additional information on the field dissipation of sulfentrazone 75DF is required at this time.

#### METHODOLOGY:

Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 75DF; 75% a.i. formulated into a dry flowable powder, FMC] was broadcast once, at 0.375 lb ai/A, onto a bare ground plot (190 x 50 feet) of silty clay loam soil (0- to 12-inch depth: 3.5% organic matter, pH 5.6; soil not further characterized) that was located in Danville, Iowa. The application was made on 5/26/93, using a CO<sub>2</sub> backpack; the herbicide was incorporated into the soil at a depth of 2 inches after treatment (time not reported).

An untreated bareground plot (190 x 20 feet) located next to the treated plot was used as a control. During the study, the site was kept free of "dense weed growth" through normal agricultural maintenance. According to the field report, Roundup was applied at a rate of 1 lb ai/A on 8/23/93 and 7/12/94. In order to provide the site with normal or above normal precipitation amounts according to 30 year normals, the site was irrigated: 2.5 inches in 4/94, 3 inches in 5/94, 1.5 inches in 6/94, 3 inches in 7/94, 2.75 inches in 8/94, and 3.25 inches in 9/94.

For sampling purposes, the treated and control plots were divided into five subplots, and each subplot was divided into 1-m<sup>2</sup> sub-subplots. Fifteen soil samples were collected from the treated plot prior to and immediately after application, and at 1, 6, 14, 21, 29, 57, 91, 120, 180, 295, 365, 455, and 531 days posttreatment. Samples were collected from the 0- to 6-inch depth using a probe (2.25-inch diameter). Samples were then collected from the entire 6- to 36-inch depth through the existing sample hole using a probe (1.5-inch diameter) equipped with an acetate liner, and the cores were divided into 6-inch segments. The soil cores collected prior to treatment were combined according to sample depth to create a single composite sample. The cores from the treated plot, except for the 0- to 6-inch segment of the 1-day posttreatment samples, were combined according to sampling interval and sample depth to create three composite samples (five cores per composite sample).

For the control plot, fifteen soil samples were collected prior to and immediately after application, and at 1, 6, 14, 21, 29, 57, 91, 120, 180, 295, 365, 455, and 531 days posttreatment; the cores were

divided into 6-inch segments, then combined to create a single composite sample.

All collected samples were frozen immediately following sampling process prior to shipping to the analytical laboratory. All samples were stored frozen (-18 C) at the analytical laboratory up to 11 months prior to extraction. Some samples collected from the top zone were re-analyzed at the end of the study to verify initial analytical results.

Subsamples of each composite sample were extracted with acetonitrile:0.25 N HCl (70:30, v:v) by refluxing for 1 hour; during the reflux procedure, the 3-carboxylic acid F6285 was decarboxylated into 3-desmethyl F6285. The mixture was cooled, and an aliquot of the extract was concentrated under nitrogen. The concentrate was diluted with 5% NaCl, then partitioned three times with hexane:ethyl acetate (80:20, v:v). The hexane:ethyl acetate fractions were combined and evaporated to dryness; the resulting residues were dissolved in hexane:ethyl acetate (80:20, v:v) and filtered through a silica gel solid-phase extraction cartridge. Residues were eluted from the cartridge with hexane:ethyl acetate (70:30, v:v), and the eluate was evaporated to dryness. The dried residues were dissolved in acetonitrile, and the acetonitrile solution was analyzed for methanesulfonamide and 3-desmethyl F6285 using GC with electron-capture detection. The limit of detection was 1 ppb, and the limit of quantitation was 5 ppb. Recovery of methanesulfonamide and 3-carboxylic acid F6285 from soil fortified with both compounds at 5-500 ppb ranged from 79 to 118% of the applied (average 100 ± 11%) for methanesulfonamide, and from 66 to 111% (average 83 ± 11%) for 3-carboxylic acid F6285.

#### DATA SUMMARY:

Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285.75DF; 75% active ingredient formulated into a dry flowable powder], at 0.375 lb ai/A, dissipated with an observed half-life of 710 days in the 0- to 6-inch depth of a bareground plot of silty clay loam soil located in Danville, Iowa. The herbicide was applied to the soil in late May 1993, and was incorporated into the soil to a depth of 2 inches after application. In the 0- to 6-inch soil depth, methanesulfonamide averaged 94-206 ppb through 29 days posttreatment, 78-176 ppb at 57 through 365 days, 104-108 ppb at 455 and 531 days (Table 1a). Methanesulfonamide was detected in the 6- to 12-inch soil depth at 8 ppb at 0 day, 1-3 ppb at 21 and 29 days, and 9-15 ppb at all samples collected at and after 57 days. Trace amounts of methanesulfonamide were detected in the 12-18 inch depth soil at 21, 57, 91, 120, and 180 days. For the samples collected at the depth of 30-36 inches, the parent compound was detected only at days 180 (Table 1a). The degradate

N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamido-3-carboxylic acid (3-carboxylic acid F6285),

which was converted to N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-desmethyl F6285) prior to analysis, was detected in all samples collected in the 0-6 inch soil zone (ranging from 4-10 ppb). This degradate was not detected in the 6-12 inch soil zone during the first month after application; trace amounts were detected at later dates (1 ppb at days 57, 4 ppb at days 120, 1 ppb at days 180, 4 ppb at days 295, 3 ppb at days 365, and 4 ppb at days 531). For the samples collected at the depth of 12-18 inches, 3-carboxylic acid F6285 was only detected (1 ppb) at days 120, and was not detected (<1 ppb) in soil collected from depths below 18 inches (Table 1a).

During the study, air temperatures ranged from -21 to 93 F; soil temperatures were not provided. Precipitation totaled 41 inches between May and December 1993. The precipitation from January to December 1994 was 25 inches. In order to provide the site with normal or above normal precipitation amounts according to 30 year normals, the site was irrigated: 2.5 inches in 4/94, 3.0 inches in 5/94, 1.5 inches in 6/94, 3.0 inches in 7/94, 2.75 inches in 8/94, and 3.25 inches in 9/94.

#### COMMENTS:

1. The study author stated that the stability of methanesulfonamide and 3-carboxylic acid F6285 in a silty clay loam soil stored at -18 C for 12 months has been established. Stability of both compounds was shown for at least 12 months under frozen storage. The data were reported separately (MRID 43345420, Barrett, G.P. Cold storage stability of FMC 97285 and FMC 129427 in/on laboratory fortified soil, February 1994, Study Number: 162CSS92R2, FMC Corporation). All soil samples collected in this study were analyzed within 11 months from the date of sampling.
2. During the conduct of the study, two sudden increases of the concentration of the parent compound in the 0-6 inch soil zone were observed between days 6 and 21, and between days 91 and 180. The concentrations of the parent compound in the 0-6 inch soil depth decreased from 206 ppb at day 0 to 94 ppb at days 6. However, the concentrations of methanesulfonamide in the soil increased to 212 ppb at days 21. After that, the concentration of methanesulfonamide dropped to 138 ppb at days 29, and then dropped to 78 ppb at 91 days. Another increase in the concentration of the parent compound was observed from days 91 to days 169 (increased from 78 ppb to 169 ppb, respectively). Using first-order linear regression equations, the study author calculated a half-life of 710 days ( $r^2 = 0.58$ ) for methanesulfonamide in the silty clay loam soil.
3. Prior to analysis, 3-carboxylic acid F6285 in the soil was converted to 3-desmethyl F6285, which is also a degradate of

methanesulfonamide. The soil was then analyzed for methanesulfonamide and 3-desmethyl F6285.

In an aerobic soil metabolism experiment (MRID 42932117) conducted using sandy loam and silty clay loam soils treated with either phenyl ring- or carbonyl-labeled [<sup>14</sup>C]methanesulfonamide at 2.5 ppm and incubated at 25 C and 75% of field moisture capacity, 3-carboxylic acid F6285 was the only degradate isolated from the soil at >10% of the applied; other degradates identified were 3-hydroxymethyl-F6285, 3-desmethyl-F6285, and 5'-desmethylsulfonyl-F6285 at maximums of 3.9, 1.1, and 4.8% of the applied, respectively (according to HPLC analysis). Methanesulfonamide degraded with a calculated half-life of 534-555 days.

4. The application rate in this study, 0.375 lb ai/A, is as same as the current proposed maximum field application rate. Based on a theoretical application of 0.375 lb ai/A, the concentration of methanesulfonamide in the 0-6 inch soil depth would be expected to be 187 ppb, which is within the range of the concentration of 169-206 ppb measured at 0 and 1 days.
5. The site description was incomplete. Soil characteristics, such as particle size distribution and CEC, and the depth to the water table were not reported. Also, the time at which methanesulfonamide was incorporated into the soil was not reported, which is a serious omission because methanesulfonamide degrades rapidly in sunlight (refer to MRIDs 43345424 and 43588601).
6. Daily precipitation amounts were not reported; the study author stated that "excessive precipitation events occurred between June and August 1993" (9.9 inches in June, 11.8 inches in July, and 10.2 inches in August). It should be noted that methanesulfonamide remained relatively stable, and significant leaching did not occur.
7. Samples collected from day 0 to days 455 were shipped frozen to the analytical laboratory, while those collected at days 531 were shipped at "ambient" temperatures overnight. According to the report, the last set of samples was shipped at ambient temperatures overnight in order to expedite analysis. At the analytical laboratory, all samples were stored frozen prior to analysis.
8. In 1988, the test plots had been planted to soybeans and treated with Dual and metribuzin; in 1989, the test plots had been planted to popcorn and treated with Bladex and atrazine; in 1990, the test plots had been planted to corn and treated with Pursuit; in 1991, the test plots had been planted to soybeans and treated with Trellan and metribuzin; and in 1992, the test plots had been planted to soybeans and treated with Trellan and metribuzin. During the study, the test plots were treated with Roundup two times at a rate of 1 lb a.i./A for vegetation control.

Self-Inspection Review

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Pages 380 through 381 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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Arkansas

DATA EVALUATION RECORD

STUDY

CHEM 129081	Methanesulfonamide (F6285)	\$164-1
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FORMULATION---DRY FLOWABLE POWDER (DF)

STUDY ID 43651008

Nagel W.D. and J.F. Culligan. 1995. Terrestrial field dissipation F6285 75DF herbicide. FMC Study No.: 162E4193E1. Unpublished study performed and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 24

REVIEWED BY: Larry Liu  
 TITLE: Environmental Scientist  
 ORG: EFGWB/EFED/OPP  
 TEL: 703-305-5372

SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study can be used towards the fulfillment of data requirements.
2. Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 75DF; 75% a.i. formulated into a dry flowable powder], at 0.375 lb ai/A, dissipated with an observed half-life of approximately 1.5 years in the 0- to 6-inch depth of a plot of bareground silty clay loam soil in Arkansas. The herbicide was applied to the soil on 6/2/93, and was incorporated into the soil to a depth of 2-3 inches after application.

In the 0- to 6-inch soil depth, methanesulfonamide averaged 68-165 ppb through 30 days posttreatment, 53-186 ppb at 61 through 276 days, 60 ppb at 360 days, and 67-95 ppb at 453 through 554 days. Trace amounts of methanesulfonamide were detected in the 6- to 12-inch soil depth: 3 ppb on day 1, 2 ppb on days 6, 1 ppb on days 90 and 128. The degradate (3-carboxylic acid F6285), which was converted to 3-desmethyl F6285 prior to analysis, was detected in all the 0-6 inch soil samples collected from days 3 to days 554 with a concentration ranging from 3-13 ppb.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the field dissipation of sulfentrazone 75DF.

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4. No additional information on the field dissipation of sulfentrazone 75DF is required at this time.

METHODOLOGY:

Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 75DF; 75% a.i. formulated into a dry flowable powder, FMC] was broadcast once, at 0.375 lb ai/A, onto an unvegetated plot (59 x 52 feet) of silty clay loam soil (0- to 12-inch depth: 1.4% organic matter, pH 6.7; soil not further characterized) that was located in Newport, Arkansas. The application was made on 6/2/93, using a CO<sub>2</sub> backpack; the herbicide was incorporated into the soil at a depth of 2-3 inches after treatment (time not reported).

An untreated bareground plot (59 x 33 feet) located "near" the treated plot was used as a control. During the study, the site was kept free of "dense weed growth" through normal agricultural maintenance. According to the field report, Roundup was applied at a rate of 1 lb ai/A on 8/17/93, 4/27/94, 6/16/94, and 7/21/94. In order to provide the site with normal or above normal precipitation amounts according to 30 year normals, the site was irrigated: 2.1 inches in 7/93, 1.2 inches in 8/93, 3 inches in 5/94, 1 inch in 9/94, and 2.5 inches in 10/94.

For sampling purposes, the treated and control plots were divided into five subplots, and each subplot was divided into 1-m<sup>2</sup> sub-subplots. Fifteen soil samples were collected from the treated plot prior to and immediately after application, and at 1, 3, 6, 14, 30, 61, 90, 128, 215, 276, 360, 453, and 554 days posttreatment. Samples were collected from the 0- to 6-inch depth using a probe (2.25-inch diameter). Samples were then collected from the entire 6- to 36-inch depth through the existing sample hole using a probe (1.5-inch diameter) equipped with an acetate liner, and the cores were divided into 6-inch segments. The soil cores collected prior to treatment were combined according to sample depth to create a single composite sample. The cores from the treated plot, except for the 0- to 6-inch segment of the 1-day posttreatment samples, were combined according to sampling interval and sample depth to create three composite samples (five cores per composite sample).

For the control plot, fifteen soil samples were collected prior to and immediately after application, and at 1, 3, 6, 14, 30, 61, 90, 128, 215, 276, 360, 453, and 554 days posttreatment; the cores were divided into 6-inch segments, then combined to create a single composite sample. All collected samples were frozen immediately following sampling process prior to shipping to the analytical laboratory. All samples were stored frozen (-18 C) at the analytical laboratory up to 9 months prior to extraction.

Subsamples of each composite sample were extracted with acetonitrile:0.25 N HCl (70:30, v:v) by refluxing for 1 hour; during

During the study, air temperatures ranged from 20 to 100 F; soil temperatures were not provided [page 83]. Precipitation totaled 28 inches between June and December 1993. The precipitation from January to December 1994 was 53 inches. In order to provide the site with normal or above normal precipitation amounts according to 30-year normals, the site was irrigated: 2.1 inches in 7/93, 1.2 inches in 8/93, 3 inches in 5/94, 1 inch in 9/94, and 2.5 inches in 10/94.

COMMENTS:

1. The study author stated that the stability of methanesulfonamide and 3-carboxylic acid F6285 in a silty clay loam soil stored at -18 C for 12 months has been established. Stability of both compounds was shown for at least 12 months under frozen storage. The data were reported separately (MRID 433454420, Barrett, G.P. Cold storage stability of FMC 97285 and FMC 129427 in/on laboratory fortified soil, February 1994, Study Number: 162CSS92R2, FMC Corporation). All soil samples collected in this study were analyzed within 9 months from the date of sampling.
2. During the conduct of the study, two sudden increases of the concentration of the parent compound in the 0-6 inch soil zone were observed during the first 3 months. The concentrations of the parent compound in the 0-6 inch soil depth decreased from 165 ppb at day 0 to 93 ppb at days 6. However, the concentrations of methanesulfonamide in the soil increased to 244 ppb at days 14, then dropped to 53 ppb at days 61. After that, the concentration of methanesulfonamide rose to 186 ppb at 90 days, and then dropped to 60 ppb at days 360. Using first-order linear regression equations, the study author calculated a half-life of 558 days ( $r^2 = 0.23$ ) for methanesulfonamide in the bareground silty clay loam soil.
3. Prior to analysis, 3-carboxylic acid F6285 in the soil was converted to 3-desmethyl F6285, which is also a degradate of methanesulfonamide. The soil was then analyzed for methanesulfonamide and 3-desmethyl F6285.

In an aerobic soil metabolism experiment (MRID 42932117) conducted using sandy loam and silty clay loam soils treated with either phenyl ring- or carbonyl-labeled [ $^{14}$ C]methanesulfonamide at 2.5 ppm and incubated at 25 C and 75% of field moisture capacity, 3-carboxylic acid F6285 was the only degradate isolated from the soil at >10% of the applied; other degradates identified were 3-hydroxymethyl-F6285, 3-desmethyl-F6285, and 5'-desmethylsulfonyl-F6285 at maximums of 3.9, 1.1, and 4.8% of the applied, respectively (according to HPLC analysis). Methanesulfonamide degraded with a calculated half-life of 534-555 days.

4. The application rate in this study, 0.375 lb ai/A, is as same as the current proposed maximum filed application rate. Based on a theoretical application of 0.375 lb ai/A, the concentration of methanesulfonamide in the 0-6 inch soil depth would be expected to be

187 ppb, which is very close to the concentration of 163-165 ppb measured at 0 and 1 days.

5. The site description was incomplete. Soil characteristics, such as particle size distribution and CEC, and the depth to the water table were not reported. Also, the time at which methanesulfonamide was incorporated into the soil was not reported, which is a serious omission because methanesulfonamide degrades rapidly in sunlight (refer to MRIDs 43345424 and 43588601).
6. Daily precipitation amounts were not reported; the study author stated that most of the monthly rainfall were "above average". It should be noted that methanesulfonamide remained relatively stable, and significant leaching did not occur.
7. Samples collected on 5/21/93 were shipped at "ambient" temperatures to the analytical laboratory by UPS, while other samples were shipped at frozen temperatures by truck. At the analytical laboratory, all samples were stored frozen prior to analysis.
8. In 1988, the test plots had been planted to rice and treated with propanil; in 1989, the test plots had been planted to soybeans and treated with treflan and bassagran; in 1990, the test plots had been planted to rice and treated with arrosolo, propanil, molinate and buctril; in 1991, the test plots had been planted to soybeans and treated with squadron, pendimethalin, and imazaquin; and in 1992, the test plots had been planted to rice and treated with propanil and bolero. During the study, the test plots were treated with glyphosate four times at a rate of 1 lb a.i./A for vegetation control.

Substantive Review

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Page \_\_\_\_\_ is not included in this copy.

Pages 387 through 388 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

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DATA EVALUATION RECORD

STUDY 6

CHEM 129081

Methanesulfonamide  
(F6285)

\$164-1

FORMULATION--14--FLOWABLE CONCENTRATE (F1C)

STUDY ID 43345434

Becker, J.M. 1994. A combined soil dissipation and small-scale prospective groundwater monitoring study with F6285 4F herbicide. Blasland, Bouck, and Lee, Inc. Study No.: 376.03. FMC Study No.: 162E6692E1. Unpublished study performed by Blasland, Bouck, and Lee, Inc., Durham, NC, and FMC Corporation, Princeton, NJ, and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 38

REVIEWED BY: K. Ferguson

TITLE: Task Leader

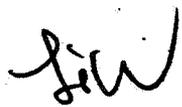
EDITED BY: C. Padova  
M. Anderson

TITLE: Staff Scientist  
Staff Scientist

APPROVED BY: W. Spangler  
ORG: Dynamac Corporation  
Rockville, MD  
TEL: 301-417-9800

TITLE: Project Manager

APPROVED BY: L. Liu  
TITLE: Environmental Scientist  
ORG: EFGWB/EFED/OPP  
TEL: 703-305-5372



SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study can be used towards the fulfillment of data requirements.
2. The DER only included the field dissipation portion of the study. The groundwater portion will be discussed separately by the Ground Water Technology Section in EFGWB.
3. Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 4F; 4 lb ai/gallon flowable

concentrate], at 0.5 lb ai/A, dissipated with an estimated half-life of 121 days in the entire 48-inch soil column of a plot of loamy sand soil in North Carolina. The herbicide was applied to the soil in mid-May 1992, and was incorporated into the soil at a depth of 4-6 inches immediately after application; the site was planted to soybeans at 6 days posttreatment. In the 0- to 6-inch soil depth, methanesulfonamide averaged 330 ppb immediately posttreatment, 146 ppb at 32 days, 56.7 ppb at 61 days, and 13.4-22 ppb at 103 through 368 days. Methanesulfonamide was detected in the soil to a depth of 48 inches, with maximum average concentrations of 36.7 ppb in the 6- to 12-inch depth, 10.9 ppb in the 12- to 18-inch depth, 6.6 ppb in the 18- to 24-inch depth, 5.2 ppb in the 24- to 30-inch depth, 10.8 ppb in the 30- to 36-inch depth, 3 ppb in the 36- to 42-inch depth, and 1 ppb in the 42- to 48-inch depth.

The degradate N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamido-3-carboxylic acid (3-carboxylic acid F6285), which was converted to N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-desmethyl F6285) prior to analysis, averaged  $\leq 11.5$  ppb in soil from the 0- to 6-inch depth and  $\leq 7.3$  ppb in soil collected from depths below 6 inches at all sampling intervals.

4. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the field dissipation of sulfentrazone 4F.
5. No additional information on the field dissipation of sulfentrazone 4F is required at this time.

#### METHODOLOGY:

Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 4F; 4 lb ai/gallon flowable concentrate, FMC] was broadcast once, at 0.5 lb ai/A, onto five subplots, each surrounded by a 10-foot buffer zone, within an unvegetated plot (440 x 200 feet) of loamy sand soil (0- to 6-inch depth: 84-90% sand, 6-8% silt, 4-8% clay, 1.1-1.3% organic matter, pH 6.3-6.8; CEC 2.5-3.1 meq/100 g) located in Edgecombe County, North Carolina (Figure 1). The application was made on May 15, 1992, using a tractor-mounted field sprayer; the herbicide was incorporated (4-6 inches) into the soil immediately after treatment. An untreated bareground plot (0.5 A), located upgradient from the treated area with respect to the groundwater flow, was used as a control; the untreated plot was divided into five subplots to correspond with the treated area. The treated plots, including the untreated buffer zones, and the control plot were planted to soybeans at 6 days posttreatment. During the study, the site was sprinkler-irrigated

with sufficient water from a nearby river to meet 120% of the historical monthly volume.

Three soil cores were collected from each treated and control subplot 2 days prior to and immediately after application, and at 1, 7, 12/14, 31/32, 61, 103/104, 124, and 159 days posttreatment; three soil cores were collected from each treated subplot and one soil core was collected from each control subplot at 186, 214, 249, 278, 305, 340, and 368 days posttreatment. Samples were collected from the 0- to 6-, 6- to 30-, and 30- to 48-inch depths (2.25-, 2-, and 1-inch diameter, respectively) using a three-stage hydraulic soil probe equipped with acetate liners. After the 0- to 6-inch soil core was removed, a protective steel casing remained in the borehole while the 6- to 30- and 30- to 48-inch depths were collected. The cores were placed in a cooler on dry ice "as soon after collection as possible." After sampling was completed, the boreholes were packed with bentonite pellets; the cores were transported to a "residue-free" trailer, where they were sectioned into 6-inch segments. The soil cores collected prior to treatment were combined according to sample depth to create a single composite sample. The cores from the treated plot, except for the 0- to 6-inch segment of the 7-day posttreatment samples, were combined according to sampling interval and sample depth to create three composite samples (five cores per composite sample). For the control plot, the fifteen cores collected at each sampling interval prior to and on 159 days posttreatment were composited as described for the treated samples; the five cores collected at each sampling interval after 159 days posttreatment were combined according to sample depth to create a single composite sample. All soil samples were shipped frozen on dry ice to the analytical laboratory via overnight delivery. Samples were stored frozen (-18 C) at the analytical laboratory prior to analysis. Most soil samples were analyzed within 5 months of collection; the maximum length of storage was 11 months.

Subsamples (50 g) of each composite sample were extracted with acetonitrile:0.25 N HCl (70:30, v:v) by refluxing for 1 hour; during the reflux procedure, 3-carboxylic acid F6285 was decarboxylated into 3-desmethyl F6285. The mixture was cooled, and the acetonitrile was evaporated from the extract under nitrogen. The concentrate was partitioned three times with hexane:ethyl acetate (80:20, v:v). The hexane:ethyl acetate fractions were combined and concentrated to dryness under nitrogen; the resulting residues were dissolved in hexane:ethyl acetate (80:20, v:v) and filtered through a silica gel solid-phase extraction cartridge. Residues were eluted from the cartridge with hexane:ethyl acetate (60:40, v:v), and the eluate was concentrated to dryness. The dried residues were dissolved in acetonitrile, and the acetonitrile solution was analyzed for methanesulfonamide and 3-desmethyl F6285 using GC with electron-capture detection. The limit of detection was 1 ppb, and the limit of quantitation was 5 ppb. Recovery of methanesulfonamide and 3-carboxylic acid F6285 from soil fortified with both compounds at 5-500 ppb ranged from 84 to 120% of the applied (average  $104 \pm 10\%$ ) for

methanesulfonamide, and from 70 to 115% (average  $80 \pm 8\%$ ) for 3-carboxylic acid F6285.

DATA SUMMARY:

Methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; sulfentrazone; F6285 4F; 4 lb ai/gallon flowable concentrate], at 0.5 lb ai/A, dissipated with an observed half-life of approximately 30 days in the 0- to 6-inch depth of a plot of loamy sand soil located in Edgecombe County, North Carolina. The herbicide was applied to the soil in mid-May 1992, and was incorporated into the soil at a depth of 4-6 inches immediately after application; the site was planted to soybeans at 6 days posttreatment. In the 0- to 6-inch soil depth, methanesulfonamide averaged 330 ppb immediately posttreatment (raw data 210.0-451.0 ppb), 157-204 ppb at 1 through 14 days (1.7-418.4 ppb), 146 ppb at 32 days (108.2-211.6 ppb), 56.7 ppb at 61 days (56.1-57.5 ppb), and 13.4-22 ppb at 103 through 368 days (9.4-32.6 ppb; Tables 1 and 19). Methanesulfonamide was detected in the soil to a depth of 48 inches; maximum concentrations were measured at 61 days posttreatment in all layers. In the 6- to 12-inch soil depth, methanesulfonamide was an average 36.7 ppb at 61 days posttreatment, 15.6-16.8 ppb at 103 through 160 days, 6.5-13.4 ppb at 186 through 340 days, and 14.1 ppb at 368 days. In the 12- to 18-inch soil depth, methanesulfonamide was an average 10.9 ppb at 61 days posttreatment, 5.2-5.6 ppb at 103 and 124 days, 1-5 ppb at 160 through 340 days, and 7.3 ppb at 368 days. With the exception of the 61-day sample, methanesulfonamide averaged  $\leq 5$  ppb in soil collected from depths below 18 inches; in the 61-day sample, methanesulfonamide averaged 6.6 ppb in the 18- to 24-inch depth, 5.2 ppb in the 24- to 30-inch depth, 10.8 ppb in the 30- to 36-inch depth, 3 ppb in the 36- to 42-inch depth, and 1 ppb in the 42- to 48-inch depth. The degradate

N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamido-3-carboxylic acid (3-carboxylic acid F6285),

which was converted to N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-desmethyl F6285) prior to analysis, averaged 10.4-11.5 ppb at 14 and 32 days posttreatment (raw data 6.3-19.2 ppb), and averaged  $\leq 6.5$  ppb at all other sampling intervals in the 0- to 6-inch soil depth (Tables 2 and 19). In the 6- to 12-inch depth, 3-carboxylic acid F6285 averaged 5.0-7.3 ppb at 32 and 61 days posttreatment, and  $\leq 4$  ppb at all other sampling intervals. 3-Carboxylic acid averaged  $\leq 3$  ppb in soil collected from depths below 12 inches.

During the study, average air temperatures ranged from 27.0 to 89.5 F, and average soil temperatures (6-inch depth) ranged from 37.1 to 91.6 F. Precipitation plus irrigation totaled 1.67 inches through 14

days posttreatment (May 15-31, 1992), 6.52 inches during June, 6.41 inches during July, 10.76 inches during August, and 15.71 inches between September and December; precipitation totaled 25.41 inches between January and July 1993. Because the site received above average rainfall and good soil moisture was present, irrigation was not deemed necessary except during June and July 1992. There was no slope to the test plots, and the depth of the water table varied from 5.7 to 10.0 feet during the study.

COMMENTS:

1. The study author stated that the stability of methanesulfonamide and 3-carboxylic acid F6286 in a loamy sand soil stored at -18 C for 12 months has been established. The data were reported separately (MRID 433454420, Barrett, G.P. Cold storage stability of FMC 97285 and FMC 129427 in/on laboratory fortified soil, February 1994, Study Number: 162CSS92R2, FMC Corporation). All soil samples collected in this study were analyzed within 11 months from the date of sampling.
2. Prior to analysis, 3-carboxylic acid F6285 in the soil was converted to 3-desmethyl F6285, which is also a degradate of methanesulfonamide. The soil was then analyzed for methanesulfonamide and 3-desmethyl F6285. The study author stated that 3-carboxylic acid F6285 was the only degradate of significance in field soil.

In an aerobic soil metabolism experiment (MRID 42932117) conducted using sandy loam and silty clay loam soils treated with either phenyl ring- or carbonyl-labeled [<sup>14</sup>C]methanesulfonamide at 2.5 ppm and incubated at 25 C and 75% of field moisture capacity, 3-carboxylic acid F6285 was the only degradate isolated from the soil at >10% of the applied; other degradates identified were 3-hydroxymethyl-F6285, 3-desmethyl-F6285, and 5'-desmethylsulfonyl-F6285 at maximums of 3.9, 1.1, and 4.8% of the applied, respectively (according to HPLC analysis). [<sup>14</sup>C]Methanesulfonamide degraded with a calculated half-life of 534-555 days.

3. The study was terminated early because the irrigation equipment overturned at 13 months posttreatment, causing deep gullies to form in the field and washing soil from the treated area into the control plot.
4. Aliquots of the tank mix solution were collected just after the addition of methanesulfonamide to the tank and again immediately after the treatment of the test plots [page 37]. The measured concentrations of methanesulfonamide were 1872 ppm "several minutes" prior to application, and 3375 ppm after application. The low concentration of methanesulfonamide in the pretreatment tank mix was attributed to insufficient time for the test substance to fully disperse in the aqueous spray solution. The theoretical concentration of methanesulfonamide in the tank mix was 3300 ppm.

5. Samples of the control soil were spiked in the field with methanesulfonamide and 3-carboxylic acid F6285 in conjunction with the 0-, 6-, and 12-month sampling intervals. Data were provided only for the 12-month sampling. Control soil samples were treated with methanesulfonamide at 100 ppb or with 3-carboxylic acid F6285 at 50 ppb. After 170 days of storage, the measured concentrations of methanesulfonamide were 85-101 ppb, and of 3-carboxylic acid F6285 were 43-50 ppb.
6. The half-life of methanesulfonamide was calculated to be 79 days based on first-order linear regression analysis of total residues detected in the entire 48-inch soil column through 61 days posttreatment. When data for the entire 1-year experiment were used, the half-life was determined to be 121 days. The author did not report the half-life of dissipation based on the residues detected in the 0-6 inch soil zone. The reviewer estimated that the half-life in the 0-6 inch soil zone is approximately 30 days.
7. The study author stated that the region in North Carolina and the sandy soil was atypical of the sites on which methanesulfonamide would be used, but was chosen to represent a worst-case situation. The soil was extremely permeable. The site was also treated with potassium bromide to trace water movement through the soil.
8. The current proposed maximum field application rate is 0.375 lb ai/A; the application rate in this study, 0.5 lb ai/A, was 1.3x the maximum proposed application rate.
9. In 1987, the test plots had been planted to cotton and treated with pendimethalin, lamda-cyhalothrin, and fluometuron; in 1988, the test plots had been planted to corn and treated with atrazine and butylate; in 1989, the test plots had been planted to peanuts and treated with pendimethalin, bentazone, butylate, and phorate; in 1990, the test plots had been planted to cotton and treated with pendimethalin, aldicarb, and fluometuron; and in 1991, the test plots had been planted to corn and treated with atrazine, butylate, and bentazone.
10. The study author stated that the incorporation depth of 4-6 inches was deeper than would occur in a normal farming situation [page 25].
11. The site located in Edgecombe County, North Carolina was selected as the study test site because of the nature of the soil profile (such as texture and uniformity) and the shallow depth of ground water classified it as the most vulnerable site.

Substantive Review

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Pages 395 through 422 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
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DATA EVALUATION RECORD

STUDY 7

CHEM 129081 Methanesulfonamide \$165-4  
(F6285)

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 43345433

Dionne, E. 1993. F6285 - Bioconcentration and elimination of <sup>14</sup>C-residues by bluegill sunfish (*Lepomis macrochirus*). SLI Study No.: 282.1091.6112.140. SLI Report No.: 92-7-4315. FMC Protocol/Project No.: 162E5491E1. FMC Report No.: PC-0186. Unpublished study performed by Springborn Laboratories, Inc., Wareham, MA, and submitted by FMC Corporation, Princeton, NJ.

DIRECT REVIEW TIME = 16

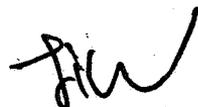
REVIEWED BY: M. Anderson TITLE: Staff Scientist

EDITED BY: C. Padova TITLE: Staff Scientist  
K. Ferguson Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation  
Rockville, MD  
TEL: 301-417-9800

APPROVED BY: Larry Liu  
TITLE: Environmental Scientist  
ORG: EFGWB/EFED/OPP  
TEL: 703-305-5372



SIGNATURE:

CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study can be used to fulfill data requirements.
2. Methanesulfonamide residues did not accumulate in the edible tissue (muscle) and accumulated only slightly in the nonedible tissue (viscera and carcass) of juvenile bluegill sunfish exposed to methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285] at 0.94 mg/L for 28 days under flow-through

conditions. Average bioconcentration factors throughout steady state were <1x, 1.8-2.4x, and 1.1-2.0x for edible tissue, nonedible tissue, and whole fish, respectively. The degradate, 3-hydroxymethyl F6285 [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide], was identified in the viscera. The  $K_{ow}$  for methanesulfonamide is 0.006.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the laboratory accumulation of phenyl ring- and carbonyl-labeled [ $^{14}C$ ]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide] in fish.
4. No additional information of the laboratory accumulation of [ $^{14}C$ ]methanesulfonamide in fish is required at this time.

#### METHODOLOGY:

Juvenile bluegill sunfish (*Lepomis macrochirus*; mean weight 2.4 g, mean length 51 mm) were held in culture tanks on a 16-hour photoperiod under fluorescent lights for  $\geq 14$  days. Flow through aquatic exposure systems were prepared using three glass aquaria (75 x 39 x 30 cm). Aerated well water (pH 6.8-7.2, average dissolved oxygen content 80-97% of saturation, total hardness 26-38 mg/L as  $CaCO_3$ , alkalinity 19-34 mg/L as  $CaCO_3$ , specific conductance 110-120  $\mu mhos/cm$ ) was delivered to the aquaria at a rate of 8.3 turnovers per day (90% replacement in 6 hours). The water in two of the aquaria was treated at 0.94 mg/L with either phenyl ring-labeled [ $^{14}C$ ]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285; radiochemical purity 98.9%, specific activity 20.1 mCi/mMol, FMC Corporation] or carbonyl-labeled [ $^{14}C$ ]methanesulfonamide (radiochemical purity 99.8%, specific activity 24.0 mCi/mMol, FMC), dissolved in acetone. The water in the third aquarium was treated at 9.3  $\mu L/L$  with acetone, and served as a control. The flow-through systems were allowed to equilibrate for approximately 1 week prior to study initiation; water samples were collected on 5 separate days during this period to establish the concentration of [ $^{14}C$ ]residues in the treated and control test water.

Following the equilibration period, 130 fish were transferred into each of the three aquaria. Following a 28-day exposure period, 30 fish from each of the treated aquaria were transferred into untreated aquaria for a 14-day depuration period. The control aquarium was maintained throughout the exposure and depuration periods. From the treated and control aquaria, water samples (5 mL) were collected on days 0, 1, 3, 7, 10, 11 (carbonyl-labeled only), 12 (carbonyl-labeled only), 14, 18, 21, and 28 days of the exposure period, and days 1, 3, 7, 10, and 14 of the depuration period. Five fish were collected

from each of the aquaria on days 1, 3, 7, 10, 14, 21, and 28 of the exposure period, and 1, 3, 7, 10, and 14 of the depuration period.

The water samples were analyzed for total [ $^{14}\text{C}$ ]residues using LSC. Recovery efficiencies from fortified water samples averaged 105%. In addition, aliquots of the 21-day water samples were analyzed by reverse-phase HPLC using a Phenomenex Ultramex C-18 column eluted with acetonitrile:water:acetic acid (40:60:0.1, v:v:v); the column was equipped with photo diode-array (220 nm) and radioactive flow detection. [ $^{14}\text{C}$ ]Compounds were identified by comparison of retention times to unlabeled reference standards of methanesulfonamide (F6285); N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl]-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-hydroxymethyl F6285); and 1-(2,4-dichloro-5-[N-(methylsulfonyl)amino]phenyl)-4-difluoromethyl-4,5-dihydro-5-oxo-1H-1,2,4-triazole-3-carboxylic acid (3-carboxylic acid F6285) analyzed on the same day. Additional aliquots of the 21-day water samples were analyzed by two-dimensional TLC on silica gel plates developed in toluene:ethyl acetate:acetonitrile (75:25:10, v:v:v) in the first direction, and methylene chloride:methanol:ammonium hydroxide (75:25:10, v:v:v) in the second direction. [ $^{14}\text{C}$ ]Compounds were located and quantified using an imaging scanner.

All fish were separated into edible (muscle) and nonedible (viscera and carcass) tissues; the tissue samples were weighed, mixed with cellulose powder to aid combustion, and air-dried at ambient temperatures for  $\geq 24$  hours but  $\leq 72$  hours. Subsamples were analyzed for total radioactivity by LSC following combustion; concentrations of [ $^{14}\text{C}$ ]residues in the whole fish were determined by calculation. Recovery efficiencies of the oxidizer averaged 98.7%. Additional subsamples of the 28-day viscera tissue were ground with dry ice in an analytical mill, then extracted according to the scheme outlined in Figure 2. The tissue samples were extracted four times with acetonitrile (method not further described); after each extraction, the samples were centrifuged, and the supernatants were combined then concentrated under nitrogen. Subsamples of the extracted tissue were analyzed by LSC following combustion. The concentrated extracts were centrifuged, and the supernatants were decanted, analyzed by LSC, and concentrated under nitrogen; the remaining residues were rinsed twice with acetonitrile, and the samples were centrifuged. The supernatants were combined with the concentrated extracts, and the remaining residues were discarded. The combined acetonitrile solutions were refrigerated for 2 days to precipitate fatty materials; after refrigeration, the samples were centrifuged. When necessary, the fatty materials were rinsed three times with acetonitrile, and the samples were centrifuged. The fatty precipitates were discarded, and the supernatants were combined with the acetonitrile extracts remaining after refrigeration. The combined solutions were concentrated under nitrogen, and aliquots were analyzed by reverse-phase HPLC as previously described.

DATA SUMMARY:

[<sup>14</sup>C]Methanesulfonamide residues did not accumulate in the edible tissue (muscle) and accumulated only slightly in the nonedible tissue (viscera and carcass) of juvenile bluegill sunfish exposed to phenyl ring- or carbonyl-labeled [<sup>14</sup>C]methanesulfonamide [N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide; F6285; radiochemical purities  $\geq 98.9\%$ ] at 0.94 mg/L for 28 days under flow-through conditions. In the fish exposed to phenyl ring-labeled [U-<sup>14</sup>C]methanesulfonamide, average bioconcentration factors throughout steady state (days 1 through 28) were  $<1x$ ,  $1.8x$ , and  $1.1x$  for edible tissue, nonedible tissue, and whole fish, respectively; in the fish exposed to carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, average bioconcentration factors throughout steady state (days 3 through 28) were  $<1x$ ,  $2.4x$ , and  $2.0x$ , respectively [pages 24-25]. The degradate,

N-(2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide (3-hydroxymethyl F6285)

was identified in the viscera.

At 1 through 28 days of the uptake phase of the study in the fish exposed to phenyl ring-labeled [<sup>14</sup>C]methanesulfonamide, total [<sup>14</sup>C]residues averaged  $\leq 0.73$  mg/kg in the edible tissue,  $\leq 2.7$  mg/kg in the nonedible tissue, and  $\leq 1.9$  mg/kg in the whole fish; maximum concentrations occurred at 7 days (Table 2). In the viscera from the fish collected on day 28, [<sup>14</sup>C]methanesulfonamide was 74% of the radioactivity recovered during HPLC analysis, and 3-hydroxymethyl F6285 was 26% (Figure 6). From days 3 through 14 of the depuration phase of the study, total [<sup>14</sup>C]residues averaged  $\leq 0.29$ ,  $\leq 0.30$ , and  $\leq 0.28$  mg/kg in the edible tissue, nonedible tissues, and whole fish, respectively (Table 2).

At 1 through 28 days of the uptake phase of the study in the fish exposed to carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, total [<sup>14</sup>C]residues averaged  $\leq 1.1$  mg/kg in the edible tissue,  $\leq 6.0$  mg/kg in the nonedible tissue, and  $\leq 2.9$  mg/kg in the whole fish; maximum concentrations occurred at 10 days (Table 3). Insufficient radioactivity was recovered in the viscera from the fish collected on day 28 for successful characterization analyses [page 26]. By day 1 of the depuration phase of the study, total [<sup>14</sup>C]residues averaged 0.46, 0.77, and 0.53 mg/kg in the edible tissue, nonedible tissue, and whole fish, respectively; and by days 3 through 14, total [<sup>14</sup>C]residues averaged  $\leq 0.32$ ,  $\leq 0.32$ , and  $\leq 0.29$  mg/kg, respectively (Table 3).

Throughout the exposure period, average [<sup>14</sup>C]residues in the treated water of the test aquaria were 0.63-1.1 mg/L, except on day 18 when the average concentrations decreased to 0.44-0.50 mg/L for part of the day due to malfunctions in the diluter systems (Tables 2 and 3).

Based on HPLC analysis, at day 21, methanesulfonamide was 0.84 and 0.92 mg/L in the test water treated with phenyl- and carbonyl-labeled [<sup>14</sup>C]methanesulfonamide, respectively; and, based on TLC analysis, was 100% of the recovered radioactivity in both test aquaria (Table 4). Throughout the study, the temperature of the water in the three aquaria was 17-19 C, and the pH was 6.6-7.1 (page 71 and Table 1).

COMMENTS:

1. During HPLC analysis of the viscera from the fish collected on day 28 from the phenyl-label treatment, two [<sup>14</sup>C]compounds were isolated: methanesulfonamide was 74% of the recovered radioactivity, and F6285 3-hydroxymethyl was 26%. Due to insufficient radioactivity, similar analysis attempts of the viscera from the 28-day sample from the carbonyl-label treatment were unsuccessful. The study author stated that approximately 1/3 of the total tissue mass was used during the preparation for HPLC analysis; had the laboratory attempted to increase the tissue mass, excessive processing and purification would have been necessary, probably resulting in significant loss of radioactivity. The presence of only parent and F6285 3-hydroxymethyl in the tissue from the phenyl-label treatment suggest that no molecular cleavage resulted during degradation, and, consequently, no additional degradates would have been isolated in the tissue from the carbonyl-label treatment.
2. No attempt was made to characterize [<sup>14</sup>C]residues isolated in the edible fish tissue; however, methanesulfonamide residues did not accumulate in the edible tissue (bioconcentration factors <1x).
3. During the night, for a period of approximately 12 hours between days 17 and 18 of the exposure period, the diluter systems malfunctioned, and prevented delivery of methanesulfonamide to the test aquaria. Consequently, average concentrations of [<sup>14</sup>C]residues in the test water decreased to 0.44-0.50 mg/L in the morning of day 18; the problem was immediately corrected, and by the evening of day 18, the average concentrations of [<sup>14</sup>C]residues had increased to 0.70-0.89 mg/L. No significant impact on the data is suspected.
4. On day 10 of the exposure period in the water treated with carbonyl ring-labeled [<sup>14</sup>C]methanesulfonamide, concentrations of [<sup>14</sup>C]residues were low at 0.63-0.67 mg/L. In order to closely monitor the water concentrations, additional aliquots were collected on days 11 and 12; on these days, concentrations of total [<sup>14</sup>C]residues were 0.78-0.81 mg/L.
5. Reportedly, extraction efficiencies were approximately 90 and 115% for the viscera from the fish collected at 28 days from the phenyl- and carbonyl-label treatments, respectively. No [<sup>14</sup>C]residues were detected in the extracted tissues.

6. The study author stated that, due to the low levels of radioactivity in the viscera tissue extracts, confirmational TLC analysis was not performed.
7. According to the study author, no [<sup>14</sup>C]residues were detected in the aquaria during the depuration phase of the study, or in the control aquaria throughout exposure and depuration.
8. According to the study author, the study sponsor stated that the water solubility of the test material was 238 (± 20) mg/L.
9. Whole fish concentrations were not determined by direct combustion, rather, were "based on calculations using sample weights and tissue concentrations of <sup>14</sup>C-residues measured in the edible and non-edible tissue portions [footnote b, page 35]".
10. During the entire 42-day study, only five fish died in the three aquaria. The study author stated that, "In general, the fish appeared healthy and exhibited normal behavior throughout the study [page 23]."
11. The nominal exposure concentration of 0.94 mg/L was 1/100 of the reported LC<sub>50</sub> for bluegill sunfish of 94 mg/L.
12. The study author stated that throughout the exposure period, no undissolved test material was observed in either the dilution system or the aquaria.
13. During the study, the fish were fed a dry pelleted food twice daily at approximately 2% of their total mass per feeding, except for the 24 hours prior to each sampling. Routine analyses indicated that the food was reasonably free of pesticides and PCBs. During the holding period, fish were fed ad libitum, except for the 24 hours prior to test initiation.
14. Detection limits for the analytical methods were not provided.
15. The K<sub>ow</sub> for methanesulfonamide is 0.006.

Self-Substantiated Review

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Pages 449 through 449 are not included in this copy.

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The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
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  - The document is not responsive to the request.
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Chemical Code: 129081

DP Barcode: D215727 & al. (see below)

**ENVIRONMENTAL FATE AND GROUND WATER MONITORING**

To: Joanne Miller, PM #23  
Registration Division (7505C)

From: Elizabeth Behl, Section Head  
Ground Water Technology Section  
Environmental Fate & Ground Water Branch/EFGW (7507C)

Thru: Henry Jacoby, Chief  
Environmental Fate & Ground Water Branch/EFGW (7507C)

*Henry Jacoby 9/21/96*

Attached, please find the EFGWE review of...

DP Barcode:	D215727, D211622, D211625, D211627
Common Name:	Sulfentrazone, methanesulfonamide, F6285
Company Name:	FMC Corp. Agricultural Chemicals Group
ID #:	000279-GRUO sulfentrazone technical
Purpose:	Progress report for a small-scale prospective ground-water monitoring study at a single site and request for permission to terminate study.

Type Product:	
Herbicide:	100, 230

**STATUS OF STUDIES IN THIS PACKAGE:**

**STATUS OF DATA REQUIREMENTS:**

Quantity									
100-1									

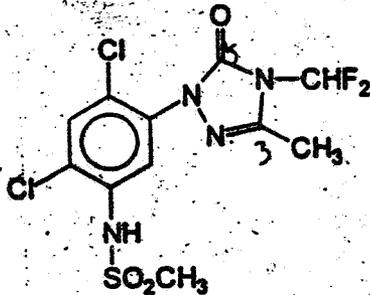
**Sulfentrazone**



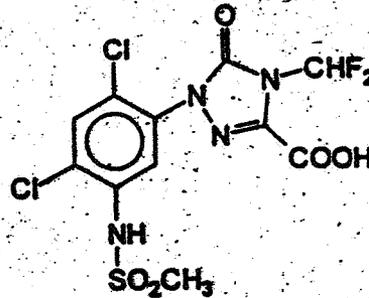
<sup>1</sup>Study Status Codes: A=Acceptable U=Upgradable C=Ancillary F=Final  
<sup>2</sup>Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved W=Waived

*450*

**1. CHEMICAL:** Sulfentrazone (F6285 4F herbicide)



Sulfentrazone



3-Carboxylic Acid-Sulfentrazone

**2. TEST MATERIAL:** formulated products.

**3. STUDY/ACTION TYPE:**

Small-scale prospective ground-water monitoring study.

**4. STUDY IDENTIFICATION:**

Becker, John M. 1995. Letter to EPA (routed by the Agency through Joanne Miller, Product Manager 23) dated 3/17/95, requesting permission to terminate the small-scale prospective ground-water monitoring study for sulfentrazone in Edgecombe County, NC.

Becker, John M. 1995. A combined soil dissipation and small-scale prospective ground-water monitoring study with F6285 4F herbicide. Study submitted by FMC Corp., Agricultural Chemical Group. EPA MRID no. 43345434. Report dated 8/3/94.

**5. REVIEWED BY:**

Michael R. Barrett, Ph.D.  
Chemist

Signature:

OPP/EFED/EFGBW/Ground-Water Section

Date:

6/26/95

**6. APPROVED BY:**

Elizabeth Behl  
Acting Section Chief  
OPP/EFED/EFGBW/Ground-Water Section,

Signature: Elizabeth Behl  
Date: 6/26/95

**7. CONCLUSIONS:**

The primary purpose of this review is to respond to the registrant's request for study termination, therefore full scientific conclusions on the utility of this study will not be made at this time. The irrigation accident which occurred 13 months after application of the herbicide precludes obtaining the full body of data normally required with these studies. Also, since many of the changes recommended by EFGBW and GWTS (5/14/92 review, DP Barcode D174353) were not made, the utility of this study will be significantly limited. Nevertheless, significant insight into sulfentrazone leaching at a very vulnerable site is still possible with this study.

Under the conditions of this study, concentrations of parent plus acid reached up to 100 ppb in soil water at a three-foot depth (average of replicates; see discussion section of this review for further details). Sulfentrazone residues persisted in the vadose zone; by the last sampling date analyzed so far (395 days after application) residues of parent + acid still averaged about 10 ppb in soil-pore water from all three depths (three, five, and seven feet). A similar pattern occurred in ground water with the peak concentrations (30 or 40 ppb) of sulfentrazone residues occurring about four to five months after application. Sulfentrazone residues clearly were both mobile and persistent at the study site and readily moved to ground water.

More general conclusions about sulfentrazone leaching to ground water that is less vulnerable than at the study site need to be made. However, only one study has been conducted at a site with very permeable soils, very shallow ground water (ca. 9-foot depth), under very wet conditions with rapid recharge of the aquifer.

**8. RECOMMENDATIONS:**

Data collection efforts may cease and site decommissioning be completed at the Edgecombe County, North Carolina site provided the registrant agrees to collect and/or provide the following data:

- (A.) To the extent possible, more detailed documentation of the extent of the damage caused by the irrigation accident at the study site should be included in the final report. Maps of the dimensions of the erosion (area covered and approximate depth) should be submitted in as much detail as possible. Field maintenance practices following the irrigation accident need to be documented. Specify how much of the soybean crop in the treated field was lost due to the irrigation accident. Indicate what agricultural practices have been used on the field since then.
- (B.) Before decommissioning the site, additional samples must be collected and analyzed for sulfentrazone, sulfentrazone 3-carboxylic acid, and bromide from all monitoring wells and, if applicable, any intact (i.e., which had no heavy erosion within a 5 meter radius) suction lysimeters remaining in the treated area. Sampling must be done for two intervals in 1995 (the interval is not critical, these data will serve only to provide a general indication of the long-term dissipation rate of sulfentrazone residues from soil water and ground water). In addition, any ground water or soil water samples that have been collected since 395 days after treatment and are in storage should be analyzed for these residues.

For the final report, in addition to the above data the following additional items should be included:

- (C.) All residue concentration data for sulfentrazone and degradates and for bromide should be submitted in electronic format such as dBASE, Microsoft Excel, Lotus 123, or Quattro Pro, and as an ASCII text file in addition to a hard copy with the final report.
- (D.) Compare the conditions of this study (regarding leaching potential) with conditions likely to be encountered in different years or with different irrigation practices at the same site. Also compare with conditions over the remainder of the intended use area. Identify, to the degree possible, areas where sulfentrazone leaching to ground water is most likely.
- (E.) Actual or predicted ground-water residue levels should be compared to dosages known to adversely affect plants and animals in ecological effect and mammalian toxicology studies.

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The Agency has not yet received any response from the registrant to our earlier recommendations made for this study in a May 14, 1992 review (DP Barcode D174353). Our original recommendations, the majority of which were not addressed in the present submission, are listed below:

- 1) It is mandatory that analyses be done for the 3-carboxylic acid degradate. EFGWB requires monitoring for all major metabolites.
- 2) The locations of the monitoring wells as proposed are unacceptable. It is necessary to place the monitoring wells on site in order to obtain the necessary monitoring-information.
- 3) The irrigation scheme proposed in the protocol is unacceptable. EFGWB generally recommends that irrigation and precipitation approximate 150 percent of the 30-year monthly average precipitation for the area unless an alternative irrigation schedule is suggested and approved. [Update: From the progress report, it does appear that the amount and timing of irrigation and rainfall at this site did indeed result in ground-water recharge and pesticide leaching potential well above that which would occur in an average year at the site.]
- 4) SULFENTRAZONE is a low application rate compound which exhibits a long persistence and high mobility. In order to adequately determine the amount of SULFENTRAZONE that may enter ground water, the application rate should be doubled to 2 times the maximum label rate (1.0 lb. a.i. per acre).
- 5) The method of soil sample compositing is acceptable for the 1 DAT sampling round as presented [In general, the registrant should be aware that compositing schemes may invalidate a study.]
- 6) The soil sampling method presented for 7 DAT to the end of the study is unacceptable. An alternative is presented in the body of the review.
- 7) Analyses for the bromide tracer must be done over the length of the study.
- 8) All samples must be analyzed for both SULFENTRAZONE and the metabolite 3-carboxylic acid. This includes all of the 0-6 inch soil samples from the 7 DAT sampling round.
- 9) The proposed method of ground-water sampling is partially acceptable. EFGWB prefers that ground-water samples be taken on the same days as the soil samples; i.e., also on Day 1, and Day 7 after application.

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- 10) The portion of the protocol that explains the soil-pore water sampling is acceptable, providing that any compositing of soil-pore water samples is done with the closest lysimeter clusters.
- 11) The study will be done on a site in the Southeast Coastal Plain; i.e., an area with probable high evaporation rates. For this reason, it is recommended that tensiometers be installed on the site at appropriate intervals to determine the matrix potential of the soil (water movement) during the growing season. One tensiometer should be placed below the crop root zone. In this case, approximately 2-3 feet below the surface. The placement of the second tensiometer will be determined by the depth to the top of the water table.
- 12) A large amount of lysimeter samples will be taken throughout the study. The registrant must verify that the test chemical does not adhere to the ceramic cup portion of the lysimeter before installation.
- 13) EPA approval must be obtained for the final study site.

## 9. BACKGROUND:

No background information on this study requirement was given in the registrant's report. However, a protocol for this study was previously reviewed by the Ground Water Technology Section (GWTS) on 5/14/92 (DP Barcode D174353). A number of recommendations were made in this review for modification of the protocol, please refer to the "Recommendations" section of this review as well as the earlier review of this study for more details on the recommendations made by GWTS.

The registrant apparently chose to begin this study without an approved protocol; they applied bromide tracer on 5/14/92 and sulfentrazone at 0.5 lb ai/A (1x the maximum label rate at that time, but 1.33x the current maximum rate, according to the registrant's study progress report) on 5/15/92. All monitoring wells were located off-site (albeit close to the treated area), contrary to the specific requirement for this study by the Agency that ground-water monitoring wells be located inside the treated area. Historically the Agency has never recommended that a study be conducted without any wells inside the treated area. Four piezometers were placed around the perimeter of the test site and used to monitor ground-water flow, however, nested tensiometers were apparently not installed as recommended by the Agency. All

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samples were analyzed for both sulfentrazone parent and sulfentrazone carboxylic acid, as requested by the Agency.

The study site selected was in Tarboro, Edgecombe County, North Carolina. The soil type and series were not specified. In four soil cores taken, the soil texture was generally a loamy sand near the surface, grading to a sand at lower depths (two cores were analyzed to a depth of about 11.5 feet and two others to a depth of 5 feet). Organic matter was about 1.2% in the upper six inches of soil.

On June 18, 1993 (about 13 months after the application of sulfentrazone) the traveling gun irrigation apparatus turned over while in operation and caused severe erosion in parts of the treated area. This accident was reported to GWTS in a telephone call; however, the registrant apparently did not follow-up on a request by GWTS to set up a meeting to discuss how to respond. The registrant states in the submitted progress report that they terminated all sample collection after 425 days, however, only the results of bromide and herbicide analyses of samples taken up to 395 days after treatment have been reported. As discussed briefly in the conclusions section of this review, sulfentrazone and its 3-carboxylic acid degradate readily leached to ground water under the conditions of this study.

## 10. DISCUSSION:

A detailed review of this study will be conducted when the final report is submitted. This study does provide information on the leaching of sulfentrazone to shallow ground water overlain by highly permeable, sandy soils. In this study, about 27 inches of rain and irrigation water reached the site in the first four months after application; 62 inches reached the site by 13 months after application. Sulfentrazone residues persisted over the entire 13-month period for which sampling data have been submitted with this progress report. Amounts of sulfentrazone leaching were substantial relative to the application rate. Residues of parent plus acid reached the following maximum concentrations in soil water (average of replicates):

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Lysimeter depth, feet	Days after application	Total residues (parent + acid), ppb	Sulfentrazone concentration, ppb
3	124	100.8	15.1
5	186	30.7	15.1
7	214	25.3	12.3

By the last sampling date analyzed so far (395 days after application) residues of parent + acid averaged about 10 ppb in soil-pore water from all three depths. This was a 10-fold decline from peak concentrations (at the 3- and 7-foot depths, respectively) that had occurred several months earlier.

A similar pattern occurred in ground water with the peak concentrations of sulfentrazone residues occurring about four to five months after application.

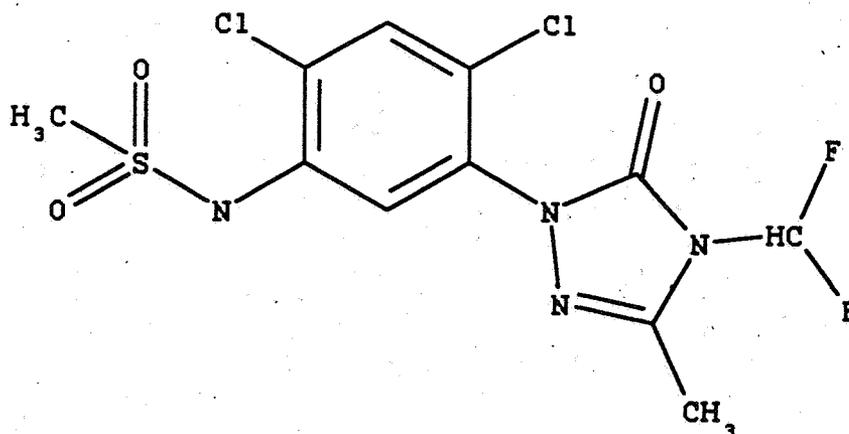
Well depth / timing	Days after application	Total residues (parent + acid), ppb	Sulfentrazone concentration, ppb
Shallow, max.	124	42.2	37.4
Shallow, final	395	13.3	7.2
Deep, maximum	160	30.6	19.2
Deep, final	395	9.3	5.1

Apparently, much of the applied sulfentrazone had moved through the soil profile within several months after application and the amount of residues leaching had declined by 13 months after application, when the last sample was taken. However, there were still significant amounts of sulfentrazone residues (parent and acid degrade) remaining in soil water at all depths sampled 13 months after treatment.

Because of the high persistence of sulfentrazone residues, their partition primarily into the soil pore water, and the relatively rapid recharge of the aquifer that occurred, residues were detected in downgradient wells (which were located outside of the treated area). Unfortunately, among the Agency recommendations that were not followed for this study were those concerning the location of the monitoring wells. The registrant located 3 of

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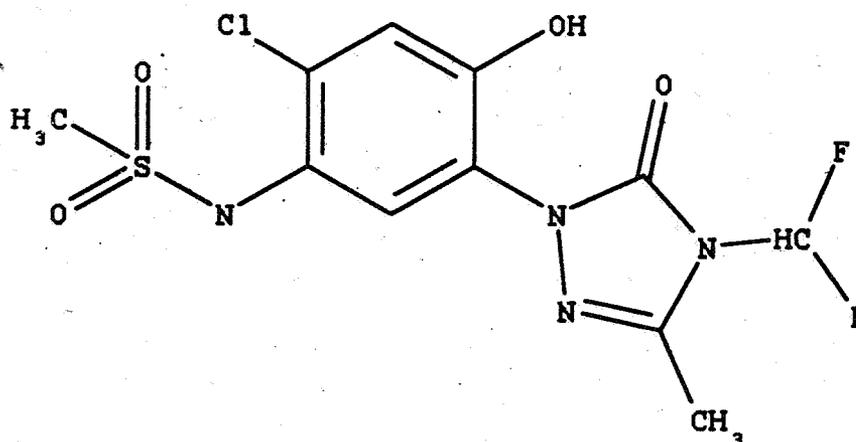
their 5 well clusters entirely upgradient of the treated area, so in reality their design consisted of three control well clusters and two monitoring well clusters. Furthermore, only a small fraction of the treated area was upgradient of one of the two monitoring well clusters. As would be expected, tracer and herbicide residues in this cluster were substantially lower than in the single well cluster that was wholly downgradient from the treatment area. Since no wells were located on site, it cannot be determined what concentrations of sulfentrazone and its degradates were present at the point of entry of the leachate into the saturated zone.



N-(2,4-Dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide

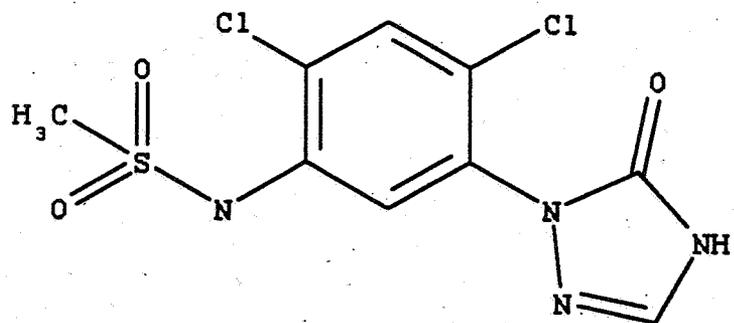
(Methanesulfonamide; F6285)

*Sulfentrazone*

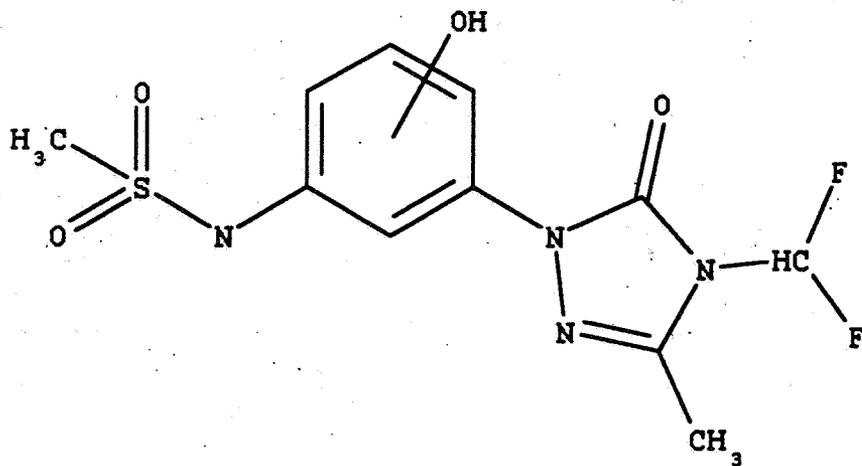


2-Hydroxy-4-chloro F6285

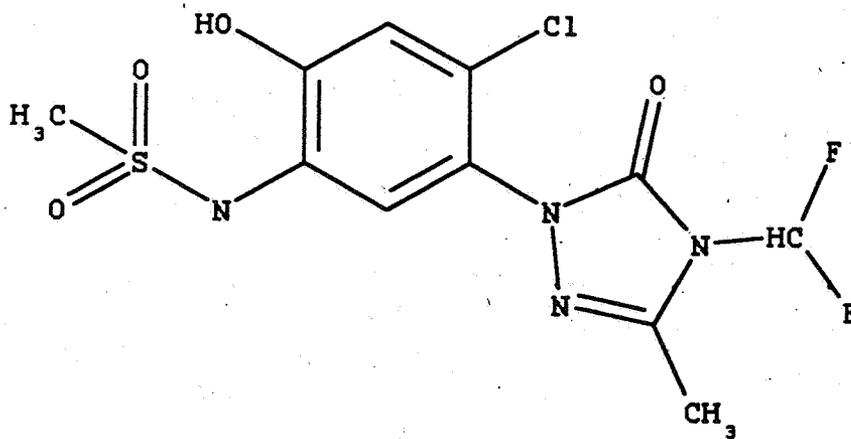
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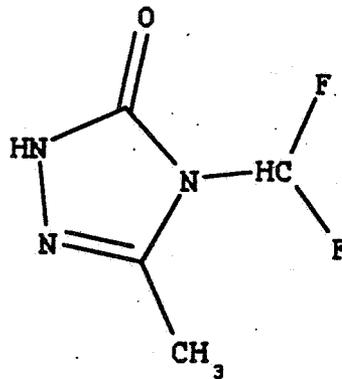
N-[2,4-Dichloro-5-(4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]methanesulfonamide  
(3-Desmethyl-4-desdifluoromethyl F6285)



Desdichloromonohydroxy F6285

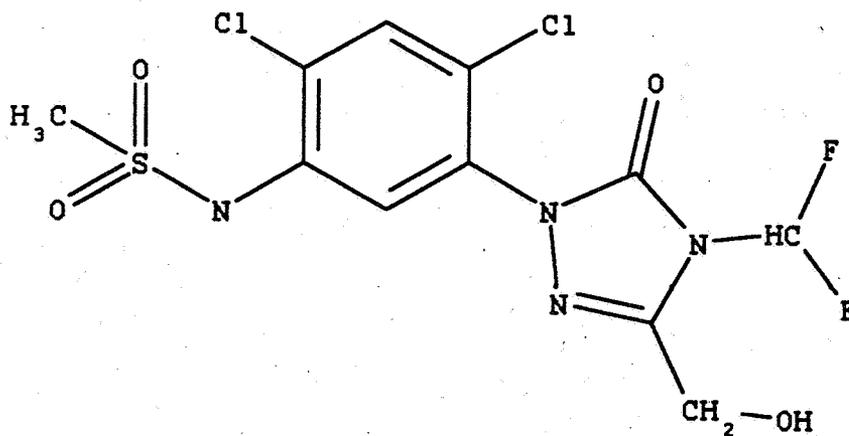


2-Chloro-4-hydroxy F6285



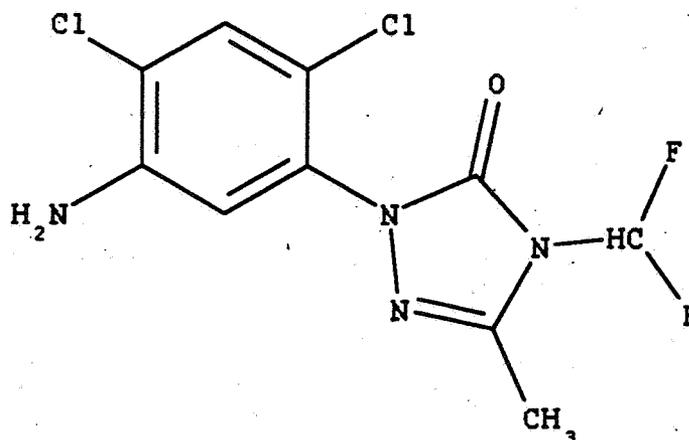
"Photodegradate 4C"

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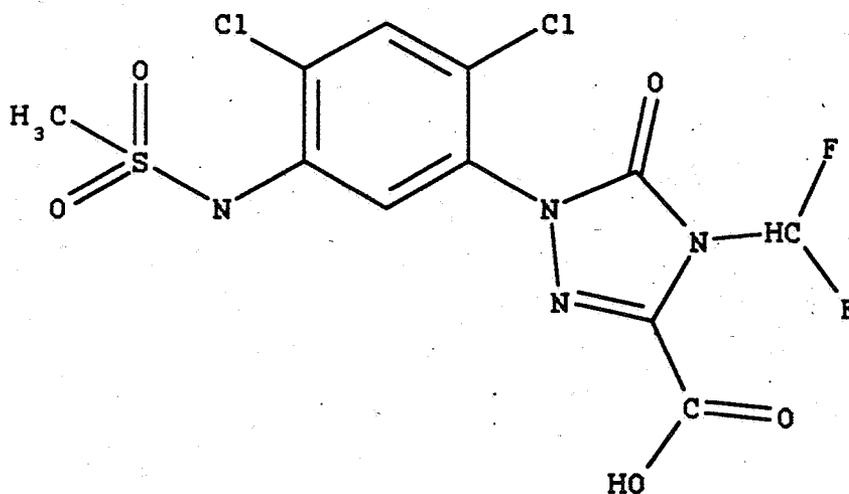
N-(2,4-Dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-hydroxymethyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonamide

(3-Hydroxymethyl F6285)



1-(2,4-Dichloro-5-aminophenyl)-4-difluoromethyl-3-methyl-1H-1,2,4-triazol-5(4H)-one

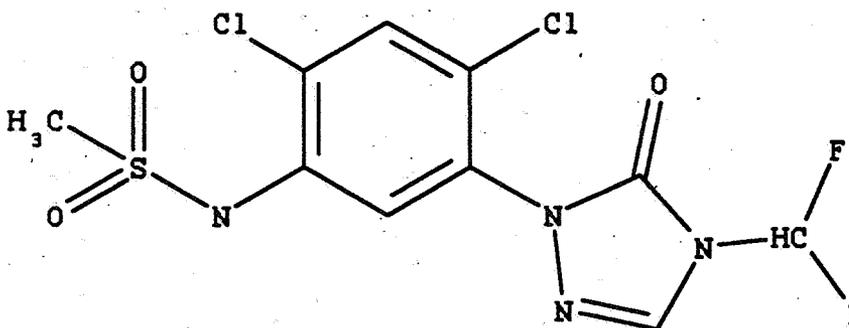
(Desmethyl sulfonyl-F6285)



**N-(2,4-Dichloro-5-[N-(methylsulfonyl)amino]phenyl)-4-difluoromethyl-4,5-dihydro-5-oxo-1H-1,2,4-triazol-3-carboxylic acid**

**N-(2,4-Dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonylamido-3-carboxylic acid**

**(3-Carboxylic acid F6285)**



**N-(2,4-Dichloro-5-[4-(difluoromethyl)-4,5-dihydro-5-oxo-1H-1,2,4-triazol-1-yl]phenyl)methanesulfonylamide**

**(3-Desmethyl F6285)**

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