

US EPA ARCHIVE DOCUMENT

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Date Out of EAB: MAR 27 1987

To: R. Taylor
Product Manager 25
Registration Division (TS-767)

From: T. Dougherty, Acting Chief
Review Section #
Exposure Assessment Branch
Hazard Evaluation Division (TS-769) *TD*

Attached, please find the EAB review of...

Reg./File # : 476-EEFL and -EEEA, 476-EUP-RNE, 476-EUP-RNG
Chemical Name: Sulfosate
Type Product : Herbicide
Product Name : Touchdown, SC-0224 Concentrate, SC-0224 4-LC
Company Name : Stauffer Chemical Company
Purpose : New chemical, request registration of product for use on non-crop areas (terrestrial nonfood and domestic outdoor)

Action Code(s): 701, 121
Date Received: 7/2/86 & 1/28/87
Date Completed: MAR 27 1987
Total EAB Reviewing Time: 1.0 days

EAB #(s) : 60707, 60708, 70214, 70215
TAIS Code: _____
Monitoring submitted: _____
Monitoring requested: _____

Deferrals to: _____ Ecological Effects Branch
_____ Residue Chemistry Branch
X _____ Toxicology Branch

INERT INGREDIENT INFORMATION IS NOT INCLUDED

1. CHEMICAL: Common name:

Sulfosate

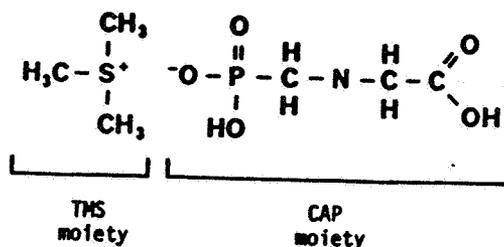
Chemical name:

Trimethylsulfonium carboxymethylaminomethylphosphonate

Trade name(s):

Touchdown, SC-0224 Concentrate, SC-0224 4-LC

Structure:



Formulations:

5 lb/gal (52.2%) concentrate, 4 lb/gal (40.8%) LC

Physical/Chemical properties:

Physical state: Liquid.

Color: Brown.

Odor: Faint, characteristic of sulfur-containing compounds.

Boiling point: 110°C at 760 Torr.

Density: 1.27 g/cc.

Vapor pressure: 8.2 torr at 10°C, 14.6 torr at 20°C,
24.9 torr at 30°C, 41.3 torr at 40°C,

Vapor pressure

of the active ingredient: $<4 \times 10^{-7}$ torr at 25°C.

pH: 3.5-5.0 (1 g in 20 mL water).

Viscosity: 38.2 centistokes at 25°C.

Molar water solubility

[pure active ingredient]: 17.6×10^6 g.

K_{ow} [pure active ingredient]: $<<10$ [no sulfosate was detected (<0.1 ppm) in the octanol phase].

2. TEST MATERIAL:

See individual studies.

3. STUDY/ACTION TYPE:

Stauffer Chemical Co. is seeking registration of sulfosate for weed control in terrestrial nonfood and domestic outdoor use sites.

4. STUDY IDENTIFICATION:

The following studies were reviewed as new or amended submittals:

Katague, D.B., G.G. Patchett, and M.G. Kleinschmidt. 1985. Residue analytical method: Determination of SC-0224 cation residues in crops, water, and soil by gas chromatography. RRC 85-33. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-06.

Kleinschmidt, M.G. 1986. Addendum to: SC-0224 4-LC field dissipation study. Prepared and submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-05.

Lee, K.S. 1986. Solubility and octanol/water partition coefficient of aminomethylpropionic acid. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-03.

McGahan, L. 1986. Addendum to: The photodegradation of SC-0224 applied to soil. Laboratory Project PMS-137, MRC-83-09. Prepared and submitted by Stauffer Chemical Company, Mountain View, CA. Acc. No. 400462-04.

Patchett, G.G., D.B. Katague, and M.G. Kleinschmidt. 1985. Residue analytical method: Determination of SC-0224 anion residues in crops, soil, and water by liquid chromatography. WRC 85-34. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-07.

Schwab, G.W. 1986. Frozen storage stability of Touchdown in soil. Project RRC 86-61. Prepared and submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-08.

Spillner, C.J., S. Carley, and I. Neeman. 1986. SC-0224 aged soil mobility study. Laboratory Project ID PMS-205, MRC-86-02. Unpublished study prepared and submitted by Stauffer Chemical Company, Mountain View, CA. Acc. No. 263552.

5. REVIEWED BY:

T. Dougherty
Chemist
EAB/HED/OPP

Signature:

Theresa M. Dougherty

Date:

3/27/87

6. APPROVED BY:

T. Dougherty
Acting Chief
Review Section #1, EAB/HED/OPP

Signature:

Theresa Dougherty

Date:

3/27/87

7. Conclusions:

- See individual studies.
- In sand soil, the trimethylsulfonium moiety was mobile based on soil TLC studies for aged (3-day) residues.
- In the terrestrial field dissipation study, samples were taken only to a depth of 6 inches, which was not adequate to establish the depth of leaching. In some soils, significant residues of the CAP anion, TMS cation and AMP were detected at 3-6" depth from 91 to 189 days.
- Protective Clothing and Reentry issues will be addressed by EAB within the next two weeks.

8. Recommendations:

Unless Toxicology Branch disagrees, EAB recommends Conditional Registration of sulfosate with the provision that acceptable Soil Field Dissipation data be submitted to demonstrate the depth of leaching of sulfosate residues in sandy soil.

If Conditional Registration is granted, we recommend a label restriction, such as that noted below, concerning leaching potential.

GROUND WATER ADVISORY

Residues of Touchdown can seep or leach through soil and can contaminate ground water which may be used as drinking water. Users are advised not to apply Touchdown where the water table (ground water) is close to the surface and where the soils are very permeable, i.e., well-drained soils such as loamy sands. Your local agricultural agencies can provide further information on the type of soil in your area and the location of ground water.

Labeling changes and/or Reentry studies may be necessary pending evaluation of Protective Clothing and Reentry issues by EAB.

- 7. CONCLUSIONS:
- 8. RECOMMENDATIONS:
- 9. BACKGROUND:

A. Introduction

INFORMATION ON PREVIOUSLY REVIEWED STUDIES

Environmental fate data requirements to support terrestrial nonfood and domestic outdoor uses of sulfosate are summarized in the table below. The registrant has removed the forestry use from the label.

| | Terrestrial nonfood | Domestic outdoor |
|------------------------------------|---------------------|------------------|
| Hydrolysis | pa | R |
| Aqueous photolysis | R | - |
| Aerobic soil metabolism | R | R |
| Leaching and adsorption/desorption | R | R |
| Field dissipation | R | R |
| Fish accumulation | CR ^b | - |

^a Required.

^b Conditionally required.

The present status of each data requirement is summarized below:

Hydrolysis

The hydrolysis study was originally reviewed on 8/18/83 in connection with an EUP request and found to be unacceptable. However, the data requirement was satisfied in a subsequent submission (3/1/84). Hydrolysis of sulfosate was determined to be essentially nonexistent at pH 5-9.

Photodegradation in Water

The aqueous photolysis data requirement was satisfied in a previous submission (3/1/84). The carboxymethylaminomethylphosphonate (CAP) anion had half-lives of 14.6, 77.9, and 41.6 days at pH 5, 7, and 9, respectively. Photoproducts were phosphoric acid and aminomethylphosphonic acid. The trimethylsulfonium (TMS) cation was stable at pH 5 and 7, but degraded with a half-life of 31.7 days at pH 9.

Photodegradation on Soil

The photodegradation on soil study was originally reviewed on 1/21/86 and found to be unacceptable. Additional data that were

requested by EAB have been submitted and are evaluated in the attached report.

Aerobic soil metabolism

The aerobic soil metabolism data requirement was satisfied by two studies in a previous submission (6/30/86). One study, using sulfosate labeled only on the TMS moiety, demonstrated that TMS had a half-life of about 3 days in soil and CO₂ was the major degradate. However, an unknown of approximately 14% of the applied and a recovery of 73% at the end of the study represent gaps in the understanding of the fate of TMS. Soil bound [¹⁴C]residues peaked at about 20% of the applied at day 8 and then slowly decreased.

Extractable [¹⁴C]residues declined from about 60% of the applied at day 0 to ~6% at day 10 (most of which was parent TMS). During the first week, approximately 50% of the applied radioactivity was evolved as ¹⁴CO₂. After 211 days, 75% of the applied radioactivity had been volatilized. Recoveries ranged from 73% to 87% of the ¹⁴C initially applied. Small scale studies, which had different temperature conditions from the large study, were used to identify the [¹⁴C]residues. In the small scale studies, most of the extractable [¹⁴C]residues (which declined from 75.3% of the applied at day 0 to 27.1% at day 4) were recovered from the ammonium formate fraction which contained only parent TMS. The acetone fraction contained about 0.5% TMS over the same time period, but also contained an unknown ¹⁴C residue that peaked at 14-17% of the applied radioactivity at 4 days and declined to about 1% of the applied at 6 days. Recoveries from the small scale studies indicated that combustion of wet soils (as opposed to dry soils in the large study) gave a more accurate determination.

The second study, using sulfosate labeled only on the CAP moiety, demonstrated that the CAP half-life was ~2-3 days. In the study, the extractable residues declined from about 57% of the applied at day 0 to 14% at day 30. Soil-bound residues were 40% of the applied initially and declined to 18% at day 30. At day 30 about 60% of the applied had been evolved as ¹⁴CO₂. Recovery was 91-102% for the one year duration of the study. Identification of residues was made in a small scale study and showed CAP comprised 78% of the applied at day 0 (97% of the extractable residues) and 8% at day 21. The degradate aminomethylphosphonic acid (AMPA) comprised 0.4% of the applied at day 0 and 15.4% (57% of the extractable residues) at day 21. The extractable [¹⁴C]residues from the large study declined from 30% of the applied at day 9 to 14% at day 30 and 8% at day 76, indicating that AMPA probably increased slightly after day 21 for a short period and then decreased following the rate of decline of the extractable [¹⁴C]residues (qualitative determinations were not made after day 21).

Soil Mobility

The soil TLC study of unaged sulfosate was originally reviewed on 8/18/83 in connection with an EUP request and found to be accept-

able. The study indicated low mobility of the parent compound in soil. It only partially satisfies the leaching and adsorption/desorption data requirements for purposes of registration because the mobility of residues obtained from soil aged aerobically with the parent was not tested. An aged leaching study has been submitted and is reviewed in this report.

Field Dissipation

The field dissipation study was originally reviewed on 1/17/86 and found to be unacceptable. Additional data that were requested by EAB have been submitted and are evaluated in the attached report.

Fish Accumulation

This data requirement has been waived for the active ingredient (3/1/84) based on the high water solubility and low K_{ow} of sulfosate. Data on the solubility and octanol/water partition coefficient for aminomethylphosphonic acid (AMPA) have been submitted and are evaluated in the attached report.

B. Directions for Use

Sulfosate is a herbicide developed to be applied postemergent at 0.44-4.1 lb ai/A to control actively growing weeds. Spray, wiper, and hand-directed spot applications are proposed. For spray applications, the product is to be mixed with surfactant (2:1) and applied in 10-30 gal water/A or in 12 gal/A if applied by Controlled Droplet Application equipment. For wiper application, two parts product are to be mixed with one part surfactant and six parts water. For hand-directed spot application, two parts of a 1-3% solution of the product in water are to be mixed with one part surfactant.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See attached report.

11. COMPLETION OF ONE-LINER:

A one-liner is on file.

12. CBI APPENDIX:

All data reviewed here are considered CBI by the registrant and must be treated as such.

SULFOSATE

Initial Draft Report

**Task 1: Review and Evaluation of
Individual Studies**

**Task 2: Environmental Fate and
Exposure Assessment**

Contract No. 68-02-4250

MARCH 27, 1987

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
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Rockville, MD 20852

SULFOSATE

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INTRODUCTION

Sulfosate is a herbicide developed to be applied postemergent at 0.44-4.1 lb ai/A to control actively growing weeds. Spray, wiper, and hand-directed spot applications are proposed. For spray applications, the product is to be mixed with surfactant (2:1) and applied in 10-30 gal water/A or in 12 gal/A if applied by Controlled Droplet Application equipment. For wiper application, two parts product are to be mixed with one part surfactant and six parts water. For hand-directed spot application, two parts of a 1-3% solution of the product in water are to be mixed with one part surfactant.

CASE GS -- SULFOSATE STUDY 1 PH --

CHEM 128501 Sulfosate

BRANCH EAB DISC --

FORMULATION 01 - TECHNICAL CHEMICAL (TECH)

FICHE/MASTER ID No MRID CONTENT CAT 01
 McGahen, L. 1986. Addendum to: The photodegradation of SC-0224 applied to soil. Laboratory Project PMS-137, MRC-83-09. Prepared and submitted by Stauffer Chemical Company, Mountain View, CA. Acc. No. 400462-04.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 (MH) START-DATE END DATE

REVIEWED BY: K. Patten
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APPROVED BY: T. Dougherty
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 ORG: EAB/HED/OPP
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SIGNATURE: *T. Dougherty*

DATE: 3/27/87

CONCLUSIONS:

Degradation - Photodegradation on Soil

Sulfosate (technical grade, 54% ai) was applied at 30 ppm to loamy sand soil TLC plates and irradiated outdoors with natural sunlight for 24 days. Following irradiation, the carboxymethylaninomethylphosphonate (CAP) anion and the trimethylsulfonium (TMS) cation were analyzed separately (Table 1). The CAP anion degraded with an initial rapid phase of ~12 days during which ~34% of the applied degraded followed by a slow phase during which only ~6% degraded during the remaining 12 days; the calculated half-life was ~48 days (assuming ~8 hours of sunlight per day). The formation of aminomethylphosphonic acid (AMPA) was directly related to the degradation of the CAP anion; together they accounted for 80-97% of the applied. In the dark controls, 84% of the CAP anion remained undegraded at 24 days posttreatment, but no AMPA was detected. The TMS cation was stable during 24 days of irradiation.

In the previous review of this study (EAB, 1/21/86, Acc. No. 258400), the acceptance of the study was withheld until the following information was supplied: method validation data (accuracy, precision, etc.); data

indicating the stability of CAP, AMPA, and TMS in frozen storage; and data indicating whether dimethylsulfide (DMS) was formed in the soil during irradiation (i.e., prior to the dealkylation step during analysis for TMS).

The method validation and frozen storage stability data have been provided and are reviewed as Studies 5, 6, and 7 in this report. Concerning the formation of dimethylsulfide, the registrant has responded that the analytical method used (extraction with 0.5 M ammonium hydroxide) would not extract dimethylsulfide. To confirm this claim, the registrant applied dimethylsulfide at 2 and 4 ppm to loamy sand soil, then extracted the samples under the conditions used in the original experiment. No dimethylsulfide was detected in the extract. Also, the registrant contends that if any dimethylsulfide had formed during irradiation, it would have volatilized from the soil at the temperatures that existed during the photodegradation study (25-35°C). Also, the registrant states that reexamination of the original analytical data for TMS revealed that the correction factor for recovery had not been applied to the TMS result, and, in fact, recovery from the irradiated soil averaged 95.4% of the applied on day 24; therefore, dimethylsulfate may not have been detected in the sample because the parent TMS did not degrade.

This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of sulfosate on soil.

Table 1. Sulfosate and its degradates (% of the applied) in loamy sand soil treated with sulfosate (54% TECH) at 30 ppm and irradiated outdoors with natural sunlight at 25-35°C.^a

| Sampling interval (days) | CAP moiety ^b | | TMS moiety ^c |
|--------------------------|-------------------------|--------------------|-------------------------|
| | CAP anion | AMPAD ^d | TMS cation |
| <u>Irradiated</u> | | | |
| 0 | 98.8 | 4.8 | 105.6 |
| 0.75 | 92.8 | 4.1 | 97.4 |
| 1.50 | 92.0 | 5.2 | 102.8 |
| 2.25 | 83.1 | 6.3 | 102.3 |
| 4.50 | 74.9 | 9.6 | 103.6 |
| 6.00 | 75.9 | 12.5 | 96.0 |
| 12.0 | 64.3 | 16.2 | 123.9 |
| 18.0 | 62.6 | 19.9 | 72.4 |
| 24.0 | 59.7 | 24.3 | 95.4 |
| <u>Dark control</u> | | | |
| 0 | 93.2 | ND ^e | 103.2 |
| 0.75 | 93.2 | 1.5 | 101.2 |
| 1.50 | 93.2 | ND | 100.0 |
| 2.25 | 85.3 | ND | 95.8 |
| 4.50 | 91.6 | ND | 111.4 |
| 6.00 | 91.1 | ND | 84.2 |
| 12.0 | 87.0 | 8.1 | 132.5 |
| 18.0 | 89.4 | ND | 67.8 |
| 24.0 | 84.1 | ND | 88.9 |

^a Data are corrected for recovery from fortified samples.

^b Carboxymethylaminomethylphosphonate moiety.

^c Trimethylsulfonium moiety.

^d Aminomethylphosphonic acid.

^e Not detected; the detection limit was 0.1 ppm.

CASE GS -- SULFOSATE STUDY 2 PM --

CHEM 128501 Sulfosate

BRANCH EAR DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01
Spillner, C.J., S. Carley, and I. Neeman. 1986. SC-0224 aged soil mobility study. Laboratory Project ID PMS-205, MRC-86-02. Unpublished study prepared and submitted by Stauffer Chemical Company, Mountain View, CA. Acc. No. 263552.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: R. Tamma
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ORG: EAB/HED/OPP
TEL: 557-0335

SIGNATURE: *T. Dougherty*

DATE: 3/27/87

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Aged (3-day) [¹⁴C]sulfosate residues were immobile to mobile in two loam, one sand, and one clay loam soils, based on soil TLC. The carboxymethylaminomethylphosphonate moiety and its sole degradate, aminomethylphosphonic acid, were immobile ($R_f < 0.02$) in all four soils. The trimethylsulfonium moiety (which produced no extractable degradates) was immobile ($R_f < 0.08$) in the two loam soils, slightly mobile ($R_f < 0.14$) in the clay loam soil, and mobile ($R_f < 0.66$) in the sand soil.
3. This study contributes towards the fulfillment of EPA Data Requirements for Registering Pesticides by providing information on the mobility of aged sulfosate residues in four soils.

MATERIALS AND METHODS:

Sorrento loam soil (Table 1) was air-dried, sieved, and transferred

(50-g samples) to four serum bottles. [^{14}C -CAP]sulfosate (labeled in the carboxymethylaminomethylphosphonate moiety, radiochemical purity 98%, specific activity 30 mCi/mmol, Stauffer Chemical Company) was added to two bottles at 20 ppm; [^{14}C -TMS]sulfosate (labeled in the trimethylsulfonium moiety, radiochemical purity 99.7%, specific activity 20 mCi/mmol, Stauffer Chemical Company) was added to the remaining two bottles at 27 ppm. The soils were moistened to 75% of their water-holding capacity, and a tube containing a 1 M KOH trapping solution was placed in each flask. The flasks were incubated aerobically for 3 days at 20-28°C. Aliquots of each trapping solution were analyzed for total radioactivity by LSC. The soils were extracted three times with water by shaking (15 minutes); the resulting extracts were not combined, but analyzed separately. All extracts were concentrated by evaporation, and aliquots of the extracts were analyzed by TLC on silica gel plates developed in either 0.1 M ammonium formate:methanol (3:1; CAP label) or 10% methylamine HCl: methanol (1:1; TMS label). Radioactive areas were located using autoradiography and quantified by LSC. Radioactive compounds were identified by comparison to unlabeled standards that were co-chromatographed with the samples.

Four soils ranging in texture from sand to clay loam (Table 1) were used in preparing soil TLC plates (0.5-mm thickness). Duplicate air-dried plates were each spotted with either the extracts from the [^{14}C -CAP]sulfosate treated soil or the extracts from the [^{14}C -TMS]sulfosate-treated soil, and with the appropriate standards. The plates were air-dried overnight, then developed in distilled water to a distance 12-15 cm from the origin. After development, the plates were air-dried, visualized using autoradiography, and quantified using TLC linear scanning and/or LSC.

REPORTED RESULTS:

Aged (3-day) [^{14}C]sulfosate residues were immobile to mobile in two loam, one sand, and one clay loam soils, based on soil TLC (Table 2). The carboxymethylaminomethylphosphonate moiety and its sole degradate, aminomethylphosphonic acid, were immobile ($R_f < 0.02$) in all four soils (Table 3). The trimethylsulfonium moiety (which produced no extractable degradates) was immobile ($R_f < 0.08$) in the two loam soils, slightly mobile ($R_f < 0.14$) in the clay loam soil, and mobile ($R_f < 0.66$) in the sand soil.

DISCUSSION:

1. [^{14}C -CAP]Sulfosate and [^{14}C -TMS]sulfosate were initially aged for 3 days, one half-life, <21% of the applied sulfosate remained undegraded.
2. The CEC's of Keeton loam, Felton sand, and Prairie clay loam soils were not provided.
3. The variability in R_f values (0.06-0.70) obtained from TLC plates of Felton sand soil for TMS-sulfosate was stated by the registrant to be an anomaly due to the low clay content of sandy soil that permitted mobility of [^{14}C]TMS-sulfosate with a paired unknown ion; however, no data were provided to support this statement.

4. Since sulfosate has a half-life of <3 days in soil, the TLC mobility method may have been inappropriate because considerable additional aging may have occurred when the plates were dried overnight, developed with water, and again dried after development in water--a lengthy process which could have allowed sulfosate to degrade further.
5. The detection limit was not reported.

Table 1. Soil characteristics.

| Soil type | Sand | Silt | Clay | Organic matter | pH | CEC (meq/100 g) |
|-------------------|------|------|------|----------------|-----|-----------------|
| | % | | | | | |
| Keeton loam | 44.0 | 42.5 | 13.5 | 1.4 | 6.6 | -- |
| Sorrento loam | 48.0 | 33.5 | 18.5 | 2.5 | 7.1 | 22.4 |
| Felton sand | 87.5 | 8.3 | 4.2 | 2.9 | 6.9 | -- |
| Prairie clay loam | 35.2 | 26.4 | 38.4 | 4.1 | 6.2 | -- |

Table 2. Mobility parameters (R_f and Freundlich K_{ads}) of [^{14}C -CAP]-sulfosate and [^{14}C -TMS]sulfosate residues on four soils.

| Label Position | Extract | Keeton loam | Sorrento loam | Felton sand | Prairie clay loam |
|-------------------------|---------|-------------|---------------|-------------|-------------------|
| R_f^a | | | | | |
| [^{14}C -CAP] | 1 | 0.00 | 0.02 | 0.02 | 0.02 |
| | 2 | 0.00 | 0.00 | 0.02 | 0.01 |
| | 3 | 0.00 | 0.00 | 0.02 | 0.02 |
| [^{14}C -TMS] | 1 | 0.04 | 0.08 | 0.54 | 0.14 |
| | 2 | 0.00 | 0.00 | 0.66 | 0.02 |
| | 3 | 0.00 | 0.00 | 0.08 | 0.00 |
| K_{ads} | | | | | |
| [^{14}C -CAP] | 1 | -- | 30 | 25 | 49 |
| | 2 | -- | -- | 25 | 74 |
| | 3 | -- | -- | 25 | 49 |
| [^{14}C -TMS] | 1 | 27 | 14 | 0.94 | 11 |
| | 2 | -- | -- | 0.68 | 36 |
| | 3 | -- | -- | 17 | -- |

^a Average of duplicate samples; K_{ads} values could not be averaged but are reported for the most mobile sample.

Table 3. Distribution of radioactivity (% of applied) from a loam soil treated with either [¹⁴C-CAP]sulfosate at 20 ppm or [¹⁴C-TMS]-sulfosate at 27 ppm after aging for 3 days at 20-28°C.

| Label position | Extractable | | | | | | Unextractable | Volatile |
|------------------------|----------------|------|------|-------------------------|------|------|---------------|----------|
| | Parent | | | Degradates ^a | | | | |
| | 1 ^b | 2 | 3 | 1 | 2 | 3 | | |
| [¹⁴ C-CAP] | 2.11 | 1.71 | 1.89 | 0.65 | 0.94 | 1.57 | 41.1 | 17.3 |
| | 1.96 | 2.09 | 2.27 | 0.61 | 0.83 | 1.25 | 41.8 | 20.6 |
| [¹⁴ C-TMS] | 12.96 | 4.22 | 2.50 | ND ^c | ND | ND | 56.7 | 1 |
| | 13.73 | 4.25 | 2.8 | ND | ND | ND | 56.2 | 0.2 |

^a The carboxymethylaminomethylphosphonate moiety degraded to aminomethylphosphonic acid (AMPA).

^b The soil was extracted three times with water; the extracts were not combined.

^c Not detected; the detection limit was not reported.

CASE GS -- SULFOSATE STUDY 3 PM --

CHEM 128501 Sulfosate

BRANCH EAB DISC --

FORMULATION 15 - SOLUBLE CONCENTRATE/LIQUID (SC/L)
-----FICHE/MASTER ID No MRID CONTENT CAT 01
Kleinschmidt, M.G. 1986. Addendum to: SC-0224 4-LC field dissipation study.
Prepared and submitted by Stauffer Chemical Company, Richmond, CA. Acc. No.
400462-05.-----
SUBST. CLASS = S.-----
DIRECT REV TIME = 8 (MH) START-DATE END DATE
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-----APPROVED BY: J. Dougherty
TITLE: Chemist
ORG: EAB/HEN/OPP
TEL: 557-0335
-----SIGNATURE: *J. Dougherty*

DATE: 3/27/87

CONCLUSIONS:Field Dissipation - Terrestrial

Sulfosate (4 lb/gal LC) was applied at 6 lb ai/A to field plots located in Virginia, California, Iowa, and Florida. The carboxymethylamino-methylphosphonate (CAP) anion and the trimethylsulfonium (TMS) cation were analyzed separately at intervals up to 189 days posttreatment (Table 1). The soils were also analyzed for aminomethylphosphonic acid (AMPA), a degradate of CAP anion. In Virginia, the CAP anion degraded with a half-life of <7 days in the 0- to 3-inch depth soil while its degradate, AMPA, was variable, ranging from <0.1 to 1.40 ppm during the 60-day study. The TMS cation was not detected during the study. In the California, Iowa, and Florida studies, significant residues of the CAP anion, TMS cation, and AMPA, occurred in both the 0- to 3-inch and 3- to 6-inch depth soil samples. Half-life values for the CAP anion were 23.2-25.8 days and for the TMS cation were 29.6-50.4 days. AMPA half-life values were 91.6 days in California and 82.8 days in Iowa. (AMPA residues in the FL study increased throughout the sampling period).

In the previous review of the Virginia study (EAB, 1/17/86, Acc. No. 250548), it was concluded that the study could not satisfy data require-

ments for field dissipation because: details of the analytical methods were not provided; no storage stability data were provided; and no acceptable aerobic soil metabolism study was available to determine whether AMPA was the sole soil degradate for which analysis is required. In the previous review of the California, Iowa, and Florida studies (EAB, 1/21/86, Acc. No. 258400), it was concluded that the studies could not satisfy environmental fate requirements for field dissipation because: details of the analytical methods were not provided; no storage stability data were provided; no acceptable aerobic soil metabolism study was available to determine whether AMPA was the sole soil degradate for which analysis is required; rainfall and irrigation data were incomplete; and samples were taken from an insufficient depth to determine the potential for leaching into groundwater.

The registrant has provided the method validation data and frozen storage stability data requested; these are reviewed as studies 5, 6, and 7 in this report. Aerobic metabolism studies (EAB, 6/30/86, Acc. No. 260670) that have been accepted to fulfill data requirements demonstrated that aminomethylphosphonic acid (AMPA) is the primary extractable degradate. Rainfall and irrigation data for the California, Iowa, and Florida sites are presented in Table 1 (data for the Virginia site were not requested by EAB). These responses by the registrant appear to be sufficient to address some of the concerns of EAB. However, data from the aged sulfosate leaching study indicate that the TMS cation is mobile in sand soil. Therefore, a study is still needed to define the potential of sulfosate and its degradates to leach under actual use conditions.

Table 1. Sulfosate and its degradates (ppm) in field plots in Virginia, California, Iowa, and Florida that were treated with sulfosate (4 lb/gal LC) at 6 lb ai/A.

| Sampling interval (days) | CAP moiety | | | | TMS moiety | | Cumulative precipitation (inches) |
|--------------------------|------------|------|------|------|-----------------|-------|-----------------------------------|
| | CAP | | AMPA | | TMS | | |
| | 0-3" | 3-6" | 0-3" | 3-6" | 0-3" | 3-6" | |
| <u>Virginia</u> | | | | | | | |
| 0 | 0.64 | -- | 0.51 | -- | ND ^a | -- | -- |
| 1 | 0.49 | -- | <0.1 | -- | ND | -- | -- |
| 2 | 0.09 | -- | 0.21 | -- | ND | -- | -- |
| 7 | 0.10 | -- | 0.22 | -- | ND | -- | -- |
| 14 | 0.19 | -- | 0.35 | -- | ND | -- | -- |
| 30 | 0.19 | -- | 1.49 | -- | ND | -- | -- |
| 60 | 0.75 | -- | 0.70 | -- | ND | -- | -- |
| <u>California</u> | | | | | | | |
| 0 | 15.7 | ND | 4.5 | ND | 8.20 | ND | -- |
| 7 | 6.5 | ND | 2.27 | ND | 4.45 | ND | 0.73 |
| 14 | 5.6 | ND | 1.98 | ND | 3.15 | ND | 0.73 |
| 28 | 1.35 | ND | 1.38 | 0.11 | 2.78 | ND | 6.73 |
| 61 | 0.48 | 0.81 | 0.46 | 0.44 | 1.64 | 0.26 | 6.73 |
| 91 | 0.20 | 0.77 | 0.28 | 1.88 | 1.18 | 0.66 | 12.73 |
| <u>Iowa</u> | | | | | | | |
| 0 | 0.92 | 0.16 | 0.38 | 0.10 | 1.2 | 0.21 | -- |
| 7 | 1.8 | ND | 1.48 | ND | 0.96 | 0.15 | 0.55 |
| 14 | 0.86 | 0.05 | 1.33 | 0.08 | 0.80 | 0.17 | 0.55 |
| 28 | 1.29 | ND | 2.77 | ND | 0.75 | ND | 1.05 |
| 63 | 0.19 | ND | 1.13 | 0.09 | 0.22 | 0.15 | 8.00 |
| 84 | ND | ND | 0.62 | 0.07 | <0.15 | <0.15 | 8.10 |
| 189 | ND | ND | 0.19 | ND | 0.19 | 0.19 | 15.20 |
| <u>Florida</u> | | | | | | | |
| 0 | ND | ND | ND | ND | ND | ND | -- |
| 7 | 1.59 | 0.25 | 0.68 | 0.05 | 1.00 | 0.24 | 2.96 |
| 14 | 0.69 | 0.25 | 0.81 | 0.27 | 0.35 | 0.18 | 6.03 |
| 30 | 0.10 | 0.06 | 0.55 | 0.15 | 0.05 | 0.07 | 6.34 |
| 60 | 0.11 | ND | 0.87 | 0.08 | ND | ND | 10.92 |
| 90 | 0.07 | ND | 0.76 | 0.17 | ND | ND | 16.62 |
| 180 | ND | ND | 1.00 | 0.29 | ND | ND | 28.05 |

^a Not detected; the detection limit was 0.05 ppm.

CASE GS -- SULFOSATE STUDY 4 PM --

CHEM 128501 Sulfosate

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01
Lee, K.S. 1986. Solubility and octanol/water partition coefficient of
aminomethylpropionic acid. Unpublished study submitted by Stauffer Chemical
Company, Richmond, CA. Acc. No. 400462-03.-----
SUBST. CLASS = S.-----
DIRECT RVW TIME = 4 (MH) START-DATE END DATE-----
REVIEWED BY: R. Tamma
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500-----
APPROVED BY: T. Dougherty
TITLE: Chemist
ORG: EAB/IED/OPP
TEI: 557-0335SIGNATURE: *T. Dougherty*

DATE: 3/27/87

CONCLUSIONS:Ancillary Study - Octanol/Water Partition Coefficients

1. This study is scientifically valid.
2. Octanol/water partition coefficient (K_{ow}) values for aminomethylphosphonic acid ranged from 1.2×10^{-5} to 9.2×10^{-5} .

MATERIALS AND METHODS:

Prior to use, octanol was saturated with water by shaking certified grade n-octanol and deionized water in a separatory funnel to equilibrate.

Aqueous solutions of aminomethylphosphonic acid (AMPA, purity 99%, Sigma Chemical Co.) were prepared at 0.1 and 0.01 M concentrations. The test solutions were combined separately with water-saturated octanol, mixed, and allowed to stand overnight in a shaker bath at 25°C. The solutions were then centrifuged and the water and octanol phases were separated.

Aliquots of the aqueous phases were diluted and analyzed by HPLC. Aliquots of the octanol phases were extracted with water, and the aqueous extract was analyzed by HPLC. The octanol/water partition coefficient (K_{ow}) value was calculated.

REPORTED RESULTS:

K_{ow} values ranged from 1.2×10^{-5} to 9.2×10^{-5} for the 0.01 M AMPA solution and from 1.2×10^{-5} to 1.1×10^{-4} for the 0.1 M solution (Table 1).

DISCUSSION:

1. Characteristics of the water, including pH, dissolved oxygen content, hardness, and alkalinity were not provided.
2. The ratio of octanol to water was not reported.

Table 1. Octanol/water partition coefficients (K_{ow}) and concentrations in the octanol and water layers (mole/L) for aminomethylphosphonic acid.

| Concentration (M) | Octanol layer | Water layer | K_{ow} |
|----------------------|----------------------|----------------------|----------------------|
| | mole/L | | |
| 0.01 | 8.7×10^{-6} | 9.4×10^{-2} | 9.2×10^{-5} |
| | 2.8×10^{-6} | 9.5×10^{-2} | 2.9×10^{-5} |
| | 1.1×10^{-6} | 9.4×10^{-2} | 1.2×10^{-5} |
| 0.1 | 1.1×10^{-6} | 1.1×10^{-2} | 1.1×10^{-4} |
| | 3.0×10^{-7} | 9.4×10^{-3} | 3.2×10^{-5} |
| | 8.7×10^{-8} | 7.2×10^{-3} | 1.2×10^{-5} |

CASE GS -- SULFOSATE STUDY 5 PM --

CHEM 128501 Sulfosate

BRANCH EAP DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID No MRID CONTENT CAT 01
Katague, D.R., G.G. Patchett, and M.G. Kleinschmidt. 1985. Residue analytical method: Determination of SC-0224 cation residues in crops, water, and soil by gas chromatography. RRC 85-33. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-06.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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DATE: 3/27/87

CONCLUSIONS:

Ancillary Study - Analytical Methodology

1. This study is scientifically valid.
2. The trimethylsulfonium (TMS) cation of sulfosate was recovered at 68-115% from fortified soil samples and 67-125% from fortified plant samples.

MATERIALS AND METHODS:

Experiment 1

The trimethylsulfonium (TMS) cation of sulfosate (purity unspecified, Stauffer Chemical Co.), dissolved in water, was added at 0.05-1.0 ppm to Florida fine sand, California sandy loam, Iowa silty clay loam, and California garden soils. After treatment, the fortified soil samples (20 g of each) were extracted (mechanical shaking) for 30 minutes with 40 mL of 10% aqueous potassium hydroxide. The extracts were immediately centrifuged for 10 minutes at 1500 rpm.

An aliquot (amount unspecified) of each sample extract was applied to the surface of a weak cation resin column (Bio-Rex 70) and the column was washed with two 5-mL and one 10-mL portions of 0.02 M HCl. The washings were discarded. Then, the TMS cation was eluted from the column with 20 mL of 0.1 M HCl.

When necessary, the eluate was washed through a strong cation resin column (AG 50 W) with 5 mL of 0.05 N HCl followed by 5 mL of 0.05 M KCl. The washings were discarded and TMS was eluted with 25 mL of 0.24 M HCl:0.1 M KCl solution. The TMS eluant was concentrated to dryness on a hot plate, dissolved in 2 mL of water and dealkylated to dimethylsulfide (DMS) by heating the sample with potassium hydroxide for 60 minutes at 100°C. The samples were cooled to room temperature (temperature unspecified) and analyzed by gas chromatography. Solutions of DMS (purity 98%, Aldrich Chemicals) at 0.1-1000 µg/mL and prepared in toluene, were stable at ambient temperature (temperature unspecified) for 2 weeks when maintained in a tightly sealed container.

When background values exceeded 0.05 ppm, the dealkylated toluene extract was filtered through a disposable pipet containing 0.9 g of CC-4 adsorbent (post column cleanup). The eluate was discarded and the column was washed with 2 mL of fresh toluene; the resulting eluate was collected.

Each sample extract (from either pre- or postdealkylation clean-up) and the calibration solutions were analyzed on a Tracor MT-22 or Tracor MT-560 gas chromatograph using flame photometric detection (Table 1). Injections were made 3 minutes apart to avoid signal suppression due to toluene tailing. Calibration solutions were injected after every ~4 sample injections to check variation in detector sensitivity. TMS in the extracts was quantified by comparing peak heights of extracts to peak heights of calibration solutions. Samples containing residues higher than calibrants were diluted and reinjected so that the concentration range fell within that of the calibration curve.

Experiment 2

TMS (purity unspecified, Stauffer Chemical Co.) dissolved in water, was added at ~0.5 and 2 ppm to fresh fruits and vegetables containing 70-90% water. Treated samples (50 g of each) were extracted for 3 minutes in a Waring blender with 210 mL of water. The extracts were allowed to settle, decanted, and centrifuged for 10 minutes at 1500 rpm. A 10-mL aliquot of the clear aqueous supernatant was acidified (pH unspecified) with 1.0 mL of an acid-modified solution of KH_2PO_4 (16 g KH_2PO_4 : 160 mL water:40 mL methanol:13.4 mL of 36% HCl). Each sample was cleaned up on a weak cation exchange resin column as described in Experiment 1 and refrigerated overnight at 6°C.

Grains, seeds, and nuts (except soybeans) containing 5-15% water were fortified with TMS at 0.5 and 0.2 ppm. Each sample (50 g) was extracted with 246 mL water as described above.

Forage crops, grasses, and animal feed samples were fortified with TMS at 0.5 and 0.2 ppm. Each sample (25 g) was extracted (mechanical shaking or blending) with the appropriate amount of water (~250 mL), based on the water content of the sample as described above.

Fortified and ground soybeans were soaked in 246 mL water, refrigerated overnight, shaken briefly by hand, decanted, centrifuged, and acidified as above. This method avoided the formation of emulsions.

All extracted samples were analyzed by GC as described in Experiment 1.

REPORTED RESULTS:

Experiment 1

Recoveries of the TMS cation of sulfosate from fortified soils ranged from 78 to 115% for Florida fine sand, 83 to 94% for California sandy loam, 74 to 103% for Iowa silty clay loam, and 84 to 94% for California garden soil (Table 2). Background residues were <0.15 ppm. Retention times of TMS ranged from 0.5 to 2 minutes (Table 1). The standard deviation for DMS was $\pm 2\%$.

Experiment 2

Recovery of the TMS cation from the different crop plants ranged from 67 to 125%. Background residues were <0.197 ppm for all crops. Detection limits were 0.01 ppm for forage grasses, animal feeds, and wheat straw and 0.05 ppm for all other crops. Retention times and standard deviation were the same as reported in Experiment 1.

DISCUSSION:

General

1. The length of time between the extraction of soil and crop samples and the GC analysis was not reported.
2. Two different sets of GC conditions were presented (Table 1); however, it is not clear as to which conditions were used for each sample.
3. The refrigeration temperature at which samples were stored was not reported.
4. The purity of the test substances (TMS) was not specified.

Soils

No GC tracings were presented for any soil sample.

Table 1. Gas chromatographic conditions used for analyzing the trimethylsulfonium cation of sulfosate from fortified crop and soil samples.^a

| | | |
|------------------------|--------------------------------|-----------------------------|
| Instrument: | Tracor MT 222 | Tracor 560 |
| Column: | 180 cm x 2 mm i.d | 180 cm x 4 mm i.d. |
| Column packing: | 10% OV-101 on Gas Chrom O | 3% OV-1 on Chrom W, H.P. |
| Inlet: | On-column or with glass insert | With aluminum sleeve insert |
| Inlet Temperature: | 190°C | 200°C |
| Column Temperature: | 105°C | 120°C |
| Detector Temperature: | 170-180°C | 120°C |
| Carrier Gas: | 35 mL/minute (He) | 54 mL/minute (N) |
| Air: | 80-100 mL/minute | 117 mL/minute |
| Hydrogen: | 40-50 mL/minute | 10 mL/minute |
| Quantitation: | Peak height | Peak height |
| Recorder chart speed: | 1 cm/minute | 0.5 cm/minute |
| Retention time of DMS: | 0.5 minute | 2.0 minutes |

^a The detection limit for forage grasses, animal feed, and wheat straw is 0.1 ppm. The detection limit for soils and all other crops is 0.05 ppm.

Table 2. Reported recoveries from four soils fortified with trimethylsulfonium cation of sulfosate (TMS) and analyzed by GC^a.

| Soil type | Fortification level (ppm) | Background (ppm) | Recovery (ppm) |
|------------------------|---------------------------|------------------|----------------|
| Florida fine sand | 0.46 | 0 | 91 |
| | 0.10 | 0.017 | 96 |
| | 0.50 | 0.074 | 115 |
| | 0.05 | 0 | 78 |
| California sandy loam | 0.10 | 0 | 83 |
| | 0.10 | 0 | 94 |
| | 1.0 | 0 | 87 |
| | 0.46 | 0 | 91 |
| Iowa silty clay loam | 0.46 | 0.15 | 103 |
| | 0.50 | 0.11 | 102 |
| | 0.05 | 0.14 | 74 |
| | 0.05 | 0.098 | 90 |
| | 0.10 | 0.10 | 90 |
| California garden soil | 0.05 | 0 | 94 |
| | 0.05 | 0 | 84 |

^a Detection limit was 0.05 ppm.

CAS# -- SULFOSATE STUDY 6 PM --

CHFM 128501 Sulfosate

BRANCH EAB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID No MRID CONTENT CAT 01
 Patchett, G.G., D.B. Katague, and M.G. Kleinschmidt. 1985. Residue analytical method: Determination of SC-0224 anion residues in crops, soil, and water by liquid chromatography. WRC 85-34. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-07.

SURST. CLASS = S.

DIRECT PVW TIME = 8 (MH) START-DATE END DATE

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DATE: 3/27/87

CONCLUSIONS:

Ancillary Study - Analytical Methodology

1. This study is scientifically valid.
2. The carboxymethylaminomethylphosphonate (CAP) anion of sulfosate and its degradate, aminomethylphosphonic acid (AMPA), were recovered at 61-111% from fortified soil samples and 61-126% from fortified plant samples.

MATERIALS AND METHODS:

The carboxymethylaminomethylphosphonate (CAP) anion of sulfosate and aminomethylphosphonic acid (AMPA) (purities unspecified, Stauffer Chemical Company), dissolved in water, were added at 0.5 and 0.2 ppm to Florida fine sand, California sandy loam, and Iowa silty clay loam soil. After treatment, each fortified soil sample (20 g) was extracted (mechanical shaking) for one hour with 100 mL of 0.5 M ammonium hydroxide. The extracts were immediately centrifuged for 10 minutes at 1500 rpm, and an aliquot was filtered through a 2 µ filter tip, and concen-

trated at 50°C. The extraction of CAP and AMPA from the soils was performed in <4 hours to minimize decomposition. The dried extracts were dissolved in 2 mL of 0.05 M borate buffer and mixed with 2 mL of 9-fluorenylmethyl chloroformate (FMCL) derivative (1.0 mg/mL of 9-FMCL in acetone). This mixture was allowed to stand for 25 minutes at ambient temperatures, then mixed with 10 mL of ethyl acetate to stop the derivatization process. An aliquot was then extracted with an unknown amount of unspecified organic solvent to remove the excess FMCL; the CAP and AMPA derivatives remained in the aqueous phase.

CAP and AMPA calibration solutions and the soil extracts were analyzed on a Perkin-Elmer HPLC using pH 2.5 phosphate buffer:acetonitrile:distilled water (Table 1) at a flow rate of 1.0 mL/minute with fluorescence detection at 254 nm.

Experiment 2

CAP and AMPA (purities unspecified, Stauffer Chemical Co.), dissolved in water, were added at 0.5 and 0.2 ppm to fresh fruits and vegetables containing 70-90% water. Each treated sample (50 g) was extracted for 3 minutes in a Waring blender with 210 mL of water. The extracts were allowed to settle, decanted, and centrifuged for 10 minutes at 1500 rpm. An aliquot of the clear aqueous supernatant was acidified with 1.0 mL of an acid-modified solution of KH_2PO_4 (16 g KH_2PO_4 :160 mL water:40 mL methanol:13.4 mL 36% HCl). The solutions were acidified to prevent enzymatic degradation of the extracts.

A 1.10-mL aliquot of each extract sample was eluted through an acidified cation exchange resin column with 0.08 N hydrochloric acid in 10% methanol. The first portion of the eluate contained sugars and interfering substances; this was discarded. The second portion of the eluate contained the CAP, and the third part contained the AMPA. The CAP and AMPA were collected separately and dried. The dried extracts were dissolved in the borate buffer, derivatized with FMCL, and analyzed as described in Experiment 1.

Grains, seeds, and nuts (except soybeans) containing 5-15% water were fortified with CAP and AMPA at 0.5 and 0.2 ppm. Each fortified sample (50 g) was extracted with 246 mL water as described above.

Forage crops, grasses, and animal feed samples were fortified with TMS at 0.5 and 0.2 ppm. Each sample (25 g) was extracted (mechanical shaking or blending) with the appropriate amount of water (~250 mL), based on the water content of the sample as described above. A 1.10-mL aliquot of the acidified extract represents 0.1 g of sample.

Fortified and ground soybeans (25 g) were soaked in 246 mL water, refrigerated overnight, shaken briefly by hand, decanted, centrifuged, and acidified as above. This method avoided the formation of emulsions. A 1.10-mL aliquot of the acidified extract represented 0.1 g of sample.

Fortified almonds and soapstock samples were extracted with water, acidified, and reextracted with chloroform by shaking. The upper fraction was acidified as above.

All extracted samples were analyzed by GC as described in Experiment 1.

REPORTED RESULTS:

Experiment 1

Recoveries of the carboxymethylaminomethylphosphonate anion of sulfosate (CAP) from fortified soils were 100-111% from Florida fine sand, 90-93% from California sandy loam, and 61-82% from Iowa silty clay loam soils (Table 2). Recoveries of aminomethylphosphonic acid (AMPA) were 83-88% from Florida fine sand, 89-92% from California sandy loam, and 79-98% from Iowa silty clay loam soils. Background residues were <0.15% for all soils. The detection limit was 0.01 ppm. Retention times of CAP ranged from 11.3-26.4 minutes and AMPA, 14.4-69.4 minutes, depending on the ratios of the three solvents used in HPLC analysis (Table 1). Derivatization and HPLC analysis of the extracts were reproducible with a standard deviation of 2.5% for both CAP and AMPA.

Experiment 2

Recoveries of CAP and AMPA from the different crop plants ranged from 61-126 and 64-111%, respectively. Background residues were 0.03 ppm for all crops. Detection limits were 0.1 ppm for forage, grasses, animal feeds, and soybeans and 0.05 ppm for all other crops. Retention times and standard deviations of results were the same as described in Experiment 1.

DISCUSSION:

General

1. The length of time between extraction of soil and crop samples and HPLC analysis was not reported.
2. Various combinations of the three solvents, pH 2.5 phosphate buffer: acetonitrile:distilled water, used in HPLC analysis and the corresponding retention times were presented (Table 1); however, it is not clear as to which ratio of the solvents were used for each sample.
3. The purities of the test substances (CAP and AMPA) were not specified.

Soils

The detection limit of soil samples were not reported.

Table 1. Retention time of derivatized carboxymethylaminomethylphosphonate anion of sulfosate (CAP) and its degradate aminomethylphosphonic acid obtained by HPLC using a fluorescence detector at a flow rate of 1.0 mL/mL.

| pH 2.5 Phosphate | Acetonitrile % | Distilled water | Retention time (minutes) | |
|------------------|-------------------|--------------------|-----------------------------|------|
| | | | CAP | AMPA |
| 16 | 22 | 62 | 11.3 | 14.4 |
| 12 | 22 | 66 | 11.4 | 15.9 |
| 11 | 22 | 67 | 13.2 | 18.8 |
| 10 | 22 | 68 | 14.6 | 22.5 |
| 7 | 22 | 71 | 18.4 | 33.0 |
| 6 | 22 | 72 | 20.3 | 40.0 |
| 5 | 19 | 76 | 26.4 | 69.4 |

Table 2. Reported recoveries from four soils fortified with carboxymethyl-aminophosphonate (CAP) anion of sulfosate and aminomethylphosphonic acid (AMPA) and analyzed by HPLC.

| Soil type | Fortification level (ppm) | Background (ppm) | Recovery (%) |
|-----------------------|---------------------------|------------------|--------------|
| <u>CAP</u> | | | |
| Florida fine sand | 0.5 | 0.03 | 100 |
| | 0.2 | 0.03 | 111 |
| California sandy loam | 0.5 | 0.0 | 93 |
| | 0.2 | 0.02 | 90 |
| Iowa silty clay loam | 0.5 | 0.02 | 82 |
| | 0.2 | 0.01 | 61 |
| <u>AMPA</u> | | | |
| Florida fine sand | 0.5 | 0.0 | 83 |
| | 0.2 | 0.0 | 88 |
| California sandy loam | 0.5 | 0.03 | 92 |
| | 0.2 | 0.03 | 89 |
| Iowa silty clay loam | 0.2 | 0.03 | 79 |
| | 0.2 | 0.01 | 98 |

CASE GS -- SULFOSATE STUDY 7 PM --

CHEM 128501 Sulfosate

BRANCH EAB DISC --

FORMULATION 15 - SOLUBLE CONCENTRATE/LIQUID (SC/L)

FICHE/MASTER ID No MRID CONTENT CAT 01
Schwab, G.W. 1986. Frozen storage stability of Touchdown in soil. Project
RRC 86-61. Prepared and submitted by Stauffer Chemical Company, Richmond,
CA. Acc. No. 400462-08.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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DATE: 3/27/87

CONCLUSIONS:

Ancillary Study - Freezer Storage Stability

1. This study is scientifically valid.
2. The concentration of the trimethylsulfonium moiety in soil from field plots treated with sulfosate (Touchdown 4-LC, 4 lb/gal LC) at 6.0 lb ai/A and stored at -20°C for up to 2 years, ranged from 0.8 to 1.3 ppm in sand soil, 6.8 to 11.0 ppm in sandy loam soil, and 0.5 to 0.84 ppm in silty clay loam soil. The concentration of the carboxymethylaminomethylphosphonate moiety ranged from 1.27 to 2.1 ppm in sand soil, 3.5 to 14.7 ppm in sandy loam soil, and 0.70 to 1.5 ppm in silty clay loam soil. The concentration of aminomethylphosphonic acid ranged from 0.51 to 0.89 ppm in sand soil, 1.9 to 7.3 ppm in sandy loam soil, and 2.0 to 2.6 ppm in silty clay loam soil.

MATERIALS AND METHODS:

Sulfosate (Touchdown 4-LC, 4 lb/gal LC, Stauffer Chemical Company), at 6.0 lb ai/A, was sprayed to field plots of St. Johns sand soil (0.5% organic matter, pH 5.4) at Sanford, Florida; sandy loam soil (2.2%

organic matter, pH 6.9) at Orange Cove, California; and silty clay soil (6.0% organic matter) at Lisbon, Iowa. Several 1-inch cores were taken of both treated and untreated soil; samples were composited and frozen in sealed plastic bags at -20°C until analysis.

Soil samples were analyzed at 0, 1, and 2 years posttreatment for the triethylsulfonium moiety (TMS), the carboxymethylaminomethylphosphonate moiety (CAP), and aminomethylphosphonic acid (AMPA). At each time of analysis, samples of each soil were fortified and analyzed for TMS, CAP, and AMPA. Samples were extracted and analyzed by procedures RRC 85-33 and RRC 85-34, which are described in Study 5 and Study 6, respectively.

REPORTED RESULTS:

The concentration of TMS during the two-year period of the study ranged from 0.8 to 1.3 ppm in sand soil, 6.8 to 11.0 ppm in sandy loam soil, and 0.5 to 0.84 ppm in silty clay loam soil. The concentration of CAP ranged from 1.27 to 2.1 ppm in sand soil, 3.5 to 14.7 ppm in sandy loam soil, and 0.70 to 1.5 ppm in silty clay loam soil. The concentration of AMPA ranged from 0.51 to 0.89 ppm in sand soil, 1.9 to 7.3 ppm in sandy loam soil, and 2.0 to 2.6 ppm in silty clay loam soil.

DISCUSSION:

1. The reported concentrations of TMS, CAP, and AMPA tended to increase with increasing storage duration. Additionally, these compounds were detected in the control samples.
2. The test soils were not adequately characterized; percent sand, silt, and clay, and CEC, were not reported. The pH of the silty clay soil was not reported.
3. It was not indicated how much time elapsed between soil treatment and the analysis of the time 0 samples.

Table 1. PPM of the trimethylsulfonium (TMS) and the carboxymethylaminomethylphosphonate (CAP) moieties of sulfosate, and aminomethylphosphonic acid (AMPA) in soil treated with sulfosate at 6 lb ai/A and frozen up to 2 years and in samples fortified at the time of analysis.

| Analyte | Storage interval (years) | Treatment designation | Soil texture | | |
|---------|--------------------------|-----------------------|------------------------|-------------------------|-------------------------|
| | | | Sand | Sandy loam | Silty clay loam |
| TMS | 0 | Control | 0.015 | <0.05 | 0.125 |
| | | Fortified | 0.110 ^a | 0.083 ^b | 0.163 ^a |
| | | Treated | 0.8 | 7.7 | 0.7 |
| | 1 | Control | <0.05 | <0.05 | 0.15 |
| | | Fortified | 0.42 ^c | 0.42 ^d | 0.62 ^c |
| | | Treated | 0.77-0.94 | 6.8-11.0 | 0.69-0.84 |
| | 2 | Control | <0.05 | <0.05 | 0.37 |
| | | Fortified | 0.40-0.46 ^c | 0.35-0.38 ^c | 0.78-0.83 ^c |
| | | Treated | 1.2 -1.3 | 8.0 | 0.5 -0.6 |
| CMP | 0 | Control | 0.029 | <0.05 | 0.011 |
| | | Fortified | 0.533 ^a | 0.48 ^a | 0.134 ^e |
| | | Treated | 1.27 | 5.3-14.7 | 1.13 |
| | 1 | Control | 0.04-0.07 | 0.04 ^a -0.08 | 0.142-0.25 |
| | | Fortified | 0.73-1.02 ^f | 0.88 -0.99 ^f | 1.15 -1.22 ^f |
| | | Treated | 1.53-1.94 | 7.22 -8.12 | 1.26 -1.5 |
| | 2 | Control | <0.05 | <0.05 | 0 |
| | | Fortified | 0.94-1.05 ^f | 0.94-1.05 ^f | 0.99-1.29 ^f |
| | | Treated | 1.9 -2.1 | 3.5 -3.8 | 0.70-0.82 |
| AMPA | 0 | Control | <0.05 | <0.03 | 0.033 |
| | | Fortified | 0.416 ^a | 0.49 ^a | 0.19 ^e |
| | | Treated | 0.54 | 1.9 -4.2 | 2.4 |
| | 1 | Control | 0.033-0.046 | 0.032-0.049 | 0.122-0.178 |
| | | Fortified | 0.70 -1.0 ^f | 0.92 -1.04 ^f | 1.12 -1.18 ^f |
| | | Treated | 0.51 -0.68 | 5.82 -6.78 | 2.04 -2.46 |
| | 2 | Control | 0 -0.06 | 0.06 | 0.12 -0.18 |
| | | Fortified | 0.83-0.98 ^f | 0.98-1.05 ^f | 1.1 -1.35 ^f |
| | | Treated | 0.77-0.89 | 6.5 -7.3 | 2.0 -2.6 |

^a Fortified at 0.5 ppm.

^b Fortified at 0.1 ppm.

^c Fortified at 0.46 ppm.

^d Fortification rate unspecified.

^e Fortified at 0.2 ppm

^f Fortified at 1.00 ppm.

EXECUTIVE SUMMARY

The data summarized here are scientifically valid data that have been reviewed in this report but do not fulfill data requirements unless noted in the Recommendations section of this report.

Hydrolysis of sulfosate was determined to be essentially nonexistent at pH 5-9.

In irradiated aqueous solutions, the carboxymethylaminomethylphosphonate (CAP) anion of sulfosate had half-lives of 14.6, 77.9, and 41.6 days at pH 5, 7, and 9, respectively. Photoproducts were phosphoric acid and aminomethylphosphonic acid. The trimethylsulfonium (TMS) cation was stable at pH 5 and 7, but degraded with a half-life of 31.7 days at pH 9.

On irradiated soil TLC plates of loamy sand soil treated with sulfosate (technical grade, 54% ai) at 30 ppm, the carboxymethylaminomethylphosphonate (CAP) anion of sulfosate degraded with an initial rapid phase of ~12 days during which ~34% of the applied degraded followed by a slow phase during which only ~6% degraded during the remaining 12 days; the calculated half-life was ~48 days (assuming ~8 hours of sunlight per day). The formation of aminomethylphosphonic acid (AMPA) was directly related to the degradation of the CAP anion; together they accounted for 80-97% of the applied. In the dark controls, 84% of the CAP anion remained undegraded at 24 days posttreatment, but no AMPA was detected. The trimethylsulfonium (TMS) cation was stable during 24 days of irradiation.

In an aerobic soil metabolism study, using sulfosate labeled only on the trimethylsulfonium (TMS) moiety, TMS had a half-life of ~3 days in soil and CO₂ was the major degradate. However, an unknown of approximately 14% of the applied and a recovery of 73% at the end of the study represent gaps in the understanding of the fate of TMS. Soil bound [¹⁴C]residues peaked at ~20% of the applied at day 8 and then slowly decreased. Extractable [¹⁴C]residues declined from about 60% of the applied at day 0 to ~6% at day 10 (most of which was parent TMS). During the first week, approximately 50% of the applied radioactivity was evolved as ¹⁴CO₂. After 211 days, 75% of the applied radioactivity had been volatilized. Recoveries ranged from 73% to 87% of the ¹⁴C initially applied. Small scale studies, which had different temperature conditions from the large study, were used to identify the [¹⁴C]residues. In the small scale studies, most of the extractable [¹⁴C]residues (which declined from 75.3% of the applied at day 0 to 27.1% at day 4) were recovered from the ammonium formate fraction which contained only parent TMS. The acetone fraction contained about 0.5% TMS over the same time period, but also contained an unknown ¹⁴C residue that peaked at 14-17% of the applied radioactivity at 4 days and declined to about 1% of the applied at 6 days. Recoveries from the small scale studies indicated that combustion of wet soils (as opposed to dry soils in the large study) gave a more accurate determination.

In an aerobic soil metabolism study using sulfosate labeled only on the carboxymethylaminomethylphosphonate (CAP) moiety, the CAP half-life was ~2-3 days. The extractable residues declined from about 57% of the applied at day 0 to 14% at day 30. Soil-bound residues were 40% of the applied initially and declined

to 18% at day 30. At day 30 ~60% of the applied had been evolved as $^{14}\text{CO}_2$. Recovery was 91-102% for the one year duration of the study. Identification of residues was made in a small scale study and showed CAP comprised 78% of the applied at day 0 (97% of the extractable residues) and 8% at day 21. The degradate aminomethylphosphonic acid (AMPA) comprised 0.4% of the applied at day 0 and 15.4% (57% of the extractable residues) at day 21. The extractable [^{14}C]residues from the large study declined from 30% of the applied at day 9 to 14% at day 30 and 8% at day 76, indicating that AMPA probably increased slightly after day 21 for a short period and then decreased following the rate of decline of the extractable [^{14}C]residues (qualitative determinations were not made after day 21).

Aged (3-day) [^{14}C]sulfosate residues were immobile to mobile in two loam, one sand, and one clay loam soils, based on soil TLC. The carboxymethylaminomethylphosphonate moiety and its sole degradate, aminomethylphosphonic acid, were immobile ($R_f < 0.02$) in all four soils. The trimethylsulfonium moiety (which produced no extractable degradates) was immobile ($R_f < 0.08$) in the two loam soils, slightly mobile ($R_f < 0.14$) in the clay loam soil, and mobile ($R_f < 0.66$) in the sand soil.

In field dissipation studies in which sulfosate (4 lb/gal LC) was applied at 6 lb ai/A to field plots located in Virginia, California, Iowa, and Florida, the carboxymethylaminomethylphosphonate (CAP) anion of sulfosate degraded with a half-life of <7 days in the 0- to 3-inch soil depth at the Virginia site, while its degradate, aminomethylphosphonic acid (AMPA), was variable, ranging from <0.1 to 1.40 ppm during the 60-day study. The trimethylsulfonium (TMS) cation was not detected during the study. In the California, Iowa, and Florida studies, significant residues of the CAP anion, TMS cation, and AMPA occurred in both the 0- to 2-inch and 3- to 6-inch depth soil samples. Half-life values for the CAP anion were 23.2-25.8 days and for TMS cation were 29.6-50.4 days. AMPA half-life values were 91.6 days in California and 82.8 days in Iowa (AMPA residues in the Florida study increased throughout the sampling period).

Sulfosate has been demonstrated to have a high water solubility and low K_{ow} . Since the octanol/water partition coefficient (K_{ow}) values for aminomethylphosphonic acid ranged from 1.2×10^{-5} to 9.2×10^{-5} , it is unlikely that either sulfosate or its primary degradate would accumulate in fish.

RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate of and the exposure of humans and nontarget organisms to sulfosate. The submission of data relevant to registration requirements (Subdivision N) for terrestrial nonfood and domestic outdoor use sites is summarized below:

Hydrolysis studies: Based on previously submitted data, no additional data are required.

Photodegradation studies in water: Based on previously submitted data, no additional data are required.

Photodegradation studies on soil: Based on previously submitted data and data submitted for this addendum, no additional data are required.

Photodegradation studies in air: No data were reviewed for this addendum; however, no data are required because the use is unlikely to result in significant exposure to workers other than applicators.

Aerobic soil metabolism studies: Based on previously submitted data, no additional data are required.

Anaerobic soil metabolism studies: No data were reviewed for this addendum; however, no data are required.

Anaerobic aquatic metabolism studies: No data were reviewed for this addendum; however, no data are required because sulfosate has no aquatic or aquatic impact uses.

Aerobic aquatic metabolism studies: No data were reviewed for this addendum; however, no data are required because sulfosate has no aquatic or aquatic impact uses.

Leaching and adsorption/desorption studies: Based on previously submitted data and data submitted for this addendum, no additional data are required.

Laboratory volatility studies: No data were reviewed for this addendum; however, no data are required.

Field volatility studies: No data were reviewed for this addendum; however, no data are required.

Terrestrial field dissipation studies: Four field dissipation studies (Acc. Nos. 250548 and 258400), which were previously reviewed but did not satisfy data requirements, have been amended for this addendum. The registrant has adequately addressed all issues but the fact that the soils were not sampled deep enough to define the extent of leaching under actual use conditions. A study is still needed to define the potential of sulfosate and its degradates to leach under actual use conditions.

Aquatic field dissipation studies: No data were reviewed for this addendum; however, no data are required because sulfosate has no aquatic or aquatic impact uses.

Forestry dissipation studies: No data were reviewed for this addendum; however, no data are required because sulfosate has no forestry uses.

Dissipation studies for combination products and tank mix uses: No data were reviewed for this addendum; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were submitted for this addendum; however, no data are required.

Confined accumulation studies on rotational crops: No data were reviewed for this addendum; however, no data are required because sulfosate has no terrestrial food crop uses.

Field accumulation studies on rotational crops: No data were reviewed for this addendum; however, no data are required because sulfosate has no terrestrial food crop uses.

Accumulation studies on irrigated crops: No data were reviewed for this addendum; however, no data are required because sulfosate has no terrestrial food crop uses.

Laboratory studies of pesticide accumulation in fish: Based on previously submitted data and data submitted for this addendum, the data requirement has been waived.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed for this addendum; however, no data are required.

Reentry studies: No data were reviewed for this addendum; however, no data are required.

REFERENCES

The following studies are new submittals reviewed in this report:

Katague, D.R., G.G. Patchett, and M.G. Kleinschmidt. 1985. Residue analytical method: Determination of SC-0224 cation residues in crops, water, and soil by gas chromatography. RRC 85-33. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA.

Kleinschmidt, M.G. 1986. Addendum to: SC-0224 4-LC field dissipation study. Unpublished study prepared and submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-05.

Lee, K.S. 1986. Solubility and octanol/water partition coefficient of aminomethylpropionic acid. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-03.

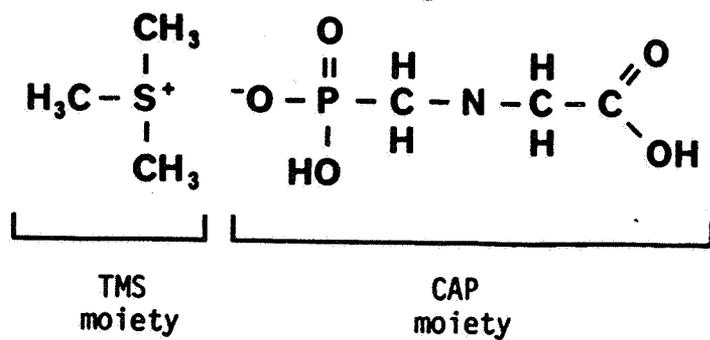
McGahan, L. 1986. Addendum to: The photodegradation of SC-0224 applied to soil. Laboratory Project PMS-137, MRC-83-09. Unpublished study prepared and submitted by Stauffer Chemical Company, Mountain View, CA. Acc. No. 400462-04.

Patchett, G.G., D.B. Katague, and M.G. Kleinschmidt. 1985. Residue analytical method: Determination of SC-0224 anion residues in crops, soil, and water by liquid chromatography. WRC 85-34. Unpublished study submitted by Stauffer Chemical Company, Richmond, CA.

Schwah, G.W. 1986. Frozen storage stability of Touchdown in soil. Project RRC 86-61. Unpublished study prepared and submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 400462-08.

Spillner, C.J., S. Carley, and I. Neeman. 1986. SC-0224 aged soil mobility study. Laboratory Project ID PMS-205, MRC-86-02. Unpublished study prepared and submitted by Stauffer Chemical Company, Mountain View, CA. Acc. No. 263552.

APPENDIX
STRUCTURE OF SULFOSATE



Sulfosate
 Trimethylsulfonium carboxymethylaminomethylphosphonate