TEXT SEARCHABLE DOCUMENT - 2010

Data Evaluation Record on the field volatility of dimethyl disulfide

PMRA Submission Number {.....}

EPA MRID Number 47377801

Data Requirement: PMRA Data Code: EPA DP Barcode: D337302 **OECD Data Point:** EPA Guideline: 835.8100

Test material: Dimethyl disulfide

End Use Product name: ATOMAL01 Formulation type: Liquid

Concentration of a.i.: ≥98% (nominal)

Active ingredient

Synonyms:

Common name: Dimethyl disulfide. Chemical name: IUPAC name: Dimethyl disulfide. Dimethyl disulfide. CAS name: CAS No.: 624-92-0.

DMDS, dimethyldisulfide, DMDS TC, dimethyl disulfide TC, ATOMAL, ATOMAL01, 2,3-dithiabutane, methyl disulfide, (methyldithio)methane, (methyldisulfanyl)methane, (methyldithio)methane, methyldithion ethane, dimethyldisulphide. S(SC)C (EPI Suite, v3.12 SMILES String).

Smiles string:

Primary Reviewer: Dan Hunt **Cambridge Environmental**

Signature: Date: 11/17/08

Secondary Reviewer: Joan Harlin **Cambridge Environmental**

QC Manager: Joan Gaidos **Cambridge Environmental**

Signature: Date: 11/17/08

Signature: Date: 11/17/08

Signature: Lie full Date: 5112/10

Final Reviewer: Gabe Rothman **EPA Reviewer:**

Company Code Active Code Use Site Category EPA PC Code: 029088

CITATION: Batrolome, J. 2007. Determination of atmospheric concentrations of dimethyldisulphide and occupational exposure to fumigators during typical shank applications with immediate covering to cultivated soil in Italy, Spain and United Kingdom in 2005. Unpublished study performed by Huntingdon Life Sciences Ltd., Karlsbad, Germany (study director) and Huntingdon Life Sciences, Occold, Suffolk, England (analytical phase; p. 5); sponsored and submitted by Cerexagri S.A., France and ARKEMA, France. Project ID:



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EFA/048. Experiment initiated August 18, 2005 and completed March 9, 2006 (p. 18). Final report issued November 29, 2007.

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EXECUTIVE SUMMARY

The volatilization of dimethyl disulfide (DMDS; formulated product containing nominal \geq 98% DMDS) was studied following one broadcast shank application at Lagosanto, Italy (Site 1) and San Guiseppe, Italy (Site 3), and following one shank application to raised beds at Matalascanas, Spain (Site 2) and Lawford, Essex, United Kingdom (Site 4), with subsequent covering of the soil with Virtually Impermeable Film (VIF) plastic film. The treated area at Site 1 and Site 3 was approximately 36 m x 140 m and 34 m x 150 m, respectively. The treated area at Site 2 was approximately 78 x 146 m, containing 74 raised beds, each approximately 40 cm high and 50-55 cm wide. The treated area at Site 4 was approximately 100 m x 100 m, containing 65 raised beds, each approximately 30 cm high and 75 cm wide. Soil was characterized for 10-cm increments to a depth of 30 cm, and found to be a loamy sand at Site 1 (pH 7.7-7.8, organic carbon: 0.7-1.0%), a sand at Site 2 (pH 6.7-7.2, organic carbon: 0.2-0.3%), a loamy sand at Site 3 (pH 7.9-8.1, organic carbon: 0.3-0.4%), and a sandy silt loam at Site 4 (pH 6.4-6.6, organic carbon: 0.9-1.0%), using a soil classification system other than the USDA soil classification system. The test sites were representative of strawberry and carrot growing regions of Italy, Spain, and the United Kingdom in which fumigation practices are conducted.

Test applications were made to each site between August 19 and October 14, 2005 at application rates of 378.4 kg DMDS/ha at Site 1, 400.8 kg DMDS/ha (80.1 g DMDS/m² for raised beds) at Site 2, 377.6 kg DMDS/ha at Site 3, and 417.7 kg DMDS/ha (84.6 g DMDS/m² for raised beds) at Site 4. The test substance was applied using typical commercial application equipment for shallow shank, injection fumigation at each test site. Immediately after injection, the treated soil was covered by VIF plastic film (25-50 μ m thickness) at each test site. Seven days after the fumigation, the middle of each row of VIF was cut open for its entire length at Site 1 and Site 3, and two parallel offset set of holes or slits were left in the top of the VIF on the raised beds at Site 2 and Site 4 for aeration.

Four air monitoring areas were located at the boundary of the treated area at the midway point between the corners of the treated area (0 m) and in each of four concentric circles at distances of approximately 5, 25, 50, and 75 m from the treated test plot (20 monitors total), with air collection tubes located 1.5 m above the soil surface. Air samples were collected from 0 to 10 days at approximately 0 to 6 hours, 6 to 12 hours, 12 to 18 hours, and 18 to 24 hours, except during the fumigation and aeration procedures at 0 and 7 days, respectively, when air samples were collected approximately every 2 hours. Air samples were collected using SKC charcoal air filter tubes containing Anasorb CSC. Following collection, the samples were maintained frozen for up to 158, 183, 136, and 167 days until analysis for Sites 1, 2, 3, and 4, respectively. The sorbent from the air filter tubes was extracted by shaking with hexane, and an aliquot of the hexane extract was analyzed by GC/MS. The LOQ was 0.1 μ g/sample and the LOD was 0.02 μ g/sample. Samples were not analyzed for transformation products of DMDS.

Maximum wind speeds recorded on the day of application were 2.8, 3.3, 2.6, and 2.8 m/s for Sites 1, 2, 3, and 4, respectively, with maximum wind speeds for the 10-day study period of 4.7 m/s for Site 1, 6.9 m/s for Site 2, 4.3 m/s for Site 3, and 6.9 m/s for Site 4 (the height of the measurement was not reported). Mean daily air temperatures for the 10-day study period ranged

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from 14.7 to 19.9°C at Site 1, 21.3 to 26.0°C at Site 2, 10.6 to 15.8°C at Site 3, and 12.3 to 18.9°C at Site 4. Mean daily soil temperatures ranged from 17.0 to 22.0°C at Site 1, 26.8 to 30.6°C at Site 2, 13.7 to 16.4°C at Site 3, and 14.3 to 21.5°C at Site 4. Mean daily relative humidity ranged from 68.9 to 99.2% at Site 1, 45.9 to 82.7% at Site 2, 70.2 to 99.4% at Site 3, and 79.6 to 97.4% at Site 4. Site 1 received a total of 4.8 cm of rainfall, with over 90% of the total rainfall occurring during the last 2 days of the study period. Site 2 received a total of 0.02 cm of rainfall. Site 3 received a total of 2.5 cm of rainfall, with 2.3 cm falling on the seventh day of the study. Site 4 received a total of 2.3 cm of rainfall.

DMDS was reported in terms of total micrograms per cubic meter environmental concentration in air $(\mu g/m^3)$. Maximum mean values were observed at the sampling stations located at the boundary of the test plots (0 m) unless otherwise specified. Mean concentrations of DMDS, based on the rolling 24-hour period, reached a maximum of approximately 200-294 μ g/m³ by 1-2 days posttreatment at all four test sites before decreasing to approximately 20-76 μ g/m³ by 6 days posttreatment (the day prior to aeration). The rolling 24-hour period was from the start of fumigation (ranging from 09:00 to 12:45) to the following 06:00 for day 0 samples, and from 06:00 to 06:00 for samples through 7-8 days posttreatment. The 9 and 10 day samples were bulked for analysis and the sampling period varied. Maximum worst-case daily DMDS concentrations (highest individual result) were approximately 1734 μ g/m³ (1 day) at Site 1 (5 m), $1554 \ \mu g/m^3$ (day 0) at Site 2, $1372 \ \mu g/m^3$ (day 0) at Site 3 (75 m), and 591 $\ \mu g/m^3$ (1 day) at Site 4. Following aeration at Site 1, mean DMDS concentrations reached a maximum of 568.639 $\mu g/m^3$ at 8 days (5 m) before decreasing to a maximum of 4.376 $\mu g/m^3$ by 10 days. Following aeration at Site 2, mean DMDS concentrations reached a maximum of 22.070 μ g/m³ at 7 days before decreasing to a maximum of 3.228 μ g/m³ by 10 days (5 m). Following aeration at Site 3, mean DMDS concentrations reached a maximum of 264.380 μ g/m³ at 8 days before decreasing to a maximum of $62.458 \,\mu\text{g/m}^3$ by 10 days (5 m). Following aeration at Site 4, mean DMDS concentrations reached a maximum of 71.217 μ g/m³ at 7 days before decreasing to a maximum of 4.841 μ g/m³ by 10 days.

Study Acceptability: This study is classified Supplemental. No significant deviations from good scientific practices were noted. Volatility was not reported in units of $\mu g/cm^2/hr$ or g/ha/day. The highest recommended label rate was not reported and the study was not conducted domestically.

MATERIALS AND METHODS

The concentration of dimethyl disulfide (DMDS, ATOMAL01; formulated product containing nominal ≥98% DMDS) in air was measured following one broadcast shank application at Lagosanto, Italy (Site 1) and San Guiseppe, Italy (Site 3), and following one shank application to raised beds at Matalascanas, Spain (Site 2) and Lawford, Essex, United Kingdom (Site 4), with subsequent covering of the soil with Virtually Impermeable Film (VIF) plastic film (pp. 17-21 and pp. 30-31). The studies were conducted from August to October to coincide with the

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potential use pattern timing for dimethyl disulfide as a soil fumigant to strawberry and carrot fields in Italy, Spain, and the United Kingdom (p. 10).

The treated area at Site 1 and Site 3 consisted of three blocks of approximately 36 m x 140 m (Site 1) or 34 m x 150 m (Site 3) separated by ditches 1.5-2 m wide, and the treated area at Site 2 and Site 4 consisted of a single block of approximately 78 x 146 m (Site 2) or 100 m x 100 m (Site 4) containing raised beds (pp. 22-25). Site 2 contained 74 raised beds, each approximately 40 cm high and 50-55 cm wide, with a space of 50-55 cm between adjacent raised beds. Site 4 contained 65 raised beds, each approximately 30 cm high and 75 cm wide, with a space of 75 cm between adjacent raised beds. Prior to application, soil was collected from twelve cores inside the treatment area at each test site to a depth of 30 cm, segmented into 10-cm increments, and composited by depth for characterization (p. 27). Soil was characterized as loamy sand texture and inceptisol taxonomy at Site 1 (pH 7.7-7.8, organic carbon: 0.7-1.0%), as sand texture and inceptisol taxonomy at Site 3 (pH 7.9-8.1, organic carbon: 0.3-0.4%) and as sandy silt loam texture and alfisol taxonomy at Site 4 (pH 6.4-6.6, organic carbon: 0.9-1.0%; all depths; pp. 27-28); however, soils were not characterized according to the USDA soil classification system. The pesticide and crop history of the test areas was not reported.

Parameter	Value	Comment
Molecular weight (g/mol)	Not reported.	
Chemical formula	C ₂ H ₆ S ₂	
Water Solubility	Not reported.	
Vapor Pressure/Volatility	Not reported.	
UV Absorption	Not reported.	
рКа	Not reported.	
K _{ow} /log K _{ow}	Not reported.	
Stability of compound at room temperature, if provided	Not reported.	

Physico-chemical properties of DMDS:

Data were obtained from p. 44 of the study report.

The test substance was applied using typical commercial application equipment for shallow shank, injection fumigation at each test site, and was performed according to typical local practices in each country (pp. 17-19). Applications were made at Sites 1-3 (Italy and Spain) by passing up each row consecutively, except that at Site 4 (the United Kingdom) where the raised beds were formed prior to the fumigation, the applicators adhered to a pre-arranged application routine that involved skipping a row and then returning to it later in the application routine (p. 11). The tanks of DMDS were weighed before and after the test application at each site to determine the weight of DMDS applied. Aeration was conducted at all sites 7 days after the fumigation (p. 35).

The application at Site 1 (Italy) was made on September 23, 2005 at an application rate of 378.4 kg DMDS/ha (337.9 lb DMDS/A; p. 32). Application equipment consisted of a tractor equipped

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with a rear-mounted shank applicator, which injected the test material at a depth of 25 to 30 cm (pp. 30, 32). Immediately after injection, the treated soil was covered by VIF plastic film (SIS Barrier Film, 4.0 m wide, 25 μ m thickness), which was covered with soil at the ends of each row by the applicator, buried into the soil, and glued to the previous row of VIF by the fumigation equipment. Seven days following application, the middle of each row of VIF was cut open for its entire length by the test subject walking down the middle of each row dragging a knife (p. 36). The VIF was removed approximately 24 hours after aeration.

The application at Site 2 (Spain) was made on August 19, 2005 to raised beds, at an application rate of 400.8 kg DMDS/ha (357.9 lb DMDS/A) to the entire plot or at an application rate of 80.1 g DMDS/m² for raised beds only (p. 33). Application equipment consisted of a tractor equipped with the raised bed-forming device mounted on the front of the tractor and a rear-mounted shank applicator, which injected the test material at a depth of 25 cm (pp. 30, 33). Immediately after injection, the treated soil was covered by VIF plastic film (1.4 m wide, 50 μ m thickness), which was covered with soil at the ends of each row by the applicator; the sides were buried into the soil by the fumigation equipment. Seven days following application, each raised bed was aerated manually by dragging a handle attached to the axle of a set of spiked wheels which left two parallel offset set of holes in the top of the VIF on the raised beds (p. 36). The VIF was not removed until after the conclusion of the study, following typical practices for a commercial strawberry crop at the test site.

The application at Site 3 (Italy) was made on October 14, 2005 at an application rate of 377.6 kg DMDS/ha (337.1 lb DMDS/A; p. 34). Application equipment consisted of a tractor equipped with a rear-mounted shank applicator, which injected the test material at a depth of 20 cm (pp. 30, 34). Immediately after injection, the treated soil was covered by VIF plastic film (SIS Barrier Film, 4.0 m wide, 25 μ m thickness), which was covered with soil at the ends of each row by the applicator, buried into the soil, and glued to the previous row of VIF by the fumigation equipment. Seven days following application, the middle of each row of VIF was cut open for its entire length by the test subject walking down the middle of each row dragging a knife (p. 36). The VIF was removed approximately 24 hours after aeration.

The application at Site 4 (United Kingdom) was made on September 6, 2005 to pre-formed raised beds, at an application rate of 417.7 kg DMDS/ha (372.9 lb DMDS/A) to the entire plot or at an application rate of 84.6 g DMDS/m² for raised beds only (p. 35). Application equipment consisted of a tractor equipped with a rear-mounted shank applicator, which injected the test material at a depth of 15 to 20 cm (pp. 31, 35). Immediately after injection, the treated soil was covered by VIF plastic film (Film Bromostop[®] black, 1.4 m wide, 50 μ m thickness), which was covered with soil at the ends of each row by the applicator; the sides were buried into the soil by the fumigation equipment. Seven days following application, each raised bed was aerated using a tractor equipped with hole punching equipment mounted in the back, which left two parallel offset set of slits in the top of the VIF on the raised beds (p. 36). The VIF was not removed until after the conclusion of the study, following typical practices for a commercial strawberry crop at the test site.

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Air monitoring areas were located at the boundary of the treated area at the midway point between the corners of the treated area and in four concentric circles at distances of approximately 5, 25, 50, and 75 m from the treated test plot, with air collection tubes located 1.5 m above the soil surface (pp. 11-12, 36-38). Four air samplers were placed in each of the four concentric circles, with the samplers placed at 5 and 50 m from the test plot, in line with the samplers located at the boundary of the treated area at the midway point between the corners of the treated area, and the samplers placed at 25 and 75 m from the test plot placed from the corners of the treated plot. Air collection tubes were oriented pointing downwards and were protected against moisture by a turned over bucket.

Air samples were collected using SKC charcoal air filter tubes containing Anasorb CSC (400/200 split; p. 38). Air flow rates were adjusted to approximately 480 to 500 mL/min before each sampling period, except for Site 2 (Spain) where some air pumps were adjusted to 600 mL/min due to a technical issue with the air pumps, which can have problems maintaining the set flow rate when the weather is very hot, as occurred at this site.

Air samples were collected from 0 to 10 days at approximately 0 to 6 hours, 6 to 12 hours, 12 to 18 hours, and 18 to 24 hours except during the fumigation and aeration procedures at 0 and 7 days, respectively, when air samples were collected approximately every 2 hours (pp. 13, 41-42). At the end of each sampling period, the pre-labeled air sampling tubes were capped, placed in a plastic bag, and placed into freezer storage within 2 hours of sampling (p. 38). Samples were maintained frozen for up to 158, 183, 136, and 167 days until analysis for Sites 1, 2, 3, and 4, respectively (Tables 6-58, pp. 69-121).

Meteorological conditions were monitored hourly at each test site by an on-site weather station that measured air and soil temperature, relative humidity, rainfall, and wind speed and direction (p. 28).

Field spikes were prepared for each test site by fortifying eleven sets of air filters with dimethyl disulfide standard solution in hexane, in duplicate, at 1, 100, and 5000 μ g/filter (pp. 38, 43). Field spikes were prepared at the analytical laboratory, shipped frozen to the field locations, and stored frozen until needed, at which time they were allowed to thaw. The fortified air filter tubes were set up in an area at least 1 km away from the treated area (upwind) to avoid contamination, and were connected to a personal air sampling pump and ran with a flow rate of approximately 500 mL/min for a period of >6 hours. At the end of the sampling period, each air sampling tube was capped at both ends, placed in pre-labeled plastic bags and stored, transported, and analyzed alongside the field samples. Field spikes were stored frozen for 10-183 days prior to analysis (Tables 59-62, pp. 122-133). An additional set of transit stability samples was prepared for each test site by fortifying air filters with dimethyl disulfide standard solution in hexane, in duplicate, at 1, 100 and 5000 μ g/filter (pp. 38, 42). Transit stability samples were prepared at the analytical laboratory, shipped frozen to the field locations, and stored and shipped in the same manner as the field samples (frozen).

The sorbent from the front section of the charcoal air filter tubes, along with the glass wool separators from both the front and the middle of the filter tube, was combined with hexane (20

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mL), vortexed for *ca*. 30 seconds, sonicated for 30 seconds, and then shaken for 30 minutes on a reciprocating shaker (p. 45). After shaking, the sample was sonicated for an additional 30 seconds, vortexed for 30 seconds, and after the sorbent material was allowed to settle, an aliquot of the hexane extract was removed for analysis. Extracts were analyzed by GC (HP-5MS capillary column, 30 m x 0.25 mm i.d., 0.25 μ m film thickness) using mass spectrometric (MS) detection (positive ion mode; p. 46). Calibration solutions were prepared with the DMDS analytical standard (Lot/batch No.: 17.08.04, analytical purity 99.9%; p. 44), dissolved in hexane, over the range of 1-100 ng/mL. The Limit of Quantification (LOQ) was 0.1 μ g/sample (previously validated) and the Limit of Detection (LOD) was determined to be 1 ng/mL or 0.02 μ g/sample (pp. 46, 48). It was not stated whether the back portions of the filter tubes were analyzed to determine if breakthrough of the residue from the front portion of the sample occurred. Samples were not analyzed for transformation products of DMDS.

RESULTS/DISCUSSION

Dimethyl disulfide concentrations in air were reported based on the rolling 24-hour worst case daily result (highest individual result), the rolling 24-hour 75th percentile result, and the rolling 24-hour mean result at each specified distance (0, 5, 25, 50, and 75 m) at each test site (pp. 51-66). The rolling 24-hour period was from the start of fumigation (ranging from 09:00 to 12:45) to the following 06:00 for day 0 samples, and from 06:00 to 06:00 for samples through 7-8 days posttreatment. The 9 and 10 day samples were bulked for analysis and the sampling period varied. DMDS was reported in terms of total micrograms per cubic meter environmental concentration in air (μ g/m³).

Following broadcast shank application at <u>Site 1 (Lagosanto, Italy)</u>, the mean concentration of DMDS in the atmosphere was a maximum of 294.259 μ g/m³ at 2 days at the boundary of the treated plot (0 m), and decreased to a maximum of 29.494 μ g/m³ by 6 days posttreatment (0 m; the day prior to aeration; p. 62). The maximum worst-case daily DMDS concentration was 1733.952 μ g/m³ at 1 day, measured at 5 m from the treated plot, and was 8.964 μ g/m³ at 10 days (5 m; p. 51). Following aeration at 7 days in which the middle of each row of VIF was cut open for its entire length, the mean concentration of DMDS was a maximum of 568.639 μ g/m³ at 8 days at 5 m from the treated plot, DMDS was a maximum of 4.376 μ g/m³ by 10 days (0 m). At a distance of 75 m from the treated plot, DMDS was a maximum mean concentration of 179.237 μ g/m³ at 8 days before decreasing to 0.699 μ g/m³ by 10 days.

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Distance	Mean daily concentration of DMDS in atmosphere ($\mu g/m^3$) at Site 1										
to test		Days after treatment									
plot (m)	0	1	2	3	4	5	6	7	8	9	10
0	106.625	261.782	294.259	156.970	169.694	58.547	29.494	185.574	540.468	44.397	4.376
5	99.484	257.055	280.419	159.642	149.854	54.473	27.597	184.150	568.639	44.364	3.852
25	112.313	168.370	161.229	155.854	81.728	29.684	14.045	81.661	360.684	16.874	1.838
50	120.298	148.774	207.084	107.659	68.714	27.217	14.309	75.760	244.079	18.576	2.361
75	80.855	115.581	95.924	95.746	49.545	14.942	6.565	31.374	179.237	9.543	0.699

Data were obtained from p. 62 of the study report. Data are means of all samples taken in 24-hour period at the specified distance from the treated plot. The day 0 mean is from the start of fumigation at 09:00 until 06:00 the following day. Means reported for days 1 through 8 are for a 24 hour period from 06:00 to 06:00. Due to bulking of day/night samples for the 9 and 10 day samples, day 9 includes the 10 day sample from 00:00 to 06:00; the day 10 mean is from 06:00 to 24:00 on day 10.

Following shank application to raised beds at <u>Site 2 (Matalascanas, Spain)</u>, the mean concentration of DMDS in the atmosphere was a maximum of 263.751 µg/m³ at 1 day at the boundary of the treated plot (0 m), and decreased to a maximum of 20.116 µg/m³ by 6 days posttreatment (0 m; the day prior to aeration; p. 63). The maximum worst-case daily DMDS concentration was 1553.818 µg/m³ at day 0, measured at 0 m, and was 8.029 µg/m³ at 10 days (5 m; p. 53). Following aeration at 7 days in which two parallel offset set of holes were left in the top of the VIF on the raised beds, the mean concentration of DMDS was a maximum of 22.070 µg/m³ at 7 days at 0 m, and decreased to a maximum of 3.228 µg/m³ by 10 days (5 m). At a distance of 75 m from the treated plot, DMDS was a maximum mean concentration of 48.550 µg/m³ at 1 day before decreasing to 3.914 µg/m³ by 6 days; following aeration, DMDS was a maximum mean concentration of 2.621 µg/m³ at 7 days before decreasing to 0.393 µg/m³ by 10 days.

Distance	Mean daily concentration of DMDS in atmosphere ($\mu g/m^3$) at Site 2										
to test		Days after treatment									
plot (m)	0	1	2	3	4	5	6	7	8	9	10
0	224.570	263.751	258.882	103.044	48.120	52.264	20.116	22.070	10.140	5.655	2.898
5	155.752	232.368	216.259	97.269	56.053	38.977	18.963	19.053	9.737	5.922	3.228
25	88.113	114.863	77.461	38.503	12.351	18.959	11.931	12.693	4.814	3.662	1.397
50	52.638	83.579	60.993	37.483	15.902	13.626	5.983	4.295	2.484	1.693	0.654
75	32.285	48.550	26.338	7.441	4.971	7.619	3.914	2.621	0.864	0.726	0.393

Data were obtained from p. 63 of the study report. Data are means of all samples taken in 24-hour period at the specified distance from the treated plot. The day 0 mean is from the start of fumigation at 09:00 until 06:00 the following day. Means reported for days 1 through 7 are for a 24-hour period from 06:00 to 06:00. Due to bulking of the 9 and 10 day samples, 9 and 10 day samples are from 00:00 to 00:00 and 8 day samples are from 06:00 to 00:00.

Following broadcast shank application at Site 3 (San Guiseppe, Italy), the mean concentration of DMDS in the atmosphere was a maximum of 232.253 μ g/m³ at 1 day at the boundary of the treated plot (0 m), and decreased to a maximum of 49.227 μ g/m³ by 6 days posttreatment (0 m; the day prior to aeration; p. 64). The maximum worst-case daily DMDS concentration was 1372.118 μ g/m³ at day 0, measured at 75 m from the treated plot, and was 113.730 μ g/m³ at 10 days (5 m; p. 54). Following aeration at 7 days in which the middle of each row of VIF was cut open for its entire length, the mean concentration of DMDS was a maximum of 264.380 μ g/m³ at

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8 days at 0 m, and decreased to a maximum of $62.458 \ \mu g/m^3$ by 10 days (5 m). At a distance of 75 m from the treated plot, DMDS was a maximum mean concentration of 102.750 $\ \mu g/m^3$ at 2 days before decreasing to 3.051 $\ \mu g/m^3$ by 6 days; following aeration, DMDS was a maximum mean concentration of 37.421 $\ \mu g/m^3$ at 8 days before decreasing to 8.609 $\ \mu g/m^3$ by 10 days.

Distance	Mean daily concentration of DMDS in atmosphere ($\mu g/m^3$) at Site 3										
to test	Days after treatment										
plot (m)	0	1	2	3	4	5	6	7	8	9	10
0	83.128	232.253	211.545	70.809	184.009	142.499	49.227	127.883	264.380	120.150	52.598
5	75.594	213.497	191.272	60.661	157.870	125.018	38.705	125.522	226.780	113.441	62.458
25	85.679	116.953	111.499	31.448	109.347	58.759	10.397	43.392	84.208	54.298	23.589
50	81.003	150.760	130.727	33.277	92.145	54.499	15.374	48.158	80.967	48.848	18.122
75	88.194	82.595	102.750	14.856	79.101	42,724	3.051	15.094	37.421	31.572	8.609

Data were obtained from p. 64 of the study report. Data are means of all samples taken in 24-hour period at the specified distance from the treated plot. The day 0 mean is from the start of fumigation at 09:00 until 06:00 the following day. Means reported for days 1 through 8 are for a 24-hour period from 06:00 to 06:00. Due to bulking of day/night samples for the 9 and 10 day samples, day 9 includes the 10 day sample from 00:00 to 06:00; the day 10 mean is from 06:00 to 24:00 on day 10.

Following shank application to raised beds at <u>Site 4 (Lawford, Essex, United Kingdom)</u>, the mean concentration of DMDS in the atmosphere was a maximum of 200.446 μ g/m³ at 1 day at the boundary of the treated plot (0 m), and decreased to a maximum of 75.523 μ g/m³ by 6 days posttreatment (the day prior to aeration; p. 65). The maximum worst-case daily DMDS concentration was 590.888 μ g/m³ at 1 day, measured at 0 m, and was 10.532 μ g/m³ at 10 days (5 m; p. 55). Following aeration at 7 days, in which two parallel offset set of slits were left in the top of the VIF on the raised beds, the mean concentration of DMDS was a maximum of 71.217 μ g/m³ at 7 days at 0 m, and decreased to a maximum of 4.841 μ g/m³ by 10 days (0 m). At a distance of 75 m from the treated plot, DMDS was a maximum mean concentration of 63.498 μ g/m³ at 2 days before decreasing to 13.669 μ g/m³ at 8 days before decreasing to 0.381 μ g/m³ by 10 days.

Distance	Mean daily concentration of DMDS in atmosphere ($\mu g/m^3$) at Site 4										
to test		Days after treatment									
plot (m)	0	1	2	3	4	5	6	7	8	9	10
0	47.184	200.446	199.584	96.326	31.196	19.292	75.523	71.217	32.555	28.884	4.841
5	45.517	169.497	174.713	80.005	30.552	17.736	56.058	63.175	28.677	25.855	4.119
25	23.193	83.676	105.131	31.140	14.755	3.737	30.425	25.362	16.395	14.126	1.372
50	26.727	28.246	86.166	25.333	5.070	6.233	26.123	22.461	12.540	8.744	2.614
75	12.473	37.555	63.498	9.987	3.355	0.751	13.669	8.802	10.002	6.630	0.381

Data were obtained from p. 65 of the study report. Data are means of all samples taken in 24-hour period at the specified distance from the treated plot. The day 0 mean is from the start of fumigation at 12:45 until 06:00 the following day. Means reported for days 1 through 7 are for a 24-hour period from 06:00 to 06:00. Due to bulking of the 9 and 10 day samples, 9 and 10 day samples are from 00:00 to 00:00 and 8 day samples are from 06:00 to 00:00.

Maximum wind speeds recorded on the day of application were 2.8, 3.3, 2.6, and 2.8 m/s for Sites 1, 2, 3, and 4, respectively, with maximum wind speeds for the 10-day study period of 4.7 m/s for Site 1, 6.9 m/s for Site 2, 4.3 m/s for Site 3, and 6.9 m/s for Site 4 (the height of the

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measurement was not reported; Appendix 3, pp. 153-177). Mean daily air temperatures for the 10-day study period ranged from 14.7 to 19.9°C at Site 1, 21.3 to 26.0°C at Site 2, 10.6 to 15.8°C at Site 3, and 12.3 to 18.9°C at Site 4 (pp. 28-29). Mean daily soil temperatures ranged from 17.0 to 22.0°C at Site 1, 26.8 to 30.6°C at Site 2, 13.7 to 16.4°C at Site 3, and 14.3 to 21.5°C at Site 4. Mean daily relative humidity ranged from 68.9 to 99.2% at Site 1, 45.9 to 82.7% at Site 2, 70.2 to 99.4% at Site 3, and 79.6 to 97.4% at Site 4. All reviewer-reported ranges exclude the meteorological data reported for the day prior to the test application. Site 1 received a total of 4.8 cm of rainfall, with over 90% of the total rainfall occurring during the last two days of the study period; Site 2 received a total of 0.02 cm of rainfall; Site 3 received a total of 2.5 cm of rainfall, with 2.3 cm falling on the seventh day of the study; and Site 4 received a total of 2.3 cm of rainfall.

Mean recovery of dimethyl disulfide from field spikes fortified with DMDS at each test site at 1, 100, and 5000 μ g/filter was 90% (range from 70 to 109%, excluding one outlier at 126%; p. 48 and Tables 59-62, pp. 122-133). Field spikes were stored frozen for 10-183 days prior to analysis.

STUDY DEFICIENCIES

- 1. Volatility was not reported. The primary purpose of the laboratory volatility study is to determine the potential of a pesticide to move into the air and to determine the rate of volatilization from soil. Volatilization should be reported in units of $\mu g/cm^2/hr$ or g/ha/day. The concentration of DMDS in the atmosphere was measured and reported in $\mu g/m^3$.
- 2. The highest recommended label rate was not reported for dimethyl disulfide, and the application rate was not verified. Subdivision N Guidelines require application at the maximum label rate. Additionally, EPA believes that soil samples should be collected to confirm that the pesticide was applied at the desired rate. The reviewer notes that the weight of DMDS applied to each plot was determined by weighing the DMDS tanks before and after application at each test site, and that the application rate was determined from the total weight of DMDS applied and the total area fumigated (pp. 11, 31-35).
- 3. The field volatility study was not conducted in the USA. The four study trials were located in Italy (two sites), Spain, and the United Kingdom. Subdivision N Guidelines require that the field volatility study be conducted domestically.
- 4. The soils at the test sites were not characterized using the USDA classification system. Soil textures were determined according to the UK classification system, which defines clay as particles <0.002 mm, silt as particles 0.002-0.063 mm and sand as particles 0.063-2.0 mm (pp. 26-27 and Appendix 4, p. 185). Soils should be characterized according to the USDA textural classification, which defines clay as particles <0.002 mm, silt as particles 0.002-0.05 mm and sand as particles 0.05-2.0 mm. Additionally, the study trials

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were located at three sites in Europe, and the study authors did not make any effort to establish comparability between the test site soils and US soils.

- 5. A plot use history was not provided for any of the four test sites as required by Subdivision N Guidelines. A plot use history is necessary to demonstrate that chemicals similar to the test material were not applied to the test plots in the previous three years.
- 6. The meteorological monitoring datasets accompanying these studies did not include solar radiation. This measurement is required to quantify atmospheric stability and turbulence which is necessary to determine flux of dimethyl disulfide. Since there are only air samplers off the treated field, the Pasquill-Gifford Stability Class is required in order to back-calculate emission rates for dimethyl disulfide over time using the ISCST3 dispersion model in the determination of the flux profile.

REVIEWER'S COMMENTS

- 1. The study was conducted according to OECD Series on Testing and Assessment No. 9 "Guidance Document for the Conduct of Studies of Occupational Exposure to Pesticides During Agricultural Application", 1997. OECD/GD(97)148, and in compliance with the UK Good Laboratory Practice Regulations (Statutory Instrument 1999 No. 3106, as amended by Statutory Instrument 2004 No. 994), OECD Principles of Good Laboratory Practice (as revised in 1997), ENV/MC/CHEM(98)17 and EC Commission Directive 2004/10/EC of 11 February 2004 (Official Journal No. L 50/44; p. 3 and p. 16). Signed and dated Data Confidentiality, GLP compliance and Quality Assurance statements were provided (pp. 2-4).
- 2. The study author reported that the analytical method was previously validated and documented in a separate report (p. 13). Additionally, the study author stated that control soil samples fortified with DMDS and analyzed alongside the field samples demonstrated recoveries in the acceptable range of 70-110% for all batches (p. 48); however, individual recoveries were not reported. The level of fortification for procedural recoveries was not reported.
- 3. The study author noted that a freezer at Site 2 (Spain) containing all samples up to 06:00 at 9 days posttreatment malfunctioned, causing the temperature in the freezer to increase above 0°C for approximately 1 hour (p. 39). However, analysis of transit and field spikes stored with the field samples indicated suitable recoveries. The study author concluded that this event had no effect on the study results.
- 4. The study author stated that the freeze/thaw and weathering stability of DMDS was confirmed over the range of 0.1 to 6000 μg/sample on activated charcoal air filter tubes in HLS study no.: EFA/049 (p. 48). The front and back sections of the air filter tubes were analyzed separately to confirm no breakthrough of DMDS on the activated charcoal air filter tubes.

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Attachment 1: Structure of Test Material

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Dimethyl disulfide [DMDS, dimethyldisulfide, DMDS TC, dimethyl disulfide TC, ATOMAL, ATOMAL01, 2,3-dithiabutane, methyl disulfide, (methyldithio)methane, (methyldisulfanyl)methane, (methyldithio)methane, methyldithion ethane, dimethyldisulphide]

IUPAC Name:	Dimethyl disulfide.		
CAS Name:	Dimethyl disulfide.		
CAS Number:	624-92-0.		
SMILES String:	S(SC)C (EPI Suite, v3.12 SM	AILES String).	
Empirical formula	: CH ₃ S	Molecular formula:	$C_2H_6S_2$

H₃C^SS^{CH}3