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



# **OPP OFFICIAL RECORD** HEALTH EFFECTS DIVISION SCIENTIFIC DATA REVIEWS **EPA SERIES 361**

OFFICE OF PREVENTION. PESTICIDES AND TOXIC SUBSTANCES

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## **MEMORANDUM**

Review of "Assessment of Exposure for MSMA and DSMA" (MRID 437204-01; SUBJECT:

DP Barcode D217733).

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This submission is a registrant analysis of dermal and inhalation handler exposure to MSMA and DSMA based on specified application rates, cacodylic acid's dermal absorption, and exposure data available in the Pesticide Handler's Exposure Database (PHED), (version not stated, before May 1995). MSMA and DSMA are both arsenical, selective post-emergent herbicides. DSMA is formulated as a granular, a soluble concentrate, and a wettable powder. MSMA is formulated as a liquid and a liquid with surfactants. The use patterns of both active ingredients are the same.

The application rates for MSMA, used in this analysis, are 2.0 lbs ai/A for cotton, orchards, non-crop areas such as ditch banks, fence rows, and rights-of way, and 2.2 lbs ai/A for lawns and turf. The applications rates for DSMA, used in this analysis, are 3.6 lbs ai/A for cotton, non-crop areas such as ditch banks, fence rows, and rights-of-way, and 3.6 to 7.2 lbs ai/A for citrus trees. The pesticides are applied to cotton using a groundboom sprayer or an aircraft and to lawns, trees and non-crop areas using liquid broadcast, low or high pressure hand wands, and backpack sprayer are used. Homeowners use either backpack sprayers or 2 to 3 gallon low pressure handwand.

PHED was used to estimate the dermal and inhalation exposure resulting from the registered uses of MSMA and DSMA formulated as a liquid water-soluble concentrate or a wettable powder. For each use pattern, a variety of subsets were created. The determination of which specific subsets to use was based on the size of the data set created, the appropriateness of the specifications, and the effect of additional specifications on the exposure data.

Six scenarios were used to determine the dose of MSMA and DSMA. The first is mixer/loader exposure to the liquid water-soluble concentrate formulation. This includes emulsifiable concentrate, aqueous suspension, or a solution with open pour mixing and loading. The inhalation data were restricted to those observations of data grades A or B. The dermal exposure data were restricted to dermal grades of A or B and hand grades of A and B or C when hand rinses or no clothing with chemical resistant gloves was used. The second scenario is mixer/loader exposure to the wettable powder formulation. The data were subseted to exclude water soluble packaging and include those that had 10 lbs ai handled or greater and a handler wearing overalls over no clothing and chemical resistant gloves. The third scenario is applicator exposure during open cab groundrig application. The data were initially subseted to exclude granular and dust formulations and restricting the vehicles to open cab only The dermal exposure is based on long pants, short sleeve shirt, and no gloves. Only A and B grade data was used for inhalation and dermal exposure, with C for the hand rinse also being included. The forth scenario is a hand-held gun applicator exposure. Homeowners must use a backpack or a low pressure handwand. The use of a hose-end sprayer is prohibited by the label. For occupational use the data was subseted into just a liquid broadcast, a low or a high pressure hand wand, and a backpack sprayer. The dermal exposure is based on long-sleeved shirt and long pants, with chemical resistant gloves for the occupational worker only. The fifth scenario is the pilots exposure. The subset excluded granular and dust formulations and application rates less than 0.09 lbs ai/A. The dermal exposure is based on long pants, short sleeved shirt and no gloves. The sixth scenario is flagger exposure. The data was subseted by excluding dust and granular applications and application rates less than 0.5 lbs ai/A. The dermal exposure was based on no clothing.

A PHED assessment was done by HED, using PHED Surrogate Exposure Guide, Version 1.1, August 1998. attempting to match HED's normal procedure for using PHED as close as possible to the study's scenarios. Table 1 compares the HED's PHED assessment to the study's PHED assessment.

Table 1. Study PHED Run Compared to PHED Surrogate Exposure Guide Data.

Job Function (HED's Scenario if Different)	Clothing (HED's clothing if different)	Study's  *Dermal Exposure (mg/lb ai) (replicates)	HED's Dermal Exposure (mg/lb/ai) (replicates)	Study's Inhalation Exposure (zg/lb al) (replicates)	HED'S Inhalation Exposure (ug/lb ai) (replicates)
Mixer/Loader liquid formulation	no clothing, chemical resistant gloves	0.018 (14-22)	0.313 (72 to 122 hand 59)	0.17 (16)	1.2 (85)
Mixer/Loader wettable powder formulation	overalls over no clothing (single layer of clothing), chemical resistant gloves	0.175 (4-26)	0.167 (22-45 hand 24)	2.5 (26)	43 (44)
Groundrig Application open cab	long pants, short-sleeved shirt (single layer of clothing), no gloves	0.014 (14-16)	0.014 (23-42 hand 21)	0.37	0.74 (22)
Occupational Hand-Spray Application (Lawn Handgun, Low Pressure Handgun, High Pressure Handgun, and Backpack Sprayer)**	long sleeved shirt, long pants (single layer of clothing), chemical resistant gloves	0.224 (4-6)	0.34 (0-14 hand 14), 7.1 (13 hand 4), 0.64 (9-11 hand 9), and 2.5 (9-11 hand 11)	20 (2)	1.4 (14), 940 (13), 79 (11), and 30 (11)
Residential Hand-Spray Application (Backpack Sprayer and Aerosol Can) <sup>b</sup>	single layer of clothing, no gloves	1.37 (2-6)	5.1 (9-11 hand 11) and 220 (30 hand 15)	1.4 (14)	30 (11) and 2400 (30)
Pilot (Enclosed Cab)	long pants, short-sleeved shirt (single layer of clothing), no gloves	0.012 (6-8)	0.005 (24-48 hand 7)	0.021	0.068 (23)
Flagger (liquid formulation)	no clothing (no gloves)	0.079 (10-30)	0.053 (17-57 hand 30)	0.46 (30)	0.35 (28)

occupational hand spray application. HED does not combined these scenarios, so each separate scenario was shown to compare it to the study's combined scenario. Also, HED usually does not assess the backpack sprayer for applicator only, but instead it assesses the mixer/loader/applicator as a more feasible scenario. The study combined a liquid broadcast sprayer (lawn handgun), a low and a high pressure hand-held spray gun, and a backpack sprayer into one scenario, the

The study combined a backpack sprayer and an aerosol can into one scenario, the residential hand spray application. HED does not combine these scenarios, so each separate scenario was shown to compare it to the study's combined scenario. Also, HED usually does not assess the backpack sprayer for applicator only, but instead it assesses the mixer/loader/applicator as a more feasible scenario.

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## **Summary of Unit Exposure Values**

The following registrant suggested unit exposure values are relatively similar to unit exposures to PHED: mixer/loader (wettable powder formulation) for dermal exposure, groundrig application for dermal exposure, and flagger for both dermal and inhalation exposure. The following registrant suggested unit exposure values are within a ten fold margin of PHED unit exposure values: mixer/loader (liquid formulation) for inhalation exposure, groundrig application for inhalation exposure, occupational hand spray application for both dermal and inhalation exposure, residential back pack sprayer application for dermal exposure, and pilot for both dermal and inhalation exposure. The rest of the unit exposure values differed from PHED by more than a 10 fold factor.

A biomonitoring study of flaggers exposed to chlopyrofos was also reported. Six flaggers were monitored over a four week period. Only three out of the seven days were spent flagging. Twelve applications were made, totaling 24,000 acres being treated with approximately 20,000 lbs ai. The estimated flagger exposure based on 65 replicates ranged from 0.065  $\mu$ g/lb ai to 21.9  $\mu$ g/lb ai. The geometric mean exposure was 2.49  $\mu$ g/lb ai. The exposure estimates reflect the clothing typically worn by flaggers.

The dermal absorption of MSMA and DSMA was estimated based on cacodylic acid's dermal absorption. The additional methyl group makes cacodylic acid slightly more lipophilic than either MSMA or DSMA and this increases it dermal absorption potential compared to MSMA or DSMA. The average percentage of the three dose levels that were absorbed after a ten hour exposure duration was 2.5%. The average potential absorption was 22.8%, which is likely an overestimate. The corrected values for MSMA and DSMA using the 22.8% dermal absorption are in table 2.

Table 2. Study's PHED Run Unit Exposure Values Corrected for Dermal Adsorption.

Job Function	Dermal Exposure (mg/lbs ai)	Inhalation Exposure (μg/lbs ai)
Mixer/Loader (liquid formulation)	0.0041	0.17
Mixer/Loader (wettable powder formulation)	0.040	2.5
Groundrig Applicator	0.0032	0.37
Occupational Hand Spray Application	0.051	20
Residential Hand Spray Application	0.312	20
Pilot	0.0027	0.021
Flagger	0.00057ª	0.46

a Value from flagger study (2.49  $\mu$ g/lbs ai) replaced PHED run number (79  $\mu$ g/lbs ai). 2.49  $\mu$ g/lbs ai \* 22.8% \* (1mg 1000  $\mu$ g) = 0.00057 mg/lbs ai.

Dose estimates were performed for cotton, orchards, non-crop, and lawns. For MSMA's and DSMA's liquid formulations, the combined mixer/loader and groundboom applicator absorbed dose is  $7.3~\mu g/lbs$  ai for dermal exposure and  $0.54~\mu g/lbs$  ai for inhalation exposure.

For DSMA's wettable powder formulations, the combined mixing/loading and groundboom application dose is 43  $\mu$ g/lbs ai for the dermal dose and 2.9  $\mu$ g/lbs ai for the inhalation dose. A small grower was estimated to handle 183 lbs ai/year of MSMA or 215 lbs ai/year DSMA. A large grower was estimated to handle either 438 lbs ai/year MSMA or 516 lbs ai/year DSMA, based on a 1994 use summary for the six major cotton producing states. For cotton using a ground boom, the annual and daily amortized absorbed dose estimates are based on a 70 kg person and are in Table 3. Daily amortized and annual doses are not calculated by HED.

#### Annual doses are calculated as follows:

Annual Dermal Dose ( $\mu$ g/kg/year) = (dermal absorbed dose ( $\mu$ g/lb ai) \* amount handled (lbs ai/year))/ body weight (kg).

Annual Inhalation Dose ( $\mu$ g/kg/year) = (inhalation absorbed dose ( $\mu$ g/lb ai) \* amount handled (lbs ai/year))/ body weight (kg).

Combined Annual Dose ( $\mu$ g/kg/year) = Annual Dermal Dose ( $\mu$ g/kg/year) + Annual Inhalation Dose ( $\mu$ g/kg/year).

# Daily Amortized Doses are calculated as follows:

Daily Dermal Amortized Dose ( $\mu$ g/kg/day) = ((dermal absorbed dose ( $\mu$ g/lb ai) \* amount handled (lbs ai/year))/ body weight (kg))/ 365 days/year.

Daily Inhalation Amortized Dose ( $\mu g/kg/day$ ) = ((inhalation absorbed dose ( $\mu g/lb$  ai) \* amount handled (lbs ai/year))/ body weight (kg))/ 365 days/year.

Combined Daily Amortized Dose ( $\mu$ g/kg/year) = Daily Dermal Amortized Dose ( $\mu$ g/kg/day) + Daily Inhalation Amortized Dose ( $\mu$ g/kg/day).

Table 3. Groundboom Application of Liquid Pesticide to Cotton.

Grower/Dose	Dermal Dose (μg/kg/day or year)	Inhalation Dose (μg/kg/day or year)	Combined Dose (µg/kg/day or year)
	MSMA		
Small grower - Annual Dose	19	1.4	20
Small Grower - Daily Amortized Dose	0.052	0.0039	0.056
Large Grower - Annual Dose	46	3.4	49
Large Grower - Daily Amortized Dose	0.13	0.0093	0.14
	DSMA		
Small grower - Annual Dose	22	1.7	24
Small Grower - Daily Amortized Dose	0.061	0.0045	0.066
Large Grower - Annual Dose	54	4.0	58
Large Grower - Daily Amortized Dose	0.15	0.011	0.16

DSMA wettable powder formulation is applied to cotton, with use estimates of 215 lbs ai/year for small growers and 516 lbs ai/year for large growers. Table 4 shows the annual and amortized daily dose of a 70 kg person estimates for the DSMA wettable powder formulation.

Table 4. DSMA, Wettable Powder Formulation, Applied to Cotton .

Grower/Dose	Dermal Dose (μg/kg/day or year)	Inhalation Dose (µg/kg/day or year)	Combined Dose (µg/kg/day or year)
Small grower - Annual Dose	132	8.9	141
Small Grower - Daily Amortized Dose	0.36	0.024	0.38
Large Grower - Annual Dose	317	21	338
Large Grower - Daily Dose	0.87	0.059	0.93

An aerial application crew of a mixer/loader, pilot, and flaggers, is assumed to handle 3000 lbs ai/year of MSMA or 5600 lbs ai/year DSMA for application to cotton. Table 5 represents the annual and amortized daily dose of a 70 kg person for MSMA and DSMA.

Table 5. MSMA and DSMA Dose Estimates for an Aerial Application Crew on Cotton.

Scenario/Dose	Dermal Dose (μg/kg/day or year)	Inhalation Dose (µg/kg/day or year)	Combined Dose (µg/kg/day or year)
	MSMA		
Liquid Mixer/Loader - Annual Dose	176	7,3	183
Liquid Mixer/Loader - Daily Dose	0.48	0.020	0.50
Pilot - Annual Dose	328	14	342
Pilot - Daily Dose	. 0.90	0.037	0.94
Flagger - Annual Dose	3200	200	3400
Flagger - Daily Dose	8.8	0.55	9.4
	DSMA		
Liquid Mixer/Loader - Annual Dose	116	0.90	117
Liquid Mixer/Loader - Daily Dose	0.32	0.0025	0.32
Powder Mixer/Loader - Annual Dose	216	<b>i</b> .7	218
Powder Mixer/Loader - Daily Dose	0.59	0.0046	0.60
Pilot - Annual Dose	12	9.9	22
Pilot - Daily Dose	0.033	0.027	0.060
Flagger - Annual Dose	23	18	41
Flagger - Daily Dose	0.062	0.049	0.11

MSMA and DSMA are applied in orchards or groves and 60 lbs ai/year is representative of their use. DSMA is used only on citrus. Table 6 contains the annual and amortized dose estimates for a 70 kg person.

Table 6. Orchard/Grove Application Dose Estimates.

Scenario/Dose	Dermal Dose (μg/kg/day or year)	Inhalation Dose (μg/kg/day or year)	Combined Dose (μg/kg/day or year)
MSMA or DSMA Liquid - Annual Dose	132	8.9	141
MSMA or DSMA Liquid - Daily Dose	0.36	0.024	0.38
DSMA Powder - Annual Dose	317	21	. 338
DSMA Powder - Daily Dose	0.87	0.059	0.93

MSMA and DSMA are applied to non-crop areas for weed control. Each crew member was estimated to handled 750 lbs ai/year of MSMA and 1350 lbs ai/year DSMA. Table 7 contains the annual and amortized estimates for a 70 kg person.

Table 7. MSMA and DSMA Non-Crop Application Estimates.

Scenario/Dose	Dermal Dose (μg/kg/day or year)	Inhalation Dose (µg/kg/day or year)	Combined Dose (µg/kg/day or year)
MSMA Liquid - Annual Dose	78	5.8	84
MSMA Liquid - Daily Dose	0.21	0.016	0.23
DSMA Liquid - Annual Dose	141	10	151
DSMA Liquid - Daily Dose	0.39	0.029	0.42
DSMA Powder - Annual Dose	829	56	885
DSMA Powder - Daily Dose	2.3	0.15	2.5

MSMA and DSMA are applied to lawns by occupational handlers. They are estimated to use 48 lbs ai/year of MSMA or DSMA. For a truck mounted hand held spray gun application, the combined absorbed dose for mixing/loading and application of liquids is 55  $\mu$ g/lbs ai for dermal exposure and 20  $\mu$ g/lbs ai for inhalation exposure. Wettable powder has a combined absorbed dermal dose of 91  $\mu$ g/lbs ai and inhalation dose of 23  $\mu$ g/lbs ai. The annual and amortized daily dose estimates for a 70 kg person are in Table 8.

Table 8. MSMA and DSMA Occupational Lawn Application Estimates.

Scenario/Dose	Dermal Dose (μg/kg/day or year)	Inhalation Dose (μg/kg/day or year)	Combined Dose (µg/kg/day or year)
MSMA or DSMA Liquid - Annual Dose	38	14	52
MSMA or DSMA Liquid - Daily Dose	0.10	0.038	0.14
DSMA Powder - Annual Dose	62	16	78
DSMA Powder - Daily Dose	0.17	0.044	0.21

MSMA and DSMA are applied to lawns by residential handlers. They are estimated to use 0.72 lbs ai year of MSMA or DSMA treating a 15,000 sq ft lawn twice annually. For compressed air sprayer or backpack sprayer application, the combined absorbed dose for mixing/loading and application of liquids is 316  $\mu$ g/lbs ai for dermal exposure and 20  $\mu$ g/lbs ai for inhalation exposure. Wettable powder has a combined absorbed dermal dose of 352  $\mu$ g/lbs ai and inhalation dose of 23

 $\mu$ g/lbs ai. The annual and amortized daily dose estimates for a 70 kg person are in Table 9.

Table 9. MSMA and DSMA Residential Lawn Application Estimates.

Scenario/Dose	Dermal Dose (μg/kg/day or year)	Inhalation Dose (μg/kg/day or ÿear)	Combined Dose (µg/kg/day or year)
MSMA or DSMA Liquid - Annual Dose	3.3	0.21	3.5
MSMA or DSMA Liquid - Daily Dose	0.0089	0.0057	0.0095
DSMA Powder - Annual Dose	3.6	0.24	3.8
DSMA Powder - Daily Dose	0.0099	0.0065	0.011

## **Summary**

The registrant conducted an analysis of dermal and inhalation handler exposure to MSMA and DSMA based on specified application rates, cacodylic acid's dermal absorption, and exposure data available in the Pesticide Handler's Exposure Database (PHED), (version not stated, before May 1995). The six scenarios identified in the study were mixer/loader (liquid formulation), mixer/loader (wettable powder formulation), groundrig applicator, occupational hand spray application, residential hand spray application, pilot application, and flaggers.

The registrant's suggested unit exposure values were compared to the unit exposures in PHED Surrogate Exposure Guide, version 1.1, August 1998. The following registrant suggested unit exposure values are relatively similar to unit exposures to PHED: mixer/loader (wettable powder formulation) for dermal exposure, groundrig application for dermal exposure, and flagger for both dermal and inhalation exposure. The following registrant suggested unit exposure values are within a ten fold margin of PHED unit exposure values: mixer/loader (liquid formulation) for inhalation exposure, groundrig application for inhalation exposure, occupational hand spray application for both dermal and inhalation exposure, residential back pack sprayer application for dermal exposure, and pilot for both dermal and inhalation exposure. The rest of the unit exposure values differed from PHED by more than a 10 fold factor.

Annual dose and daily amortized dose were calculated for both MSMA and DSMA. HED dose not calculate annual and daily amortized doses. For MSMA used on cotton, a small grower's annual dose is  $20~\mu g/kg/year$  and a large grower's annual dose is  $49~\mu g/kg/year$ . A small grower's daily amortized dose is  $0.056~\mu g/kg/day$  and a large grower's daily amortized dose is  $0.14~\mu g/kg/day$ . A mixer/loader's annual dose is  $183~\mu g/kg/year$  and daily amortized dose is  $0.5~\mu g/kg/day$ . A pilot's annual dose is  $342~\mu g/kg/year$  and daily amortized dose is  $0.94~\mu g/kg/day$ . A flagger's annual dose is  $3400~\mu g/kg$  year and daily amortized does is  $9.4~\mu g/kg/day$ .

For liquid DSMA used on cotton, a small grower's annual dose is  $24 \,\mu g/kg/year$  and a large grower's annual dose is  $58 \,\mu g/kg/year$ . A small grower's daily amortized dose is  $0.066 \,\mu g/kg/day$  and a large grower's daily amortized dose is  $0.16 \,\mu g/kg/day$ . A mixer/loader's annual dose is  $141 \,\mu g/kg/year$  and daily amortized dose is  $0.32 \,\mu g/kg/day$ . For the wettable powder formulation of DSMA, a small grower's annual dose is  $141 \,\mu g/kg/year$  and a large grower's annual dose is  $338 \,\mu g/kg/year$ . A small grower's daily amortized dose is  $0.38 \,\mu g/kg/day$  and a large grower's daily amortized dose is  $0.93 \,\mu g/kg/day$ . A mixer/loader's annual dose is  $218 \,\mu g/kg/year$  and daily

amortized dose is 0.6  $\mu$ g/kg/day. A pilot's annual dose is 22  $\mu$ g/kg/year and daily amortized dose is 0.060  $\mu$ g/kg/day. A flagger's annual dose is 41  $\mu$ g/kg/year and daily amortized does is 0.11  $\mu$ g/kg/day.

For the remaining occupational uses of MSMA and DSMA, such as orchards, non-crop, and lawn application, the annual dose of MSMA liquid ranges from 141 to 52  $\mu$ g/kg/year and the daily amortized dose ranges from 0.38 to 0.14  $\mu$ g/kg/day. The annual dose of DSMA liquid ranges from 151 to 52  $\mu$ g/kg/year and the daily amortized dose ranges from 0.42 to 0.14  $\mu$ g/kg/day. The annual dose of DSMA wettable powder ranges from 885 to 78  $\mu$ g/kg/year and the daily amortized dose ranges from 2.5 to 0.21  $\mu$ g/kg/day.

For residential lawn application, the annual dose of MSMA and DSMA liquid is 3.5  $\mu$ g/kg/year and daily amortized dose is 0.0095  $\mu$ g/kg/day. The annual dose of DSMA wettable powder is 3.8  $\mu$ g/kg/year and daily amortized does is 0.011  $\mu$ g/kg/day.

#### Conclusion

It is HED's policy to use the PHED Surrogate Exposure Guide, Version 1.1, August 1998 when assessing handler exposure. Use of the Surrogate Exposure Guide offers certain advantages over attempting to subset PHED for each individual exposure assessment. For example, use of the Guide results in consistency among exposure assessments for similar pesticide exposure scenarios, and use of the Guide is relatively easy and, therefore, saves resources by reducing the time spent on analyzing individual data sets. Moreover, restrictive subsets (e.g., one exposure study) may not encompass the variety of agricultural equipment in use throughout the country and the inter-variability of exposures among handlers. Also, HED does not amortize doses for occupational exposures. Therefore, the unit exposures from the PHED Surrogate Exposure Guide, Version 1.1, August 1998 will be used in the MSMA and DSMA Occupational and Residential Exposure Assessment.