MRID 43314801
MRID 43322801

DP Barcode :D206247, 206296, 206535
PC Code No.:013803
EFGWB Out : OCT 11 1994

TO: Virginia Dietrich
Product Manager PM 51
Special Review and Reregistration Division (H7508W)

FROM: Akiva Abramovitch, Chief
Environmental Chemistry Review Section #3
Environmental Fate & Ground Water Branch/EFED (H7507C)

THRU: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C) Henry Jacoby 10/11/94

Attached, please find the EFGWB review of...

Reg./File #: 2395

Common Name: MSMA

Product Name: Ansar, Target, Bueno, Daconate, Merge

Company Name: MAA Task Force Three

Purpose: 1) review of 162-4 study, 2) protocol review, 2) response to 164-1 deficiencies, ~~Review of 162-1, 162-2, 164-1 studies for registration; response to data waiver requests~~ (conditions noted by HJ on 4/4/02.)

Type Product: Herbicide Action Code: 606, 627, 635 Review Time: 2.5 days

EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

161-1		162-4	43314801 ✓	Y	164-4		166-1	
161-2		163-1			164-5		166-2	
161-3		163-2			165-1		166-3	
161-4		163-3			165-2		167-1	
162-1		164-1	43322801 ✓	N	165-3		167-2	
162-2		164-2			165-4		201-1	
162-3		164-3			165-5		202-1	

Y = Acceptable (Study satisfied the Guideline)/Concur U = Upgradeable (Study may become satisfactory with the submission of additional information)
S = Supplemental (Study provided useful information, but Guideline was not satisfied) N = Unacceptable (Study was rejected)/Non-Concur

DP BARCODE: D206247 REREG CASE # 2395

CASE: 818606 DATA PACKAGE RECORD DATE: 08/05/94
SUBMISSION: S471322 BEAN SHEET Page 1 of 1

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REREGISTRATION ACTION: 606 GENERIC DATA
CHEMICALS: 013803 MSMA 100.00 %

ID#: 013803
COMPANY:
PRODUCT MANAGER: 51 VIRGINIA DIETRICH 703-308-8157 ROOM: CS1 3H3
PM TEAM REVIEWER: RON KENDALL 703-308-8068 ROOM: CS1 4L3
RECEIVED DATE: 07/26/94 DUE OUT DATE: 11/23/94

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 206247 EXPEDITE: N DATE SENT: 08/05/94 DATE RET.: / /
CHEMICAL: 013803 MSMA
DP TYPE: 999 Miscellaneous Data Package
CSF: N LABEL: N

ASSIGNED TO	DATE IN	DATE OUT
DIV : EFED	08/10/94	/ /
BRAN: EFGB	/ /	/ /
SECT:	/ /	/ /
REVR :	/ /	/ /
CONTR:	/ /	/ /

ADMIN DUE DATE: 12/03/94
NEGOT DATE: / /
PROJ DATE: / /

* * * DATA REVIEW INSTRUCTIONS * * *

Please review MRID# 43314801 for GDLN 162-4. 0.15. ots 4/4/02

Thank you for your time, if you have questions please call me at 308-8068.

* * * DATA PACKAGE EVALUATION * * *

No evaluation is written for this data package

* * * ADDITIONAL DATA PACKAGES FOR THIS SUBMISSION * * *

DP BC	BRANCH/SECTION	DATE OUT	DUE BACK	INS	CSF	LABEL

2

DP BARCODE: D206296 REREG CASE # 2395

CASE: 818606 DATA PACKAGE RECORD DATE: 08/08/94
SUBMISSION: S471371 BEAN SHEET Page 1 of 1

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REREGISTRATION ACTION: 627 CORE DATA
CHEMICALS: 013803 MSMA 100.00 %

ID#: 013803
COMPANY:
PRODUCT MANAGER: 51 VIRGINIA DIETRICH 703-308-8157 ROOM: CS1 3H3
PM TEAM REVIEWER: RON KENDALL 703-308-8068 ROOM: CS1 4L3
RECEIVED DATE: 08/05/94 DUE OUT DATE: 12/03/94

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 206296 EXPEDITE: N DATE SENT: 08/08/94 DATE RET.: / /
CHEMICAL: 013803 MSMA
DP TYPE: 999 Miscellaneous Data Package
CSF: N LABEL: N

ASSIGNED TO	DATE IN	DATE OUT
DIV : EFED	08/11/94	/ /
BRAN: EFGB	/ /	/ /
SECT:	/ /	/ /
REVR :	/ /	/ /
CONTR:	/ /	/ /

ADMIN DUE DATE: 12/06/94
NEGOT DATE: / /
PROJ DATE: / /

* * * DATA REVIEW INSTRUCTIONS * * *

Registrant is presenting additional information/explanation to upgarde previous submission MRID# 42616201, This submission is MRID# 43322801. Please review.

O.K. DTK 1/4/02

* * * DATA PACKAGE EVALUATION * * *

No evaluation is written for this data package

* * * ADDITIONAL DATA PACKAGES FOR THIS SUBMISSION * * *

DP BC	BRANCH/SECTION	DATE OUT	DUE BACK	INS	CSF	LABEL

DP BARCODE: D206535

REREG CASE # 2395

CASE: 818606
SUBMISSION: S471752

DATA PACKAGE RECORD
BEAN SHEET

DATE: 08/15/94
Page 1 of 1

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REREGISTRATION ACTION: 635 PROTOCOL
CHEMICALS: 013803 MSMA 100.00 %

ID#: 013803
COMPANY:
PRODUCT MANAGER: 51 VIRGINIA DIETRICH 703-308-8157 ROOM: CS1 3H3
PM TEAM REVIEWER: RON KENDALL 703-308-8068 ROOM: CS1 4L3
RECEIVED DATE: 08/10/94 DUE OUT DATE: 11/18/94

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 206535 EXPEDITE: N DATE SENT: 08/15/94 DATE RET.: / /
CHEMICAL: 013803 MSMA
DP TYPE: 999 Miscellaneous Data Package
CSF: N LABEL: N

ASSIGNED TO	DATE IN	DATE OUT
DIV : EFED	08/17/94	/ /
BRAN: EFGB	/ /	/ /
SECT:	/ /	/ /
REVR :	/ /	/ /
CONTR:	/ /	/ /

ADMIN DUE DATE: 11/13/94
NEGOT DATE: / /
PROJ DATE: / /

* * * DATA REVIEW INSTRUCTIONS * * *

Please review and advise if attached protocol for MSMA will answer our outstanding question s for GDLNs 162-1, and 162-3. o.k. jtk 9/4/02

If you have questions please call Ron Kendall at 308-8068.

* * * DATA PACKAGE EVALUATION * * *

No evaluation is written for this data package

* * * ADDITIONAL DATA PACKAGES FOR THIS SUBMISSION * * *

DP BC	BRANCH/SECTION	DATE OUT	DUE BACK	INS	CSF	LABEL

4

1. CHEMICAL: Common name:

MSMA.

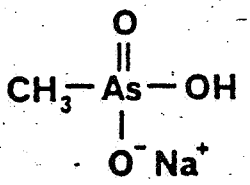
Chemical name(s):

Monosodium methanearsonate.
Methylarsonic acid, monosodium salt

Trade name(s):

MSMA, Ansar 529, Ansar 170, Target MSMA, Daconate, Mesamate, Bueno, Merge 823, Dal-E-Rad, Weed-E-Rad, Arsonate Liquid, Weed-Hoe, and Super Arsonate.

Structure:



Formulations:

Liquid, and liquid plus surfactants.

Physical/Chemical properties:

Molecular formula:	CH_4AsNaO_3.
Molecular weight:	162.0.
Physical state:	Colorless crystalline solid.
Melting point:	132-139 C.
Solubility (25 C):	104 g/mL water.

2. TEST MATERIAL:

Study 1: Active ingredient.

3. STUDY/ACTION TYPE:

Review of aerobic aquatic metabolism study, comments on protocol for aerobic soil metabolism study, and response to registrant comments on EFGWB review of terrestrial field dissipation study submitted in support of reregistration.

4. STUDY IDENTIFICATION:

162-4: Aerobic aquatic metabolism
Atkins, R.H. 1994. Aerobic aquatic metabolism of [^{14}C]MSMA. PTRL Project No. 757; PTRL Report No. 1573. Unpublished study performed by PTRL East, Inc., Richmond, KY, and submitted by Luxembourg Industries (PAMOL), Ltd., Tel Aviv, Israel. (43314801)

164-1: Terrestrial Field Dissipation
Coody, P.N. 1994. Supplemental attachment to MRID number 42616201: Terrestrial field dissipation study in Arkansas soil. Submission of response to deficiencies noted in EPA letter of 2/9/94. Response prepared by PTRL-East, Richmond, KY; and submitted by MAA Research Task Force Three, Memphis, TN. (43322801)

5

5. REVIEWED BY:

David Edelstein
Soil Scientist
EFGWB/EFED/OPP
Review Section #3

Signature: David Edelstein

Date: OCT - 5 1994

6. APPROVED BY:

Akiva D. Abramovitch
Chief
EFGWB/EFED/OPP
Review Section #3

Signature: K. A. Barrett for AA

Date: OCT - 5 1994

7. CONCLUSIONS:

162-1: Aerobic soil metabolism (test protocol)
The submitted protocol appears to provide a reasonable basis for assessing the metabolism of MSMA in aerobic soil. However, due to the protocol's similarity to the 162-4 study reviewed in this package, the EFGWB reviewer raises the following concerns:

1) pH, Eh, and dissolved oxygen measurements should be made before the system is purged with pure ~~oxygen~~, so that the actual conditions existing in the flask during incubation can be determined. Also, the use of a flow-through system rather than a closed system might simplify this issue.

2) The protocol calls for sampling for total arsenic in soil at time 0, 6 months, and 12 months posttreatment. As inorganic forms of arsenic are believed to be MSMA degradates, total soil arsenic should be sampled at each sampling interval.

3) Colony forming units should be enumerated both before and after the experiment, and results of both counts reported.

4) It is recommended that the study author address the relationship between the results of the aerobic soil metabolism study and the reported results of the field studies (MRID 42526001, 42616201).

O.K. per 4/4/02

162-4: Aerobic aquatic metabolism (MRID 43314801; acceptable)
Although there are a number of uncertainties in this study, it is marginally acceptable. Methyl-labeled [^{14}C] monosodium methanearsonate (MSMA) degraded slowly on sandy loam soil that was flooded with HPLC-grade water and incubated in the dark at 25.0 ± 0 °C. One [^{14}C]degradate was identified: cacodylic acid, maximum 4.5-5.3% of the applied 30 days posttreatment. By day 30, 0.9-2.0% of the applied radioactivity had been released as CO_2 and 7.5-7.8% of the applied radiocarbon was bound residue.

164-1: Terrestrial Field Dissipation (MRID 42616201, ~~43314801~~ 43732801 (response to deficiencies) upgradeable)
The registrant's response does not satisfy the purpose of the terrestrial field dissipation study, which is to identify the routes of dissipation of MSMA in the field. In the laboratory, MSMA is stable to abiotic processes, biodegrades very slowly, and is not mobile. Yet, in the field, the half-life was reported to be 11 days in one study and 55 days in another. The registrant has not provided any explanation of this difference, although the EFGWB reviewer suspects that the problem lies in the laboratory biodegradation data. New laboratory studies have been

Reassigned to 162-4 dtd 4/4/02

6

required, and EFGWB will revisit the field study when acceptable aerobic soil metabolism and mobility data are received, as this should aid in the interpretation of field results. The registrant is encouraged to discuss laboratory study results in terms of their implications for the field study.

With regard to certain specific comments, the registrant response offers a degradation pathway for MSMA, it does not provide data on the pattern of degradate formation and decline. The pattern is established from measured degradate concentrations, which can be compared to one another and the parent concentration over the time period of the experiment. The terrestrial field dissipation study did not establish a pattern of degradate formation, as concentrations were highly variable, but only established a decline in parent concentration over time. As the rapid disappearance of parent MSMA was unexpected, a corresponding rise in degradate concentrations could have provided an explanation for that result.

The question of arsenic speciation is not simply a matter of academic interest. Arsenite is believed to have more serious toxicological effects than arsenate. However, EFGWB agrees that arsenate-arsenite speciation is primarily a function of site conditions, not a direct consequence of MSMA use. As inorganic arsenic speciation is a site-specific effect, there would be little purpose in requiring data beyond the submitted Eh-pH diagram. No further data on inorganic arsenic speciation is required at this time.

ENVIRONMENTAL FATE ASSESSMENT

Laboratory data indicate that monosodium methanearsonate (MSMA) is to be persistent, but not mobile. Some MSMA degradates may be volatile. In water, the sodium ion dissociates from MSMA to form the methanearsonate anion and methanearsonic acid, which are stable to hydrolysis. MSMA is stable to photolysis in soil and water. While MSMA mobility data are incomplete, inorganic arsenic can form insoluble salts in soil solution, and is not believed to be mobile. MSMA appears to resist aerobic biodegradation. The anaerobic metabolism pathway of MSMA is not clear; the primary anaerobic metabolites of MSMA were said to volatilize, but no evidence was provided for this assertion.

In the field, MSMA appeared to dissipate far more rapidly than would be expected from the laboratory data. The route of dissipation is unclear, as little MSMA appeared to degrade to cacodylic acid, and MSMA does not appear to be mobile. Additional data on MSMA dissipation in the field will be needed. However, the presumed immobility of inorganic arsenic and the fact that it cannot be degraded indicate that repeated applications of MSMA will increase the probability of environmental exposure (i.e., surface water exposure, wildlife exposure) to arsenic.

MSMA does not accumulate in fish.

8. RECOMMENDATIONS:

Inform the registrant that the study aerobic aquatic metabolism is acceptable. However, the registrant's response to comments is not sufficient to permit acceptance of the terrestrial field dissipation studies without the required aerobic soil metabolism and mobility data. The short half-lives reported in the field study must be reconciled with MSMA's apparent persistence in the laboratory.

Data requirement status for MSMA are listed in Table 1.

7

9. BACKGROUND:

A. Introduction

B. Directions for Use

MSMA (monosodium methanearsonate) is a selective contact herbicide registered for use to control bahiagrass, barnyardgrass, chickweed, cocklebur, crabgrass, dallisgrass, Johnson grass, foxtails, mustard, nutgrass, pigweed, punctureVine, ragweed, sandbur, tules, wild oats and wood sorrel in terrestrial food crops (cotton, bearing citrus, and nonbearing orchards), noncropland areas, and turf. In addition, MSMA may be used to kill trees. Single active ingredient formulations include liquid and liquid plus surfactants. Multiple active ingredient formulations include cacodylic acid, fluometuron, mecoprop, and dicamba.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Refer to attached review.

11. COMPLETION OF ONE-LINER:

The one-liner has been updated and is attached.

12. CBI APPENDIX:

No claims of confidentiality are made for any of the data reviewed in this package.

DATA REQUIREMENT STATUS: MSMA (TERRESTRIAL FOOD CROPS)

GUIDELINE	MRID #	EFGWB#	DATE	STATUS
HYDROLYSIS (of MAA)	42363001	92-1115	4/93	NOT SATISFIED
AQUEOUS PHOTOLYSIS	41903902	91-0686	4/93	SATISFIED
PHOTOLYSIS ON SOIL	41903901	91-0686	4/93	SATISFIED
AEROBIC SOIL METABOLISM	41886901	91-0689	4/93	NOT SATISFIED
ANAEROBIC AQUATIC METABOLISM	41996501	91-0689	4/93	NOT SATISFIED
AEROBIC AQUATIC METABOLISM	43314801		9/94	SATISFIED
LEACHING/ ADSORPTION/ DESORPTION		6171	12/86	NOT SATISFIED[1]
TERRESTRIAL FIELD DISSIPATION	42526001 42616201 43322801 (O.K. response to Silwood ltr 4/14/94)	93-0106	4/93 9/94	NOT SATISFIED
BIOACCUMULATION IN FISH	42432501	92-1283	4/93	SATISFIED
DROPLET SIZE SPECTRUM				NOT SATISFIED
DRIFT FIELD EVALUATION				NOT SATISFIED

1/ Although an adsorption/desorption study of MSMA mobility was accepted on 12/5/86 (EAB #6171), it should be considered supplemental. This study does not fully satisfy the mobility data requirement because three of the four tests were not performed on actual soils.

9

Response to EPA Review of MRID 42526001 and 42616201

The review concludes that both studies are scientifically sound but require additional detail and/or information to meet the Subdivision N guidelines. The following detail is given to address the Agency's specific concerns.

Item 1. "...an adequate freezer storage stability experiment was not provided..."

Stability of the test material in the test soil, both from Arkansas (MRID 42526001) and California (MRID 42616201) during frozen shipment and storage was quantified by spiking a number of preweighed soil samples (at the study sites) on the day of the first chemical applications. Organic spiking solutions containing MSMA and cacodylic acid were used. The samples were placed into frozen storage at the study site and were later shipped to the analytical laboratory. Upon receipt at the laboratory the samples were placed into frozen storage until they were thawed for analysis. The details of the spiking are provided on page 15 of MRID 42526001 as an example of the procedure used. The results of the storage stability for the organic species is included in each report with the data tables attached for convenience. Table XII in MRID 42526001 (attached) indicates that an average of 86.9 and 97.7% of the nominal spike was recovered for MSMA and cacodylic acid up to 588 days after treatment. With the exception of a single sample (CA-78), which was excluded as a being improperly spiked, all samples spiked and analyzed showed recovery >70% of nominal. A chemical recovery >70% is generally considered acceptable for residue methods when a sample is spiked immediately prior to analysis. Based on this criterion, reproducible recoveries > 70% up to 588 days post treatment documents excellent storage stability for this field study.

The results for chemical frozen storage stability in the Arkansas study (MRID 42616201, attached as Table X) also demonstrate excellent results. An average recovery of 78.1 and 99.2% of the nominal spike was observed for MSMA and cacodylic acid, respectively, after up to 512 days of frozen storage. In this study several low recoveries (53.2-69.6%) were observed for MSMA after 400 days of frozen storage. The recovery of MSMA was higher on days 433 and 512, however, ranging from 78.1-93.1% and averaging 84.1% of the nominal spike. These data suggest that the analyses performed on day 400 may have been suspect, particularly in light of low recoveries for cacodylic acid in the same samples. The data does show excellent stability of the analytes late in the study (433 to 512 days after spiking), however, and therefore confirm excellent storage stability.

It is not possible in remote field studies to perform a "time 0" analysis of field spikes because the samples are frozen at the study site and later shipped frozen to the analytical laboratory, in this case by overland carrier. Time 0 spike recovery data are available for the concurrent recovery samples prepared at the laboratory in conjunction with each analytical run. The concurrent recoveries for all analytical runs presented in MRID 42526001 are summarized below:

Parameter	MSMA	Cacodylic Acid
Experiment-Wide Average Recovery	101.2%	108.0%
Observations (n)	146	122
Standard Deviation	17.6%	12.5%

These results indicate that excellent time 0 recovery of spiked soil was achieved and that the compound is stable through the analytical methodology.

In summary, the data presented in both study reports document excellent stability of MSMA and cacodylic acid after hundreds of days of frozen storage.

Item 2. "The aerobic soil metabolism study...found that arsenic acid was the major soil metabolite of MSMA, but this study did not distinguish between arsenic acid and total soil arsenic."

Response:

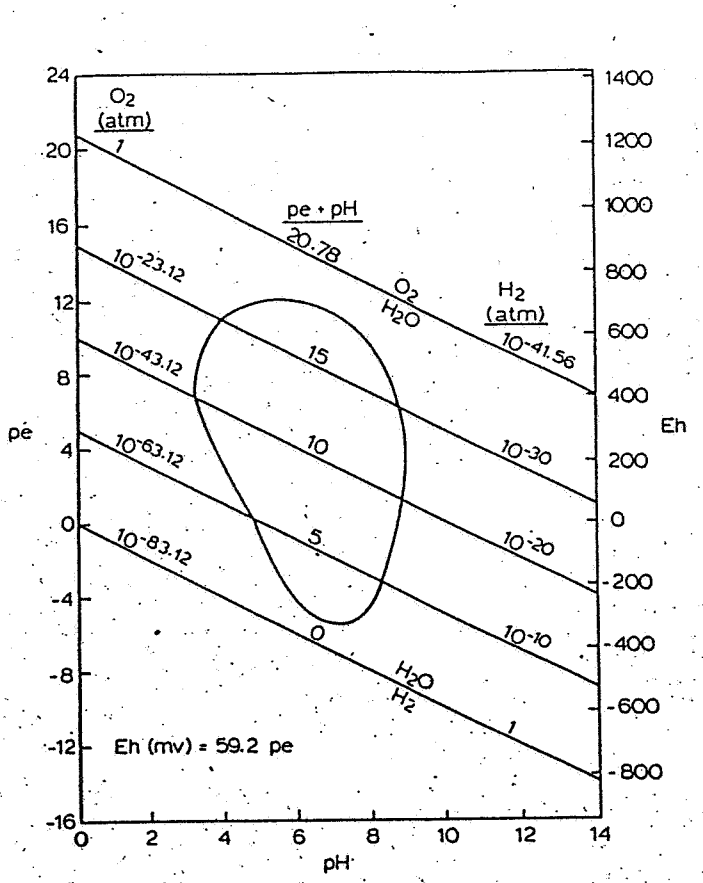
The aerobic soil metabolism study (MRID 41886901) is currently being repeated to address scientific shortcomings. Therefore, comparison of the reaction rates observed in the terrestrial field dissipation study to the current aerobic soil metabolism study is not appropriate at this time.

With respect to the ability to speciate soil arsenic in the terrestrial field dissipation study, it was determined during preliminary method development that elemental arsenic speciation of soil extracts based on valence (As^{3+} vs As^{5+}) as described in MRID 41886901 could not be reproduced. Further it was determined that the extraction procedure required to obtain acceptable recovery of the test material was oxidative in nature, and therefore would not support speciation of the elemental arsenic in the original soil. As presented in Appendix 7 of the study report, the extraction step in the analytical procedure involved shaking the soil in a 2M NH_4OH solution for one hour with a subsequent extraction using fresh extractant with shaking for 30 minutes. This procedure reliably extracted MSMA and its degredate, cacodylic acid, as indicated by experiment-wide concurrent recoveries of 101.2 and 108.0%, respectively for MSMA and cacodylic acid (MRID 42616201). However, it is likely that the shaking in an alkaline solution would affect the oxidation/reduction status of the soil and thereby not support a meaningful speciation of the As^{3+} and As^{5+} as it existed in the original soil.

The soil samples obtained in the terrestrial dissipation studies were also subjected to an elemental arsenic analysis as a means of examining the residual levels of arsenic resulting from three applications of MSMA. In this case, soil was subjected to a harsh digestion in a mixture of HCl and HNO_3 which was heated until nearly dry. It was determined that such a digestion procedure was required to release the soil arsenic for analysis by atomic absorption. This procedure is highly oxidative in nature, however, and once again the method needed to release the arsenic did not support speciation based on the initial redox status. It should be emphasized that the analysis As in this study was based on a desire to quantify possible accumulation in the soil profile resulting from multiple applications of MSMA. Thus, the arsenic present was determined with both As^{3+} and As^{5+} analyzed together.

It is interesting that the Agency is specifically concerned with the redox status of elemental arsenic in the soil. The redox potential of soil is known to be variable geographically and to fluctuate seasonally. The following figure (Lindsay, 1979) indicates the range of equilibrium redox conditions in soil:

11

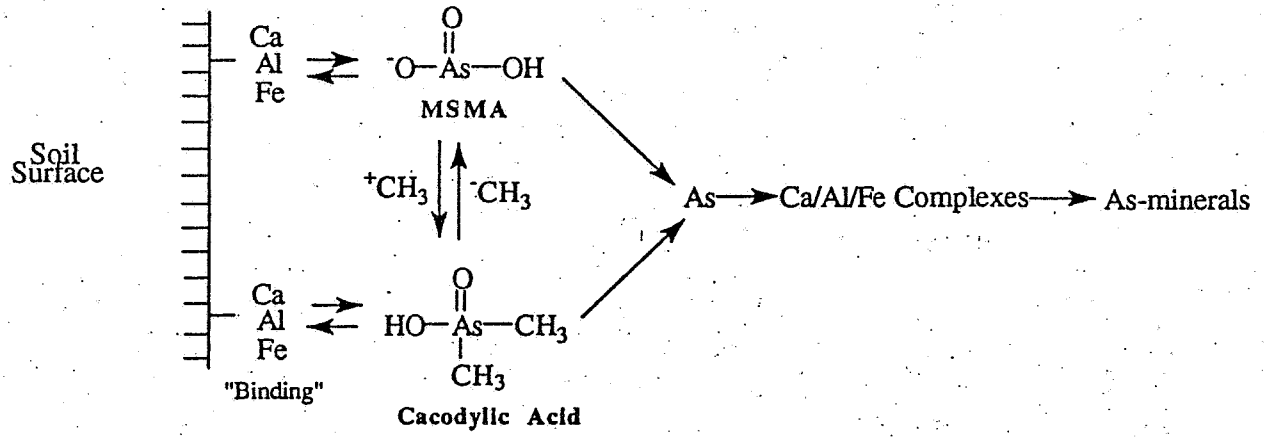


Based on this range of redox relationships, it is possible that the ratio of As^{3+} to As^{5+} would change over time even though the total As concentration is constant. An analysis to describe the redox status of the soil is seemingly beyond the scope of a guideline terrestrial field dissipation study. While the valence of the elemental species is important in determining the mineral species which may from under conditions of thermodynamic equilibrium (Lindsay, 1979) or to complex with other soil constituents (such as iron, aluminum or calcium), it does not appear to be relevant to the determination of the fate of MSMA if the total arsenic level in the soil is measured by soil depth over time as part of the field study.

Item 3. "...the pattern of formation and decline of degredates was not adequately addressed."

Response:

A proposed reaction pathway for MSMA added to the California or Arkansas soil was not presented in either study report. The proposed pathway is simple, as illustrated below:



This pathway shows that MSMA degrades to elemental arsenic directly or through methylation to cacodylic acid. Strong binding of either organic arsinical to soil is possible. Alternatively arsenicin MSMA can be mineralized with subsequent complexing of elemental arsenic to iron or phosphate species leading to the eventual formation of stable minerals.

Reference:

Lindsay, W. L. 1979. Chemical Equilibria in Soils. John Wiley & sons. New York. 449 pp.

13

Page_____ is not included in this copy.

Pages 14 through 15 are not included.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

_____ Information about a pending registration action.

✓ FIFRA registration data.

_____ The document is a duplicate of page(s) _____.

_____ The document is not responsive to the request.

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

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
MSMA
Last Update on September 14, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer:	Section Head:	Date:

Common Name:MSMA
Smiles Code:
PC Code # : 13803 CAS #:2163-80-6 Caswell #:

Chem. Name :MONOSODIUM METHANEARSONIC ACID

Action Type:HERBICIDE

Trade Names:ANSAR; BUENO; DACONATE;DAL-E-RAD
(Formul'tn): LIQUID; LIQUID + SURFACTANT
Physical State:

Use :TURF, COTTON, NON-CROP SITES
Patterns :
(% Usage) :
:

Empirical Form: CH_4AsO_3-Na
Molecular Wgt.: 162.00 Vapor Pressure: E Torr
Melting Point : 132-139 C °C Boiling Point: °C
Log Kow : -3.100 pKa: @ °C
Henry's : E Atm. M3/Mol (Measured)

Solubility in ...					Comments
Water	1.00E 6	ppm	@20.0	°C	104 g/ml
Acetone	E	ppm	@	°C	
Acetonitrile	E	ppm	@	°C	
Benzene	E	ppm	@	°C	
Chloroform	E	ppm	@	°C	
Ethanol	E	ppm	@	°C	
Methanol	E	ppm	@	°C	
Toluene	E	ppm	@	°C	
Xylene	E	ppm	@	°C	
	E	ppm	@	°C	
	E	ppm	@	°C	

Hydrolysis (161-1)
[V] pH 5.0:stable
[ ] pH 7.0:stable
[ ] pH 9.0:stable
[ ] pH :
[ ] pH :
[ ] pH :

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
MSMA
Last Update on September 14, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Photolysis (161-2, -3, -4)
[S] Water:STABLE UNDER ARTIFICIAL LT
[V] :STABLE UNDER NATURAL LIGHT
[ ] :
[ ] :

[V] Soil :STABLE UNDER NATURAL LIGHT
[ ] Air :

Aerobic Soil Metabolism (162-1)
[S] 831 DAYS (PROBABLY HIGH DUE
[ ] TO APPL OF 100 PPM)
[S] 119 DAYS (SOIL ENRICHED WITH
[ ] 16% OM)
[ ]
[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[S] DEGRADATION RATE LESS THAN
[ ] UNDER AEROBIC CONDITIONS
[ ]
[ ]
[ ]
[ ]
[ ]

Anaerobic Aquatic Metabolism (162-3)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Aerobic Aquatic Metabolism (162-4)
[V] degraded slowly in HPLC-grade water over sandy loam; qualitative
[ ] half-life was 245 days, based on 30 day experiment. Greatest
[ ] sink was soil binding of the radioactive methyl group. Arsenate
[ ]
[ ]
[ ]
[ ]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
MSMA
Last Update on September 14, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Soil Partition Coefficient (Kd) (163-1)

	s	s	c	%OC	K
[V]					
[ ]	100	-	-	.06	2.5
[ ]	84	11	5	.49	13
[ ]	HEAVY CLAY			9.03	40
[ ]	HEAVY CLAY			9.73	56
[ ]	SAND CLAY			.22	110

Soil Rf Factors (163-1)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Laboratory Volatility (163-2)
[ ]
[ ]

Field Volatility (163-3)
[ ]
[ ]

Terrestrial Field Dissipation (164-1)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Aquatic Dissipation (164-2)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Forestry Dissipation (164-3)
[ ]
[ ]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
MSMA
Last Update on September 14, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Long-Term Soil Dissipation (164-5)
[ ]
[ ]

Accumulation in Rotational Crops, Confined (165-1)
[ ]
[ ]

Accumulation in Rotational Crops, Field (165-2)
[ ]
[ ]

Accumulation in Irrigated Crops (165-3)
[ ]
[ ]

Bioaccumulation in Fish (165-4)
[V] <1x; little or no accumulation
[ ]

Bioaccumulation in Non-Target Organisms (165-5)
[ ]
[ ]

Ground Water Monitoring, Prospective (166-1)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Small Scale Retrospective (166-2)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Large Scale Retrospective (166-3)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Miscellaneous Data (158.75)
[ ]
[ ]
[ ]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
MSMA
Last Update on September 14, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Field Runoff (167-1)
[ ]
[ ]
[ ]
[ ]

Surface Water Monitoring (167-2)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Droplet Spectrum (201-1)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Field Evaluation (202-1)
[ ]
[ ]
[ ]
[ ]

Degradation Products

Inorganic arsenic
After 160 days under anaerobic conditions, soil residues contained 58% MSMA, 42% cacodylic acid, plus trimethyl arsines.
Arsenic 5+ acid

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
MSMA
Last Update on September 14, 1994
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Comments

MSMA appears to be persistent, but not mobile. Some degradates may be volatile. In water, the sodium ion dissociates to form the methanearsonate anion and methanearsonic acid. MSMA is stable to hydrolysis,aqueous photolysis and soil photoysis. Supplemental data suggest an aerobic soil half-life of 313 days.

References: EFGWB reviews
Writer : DME

DATA EVALUATION RECORD

STUDY 1

CHEM 013803 MSMA §162-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 43314801
Atkins, R.H. 1994. Aerobic aquatic metabolism of [^{14}C]MSMA. PTRL Project No. 757; PTRL Report No. 1573. Unpublished study performed by PTRL East, Inc., Richmond, KY, and submitted by Luxembourg Industries (PAMOL), Ltd., Tel Aviv, Israel.

DIRECT REVIEW TIME = 12

REVIEWED BY: D. Edelstein
TITLE: Soil Scientist
ORG: EFGWB/EFED/OPP
TEL: 703-305-5935

SIGNATURE: D. Edelstein 10/5/94

CONCLUSIONS:

Metabolism - Aerobic Aquatic

1. This study can be used to fulfill data requirements.

2. Methyl-labeled [^{14}C] monosodium methanearsonate (MSMA) degraded slowly on sandy loam soil that was flooded with HPLC-grade water and incubated in the dark at 25.0 ± 0 °C. One [^{14}C]degradate was identified: cacodylic acid, maximum 4.5-5.3% of the applied 30 days posttreatment. By day 30, 0.9-2.0% of the applied radioactivity had been released as CO_2 and 7.5-7.8% of the applied radiocarbon was bound residue.

3. This study is acceptable and fulfills the 162-4 Aerobic aquatic metabolism data requirement for MSMA. No additional data is required at this time.

METHODOLOGY:

Air-dried, sieved (2 mm) Hanford sandy loam soil (59.2% sand, 33.6% silt, 7.2% clay, 0.60% organic matter, pH 6.7, CEC 5.33 meq/100 g) was weighed (20 g) into 500-mL Erlenmeyer flasks with 100 ml of HPLC-grade water. The system was treated at 5.91 ppm (based on total weight of soil and water) with methyl-labeled [^{14}C]MSMA (monosodium methanearsonate; radiochemical purity >98.1%, specific activity 2.4

22

mCi/mMol, Wil Research Laboratories) dissolved in HPLC-grade water. The sample flasks were stoppered and equipped with gas inlet and outlet tubes. The inlet and outlet tubes were designed to release CO_2 and volatiles while providing a means to replace headspace gas with oxygen. The flasks were incubated in the dark at 25 ± 0.0 C. At each sampling interval, the flasks were flushed with oxygen; the oxygen was vented through a polyurethane foam plug and KI/I_2 (to trap possible volatile arsines), ethylene glycol and 10% KOH trapping solutions (Figure, p. 60). Duplicate flasks of treated soil were collected at 0, 1, 7, 14, 20 and 30 days posttreatment.

A sterile system was also established using the same protocol except that dosing was 6.11 ppm. The foam plug and KI/I_2 traps were not used, as little or no radioactivity were collected in these traps during the viable system experiment. Sampling of the sterile system was on 0, 1, 3 and 7 days posttreatment.

Duplicate flasks were removed at each sample time and flushed with oxygen (120 ml/min for 10 min) for volatile collection. The samples were then centrifuged, and the supernatant aqueous solution decanted. The solution was centrifuged a second time and decanted directly into a vacuum filtration apparatus. The filtered water samples were measured and radioassayed. Subsamples were taken for HPLC and/or TLC analysis and stored at approximately 4°C. The remaining aqueous sample material was stored at -20°C.

Subsamples of each soil sample were analyzed for total radioactivity using LSC following combustion. Additional subsamples were extracted twice with 1.0 N ammonium hydroxide by shaking on a wrist-action shaker for approximately 30 minutes. Between extractions, the samples were centrifuged and the supernatants were decanted. Day 7, 14, and 20 subsamples (5 g) and the entire day 30 sample were extracted a third time with 1.0 N ammonium hydroxide by shaking overnight. These samples were also centrifuged and the supernatant decanted. The three supernatants were pooled (Extract 3), and aliquots were analyzed for total radioactivity using LSC. On day 7, replicate B, filtered water and Extract 1 were mistakenly pooled; this was referred to as Extract 2. When this sample was extracted overnight, the supernatant was pooled with extract 2 to make Extract 4.

Subsamples of the Day 0-Day 1 (Extract 1) and subsamples of Day 7-Day 30 (Extract 3) were radioassayed and stored at 4 °C. Aliquots of the soil extracts were applied to solid phase extraction columns using a vacuum manifold and a vacuum pump. After extraction, volumes were measured and the samples radioassayed. The extracts were also concentrated under nitrogen, then measured and radioassayed. Extracted soil was air dried, and subsamples (number and size not specified) were combusted and analyzed by LSC.

To confirm the presence of cacodylic acid in the viable system, an approximate 70 ml subsample of the water phase of Flask B, Day 30,

Replicate A was lyophilized and resuspended in HPLC-grade water. Multiple injections of this solution on the HPLC column and the early peak collected. These fractions were pooled and lyophilized to concentrate the sample. The sample was derivatized with methylthioglycolate to aid GC analysis. Following reaction, the derivative was extracted from the aqueous phase with hexane.

A sterile incubation was performed to determine whether cacodylic acid was a product of microbial activity. The soil and flasks were sterilized by autoclaving twice at 121 °C and 15 psi for 30 minutes. In opther respects, the sterile system was the same as the viable system: Duplicate flakss were sampled at 0, 1, 3 and 7 days posttreatment. Flasks were flushed with oxygen, then pH, Eh and dissolved oxygen were measured. The contents of the flasks were centrifuged, and the supernatant water decanted, filtered, measured, and radioassayed. A 10-ml subsample was cleaned up on a Varian Florosil ssolid phase extraction column; the eluate and rinse were radioassayed. Water samples were then analyzed by HPLC.

Sterile soil pellets were extracted in the same manner as in the viable soil study, with overnight extraction being performed on the day 3 and day 7 samples only. The extract from the day 0 and 1 samples was referred to as Extract 1, while the day 3 and 7 extracts were called Extract 5. Post extraction soils were dried, combusted and analyzed by LSC.

Extracts from the viable system and aqueous samples were analyzed by reverse-phase HPLC using a LC-NH_2 column eluted with either an HPLC-grade water or a 1% acetic acid gradient; the column was equipped with UV (265 nm) and radioactivity detection. The gradient for the sterile system extracts was acetonitrile:HPLC-grade water (1:1, v:v) or 2% acetic acid. Eluate fractions were collected and analyzed using LSC. The method detection limit was twice the background radiation, or 0.01 ppm. Further evidence of the presence of cacodylic acid in the water phase of a representative sample was provideded by comparing Day 1 and Day 30 samples of the ^{14}C-labeled material from the extract to the known R_f value of cacodylic acid. Cellulose TLC plates were developed in ethyl acetate:17.4 N glacial acetic acid:water (3:2:1,v:v:v). The radiolabeled areas were visualized, then scraped and quantitated by LSC. Identification of the methylthioglycolate derivatives of ^{14}C-MSMA and ^{14}C-cacodylic acid were provided by GC and GC/MS.

Aliquots of the trapping solutions and an acetonitrile extract of the polyurethane foam plug were analyzed for total radioactivity using LSC. The identification of [^{14}C]residues in the KOH trapping solutions as $^{14}CO_2$ was confirmed using barium chloride precipitation.

DATA SUMMARY:

Methyl-labeled [^{14}C]MSMA (monosodium methanearsonate; radiochemical purity >98%), at 5.91 ppm, degraded with a registrant-calculated half-life of 245 days on sandy loam soil that was flooded and incubated in the dark at 25.0 ± 0.0 C. The study author reported that, based on HPLC and peak integration analyses, [^{14}C]MSMA comprised an average of 96.7% of the applied immediately posttreatment, 87.5-97.6% at 1 through 20 days, and 85.6-87.1% at 30 days posttreatment (Table VII). In the viable soil system, one other [^{14}C]degradate was identified:

cacodylic acid (CA)

was a maximum of 9.1% of the applied 1 day posttreatment, but was found at approximately 1-5% of the applied at all sampling intervals. [^{14}C]Residues that were not extracted from the soil were 1.7-2.0% of the applied at time 0, 4.7-5.0% at 1 day, and reached a maximum of 7.5-7.8% by 30 days (Table VI). [^{14}C]Residues in the KOH volatile trapping solution were 0.9-2.0% of the applied at 30 days; no [^{14}C]volatiles were detected in the potassium iodide/iodine trapping solution. During the study, the material balances ranged from 99.9 to 103.0% of the applied with no discernable pattern of loss.

No cacodylic acid was recovered from the sterile system, suggesting that cacodylic acid is a microbial degradate of MSMA. The rate of soil binding in that system seemed to be somewhat faster than in the viable system.

COMMENTS:

1. It is not certain that aerobic conditions were maintained throughout the experiment. Aerobic soil and aquatic metabolism experiments are typically run with flow-through aeration systems, but the system flasks in this study were closed, rasing the possibility that microbial activity could be sufficient to consume the available oxygen. Although the headspace filled with oxygen on a weekly basis, there is no evidence that this was enough to maintain aerobic conditions. pH, Eh, and dissolved oxygen were measured <u>after</u> the flask was purged with oxygen in order to collect volatiles, which means that the measurements in Table V are of the effect of purging a 500 ml flask containing 100 ml of water with 120 ml/min of oxygen for 10 minutes, not of the conditions existing in the flask during incubation.

   However, indirect evidence suggests that aerobic conditions were maintained. The headspace had a volume of nearly 400 ml, and the water presumably contained some dissolved oxygen at study initiation. Little CO_2 was released, further suggesting that not all of the available oxygen was consumed during the experiment. While this aspect of the experiment was handled poorly, there does not seem to be any benefit to be gained by requiring a new study.

2. No measurements were made of background levels of arsenic; it was not possible to determine if any MSMA was transformed to arsenate. It appears that a methylation/demethylation process was ocurring in the system to transform some of the MSMA into cacodylic acid and some of the radiocarbon into bound residue. It would have been helpful to see whether total soil arsenic showed a rise comparable to the rise in bound radiocarbon. In an earlier aerobic soil metabolism study (MRID 41886901, reviewed 1/6/94) the study author reported that the major degradate of MSMA was arsenic (V) acid.

3. A count was provided of "colony forming units" to demonstrate that there was an active microbial population in the test system (Table II). However, it was not stated whether the count was made before or after the study.

4. The study author notes that "pooling the initial extract representing the entire soil sample (Extract 1) and a 5-g subsample extract as was done for Day 7, 14, and 20 samples, does not provide a totally representative extract sample for subsequent chromatographic analysis." The study author suggests that the importance of this is limited as only MSMA was found in the soil extracts.

5. The study author notes that "the duration of the aerobic aquatic incubation (30 days) under viable microbial conditions is not sufficiently long for determination of an accurate rate of degradation (and/or dissipation) of [^{14}C]MSMA." Therefore, the projected dissipation half-lives (245 days in viable soil, 128 days in sterile soil) should only be regarded as qualitative values implying considerable persistence for MSMA in soil.

6. Results of the TLC anaylses, which are given in terms of % of the recovered radioactivity, are comparable to HPLC results when adjusted for over all recovery.

Page _____ is not included in this copy.

Pages 27 through 49 are not included.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

_____ Information about a pending registration action.

✓ FIFRA registration data.

_____ The document is a duplicate of page(s) _____.

_____ The document is not responsive to the request.

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