US ERA ARCHIVE DOCUMENT

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To:	Werdig		
	Product Manager 50 Registration Division (TS-	7671	
	Registration Division (15-	- 767)	
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From:	Herbert Manning Ph.D., Act		
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#### 1. CHEMICAL:

Common name: MSMA

Chemical name: Monosodium methylarsenate

Structure:

## 2. TEST MATERIAL:

The individual test materials are described in each of the individual studies discussed in Section 10.

## 3. STUDY/ACTION:

All of these studies reviewed herein were submitted in response to the GWDCI. The following review is an assessment of the leaching potential of MSMA based on the completed data package.

## 4. STUDY IDENTIFICATION: Accession # 259484.

The Photodecomposition of Methanearsonic Acid in Aqueous Solution. R.A. Zingaro. August 1985.

The Photodegradation of Methanearsonic Acid on Soil Surfaces. R.A. Zingaro. October 1985.

Von Endt, D.W. et al., "Degradation of Monosodium Methane Arsonic Acid by Soil Microorganisms," Ag. Food Chem., Vo. 16, No.1, 1968, P.17.

Woolson, E.A., "Generation of Alkylarsines from Soil", Weed Science, Vol. 25, 5, Sept. 1977, 412-416.

Mason et.al. Dept. Env. Health Sci., Tulane Univ. New Orleans, La., Int'l. Cong. Environ. Sensing Assess. Proc. 1975, (Published 1976) 2, 102, IEEE, NY, NY.

Hilthold, A.E. et al., "Distribution of Arsenic in Soil Profiles after Repeated Applications of MSMA", Weed Sci., Volume 22, Issue 3, (May), 1974, 272-275.

#### 5. REVIEWED BY:

Catherine Eiden Section # 1 EAB

# Date: Dec. 2, 1986

## 6. APPROVED BY:

Herbert Manning, Ph.D. Acting Section Chief Section # 1, EAB

## Herbert J. Manning Date: Doc 5, 1986

## 7. CONCLUSION:

The EAB cannot conclude that MSMA has no potential to reach ground water when used agriculturally. Each of the studies submitted under the GWDCI is discussed under section 10. The following conclusions apply to the acceptability of each of the studies for the purpose of the GWDCI screen.

l. No hydrolysis study (161-1) was submitted; however, from previous work on cacodylic acid (E.A. Woolson) and DSMA, EAB concludes that the hydolytic fate of MSMA will be similar. There will be hydrolysis of the OH bond and dissolution of the ONA<sup>+</sup> bond when MSMA is dissolved in water. No hydrolysis of the C-As bond is expected.

The hydrolysis study requirement for MSMA is waived.

- 2. The aqueous photolysis study (161-2) may be acceptable pending the receipt of data showing that: dark controls were used; a comparison of the light source used with natural sunlight spectra; the borosilicate glass casing acted as a filter to blockout wavelengths <280 nm. References cited should be sent in. MSMA was stable to aqueous photolysis under artificial light.
- 3. The soil photolysis study (161-3) may be accepted pending the submission of data comparing the light source used with natural sunlight. A half-life of 6 days was calculated for MSMA.
- 4. The aerobic soil study(s) (162-1) is acceptable for the purposes of the GWDCI screen. However, this study concludes that MSMA has a half-life of 831 days. This study used a 100 ppm application of MSMA to soil. This application rate is considered high and may unrealistically exaggerate the half-life of MSMA in soil under aerobic conditions. The registrant may want to repeat



the study at more realistic use rates.

Also, the following supporting information must be supplied:

- ° Was the study conducted in the dark?
- Was the soil stored prior to use? Was it microbially active?
- $^{\circ}$  Was all the remaining radioactivity in the soil after accounting for  $\text{CO}_2$ , MSMA or other As species?
- 5. The anerobic soil study (162-2) is acceptable for the purposes of the screen pending the submission of the following information:
- Was the study conducted in the dark?
- \* Was there only one data-point at 160 days? There was little degradation of MSMA under anaerobic conditions. Cavodylic acid plus trimethyl arsines (42%0 formed).
- 6. Leaching studies (163-1) are acceptable for the purposes of the GWDCI screen. MSMA plus associated As are adsorbed to clays and even low organic matter soils.
- 7. No field dissipation study (164-1) submitted was acceptable for the purposes of the GWDCI screen. A new Field Dissipation study is necessary and required. Several soil types should be selected on which MSMA is typically applied. Plots representative of these soil types with crops typical for MSMA should be selected (include one plot of cotton rotated to rice on a Mississippi delta sand loam soil). The plots selected should be representative of actual use situations, crops and irrigation practices. One plot could be a bare soil situation without crops, with irrigation.

Sample all representative soils from plots prior to application of MSMA for the specific study. Because As is ubiquitous in the environment, and because there may be residual As in the soil from previous use, an estimate of background As will be necessary.

Sample soils at time-zero, immediately after MSMA application. Sample soils deeply enough to define the extents of leaching of total As. Then analyze the remaining soil samples in order to speciate the total As to the zone of maximum leaching.

#### 8. RECOMMENDATION:

EAB recommends the following:

(1) A new Field Dissipation study (164-1) is required that speciates MSMA. A Mississippi delta soil (SL) planted to cotton and rotated to rice should be used as one representative plot. Include typical flood irrigation used on rice.

Estimate the background As levels before application.

Define the leaching front (as deep as is necessary) with total As first. Then speciate total As to zone of maximum leaching.

(2) waive the hydrolysis study as non-essential to determining the environmental fate of MSMA.

(3) Require an Anaerobic Metabolism study (162-2) with speciated arsenic analysis.

(4) Require an Aerobic Metabolism study (162-1) with speciated arsenic at a lower application rate than 100 ppm, i.e., 10 ppm.

#### 9. BACKGROUND:

For postemergent control of johnsongrass and other grassy weeds on ditch banks, right-of-ways, storage yards, and other non-crop areas; pre-plant cotton; bearing citrus (except Florida); non-bearing orchards; and for crabgrass and certain broadleaf control in turf.

## 10. DISCUSSION OF INDIVIDUAL STUDIES:

10.1 Hydrolysis. No study was submitted. No study is required. This study requirement has been waived because MSMA is a salt and its hydrolysis reaction is known.

#### 10.2

#### A. STUDY IDENTIFICATION

The Photodecomposition of Methanearsonic Acid in Aqueous Solution. R.A. Zingaro. August 1985.

## B. MATERIALS AND METHODS

The experiment used redistilled, deionized water, buffers made from reagent grade chemicals. A photoreactor as given by Crosby & Tang was used for irradiation, i.e., a 40-watt G.E. F40 BL Blacklight fluorescent lamp inside of borosilicate glass. The MSMA solution was irradiated continuously. The reaction temperature was 24.5+ 1.0°C. The experiment was conducted in the dark, except for the lamp light. (The solution pH was 5.0). There were no dark controls) Sample aliquots were taken periodically (16 days total exposure time.)

#### C. RESULTS

MSMA is converted to  $MeAsH_2$  (the hydride) with Na borohydriate for analysis by plasma emission spectrometry (LPS). There was no degradation after 192 hours continuous irradiation.

The method of analysis LPS allowed for detection of each of the As species (MeAsH<sub>2</sub>, Me<sub>2</sub>AsH<sub>1</sub> EtAsH<sub>2</sub>, Me3As, AsH<sub>3</sub>). The technique has an absolute sensitivity of 0.1 ng. Because there was no breakdown of MSMA, no half-life (t1/2) as calculated, no degradates were identified.

## D/E. DISCUSSIONS/CONCLUSIONS

- \* The study was not conducted for 30 days (192 hrs) <20 days approximately 16 days of light exposure.
- \* no dark controls were used.
- \* borosilicate glass was used as a filter, there was no mention of

the wavelengths excluded by the filter.

- \* no comparison of the spectra of light source vs sunlight was provided.
- \* send in references cited.
- \* is pH 5 the most stable ph for hyrolysis?

#### 10.2

## A. STUDY IDENTIFICATION

The Photodegradation of Methanearsonic Acid on Soil Surfaces. R.A. Zingaro. October 1985.

## B. MATERIALS AND METHODS

The soil used, called Houston black, with % ssc=7.8,54.8,37.4, %FC=36.2,%wp = 7.9, CEC = 40.8 % OM = 0.7 was revitalized with moisture - silty clay texture. All containers used to hold soils were washed with HNO3, distilled H<sup>2</sup>O, and HCL and more H<sub>2</sub>O before As addition to remove any surface traces of As. 20g of soil were added to each dish. Aqueous MSMA (5.42 x  $10^{-4}$ M) was added to soils with a calibrated pipette. Soil samples were placed under several Sylvania Cool White CF96CW 215 W lamps in a chamber. Dark controls were used. Exposure time was 16 hours/day. The wavelength distribution was given as < 380 nm 1.7%, not all < 290 nm was excluded. The use of a glass filter was not mentioned. The light source was not compared to natural sunlight. Soil aliquots were removed periodically and analyzed.

Soil aliquots were extracted with 5M HCL, filtered, washed with water, all filtrates were combined and analyzed for AS, MeAS, Me2As, Me3As species.

The As species are reduced to hydrides as in the aqueous photolysis experiment with BHy. The species are then carried to a liquid N2 trap separated by fractional distillation and analyzed for as AsH3 MeAsH2, EtAsH2, Me2as H, Me3As. These gases are decomposed and ionized in the helium liquid plasma. The ionized gaseous As ions in returning to ground state emit energy characteristic of their particuliar energy level. Intensity of the emission lines is proportional to the concentration.

Background As was measured as 2.1 ug/g.

#### C. RESULTS

Breakdown of MSMA to inorganic arsenic (arsenate) via demethylation. After 9.1 days, 59% of the original As as MSMA was converted to inorganic As. At 5.8 days > 1/2 of MSMA originally present has been decomposed in the controls —microbial process of demethylation. Approximately 10% was lost as gaseous methyl arsine at 21% hours (9.1 days). No traps were used to trap volatiles, no actual identification of degradates was given. The final percentage of conversion was given as 69.67% MSMA as inorganic As. Authors believe light is less important than microbial degradation. The exposure time (21% hours) approximates 13-18 days.

#### D/E. CONCLUSIONS

Before the study can be accepted for the purposes of the screen, EAB needs a comparison of the light source used with that of natural sunlight. Pending this submission of data, study can be accepted. Otherwise, the study is valid. No trapping of volatiles is noted, but it is known that methanearsenic acid gives off volatile methyl arsines.

#### 10.3

#### A. STUDY IDENTIFICATION

Von Endt, D.W. et al., "Degradation of Monosodium Methane Arsonic Acid by Soil Microorganisms," Ag. Food Chem., Vo. 16, No.1, 1968, P.17.

#### B. MATERIALS AND METHODS

Radio-labelled MSMA was used ( $C^{14}$ ) specific activity of 0.91 uc/mg. The MSMA -  $^{14}$ C was tested for purity. The other chemicals used were reagent grade. Four soil types were used; clay, silty clay loam, sandy clay loam and silty clay loam. Their characteristics are outlined below:

Soil Type	рН	% OM	% FC
clay	6.2	3.9	38.4
SiCL	6.8	2.5	25.8
SCL	5.3	1.9	17.8
SiCL	5.0	1.7	24.3

Soils were kept at 28-30°C and kept at field capacity. 10-100 ppm MSMA was added to samples of each of the 4 soil types. 14C02 was monitored only and species present as residues were identified by thin layer chromatography (TLC). 14C02, MSMA residues, AsO4-3 were identified. No AsO3-4 was identified. Soils were incubated up to 60 days. A half-life of 365-2465 days was estimated. Between 1.7-10% MSMA was degraded by day 60. This estimate is based on 14CO2 measurements. Enriching the soils with microbes increased degradation of MSMA up to 20% in 3 days. In sterilized soil there was no evidence of degradation. These data are taken from a peer-reviewed journal article, "Von Endt, D.W. et al., "Degradation of Monosodium Methane Arsonic Acid by Soil Microorganisms," Ag. Food Chem., Vo. 16, No.1, 1968, P.17.

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## D/E. CONCLUSIONS

- \* No raw data were provided, but there were decline curves.
- \* Was soil stored & aged?
- \* Results from this conflict with results from soil photolysis.
- \* Was the study conducted in dark?
- \* A limited description of methods of analysis was provided.
- \* 100 ppm dosing rate seems high.

The study cannot be accepted at this point for the purposes of the screen/review.

A second study using similar conditions reported a t1/2 of 119 days. But the soil was enriched with 16% O.M. Unamended soils with MSMA added showed 5.5% decomposition in 30 days. The t1/2 for this unamended soil = >365 days. Decomposition of MSMA was demonstrated by  $^{14}\mathrm{CO}_2$  evolution. No other degradates were identified. The study is not acceptable as is.

A third study was conducted using a Mattapeake SiL with \$ ssc = 38.4, 49.4, 12.2; pH = 5.3; \$OM = 1.5. 60 uCi of  $^{14}\text{C-MSMA}$  at 10 ppm was added to 100 g soil at room temperature adjusted to 25-30% FC. Soils were kept aerobic and anaerobic conditions were established by N<sub>2</sub> flushing a second set of soils with N<sub>2</sub>. Whether the soils were kept in the dark is unclear. The soils were incubated for 160 days. Trapping solutions (KI) were set up to trap volatile degradates, but not CO<sub>2</sub>.

Soils were extracted with water and analyzed by liquid scintillation chromatography (LSC). Then they were extracted with acid (H<sub>2</sub>SO<sub>4</sub>:HCLO<sub>4</sub>) and counted by LSC. Trapping solutions were analyzed by gas chromatography (GC) and atomic absorption (AA). The frequency of sampling and analysis were not reported. Data for the 160 day sampling interval are given, only.

After 160 days, 44% of the As species were H<sub>2</sub>0-soluble and extracted with only water. Acid digestion liberated a total of 62% of the total As species. Combustion liberated a total of 65% of the total As species. The traps contained approximately 12.5% of the initial radioactivity as volatilized degradates. Total recovery was approximately 82% of the total radioactivity. This includes CO<sup>2</sup> measured from combustion plus trap contents. A half-life estimate of 831 days is given, but no data to support this are given. This figure is based on the percentage (12.5%) of volatile degradates trapped over a 160 day period. Under aerobic conditions, 5% MSMA remained in the soil at 160 days, and di and tri-methyl arsines plus cacodylic acid (CACO) made up the remaining 95% (12.5% of this is attributed to volatilized di-and tri-methyl arsines).

#### 10.4

#### A. STUDY IDENTIFICATION

Woolson, E.A., "Generation of Alkylarsines from Soil", Weed Science, Vol. 25, 5, Sept. 1977, 412-416.

#### B. MATERIALS AND METHODS

The anaerobic study was performed much as the aerobic regarding materials, methods and analysis procedures. A total of 30% As was extractable with water, a total of 68% of the total As was extracted with acid, a total of 89% of the total AS was recovered through combustion.

#### C. RESULTS

Under anaerobic conditions, the degradation rate is reduced. Most of the extractable residue in the soil remaining is a trimethyl arsenic species regardless of MSMA, CACO or AsO<sub>4</sub><sup>-3</sup> substrate. Most of the volatilized As species was CACO or trimethylarsine. Only 0.8% was evolved as <sup>14</sup>CO<sub>2</sub>. No tl/2 was estimated as only 0.8% CO<sub>2</sub> evolved in 160 days. Soil residues contained 58% MSMA, 42% cacodylic acid plus trimethyl arsines, respectively, at 160 days. There was Little to no breakdown of MSMA to CO<sub>2</sub> under anaerobic conditions.

#### D/E. CONCLUSIONS

These data are taken from a peer-reviewed journal article. Woolson, E.A., "Generation of Alkylarsines from Soil", Weed Science, Vol. 25, 5, Sept. 1977, 412-416. The study is not acceptable for the purposes of the screen/review. Before the study can be accepted the following questions mut be answered: Was the study conducted in the dark? Was there only one sampling point at day 160.

#### 10.5

#### A. STUDY IDENTIFICATION

Mason et.al. Dept. Env. Health Sci., Tulane Univ. New Orleans, La., Int'l. Cong. Environ. Sensing Assess. Proc. 1975, (Published 1976) 2, 102, IEEE, NY, NY.

Hilthold, A.E. et al., "Distribution of Arsenic in Soil Profiles after Repeated Applications of MSMA", Weed Sci., Volume 22, Issue 3, (May), 1974, 272-275.

#### B. MATERIALS AND METHODS

An adsorption/desorption study with 5 soils was performed: the soils had the following characterics:

Type	% ssc	% OC	<u>K</u>	<u>1/n</u>	<u>r</u>	pH(sol'n)
sand sand	100(fine & coarse) 84,11,5	0.06 0.49	2.5 13	0.92	0.98	6.7 6.9
clay Clay	(heavy clay) (heavy clay)	9.03 9.73	40 56	0.56 0.50	0.99 0.94	6.9 6.9
sand-clay	?	0.22	110	0.27		6.0

The tests were run using MSMA in concentrations of 0,5,10,25,50 mg/l of arsenic. The soil/water ratio was not given. The shaker flasks used were kept at consant temperature and shaken for 24 hours in a shaker bath. After equilibration, the samples were centrifuged to separate soil and water phases. After an aliquot was removed, desorption tests were made by replacing MSMA solution removed for sorption analyses with distilled water. The samples were re-equilibrated and analyzed. No methods of analysis for As were given.

#### C. RESULTS

The data were fitted to the Freundlich equation. The data are given in the table above.

## D/E. DISCUSSION/CONCLUSION

These data indicated that As from MSMA or MSMA plus associated As adsorbed strongly to clays and even to sandy soils with a low percentage of organic matter. This study is acceptable pending the receipt of information on how the As was analyzed for. Data were obtained from a peer reviewed journal article: Mason et.al. Dept. Env. Health Sci., Tulane Univ. New Orleans, La., Int'l. Cong. Environ. Sensing Assess. Proc. 1975, (Published 1976) 2, 102, IEEE, NY, NY.

The following is taken from a second experiment taken from a peer-reviewed journal article, Hiltbold, A.E. et al., "Distribution of Arsenic in Soil Profiles after Repeated Applications of MSMA", Weed Sci., Volume 22, Issue 3, (May), 1974, 272-275. A batch equilibrium sorption experiment was performed using 3 soils: SiL,fsl,LS. The soils were not characterized as to %s,s,c, %OM etc. 5 ml aliquots at 50ppm MSMA-As Sol'n. were added to 5g soil samples, a 1:1 soil/water ratio. Sample were equilibrated overnight. No temperature was reported. After centrifugation the As content was analyzed for by X-ray spectrochemical analysis. Background As was checked in a blank soil sample.

The Kd values are given for three separate soil horizons as given below:

Type	Horizon	Depth(cm)	$\frac{(ml/g)kd}{}$	8 OM	% SSC
sil	Ap	0-18	5.4	?	3
	B22T	50-77	38.4		
	B22T	77-144	63.6		
fsl	AP	0-15	0.4		
	A2	15-30	$\frac{1.1}{2}$		
	B2lT	30-45	8.7		
ls	AP	0-15	0.2		
	Al	15-30	1.7		
	BlT	30-45	21.6		

Pending the submission of the information listed below, the study may be accepted:

experiment temperatures and soil characteristics.

10.6

#### A. STUDY IDENTIFICATION

Several studies were submitted, but none are reviewed in detail here as they were all found to be woefully inadequate.

#### B. MATERIALS AND METHODS

EAB requires a good field dissipation study (164-1) using several soil types and including normal agricultural practices, cropping patterns and irrigation. A control plot will be needed without application for background checks, and a bare soil plot will be needed. To the bare soil plot nothing would be added except the MSMA. There would be no crops present, no irrigation practiced. Climate information must be included.

#### C. RESULTS

Not applicable.

#### D/E. DISCUSSION/CONCLUSIONS

Not applicable.

## Product Chemistry

Solubility in water 25°C 25°C + 1°C 5 g/10ml sat'd. sol'n.

#### 11. ONE-LINER:

No one-liner completed.

#### 12. CBI:

No CBI included with this package.