

US EPA ARCHIVE DOCUMENT

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Date Out EFB: 09 AUG 1982

To: Product Manager 23 Mountfort
TS-767

From: Samuel M. Creeger *SAC*
Acting Chief, Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 677-269

Chemical: Monosodium methanearsonate (MSMA)

Type Product: Herbicide

Product Name: Bueno 6

Company Name: Diamond Shamrock

Submission Purpose: Applicator exposure studies with MSMA

ZBB Code: 3(c)(5)

ACTION CODE: 401

Date in: 4/22/82

EFB # 298

Date Completed: 09 AUG 1982

TAIS (level II) Days

Deferrals To:

67

6

 Ecological Effects Branch

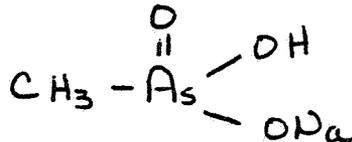
 Residue Chemistry Branch

 X Toxicology Branch

1.0 INTRODUCTION

Diamond Shamrock has submitted applicator exposure studies with monosodium methane arsonate herbicide. Acc. No. 247265.

2.0 Bueno 6: MSMA Monosodium methane arsonate



3.0 DISCUSSION

The MSMA formulation used in this study contains 6 lb ai/gal. MSMA is registered for use on cotton, certain bearing and non-bearing citrus trees, non-bearing deciduous fruit and nut orchards, highway rights-of-way (ROW), drainage ditch-banks, lawn and ornamental turf, fence rows and storage yards.

This study measured the dermal and respiratory exposure of field applicators using MSMA under typical working conditions. Residues in urine were also measured to determine the relationship between exposure and absorption of MSMA and its subsequent excretion.

Three application scenarios were chosen as representative of all MSMA uses:

- Aerial application on cotton fields
- Ground application on cotton fields
- Ground application along highway ROW.

The studies were conducted in the Mississippi delta region. The application rate for these studies was 2 lb MSMA/acre or 2 2/3 pt Bueno 6 in 40 gal of water.

Dermal exposure samples consisted of measuring MSMA residues on 4" x 4" patches of absorbent paper (1 mm thick Acetanier P-FA on glassine paper) placed on the head, upper forearms and front of the thighs (Exhibit I). Respiratory exposure was determined by measuring MSMA residues collected on a 0.8 micron filter placed in the worker's breathing zone (Exhibit II). Table 0 shows the number of people monitored and their responsibilities in this study. Exhibits VI and VII summarize data on application equipment and personnel used during the three phase study. A brief description of the monitoring taking place during the these phases is given below.

Phase I--Aerial Application on Cotton Fields

Each spraying cycle was about 15 to 30 minutes in duration. The two cycles comprising each exposure period were made in quick succession without any lag time. Samples from nine such exposure periods were taken in this study over four days as indicated below:

<u>Date</u>	<u>Day</u>	<u>Number of Exposure Periods During Which Samples were Collected</u>	<u>Urine Samples Per Person</u>
5/21/79	1	3	Pre-exposure sample at start of day
5/22/79	2	1	24-hour composite sample
5/23/79	3	4	Sample at start of day
5/24/79	4	1	None
5/25/79	5	None	Sample at start of day (end of week sample)

Phase II--Ground Application on Rights-of-Way

For each exposure sample, the sprayer and mixer were outfitted with the air sampling unit and the dermal patches as described earlier. The airpumps were switched on and adjusted to draw 1.8 liters/min of air, marking the beginning of the exposure period. The individuals were then allowed to perform their normal duties for a period of 2 2/3 hours. At the end of this period, the dermal patches and air samples were carefully collected and stored.

Twelve exposure samples were collected over four days as indicated as below:

<u>Date</u>	<u>Day</u>	<u>Number of Exposure Periods During Which Samples Were Collected</u>	<u>Urine Samples Per Person</u>
6/25/79	1	3	◦ Pre-exposure sample at start
6/26/79	2	3	◦ Sample at start of day
6/27/79	3	3	◦ 24-hour composite sample ◦ Sample at start of day
6/28/79	4	3	◦ Sample at start of day ◦ Sample at end of day

Phase III--Ground Application on Cotton Field

The sprayer/mixer was outfitted with the air sampling unit and dermal patches as described earlier. The sampling was conducted on this individual for three days in a manner similar to that described for Phase II--three exposure samples per day of 2-2/3 hours exposure period each, for three days and urine sample each day, as follows:

<u>Date</u>	<u>Day</u>	<u>Number of Exposure Period During Which Samples were Collected</u>	<u>Urine Samples</u>
8/29/79	1	3	◦ Pre-exposure samples at start of day
8/30/79	2	3	◦ Sample at start of day ◦ 24-hour composite sample
8/31/79	3	3	◦ Sample at start of day ◦ End of day sample could not be collected

Results

During analysis, MSMA residues in/on the samples collected were converted through a digestion process to inorganic arsenic for measurement. In order to report results in terms of residue MSMA, the arsenic reported results were multiplied by 2.16 (MW of MSMA (161.94) divided by MW of AS (74.92)).

The residues found on the forearms are interpreted as exposure of the hands to MSMA. Respiratory residue values found as a result of sampling at 1.8 l/min were scaled up to reflect respiration rate of worker estimated to be 20 l/min.

Average exposure levels are found in Exhibit VIII. The order of increasing dermal and respiratory exposure is shown below. The average arsenic levels in urine are in Exhibit X.

Dermal Exposure

<u>Rank</u>	<u>Average (1) Exposure Level ug MSMA/in²/hr</u>	<u>Participant in the Exposure Study</u>
1	1.57	Pilot--Aerial Application on Cotton (Phase I)
2	2.86	Mixer--Aerial Application on Cotton (Phase I)
3	5.92	Mixer--Highway Application (Phase II)
4	15.90	Mixer/Sprayer--Ground Application on Cotton (Phase III)
5	55.9	Sprayer--Highway Application (Phase II)
6	435	Flagman--Aerial Application on Cotton (Phase I)

Respiratory Exposure

<u>Rank</u>	<u>Average Exposure (ug MSMA/hr)</u>	<u>Participant in the Exposure Study</u>
1	22.4	Mixer--Highway Application (Phase II)
2	34.0	Pilot--Aerial Application on Cotton (Phase I)
3	52.8	Mixer--Aerial Application on Cotton (Phase I)
4	215	Mixer/Sprayer--Ground Application on Cotton (Phase III)
5	252	Sprayer--Highway Application (Phase II)
6	966	Flagman--Aerial Application on Cottor (Phase I)

4.0 CONCLUSIONS

EFB finds this study to have some shortcomings that make it difficult to interpret conclusively the exposure values received.

One difficulty stems from the apparent interpretation that forearm exposure is the same as hand exposure. This interpretation could lead to gross inaccuracies. Actual hand exposure could account for about 90% of a mixer/loader's total dermal exposure. In addition more pesticide could be absorbed through the hands than through the forearms. From the photo's provided, it seems that typical work clothes include a short-sleeved shirt and no gloves (one worker did wear gloves). Consequently, residues found on the forearm patches should be included as exposure to the forearms and not the hands. In addition, it could be assumed that exposure to the legs is minimal since long-legged pants are worn and are expected to serve as a barrier to the pesticide to some unknown degree. Finally, the summary table (Exhibit VIII) contained some errors of transposition. These have been corrected using the raw data provided.

This reviewer has recalculated the corrected exposure values found in Exhibit VIII for the forearms (not hands) and head representing the face, back of neck, front of neck and "v" of chest. Standard body areas were used (forearms, 1210 cm²; head, 910 cm²). To determine exposure on a per kg body weight basis, these figures are divided by 70 kg, the assumed standard mass of a male worker.

Sample calculation using exposure to pilot:

Forearms:

$$1.39 \text{ ug/in}^2/\text{hr} \times \text{in}^2/6.25 \text{ cm}^2 = 0.22 \text{ ug/cm}^2/\text{hr}$$

$$\text{Area of forearms} = 1210 \text{ cm}^2$$

Exposure to forearms:

$$0.22 \text{ ug/cm}^2/\text{hr} \times 1210 \text{ cm}^2 = 266 \text{ ug/hr}$$
$$0.26 \text{ mg/hr}$$

or

$$\text{dividing by body weight: } 3.8 \text{ ug/kg/hr}$$

Table 1 gives all of the recalculated exposure values. Note that respiratory exposure is at least an order of magnitude less than dermal exposure.

EXHIBIT I
Diamond Shamrock Corporation
DERMAL EXPOSURE SAMPLING APPARATUS

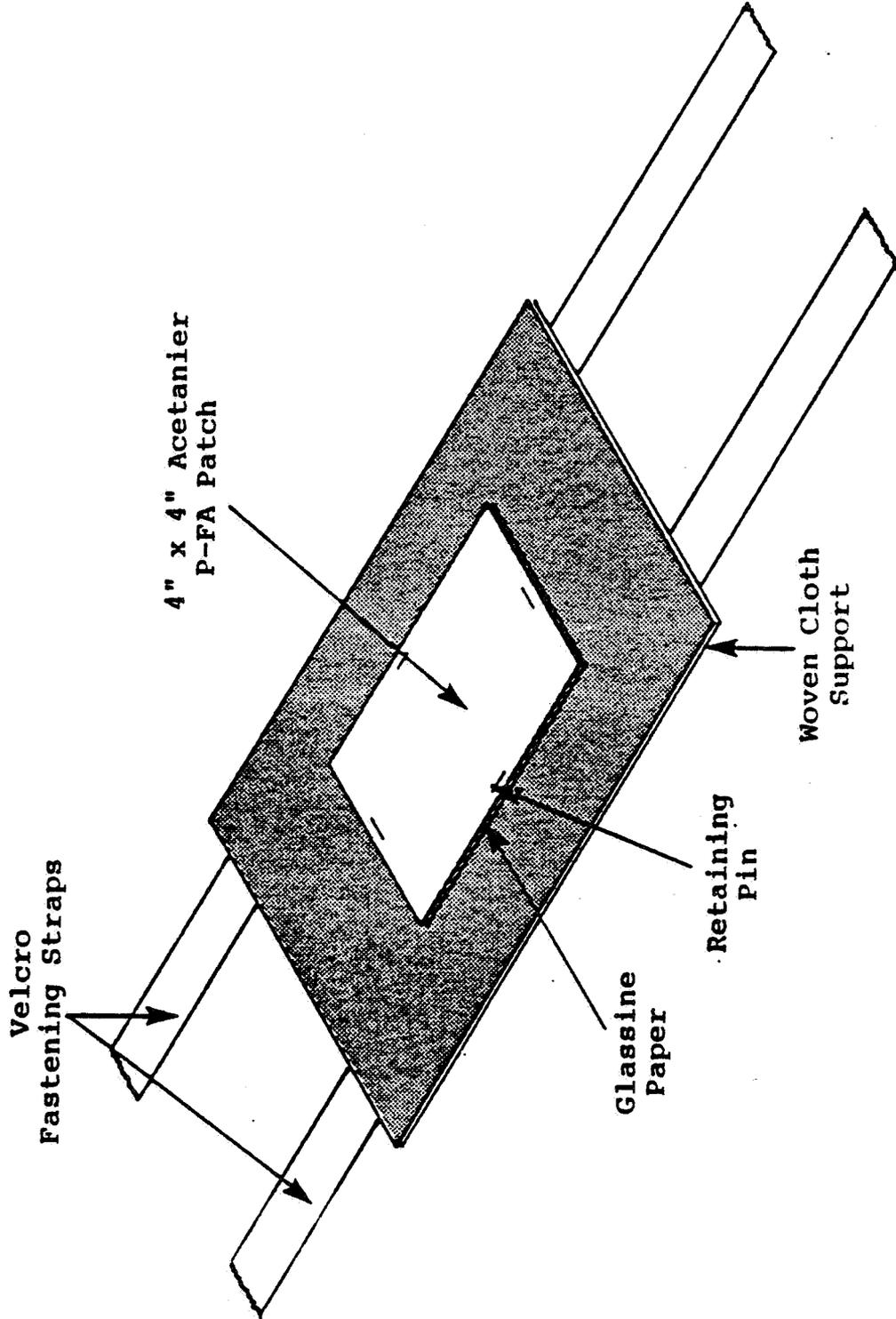
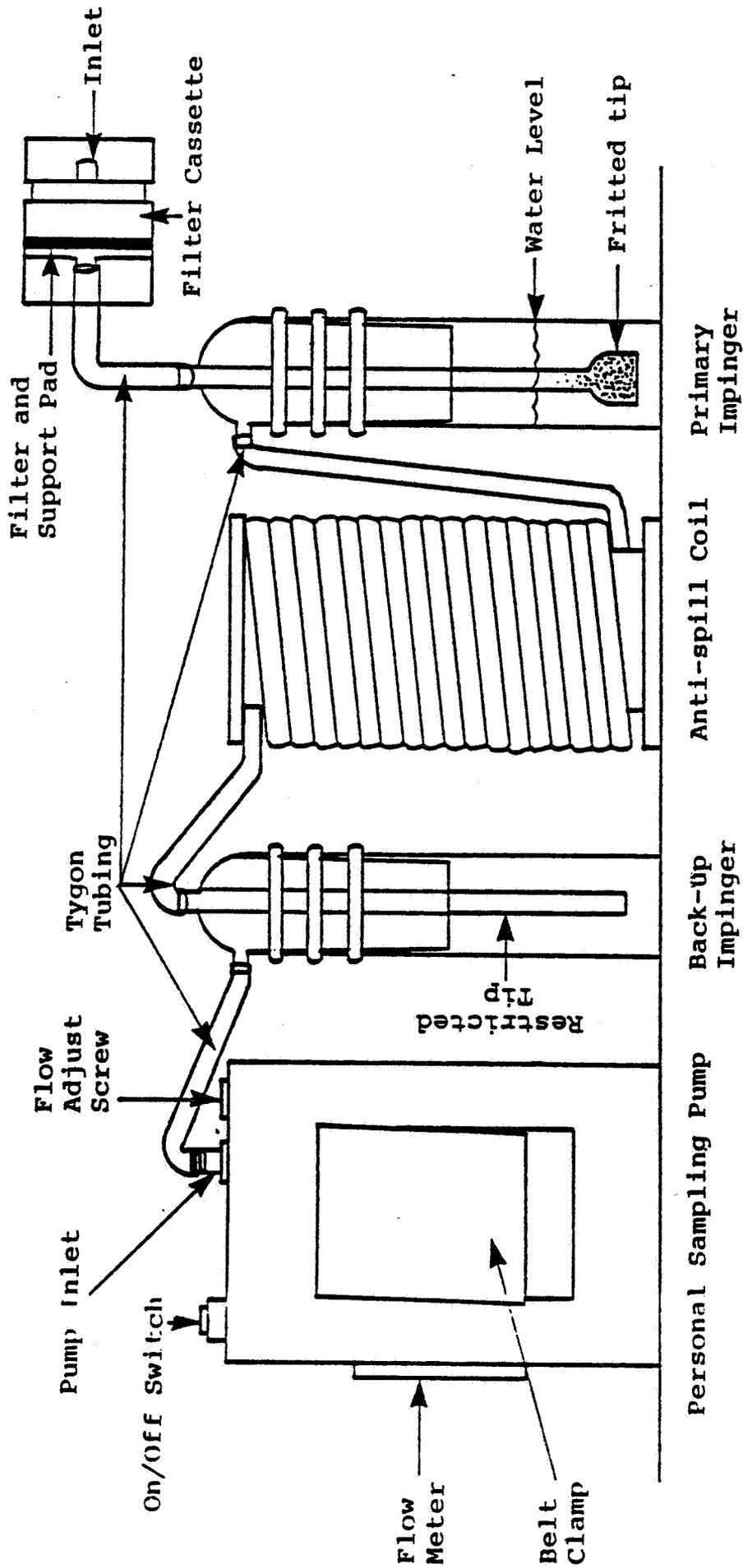


EXHIBIT II
Diamond Shamrock Corporation
RESPIRATORY EXPOSURE SAMPLING APPARATUS



Source: Booz, Allen & Hamilton Inc.

Table 0.

<u>Application Situation</u>	<u>Number of People Monitored</u>	<u>Responsibility of Person Monitored</u>	<u>Relevant Activities</u>
Aerial Application on Cotton Fields	3	Pilot Mixer Flagman	. Aerial spraying . Mixing and loading of spray mixture into the airplane . Optionally used by pilots as field markers
Ground Application on Cotton Fields	1	Sprayer/Mixer	. Duties include mixing, loading and spraying
Ground Application on Highways	2	Sprayer (Tractor Driver) Mixer (Truck Driver)	. Conducts the actual spraying work . Also participates in mixing and loading activities. . Follows the spray tractor with reserve spray mixture . Also participates in mixing and loading activities

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EXHIBIT VI
Diamond Shamrock Corporation
SUMMARY OF APPLICATION EQUIPMENT DESCRIPTIONS

- 10 -

<u>Phase</u>	<u>Application Equipment Description</u>
I--Aerial Application on Cotton	<ul style="list-style-type: none">• Cessna AGTRUCK, single engine, closed cabin, low wing mono-plane equipped with 46 nozzles.• 80 psi spraying pressure.• Spraying conducted from about 10 feet above ground at an indicated ground speed of about 120 mph.• Standard No. 8 nozzles with #45 core.• About 40 feet spraying width.• A 3' diameter x 4' height cylindrical mixing tank.
II--Highway Application	<ul style="list-style-type: none">• Spraying tractor designed and fabricated by the Arkansas State Highway Department using FORD 5000 tractor.• A standard #80 spraying nozzle.• 4-5 psi pressure at the spray nozzle.• About 12 feet spray width.
III--Ground Application on Cotton	<ul style="list-style-type: none">• A John Deere spray tractor (with open windows) fitted with 8003E nozzles and a 200 gallon tank.• 25 psi spray pressure.

Source: Roop, Allen & Hamilton Inc.

EXHIBIT VII
Diamond Shamrock Corporation
HEIGHT AND WEIGHT OF THE APPLICATORS MONITORED

<u>Phase</u>	<u>Individual</u>	<u>Height</u>	<u>Weight</u>
I (Aerial)	Pilot	5' 5"	160
	Mixer	5' 8"	200
	Flagman	5' 7"	180
II (Highway)	Sprayer	5' 8"	170
	Mixer	6' 0"	180
III (Ground)	Sprayer/Mixer	6' 1"	235

Source: Booz, Allen & Hamilton Inc.

EXHIBIT VIII
Diamond Shamrock Corporation
SUMMARY RESULTS OF
AVERAGE (1) EXPOSURE LEVELS

	Phase I		Phase II		Phase III Ground Application on Cotton Mixer-Sprayer	
	Aerial		Highway			
	Pilot	Mixer	Mixer	Sprayer		
	Application on Cotton					
		Flagman				
DERMAL EXPOSURE: (µg MSMA/sq. inch/ hour) (2)	Hands	1.39	347	9.10	67.3	32.80
	Legs	2.08	176	7.23	90.2	7.51
	Head	1.26 1.91	783	1.43	10.1	7.40
	Average	1.57 1.79	435	5.92	55.9	15.90
RESPIRATORY EXPOSURE: (µg MSMA/hour) (3)		34.0	52.8	22.4	252	215

- (1) Detailed results are in Exhibit IX and Appendix E, Volume II.
 (2) Can be converted to µg MSMA/sq cm by dividing the data by 6.25.
 (3) Based on average inhalation of 1,200 liters of air per hour.

Source: Booz, Allen & Hamilton Inc.

EXHIBIT X
Diamond Shamrock Corporation
AVERAGE ARSENIC LEVELS IN URINE ($\mu\text{g}/\text{ml}$)

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Type of Sample	Phase I		Phase II		Phase III	
	<u>Aerial Application on Cotton Pilot</u>	<u>Mixer</u>	<u>Highway Application Sprayer</u>	<u>Mixer</u>	<u>Ground Application on Cotton Sprayer/Mixer</u>	<u>Mixer</u>
Pre-Exposure (Day 1)	0.025	0.03	0.02	0.02	<0.02	<0.02
Mid-Week (Post Exposure)						
Day 2	(b)	(b)	(b)	0.08	0.11	0.11
Day 3	0.02	<0.02	0.06	0.14	0.04	0.04
Day 4	(b)	(b)	(b)	0.22	(a)	(a)
End of Week Sample	0.02	0.03	0.12	0.50	(b)	(b)
24-Hour Cumulative	0.02	0.03	0.03	0.93	0.18	0.18

(b) Not applicable
 (t) Sample not collected; not required by protocol

Source: Booz, Allen & Hamilton Inc.

Table 1.1 Average Exposure Values (mg/hr)

	<u>Phase I</u>			<u>Phase II</u>		<u>Phase III</u>
	<u>Pilot</u>	<u>Mixer</u>	<u>Flagman</u>	<u>Mixer</u>	<u>Sprayer</u>	<u>Mixer/Sprayer</u>
Forearms	0.26	0.52	67	1.7	13	6.3
Head	0.18	0.33	114	0.20	1.4	1.0

Table 1.2 Average Exposure Values (ug/kg/hr)

	<u>Phase I</u>			<u>Phase II</u>		<u>Phase III</u>
	<u>Pilot</u>	<u>Mixer</u>	<u>Flagman</u>	<u>Mixer</u>	<u>Sprayer</u>	<u>Mixer/Sprayer</u>
Forearms	3.8	7.5	959	25	186	90
Head	2.6	4.8	1628	2.9	21	15
Respiratory	0.48	0.75	13.8	0.32	3.6	3.0

4.0 RECOMMENDATION

If dermal exposure to the hands had been measured along with additional patches for head and neck exposure determinations (such as on the chest and back or shoulders), it would have been a complete study. EFB does not believe this study provides enough data to be an acceptable exposure study. EFB defers to Toxicology Branch for a possible risk assessment determination.



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Environmental Fate Branch, HED