

Shaughnessy No.: 123301

Date Out of EAB: JAN 24 1986

To: H. Jacoby
Product Manager 21
Registration Division (TS-767)

From: Samuel M. Creeger, Chief *SMC*
Review Section #1
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached, please find the EAB review of...

Reg./File #: 359-706
Chemical Name: fosetyl-Al
Type Product: fungicide
Product Name: Aliette
Company Name: Rhone-Poulenc, Inc.
Submission Purpose: New use on bearing citrus.

Date Received: 6/28/85 Action Code(s): 335

Date Completed: JAN 24 1986 EAB #(s) : 5727

days: 3.0

Deferrals to: _____ Ecological Effects Branch
_____ Residue Chemistry Branch
_____ Toxicology Branch

Monitoring study requested by EAB:

Monitoring study voluntarily conducted by registrant:

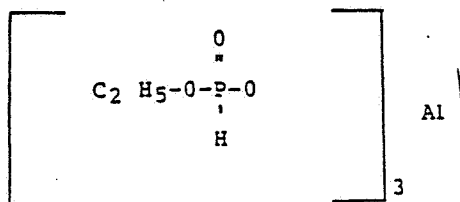
1. CHEMICAL:

Common name: Fosetyl-Al

Chemical name: Aluminum tris(O-ethyl phosphonate)

Trade name: Aliete - 80% WP

Chemical Structure :



Physical/Chemical Properties: see EAB one-liner (attached)

2. TEST MATERIAL:

Batch GHS-352-1: aluminum tris-O-[1-¹⁴C]-ethylphosphonate
(sp. act. = 25.5 uCi/mg; 98% pure)

Batch MJA-413: ammonium tris-O-[1-¹⁴C]-ethylphosphonate
(sp. act. = 34.7 uCi/mg; 100% pure)

3. STUDY/ACTION TYPE:

Rhone-Poulenc, Inc. is submitting an anaerobic aquatic metabolism study in support of a label amendment to register use of Alliete® on bearing citrus.

4. STUDY IDENTIFICATION:

Chabassol, Yves (Rhone-Poulenc Agrochimie). 1984. Fosetyl-Al: Anaerobic aquatic metabolism study. (Unpublished study submitted under PP#5F3267; Accession No. 073643)

5. REVIEWED BY:

Debra Edwards, Ph.D.
Review Section 1/EAB/HED/OPP

Debra Edwards
JAN 24 1986

6. APPROVED BY:

Samuel M. Creeger, Chief
Supervisory Chemist
Review Section 1/EAB/HED/OPP

Samuel M Creeger
JAN 24 1986

7. CONCLUSIONS:

According to the Registration Standard for fosetyl-Al, the following environmental fate data requirements for purposes of registration have been met: hydrolysis; photolysis in water, soil, and air; aerobic soil metabolism; and leaching

and adsorption/desorption. The fish accumulation data requirement was waived, based on the low K_{ow} (1.7×10^{-3} to 5.2×10^{-3}) and the short $t_{1/2}$ in aerobic soil (1-1 1/2 hours). Also, the field dissipation data requirement was waived, based on the short $t_{1/2}$ found in the aerobic soil metabolism study. The reviewer does not concur with the decision to waive the field dissipation study with regard to this citrus use. Fosetyl-Al is stable to hydrolysis and photolysis, and laboratory soil mobility studies indicate a high potential for leaching (refer to EAB one-liner - attached to this review). Therefore, fosetyl-Al may leach below the zone of soil microbial activity, where it may persist and be available for leaching to ground water.

The present submission (anaerobic aquatic metabolism) was submitted in lieu of an anaerobic soil metabolism study because in an anaerobic soil metabolism study, application of the test substance is made before establishing anaerobic conditions. Due to the short $t_{1/2}$ of fosetyl-Al in aerobic soil, the anaerobic soil metabolism procedure was impractical. Thus, the anaerobic aquatic metabolism study was conducted in which application of the test substance was made after having established anaerobic conditions. The submitted study indicates that most of the parent remains in the aqueous phase where it is degraded to ethanol, CO_2 and, presumably, phosphorous acid. Half-life values for the parent in the aqueous phase were 1440 hours. The study does not satisfy environmental fate requirements for registration, however, because the material balance was not adequate (approximately 80% recovered in the sandy loam test after 32 hours) and residues were not characterized in the soil sediment extracts (refer to section 10.1 E for details).

8. RECOMMENDATIONS:

EAB cannot fully assess the proposed registration of Aliete on bearing citrus until adequate anaerobic aquatic metabolism (in lieu of anaerobic soil metabolism) and field dissipation studies have been submitted. Field dissipation studies should at least be conducted in citrus production areas of Florida and Texas.

The registrant is encouraged to submit test protocol for our comment before initiating these studies.

9. BACKGROUND:

A. Introduction:

Phone-Poulenc, Inc. is seeking to amend the registration of Aliete (80% WP) by adding a use on bearing citrus.

B. Directions for use:

Aliete (80% WP) is to be used on bearing citrus in all areas except CA, to control Phytophthora foot and root rot. Application is to be by ground equipment, at 4 lb ai/100-250 gal/A. Foliar sprays are to be made at each leaf flush (March, May, July, September) up to four times per year, but not within 90 days of harvest.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

0.1 A. Study Identification: Anaerobic aquatic metabolism.

Chabassol, Yves (Rhone-Poulenc Agrochemie). 1984. Fosetyl-Al: Anaerobic aquatic metabolism study. (Unpublished study submitted under PP#5F3267; Accession No. 073643)

B. Materials and Methods:

Five gram aliquots of air-dried, sieved (2 mm sieve) soil (sandy loam or silty clay loam - see Attachment 1 for soil characteristics) combined with 50 mg of alfalfa meal (to provide organic matter) were placed in 50 ml glass centrifuge bottles along with 20 ml of water. Bottles were capped, and the contents homogenized. Bottles were then incubated in the dark at $20 \pm 2^\circ\text{C}$ for 29-34 days to establish anaerobic conditions. After the 29- to 34-day incubation period, aluminum tris-O-[1- ^{14}C]-ethylphosphonate (batch GHS 352-1), ammonium tris-O-[1- ^{14}C]-ethylphosphonate (batch MJA-413), or [1- ^{14}C]-ethanol was added to the bottles; a summary of test conditions (specific activity and concentration of test substance, and sampling times) is given in Attachment 2. After addition of the test substance, the soil-water mixture was homogenized for 10 minutes, and the bottles were covered with aluminum foil and attached to a gas collection system in which nitrogen gas was bubbled through the aqueous phase and passed through three gas trapping bottles. The first and second bottles contained 0.1 N NaOH and the third bottle contained concentrated sulfuric acid. The incubation temperature was $20 \pm 2^\circ\text{C}$.

The contents of gas trapping bottles were analyzed by LSC. Also, the contents of the first 0.1 N NaOH bottle were analyzed via HPLC and the presence of $^{14}\text{CO}_2$ confirmed via LSC before and after barium carbonate precipitation. After centrifugation, the aqueous phase was extracted via LSC, radio-HPLC and, in some cases, analysis was repeated after removal of dissolved ^{14}C -carbonate by precipitation with barium. Soil sediment was extracted successively with 0.1 N sulfuric acid, water, ammonium hydroxide, water, and methanol. The extracted soil was air-dried and analyzed for total ^{14}C by LSC after combustion.

C. Reported Results:

The distribution of radioactivity (volatiles, aqueous phase, soil sediment extracts, bound) for the individual soil/fosetyl-Al combinations is given in Attachments 3 and 4.

"The portion of the dose recovered in the aqueous phase, initially 87-89%, decreased to about 25% after 240 hours. The radioactivity recovered in the sulfuric acid extract and subsequent rinse of the soil sediment varies in the same way. At all incubation times (including time zero), it accounts for ca 8% of the amount recovered in the aqueous phase, which in fact corresponds approximately to the amount of aqueous phase remaining in the damp soil sediment separated by centrifugation. . . . the contents of the sulfuric acid extract are essentially the same as in the aqueous phase."

Total recovery of the initial dose declined throughout the sampling period. The authors attributed this loss to evolution of degradation products of high volatility. In this regard, a preliminary study was conducted during method development, in which ethanol followed by isooctane, mercuric perchlorate, potassium permanganate in 0.1 N sulfuric acid, and porous polymer Tenax GC were used individually as part of a trapping system. Only Tenax trapped any significant radioactivity. In triplicate LSC analyses of the polymer, ^{14}C -recovery decreased (1.1, 0.33, and 0.17% of the dose), " . . . as if a volatile compound was leaving the Tenax resin during its analysis."

"Radio-HPLC of the contents of the first trap (sodium hydroxide) consistently showed a single peak matching standard labelled carbonate. The identity of the carbonate was confirmed through the precipitation of barium carbonate, which resulted in the virtually complete disappearance of radioactivity detectable by HPLC and by LSC."

Quantitation of parent and metabolites in the aqueous phase of the various tests in which fosetyl-Al was used as the test substance is presented in Attachments 5 and 6. Half-life values for fosetyl were 40 hours (silty clay loam) and 14 hours (sandy loam). Ethanol was present at the maximum concentration in the aqueous phase at the 120-hour sampling time.

Results from the $[1-^{14}\text{C}]$ ethanol test are presented in Attachments 7 and 8. "With respect to the results obtained on the soil sediment, it is observed that the sulfuric acid extract contains 8% (average) of the amount of radioactivity recovered in the aqueous phase. This suggests the same comments as for the sulfuric acid extract in the test with fosetyl" The $t_{1/2}$ for ethanol, applied as the test substance, was 8 hours.

D. Study Author's Conclusions:

"The degradation proceeds through hydrolysis into ethanol (and presumably phosphorous acid, which was not monitored in this study). . . . degradation products appear to be carbon dioxide and, most probably, another very volatile degradation product which was not accounted for in this study (methane or ethane?)"

"Of the extraction solvents tested, aqueous ammonium hydroxide was the only one found to extract a significant portion (about one-half) of the residue present in the soil sediment. The fact that partial dissolution of the soil residue could be achieved only under alkaline conditions suggests that the residue is closely related to the organic matter of the soil."

"In tests carried out with ethanol, a portion of the radioactive dose was also unaccounted for, as in the tests with fosetyl. Other similarities were observed with respect to the patterns of formation of carbon dioxide, of soil residues extractable with ammonium hydroxide, and of bound residues. This further supports the hypothesis that the degradation of fosetyl proceeds mostly, if not exclusively, through the hydrolysis into ethanol."

E. Reviewer's Conclusions and Interpretation of Study Results:

The reviewer is in agreement with the study author's conclusions regarding $t_{1/2}$ values and degradation products (ethanol and CO_2) in the aqueous phase. However, the study does not meet the environmental fate requirements for anaerobic aquatic metabolism data because (i) residues were not characterized in the soil sediment extracts, and (ii) recoveries (material balance) of ^{14}C -residues were not adequate (approximately 80% from the sandy loam tests after 32 hours). [The authors attribute this loss to "degradation products of very high volatility."]

^{14}C -Residues in combined soil sediment extracts ranged from 6.3-15.6% of the applied dose, which is approximately equivalent to 6-14 ppm, expressed as parent. The Environmental Fate Guidelines (Subdivision N) state, "Residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified, when feasible." The initial dose in the submitted test was approximately 100 ppm with reference to the soil and 25 ppm with reference to the aqueous phase. The authors stated that the 100 ppm concentration in the soil "would be that obtained at the highest recommended rate (direct soil treatment at 80 kg/ha for ornamentals), assuming a homogeneous distribution in a 6 cm soil layer." The authors also stated that the limit of detection of the radio-HPLC method used was

approximately 5% of the radioactive dose (i.e., 20-25 ug expressed as parent). In the aqueous phase, this limit permits detection of residues, expressed as parent, at 1-1.25 ppm. In the soil sediment, 20-25 ug would be approximately equivalent to 4-5 ppm, expressed as parent.

The reviewer recognizes that it may not have been possible to detect 0.01 ppm in the soil and water because this would have required detection of 0.05 and 0.2 ug of ¹⁴C-residue, expressed as parent, respectively. These levels are approximately equivalent to 0.01 and 0.04% of the applied dose, respectively. However, the registrant should attempt to achieve the lowest possible limit of detection, and provide a valid justification as to why detection of residues at 0.01 ppm is not possible. In addition, a better material balance must be achieved in which volatiles are trapped and characterized.

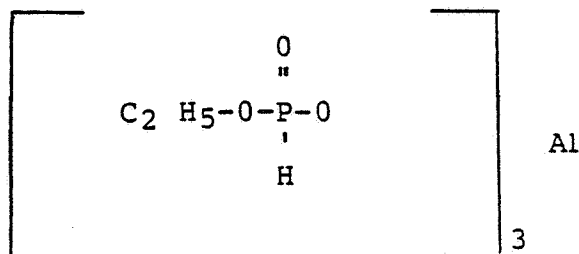
11. COMPLETION OF ONE-LINER: One-liner updated (appended).
12. CBI APPENDIX: No CBI appendix.

EAB File No. 123301

COMMON NAME: Fosetyl-Al TYPE PESTICIDE: Fungicide

CHEMICAL NAME: Aluminum tris (0-ethyl phosphonate)

STRUCTURE:



CHEMICAL PROPERTIES

Molecular weight: 354 Aqueous solubility: 120g/L (120,000 ppm)Vapor Pressure: no data (fosetyl-Al is a salt)Partition Coefficients:Octanol/water (kow): 2×10^{-3} (range = 1.7×10^{-3} to 5.2×10^{-3})Soil Adsorption: (Adsorption of Phosphorous acid correlates with % O.M.)

<u>Soil Type:</u>	% soil <u>Organic matter</u>	% <u>ads.</u>	<u>Adsorption Coefficient</u>
Sandy Loam	3.6	84	$K = 6.5$ ($1/N = 0.613$) <u>Koc</u>
Silt loam	2.3	51	—
Loamy sand	1.3	27	—

Hydrolysis:

Soil TLC: Rf = 1 (Helling's mobility class 1 - very mobile)

<u>pH</u>	<u>Half-life</u>	
5	(Stable)	less than 10% degradation in 1 month
9	(Stable)	less than 10% degradation in 1 month

Photolysis

Water: (Stable) very little adsorption at 290 nm

Soil Surface: (Stable) very little adsorption at 290 nm

Degradation:Lab Studies

Aerobic Soil half-life: 1 - 1 1/2 hrs.
20 minutes in
sandy loam

Anaerobic soil half-life: no data

Anaerobic aquatic half-life: 14-40 hours

Fish Bioaccumulation Factors

<u>Species</u>	<u>Tissue</u>		<u>Whole Fish</u>	<u>Depuration half-life</u>
	<u>Edible</u>	<u>Viscera</u>		
Bluegill	No data	No data	No data	No data
Catfish	No data	No data	No data	No data
<u>Found in Ground Water?</u>		No data		
<u>Established Reentry Internal:</u>	N/A			
<u>Rotational Crop Restrictions:</u>	No data			

Summary Comments: Fosetyl-Al is degraded by soil microbes. The first aerobic degradates are ethanol and phosphorous acid; the maximum half-life was 1 1/2 hours. Degradation by hydrolysis or photolysis will be relatively non-existent.

References

Exposure Assessment Branch Files

Updated (Anaerobic aquatic half-life) on 1/21/86 by D. Edwards