Shaughnessy No.: 125401

Date Out EAB: AUG 27 1985

TO: R. Taylor/Yowell
Product Manager # 25
Registration Division
TS-767

FROM: Samuel M. Creeger, Chief
Environmental Chemistry Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

Attached please find the environmental fate review of:

Reg./File No.: 279-GNLE, -GNLG and -GNLO

Chemical: FMC 57020 (Dimethazone)

Type Product: Herbicide

Product Name: Command®

Company Name: FMC

Submission Purpose: Registration on soybeans, response to previous review

Action Code: 106

Date In: 7/18/85

EAB # 5763-5765

Date Completed: AUG 27 1985

TAIS (Level II) 61

Days 5.5

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

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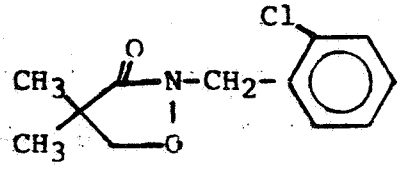
1. CHEMICAL:

- o Common name: Dimethazone (proposed? accepted?)
- o Trade name: Command® Herbicide
- o Company code: FMC 57020
- o Chemical name: 2-(2-chlorophenyl)methyl-4,4-dimethyl-3-isoxasolidinone
- o Chemical structure:



2. TEST MATERIAL:

Aromatic ring-^{14}C-FMC 57020 (28.15 mCi/mmol, 96.7 % pure)

3. STUDY/ACTION TYPE:

Registration on soybeans. Response to previous review.

4. STUDY IDENTIFICATION:

- o Wu, J., "Photodegradation of FMC 57020 in Water - Study II. Comparative Behavior in Artificial and Natural Sunlight. Nature of Volatile Degradates." FMC Corp. Study No. 164E12E02, P-1136, 6/13/85, EPA Acc. No. 073672 (Tab 3).

- o Wu, J., "Photodegradation of FMC 57020 in/on Soil - Study II. Comparative Behavior in Artifical (Artificial) and Natural Sunlight," FMC Corp. Study No. 164E13E02, P-1137, 6/13/85, EPA Acc. No. 073672 (Tab 4).

5. REVIEWED BY:

Soobok Hong, Ph.D. S Creeger for
Chemist
Environmental Chemistry Review Section 1/EAB/HED

6. APPROVED BY:

Samuel M. Creeger, Chief Samuel M Creeger
Supervisory Chemist
Environmental Chemistry Review Section 1/EAB/HED AUG 27 1985

7. CONCLUSIONS:

7.1 All environmental fate data requirements have been addressed in support of registration of Command Herbicide on soybeans. However, information is needed to complete our review of the photolysis studies as discussed in section 8, RECOMMENDATIONS.

7.2 The following is the summary of environmental fate of Command Herbicide (FMC 57020):

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- o Hydrolysis - FMC 57020 is stable to hydrolysis in acidic, neutral and basic solutions maintained at temperature of 25 ± 0.5°C.

- o Aqueous photolysis - ^{14}C-phenyl-FMC 57020 photodegrades in water under natural sunlight ($t_{1/2}$=87.7 d) and artificial sunlight ($t_{1/2}$=61 d. assuming a 12 hr/day photoperiod) with the major photoproduct being $^{14}CO_2$. Acetone accelerated photolysis rates ($t_{1/2}$=23.8 and 5.7 days in 0.1 and 2.0 % acetone sensitized solution under artificial sunlight).

- o Soil photolysis - FMC 57020 is stable to photolysis in/on soil.

- o Aerobic soil metabolism - FMC 57020 is mineralized in soil under aerobic conditions. CO_2 evolution and soil binding increase with time. The rate and the degree of mineralization and soil binding vary with soil types. Both rings of the molecule are susceptible to the mineralization process. Unchanged FMC 57020 is the primary residue in soil, and polar/non-polar metabolites are minor residues. The estimated half-lives varied from 56 to 173 days depending on soil type.

- o Anaerobic soil metabolism - FMC 57020 readily degrades to FMC 65317 as a major product under anaerobic conditions. Another 12 minor degradation products were detected. No CO_2 evolution was observed. Data indicate that FMC 65317 persists under anaerobic conditions.

- o Laboratory leaching - FMC 57020 appears to have a low to intermediate mobility in sandy loam, silt loam and clay loam soils but a high mobility in sand soil. FMC 65317, an anaerobic soil degradate of FMC 57020, has a very high mobility in all soil types.

- o Field leaching - FMC 57020 appears to have a low leaching potential under actual field conditions (loamy sand, 1.2 % OM, 2.0 lb ai/A, 13.9 inches of water in 61 days) since no detectable levels (less than 0.02 ppm) of the compound or its metabolites were found in soil samples taken deeper than 1 foot. FMC 65317 was not detected in any soil sample at any depth.

- o Rotational crops - The application of ^{14}C-FMC 57020 at the rate of 2 lb ai/A (1.6-1.7x maximum label rate) results in low residues in rotational crops (corn, oat, cabbage and sugar beet) planted 10 months after chemical application. A majority of these residues are either plant tissue bound or polar. Organosolubles accounted for less than 0.02 ppm. Residue levels were higher in the mature rotational crops as compared to the immature ones. Total ^{14}C did not exceed 0.063 ppm in corn, cabbage or sugar beet, but reached a maximum of 0.118 ppm in mature oat straw. The data support a 9 month rotational crop interval (see EAB review of 7/2/85

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[Holst and Hong] for the rotational crop interval reduction from 10 months to 9 months).

- o Fish accumulation - FMC 57020 has a moderate tendency to bioaccumulate in bluegill sunfish under flow-through conditions. A bioaccumulation factor of 40x for whole fish was found, but depuration occurs rapidly to low but measurable levels upon removal of the fish to uncontaminated water. FMC 57020 appears to be metabolized in the fish by a variety of processes including oxidation, hydroxylation, heterocyclic ring opening, methylation, and decarboxylation. There are indications that the methylene carbon is incorporated into fats/oils and higher molecular weight lipophilic/polar conjugates.

8. RECOMMENDATIONS:

It is recommended that the registrant address the questions raised in section 10.2 E and provide the structure of arylamide as discussed in section 10.3.E. When these issues are satisfactorily addressed, then there will be no data gaps for the proposed soybean use.

9. BACKGROUND:

A. Introduction

In response to EAB review of 6/17/1985, FMC has submitted the final reports for new aqueous photolysis and soil photolysis studies. Also, the submission (Acc. No. 073672) includes FMC's response to the EAB's comments concerning field dissipation data.

B. Directions for Use

No label was included with the submission. Previous reviews reveal that Command® Herbicide may be used alone, or in combination with other herbicide for pre-emergence and post-emergence control of broadleaf and grass weeds on soybeans. The maximum use rate when used alone is 1.2 lb ai/A. For detailed information, see the attachment (labels) of 11/23/84 review.

10. DISCUSSION OF INDIVIDUAL STUDIES:

10.1 A. Study Identification

Field Dissipation (FMC Report No. P-0896, Section 10.5 of EAB review of 6/17/85 and Section 3.14 of 11/23/84 review).

B. EAB Cited Deficiencies

The data points used for plotting dissipation curves need to be provided in tables.

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It was recommended that soil concentrations in 0-12 inch depth be recalculated and dissipation rates be recalculated.

C. FMC's Response

In order to obtain calculated or theoretical concentrations for the entire soil profile of 0-12 inch depth as recommended by EAB, the densities of the soils in 0-6 inch and 6-12 inch depth were determined, and equal density was observed for 0-6" and 6-12" depth soils in every soil type, i.e., silt loam soil (IL): 1.02 vs. 1.03; sandy loam soil (NJ): 1.42 vs. 1.41; sandy clay loam soil (NC): 1.04 vs 1.04 and silt loam soil (AR): 1.17 vs. 1.16.

Therefore, to incorporate 0-6" and 6-12" residues, FMC residues in 0-6" and 6-12" depth were added and divided by two. The resulting calculated 0-12" soil residues are presented in Tables 2a, 3a, 4a, and 5a. Based on the "best fit" principle, the residue data in Tables 2a, 4a, and 5a were plotted using second-order decay law and data in Table 3a were ploted using 1.5-order decay law. The resulting half-lives are presented in Table 6.

D. Reviewer's Comment

The FMC's response adequately address the EAB's concern on field dissipation studies.

FMC 57020 dissipates under field conditions with a half-life range of 24-82 days depending on soil type and the method of application (pre-emergence and preplant incorporated application).

The field dissipation data requirement for Command Herbicide on soybeans is satisfied.

10.2 A. Study Identification

Wu, J., "Photodegradation of FMC 57020 in Water - Study II. Comparative Behavior in Artificial and Natural Sunlight. Nature of Volatile Degradates." FMC Corp. Study No. 164E12E02, P-1136, 6/13/85, EPA Acc. No. 073672 (Tab 3).

B. Materials and Methods

^{14}C-FMC 57020 (aromatic ring labeled, 28.15 mCi/mmol, 96.7 % pure) was subjected to photolysis in water (pH 6.7) under natural (outdoor) and simulated (indoor) sunlight in the presence or absence of acetone (0.1 % or 2.0 %).

Indoor tests.

Dynamic (moving air) - One hundred ml of water was fortified with 1 ppm (ug/ml) of ring-^{14}C-FMC 57020 (@ 2 uCi), and

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___ Description of product 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

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placed in a 250 ml sterilized gas washing bottle. A dark control sample was also prepared accordingly. The experimental set-up is shown in Figure 1. The sample bottle was continuously irradiated with a 275 W G.E. sunlamp (@ 1500 uw/cm^2, Appendix D)

Static - Aliquots of 5 ml of the 1 ppm ^{14}C-FMC 57020 were pipetted into a 10 ml capacity sterilized borosilicate ampules. The ampules were sealed, placed in a water bath (25°C) and irradiated. Acetone sensitized (0.1 %) aqueous samples were prepared in the same manner. A 2 % acetone sensitized solution (5 flasks, 15 ml each) was also irradiated in a 100 ml flask equipped with a CO_2 trap (0.1 N KOH). Dark control samples were prepared accoringly.

Outdoor tests.

Sealed ampule samples containing 5 ml of the 1 ppm ^{14}C-FMC 57020 solution were placed in a water-cooled flat glass tray and irradiated directly by natural sunlight for 30 days. The glass tray was cooled by constant temperature water bath at 25°C. Dark control samples were prepared accordingly.

Samples were harvested at predetermined intervals and analyzed by LSC and HPLC (Waters, CH_3CN/H_2O). A summary of the retention times for the various components is shown in Figure 2. The summary of the photolysis conditions and sampling intervals is shown in Table 1.

C. Reported Results

The recoveries of total radioactivity exceeded 90 % in most cases.

The results obtained from photolysis of non-sensitized solutions are shown in Tables 2 and 3.

To obtain the trapping efficiency, 1 uCi of $NaH^{14}CO_3$ (10.0 ug of $NaH^{14}CO_3$ in 1.0 ml water, pH 9.5) was placed in a 125 ml filtering flask containing 25 ml of distilled water. One hundred ul of 1 N HCl was injected through a septum to generate $^{14}CO_2$. The evolved $^{14}CO_2$ was bubbled through 0.1 N KOH trap by vacuum for 5 minutes. The CO_2 trapping efficiency was 38.6 % when one KOH trap was used and 41.0 % when two KOH traps were used. Adjusted by the trapping efficiency (38.6 %), a total of 94.7 % of the applied radiochemical was recovered (Table 2).

^{14}C recoveries from the 2 % acetone sensitized solution are listed in Table 5. Over the 3-day period, radiochemical trapped in the KOH trap incresed.

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Tables 6 and 7 present the results obtained from the dynamic system.

Table 8 summarizes the photolysis rates and half-lives at various test conditions.

The volatile ^{14}C gas trapped in KOH solution (test #5) was confirmed as $^{14}CO_2$ by adding $Ba(OH)_2$ solution into the KOH solution. The white precipitate (ppt) was separated, rinsed and a portion of the $Ba^{14}CO_3$ suspended in Hydrocount/H_2O for LSC. The majority (94.2 %) of the radioactivity in the KOH trap solution was in $Ba^{14}CO_3$ precipitate while the supernatant contains 5.8 % of the total radioactivity. Volatile radioactive gases (in KOH solution, #8) were also analyzed by GC/MS after purging the KOH solution with He gas or after neutralization with 6 N HCl and the adsorbing the the volatiles onto a Carbosieve-B adsorption column. The mass spec peak was indicative of CO_2 (m/z 44).

It appears that the photolysis of FMC 57020 proceeds via triplet excited energy states because the reaction was considerably enhanced in the presence of acetone, a known triplet state sensitizer. To confirm the quenching effect caused by molecular oxygen, an experiment was conducted to compare FMC 57020 breakdown in a degassed solution with that in oxygenated solution. Table 10 presents the results. The photodegradation rate of FMC 57020 in aqueous solution can vary depending on the levels of dissolved oxygen in the test solution.

Tables 11-14 list the % of product distribution from HPLC analyses for all indoor and outdoor solution studies. Figure 6 illustrates the proposed FMC 57020 photodegradation pathways. The minor photoproducts in descending order were o-chlorobenzoic acid, benzoic acid, o-chlorobenzaldehyde, o-chlorobenzamide and o-chlorobenzalcohol.

D. Study Author's Conclusion

FMC 57020 is slowly photodegraded in water under natural or simulated sunlight. Acetone, a triplet state photosensitizer, accelerates the photodegradation rate. Molecular oxygen, on the other hand, is able to quench the reaction efficiently. CO_2 has been shown to be the primary volatile constituent formed during the photodecomposition of FMC 57020. Its rate and level of formation can be significantly enhanced by the addition of acetone.

E. Reviewer's Discussion and Interpretation of Study Results

^{14}C-phenyl-FMC 57020 appears to photodegrade slowly in water under natural sunlight ($t_{1/2}$=87.7 d) and artificial sunlight ($t_{1/2}$=61 assuming a 12 hr/day photoperiod) with the major photoproduct being $^{14}CO_2$. Other minor photoproducts include

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o-chlorobenzoic acid, benzoic acid, o-chlorobenzaldehyde, o-chlorobenzamide and o-chlorobenzalcohol. Acetone accelerates photolysis rates ($t_{1/2}$=23.8 and 5.7 days in 0.1 and 2.0 % acetone sensitized solution under artificial sunlight).

The registrant should address the following questions:

- Does the glassware (ampoules, flasks and glass tops) used in the tests transmit sunlight without any absorption?
- What is the fate of isoxasolidine ring of FMC 57020 molecule? What data is used to support the degradation pathway of the isoxasolidine ring proposed in fig. 6?

10.3 A. Study Identification

Wu, J., "Photodegradation of FMC 57020 in/on Soil - Study II. Comparative Behavior in Artifical (Artificial) and Natural Sunlight," FMC Corp. Study No. 164E13E02, P-1137, 6/13/85, EPA Acc. No. 073672 (Tab 4).

B. Materials and Methods

^{14}C-FMC 57020 (aromatic ring-labeled, the same as described in section 10.2 B), was subjected to soil photolysis under natural sunlight or simulated sunlight for a period of 30 days.

Dried, sieved and autoclaved Dunkirk silt loam soil (4.9 g) (%sand 24.8; %silt 60.0; %clay 15.2; %OM 2.1; CEC 10.9; pH 4.8; bulk density 1.2) was mixed with 10 ml of distilled water in a 5.1 cm i.d. Pyrex petri plate. The soil plate was allowed to dry overnight yielding a thickness of 0.5 mm. Each plate was evenly treated with 2.0 ml of ^{14}C-FMC 57020 in CH_2Cl_2 (0.72 mg, 2.0 uCi/plate) equivalent to a broadcast treatment rate of 3 lb ai/A.

Outdoor (natural sunlight) tests:

Twenty sealed soil plates were placed in a water bath cooled stainless soil chamber. Half of the plates were wrapped with aluminum foil placed side by side with the other 10 plates as dark controls. The chamber was covered with a Pyrex glass top to prevent rainfall, but a gap of 1" between the chamber edge and glass plate was reserved to allow for air cooling effect. The soil chamber was immersed into a cold water styrofoam chest to maintain a chamber temperature 20-30°C (Figure 1).

Indoor tests:

The light source was the same as used for aqueous photolysis (section 10.2, above).

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Dynamic (moving air) system - A 9" X 18" Pyrex glass pipe fitted with aluminum flange (Figure 2) was connected with a series of traps consisting of a polyurethane foam stopper, a 0.25 N H_2SO_4 (100 ml) trap and two 0.25 N KOH (100 ml each) traps (Figure 3). The uncovered soil plates were then placed in the center of the glass pipe on an aluminum holding plate. Air was allowed to flow through the chamber at @80 ml/min after passing through DRIERITE® and Hydro-Purge® II to remove corrosive gas including CO_2 and a water flask to moisten the air. A second control chamber was established identically and placed side by side with the first one except the entire glass chamber was wrapped with aluminum foil.

Static (sealed plate) system - Ten soil plates were covered with a borosilicate (Pyrex) glass cover and sealed with plastic adhesive tape around the bottom edge. The sealed soil plates were then placed in a stainless steel chamber with water cooling reservoir (Figure 4). Dark controls were done in the same manner. The temperature for both indoor and outdoor soil photolysis were monitored periodically and kept 20-30°C.

Both the indoor and outdoor soil plates were sampled in duplicate at 0, 3, 7, 21 and 30 days after irradiation. For moving air system, all of the traps were changed at each sampling interval.

Soil was scraped from the plates, and triplicate subsamples (0.05-0.1 g)were radioassayed by combustion/LSC. The plates were thoroughly rinsed with methanol and radioassayed. Aliquots of trapping solutions were also counted by LSC.

Soil samples were extracted according to the scheme in Figure 5. Aliqots from each fraction (I and IV of Figure 5) of each sample were isotopically diluted with unlabeled FMC 57020 standard and analyzed by HPLC. Radioactivity in the CH_2Cl_2 and MeOH extracts, various trapping solutions and HPLC fractions were determined.

C. Reported Results

The results are shown in Tables 2-6.

Photodecomposition of FMC 57020 in/on soil surface proceeded very slowly under either simulated or natural sunlight. Under indoor simulated sunlight conditions, both the static and dynamic photodegradation systems also show very slow decomposition.

HPLC analysis indicated that more than 90 % of the organo-soluble were unchanged FMC 57020 at all sampling intervals. Polar residues increased slowly, but not significantly, through the 30 day irradiation period. o-Chlorobenzamide, arylamide, o-chlorobenzaldehyde, o-chlorobenzoic acid and

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benzoic acid are the few detectable products but non of them exceeded 1 % at all time intervals. Radioactivity in various traps was negligible (Table 8).

Table 7 lists all photodegradation rates and half-lives for the three tests.

D. Study Author's Conclusion

Data indicate that a slow breakdown of FMC 57020 occurs in/on soil surface when exposed to either simulated or natural sunlight. Loss of parent compound and volatile material as well as thermal and microbial decomposition is negligible under both dynamic and static photodegradation conditions.

E. Reviewer's Discussion and Interpretation of Study Results

FMC 57020 seems to be very stable to photolysis on soil (estimated half-lives of 600-1000 days).

The registrant should be asked to provide the structure of arylamide, one of the claimed phototransformation products.

11. ONE-LINER: An updated one-liner is attached.

12. CBI: No CBI is included in this review.