~~5/21/75~~ 5-15-75

Environmental Chemistry Review for Dimethyl phosphate of 3-hydroxy-NN-dimethyl-cis-crotonamide(dicrotophos)

Date Div. Received: 2/14/72 Date of Submission: 2/10/72
Product Name: Bidrin Type Product: Insecticide
Company Name: Shell
Submission Purpose: None: Date package for 70-15

comment out 201-274
15 May 1975

1. CONCLUSIONS

1.1 Data submitted are inadequate to characterize hazards associated with this product. Data submitted do show an oxidative conversion of Bidrin to Azodrin for which some additional 70-15 information is available. It is concluded that, for those circumstances that involve metabolic conversion of Bidrin to Azodrin, environmental hazards of Bidrin use will be similar to those found for Azodrin. Bidrin persistence will be greater than that of Azodrin and some circumstances will result in a conversion of Bidrin to products other than Azodrin. Thus, to completely assess environmental hazards associated with Bidrin's environmental fate, the following are needed:

1.2.1 A photodegradation study. See enclosure. (Enclosed Second Draft Guidelines, p. V40 - V44)

1.2.2 A leaching study. See enclosure. (Enclose Draft Guidelines, p. V-29 to V-30)

1.2.3 A fish accumulation study. See enclosure. (Enclose Second Draft Guidelines, p. V-37 to V-38)

[Note: A study on degradation product Azodrin is useful, but since Bidrin may not hydrolyze at near-neutral pH at normal ambient temperatures, breakdown is not assured in water and thus a study on the parent is needed.]

1.2.4 Hydrolysis studies at pH 5 and 7. See enclosure. (Enclose Second Draft Guidelines, p. V33)

1.2.5 Effects on microorganisms. The studies reported were inadequate. The following study is needed. An assessment of pesticide impact on soil microorganisms is needed.

To assess the impact of pesticides on soil microbial functions the following are suggested:

a. The effects on the transformations of nitrogen compounds should be determined. This includes nitrification, nitrogen fixation and denitrification.

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b. Effects on pesticide degratory enzyme activities should be determined. Additionally, effects on general soil enzyme a-tivities such as soil dehydrogenase and phosphatase should be determined.

c. Effects on common pesticide degraders such as Bacillus sp., actinomycetes, pseudomonads, coryneform bacteria, Trichoderma, Aspergillus, etc., should be determined.

d. Effects on carbohydrate transformations should be determined.

e. Population analyses using a variety of selective procedures including the use of restrictive growth media, the use of special isolation techniques (i.e., Anaerobic isolation, thermophilic isolation) and direct counting procedures are to be made to determine the effect of the chemical on normal soil microflora.

1.3 The above represent minimal requirements for data needed to assess environmental hazards. Additional studies may be needed pending reviews of individual use patterns.

2. INTRODUCTION

2.1 This is a first 70-15 review for Bidrin.

2.2 Data was submitted in response to a letter of 1/7/72.

2.3 Bidrin is registered for use on cotton, soybeans and various ornamentals.

3. REVIEW OF DATA

3.1 The data package consisted of 30 separate reports of which 17 had some bearing on 70-15 needs. Most were published papers not designed to meet environmental chemistry requirements directly but which contained some useful information.

3.2 Residue dissipation studies

3.2.1 Report No. 1 "Stability of Bidrin in Soil".

This is a lab study using two soils, a sandy loam (air dry) and a fresh loam. Tabular data are not presented, but a graphical representation of dissipation in the loam shows a half-life of about 7 days and 90% loss of Bidrin by 20 days. The dry sandy loam was reported to have had little decomposition (< 10%) in 28 days. Sterile loam soil was reported to show no decomposition in 30 days (no data presented). Analysis was for parent only using spectrophotometric techniques following sodium sulphate, chloroform and, finally, carbon tetrachloride extractions.

3.2.2 Report #2. This study used the same techniques as Report #1. Different formulations of Bidrin were used, all containing 5.6% active ingredients. Half-lives were between 3 and 6 days for all formulations.

3.2.3 Report #5. Part of this report refers to a ^{14}C-Bidrin application to sandy loam. Soils of various moisture content were compared as follows:

STABILITY OF BIDRIN IN SANDY LOAM FIELD SOIL

MOISTURE CONTENT FIELD CAPACITY, %	WT, %	^{14}C-BIDRIN RECOVERED AFTER 7-8 DAYS, %
Air-dry	1.2	80.5
50	4.0	18.5
75	6.8	8.8
100	9.8	6.8

This data supports the observations of Report #1 on effects of moisture.

3.2.4 Report #3. Part of this study compared ^{14}C-labeled Bidrin in sandy loam soil (75% moisture capacity) under sterile and non-sterile conditions. These data show that only 65% is initially recoverable on day 0 but that 60% is still present in sterile soil on day 8 while only 15% is present in non-sterile soil. No other soil dissipation data is given.

Fig's from Tab "4

3.2.5 Study ~~5~~ 4. A last report on lab studies using Bidrin showed that high organic matter retarded decomposition of Bidrin. Several soils with O.M. values of 2-16.5% were tested and half-lives only were reported for Bidrin and Azodrin (c.f.). Adsorption contents showed values varying directly with organic matter. Half-lives for the 16.5% soil were 15 days and for a sandy loam of undefined O.M., 11 days. However, for soils of O.M. 6.5% or less, half-lives were 3 days. Azodrin was slightly more persistent than Bidrin.

3.2.6 Report #6 and #7. These reports are of field studies of Bidrin dissipation. One set was done in Arkansas and the other in Great Britain. In each, the computed half-lives were about 5-6 days. The 90% dissipation was much quicker in Arkansas (2 weeks) versus Great Britain (6-7 weeks).

3.2.7 General conclusions. Dissipation of parent Bidrin in soil is relatively short except where soil microbes are inhibited by direct sterilization or drying. Bidrin loss is also slowed by adsorption to organic matter, especially above 6.5% O.M.

3.3 Route of degradation. A proposed set of degradation pathways mediated by microbial and/or other metabolic activities is shown on page 9 of the data package and derived from several studies (Reports 3, 7, 8, 9, 10, 11, 12, 13). Some studies involved use of ^{14}C and other ^{32}P labeled pesticides. These studies all point to the initial degradation of Bidrin to form Azodrin (N-methyl Bidrin) via hydroxymethyl Bidrin as one important degradation route (p. 57-59). Azodrin can be more toxic than Bidrin to several organisms and is itself a registered insecticide. Other routes involve hydrolysis of the phosphate giving N,N dimethyl-acetoacetamide which is further degraded. Conjugates can be formed in plants which can be further degraded by loss of dimethyl-phosphate.

As was noted earlier in Section 3.2, Azodrin is slightly more persistent in soil than Bidrin. Thus, though loss of parent can occur rapidly,cholinesterase inhibiting products are produced by oxidative degradation of Bidrin which persist longer than the parent.

3.4 Photodegradation. A photodegradation study is mentioned on p. 10. It was reported that no photodegradation occurred after 4 hours sunlamp exposure on glass slides. No data is given.

3.5 Effects on microorganisms. A report of primary screening tests for activity to microorganisms is alluded to on p. 12 of the summary. One set of data purported to show no effect versus microorganisms except *Erwinia caratovora*, is need given. The other set, consisting of a page from a lab worksheet, shows no effect at 32 ppm versus all except *Polyp(e)rus* (sic.) *tulipferus* (at 25 ppm) and *P. italicum* (32 ppm). Of those tested, many were plant pathogens, but not normal microflora involved in soil fertility.

These tests appear unsatisfactory as indicators of lack of effect on important soil microbial functions.

3.6 Hydrolysis. No study was performed involving hydrolysis of Bidrin at pH's 5, 7 and 9, or similar pH at less than 55°C. At elevated temperatures (or extreme pH), half-lives ranged from less than one to 160 hours. Bidrin appears to degrade more rapidly at extreme basic pH (9-12) than neutral or acid pH (2.5-7.0). At cooler temperatures, Bidrin was stable for > 40 to > 80 days (38°C) or 100 days (r.t.) at pH 1.1 and pH 9.1.

The stability at room temperature of Bidrin at pH 5 and 7 is still undefined. However, if pH 9.1 data is an indicator, one would expect persistence greater than 100 days.

3.6 Leaching and Movement. The only data indirectly applicable were found in Report #5. These involve the leaching of Bidrin through 3" of soil and bioassay of the leachate. These data show easy movement through 3" of soil. However, this data is insufficient to define movement of Bidrin.

4. SUMMARY

4.1 The data show potential rapid conversion of Bidrin in soil to Azodrin. Parent Bidrin is rapidly lost (3-7 days) while Azodrin also degrades quickly, though not as fast as Bidrin (6-18 days).

4.2 Bidrin appears to be degraded by microbial activity. Other modes of degradation were either not reported or inadequately described.

4.3 Bidrin adsorbs to organic matter which slows down dissipation in high organic soils.

4.4 The following conclusions are found with Bidrin metabolite Azodrin (201-GUE and 201-GUO (3/6/73)):

1. The 1/2 life in 4 or more tested soils is short; except for granular formulations which may carry over into rotational crops. At this submission there is no proposed use for granular formulations.

2. Azodrin photodegrades.

3. Hydrolyzes rapidly at pH above 8. Most soils are below pH 7 so hydrolysis would be slow.

4. Can degrade thermally.

5. Possible leacher.

6. Microorganism can degrade Azodrin. No or little effect on organism test.

7. Bound or unextractable residues are present and degrades with time. Again, crop rotational data will be needed for granular formulation if proposed.

8. Note no decline curve for soil, field residue soil study.

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