THIS REPORT CONTAINS CONFIDENTIAL BUSINESS INFORMATION. #8455A

Shaughnessy #: 079101

EAB Logout Due Date: 07 SEP 1984

Init:

To:
Wm. Miller
Product Manager # 16
Registration Division (TS-767)

From:
Lionel A. Richardson Chief,
Environmental Chemistry Review Section # 3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769c)

Attached please find the EAB review of...

Reg./File No.: 476-2109

Chemical: Aspon

Type Product: I

Product Name:

Company Name: Stauffer Chemical Company

Submission Purpose: Registration Standard

ZBB Code: 3 (c)(5)

ACTION CODE: 606

Date In: 7/11/84

EAB # 4458

Date Completed: 9/7/84

TAIS (level II) Days

42 13.5

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

DATA EVALUATION RECORD CONFIDENTIAL

CASE GS 079101 DISC 30 TOPIC 050520 GUIDELINE 40 CFR 162-1

CHEM ASPON

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No Fisch CONTENT CAT -- 01

Aspon aerobic soil metabolism study (MIR 24-7-83). Interim Reports No. 1 and 2. Unpublished. Submitted by Stauffer Chemical Company, July 2, 1984 in support of Registration Standard.

SUBST. CLASS =

DIRECT RVW TIME = (MH) START-DATE END DATE

REVIEWED BY: H.L. Boyd
TITLE: Chemist
ORG: EAB
LOC/TEL: Room 807 - I 557-0267

SIGNATURE: Hudson L Boyd DATE: 9-7-8

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

1. The validity of this study cannot be evaluated for reasons enumerated on the attached.

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PROJECT 148250 - Aspon (MIR 24-7-83)

Interim Reports No. 1 & 2

The validity of this study and the value of the data derived therefrom cannot be evaluated from the rambling, incoherent write-ups (Reports 1 and 2). If the report writers know how the experiment was conducted and what was accomplished, they failed to communicate the fact. In some points, Report #2 (a follow-up) differs from Report #1 about the same steps in the method.

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A few questions are:

In what solvent was Aspon dissolved for the biometer flask study(s)? Was this the same solvent used for treating the flasks without soil?

Were any flasks without soil treated with Aspon?

Was the value of soil treatment 7.xxx ppm or 6.xxx ppm?

It is stated: "Control flasks included two flasks treated with solvent only" (what was the solvent?), and "two flasks without soil (blank controls)". Yet, Table 2 Report 2, describes the four control flasks as two being blank controls (no soil) and two being "untreated controls (soil not treated with Aspon)." It is difficult to visualize just what happened.

Again: In the discussion of results (Study 2) reference is made of flask treatment with several dilutions of Aspon, yet in the materials and methods section for soil preparation and treatment no mention is made of the dilutions. Obviously, the statement that sixteen flasks were treated with about 6.63 - 6.72 ppm Aspon is not wholely true.

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It is not intended that the above are all of the questions unanswered by the write ups. The researchers should know what they did, how they did it, and what the results were. Given that information in clear, straight-forward English we will be in a position to judge whether registration requirements (re: aerobic metabolism) have been satisfied.

DATA EVALUATION RECORD CONFIDENTIAL

CASE GS 079101 DISC 30 TOPIC 050515 GUIDELINE 40 CFR 163.1

CHEM Aspon

BRANCH EAB

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No fiche CONTENT CAT.: 01

Studies on the adsorption/desorption of [^{14}C] Aspon and its metabolites in soil. Unpublished study PMS 131; MRC-83-05; dated June 1, 1983, and submitted by Stauffer Chemical Co., July 2, 1984, in support of Registration Standard.

SUBST. CLASS =

DIRECT RVW TIME = (MH) START-DATE END DATE

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CONCLUSION:

1. This study is scientifically valid, but see Discussion section.
2. Neither Aspon nor its soil metabolites are expected to be significantly mobile in sand, loam, nor sandy loam soils, and should not contaminate ground water by leaching through the soil.
3. This study fulfills EPA Data Requirements for Registering Pesticides (1983) Sec. 163.1 (leaching) by providing data on adsorption/desorption and mobility in four soils.

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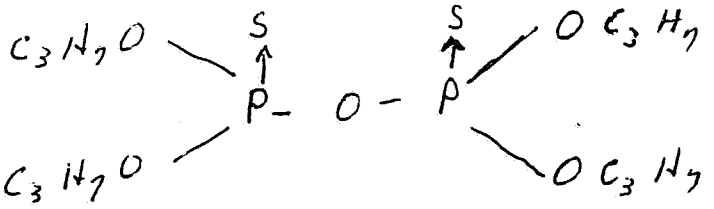
MATERIALS AND METHODS



0,0,0,0-Tetra-n-propyl dithiopyrophosphate - Aspon

Chemicals. ^{14}C-Aspon, 90.2% purity (by 2-D TLC) from the DeGuine Technical Center, Stauffer Chemical Co., with a specific activity of 14.16 mCi/m Mole (83,200 dpm/ug) was used in these studies. For the mobility studies, ^{14}C-2,4-D, carboxy label, and a specific activity of 5.1 mCi/m Mole (51,200 dpm/ug) was used. It appears from the results section of the report that the radiopurity of the 2,4-D was 96.8%. (See remarks in the conclusion section). The 2,4-D was obtained from ICN Pharmaceuticals, Inc., Irvine, CA.

Soils. Four soils, Keeton sandy loam, Sorrento loam, Felton sand, and Prairie loam, were used for soil thin-layer mobility studies and for adsorption/desorption studies. Soil organic matter contents ranged from 1.1 - 6.2% and soil pH ranged from 5.7 to 6.9. Soils were screened to 500u for these studies.

Soil metabolites of Aspon were studied from ^{14}C-Aspon applied to the Sorrento loam at 8 ppm and aged for 28 days in a dark environment at 22°C. The treated soil was extracted with acetone/methanol (ratio not given). After concentration on a rotary vacuum evaporator the extract was partioned with diethylether. The ether extract was further concentrated, assayed by liquid scintillation counting (LSC) and percent distribution of ^{14}C made by 2-D TLC.

Stock solutions of ^{14}C-Aspon were prepared by evaporating measured (unspecified) volumes of the chemical in ether to dryness in a nitrogen atmosphere and then taking up the residues in distilled water. After sonic mixing the resulting solution was assaying by LSC and labeled 1X. Subsequently, by serial dilution, solutions of 0.1x and 0.01x were prepared. Aliquots of these solutions were also assayed by LSC.

Liquid scintillation counting of "appropriately sized aliquots" was accomplished in triplicate using a scintillation cocktail (3a70B from Research Products Corp, Elk Grove Village, Ill.) and a Packard Liquid Scintillation Spectrometer equipped with an automatic external standard (AES). Background noise was accounted for and counting efficiencies were determined from an AES ratio or channels ratio vs counting efficiency curve.

Radioactivity in soil samples was determined by combustion in a Packard Sample Oxidizer, with $^{14}CO_2$ being trapped in Carbosorb combined with a scintillation cocktail prior to LSC analysis.

Soil thin-layer chromatography was employed to predict the leaching potential of Aspon and its degradates; ^{14}C-2,4-D was used as a reference for comparative purposes. Solvent systems of hexane/ether (1:1) and toluene were used for ^{14}C-Aspon and ether/hexane/ formic acid (70/80/2) for ^{14}C-2,4-D. Samples were spotted on Merck silica gel 60 F254 plates, 20 x 20 cm with 0.60 mm thick layers. Non-radioactive Aspon was detected by use of a spray reagent, DCQ (2,6-dibromo-N-chloro-p-benzoquinone imine) in cyclohexane, followed by exposure to HCl vapors ---- Aspon appeared as an orange spot on a yellow background.

Radioactive spots were visualized by autoradiography using Kodak SB-5 x-ray film. Radioactive areas of TLC plates were scraped into scintillation vials containing 1 ml MeOH and scintillation cocktail and assayed by LSC.

Mobility studies. Water slurries of each soil were prepared and applied as 0.5mm layers to individual 20 x 20cm glass plates and allowed to air dry. Aliquots of an acetone solution of ^{14}C-Aspon (41 ug in 10 uL) were applied to the origins of triplicate plates of each soil type.

"Aged" Aspon extract (9.1 ug in 60 uL) (apparently from each of the four soils) was applied to two sets of plates and ^{14}C-2,4-D (38 ug in 10 uL acetone) was applied to the third set of plates.

When the plates were air dry they were placed in TLC tanks with distilled H_2O until movement had proceeded 12 cm or until 6-hrs had elapsed.

After removal of the plates from the TLC tank they were allowed to air dry for a short period. They were then wrapped in plastic film and "autoradiographed" against Kodak SB-5 film. Movement of the chemicals was recovered as Rf values: Top of origin spot to top of leading edge of the mobile compound divided by the value of a similar measurement to the water front. By scraping 1cm sections of soil from one of the triplicate plates of each soil and analyzing by combustion the percent distribution of the chemical in the chromatographic zone was calculated.

Adsorption Determinations. To 2.5g soil in a 30ml screw cap centrifuge tube was added 10 ml of a stock solution containing Aspon. After sealing with a cap this tube was agitated for 45-90 minutes in the laboratory at 20-21°C. Following agitation the tubes were centrifuged for 10 min @ 3000 rpm (800xg) and triplicate aliquots of the supernatant were assayed by LSC. Controls, tubes with solution but no soil, and tubes with soil and distilled H_2O but without Aspon, were run to determine how much Aspon was adsorbed on/by the glass.

Data were recorded as follows:

C = Concentration of ^{14}C-Aspon in aqueous stock solution (ug/ml)

Co = Concentration in blank solutions (no soil) after equilibration for 45 min. @ 20°C (ug/ml)

Cw = Solution concentration after equilibration with soil 45 min. @ 20°C (ug/ml)

Cs = Soil concentration following equilibration for 45 min. @ 20°C (ug/g)

Adsorption coefficients Ka for Aspon were determined from the Freundlich equation as follows:

(1) $C_s = KC_w^{1/n}$

(2) $\log C_s = \log K + 1/n \log Cw$

where K = adsorption coefficient

n = constant

Cw was measured directly by assaying the solution after equilibration. C_s was calculated from

(3) $C_s = \frac{(Co - Cw)}{m} V$

where, Co = see above

V = Total volume of solution (ml)

m = mass of soil in grams

Least-squares linear regression analysis was performed on the data using equation (2) previously mentioned.

Desorption Determinations.

Stock solutions of ^{14}C-Aspon in ether were prepared at CA 20, 2.0, and 0.2 ppm, and 1-ml aliquots were applied to 2.5g soil in centrifuge tubes as described under adsorption. The ether was evaporated in vacuo, 10 ml dist. H_2O was added, and the tubes were agitated on a wrist-action shaker for 60 min. The tubes were then centrifuged and contents assayed by LSC as previously described. Controls included untreated solution/soil mixtures used for LSC background measurements and treated solutions without soil to determined amounts not desorbed from glass.

Desorption, Kd values, were calculated from C, Co, C_w and C_s as described for adsorption and $C_s = KC_w^{1/n}$ ($\log C_s = \log K + 1/n \log C_w$).

Following adsorption and desorption runs the supernatants were extracted with ether and the soils with acetone followed by ether. After drying over anhydrous sodium sulfate and concentrated on a RVE the extracts were analyzed by TLC.

Similarly, plates from Keeton and Sorrento soils were extracted and aliquots subjected to LSC analysis for ^{14}C; extracted soils were combusted to account for unextractable ^{14}C. From these results the purity of the Aspon on soil thin-layer plates was ascertained.

RESULTS

The extract of the 28-day "soil aged" (Sorrento loam) Aspon reportedly contained 75% of the originally applied ^{14}C and 87% of the soil bound residue (13% bound ^{14}C). The extract consisted of 90.8% Aspon, 5.1% of an unknown [redacted] 2.3% ^{14}C at the origin on a 2-D TLC plate, and 1.8% other non-polar compounds. Note: Just what this means in terms of adsorption/desorption/mobility was not explained. It appears that Aspon would be expected to metabolize slowly in Sorrento loam and under the test conditions. See "metabolites" in the Materials and Methods section of this report.

Information which may reveal the manufacturing process is not included

To assure that the observed results in the adsorption/desorption studies were representative of Aspon rather than of an impurity or a degradate certain confirmation tests were made:

a. In the preparation of stock solutions Aspon was equilibrated with water in the absence of an organic solvent to eliminate inconsistencies arising when a aliquot of ^{14}C-Aspon in ether was added to water.

b. Equilibration of Aspon solutions was limited to 45-60 minutes to reduce the adsorption of the pesticide to glass.

c. Stock solutions were prepared daily because of the general instability of Aspon in water even at refrigerator temperatures. Solutions were shown to be stable for at least 24 hours, a period in excess of the equilibration times.

d. Ether extractions (>90% ^{14}C removed from soil and water samples) followed by TLC analyses of extracts confirmed the stability of Aspon in adsorption and desorption runs. Calculated values for ^{14}C-Aspon adsorbed to the soil were confirmed by combustion analyses of the soils and by assays of ether soil extracts.

Adsorption coefficient (Ka) values for Aspon in Keeton soil ranged from 32 to 61 with an average of 48 $\pm$ 12; for Sorrento soil the Ka values ranged from 53 to 61 with an average of 61 $\pm$ 8. Ka values varied widely due to the adsorption of Aspon on glass;

the amount of ^{14}C adsorbed to glass varied from 10-30% depending upon solution concentration (greated adsorption to glass with more dilute solutions). Ka correlation coefficients, determined from plotting the data using the Freundlich equation, exceeded 0.99, indicating excellent correlation over a range of concentrations from 0.01 to 1.0. It was proposed that some correlation existed between Ka and organic matter content and that:

$$K_{OC} = (Ka/\%OC) \times 100 = (Ka/ (\%OM/1.724)) \times 100$$

oc = organic carbon adsorption coefficient

K_{OC} for Keeton and Sorrento soils was reported to be 7500 and 6200, respectively, indicating a material with little soil mobility.

Desorption coefficient (Kd) values ranged from 36 to 75 with an average of 57 $\pm$ 26 for Keeton sandy loam and from 84 to 141 with an average of 109 $\pm$ 27 for Sorrento loam. Glass tubes retained a portion of the applied ^{14}C-Aspon, just as happened in the adsorption studies. All correlation coefficient values exceeded 0.99 indicating good correlation with the Freundlich isotherm. Moreover, the desorption Freundlich constants were all greater than the corresponding adsorption constants. It was judged that Aspon does not desorb as readily as it adsorbs (to the soils tested) and that the factors influencing desorption differ from those influencing adsorption.

Rf values for Aspon and its 28-day soil metabolites ranged from 0.0 $\pm$ 0 to 0.08 $\pm$ 0.08 on the soils tested placing them in EPA mobility class 1 for immobile compounds. By comparison, the Rf values for ^{14}C-2,4-D ranged from 0.74 to 0.90 for a mobility class 4. Combustion analyses of the chromatography zones of the TLC plates confirmed the Rf values reported. Moreover, confirmatory tests were made to assure that the results from the mobility studies truely reflected ^{14}C-Aspon and not a breakdown product or an impurity. The immobility of Aspon on soil thin layers corresponded with the large adsorption/desorption coefficients.

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DISCUSSION

1. Despite a grossly deficient report on research to fill data gaps on the registrant's pesticide it was concluded that the study(s) was/were valid. An exhorbitant amount of time and effort was required by this reviewer to rearrange, rewrite, and/or abstract the submitted report to avoid outright rejection. It would be in the registrant's interest to assure that technical reports clearly tell what was done, how it was done, and what the results were - step-by-step. In other words, to see that the technical report is as well presented as was the experiment performed. This message should be relayed to the registrant.

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DATA EVALUATION RECORD

CASE GS 079101 DISC 30 TOPIC 051015 GUIDELINE 40 CFR 161-2

CHEM ASPON

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No Fiche CONTENT CAT -- 01

Photolysis of Aspon in Water. Lee, R.E., de Guigne Technical Center. Report No. RRC 83-28. Unpublished. Submitted by Stauffer Chemical Company July 2, 1984, in support of Registration Standard.

SUBST. CLASS =

DIRECT RVW TIME = (MH) START-DATE END DATE

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SIGNATURE: Hudson L Boyd DATE: 9-7-8

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ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSION:

1. This study was not conducted in nor reported in a scientific manner and cannot be accepted as valid for the re-registration of Aspon.

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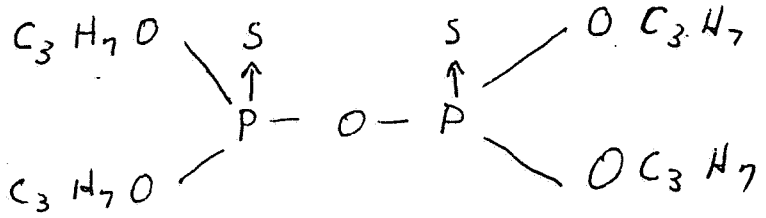
MATERIALS AND METHODS



O,O,O,O-Tetra-n-propyl dithiopyrophosphate = Aspon

Aspon, "analytical reference standard" of 97.0% purity, obtained from Stauffer Chemical Company was dissolved in methanol and added to millipore water (supposedly sterile water) to prepare a stock solution (concentration not stated).

Unspecified volumes of the stock solution were transferred to two bottles and kept as dark controls.

Apparently some quantity of the stock solution was exposed to artificial sunlight although the description is too vague to be sure. Aliquots of "the photolysis solution" and of solutions from dark controls were taken at "various times", extracted with toluene, dried over Na_2SO_4 and analyzed on an "NP-GC (HP5880A)" whatever that is.

RESULTS

It is stated under "Results and Discussion" rather than "Methods" that a concentration of 0.04 ppm was chosen for this study. Judging from data submitted it appears that Aspon was subject to photolysis (time not specified) but it is impossible to state factually to what degree. For instance, although a concentration

of 0.04 ppm was used, the concentration at Day 0 was only 0.022 ppm.

DISCUSSION

1. The experiment was not reported in a scientific manner and lacks evidence of having been conducted scientifically. Consequently any work performed or reported is unacceptable for the reregistration of Aspon.

DATA EVALUATION RECORD

CASE GS 079101 DISC 30 TOPIC 050530 GUIDELINE 40 CFR 164-1

CHEM Aspon

BRANCH EAB

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No Fiche CONTENT CAT.: ?

Dissipation study - soil & turf. Stauffer Chemical Co., Residue Report FSDS No. A-13592 Project No. I-24-DRS-TI A-13592-0 thru -7.

SUBST. CLASS =

DIRECT RVW TIME = (MH) START-DATE END DATE

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CONCLUSION:

1. The data from this project cannot be evaluated because of the lack of protocols. The report consists of a lot of numbers without any description of how the study was conducted, how the samples were analyzed, what controls were used, or any other information incumbent upon any scientist preparing a technical report intended to inform his audience.