4-21-89

DATA EVALUATION RECORD

DPX-L5300 STUDY 4

SHAUGHNESSY No. 128887
COMMON NAME: DPX-L5300
CHEMICAL NAME: Methyl 2-[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) methylamino] carbonyl] amino] sulfonyl] benzoate
FORMULATION: Active ingredient
DATA REQUIREMENT: Aerobic Soil Metabolism (162-1)

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(1) FICHE/MASTER ID 40245522
Rapisarda, C. and M.T. Scott. 1985. Aerobic soil metabolism of [triazine2-^{14}C]DPX-L5300. Laboratory Project ID: AMR-360-85. Prepared and submitted by E.I. du Pont de Nemours and Company, Wilmington, DE. No. 7F3540.

(2) FICHE/MASTER ID 40927204
M.T. Scott. 1988. Supplement to: Aerobic soil metabolism of [triazine-2-^{14}C] DPX-L5300. Laboratory Project ID: AMR-360-85. Prepared and submitted by E.I. du Pont de Nemours and Company, Wilmington, Delaware.

SUBST. CLASS = S

DIRECT RVW TIME = 8

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CONCLUSIONS:

Metabolism - Aerobic Soil

(1) This study is acceptable and partially fulfills the aerobic soil metabolism (162-1) data requirement by providing information on the aerobic metabolism of triazine-labeled [^{14}C]DPX-L5300 in two silt loam soils. The information on the aerobic soil metabolism of the phenyl portion of the molecule which is included in the supplement is inadequate and must be expanded for the aerobic soil metabolism (162-1) data requirement to be completely satisfied.

(2) The aerobic soil metabolism of the phenyl portion of DPX-L5300 was not followed in this study. Based upon the results of aerobic soil metabolism studies on DPX-T6376, and on the results of a field dissipation study on DPX-L5300, phenyl moiety degradates are expected to be methyl 2-(aminosulfonyl) benzoate, 2-(aminosulfonyl)benzoic acid, and saccharin (Figures 2 and 3 of Supplement No. 1). However, the information included in the supplement on the aerobic soil metabolism of the phenyl portion of the molecule is inadequate because only the degradative pathway was provided. Information on the kinetics of the degradation of the phenyl containing degradates (eg., the concentrations of methyl 2-(aminosulfonyl) benzoate, methyl 2-(aminosulfonyl) benzoic acid, and saccharin after various incubation times) should have also been included along with a discussion of the data. The registrant should submit a new supplement which includes all pertinent information on the aerobic soil metabolism of methyl 2-(aminosulfonyl) benzoate.

(3) Triazine labeled [^{14}C]DPX-L5300 incubated in the dark at 25°C at an initial concentration of 60 ppb degraded with half-lives of less than 3 days in non-sterile Keyport silt loam soil (pH 4.3, organic matter 4.7%) and less than 12 days in non-sterile Gardena silt loam soil (pH 7.5, organic matter 5.4%). The difference between the degradative half-lives in the two test soils appears to be at least partially due to the pH dependence of the hydrolysis rate. The major triazine moiety degradate in both soils was triazine amine at all incubation times up to 365 days (Figure 3 of Supplement No. 1). Triazine amine was very persistent in the Keyport silt loam reaching a maximum of 91.1% of applied after 14 days incubation and then remaining at relatively constant levels fluctuating between 83.5% and 90.3% of applied for the duration of the 365 day study (Table 7). Triazine amine levels continually increased in the Garden silt loam from 14.3% of applied at day 0 to 71.4% of applied after 365 days (Table 9). The triazine moiety degradates slowly degrade to $^{14}CO_2$ which represented 6.1% and 16.7% of applied after 365 days in the Keyport silt loam and Gardena silt loam, respectively.

(4) The proposed degradative pathway of DPX-L5300 in soil under aerobic conditions is presented in Figure 7. DPX-L5300 appears to undergo hydrolysis of the sulfonyl-urea bridge to form methyl 2-(aminosulfonyl) benzoate (ester sulfonamide) and triazine amine.

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The ester sulfonamide can undergo hydrolysis to form methyl 2-(aminosulfonyl) benzoic acid (acid sulfonamide) or ring closure to form saccharin. The acid sulfonamide can also undergo ring closure to form saccharin. An equilibrium between saccharin and the acid sulfonamide may sometimes be established due to the ability of saccharin to undergo ring opening to reform the acid sulfonamide. Triazine amine undergoes demethylization to form N-demethyl triazine amine and O-demethyl triamine.

SUMMARY OF DATA BY REVIEWER:

Triazine-labeled [^{14}C]DPX-L5300 (radiochemical purity 99%, specific activity 41.2 uCi/mg), at 60 ppb (70 g a.i./ha), degraded with half-lives of < 3 days in nonsterile Keyport silt loam soil (pH 4.3) and < 12 days in nonsterile Gardena silt loam soil (pH 7.5), both adjusted to 70% of moisture capacity and incubated at 25°C in the dark. At 365 days posttreatment, [^{14}C]DPX-L5300 was 0.3-1.6% of the applied in both soils (Tables 7 and 9). The major triazine labeled degradate in both soils was triazine amine (formed via a hydrolytic pathway), which comprised 79.5%-91.1% of the applied in the Keyport silt loam soil between days 1 and 365 (maximum at day 14) and which increased from 14.3 to 71.4% of the applied in the Gardena silt loam soil between days 0 and 365. Other degradates included O-demethyl triazine amine (maximum 7.6% of the applied, formed from O-demethyl DPX-L5300 or from triazine amine directly), N-demethyl triazine amine (maximum 7.8% of the applied, formed from triazine amine), and one unknown (maximum 7.6% of the applied). At 365 days posttreatment, 5.4-8.1% of the applied radioactivity was unextractable, and a total of 6.1% from the Keyport soil and 16.8% from the Gardena soil was volatilized as $^{14}CO_2$. The material balance in both soils ranged from 99.3 to 101.5% of the applied. In sterilized soils, DPX-L5300 declined from 11.9% of the applied at 1 day posttreatment to 5.7% of the applied at 5 days posttreatment in the Keyport silt loam soil, and from 48.3% of the applied at 1 day posttreatment to 19% of the applied at 14 days posttreatment in the Gardena silt loam soil.

Based upon the aerobic soil metabolism of phenyl labeled [^{14}C]DPX-T6376 (Figure 2 of Supplement No.1) and upon the field dissipation of phenyl and triazine labeled [^{14}C]DPX-L5300 (Figure 3 of Supplement No. 1), the phenyl moiety degradates of the aerobic soil metabolism of DPX-5300 are expected to be methyl 2-(aminosulfonyl)benzoate, 2-(aminosulfonyl)benzoic acid, and saccharin. Information on the relative levels of the phenyl moiety degradates after various incubation times were not included in the supplement.

DISCUSSION:

(1) No data were provided in the study on the aerobic metabolism of phenyl-labeled [^{14}C]DPX-L5300. In the addendum, the registrant contends that such data is unnecessary because previously submitted data on the aerobic soil metabolism of phenyl labeled [^{14}C]DPX-T6376 and phenyl labeled [^{14}C]DPX-5648 are sufficient to

determine the fate of the phenyl portion of the DPX-L5300 molecule for the following reasons:

(a) The initial step in the aerobic soil metabolism of DPX-T6376, DPX-5648, and DPX-5300 is the hydrolytic cleavage of the sulfonyl-urea bridge which results in different triazine fragments, but the same phenyl fragment [methyl 2-(aminosulfonyl) benzoate] (see Figures 2 and 3 of Supplement No. 1)

(b) The aerobic soil metabolism of the phenyl fragment in Keyport silt loam (one of the soils used in the DPX-L5300 study) was determined in the previously submitted aerobic soil metabolism studies on DPX-T6376 and DPX-5648.

EFGWB may be able to concur with the registrant because the DPX-T6376 study was previously judged to be acceptable. (The DPX-5648 study has not as yet been reviewed). However, the information included in the supplement on the aerobic soil metabolism of methyl 2-(aminosulfonyl) benzoate is inadequate because only the degradative pathway was provided. Information on the kinetics of the degradation of the phenyl moiety containing degradates (eg., the concentrations of methyl 2-(aminosulfonyl)benzoate, methyl 2-(aminosulfonyl) benzoic acid, and saccharin after various incubation times) should have also been included in the supplement along with a discussion of the data. The registrant should submit a new supplement which includes all pertinent information on the aerobic soil metabolism of methyl 2-(aminosulfonyl) benzoate.

(2) The registrant attributes the more rapid degradation of DPX L5300 in the Keyport silt loam soil to the fact that the pH is much lower than that of the Gardena silt loam soil (pH 4.3 vs. pH 7.5). A previous hydrolysis study indicated that DPX-L5300 degraded more rapidly in acid solutions.

(3) Assuming single slope first-order reaction kinetics over the entire decline curve, the registrant determined that the half-lives for triazine-labeled [^{14}C]DPX-L5300 were 3 days in the Keyport silt loam soil and 12 days in the Gardena silt loam soil. These values are obviously too high since at day 1, only 15.8% of the applied DPX-L5300 remained undegraded in the Keyport soil (compared to 86% at time 0) and only 53.7% remained undegraded in the Gardena soil (compared to 85.1% at time 0). As is the case for most pesticides in soil, the degradation of DPX-L5300 appears to follow second-order or other non-first-order kinetics rather than first-order kinetics. In such cases, the "goodness-of-fit" to first-order kinetics can often be improved by dividing the decline curve into 2 or more regions and fitting the data within each region to a separate first order equation. Unfortunately, that could not be done for either the Keyport silt loam or Gardena silt loam data because only 2 samples were collected during the first day of each study (one at time 0 and the other at day 1). However, due to the rapid decline of DPX-L5300 during

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the first day of each study, the half-lives calculated from the entire decline curves overestimate the true half-lives. The above comments are still applicable because the registrant's response in the supplement to similar comments on the original study did not address the issues raised. However, despite the cited deficiencies, the data is adequate for the primary purpose of developing sampling and analysis protocols for the terrestrial field dissipation studies.

(4) Soil extracts and reference standards were chromatographed on separate TLC plates due to a lack of space on the plates. However, reference standards were spotted on the same type of TLC plates as soil extracts. In addition, reference standard and soil extract TLC plates were developed in the same TLC tank at the same time. Therefore, identification of soil extract fractions could be obtained by a comparison of R_f values to those of reference standards.

(5) Although the detection limit for DPX-L5300 and its degradates in soil was not specifically reported in the text, the registrant reported non-detectable values as "<0.1%" (of the applied). Since 0.1% of 60 ppb is 0.00006 ppm, this value was assumed to be the limit of detection for this study.

MATERIALS AND METHODS

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