DATA EVALUATION RECORD

STUDY 12

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STUDY ID 44505203
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CONCLUSIONS

Mobility - Leaching & Adsorption/Desorption

1. This study is scientifically valid ***(acceptable)*** and provides useful information on the soil mobility (batch equilibrium) of mesotrione (ZA1296) in four soils (two U.S. and two foreign). This study is one of a series of three batch equilibrium studies for parent mesotrione (this MRID and MRIDs 44373532 and 44505204). There is also a separate batch equilibrium submission for the transformation product MNBA (MRID 44505201), and another for the transformation product AMBA (MRID 44505202).

   In combination with other studies, EPA Subdivision N Guideline requirements for soil mobility (batch equilibrium) for parent and transformation products are ***satisfied***. However, the registrant should carefully consider the critical elements in the Comments section of this report, as these may affect the validity and consequent acceptability of future study submissions.

2. Sorption of mesotrione to the four tested soils was low. [Because of some possible instability of parent compound (even though soils were sterilized), ostensible results for parent actually may be for parent plus transformation products (Comment 4).]

   The mobility of nonradiolabeled (1.0 and 2.0 µg/mL rates only) plus uniformly phenyl ring-labeled [^{14}C]mesotrione, at nominal concentrations of 0.05, 0.1, 0.2, 1.0, and 2.0 mg/mL, was determined in silt loam (from Wisconsin), sandy loam (from North Carolina), French loam, and British clay loam soil:solution slurries (1:2, w:v) that were equilibrated for 16 hours at **20 ± 2°C**. **Freundlich K_{ads} values** were **0.33** for the sandy loam (1.0% o. m.), **0.16** for the loam (1.5% o. m.), **0.61** for the silt loam (2.2% o. m.), and **0.97** for the clay loam (5.7% o. m.); corresponding **Freundlich K_{oc} values for sorption were 58, 19, 48, and 29 mL/g**. Respective 1/N values were 0.95, 0.95, 0.95, and 0.93 for adsorption. K_{des} values were determined from separate samples than those used to determine K_{ads} values. **Freundlich K_{des} values** determined following a 19-hour equilibration period were **0.74** for the sandy loam, **0.28** for the loam, **0.78** for the silt loam, and **1.7** for the clay loam soil; corresponding **K_{oc} values for desorption were 130, 33, 61, and 50 mL/g**. However, the K_{ads} and K_{des} values may not be comparable because separate test systems were utilized for the adsorption and desorption phase of the study. The 1/N values were not reported for the desorption phase. The reviewer-calculated coefficients of determination (r^2) for the relationships K_{ads} *vs.* organic matter content, K_{ads} *vs.* pH, and K_{ads} *vs.* clay content (%) were 0.83, 0.05, and 0.52 respectively.

METHODOLOGY

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Based on the results of a preliminary study for the adsorption of uniformly phenyl ring-labeled [^{14}C]mesotrione {2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione; radiochemical purity >96%, specific activity 1.12 GBq/mmol; pp. 14, 15} to silt loam soil (collected from Wisconsin), an equilibration period of 16 hours was chosen for all soils (Appendix 1, Table 8, p. 31). In the preliminary study, aliquots of 0.01 M $CaCl_2$ solution treated with uniformly phenyl ring-labeled [^{14}C]mesotrione were utilized to determine the stability of the parent and adsorption to the Teflon centrifuge tubes; degradation of the test compound was not observed through 16 hours of equilibration (Appendix 1, p. 30), and data for the adsorption of the test compound to the Teflon centrifuge tubes were not reported.

For the adsorption phase of the definitive study, subsamples (10 g) of sieved (2 mm), air-dried, sterilized (gamma irradiation) sandy loam (from North Carolina), French loam, silt loam (from Wisconsin), and British clay loam soils (Table 1, p. 12) were placed into Teflon® centrifuge tubes and equilibrated (prior to treatment) overnight by shaking with autoclaved 0.01 M $CaCl_2$ solution (19 mL) at 20 ± 2°C (p. 11). Aliquots (1 mL) of 0.01 M $CaCl_2$ solution treated with nonradiolabeled (1.0 and 2.0 µg/mL rates) plus uniformly phenyl ring-labeled [^{14}C]mesotrione (dissolved in acetonitrile) at nominal concentrations of 0.05, 0.1, 0.2, 1.0, and 2.0 µg/mL were added to the soil:solution slurries (pp. 14, 15). Duplicate tubes were prepared for each soil type/treatment rate combination; additional tubes containing untreated 0.01 M $CaCl_2$ solution and soil, and 0.01 M $CaCl_2$ solution without soil were prepared as controls. The soil:solution slurries (1:2, w:v) were equilibrated by shaking for 16 hours at **20 ± 2°C**; light conditions were not reported. Following the adsorption equilibration period, soil:solution slurries were centrifuged and triplicate aliquots of the adsorption supernatant were analyzed for total radioactivity by LSC (p. 19); the limit of detection was not reported. Samples were stored frozen (duration not reported) at -20 ± 5°C until further analysis (p. 16).

For the desorption phase of the definitive study, samples were prepared, equilibrated, treated, re-equilibrated, and centrifuged as in the adsorption phase (p. 19); aliquots of the supernatants were analyzed by LSC. A volume of pesticide-free 0.01 M $CaCl_2$ solution equivalent to the volume decanted following adsorption was added to the soil. Tubes containing the soil:solution slurries were equilibrated for 19 hours at **20 ± 2°C**. Following equilibration, soil:solution slurries were centrifuged, decanted, and analyzed for total radioactivity by LSC. Samples were stored frozen (duration not reported) at -20 ± 5°C until further analysis.

To determine compound stability (in solution) during the adsorption and desorption phases, selected supernatants from frozen samples were thawed and evaporated to dryness by compressed air (p. 17). Samples were re-suspended in acetonitrile and analyzed by TLC on Sorbsil-C_{30} plates which were developed with chloroform:methanol:ammonia (25% by weight; 69:27:4, v:v:v; p. 20). Samples were co-chromatographed with nonradiolabeled and radiolabeled reference standards. Radioactive areas on the TLC plates were detected by radioimage scanning; the method of visualization for the nonradiolabeled reference standards was not reported.

To determine compound stability (in soil) during the adsorption and desorption phases, selected samples of frozen adsorbed and desorbed soil were extracted three times by shaking with methanol:water plus 0.5% HCl (9:1, v:v; p. 17). Samples were centrifuged and the supernatants were combined and diluted with methanol. The extract was partitioned into dichloromethane, concentrated under compressed air, and analyzed by TLC as described previously for the supernatants.

Triplicate subsamples of the post-extracted soil from both the adsorption and desorption phases were dried and analyzed for total radioactivity by LSC following combustion; data were corrected for combustion efficiencies (pp. 19, 20).

DATA SUMMARY

The mobility of nonradiolabeled (1.0 and 2.0 μg/mL rates only) plus uniformly phenyl ring-labeled [^{14}C]mesotrione (radiochemical purity >96%), at nominal concentrations of 0.05, 0.1, 0.2, 1.0, and 2.0 mg/mL, was determined in silt loam (from Wisconsin), sandy loam (from North Carolina), French loam, and British clay loam soil:solution slurries (1:2, w:v) that were equilibrated for 16 hours at 20 ± 2°C. Freundlich K_{ads} values were 0.33 for the sandy loam (1.0% o.m.), 0.16 for the loam (1.5% o. m.), 0.61 for the silt loam (2.2% o. m.), and 0.97 for the clay loam (5.7% o.m.) (Table 5, p. 25); corresponding K_{oc} values were 58, 19, 48, and 29 mL/g. Respective 1/N values were 0.95, 0.95, 0.95, and 0.93 for adsorption (Table 6, p. 25). K_{des} values were determined from separate samples than those used to determine K_{ads} values. Freundlich K_{des} values determined following a 19-hour equilibration period were 0.74 for the sandy loam, 0.28 for the loam, 0.78 for the silt loam, and 1.7 for the clay loam (Table 7, p. 26); corresponding K_{oc} values were 130, 33, 61, and 50 mL/g. The 1/N values were not reported for the desorption phase. The reviewer-calculated coefficients of determination (r^2) for the relationships K_{ads} *vs.* organic matter content, K_{ads} *vs.* pH, and K_{ads} *vs.* clay content (%) were 0.83, 0.05, and 0.52 respectively.

During the 16-hour adsorption equilibration period, 14-16% of the applied radioactivity was adsorbed to the sandy loam soil (across all application levels), 6.0-9.7% of the applied was adsorbed to the loam soil, 23-26% was adsorbed to the silt loam soil, and 33-39% was adsorbed to the clay loam soil (Table 5, p. 25). Data indicating the percentages of the applied radioactivity desorbed from the four soils were not provided; raw data were reported in Appendix 4 (Table 12, p. 42).

The stability of uniformly phenyl ring-labeled [^{14}C]mesotrione was confirmed by analysis of supernatants and soil extracts (adsorption and desorption) by TLC (p. 22); data were reported in Appendix 5 (Tables 13, 14; pp. 48, 49; see Comment #4).

Material balances (based on LSC analysis for individual replicates across all application rates) following the adsorption and desorption phases were 94.6-103% for the loam soil (Appendix 2, Table 9, p. 34; see Comment #3). Material balances (for individual replicates at the 0.2 μg/mL application rate) were 95-104%, 95.4-98.1%, and 91.5-93.3% for the sandy loam, silt loam, and clay loam soils, respectively (Appendix 2, Table 10, p. 35).

COMMENTS

1. Desorption of the test compound was not studied using the same test samples from the adsorption phase of the study. Separate samples were prepared, equilibrated with 0.01 M $CaCl_2$ solution, treated with [^{14}C]mesotrione, and re-equilibrated prior to the desorption phase of the definitive study. Generally, a batch equilibrium study requires that adsorption and desorption data be determined from the same soil:water systems.

2. Soils were sterilized with gamma irradiation prior to use in order to inhibit microbial degradation of the compound (p. 11). However, the batch equilibrium study did not include data for reference chemicals of known mobility, as required by Subdivision N Guidelines. Sterilized soils may have significantly altered physical and chemical properties, which may affect the adsorption of pesticides by the soils.

3. Material balances were calculated separately for adsorption and desorption samples because separate samples were prepared and treated with [^{14}C]mesotrione for each phase; the reviewer reported material balances as an overall range for the adsorption and desorption samples. Additionally, material balances were not reported across all application rates for the sandy loam, silt loam, and clay loam soils (Appendix 2, Table 10, p. 35); material balances were only reported for soil:solution slurries treated with [^{14}C]mesotrione at a nominal concentration of 0.2 μg/mL. It is necessary that complete material balances be reported to allow the reviewer to account for all residues throughout the study and to aid in determining the validity of the study.

4. The stability of the test compound was questionable in the $CaCl_2$ solution and the soil extracts from the adsorption and desorption equilibration periods. For the sandy loam soil, 71.4-84.4% and 83.6-90.6% of the radioactivity present in the $CaCl_2$ solution and the soil extracts, respectively, was present as parent (Appendix 5, Tables 13, 14; pp. 48, 49); respective recoveries of the parent from the $CaCl_2$ solution and the soil extracts were 74.4-93.3% and 86.1-94.8% for the loam soil, 68-83.9% and 90.1-91.5% for the silt loam soil, and 86.1-88.7% and 90.2-94.5% for the clay loam soil. Adsorption and desorption

coefficients were calculated assuming all radioactivity present in the $CaCl_2$ solution and the soil extracts was present as parent (p. 22).

5. The study authors did not indicate whether the preliminary and definitive studies were conducted in darkness.

6. The equilibration period may have been too short for the sandy loam and loam soils; 14-16% of the applied radioactivity was adsorbed to the sandy loam soil and 6.0-9.7% of the applied was adsorbed to the loam soil following the 16-hour equilibration period (Table 5, p. 25). An adsorption of 20-80% is necessary for the valid use of the Freundlich equation. The equilibration period for all soils was determined based on the results of a preliminary study for the adsorption of uniformly phenyl ring-labeled [^{14}C]mesotrione to silt loam soil collected from Wisconsin (pp. 30, 31). The equilibration period for each soil should be determined separately, based on preliminary studies conducted using each soil utilized in the definitive study.

7. The study was conducted with two domestic (U.S.) and two foreign (U.K. and France) soils. The EPA prefers that domestic soils be used in mobility studies. However, the EPA will accept foreign soils for two of the four required soils if the soils are characterized according to the USDA system. The soils were characterized using the USDA classification system (Table 2, p. 13); however, the reviewer noted that the study authors inadvertently referred to micrometers as millimeters.

8. The study authors stated that "Kd values tended to increase more in those soils in which initial adsorption had been least" (p. 24), and that "the data therefore suggest that adsorption of ZA1296 [mesotrione] is not entirely reversible, resulting in a reduction in the potential mobility of the compound." The initial Kd values were lowest for the French loam (0.18) and sandy loam (0.35) soils (Table 5, p. 25); following desorption, Kd values increased 76% and 100%, respectively (Table 7, p. 26). The reviewer noted that the initial Kd value was highest for the British clay loam soil (1.1) and increased 68% following desorption.

9. The study authors stated that mesotrione shows a greater affinity for adsorption to soil organic matter as the pH is reduced (p. 9); however, the study authors also stated "that a larger data base would be needed to confirm this conclusion" (p. 23). The greatest adsorption was observed in the high organic matter clay loam soil; however, the study authors stated that "when the organic matter remains at a similar level i.e. 'Garonne' soil and 'Wisconsin' soil the adsorption is greater in the soil with a lower pH" (pp. 8, 9). The reviewer-calculated coefficients of determination (r^2) for the relationships K_{ads} *vs.* organic matter content and K_{ads} *vs.* pH were 0.83 and 0.05 respectively. The coefficient of determination (r^2) for the relationship K_{ads} *vs.* pH was negatively affected by the strong relationship between K_{ads} and organic matter; the greatest adsorption was observed in the high organic matter (5.7%) clay loam soil despite an elevated pH (7.1). The study authors

stated that as the pH is reduced, the test compound "becomes more associated and lypophilic in nature" and shows a greater affinity for adsorption to soil organic matter (p. 9); the pKa of mesotrione is 3.1. The reviewer notes that the reviewer-calculated coefficient of determination (r^2) values for the relationships K_d *vs.* organic matter and K_d *vs.* pH were 0.12 and 0.43, respectively, in a supplemental batch equilibrium study of mesotrione in 13 soils (MRID 44505204).

10. Method detection limits and limits of quantitation were not reported. Both method detection limits and limits of quantitation should be reported to allow the reviewer to evaluate the adequacy of the method.

11. The study authors reported the Freundlich adsorption (K_{ads}) and desorption (K_{des}) coefficient values as K_F in the study (Tables 5, 7; pp. 25, 26). In addition, K_{oc} values were reported as K_{Foc} in the study.

12. The reviewer confirmed that the silt loam soil (from Wisconsin) utilized in this study was the same type of soil used in two submitted aerobic soil metabolism studies (MRIDs 44505130 and 44373531).

13. The soil series names were not reported. Instead, the soils were referred to by their geographic locations or descriptions of their location (Table 1, p. 12). Soils were referred to as 'ERTC' (sandy loam soil from North Carolina), 'Garonne' (French loam soil), 'Wisconsin' (silt loam soil from Wisconsin), and 'Picket Piece' (British clay loam soil) throughout the study.

14. The solubility of mesotrione in water or in the test solution was not reported.

15. The study authors inadvertently labeled Table 9 "Synopsis of Mass Balance Results from the Adsorption/Desorption Samples for 'Toulouse' Soil" (p. 34). Toulouse soil was not used in this study; the reviewer assumed that the study author was referring to the French loam soil ('Garonne') because data for the remaining three soils were reported in Table 10 (Appendix 2, p. 35).

16. The study authors inadvertently stated that the results from the TLC analysis were reported in Appendix 3 (p. 22); results from the TLC analysis were provided in Appendix 5 (p. 43).

MRID 44505203

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