

US EPA ARCHIVE DOCUMENT

CONCLUSIONS

Mobility - Leaching & Adsorption/Desorption

1. This study is scientifically valid and provides useful information on the soil mobility (batch equilibrium) of difenoconazole in eight soils. However, in the one study (MRID 42245136), the material balances for many of the replicates were outside of the acceptable range of 90-110%, and were determined only after the adsorption phase of the experiment; material balances following desorption were not determined. In the other study (MRID 42245135), it was not confirmed that the parent was stable in the test system; therefore, it was not adequately demonstrated that the observed desorption was due solely to adsorption of the parent compound.

2. This study does not meet Subdivision N Guidelines for the fulfillment of EPA data requirements on mobility (batch equilibrium) in the soil for the following reasons:
 - (i) material balances were not within the acceptable range of 90-110% of the applied radioactivity (MRIDs 42245135 and 42245136);
 - (ii) autoclaved sterilized soils were used, but data for reference chemicals of known mobility were not included (MRID 42245136) and;
 - (iii) parent compound stability during the study was not confirmed (MRID 42245135).

3. Triazole ring-labeled [3,5-¹⁴C]difenoconazole (MRID 42245135), at nominal concentrations of 0.1, 0.2, 0.4, 0.7, and 1.0 ppm, was studied in sand, sandy loam, silt loam, and silty clay loam soil:solution slurries that were equilibrated for 24 hours in darkness at 25 ± 0.0°C. Freundlich K_{ads} values were 12.8 for the sand soil (0.62% o.m.), 63.0 for the sandy loam soil (3.4% o.m.), 54.8 for the silt loam soil, and 47.2 for the silty clay loam soil; corresponding K_{oc} values were 3867, 3518, 3471, and 7734 mL/g. Respective 1/N values (reviewer-calculated) were 0.74, 0.76, 0.85, and 0.91 for adsorption. Freundlich K_{des} values determined following a 24-hour equilibration period were 18.6 for the sand soil, 95.2 for the sandy loam soil, 57.2 for the silt loam soil, and 71.4 for the silty clay loam soil; corresponding K_{oc} values were 5624, 5320, 3620, and 11700 mL/g. Respective 1/N values (reviewer-calculated) were 0.75, 0.80, 0.76, and 0.93 for desorption. The reviewer-calculated coefficients of determination (r^2) for the relationships K_{ads} vs. organic matter, K_{ads} vs. pH, and K_{ads} vs. clay content were 0.74, 0.18, and 0.21, respectively.

Triazole ring-labeled [3,5-¹⁴C]difenoconazole (MRID 42245136), at nominal concentrations of 0.02, 0.05, 0.1, 0.5 and 1.0 µg/mL, was studied in autoclave sterilized clay, sand, silt loam, and sandy loam soil:solution slurries that were equilibrated for 8 hours at 25 ± 1°C. Freundlich K_{ads} values were 97.9 for the clay soil (4.8% o.m.), 2.1 for

the sand soil (0.9% o.m.), 35.0 for the silt loam soil, and 11.5 for the sandy loam soil; corresponding K_{oc} values were 3466, 400, 5663, and 1956 mL/g. Respective $1/N$ values (reviewer-calculated) were 0.89, 0.80, 0.88, and 0.94 for adsorption. Freundlich K_{des} values determined following a 8-hour equilibration period were 119.1 for the clay soil, 4.2 for the sand soil, 66.7 for the silt loam soil, and 17.3 for the sandy loam soil; corresponding K_{oc} values were 4217, 790, 10792, and 2939 mL/g. Respective $1/N$ values (reviewer-calculated) were 0.86, 0.85, 0.89, and 0.94 for desorption. The reviewer-calculated coefficients of determination (r^2) for the relationships K_{ads} vs. organic matter, K_{ads} vs. pH, and K_{ads} vs. clay content were 0.91, 0.36, and 0.93, respectively.

METHODOLOGY

MRID 42245135

Based on the results of a preliminary study of the adsorption of triazole ring-labeled [3,5- ^{14}C]difenoconazole {CGA-169374; chemical name not provided; radiochemical purity 97.2%, specific activity 27.4 $\mu Ci/mg$; Figure 1, p. 42} to sand, sandy loam, silt loam, and silty clay loam soils (Table I, p. 26), equilibration periods of 24 hours were chosen for both the adsorption and desorption phases (p. 16); data were not reported. Based on the results of a preliminary study, soil:solution ratios of 1:12 (w:v; sand soil) and 1:60 (w:v; sandy loam, silt loam, and silty clay loam soils) were chosen for the definitive study (reviewer-calculated; p. 16; Tables II-V, pp. 27-30). The adsorption of the test compound to glass was not studied. The stability of the test compound in the test system was not studied.

For the adsorption phase of the definitive study, aliquots (30 mL) of 0.01 M $CaCl_2$ solution treated with triazole ring-labeled [^{14}C]difenoconazole, at nominal concentrations of 0.1, 0.2, 0.4, 0.7, and 1.0 ppm, were added to Teflon[®] centrifuge tubes containing samples (2.5 g sand; 0.5 g sandy loam, silt loam, and silty clay loam) of air-dried, sieved (2 mm) Huntington sand, Huntington sandy loam, Armour silt loam, and Salvisa silty clay loam soils (pp. 15, 16). Duplicate samples were prepared for each soil type/treatment rate combination. The soil:solution slurries (1:12, w:v, sand soil; and 1:60, w:v, sandy loam, silt loam, and silty clay loam soils) were equilibrated by shaking for 24 hours in darkness at $25 \pm 0.0^\circ C$. Following the adsorption equilibration period, soil:solution slurries were centrifuged and the supernatants decanted. Triplicate aliquots of each supernatant were analyzed for total radioactivity by LSC; the limit of detection was twice the background (p. 17). Characterization of the recovered radioactivity to demonstrate the stability of the test compound in the soil:solution slurry was not performed.

For the desorption phase of the definitive study, an aliquot of pesticide-free 0.01 M $CaCl_2$ solution equivalent to the volume of supernatant decanted following adsorption was added to each of the soil pellets from the adsorption phase of the study (p. 17). The

soil:solution slurries were equilibrated by shaking for 24 hours in darkness at $25 \pm 0.0^\circ\text{C}$. Following equilibration, the soil:solution slurries were centrifuged and the supernatants were decanted. Triplicate aliquots of each supernatant were analyzed for total radioactivity by LSC. Characterization of the recovered radioactivity to demonstrate the stability of the test compound in the soil:solution slurry was not performed.

Following the desorption phase of the definitive study, post-extracted soil samples were air dried and analyzed for total radioactivity by LSC following combustion (p. 17).

MRID 42245136

In a preliminary study of the adsorption of triazole ring-labeled [3,5- ^{14}C]difenoconazole {CGA-169374; 1-(2-[4-(4-chlorophenoxy)-2-chlorophenyl-(4-methyl-1,3-dioxolan-2-yl)-methyl])-1H-1,2,4-triazole; radiochemical purity 99%, specific activity 49284 dpm/ μg ; p. 11; Figure 1, p. 28; Appendix C, p. 78} to autoclave sterilized clay, sand, silt loam, and sandy loam soils (Table 1, p. 18), equilibration periods of 8 hours were chosen for both the adsorption and desorption phases (p. 15; Table 2, p. 19). Based on the results of a preliminary study, soil:solution ratios of 1:5 (w:v; sand and sandy loam soils) and 1:100 (w:v; silt loam and clay soils) were chosen for the definitive study (p. 15; Table 3, p. 20). The adsorption of the test compound to glass was not studied. The stability of the test compound in the test system was not studied.

For the adsorption phase of the definitive study, aliquots (25 mL for sand and sandy loam soils; 50 mL for silt loam and clay soils) of 0.01 M calcium acetate solution treated with triazole ring-labeled [^{14}C]difenoconazole, at nominal concentrations of 0.02, 0.05, 0.1, 0.5 and 1.0 $\mu\text{g}/\text{mL}$, were added to glass centrifuge tubes containing samples (5 g for sand and sandy loam soils; 0.5 g for silt loam and clay soils) of autoclave sterilized, oven-dried clay, sand, silt loam, and sandy loam soils (pp. 10, 13). Duplicate samples were prepared for each soil type/treatment rate combination. The soil:solution slurries (1:5, w:v, sand and sandy loam soils; and 1:100, w:v; silt loam and clay soils) were equilibrated by shaking for 8 hours at $25 \pm 1^\circ\text{C}$ (light conditions not reported). Following the adsorption equilibration period, soil:solution slurries were centrifuged and the supernatants were decanted. Duplicate aliquots of each supernatant were analyzed for total radioactivity by LSC (p. 14); the limit of detection was not reported. Soils were analyzed for total radioactivity by LSC following combustion (p. 13; see Comment #4).

For the desorption phase of the definitive study, an aliquot of pesticide-free 0.01 M calcium acetate solution equivalent to the volume of supernatant decanted following adsorption was added to each of the soil pellets from the adsorption phase of the study (p. 13). The soil:solution slurries were equilibrated by shaking for 8 hours at $25 \pm 1^\circ\text{C}$ (light conditions not reported). Following equilibration, the soil:solution slurries were centrifuged and the supernatants decanted. Duplicate aliquots of each supernatant were analyzed for total radioactivity by LSC.

Following the desorption phase of the definitive study, post-extracted soil samples were analyzed for total radioactivity by LSC following combustion (p. 13).

Following both the adsorption and desorption phases of the definitive study, aliquots of selected samples (1.0 $\mu\text{g}/\text{mL}$ treatment) were analyzed by TLC (conditions were not reported; p. 16).

DATA SUMMARY

MRID 42245135

Triazole ring-labeled [3,5- ^{14}C]difenoconazole (radiochemical purity 97.2%), at nominal concentrations of 0.1, 0.2, 0.4, 0.7, and 1.0 ppm, was studied in sand, sandy loam, silt loam, and silty clay loam soil:solution slurries that were equilibrated for 24 hours in darkness at $25 \pm 0.0^\circ\text{C}$. Freundlich K_{ads} values were 12.8 for the sand soil (0.62% o.m.), 63.0 for the sandy loam soil (3.4% o.m.), 54.8 for the silt loam soil, and 47.2 for the silty clay loam soil (Tables XII-XVI, pp. 37-41; Figures 5-8, pp. 46-49); corresponding K_{oc} values were 3867, 3518, 3471, and 7734 mL/g. Respective 1/N values were 0.74, 0.76, 0.85, and 0.91 for adsorption (reviewer-calculated using data from Table XVI, p. 41). The reviewer-calculated coefficients of determination (r^2) for the relationships K_{ads} vs. organic matter, K_{ads} vs. pH, and K_{ads} vs. clay content were 0.74, 0.18, and 0.21, respectively. Freundlich K_{des} values determined following a 24-hour equilibration period were 18.6 for the sand soil, 95.2 for the sandy loam soil, 57.2 for the silt loam soil, and 71.4 for the silty clay loam soil (Tables XII-XVI, pp. 37-41); corresponding K_{oc} values were 5624, 5320, 3620, and 11700 mL/g. Respective 1/N values (reviewer-calculated) were 0.75, 0.80, 0.76, and 0.93 for desorption.

During the 24-hour equilibration period, $64.3 \pm 7.2\%$ of the applied radioactivity was adsorbed to the sand soil, $63.1 \pm 6.1\%$ of the applied was adsorbed to the sandy loam soil, $54.6 \pm 3.7\%$ of the applied was adsorbed to the silt loam soil, and $48.0 \pm 2.5\%$ of the applied was adsorbed to the silty clay loam soil (across all application levels; Table XI, p. 36). Following a single 24-hour desorption period, $24.0 \pm 5.6\%$, $26.8 \pm 3.8\%$, $36.9 \pm 5.0\%$, and $40.7 \pm 2.2\%$ of the previously adsorbed radioactivity was desorbed from the sand, sandy loam, silt loam, and silty clay loam soils, respectively.

The stability of the test compound in the soil:solution slurries following the adsorption and desorption phases was not determined; [^{14}C]residues were not characterized (see Comment #3).

Material balances (based on LSC analysis of individual replicates) across all application rates were 95.0-128.4% of the applied radioactivity (nominal basis) for the sand soil, 100.9-112.2% of the applied for the sandy loam soil, 95.2-107.2% for the silt loam soil,

and 92.0-110.6% of the applied for the silty clay loam soil (Tables VI-X, pp. 31-35; see Comment #1).

MRID 42245136

Triazole ring-labeled [3,5-¹⁴C]difenoconazole (radiochemical purity 99%), at nominal concentrations of 0.02, 0.05, 0.1, 0.5 and 1.0 $\mu\text{g/mL}$, was studied in autoclave sterilized clay, sand, silt loam, and sandy loam soil:solution slurries that were equilibrated for 8 hours at $25 \pm 1^\circ\text{C}$. Freundlich K_{ads} values were 97.9 for the clay soil (4.8% o.m.), 2.1 for the sand soil (0.9% o.m.), 35.0 for the silt loam soil, and 11.5 for the sandy loam soil (Table 9, p. 26; Figure 2, pp. 29-30); corresponding K_{oc} values were 3466, 400, 5663, and 1956 mL/g. Respective 1/N values (reviewer-calculated) were 0.89, 0.80, 0.88, and 0.94 for adsorption. The reviewer-calculated coefficients of determination (r^2) for the relationships K_{ads} vs. organic matter, K_{ads} vs. pH, and K_{ads} vs. clay content were 0.91, 0.36, and 0.93, respectively. Freundlich K_{des} values determined following a 8-hour equilibration period were 119.1 for the clay soil, 4.2 for the sand soil, 66.7 for the silt loam soil, and 17.3 for the sandy loam soil (Table 10, p. 27; Figure 3, pp. 31-32); corresponding K_{oc} values were 4217, 790, 10792, and 2939 mL/g. Respective 1/N values (reviewer-calculated) were 0.86, 0.85, 0.89, and 0.94 for desorption.

Data indicating the percentages of the applied radioactivity adsorbed to and desorbed from the four soils were not provided (raw data were reported in Tables 5-8, pp. 22-25).

Based on TLC analysis of selected samples (1.0 $\mu\text{g/mL}$) the parent compound was stable in the supernatants following adsorption and desorption (p. 16); tabular data were not provided.

Material balances (based on LSC analysis individual replicates) were 83.2-131.3% of the applied radioactivity for the sand soil, 86.4-92.9% for the sandy loam soil, 85.4-93.8% for the silt loam soil, and 89.3-98.3% for the clay soil (Appendix C, pp. 80, 84, 88, and 92; see Comments #1 and 4).

COMMENTS

1. In both studies, material balances were not within the acceptable range of 90-110% as required by Subdivision N Guidelines. In the one study, the material balances were greater than 110% of the applied radioactivity once in the sand (128.4%), once in the sandy loam (112.2%), and once in the silty clay loam (110.6%) soil:solution slurries (MRID 42245135, Tables VI-X, pp. 31-35). The reviewer notes that it is unlikely that the material balance problems in MRID 42245135 had a significant impact on the mobility determinations. However, in the other study, the material balances were greater than 110% of the applied radioactivity twice in the sand soil (131.3% and 114.4%)

soil:solution slurries (MRID 42245136, pp. 80, 84, 88, and 92). The material balances were less than 90% of the applied radioactivity five times (71.5-88.9%) in the sand, five times in the sandy loam (86.4-89.1%), seven times in the silt loam (85.4-89.3%), and once in the clay (89.3%) soil:solution slurries (MRID 42245136, pp. 80, 84, 88, and 92). The reviewer noted that the material balances obtained for the four soils in MRID 42245136 were determined using the supernatant and combusted soils following the adsorption period only (also see Comment #4). Additionally, in MRID 42245136, the study author reported using borosilicate glass tubes due to possible adsorption to the glass (p. 15); however, the reviewer notes that adsorption to glass was not tested in either of the preliminary or definitive studies.

2. In one of the studies (1988), test soils were sterilized in an autoclave at 121 °C and 15 psi for 60 minutes prior to use (MRID 42245136, p. 10). Sterilization techniques may alter the physical or chemical properties of the soil, which may affect the adsorption and desorption of pesticides. If the registrant chooses to sterilize the soils, then the batch equilibrium study must include reference chemicals of known mobility (*Pesticide Reregistration Rejection Rate Analysis*. 1993. U.S. EPA Document: EPA 738-R-93-010, p. 118). Data for reference chemicals of known mobility were not reported, and the study author did not address the issue of potential alteration of the soils due to sterilization. The reviewer noted that a published study examining the effects of sterilization techniques on soil properties indicated that autoclaving (two hours at 103.4 kPa and 121 °C) resulted in increased exchangeable Mn and decreased extractable Fe, thus changing the chemical properties in the soils ("Influence of Sterilization Methods on Selected Soil Microbiological, Physical, and Chemical Properties." 1989. D. C. Wolf, T. H. Dao, H. D. Scott, and T. L. Lavy. *Journal of Environmental Quality*, Volume 18, pp. 39-44).
3. In one of the studies (1991), it could not be determined whether the parent compound was stable following the adsorption and desorption phases of the definitive study (MRID 42245135). Radiolabeled [¹⁴C]residues in the adsorption and desorption soil:solution slurries were not characterized. The [¹⁴C]difenconazole in the acetonitrile dosing solution was analyzed by HPLC and determined to be stable following incubation (pp. 17, 23); however, this does not confirm the stability of the parent compound in the soil:solution slurries. Also, a hydrolysis study was not available for the reviewer to confirm hydrolytic stability. Clarification by the registrant is necessary.
4. In one of the studies (1988), it was stated in the protocol that following the adsorption phase of the study (MRID 42245136) subsamples of the soils were combusted to determine the actual amount of soil adsorbed (p. 35). However, in the methods section of the study, it is not clear whether subsamples were combusted and the remaining soil was used for desorption, or whether the whole sample was sacrificed and combusted and separate replicate samples were used for desorption (p. 13); a protocol deviation was not reported. This discrepancy makes it difficult for the reviewer to determine if the method

used was adequate to determine the desorption of the parent compound. Additionally, the recovered radioactivity from the combusted soils following adsorption were utilized for the calculation of the material balances rather than data obtained from combusting the soils following desorption (pp. 80, 84, 88, and 92); generally material balances are calculated following the desorption phase of the experiment. Also, the reviewer was unable to reproduce the calculations of the material balances reported on pages 80, 84, 88, and 92 using the raw data provided. Clarification by the registrant is necessary.

5. In one study, the $1/N$ values associated with adsorption were 0.74, 0.76 and 0.85 for the sand, sandy loam, and silt loam soils, respectively; corresponding $1/N$ values associated with desorption were 0.75, 0.80 and 0.76 (reviewer-calculated based on N values reported in Table XVI, p. 41; MRID 42245135). In the other study, the $1/N$ values associated with adsorption were 0.89, 0.80, and 0.88 for the clay, sand and silt loam soils, respectively; corresponding $1/N$ values associated with desorption were 0.86, 0.85, and 0.89 (reviewer-calculated bases on N values reported in Table 9, p. 26; MRID 42245136). If the $1/N$ value is not within the range of 0.9 to 1.1, then the Freundlich isotherm may not adequately or accurately represent the adsorption of the compound across all concentrations.
6. The reviewer noted that in one of the two studies (1988), the adsorption and desorption phases were conducted in a 0.01 M calcium acetate solution (MRID 42245136, p. 11); generally a 0.01 N or M CaCl_2 solution is used.
7. The limits of detection and quantitation were not reported for LSC or TLC analyses. Both limits of detection and quantitation should be reported for each analytical method utilized to allow the reviewer to evaluate the adequacy of the methods.
8. In both studies, a preliminary study was not performed to determine whether the test compounds adsorbed to the test vessels, nor were controls used to determine this during the definitive study. The reviewer notes that adsorption to the glass may have occurred since material balances were out of the acceptable range of 90-110% as required by Subdivision N Guidelines (also see Comment #1).
9. In one of the studies (1988), light conditions (darkness or ambient light) were not reported (MRID 42245136).
10. In one of the studies (1988), the soil series names were not reported as required by Subdivision N Guidelines (MRID 42245136). In future studies submitted to the EPA, it is necessary that the soil series names be reported.
11. The study author reported that the sandy loam soil utilized in each study is the same soil type used in an aerobic soil metabolism study (MRID 42245135, p. 15; MRID 42245136, p. 10).

12. The aqueous solubility of the parent compound was reported as 3 ppm at 20°C at pH 7 (MRID 42245135, p. 14); and 20 ppm at 20°C (unspecified pH; MRID 42245136, p. 50). The reviewer notes that the aqueous solubility of the compound was reported as 15 mg/L at 25°C (unspecified pH) in *The Pesticide Manual* (11th edition, 1997; British Crop Protection Council). The solubility of the test compound in the test solutions was not reported in either study.