

US EPA ARCHIVE DOCUMENT

ABSTRACT

Mobility - Leaching & Adsorption/Desorption

Unaged

The mobility of thiazolyl ring-labeled [2-¹⁴C]thiamethoxam {CGA-293343; 3-(2-chloro-thiazol-5-ylmethyl)-5-methyl-[1,3,5]oxadiazinan-4-ylidene-N-nitroamine; radiochemical purity 96.9%; specific activity 28.5 μCi/mg}, at a nominal concentration of 0.6 ppm, was determined in muck and sand soil:solution slurries that were equilibrated for 24 hours at 25 ± 1°C. Simple K_d values for the muck (o.m. 48.7%) and sand (o.m. 0.6%) soils were 16.5 and 0.13, respectively, for adsorption; corresponding K_{oc} values were 58.4 and 37.4. Simple K_d values for the muck and sand soils were 29.9 and 0.74, respectively, for desorption; corresponding K_{oc} values were 105.7 and 213.5. During the 24-hour equilibration period, 33.8-34.7% and 10.8-11.6% (individual replicates) of the applied radioactivity was adsorbed to the muck and sand soils, respectively. Following a 24-hour desorption equilibration period, 16.3-16.9% and 5.6-5.7% (individual replicates) of the adsorbed radioactivity was desorbed from the muck and sand soils, respectively.

Aged

The mobility of thiazolyl ring-labeled [2-¹⁴C]thiamethoxam (CGA-293343; radiochemical purity 98.9%; specific activity 47.1 μCi/mg) and formulated thiazolyl ring-labeled [2-¹⁴C]thiamethoxam (2SC formulation), at a nominal concentration of 0.6 ppm, was determined in muck and sand soil:solution slurries that were incubated for up to 30 days at 25 ± 1°C. Duplicate samples were removed at designated sampling intervals to determine the adsorption of the parent compound to the soil prior to and following a 24-hour desorption equilibration period, and to characterize [¹⁴C]residues. Data are means of replicate samples.

For the muck soil samples treated with the parent (analytical grade), mean simple K_d values calculated at each sampling interval were 10.9-16.7; corresponding K_{oc} values were 38.7-59.2. Following a 24-hour desorption equilibration period, 92.0% (day 0) to 94.5% (7 days) of the applied radioactivity was adsorbed to the soil. Based on TLC analysis, the parent compound was present at 72.2-78.3% of the applied radioactivity throughout the incubation period. The degradates,

4H-1,3,5-oxadiazin-4-one, 3-[(2-chloro-5-thiazolyl)methyl]tetrahydro-5-methyl- (CGA-355190) and

guanidine, N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitro (CGA-322704),

were each detected at ≤0.8% of the applied radioactivity. Nonextractable [¹⁴C]residues were initially (day 0) 16.1% of the applied radioactivity and were 20.1-23.7% from 2 to

30 days posttreatment. Evolved $^{14}\text{CO}_2$ accounted for 0.19% of the applied radioactivity at 30 days posttreatment.

For the sand soil samples treated with the parent (analytical grade), mean simple K_d values calculated at each sampling interval increased from 0.14 at day 0 to 0.43 at day 30; corresponding K_{oc} values were 38.9-122.6. Following a 24-hour desorption equilibration period, 11.4% (day 0) to 30.4% (30 days) of the applied radioactivity was adsorbed to the soil. Based on TLC analysis, the parent compound was initially present at 99.5-99.8% of the applied radioactivity at 0-2 days and decreased to 91.0% by 30 days posttreatment. The degradates, CGA-355190 and CGA-322704, were each detected at $\leq 0.6\%$ of the applied radioactivity. Nonextractable [^{14}C]residues were initially (day 0) 0.9% of the applied radioactivity and increased to a maximum of 7.7% by 30 days posttreatment. Evolved $^{14}\text{CO}_2$ accounted for $\leq 0.08\%$ of the applied radioactivity throughout the incubation period.

For the muck soil samples treated with the formulated parent (2SC formulation), mean simple K_d values calculated at each sampling interval were 14.3-17.6; corresponding K_{oc} values were 50.4-62.2. Following a 24-hour desorption equilibration period, 93.8-94.2% of the applied radioactivity was adsorbed to the soil. Based on TLC analysis, the parent compound was initially (day 0) present at 78.6% of the applied radioactivity and decreased to 65.3% by 30 days posttreatment. The degradates, CGA-355190 and CGA-322704, were each detected at $\leq 1.6\%$ of the applied radioactivity. Nonextractable [^{14}C]residues were initially (day 0) 15.3% of the applied radioactivity, were 18.7-19.6% from 2 to 21 days, and were a maximum of 27.2% at 30 days posttreatment. Evolved $^{14}\text{CO}_2$ accounted for 0.71% of the applied radioactivity at 30 days posttreatment.

For the sand soil treated with the formulated parent (2SC formulation), mean simple K_d values calculated at each sampling interval increased from 0.14 at day 0 to 0.38 at day 30; corresponding K_{oc} values were 41.3-109.7. Following a 24-hour desorption equilibration period, 11.5% (day 0) to 29.3% (30 days) of the applied radioactivity was adsorbed to the soil. Based on TLC analysis, the parent compound was initially (day 0) present at 99.7% of the applied radioactivity and decreased to 85.9% by 30 days posttreatment. The degradates, CGA-355190, CGA-322704, and

urea, N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl- (CGA-353968),

were each detected at $\leq 1.4\%$ of the applied radioactivity. Nonextractable [^{14}C]residues were initially (day 0) 1.0% of the applied radioactivity and increased to a maximum of 9.3% by 30 days posttreatment. Evolved $^{14}\text{CO}_2$ accounted for 1.4% of the applied radioactivity at 30 days posttreatment.

MATERIALS AND METHODS

Unaged

For the adsorption phase, aliquots of 0.01 M aqueous CaCl₂ solution treated with thiazolyl ring-labeled [2-¹⁴C]thiamethoxam (3-(2-chloro-thiazol-5-ylmethyl)-5-methyl-[1,3,5]oxadiazinan-4-ylidene-N-nitroamine; radiochemical purity 96.9%; specific activity 28.5 μCi/mg; Lot No.: CL-XLVI-49; p. 25; Figure 1, p. 104), dissolved in acetonitrile, at a nominal concentration of 0.6 ppm, were added to centrifuge tubes containing subsamples of sieved (2 mm) sand soil (7 g; wet-weight equivalent) or muck soil (1.75 g; wet-weight equivalent; p. 39). The soil:solution slurries (7:7, w:v, sand soil; 1.75:35, w:v, muck soil) were equilibrated by shaking for 24 hours at 25 ± 1°C. Following the adsorption equilibration period, the tubes were vortexed, sonicated for five minutes, and centrifuged for ten minutes (p. 40). Triplicate aliquots of the supernatants were analyzed by LSC.

For the desorption phase, an aliquot of pesticide-free 0.01 M aqueous CaCl₂ solution equivalent to the volume of supernatant that was removed following the adsorption phase was added to the soil pellets from the adsorption phase of the study (p. 40). The samples were vortexed for 30 seconds and equilibrated by shaking for 24 hours at 25 ± 1°C. Following equilibration, the soil:solution slurries were vortexed, sonicated, and centrifuged for ten minutes. Triplicate aliquots of the supernatants were analyzed by LSC. The soil pellets were extracted twice with acetonitrile:0.5 N HCl (adjusted to pH 5.6; 3:1, v:v), and the samples were vortexed for five minutes, sonicated for five minutes, and centrifuged for ten minutes. The supernatants were decanted, combined, and analyzed by LSC. To determine compound stability, extracts were analyzed by two-dimensional TLC using silica gel 60 F-254 plates developed in methylene chloride:methanol (9:1, v:v) and chloroform:methanol:ammonium hydroxide:water (80:30:4:2, v:v:v:v; p. 33). Samples were co-chromatographed with nonradiolabeled reference standards of the parent and the potential degradates, 4H-1,3,5-oxadiazin-4-one, 3-[(2-chloro-5-thiazolyl)methyl] tetrahydro-5-methyl- (CGA-355190), guanidine, N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitro (CGA-322704), and urea, N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl- (CGA-353968); nonradiolabeled reference standards were visualized with UV light. Areas of radioactivity on the plates were quantified by radioimage scanning. [¹⁴C]Residues were also scraped from selected TLC plates and analyzed by LSC. Stability was confirmed (one replicate from each soil type) by reverse-phase HPLC (YMC ODS- AQ C18 column) with UV (260 nm) and radioactive flow detection (p. 34). HPLC conditions were as follows:

Minutes:	Mobile Phase Gradient:
0-5	Isocratic, 100% of acidified water (0.025% HCl)
5-15	Linear gradient from 0% to 10% acetonitrile in acidified water

15-20	Isocratic, 10% acetonitrile in acidified water
20-30	Linear gradient from 10% to 15% acetonitrile in acidified water
30-40	Isocratic, 15% acetonitrile in acidified water
40-50	Linear gradient from 15% to 18% acetonitrile in acidified water
50-55	Isocratic, 18% acetonitrile in acidified water
55-65	Linear gradient from 18% acetonitrile in acidified water to 100% methanol
65-75	Linear gradient from 100% methanol to 100% acidified water

Samples were co-chromatographed with nonradiolabeled reference standards of the parent and the potential degradates CGA-355190, CGA-322704, and CGA-353968.

Post-extracted soil samples were air dried and triplicate subsamples were analyzed by LSC following combustion (p. 40).

Aged

Subsamples (50 g; dry weight equivalent) of sieved (2 mm), Florida sand (o.m. 0.6%) and Florida muck (48.7% o.m.) soils (Table 1, p. 56) were weighed into sample flasks, adjusted to 75% of 0.33 bar moisture content, and pre-incubated at $25 \pm 1^\circ\text{C}$ for 16 days (p. 28; Table 2, p. 57). Following the pre-incubation period, samples were treated by syringe with thiazolyl ring-labeled [2- ^{14}C]thiamethoxam {CGA-293343; radiochemical purity 98.9%; specific activity 47.1 $\mu\text{Ci}/\text{mg}$; Lot No.: CL-XLVIII-34; p. 24} OR formulated thiazolyl ring-labeled [2- ^{14}C]thiamethoxam (2SC formulation), both dissolved in acetonitrile, at a nominal application rate of 0.6 ppm (pp. 29, 36). Samples were incubated at $25 \pm 1^\circ\text{C}$ for up to 30 days. The moisture content of the samples was maintained at 75% of 0.33 bar moisture by the weekly addition of water. To trap [^{14}C]volatiles, sterile air was continuously pumped through the test systems and through an ethylene glycol trap and two 10% aqueous KOH traps (p. 27; diagram presented in Figure 4, p. 108). Duplicate samples were removed for analysis at 0, 2, 7, 14, 21, and 30 days posttreatment (p. 37).

At each sampling interval, samples were shaken with a 0.01 M aqueous CaCl_2 solution for 24 hours at $25 \pm 1^\circ\text{C}$ (p. 37). Following the desorption period, samples were centrifuged for 15 minutes, and the supernatants were decanted and aliquots were analyzed for total radioactivity by LSC. Supernatants from the muck soil samples were concentrated by solid phase extraction (Varian Bond Elut ENV Column) prior to further analysis. Supernatants were analyzed by two-dimensional TLC as previously described (p. 33). Selected supernatants were further analyzed by reverse-phase HPLC as previously described (p. 34).

Soil pellets were extracted twice by shaking on a wrist-action shaker for 30 minutes with acetonitrile:0.5 N HCl (adjusted to pH 5.6; 3:1, v:v) and centrifuged (p. 38); extracts from the sand soil samples were concentrated under a stream of nitrogen prior to analysis. Aliquots were combined and analyzed by LSC and two-dimensional TLC as previously described. Selected extracts were further analyzed by reverse-phase HPLC as previously described. Post-extracted soil samples were air dried and analyzed by LSC following combustion; combustion efficiency was $>90\%$.

To determine the stability of the parent compound during the acetonitrile:0.5 N HCl extraction, duplicate control samples were fortified with thiazolyl ring-labeled [2- ^{14}C]thiamethoxam and extracted twice by shaking as previously described (p. 47).

Results indicated that 83.3-84.9% of the applied radioactivity was extracted (p. 47); TLC analysis of the extracts indicated that 98.0% of the radioactivity present in the extract was present as the parent compound.

To determine soil viability at the beginning and end of the study, the test soils were weighed into flasks and the metabolically active microbial community was estimated based on the substrate-induced respiration method (p. 28). Biomass analyses indicated that the soils were viable; 39.2 and 57.5 mg C/kg soil for the sand soil and 159.4 and 215.9 mg C/kg soil for the muck soil prior to treatment and at 33 days posttreatment, respectively (Table 3, p. 58).

RESULTS/DISCUSSION

Unaged

The mobility of thiazolyl ring-labeled [2-¹⁴C]thiamethoxam (CGA-293343), at a nominal concentration of 0.6 ppm, was determined in muck and sand soil:solution slurries that were equilibrated for 24 hours at 25 ± 1°C. Simple K_d values for the muck (o.m. 48.7%) and sand (o.m. 0.6%) soils were 16.5 and 0.13, respectively, for adsorption; corresponding K_{oc} values were 58.4 and 37.4 (Appendix 14, p. 196). Simple K_d values for the muck and sand soils were 29.9 and 0.74, respectively, for desorption; corresponding K_{oc} values were 105.7 and 213.5. During the 24-hour equilibration period, 33.8-34.7% and 10.8-11.6% of the applied radioactivity was adsorbed to the muck and sand soils, respectively (individual replicates; Appendix 4, p. 186). Following a 24-hour desorption equilibration period, 16.3-16.9% and 5.6-5.7% of the adsorbed radioactivity was desorbed from the muck and sand soils, respectively (individual replicates; Appendix 5, p. 187).

Based on TLC analysis, the parent compound was stable in adsorption and desorption supernatants and soil extracts (Appendix 11, p. 193); ≥98.1% of the applied radioactivity present in the supernatants and extracts was present as parent.

Material balances (based on LSC analysis of individual replicates) for the muck and sand soils treated with thiazolyl ring-labeled [2-¹⁴C]thiamethoxam were 98.0-98.2% and 98.5% of the applied radioactivity, respectively (Appendix 2, p. 184).

Aged

The mobility of thiazolyl ring-labeled [2-¹⁴C]thiamethoxam (CGA-293343), at a nominal concentration of 0.6 ppm, was determined in muck soil:solution slurries that were incubated for up to 30 days at 25 ± 1°C. Mean simple K_d values calculated at each

sampling interval were 10.9-16.7; corresponding K_{oc} values were 38.7-59.2 (Table 24, p. 100). Data are means of replicate samples. Following a 24-hour desorption equilibration period, 92.0% (day 0) to 94.5% (7 days) of the applied radioactivity was adsorbed to the soil (Table 12, p. 73). Based on TLC analysis, the parent compound was present at 72.2-78.3% of the applied radioactivity throughout the incubation period (Table 16, pp. 87-88). The degradates,

4H-1,3,5-oxadiazin-4-one, 3-[(2-chloro-5-thiazolyl)methyl]tetrahydro-5-methyl- (CGA-355190) and

guanidine, -[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitro (CGA-322704),

were each detected at $\leq 0.8\%$ of the applied radioactivity. Unidentified minor degradates and uncharacterized [^{14}C]residues (origin material) were each detected at $\leq 1.5\%$ of the applied radioactivity. Nonextractable [^{14}C]residues were initially (day 0) 16.1% of the applied radioactivity and were 20.1-23.7% from 2 to 30 days posttreatment (Table 9, p. 65). Evolved $^{14}\text{CO}_2$ accounted for 0.19% of the applied radioactivity at 30 days posttreatment.

The mobility of thiazolyl ring-labeled [2- ^{14}C]thiamethoxam (CGA-293343), at a nominal concentration of 0.6 ppm, was determined in sand soil:solution slurries that were incubated for up to 30 days at $25 \pm 1^\circ\text{C}$. Mean simple K_d values calculated at each sampling interval increased from 0.14 at day 0 to 0.43 at day 30; corresponding K_{oc} values were 38.9-122.6 (Table 24, p. 101). Data are means of replicate samples. Following a 24-hour desorption equilibration period, 11.4% (day 0) to 30.4% (30 days) of the applied radioactivity was adsorbed to the soil (Table 12, p. 74). Based on TLC analysis, the parent compound was initially present at 99.5-99.8% of the applied radioactivity at 0-2 days and decreased to 91.0% by 30 days posttreatment (Table 17, pp. 89-90). The degradates, CGA-355190 and CGA-322704, were each detected at $\leq 0.6\%$ of the applied radioactivity. Unidentified minor degradates and uncharacterized [^{14}C]residues (origin material) were each detected at $\leq 0.2\%$ of the applied radioactivity. Nonextractable [^{14}C]residues were initially (day 0) 0.9% of the applied radioactivity and increased to a maximum of 7.7% by 30 days posttreatment (Table 9, p. 66). Evolved $^{14}\text{CO}_2$ accounted for $\leq 0.08\%$ of the applied radioactivity throughout the incubation period.

The mobility of formulated thiazolyl ring-labeled [2- ^{14}C]thiamethoxam (CGA-293343; 2SC formulation), at a nominal concentration of 0.6 ppm, was determined in muck soil:solution slurries that were incubated for up to 30 days at $25 \pm 1^\circ\text{C}$. Mean simple K_d values calculated at each sampling interval were 14.3-17.6; corresponding K_{oc} values were 50.4-62.2 (Table 24, p. 102). Data are means of replicate samples. Following a 24-hour desorption equilibration period, 93.8-94.2% of the applied radioactivity was adsorbed to the soil (Table 12, p. 75). Based on TLC analysis, the parent compound was

initially (day 0) present at 78.6% of the applied radioactivity and decreased to 65.3% by 30 days posttreatment (Table 18, pp. 91-92). The degradates, CGA-355190 and CGA-322704, were each detected at $\leq 1.6\%$ of the applied radioactivity. Unidentified minor degradates and uncharacterized [^{14}C]residues (origin material) were each detected at $\leq 0.3\%$ of the applied radioactivity. Nonextractable [^{14}C]residues were initially (day 0) 15.3% of the applied radioactivity, were 18.7-19.6% from 2 to 21 days, and were a maximum of 27.2% at 30 days posttreatment (Table 9, p. 67). Evolved $^{14}\text{CO}_2$ accounted for 0.71% of the applied radioactivity at 30 days posttreatment.

The mobility of formulated thiazolyl ring-labeled [2- ^{14}C]thiamethoxam (CGA-293343; 2SC formulation), at a nominal concentration of 0.6 ppm, was determined in sand soil:solution slurries that were incubated for up to 30 days at $25 \pm 1^\circ\text{C}$. Mean simple K_d values calculated at each sampling interval increased from 0.14 at day 0 to 0.38 at day 30; corresponding K_{oc} values were 41.3-109.7 (Table 24, p. 103). Data are means of replicate samples. Following a 24-hour desorption equilibration period, 11.5% (day 0) to 29.3% (30 days) of the applied radioactivity was adsorbed to the soil (Table 12, p. 76). Based on TLC analysis, the parent compound was initially (day 0) present at 99.7% of the applied radioactivity and decreased to 85.9% by 30 days posttreatment (Table 19, pp. 93-94). The degradates, CGA-355190, CGA-322704, and urea, N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl- (CGA-353968),

were each detected at $\leq 1.4\%$ of the applied radioactivity. Unidentified minor degradates and uncharacterized [^{14}C]residues (origin material) were each detected at $\leq 0.3\%$ of the applied radioactivity. Nonextractable [^{14}C]residues were initially (day 0) 1.0% of the applied radioactivity and increased to a maximum of 9.3% by 30 days posttreatment (Table 9, p. 68). Evolved $^{14}\text{CO}_2$ accounted for 1.4% of the applied radioactivity at 30 days posttreatment.

Material balances (based on LSC analysis of individual replicates) for the muck and sand soils treated with thiazolyl ring-labeled [2- ^{14}C]thiamethoxam were 94.6-99.0% and 99.4-103.1% of the applied radioactivity, respectively, throughout the incubation period (Table 9, pp. 65-66). Material balances (based on LSC analysis of individual replicates) for the muck and sand soils treated with formulated thiazolyl ring-labeled [2- ^{14}C]thiamethoxam (2SC formulation) were 93.9-97.5% and 93.1-102.1% of the applied radioactivity, respectively, throughout the incubation period (Table 9, pp. 67-68).

DEFICIENCIES/DEVIATIONS

1. Freundlich K_{ads} and K_{des} values could not be determined because the soils were treated with the parent compound at a single concentration. The study author calculated simple K_d values (concentration of parent sorbed/concentration of parent desorbed) to determine the mobility of the parent in sand and muck soils. K_{oc} values were calculated by adjusting the K_d values for the percentage of organic carbon present in the two soils.
2. The study author stated that the application rate (0.6 ppm) was approximately equal to the proposed maximum use rate for the parent compound in furrow treatments (p. 29).
3. The limits of detection and quantitation for TLC and HPLC analyses were reported in dpm/ μ g (pp. 31-32).
4. The formulation of the test compound used in the aged soil study was reported as 2SC throughout the study. The reviewer reported the formulation as a soluble concentrate (formulation code 15).
5. The soil series name of the sand soil was reported as "St. Johns, Malabar, Wabasso" (Table I, p. 56); clarification by the registrant may be necessary. A soil series name was not reported for the muck soil.
6. The study author stated that the study is a supplemental study to the existing batch equilibrium studies of the parent, and was designed to determine the effect of time on desorption (p. 21).
7. The study author stated that, for the unaged study, two empty centrifuge tubes were treated with the test solution to determine whether the test compound adsorbed to the Teflon centrifuge tubes (p. 39). The results were not reported.

ATTACHMENT 1

Tables cited in DER

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