

applied, respectively, at 33 days posttreatment). The degradates identified in the aniline-labeled pH 9 solutions were 3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenylurea (maximum of 59% of the applied at 37 days posttreatment), and 3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)-phenylamine (maximum of 10% of the applied at 33 days posttreatment).

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of benzoyl ring-labeled [^{14}C]hexaflumuron in aqueous buffered solutions at pH 5, 7, and 9.
4. No additional information on the hydrolysis of hexaflumuron is needed at this time.

METHODOLOGY:

Uniformly benzoyl ring-labeled [^{14}C]hexaflumuron [1-(3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenyl)-3-(2,6-difluorobenzoyl)urea; radiochemical purity >99%, specific activity 932.4 KBq/mg, Dow Chemical], dissolved in propan-2-ol, was added at 0.015 ug/mL to 100-mL glass bottles containing sterile (autoclaved) aqueous buffer solutions (50 mL; concentration of buffers not specified) adjusted to pH 5 (phthalate, containing mercuric chloride at 10 ppm), pH 7 (phthalate, mercuric chloride-free), and pH 9 (borate). In addition, uniformly aniline ring-labeled [^{14}C]hexaflumuron (radiochemical purity >99%, specific activity 802.9 KBq/mg, Dow Chemical) dissolved in propan-2-ol was added at 0.015 ug/mL to additional bottles containing sterile aqueous buffer solutions adjusted to pH 9 (borate). In all treated solutions, the final concentration of cosolvent (propan-2-ol) was 0.8% by volume. The samples were shaken, then incubated in the dark at 25 ± 1 C. Duplicate bottles of each solution were collected at 0, 1, 3, 7, 14, 21, and 33 days posttreatment; the aniline ring-labeled pH 9 solution was also collected at 37 days.

At each sampling interval, triplicate aliquots of each test solution were analyzed for total radioactivity using LSC. The remaining solutions were then extracted three times with methylene chloride (5 mL) by shaking; after each extraction, the solutions were centrifuged and the methylene chloride layers decanted. Aliquots of the extracted test solutions were analyzed for total radioactivity by LSC; due to the low amounts of radioactivity remaining, the pH 5 and 7 solutions, and the pH 9 aniline ring-labeled solutions were not further analyzed.

The three methylene chloride extracts from each sample were combined; aliquots were analyzed by LSC, and the remainder of the combined extracts was evaporated to dryness under nitrogen. The resulting residues were redissolved in methylene chloride, and aliquots were analyzed by LSC to determine procedural recovery; recoveries were > 90%. Additional aliquots were analyzed by one-dimensional TLC on silica gel plates developed in toluene:propan-2-ol:acetic acid (9:1:1, v:v:v) or trimethylpentane:ethyl acetate (2:1, v:v). Unlabeled reference standards were cochromatographed with the samples and visualized under UV light. Radioactive areas on the plates were located and quantified by radioscanning.

The methylene chloride-extracted pH 9 solutions containing benzoyl ring-labeled [¹⁴C]hexaflumuron were mixed with 2 N sulfuric acid and sodium chloride, then extracted twice with diethyl ether. The ether extracts were combined, and aliquots were analyzed by LSC and TLC as previously described.

In order to produce large quantities of the [¹⁴C]hexaflumuron degradates, portions (2.5 L) of the pH 9 buffer solution were spiked with either benzoyl or aniline ring-labeled [¹⁴C]hexaflumuron, "saturated" with unlabeled hexaflumuron, and incubated in a water bath at 50°C for 7 days. Both test solutions were then extracted as described previously; all extracts were analyzed by LSC and TLC as previously described. Also, aliquots of both the benzoyl and aniline ring-labeled [¹⁴C]hexaflumuron methylene chloride extracts were analyzed by HPLC using a Spherisorb ODS 2 column eluted with acetonitrile:water (65:35, v:v). To confirm the identification of the degradation products, [¹⁴C]residues were derivitized with BSTFA reagent; the resulting trimethyl silyl derivatives were analyzed by GC/MS.

DATA SUMMARY:

Uniformly benzoyl ring-labeled [¹⁴C]hexaflumuron [1-(3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenyl)-3-(2,6-difluorobenzoyl)urea; radiochemical purity >99%], at 0.015 ug/mL, was stable in sterile aqueous pH 5 buffer solutions (containing 10 ppm mercuric chloride) and relatively stable (<5% degraded) in pH 7 buffer solutions (no mercuric chloride); the solutions were incubated in the dark at 25 ± 1°C for 33 days. In pH 9 buffer solutions (no mercuric chloride), uniformly benzoyl and aniline ring-labeled [¹⁴C]hexaflumuron (radiochemical purities >99%) degraded with registrant-calculated half-lives of 21-22.5 days. Degradates identified in the benzoyl-labeled pH 9 solutions were:

2,6-difluorobenzoic acid (maximum of 55% of the applied at 33 days posttreatment); and

2,6-difluorobenzamide (maximum of 8% of the applied at 33 days posttreatment).

Degradates identified in the aniline-labeled pH 9 solutions were:

3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenylurea (maximum of 59% of the applied at 37 days posttreatment); and

3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenylamine (maximum of 10% of the applied at 33 days posttreatment).

In the pH 5 buffered solutions, [¹⁴C]hexaflumuron comprised 100% of the recovered radioactivity at all sampling intervals (Table V). During the study, the material balances were 92.8-106.7% of the applied with no discernable pattern of decline (Table I).

In the pH 7 buffered solutions, [¹⁴C]hexaflumuron comprised 100% of the recovered through 14 days posttreatment, 92-96% at 21 days, and 92-93% at

33 days (Table VI). Unidentified "others" (not extractable by methylene chloride) totaled a maximum of 6% of the recovered at 33 days posttreatment. During the study, the material balances were 94.6-100.0% of the applied with no discernable pattern of decline (Table II).

In the pH 9 buffered solutions treated with benzoyl ring-labeled [¹⁴C]hexaflumuron, [¹⁴C]hexaflumuron was 100% of the recovered radioactivity immediately posttreatment, 53% at 21 days, and 35-36% at 33 days (Table VII). 2,6-Difluorobenzoic acid and 2,6-difluorobenzamide increased to maximums of 49-55 and 4-8% of the recovered, respectively, at 33 days posttreatment. Material balances were 98.2-102.0% of the applied at 0 days posttreatment, 93.2-97.1% at 1 through 21 days, and 91.4-93.9% at 33 days (Table III).

In the pH 9 buffered solutions treated with aniline ring-labeled [¹⁴C]hexaflumuron, [¹⁴C]hexaflumuron was 100% of the recovered radioactivity immediately posttreatment, 50% at 21 days, and 32-37% at 33 and 37 days (Table VIII). 3,5-Dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenylurea increased to a maximum of 55-59% of the recovered at 37 days posttreatment; 3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenylamine increased to a maximum of 10% at 33 days, and was 4-5% at 37 days. Material balances were 88.6-93.3% of the applied at 0 days posttreatment, 88.5-98.3% at 1 through 21 days, and 80.0-86.7% at 33 and 37 days (Table IV).

COMMENTS:

1. The pH 5 buffer solutions were amended with mercuric chloride as a "stabilizer"; no degradation was observed. Mercuric chloride was not added to either the pH 7 or 9 solutions; hexaflumuron was not stable at these pHs (7-8 and approximately 65% degradation at 33 days posttreatment, respectively). The study author did not explain the addition of mercuric chloride to the pH 5 solution. However, since hexaflumuron is a substituted urea, and as a class, substituted ureas are most susceptible to hydrolysis at high pH (as was observed in this study), it is not likely that the addition of mercuric chloride to the pH 5 solutions affected the hydrolysis of hexaflumuron at that pH.
2. LSC analysis of the buffer solutions before extraction showed that not all of the applied radioactivity was in solution; percentages in solution were as low as 17% (Tables I, II, and III).
3. At 15-33 days posttreatment, the pHs of the buffer solutions were 4.98-5.03, 6.96-7.01, and 8.94-8.96.
4. The aqueous solubility of hexaflumuron was reported to be 0.027 ug/mL at 18°C; concentrations during the study were 0.015 µg/mL.
5. A hydrolytic degradation pathway for hexaflumuron was provided in Figure 9.
6. Recovery of the radioactivity after TLC was determined by scraping the silica gel support from the glass and analyzing it by LSC. The recovery from the day 33 extracts of the pH 9 benzoyl-labeled solutions was 98.5%.

HEXAFLUMURON

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