

US EPA ARCHIVE DOCUMENT

and irradiated with a xenon lamp, showed little degradation after 29 days.

Also, the acetone added as a sensitizer in Study 3 seemed to decrease apparent photodegradation of quinclorac, while acetone added in this study slightly increased photodegradation.

METHODOLOGY:

[3-¹⁴C]Quinclorac (radiochemical purity 99.6%, specific activity 40.4 uCi/mg, BASF Corporation) dissolved in pH 7 buffer solution (0.1 M phosphate) was added at 54 ppm to two volumetric flasks, one containing additional pH 7 buffer solution and the second containing pH 7 buffer that had been sensitized by the addition of 0.5% acetone. The test solutions were filter-sterilized (0.22-micron) as they were introduced into two sterilized "reaction vessels" via liquid ports. CO₂-free, sterile (0.22-micron filter) air was drawn (375 mL/minute) through the reaction vessels using a vacuum pump; before exiting the system, the air was drawn through NaOH and HCl trapping solutions and a charcoal filter (Figure 6). Both vessels were purged for 10 minutes/day on 5 days during each week. The reaction vessels were sealed on the top with a quartz glass plate and were surrounded by a jacket through which cooling water was pumped to maintain the test solutions at 25 °C. The vessels were placed below a xenon arc lamp housed in a Hanau Suntest irradiation apparatus containing various filters and reflectors designed to produce irradiation that approximated sunlight (Figure 4). Radiation below 290 nm was minimal to zero (Figure 5); the measured light intensity at sample level was 805 ± 33 watts/m², compared to an intensity of 931 watts/m² for natural sunlight (measured under sunny conditions near noon in May at a New Jersey location). After removing an initial subsample from the two reaction vessels, the arc lamp was ignited and the solutions were irradiated on a 15-hour light:9-hour dark cycle for 5 days each week the experiment was continued; on the sixth and seventh day of each 7-day cycle, the solutions were irradiated 24 hours per day. Aliquots of the irradiated solutions were removed through sampling ports of the photolysis chambers after 115.9, 237.8, 363.8, 586.5, and 697.0 hours of cumulative irradiation.

Total [¹⁴C]residues in the test solutions, trapping solutions, and methanol washes of the reaction vessels were quantified directly using LSC. Aliquots of the test solutions from each sampling interval were analyzed for quinclorac and its degradates using reverse-phase HPLC with a methanol:0.1 M ammonium acetate mobile phase and with UV (230 nm) and radioactive flow detection. Additional aliquots of the test

solutions were analyzed by one-dimensional TLC on silica gel plates developed in ethyl acetate:methanol:acetic acid (80:15:5); radioactive areas were located and quantified with a radiochromatogram analyzer. The charcoal filters were analyzed for total radioactivity by LSC following combustion.

DATA SUMMARY:

[3-¹⁴C]Quinlorac (radiochemical purity 99.6%), at 54 ppm, degraded slightly (<10% of the applied) in a sterile aqueous pH 7 buffer solution that was irradiated for 697 hours using a xenon arc lamp at 25 °C (Figure 10). The intensity of the xenon lamp at sample level was 805 watts/m², compared to a measured intensity of 931 watts/m² for sunlight. After 697 hours of irradiation, quinlorac comprised 92% of the recovered radioactivity, an unidentified degradate comprised 1.6%, and 2.7% remained near the origin of the TLC plate (Figure 10). At the completion of the study, cumulative volatiles were 0.1% of the applied radioactivity and the material balance was 97.9% (Table II).

Photodegradation of quinlorac was more rapid in the presence of a photosensitizer (0.5% acetone). After 697 hours of irradiation using the xenon arc lamp, quinlorac comprised 84.5% of the recovered and 6.5% remained near the origin of the TLC plate; no other degradates were detected (Figure 10). At the completion of the study, cumulative volatiles were 1.1% of the applied and the material balance was 91.1% (Table III).

REVIEWERS COMMENTS:

1. The registrant did not explain the disparity between this study and the following two aqueous photolysis studies (Study 3 and 4). The latter studies show fairly rapid degradation of quinlorac (half-lives of 5 and 10 days) in unsterilized non-buffered rice-paddy and river waters and water containing activated sludge when exposed to sunlight, while the half-life in this study, using sterilized water buffered at pH 7 and irradiated with xenon, showed little if any degradation after 29 days.

Also, the acetone added as a sensitizer in Study 3 seemed to decrease apparent photodegradation of quinlorac, while acetone added in this study slightly increased photodegradation.

2. The study author stated that "...two other samples (one after 8 h of darkness, the other after 24 h) were withdrawn from the sensitized and nonsensitized reaction solutions at the end of the experiment to verify that no dark-dependent changes in reaction components occurred. The HPLC traces...indicate that

within experimental limitations, the solutions at the beginning and end of the dark period were identical."

It is uncertain whether these two dark samples are meant to represent the storage stability of the irradiated solution or to demonstrate that the dark periods interspersed with irradiation had no effect on degradation (so that the irradiation could be considered cumulative). Two data points are not considered adequate for the dark control required by Subdivision N guidelines; the study author referred to 40320816 (Study 1) for information about the hydrolytic behavior of quinclorac.

3. The study author calculated the half-lives of quinclorac in the nonsensitized and sensitized solutions to be 2416-3240 hours and 1030-1238 hours, respectively. However, the statistical estimations of the photodegradation half-lives of quinclorac reported in these experiments are of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.
4. The study author noted that quinclorac ionizes over the pH 5-9 range. Since quinclorac was shown to be stable to hydrolysis over this range, pH 7 was chosen for this study as a value in the middle of a stable pH range.
5. EFGWB prefers that [¹⁴C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

In this study, the sample extracts were analyzed using one-dimensional TLC with one solvent system and by HPLC with UV and radioactive flow detection. Although analytical reference standards of quinclorac were used in the HPLC-UV analyses, it could not be determined from the "Experimental Section" whether reference standards were used with the TLC and [¹⁴C]HPLC analyses.

6. The absorbance spectrum of the pesticide in the test solution was provided (Figure 1).
7. The method detection limit was not reported. Recovery efficiencies are not required because the samples were analyzed directly without extraction.