9-15-92

DATA EVALUATION RECORD

STUDY 1

CHEM 128974 Quinclorac 161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY MRID 422941-01
Goetz, A.J. and V.W. Winkler. 1991. Photolysis of ^{14}C-BAS 514 H in rice field water and paddy sediment. BASF Protocol No. 91095. BASF Report No. M9126. BASF Registration Document No. 91/5168. Unpublished study performed and submitted by BASF Corp. Research Triangle Park, NC.

DIRECT REVIEW TIME = 3

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. EFGWB concludes that this non-guideline study is scientifically valid and provides supplementary information that unequivocally shows quinclorac to degrade photolytically in the presence of rice paddy water and sediment. This is in contrast to the guideline study (EFGWB Study 2, MRID 41063560, in EFGWB Science Chapter dated 12/3/90) that showed little degradation of quinclorac in sterile and buffered water after 29 days.

2. The half-lives of quinclorac were 15.7 days for the chemical without the formulation ingredients added to soil and water and 5.3 days for the chemical with the formulation ingredients added to soil and water.

METHODOLOGY:

One ml (57.4 *ug*) of an aqueous solution of ^{14}C-BAS 514 H (5.7×10^6 dpm) was added to 10 g of sediment (pH: 7.6, CEC: 24 meg/100g, BD: 0.98 g/cc, %

moisture at 1/3 bar: 36.8, % OM: 1.9, % sand: 27.3, % silt: 29.2, % clay: 43.5, USDA textural class: clay) and 19 ml of rice paddy water (pH: 7.49, conductivity: 0.48 mmhos, Ca: 62 mg/l, Mg: 19 mg/l, hardness (as mg eq $CaCO_3$): 234 mg/l) obtained from a typical rice growing soil near Stoneville, MS. This amount of quinclorac is equivalent to about 10 times the normal application rate of 0.5 lb ai/A. The effect of formulation ingredients was also tested by adding 50 *u*g of the formulation material and quinclorac to one set of samples for irradiation and to one set of dark controls.

Samples were irradiated using a xenon lamp (Hanau Suntest with filters to exclude wavelengths <290 nm) at 1900 $uE.m^{-2}.s^{-1}$ at 26-27°C and pH 7.5 with intermittent 12-hour light and dark periods for 30 days. Light intensity measurements were made with a Li-Cor model LI-185B. Photolysis was carried out in the reaction vessel depicted in Figure 3. The tops of the vessels were quartz plates sealed to the bodies with teflon grease. The light intensity used in the study was reported to be equivalent to a clear November day in Research Triangle Park, NC.

Quantitative analysis was conducted at 0, 15 and 30 days. Volatile components were trapped in carbitol for organics and NaOH for CO_2 and samples were collected on 1, 2, 3, 5, 7, 9, 11, 13, 15, 20 and 30 days after treatment. The rice paddy water was separated from the sediment and analyzed for BAS 514 H and photolytic products. Borate buffer (25 *m*M, p 10.8) and 1*N* NaOH extracts of the sediment were analyzed in a similar manner. Briefly, the method consisted of acidifying the aqueous fraction and filtering out precipitated humic material. The filtrate was then passed through a uC_{18} column and washed with 0.1*N* HCl. The non retained material was considered to be polar photoproducts. The uC_{18} column-adsorbed, nonpolar material was eluted with methanol/NH_4OH (*ca* 10%, pH 12), concentrated, and subjected to normal and reversed-phase thin-layer chromatography (TLC) using acidic developing systems to determine the amounts of quinclorac and photodegradation products.

Radioactivity was quantified by LSC using Beckman LS 6000 11 Series LSC systems and/or Beckman LS 9800 Series LSC Systems. The radioactivity in sediment was quantified by combustion in a R. J. Harvey Biological Oxidizer OX-300 and trapping the $^{14}CO_2$ in harvey cocktail. The radioactivity on the thin-layer plates was analyzed by a Bioscan Imaging Scanner 200.

DATA SUMMARY:

The mass balance for the samples, shown in Table 11, ranged from 97.8 to 105% Total Radioactive Residues (TRR)[1]. Mass balance for 15- and 30-day irradiated samples ranged from 78.0 to 91.5% of the applied TRR. The lower values for the irradiated samples are attributed by the author to the analysis of many different fractions of photodecomposition products which were not present in the dark controls.

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[1]The % TRR in the tables was calculated by dividing the dpm of each fraction by 5,147,623 dpm (the applied radioactivity) and multiplying times 100.

A significant amount of quinclorac was converted to volatile inorganic material since after 30 days, 8.1 and 20.5% of the applied TRR was CO_2, respectively, for the nonformulated and formulated treatments. For both treatments, the majority of CO_2 production occurred between 0 and 9 DAT, and the rate of production decreased after 9 DAT (Table 1 and Figure 5). Organic volatiles were <0.5% of the applied TRR (Table 1).

Table A summarizes the 30-day results of the study; while Tables 2 and 3 and Figures 6 and 7 provide distribution of residues in water and sediment. The results indicate that quinclorac is rapidly degraded when irradiated in rice paddy water and sediment. Furthermore, the degradation was accelerated in the presence of the formulation ingredients. The amount of quinclorac remaining in the irradiated rice paddy water was 23.0 and 0.8% of the applied TRR for the non-formulated and formulated treatments, respectively, after 30 days. However, in the dark controls 92.4 and 88.3% of the applied TRR remained as quinclorac in the nonformulated and formulated treatments, respectively, after 30 days. The amount of TRR remaining in the sediment of irradiated samples was 61.5 and 70.0%, respectively, for nonformulated and formulated treatments; while the amount of TRR remaining in the sediment of the dark controls was <10%.

The half-lives of quinclorac in the non-formulation and formulation treatments were calculated from the data in Table 12 using first order model. The coefficient of determination for both treatments was 0.97 and the calculated half-lives for the nonformulated treatments and formulated treatment were 15.7 and 5.3 days, respectively. Although the addition of the formulation decreased the half-life, the half-life without formulation was 15.7 days, indicating that natural rice paddy water possesses a sufficient concentration of photosensitizers to result in rapid photodecomposition of quinclorac. The increase in photolysis rate with the addition of the formulation materials is probably due to the ability of the some of the ingredients to act as photosensitizers. Whether or not the formulation ingredients would enhance photodegradation under actual field use is not known, but it is likely that the naturally occurring photosensitizers would contribute more to photolysis.

These results indicate that within the parameters of this study, quinclorac is rapidly photolyzed to many polar and nonpolar products which are mainly bound to sediment or converted to CO_2.

REVIEWER'S COMMENTS:

Previous studies [Stewart, J. January 1991. Freezer storage stability of quinclorac and its metabolites in soil - 0, 17, 21 month analysis. Registration Document No. 91/5016. Unpublished study performed and submitted by BASF Corp., Research Triangle Park, NC. MRID 417814-32 and Eswein, R. P. 1991. Freezer storage stability of quinclorac (BAS 514 H) in water: Final report. BASF Registration Document No. 9/5151. Unpublished study performed and submitted by BASF Corp. Agricultural Products, Research Triangle Park, NC. 31 pp. MRID 422941-10, reviewed in this report as DER 11, see attached] have shown that quinclorac is stable in water and soil that has been stored frozen for up to 21 and 39 months, respectively. Although no mention was made in this report in relation to length of storage of the samples, it appears that

most of the samples were analyzed almost immediately after sampling. Therefore, no further information is needed related to storage stability of quinclorac in water and soil in regards to this study.