

9-1-88

DATA EVALUATION RECORD

STUDY 2

SHAUGHNESSY NO. 128994

MON-15151

Sec. 161-2 and 161-3

FORMULATION—00—ACTIVE INGREDIENT

MRID NO. 40638628

Klemm, G.H., R.G. Nadeau, and R.T. Solsten. 1988. The photolysis of MON-7200 [3,5-pyridine-dicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-,S,S-dimethyl ester] in water and in soil. Laboratory Project Identification MSL-7049, R. D. No. 866. Unpublished study prepared and submitted by Monsanto Agricultural Company, St. Louis, MO.

DIRECT REVIEW TIME = 24

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CONCLUSIONS:

Degradation - Photodegradation in Water

This part of the report is acceptable and fulfills EPA Data Requirements for an aqueous photolysis study by providing information on the photodegradation of ring-labeled [¹³C/¹⁴C]MON-15151 in sterile pH 7 buffered nonsensitized and sensitized aqueous solutions.

Degradation - Photodegradation on Soil

For the purposes of an EUP this part of the report satisfies the requirement for a photolysis study on soil by providing information on the photodegradation of ring-labeled [¹³C/¹⁴C]MON-15151 on a silt loam soil.

SUMMARY OF DATA BY REVIEWER:

Degradation - Photodegradation in Water

Ring-labeled [$^{13}\text{C}/^{14}\text{C}$]MON-15151 (radiochemical purity >99%), at 0.7 ppm, degraded with a half-life of 61.8 hours in a sterile, nonsensitized pH 7 buffered aqueous solution and 72.4 hours in a similar solution amended with humic acid (as a photosensitizer) during continuous irradiation under artificial light at 25°C. The intensity of the light source (one 500-watt xenon arc lamp) was 198 mW/cm² compared to a registrant-computed sunlight intensity of 58 mW/cm². Half-lives in sunlight days, as computed by the registrant using 58 mW/cm² as a reference, were 17.6 and 20.6 for the nonsensitized and humic acid solutions, respectively. At the termination of the photolysis experiment (≈128 hours artificial light or 36.4 sunlight days) with nonsensitized solution, MON-15151 comprised 24.5% of the applied radioactivity and two degrade monoacids, . . .

2-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-6-(trifluoromethyl)-3-pyridinecarboxylic acid (normal acid; II) and

6-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-2-(trifluoromethyl)-3-pyridinecarboxylic acid (reverse acid; III) . . .

comprised 27.3 and 14.2%, respectively, of the applied radioactivity. Two minor degradates, each of which comprised ≈4-5% of the applied radioactivity, were . . .

2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarboxylic acid (diacid; IV) and

3,5-bis(methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine (V).

Two additional minor degradates together comprised 7.3% of the applied radioactivity . . .

3-(methylthiocarbonyl)-2-difluoromethyl-4-(2-methylpropyl)-6-trifluoromethylpyridine (VI) and

3-(methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethylpyridine (VII).

Similar degradates and percentage recoveries were obtained with the humic acid-sensitized solutions. MON-15151 was stable in all control solutions maintained in the dark.

Degradation - Photodegradation on Soil

Ring-labeled [$^{13}\text{C}/^{14}\text{C}$]MON-15151 (radiochemical purity >99%), at 1 lb/A on silt loam soil, was slightly degraded to 2-(difluoromethyl)-4-(2-methyl-

propyl)-5-[(methylthio)carbonyl]-6-(trifluoromethyl)3-pyridinecarboxylic acid (normal acid; II), which comprised ~5% of the applied radioactivity after continuous exposure to 118 hours of artificial light (one 500-watt xenon arc lamp). MON-15151 was stable in the dark control soil.

DISCUSSION:

Degradation - Photodegradation in Water

1. The absorption spectra of MON-15151 in buffer or buffer plus humic acids was not provided.
2. Emission spectra for the xenon arc lamp with two types of filtering devices were provided as was a spectrum for sunlight. However, it was not possible to make a realistic comparison of the wavelength-energy distribution between the artificial light sources and sunlight because of large differences in scale values on the figures depicting the spectra.
3. Intensity measurements were provided for the light system used, but it could not be determined what the relationship was between the values provided and the actual intensity within the photolysis chamber.
4. Although the temperature of the solutions within the photolysis chamber was apparently predetermined to be 25°C with a coolant temperature of 19.8°C (the protocol specified 5°C) and the temperature of the solutions was measured prior to analyses, sample data were not provided to substantiate that the photolysis experiments were actually conducted at 25°C.
5. Filter-sterilized deionized water was used in these experiments, but it could not be determined whether the humic acid solutions were sterilized after addition of the humic acids.
6. A study was also conducted using filter-sterilized rice paddy water (pH 8.0); the half-life calculations for MON-15151 differed by less than 1 day between pH 7 buffered water and rice paddy water. The data were not evaluated in detail because they are not required by current EPA Guidelines for Registering Pesticides.

Degradation - Photodegradation in Soil

1. The photolytic degradation of MON-15151 on soil was stated as having been conducted at 25°C. However, this value appears to have been based upon a personal communication that a coolant temperature of 10°C would maintain the soil surface at 25°C rather than upon actual soil temperature measurements.
2. The registrant is advised that continuous (24 hrs/day) ^{photolytic Exposure} is not an acceptable procedure. Alternating light/dark periods of 12 hours are recommended to allow bacterial recovery. The intensity of the artificial light must be comparable to natural sunlight, not many times greater.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Degradation - Photodegradation in Water

Ring-labeled [$^{13}\text{C}/^{14}\text{C}$]MON-15151 (radiochemical purity of the mixture was >99% and specific activity was 17.87 mCi/mmol, Monsanto Company) was added at 0.7 ppm to sterile pH 7 phosphate buffer and buffer containing 25.8 mg/L humic acids as photosensitizers. The solutions were irradiated in a cylindrical Pyrex chamber at 25°C under continuous light from a xenon arc lamp with a light intensity of 198 mW/cm² between 300 and 750 nm. Samples were removed at intervals from 0.5 to ca. 128 hours for degradate analysis, pH, and temperature measurements. A foam plug used to trap volatiles was removed from the photolysis chamber for analysis at each sampling period. A control solution was kept in the dark at 25°C and sampled at an unspecified time period for degradate formation.

Total radioactivity of the test solution and foam plug was determined at each sampling period by ISC. Solutions were then extracted with ether, acidified, extracted with ethyl acetate, and concentrated. The fractions from the extraction of the nonphotosensitized solutions were analyzed by HPLC with a radioactive flow detector, identification of degradates was based upon comparison of retention times with standards, and structure confirmation was determined by MS. Degradates in extracts of the sensitized solutions were identified by comparison of their retention times with those of the identified degradates from the nonsensitized solutions.

Degradation - Photodegradation on Soil

A slurry of sieved (2 mm) silt loam soil (24% sand, 68% silt, 8% clay, pH 7.5, and CEC 10.7 meq/100 g) was added to petri dishes to a depth of 1 mm and air-dried overnight. Ring-labeled [$^{13}\text{C}/^{14}\text{C}$]MON-15151 (properties as previously described for photodegradation in water) in hexane was added to the soil at 1 lb/A, allowed to air dry for evaporation of the hexane, and continuously exposed to the xenon arc lamp source (radiant properties as previously described) in an enclosed cylindrical Pyrex chamber at ca. 25°C for intervals varying from 3.6 to ca. 118 hours. Comparable control dishes of soil were sealed and maintained in the dark for 2.4 and ca. 118 hours prior to sampling. The Pyrex chamber was vented through two ports fitted with foam plugs to trap volatiles.

At each sampling period, the chamber was flushed with air and the foam plugs and one dish of soil were removed for extraction and analysis. The plugs were extracted with ether and the soil was extracted with water:acetonitrile (50:50). Radioactivity was determined by both combustion and ISC; analysis and confirmation was based upon HPLC with radioactive flow monitoring and comparisons to known standards.

Dithiopyr Science Review

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