DATA EVALUATION REVIEW

I. Study Type: Aqueous photolysis

II. Citation: Brehm, M., W63-Thidiazuron: The Photodegradation of
            Thidiazuron in Aqueous Solutions. preformed by
            Schering AG, Federal Republic of Germany,
            sponsored and submitted by NOR-AM Chemical
            Company. dated 5/23/89. received EPA 8/28/89,
            MRID # 411882-1.

III. Reviewer:

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V. Conclusions:

   EFGWB concludes this study is scientifically sound but it cannot be
used to satisfy the data requirements for the following reasons:

   1. The mercury (Hg)-arc light experiments are not acceptable
      because the spectral distribution of light is not continuous
      and, the light intensity is approximately 3.5 times greater
      than natural light.

   2. There were inconsistent light sources used between the
      photodegradation rate and photodegradate identification studies.

   3. The structural identification for photodegradates did not provide
      definitive characterization of specific compounds.

   Based on this supplemental data, thidiazuron has a short photolysis half-
life ranging from 32 to 49 min^{-1} for buffered aqueous solutions. The
identification of photolysis degradates suggest that solution pH regulated
the degradate end-product. Structural photodegradate identification show
the phenyl-urea parent compound is retained in both degradates; however,
the chemical properties were different between degradates. Based on the
results of this study, EFGWB tentatively concludes that thidiazuron will
not persist in aqueous environments exposed to natural light.

VI. Materials and Methods:

A. Hg-Arc

The photolysis experiments were conducted using a double-filtered (e.g., borosilicate and quartz filter) mercury (Hg)-arc light with an integrated light intensity of 0.91 mWatt cm^{-2} in the 290-320 nm wavelength range. Unlabelled thidiazuron buffered solutions containing 10 ug ml^{-1} thiadizuron were prepared using a 1% acetonitrile/D*H2O solvent in the appropriate buffer solutions (e.g., acetate, phosphate, and borate). The thidiazuron buffer solutions were placed in heat-treated quartz vials and exposed to light for 0, 2, 5, 10, 15, 20, 30, 40, and 60 minutes. The temperature was held nearly constant at 27+/- 2°C. After light exposure, the remaining thidiazuron in solution was determined in a MeOH/phosphate (pH=7) eluent using a HPLC (HP 1090L) equipped with a filter photomer detector set at 210 nm. The thidiazuron first-order rate constant was estimated using linear regression.

> HPLC Calibration Curve (Unlabelled thidiazuron, pH 5)
> Peak Area = 266.20 + 972.96*(thidiazuron, ug ml^{-1}) R^2=0.9995
> Range of Standards low = 1.00 ug ml^{-1}
> high = 10.00 ug ml^{-1}

> First-Order Rate Constant Estimation (Unlabelled thidiazuron, pH 5)
> LnC = 4.6163 - 0.0525*(time) R^2=0.9995

B. Quantum Yield Experiment

The photolysis half-life was calculated using quantum degradation efficiency estimates (molecules degraded/photon absorbed) in conjunction with the Hg-arc light intensity distribution. The absolute light intensity distribution for the Hg-arc lamp was measured using an actinometric procedure, 0.01 M uranylsulfate and 0.05 M oxalic acid, with a constant quantum yield of 0.56 in the 290-500nm wavelength range. Therefore, the overlap of the thidiazuron light absorption spectra and absolute light intensity provide an estimate of the photons absorbed by thidiazuron. The photolysis rate constants were calculated using a photochemical efficiency equation.

C. Computer Simulation (GCSOLAR)

Thidiazuron aqueous photolysis rates were estimated using computer generated light intensities. The simulated environmental conditions represented midseason conditions with solar declinations from +20 to -10 at latitudes of 30, 40, and 50° N. The photolysis rate constant was calculated using the quantum yield estimate (i.e., determined in the quantum yield experiment) multiplied by the rate of light absorption for thidiazuron.

D. Natural light

Buffer solutions containing 10 ug ml^{-1} unlabelled thidiazuron were placed in heat-treated quartz vials and exposed to natural light for 0, 15, 30, 60, 90 minutes. The vials were exposed to sunlight at 11:00 am on March 28, 1989 under clear skies with an integrated energy of 58.2 mWh cm^{-2}. After light exposure, the remaining thiodiazuron in solution was determined using HPLC. The rate constant was calculated assuming first-order kinetics using linear regression.

E. Degradate Determination and Material Balance

Thidiazuron photolysis degradate identification and quantification was assessed using Hg-arc irradiated radiolabelled thidiazuron solutions and HPLC reference compounds. Degradate formation was assessed as a function of time using a similar experimental procedure as described for the Hg-arc photolysis studies. The specific activity of thidiazuron was quantified using both HPLC (equipped with a variable wavelength monitor and radioactivity detector) and LSC. The quantity of thidiazuron and degradates were assessed using the initial ^{14}C solution specific activity as a 100% index. Further characterization of the degradates included degradate synthesis using Xenon irradiated thidiazuron solutions; thereafter, degradates were concentrated and purified for structural analysis with NMR/IR/MS.

Test compounds: thidiazuron unlabelled, 98.9 w/w purity; thidiazuron ^{14}C labelled at the fifth carbon of the thiadizol ring, specific activity 2.5 MBq mg^{-1}, purity 98%; thidiazuron ^{14}C-labelled [$-U-^{14}C$] attached to the phenyl group, specific activity 11.8 MBq mg^{-1}, purity 98%.

HPLC Reference Compounds: 5-amino-1,2,3 thiadiazole; N-phenyl-N'-1,2,5-thiadiazol 3-yl urea; N,N - diphenyl urea; N-phenyl urea; N-phenyl; urethane.

VII. Study Author's Results and/or Conclusions:

A. The absorption spectra of thidiazuron has maximum light absorption at a wavelength of 298nm in pH 5 and 7 buffered solutions (Figure 1). In contrast, maximum light absorption in pH 9 buffer solution occurs at 327 nm. The shift in thidiazuron spectral properties with pH was attributed to ionization (i.e., pKa=8.8).

B. The first-order rate constant for aqueous photolysis using Hg-arc irradiation was similar to natural light when corrected for light intensity differences in the wavelength range of 290-320 nm (Tables 1 and 2). The average corrected half-life of thidiazuron under Hg-arc and natural light was 37.1 and 41.8 min^{-1}, respectively.

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C. Thidiazuron was stable in the buffered solutions suggesting hydrolysis did not account for degradate formation (Table 3).

D. The average quantum-yield for thidiazuron degradation in aqueous environments is 0.075 molecules degraded photon^{-1} (Table 4).

E. The material balance using radiolabelled thidiazuron was between 100-105% (Table 5).

F. Degradate identification studies show that at least two products formed during Hg-arc light irradiation. The mass balance calculations suggest solution pH regulated the degradate formation. In slightly-acidic solutions (pH 5), the predominate degradate (i.e., 72% of the original mass) had an HPLC retention time of 16 minutes (Table 5, Figure 2). In contrast, the predominate degradate (i.e., 64% of the original mass) in neutral and alkaline solutions (pH 7 and pH 9) had a HPLC retention time of 2.5 minutes. The radioactive tracing experiments suggest both degradates retained the phenyl and fifth carbon of the thiadizol group of the parent urea compound after photolysis (Figure 3). Further identification using NMR/IR/MS suggest the degradate formed in neutral and alkaline solutions retained only the phenyl-urea parent compound.

VIII. Reviewer's Comments:

A. The Hg-arc experiments are not acceptable because the spectral distribution of light is not continuous and, the light intensity is approximately 3.5 times greater than natural light. The commonly accepted artificial light source for photolysis experiments is Xenon because it has a continuous spectral distribution of light and, the normalized photon irradiance simulates natural light over a broad wavelength range (i.e., 250-410 nm).

B. There were inconsistent light sources used between the photodegradation rate and photodegradate identification studies. The photolysis rate experiments were conducted under Hg-arc light and natural light; however, the degradate identification experiment was conducted under a Xenon light source. There should be a consistent light source (e.g., natural light or Xenon lamp) used for both the photolysis rate and degradate identification experiments.

C. The exact structural identification is necessary for photodegradates exceeding 10% of the mass balance. The photodegradates , representing HPLC peak 1 and 3, are only partially identified as retaining the parent urea-phenyl compound.

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D. Photolysis half-life estimates calculated from computer generated light intensities (i.e., GCSOLAR) are not accepted _in lieu_ of experimental results. Therefore, model simulations are considered strictly supplemental and cannot be used in the data evaluation review.

IX. CBI Appendix