DATA EVALUATION RECORD

CASE GS   PROMETRYN   STUDY 8   PM   25

CHEM   080805

BRANCH: ENVIRONMENTAL FATE AND GROUND-WATER

FORMULATION 00 - ACTIVE INGREDIENT

Saxena, A.M. 1987. Determination of the Volatility of Prometryn
From CAPAROL 4L. Study No. 1073. Conducted by Colorado
Analytical Research and Development Corporation. Submitted by
Ciba-Geigy Corporation. Accession Number 405737-14.

DIRECT RVW TIME = 1 day

REVIEWED BY: R.C. DOYLE
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SIGNATURE:
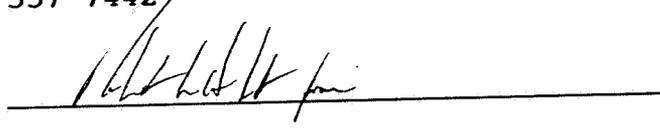
CONCLUSIONS:

     The scientific validity of this study cannot be demonstrated
in the present submission. Estimates of prometryn volatilization
from soil may be underestimated because of inadequate trapping
procedures. The submission lacks information to fully evaluate
all procedures. The study is unacceptable to meet the
requirements to register pesticides (Subdivision N Guidelines
Section 163-2).

MATERIALS AND METHODS:

     Two laboratory volatility tests were conducted: one using
technical grade uniformly ring labeled ^{14}C-prometryn (supplied by
Ciba-Geigy Corporation, 97.2% radiochemical purity, 6.5 x 10^{10}
dpm/gram; the second using Caparol 4L (43.7% prometryn). A
California sandy loam soil (61% sand, 31% silt, 8% clay, 0.36%
organic matter, pH 4.33, 27.77% moisture at field capacity, 4.1
meq/100 g CEC) was used for both studies. The studies were
conducted in aeration chambers (12" x 12" x 12"), material not

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specified. The chambers were fitted with an intake and an exhaust port, through which perforated pipe (nominally 2.5 cm in diameter) extended into the chamber. The pipes were positioned at a height of approximately 23 cm, on opposite walls of the chamber, offset from each other by approximately 6.5 cm. Outflow from the chamber passed through two ethylene glycol traps and then through a 10% sodium hydroxide trap.

The preliminary study was conducted by spraying an acetonitrile solution of ^{14}C-prometryn (90% nonradiolabeled mixed with 10% radiolabeled) onto an 11.25 x 11.25-inch surface of soil ((1-inch thick, sieved to pass 2 mm) at a rate equivalent to 3.2 lb ai/acre. Plastic-backed paper was used to line the chamber during the aerosol application to prevent contamination of non-soil surfaces. Testing with dry soil (0% moisture) was conducted at 25°C and 55°C with air flow rates of 15 and 30 l/hr. Volatile losses from moist soil (75% of field capacity) were measured at 40°C with an air flow rate of 30 l/hr. Aliquots of the ethylene glycol and NaOH traps were analyzed by radiochemistry techniques at 1, 3, 6, 8, and 24 hours. Ten samples of treated soil were analyzed by combustion and radiochemical analysis.

In the definitive study, Caparol 4L was applied as in the preliminary study. Volatilization from dry soil (97% of field capacity) was measured at 25°C and 55° with air flow rates of 15 and 30 l/hr. Measurements were made with moist soil at 6.94 and 20.83% of field capacity. The air flow and temperature were held at 15 l/hr and 25°C for these measurements. After 24 hours, 5-ml aliquots of each ethylene glycop trap was diluted in water. Prometryn in each sample was sorbed to a C-18 Sep-Pak and then eluted off with acetonitrile. The acetonitrile was volatilized off (rotary evaporation at 35°C) and the residue was taken up in 2 ml of ethyl acetate. Prometryn in the ethyl acetate was quantified by gas chromatography (GC) with a nitrogen detector. All data were corrected for recovery as determined using a fortified control.

RESULTS:

Data from the preliminary study are summarized in Table 1. Volatile losses appear low. The total number of micrograms of prometryn trapped within sampling was less than 0.12 ug (with one exception of 0.57 ug during the 8-hour samples of the moist soil. Accumulation of radioactivity in the NaOH trap was also low (< 0.009% of applied ^{14}C, reviewer's calculation). Recovery of total radioactivity from treated soil indicated that the average quantity of prometryn applied was 67.2 mg (102.8% of intended application).

Results of the definitive study are presented in Table 2. Average rates of prometryn volatilization over a 24-hour period were low, < 10.97 ug/cm^2/hr. In all samples, prometryn was found in both ethylene glycol traps. Recovery of prometryn from spiked

controls ranged from 58.1 to 193.0% (8 samples) with an average of 115.9± 43.3%. Using a ^{14}C-prometryn spike, a recovery of 91.2% was obtained.

AUTHOR'S CONCLUSIONS

The volatility of ^{14}C-prometryn (technical) and its formulated product, Caparol 4L, is low. Volatility of Caparol 4L, based on the average quantity of prometryn found in the ethylene glycol traps over all treatments, is of the order of magnitude of 1.19 x 10^{-2} ug/cc/hour/acre. Variation in temperature, air flow, and soil moisture did not effect volatilization.

The recovery data from spiked controls demonstrated the validity of the analytical methodology.

REVIEWER'S DISCUSSION

Insufficient information has been submitted to completely evaluate this study. The description of radiation counting techniques was not adequate. The following information on liquid scintillation counting must be reported: method of quench correction, calibration (quench) curve(s), method and date(s) of calibration, and sample calculations. No counting data (counts per minute, disintegrations per minute (DPM), typical counting times, and quench measuring values such as H number, internal standard, channels ratio, etc.) were submitted. At a minimum, representative data are necessary for EFGWB to estimate the reliability of these data.

Sample calculations and data for making up test solutions were not submitted. Sample calculations for converting DPM to ug of prometryn were not submitted. The quantities of prometryn (non-radioactive) found in the ethylene glycol traps were not reported and the calculations used to determine the rates of prometryn volatilization (the only data reported for the definitive study) were not explained. All of this information is required.

It was reported that 65.4 mg applied to an 11.25- by 11.25- inch surface of soil was equivalent to 3.2 lb/acre. This is incorrect as shown below:

$$11.25 \times 11.25 = 126.6 \text{ in}^2$$
$$126.6 \text{ in}^2/6272640 \text{ in}^2/\text{acre} = 2.018 \times 10^{-5} \text{ acre}$$
$$3.2 \text{ lb/acre} \times 2.018 \times 10^{-5} \text{ acre} = 6.46 \times 10^{-5} \text{ lb}$$
$$6.46 \times 10^{-5} \text{ lb} \times (453.6 \times 10^{3} \text{ mg/lb}) = 29.3 \text{ mg}$$
$$29.3 \text{ mg/11.25 in} \times 11.25 \text{ in} = 3.2 \text{ lb/acre}$$

It cannot be determined by EFGWB if the rate of prometryn application and/or the quantity of prometryn applied is correct.

Recovery data for the GC determination of prometryn was highly variable, recovery ranging from 58.1 to 193.0%. Recovery data and other QC data for the combustion of ^{14}C were not reported.

A substantial quantity of prometryn was found in the second ethylene glycol trap in all samples were volatilization was apparent. In some samples, more prometryn was found in the second trap than in the first trap. This strongly suggests that the traps may not have collected all of the volatile prometryn that passed through them. No trapping efficiency data were submitted, nor was a material balance determined. Therefore, it is possible that the reported data significantly underestimate the volatilization of prometryn from soil. The scientific validity of this study is questionable.

Table 1. Initial Preliminary Volatility Studies of ^{14}C-Prometryn from Sandy Loam Soil Surfaces

Temperature	Air Flow Rate	% FMC[1]	Elapsed Time	Total Micrograms of Equivalent Prometryn Found by Radioanalysis		
				First Ethylene Glycol Trap	Second Ethylene Glycol Trap	10% NaOH CO_2 Trap
25°	15 Liters/ hour	0	1 hour	0.0000	0.0000	0.5851
			3 hours	0.0610	0.0000	0.6119
			6 hours	0.0000	0.0000	0.6464
			8 hours	0.0569	0.0338	0.8657
			72 hours	0.0000	0.0000	0.3628
25°	30 Liters/ hour	0	1 hour	0.0000	0.0000	0.2352
			3 hours	0.0000	0.0000	0.1844
			6 hours	0.0000	0.0000	0.2140
			8 hours	0.0000	0.0000	0.1416
			24 hours	0.0567	0.0000	0.3149
55°	15 Liters/ hour	0	1 hour	0.0000	0.0000	0.1335
			3 hours	0.0000	0.0000	0.0854
			6 hours	0.0000	0.0000	0.0920
			8 hours	0.0000	0.0000	0.0430
			24 hours	0.0000	0.0000	0.2134
55°	30 Liters/ hour	0	1 hour	0.0364	0.0283	0.3520
			3 hours	0.0437	0.0297	0.3426
			6 hours	0.0134	0.0193	0.3204
			8 hours	0.0347	0.0280	0.5135
			24 hours	0.0000	0.0000	0.2845
40°	30 Liters/ hour	75	1 hour	0.0543	0.0615	0.4802
			3 hours	0.0096	0.0372	0.4310
			6 hours	0.0548	0.0712	0.4639
			8 hours	0.3710	0.1984	0.5239
			24 hours	0.0000	0.0000	0.6923

[1] FMC = field moisture capacity

Table 2. Determination of Volatility of Prometryn Caparol 4L Treated Soil

Volatility of Prometryn
Expressed as micrograms/cc/hour

Temperature	Air Flow Rate	Field Moisture Capacity (FMC)[1]	Rep	First Ethylene Glycol Trap	Second Ethylene Glycol Trap	Total Ethylene Glycol Traps[2]
$25°$	15 L/hr.	Dry, 0.97%	1	3.50×10^{-7}	1.42×10^{-7}	4.92×10^{-7}
			2	8.61×10^{-8}	2.08×10^{-7}	2.94×10^{-7}
			average	2.18×10^{-7}	1.75×10^{-7}	3.93×10^{-7}
$25°$	30 L/hr.	Dry, 0.97%	1	4.86×10^{-8}	6.53×10^{-8}	1.14×10^{-7}
			2	4.31×10^{-8}	1.94×10^{-8}	6.25×10^{-8}
			average	4.58×10^{-8}	4.24×10^{-8}	8.82×10^{-8}
$55°$	15 L/hr.	Dry, 0.97%	1	5.56×10^{-8}	4.72×10^{-8}	1.03×10^{-7}
			2	9.17×10^{-8}	2.50×10^{-8}	1.17×10^{-7}
			average	7.36×10^{-8}	3.61×10^{-8}	1.10×10^{-7}
$55°$	30 L/hr.	Dry, 0.97%	1	1.88×10^{-7}	1.19×10^{-7}	3.07×10^{-7}
			2	1.32×10^{-7}	1.47×10^{-7}	2.79×10^{-7}
			average	1.60×10^{-7}	1.33×10^{-7}	2.93×10^{-7}
$25°$	15 L/hr.	25%FMC,6.94%	1	3.58×10^{-7}	3.75×10^{-7}	7.33×10^{-7}
			2	4.89×10^{-7}	8.44×10^{-7}	1.33×10^{-6}
			average	4.24×10^{-7}	6.10×10^{-7}	1.03×10^{-6}
$25°$	15 L/hr.	75%FMC,20.83%	1	3.75×10^{-7}	4.00×10^{-7}	7.75×10^{-7}
			2	2.72×10^{-7}	8.67×10^{-7}	1.14×10^{-7}
			average	3.24×10^{-7}	6.33×10^{-7}	4.94×10^{-7}

1 FMC = field moisture capacity

2 Calculated by reviewer