Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Diuron

MRID #: 417193-05

Matrix: Soil

Analysis: HPLC/UV

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ANALYTICAL METHODS

Reference Standards

Reference standards of diuron and DCPMU were obtained from Agricultural Products, E. I. du Pont de Nemours and Company, Wilmington, Del. The diuron standard (IN-14740; Lot #149) was 99.6% chemically pure, and the DCPMU standard (IN-15654; Lot #12) was 99.0% chemically pure. Stock solutions of the reference standards were prepared in methanol; the HPLC analytical standards were prepared from these stock solutions in acetonitrile/water (3:7).

Extraction and Analysis of Soil Samples

The extraction and analysis of soil samples at Enviro-Test Laboratories were performed according to the U.S. EPA Good Laboratory Practice regulations. Storage, preparation, extraction, and analyses were conducted by Enviro-Test personnel.

Portions (*ca.* 50 g) of air-dried homogenized soil were shaken for ~30 min in methanol with a wrist-action shaker. The mixtures were centrifuged to sediment the solids, and the supernatant fluids were decanted. The extraction was repeated, and the two extracts from each sample were combined and concentrated to near dryness (rotary evaporation, *ca.* 42°C). The concentrate was quantitatively transferred to a separatory funnel, diluted with water, and extracted two times with methylene chloride. The methylene chloride extracts were dried by passage through Na_2SO_4 and evaporated to dryness. The residues were dissolved in

5 mL of acetonitrile/water (3:7). Aliquots (500 µL) of these solutions were filtered (Millipore, 0.45 um) and analyzed by HPLC.

The chromatographic conditions used were as follows:

Instrument:	Varian 5500 Liquid Chromatograph with Spectra Physics 4290 integrator
	or
	Waters 600A Liquid Chromatograph with Hewlett Packard 3388A integrator
Column:	Zorbax Rx, 4.6 x 250 mm, 5 µm
	or
	Supelco C18, 4.6 x 250 mm, 5 µm
Temperature:	Ambient or 35°C
Typical Mobile Phases:	Acetonitrile/water:30/70
	or
	Acetonitrile/water:32/68
Flow Rate:	1.2 mL/min
Sample Volume:	50 - 100 µL
Wavelength:	254 nm
Chart Speed:	0.25 cm/min
Retention times:	DCPMU: *ca.* 16 min; diuron: *ca.* 21 min (the retention times varied slightly, depending on the conditions).

Sample chromatograms are presented in Appendix III.

Calculation of Sample Residues

Standard curves based on peak response (in thousands) were constructed by analyzing suitable concentrations of standards containing diuron and DCPMU. The amount of diuron or DCPMU residue was calculated using the following equation:

$$\text{ppm of diuron or DCPMU} = \frac{\text{peak response} \times \text{avg. R.F.}}{\text{injection volume (mL)}} \times \frac{V}{W}$$

where

peak response	=	peak response of analyte in either area or height
avg. R.F.	=	average response factor (the sum of the response factors divided by the number of determinations)
R.F.	=	response factor (the concentration of the standard/peak height of standard)
V	=	total volume (in mL) of sample solution
W	=	sample weight (in g)

Residue values in the control and treated samples were expressed in parts per million (ppm). The quantitation limit of this method is 0.01 ppm for both diuron and DCPMU, based on a 50-g sample.

Protocol Deviations

Additional samples were taken of Day 418 and Day 538 at the Newark, Delaware site and on Day 415 at the Madera, California site.

Ninety-centimeter samples were taken on Days 210, 243, 299, 359, and 418 at Newark, Delaware.

An equipment breakdown shortly before application at the Madera, California site resulted in pretreatment samples being taken at -19 days rather than -1 day.

None of these deviations had a significant effect on the study results.

RESULTS AND DISCUSSION

Analyses of Soil Samples

Analytical results for the soil samples by depth and PHI are presented in Tables IV (Newark, Delaware) and V (Madera, California). A summary of the residues in the total soil column are presented in Tables VI (Newark, Delaware) and VII (Madera, California).

Recovery data for diuron and DCPMU analyses are provided in Tables VIII and IX, respectively. The average recoveries were:

Diuron: 87% (S.D. = ±15)

DCPMU: 85% (S.D. = ±15)

Dissipation of Diuron

The half-life of diuron was calculated from the equation

$$t_{\frac{1}{2}} = \frac{0.693}{-k}$$

where k is the rate constant in days^{-1}. The rate constant is the slope of the straight line that results by plotting the ln of the diuron concentration vs. time and subjecting the plot to least-squares regression analysis (Figures 1 and 2). The concentration of diuron in the soil at each sampling time was calculated by summing the means of the diuron concentrations at the

various depths (for some segments there was only one determination, but in others there were two or three; Tables IV and V).

The rate constants and half-lives are as follows:

Site	Rate Constant days^{-1}	Half-Life (days)
Newark, Delaware	-5.169×10^{-3}	134
Madera, California	-6.774×10^{-3}	102

Diuron was degraded much faster in this field dissipation study than in the aerobic soil metabolism study (Reference 1), in which the calculated half-life was 372 days. The aerobic soil metabolism study was conducted in the dark at 25°C. The rate of diuron degradation is affected by soil temperature, sunlight, and microbial action. In the field, the degradation of diuron is hastened by higher average temperatures and the photolytic effect of sunlight.

Diuron is degraded slightly faster at Madera, California than at Newark, Delaware. Ambient soil temperature at Madera is, on average, higher than at Newark.

Mobility of Diuron in Soil

Diuron appeared to be present in the deeper segments for the first 14 days in Delaware soil (Table IV) and for the first 89 days in California soil (Table V). However, this is probably due to contamination of the lower depths by the sampling probe; it is difficult to imagine how diuron (which is of low mobility or immobile in soil) could have penetrated 45-60 cm

of soil only a few hours after application. It was not found in the lower soil segments at later times, probably because the contaminating concentrations dropped below the limit of quantitation.

Apart from these sampling artifacts, diuron remained in the upper 15 cm of soil at both sites, with only rare penetration below that (Figures 3 and 4).

The Rise and Fall of DCPMU

The total concentration of DCPMU was calculated by summing the DCPMU concentrations at various depths for each sampling time.

In Newark, Delaware, the total DCPMU concentration rose gradually to a maximum of *ca.* 0.3 ppm by Day 300, then declined to *ca.* 0.1 ppm by Day 418 (Table IV).

In Madera, California, the total DCPMU concentration rose gradually and irregularly to a maximum (*ca.* 0.335 ppm) by Day 219, then gradually declined to less than 0.10 ppm by Day 358 (Table V).

In the aerobic soil metabolism study of diuron (Reference 1), the concentration of DCPMU rose gradually over the life of the study. However, in this field study, DCPMU was degraded faster, perhaps due to higher average temperatures and sunlight. The results of this study show that DPCMU does not accumulate in the soil under field conditions.

Mobility of DCPMU in Soil

DCPMU was found consistently in the upper 15 cm of soil, with occasional presence in the 15- to 30-cm segment (Tables IV and V; Figures 5 and 6). The presence of DCPMU at lower depths in the early

samples from Newark, Delaware were most likely due to contamination during sampling.

CONCLUSIONS

Diuron, the active ingredient of Karmex® DF Herbicide, dissipates in the field with a half-life of 134 days in silty clay loam at Newark, Delaware and 102 days in sandy loam at Madera, California. Its mobility is low; all of the applied diuron remained in the top 15 cm of soil at both sites.

The concentration of DCPMU (the principal degradate of diuron) rose to a maximum of *ca.* 0.3 ppm in 220-300 days, then declined to less than 0.1 ppm by 300 days (Delaware) and 418 days (California). It also is of low mobility; it was not found consistently below the top 15 cm at either site.