

STANDARD OPERATING PROCEDURE

Calculation of Pesticide Half-life from a Terrestrial Field Dissipation Study

KEY WORDS

Linear regression, TFD, mass, first order decay

APPROVALS

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1.0 INTRODUCTION

For pesticide products being registered in California, the Department of Pesticide (DPR) characterizes various physical-chemical properties of the products' active ingredients (A.I.s). Terrestrial field dissipation (TFD) half-life is one property that is characterized. The half-life of a substance is defined as the time it takes for a substance to decrease its amount by half. Of the various methods for determining a half-life of an A.I., DPR has adopted the method described by Johnson et al. (1992). However, a lack of specificity in data preparation prior to the half-life calculation has resulted in inconsistency in the determination of TFD half-life values.

Current DPR procedure, as specified by Johnson et al. (1992), utilizes the first order decay function:

$$\text{Eq. 1} \quad Y = A \times e^{-kt}$$

Where:

Y= amount of pesticide at time=t, mg/m²

A = initial amount of pesticide, mg/m²

k = dissipation rate constant, days⁻¹

t = time, days

Note that *k* is taken to be positive and Eq. 1 explicitly uses a negative sign in order to represent the loss rate. The remaining problem is to find *k*, the dissipation rate constant. In order to find *k*, perform a natural log transformation on Eq. 1, which yields:

$$\text{Eq. 2} \quad \ln(Y) = \ln(A) - kt$$

A linear regression of ln (Y) on t can now be used to estimate *k*. With an estimate for *k*, the half-life (days) can be calculated by setting $y=0.5A$ in Eq. 1 and then solving for *t*. After taking the natural log of both sides, and rearranging, the result is [Eq. 4](#). Eq. 4 is then used to estimate the terrestrial field dissipation half-life of the pesticide.

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1.1 Purpose

The purpose of this document is to standardize the calculation of a terrestrial field dissipation half-life, using a first-order decay function.

1.2 Definitions

- 1.2.1 DAFT- Days After Final Treatment: The time interval between sampling event and date of pesticide application.
- 1.2.2 MDL- Method Detection Limit: The lowest concentration of a substance that a method of analysis can quantify reliably.
- 1.2.3 ND- Nondetect: No pesticide residue was found in an analyzed soil sample at detectable levels.

2.0 MATERIALS TFD STUDY

- 2.1 Computer program capable of performing a regression using least squares methodology (SAS, Minitab, etc.)

3.0 PROCEDURES

3.1 Unit Conversions

- 3.1.1 Convert all concentrations to mg/kg (ppm), if they are not already reported as such.
 - 3.1.1.1 Concentrations must be reported on a dry soil-weight basis. See SOP METH006.00 for more information.
- 3.1.2 Convert all soil core segment lengths into meters. A 6 in. long segment is equivalent to 0.1524 m.
- 3.1.3 Convert residue data from a mass per dry soil-weight basis to a mass per surface area basis for each segment in the soil column; mg/kg to mg/m². See [Eq. 3](#).

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3.2 Data Aggregation

3.2.1 At each sampling event in the TFD study, sum all residues in the soil column.

3.2.1.1 If the residue in a soil core is below the detection limit, then treat it as zero for purposes of summation.

3.2.2 Determine the natural log of the total residue mass of the soil column at each sampling event.

3.2.2.1 If a study has multiple replications during each sampling event, see section [5.1: Field Subdivided into Blocks](#).

3.3 Linear Regression

3.3.1 Perform linear regression on the natural log-transformed residues. The natural log-transformed total residue mass is the y-axis variable and the corresponding sampling event, as DAFT, is the x-axis variable.

3.3.1.1 Record the p-value of the regression slope and indicate its significance at $P \leq 0.05$.

Figure 1: Regression Performed with Statistical Software
(Data used in this regression is located in Table 2, column "Average ln")

Regression Analysis: Residues versus DAFT				
The regression equation is				
$Y = 4.61 - 0.00609 X$				
Predictor	Coeff	SE Coeff	T Stat	P-value
Intercept	4.61275	0.07126	64.73	0.00
Slope	-0.00609	0.0002847	-21.38	0.00
R-Squared=0.96				

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3.3.1.2 The coefficient of the predictor variable Slope in Fig. 1(-0.00609) is the slope of the regression line and is equal to k, the dissipation rate constant.

3.3.1.3 The R-Squared value in Fig.1 is 0.96. Values approaching 1.0 indicate a better fit to the regression model.

3.3.1.4 The p-value for the slope should be equal to or less than 0.05, indicating a statistically significant regression, and thus giving some confidence in the model.

3.3.2 Convert the rate constant into a half-life value. The units are consistent with those used for the x-axis variable and are typically in days. See [Eq. 4](#).

4.0 CALCULATIONS

4.1 Preliminary Calculations

This conversion addresses problems associated with calculating half-lives on a concentration basis by accounting for the in-field variation of bulk density and differences in soil segment length between samples. Pesticide residues in each soil segment are converted from a concentration value to a mass per surface area value.

4.1.1 Eq. 3
$$M = C \times \rho \times l \times F$$

Where

M = mass of pesticide residue on an area basis, mg/m²

C = concentration of pesticide residue, mg/kg (ppm by dry weight)

ρ = bulk density of soil segment, kg/dm³ (g/cm³)

l = length of soil segment, m

F = scaling factor, 1000 dm³/m³

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4.2 Conversion of Rate Constant to Half-Life

4.2.1 Eq. 4
$$t_{1/2} = \frac{\ln(0.5)}{k}$$

Where

$t_{1/2}$ = half-life of pesticide, days

k = dissipation rate constant, days⁻¹

5.0 STUDY-SPECIFIC CONSIDERATIONS

5.1 Field Subdivided into Blocks

5.1.1 Studies often divide the field into different blocks and report the resulting residues from each block separately. Ensure residue mass is summed from soil columns *within* the block at each sampling time, not amongst the blocks (Table 1).

DAFT	Block A				Block B				Block C				Block D			
	0-6"	6-12"	12-18"	Sum	0-6"	6-12"	12-18"	Sum	0-6"	6-12"	12-18"	Sum	0-6"	6-12"	12-18"	Sum
0	159.7			159.7	154.5			154.5	127.3			127.3	158.5			158.5
3	125.8			125.8	86.5			86.5	120.9			120.9	174.7	2.4		177.1
7	158			158	104.6			104.6	112.9			112.9	89.3			89.3
14	92.6			92.6	67			67	92.1			92.1	56			56
21	91.4			91.4	83.2			83.2	98			98	71.8	2.7		74.5
28	82.5		3.3	85.8	103.3			103.3	66.4			66.4	72.3			72.3
59	79.5	2.3		81.8	52.3			52.3	56.2	8.7		64.9	45.3	4.3		49.6
89	44.9	6.3		51.2	37.3	4.4		41.7	42.2	6.3		48.5	41.8	5.5		47.3
119	23.8	8.2	2.1	34.1	28	4.3		32.3	45.2	4.8		50	34.4	6		40.4
150	31.7	5.8		37.5	25.3	7.6		32.9	32.3	5.2		37.5	24.6			24.6
180	21.7	5		26.7	23.8	5.7		29.5	23.2	3.5		26.7	24.4	4		28.4
243	27.2	7.2		34.4	17.5	6.4		23.9	20.2	4.5	3.6	28.3	12.7	6.8	2.9	22.4
300	16	5.5	2.8	24.3	17.7	5	2.8	25.5	16.5	6.1		22.6	12.7	2.6		15.3
361	11.7	2.3		14	10.7			10.7	15.7	2		17.7	13.2			13.2
421	7.9			7.9	5.5			5.5	9.7		2.9	12.6	7			7
486	4			4	4.2			4.2	10.8			10.8	3.8			3.8
539	3			3	2.5			2.5	3			3	5.7			5.7

Table 1: Aggregation of Residues (mg/m²) by Block. In this table, concentrations have already been converted to mass per unit area using Eq. 3

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- 5.1.2 At each sampling time, the summed residue mass in each soil column of each block must be log-transformed individually (Table 2). If the study has 4 blocks, then there are 4 values per sampling event to log transform.
- 5.1.3 Average the natural log-transformed residues of all blocks to get only one value for each sampling time. The bold values in Table 2, in the column labeled “Average ln”, are regressed against DAFT in the first column of Table 2. For blocks with nondetects, see [5.2](#).

DAFT	ln(Block A)	ln(Block B)	ln(Block C)	ln(Block D)	Average ln
0	5.07	5.04	4.85	5.07	5.01
3	4.83	4.46	4.79	5.18	4.82
7	5.06	4.65	4.73	4.49	4.73
14	4.53	4.20	4.52	4.03	4.32
21	4.52	4.42	4.58	4.31	4.46
28	4.45	4.64	4.20	4.28	4.39
59	4.40	3.96	4.17	3.90	4.11
89	3.94	3.73	3.88	3.86	3.85
119	3.53	3.48	3.91	3.70	3.65
150	3.62	3.49	3.62	3.20	3.49
180	3.28	3.38	3.28	3.35	3.33
243	3.54	3.17	3.34	3.11	3.29
300	3.19	3.24	3.12	2.73	3.07
361	2.64	2.37	2.87	2.58	2.62
421	2.07	1.70	2.53	1.95	2.06
486	1.39	1.44	2.38	1.34	1.63
539	1.10	0.92	1.10	1.74	1.21

Table 2: Transformation and Averaging of Data. For example, 5.07 is the transformed sum from Block A of Table 1 at DAFT=0 [5.07=ln (159.7)].

5.2 Nondetects and Uneven Sampling Times (“1/2 MDL Rule”)

- 5.2.1 For studies with multiple blocks, ensure that all the blocks have residue values ending at the same final sampling time. If the blocks have residue values ending at different sampling times, then follow the procedure below.
 - 5.2.1.1 First, identify the block or blocks with the last measurable residue value. This will dictate the number of sampling times to be used in the determination of the half-life.

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5.2.1.2 Next, replace earlier nondetects (NDs) in the remaining blocks with residue values (see below) until all the blocks end at the same final sampling time.

5.2.1.2.1 Assign $\frac{1}{2}$ MDL for the first (earliest) ND, $\frac{1}{4}$ MDL for the next ND, $\frac{1}{8}$ MDL for the next ND, etc.

DAFT	Block A	Block B	Block C
0	35	37	40
1	30	29	25
2	15	12	10
5	10	7	6
10	5	7	2
20	2	2	ND
30	ND	1	ND
50	ND	ND	ND
70	ND	ND	ND

→

DAFT	Block A	Block B	Block C
0	35	37	40
1	30	29	25
2	15	12	10
5	10	7	6
10	5	7	2
20	2	2	0.5
30	0.5	1	0.25
50	-	-	-
70	-	-	-

Table 3: Raw Data from Registrant (ppm)

Table 4: Data after “1/2 MDL Rule” (ppm)

5.2.1.3 Table 3 shows the raw data as presented by the registrant. Table 4 shows the raw data transformed by the “1/2 MDL Rule” (MDL=1 ppm). Block B has the last measurable residue detection (DAFT 30). Blocks A and C have successive fractions of the MDL added until they have the same number of data points as Block B, all ending at DAFT 30. Then follow section 4.1 to convert the concentrations to a mass and then [5.1.2](#) to complete the regression.

5.3 Biphasic Degradation

5.3.1 It sometimes appears that dissipation proceeds at two different rates over the course of a study: often an initial fast rate followed by a slow rate.

5.3.2 DPR policy will be to use all of the data when performing the linear regression, unless there is a good reason to omit some data points. This provides a consistent way to compare the dissipation rates of different pesticides.

5.3.2.1 A good reason to omit data points would be something going wrong with the experiment itself.

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5.4 Multiple Applications

5.4.1 If multiple pesticide applications are made to a TFD study, then linear regression should only be conducted on residue data measured after the final pesticide application.

5.4.1.1 Example: Pesticide in a TFD study is applied 3 times at 30 day intervals to the same site. The DAFT starts after the third application.

5.4.1.2 Note in any write-up or summary that multiple applications to a site occurred during the TFD study.

5.5 Missing Data Needed for Mass Conversion

5.5.1 Sometimes soil bulk density is omitted from TFD reports, making it impossible to convert pesticide concentration values into mass per surface area values.

5.5.1.1 Soil bulk density can be estimated from soil texture, organic matter content and the degree of soil compaction by utilizing the empirical equations from Saxton and Rawls (2006). These equations are in the “Soil Water Characteristics” calculator, which can be used to estimate soil bulk density. The calculator is located at:
<https://www.ars.usda.gov/research/software/download/?softwareid=492&modecode=80-42-05-10%20?#downloadForm>

5.5.2 TFD turf studies often omit bulk density data for the thatch layer. However, pesticide concentrations can be converted to a mass per surface area basis if the study provides the weight and the surface area of the thatch sample. See [Eq. 5](#).

5.5.2.1 Eq. 5
$$M = \frac{C \times W}{A}$$

Where

M = mass of pesticide residue on an area basis, mg/m²

C = concentration of pesticide residue in thatch, mg/kg

W = weight of thatch, kg

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A = surface area of thatch, m²

5.5.2.2 If all descriptive information on the thatch layer is missing, then you may use the thatch parameters from the PRZM turf scenarios (U.S. EPA, 2006).

5.5.2.2.1 Bulk Density = 0.37 g/cm³; Turf Thickness = 2 cm

6.0 REFERENCES

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