

Nonlinear Pesticide Dissipation in Soil: A New Model Based on Spatial Variability

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■ In both laboratory and field studies, the dissipation of pesticides in soil often fails to follow simple first-order reaction kinetics. Rather than being linear when plotted as $\ln C$ versus time, the dissipation data are curved, typically concave upward. This nonlinear behavior has now been described successfully through the use of a new first-order, nonlinear kinetic model. The nonlinear model is based on the assumption of a spatially variable first-order rate constant, and it reduces to the linear case when the rate constant is spatially uniform. Excellent fits to both laboratory and field data are obtained for all pesticides modeled. Interestingly, the relative variability found for the rate constant is similar for laboratory and field studies, suggesting that the length scale of the spatial variability is very small, possibly on the order of pore-size dimensions.

Introduction

Soils are heterogeneous (1-6). In spite of this, most theoretical descriptions of pesticide dissipation kinetics in soil have relied upon models that assume some degree of homogeneity (7-16). This fundamental discrepancy may be responsible for the general failure of these models to adequately characterize observed dissipation curves (17-19). We take a new approach in this paper and show, by explicitly acknowledging the heterogeneity or spatial variability of soil, that one can derive a simple, nonlinear, first-order kinetic model of pesticide dissipation giving excellent fits to observed data.

As used in this paper, the term dissipation refers to the group of processes that reduces the concentration (e.g., percent remaining or pounds/acre) of a pesticide following its application to a laboratory aliquot of soil or an experiment field plot. As such, it includes a host of biological,

chemical, and physical phenomena that are in turn dependent on a number of soil, environmental, and cultural factors. Processes most often associated with dissipation are microbial degradation, chemical hydrolysis, volatilization, runoff, wind erosion and photolysis (7, 12). Factors affecting the rates of these processes include microbial population density, temperature, amount and intensity of precipitation, solar intensity, soil properties (moisture, organic matter, texture, sorptive capacity), tillage, and cropping practices (7, 12). Several of these processes and factors are either unimportant, controllable, or ignored in laboratory studies, but all play a role in field studies to some degree.

All of the factors affecting dissipation rates are spatially variable to some degree (1-6). For instance, the spatial variations in temperature across a newly planted cornfield are generally moderate, but the soil organic matter content can vary by at least an order of magnitude (1, 20). Certainly at the microscopic level (where most dissipative processes occur) there are large variations in water content and soil sorptive capacity as different size soil pores are encountered (1). If the applied pesticide were able to diffuse readily throughout the entire treated field or laboratory beaker, such spatial variability would not be as critical because the system would behave more like a single, well-mixed reactor. However, diffusion rates in soil are notoriously slow for all but the most volatile of pesticides (21), and the applied material is thereby confined to rather small regions of soil, which may be very different from others only a short distance away.

Given the apparent complexity of dissipation, it is reasonable to question whether any single model could adequately characterize its rate in a quantitative manner. In fact, in a recent U.S. Environmental Protection Agency (EPA) document (17) it is stated that "it is doubtful that any single rate equation will ever be found which is applicable to all or most pesticides in soil". This caveat does

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dissipation of most pesticides from soils can be considered as following a first-order reaction at least over a portion of the degradation curve". Regulatory agencies such as the U.S. EPA have dual needs for an accurate kinetic model of dissipation curves:

(1) Some form of dissipation kinetics must be assumed in order to model pesticide fate and transport in the environment, such as in PRZM (a leaching model) (22) or HSPF (a runoff model) (23).

(2) The kinetic model, if it fits, allows estimates of "benchmark" dissipation times, such as the periods required for 50% or 90% of the applied material to dissipate (generally known as DT_{50} or DT_{90} , respectively).

These benchmark dissipation times are finding increasing use in screening procedures for the assessment of leachability or other undesirable environmental properties (24, 25). As extensively discussed in the literature (17-19), the dissipation model of most widespread use (linear, first-order kinetics) is often inadequate for the purpose of estimating DT_{50} and DT_{90} , because the assumption of linearity is generally violated to a wide degree by the time 90% of the material has dissipated.

The effect of spatial variability on pesticide fate has been widely discussed in the literature as it affects sampling requirements (5), sorption (20), and transport (2). Thus far, however, no one has described the nonlinear effects of spatial variability on dissipation kinetics—the subject of this paper. We will show that acknowledgment of spatial variability in the dissipation process leads directly to a simple nonlinear model that gives excellent fits to both laboratory and field dissipation data. The new model allows reliable estimates to be made of DT_{50} , DT_{90} , and any other aspects of the dissipation curve. Its use in environmental fate models would undoubtedly lead to improved predictions of fate and transport.

Theory

The new kinetic model is outlined in this section by first describing the traditional linear, first-order model and then discussing the various "compartmental" models that have been used. A shift in paradigm is then accomplished by considering an infinite-compartment model to be representative of spatial variability of the dissipation process. In the equations that follow, the concentration of the pesticide (generally expressed as percent remaining or pounds/acre) is considered a function of time and is denoted by $C = C(t)$. The theory pertains only to the dissipation of the parent compound and does not consider subsequent metabolite formation and decline.

Linear First-Order Model. A first-order reaction model is commonly used to describe dissipation kinetics (7-16). The model is defined by the relation

$$dC/dt = -kC \quad (1)$$

in which the time derivative of the concentration, dC/dt , is directly proportional to the concentration. The proportionality coefficient, k , is usually termed the first-order reaction rate constant. Reaction models of order other than 1 have sometimes found empirical use due to an improved fit with experimental data. In particular, Timme et al. (10) showed that models based on 1.5- and 2-order kinetics and/or a square root of time transformation often yield significantly better fits to dissipation data. However, such models have no sound theoretical basis because all known dissipation reactions are unimolecular with respect to the pesticide (at least at the very dilute levels typically found in the environment). The rare exceptions to this rule of unimolecularity are certain less important physical

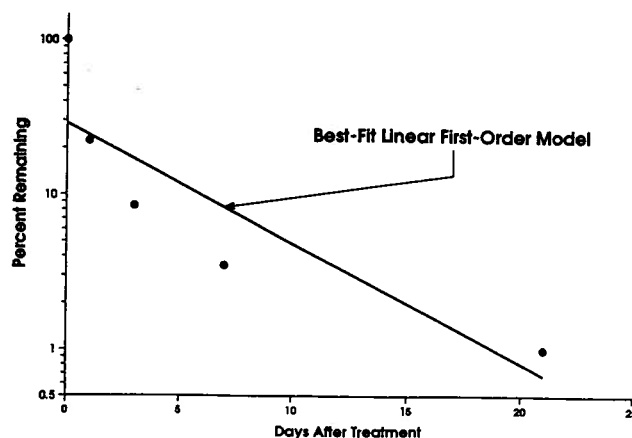


Figure 1. Data of ref 27 showing fluzifop butyl dissipation in an aerobic laboratory study. The line was fit by using an ordinary least-squares regression of $\ln C$ onto time.

loss mechanisms such as runoff or erosion, which do not have a molecular basis.

Other modifications of eq 1 have been achieved by allowing the rate "constant" to be a function of time, as in so-called "fractal reaction kinetics" (26), or by using a dependent variable that is both a function of temperature and time, as with the degree-days approach (12, 13).

Integrating eq 1 and taking logarithms of each side yields a linear relationship:

$$\ln C = \ln C_0 - kt \quad (2)$$

where $C_0 = C(0)$ is the initial concentration. Thus, the two parameters, C_0 and k , are commonly estimated by using a simple linear regression of the natural logarithm of the concentration onto time. Since the standard deviation of individual concentrations generally increases proportionately with the average concentration, the logarithmic transformation induces an efficient weighted regression. This beneficial effect is generally lost at very low concentration levels, near the detection limit, where the relative variability increases.

An interesting and useful feature of the kinetic model described by eq 2 is that the time necessary for the concentration to decline by 50% is a constant, determined entirely by the first-order rate constant. This time is usually called the half-life, $t_{1/2}$, and is related to k by

$$t_{1/2} = \ln 2/k \quad (3)$$

Unfortunately, the dissipation data for most pesticides that we have examined appear nonlinear when plotted as $\ln C$ versus time. This is illustrated in Figure 1 (a laboratory study) (27) and Figure 2 (a field study) (28). This curvature demonstrates that herbicide dissipation is not adequately described by the traditional first-order model presented above.

Compartment Models. A simple extension of the first-order kinetic model, which yields curvature in the $\ln C$ versus t plot, is the so-called "two-compartment" model. Various forms of the two-compartment model have been proposed in the literature (15, 18, 29). Three of these are illustrated schematically in Figure 3. Hamaker and Goring proposed (15) a five-parameter model comprised of two compartments between which compound moves freely but dissipation occurs only while the pesticide is in the first. Conceptually, the two compartments represent dissolved and sorbed phases within soil, with dissipation only possible while the pesticide is in solution. Hill and Schaalje proposed (29) a similar system, except that the second compartment is initially empty, no movement occurs back

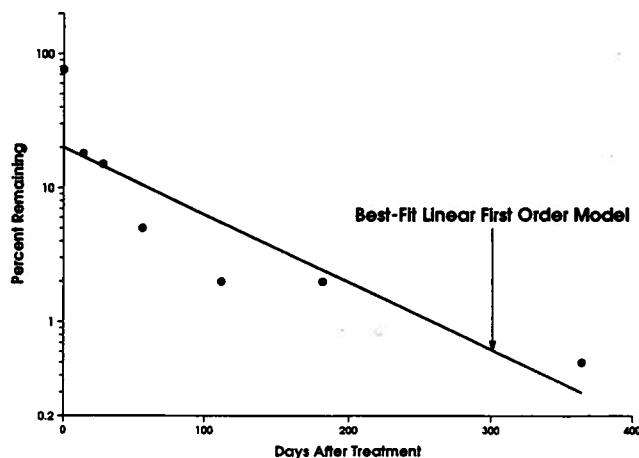


Figure 2. Data of ref 28 showing sulfometuron dissipation in a field study at Raleigh, NC. The line was fit by an ordinary least-squares regression of $\ln C$ onto time.

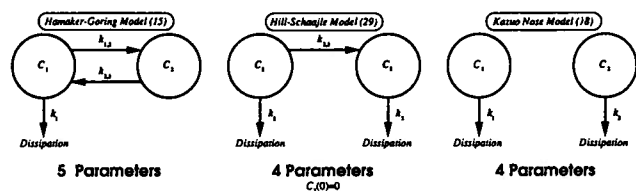


Figure 3. Schematic representation of three two-compartment models that have been proposed for the description of pesticide dissipation in soil.

from the second to the first, and dissipation is assumed to occur in both compartments, although at different rates. The physical interpretation in this case is that the first compartment represents a surface soil layer in which dissipation is more rapid and the second compartment represents a deeper soil layer described by slower dissipation kinetics. Kazuo Nose proposed (18) yet another modification to the two-compartment model in which dissipation occurs in both but no movement between compartments is allowed. In this case, the compartments represent two classes of spatially segregated sites within the soil matrix. All three of these two-compartment models have a relatively large number of parameters (four or five). Often, a dissipation study contains only five or fewer time points, rendering it impossible to evaluate the fit of the model. A reduction in the number of parameters, and a simplification in the model, may be achieved by a theoretical extension to the independent compartmental concept.

As part of his paper describing the use of a two-compartment model, Nose suggested (18) that any number of independent compartments could be assembled to yield a dissipation model that could be expressed as a sum of exponentials:

$$C(t) = \sum_{i=1}^n C_i(t) = \sum_{i=1}^n C_i e^{-k_i t} \quad (4)$$

At each point in time, $C(t)$ is just the sum of the separate concentrations, $C_i(t)$, over all n individual compartments. Simple first-order dissipation (eq 1) holds within each compartment. The two-compartment model actually used by Nose to fit his data is a special case ($n = 2$) of this more general form.

To proceed to the next section, we note that rather than considering each of the n individual compartments separately, we can combine all those, if any, that have the same rate constant. Denote by m ($m \leq n$) the number of these unique values of k_i . Let p_j denote the fraction of the initial

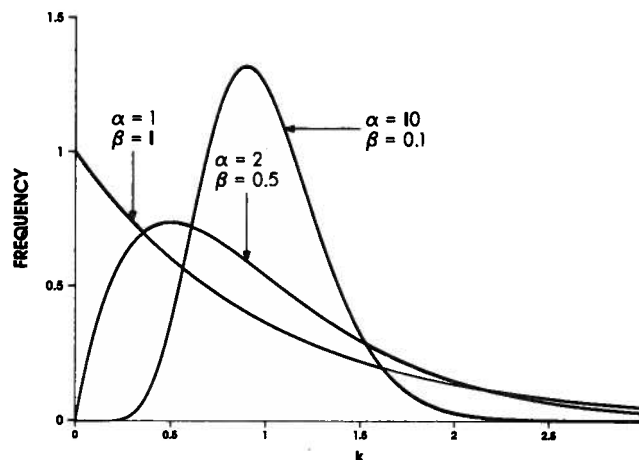


Figure 4. Typical shapes of the Γ distribution for three different sets of parameters. Each distribution shown has a mean of 1.

concentration that is allocated to compartments with rate constant k_j . That is

$$p_j = \sum_{k_i=k_j} C_i(0)/C(0) \quad (5)$$

where the sum in the numerator is over all compartments with $k_i = k_j$. Then eq 4 can be rewritten as

$$C(t) = \sum_{i=1}^n C_i e^{-k_i t} = \sum_{j=1}^m p_j C_0 e^{-k_j t} = \sum_{j=1}^m p_j u(k_j, t) \quad (6)$$

In other words, $C(t)$ is just the mean of all the contributions from a population of m simple first-order dissipation processes, $u(k_j, t)$.

From Many Compartments to Continuous Spatial Variability. As the number of compartments gets larger and larger, the summation of eq 6 can be replaced by the integral

$$C(t) = \int_0^\infty p(k) u(k, t) dk = \int_0^\infty p(k) C_0 e^{-k t} dk \quad (7)$$

where $p(k)$ replaces p_j . This simple extension to the multicompartment model (eq 6) implies that there is a continuum of spatially segregated compartments, each undergoing a simple first-order dissipation process determined by k . A probability density function (or pdf), $p(k)$, has been used to describe the relative allocation of the initial concentration, C_0 , to the continuous array of possible k 's. As was the case with only m discrete values of k , in eq 6, $C(t)$ is still simply the mean of $u(k, t)$. The only logical constraint on $p(k)$ is that it be positive only for positive values of k (otherwise a compartment would be producing, rather than dissipating, the pesticide). While any pdf satisfying this constraint can be employed, a common distribution for such nonnegative random variables is the gamma (Γ), (30), whose pdf is given by

$$f(k) = \frac{k^{\alpha-1} e^{-k/\beta}}{\beta^\alpha \Gamma(\alpha)} \quad \alpha > 0, \beta > 0, k > 0 \quad (8)$$

As illustrated in Figure 4, this distribution can take on a variety of shapes ranging from near-normal (Gaussian) for large α to highly positively skewed for smaller α . The parameter α is dimensionless and the parameter β has units of the rate constant, typically days⁻¹. The moments of the distribution are simple functions of the two parameters:

$$\mu = \alpha\beta \quad (9)$$

for the mean, and

$$\sigma^2 = \alpha\beta^2 = \mu\beta \quad (10)$$

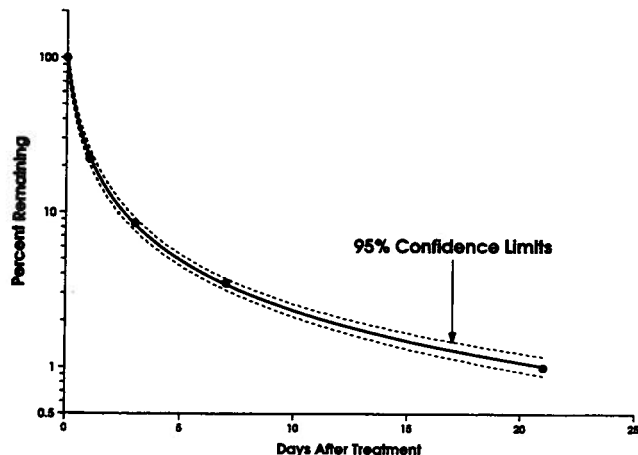


Figure 5. Data of ref 27 showing fluazifop butyl dissipation in an aerobic laboratory study. The new nonlinear model described in this work was fit to the data by the methods described herein.

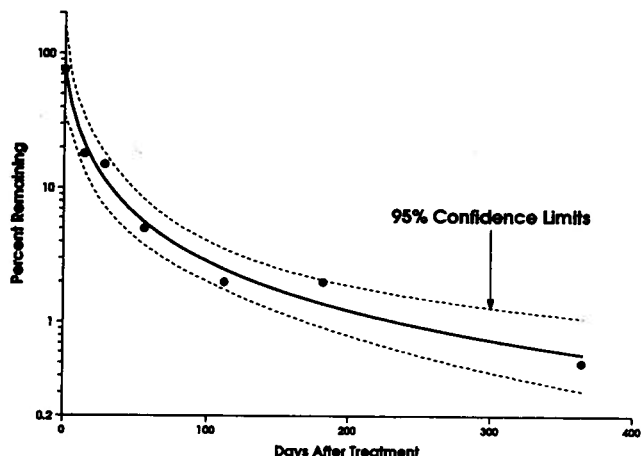


Figure 6. Data of ref 28 showing sulfometuron dissipation in a field study at Raleigh, NC. The new nonlinear model described in this work was fit to the data by the methods described herein.

for the variance.

If the rate constants in eq 7 are assumed to follow the Γ distribution, then the following simple form for the concentration results:

$$C = C_0(1 + \beta t)^{-\alpha} \quad (11)$$

This equation is the smooth curve appearing in Figures 5 and 6, in which the data of Figures 1 and 2 are replotted in order to exemplify the much-improved fit over the traditional linear model. In practice, and by analogy with the methods typically used to fit data to the linear, first-order model, the logarithm of each side of eq 11 is taken (the alternative form is found by making the substitution, $\mu = \alpha\beta$):

$$\ln C = \ln C_0 - \alpha \ln(1 + \beta t) \quad (12a)$$

$$\ln C = \ln C_0 - \mu \frac{\ln(1 + \beta t)}{\beta} \quad (12b)$$

This transformation of the data would give a straight line if $\ln C$ were plotted versus $\ln(t + \text{a constant})$. The linear nature of such plots has been noted previously, with similar transformations having been used in the literature (14, 19). However, they have always been used only as an empiricism, without any theoretical justification ever given for this particular form. As β approaches zero in eq 12b, this model reduces to the simple, linear, first-order model described by eq 2, with $k = \mu = \alpha\beta$. In such a case, the Γ distribution becomes degenerate, i.e., all the compartments

have k equal to μ . This gives a satisfying physical rationale for the reason behind the linearity that is sometimes observed in $\ln C$ versus time plots: the spatial variability is reduced nearly to zero in such cases.

Of course, what is usually of most interest is to estimate how long it takes for a specified fraction or percentage of the applied material to dissipate. In the case of linear kinetics, the half-life, $t_{1/2}$, was sufficient for this purpose. With nonlinear dissipation kinetics, however, the time for residues to decline by 50% is no longer constant. By first defining x to be the fraction of applied chemical that has dissipated, a general dissipation time, DT_{100x} , can be defined as the time necessary for the concentration to reach $100(1 - x)\%$, of the applied amount. This general dissipation time is a function of the two parameters in the Γ distribution describing the spatial variability of the k 's:

$$DT_{100x} = [(1 - x)^{-1/\alpha} - 1]/\beta \quad (13)$$

Because this is still a first-order (though nonlinear) model, the dissipation times are independent of the initial concentration or application rate, just as in the linear, first-order model. For DT_{50} and DT_{90} , the 50% and 90% dissipation times, respectively, we have

$$DT_{50} = [0.5^{-(1/\alpha)} - 1]/\beta \quad (14)$$

and

$$DT_{90} = [0.1^{-(1/\alpha)} - 1]/\beta \quad (15)$$

Estimation of Parameters. Any nonlinear regression program can be used to fit the parameters from the new model (eq 11) from experimental dissipation data. We use the SAS procedure, PROC NLIN (31), to estimate the parameters as they appear in eq 12a. We use the log-transformed version (eq 12a) rather than eq 11 in order to achieve the beneficial weighting and in order to spot deviations from the simple first-order model (eq 2). NLIN fits nonlinear regression models by least squares. The default GAUSS-NEWTON iterative method within NLIN was used since the derivatives of the parameters α , β , and C_0 can be easily derived (see the Appendix). PROC NLIN also allows the user to restrict all three parameters to positive values as required by eq 8. As with any nonlinear iterative solution, we have occasionally encountered numerical difficulties with certain sets of particularly "noisy" dissipation data, but convergence has been achieved quite readily in the vast majority of cases attempted.

As indicated above, a small value for β is indicative of nearly linear (more spatially uniform) behavior. The hypothesis of simple linear first-order behavior in the dissipation data is easily obtained by testing if the parameter β is equal to zero. A commonly used approximate F test for this hypothesis is described in ref 32. Denote by RSS_L and RSS_N the residual sums of squares for a fit to the linear model (eq 2) and the nonlinear model (eq 12a), respectively. Define the test statistic F as

$$F = \frac{RSS_L - RSS_N}{RSS_N} (n - 3) \quad (16)$$

If F is greater than the appropriate percentile from an F distribution with 1 and $n - 3$ degrees of freedom, then β is significantly greater than zero. That is, the new kinetic model provides a significantly improved fit to the dissipation data.

Application to Experimental Data

A literature search was conducted to gather several sets of dissipation data in order to test the utility of the new kinetic model. A total of 45 data sets were examined. The

Table I. Summary of Fits Obtained While Fitting the New Kinetic Model to Various Sets of Dissipation Data Taken from the Literature (Dissipation Times Are Given in Days)

ref	compound	\hat{DT}_{50}	\hat{SE}	\hat{DT}_{90}	\hat{SE}	$\hat{\mu}, (\hat{\alpha}, \hat{\beta})^a$	lab/field	soil
43	aldicarb	10.43	5.18	67.26	25.68	0.0856 (1.4221, 0.0602)	field (1)	sand
43	aldicarb	33.24	6.43	110.43	21.37	0.0209	field (2)	silt
38	asulam	12.97	2.59	43.08	8.61	0.0535	lab (1)	clay
38	asulam	1.56	3.91	17.39	38.18	0.6885 (0.8476, 0.8123)	lab (2)	clay
44	atrazine	19.20	2.89	133.21	10.93	0.0477 (1.2974, 0.0368)	field (1)	sand
44	atrazine	25.72	2.88	193.01	13.83	0.0366 (1.1883, 0.0308)	field (2)	sand
34	avermectin	21.58	2.97	107.22	7.95	0.0377 (2.2207, 0.0170)	lab (1)	silt
34	avermectin	16.68	2.01	83.86	5.79	0.0490 (2.1644, 0.0226)	lab (2)	silt
34	avermectin	61.33	14.03	278.21	33.57	0.0128 (2.8110, 0.0046)	lab (3)	sand
34	avermectin	23.19	5.39	183.42	26.32	0.0413 (1.1258, 0.0367)	lab (4)	clay
34	avermectin	30.81	15.03	281.62	92.42	0.0326 (0.9869, 0.0331)	lab (5)	clay
39	chlorimuron ethyl	17.12	2.90	122.53	10.90	0.0541 (1.2515, 0.0432)	lab (1)	sand
39	chlorimuron ethyl	1.88	1.22	14.99	7.68	0.5093 (1.1195, 0.4549)	lab (2)	silt
42	fenvalerate	74.50	12.43	555.21	61.61	0.0126 (1.1970, 0.0105)	lab (1)	sand
42	fenvalerate	130.86	5.84	434.72	19.39	0.0053	lab (2)	clay
27	fluazifop butyl	15.40	0.82	51.15	2.74	0.0450	lab (1)	silt
27	fluazifop butyl	0.72	0.10	3.62	0.41	1.1252 (2.1897, 0.5138)	lab (2)	silt
27	fluazifop butyl	0.32	0.02	2.50	0.11	2.9895 (1.1365, 2.6305)	lab (3)	silt
27	fluazifop butyl	0.54	0.13	3.06	0.56	1.5889 (1.7088, 0.9299)	lab (4)	silt
27	fluazifop butyl	3.02	0.10	10.57	0.23	0.2349 (15.5168, 0.0151)	lab (5)	silt
33	flufosinate	2.55	1.23	21.84	7.58	0.3851 (1.0456, 0.3683)	lab (1)	clay
33	glufosinate	9.05	4.55	45.62	12.80	0.0903 (2.1530, 0.0419)	lab (2)	silt
33	glufosinate	2.06	0.76	15.56	4.33	0.4579 (1.1800, 0.3881)	lab (3)	sand
37	linuron	57.10	19.83	368.57	89.78	0.0157 (1.4195, 0.0110)	field (1)	sand
37	linuron	49.83	30.83	2135.11	1959.90	0.0326 (0.4578, 0.0712)	field (2)	sand
37	linuron	69.10	20.27	1981.38	1552.48	0.0208 (0.5265, 0.0395)	field (3)	sand
36	metolachlor	46.58	1.89	186.05	15.04	0.0165 (3.7158, 0.0044)	field (FL)	sand
36	metolachlor	12.96	8.31	468.12	267.83	0.1189 (0.4845, 0.2454)	field (MD)	silt
35	metolachlor	52.69	7.27	313.00	131.22	0.0165 (1.5969, 0.0103)	field (2)	sand
35	metolachlor	47.60	2.26	158.13	7.49	0.0146	field (3)	sand
40	metolachlor	13.64	6.64	101.77	28.53	0.0689 (1.1957, 0.0576)	field (1)	sand
40	metolachlor	17.09	3.71	122.85	14.76	0.0543 (1.2456, 0.0436)	field (2)	sand
44	metolachlor	12.00	1.95	86.52	8.33	0.0774 (1.2406, 0.0624)	field (1)	sand
44	metolachlor	16.84	2.39	86.20	6.74	0.0488 (2.0822, 0.0235)	field (2)	sand
35	propachlor	10.43	1.83	55.89	5.21	0.0802 (1.8993, 0.0422)	field (1)	sand
35	propachlor	22.44	2.79	74.55	9.26	0.0309	field (2)	sand
35	propachlor	10.14	0.76	33.67	2.52	0.0684	field (3)	sand
28	sulfometuron	4.04	8.14	34.89	55.55	0.2438 (1.0379, 0.2349)	field (DE)	silt
28	sulfometuron	6.20	2.42	43.17	13.32	0.1478 (1.2930, 0.1143)	field (NC)	sand
28	sulfometuron	93.93	32.44	393.57	76.79	0.0081 (3.6999, 0.0022)	field (OR)	silt
28	sulfometuron	37.92	29.58	563.75	304.16	0.0310 (0.7102, 0.0436)	field (SK)	clay
28	sulfometuron	79.72	31.26	496.25	110.88	0.0111 (1.4914, 0.0074)	field (CO)	silt
41	terbufos	11.16	2.15	40.76	5.98	0.0646 (8.7692, 0.0074)	field	silt
44	terbuthylazine	10.44	5.83	105.44	37.33	0.0995 (0.9115, 0.1091)	field (1)	sand
44	terbuthylazine	28.21	7.09	671.50	227.81	0.0481 (0.5671, 0.0849)	field (2)	sand

^aThe absence of estimates for α and β indicates that β was not significantly greater than 0 and the simple linear model was used to estimate dissipation times.

new nonlinear, first-order model was found to be no better than the linear model in only seven (16%) of the cases. In all other instances, a significantly improved fit was achieved through the use of eq 12. All 45 analyses are summarized in Table I.

The parameter estimates of α and β , $\hat{\alpha}$ and $\hat{\beta}$, are plotted in Figure 7, using different symbols for laboratory and field studies. It is clear from this plot that $\hat{\beta}$ varies over many more orders of magnitude than $\hat{\alpha}$. The value for $\hat{\alpha}$ is often near 1, and this value should probably be assumed in cases where only a few of data points are available and predictions of future behavior need to be made. Somewhat surprisingly, the parameter estimates for the laboratory data fall in the same range as those for the field data. This indicates that (assuming our model is valid) the spatial variability responsible for the observed behavior must have a very small length scale, possibly on the order of pore-size dimensions. Others have shown (45) that EDB, a pesticide of relatively small molecular volume, can become physically entrapped in soil pores and thereby resist further dissipation. Similarly, paraquat has been reported (46) to form tight charge-transfer complexes with clay layers, leading to unexpected persistence.

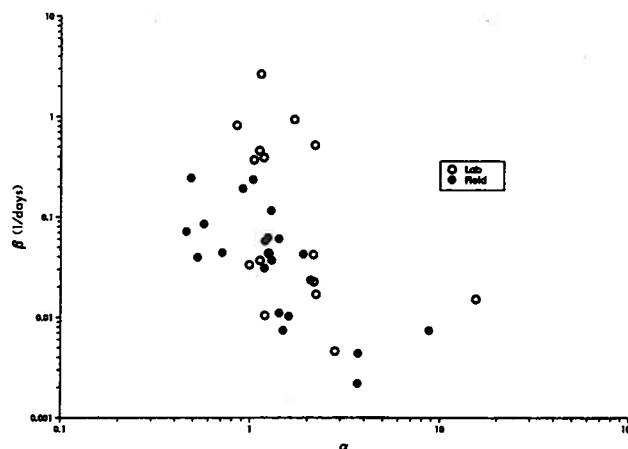


Figure 7. Scatter diagram of the parameter estimates giving best fits to the various sets of dissipation data examined in this work.

The possibility that pore-scale phenomena cause the nonlinearity was investigated further by examining the effect of soil texture on the parameter estimates. Although there were some weak trends present, with the predomi-

nantly clayey soils tending to have lower $\hat{\alpha}$ values (and therefore more curvature in the dissipation function), the variability in the data set prevented any fine distinctions from being made. It does seem reasonable that diversity in pore sizes, particularly the very small pores present in clays, may give rise to more curvature in the dissipation kinetics. Under this hypothesis the sandy soils, on the other hand, should tend to give more linear dissipation curves, and there were some weak indications of this in the examined data.

Conclusions

We have shown that acknowledgment of spatial variability in the dissipation process leads to a nonlinear, first-order kinetic model giving excellent fits to a wide range of pesticide dissipation data, whether derived from laboratory or from field studies. The new technique allows reliable estimates to be made of DT_{50} , DT_{90} , and any other aspects of the dissipation curve. Its use in environmental fate models would undoubtedly lead to improved predictions of fate and transport. A physical explanation for the curvature in the dissipation behavior is that certain regions in the soil exhibit relatively rapid dissipation, causing an initially steep slope, but these areas become exhausted of pesticide, leaving behind a residue that dissipates somewhat less rapidly.

The length scale of the spatial variability in the dissipation process must be very small, because data derived from very small laboratory aliquots of soils suggest variability of the same degree as determined with field data. Clays appear to give more curvature in the dissipation plot than sands, further suggesting a microscopic, pore-scale source of the spatial variability. Further experimental work controlling the other parameters in the dissipation process while varying only heterogeneity on various length scales would be necessary in order to further explore this relationship. Hopefully, our proposed justification for the observed nonlinearity in pesticide dissipation kinetics will stimulate more research into the various phenomena that would cause dissipation rates to vary spatially in soil.

A further complication not considered in this paper is the formation of metabolites from the parent chemical and their subsequent degradation. The assumption of spatially variable rate constants for these various processes forces us to consider the multivariate distributions of dissipation rates, quickly leading to intractable mathematics and a large number of parameters. We are currently investigating simplifications that would result in practical ways to model such a system.

Appendix I. Statistical Details

Nonlinear regression techniques are needed to estimate, from a given set of data, best-fit values for the parameters appearing in eqs 12a and 13. Most nonlinear regression software requires that partial derivatives of the function with respect to the parameters be calculated. Defining the dependent variable in eq 12a as

$$Y = Y(t) = \ln C(t) \quad (I.1)$$

and the intercept as

$$\theta = \ln C_0 \quad (I.2)$$

then the required partial derivatives are

$$\frac{\partial Y}{\partial \theta} = 1 \quad (I.3)$$

$$\frac{\partial Y}{\partial \alpha} = -\ln(1 + \beta t) = Y_\alpha \quad (I.4)$$

$$\frac{\partial Y}{\partial \beta} = \frac{-\alpha t}{(1 + \beta t)} = Y_\beta \quad (I.5)$$

The estimated variance of the predicted concentration (or, more properly, $\ln C$) can be expressed in terms of these partial derivatives and the estimated variances and covariances of the parameter estimates:

$$\begin{aligned} \text{var } Y = & \text{var } \hat{\theta} + Y_\alpha^2 \text{var } \hat{\alpha} + Y_\beta^2 \text{var } \hat{\beta} + \\ & 2Y_\alpha Y_\beta \text{cov}(\hat{\alpha}, \hat{\beta}) + 2Y_\alpha \text{cov}(\hat{\alpha}, \hat{\theta}) + 2Y_\beta \text{cov}(\hat{\beta}, \hat{\theta}) \end{aligned} \quad (I.6)$$

The estimated variance of the dissipation time estimates, \hat{DT}_{100x} , and hence the confidence intervals for DT_{100x} , are derived in a manner similar to that used for the concentration itself. The partial derivatives are once again required:

$$\left. \frac{\partial DT_{100x}}{\partial \alpha} \right|_{\hat{\alpha}, \hat{\beta}} = \frac{(1-x)^{-1/\hat{\alpha}} \ln(1-x)}{\hat{\beta} \hat{\alpha}^2} = \Delta_{X\hat{\alpha}} \quad (I.7)$$

$$\left. \frac{\partial DT_{100x}}{\partial \beta} \right|_{\hat{\alpha}, \hat{\beta}} = \frac{1-(1-x)^{-1/\hat{\alpha}}}{\hat{\beta}^2} = \Delta_{X\hat{\beta}} \quad (I.8)$$

and the estimated variance of the general dissipation time is

$$\begin{aligned} \text{var } \hat{DT}_{100x} = & \Delta_{X\hat{\alpha}}^2 \text{var } \hat{\alpha} + \Delta_{X\hat{\beta}}^2 \text{var } \hat{\beta} + 2\Delta_{X\hat{\alpha}}\Delta_{X\hat{\beta}} \text{cov}(\hat{\alpha}, \hat{\beta}) \end{aligned} \quad (I.9)$$

Approximate 95% confidence intervals for any parameter or functions of parameters, $\omega = \omega(\alpha, \beta, \theta)$, can be computed as

$$\hat{\omega} \pm t^*_{n-3} \hat{\sigma}_{\hat{\omega}} \quad (I.10)$$

where $\hat{\omega}$ is the estimate of ω , and $\hat{\sigma}$ is its estimated standard error (the square root of the estimated variance). The coefficient t^* is the 5% two-tailed percentile from the Student's t distribution with $n - 3$ degrees of freedom.

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