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THE APPLICATION OF MATHEMATICAL MODELING TO THE SOIL PERSISTENCE AND ACCUMULATION OF PESTICIDES

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INTRODUCTION

The immediate practical justification for modeling the persistence of pesticides in soil lies in the ability that it would give us to predict residues of pesticides in soil. Because of the great concern for pollution, information on soil residues at the end of the season and beyond is now required for each pesticide reaching the soil and, therefore, virtually every agricultural pesticide. The method used to satisfy this requirement is the empirical one of analyzing the soil residues in many locations and for several seasons. As is generally the case for the purely empirical approach, this is time-consuming and expensive. Laboratory studies may be required, but because these cannot now be well correlated with field results, much the greater weight is placed on the field studies. A valid model for persistence of pesticides in soil would allow a better utilization of information from the laboratory and, thus, fewer field studies would be needed.

Beyond this practical consideration, such a model would give us a greater understanding of the nature of the processes by which pesticides disappear from soil and of the nature of the soil itself. In the long run, this will be of even greater value.

Empirical and Analytical Models

Since an immediate object for modeling soil persistence is the successful model for the field situation, we will examine some of the attempts that have been made to develop such models. For this examination, we will find certain features and aspects of models that are important, as the following:

1. Models range from empirical to analytical or theoretical with intermediate types also observed.
2. Initial conditions are complex and more difficult to model than the final stabilized condition or steady state.
3. Models usually assume first-order kinetics.
4. The variability inherent in field studies makes statistical treatment of models necessary.
5. The rate of degradation varies significantly with climatic and soil conditions.

It is useful to classify mathematical models into empirical, semi-empirical and analytical types. An empirical model is justified solely by its ability to fit the data, while an analytical model is derived from theory and uses directly measurable quantities. The semi-empirical model lies between these two extremes in that it has a basis in theory but the parameters in the equation are derived indirectly from the data. The importance of the distinction is that an empirical model cannot usually be extrapolated beyond the data used to establish it. An analytical model, if valid, should extrapolate or predict. Examples of semi-empirical models will appear later in the paper.

An example of an empirical model for soil persistence is provided by the work of Menn, *et al.* (1965) who used the following model to describe the disappearance of phosmet from soil:

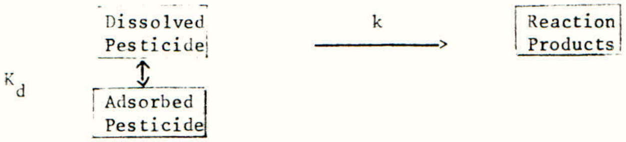
$$\text{Conc.} = A + B(\text{time}) + C\sqrt{\text{time}} \qquad /1/$$

For 2-percent chemical in a Sorrento loam soil:

$$A = 8.423, \quad B = -0.072; \quad C = 0.607$$

Although this model can be fitted to their data by the proper choice of the coefficients, A, B and C, it is doubtful if these coefficients have any real meaning. It certainly cannot be extrapolated, since for longer times the second terms will dominate and the concentration will become negative--a meaningless result certainly not intended by the authors.

An excellent example of an analytical model is provided by the early work of Furmidge and Osgerby (1967). Their model assumed that the pesticide dissolved in soil solution degraded according to first-order kinetics, but that the absorbed pesticide was protected from degradation. This can be represented by the following compartment model:



where K_d is the distribution adsorption coefficient (ppm in oil/ppm in water) and k is the first-order rate constant for degradation of the pesticide in water. If it is assumed that the adsorption equilibrium is rapid compared with the degradation reaction, the reaction rate in soil can be calculated by the following equation:

$$dc/dt = \frac{kc}{1 + (\text{wt soil}/\text{wt } H_2O)\ K_d} \qquad /2/$$

where c is the concentration of pesticide expressed as total amount of pesticide (adsorbed and dissolved) per weight of dry soil. It should be noted that, according to this model, reaction in soil still follows first-order kinetics with, however, a smaller rate constant.

Furmidge and Osgerby found that the model worked well for an N-phosphorylated atrazine, although the total amount of degradation was somewhat small. They followed the reaction 1.2 half-lives and 3 half-lives is the rule of thumb for accurate kinetic work. An attempt to apply this model to the decomposition of monocrotophos in soil was less successful, probably because the decomposition is microbial in character, and disappearance from the culture media was used to estimate the degradation rate in soil solution. The environment experienced by the microorganisms in soil is, of course, quite different from that in a culture media.

Models for Persistence Under Field Conditions

The first model with which we concern ourselves is a qualitative one proposed by Edwards (1966). Edwards pointed out that a pesticide does not immediately become fully incorporated into the soil but passes through an initial period of dispersion.

During this period, it is differently subject to loss by various processes. During application, for example, the pesticide may be lost by drift and has a maximum exposure to volatilization. In a second stage, the pesticide has reached the soil but has not yet become molecularly incorporated so is still relatively exposed to loss by volatilization, leaching and degradation; photochemically, chemically or biochemically. Eventually, the chemical approaches a state of molecular dispersion in the soil and becomes somewhat isolated from the forces that cause its loss and breakdown. At usual water contents, most pesticides are almost completely adsorbed in the soil, and this tends to slow down movement by leaching and volatilization and to protect the chemical from degradation. From the Edwards model, we would conclude that the early portion of the disappearance curve would show more rapid loss than later portions when the chemical is dispersed in the soil. Figure 1 is Edwards' graphical representation of this model.

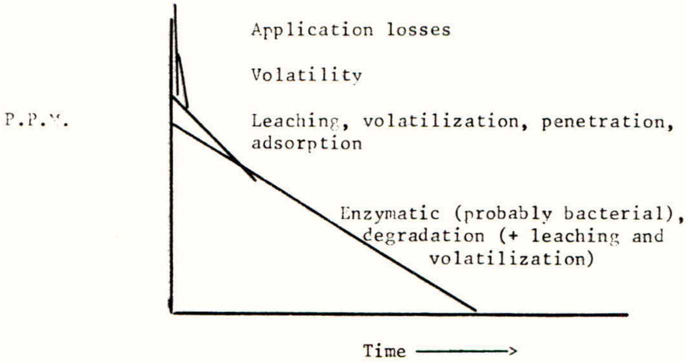


Figure 1 Theoretical breakdown curve for soil insecticides

The initial phases of this dissipation processes described by Edwards are very difficult to model because they are so dynamic and complex and they are, therefore, either minimized and/or bypassed. Soil incorporation should, for example, hasten the dispersion process and shorten the time required for the soil-pesticide system to equilibrate. Frequently, this initial period is bypassed simply by extrapolating back to an initial concentration which represents the later stages of decomposition or disappearance. For example, when modeling the exposure of workers to pesticide residues on foliage, Sarat (1973) found it necessary to use an extrapolated initial value for foliar deposit that was only 70 percent of the actual value found by analysis soon after application.

An even more extreme example was reported by Hermanson, et al (1971) in modeling soil residues of organically bound chlorine from eight organochlorine insecticides. These insecticides were applied for each of 5 years and then allowed to disappear and decay for an additional 6 years, so the initial phases should be short compared with the time of the experiment. The full mathematical formulation of Edwards' hypothesis, i.e. containing terms for losses from application, volatilization, leaching, chemical degradation and biochemical degradation was discussed and then simplified to a form:

$$\log Cl = \log A + Bt \qquad /3/$$

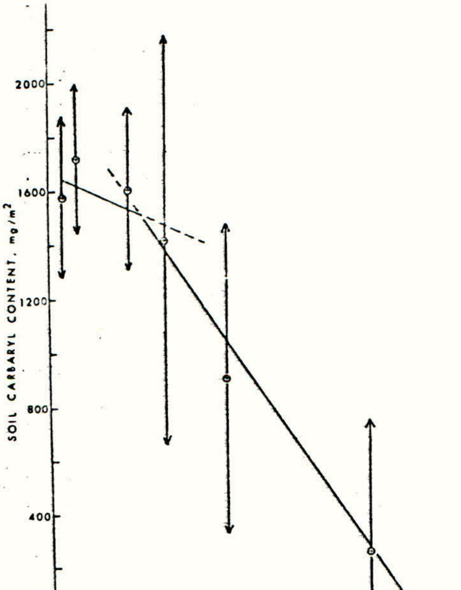
where A represents the initial conditions and B represents the contributions of volatilization, chemical degradation and biochemical breakdown after the system has settled down. This equation is exactly equivalent to first-order reaction kinetics:

$$\log c = \log c_o + Bt \qquad /4/$$

where c_o is the initial concentration and t is the time. The actual model was a system of such equations, expressing each annual addition and the final 5-year period of degradation. By appropriate statistical methods, the best single values of A and B were determined for the entire experiment. In the case of DDT, for example these values were, respectively, 2.7 ppm and -0.084 years^{-1}. However, the actual application rate for DDT was supposed to have been 20.7 pounds/acre or approximately 10 ppm in the top 6 inches, which is much higher than this. In the case of aldrin, the value of A was only 9 percent of the expected value of 2.43 ppm. It is not clear why there should be such a large discrepancy in this case, but if the literature on soil pesticides is examined, many other instances will be found of discrepancy between soil residues found by analysis and those calculated from the application dose. As Edwards puts it, "Only rarely does the quantity of insecticide intended to be applied actually become incorporated in the soil".

Another case of rapid initial change was reported by Decker, Bruce and Bigger (1965) for aldrin. In this case, although aldrin was applied to the soil, the soil residues were dieldrin. They were able to use a first-order rate model by assuming that there was a fairly rapid disappearance of aldrin with 10 to 20 percent conversion to dieldrin, and this was followed by disappearance of dieldrin with a 2 to 4-year half-life. This data was only for a limited area in the state of Illinois and the climatic factors were ignored, i.e. assumed to be constant.

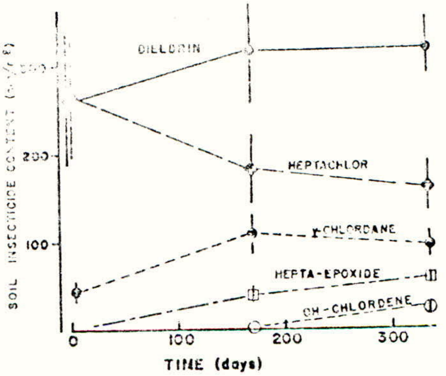
Any attempt to model pesticide persistence in soil under field conditions must take into account the variability which is inherent in sampling and analyzing soil samples. Work with carbaryl by Caro, et al. (1974) presented in Figure 2 shows how large a factor this can be. The vertical lines in this graph are standard deviations



Arrows: = one standard deviation about mean

Figure 2 The disappearance curve for carbaryl in Coshocton silt loam soil (Caro, et al, 1974) from the set of replicates, which in this case, are also approximately the 90 percent confidence interval for the means themselves. It seems doubtful that a very accurate idea of the kinetics of carbaryl degradation could be obtained from these field data. Comment should be made on the initial slow rate or lag. It is possible that this is due to an initial build-up of a microbial population able to use carbaryl as a food. It may, however, also be a reflection of the spring planting date (lower soil temperature) and application of a granular formulation (temporary unavailability of the chemical to soil degradative forces).

A field study of dieldrin and heptachlor disappearance by Taylor et al. (1971) provides another example of field variability. Dieldrin and heptachlor were sprayed in this field, disked in, and sampled extensively. Initially 12 and finally 75 soil cores for each of the 5 sub-sections were taken. Again we see considerable variability in the experimental points (Figure 3).



Bars = one standard deviation about the means

Figure 3 Measured changes in concentration in a field soil from a dieldrin and heptachlor application (Taylor, et al., 1971)

The use of statistical analysis is illustrated by treatment of a 6-year sampling from the same experiment (Freeman et al., 1973). Linear regression of the data yielded the following equations:

$$\text{ppm dieldrin} = 2.72 - 0.202\ (\pm\ 0.155)\ \text{years} \quad \text{(with 80\% confidence interval)} \qquad /5/$$

$$\log\ \text{ppm heptachlor} = 2.43 - 0.364\ (\pm\ 0.1)\ \text{years},\ R = 0.99 \quad \text{(99\% confidence interval)} \qquad /6/$$

These show clearly that the straight line model for dieldrin is very poorly determined compared to that of heptachlor and in spite of an extended time period. Taylor concludes that accurate determination of the persistence of a long-lived pesticide is almost impractical in the field.

Hamaker, et al. (1967) have attempted to model the disappearance of picloram from soil under field conditions. These data were for locations distributed over the continental United States and Canada, so climatic factors could not be ignored as was done in the model thus far described. In addition, first-order kinetics did not adequately represent the rate of loss of picloram from the soil. In general, the lower the concentration of picloram in the soil, the shorter the time during which a given fraction of the chemical disappears, i.e. the half-life is shorter for lower concentrations. This corresponds to a pseudo-order that is less than 1.

It is assumed by Hamaker, et al., that one-half-order kinetics would adequately represent the rate of loss of picloram from soil. This corresponds simply to the statement that the rate depends upon the square root of the concentration and, accordingly, half-order rate constants were calculated from the data on the disappearance of picloram. A single constant such as this half-order constant was necessary because in almost every location, the only information available was the initial and final soil concentrations. A multiple regression of this rate constant against temperature (annual days over 90^oF), moisture (inches of rainfall), rate of application (ounces/acre), and three soil factors (percent clay, percent organic matter, and pH) against half-order constants gave a correlation coefficient of 0.7. Moreover, most of the significance lay with days over 90^oF and annual precipitation, so that an equation with these factors only was proposed as a useful tool in dealing with the disappearance of picloram from soil in the United States and Canada. Data published later (Goring and Hamaker, 1971) as well as some further data of Australian origin (Hamaker; unpublished data) were also found to fit the model to the same degree.

This is an example of a purely empirical model based on the multiple linear regression and has many limitations. Certainly, half-order kinetics is an arbitrary assumption and Meikle, et al. (1973) have found, for example, a pseudo-order of 0.8 best fitted one set of laboratory data. Furthermore, the variables used for climatic conditions are only crude indicators, at best, of the actual soil temperature and moisture and the assumption of the linear dependence of the rate of constant upon them can only be an approximation. The justification of an empirical model such as this lies in its usefulness, and for many purposes this model has been a useful tool.

Simulation Model

Certainly the most sophisticated and analytical model that has yet been developed is the one used by Walker for propyzamide and napropamid (Walker, 1973; 1974). In this case, the disappearance of these chemicals from soil follows first-order kinetics, so the first-order rate constant can be used to represent the reaction. By appropriate laboratory studies, the dependence of this constant upon temperature and soil moisture was determined for a field soil, and the resulting relationships were used in the computer simulation for a field situation. Results of this simulation are shown in Figure 4 and 5. The irregular variation in the lines describing the decrease of propyzamide in the soil is probably due to the normal variation of residues in sampling field soils.

The actual relationships used by Walker were the following:

$$\log \frac{(\text{Half-life})_1}{(\text{Half-life})_2} = \frac{\Delta E^*}{2.303R} \left(\frac{1}{\text{Temp}_1\ (^oK)} - \frac{1}{\text{Temp}_2\ (^oK)} \right) \qquad /7/$$

$$\text{Half-life} = a \times (\text{Moisture Content})^{-b} \qquad /8/$$

For propyzamide: ΔE^* = 17.5 Kcal/mol @ 12% moisture
a = 229.1, b = 0.823 @ 23^oC

For napropamid: ΔE^* = 7.83 Kcal/mole @ 7.5 and 10% moisture
a = 189.3, b = 0.550 @ 28^oC

These relationships for temperature and for moisture content are used consecutively; that is, the values for k are corrected to constant temperature and then the

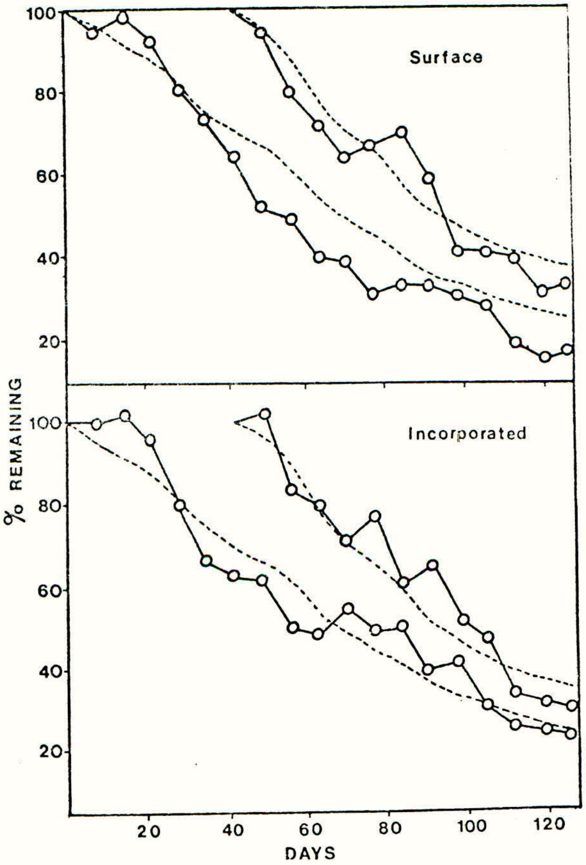
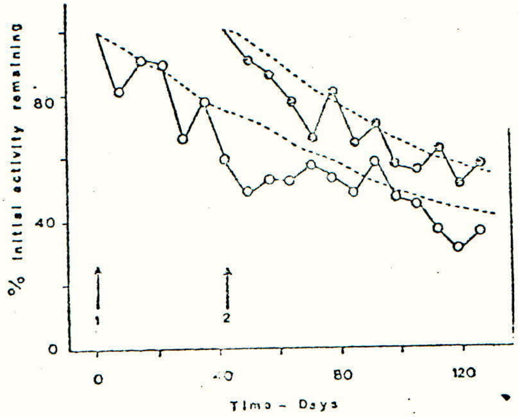


Figure 4 The persistence of propyzamide in the field: (Walker, 1973)



(-----Simulated Curve).

Figure 5 Persistence of napropamid in the field (Walker, 1974) moisture relationship is applied or vice versa. When used in this manner, the two relationships are equivalent to a single expression:

$$dc/dt = (k_o e^{-\Delta E^*/RT} \times (H_2O)^{-b})c \qquad /9/$$

where the expression in parentheses is equal to the first-order rate constant for the decomposition. This says that the first-order rate constant depends upon the moisture and the temperature in a rather special manner: as a product of a function in moisture and a function in temperature. In general, we might have expected a single function in both variables, not separable in this fashion, but, in this case, the interaction of the two variables is evidently small.

The temperature relationship is the standard Arrhenius equation for the effect of temperature upon a rate of chemical reaction and has, therefore, a real theoretical basis. The moisture relationship, however, appears to be entirely empirical and is based on the assumption of a straight line in a log k vs. log moisture plot. The adsorption model suggested by Furmidge and Osgerby provides an interesting possibility in this connection. If equation 2 is inverted, it gives the following linear form:

$$1/k_{obs} = 1/k_{aq} + K_d/k_{aq} \; (1/(g\ H_2O/g\ soil)) \qquad /10/$$

so a graph of $1/k_{obs}$ vs. $1/\%H_2O$ should be a straight line (where percent H_2O is defined as g H_2O/g soil x 100). When this is applied to Walker's data, a better fit is obtained than with the exponential relationship. However, the adsorption coefficients obtained are much smaller than has been obtained by direct measurement. Evidently, the model is not an accurate map of the system, probably because some of the adsorbed material undergoes decomposition.

Propyzamide: $(K_d)_{calc} = 0.14$

$(K_d)_{obs} = 2.25 - 13.6^*$ (Leistra, et al., 1974)

Napropamid: $(K_d)_{calc} = 0.525$

$(K_d)_{obs} = 2.10 - 8.8^*$ (Wu, et al., 1975)

*the range of K_d values for several soils

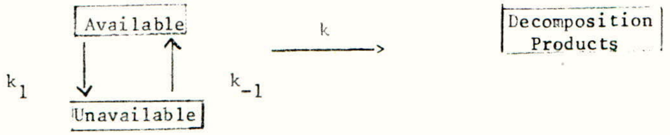
As originally developed, Walker's model for propyzamide had three limitations: data on soil moisture and temperature were needed, first-order kinetics was used, and only one soil was included. These limitations need to be removed before the model can be applied more generally. For example, much weather data is given as precipitation and air temperatures instead of soil moisture and soil temperatures. In the case of napropamid, Walker simulated soil moisture content from rainfall data and used this to successfully simulate napropamid disappearance when incorporated. Apparently, napropamid on the soil surface is photodegraded to a significant extent, and this is a factor not included in the model. The further useful step of estimating soil temperatures from air temperatures appears quite feasible from published reports.

Kinetics of Degradation in Soil

In order to use this model so well demonstrated by Walker, it is necessary to know the kinetics of degradation in soil. In the case of propyzamide and napropamid, the kinetics were first-order, but in other cases the kinetics are more complex, in keeping with the complexity of soil. The kinetics of reaction in homogeneous solution do not appear to apply directly, as might be expected, and the actual kinetics, as yet, are not well understood. Because of this, some cases where degradation deviates only slightly from first-order are treated as first-order, e.g. Herlihy and Quirke (1975), Zimdahl, et al., (1970). This procedure is risky, since deviations that are insignificant for short time periods may become very significant for longer periods.

Disappearance curves of pesticides in soil can be divided into three classes, based on the shape of the curve when plotted on semilog axes (log concentration vs. time). Those that are concave upward, those concave downward, and those that give straight line (i.e., first-order). The first class, which is much more common, is illustrated in Figures 6 and 7 for diazinon and thionazin, taken from the work of Getzin (1968). The second case of a concave downward curve is suggested by Figure 8 on picloram from Hamaker, et al. (1968). It may also suggest cases of lag due to enrichment, as in Figure 9 from the work of Engvild and Jensen (1969) on pyrazon. The third class is represented by propyzamide, napropamid and others.

Figures 6 and 7 for degradation of diazinon and thionazine have dashed curves as well as the experimental points. These are claculated curves obtained from the following modification of the Furmidge and Osgerby model:



The modification is to replace "adsorbed" with "unavailable" and introduce slow rates of transfer into and out of the "unavailable". Because freshly added chemical is mainly in the available state, the initial rate is rapid but falls off as chemical transfers to the unavailable condition. Eventually a steady state is achieved which is represented by a straight line on the graph because k, k_1 and k_{-1} are first-order constants. The degree of fit for these and other cases (Hamaker and Goring) raises hopes that simulation can be applied to degradations that are not first-order. It may, of course, be necessary to adjust the model for any irreversible fixation that might occur.

Table 1 gives an indication of how temperature may affect the three constants in question. The values for k, the rate of constant for degradation, behave normally. Diazinon has, for example, about the same activation energy as reported for hydrolysis in aqueous solution by Gomaa and Faust (1969). The values of k_1 and k_{-1}, transfer rate constants, appear to be less sensitive to temperature. In the case of diazinon, it is likely that the uncertainties of determining these constants are greater than the difference between them. They probably can be assumed to be the same and an average used. In the case of thionazin, it may be that the constant at 15^{o}C are in error for some reason. The quantity m_1 shown in the next to last column of the table is the slope approached by the degradation for long time periods.

Effect of Soil Organic Matter

This model has been described more completely by Hamaker and Goring (to be published) and Figures 10 and 11 for triclopyr in two different soils are taken from that source. It will be noted that the soil with higher organic carbon (Illinois - 4.2%; California - 0.8%) has a greater inherent decomposition rate, i.e., k, but also a greater capacity to make the chemical unavailable, i.e. k_1/k_{-1}. Thus, the decomposition in the soil with higher organic matter content is initially more rapid, but the steady-state degradation rate is slower. In this case, the amount of residue is about the same in the end, rather like the tortoise and the hare. This phenomenon is probably why it has been so difficult to establish the relationship between soil properties and rates of degradation in soil. Degradation in soil is usually microbiological, and one would expect the rate to depend primarily on the organic matter content of soil as support for the soil microorganisms. However, the above analysis suggests that the situation is too complex for the linear regression type of analysis that has thus far been used. It seems more likely that the time required for disappearance of, say 90%, will be long for both very low and very high organic matter contents, and will be a minimum for some intermediate organic matter content. Analysis appropriate to such a model does not seem to have been done.

The second type of deviation from first-order, namely equivalent to an order less than 1 or concave downward, may be difficult to model. In cases of lag time due to enrichment, the initial period of low rate will depend upon the previous treatment of the soil. It may be possible to consider the lag period as an initial non-equilibrium phase in the sense of Edwards' model and model the degradation after the microbial system has stabilized. Fortunately, the authenticated cases of lag time are associated with relatively rapid degradation, e.g. 2,4-D, dalapon, pyrazon, etc., are not large. This would probably only give some sort of maximum or minimum value for the disappearance of the chemical, depending upon whether fresh or enriched soil is used.

This analysis suggests that it may be possible to apply the analytical model due to Walker to soil persistence of pesticides generally with soil factors being the least understood. However, the work of Hamaker et al. (1967) on picloram suggests that this factor is less significant than the climatic factors of temperature and moisture. A final disclaimer should be added relative to the difficulty of prediction where microbial population is varying either in quantity or quality of the of the microbiological community. This applies certainly to cases showing enrichment. In most cases, however, the microbiological community is relatively stable and subject to slow changes as the organic matter degrades in quantity and nutritional value.

Figure 6.

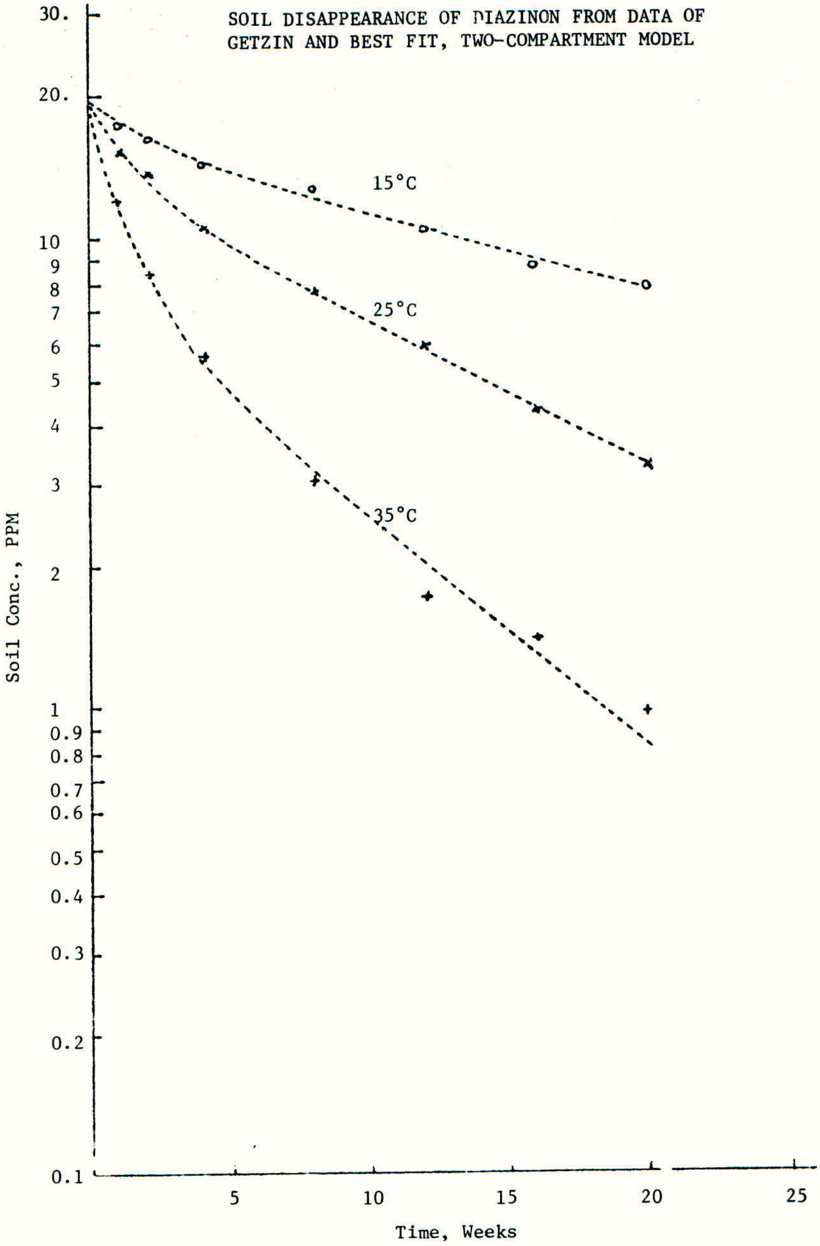
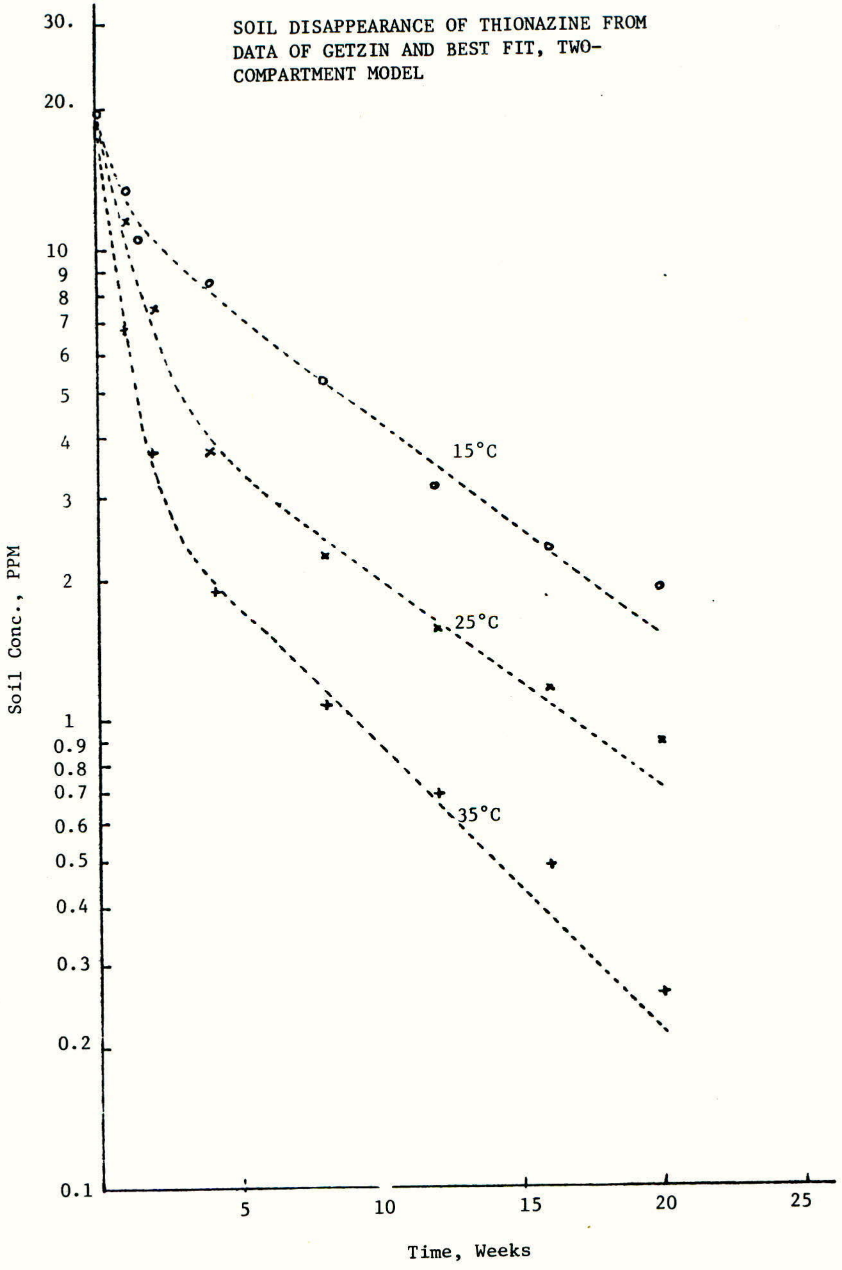

SOIL DISAPPEARANCE OF DIAZINON FROM DATA OF GETZIN AND BEST FIT, TWO-COMPARTMENT MODEL
30.
20.
10
9
8
7
6
5
4
3
2
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Soil Conc., PPM
15°C
25°C
35°C
5
10
15
20
25
Time, Weeks

FIGURE 7.



SOIL DISAPPEARANCE OF THIONAZINE FROM DATA OF GETZIN AND BEST FIT, TWO-COMPARTMENT MODEL

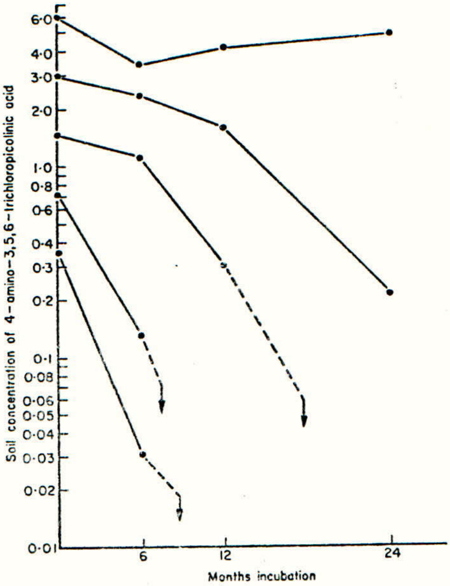


Figure 8 Detoxification rate of 4-amino-3,5,6-trichloropicolinic acid in soil N-1. Broken lines represent loss to below detectable level, approximately 0.01 ppm. (Hamaker, Youngson and Goring, 1968)

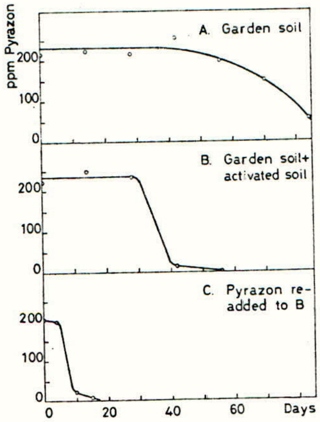
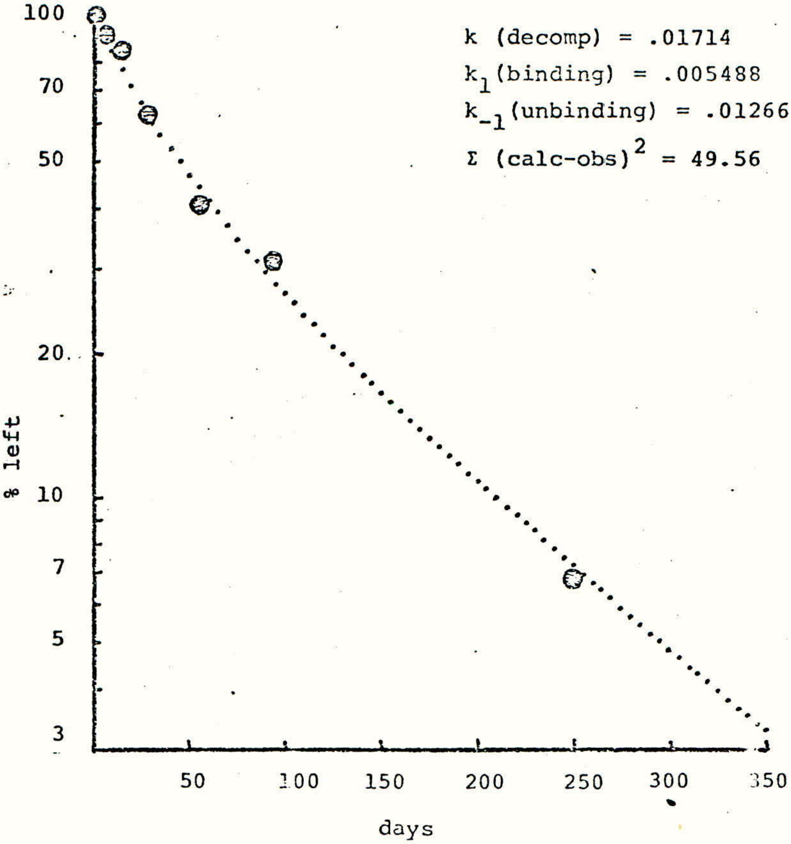


Figure 9 Time course of breakdown of 250 ppm of pyrazon in different soils.

A. Untreated garden soil (No 3).
B. Addition of 10% pyrazon decomposing soil (No. 1) to untreated garden soil (No. 3) causes accelerated breakdown.
C. The garden soil has become enriched with pyrazon decomposers and further additions of pyrazon are rapidly decomposed.
(Engvild and Jensen, 1969)

BEST FIT FOR DISAPPEARANCE OF 1 ppmw TRICLOPYR FROM A CALIFORNIA SOIL AT 35°C, 1/3 BAR MOISTURE 0.8% ORGANIC CARBON



k (decomp) = .01714

k_1 (binding) = .005488

k_{-1} (unbinding) = .01266

Σ (calc-obs)^2 = 49.56

FIGURE 10

BEST FIT FOR DISAPPEARANCE OF 1 ppmw TRICLOPYR FROM AN ILLINOIS SOIL AT 35°C AND 1/3 BAR MOISTURE 4.2% ORGANIC CARBON

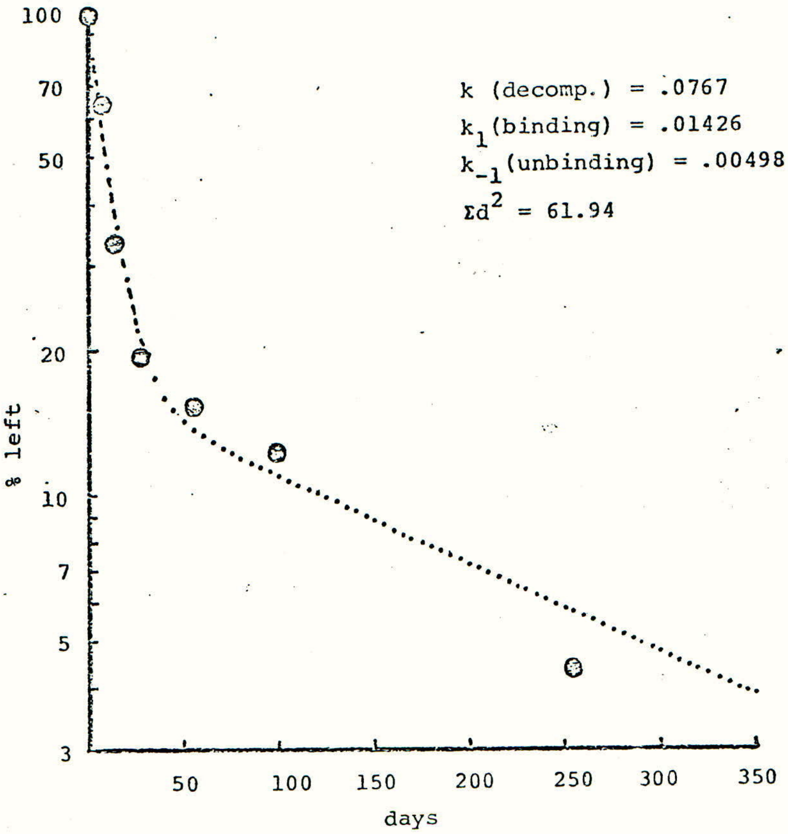


FIGURE 11

TABLE 1 - TWO-COMPARTMENT MODEL FOR SOIL DEGRADATION: VARIATION OF RATE CONSTANTS WITH TEMPERATURE

Chemical	Temperature	k (wk^{-1})	ΔE^* a/ (Kcal/mole)	k_1 (wk^{-1})	k_{-1} (wk^{-1})	k_1/k_{-1} b/	m_1 c/	ΔE^* a/ (Kcal/mole)
Diazinon	15°C	0.08796)	15.78 d/	0.1969	0.1456	1.35	-0.03215)	
	25°C	0.2415)		0.2980	0.1968	1.51	-0.07147)	11.17
	35°C	0.5250)		0.2242	0.1758	1.27	-0.1138)	
Thionazin	15°C	0.4936)		0.5166	0.2439	2.12	-0.1047)	
	25°C	0.6721)	9.78	0.1852	0.1332	1.39	-0.1006)	--
	35°C	1.225)		0.2088	0.1645	1.26	-0.1380)	

a/ Calculated by linear regression of 1/T against ln k, i.e., the Arrhenius equation, $\ln k = A - \Delta E^*/R\ (1/T)$

T = Absolute temperature (°K); R = Gas constant (1.987 cal. /deg. x mole); ΔE^* = Activation energy.

b/ k_1/k_{-1} is the equilibrium value for the ratio of unavailable chemical/available chemical.

c/ m_1 is the slope of the steady-state decomposition rate calculated according to the equation,

$$m_1 = \frac{-(k + k_1 + k_{-1}) - \sqrt{k^2 + k_1^2 + k_{-1}^2 + 2kk_1 - 2kk_{-1} + 2k_1k_{-1}}}{2}$$

d/ Comaa et al. (1969) report an activation energy of about 14 Kcal/mole for hydrolysis in aqueous solution.

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