Pesticide Degradation Kinetics

Probably because it is mathematically simple and can be easily fit to experimental data (as in the days before everyone had a high-speed computer), the first-order model has been widely used to describe pesticide degradation kinetics. In differential form,

$$\mathbf{dC / dt = -kC}$$

where C is pesticide concentration, t is time and k is the degradation rate constant. The model is often written using half-life, H, instead of k. The half-life is the time required for half of the mass of pesticide to be degraded. From integration of the above,

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

so that $k = (\ln 2) / t_{1/2}$ and

$$\mathbf{dC / dt = - (0.693 /\ t_{1/2}\ ) C}$$

Applicability of the first-order model makes several assumptions and, in some cases, either the assumptions do not hold or, for some other reason, the degradation data cannot be adequately described by first-order kinetics.

Assumptions

Typically degradation of a pesticide is a biotic process, however, there are abiotic degradation processes as well. The latter include photodegradation (that can produce a wild array of products) and various types of chemical degradation processes. Restricting degradation to the soil interior (no photodegradation component) and assuming negligible chemical degradation, pesticide degradation is an enzyme-catalyzed transformation. The rate of an enzyme-catalyzed reaction can be described by Michaelis-Menten kinetics

$$\mathbf{dC / dt = -(V_{max}\ C) / (K_m + C)}$$

where C is concentration in solution, V_{max} is maximum reaction rate (which includes contributions from extracellular soil enzyme activities and intracellular soil microbial activities catalyzing the transformation reactions), K_m is the Michaelis constant, and t is time. Since the value of maximum reaction rate, V_{max}, changes with the concentrations of extra- and intra-cellular enzymes in a system, Michaelis-Menten kinetics is applicable to a situation in which the microbial cells participating in the degradation are not growing to any appreciable degree. If this is the case and if $C << K_m$ (i.e.,. C is very low), then first-order kinetics are consistent with Michaelis-Menten kinetics and degradation may be described by the first-order model.

If degradation is dominated by intracellular microbial activities, the degradation kinetics may be represented by the modified Monod equation

$$\mathbf{dC / dt = - (\mu_{max}\, BC) / [Y(K_s + C)]}$$

where μ_{max} is the maximum specific growth rate, B is the density of active microbial cells, Y is the yield coefficient or the amount of biomass produced out of unit amount of substrate consumed, and K_s is the Monod constant at which the rate of growth is half the maximum rate. If the initial bacterial cell density is high relative to the substrate concentration, little or no increase in cell numbers is possible. Under these conditions, this Monod equation may be reduced to the Michaelis-Menten equation by setting $V_{max} = \mu_{max}\, B_0/Y$ and $K_m = K_s$, where B_0 is the initial density of microbial cells. And as with the Michaelis-Menten equation, if $K_s >> C$, it reduces to the first-order model.

If the number of microbial cells active in a degradation process increases significantly, the increase should be incorporated into the degradation model. For a degradation process dominated by microbial activity, the Monod equation given below can be used to simulate the increase in the density of microbial cells.

$$\mathbf{(1 / B)\, (dB / dt) = \mu_{max}\, C / (K_s + C)}$$

Among factors affecting soil microbial populations and activities are temperature and soil water. Although studies on pesticide degradation are conducted under constant temperature and moisture, degradation in the field are subject to substantial fluctuations in these and other parameters. Temperature dependence of biotic (and abiotic) degradation rate may be accounted for by use of the Arrhenius equation. If the first-order rate constant is determined at two different temperatures, then this model can be used to predict the rate constant at another temperature.

$$\mathbf{k(T) = k(T_0)\, exp\, [a\, (1/T - 1/T_0)]}$$

where T is absolute temperature, T_0 is the temperature for which $k(T) = k(T_0)$ and a is known from separate determinations of k at two different temperatures.

Other Degradation Models

Even under controlled conditions of temperature, soil moisture and soil fertility, i.e., conditions for which microbial populations and activities are expected to be rather constant, a low concentration of pesticide may exhibit deviation from first-order kinetics. Some researchers have found that such degradation behavior is adequately described by an N^{th}-order model,

$$\mathbf{dC / dt = -kC^N}$$

where N is an empirical constant. Although the N^{th}-order model may adequately describe degradation kinetics, it is not founded on any underlying mechanism. However, the dependence of C on t in this model is similar to the dependence of C on t in an extension of the first-order model in which the pesticide is presumed to be partitioned into two physically separate compartments, 1 and 2, each with different degradation rate constants.

$$\mathbf{dC / dt = (-k_1C_1) + (-k_2C_2)}$$

$$\mathbf{C = - k_1C_{10} \exp(-k_1t) – k_2C_{20} \exp (-k_2t)}$$

And since $C_0 = C_{10} + C_{20}$, the initial concentrations in these compartments, and there is no transfer between compartments

$$\mathbf{C = - k_1fC_0 \exp(-k_1t) – k_2(1-f)C_0 \exp (-k_2t)}$$

The number of such separate compartments can be increased without bound and the frequency of different rate constants statistically distributed, leading the same type of degradation behavior described by the N^{th}-order model. In other words, the N^{th}-order model is consistent with a large number of quire different degradation micro-environments.

Describing Appearance / Disappearance of Degradation Products

From the standpoint of environmental fate assessment and modeling, disappearance of the parent compound may be all that is needed. However, some degradation products may be as (or more) toxic as the parent so that their fate is also of interest. Tracking the whole suite of intermediates leading to complete degradation (i.e., release of CO_2 from the parent compound) is probably impossible. But being able to report as much detailed data as is possible and account for it within the framework of a kinetic model gives a sense of confidence that we have an adequate understanding of the fate of a pesticide.

If one or more intermediates can be identified and measured, it may be possible to describe the kinetics of pesticide degradation further than just the disappearance of the parent compound. For example, if loss of a functional group (whether directly or via a series of reaction intermediates) gives a fairly persistent degradation product, its appearance may be described based on the concentration of remaining parent compound. In the case of first-order kinetics,

$$\mathbf{dC_I / dt = k^*C_P = kC_{P0} \exp(-kt)}$$

where C_I and C_P are concentrations of the intermediate and parent, respectively. Including degradation of the intermediate,

$$\mathbf{dC_I / dt = k^*C_{P0} \exp(-kt) - k_I C_I}$$

where k_I is the rate constant for degradation of the intermediate, I.

Figure 1 shows disappearance of parent compound, norflurazon, and appearance of the intermediate, desmethyl norflurazon.

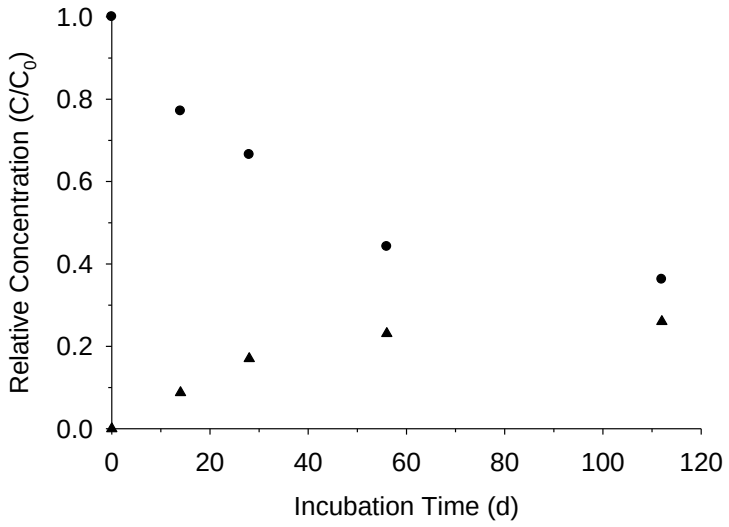

Figure 1. Relative concentrations of norflurazon (circles) and desmethyl norflurazon (triangles) as a function of incubation in a conventionally tilled Dundee surface soil.

If degradation is tracked using a radiolabel (^{14}C), it is often found to proceed with the development of an apparently bound fraction, so called because it is unextractable by the solvent(s) used to recover the parent compound. This fraction is strongly sorbed, shows faster rate of sorption than desorption, and perhaps is irreversibly sorbed. The rate of release of bound ^{14}C is of interest because it provides an estimate of whether or how fast highly sorbed intermediates might be released back into the biological environment. The degradation of norflurazon (Fig. 1) proceeds with development of bound residue. A broad overview of norflurazon degradation would therefore include disappearance of extractable compounds (norflurazon, desmethyl norflurazon and unidentified polar intermediates), unextractable ^{14}C and ^{14}C that appears in $^{14}CO_2$ (mineralized). The behavior of these three pools might be described with a first-order model that assumes reversible (forward and reverse rate constants) sorption of extractable compounds to produce the unextractable pool and mineralization from the extractable pool,

$$\mathbf{dE / dt = -(k_m + k_f)E + k_rU}$$

$$\mathbf{dU / dt = k_fE – k_rU}$$

$$\mathbf{dV / dt = k_mE}$$

where E, U and V are concentrations (or relative concentrations) of extractable, unextractable and mineralizad ^{14}C and the various ks are rate constants.

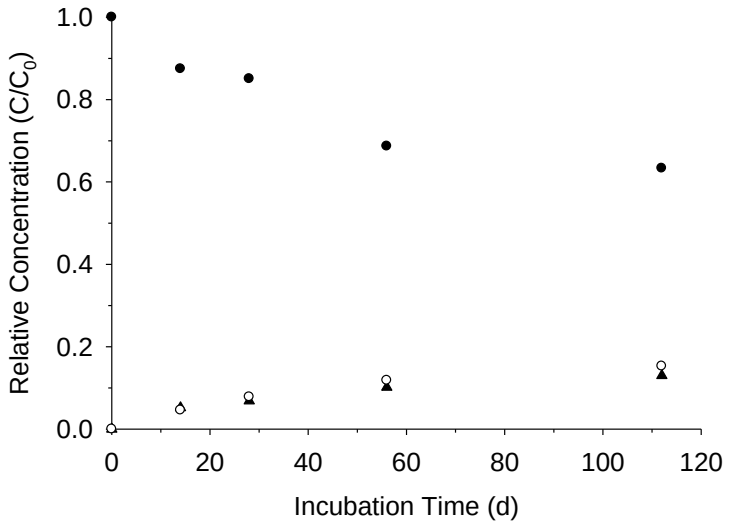

Figure 2. Fate of ^{14}C during degradation of ^{14}C-labeled norflurazon: filled circles = extractable, unextractable or bound = open circles and mineralized = filled triangles ^{14}C.

Glossary

Catabolic Degradation: Catabolic degradation refers to the microbial degradation from which the substrates are utilized as sources of energy and carbon for microbial growth.

Cometabolic Degradation: Cometabolic degradation refers to the microbial degradation from which no energy or carbon is derived from substrate oxidation.

Density of Active Microbial Cells : Density of active microbial cells is the number of microbial cells active in a degradation process per unit bulk volume of soil.

Extracellular Degradation: Extracellular degradation refers to the transformation of a chemical compound by accumulated extracellular soil enzymes (enzymes that are not associated with active microbial cells).

First-order Rate Constant: First-order rate constant is a coefficient in an equation describing the rate of a first-order kinetics. The product of the coefficient and the reactant concentration yields the reaction rate.

Half-life: The half-life of a reaction is the time required for the concentration of one of the reactants to decrease to half of its initial value.

Maximum Reaction Rate: Maximum reaction rate is the reaction rate under the conditions that the substrate concentration is high enough not to impose any limitation on the reaction process.

Maximum Specific Growth Rate: Maximum specific growth rate is the specific growth rate under the conditions that the substrate concentration is high enough not to impose any limitation on the growth of microbial cells.

Michaelis Constant: Michaelis constant is a substrate concentration at which the reaction rate is half the maximum reaction rate.

Microbial Degradation: Microbial degradation refers to the transformation of a chemical compound by the activity of microorganism, which are essentially intracellular, enzyme-catalyzed reactions encountered in the regular metabolic activity of microbes.

Monod Constant: Monod constant is a substrate concentration at which the growth rate of the biomass of microbial cells participating in the reaction is half the maximum growth rate.

Specific Growth Rate: Specific growth rate is the growth rate per unit amount of microbial cells.

Yield Coefficient: Yield coefficient represents the amount of microbial biomass produced out of unit amount of substrate consumed

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