First-Order Degradation

Degradation in soils is the result of a combination of chemical and, predominantly, biological events (Bollag and Liu, 1990; Wu and Nofziger, 1999). A first-order degradation model is often used to simulate the decrease of residual mass of a chemical compound in a soil system after its application (Dykaar and Kitanidis, 1996; Walker, 1974). If the first-order rate constant or half-life remains unchanged in the degradation process, the residual mass of the chemical degraded decreases exponentially with time. This program displays the changing concentration of a chemical undergoing first-order degradation for user-specified degradation rates and initial concentrations.

Model Description

The first-order degradation kinetics may be expressed as (Dykaar and Kitanidis, 1996; Wu and Nofziger, 1999)

$$\frac{dC}{dt} = -kC$$

where C is the concentration of the product of interest, k is the first-order rate constant, and t is time. In practice, the first-order rate constant often is replaced by a half-life, H, where H = ln(2.0)/k. The first-order equation can then becomes written as

$$\frac{dC}{dt} = -\frac{0.693}{H}C$$

(Rocha and Walker, 1995). If the degradation rate remains constant during the degradation process, the residual concentration, C(t), is given by

$$C(t) = C_o e^{-kt} = C_o e^{-0.693t/H} = C_o\left(0.5^{t/H}\right)$$

where C_0 is the initial concentration. From the expression above, we see that the logarithm of the concentration is a linear function of time.

Assumptions and Simplifications

The simplifications for the computer program can be summarized as follows:

1. The degradation process can be adequately described by the first-order model.
2. The half-life or degradation rate constant does not change with time. This may require that the environmental factors such as soil temperature and water content remain constant throughout the degradation period.

Let us examine the degradation of pesticides in more detail to gain insight into conditions that can be described by the first-order model. Biodegradation of pesticides in soils is an enzyme-catalyzed transformation of organic compounds. The rate of an enzyme-catalyzed reaction can be described by the Michaelis-Menten equation (Alexander, 1994; Paul and Clark, 1989):

$$\frac{dC}{dT} = -\frac{V_{max}C}{K_m + C} \qquad [1]$$

where C is the concentration of a chemical compound in a soil solution, V_{max} is the maximum reaction rate, which includes contributions from extracellular soil enzyme activities and intracellular soil microbial activities catalyzing the transformation reactions, K_m is a Michaelis constant, and t is time. The value of maximum reaction rate, V_{max}, changes with the concentrations of extra- and intra-cellular enzymes in a soil system. Because the Michaelis-Menten kinetics was formulated on the basis of constant catalyzing material (enzymes), it is applicable to a situation in which the microbial cells participating in the degradation are not growing to any significant degree.

If degradation is dominated by intracellular microbial activities, the degradation kinetics may be represented by the modified Monod equation (Alexander, 1994)

$$\frac{dC}{dt} = -\frac{\mu_{max}BC}{Y(K_s + C)} \qquad [2]$$

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, equation [2] may be reduced to equation [1] by setting $V_{max} = \mu_{max} B_0/Y$ and $K_m = K_s$, where B_0 is the initial density of microbial cells.

Both equation [1] and [2] are reduced to the first-order equation if the substrate concentration is very low. That is, if $C \ll K_m$ for equation [1] or $C \ll K_s$ for equation

[2]. 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 (Alexander, 1994).

$$\frac{1}{B}\frac{dB}{dt} = \frac{\mu_{max} C}{K_S + C}$$

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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