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SUBJECT: BACK CALCULATION TO APPLICATION RATE USING PESTICIDE SOIL CONCENTRATION AND ESTIMATED TERRESTRIAL FIELD DISSIPATION HALF-LIFE

Background

The Department of Pesticide Regulation has received requests on methodology to calculate potential application rates or dates of application based on measured concentration of pesticides in soil samples. The samples are usually taken some time after the application date so the pesticide has been subject to dissipation from the site of application through chemical and biological degradation and offsite movement in water. During registration of a product, registrants are required to provide environmental fate data to the U.S. Environmental Protection Agency (EPA). One requirement is denoted as terrestrial field dissipation (TFD) where the pesticide is applied to a soil and soil samples are taken over time to provide an estimate of the rate of disappearance. The rate of disappearance denoted TFD half-life (t ½) can be used in a back calculation to provide estimates of initial soil application rates.

Methodology

The U.S. EPA and Health Canada issued a collaborative North American Free Trade Agreement guidance document on the conduct of a TFD study and eventual mathematical derivation of t ½ value (Corbin et al., 2006). The document explains the use of a first-order kinetic decay function to describe pesticide dissipation. The equation is:

Eq. 1. $$M = M_0 e^{-kt}$$

In this equation, M is the mass of compound at time t, M_o is the initial mass applied to the soil, k is the rate constant for disappearance, and t is time. One method to obtain a solution to this equation is to linearize the function by converting to natural logarithms as in Eq. 2.

Eq. 2. $\ln(M) = \ln(M_{0)} + kt$

Equation 3 provides a method to express k in terms of a half-life by indicating the time it takes for the concentration to be reduced to half its value:

Eq. 3. $t\,½ = \ln(0.5)/k$

Ln(0.5) is the degradation of a concentration to 50 percent of its value. When t ½ is known the relationship can be reversed as in Eq.4 and k can be estimated.

Eq. 4. $k = \ln(0.5)/t\,½$

For example, if the t ½ is known at 25 days then the rate constant is:

Eq. 5. $k = \ln(0.5)/25 = -0.693/25 = -0.02772$

Once the rate constant is computed, the concentration from a known starting value can be forecasted for any future time. Assumption of first-order kinetics means that the relationship is constant whether calculating forward or backward in time. Thus, if a soil concentration after application is known, then an estimated concentration can be back calculated. For example, if a soil concentration is measured at 0.4 ppm and the t ½ is known at 25 days, one might ask what the concentration was 120 days before. Since the time span is 120 days and the t ½ is 25 days the pesticide would have undergone 4.8 half-lives, which is calculated as 120 days/25 days. Equation 6 is used for estimating the soil concentration back to 120 days:

Eq. 6. $Mi = M/(0.5^{tn}) = 0.4\text{ ppm}/(0.5^{4.8}) = 11.14\text{ ppm}$

Where Mi is the calculated concentration at 120 days earlier and tn is the number of half-lives for a given time period.

Calculation of the mass of pesticide residue in a sampled soil core requires the bulk density value for each soil segment, the depth of the sample, and the residue concentration on a dry soil basis. From the soil concentration, the residue mass is expressed on a soil area basis using Eq. 7.

Eq. 7. $$\frac{mg\text{ pesticide}}{kg\text{ dry soil}} \text{ x } \frac{kg\text{ dry soil}}{L\text{ soil}} \text{ x } \frac{1000L\text{ soil}}{m^3\text{ soil}} \text{ x } \frac{m\text{ soil segment length}}{1} = \frac{mg\text{ pesticide}}{m^2\text{ soil}}$$

For example if residue concentration on a dry soil basis is 11.14 mg/kg (11.14 ppm from Eq. 6), soil bulk density is 1.45 kg/L, standardizing units from liters to cubic meters is1000 L/m^3, and the soil segment length is 0.15 m (6 inches), then residue mass on square meter basis is:

Eq. 8. $11.14 \text{ x } 1.45 \text{ x } 1000 \text{ x } 0.150 = 2423 \text{ mg/m}^2$

Residue mass is now expressed on a standardized metric basis and can be converted to lbs per acre according to Eq. 9:

Eq. 9. $\text{lbs/acre} = \text{mg/m}^2 \text{ x } 1 \text{ lb/454,000 mg x } 4{,}046.9 \text{ m}^2\text{/acre} = \text{mg/m}^2 \text{ x } 0.0089$

For this example where 0.4 ppm of a pesticide with a known t ½ of 25 days was measured in a soil sample taken down to 0.15 m with a bulk density of 1.45 kg/L, the back calculation to lbs/acre is 2423 mg/m^2 x 0.0089, which equals 21.6 lbs/acre.

References

Corbin, M., M. Eckel, M. Ruhman, D. Spatz, N. Thurman, R. Gangaraju, T. Kuchnicki, R. Mathew, and I. Nicholson. 2006. NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies. U.S. EPA and Health Canada. March 31, 2006.