Appendix O. Use of fugacity approach to estimate exposures to small mammals consuming earthworms contaminated with dicofol from treatment sites

The T-REX model (USEPA 2008) is useful for assessing exposures of terrestrial animals to pesticide residues on foliar surfaces of crops and seeds. The model cannot be used to assess pesticide exposures to terrestrial animals resulting from consumption of earthworms contaminated with pesticide mass present in the soil of the application site. In order to explore the potential exposures of mammals to dicofol present in the soil and earthworms present on the treatment site, a simple fugacity approach was employed to estimate dicofol concentrations in earthworms.

Fugacity is most often regarded as the "escaping tendency" of a chemical from a particular phase. Fugacity (F) has units of pressure, generally pascals (Pa), and can be related to phase concentrations. For any particular environmental phase (e.g., water, soil, air, or biota) there is a corresponding "fugacity capacity" with units of mol/m^3-Pa and is denoted by Z. The relationship between fugacity, fugacity capacity and chemical concentration (C) is defined by Equation 1.

$$Equation\ 1. \quad C = Z * F$$

Fugacity capacities for a given chemical are calculated for the phases of interest as part of the exposure point estimation methodology (Mackay and Paterson 1981). The following calculations of fugacity capacities for water (Z_W), soil (Z_S) and earthworms (Z_E) (Equations 2-4) require several chemical-specific parameters and assumptions of system temperature (25^{o}C) and steady state equilibrium. Parameter values relevant to Equations 2-4 are defined in Table O1.

$$Equation\ 2. \quad Z_W = \frac{1}{H}$$

$$Equation\ 3. \quad Z_S = \frac{K_d * \rho_S}{H}$$

$$Equation\ 4. \quad Z_E = \frac{L * K_{OW}}{H}$$

Table O1. Summary of parameters relevant to earthworm fugacity model.

Symbol	Definition	Units
C_E	Chemical concentration in earthworm tissue	mol/m^3
C_E'	Chemical concentration in earthworm tissue	g/kg
C_S	Chemical concentration in soil	mol/m^3
C_W	Chemical concentration in pore water of soil	mol/m^3
H	Henry's Law constant	m^3-Pa/mol
K_d	Soil partitioning coefficient	cm^3/g
K_{OW}	Octanol to water partition coefficient	none
L	Lipid fraction of earthworm	none
MW	molecular weight of chemical	g/mol
Z_E	Fugacity capacity of pesticide in earthworms	mol/m^3-Pa
Z_S	Fugacity capacity of pesticide in soil	mol/m^3-Pa
Z_W	Fugacity capacity of pesticide in (pore) water	mol/m^3-Pa
ρ_E	density of earthworm	kg/m^3
ρ_S	Bulk density of soil	g/cm^3

Fugacity capacities for a given chemical are calculated for the phases of interest as part of the exposure point concentration estimation methodology. By definition, the ratio between Z values of different phases (compartments) equals the partitioning coefficient (for example, see Equation 5).

$$\textit{Equation 5.} \quad \frac{Z_{octanol}}{Z_{water}} = K_{OW}$$

In this approach, it is assumed that a pesticide partitions between the soil, the (pore) water and the air contained within the soil of the treatment site. It is assumed that earthworms dwelling within the soil are exposed to a pesticide via ingestion of contaminated soil and pore-water (Belfroid et. al 1994). The concentration of a pesticide in earthworm tissues can be calculated according to Equation 6. The parameters of equation 6 are defined in Table O1.

$$\textit{Equation 6.} \quad C_E = C_S * \left(\frac{Z_E}{Z_S}\right) + C_W * \left(\frac{Z_E}{Z_W}\right)$$

Equation 6 can be redefined using equations 2-4 as follows in Equation 7. Equation 7 is used to calculate the concentration of a pesticide in earthworms inhabiting the soil of treatment sites.

$$\textit{Equation 7.} \quad C_E = K_{OW} * L * \left(\frac{C_S}{K_d * \rho_s} + C_W\right)$$

C_S and C_W are calculated using PRZM, where C_S = 0.027 mol/m^3 and C_W = 4.32x10^{-4} mol/m^3, based on estimates generated from the CA fruit scenario for applications of dicofol to pome fruit. These concentrations were selected to be representative of the steady-state concentrations of dicofol in soil and soil-pore water (see Figures 8 and 9 of the risk assessment; values converted using molecular weight of dicofol = 370.5 g/mol). Kd and Kow were 64.6 cm^3/g and 1148154 (= log Kow value of 6.06), based on available data for dicofol. ρ_S is which is 1.65 g/cm^3, based on the properties of the soil of the CA fruit scenario. L is based on the lipid content of earthworms, which was assumed to be 0.01 (Cobb et al. 1995). The resulting C_E value is in units of mol/m^3. This value is converted to units of g/kg using equation 8. The density of the earthworm (ρ_E) is assumed to be 1000 kg/m^3 (equivalent to density of water). **The resulting concentration of dicofol in earthworms (C_E') is 2.914 g/kg.**

$$\textit{Equation } 8. \quad C_E^{'} = \frac{C_E * MW}{\rho_E}$$

References:

Belfroid, A., M. Sikkenk, W. Seinen, K.V. Gestel, J. Hermens. 1994. The toxicokinetic behavior of chlorobenzenes in earthworm (*Eisenia andrei*) experiments in soil. Environ. Toxicol. Chem. 13: 93-99.

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Mackay, D. and S. Paterson. 1981. Calculating fugacity. Environ. Sci. Technol. 15: 1006-1014.

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