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

The T-REX model is useful for assessing exposures of terrestrial animals to pesticides applied to foliar surfaces of crops. The model cannot be used to assess pesticide exposures to terrestrial animals resulting from applications involving soil incorporation.

In order to explore the potential exposures of mammals to oxamyl following applications involving ground application, a simple fugacity approach was employed to estimate oxamyl concentrations in earthworms and subsequent exposures to mammals consuming earthworms. In this approach, it is assumed that oxamyl partitions between the organic carbon, 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 oxamyl in earthworm tissues is calculated according to Equation 1. Some parameters in Equation 1 are calculated using equations 2-8. The parameters and their values in Equations 1-8 are defined in Table K.1. In equations 1, 6, 7 and 8, fugacity capacities (Z) for oxamyl are calculated for different phases of the system (specifically, soil, earthworm and pore-water) (Mackay and Paterson 1981).

Equation 1. $C_E = C_S * \left(\frac{Z_E}{Z_S} \right) + C_W * \left(\frac{Z_E}{Z_W} \right)$

Equation 2. $C_W = \frac{C_S}{K_{bw}}$

Equation 3. $K_{bw} = \rho_s * K_d + \theta + (\varepsilon - \theta) * K_{aw}$ (Trapp and McFarlane 1995)

Equation 4. $K_{aw} = \frac{H}{R * T}$

Equation 5. $H = \left(\frac{V * MW}{Sol} \right)$

Equation 6. $Z_E = \frac{L * K_{OW}}{H}$

Equation 7. $Z_S = \frac{K_d * \rho_S}{H}$

Equation 8. $Z_W = \frac{1}{H}$

Table K.1. Parameters and results of Equations 1-9.

Symbol	Definition	Value	Units
C_E	Chemical (i.e. oxamyl) concentration in earthworm tissue	1.3 to $4.3x10^{-4}$	mol/m^3
C_S	Chemical (i.e. oxamyl) concentration in soil	0.014	mol/m^3
C_W	Chemical (i.e. oxamyl) concentration in pore water of soil	0.015-0.030	mol/m^3
H	Henry's Law constant, value specific to oxamyl	$4.0\ x10^{-8}$	m^3-Pa/mol
K_{aw}	Air-to-water partitioning coefficient for oxamyl	$1.6\ x10^{-11}$	none
K_{bw}	Bulk soil-to-water partitioning coefficient	0.46-0.94	none
K_d	Soil partitioning coefficient, value specific to oxamyl	0.12-0.49	cm^3/g
K_{OW}	Octanol to water partition coefficient for oxamyl	0.36*	none
L	Lipid fraction in earthworm	0.01	none
R	Universal gas constant	8.31	Pa-m^3/mol-K
T	temperature	298	K
Z_E	Fugacity capacity of oxamyl in earthworms	90000	mol/m^3-Pa
Z_S	Fugacity capacity of oxamyl in soil	0.39 to $1.6\ x10^7$	mol/m^3-Pa
Z_W	Fugacity capacity of oxamyl in (pore) water	$2.5x10^7$	mol/m^3-Pa
ρ_S	Bulk density of soil	1.3	g/cm^3
θ	Volumetric fraction of soil	0.30	none
ε	Volumetric total porosity of soil	0.50	none

*MRID 40499702

Equation 1 can be redefined using equations 2-8 as follows in Equation 9. Equation 9 is used to calculate the concentration of oxamyl in earthworms inhabiting the soil of treatment sites.

$$Equation\ 9. \quad C_E = K_{OW} * L * \left(\frac{C_S}{K_d * \rho_s} + C_W \right)$$

Formulated product labels for oxamyl allow for a maximum single application of 4.0 lb a.i./A (0.0020 mol/m^2) via soil incorporation to several uses, including apples, cherries, citrus, cucumber, melons, peaches, pears, potatoes, pumpkin and squash. If it is assumed that earthworms inhabit the top 0.15 m of soil and that an application of oxamyl made via soil incorporation results in a homogenous distribution of oxamyl within the volume of soil inhabited by earthworms, the soil concentration (C_S) of oxamyl is 0.014 mol/m^3.

Using the vapor pressure (V = 3.8 $x10^{-7}$ torr = 5.07 $x10^{-5}$ Pa; MRID 42526101), the molecular weight (MW = 219 g/mol; MRID 40499702) and the solubility (Sol = 2.8$x10^{5}$ mg/L = 2.8$x10^{5}$ g/m^3; MRID 40499702) the Henry's Law constant (H) can be calculated according to Equation 5 (U.S. EPA 2002). The resulting H for oxamyl is 4.0 $x10^{-8}$ Pa-m^3/mol.

The air-to-water partition coefficient (Kaw) for oxamyl is calculated using Equation 4 along with the Henry's law constant calculated above and the universal gas constant (8.31 Pa-m^3/mol-K). Assuming that the temperature of the soil is 298 K, the K_{aw} value for oxamyl is 1.6 $x10^{-11}$.

The bulk soil-to-water partitioning coefficient (K_{bw}) is calculated using Equation 3 along with the K_d and K_{aw} values for oxamyl. It is assumed that the bulk density of the soil (ρ_S) is 1.3 g/cm^3. It is also assumed that the volumetric fraction of the soil (θ) and volumetric total porosity of the soil (ε) are 0.30 and 0.50, respectively. Based on these assumptions, K_{bw} ranges 0.46-0.94.

Equation 2 is used to calculate the concentration of oxamyl in the pore water of the soil (C_W). Considering the range of K_{bw} values, C_W for oxamyl ranges 0.015-0.030 mol/m^3.

With the assumption that the lipid fraction (L) of the earthworm is 0.01 (Cobb et al. 1995), the range of chemical concentrations of oxamyl in the earthworm (C_E) is 1.3 to 4.3$x10^{-4}$ mol/m^3 (= 0.029-0.094 g/m^3). If the density of the earthworm is 1 g/cm^3 (equivalent to 1$x10^{6}$ g/m^3), **the concentrations of oxamyl in earthworm tissues are 0.029-0.094 mg oxamyl/kg earthworm.** This information can be used to estimate (acute) dose-based exposures of small mammals (representing prey of terrestrial-phase CRLF) to oxamyl through consumption of contaminated earthworms.

Daily fresh food intake (F; g/day) of a mammal can be calculated according to Equation 10 (U.S. EPA 1993, U.S. EPA 2006), where BW = body mass of the animal (in g) and W = fraction of water in food. In this case, it is assumed that the BW of the animal is 20 g and the W of the earthworm is 0.8. Therefore, F = 16.8g/day = 0.0168 kg/day.

$$Equation\ 10. \quad F = \frac{0.621 * BW^{0.564}}{1 - W}$$

If it is assumed that the small mammal being assessed eats only earthworms on the day of treatment (meaning that there would be no degradation of oxamyl), the acute dose of oxamyl to a 20 g mammal would be 0.024 to 0.078 mg/kg-bw. This range of exposure values is 2 orders of magnitude below the LD_{50} values for rats (2.5-3.1 mg/kg-bw; MRID 00063011) exposed to oxamyl.

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