Appendix K. Methods for Calculating PCNB Residues in Soil and Worms.

(a) Accumulation of PCNB Residues on Soil

In order to compare soil residues of PCNB to toxicity data from earthworms (Roark and Dale, 1979; Van Gestel *et al.*, 1991), a modeling analysis of soil residues was frst conducted for a treated site following 30 years of application. PRZM/EXAMS runs were conducted for ground applications to cotton, potatoes, and cole crops, and total soil concentrations were estimated for the upper 10 cm soil horizon (turf analysis was not conducted because uses are not incorporated into soil). The resulting 1-in-10-year peak concentrations in the soil for total PCNB were 5, 7, and 78 mg/kg-soil for cotton, potatoes, and cole crops, respectively, which translates to soil concentrations of 7800, 10,780, and 117,000 mg/m^3, respectively (based on soil bulk density conversions of 1.56, 1.54, and 1.5 g/cm^3 for CA cotton, potato, and cole crop scenarios, respectively). The 1-in-10- year peak concentrations in the pore water for total PCNB were 257, 794, and 689 mg/m^3, respectively. Estimated annual average peak PCNB soil concentrations tended to increase for the first several years of the 30-year period before reaching a plateau.

(b) Use of fugacity approach to estimate exposures to small mammals consuming earthworms contaminated with PCNB from treatment sites

The T-REX[1] model 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 CTS, CCR, and SFGS to PCNB present in the soil and earthworms present on the treatment site, a simple fugacity approach was employed to estimate PCNB 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. $C = Z * F$

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°C) and steady state equilibrium. Parameter values relevant to Equations 2-4 are defined in **Table 1**.

[1] Available at http://www.epa.gov/oppefed1/models/terrestrial/index.htm

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

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

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

Table 1. 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 1**.

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

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.

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

C_S and C_W are calculated using PRZM. C_S values are 0.026, 0.036, and 0.396 mol/m^3 for cotton, potato, and cole crop uses, respectively; C_W values were 8.7x10^{-4} 2.7x10^{-3}, and 2.3x10^{-3} mol/m^3 for cotton, potato, and cole crop uses, respectively. Kd and Kow values were 15.5 cm3/g and 100000 (= log Kow value of 5), respectively, based on available data for PCNB. ρ_S was 1.56, 1.54, and 1.5 g/cm^3, based on the properties of the soil of the CA cotton, potato, and cole crop scenarios, respectively. 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 concentrations of PCNB in earthworms (C_E') are 0.58, 1.2, and 5.7 g/kg-bw for cotton, potato, and cole crop uses, respectively.** These values were used to represent earthworms as an additional source of dietary exposure that could be compared to chronic dietary endpoint values for the CTS, CCR, and SFGS in the risk characterization portion of the assessment.

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

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.

Cobb, G.P., E.H. Hol, P.W. Allen, J.A Gagne, R.J. Kendall. 1995. Uptake, metabolism, and toxicity of terbufos in the earthworm (Lumbricus terrestris) exposed to COUNTER-15G in artificial soils. Environ. Toxicol. Chem. 14(2):279-285.

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

Roark J.H., Dale J.L. 1979. The Effect of Turf Fungicides on Earthworms. Ark.Acad.Sci.Proc. 33: 71-79.

USEPA. 2008. User's Guide: T-REX Version 1.4.1 (Terrestrial Residue Exposure model). United States Environmental Protection Agency. Environmental Fate and Effects Division.

Van Gestel C.A.M., Ma W.C., Smit C.E. 1991. "Development of QSARs in Terrestrial Ecotoxicology: Earthworm Toxicity and Soil Sorption of Chlorophenols, Chlorobenzenes and Dichloroaniline". Sci. Total Environ. 109/110.