APPENDIX G. Fugacity Model- Terrestrial Chronic Exposure Estimates for Granular Applications of Permethrin

There is potential for exposure of birds and mammals to granular permethrin by direct ingestion of granules or ingestion of contaminated food items. They also may be exposed by other routes, such as incidental ingestion of contaminated soil, dermal contact with treated granular surfaces and soil during activities in the treated areas, preening activities, and ingestion of drinking water contaminated with pesticide. It should be noted, however, that the primary route of exposure to permethrin granules will be via the oral route because it is not volatile and it is not expected to appreciably absorb through the skin relative to absorption via the gut following direct consumption (the estimated conservative dermal absorption factor is 15%; refer to the Health Effects Division's chapter for the Reregistration Eligibility Decision Document (RED) for permethrin (Dated April 4th 2006; DP Barcode D324993)). Therefore, ingestion of granules and consumption of terrestrial invertebrates that have bioconcentrated pesticide residues were considered as routes of exposure in this assessment.

Although a bird's or mammal's habitat is not limited to a square foot, there is presumably a direct correlation between the concentration of a pesticide in the environment (mg/ft^2) and the chance that an animal will be exposed to a concentration that could adversely affect its survival. For granular applications of permethrin, acute exposure and risks to terrestrial wildlife are estimated with the conceptual approach and the LD_{50}/ft^2 method given in the model T-REX and discussed elsewhere. EFED has no standard methodology for assessing chronic risk to terrestrial organisms from granular applications. The chronic exposure estimation and risk characterization for terrestrial wildlife (birds and mammals) in this risk assessment considers granular routes of exposure including direct ingestion of soil invertebrates that have bioconcentrated permethrin residues of granules in soil. In addition, exposure and risk to terrestrial soil-dwelling invertebrates resulting from granular permethrin were also considered using the methodology described below.

<u>Concentrations in Soil</u>

Soil concentrations of permethrin were calculated based on a depth of 7.6 cm (three inches; a chemical concentration averaged over a 7.6 cm soil depth was used to reflect a concentration across the earthworm occupied area of soil), the maximum application rate, number of applications, and the minimum interval for each use selected as the representative use for a "Use Category", and a 1-acre terrestrial environment. The general expression for any concentration term is given by Equation 1:

$$C_i = \frac{mass}{volume} \qquad \text{Equation (1)}$$

The mass of permethrin is determined by the application rate, while the volume of soil is determined by the soil depth (z) and soil bulk density (ρ). Adding these terms to Equation 1 and applying unit conversions yields a more detailed equation for C_{soil} in units of mg/kg:

$$C_{soil\ i} = \frac{application\ rate}{soil\ depth \times soil\ density} = \frac{AR \times CF_1 \times CF_2}{z \times CF_3 \times \rho_{soil}} \quad \text{Equation (2)}$$

where,

$C_{soil\ i}$	=	concentration in soil immediately following a single application (mg/kg)
AR	=	application rate (lb ai/acre)
z	=	soil depth (cm)
ρ_{soil}	=	soil bulk density (g/cm^3)
CF_1	=	conversion factor, 453582.4 mg = 1 lb
CF_2	=	conversion factor, 1 acre = 40468730 cm^2
CF_3	=	conversion factor, 0.001 kg = 1 g

Note that Equation 2 does not require a term for surface area as long as it is assumed that the application rate and soil characteristics are homogeneous throughout the area of application. Assuming $\rho = 1.3\ g/cm^3$, and combining all conversion factors yields Equation 3, in which soil concentration is determined by the ratio of the application rate (lb a.i./A) divided by the soil depth (cm) multiplied by a constant, 8.62:

$$C_{soil\ i} = 8.62 \times \frac{AR}{z} \quad \text{Equation (3)}$$

This equation provides an estimate of the soil concentration immediately following a single pesticide application. This approach does not model possible accumulation of chemical in surface soil following multiple applications, nor does it account for dissipation kinetics. In order to determine the maximum soil concentration *under a multiple application scenario with a uniform application rate and interval throughout*, a measure of dissipation in surface soil (the aerobic soil metabolism half-life of 111 days for permethrin used in the PRZM/EXAMS modeling; three times the single available value of 37 days) and the following equation was used:

$$C_{soil_{max}} = \sum_{i=1}^{n} C_{soil_i} * e^{(-k * T)} \quad \text{Equation (4)}$$

where,

$C_{soil\ max}$	=	the maximum concentration of chemical found in bulk soil under a multiple application scenario (mg/kg)
n	=	the maximum number of applications
$C_{soil\ i}$	=	concentration in soil resulting solely from the i^{th} application of a pesticide (mg/kg) = Equation 3
T	=	the time in days from the i^{th} application until the final application
k	=	soil degradation rate constant = calculated assuming first order kinetics with the following equation = ln(0.5) / ((aerobic soil metabolism half-life)(-1))

<u>Concentrations in Soil Invertebrates</u>

An estimation of permethrin concentrations potentially accumulated in the tissues of earthworms (the model invertebrate) was required to complete the exposure estimates for terrestrial invertebrates and insectivorous birds and mammals. This estimation of earthworm concentration was calculated using a fugacity-based (equilibrium partitioning) approach based on the work of Trapp and McFarlane (1995) and Mackay and Paterson (1981). Earthworms dwelling within the soil are exposed to contaminants in both soil pore water and via the ingestion of soil (Belfroid et al. 1994). The concentration of permethrin in earthworms was calculated as a combination of uptake from soil pore water and gastrointestinal absorption from ingested soil:

$$C_{earthworm} = [(C_{soil\ max})(Z_{earthworm}/Z_{soil})]+[(C_{soil\ water})(Z_{earthworm}/Z_{water})] \qquad \text{Equation (5)}$$

where,

$C_{soil\ max}$ = the maximum concentration of chemical found in bulk soil under a multiple application scenario
$Z_{earthworm}$ = the fugacity capacity of chemical in earthworms = $(lipid)(K_{ow})(\rho_{earthworm})/H$
Z_{soil} = fugacity capacity of chemical in soil = $(K_d)(\rho_{soil})/H$
Z_{water} = fugacity capacity of chemical in water = 1/H
$C_{soil\ water}$ = concentration of chemical in soil water = $C_{soil\ max}/K_{bw}$
K_{bw} = bulk soil-to-water partitioning coefficient = $(\rho_{soil})(K_d)+\theta+(\varepsilon-\theta)(K_{aw})$
K_{aw} = air-to-water partitioning coefficient = H/RT
H = Henry's Constant specific to permethrin = $1.4\text{x}10^{-6}$ atm-m^3/mol
R = universal gas constant =8.31 Joules-m^3/mol-^oK
T = temperature ^oK =assumed to be 298 ^oK
K_{oc} = pesticide organic carbon/ water partitioning coefficient = 76,800L/kg
K_d = soil partitioning coefficient for permethrin = (K_{oc} * 0.02 (assumed fraction of soil organic carbon))
ρ_{soil} = bulk density of soil =assumed to be 1.3 g/cm^3
θ = volumetric fraction of the soil =assumed to be 0.30
ε = volumetric total porosity of the soil = (1-(ρ_{soil} /partical densitiy of 2.65 mineral soils)
lipid = fraction of lipid in organism = 0.01 (Cobb et al. 1995)
K_{ow} = the octanol to water partitioning coefficient for permethrin =$1.26\text{x}10^6$
$\rho_{earthworm}$ = the density of the organism g/cm^3 = assumed to be 1 g/cm^3

Table G.1 summarizes the model inputs and exposure estimates (i.e., earthworm concentrations in ppm) for insectivorous birds, insectivorous mammals, and terrestrial invertebrates, based on granular permethrin applications.

Table G.1. Fugacity model input parameters and exposure estimates for avian, mammalian, and terrestrial invertebrate receptors.

Parameter	**Use Category[1]**		
	Nuts (0.3 lb a.i./A, 3 apps, 10-day interval)	**Corn and Sod & Golf Turf [2] (0.20 lb a.i./A, 4 apps, 3-day interval)**	**Residential (1.00 lb a.i./A, 4 apps, 7-day interval) [3]**
$C_{soil\ max}$ (mg/kg @ 7.6 cm depth)	0.9604	0.8826	4.2548

Table G.1. Fugacity model input parameters and exposure estimates for avian, mammalian, and terrestrial invertebrate receptors.			
Parameter	**Use Category[1]**		
	Nuts **(0.3 lb a.i./A, 3 apps, 10-day interval)**	**Corn and Sod & Golf Turf [2]** **(0.20 lb a.i./A, 4 apps, 3-day interval)**	**Residential** **(1.00 lb a.i./A, 4 apps, 7-day interval) [3]**
Earthworm Concentration ($C_{earthworm}$) (mg/kg)	12.1199	11.1377	53.6928
K_d (L/kg)	1536	1536	1536
Z_{water} (1/H or moles/Pa-m^3)	7.14 x10^5	7.14 x10^5	7.14 x10^5
Z_{soil} ((K.·ρ_{soil})/H)	1.43 x10^9	1.43 x10^9	1.43 x10^9
$Z_{earthworm}$ ((lipid·K_{ow}·$\rho_{earthworm}$)/H)	9.00x10^9	9.00x10^9	9.00x10^9
ρ_{soil} (g/cm^3)	1.3	1.3	1.3
$\rho_{earthworm}$ (g/cm^3)	1	1	1
θ (unitless)	0.3	0.3	0.3
ε (unitless)	0.509434	0.509434	0.509434
K_{aw} (H/RT)	5.65x10^{-10}	5.65x10^{-10}	5.65x10^{-10}
K_{bw} ((ρ_{soil}·Kd)+θ+(ε-θ)(K_{aw}))	1997.1	1997.1	1997.1

[1] Please refer to the main assessment for details regarding which uses are covered under each "Use Category."

[2] The two "Use Categories" for granular uses on "Corn" and on "Sod and Golf Turf" have been considered together for the fugacity model analysis since they share the same use parameters (*ie.*, rate, # of applications, and interval).

[3] The application interval and number of applications for the residential uses of granular permethrin (based on use parameters for Fire Ant Mound treatment) were assumed. Please refer to the "Aquatic Exposure Assessment" section of the main assessment for a description of the assumptions regarding input parameters and the reasoning behind them.

Chronic Risk Characterization for Terrestrial Wildlife

Chronic risks for birds and mammals that consume terrestrial invertebrates as the majority of their diet were estimated based on comparison of the concentration of permethrin in earthworm tissue ($C_{earthworm}$) with chronic toxicity values for birds and mammals. In addition to dietary estimates for birds and mammals, residue concentrations in terrestrial invertebrates were converted to daily oral doses for mammals based on the fraction of body weight consumed as estimated through mammalian allometric relationships, and were then compared with chronic oral toxicity values for mammals. Lastly, the concentration of permethrin in earthworms, used as a surrogate for all terrestrial soil-dwelling invertebrates, was compared to the most sensitive acute contact LD_{50} value for terrestrial invertebrates in order to evaluate the potential for risk to this taxonomic group resulting from granular permethrin use.

Insectivorous Birds

Chronic risks for insectivorous birds were estimated by comparing the $C_{earthworm}$ in ppm by the avian chronic NOAEC for permethrin (125 ppm). The highest estimated earthworm residue for insectivorous avian receptors (12.12 ppm) is less than the avian chronic endpoint (125 ppm) for granular permethrin applications. Therefore, as shown in **Table G.2**, chronic risks to birds associated with ingestion of earthworms that have bioconcentrated permethrin granules are not expected and are below the Agency's chronic risk LOC. However, it is unclear whether other routes of granular permethrin exposure (i.e., direct consumption of granules, ingestion of granules that adhere to soil invertebrates, partitioning of dissolved permethrin to on-site sources of wildlife drinking water, and dermal exposure of granules released to surrounding soil and on-site puddles) or combined routes of exposure would result in chronic risk concerns for avian receptors.

Insectivorous Mammals

Chronic risks for insectivorous mammals were estimated by considering both dietary- and dose-related exposures and effects. In the dietary method, risks were estimated by comparing the $C_{earthworm}$ by the mammalian chronic NOAEC for permethrin (55.44 ppm). Based on the dietary method and the maximum granular permethrin application rate for the Residential "Use Category", chronic LOCs are not exceeded for insectivorous mammals because the highest earthworm residue concentration (53.69 ppm) is less than the NOAEC (55.44 ppm).

However, dose-based RQs are likely to provide more accurate estimates of risk to insectivorous mammals because they are based on earthworm residues that are consumed by a mammal in a given day and an adjusted NOAEL value for a relevant size class of mammals, while the dietary-based RQs use no such adjustments to account for feeding behavior and varying size classes. Earthworm residue concentrations derived based on the dose method are first converted to a daily dose by multiplying the dietary $C_{earthworm}$ by the percentage BW consumed for 15 gram mammals (95% BW). In addition the NOAEL value (2.77 mg/kg-BW/day) is adjusted to account for the size class of mammals relevant to this assessment (15 grams) according to the following equation:

$$Adjusted\ NOAEL = NOAEL\ (TW/AW)^{(0.25)}$$

where:

TW = body weight of tested animal (350 g rat); and
AW = body weight of assessed animal (15g).

As shown in **Table G.2**, estimated chronic doses for insectivorous mammals, based on the modeled granular applications of permethrin and the adjusted NOAEL for 15 g mammals do exceed the Agency's chronic risk LOC for all three modeled scenarios with RQ values ranging from 1.74 to 8.38. The results of the assessment indicate that, when risk to mammals is assessed on the basis of daily ingested dose, permethrin bioconcentrated in terrestrial invertebrates does, by itself, represent a biologically significant pathway for exposure. However, it is unclear whether other routes of granular permethrin exposure (i.e., direct consumption of granules, ingestion of granules that adhere to soil invertebrates, partitioning of dissolved permethrin to on-site sources of wildlife drinking water, and dermal exposure of granules released to surrounding soil and on-site puddles) or combined routes of exposure would result in elevated chronic risk concerns for mammalian receptors.

Soil-dwelling Invertebrates

To evaluate the potential for risks to terrestrial soil-dwelling invertebrates resulting from granular applications of permethrin, EECs (mg a.i./kg-bw) in earthworms were estimated using the fugacity-based approach. In the case of permethrin, the honey bee was used as a surrogate for evaluating risks of permethrin to terrestrial invertebrates. The toxicity value for terrestrial invertebrates was calculated by multiplying the lowest available acute contact LD_{50} of 0.024 mg a.i./bee by 1 bee/0.128g, which is based on the weight of an adult honey bee. The EECs in earthworms in ppm (mg a.i./kg-bw) were then divided by the calculated toxicity value for terrestrial invertebrates, which is 0.1875 µg a.i./g of bee, to derive RQs.

As shown in **Table G.2**, for all modeled granular applications of permethrin, RQs for soil-dwelling terrestrial invertebrates exceed the Agency's interim LOC (RQ≥0.05) for listed terrestrial invertebrates (RQs range from 59.41 to 286.35). Therefore, granular permethrin applications do appear to pose a risk to soil-dwelling invertebrates.

Table G.2. RQs for terrestrial soil invertebrates and insectivorous birds and mammals estimated using a fugacity-based (equilibrium partitioning) approach for the maximum granular permethrin application scenarios. [1]

Use Category [2]	App Rate (lbs a.i./A), Interval (Days), # of Apps[3]	$C_{soil\ max}$ (mg/kg) [4]	$C_{earthworm}$ (mg/kg) [5]	Dose-adjusted $C_{earthworm}$ (mg/kg-BW)[6]	Dose-Based Chronic RQ for Mammals [7]	Dietary-Based Chronic RQ for Mammals[8]	Dietary-Based Chronic RQ for Birds[8]	RQ for Terrestrial Soil Invertebrates[9]
Nuts	**0.3, 10, 3**	0.96	12.12	11.51	**1.89**	0.22	0.10	**64.64**
Corn and Sod & Golf Turf	**0.20, 3, 4**	0.88	11.14	10.58	**1.74**	0.20	0.09	**59.41**
Residential	**1.00, 7, 4**	4.25	53.69	51.01	**8.38**	0.97	0.43	**286.35**

[1] All bolded and shaded RQs exceed the Agency's chronic risk LOC (1) for birds and mammals, or the Agency's interim LOC for listed terrestrial invertebrates (0.05).
[2]Please refer to the main assessment for details regarding which uses are covered under each "Use Category."
[3] The maximum number of applications per year, the minimum application intervals, and the maximum application rates for each use selected as the representative use for a "Use Category" were derived from the product labels and used to model EECs.
[4] $C_{soil\ max}$ = the maximum soil concentration (mg/kg) predicted by the model.
[5] $C_{earthworm}$= the earthworm concentration (mg/kg) predicted by the model.
[6] Dose-adjusted $C_{earthworm}$ = $C_{earthworm}$ (ppm) * (%Body weight consumed/100), where % body weight consumed equals 95% for a 15 g mammal.
[7] Dose-based Chronic RQ = Dose-adjusted $C_{earthworm}$ / Adjusted NOAEL, where the Adjusted NOAEL = NOAEL $(TW/AW)^{0.25}$. Equivalent to 6.09 for a 15 g mammal.
[8] Dietary-based Chronic RQ = $C_{earthworm}$ / Avian or Mammalian NOAEC.
[9] RQs for terrestrial invertebrates exposed to granular permethrin are calculated as follows: [$C_{earthworm}$ (mg-kg-bw)]/[(48-hour contact LD_{50} = 0.024 µg a.i./honey bee*(1 bee/0.128 g)].

There are a number of uncertainties associated with the fugacity model used to estimate permethrin concentrations in earthworm tissue and subsequent risks to terrestrial soil-dwelling invertebrates and insectivorous terrestrial wildlife. It may be possible to further refine this assessment with additional information addressing the following uncertainties:

- A 7.6-cm soil depth was used to reflect a concentration across the earthworm occupied area of soil to derive the $C_{earthworm}$. Although earthworms may live at lower depths in the soil horizon, a 7.6-cm depth represents a reasonably conservative scenario; if risk is acceptable at this depth, it will be acceptable if concentrations are averaged over greater depths.

- The fugacity-based model assumes equilibrium partitioning between bulk soil and soil pore water. In addition, the model assumes a fixed value for soil density, earthworm density, temperature, pore space, organic carbon, and the lipid content of the earthworm. Resulting concentrations of permethrin in earthworm tissue may be either under- or over-estimated depending on the soil type, temperature, and size/lipid content of the earthworm, at the time of exposure.

- This assessment considers only one route of exposure (i.e., ingestion of terrestrial invertebrates that have bioconcentrated permethrin from granules in the soil) for insectivorous birds and mammals. In addition, it is assumed that 100% of the diet is comprised of terrestrial soil invertebrates. Given species-specific feeding habits and dietary requirements, this assumption may overestimate risks associated with ingestion of soil invertebrates that have accumulated permethrin. Other potential routes of exposure including direct ingestion of granules, ingestion of granules that adhere to soil invertebrates, partitioning of dissolved permethrin to sources of wildlife drinking water, and dermal exposure of granules released to surrounding soil and puddles) or combined routes of exposure were not considered. The results of the assessment indicate that, when risk to mammals is assessed on the basis of daily ingested dietary dose, permethrin bioconcentrated in terrestrial invertebrates does, by itself, represent a biologically significant pathway for exposure. However, it is unclear whether other routes of granular permethrin exposure (i.e., direct consumption of granules, ingestion of granules that adhere to soil invertebrates, partitioning of dissolved permethrin to on-site sources of wildlife drinking water, and dermal exposure of granules released to surrounding soil and on-site puddles) or combined routes of exposure would result in risk to birds or elevated chronic risk concerns for mammalian receptors.

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'

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

Trapp, S. And J.C McFarlane (eds.). 1995. Plant Contamination Modeling and Simulation of Organic Chemical Processes. Lewis Publishers. Boca Raton, Florida.

USEPA. 2006. Permethrin. Fifth Revision of the HED Chapter of the Reregistration Eligibility Decision Document (RED). PC Code 109701, Case No. 52645-53-1, DP Barcode D324993. Office of Prevention, Pesticides, and Toxic Substances. Health Effects Division of the Office of Pesticide Programs. Washington, D.C. April 4, 2006.