Appendix I
Terrestrial Chronic Exposure Estimates for Granular Applications of Simazine (Earthworm Fugacity Model)

Simazine exposure to terrestrial wildlife from non-granular applications is evaluated by estimating pesticide residues on food items including grasses, plants, insects, fruits, pods, and seeds. For the purposes of this CRLF assessment, terrestrial wildlife is assumed to include birds, which are used as a surrogate for the terrestrial-phase CRLF, and mammals, which are food items for terrestrial-phase CRLFs. For granular applications, terrestrial EECs and acute risks were derived based on an estimation of loadings of pesticide per unit area (ft^2). EFED has no standard methodology for assessing chronic risk to terrestrial organisms from granular applications. The following chronic exposure estimation and risk characterization for terrestrial wildlife considers granular routes of exposure including direct ingestion of soil invertebrates that have bioconcentrated pesticide residues of granules in soil.

Direct Ingestion of Soil Invertebrates

An estimation of simazine concentrations potentially accumulated in the tissues of earthworms was required to complete the exposure estimates for 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 simazine in earthworms was calculated as a combination of uptake from soil pore water and gastrointestinal absorption from ingested soil:

$$C_{earthworm} = [(C_{soil})(Z_{earthworm}/Z_{soil})]+[(C_{soil\ water})(Z_{earthworm}/Z_{water})]$$

where: C_{soil} is the concentration of chemical in bulk soil (note: a chemical concentration averaged over a 15-cm soil depth was used to reflect a concentration across the earthworm occupied area of soil)
$Z_{earthworm}$ is the fugacity capacity of chemical in earthworms = $(lipid)(K_{ow})(\rho_{earthworm})/H$
Z_{soil} is the fugacity capacity of chemical in soil = $(K_d)(\rho_{soil})/H$
Z_{water} is the fugacity capacity of chemical in water = $1/H$
$C_{soil\ water}$ is the concentration of chemical in soil water = C_{soil}/K_{bw}
K_{bw} is the bulk soil-to-water partitioning coefficient = $(\rho_{soil})(K_d)+\theta+(\varepsilon-\theta)(K_{aw})$
K_{aw} is the air-to-water partitioning coefficient = H/RT
H = Henry's Constant specific to simazine (3.2E-10)
R = universal gas constant, 8.31 Joules-m^3/mol-^oK
T = temperature ^oK, assumed to be 298 ^oK
K_d = soil partitioning coefficient for simazine (1.7)
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, assumed to 0.50
lipid = fraction of lipid in organism 0.01 (Cobb et al., 1995)
K_{ow} = the octonal to water partitioning coefficient for simazine (122)
$\rho_{earthworm}$ = the density of the organism, assumed to be 1 g/cm^3

Table I.1 summarizes the estimated immediate post-treatment soil concentrations of simazine, assuming 15 cm (3-inch) averaging depth, a soil density of 1.3 g/cm^3, and granular application rates of simazine including 8 lb ai/A (non-bearing fruit), 4 lb ai/A (berries), and 2 lb ai/A (turf).

Table I.1. Estimated Soil Concentrations for Simazine (Immediately Post-treatment)

Application Rate (lb ai/A)	Soil Concentration (mg/kg-soil) ca 15 cm
8	4.57
4	2.28
2	1.14

Table I.2 summarizes the model inputs and exposure estimates (i.e., earthworm concentrations in ppm) for insectivorous birds (used as a surrogate for terrestrial-phase CRLFs that consume invertebrates) and mammals (food item of the terrestrial-phase CRLF), based on granular simazine application rates ranging from 2 to 8 lb ai/A.

Table I.2. Model Input Parameters and Dietary Exposure Estimates for Avian and Mammalian Receptors (for Soil Concentrations Immediately Post-treatment)

Parameter	8 lb/A	4 lb/A	2 lb/A
C_{ss} (mg/kg @ 15 cm depth)	4.57	2.28	1.14
Earthworm Concentration (mg/kg) ($C_{earthworm}$)	4.74	2.37	1.18
K_d (L/kg)	1.7		
Z_{water} (1/H or moles/Pa-m^3)	3.1E+09		
Z_{soil} (($K_{\bullet} \bullet \rho_{soil}$)/H)	6.9E+09		
$Z_{earthworm}$	3.8E+09		

Parameter	8 lb/A	4 lb/A	2 lb/A
$((lipid \bullet K_{ow} \bullet \rho_{earthworm})/H)$			
ρ_{soil} (g/cm^3)	1.3		
$\rho_{earthworm}$ (g/cm^3)	1		
θ (unitless)	0.3		
ε (unitless)	0.5		
K_{aw} (H/RT)	1.1E-08		
K_{bw} $((\rho_{soil} \bullet Kd)+\theta+(\varepsilon-\theta)(K_{aw}))$	2.51		

Chronic Risk Characterization for Terrestrial Wildlife

Chronic risks for birds (used as a surrogate for terrestrial-phase CRLFs) and mammals that consume terrestrial invertebrates as the majority of their diet were estimated based on comparison of the concentration of simazine in earthworm tissue ($C_{earthworm}$) with chronic toxicity values for birds and mammals. Given that earthworms are likely to be present in the top 6 inches of soil, a 15-cm soil depth was used to reflect a concentration across the earthworm occupied area of soil to derive the $C_{earthworm}$. It is important to note that this estimation of risk assumes that 100% of the diet is comprised of terrestrial soil invertebrates.

Insectivorous Birds

Chronic risks for insectivorous birds were estimated by comparing the $C_{earthworm}$ in ppm by the avian chronic NOAEC for simazine (100 ppm). Estimated earthworm residues for insectivorous avian receptors (1.18 to 4.74 mg/kg) are less than the avian chronic endpoint (100 mg/kg; based on reproductive effects) for non-granular simazine applications ranging from 2 to 8 lb ai/A. Therefore, chronic risks to terrestrial-phase CRLFs associated with ingestion of terrestrial invertebrates (i.e., earthworms) that have bioaccumulated simazine granules are not expected. However, it is unclear whether other routes of granular simazine exposure (i.e., direct consumption of granules, ingestion of granules that adhere to soil invertebrates, partitioning of dissolved simazine 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 terrestrial-phase amphibians.

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 simazine (10 ppm; based on reduction in body weight gain). In the dose method, the residue concentration in earthworms was converted to a daily oral dose based on the fraction of body weight consumed as estimated through mammalian allometric relationships. The dose was then compared to the NOAEL (0.56 mg/kg-BW/day) for mammalian receptors.

Based on the dietary method and simazine granular application rates of 2 to 8 lb ai/A, chronic LOCs are not exceeded for insectivorous mammals because the respective earthworm residue concentrations (1.18 to 4.74 mg/kg) are greater than the NOAEC (10 mg/kg). 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 the small mammals (15g = 95% BW). In addition, the NOAEL value (0.56 mg/kg-BW/day) is adjusted to account for the size of the mammals according to the following equation:

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

where:

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

As shown in Table I.3, estimated chronic doses for insectivorous mammals, based on the two highest granular applications of simazine (4 and 8 lb ai/A) and adjusted NOAELs for small sized mammals exceed chronic LOCs with RQ values ranging from 1.83 to 3.66. However, chronic LOCs are not exceeded for granular applications of simazine at the 2 lb ai/A rate. The results of the assessment indicate that, when growth effect risks for mammals are assessed on the basis of daily ingested dietary dose, the accumulation of simazine in terrestrial invertebrates may represent, by itself, a biologically significant pathway for exposure. 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 adjusted NOAEL values for three sizes of mammals, while the dietary-based RQs use no such adjustments to account for feeding behavior and varying size classes.

Table O3. Dose-based Chronic RQs for Insectivorous Mammals

Application Rate	Body Weight (g)	Dose-adjusted EEC_w (mg/kg-BW/day)[a]	Adjusted NOAEL (mg/kg-BW/day)[b]	Chronic RQ[c]
8 lb ai/A	15	4.50	1.23	**3.66**[e]
4 lb ai/A	15	2.25	1.23	**1.83**[e]
2 lb ai/A	15	1.12	1.23	0.91

[a] Dose-adjusted EEC_w = Dietary EEC_w (ppm) * (%BW consumed/100).
[b] Adjusted NOAEL = NOAEL $(TW/AW)^{0.25}$.
[c] Chronic RQ = Dose-adjusted EEC_w / Adjusted NOAEL.

[e] Exceeds chronic risk level of concern (RQ ≥ 1.0).

Uncertainties

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

- A simazine concentration averaged over a 15-cm soil depth was used to reflect a concentration across the earthworm occupied area of soil. However, it is possible that earthworms may be present at deeper soil depths, resulting in a lower concentration of simazine in bulk soil and earthworm tissue.

- 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 simazine 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 bioaccumulated simazine 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 simazine, especially for terrestrial-phase amphibians, which have lower metabolic rates than birds. Other potential routes of exposure including direct ingestion of granules, ingestion of granules that adhere to soil invertebrates, partitioning of dissolved simazine 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.

References

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