APPENDIX 1-8. Evaluation of Residues of Concern for Triazine ESA Biological Evaluations

**Aquatic Exposure**

Previous ecological risk assessments of the triazines (atrazine, simazine and propazine) concluded the residues of concern for aquatic species consist of parent only. This conclusion was based on a review of the degradate toxicity data available at that time and the impact of the inclusion of these degradates on aquatic EECs, considering the persistence of the parent compound. These analyses are provided in several published documents and are not repeated herein.[[1]](#footnote-2),[[2]](#footnote-3),[[3]](#footnote-4),[[4]](#footnote-5) The analysis for this BE builds on the information from previous risk assessments and considers new degradate data that are available in the ECOTOX database.

Major degradates and the maximum % formed for each triazine are shown in **Table 1** below (details on fate studies and the formation of degradates can be found in **Chapter 3**). While there are a few degradates specific to each individual chemical, the triazines share several common degradates. Major degradates, those with approximately greater than 10% formation, were considered for inclusion in aquatic modeling.

**Table 1. Percent formation of major degradates across triazines**

|  |  |  |  |
| --- | --- | --- | --- |
| **Degradate** | **Chemical and % formed** | | |
| **Atrazine** | **Simazine** | **Propazine** |
| Deethylatrazine (DEA) | X (16%) |  |  |
| Deisopropylatrazine (DIA) |  | X (18%) |  |
| Diaminochlorotriazine (DACT)\* | X (18%) |  | X (12%) |
| Hydroxyatrazine (HA) | X (15%) |  |  |
| Hydroxysimazine (HS) |  | X (62%) |  |
| Hydroxypropazine (HP)\*\* |  |  | X (31%) |

\* Also referred to as Diadealkylatrazine (DDA)

\*\* Also referred to as Propazine-2-hydroxy

Acute and chronic toxicity studies for the DEA, DIA, DACT, and HA degradates have been submitted by the registrants and are available in the open literature. A comparison of the toxicity data for the parent triazines and major degradates is presented in **Table 2**, **Table 3**, and **Table 4** for fish, aquatic invertebrates, and aquatic plants, respectively. Based on the review of new ECOTOX literature on the degradates, 5 additional studies were found with information that was suitable for consideration in the toxicity of degradates. Upon review of each of these studies, however, concerns with the quality of the data or relevancy of the endpoint assessed to survival or reproduction were noted (additional comments provided in **APPENDIX 2-2**). No degradate data were available on hydroxysimazine or hydroxypropazine through submitted studies, ECOTOX review or other database reviews. In the 2006 Interim Registration Eligibility Decision (IRED)[[5]](#footnote-6) in the discussion of hydroxysimazine and hydroxypropazine with regard to human health risk concerns, an analogy was made of the suspected toxicity of hydroxysimazine and hydroxypropazine being similar to that of hydroxyatrazine, based on the mechanism of degradate formation, which is different from those of the chlorinated degradates. Based on this comparison and the risk assessment for hydroxyatrazine showing minimal exposure and risk, hydroxysimazine and hydroxypropazine were not included in the assessment of human health risk. It is uncertain if the same analogy can be made for aquatic species; however, acute toxicity values for hydroxyatrazine are all non-definitive greater than values at concentrations ranging from 1.9 to 100 mg a.i./L.

**Table 2. Comparison of Available Fish Toxicity Data for the Triazines and Major Degradates**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Test Substance** | **Test Species** | **Endpoint** | **Value**  **(mg/L)** | **Reference** |
| **Acute** | | | | |
| Atrazine | Sheepshead minnow (*Cyprinodon variegatus*) | 96-hr LC50 | 2 | MRID 45208303/45227711 |
| Propazine | Sheepshead minnow (*Cyprinodon variegatus*) | 96-hr LC50 | 4.3 | MRID 48036204 |
| Simazine | Sheepshead minnow (*Cyprinodon variegatus*) | 96-hr LC50 | 4.3 | MRID 42503702 |
| DACT | Rainbow trout (*Oncorhynchus mykiss*) | 96-hr LC50 | >100 | MRID 47046104 |
| DIA | Rainbow trout (*Oncorhynchus mykiss*) | 96-hr LC50 | 17 | MRID 47046103 |
| HA | Sheepshead minnow (*Cyprinodon variegatus*) | 96-hr LC50 | >1.9 | MRID 46500006 |
| HA | Rainbow trout (*Oncorhynchus mykiss*) | 96-hr LC50 | >3 | MRID 46500004 |
| HA | Bluegill sunfish (*Lepomis macrochirus*) | 96-hr LC50 | >3.8 | MRID 46500005 |
| **Sublethal** | | | | |
| Atrazine | Atlantic salmon (*Salmo salar*) | NOAEC | 0.0085 | MRID |
| Propazine | FW | NOAEC | 0.772 | MRID 48036205 |
| Simazine | African clawed frog1 | NOAEC | 0.0012 | E178653 |
| DACT |  | NOAEC | <0.03 | Liu et al., 2019 |
| DEA |  | NOAEC | <0.03 | Liu et al., 2017 |
| DIA |  | NOAEC | 0.03 | Liu et al., 2018 |

1 Surrogate for fish

**Table 3. Comparison of Available Aquatic Invertebrate Toxicity Data for the Triazines and Major Degradates**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Test Substance** | **Test Species** | **Endpoint** | **Value**  **(mg/L)** | **Reference** |
| **Acute** | | | | |
| Atrazine | Opposum shrimp (*Neomysis integer*) | EC50 | 0.048 | E103334 |
| Propazine | Mysid Shrimp (Americamysis bahia) | EC50 | 4.2 | MRID 44184801 |
| Simazine | Stonefly (*Pteronarcys californiaca*) | EC50 | 1.9 | MRID 40098001 |
| DACT | Waterflea (Daphnia magna) | EC50 | >100 | MRID 47046102 |
| DIA | Waterflea (Daphnia magna) | EC50 | >100 | MRID 47046101 |
| HA | Waterflea (Daphnia magna) | EC50 | >4.1 | MRID 46500001 |
| DEA | Amphipod | LC50 | 7.2 | E118745 |
| DEA | Amphipod | LC50 | >3 | E118745 |
| DIA | Amphipod | LC50 | 7.2 | E118745 |
| DIA | Amphipod | LC50 | >3 | E118745 |
| HA | Mysid Shrimp (*Americamysis bahia*) | LC50 | >2 | MRID 46500003 |
| DEA | *Gammarus pulex* | LC50 | 2.8 | Maazouzi et al, 2016 |
| DEA | *Gammarus cf. orinos* | LC50 | 10.1 | Maazouzi et al, 2017 |
| DEA | *Asellus aquaticus* | LC50 | 15.4 | Maazouzi et al, 2018 |
| DEA | *Niphargus rhenorhoda-nensis* | LC50 | 112.3 | Maazouzi et al, 2019 |
| **Sublethal** | | | | |
| Atrazine | Copepod (*Amphiascus tenuiremis*) | NOAEC | 0.0035 | E73333 |
| Propazine | Waterflea (Daphnia magna) | NOAEC | 0.047 | MRID 44327602 |
| Simazine | Mysid Shrimp (Americamysis bahia) | NOAEC | 0.063 | MRID |

**Table 4. Comparison of Available Aquatic Plant Toxicity Data for the Triazines and Major Degradates**

| **Test Substance** | **Test Species** | **Endpoint** | **Value**  **(mg/L)** | **Reference** |
| --- | --- | --- | --- | --- |
| Atrazine | HC05 species of the SSD | EC50 | 0.014 | Appendix 2-5 |
| Propazine | Diatom (*Navicula pelliculosa*) | EC50 | 0.025 | MRID 44287310 |
| Simazine | HC05 species of the SSD | EC50 | 0.012 | Appendix 2-5 |
| DEA | Blue-green algae (*Anabaena variabilis*) | EC50 | 0.7 | MRID 45087404 |
| DEA | Blue-green algae (*Anabaena inaequalis*) | EC50 | 1 | MRID 45087401 |
| DEA | Green algae (*Scenedesmus quadricauda*) | EC50 | 1.2 | MRID 45087402 |
| DEA | Green algae (*Chlorella pyrenoidosa*) | EC50 | 1.8 | MRID 45087403 |
| DEA | Blue-green (*Anabaena cylidrica*) | EC50 | 4.8 | MRID 45087405 |
| DEA | *Lemna minor* | EC50 | 0.00825 | Havelkova et al 2019 |
| DIA | Blue-green algae (*Anabaena inaequalis*) | EC50 | 2.5 | MRID 45087406 |
| DIA | Green algae (*Chlorella pyrenoidosa*) | EC50 | 3.6 | MRID 45087408 |
| DIA | Green algae (*Scenedesmus quadricauda*) | EC50 | 4 | MRID 45087407 |
| DIA | Blue-green algae (*Anabaena variabilis*) | EC50 | 4.7 | MRID 45087409 |
| DIA | Blue-green (*Anabaena cylidrica*) | EC50 | 9.3 | MRID 45087410 |
| DIA | Green algae (*Scenedesmus subspicatus*) | EC50 | 1.3 | MRID 47046105 |
| DIA | *Algae* | EC50 | 0.002 | Sbrilli et al 2005 |
| HA | Blue-green algae (*Anabaena inaequalis*) | EC50 | >100 | MRID 45087410 |
| HA | Green algae (*Scenedesmus quadricauda*) | EC50 | >100 | MRID 45087411 |
| HA | Green algae (*Chlorella pyrenoidosa*) | EC50 | >100 | MRID 45087412 |
| HA | Blue-green algae (*Anabaena variabilis*) | EC50 | >100 | MRID 45087413 |
| HA | Blue-green (*Anabaena cylidrica*) | EC50 | >100 | MRID 45087414 |

The toxicity data give a general conclusion that degradates tend to be less toxic than the parent, but may, based on some studies for sublethal or chronic effects, have a similar toxicity to the parent. It is useful then to consider the impact of the % formation of the degradates on the decision to include them in the analysis. As stated in the propazine assessment, based on the long half-lives already utilized for aquatic modeling, additional degradates would likely have little impact on the results of the predicted EECs. A similar conclusion could be reached for atrazine and simazine, even though their half-lives are shorter than propazine, based on the relatively low maximum % formation of the degradates (18% or less). The exception to this is hydroxysimazine and hydroxypropazine, which maximally formed at 62% and 31%, respectively (formed in aerobic soil metabolism studies). However, using hydroxyatrazine toxicity as a surrogate value, the available evidence suggests these are less toxic than the parent compound. Aquatic monitoring data also supports the lower formation of degradates in the aquatic environment, as detected values are generally observed at concentrations an order of magnitude lower than values of the parent compounds. Considering these factors overall, aquatic modeling of the parent compound alone for each of the triazines is considered adequate for determining potential exposure concentrations to aquatic organisms.

**Terrestrial Exposure**

The DEA degradate has been shown to be of similar toxicity to birds and mammals on an acute oral basis. Other dealkylatrazine degradates have been shown to be more acutely toxic to rats and more developmentally toxic to gestating rat pups than the parent chlorotriazines (**Table 4**). Acute avian studies suggest that DIA is less toxic than atrazine to birds on an acute oral basis. No avian toxicity data for DACT are available; therefore, based on the equivalent toxicity in mammals, DACT may also be of toxicological concern in birds.

To further evaluate degradates in the terrestrial environment, magnitude of residue studies that included degradate formation were evaluated. In a magnitude of residue study evaluating residues in or on sugarcane (MRID 47089002), there was limited degradate formation at 120 days after treatment. In a study on grass/hay/forage, atrazine was applied at 12 different sites at an application rate of 2.1 lb a.i./A. Residues on day 0 ranged from approximately 130 to 220 ppm of atrazine on forage and hay, but total formation at 30 days maximally ranged from approximately 1 to 2 ppm. Based on the generally low formation of degradates in these studies and the use of foliar half-lives of 17-35 days, use of parent toxicity data for terrestrial modeling is considered protective. When toxicity data for a degradate exists for a taxon, this data may be considered in the selection of a toxicity endpoint for the parent compound if multiple studies exist (*i.e.* if varying endpoints are available for parent, may consider magnitude of degradate toxicity endpoints).

**Table 4. Summary of Available Degradate Toxicity Data in Birds and Mammals**

|  |  |  |  |
| --- | --- | --- | --- |
| **Chemical** | **Acute Bird LD50 (mg/kg-bw)** | **Acute Mammal LD50 (mg/kg-bw)** | **Mammal Developmental NOAEL (mg/kg-bw)** |
| Atrazine | 783 (MRID 00024721) | 1869 (MRID 00024706) | 10 (MRID 40566302) |
| Simazine | >4640 (MRID 00072798) | 2014 (E70756) | 30 (MRID 40614403) |
| Propazine | >1640 (MRID 44287301) | >5050 (MRID 43474101) | 10 (MRID 00150242) |
| HA | >2000 (MRID 46500008) | Not available | 25 (MRID 41065202) |
| DEA | 768 (MRID 46500009) | 1240 (MRID 43013201) | 5 (MRID 43013209) |
| DIA | >2000 (MRID 46500007) | 1100 (MRID 43013202) | 5 (MRID 43013208) |
| DACT | Not available | Not available | 2.5 (MRID 41392402) |

1. U.S. Environmental Protection Agency (USEPA). 2016. Refined Ecological Risk Assessment for Atrazine. Office of Pesticide Programs, Environmental Fate and Effects Division. DP Barcode 418317. April 12, 2016. [↑](#footnote-ref-2)
2. USEPA. 2015. Preliminary Risk Assessment for Registration Review of Propazine. Office of Pesticide Programs, Environmental Fate and Effects Division. DP Barcode 428090. October 28, 2015 [↑](#footnote-ref-3)
3. U.S. Environmental Protection Agency (USEPA). 2016. Preliminary Ecological Risk Assessment for Simazine. Office of Pesticide Programs, Environmental Fate and Effects Division. DP Barcode 424724. April 12, 2016. [↑](#footnote-ref-4)
4. U.S. Environmental Protection Agency (USEPA). 2009. Potential Risks of Atrazine Use to Federally Threatened California Red-legged Frog (Rana aurora draytonii) and Delta Smelt (Hypomesus transpacificus) Pesticide Effects Determination. Office of Pesticide Programs, Environmental Fate and Effects Division. February 19, 2009. [↑](#footnote-ref-5)
5. U.S. Environmental Protection Agency (USEPA). 2006. Atrazine Reregistration Eligibility Decision Document [↑](#footnote-ref-6)