MEMORANDUM

SUBJECT: Simazine (SRR) Registration Standard

FROM: Charles L. Trichilo, Ph.D., Chief
Dietary Exposure Branch
Health Effects Division (TS-769C)

TO: Reto Engler, Ph.D., Chief
Science Analysis and Coordination Branch
Health Effects Division (TS-769C)

and

J. Frane, Acting Chief
Reregistration Branch (TS-767)
Special Review and Reregistration Division (TS-767)

Attached are the Product and Residue Chemistry chapters for the simazine Second Round Review (SRR) prepared by Dynamac Corporation under supervision of Dietary Exposure Branch, HED. The original Standard was published in April, 1984. Please note that the SACB copy of this cover memo does not have the chemistry chapters attached.

The due date for these chapters is February 28, 1989.

This standard includes data available and reviewed up to December 30, 1988.

The Agency has determined that product chemistry data for all technical and manufacturing-use products must be resubmitted for each pesticide because new requirements have been introduced and previously submitted data must be updated. Therefore, in this SRR chapter, only product chemistry data for the technical grade of the active ingredient received in response to data submissions required in the Guidance Document dated April, 1984 will be evaluated with regard to adequacy in meeting the requirements of 40 CFR Part 158.120. New and/or updated data are still required for all
other product chemistry Guidelines topics.

Attached to the Product Chemistry chapter are comprehensive
generic and product specific data requirement tables for the
technical grade of the active ingredient and manufacturing-use
products, respectively, of simazine.

These chapters have undergone secondary review in Dietary
Exposure Branch and have been revised to reflect the Branch
policies.

It should be noted that a major portion of the Residue
Chemistry data gaps in this SRR arise from Toxicology’s heightened
interest in the chloro- and hydroxy- metabolites of simazine. In
the original standard, TOX had considered these metabolites to be
insignificant and that the parent molecule was the only residue of
concern.

SACB will provide the TAS calculations for simazine in a
separate memo. If numbers other than tolerances are needed to
obtain a more realistic estimate of dietary exposure to simazine,
SACB is encouraged to consult with the Branch regarding the use
of anticipated residues.

The Product Chemistry chapter contains Appendices A, B, C, D and
E. These are to be protected. Only the copies of the standard in
Dietary Exposure Branch and those sent to J. Frane, E. Eldredge and
Toxicology Branch contain such information.

Finally, Special Review and Reregistration Division, please
note that Dietary Exposure Branch has completed the data tables
for the Residue Chemistry chapter and they are included in this
package.

If you need additional input please advise.

Attachment 1 : Simazine Residue Chemistry Review
Attachment 2 : Simazine Product Chemistry Review
Attachment 3 : Confidential Appendices to Product Chemistry
Review

cc: With Attachments 1, 2 and 3: R. B. Perfetti, J. Stewart (TOX),
E. Eldredge (PMSD/ISB), Simazine Registration standard file.

cc: With Attachments 1 and 2: P. Lombardo (FDA) and M. Cordle
(USDA)

cc: Without Attachments: W. Burnam (HED), S. Rathman (HED), F.
Bishop (RD), H. Jamerson (RD), Atrazine SF, Circulation (7) and
RF.
Final Report

SIMAZINE (SRR)
Task 1: Product Chemistry

Contract No 68-D8-0080

January 11, 1989

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852
SIMAZINE
SECOND ROUND REVIEW
PRODUCT CHEMISTRY

INTRODUCTION

The Federal Insecticide, Fungicide, and Rodenticide Act [FIFRA §3(c)(2)(A)] requires the Environmental Protection Agency to establish guidelines for registering pesticides in the United States. The Agency, in turn, requires registrants to provide quantitative data on all added ingredients, active and inert, which are equal to or greater than 0.1% of the product by weight.

To establish the composition of products to be registered, the Agency requires detailed information on the manufacturing and/or formulation processes, and a discussion on the formation of manufacturing impurities. Furthermore, to assure that the composition of the product as marketed will not vary from that evaluated at the time of registration, prospective pesticide registrants are required to propose certified upper and lower composition limits for the added ingredients, and upper limits for toxicologically significant impurities. Standard certified limits for pesticide product ingredients are established according to 40 CFR §158.175(b)(2); these limits may be modified with appropriate and acceptable explanation by the registrant.

The Agency also requires data on the physical and chemical properties of the pesticide active ingredient and its formulations, such as melting and boiling points, ambient vapor pressure, and solubility in various solvents. Corresponding to each of the Topical Discussions listed below are the Guideline Reference Numbers from "Pesticide Assessment Guidelines - Subdivision D - Product Chemistry", referred to in Title 40 of the Code of Federal Regulations (40 CFR), Part 158, "Data Requirements for Registration", Subpart C, "Product Chemistry Data Requirements". These regulations and guidelines explain the minimum data that the Agency needs to adequately assess the product chemistry of simazine.

Guidelines Reference No.
from 40 CFR §158.155-190

Product Composition and Manufacture . . . . . . . . . . 61-(1-3)
Analysis and Certification of Product Ingredients . . 62-(1-3)
Physical and Chemical Characteristics . . . . . . . . . . 63-(2-20)

Current Agency policy requires that recent product chemistry data be available for each pesticide. Although product chemistry data may have been submitted in the past, the Agency has determined
that these data must be updated and resubmitted for each pesticide to satisfy current data requirements.

PRODUCT IDENTITY AND COMPOSITION

61-1. Product Composition

Simazine is the common name approved by ANSI, BSI, Z-ISO, (f) F-ISO, and WSSA for a herbicide having manufacturing-use products registered in the U.S. by Aceto Agricultural Chemicals Corp., Ciba-Geigy Corp., Drexel Chemical Co., Griffin Corp., and Makhteshim-Agan (America) Inc. The molecular structure is illustrated below:

```
\begin{center}
\includegraphics[width=0.5\textwidth]{molecular_structure.png}
\end{center}
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The IUPAC-approved chemical names are 6-chloro-N²,N⁴-diethyl-1,3,5-triazine-2,4-diamine or 2-chloro-4,6-bis(ethylamino)-1,3,5-triazine. Variations in chemical nomenclature include: 6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine (Chemical Abstracts 9th Collective Index); and 2-chloro-4,6-bis(ethylamino-s-triazine (Chemical Abstracts 8th Collective Index). Other common and trade names include CAT (JMAF); G-27692; Gesatop, Weedex; Aquazine; Princep; Gesapun; Amizine; Primatol S; CDT; CET; CFT; Simadex; Simflow; Cekusan; Simanex; Sim-Trol; and Framed (discontinued). Formulation mixtures include Aventox; Rentol; Dosamix; Fylene; Hermes; Erbitox Totale; Etazine; Fogard S; Gesaprim S; Forte; Gesatop Z; Gramazine; Terraklene; Groundhog; Pathclear; Herbon Blue; Hytrol; Primatol; Primatol SE; Weedazin; Siden; Soltair; Telok; Simazol; and Amizine.

Other identifying characteristics and codes are:

- **Empirical Formula:** $\text{C}_9\text{H}_8\text{ClN}_5$
- **Molecular Weight:** 201.7
- **CAS Registry No.:** 122-34-9
  - (simazine + metoxuron) 53126-75-3
  - (simazine + secbumeton) 61952-98-5
  - (simazine + atrazine) 39331-45-8
  - (simazine + paraquat) 39312-80-6
- **Shaughnessy No.:** 080807
- **Wiswesser Line-Formula Notation:** T6N CN ENJ BM2 DM2 FG

A Product Search Listing (PRD-284C) conducted 12/12/88 identified the simazine manufacturing-use products listed below in Table 1. Refer to Confidential Appendix A for disclosure of the ingredients in the indicated products.

Table 1. Simazine manufacturing-use products.

<table>
<thead>
<tr>
<th>Product</th>
<th>EPA Reg. No.</th>
<th>Registrant</th>
<th>Ingredients Disclosure</th>
</tr>
</thead>
<tbody>
<tr>
<td>97% T</td>
<td>100-541</td>
<td>Ciba-Geigy Corp., Agricultural Division</td>
<td>Reviewed</td>
</tr>
<tr>
<td>98% T</td>
<td>1812-262</td>
<td>Griffin Corp.</td>
<td>Yes</td>
</tr>
<tr>
<td>95% T</td>
<td>2749-292</td>
<td>Aceto Agricultural Chemicals Corp.</td>
<td>Yes</td>
</tr>
<tr>
<td>98% T</td>
<td>11603-24</td>
<td>Makhteshim-Agan (America) Inc.</td>
<td>Yes</td>
</tr>
<tr>
<td>95% T</td>
<td>19713-59</td>
<td>Drexel Chemical Co.</td>
<td>Yes</td>
</tr>
<tr>
<td>80% FI</td>
<td>11603-11</td>
<td>Makhteshim-Agan (America) Inc.</td>
<td>Yes</td>
</tr>
<tr>
<td>90% FI</td>
<td>40810-9</td>
<td>Ciba-Geigy Corp. Plastics &amp; Additives Division</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The Simazine Guidance Document dated 3/1/84 required no additional generic or product-specific data concerning product composition; however, additional data have been submitted.

Data submitted by Ciba-Geigy Corp. (1984; MRID 00143169) in response to the Guidance Document have been reviewed by the Agency (EPA Memorandum RCB No. 1791 dated 2/9/87) and found to satisfy the requirements of 40 CFR 158.155 (Guideline Reference No. 61-1) regarding product composition of the 97% T (EPA Reg. No. 100-541). The data reviewed in Confidential Appendix A regarding product composition of the Makhteshim-Agan 80% FI (EPA Reg. No. 11603-11) and the Ciba-Geigy 90% FI (EPA Reg. No. 40810-9) also satisfy those requirements. No additional data are required on this topic for these products.
Additional product composition data reviewed in Confidential Appendix A do not fully satisfy those requirements for the other simazine manufacturing-use products. Certified limits for and purposes of ingredients were not reported for the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), or Makhteshim-Agan 98% T (EPA Reg. No. 11603-24). Furthermore, the statement of composition for the Aceto 95% T does not agree with the percent active ingredient claimed on the product label. Nominal concentrations and purposes were not reported for the ingredients in the Drexel 95% T (EPA Reg. No. 19713-59); also, the proportions described do not account for 100% of the product. The following additional data are required:

- For the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), and Drexel 95% T (EPA Reg. No. 19713-59), nominal concentrations, certified limits (in accordance with 40 CFR §158.175), and purposes must be provided for all components (impurities must be identified as such). The nominal concentrations of the active ingredients reported on the product labels shall be equal to the corresponding lower certified limits.

61-2. Starting Materials and Manufacturing Process


Data submitted by Ciba-Geigy Corp. (1984; MRID 00143169) in response to the Guidance Document have been reviewed by the Agency (EPA Memorandum RCB No. 1791 dated 2/9/87) and found to satisfy the requirements of 40 CFR 158.160-165 (Guideline Reference No. 61-2) regarding beginning materials and the production/formulation process for the 97% T (EPA Reg. No. 100-541). Data discussed in Confidential Appendix B satisfy the corresponding requirements for the Makhteshim-Agan 80% FI and 98% T (EPA Reg. No. 11603-11 and -24, respectively). No additional information is required on these topics for these products.

Data discussed in Confidential Appendix B for the Drexel 95% T (EPA Reg. No. 19713-59) do not satisfy these requirements because the nature of the process (batch or continuous) and the equipment used were not described. No information on beginning materials and production/formulation processes was available for the
remaining products listed above in Table 1. The following additional data are required:

- For each manufacturing-use product that is produced from an EPA-registered product, the following information must be provided: (i) the name and EPA registration number of the EPA-registered product; (ii) the brand name, trade name, or other commercial designation and information concerning the composition of each inert ingredient; (iii) a general characterization of the formulation or production process (e.g., batch or continuous); the identity of the materials used to produce the product, their relative amounts, and the order in which they are added; (iv) a description of the equipment used; (v) a description of the conditions (e.g., temperature, pressure, pH, humidity) that are controlled during each step of the process; and (vi) a description of the procedures used to assure consistent composition of the substance produced (quality control methods). For each manufacturing use product that consists of the technical grade of the active ingredient only or is produced by an integrated system, the following information must be provided in addition to that listed above: (i) the name and address of the producer if different from the registrant; (ii) the brand name, trade name or other commercial designation of each starting material, the name and address of its producer, and information concerning its composition; (iii) a flow chart of the chemical equations of each intended reaction occurring at each step of the process and of the entire process; and (iv) a description of any purification procedures (including procedures to recover or recycle starting materials, intermediates or the substance produced). All of this information is required for the Griffin 98% T, Aceto 95% T, and Ciba-Geigy 90% FI (EPA Reg. No. 1812-262, 2749-292, and 40810-9, respectively). For the Drexel 95% T (EPA Reg. No. 19713-59), the nature of the process (batch or continuous) and the equipment used must be described.

61-3. Discussion of the Formation of Impurities

The Simazine Guidance Document dated 3/1/84 specified generic and product-specific data requirements for simazine regarding discussion of formation of impurities.

Data submitted by Ciba-Geigy Corp. (1984; MRID 00143169) in response to the Guidance Document have been reviewed by the Agency (EPA Memorandum RCB No. 1791 dated 2/9/87) and found to satisfy the requirements of 40 CFR 158.167 (Guideline Reference No. 61-3) regarding formation of impurities in the 97% T (EPA Reg. No. 100-541). Information discussed in Confidential Appen-
The information discussed in Confidential Appendix C regarding formation of impurities in the Makhteshim-Agan 80% FI (EPA Reg. No. 11603-11) also satisfies these requirements. No additional data are required on this topic for these products.

Information discussed Confidential Appendix C regarding formation of impurities in the Makhteshim-Agan 98% T (EPA Reg. No. 11603-24) does not satisfy the requirements of 40 CFR §158.167 (Guidelines Reference No. 61-3) because the individual impurities and the chemical reactions by which they form were not adequately described. No data were available that described the formation of impurities in the other manufacturing-use products listed in Table 1. The following additional data are required:

- For each manufacturing use product that consists of the technical grade of the active ingredient only or is produced by an integrated system, a discussion regarding the origin of the following potential impurities must be provided: (i) each impurity associated with the active ingredient which was found to be present in any analysis of the product conducted by or for the registrant, and (ii) each impurity which the registrant has reason to believe may be present in the product at a level equal to or greater than 0.1% (w/w) based on the composition of each starting material, intended and side reactions which may occur in the production of the product, the possible degradation of ingredients in the product after production, post-production reactions between the ingredients in the product, possible contamination from packaging materials or production equipment, and process control, purification and quality control measures. For each manufacturing use product that is produced from an EPA-registered product, a discussion must be provided for each impurity associated with the active ingredient which the registrant has reason to believe may be present in the product at a level equal to or greater than 0.1% (w/w) based on the possible carryover of impurities present in the registered product which serves as the source of the active ingredient, the possible carryover of impurities present in the inert ingredients in the product, possible reactions occurring during the formulation of the product, post-production reactions between any of the product's active ingredients and any other component of the product or its packaging, and possible contamination from packaging materials or production equipment. All of these data are required for the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), Drexel 95% T (EPA Reg. No. 19713-59), and Ciba-Geigy 90% FI (EPA Reg. No. 40810-9). For the Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), the individual impurities and chemical reactions by which they form must be adequately described.
ANALYSIS AND CERTIFICATION OF PRODUCT INGREDIENTS

62-1. Preliminary Analysis


Data submitted by Ciba-Geigy Corp. (1984; MRID 00143169, and 1988; MRID 40765102) in response to the Guidance Document have been reviewed by the Agency (EPA Memoranda RCB No. 1791 dated 2/9/87 and RCB No. 4295 dated 9/16/88) and found to satisfy the requirements of 40 CFR 158.155 (Guideline Reference No. 62-1) regarding preliminary analysis of the 97% T (EPA Reg. No. 100-541). No additional data are required on this topic for this product.

Data discussed in Confidential Appendix D regarding preliminary analysis of the Aceto 95% T (EPA Reg. No. 2749-292), the Makhteshim-Agan 80% FI (EPA Reg. No. 11603-11), and the Drexel 95% T (EPA Reg. No. 19713-59) do not satisfy the requirements of 40 CFR §158.150 (Guidelines Reference No. 61-3); the Aceto data do not represent individual samples and batches or describe the analytical methods; the Makhteshim-Agan data do not include nitrosamine analysis; and the Drexel data do not depict the change in nitrosamine content over a reasonable storage interval following manufacture. The following additional data are required:

1. For each manufacturing use product produced by an integrated system, the registrant must provide preliminary analyses of five or more representative samples of each technical grade of active ingredient contained in the product to identify all impurities present at 0.1% or greater of the TGAI. If the product is produced by a batch process, at least five separate batches should be represented. The preliminary analysis should be conducted at the point in the production process after which no further chemical reactions designed to produce or purify the substance are intended. Complete and detailed descriptions of the methods used for sample analysis must be submitted, including statements of their precision and accuracy. The preliminary analysis report should include the identity and quantity of each ingredient for which analysis is conducted, along with the mean and relative standard deviation of the analytical results. Based on the preliminary analysis, a statement of the composition of the technical grade of active ingredient must be provided. If the technical grade of active ingredient cannot be isolated, a statement of the composition of the practical equivalent of the technical grade of active ingredient must be submitted. In addition, all nitrosamines must be identified and quantified by methods.
sensitive to 1 ppm of N-nitroso contaminants in six samples of each manufacturing-use product; two samples of each must be analyzed shortly after production, two at 3 months after production, and two at 6 months after production. Upper limits must be proposed for all nitrosamines found. These data are required for all simazine manufacturing products with the exception of the Ciba-Geigy 97% T (EPA Reg. No. 100-541).

62-2. Certified Limits


Data discussed in Confidential Appendix A satisfy the requirements of 40 CFR §158.175 (Guidelines Reference No. 61-2) regarding certified limits for the Makhteshim-Agan 80% FI and the Ciba-Geigy 90% FI (EPA Reg. No. 11603-11 and 40810-9, respectively). No additional data are required on this topic for these products.

Data submitted by Ciba-Geigy Corp. (1984; MRID 00143169, and 1988; MRID 40765101) in response to the Guidance Document have been reviewed by the Agency (EPA Memoranda RCB No. 1791 dated 2/9/87 and RCB No. 4295 dated 9/16/88), but do not satisfy the requirements of 40 CFR 158.175 (Guideline Reference No. 62-2) regarding certified limits for the 97% T (EPA Reg. No. 100-541).

The data reviewed in Confidential Appendix A for the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), and the Makhteshim-Agan 98% T (EPA Reg. No. 11603-24) do not satisfy the requirements of 40 CFR §158.175 (Guideline Reference Nos. 62-2) because certified limits were not reported for all ingredients and impurities of actual or potential toxicological significance. Furthermore, the statement of composition does not agree with the percent active ingredient claimed on the Aceto product label. Additionally, data for the Drexel 95% T (EPA Reg. No. 19713-59) provided no explanation of how certified limits were established, while the quantities described do not account for 100% of the product.

The following additional data are required:

- The registrant must propose upper and lower limits for each active and inert ingredient, if such limits would differ from the standard certified limits determined by the Agency according to 40 CFR §158.175(b)(2). Also, if the manufacturing use product contains the technical grade of the active ingredient only or is produced by an integrated system, upper limits must be proposed for each...
toxicologically significant impurity associated with the active ingredients and found to be present in any sample of the product (standard certified limits cannot be used for impurities). Certified limits should be based on the sources and magnitude of variability in the manufacturing process and the stability of the ingredients following production. The registrant must certify the accuracy of the information presented, and that the certified limits will be maintained. An explanation of how each certified limit was established (e.g., sample analysis using a validated analytical procedure, quantitative estimate based on the amounts of ingredients used, etc.) must be provided, along with information on the accuracy and precision of any analytical procedures used. Certifications must be submitted on EPA Form 8570-4 (Rev. 2/85). These data are required for the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), and Drexel 95% T (EPA Reg. No. 19713-59). For the Ciba-Geigy 97% T (EPA Reg. No. 100-541), certified limits for nitrosamines must be reported on the Confidential Statement of Formula [EPA Form 8570-4 (Rev. 2-85)].

62-3. Enforcement Analytical Methods


Makhteshim-Agan (America) Inc. (1982; 00120338) submitted the gas-liquid chromatography (GLC) method from the CIPAC Handbook, Vol. 1A, 1980, p. 1345-1346, for determination of the simazine content in formulations, which is very similar to the AOAC method discussed above. The product sample and dioctyl phthalate (as an internal standard) are dissolved in dimethylformamide and analyzed by GLC on a DC 200 + QP, column using a flame ionization detector. No validation data were submitted. In a variation of this method also submitted by Makhteshim-Agan (1984; MRID 00149785), diethyl phthalate is used as the internal standard, and a carbowax 20M column is used for GLC analysis.

Makhteshim-Agan (1982; 00120338) also submitted the potentiometric titration method from Zweig, G., ed., Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, 1964, pp. 216-217, for analysis of simazine in wettable powder formulations. The chlorine atom of simazine is converted to ionic chlorine by reaction with excess morpholine; the ionic chloride is then determined in aqueous solution by potentiometric
titration with silver nitrate following acidification with sulfuric acid. The potentiometric reading for ionic chloride of other origin (determined prior to reaction of the sample with morpholine) is subtracted. This method does not distinguish between simazine and other chlorotriazines, and thus is not suitable for enforcement. Alternatively, the product sample may be extracted exhaustively with acetone. After the solvent is evaporated to dryness, the residue is dissolved in acetonitrile and titrated potentiometrically with perchloric acid. This method does not distinguish between simazine and other s-triazines having at least two amino groups, and thus is not suitable for enforcement.

Drexel Chemical Co. (1984; MRID 00146393) submitted a GLC method for analysis of simazine in the technical product. Product samples are dissolved in acetone containing terbutryn as an internal standard and analyzed by GLC on an OV 225 column using a flame ionization detector. Triplicate determinations of the same sample solution should agree within 2% error. No validation data were provided.

The Simazine Guidance Document dated 3/1/84 specified generic and product-specific data requirements for simazine regarding analytical methods to verify certified limits.

Data submitted by Ciba-Geigy Corp. (1988; MRID 40765102) in response to the Guidance Document have been reviewed by the Agency (EPA Memorandum RCB No. 4295 dated 9/16/88), but do not satisfy the requirements of 40 CFR 158.180 (Guideline Reference No. 62-3) regarding enforcement analytical methods for the 97% T (EPA Reg. No. 100-541) because complete descriptions were not submitted for the analytical methods.

The data discussed in Confidential Appendix E do not satisfy the requirements of 40 CFR 158.180 (Guideline Reference No 62-3) regarding enforcement analytical methods for impurities occurring in the Aceto 95% T and Drexel 95% T (EPA Reg. No. 2749-292 and 19713-59, respectively) because no validation data or statements regarding precision and accuracy were provided for the methods. Furthermore, because additional data are required for these products on product composition, discussion of the formation of impurities and preliminary analysis, additional impurities of toxicological significance may yet be identified. No enforcement analytical methods have been submitted for the Griffin 98% T (EPA Reg. No. 1812-262) and Makhteshim-Agan 98% T (EPA Reg. No. 11603-24).

The following additional data are required:

○ Analytical methods which are suitable for enforcement purposes must be provided for each active ingredient and each additional ingredient or impurity that is determined
to be toxicologically significant. Suitability for enforcement purposes shall be determined from validation studies of method accuracy and precision submitted by the registrant. These data are required for the Griffin 98% T (EPA Reg. No. 1912-262) and Makhteshim-Agan 98% T (EPA Reg. No. 11603-24). For the Ciba-Geigy 97% T (EPA Reg. No. 100-541), complete descriptions must be provided of Methods ASM-183-R and ASM-186-R (MRID 40765102) used to quantitate simazine and impurities that require certified limits. Validation data are also required for the analytical methods submitted by Aceto Agricultural Chemicals Corp. (Registration jacket) for analysis of impurities in the 95% T (EPA Reg. No. 2749-292), and by Drexel Chemical Co. (MRID 00146393) for analysis of simazine and impurities in the 95% T (EPA Reg. No. 19713-59).

PHYSICAL AND CHEMICAL CHARACTERISTICS

The Simazine Guidance Document dated 3/1/84 specified generic and product-specific data requirements for all physical and chemical characteristics pertinent to the technical grade of the active ingredient and manufacturing-use products.

The physical and chemical characteristics of the simazine purified active ingredient (PAI), technical grade of the active ingredient (TGAI), and manufacturing-use products (MP) are summarized below in Table 2. Unless otherwise stated here, these data satisfy the corresponding requirements of 40 CFR 158.190 (Guideline Reference No. 63-2 through 63-20) regarding physical and chemical characteristics of the indicated products. The stability data (63-13) for EPA Reg. No. 2749-292 and the storage stability data (63-17) for EPA Reg. No. 2749-292 and 19713-59 do not provide quantitative results of actual tests. Data submitted on solubility and vapor pressure of the PAI are from a desk reference (Herbicide Handbook of the Weed Science Society of America, 5th ed., 1983, p. 433-437) and have not been properly validated. Data on solubility, vapor pressure, dissociation constant, and octanol/water partition coefficient of the PAI may be shared among registrants upon proper request.

Data submitted by Ciba-Geigy Corp. (1984; MRID 00143169, and 1988; MRID 40765101) in response to the Simazine Guidance Document dated 3/1/84 have been reviewed by the Agency (EPA Memoranda RCB No. 1791 dated 2/9/87 and RCB No. 4295 dated 9/16/88) and found to satisfy the requirements of 40 CFR 158.190 (Guideline Reference No. 63-2 through 61-20) regarding most physical and chemical characteristics of the 97% T (EPA Reg. No. 100-541). However, no data were submitted concerning corrosion characteristics; this data requirement remains outstanding for this product.
The following additional data are required:

- As required by 40 CFR §158.190 and more fully described in the Pesticide Assessment Guidelines, Subdivision D, Guidelines Reference Nos. 63-2 through 63-13, data must be submitted on physicochemical characteristics (color, physical state, odor, melting point, boiling point, specific gravity, solubility, vapor pressure, dissociation constant, octanol/water partition coefficient, pH, and stability) of the technical grade of the active ingredient (TGAI). As required in 40 CFR §158.190 and more fully described in the Pesticide Assessment Guidelines, Subdivision D, Guidelines Reference Nos. 63-2 through 63-20, data must be submitted on physicochemical characteristics of each manufacturing-use product (color, physical state, odor, specific gravity, pH, oxidizing or reducing action, flammability, explodability, storage stability, viscosity, miscibility, and corrosion characteristics). All of these data are required for the Griffin 98% T (EPA Reg. No. 18152-262). For the Ciba-Geigy 97% T (EPA Reg. No. 100-541), data are required on corrosion characteristics. For the Aceto 95% T (EPA Reg. No. 2743-292), data are required on solubility, vapor pressure, octanol/water partition coefficient, stability, and storage stability. For the Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), data are required on solubility, vapor pressure, octanol/water partition coefficient, pH, stability, oxidation/reduction potential, flammability, explodability, and corrosiveness. For the Drexel 95% T (EPA Reg. No. 19713-59), data are required on solubility, vapor pressure, octanol/water partition coefficient, stability, oxidation/reduction potential, flammability, explodability, storage stability, and corrosiveness. For the Makhteshim-Agan 80% FI (EPA Reg. No. 11603-11), data are required on corrosiveness. For the Ciba-Geigy 90% FI (EPA Reg. No. 40810-9), data are required on color, physical state, odor, oxidation/reduction potential, flammability, explodability, storage stability, and corrosiveness.
Table 2. Physical and chemical properties of the simazine purified active ingredient (PAI), technical grade of the active ingredient (TGAI), and manufacturing-use products.

<table>
<thead>
<tr>
<th>Guidelines Reference Name of Property</th>
<th>Description [Method] (Product: Substrate; EPA Reg. No.; MRID or Jacket)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63-2. Color</td>
<td>white (95% T; TGAI; 2749-292: Jacket)</td>
</tr>
<tr>
<td></td>
<td>(80% FI; MP; 11603-11; 00149785)</td>
</tr>
<tr>
<td></td>
<td>(98% T; PAI &amp; TGAI; 11603-24; 00120338)</td>
</tr>
<tr>
<td></td>
<td>(95% T; TGAI; 19713-59; 00146393)</td>
</tr>
<tr>
<td>63-3. Physical state</td>
<td>fine or crystalline powder (95% T; TGAI; 2749-292: Jacket)</td>
</tr>
<tr>
<td></td>
<td>(80% FI; MP; 11603-11; 00149785)</td>
</tr>
<tr>
<td></td>
<td>(95% T; TGAI; 19713-59; 00146393)</td>
</tr>
<tr>
<td></td>
<td>solid (98% T; TGAI; 11603-24; 00120338)</td>
</tr>
<tr>
<td>63-4. Odor</td>
<td>none (95% T; TGAI; 2749-292: Jacket)</td>
</tr>
<tr>
<td></td>
<td>(98% T; P &amp; TGAI; 11603-24; 00120338)</td>
</tr>
<tr>
<td></td>
<td>(95% T; TGAI; 19713-59; 00146393)</td>
</tr>
<tr>
<td></td>
<td>slight characteristic odor (80% FI; MP; 11603-11; 00149785)</td>
</tr>
<tr>
<td>63-5. Melting point</td>
<td>228.2-228.8 C</td>
</tr>
<tr>
<td></td>
<td>(97% T; TGAI; 100-541; 40765103)</td>
</tr>
<tr>
<td></td>
<td>225 C minimum</td>
</tr>
<tr>
<td></td>
<td>(95% T; PAI?; 2749-292: Jacket)</td>
</tr>
<tr>
<td></td>
<td>225-227 C (PAI), 224-227 C (TGAI)</td>
</tr>
<tr>
<td></td>
<td>(98% T; 11603-24; 00120338)</td>
</tr>
<tr>
<td></td>
<td>225-227 C [Buchi equipment]</td>
</tr>
<tr>
<td></td>
<td>(95% T; PAI?; 19713-59; 00146393)</td>
</tr>
<tr>
<td>63-6. Boiling point</td>
<td>Simazine is a solid at room temperature.</td>
</tr>
<tr>
<td>63-7. Density, bulk density, or specific gravity</td>
<td>220 ± 50 g/L</td>
</tr>
<tr>
<td></td>
<td>(95% T; TGAI?; 2749-292: Jacket)</td>
</tr>
<tr>
<td></td>
<td>0.32-0.35 g/ml at 25 C</td>
</tr>
<tr>
<td></td>
<td>(80% FI; MP; 11603-11; 00149785)</td>
</tr>
<tr>
<td></td>
<td>1.21 at 20 C</td>
</tr>
<tr>
<td></td>
<td>(98% T; PAI; 11603-24; 00120338)</td>
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<tr>
<td></td>
<td>23.6 lb/ft³</td>
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<td>(95% T; TGAI; 19713-59; 00146393)</td>
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<tr>
<td></td>
<td>23-27 lb/ft³</td>
</tr>
<tr>
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<td>(90% FI; MP; 40810-9; jacket)</td>
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</table>

(Continued)
Table 2. (Continued.)

Guidelines Reference No., 40 CFR §158.190; Name of Property

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<tr>
<th>Solubility</th>
<th>Solvent</th>
<th>Solubility</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
<td>2 ppm</td>
<td>0°C</td>
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<tr>
<td></td>
<td>water</td>
<td>5 ppm</td>
<td>20°C</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>84 ppm</td>
<td>35°C</td>
</tr>
<tr>
<td></td>
<td>methanol</td>
<td>400 ppm</td>
<td>20°C</td>
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<tr>
<td></td>
<td>n-pentane</td>
<td>3 ppm</td>
<td>25°C</td>
</tr>
<tr>
<td></td>
<td>ethyl ether</td>
<td>300 ppm</td>
<td>25°C</td>
</tr>
<tr>
<td></td>
<td>chloroform</td>
<td>900 ppm</td>
<td>20°C</td>
</tr>
</tbody>
</table>

(95% T; PAI?; 19713-59; 00146393)
(98% T; PAI; 11603-24; 00120338)

100 mg/20 ml tetrahydrofuran
(97% T; PAI; 100-541; 40765103)

3.5 mg/L of water at 20°C
(95% T; PAI?; 2749-292: Jacket)

Vapor pressure

<table>
<thead>
<tr>
<th>Solubility</th>
<th>Solvent</th>
<th>Solubility</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.2 x 10^-10</td>
<td>mm Hg at 10°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.1 x 10^-9</td>
<td>mm Hg at 20°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.6 x 10^-8</td>
<td>mm Hg at 30°C</td>
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</tr>
<tr>
<td></td>
<td>9.0 x 10^-7</td>
<td>mm Hg at 50°C</td>
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</tbody>
</table>

(95% T; PAI?; 19713-59; 00146393)
(98% T; PAI; 11603-24; 00120338)

2.21 x 10^-8 mm Hg at 25°C; extrapolated from measurements between 36.5 and 140.2°C [OECD Guideline No. 104]
(97% T; PAI; 100-541; 40765103)

Dissociation constant

pKa = 1.7 (95% T; PAI?; 19713-59; 00146393)

pKa = 1.65 in water at 22°C
[Residue Reviews 32:100 (1970)]
(98% T; PAI & TGAI; 11603-24; 00120338)
pKa = 1.65 at 16°C
(95% T; PAI?; 2749-292: Jacket)

Octanol/water partition coefficient

K = 122 (log P = 2.1)
(97% T; PAI; 100-541; 40765103)
p = 0.9482; K = 18.30
(95% T; PAI?; 2749-292: Jacket)
1.4 g/kg water, 5 mg/kg octanol
(95% T; TGAI?; 19713-59; 00146393)
<table>
<thead>
<tr>
<th>Guidelines Reference No., 40 CFR §158.190; Name of Property</th>
<th>Description [Method] (Product; Substrate; EPA Reg. No.; MRID or Jacket)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63-12. pH</td>
<td>6.5 [FAO 22/3/M/2.9] (80% FI; MP; 11603-11; 00149785)</td>
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<tr>
<td></td>
<td>6-7 (95% T; TGAI?; 2749-292: Jacket)</td>
</tr>
<tr>
<td></td>
<td>7.9 [5 g product in 50 ml water] (95% T; TGAI; 19713-59; 00146393)</td>
</tr>
<tr>
<td></td>
<td>7-10, 10% suspension in water (90% FI; MP; 40810-9; jacket)</td>
</tr>
<tr>
<td>63-13. Stability</td>
<td>stable in neutral, slightly acidic or basic media; strong acids (sic) (95% T; PAI?; 2749-292: Jacket)</td>
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<tr>
<td>63-14. Oxidizing or reducing action</td>
<td>Undergoes no hazardous reactions whatsoever when in contact with common oxidizing and reducing agents, fire extinguishing agents, or solvents (MP; MP; 11603-11; 00149785)</td>
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<tr>
<td></td>
<td>non-oxidizer (95% T; TGAI?; 2749-292: Jacket)</td>
</tr>
<tr>
<td>63-15. Flammability</td>
<td>Contains no volatile or readily ignitable components; no danger of autoignition proximity with hot surfaces (80% FI; MP; 11603-11; 00149785)</td>
</tr>
<tr>
<td></td>
<td>non-flammable (95% T; TGAI?; 2749-292: Jacket)</td>
</tr>
<tr>
<td>63-16. Explodability</td>
<td>No tendency to undergo violent reactions in tests for impact explosivity (80% FI; MP; 11603-11; 00149785)</td>
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<tr>
<td></td>
<td>non-explosive (95% T; TGAI?; 2749-292: Jacket)</td>
</tr>
<tr>
<td>63-17. Storage stability</td>
<td>No loss of active ingredient during 28 months storage under unspecified conditions [FAO 22/3/M2.2] (80% FI; MP; 11603-11; 00149785)</td>
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</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Guidelines Reference No., 40 CFR §158.190; Name of Property</th>
<th>Description [Method] (Product; substrate; EPA Reg. No.; MRID or Jacket)a</th>
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</thead>
<tbody>
<tr>
<td>63-17. Storage stability (cont.)</td>
<td>stable under normal storage conditions (95% T; TGA1; 2749-292: Jacket)</td>
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<tr>
<td></td>
<td>minimum 2 years (95% T; TGA1; 19713-59; 00146393)</td>
</tr>
<tr>
<td></td>
<td>Samples from 7 batches showed 0-0.5% loss in active ingredient after 1 year at 8-28 C, and 0.2-0.4% after 2 years. (98% T; TGA1; 11603-24; 00120338)</td>
</tr>
<tr>
<td>63-18. Viscosity</td>
<td>All simazine T and FI products are solids at room temperature.</td>
</tr>
<tr>
<td>63-19. Miscibility</td>
<td>All simazine T and FI products are solids at room temperature.</td>
</tr>
<tr>
<td>63-20. Corrosiveness</td>
<td>non-corrosive (95% T; PAI; 2749-292: Jacket)</td>
</tr>
</tbody>
</table>

a PAI = purified active ingredient. TGA1 = technical grade of the active ingredient. MP = manufacturing-use product. FI = formulation intermediate. Hyphenated numbers represent EPA Registration Numbers. Eight-digit numbers are MRID documents from the Pesticide Document Management System (PDMS). "Jacket" refers to the pesticide registration jacket maintained for the specified product by Registration Division, OPP, EPA.
References (used):

(This list was obtained from a search of the Pesticide Document Management System database conducted 10/5/89 for documents dealing with the product chemistry of simazine. References preceded by an asterisk (*) were reviewed for this Second Round Review. Other references were reviewed for the Simazine Guidance Document dated 3/1/84.)


GS-650060-6 Confidential Statement of Formula (EPA Reg. No. 100-541).

GS-650060-11 Confidential Statement of Formula (EPA Reg. No. 39511-5).

00023954 Aceto Agricultural Chemicals Corporation (19??) Simazine (Aquasim): General Chemistry Data. (Unpublished study received Mar 13, 1979 under 2749-444; CDL:237791-A)

00023955 Ciba-Geigy Corporation (1977) Chemical Data Section for Simazine. (Unpublished study received Apr 27, 1977 under 100-541; CDL:229606-A)

00023956 Ciba-Geigy Corporation (1977) Composition of Technical Simazine. (Unpublished study received Apr 27, 1977 under 100-541; CDL:229606-B)

00023957 Ciba-Geigy Corporation (1977) Manufacturing Process for Simazine. (Unpublished study received Apr 27, 1977 under 100-541; CDL:229606-C)


Agan Chemical Manufactures, Limited (19??) Simanex: Herbicide. (Unpublished study received Jul 17, 1972 under 11603-11; CDL:014051-A)


Drexel Chemical Co. (19??) Simazine Technical. (Compilation; unpublished study received Jul 21, 1982 under 19713-59; CDL:247889-A)


Agan Chemical Mfg., Ltd. (1982) [Simanex: Chemical Study]. (Compilation; unpublished study received Dec 9, 1982 under 11603-24; CDL:249045-A)


References (not used):

[The following references pertain only to end use products or contain only duplicate or irrelevant data.]

00012172 Ciba-Geigy Corporation (19??) [Physical and Chemical Tank-Mix Compatibilities]. (Unpublished study received Jan 18, 1973 under 100-437; CDL:000242-BY)


00023239 Ciba-Geigy Corporation (1975) Simazine: Name, Chemical Identity, and Composition of the Pesticide Chemical. (Unpublished study received Jan 6, 1976 under 6E1725; CDL:097505-C)


00023267 Monsanto Company (19??) Physical and Chemical Compatibility of the Tank Mixture. (Unpublished study received Dec 19, 1977 under 524-308; CDL:232519-A)

00023269 Monsanto Company (19??) Reasonable Grounds in Support of the Request: [Roundup plus Lasso plus Princep]. (Unpublished study received Dec 19, 1977 under 524-285; CDL:232519-C)

00023281 Geigy Chemical Corporation (19??) Name, Chemical Identity and Composition of Simazine. (Unpublished study received Sep 19, 1966 under 7F0534; CDL:092912-D)

00023335 Monsanto Company (19??) Physical and Chemical Compatibility of the Tank Mixture. (Unpublished study received Dec 19, 1977 under 524-308; CDL:232518-A)
Lee, T.C. (1978) [Compatibility Studies of Princep and Evik]; AG 4710. (Unpublished study including AG 4884, received Mar 9, 1978 under 100-437; submitted by Ciba-Geigy Corp., Greensboro, N.C.; CDL:233012-B)


Geigy Chemical Corporation (197?) Determination of Atrazine, Propazine and Simazine in Commercial Formulations. Ardsley, N.Y.: Geigy. (Analytical bulletin no. 2; also In unpublished submission received Jan 15, 1966 under 7F0534; CDL:090651-A)


Ciba-Geigy Corporation (1977) Princep 4L: Chemistry Data Section. (Unpublished study received Aug 26, 1977 under 100-526; CDL:231408-A)

Ciba-Geigy Corporation (1977) Princep 4L: Confidential Formulation. (Unpublished study received Aug 26, 1977 under 100-526; CDL:231408-B)


NCH Corporation (1973) Cimacide Algaecide. (Unpublished study received May 12, 1975 under 1769-234; CDL:220067-B)


Dobbins, L. (1978) [Physical Compatibility Data for Mixtures of Princep 90WG and Other Herbicides]. (Unpublished study received Dec 27, 1978 under 100-603; submitted by Ciba-Geigy Corp., Greensboro, N.C.; CDL:236738-C)

00024034 Aceto Chemical Company (1973) Determination of: 2-Chloro-4-ethylamino-6-isopropylamino-s-triazine (Atrazine), 2-Chloro-4,6-bis-ethylamino-s-triazine (Simazine), 2-Chloro-4,6-bis(isopropylamino-s-triazine (Propazine) by Hydrolysis. Undated method. (Unpublished study received Jun 24, 1976 under 2749-430; CDL:236375-A)


00024345 Rumianca, S.p.a. (1977) [Atrazine: General Chemistry Data]. Includes eighteen undated methods. (Unpublished study received Aug 29, 1977 under 40643-1; CDL:231465-A)

00024410 Ciba-Geigy Corporation (1977) Tank-Mix Compatibility. (Unpublished study received Jun 22, 1977 under 100-439; CDL:230747-B)


00025439 Geigy Chemical Corporation (19??) Simazine. (Unpublished study received Oct 27, 1970 under 10826-1; submitted by Laing Chemical Co., Inc., Sacramento, Calif.; CDL:110884-A)

00025453 Geigy Chemical Corporation (19??) Name, Chemical Identity and Composition of Simazine. (Unpublished study received Mar 19, 1965 under 5F0447; CDL:092911-I)
Geigy Agricultural Chemicals (19??) Simazine Herbicides for Agricultural use. Ardsley, N.Y.: Geigy. (Herbicide technical bulletin no. 60-1; also In unpublished submission received on unknown date under unknown admin. no.; CDL:000213-L)


Geigy Chemical Corporation (1964) Simazine. (Unpublished study received on unknown date under unknown admin. no.; CDL:128063-K)

Ciba-Geigy Corporation (1977) Princep(R): 80W Chemistry Data Section. (Unpublished study received Aug 23, 1977 under 100-437; CDL:231369-A)

Ciba-Geigy Corporation (1977) Princep 80W: Confidential Ingredient Statement. (Unpublished study received Aug 23, 1977 under 100-437; CDL:231369-B)

Ciba-Geigy Corporation (1977) [Princep 80W: Manufacturing Procedures]. (Unpublished study received Aug 23, 1977 under 100-437; CDL:231369-C)


Ciba-Geigy Corporation (1977) Pramis(TM): 80W; Chemistry Data Section. (Unpublished study received Oct 10, 1978 under 100-602; CDL:235343-A)


00027860 Agan Chemical Manufactures, Limited (19??) Method of Analysis for Simanex (Simazine)--for Technical Material and Wettable Powders. (Unpublished study received Jul 17, 1972 under 11603-11; CDL:014051-B)

00027885 Geigy Chemical Company (19??) Name, Chemical Identity and Composition of Simazine. (Unpublished study received Jan 13, 1969 under 9F0792; CDL:093100-B)


00029640 Geigy Chemical Corporation (19??) Simazine and Related Compounds. Ardsley, N.Y.: Geigy. (Herbicide technical bulletin no. 58-2; also In unpublished submission received Nov 20, 1959 under 264-119; submitted by Union Carbide Agricultural Products Co., Ambler, Pa.; CDL:001891-C)


00030142 Bailey, G.W.; White, J.L. (19??) Herbicides: A compilation of their physical, chemical, and biological properties. Residue Reviews 10(?):? - ?. (Incompletes; 4 pages; also In unpublished submission received Jul 19, 1978 under 201-403; submitted by Shell Chemical Co., Washington, D.C.; CDL:234473-E)


00031533 Ciba-Geigy Corporation (19??) Storage Stability Data for Simazine-Fertilizer Combination (0-10-30). (Unpublished study received Aug 12, 1969 under 100-499; CDL:000533-A)

00031534 Ciba-Geigy Corporation (19??) Formulation Sheet. (Unpublished study received Aug 12, 1969 under 100-499; CDL:000533-B)


Geigy Chemical Corporation (19??) Simazine Herbicides for Selective and Non-Selective Uses. Ardsley, N.Y.: Geigy. (Simazine technical bulletin no. 62-1; also In unpublished submission received Feb 8, 1963 under 7401-192; submitted by Voluntary Purchasing Group, Inc., Bonham, Tex.; CDL:009207-A)

Ciba-Geigy Corporation (1978) Princep(R): 90WDG Chemical Data Section. (Unpublished study received Dec 27, 1978 under 100-603; CDL:236685-A)


Ciba-Geigy Corporation (1957) Graph Showing Hydrolysis Curve of Simazine. (German text: unpublished study received Mar 19, 1958 under unknown admin. no.; CDL:222507-C)


Behrens, R. (19??) [Without title]. Residue Reviews 32(?):364-365. (Incomplete; also in unpublished submission received Sep 8, 1980 under 11773-1; submitted by Van Diest Supply Co., Webster City, Iowa; CDL:243178-A)

Van Diest Supply Company (1973) Field Dissipation of Atrazine. Summary of studies 243178-B through 243178-G. (Unpublished study received Sep 8, 1980 under 11773-1; CDL:243178-H)


United States Borax & Chemical Corporation (19??) Analysis for Simazine in Metaborate-Chlorate Formulations. Undated method. (Unpublished study received Aug 1, 1966 under unknown admin. no.; CDL:104755-D)


Ciba-Geigy Corporation (1977) Princep 1% Algicide. (Unpublished study received Apr 27, 1977 under 100-588; CDL:229642-A)


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Griffin Corporation (1976) Atrazine 4L Shelf-life Study. (Unpublished study received Nov 10, 1976 under 1812-218; CDL:226865-C)


0011686 Geigy Chemical Corp. (1967) [Chemical Study: Propazine]. (Compilation; unpublished study received Dec 27, 1967 under 8F0687; CDL:092992-A)


00133019 Ciba-Geigy Corp. (1983) [Study--Chemistry: Simazine]. (Unpublished study received Nov 22, 1983 under 100-541; CDL:251986-A)


00145069 Setre Chemical Co. (19??) [Product Chemistry Data of Simazine/40% Bromacil]. Unpublished study. 8 p.


Bishop Chemical, Inc. (1987) Submission of Chemistry Data on Simazine 1G. Transmittal of 1 study.


40589200 Great Lakes Chemical Corp. (19??) Submission of Data To Support the Registration of Bromazine S Tablets: Product Chemistry Data. Transmittal of 3 studies.


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<tr>
<th>Data Requirement</th>
<th>Test Substance</th>
<th>Does EPA have data to satisfy this requirement?</th>
<th>Bibliographic Citation</th>
<th>Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?</th>
<th>Time Frame for Data Submission</th>
</tr>
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<tbody>
<tr>
<td>61-3. Formation of Impurities</td>
<td>TGA1</td>
<td>Partially</td>
<td>00120338*. 00143169*</td>
<td>Yes4</td>
<td>6 months</td>
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<td>62-1. Preliminary Analysis</td>
<td>TGA1</td>
<td>Partially</td>
<td>00143169*</td>
<td>Yes5</td>
<td>12 months</td>
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<td>63-2. Color</td>
<td>TGA1</td>
<td>Partially</td>
<td>00023955. 00023956. 00120338*. 00146393*.</td>
<td>Yes6</td>
<td>6 months</td>
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<tr>
<td>63-3. Physical State</td>
<td>TGA1</td>
<td>Partially</td>
<td>00023955. 00023956. 00120338*. 00146393*</td>
<td>Yes6</td>
<td>6 months</td>
</tr>
<tr>
<td>63-4. Odor</td>
<td>TGA1</td>
<td>Partially</td>
<td>00023955. 00023956. 00120338*. 00146393*</td>
<td>Yes6</td>
<td>6 months</td>
</tr>
<tr>
<td>63-5. Melting Point</td>
<td>TGA1</td>
<td>Partially</td>
<td>00023955. 00120338*. 00146393*. 40765103*.</td>
<td>Yes6,7</td>
<td>6 months</td>
</tr>
<tr>
<td>63-6. Boiling Point</td>
<td>TGA1</td>
<td>No</td>
<td>N/A</td>
<td>No8</td>
<td>6 months</td>
</tr>
<tr>
<td>63-7. Density/Specific Gravity</td>
<td>TGA1</td>
<td>Partially</td>
<td>00023955. 00023956. 00120338*. 00146393*</td>
<td>Yes6</td>
<td>6 months</td>
</tr>
<tr>
<td>63-8. Solubility</td>
<td>TGA1 or PAI</td>
<td>Partially</td>
<td>00023955. 00023956. 00120338*. 00149393*. 40765103*</td>
<td>Yes6</td>
<td>6 months</td>
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(Continued, footnotes follow)
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<th>Test Substance</th>
<th>Does EPA have data to satisfy this requirement?</th>
<th>Bibliographic Citation</th>
<th>Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?</th>
<th>Time Frame For Data Submission</th>
</tr>
</thead>
<tbody>
<tr>
<td>63-9. Vapor Pressure</td>
<td>TGAI or PAI</td>
<td>Partially</td>
<td>00023955.</td>
<td>Yes⁶</td>
<td>6 months</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>00120338*</td>
<td></td>
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<td></td>
<td></td>
<td>00149393*</td>
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<td></td>
<td>40765101*</td>
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<tr>
<td>63-10. Dissociation Constant</td>
<td>TGAI or PAI</td>
<td>Partially</td>
<td>00143169*</td>
<td>Yes⁶</td>
<td>6 months</td>
</tr>
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<td></td>
<td></td>
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<td>00120338*</td>
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<td>00146393*</td>
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<td></td>
<td></td>
<td></td>
<td>40765103*</td>
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<td>63-11. Octanol/Water Partition Coefficient</td>
<td>PAI</td>
<td>Partially</td>
<td>00146393*</td>
<td>Yes⁶,⁹</td>
<td>6 months</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40765101*</td>
<td></td>
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<tr>
<td>63-12. pH</td>
<td>TGAI</td>
<td>Partially</td>
<td>00146393*</td>
<td>No¹⁰</td>
<td>6 months</td>
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<tr>
<td>63-13. Stability</td>
<td>TGAI</td>
<td>Partially</td>
<td>0023955</td>
<td>Yes⁶</td>
<td>6 months</td>
</tr>
</tbody>
</table>

Other Requirements:

| 64-1. Submittal of Samples | N/A | N/A | N/A | No |

1. Additional data requirements are listed in the following Table B, "Generic Data Requirements for Simazine Manufacturing-Use Products", for registered technical products.

2. Test substance: PAI = purified active ingredient; TGAI = technical grade of the active ingredient; MP = manufacturing-use product.

3. The following information must be provided: (i) the name and address of the producer of the technical grade of the active ingredient; (ii) the brand name, trade name or other commercial designation, the name and address of the producer, and information concerning the composition of each starting material; (iii) a general characterization of the process (e.g., batch or continuous); (iv) a flow chart of the chemical equations of each intended reaction occurring at each step of the process, the necessary reaction conditions, and the duration of each step of the process and of the entire process; (v) the identity of the materials used to produce the product, their relative amounts, and the order in which they are added; (vi) a description of the equipment used; (vii) a description of the conditions (e.g., temperature, pressure, pH, humidity) that are controlled during each step of the process; (viii) a description of any purification procedures (including procedures to recover or recycle starting materials, intermediates or the substance produced); and (ix) a description of the procedures used to assure consistent composition of the substance produced (quality control methods). All of this information is required for the Griffin 98% T and Aceto 95%
T (EPA Reg. No. 1812-262 and 2749-292, respectively). For the Drexel 95% T (EPA Reg. No. 19713-59), the nature of the process (batch or continuous) and the equipment used must be described.

4. A discussion regarding the origin of the following potential impurities must be provided: (i) each impurity associated with the active ingredient which was found to be present in any analysis of the product conducted by or for the registrant, and (ii) each impurity which the registrant has reason to believe may be present at a level equal to or greater than 0.1% (w/w) based on the composition of each starting material, intended and side reactions which may occur during production, the possible degradation of ingredients after production, post-production reactions between ingredients, possible contamination from packaging materials or production equipment, and process control, purification and quality control measures. All of these data are required for the Griffin 98% T, Aceto 95% T, and Drexel 95% T (EPA Reg. No. 1812-262, 2749-292, and 19713-59, respectively). For the Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), the individual impurities and chemical reactions by which they form must be adequately described.

5. Five or more representative samples must be analyzed for the amount of active ingredient and each impurity present at 0.1% or greater. If the product is produced by a batch process, five separate batches should be represented in preliminary analyses. Complete and detailed descriptions of the methods used for sample analysis must be submitted, including statements of their precision and accuracy. The preliminary analysis report should include the identity and quantity of each ingredient for which analysis is conducted along with the mean and relative standard deviation of the analytical results. Based on the preliminary analysis, a statement of the composition of the technical grade of active ingredient must be provided. These data are required for all simazine manufacturing products with the exception of the Ciba-Geigy 97% T (EPA Reg. No. 100-541).

6. As required by 40 CFR §158.190 and more fully described in the Pesticide Assessment Guidelines, Subdivision D, Guidelines Reference Nos. 63-2 through 63-13, data must be submitted on physiochemical characteristics (color, physical state, odor, melting point, boiling point, specific gravity, solubility, vapor pressure, dissociation constant, octanol/water partition coefficient, pH, and stability). There are additional data requirements listed in Table B pertaining to physiochemical characteristics of those technical products which are also manufacturing use products. All of these data are required for the Griffin 98% T (EPA Reg. No. 18152-262). For the Aceto 95% T (EPA Reg. No. 2749-292), data are required on solubility, vapor pressure, octanol/water partition coefficient, and stability. For the Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), data are required on solubility, vapor pressure, octanol/water partition coefficient, pH, and stability. For the Drexel 95% T (EPA Reg. No. 19713-59), data are required on solubility, vapor pressure, octanol/water partition coefficient, and stability.
7. Data on melting point are required if the technical chemical is a solid at room temperature.

8. Data on boiling point are not required because the simazine technical product is a solid at room temperature.

9. Data on octanol/water partition coefficient are required if the technical chemical is organic and nonpolar.

10. Data are required on pH because simazine is practically insoluble in water.
### TABLE B. GENERIC DATA REQUIREMENTS FOR SIMAZINE MANUFACTURING-USE PRODUCTS.

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<th>Bibliographic Citation</th>
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<th>Time Frame For Data Submission</th>
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<td>62-1. Preliminary Analysis</td>
<td>MP</td>
<td>Partially</td>
<td></td>
<td></td>
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<th>Bibliographic Citation</th>
<th>Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?</th>
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**Physical and Chemical Characteristics**

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<th>Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?</th>
<th>Time Frame For Data Submission</th>
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<tr>
<td>63-2. Color</td>
<td>MP</td>
<td>Partially</td>
<td>00023956. 00120338*. 00149785*. 00146393*.</td>
<td>Yes*</td>
<td>6 months</td>
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<tr>
<td>63-4. Odor</td>
<td>MP</td>
<td>Partially</td>
<td>00023956. 00120338*. 00146393*. 00149785*.</td>
<td>Yes*</td>
<td>6 months</td>
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<tr>
<td>63-12. pH</td>
<td>MP</td>
<td>Partially</td>
<td>00146393*. 00149785*. 00149785*.</td>
<td>Yes*</td>
<td>6 months</td>
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(Continued, footnotes follow)
TABLE B.  (Continued).

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<th>Data Requirement</th>
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<th>Bibliographic Citation</th>
<th>Must additional data be submitted under FIFRA Sec. 3(c)(2)(B)?</th>
<th>Time Frame For Data Submission</th>
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<td>63-16. Explodability</td>
<td>MP</td>
<td>Partially</td>
<td>00143169* 00149785*</td>
<td>Yes\textsuperscript{9,13}</td>
<td>6 months</td>
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<tr>
<td>63-17. Storage Stability</td>
<td>MP</td>
<td>Partially</td>
<td>00023956 00120338*</td>
<td>Yes\textsuperscript{9}</td>
<td>15 months</td>
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<tr>
<td>63-18. Viscosity</td>
<td>MP</td>
<td>No</td>
<td>N/A</td>
<td>No\textsuperscript{14}</td>
<td></td>
</tr>
<tr>
<td>63-19. Miscibility</td>
<td>MP</td>
<td>No</td>
<td>N/A</td>
<td>No\textsuperscript{14}</td>
<td></td>
</tr>
<tr>
<td>63-20. Corrosion Characteristics</td>
<td>MP</td>
<td>Partially</td>
<td></td>
<td>Yes\textsuperscript{9}</td>
<td>15 months</td>
</tr>
</tbody>
</table>

Other Requirements:

64-1. Submittal of Samples        | N/A            | N/A                                           | N/A                      | No                                                            |                                |

1. Additional data requirements are listed in the preceding Table A, "Generic Data Requirements for the Simazine Technical Grade of the Active Ingredient", for those manufacturing-use products which consist only of the TGAI.

2. Test substance: PAI = purified active ingredient; TGAI = technical grade of the active ingredient; MP = manufacturing-use product.

3. For the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), and Drexel 95% T (EPA Reg. No. 19713-59), nominal concentrations, certified limits (in accordance with 40 CFR §158.175), and purposes must be provided for all components (impurities must be identified as such). The nominal concentrations of the active ingredients reported on the product labels shall be equal to the corresponding lower certified limits.

4. For each manufacturing-use product that is produced from an EPA-registered product, the following information must be provided: (i) the name and EPA registration number of the EPA-registered product; (ii) the brand name, trade name, or other commercial designation and information concerning the composition of each inert ingredient; (iii) a general characterization of the formulation or production process (e.g., batch or continuous); the identity of the materials used to produce the product, their relative amounts, and the order in which they are added; (iv) a description of the equipment used; (v) a description of the conditions (e.g., temperature, pressure, pH, humidity) that are controlled during each step of the process; and (vi) a description of the procedures used to assure consistent composition of the substance produced.
(quality control methods). For each manufacturing use product that consists of the technical grade of the active ingredient only or is produced by an integrated system, the following information must be provided in addition to that listed above: (i) the name and address of the producer if different from the registrant; (ii) the brand name, trade name or other commercial designation of each starting material, the name and address of its producer, and information concerning its composition; (iii) a flow chart of the chemical equations of each intended reaction occurring at each step of the process and of the entire process; and (iv) a description of any purification procedures (including procedures to recover or recycle starting materials, intermediates or the substance produced). All of this information is required for the Griffin 98% T, Aceto 95% T, and Ciba-Geigy 90% FI (EPA Reg. No. 1812-262, 2749-292, and 40810-9, respectively). For the Drexel 95% T (EPA Reg. No. 19713-59), the nature of the process (batch or continuous) and the equipment used must be described.

5. For each manufacturing use product that consists of the technical grade of the active ingredient only or is produced by an integrated system, a discussion regarding the origin of the following potential impurities must be provided: (i) each impurity associated with the active ingredient which was found to be present in any analysis of the product conducted by or for the registrant, and (ii) each impurity which the registrant has reason to believe may be present in the product at a level equal to or greater than 0.1% (w/w) based on the composition of each starting material, intended and side reactions which may occur in the production of the product, the possible degradation of ingredients in the product after production, post-production reactions between the ingredients in the product, possible contamination from packaging materials or production equipment, and process control, purification and quality control measures. For each manufacturing use product that is produced from an EPA-registered product, a discussion must be provided for each impurity associated with the active ingredient which the registrant has reason to believe may be present in the product at a level equal to or greater than 0.1% (w/w) based on the possible carryover of impurities present in the registered product which serves as the source of the active ingredient, the possible carryover of impurities present in the inert ingredients in the product, possible reactions occurring during the formulation of the product, post-production reactions between any of the product's active ingredients and any other component of the product or its packaging, and possible contamination from packaging materials or production equipment. All of these data are required for the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), Drexel 95% T (EPA Reg. No. 19713-59), Ciba-Geigy 90% FI (EPA Reg. No. 40810-9). For the Makhsheshim-Agan 98% T. (EPA Reg. No. 11603-24), the individual impurities and chemical reactions by which they form must be adequately described.

6. For each manufacturing use product produced by an integrated system, the registrant must provide preliminary analyses of five or more representative samples of each technical grade of active ingredient contained in the product to identify all impurities present at 0.1% or greater of the TGAI. If the product
is produced by a batch process, at least five separate batches should be represented. The preliminary analysis should be conducted at the point in the production process after which no further chemical reactions designed to produce or purify the substance are intended. Complete and detailed descriptions of the methods used for sample analysis must be submitted, including statements of their precision and accuracy. The preliminary analysis report should include the identity and quantity of each ingredient for which analysis is conducted, along with the mean and relative standard deviation of the analytical results. Based on the preliminary analysis, a statement of the composition of the technical grade of active ingredient must be provided. If the technical grade of active ingredient cannot be isolated, a statement of the composition of the practical equivalent of the technical grade of active ingredient must be submitted. In addition, all nitrosamines must be identified and quantified by methods sensitive to 1 ppm of N-nitroso contaminants in six samples of each manufacturing-use product; two samples of each must be analyzed shortly after production, two at 3 months after production, and two at 6 months after production. Upper limits must be proposed for all nitrosamines found. These data are required for all simazine manufacturing-use products with the exception of the Ciba-Geigy 97% T (EPA Reg. No. 100-541).

7. The registrant must propose upper and lower limits for each active and inert ingredient, if such limits would differ from the standard certified limits determined by the Agency according to 40 CFR §158.175(b)(2). Also, if the manufacturing use product contains the technical grade of the active ingredient only or is produced by an integrated system, upper limits must be proposed for each toxicologically significant impurity associated with the active ingredients and found to be present in any sample of the product (standard certified limits cannot be used for impurities). Certified limits should be based on the sources and magnitude of variability in the manufacturing process and the stability of the ingredients following production. The registrant must certify the accuracy of the information presented, and that the certified limits will be maintained. An explanation of how each certified limit was established (e.g., sample analysis using a validated analytical procedure, quantitative estimate based on the amounts of ingredients used, etc.) must be provided, along with information on the accuracy and precision of any analytical procedures used. Certifications must be submitted on EPA Form 8570-4 (Rev. 2/85). These data are required for the Griffin 98% T (EPA Reg. No. 1812-262), Aceto 95% T (EPA Reg. No. 2749-292), Makkhteshim-Agan 98% T (EPA Reg. No. 11603-24), and Drexel 95% T (EPA Reg. No. 11603-24). For the Ciba-Geigy 97% T (EPA Reg. No. 100-541), certified limits for nitrosamines must be reported on the Confidential Statement of Formula (EPA Form 8570 (Rev. 2-85)).

8. Analytical methods which are suitable for enforcement purposes must be provided for each active ingredient and each additional ingredient or impurity that is determined to be toxicologically significant. Suitability for enforcement purposes shall be determined from validation studies of method accuracy and precision submitted by the registrant. These data are required for the Griffin 98% T (EPA Reg. No. 1812-262).
TABLE B. (Continued).

1812-262) and Makhteshim-Agan 98% T (EPA Reg. No. 11603-24). For the Ciba-Geigy 97% T (EPA Reg. No. 100-541), complete descriptions must be provided of Methods ASM-183-R and ASM-186-R (MRID 40765102) used to quantitate simazine and impurities that require certified limits. Validation data are also required for the analytical methods submitted by Aceto Agricultural Chemicals Corp. (Registration jacket) for analysis of impurities in the 95% T (EPA Reg. No. 2749-292), and by Drexel Chemical Co. (MRID 00146393) for analysis of simazine and impurities in the 95% T (EPA Reg. No. 19713-59).

9. As required in 40 CFR §158.190 and more fully described in the Pesticide Assessment Guidelines, Subdivision D, Guidelines Reference Nos. 63-2 through 63-20, data must be submitted on physicochemical characteristics of each manufacturing-use product (color, physical state, odor, specific gravity, pH, oxidizing or reducing action, flammability, explodability, storage stability, viscosity, miscibility, and corrosion characteristics). All of these data are required for the Griffin 98% T (EPA Reg. No. 18152-262). For the Ciba-Geigy 97% T (EPA Reg. No. 100-541), data are required on corrosion characteristics. For the Aceto 95% T (EPA Reg. No. 2749-292), data are required on storage stability. For the Makhteshim-Agan 98% T (EPA Reg. No. 11603-24), data are required on pH, oxidation/reduction potential, flammability, explodability, and corrosiveness. For the Drexel 95% T (EPA Reg. No. 19713-59), data are required on oxidation/reduction potential, flammability, explodability, storage stability, and corrosiveness. For the Makhteshim-Agan 80% FI (EPA Reg. No. 11603-11), data are required on color, physical state, odor, oxidation/reduction potential, flammability, explodability, storage stability, and corrosiveness. Additional data requirements regarding physicochemical properties of manufacturing-use products which contain only the technical grade of the active ingredient are listed in Table A, "Generic Data Requirements for the Simazine Technical Grade of the Active Ingredient."

10. Data on pH are required if the test substance is dispersible in water.

11. Data are required on oxidizing/reducing potential if product contains an oxidizing or reducing agent.

12. Data are required on flammability if the product contains combustible liquids.

13. Data are required if the product is potentially explosive.

14. Data are not required on viscosity or miscibility because all manufacturing-use products are solids.
Final Report

SIMAZINE (SRR)
Task 2: Residue Chemistry

Contract No 68-D8-0080

January 11, 1989

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852
# SIMAZINE (SRR)

**RESIDUE CHEMISTRY**

**Task - 2**

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<td>Grapes</td>
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<td>Strawberries</td>
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<td>Miscellaneous Commodities</td>
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SIMAZINE
SECOND ROUND REVIEW
RESIDUE CHEMISTRY

Task - 2

INTRODUCTION

Simazine (2-chloro-4,6-bis(ethylamino)-g-triazine) is a chlorinated triazine herbicide registered for use on almonds, apples, artichokes, asparagus, avocados, bananas, blackberries, blueberries, boysenberries, cherries, corn (field and sweet), cranberries, filberts, grapefruit, grapes, lemons, loganberries, macadamia nuts, olives, oranges, peaches, pears, pecans, plums (fresh prunes), raspberries, strawberries, sugarcane, and walnuts. In addition, simazine may be applied to aquatic sites, tree nurseries, and other non-crop and industrial sites. Registration of simazine for use on alfalfa, bermudagrass, and grasses (all forage and hay) has been cancelled and the registrant has deleted these crops from all product labels. Formulations of simazine registered as a single active ingredient end-use product for use on food and feed crops include 80% wettable powder (WP), 90% dry flowable (DF), 4% granular (G), and 4 lb/gal flowable concentrate (FLC). Soil applications are made using both ground and aerial equipment.

According to the Preliminary Quantitative Usage Analysis of Simazine (R.F. Torla, December 1988), 29% of the domestically available simazine is used on field corn, 10% on alfalfa, and 9% on citrus. Additional food/feed crop uses account for less than 4% of the domestic usage, while aquatic sites account for 27% of the non-food crop uses. Seventy-five percent of the U.S. artichoke and cherry crops is treated with simazine along with 45% of each of the pear and walnut crops.

Residue tolerances are expressed in terms of simazine per se [40 CFR §180.213] or simazine and its metabolites 2-amino-4-chloro-6-ethylamino-g-triazine and 2,4-diamino-6-chloro-g-triazine in bananas and fish [40 CFR §180.213(a)]. The food additive tolerance for residues in sugarcane molasses and syrup are defined as simazine per se, while the potable water tolerance food additive definition includes the two chlorometabolites [40 CFR §185.5350(a), formerly 21 CFR §193.400].

The Simazine Guidance Document dated 3/1/84 identified residue chemistry data gaps for magnitude of the residue in plants and potable water, nature and magnitude of the residue in animals, and storage stability. Data submitted in response to this document and all previously reviewed data have been evaluated in this Second Round Review (SRR) to determine their adequacy for meeting current regulatory requirements.
QUALITATIVE NATURE OF THE RESIDUE IN PLANTS

Conclusions:

The Simazine Guidance Document dated 3/84 concluded that the nature of the residue in plants is adequately understood, based on data translated from atrazine; no additional data were required. The existing data are no longer acceptable for this topic because: (i) identification of metabolites by translation of data is no longer acceptable; (ii) Branch policy regarding characterization of water-soluble residues has become more strict; and (iii) hydroxymetabolites have recently been recognized as metabolites of potential toxicological concern. The following additional data are required:

○ Data depicting the total terminal residue of uniformly ring-labeled [14C]simazine in corn and two additional dissimilar crops (we recommend asparagus and a representative citrus fruit). A completely characterized test substance representative of technical simazine used in commercial formulations must be applied under conditions representing normal cropping practices and at rates high enough to result in sufficient radiolabeled residues for characterization. The identities and quantities of residues in or on all relevant raw agricultural commodities must be determined in order to elucidate terminal residues.

○ Representative samples from these studies must also be analyzed by the residue analytical methods developed for data collection and tolerance enforcement to ascertain that the methods are capable of adequately recovering and quantifying all residues of concern.

Additional simazine plant metabolism data, either submitted since the guidance document or otherwise not previously reviewed, are discussed below. The molecular structures of simazine and its metabolites in plants and animals are depicted in Table 3 beginning on page 8.

Data reviewed in the Residue Chemistry Chapter dated 10/13/83 showed that [14C]simazine is taken up and metabolized by grapes (MRID 00026286), pineapple (MRID 00029632), sugarcane (MRIDs 00024025, 00024026 and 00084431), and strawberry (MRID 00023913) plants; however, the terminal residues were not characterized. The additional data summarized below (MRIDs 40614436 and 40614437) confirm earlier findings that simazine is readily absorbed by plant roots. They further demonstrate that the parent compound is rapidly metabolized via dealkylation, hydroxylation, and conjugation. The major terminal residues which have been identified in corn grain and forage are the hydroxymetabo-
lites G-30414 (IV), GS-17792 (VI), GS-10813 (VII), GS-35713 (IX), and GS-10813 with the side chain hydroxylated (VIII, putative); however, the relative ratio and significance of these metabolites as a function of plant tissue, and age is highly variable. The parent compound (I), its chlorometabolites G-28273 (III) and G-28279 (II), and the hydroxymetabolites GS-17791 (V) and cyanuroic acid (X) have also been found in corn plants, though only in small amounts, and the glutathione conjugate of simazine (XI) has been tentatively identified in corn extracts. The metabolism of simazine in plants has not been adequately elucidated because high levels of polar and insoluble residues (49-84% of the recoverable radioactivity) in corn forage and grain have not been adequately characterized. The variable ratios of occurrence of polar metabolites in the submitted corn data also lead to the conclusion that the terminal residue of simazine in other plant commodities cannot be predicted from available information.

References (used):

MRID(s): 00023913. 00024025. 00024026. 00026286. 00029632. 00024431. 40614436*. 40614437*.

References (not used):

[The following reference(s) contain only duplicate data or material which is not useful in determining the qualitative nature of the terminal residue of simazine in plants.]


Discussion of the data:

Ciba-Geigy Corporation (Report No. ABR-78073; 1978; MRID 40614437) submitted a study of the fate of [14C]simazine (specific activity 30.0 µCi/mg; >99% radiochemical purity) following preemergence application at 1 lbs ai/A to field-grown corn in NE. Plants were harvested 5 (25% mature), 10 (50% mature), 15 (75% mature), and 20 (mature harvest) weeks after planting. Tissues were extracted using a biphasic procedure (Ciba-Geigy Method AG-214; MRID 40114006) giving organic, polar and insoluble fractions. Total radioactivity in plant samples was assayed by liquid scintillation spectrometry (LSS) following sample combustion. Total triazine content of mature corn stalks and grain was
quantified via thin-layer chromatography (TLC) of \(^{14}\)Ccyanuric acid following hydrolysis of tissues in nitric acid. Organosoluble and polar \(^{14}\)C-residues were analyzed by TLC and cation exchange chromatography (Aminex A-5), respectively. Metabolite identifications were based on cochromatography of residues with known standards.

\(^{14}\)C-Simazine was readily taken up and translocated by corn roots (Table 1). Simazine-equivalent \(^{14}\)C-activity in or on plants ranged from 3.15 ppm in the 25% mature stalks to 0.77 ppm in stalks harvested at 75% maturity. Mature plants contained 1.48 ppm in stalks, 0.20 ppm in cobs, and 0.15 ppm in grain. Metabolism of residues was extensive in all of the plant samples analyzed. Organosoluble residues (parent simazine and its chloro- and hydroxymetabolites) accounted for only 3-15% of the total \(^{14}\)C-activity in immature plants and <0.1-1.9% of \(^{14}\)C-residues in mature plant tissues. Polar residues accounted for 66-81% of the total \(^{14}\)C-activity in immature plants and 45-67% of the residues in mature plant. Unextractable residues increased with maturity of the plant as the organic and polar residues decreased.

TLC analysis of organosoluble residues from plants harvested 5 and 10 weeks post-treatment revealed small amounts of parent simazine (<0.1-2.1% of total \(^{14}\)C-activity) and its chloro- and hydroxymetabolites, G-28279 (<0.1-1.6%) and G-28273 (<0.1%). Cation exchange chromatography of the polar metabolites identified the hydroxy- and chloro-metabolites, GS-17792 and G-30414, as the major metabolites, accounting for 17.7 and 10% of recovered \(^{14}\)C-activity 5 weeks post-treatment. Other metabolites present in quantities less than 5% were cyanuric acid, GS-35713, GS-10813, and GS-17791. Nine other unknown metabolites were present at levels of less than 6% each, for a cumulative total of 16.4% of the radioactivity. As the stalk matured, levels of cyanuric acid and GS-35713 remained essentially unchanged; GS-17791 disappeared completely, and GS-17792 and G-30414 decreased to less than 4% of the remaining radioactivity. GS-10813 was the only major metabolite (23.2%) present 15 weeks post-treatment, and at 20 weeks none of the metabolites exceeded 10% of \(^{14}\)C-residues in stalk tissue. The decrease in resolvable metabolites was accompanied by an increase in unextractable residues to ca. 54% of the \(^{14}\)C-activity in mature stalks. The major metabolite in mature grain was GS-35713 (24.1%), with minor amounts of GS-10813 (3.3%) and GS-17792 (3.1%). Three unknown metabolites collectively accounted for 27.1% (8.4%, 8.4%, and 10.3%) of the recoverable radioactivity. Although these metabolites were not precisely identified, chromatographic evidence pointed to glutathione or similar conjugates of simazine for two of them. Triazines accounted for >85% of the radioactivity in mature stalks and grain. Only 16-31% of the \(^{14}\)C-activity in mature plant tissues was associated with identified metabolites of simazine; however, based on solubility and chromatographic properties, most of the remaining radioactivity
could tentatively be associated with conjugated forms of simazine hydroxymetabolites.

Table 1. The uptake and partitioning of $[^{14}\text{C}]$simazine metabolites in field grown corn (Ciba-Geigy Corp Report ABR-78073, 1978; MRID 40614437).

<table>
<thead>
<tr>
<th>Post treatment Interval (wks.)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant part</td>
<td>Stalks</td>
<td>Stalks</td>
<td>Stalks</td>
<td>Stalks Cobs Grain</td>
</tr>
<tr>
<td>Total ppm$^a$</td>
<td>3.15</td>
<td>1.24</td>
<td>0.77</td>
<td>1.48 0.20 0.15</td>
</tr>
<tr>
<td>Metabolite Distribution</td>
<td>percent of total $[^{14}\text{C}]$ in plants</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic solubles</td>
<td>14.8</td>
<td>10.5</td>
<td>3.1</td>
<td>1.9 1.3 &lt;0.1</td>
</tr>
<tr>
<td>Polar solubles</td>
<td>81.3</td>
<td>71.8</td>
<td>66.0</td>
<td>45.7 44.9 66.8</td>
</tr>
<tr>
<td>Nonextractables</td>
<td>15.5</td>
<td>17.8</td>
<td>30.0</td>
<td>53.9 51.4 32.9</td>
</tr>
<tr>
<td></td>
<td>111.6</td>
<td>100.1</td>
<td>99.1</td>
<td>101.5 97.6 99.7</td>
</tr>
</tbody>
</table>

$^a$ Expressed as $[^{14}\text{C}]$simazine equivalents.

Ciba-Geigy Corporation (Report No. ABR-88055, 1988; MRID 40614436) submitted a study of the fate of $[^{14}\text{C}]$simazine (specific activity 28.0 µCi/mg, 98% radiochemical purity) in greenhouse-grown corn. Preemergence applications of 2 lbs ai/A were made to corn in a loamy sand soil. Plants were harvested at 5 (25% mature), 12 (75% mature), and 16 (mature) weeks following planting. Harvests of immature plants included the whole plant; mature harvests were separated into stalks, husk and ears. The stalks and husks were combined, and the grain and cobs were separated prior to analysis. Tissues were extracted using an adaptation of a biphasic procedure (Ciba-Geigy Method AG-214; MRID 40114006) giving organic, polar, and insoluble fractions. Total radioactivity in plant samples was assayed by LSS following sample combustion. Polar $^{14}\text{C}$-residues were analyzed by two-dimensional thin layer chromatography (TLC), cation exchange chromatography (Aminex A-5), anion exchange chromatography (DEAE Sephadex A-25), and HPLC. Metabolite identifications were based on cochromatography of residues with known standards. Major unknown polar metabolites were analyzed by one-dimensional TLC following enzymatic hydrolysis ($\beta$-glucosidase), acetylation, and esterification reactions. Insoluble residues in corn cobs were subjected to acid hydrolysis in an attempt to further characterize them.
There was substantial uptake and translocation of $[^{14}C]$simazine to the corn shoots (table 2).

<table>
<thead>
<tr>
<th>Post treatment Interval (wks.)</th>
<th>5</th>
<th>12</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant part</td>
<td>Whole Plant</td>
<td>Whole Plant</td>
<td>Stalks</td>
</tr>
<tr>
<td>Total ppm*</td>
<td>1.40</td>
<td>2.14</td>
<td>5.32</td>
</tr>
<tr>
<td>Metabolite Distribution</td>
<td>percent of total $^{14}$C in plants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic solubles</td>
<td>9.8</td>
<td>7.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Polar solubles</td>
<td>83.5</td>
<td>77.7</td>
<td>66.1</td>
</tr>
<tr>
<td>Nonextractables</td>
<td>6.8</td>
<td>19.4</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>100.1</td>
<td>104.2</td>
<td>91.8</td>
</tr>
</tbody>
</table>

* Expressed as $[^{14}C]$simazine equivalents.

Simazine was rapidly metabolized to polar (66-84%) and insoluble (7-22%) compounds 5-16 weeks after treatment. Cation exchange chromatography of the polar metabolites identified the hydroxy-metabolites, GS-17792 and G-30414 as the major metabolites at 5 weeks, accounting for 41 and 22%, respectively, of the recovered radioactivity. These identifications were confirmed by anion exchange chromatography, HPLC and two-dimensional TLC. Another 21% of the radioactivity was accounted for in eight unidentified cation exchange chromatographic peaks, each containing less than 3.6% of the total radioactivity. At plant maturity GS-17792 had decreased to levels of 22.6%, 9.8%, and 10.6% of the radioactivity in stalks, grain, and cobs, respectively. G-30414 levels in stalks had diminished to ca. 5% and 2% of $^{14}$C-activity by 12 and 16 weeks, respectively. The reduction of these two hydroxymetabolites was accompanied by an increase in two unknown peaks in the cation exchange chromatograms, P-1 and P-3. Peak P-1 accounted for 8.5%, 16.2%, and 6.2% and peak P-3 accounted for 8.4%, 19% and 34%, of the total radioactivity in mature stalk, grain and cobs, respectively. Analysis of unknown P-1 by TLC following esterification, acetylation, and enzymatic hydrolysis indicated that it was composed of three or four sugar conjugates of simazine. Similar analysis of unknown P-3 did not confirm its identity but it was postulated to be dihydroxysimazine (GS-10813), having a side chain hydroxyl group. Therefore, 41.3%, 45%, and 50.8% of the total radioactive residues in mature
stalks, grain and cobs, respectively, was at least partially identified. Nine unknown cation exchange peaks, collectively accounted for 17-27% of the radioactivity in mature tissues, were found in amounts that varied among the different samples analyzed. One of these peaks individually accounted for 8.9% of the radioactivity in both mature grain and cobs but none of the other peaks was present in quantities exceeding 6.6%.

In summary, [¹⁴C]simazine is readily taken up by the roots of corn and translocated throughout the plant. The parent compound is rapidly metabolized by way of dealkylation, hydroxylation, and conjugation to the extent that the parent compound and its chlorometabolites are only minor components of the terminal residue of simazine. In the two studies of [¹⁴C]simazine metabolism in corn reviewed above, the major identified metabolites were all hydroxymetabolites: G-30414, GS-17792, GS-10813, GS-35713, and GS-10813 with the side chain hydroxylated (tentative). The presence and relative ratio of these metabolites was highly variable among the samples analyzed and unidentified residues accounted for 49-84% of the radioactivity in mature tissues. Analysis of total triazines in corn revealed that more than 85% of the radioactivity from a preemergence treatment with [¹⁴C]simazine remained in the triazine moiety at plant maturity. Therefore, the terminal residue of simazine in corn plants is distributed mostly among polar and unextractable fractions and is not readily metabolized to natural constituents of the plant. Free and conjugated hydroxymetabolites have been identified in the polar fraction but the nature of the terminal residue of simazine is not adequately understood because of the high levels of unidentified polar and insoluble metabolites and because of the absence of data concerning the identity of the metabolites in other plant commodities.
<table>
<thead>
<tr>
<th>Code</th>
<th>Chemical name</th>
<th>Substrate</th>
<th>MRID</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>2-chloro-4,6-bis(ethylamino)-s-triazine</td>
<td>Corn</td>
<td>40614437</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chicken egg, urine</td>
<td>40614429</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chicken tissues</td>
<td>40614431</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bluegill Sunfish GS-650070-20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Goat milk &amp; tissue</td>
<td>40614432</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Simazine, G-27692</td>
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</tr>
<tr>
<td>II</td>
<td>2-amino-4-chloro-6-ethylamino-s-triazine</td>
<td>Corn</td>
<td>40614437</td>
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<td></td>
<td>Chicken egg, urine</td>
<td>40614429</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chicken tissues</td>
<td>40614431</td>
</tr>
<tr>
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<td></td>
<td>Bluegill Sunfish GS-650070-20</td>
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<td>40614432</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>G-28279</td>
</tr>
<tr>
<td>III</td>
<td>2,4-diamino-6-chloro-s-triazine</td>
<td>Corn</td>
<td>40614437</td>
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<td>Chicken egg, urine</td>
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<td>Bluegill Sunfish GS-650070-20</td>
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<td>G-28273</td>
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<tr>
<td>IV</td>
<td>2-hydroxy-4,6-bis(ethylamino)-s-triazine</td>
<td>Bluegill Sunfish GS-650070-20</td>
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<td>Corn</td>
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<td>hydroxysimazine, G-30414</td>
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<td>V</td>
<td>2,4-diamino-6-hydroxy-s-triazine</td>
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<td>Corn</td>
<td>GS-17791</td>
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<td>VI</td>
<td>2-amino-4-hydroxy-6-ethylamino-s-triazine</td>
<td>Corn 40614437</td>
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<td></td>
<td>Chicken tissues 40614431</td>
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<td>Bluegill Sunfish GS-650070-20</td>
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<td>Goat tissues 40614431</td>
<td>GS-17792</td>
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<td>VII</td>
<td>2,4-(bis)hydroxy-6-ethylamino-s-triazine</td>
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<td>VIII</td>
<td>2,4-(bis)hydroxy-6-hydroxyethylamino-s-triazine</td>
<td>Corn (putative) 40614436</td>
<td>Hydroxylated GS-10813</td>
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(Continued)
Table 3. Simazine and its metabolites (continued).

<table>
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<td>IX</td>
<td>2,4-(bis)hydroxy-6-amino-s-triazine</td>
<td>Corn</td>
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<td>GB-35713</td>
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<td>X</td>
<td>2,4,6-trihydroxy-s-triazine</td>
<td>Corn</td>
<td>40614437</td>
<td>Cyanuric acid</td>
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<tr>
<td>XI</td>
<td>N-1-(((4,6-bis(ethylamino)-1,3,5-triazin-2-yl)thio)methyl)-2-((carboxymethyl)amino)-2-oxoethyl)-glutamine</td>
<td>Corn (putative)</td>
<td>40614437</td>
<td></td>
</tr>
<tr>
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<td><img src="image" alt="Structure XI" /></td>
<td>Goat milk (putative)</td>
<td>40614432</td>
<td>Glutathione conjugate</td>
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<tr>
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</tr>
<tr>
<td>XII</td>
<td>N-1-(((4-chloro-6-ethylamino)-1,3,5-triazin-2-yl)thio)methyl)-2-((carboxymethyl)amino)-2-oxoethyl)-glutamine</td>
<td>Chicken tissues</td>
<td>40614431</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Structure XII" /></td>
<td>Goat tissues</td>
<td>40614431</td>
<td>Glutathione conjugate of G-28279</td>
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Table v3. Simazine and its metabolites (continued).

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<th>Chemical name</th>
<th>Substrate (putative)</th>
<th>MRID</th>
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</thead>
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<tr>
<td>XIII</td>
<td>gamma-glutamyl-5-((4,6\text{-ethylamino-9\text{-triazin-2-yl}) cysteine)</td>
<td>Goat milk</td>
<td>40614432</td>
</tr>
<tr>
<td></td>
<td><img src="image1.png" alt="Structure" /></td>
<td>gamma-glutamylcysteine conjugate</td>
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</tr>
<tr>
<td>XIV</td>
<td>2-([N\text{-bis}(2\text{-amino-2\text{-carboxyethyl})sulfide}]-4,6\text{-ethyl-amino)-9\text{-triazine})</td>
<td>Goat milk</td>
<td>40614432</td>
</tr>
<tr>
<td></td>
<td><img src="image2.png" alt="Structure" /></td>
<td>lanthionine conjugate</td>
<td></td>
</tr>
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</table>

QUALITATIVE NATURE OF THE RESIDUE IN ANIMALS

Conclusions:


The metabolite patterns, as identified, were similar in the tissues of goats and poultry; however, 26-84% of the residues in
milk, eggs, and tissues were unidentified. Therefore, the following data are required:

- Metabolism studies characterizing the total terminal residue of simazine in ruminants and poultry. Animals must be dosed orally for a minimum of three days with ring-labeled $[^{14}\text{C}]$simazine, at a level sufficient to make residue identification and quantitation possible. Eggs must be collected twice a day during the dosing period, and test animals must be sacrificed within 24 hours of the final dose. The distribution and identity of residues must be determined in eggs, liver, kidney (ruminants only), muscle, and fat. Representative samples from these studies must also be analyzed by the residue analytical methods developed for tolerance enforcement to ascertain that the methods are capable of adequately recovering and identifying all residues of concern.

- Should the metabolism of simazine or its metabolites in ruminants and/or poultry following oral dosing differ significantly from that in rats, swine metabolism data may also be required.

The chemical structures of simazine and its known or putative metabolites in plants and animals are illustrated in Table 3 beginning on page 8. The available data (MRIDs 40614429, 40614431, 40614432, and 40614435) identify simazine (I), G-28273 (III), G-28279 (II), and conjugated forms of one or more of these chlorometabolites as major components of the terminal residue of $[^{14}\text{C}]$simazine in goat tissues and milk and chicken tissues and eggs. Conjugated forms reported include the glutathione conjugate of simazine (XI) and G-28279 (XII), the gamma-glutamyl-cysteine conjugate of simazine (XIII), and the lanthionine conjugate of simazine (XIV). The hydroxymetabolite GS-17792 (VI) was also identified as a major residue in tissues of these animals, but evidence suggests that this is actually an artifact of the proteolysis reaction. No free or bound hydroxymetabolites were detected in milk, eggs, or tissues.

References (used):

MRID(s): 40614429*. 40614431*. 40614432*. 40614435*.

References (not used):

[The following reference(s) were not used because they contained either duplicate data or were not useful in evaluating the qualitative nature of the residue in animals.]

MRID(s): 00021578. 00024009. 00025428. 00117187. 40431350. 40614428.
Discussion of the data:

Ruminants: Ciba-Geigy Corp. (1986; MRID 40614435) submitted data from a study of simazine metabolism in a single lactating goat (Report ABR-87125). The test animal received a daily capsular dose of ca. 1.1 mg/kg of uniformly ring labeled $[^{14}C]$simazine (specific activity 15.6 μCi/mg; radiochemical purity 97.5%) for 10 consecutive days (equivalent to 33.3 ppm in the feed). Milk was collected twice daily, urine and feces daily, and blood sampled on days 1, 2, 4, 6, 8 and at sacrifice. Muscle, liver, kidneys, and fat were collected when the animal was sacrificed 23 hours following the last dose. Total $^{14}C$-activity was quantified in urine and milk directly by LSS and in tissue, feces, and blood by LSS following combustion. Overall, 98.3% of the radioactivity was recovered. Excretion via urine and feces accounted for 97.2% of the radioactive dose and 0.4% was recovered in the blood. Less than 0.02% of the dose was found in the fat of the animal. Muscle (0.07%), kidney (0.08%), liver (0.40%), and milk (0.24%) accounted for the remaining radioactivity. Radioactivity in milk reached a maximum simazine-equivalent level of 0.3 ppm on the second day, and thereafter gradually decreased to a level of 0.13 ppm on the tenth day. Residues were not further characterized.

Ciba-Geigy Corp. (1972; MRID 40614432) submitted data from a study in which uniformly ring labeled $[^{14}C]$simazine was fed to a single lactating goat (study No. GAAC-72129). The test animal received a daily capsular dose of ca. 0.11 mg/kg of $[^{14}C]$simazine (specific activity 13.7 μCi/mg; 7.08 mCi/mM) for 10 consecutive days (equivalent to 5 ppm in the feed). Urine, feces, and milk were collected daily; blood was collected every other day, and volatiles (including $^{14}CO_2$) were collected over a 24-hour period after excretion of radioactivity had reached a plateau. The animal was sacrificed 48 hours after the last dose, and blood, brain, fat, muscle, heart, kidneys, liver, and rumen intestinal contents were collected. Total $^{14}C$-activity was quantified in urine and milk directly by LSS and in tissues, feces, blood and rumen contents by LSS following combustion. Respiratory CO$_2$ was trapped in aqueous sodium hydroxide, transferred to phenyl-ethylamine, and quantified by LSS. Other volatile compounds were dissolved in methanol for LSS.

Milk collected on the sixth day was fractionated by methanol precipitation of the casein fraction, and partitioning of the remaining soluble residues between ethyl acetate and the aqueous phase. Liquid fractions were radioassayed by LSS, and casein was radioassayed by combustion/LSS. Organic soluble residues were characterized on TLC plates by cochromatography with standard compounds. The aqueous phase was chromatographed on an Aminex A-5 cation exchange column equilibrated in 0.1 M ammonium formate (pH 4.0). The elution volume of radioactive peaks and standards
were determined in a linear gradient of increasing pH and ionic strength. Water-soluble \(^{14}C\)-residues in the pronase enzymatic hydrolysate of the casein fraction were chromatographed in the same manner as the aqueous fraction. Major radioactive peaks from both fractions were hydrolyzed in performic acid and further analyzed by TLC.

Of the total radioactive dose fed the animal, 96% was recovered in the urine (70%), feces (19.0%), tissues (5.8%), blood (0.5%), rumen and intestinal contents (0.4%), milk (0.3%), and CO\(_2\) and volatiles (0.2%). Residues in tissues collected 48 hours after the final dose ranged from 0.02 ppm in omental fat to 0.93 ppm in the liver. The nature of the residues in tissues was not further characterized. Simazine-equivalent \(^{14}C\)-active residues in milk reached a plateau of 0.10 ppm by the 5th day of the study. The residues in milk collected on the sixth day were found to be 39.3% in casein, 32.7% water-soluble and 28% organosoluble. The major organosoluble metabolite was G-28273 (23.5% of the radioactivity in milk). Simazine (0.25%) and G-28279 (1.3%) were also identified. Greater than 95% of the radioactivity in the casein fraction was solubilized by the enzyme hydrolysis. Major cation exchange peaks in the aqueous fraction and casein hydrolysate (not quantified) had Rf values on TLC similar to glutamyl-cysteine, lanthionine, and glutathione conjugates of simazine. The registrant suggested that these metabolites are amino acid and peptide conjugates of simazine.

Ciba-Geigy Corp. (Report ABR-88049, 1988; MRID 40614431) submitted data from a study in which a single lactating goat received a daily capsular dose of ca. 1.7 mg/kg of \(^{14}C\)simazine (specific activity 9.00 \(\mu\)Ci/mg; 99.5% radiochemical purity) for 7 consecutive days (equivalent to 50 ppm in the feed). The animal was handled and samples taken in a similar manner to that reported above in study GAAC-72129 with the major exception being that tissue samples were collected 24 hours following the final dose instead of 48 hours.

\(^{14}C\)-Residues in milk samples were extracted with ethyl acetate. The organic, aqueous (whey), and casein fractions were separated, and the casein fraction was incubated with protease overnight. \(^{14}C\)-Residues were quantified in the filtrate from the protease digestion and in the organic and aqueous phases from the solvent extraction. Both the residue from the methanol:ethyl acetate extraction and the original sample were subjected to a general protease treatment and proteins were separated from the reaction mixture by alcohol precipitation. The supernatant was subjected to cation exchange chromatography and the major elution peaks further purified through either a C-18 bond elute cartridge or via XAD-4 chromatography and preparative TLC. Radioactive residues isolated by various combinations of the above procedures were analyzed by two-dimensional TLC, analytical cation exchange chromatography, and/or HPLC.
of the $^{14}$C-activity administered to the animal, 87% was accounted for in urine (67%), feces (18%), milk (0.66%), blood (0.5%), and tissues (0.76%). Simazine-equivalent $^{14}$C-residues were 0.06-0.10 ppm in fat, 0.69-0.71 ppm in muscle, 3.03 ppm in kidneys, 2.59 ppm in brain, 0.78 ppm in heart, and 3.24 ppm in liver. Total $^{14}$C-residues in milk during the 7-day study were 0.71-1.07 ppm. Of the total recovered radioactivity from goat tissues, only 15-33% was soluble in methanol:ethyl acetate (1:1). Protease treatment of the insoluble residues released an additional 45-83% of the radioactivity. The remainder of the radioactivity (2.3-19%) contained in the proteolysis residue represents unextractable residues. Five major radioactive peaks were resolved by cation exchange chromatography of tissue extracts.

Table 4. Distribution of $^{14}$C-activity in protease filtrate of selected tissues of a goat fed 50 ppm $[^{14}$C]simazine in the diet for 7 days.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Liver</th>
<th>Kidney</th>
<th>Tenderloin</th>
<th>Heart</th>
<th>Milk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simazine</td>
<td>6.96</td>
<td>3.84</td>
<td>10.79</td>
<td>8.83</td>
<td>-</td>
</tr>
<tr>
<td>G-28273</td>
<td>5.20</td>
<td>4.20</td>
<td>13.78</td>
<td>11.00</td>
<td>28.94</td>
</tr>
<tr>
<td>G-28279</td>
<td>10.70</td>
<td>16.93</td>
<td>-</td>
<td>9.54</td>
<td>-</td>
</tr>
<tr>
<td>GS-17792a</td>
<td>32.94</td>
<td>12.73</td>
<td>6.52</td>
<td>5.61</td>
<td>-</td>
</tr>
<tr>
<td>Conjugateb</td>
<td>-</td>
<td>18.70</td>
<td>-</td>
<td>9.08</td>
<td>14.90</td>
</tr>
<tr>
<td>Unident. c</td>
<td>44.21</td>
<td>43.60</td>
<td>68.91</td>
<td>55.93</td>
<td>54.84</td>
</tr>
</tbody>
</table>

a May be an artifact of proteolysis.
b Tentatively identified as the glutathione conjugate of G-28279.
c Uncharacterized cation exchange fractions, organosoluble residues, and unextractable residues.

The reported identities of these peaks and the method of identification are as follows: (i) G-28273, identified by cochromatography with the standard compound on cation exchange and two-dimensional TLC; (ii) the glutathione conjugate of the monodeethylated metabolite of simazine, proposed by the registant based on identical ion exchange chromatographic migration to the glutathione conjugates of simazine and diaminos-triazine and similar Rfs to these same standards on two-dimensional TLC; (iii) G-28279, identified by cochromatography with the standard compound on cation exchange and TLC; (iv) GS-17792, identified by cochromatography on cation exchange, two-dimensional TLC, and HPLC; and (v) simazine, identified by cochromatography on cation exchange and two-dimensional TLC. There were no other significant peaks of radioactivity eluting from the cation exchange column. It was suggested that metabolite GS-17792 was an artifact of the enzymatic hydrolysis procedure. This was supported by the
demonstration that several thiotriazine standards, with various oxidation states of the aryl sulfur, were converted to the corresponding hydroxy derivative by the hydrolytic enzyme.

**Poultry:** Ciba-Geigy Corp. (Report ABR-86042, 1986; MRID 40614429) submitted data depicting the nature and distribution of $^{14}$C-residues in tissues and eggs from two Leghorn hens that had received daily oral capsular doses of 3.44 mg/kg of $^{14}$Csimazine (specific activity 15.3 $\mu$Ci/mg; radiochemical purity >98%) for 20 consecutive days (equivalent to ca. 50 ppm in the feed). Eggs and excreta were collected daily. The animals were sacrificed 22 hours following the final dose, and muscle, peritoneal fat, skin plus attached fat, blood, kidney, and liver were sampled. Tissue samples were radioassayed by LS following combustion. Biphasic extraction of radioactivity was performed according to a modification of the Bligh-Dyer procedure (Ciba-Geigy method AG-214; MRID 40114006), yielding organosoluble, polar, and unextractable phases. Radioactive residues in excreta and eggs were further analyzed by thin layer chromatography. Identification of metabolites was based on cochromatography with standards of simazine, G-28279 and G-28273 on TLC plates.

Of the total radioactive dose fed to the hens, 83-85% was recovered from the excreta (81-83%), blood (0.44-0.47%), tissues (0.67-0.70%), and eggs (0.58-0.60%). Simazine-equivalent residues levels were <0.1 ppm in peritoneal fat and ca. 1-3 ppm in samples of skin with attached fat, muscle, kidney, and liver. Residues in egg whites reached a plateau of about 0.5 ppm on the 2nd day, while residues in egg plateaud at ca. 1.1 ppm on days 12-14. The balance of radioactivity in selected samples of tissues, eggs and excreta are shown in Table 5.

<table>
<thead>
<tr>
<th>Tissue</th>
<th>Organic Soluble</th>
<th>Aqueous Soluble</th>
<th>Non-extractable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liver</td>
<td>0.00</td>
<td>27.40</td>
<td>70.03</td>
</tr>
<tr>
<td>Muscle</td>
<td>0.90</td>
<td>21.36</td>
<td>62.37</td>
</tr>
<tr>
<td>Egg Yolk, Day 10</td>
<td>12.18</td>
<td>43.02</td>
<td>45.78</td>
</tr>
<tr>
<td>Egg White, Day 10</td>
<td>14.26</td>
<td>80.73</td>
<td>11.57</td>
</tr>
<tr>
<td>Excreta, Day 1</td>
<td>41.18</td>
<td>44.20</td>
<td>5.77</td>
</tr>
<tr>
<td>Excreta, Day 10</td>
<td>25.66</td>
<td>70.04</td>
<td>12.30</td>
</tr>
<tr>
<td>Excreta, Day 20</td>
<td>24.20</td>
<td>66.41</td>
<td>7.49</td>
</tr>
</tbody>
</table>
Organosoluble residues were essentially absent from tissue samples and comprised only ca. 12-14% of the residues in eggs. The major proportion of the radioactivity in tissues was insoluble, although significant levels of polar residues were extracted from eggs. TLC analysis of polar residues from excreta samples indicated the presence of simazine (10.56-20.93%), G-28279 (5.93-13.90%), and G-28273 (7.81-10.38%). The major polar metabolites in eggs were G-28273 (24.09-43.09%) and G-28279 (7.40-15.62%). From ca. 1 to 3.75 of the radioactivity in the egg samples was identified as simazine and ca. 8-22% of the radioactivity remained unidentified at the TLC origin. There was no further identification of metabolites in eggs or tissues. We note that all of the metabolites identified in this study are of limited solubility in water and have been identified by the registrant as organosoluble residues in plant metabolism studies (see the section "Qualitative Nature of the Residue in Plants"). Therefore, this study would require clarification from the registrant to be useful in evaluating the nature of the terminal residue in eggs.

Ciba-Geigy Corp. (Study No. ABR-88049, 1988: MRID 40614431) submitted data depicting the nature and distribution of $^{14}$C-residues in tissues and eggs from four Leghorn hens which had received daily oral capsular doses of ca. 3.5 mg/kg of $[^{14}]$C-simazine (specific activity 24.3 μCi/mg; radiochemical purity 98.3%) for seven consecutive days (equivalent to ca. 50 ppm in the feed). Eggs were collected daily and separated into whites and yolks. Excreta was also collected on a daily basis. Muscle, liver, kidney, and fat tissues were sampled when the chickens were sacrificed 24 hours following the last dose. This study was conducted in conjunction with the goat study discussed above (MRID 40614431) and used the same techniques of extraction, separation and analysis of $^{14}$C-residues. Samples from the four hens were composited for analysis.

Approximately 84% of the total radioactive dose fed to the hens was recovered in the excreta (81%), blood (1.73%), tissues (0.93%), and eggs (0.38%). Simazine-equivalent residues were 0.09 ppm in perirenal fat, 1.57 ppm in skin and attached fat, 1.98 ppm in muscle, 3.00 ppm in liver, and 3.65 ppm in kidney. Residues in egg whites and yolks did not reach a plateau value but gradually increased from 0.02 ppm on day 1 to ca. 1.2 ppm on day 7. Treatment of samples of hen tissues and eggs with a general protease released 94-100% of the insoluble radioactivity to the aqueous protease filtrate. Cation exchange chromatography of the protease hydrolysates revealed the same five major peaks (described for the goat study, MRID 40614431), collectively comprising 18-77% of $^{14}$C-activity in tissue samples and 75% of $^{14}$C-activity in egg yolk (see Table 6).
Table 6. Distribution of $^{14}$C-activity in protease filtrate of selected tissues of hens fed 50 ppm $[^{14}$C]simazine in the diet for 7 days.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Liver</th>
<th>Kidney</th>
<th>Lean meat</th>
<th>Skin&amp;fat</th>
<th>Egg yolk</th>
</tr>
</thead>
<tbody>
<tr>
<td>simazine</td>
<td>6.79</td>
<td>8.06</td>
<td>16.93</td>
<td>15.68</td>
<td>14.89</td>
</tr>
<tr>
<td>G-28273</td>
<td>12.68</td>
<td>6.67</td>
<td>11.23</td>
<td>-</td>
<td>28.94</td>
</tr>
<tr>
<td>G-28279</td>
<td>14.72</td>
<td>19.45</td>
<td>7.78</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GS-17792$^a$</td>
<td>10.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Conjugate$^b$</td>
<td>29.70</td>
<td>29.36</td>
<td>6.46</td>
<td>-</td>
<td>28.68</td>
</tr>
<tr>
<td>Unident.$^c$</td>
<td>26.06</td>
<td>36.46</td>
<td>57.60</td>
<td>84.32</td>
<td>27.49</td>
</tr>
</tbody>
</table>

$^a$ May be an artifact of proteolysis.
$^b$ Tentatively identified as the glutathione conjugate of G-28279.
$^c$ Uncharacterized cation exchange fractions, organosoluble residues, and unextractable residues.

In summary, simazine is extensively metabolized by goats and chickens. Most of the radioactivity from $[^{14}$C]simazine feeding studies is excreted rapidly by these animals. Of the residues that are not excreted, large proportions are unextractable by normal organic/aqueous solvents. However, protease hydrolysis solubilizes >90% of the unextractable residues. Five major metabolites have been separated and identified as simazine, G-28279, G-28273, GS-17792, and a glutathione conjugate of G-28279. The hydroxymetabolite GS-17792 may be an artifact derived from hydrolysis of a conjugated form of a chlorometabolite (presumably G-28279) by the protease. These studies indicate that the metabolite pattern is similar in tissues of poultry and goats; however, uncharacterized radioactivity accounted for as much as 26-84% of the radioactivity in hen eggs and tissues and 44-69% of the radioactivity in goat milk and tissues. Further characterization of the terminal residue is required.

**RESIDUE ANALYTICAL METHODS**

**Conclusions:**

The qualitative nature of the residue in plants and animals has not been adequately described. Methods to be used in the future for data collection and tolerance enforcement will be determined following receipt of the requested metabolism data. Therefore, the adequacy of the available analytical methods cannot be ascertained. The Simazine Guidance Document dated 3/1/84 concluded that adequate analytical methods are available for purposes of data collection and tolerance enforcement for: (i) residues of simazine **per se** in or on plants and animals; (ii) for the
combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on bananas, fish, and potable water; and (iii) combined residues of simazine and its chlorometabolites (G-28279 and G-28273) on other crops pending submission of validation data.

The current preferred enforcement methods are (i) a GLC method using a microcoulometric detector (MC) for residues in milk (Method III in PAM Vol. II, section 180.213); (ii) a spectrophotometric method for residues in meat (Method I in PAM Vol. II, Section 180.213); (iii) a spectrophotometric method or a GLC/MC method for plant commodities (Methods I or II in PAM Vol. II, Section 180.213); and (iv) a GLC/MC method for residues in fish (Method IV in PAM Vol. II, Section 180.213). We note that the limits of detection for PAM Vol. II "methods I and III are ca. 0.05 ppm, which is higher than the established tolerances for residues in animal commodities (0.02 ppm for simazine per se); therefore, these methods are unsuitable for data collection.

Additional GLC methods submitted since completion of the Guidance Document quantify residues of simazine and its chlorometabolites (G-28273, G-28279) in plant and animal commodities. Method AG-539 (MRID 40614440) is available for data collection on residues of simazine per se or simazine and its three chlorometabolites in or on plant commodities. Method AG-497 (MRID 40431382) is available for data collection on residues of simazine per se or simazine and its three chlorometabolites in milk. Method AG-540 (MRID 40614439) is available for data collection on residues of simazine per se or simazine and its three chlorometabolites in ruminant tissues, poultry tissues, and eggs. Insufficient data are available to evaluate analytical methods for residues of hydroxymetabolites of concern in plant and animal commodities.

Residues of simazine per se are completely recovered (>80%) by PAM Vol. I method 232.4 (multiresidue protocol III). Simazine residues are partially recovered (50%) by method 252 involving elution from a Florisil column with ethyl ether:petroleum ether; not recovered by method 212.1; and not recovered by method 252 involving elution from Florisil with methylene chloride:hexane:acetonitrile (multiresidue protocol I). No data are available concerning recovery of the simazine metabolites by any of the multiresidue protocols I-IV.

The following additional data are required:

- Residue analytical methods must be developed and validated which will quantify residues of the simazine hydroxymetabolites of concern in or on plant commodities, meat, poultry, eggs, fish, and potable water.
Successful confirmatory trials of the proposed methods for determination of hydroxymetabolites of concern in plant and animal commodities must be conducted by an independent laboratory. Results of at least one set of samples each for an oily crop, a non-oily crop, meat and milk (a total of six samples, including two control samples, two control samples fortified at the tolerance level, and two control samples fortified at 2-5 times the tolerance level per commodity) must be submitted. No more than three sets of samples per commodity may be tested to achieve successful recovery rates of 70-120% with negligible interference compared to the established tolerances. For additional details of data requirements, refer to PR Notice 88-5, Tolerance Enforcement Methods - Independent Laboratory Confirmation by Petitioner.

Representative plant and animal tissue samples bearing residues of simazine chlorometabolites (G-28273, G-28279) and hydroxymetabolites of concern must be subjected to analysis by multi-residue protocols I and III from PAM Vol. I, Appendix II. Multi-residue protocols I-IV are available from the National Technical Information Service under Order No. PB 203734/AS.

The nature of the residue in plants and animals is not adequately understood. If the metabolism studies requested in the sections "Qualitative Nature of the Residue in Plants" and "Qualitative Nature of the Residue in Animals" reveal the presence of additional metabolites of concern, additional validated methods for data collection and tolerance enforcement will be required.

References (used):

MRID(s): 00023328. 00023897. 00024057. 00025447. 00025457. 00025458. 00027819. 00027835. 00027986. 00139356. 40431382*. 40614439*. 40614440*.

References (not used):

[The following reference(s) contain only duplicate not useful data.]

Discussion of the data:

Ciba-Geigy Corp. (1986; MRID 40431382) submitted gas-liquid chromatography (GLC) method AG-497 for determination of residues of simazine and its chlorometabolites in milk. Protein is precipitated from the milk sample by addition of acetone, vigorous mixing, and centrifugation. Acetone is evaporated from the supernatant under reduced pressure and the aqueous solution is cleaned up on a strong cation exchange column. The column is washed with water, and residues of interest are eluted with 0.5 M aqueous sodium chloride:methanol (1:1). Methanol is evaporated from the eluate under reduced pressure, and the solid residue is dissolved in toluene:methanol (96:4). Levels of simazine, G-28279, and G-28273 are analyzed by GLC on a DB-5 capillary column using a nitrogen specific detector. Recovery efficiencies from 17 samples of fresh and sour milk (fortified with 0.01-0.10 ppm of each compound) were 67-110% for simazine, 80-117% for G-28279, and 66-107% for G-28273. The limits of detection are 0.01 ppm for each compound. This method is adequate for collection of data pertaining to residues of these three compounds in milk.

Ciba-Geigy Corp. (1988; MRID 40614439) submitted GLC method AG-540 for determination of residues of simazine, atrazine, and their chlorometabolites in beef tissues, poultry tissues, and eggs. Tissue and egg samples (except fat and skin) are homogenized in water:methanol (1:4) and filtered. Fat and skin samples are homogenized in acetonitrile and filtered. After the oil layer settles and is removed, water is added to the filtrate. For all samples, the filtrate is concentrated by evaporation to the aqueous phase. This phase is adsorbed onto Extrelut adsorbent and packed into a column. Simazine, atrazine, the deethylated metabolite of atrazine (G-30033), and G-28279 are eluted with 250 ml of ethyl acetate:hexane (15:85). The eluate is evaporated to dryness, dissolved in toluene plus hexane; and cleaned up on an alumina B column. The column is rinsed with ethyl acetate:acetonitrile (1:1), and residues of interest are eluted with methanol:acetonitrile (3:7). The residues are evaporated to dryness, dissolved in ethyl acetate:methanol (95:5) and analyzed by GLC on either a DB-5 capillary column or a DB-17 megabore column using a nitrogen/phosphorus detector. Residues of G-28279 are eluted from the Extrelut column with 225 ml of ethyl acetate:hexane (1:1); the eluate is evaporated to dryness, dissolved in ethyl acetate plus toluene, and cleaned up on a Florisil column. This column is rinsed with dichloromethane, and residues of interest are eluted with methanol:ethyl acetate (1:4). The residues are evaporated to dryness, dissolved in ethyl acetate:methanol (95:5), and analyzed by GLC as above. The limits of detection are 0.01 ppm for each compound in each matrix. Validation data for this method are summarized below in Table 7. This method is adequate for collection of data from
ruminant and poultry tissues and eggs on residues of simazine and its chlorometabolites.

Table 7. Percent recovery of simazine and its chlorometabolites G-28279 and G-28273 from eggs and animal tissues by GLC method AG-540 (Ciba-Geigy, 1988; MRID 40614439).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Fortification</th>
<th>Percent Recovery (samples)</th>
<th>Simazine</th>
<th>G-28279</th>
<th>G-28273</th>
</tr>
</thead>
<tbody>
<tr>
<td>beef, muscle</td>
<td>0.01-0.25</td>
<td>72-126 (10)</td>
<td>78-125 (10)</td>
<td>71-105 (10)</td>
<td></td>
</tr>
<tr>
<td>liver</td>
<td>0.01-0.25</td>
<td>74-149 (7)</td>
<td>67-138 (7)</td>
<td>68-101 (7)</td>
<td></td>
</tr>
<tr>
<td>kidney</td>
<td>0.01-0.20</td>
<td>91-106 (3)</td>
<td>74-100 (3)</td>
<td>63-95 (5)</td>
<td></td>
</tr>
<tr>
<td>fat</td>
<td>0.01-0.25</td>
<td>68-143 (12)</td>
<td>82-139 (12)</td>
<td>77-104 (11)</td>
<td></td>
</tr>
<tr>
<td>poultry, fat</td>
<td>0.01-0.20</td>
<td>60-84 (3)</td>
<td>78-89 (3)</td>
<td>78-91 (3)</td>
<td></td>
</tr>
<tr>
<td>lean meat</td>
<td>0.01-0.25</td>
<td>76-103 (7)</td>
<td>67-95 (7)</td>
<td>69-127 (7)</td>
<td></td>
</tr>
<tr>
<td>skin</td>
<td>0.01-0.20</td>
<td>71-86 (3)</td>
<td>76-109 (3)</td>
<td>76-112 (3)</td>
<td></td>
</tr>
<tr>
<td>liver</td>
<td>0.01-0.50</td>
<td>69-101 (3)</td>
<td>67-91 (3)</td>
<td>66-76 (3)</td>
<td></td>
</tr>
<tr>
<td>eggs</td>
<td>0.01-0.25</td>
<td>67-100 (8)</td>
<td>69-103 (8)</td>
<td>62-89 (8)</td>
<td></td>
</tr>
</tbody>
</table>

Ciba-Geigy Corp. (1988; MRID 40614440) submitted GLC method AG-539 for analysis of residues of simazine and its chlorometabolites in or on plant raw and processed commodities. Residues are extracted from the homogenized or ground sample by refluxing or shaking with water:acetonitrile (1:4). For corn soapstock, residues are first extracted with hexane:ethyl acetate (1:3), and then partitioned into water:acetonitrile (1:4). The aqueous extract is concentrated by evaporation of the organic solvent, then adsorbed onto an Extrelut column. Simazine, and G-28279 are eluted from the column with 250 ml of ethyl acetate:hexane (15:85), evaporated to dryness, dissolved in toluene plus hexane, and cleaned up on an alumina B column; extracts from avocados required additional hexane/acetonitrile partitioning prior to the cleanup step. The column is rinsed with ethyl acetate:acetonitrile, and residues of interest are eluted with methanol:acetonitrile (3:7), concentrated to dryness, dissolved in ethyl acetate: methanol (95:5) and analyzed by GLC on a DB-5 capillary column or a DB-17 megabore column using a nitrogen/phosphorus detector. Residues of G-28273 are eluted from the Extrelut column with 225 ml of ethyl acetate:hexane (1:1), concentrated to dryness, dissolved in ethyl acetate plus toluene, and further cleaned up on a Florisil column. The column is rinsed with dichloromethane, and G-28273 residues are eluted with methanol:ethyl acetate, concentrated to dryness, dissolved in ethyl acetate:methanol (95:5), and analyzed by GLC as described above. Extracts of olives and dry grape pomace must be subjected to a second Florisil cleanup prior to GLC analysis. Recovery efficiencies of these compounds from various plant commodities are summarized below in Table 8. The average recovery ± standard deviation was
93 ± 11% for simazine (177 samples), 87 ± 11% for G-28279 (173 samples), and 83 ± 16% for G-28273 (169 samples). This method is adequate for collection of data from plant commodities on residues of simazine and its chlorometabolites.
Table 8. Percent recovery of simazine and its chlorometabolites G-28279 and G-28273 from raw and processed plant commodities by GLC method AG-539 (Ciba-Geigy, 1988; MRID 406144440).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Fortification</th>
<th>Percent Recovery (samples)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Simazine</td>
<td>G-28279</td>
<td>G-28273</td>
</tr>
<tr>
<td>artichokes</td>
<td>0.05-1.00</td>
<td>76-105 (6)</td>
<td>86-96 (6)</td>
<td>68-101 (6)</td>
</tr>
<tr>
<td>asparagus</td>
<td>0.05-20.00</td>
<td>69-128 (17)</td>
<td>69-105 (15)</td>
<td>58-127 (15)</td>
</tr>
<tr>
<td>avocados</td>
<td>0.05-0.50</td>
<td>73-107 (6)</td>
<td>66-103 (6)</td>
<td>63-88 (6)</td>
</tr>
<tr>
<td>olive, oil</td>
<td>0.05</td>
<td>91-093 (2)</td>
<td>98-101 (2)</td>
<td>75 (1)</td>
</tr>
<tr>
<td>olive, fruit</td>
<td>0.05-0.2</td>
<td>81-110 (3)</td>
<td>80-106 (3)</td>
<td>57-67 (3)</td>
</tr>
<tr>
<td>apple, fruit</td>
<td>0.05-0.5</td>
<td>69-101 (11)</td>
<td>63-103 (11)</td>
<td>73-97 (12)</td>
</tr>
<tr>
<td></td>
<td>juice</td>
<td>104</td>
<td>101</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>sauce</td>
<td>105</td>
<td>91</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>dry pomace</td>
<td>75</td>
<td>80</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>wet pomace</td>
<td>79</td>
<td>82</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>peel &amp; core</td>
<td>97</td>
<td>103</td>
<td>86</td>
</tr>
<tr>
<td>peach, fruit</td>
<td>0.05-0.2</td>
<td>87-106 (8)</td>
<td>86-108 (8)</td>
<td>67-150 (8)</td>
</tr>
<tr>
<td>blueberry</td>
<td>0.05-0.5</td>
<td>87-104 (5)</td>
<td>75-90 (5)</td>
<td>70-88 (5)</td>
</tr>
<tr>
<td>grape</td>
<td>0.05-0.2</td>
<td>87-102 (5)</td>
<td>84-99 (5)</td>
<td>65-89 (5)</td>
</tr>
<tr>
<td></td>
<td>juice</td>
<td>111</td>
<td>103</td>
<td>75</td>
</tr>
<tr>
<td>raisins</td>
<td>0.05</td>
<td>100</td>
<td>75</td>
<td>69</td>
</tr>
<tr>
<td>wine</td>
<td>0.05</td>
<td>101</td>
<td>83</td>
<td>85</td>
</tr>
<tr>
<td>wet pomace</td>
<td>0.10</td>
<td>73</td>
<td>74</td>
<td>88</td>
</tr>
<tr>
<td>rachis</td>
<td>0.10</td>
<td>82</td>
<td>84</td>
<td>58</td>
</tr>
<tr>
<td>yeast</td>
<td>0.10</td>
<td>101</td>
<td>103</td>
<td>95</td>
</tr>
<tr>
<td>dry pcmace</td>
<td>0.20</td>
<td>87</td>
<td>83</td>
<td>56</td>
</tr>
<tr>
<td>raspberries</td>
<td>0.05-0.2</td>
<td>86-95 (3)</td>
<td>84-87 (3)</td>
<td>74-94 (3)</td>
</tr>
<tr>
<td>corn, forage</td>
<td>0.05-1.0</td>
<td>82-119 (12)</td>
<td>75-112 (12)</td>
<td>70-101 (12)</td>
</tr>
<tr>
<td>silage</td>
<td>0.10-0.5</td>
<td>81-111 (18)</td>
<td>78-110 (18)</td>
<td>62-114 (18)</td>
</tr>
<tr>
<td>fodder</td>
<td>0.20-1.0</td>
<td>70-102 (13)</td>
<td>66-99 (13)</td>
<td>63-102 (13)</td>
</tr>
<tr>
<td>grain</td>
<td>0.05-0.2</td>
<td>67-111 (13)</td>
<td>61-105 (13)</td>
<td>68-92 (13)</td>
</tr>
<tr>
<td>ears</td>
<td>0.05-0.2</td>
<td>79-108 (5)</td>
<td>80-94 (5)</td>
<td>55-76 (5)</td>
</tr>
<tr>
<td>flour</td>
<td>0.05</td>
<td>103</td>
<td>81</td>
<td>70</td>
</tr>
<tr>
<td>germs</td>
<td>0.10</td>
<td>88</td>
<td>86</td>
<td>77</td>
</tr>
<tr>
<td>grits</td>
<td>0.10</td>
<td>97</td>
<td>93</td>
<td>82</td>
</tr>
<tr>
<td>meal</td>
<td>0.10</td>
<td>100</td>
<td>84</td>
<td>77</td>
</tr>
<tr>
<td>hulls</td>
<td>0.20</td>
<td>86</td>
<td>76</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>oil</td>
<td>0.10-0.5</td>
<td>87-110 (5)</td>
<td>84-98 (5)</td>
</tr>
<tr>
<td>soapstock</td>
<td>0.20</td>
<td>77</td>
<td>77</td>
<td>51</td>
</tr>
<tr>
<td>orange, fruit</td>
<td>0.01-0.5</td>
<td>79-111 (13)</td>
<td>72-97 (13)</td>
<td>73-121 (12)</td>
</tr>
<tr>
<td>molasses</td>
<td>0.01-0.2</td>
<td>86-92 (3)</td>
<td>83-86 (3)</td>
<td>78</td>
</tr>
<tr>
<td>peel</td>
<td>0.01-0.5</td>
<td>79-87 (4)</td>
<td>66-86 (4)</td>
<td>73-77 (2)</td>
</tr>
<tr>
<td>oil</td>
<td>0.01-0.2</td>
<td>95-124 (4)</td>
<td>72-101 (2)</td>
<td>80-90 (2)</td>
</tr>
<tr>
<td>juice</td>
<td>0.01</td>
<td>89</td>
<td>66</td>
<td>80</td>
</tr>
<tr>
<td>press liquor</td>
<td>0.05</td>
<td>71</td>
<td>67</td>
<td>73</td>
</tr>
<tr>
<td>pulp</td>
<td>0.05</td>
<td>91</td>
<td>85</td>
<td>74</td>
</tr>
</tbody>
</table>
STORAGE STABILITY DATA

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the storage stability of simazine residues is partially understood; additional data were required depicting the storage stability of simazine and its chlorometabolites (G-28279 and G-28273), in or on plant, fish and mammalian samples stored at freezing temperatures for a period of time analogous to actual storage of residue field data.

Data submitted in response to the Guidance Document (MRIDs 40614441, 40614442, and 40614443) indicate that: (i) residues of simazine and its chlorometabolites G-28279 are stable in or on apple fruit, in apple pomace and juice but that moderate (ca. 25%) loss of G-28273 may occur in these commodities during storage at -15 C for a period of up to 427 days; and (ii) residues of simazine and its chlorometabolites G-28279 and G-28273 are stable in or on field corn, sweet corn, and field corn fractions, except crude corn oil; and in animal fractions, except beef liver (where only G-28273 was unstable), when stored at -15 C for a period of 1 year.

No data were submitted regarding storage stability of simazine residues of concern in fish, nor were data submitted regarding the storage stability of the simazine hydroxymetabolites of concern in plant and animal matrices. The following additional data are required:

○ The sample storage conditions and intervals must be supplied for all required and previously submitted residue data for plant and animal commodities. Data are also required which depict the decline in levels of simazine residues of concern in commodities stored under the range of conditions and for the range in intervals specified. Crop samples bearing measurable weathered residues or fortified with atrazine residues of concern and fortified meat, milk, and egg samples must be analyzed immediately after harvest or fortification and again after storage intervals that represent actual residue sample storage conditions and allow for reasonable unforeseen delays in sample analysis. In laboratory tests using fortified samples, the pure active ingredient and pure metabolites must be used. However, if field weathered samples are used, the test substance must be a typical end-use product. For additional guidance on conducting storage stability studies, the Registrant is referred to an August 1987 Position Document on the Effects of Storage on Validity of Pesticide Residue Data available from NTIS under order no. PB88112362/AS.

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The qualitative nature of the residue in plants and animals is not adequately understood. If the requested data on plant and animal metabolism indicate the presence of additional metabolites of toxicological concern, data depicting the stability of those residues during storage will be required.

References (used):

MPID(s): 00025458, 40614441*, 40614442*, 40614443*.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614441) submitted data pertaining to the stability of residues of simazine and its chlorometabolites, G-28279 and G-28273, in or on apple fruit, dry pomace, and juice. Samples were fortified with each compound at 1.0 ppm and stored at -15 C for up to 427 days. Two fortified samples and one control sample of each commodity were analyzed at intervals of 126-132, 190-194, and 427 days using analytical method AG-539; 0-day samples (stability spikes and controls) were fortified just prior to analysis. The concentration of simazine, G-28279, and G-28273 in all commodities after 427 days was 92-108%, 90-104%, and 66-76%, respectively, of the initial fortification level. All of the untreated control samples had nondetectable (<0.05 ppm) residues of simazine and each metabolite. These data indicate that residues of simazine and its chlorometabolite G-28279 are stable in apple fruit, dry pomace and apple juice, but that moderate (ca. 25%) loss of G-28273 may occur in these commodities during storage at -15 C for a period of up to 427 days.

Ciba-Geigy Corp. (1988; MRID 40614442) also submitted data pertaining to the stability of residues of simazine and its chlorometabolites G-28279 and G-28273 in the animal commodities: beef tenderloin, beef liver, beef fat, poultry lean meat, milk, and eggs. Samples were fortified with each compound at 0.25 ppm and stored at -15 C for up to 405 days. Two samples of each commodity were analyzed at intervals of 0, 4 months, 7 months and 1 year using analytical method AG-540 for tissues, and method AG-496 for milk. Average recovery values following the 405 days were 76-110% for simazine and G-28279, and 62-98% for G-28273 in all of the commodities with the exception of beef liver. Average recoveries for beef liver following 402 days were 92% and 74% for simazine and G-28279 respectively, yet in G-28273 declined from 96% to 30% from 0 to 402 days. No data depicting recoveries in fortified control samples were provided; untreated control samples all depicted nondetectable (<0.05 ppm) residues of simazine and each metabolite. These data indicate that residues of simazine and its chlorometabolites (G-28279 and G-28273) are stable in the animal commodities, beef tenderloin, beef fat, poultry lean meat, milk and eggs, and that in beef liver, only
the parent compound simazine and G-28279 are stable and not the metabolite G-28273 when stored at -15 C for a period of 13 months.

Ciba-Geigy Corp. (1988; MRID 40614443) submitted data pertaining to the stability of residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on field corn silage, field corn grain, sweet corn ears, corn meal, corn flour, crude corn oil, and soapstock. Samples were fortified with each compound at 1.0 ppm and stored at -15 C for up to 412 days. Two samples of each commodity were analyzed at intervals of 0, 4 months, 6 months and 1 year using the analytical method AG-539. Two control samples were also analyzed per each time interval: one untreated sample and one sample fortified with each compound at 1.0 ppm just prior to analysis. Average recoveries following ca. 412 days were 92-124% for simazine and each metabolite, in corn grain and corn fractions with the exception of corn crude oil. The three compounds, in crude oil, declined from 98-123% at 187 days to 69-79% at 427 days. Fortification recoveries, in all fractions except soapstock, ranged from 77-106% following 412 days. (The fortification percentages in soapstock were low, reportedly due to matrix difficulty). Untreated control samples all bore nondetectable (<0.05 ppm) residues of simazine and each metabolite. These data indicate that residues of simazine and metabolites, G-28279 and G-28273, are stable in field corn silage, field corn grain, sweet corn ears, corn meal, corn flour and soapstock when stored at -15 C for up to 412 days. The data also indicate the possibility of degradation of the three compounds occurring in crude corn oil, at about 6 months.
MAGNITUDE OF THE RESIDUE IN PLANTS

The Simazine Guidance Document dated 3/1/84 identified field residue data requirements for oranges, apples, peaches, blueberries, grapes, raspberries, corn, corn forage and fodder, bermuda grass, grasses, alfalfa, artichokes, asparagus, avocados, olives, and sugarcane. All of these data gaps related to the need for data on simazine chloro metabolites which have not yet been included in all tolerance definitions. Processing studies were required or conditionally required for oranges, apples, raisins, field corn grain, alfalfa, olives, and sugarcane.

The Agency has informed registrants of products containing simazine (EPA letter from R.F. Mountfort to simazine registrants dated 4/29/87) that Ciba-Geigy Corp., the principal registrant for simazine, has elected not to reregister uses of alfalfa, bermudagrass, and grasses grown for seed, rather than provide the residue data required for those specific commodities. Although these uses are still listed in the "EPA Compendium of Acceptable Uses (SRR) -- Simazine", registrants of simazine technical products have amended their labels to prohibit formulation of the technical products in end-use products intended for use on these crops. Therefore, no residue data for these uses have been reviewed in this SRR.

The Agency has recently determined that triazine hydroxymethylates may be of toxicological concern. Although the qualitative nature of the simazine residue in plants has not been adequately determined, the available plant metabolism residue data demonstrate that simazine hydroxymethylates constitute a significant, if not major, portion of the terminal residue of simazine in plants. Therefore, although field residue data submitted in response to the Guidance Document have fulfilled most of the specified data gaps, additional data on residues of simazine hydroxymethylates are required for all food and feed crops having registered simazine uses, except in cases where data can be translated from another crop. This situation also requires the submission of new processing studies for applicable crops.

Any discrepancies which occur between the "EPA Compendium of Acceptable Uses (SRR) -- Simazine" and use directions summarized for specific crops in this Residue Chemistry Chapter have resulted from consultation of individual simazine end-use product labels for clarification.
Citrus Fruits Group

Conclusions for the Citrus Fruits Group:

The available data are insufficient to determine if a crop group tolerance is appropriate. If the registrants seek a crop group tolerance, the following additional data are required:

- Additional residue data are required to support the existing tolerance for the representative crop group member oranges (see individual crop section for details).

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on grapefruit harvested at normal crop maturity after the following spring broadcast treatments: (i) representative WP, DF, or FlC formulations at 4 lb ai/A in CA; (ii) representative G, WP, DF, or FlC formulations at 9.6 lb ai/A in FL; and (iii) a G formulation at 5 lb ai/A in TX. Spray treatments must be applied as a directed spray to grove floor in 20-40 gal of water/A using ground equipment, avoiding spray contact with fruit, foliage, and stems.

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on lemons harvested at normal crop maturity following spring broadcast application of representative WP, DF, or FlC formulations at 4 lb ai/A in CA where this use is registered. Spray treatments are to be applied to the grove floor in 20-40 gal of water/A using ground equipment, avoiding spray contact with fruit, foliage, and stems.

Grapefruit

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on grapefruit [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for the following uses in grapefruit groves: (i) a single application/season at 2-4 lb ai/A in CA; (ii) a split application of 2 lb ai/A in the fall followed by 2 lb ai/A in the spring in CA (except Imperial, Coachella, and Palo Verde Valleys); (iii) a single application/season at 3.2-9.6 lb ai/A in the spring in FL, and; (iv) a single application/season at 4-4.8 lb ai/A in the
spring in TX. These formulations may be tank mixed with other herbicides.

The 4% G formulation is registered for use in TX at 4-5 lb ai/A and in FL at 6.4-9.6 lb ai/A. The 50% WP MAI formulation is registered for use in FL as a single postemergence application at 4 lb ai/A in a minimum of 40 gal of water/A using ground equipment.

Granular formulations are broadcast, while spray formulations are applied as directed sprays to the grove floor in 20-40 gallons of water/A using ground equipment, avoiding spray contact with fruit, foliage, and stems. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on grapefruit. However, additional data were required on residues of simazine chlorometabolites in or on oranges, which were to be translated to fulfill corresponding data requirements for grapefruit. No additional grapefruit residue data have been submitted. The available data do not depict residues of simazine hydroxymetabolites in or on grapefruit. Also, no data are available concerning the potential for simazine residues of concern to concentrate in processed products of grapefruit. However, no additional data are required, since data requested for oranges will be translated to fulfill these requirements for grapefruit.

A Canadian tolerance of 0.1 ppm (negligible residues) has been established for residues of simazine per se in or on fruit (from fruit tree orchards). No Mexican tolerances or Codex MRLs have been established; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): None

References (not used):

[The following reference(s) contain grapefruit residue data that are not useful for assessing the tolerance.]

MRID(s): 00023975. 00024033. 00025409. 00032571. 00035665. 00106691. 00113821.
Discussion of the data:
N/A.

Lemons

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on lemons [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for the following uses in lemon groves: (i) a split application of 1.6 lb ai/A in the fall followed by 1.6 lb ai/A in the spring in AZ; (ii) a single application/season at 2-4 lb ai/A in CA; and (iii) a split application of 2 lb ai/A in the fall followed by 2 lb ai/A in the spring in CA (except Imperial, Coachella, and Palo Verde Valleys). Applications made in AZ, may be tank mixed with paraquat, glyphosate, or oryzalin. Spray formulations are applied as a directed spray to grove floor in 20-40 gallons of water/A using ground equipment, avoiding spray contact with fruit, foliage, and stems. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on lemons. Additional data were required on residues of simazine chlorometabolites in or on oranges, which were to be translated to fulfill corresponding data requirements for lemons. The available data do not depict residues of simazine hydroxymetabolites in or on lemons. Also, no data are available regarding the potential for concentration of simazine residues of concern in processed products of lemon. However, no additional data are required, since the data requested on oranges will be translated to fulfill these requirements for lemons.

Additional data (not reviewed for the Guidance Document) that are summarized below also support the existing tolerance.

A Canadian tolerance of 0.1 ppm (negligible residues) has been established for residues of simazine per se in or on fruit (from fruit tree orchards). No Mexican tolerances or Codex MRLs have been established; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.
References (used):

MRID(s): 00023329*

References (not used):

[The following reference(s) contain insufficient data for adequate assessment of the tolerance.]

MRID(s): 00023354 00033035 0035665

Discussion of the data:

Ciba-Geigy Corp. (1978; MRID 00023329) submitted field residue data from three tests in CA (not reviewed for the Simazine Guidance Document dated 3/1/84) pertaining to the residues of simazine per se in or on lemons harvested 49 days following a single directed spray application of the 80% WP formulation at 4 lb ai/A (1x the maximum registered rate for CA). Three treated samples and one untreated control sample each bore residues of <0.05 ppm (nondetectable). Data were collected using method AG-126. The limit of detection is 0.05 ppm. Simazine recovery was 106% from one lemon sample fortified at 0.05 ppm. Samples were stored for unreported intervals under unspecified storage conditions prior to analysis.

The test state of CA represents the limited region where simazine use on lemons is registered, and accounts for ca. 75% of the 1987 U.S. lemon production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA); therefore, geographic representation of the data is adequate.

Oranges

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on oranges [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FLC formulations are registered for the following uses in orange groves: (i) a split application of 1.6 lb ai/A in the fall followed by 1.6 lb ai/A in the spring in AZ; (ii) a single application/season at 2-4 lb ai/A in CA; (iii) a split application of 2 lb ai/A in the fall followed by 2 lb ai/A in the spring in CA (except Imperial, Coachella, or Palo Verde Valleys); (iv) a single application/season at 3.2-9.6 lb ai/A in the spring in FL; and (v) a single application/season at 4-4.8 lb ai/A in the spring in TX. These formulations may be tank mixed with other herbicides.
The 4% G formulation is registered for use in TX at 4-5 lb ai/A and in FL at 6.4-9.6 lb ai/A in the spring. The 50% WP MAI is registered for a single postemergence application/season in FL at 4 lb ai/A in a minimum of 40 gallons/A using ground equipment. The 34.67% EC MAI is registered for use in bedded oranges in FL at 3.2 lb ai/A or in CA (except Imperial, Coachella, and Palo Verde Valleys) as a single broadcast application at 2-4 lb ai/A in 20-60 gallons of water/A using ground equipment; a nonionic surfactant may be added to the finished spray.

Granular formulations are broadcast, while spray formulations are applied as directed sprays to the grove floor in 20-40 gallons of water/A using ground equipment, avoiding spray contact with fruit, foliage, and stems. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 required additional field residue data regarding residues of simazine and its metabolites in or on oranges; it also required an orange processing study, conditional upon outcome of field residue tests. Data submitted in response to the Guidance Document (MRID 40614450) indicate that combined residues of simazine and its chlorometabolites in or on oranges will not exceed the established tolerance level following simazine application according to the maximum registered use pattern. The submitted processing study for oranges used fruit that did not bear measurable weathered residues; nevertheless, finite simazine residues did occur in crude orange oil. Therefore, concentration factors cannot be calculated. The available data do not depict residues of simazine hydroxymetabolites in or on oranges. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on oranges harvested at normal fruit maturity after spring broadcast application of representative WP, DF, or FL formulations at the following rates: (i) 4 lb ai/A in CA; (ii) 9.6 lb ai/A in FL; and (iii) 4.8 lb ai/A in TX. Granular formulations may be used for the FL and TX tests. Spray formulations must be applied in 20-40 gal of water/A using ground equipment.

- A processing study depicting the potential for concentration of simazine residues of concern in dried pulp, oil, and molasses processed from oranges bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these commodities, appropriate food/feed additive tolerances must be proposed. The need for a processing study may be
waived if field residue tests using rates exaggerated by
the highest theoretical concentration factor for any one
of the processed products indicate that no detectable
residues of concern occur in or on oranges.

A Canadian tolerance of 0.1 ppm (negligible residues) has been
established for residues of simazine per se in or on fruit (from
fruit tree orchards). No Mexican tolerances or Codex MRLs have
been established; therefore, no questions of compatibility exist
with respect to U.S. tolerances and Codex MRLs for this commodi-
ty.

References (used):

MRID(s):  00023976.  40614450*.

References (not used):

[The following reference(s) contain data that represent less than
the maximum residue exposure potential.]

MRID(s):  00023329.  00024033.  00025409.  00032571.  00033035.
         00035665.  00087676.  00106691.  00113821.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614450) submitted data from three
tests conducted in CA, FL, and TX pertaining to residues of
simazine and its chlorometabolites (G-28279 and G-28273) in or on
oranges harvested 14 days (CA and FL) or 203 days (TX) following
application of the 80% WP and 4 lb/gal FLIC formulations at 4.8 lb
ai/A in CA (1.2x maximum registered rate) and TX (1x), and at 9.6
lb ai/A in FL (1x). Combined residues in or on 10 treated
samples and two control samples were all nondetectable (<0.15
ppm, including <0.05 ppm each of simazine, G-28279, and G-28273).

The same submission described a processing study which used
oranges from the FL study. Combined residues of simazine,
G-28279, and G-28273 were <0.03 ppm (nondetectable, including
<0.01 ppm for each compound) in or on samples of washed and
unwashed fruits, finisher pulp, molasses, juice, chopped peel,
peel frit, and press liquor. In two crude oil samples residues of
simazine were 0.26-0.30 ppm, while chlorometabolite residues
were <0.01 ppm each (nondetectable). Because the raw fruit did
not bear measurable weathered residues, concentration factors
cannot be determined for these processed fractions. Apparent
residues of simazine, G-28279, and G-28273 were all <0.01 ppm
(nondetectable) in or on control samples of washed and unwashed
fruit, finisher pulp, molasses, juice, chopped peel, peel frit,
press liquor, and crude oil.
All data discussed above were collected using GLC Method AG-539. The limit of detection was 0.05 ppm for each compound in or on oranges and 0.01 ppm in orange fractions. Recovery efficiencies from whole fruit fortified at 0.01-0.2 ppm were 111-121% for simazine, 97-109% for G-28279, and 88-112% for G-28273. Recoveries were 80-87% for simazine and 72-86% for G-28279 from juice and molasses samples fortified at 0.01-0.05 ppm. Recoveries were 95-124% for simazine, 72-101% for G-28279, and 80-92% for G-28273 from two crude oil samples fortified at 0.01-0.2 ppm. Samples were stored frozen at -15 C for 372-1,086 days prior to analysis.

Additional residue data submitted by various registrants pertaining to simazine residues in or on oranges have not been reviewed here because they represent less than the maximum exposure potential under registered uses (MRIDs 00023329, 00024033, 00025409, 00032571, 00033035, 00035665, 00087676, 00106691, 00113821).

Geographic representation is adequate because the test states of CA (66%), FL (32%), and TX (<1%) accounted for ca. 100% of 1987 U.S. commercial orange production. Field residue data from CA, FL, and TX submitted in response to the Guidance Document indicate that combined residues of simazine and its chlorometabolites will not exceed the established tolerance level for residues of simazine per se (0.25 ppm) in or on orange fruits harvested 14-203 days following simazine application at 1x rates. The submitted processing study for oranges used fruit that did not bear measurable weathered residues, but did find finite simazine residues occurred in crude oil. Therefore, concentration factors cannot be calculated. The available data do not depict residues of simazine hydroxymetabolites in or on oranges. Therefore, additional data are required.

**Pome Fruits Group**

**Conclusions for the Pome Fruits Group:**

The available data are insufficient to determine if a crop group tolerance is appropriate. We note that translated data cannot be used to support a group tolerance. If the registrants seek a crop group tolerance, the following additional data are required:

- Additional data are required for the representative crop group members apples and pears (see individual crop sections below for details).

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on pears harvested at regular intervals following application of representative G, WP, DF, and
F1C formulations at 4.0 lb ai/A. Tests must be performed in the states of CA(36%), OR(23%), and WA(36%), which collectively represent >90% of the U.S. commercial pear production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). The registrants must propose label amendments specifying a PHI that is supported by the requested residue data.

**Apples**

**Tolerance(s):**

A tolerance of 0.25 ppm been established for residues of simazine per se in or on apples [40 CFR §180.213].

**Use directions and limitations:**

The 4% G, 80% WP, 90% DF, and 4 lb/gal F1C formulations are registered for directed broadcast or banded application to apple orchards at 2-4 lb ai/A. Spray application may be made in 20-40 gal of water/A. The 4 lb/gal F1C and 80% WP may be tank mixed with other herbicides. The 34.67% MAI EC formulation (formulated with paraquat) may be applied at the same use rate in 50-200 gal of water/A, using a nonionic surfactant in the spray solution. Spray must not contact fruit, foliage, or stems. No PHI has been established. The 4% G formulation may be applied as a dormant treatment at 6-8 lb ai/A in February or March to young nonbearing apple orchards that have been established for a minimum of 1 year. Livestock grazing is restricted on areas treated with formulations or tank mixes containing paraquat.

**Conclusions:**

The Simazine Guidance Document dated 3/1/84 required additional data depicting residues of simazine and its chlorometabolites in or on apples; a processing study was conditionally required. Data submitted in response to the guidance document (MRIDs 00132787 and 40614451) are insufficient to assess the tolerance for residues of simazine per se in or on apples because they do not represent samples harvested at an established PHI. Likewise, the level of combined residues of simazine and its chlorometabolites resulting from the maximum registered use cannot be evaluated. Potential concentration factors for simazine residues of concern in processed apple products cannot be determined because the submitted processing study (MRID 40614451) did not use fruit bearing measurable weathered residues. The available data do not depict residues of simazine hydroxymetabolites in or on apples, nor has a PHI been established. The following additional data are required:
Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on apples harvested at regular intervals following application of representative G, WP, DF, and FlC formulations at 4.0 lb ai/A. Tests must be performed in the states of MI(11%), NY(10%) or PA(5%), and WA(42%), which collectively represent ca. 70% of the U.S. commercial apple production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). The registrants must propose label amendments specifying a PHI that is supported by the requested residue data.

A processing study depicting the potential for concentration of simazine residues of concern in dry pomace and juice processed from apples bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these commodities, appropriate food/feed additive tolerances must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the highest theoretical concentration factor for any one of the processed products indicate that no detectable residues of concern occur in or on apples.

A Canadian tolerance has been established at 0.1 ppm (negligible residues) for residues of simazine per se in or on apples. No Mexican or Codex MRLs have been established for simazine residues in or on apples; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):
MRID(s): 00012166*. 00023898. 00024059*. 00106691*. 00132787*. 40614451*.

References (not used):
[The following reference(s) were not used because they contain duplicate data, incomplete data, or data that are not useful in assessing the tolerance.]
MRID(s): 00012165. 00012167. 00023313. 00023888. 00023914. 00023924. 00024076. 00024080. 00024110. 00032359. 00035664. 00113821.

Discussion of the data:
Ciba-Geigy Corp. (1988; MRID 40614451) submitted data from seven tests conducted in CA, MI, MO, NY, PA, WA, and WV depicting combined residues of simazine and its chlorometabolites (G-28279
and G-28273) in or on apples harvested 114-229 days following application of a WP formulation at 4.0 lb ai/A in 20-100 gal of water using ground equipment (1x the maximum registered application rate). Combined residues in or on the 14 treated and seven control samples were <0.15 ppm (nondetectable, including simazine, G-28279, and G-28273 at <0.05 ppm each). Samples were stored at -15 C for 279-346 days prior to analysis.

In this same submission, were data from a processing study depicting simazine residues in apple processed products. All samples of processed products bore nondetectable residues (<0.05 ppm each) of simazine and its chlorometabolites. Since the fruit samples also bore no measurable weathered residues, the potential for concentration of simazine residues of concern cannot be determined from these data.

All data discussed above were collected using GLC Method AG-539, which has a limit of detection of 0.05 ppm for each compound. Recovery efficiencies were 69-105% from samples fortified with simazine and its metabolites at 0.05-0.5 ppm.

Another study submitted by Ciba-Geigy Corp. (1983; MRID 00132787) reported residue data on simazine and its chlorometabolites in or on apples from tests conducted in MI, NY, and WA in 1982. Three samples harvested 145-178 days following application of simazine at 4.0 lb ai/A (1x) bore nondetectable residues (<0.05 ppm each for simazine and G-28279; <0.10 ppm for G-28273). Samples were stored at -15 C for 253-284 days prior to analysis by method AG-295 for simazine and G-28279, and by method AG-281 for G-28273. These two methods have limits of detection of 0.05 and 0.10 ppm, respectively.

Ciba-Geigy Corp. and Elanco Products (1976; MRID 00106691, 1974; MRID 00024059, and 1969; MRID 00012166 - not reviewed in the interim residue chemistry chapter) submitted data from four tests conducted in CA(2), IL(1), and NY(1) depicting residues of simazine per se in or on apples harvested 112-219 days following application of 1-2x rates. Eight samples bore residues of <0.05 ppm (nondetectable). Samples were analyzed using a GLC method (PAM Vol. II or AG-126). Recoveries were 64-104% from samples fortified at 0.05-0.1 ppm.

Additional apple residue data were not reviewed because they represent less than the maximum exposure potential under registered uses (less than maximum registered use rate, inadequate storage of samples, or unspecified analytical methods).

Geographic representation of the data is adequate, as the states of CA(7%), IL(1%), MI(11%), MO(1%), NY(10%), PA(5%), WA(42%) and WV(2%) account for ca 80% of the 1987 U.S. apple production (Crop Database, Jan. 1988, Ag. Statistics board, NASS, USDA). The submitted data support the tolerance for residues of simazine per
se in or on apples and indicate that the maximum registered use pattern would not result in combined residues of simazine and its chlorometabolites exceeding that tolerance level.

Pears

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on pears [40 CFR §180.213].

Use directions and limitations:

The use directions for simazine in pear orchards are identical to those described above for apple orchards.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data (MRID 00023920) support the tolerance for residues of simazine per se in or on pears; however, additional data were required depicting residues of simazine and its chlorometabolites in or on apples, and were to be translated to fulfill corresponding requirements for pears. The data translated from apples indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites exceeding the established tolerance level for residues of simazine per se in or on pears. The available data do not depict residues of simazine hydroxymetabolites in or on pears. No additional data will be required specifically for pears, since the data requested for apples will be translated to satisfy this requirement. However, the following action must be taken. We note also that translated data cannot be used to support a crop group tolerance.

The registrants must propose label amendments specifying a PHI for simazine application to pears that is supported by the translated residue data.

A Canadian tolerance has been established at 0.1 ppm (negligible residues) for residues of simazine per se in or on fruit tree orchards. No Mexican or Codex MRLs have been established for simazine residues in or on pears; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023920.
References (not used):

[The following reference(s) were not used because they contain duplicate data or data that are not useful in assessing the tolerance.]

MRID(s): 00024076. 00032359. 00035664. 00106691. 00113821.

Discussion of the data:

N/A.

Additional data that were not reviewed included tests conducted at less than the maximum registered use rate.

Stone Fruits Group

Conclusions for the Stone Fruits Group:

The available data are insufficient to determine if a crop group tolerance is appropriate. If the registrant seeks a crop group tolerance, the following data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273) and hydroxymetabolites of concern in or on cherries harvested at normal fruit maturity after directed broadcast or banded application of representative WP, DF, or FlC formulations at the rates 4 lbs ai/A in the states of MO and MI. Spray formulations must be applied in 20-40 gallons of water/A using ground equipment.

- Additional residue data are required for the representative crop group members peaches and plums or fresh prunes (see individual section below for details of data requirements).

Cherries (sweet and sour)

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on cherries [40 CFR §180.213].

Use directions and limitations:

Sour cherries: The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for directed broadcast application to sour cherry orchards at 2-4 lb ai/A in 20-40 gal of water/A. The 34.67% MAI EC formulation (formulated with paraquat) may be applied at the
same rate in 50-200 gal of water/A; this use is limited geographically to MO and the states east of the Mississippi River except TN.

**Sweet cherries:** The 80% WP, 90% DF, and 4 lb/gal F1C formulations are registered for broadcast or banded application at 1.6-4 lb ai/A in 20 to 40 gal of water/A between late fall and early spring prior to weed emergence. These uses are limited to MO and the states east of the Mississippi River except TN. The 80% WP and 90% DF formulations are registered for the same use (except tank mix) in OR (EPA SLN Nos. OR810079 and OR810080) in sweet cherry orchards established for at least 2 years.

**All cherries:** The 4 lb/gal F1C formulation may be tank mixed with other herbicides. Spray must not contact fruit, foliage, or stems. Simazine should not be applied on sandy or gravelly soils. Livestock grazing is restricted on areas treated with formulations or tank mixes containing paraquat. No PHI has been established.

**Conclusions:**

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine *per se* in or on cherries. No additional data were requested specifically for cherries; however, additional data on residues of simazine chlorometabolites required for peaches were to be translated to fulfill corresponding data requirements for cherries. The data translated from peaches along with additional field residue data from cherries not previously reviewed (MRIDs 00023329 and 00131376) indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites exceeding the established tolerance level for residues of simazine *per se* in or on cherries. The available data do not depict residues of simazine hydroxymetabolites in or on cherries. No additional data will be required specifically for cherries. The data requested on plums will be translated to satisfy this requirement. We note, however, that translated data cannot be used to support a crop group tolerance.

No Canadian or Mexican tolerances or Codex MRLs exist for simazine residues in or on cherries; therefore, there are no questions of compatibility with respect to U.S. tolerances and Codex MRLs for these commodities.

**References (used):**

MRID(s): 00023329*. 00023922. 00131376*.
References (not used):

[The following reference(s) were not used because they contain duplicate data or data that was not useful in assessing the tolerance.]

MRID(s): 00023883. 00023968. 00023989. 00027924. 00027964. 00027965. 00033035. 00106691. 00113821.

Discussion of the data:

Ciba-Geigy Corp. (1983; MRID 00131376, 1978; MRID 00023329) submitted data from three tests conducted in MI(2) and WA(1) depicting combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on cherries harvested 25-75 days following a single broadcast application of a WP formulation at 4.0 lb ai/A (1x the maximum registered application rate) applied in 30-36 gallons of water using ground equipment. Combined residues in or on six samples were <0.20 ppm (nondetectable, including <0.05 ppm each for simazine and G-28279, and <0.10 ppm for G-28273). Samples were stored at -15 C for 210-324 days and analyzed by GLC Method AG-295 for simazine and G-28279 (limit of detection = 0.05 ppm) and GLC Method AG-281 for G-28273 (limit of detection = 0.10 ppm).

Other studies submitted concerning simazine residues in or on cherries were not reviewed here because they include data that do not reflect the maximum registered use rate (MRIDs 00023883, 00023968, 00023989, 00027924, 00027964, 00027965, 00033035, 00106691, 00113821).

These data indicate that combined residues of simazine and its chlorometabolites will not exceed the established tolerance level for residues of simazine per se (0.25 ppm). Geographical representation is adequate; MI represents 74% of the U.S. commercial sour cherry production and 15% of sweet cherry production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). WA can be considered representative of OR, the only state where simazine use is registered on sweet cherries. Although the available data do not depict residues of simazine hydroxymetabolites in or on cherries, no additional data will be required for cherries, since the data requested on plums will be translated to fulfill these requirements. We note, however, that translated data cannot be used to support a crop group tolerance.
Peaches

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on peaches [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for directed broadcast or banded application to peach orchards at 1.6-4 lb ai/treated A in 20-40 gal of water/A between late fall and early spring before weeds emerge. The 4 lb/gal FlC and 80% WP formulations may be tank mixed with other herbicides. The 34.67% MAI EC formulation may be applied at the same use rate in 50-200 gal of water/A, using a nonionic surfactant in the spray solution. These uses are limited geographically to AR, LA, MO, OK, TX, and states east of the Mississippi River. In CA, the 90% DF and 4 lb/gal FlC formulations may be applied at 1-2 lb ai/A. Spray must not contact fruit, foliage, or stems. Livestock grazing is restricted on areas treated with formulations or tank mixes containing paraquat. Simazine should not be applied on sandy or gravelly soils.

Conclusions:

The Simazine Guidance Document dated 3/1/84 required additional data regarding residues of simazine and its chlorometabolites in or on peaches. Data submitted in response to the Guidance Document (MRIDs 00131376 and 40614452) indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites that exceed the established tolerance level for residues of simazine per se in or on peaches. However, the available data do not depict residues of simazine hydroxymetabolites in or on peaches. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on peaches harvested at normal fruit maturity after spring directed broadcast or banded application of representative WP, DF, or FlC formulations at 4 lbs ai/A in GA(7%) or SC(23%) and NJ(5%) or PA(6%) and at 2 lbs ai/A in CA(34%), representing the major U.S. areas of peach production and the geographic limitations on simazine use. Spray formulations must be applied in 20-40 gal of water/A.

No Canadian or Mexican tolerance nor Codex MRL exists for simazine residues in or on peaches; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.
References (used):

MRID(s): 00023908. 00131376* 40614452*.

References (not used):

[The following reference(s) were not used because they represent duplicate data or data that was not useful in assessing the tolerance.]

MRID(s): 00012134. 00012158. 00012169. 00012170. 00012171.
00023883. 00023919. 00023989. 00027826. 00031663.
00033035. 00035663. 00106691. 00113821.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614452) submitted residue data from eight tests conducted in CA(1), GA(1), MI(1), MO(1), PA(2), SC(1), and TX(1) depicting combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on peaches harvested 60-129 days following application of a WP formulation at 4.0 lb ai/A (1x the maximum registered use rate) in 20-34 gal of water. Thirteen treated and seven control samples all bore combined residues of simazine, G-28279, and G-28273 of <0.15 ppm (nondetectable, including <0.05 ppm for each compound). Samples were stored at -15 C for 228-651 days prior to analysis by GLC Method AG-539, which has a limit of detection of 0.05 ppm. Recovery efficiencies were 64-150% from samples fortified with simazine and its chlorometabolites at 0.05-0.2 ppm.

Ciba-Geigy (1983; MRID 00131376) also reported data from a PA test depicting residues of simazine and its chlorometabolites in or on peaches harvested at unreported intervals following application of an unspecified formulation at 4.0 lb ai/A (1x). Two samples bore combined residues of <0.20 ppm (nondetectable, including <0.05 ppm each for simazine and G-28279, and <0.10 ppm for G-28273). Samples were stored at -15 C for 230-263 days prior to analysis by GLC Method AG-295 for simazine and G-28279 and Method AG-281 for G-28273. These methods have limits of detection of 0.05 and 0.10 ppm, respectively.

Geographic representation is adequate since the states of CA(34%), GA(7%), MI(4%), MO(1%), NJ(5%), PA(6%), and SC(23%) account for >70% of the 1987 U.S. commercial peach production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). These data indicate that combined residues of simazine and its chlorometabolites in peaches harvested 60-129 days following simazine application at 1x rates will not exceed the established tolerance level of 0.25 ppm for residues of the established tolerance for residues of simazine per se. However, the available data do not depict residues of simazine hydroxymetabolites.
in or on peaches. Therefore, additional residue data are required.

**Plums (fresh prunes)**

**Tolerance(s):**

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on plums [40 CFR §180.213].

**Use directions and limitations:**

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for directed broadcast or banded application to plum orchards at 1.6-4 lb ai/A in 20-40 gal of water/A. The 4 lb/gal FlC formulation may be tank mixed with other herbicides. These uses are limited to MO and the states east of the Mississippi River except TN. Spray must not contact fruit, foliage, or stems. Livestock grazing is restricted on areas treated with tank mixes containing paraquat. Simazine must not be applied to sandy or gravelly soils.

**Conclusions:**

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on plums. No additional data were requested specifically for plums; however, additional data on residues of simazine chlorometabolites required for peaches were to be translated to fulfill corresponding data requirements for plums. The data translated from peaches along with additional field residue data from plums not previously reviewed (1978; MRID 00023329) indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites exceeding the established tolerance level for residues of simazine per se in or on plums. The available data do not depict residues of simazine hydroxymetabolites in or on plums. The requirement for a processing study to determine potential concentration of residues in dried prunes will be waived because virtually all production of dried prunes occurs in the state of CA where this use of simazine is not registered. The following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273) and hydroxymetabolites of concern in or on plums harvested at normal fruit maturity after directed broadcast or banded application of representative WP, DF, or FlC formulations at the rates 4 lbs ai/A in MI. Spray formulations must be applied in 20-40 gallons of water/A using ground equipment.
No Canadian or Mexican tolerance nor Codex MRL exists for simazine residues in or on plums; therefore, there are no compatibility questions with regard to the Codex MRL.

References (used):

MRID(s): 00023329*, 00023910, 00023921.

References (not used):

[The following reference(s) were not used because they represent duplicate data or data that was not useful in assessing the tolerance because less than maximum use rates were used or the use was not registered in the test state.]

MRID(s): 00023883, 00023989, 00027923, 00031663, 00033035, 00106691.

Discussion of the data:

Ciba-Geigy Corp. (1978; MRID 00023329) submitted data from two tests conducted in MI and NY depicting residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on plums. Four samples were harvested 94-103 days following a single broadcast application of a WP formulation at 4.0 lb ai/A in 36 or 76 gal of water using ground equipment (1x the maximum registered use rate). Combined residues in or on all of the samples were nondetectable (<0.20 ppm, including <0.05 ppm each for simazine and G-28279 and <0.10 ppm for G-28273). Samples were stored frozen for 153-215 days prior to analysis by GLC Method AG-295 for simazine and G-28279 (limit of detection = 0.05 ppm) and AG-281 for G-28273 (limit of detection = 0.10 ppm).

Geographic representation of the data is adequate because the test states of NY(<1%), PA(<1%), and MI(2%) represent the major areas of plum production in the eastern U.S. where this use of simazine is registered (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). These data, along with data translated from peaches, indicate that combined residues of simazine and its chlorometabolites in or on cherries will not exceed the established tolerance level for residues of simazine per se following the maximum registered use pattern.

Small Fruits and Berries Group

Conclusions for the Small Fruits and Berries Group:

The available data are insufficient to determine whether a crop group tolerance is appropriate. If the registrants seek a crop group tolerance, the following additional data will be required:
Additional residue data are required to support the existing tolerances for the representative crop group members blueberries, grapes, and raspberries (see individual crop sections below for details).

Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on cranberries harvested at normal fruit maturity after spring broadcast application of representative G, WP, DF, or FlC formulations at 2 lb ai/A in WI and 4 lb ai/A in MA (representing ca 80% of U.S. cranberry production; Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). Spray formulations must be applied in 20-40 gal of water/A using ground equipment.

Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on strawberries sampled at normal crop harvest following postharvest application of a DF or FlC formulation at 1 lb ai/A in OR or WA, and following posttransplant application of a WP or FlC formulation at 2 lb ai/A to watering furrows between raised strawberry beds in LA.

Blueberries

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on blueberries [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for directed application to established blueberries in the spring at 2-4 lb ai/A in a minimum of 40 gal of water/A, or for split application of 2 lb ai/A in the spring followed by 2 lb ai/A in the fall. The 4% G formulation is registered for the same use as a broadcast application. Spray must not contact foliage or stems, and the herbicide must not be applied when fruit is present. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on blueberries; however, additional field data were required regarding residues of simazine and its chlorometabolites (G-28273 and G-28279). Data submitted in response to the Guidance Document (MRID 40614453) indicate that combined residues of
simazine and its chlorometabolites will not exceed the established tolerance level in or on blueberries following simazine application according to the maximum registered use pattern. The available data do not depict residues of simazine hydroxymetabolites in or on blueberries. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on blueberries harvested at normal fruit maturity after spring application of representative G, WP, DF, or F1C formulations to established blueberry orchards at 4 lb ai/A according to label directions. Tests must be conducted in MI(41%), NJ(34%), NC(5%) or GA(2%), and OR(3%) or WA(5%) which represent ca. 90% of the 1982 U.S. blueberry acreage (1982 Census of Agriculture, Vol. 1, Part 51, p. 371).

A Canadian tolerance of 0.1 ppm (negligible residues) has been established for residues of simazine per se in or on blueberries. No corresponding Mexican tolerance or Codex MRL has been established; therefore, no questions of compatibility exist with regard to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023900. 40614453*.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614453) submitted field residue data from ten tests conducted in ME(2), MI(2), NJ(2), NC(2), and OR(2) pertaining to residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on blueberries harvested 89-119 days following a single spring soil application of the 80% WP formulation at 4 lb ai/A (1x the maximum registered single application rate). Combined residues of simazine and its chlorometabolites were <0.15 ppm (nondetectable including simazine, G-28279, and G-28273 at <0.05 ppm each) in or on 10 treated and five control samples. Data were collected using method AG-539. The limit of detection was 0.05 ppm for each compound. Recoveries were 88-104% for simazine, 75-90% for G-28279, and 70-88% for G-28273 from samples fortified at 0.05-0.5 ppm. Samples were stored frozen at -15 C for ca. 408-502 days prior to analysis.

Geographic representation is adequate since the test states of ME(2%), MI(41%), NJ(34%), NC(5%), and OR(3%) accounted for ca. 85% of the 1981 U.S. blueberry production (Census of Agriculture, 1982, Vol. 1, Part 51, p. 371). The available data indicate that combined residues of simazine and its chlorometabolites are <0.15 ppm (nondetectable) in or on blueberries following simazine application at 1x. However, The available data do not depict
residues of simazine hydroxymetabolites in or on blueberries. Therefore, additional data are required.

Caneberries (blackberries, boysenberries, loganberries, and raspberries)

Tolerance(s):

Tolerances of 0.25 ppm have been established for residues of simazine per se in or on blackberries, boysenberries, loganberries, and raspberries [40 CFR §180.213].

Use directions and limitations:

The registered uses for simazine on caneberries (including blackberries, boysenberries, loganberries, and raspberries) are identical to those described above for blueberries.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerances for residues of simazine per se in or on blackberries, boysenberries, loganberries, and raspberries. However, additional data were required on residues of simazine chlorometabolites (G-28273 and G-28279) in or on raspberries; these data were to be translated to fulfill corresponding data requirements for blackberries, boysenberries, and loganberries. Field residue data submitted in response to the Guidance Document (MRID 40614453) indicate that combined residues of simazine and its chlorometabolites in or on raspberries harvested following simazine application reflecting the maximum registered use pattern will not exceed the established tolerance level of 0.25 ppm for residues of simazine per se.

The available data do not depict residues of simazine hydroxymetabolites in or on caneberries. Additional data are required only for raspberries. These data will be translated to fulfill corresponding requirements for blackberries, boysenberries, and loganberries. The following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273) and hydroxymetabolites of concern in or on raspberries harvested at normal fruit maturity after directed spring application of representative G, WP, DF, or FLC formulations to established plants at 4 lb ai/A according to established use directions. Tests must be conducted in CA(7%) and OR(38%) or WA(44%) which collectively represent ca. 80% of the 1982 U.S. raspberry acreage (Census of Agriculture, 1982, Vol.1, Part 51, p. 372).
Canadian tolerances of 0.1 ppm (negligible residues) have been established for residues of simazine per se in or on blackberries, loganberries, and raspberries. No Mexican tolerances or Codex MRLs have been established; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for these commodities.

References (used):

MRID(s): 00023895. 00023901. 00023902. 00023903. 40614453*.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614453) submitted field residue data from six tests conducted in CA(2), OR(2), and WA(2) pertaining to residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on raspberries harvested 84-102 days following a single spring soil application of the 80% WP formulation at 4 lb ai/A (1x the maximum registered single application rate). Combined residues of simazine and its chlorometabolites were <0.15 ppm (nondetectable, including simazine, G-28279 and G-28273 at <0.05 ppm each) in or on six treated and three control samples. Data were collected using method AG-539. The limit of detection is 0.05 ppm for each compound. Recoveries were 86-95% for simazine, 84-87% for G-28279, and 74-94% for G-28273 from samples fortified at 0.05-0.2 ppm. Samples were stored frozen at -15 C for 442-471 days prior to analysis.

Geographic representation of the data is adequate since the test states of CA(7%), OR(38%), and WA(44%) represent for ca. 90% of 1982 U.S. raspberry acreage (1982 Census of Agriculture, Vol. 1, Part 51, p. 372). The available data indicate that combined residues of simazine and its chlorometabolites in or on raspberries harvested 84-102 days following simazine application at 1x rates will not exceed the established tolerance level of 0.25 ppm for residues of simazine per se. However, The available data do not depict residues of simazine hydroxymetabolites in or on caneberrys. Additional data are required.

Cranberries

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on cranberries [40 CFR §180.213].
Use directions and limitations:

The 4% G, 80% WP, 90% DF, 4 lb/gal F1C formulations are registered for broadcast application at 2 lb ai/A to established cranberries before spring growth begins. In MA, the same formulations may be applied at 4 lb ai/A in the spring before growth begins or after harvest in the fall. Spray applications are made in 20-40 gal of water/A and must not contact fruit or foliage.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on cranberries; data were required on residues of simazine and its chlorometabolites (G-28273 and G-28279) in or on blueberries, which were to be translated to cranberries. The available data do not depict residues of simazine hydroxymetabolites in or on cranberries. However, no additional data are required since the data requested on these metabolites for blueberries will be translated to fulfill this requirement for cranberries. We note, however that translated data cannot be used to support a crop group tolerance.

No Mexican or Canadian tolerances or Codex MRLs exist for simazine residues in or on cranberries; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023905.

Discussion of the data:

N/A.

Grapes

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on grapes [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal F1C formulations are registered for directed application to grape vineyards between harvest and early spring at 2-4.8 lb ai/A in 20-40 gal of water/A. The 34.67% MAI EC formulation (formulated with paraquat) is also registered for directed application at the same rate in 50-200 gal of water/A; nonionic surfactant may be added at 0.25-0.5
gal/100 gal of spray solution. Spray must not contact fruit, foliage or stems. Simazine must not be used in vineyards that have been established less than 3 years. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine required per se in or on grapes; however, additional field residue data were required concerning residues of simazine and its chlorometabolites (G-28273 and G-28279). A grape processing study was also required, conditional upon the outcome of field residue tests. Field residue data submitted in response to the Guidance Document (MRID 40614454) indicate that combined residues of simazine and its chlorometabolites in or on grapes following simazine application according to the maximum registered use rate will not exceed the established tolerance level. The submitted processing data cannot be used to determine potential concentration factors because products were processed from fruit which did not bear measurable weathered residues. Furthermore, The available data do not depict residues of simazine hydroxymetabolites in or on grapes. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on grapes harvested at normal fruit matur- ity following early spring directed application of representative WP, DF, or F1C formulations to vineyards at 4.8 lb ai/A in 20-40 gal of water/A. Tests must be conducted in CA which accounted for ca. 90% of the 1987 U.S. grape production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA).

- A processing study depicting the potential for concentration of simazine residues of concern in raisins, raisin waste, dry pomace, and juice processed from grapes bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these products, appropriate food/feed additive tolerance must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the highest theoretical concentration factor for any one of the processed pro- ducts indicate that no detectable residues of concern occur in or on grapes.

A Canadian tolerance of 0.1 ppm (negligible residues) has been established for residues of simazine per se in or on grapes. No corresponding Mexican tolerance or Codex MRL has been estab-
lished; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023906. 00027967*. 40614454*.

References (not used):

[The following reference(s) contain insufficient data for adequate assessment of the tolerance.]

MRID(s): 00027968. 00033035. 00106691.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614454) submitted data from 11 tests conducted in CA(4), MI(2), PA(1), NY(2), and WA(2) pertaining to residues of simazine and its chlorometabolites in or on grapes following a single soil application of the 80% WP formulation at 4.8-9.6 lb ai/A (1-2x the maximum registered single application rate) in 20-40 gal of water/A. Combined residues of simazine, G-28279, and G-28273 were <0.15 ppm (nondetectable, including each compound at <0.05 ppm) in or on 11 treated and two control samples harvested 140-163 days posttreatment.

In this same submission were results of a processing study which found no detectable residues of simazine, G-28279, or G-28273 (<0.05 ppm each) in raisins, wet pomace, dry pomace, juice, rachis, yeast, and wine processed from grapes which also bore nondetectable residues.

Samples were stored frozen at -15 C for 550-580 days prior to analysis by GLC Method AG-539. The limit of detection was 0.05 ppm for each compound. Recoveries were as follows: 87-111% for simazine, 84-103% for G-28279, and 65-106% for G-28273 in or on five fruit samples fortified at 0.05-0.2 ppm; 100% for simazine, 75% for G-28279, and 69% for G-28273 in one raisin sample fortified at 0.05 ppm; 73% for simazine, 74% for G-28279, and 88% for G-28273 in one wet pomace sample fortified at 0.10 ppm; 87% for simazine, 83% for G-28279, and 56% for G-28273 in one dry pomace sample fortified at 0.20 ppm; 111% for simazine, 103% for G-28279, and 75% for G-28273 in one juice sample fortified at 0.05 ppm.

Ciba-Geigy Corp. (1973; MRID 00027967) submitted data from six tests conducted in NY pertaining to residues of simazine per se in or on grapes following a single banded soil application of the 80% WP and 4 lb/gal F1C formulations at 4.8-9.6 lb ai/treated A (1-2x the maximum registered single application rate) in 30 gal of water/A. Residues of simazine were <0.05 ppm (nondetectable) in or on one control sample and six treated samples harvested
140-163 days posttreatment. Samples were stored for an unreported number of days under unspecified conditions prior to analysis by GLC method AG-126. The implied limit of detection was 0.05 ppm. Recovery was 105% from one sample fortified with simazine at 0.05 ppm.

Additional residue data submitted by various registrants pertaining to simazine residues in or on grapes have not been reviewed here because they represent less than the maximum exposure potential under registered uses and no analytical methods were submitted (MRIDs 00027968, 000333035, and 00106691).

Geographic representation of the data is adequate since the test states of CA (89%), MI (1%), NY (1%), PA (1%), and WA (5%) accounted for ca. 100% of the 1987 U.S. grape production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). The available data indicate that combined residues of simazine and its chlorometabolites will not exceed the established tolerance level of 0.25 ppm for residues of simazine per se. However, the submitted processing study is inadequate because it did not use fruit bearing measurable weathered residues were not used. The available data do not depict residues of simazine hydroxymetabolites in or on grapes. Therefore, additional data are required.

Strawberries

Tolerance(s):
A tolerance of 0.25 ppm has been established for residues of simazine per se in or on strawberries [40 CFR §190.213].

Use directions and limitations:

The 90% DF and 4 lb/gal FlC formulations are registered in OR and WA only for postharvest broadcast application to strawberries at 1 lb ai/A in a minimum of 20 gal of water/A. Overhead irrigation may be made after harvest during bed renovation; in fields where overhead irrigation is not available, application should be made during the period of early October through November.

The 80% WP and 4 lb/gal FlC formulations are registered for SLN use in LA (LA790027 and LA790028) as a banded application at 1-2 lb ai/A in a minimum of 20 gal of water/A to watering furrows between raised strawberry beds covered with plastic mulch. Treatment should be made after transplanting and before weeds emerge, while furrows are free of standing water.
Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that residue data to support the registered use on strawberries could be waived because the application rate of 1 lb ai/A is considerably less that for most other crop group members. Review of the current registered uses, including the SLN posttransplant use at up to 2 lb ai/A which was not considered in the original standard, also concludes that requirements for residue data may be waived. Should the registrant wish to substantively amend the current registered use or seek a crop group tolerance, additional data for this topic will be required.

A Canadian tolerance of 0.1 ppm (negligible residues) has been established for residues of simazine per se in or on strawberries. No corresponding Mexican tolerance or Codex MRL has been established; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): N/A.

References (not used):

[The following reference(s) contains insufficient data (no analytical method) for adequate assessment of the tolerance]

MRID(s): 00027322.

Discussion of the data:

N/A.

Tree Nuts Group

Conclusions for the Tree Nut Group:

The available data are insufficient to determine if a crop group tolerance is appropriate. We note that translated data cannot be used to support a crop group tolerance. If the registrants seek a crop group tolerance, the following data are required:

- Additional residue data are required for the representative crop group members pecans and walnuts (see individual crop sections for details).
- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of
concern in or on almonds following banded application of representative DF or FLC formulations at 2 lb ai/A in 20-40 gallons of water/A during fall or early winter. Spray must not contact fruit, foliage, or stems. Tests must be conducted in CA where this use is permitted.

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on walnuts harvested at regular intervals following directed application of representative WP, DF, or FLC formulations at 4 lb ai/A. Tests must be conducted in CA which accounted for ca. 100% of the 1987 U.S. walnut production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). Registrants must also propose label amendments to specify a PHI which is supported by the available residue data.

Almonds

Tolerance(s):

Tolerance of 0.25 ppm each have been established for residues of simazine per se in or on almonds and almond hulls [40 CFR §180.213].

Use directions and limitations:

The 90% DF and 4 lb/gal FLC formulations are registered for directed application to established almond orchards in a 2- to 4-foot band on either side of the tree row in late fall or early winter before weeds emerge; the use rate is 1-2 lb ai/A in 20-40 gal of water/A. The 4 lb/gal FLC may be tank mixed with other herbicides. The 34.67% EC MAI formulation (formulated with paraquat) may be applied at the same rate with a nonionic surfactant in 50-200 gal of water/A. Spray must not contact fruit, foliage, or stems. Simazine must not be used on (i) Mission (Texas) variety of almonds; (ii) almond trees propagated on plum rootstocks; (iii) trees established less than 3 years; and (iv) soil with <1% organic matter.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on almond nutmeats and hulls. Data translated from pecans and additional almond residue data not previously reviewed (MRID 00131377) indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites exceeding the tolerance level for residues of simazine per se. The available data do not depict residues of simazine hydroxymetabolites in or on almond nutmeats and hulls.
However, no additional data will be required, since the data requested on these metabolites for pecans will be translated to almonds. We note, however, that translated data cannot be used to support a crop group tolerance.

No Mexican or Canadian tolerance or Codex MRL exists for simazine residues in or on almonds; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023917. 00035666.* 00131377.*

References (not used):

[The following reference(s) contain data that represents less than the maximum registered use pattern for almonds.]

MRID(s): 00033035.

Discussion of the data:

Stauffer Chemical Co. (1980; MRID 00035666) submitted field residue data from two tests conducted in CA which were not reviewed in the previous Residue Chemistry Chapter pertaining to the residues of simazine per se in or on almond nutmeats and hulls harvested 147 days following a single directed spray application of the 80% WP formulation at 2 lb ai/A (1x the maximum registered single application rate). Residues of simazine per se were <0.05 ppm (nondetectable) in or on 14 samples of nutmeats and hulls and an untreated control sample (one each). Data were collected using method WRC 73-56. The limit of detection was 0.05 ppm. Recoveries were 76% from one nutmeat sample and 116% from one hull sample fortified with simazine at 0.05 ppm. Samples were stored for 254 days under unspecified conditions prior to analysis.

Ciba-Geigy Corp. (1983; MRID 00131377) submitted field residue data from one CA tests depicting residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on almond nutmeats and hulls harvested 123 days following application of the 80% WP formulation at 2 lb ai/A (1x the maximum registered single application rate). Combined residues were <0.20 ppm (nondetectable; including <0.05 ppm each for simazine and G-28279, and <0.1 ppm for G-28273) in or on three treated nutmeat and hull samples, and untreated control samples (one each). Data were collected using method AG-295 for simazine and G-28279 and method AG-281 for G-28273. The limits of detection are 0.05 ppm for simazine and G-28279 and 0.1 ppm for G-28273. Recoveries were 55% for simazine, 54% for G-28279, and 126% for G-28273 in or on one nutmeat sample fortified at 0.1-0.2 ppm. Recoveries were 100%
for simazine, 85% for G-28279, and 71% for G-28273 in or on one hull sample fortified at 0.05-0.1 ppm. Samples were stored frozen for 274-283 days prior to analysis.

Additional data concerning simazine residues in or on almonds have not been reviewed here because they represent less than the maximum exposure potential under registered uses and no analytical method was submitted (MRID 00033035).

Geographic representation is adequate since all available data are from tests conducted in CA which accounts for virtually all commercial U.S. almond production. The available almond residue data along with data translated from pecans indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites exceeding the tolerance level for residues of simazine per se. The available data do not depict residues of simazine hydroxymetabolites in or on almonds. However, no additional data are required since the data requested for pecans will be translated to fulfill this requirement for almonds.

**Filberts**

**Tolerance(s):**

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on filberts [40 CFR §180.213].

**Use directions and limitations:**

The 80% WP, 90% DF, and 4 lb/gal FL/C formulations are registered for application to filbert orchards at 2-4 lb ai/A in the fall, or split application of 2 lb ai/A in the fall followed by 2 lb ai/A the next spring. The 4 lb/gal FL/C may be tank mixed with other herbicides. Applications must not be made when nuts are on the ground. A 21-day PHI is effect for the glyphosate tank mix; otherwise no PHI has been established for simazine treatments. These uses are limited geographically to OR and WA.

**Conclusions:**

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on filberts. Data translated from pecans and additional filbert residue data (not previously reviewed) indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites exceeding the tolerance level for residues of simazine per se. The available data do not depict residues of simazine hydroxymetabolites in or on filberts. However, no additional data will be required, since
the data requested on these metabolites for pecans will be translated to filberts.

No Mexican or Canadian tolerance or Codex MRL exists for simazine residues in or on filberts; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023329*. 00023932. 00035666*.

References (not used):

[The following reference(s) contains insufficient data for adequate assessment of the tolerance.]

MRID(s): 00113821.

Discussion of the data:

Ciba-Geigy Corp. and Stauffer Chemical Co. (1978; MRID 00023329 and 1980; MRID 00035666, not previously reviewed) submitted field residue data from four OR tests depicting residues of simazine per se in or on filberts harvested 134-144 days following direct-spray application of the 80% WP formulation at 4 lb ai/A (1x the maximum registered use rate). Residues were <0.05 ppm (nondetectable) in or on three treated nutmeat samples, one whole nut sample, and two control samples. Samples were analyzed by methods AG-126 or WRC 73-56. The implied limit of detection was 0.05 ppm for both methods. Recovery was 95-124% from two nutmeat samples fortified with 0.05-0.1 ppm simazine. Samples were stored for 165 days or unreported intervals under unspecified conditions prior to analysis.

Additional residue data concerning simazine residues in or on filberts have not been reviewed here because they represent less than the maximum registered use pattern (MRID 00113821).

Geographic representation of the data is adequate because the test state of OR accounted for ca. 100% of the 1982 U.S. filbert acreage (Census of Agriculture, 1982 Vol. 1, Part 51, p. 367). These data along with previously reviewed filbert residue data support the tolerance for residues of simazine per se in or on filberts. Although the available data do not depict residues of simazine hydroxymetabolites in or on filberts, data requested for pecans will be translated to fulfill the corresponding requirement for filberts.
Macadamia Nuts

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on macadamia nuts [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FC formulations are registered for multiple applications to established macadamia nut orchards at 2-4 lb ai/A/application in 50 gal of water/A, repeated as necessary. The 4 lb/gal EC may be tank mixed with other herbicides including glyphosate. Spray must not contact fruit, foliage, or stems. Application must not be made during the harvest period when nuts are on the ground. A 21-day PHI is in effect for the glyphosate tank mix; otherwise no PHI has been established for simazine treatments.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on macadamia nuts. No additional data were required, and none have been submitted. Data were translated from pecans to satisfy the requirement for data on combined residues of simazine and its chloromethylates. The available data do not depict residues of simazine hydroxymethylates in or on macadamia nuts. However, no additional data will be required, since the data requested on these metabolites for pecans will be translated to macadamia nuts. The use directions for macadamia nuts do not specify either a maximum application rate per season or an appropriate PHI; therefore, the following changes in use directions are required:

- The registrant must propose a maximum application rate per season and an appropriate PHI which are supported by the available residue data.

No Mexican or Canadian tolerance or Codex MRL exists for simazine residues in or on macadamia nuts; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023907.
Discussion of the data:

N/A.

Pecans

Tolerance(s):

A tolerance of 0.1 ppm (negligible residues) has been established for residues of simazine per se in or on pecans 40 CFR §158.

Use directions and limitations:

The 80% WP, 90% DF and 4 lb/gal FlC formulations are registered for directed application to pecan groves at 2-4 lb ai/A in 20-40 gal of water/A in the spring before weeds emerge. Simazine must not be used (i) when nuts are on the ground; (ii) in areas west of the Pecos River in TX or in AZ, CA, and NM; or (iii) on trees established less than 2 years. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance of 0.1 ppm for residues of simazine per se in or on pecans, and recommended that the tolerance for the combined residues of simazine, G-28279, and G-28273 in or on pecans be set at 0.15 ppm to match the combined limits of detection of available analytical methods. No additional residue data were required, but additional pecan residue data (MRIDs 000131137 and 00023229) indicate that combined residues of simazine and its chlorometabolites will not exceed 0.20 ppm (combined limits of detection for an alternate method) following the maximum registered use pattern. The available data that depict residues of simazine hydroxymetabolites in or on pecans were collected with an analytical method that is inadequate. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on pecan nutmeats harvested at normal maturity after directed application of representative WP, DF, or FlC formulations at 4 lbs ai/A in 20-40 gal of water/A in the spring before weeds emerge. Tests must be conducted in AL(9%) or GA(41%) and NM(11%) or TX(18%) which collectively accounted for ca. 80% of the 1987 U.S. pecan production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA).

No Mexican or Canadian tolerance or Codex MRL exists for simazine residues in or on pecans; therefore, no questions of compatibi-
lity exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRIDs: 00013137*. 00023327. 00023329*.

References (not used):

[The following references contain insufficient data for adequate assessment of the tolerance.]

MRIDs: 00035666. 00113821.

Discussion of the data:

Ciba-Geigy Corp. (1978-1983; MRIDs 00013137 and 00023329, not previously reviewed) submitted data from four tests conducted in AL(1), GA(1), and SC(2) depicting residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on pecan nutmeats harvested 161-188 days following a broadcast application of the 80% WP formulation at 4 lb ai/A (1x the maximum registered single application rate). Combined residues of simazine and its chlorometabolites were <0.2 ppm (nondetectable; including <0.05 ppm each for simazine and G-28279, and <0.1 ppm for G-28273) in or on four treated and four control samples. Data were collected using method AG-295 for simazine and G-28279 and method AG-281 for G-28273. The limit of detection is 0.05 ppm for simazine and G-28279 and 0.1 ppm for G-28273. Recoveries were 76-92% for simazine, 76-114% for G-28279, and 85-122% for G-28273 from nutmeat samples fortified at 0.05-0.2 ppm. Samples were stored frozen for 130-215 days prior to analysis.

Additional data concerning simazine residues in or on pecans have not been reviewed here because they represent less than the maximum registered use pattern (MRIDs 00035666 and 00113821).

Geographic representation is adequate since the test states of AL(9%), GA(41%), LA(6%), SC(3%), and TX(18%) (tests from LA and TX were reviewed in the previous Residue Chemistry Chapter) accounted for ca. 77% of the 1987 U.S. crop production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). The available data indicate that combined residues of simazine and its chlorometabolites are <0.15 or <0.20 ppm (nondetectable) in or on pecan nutmeats following a single broadcast application of the WP formulation at the maximum registered rate of 4 lb ai/A. However, adequate data depicting residues of simazine hydroxymetabolites in or on pecans are needed. Additional data are therefore required.
Walnuts

Tolerance(s):

A tolerance of 0.2 ppm has been established for residues of simazine *per se* in or on walnuts [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF and 4 lb/gal FLC formulations are registered for directed application to walnut orchards at 2-4 lb ai/A in 20-40 gal of water/A. The 4 lb/gal EC may be tank mixed with other herbicides. The 34.67% EC MAI formulation (formulated with paraquat) may be applied at the same rate in 50-200 gal of water/A with a nonionic surfactant (for use in CA only). A 21-day PHI is effect for the tank mix of simazine with glyphosate; otherwise, no PHI has been established for simazine treatments. Application must not be made when nuts are on the ground.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine *per se* in or on walnuts. Pecan residue data were translated to satisfy the requirement for data on residues of simazine chlorometabolites in or on walnuts. However, because no PHI has been established for simazine use on walnuts, the maximum registered use pattern cannot be determined. Therefore, the levels of combined residues of simazine and its chlorometabolites cannot be assessed properly. The available data do not depict residues of simazine hydroxymetabolites in or on walnuts. However, no additional data will be required since the data requested on these metabolites for pecans may be translated to fulfill the requirements for simazine metabolite data from walnuts, provided that the posttreatment intervals corresponds to the PHI that is to be established. We note, however, that translated data cannot be used to support a crop group tolerance. The following amendments to use directions on simazine product labels are required:

- The registrants must propose label amendments that specify a PHI for simazine use on walnuts that is supported by the available field residue data.

No Mexican or Canadian tolerance or Codex MRL exists for simazine residues in or on walnuts; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.
References (used):

MRID(s): 00023923, 00131377.

References (not used):

[The following reference(s) contain insufficient data for adequate assessment of the tolerance.]

MRID(s): 00027971, 00035666.

Discussion of the data:

Ciba-Geigy Corp. (1983; MRID 00131377, not previously reviewed) submitted data from a CA test depicting residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on walnut nutmeats harvested 159 days following broadcast application of the 80% WP formulation at 4 lb ai/A (1x the maximum registered single application rate). Combined residues were <0.20 ppm (nondetectable; including <0.05 ppm each for simazine and G-28279, and <0.1 ppm for G-28273) in or on one treated sample and one control sample. Data were collected using method AG-295 for simazine and G-28279, and method AG-281 for G-28273. The limit of detection was 0.05 ppm for simazine and G-28279 and 0.1 ppm for G-28273. Recovery from one nutmeat sample was 65% for simazine fortified at 0.0625 ppm, 80% for G-28279 fortified at 0.125 ppm, and 136% for G-28273 fortified at 0.1 ppm. Samples were stored frozen for ca. 226-245 days prior to analysis.

Additional data concerning simazine residues in or on walnuts have not been reviewed here because they represent less than the maximum registered use pattern (MRIDs 00027971 and 00035666).

Geographic representation of the data is adequate since the test state of CA accounted for ca. 100% of the 1987 U.S. walnut production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). Because no PHI has been established, the maximum registered use pattern for simazine on walnuts cannot be determined; therefore, the levels of combined residues of simazine and its chlorometabolites in or on walnuts cannot be assessed properly. The available data do not depict residues of simazine hydroxymetabolites in or on walnuts. However, the data required for pecans may be translated to satisfy this requirement for walnuts, provided that the posttreatment intervals correspond to the PHI that is to be established.
Cereal Grains Group

Conclusions for the Cereal Grains Group:

The available data are insufficient to determine if a crop group tolerance is appropriate. If the registrant seeks a crop group tolerance, the following data are required:

○ Additional residue data are required for the representative crop group member corn (see crop section below for details).

○ Use directions must be proposed and appropriate supporting residue data must be submitted for the additional representative group members rice, sorghum, and wheat.

Corn (field and sweet)

Tolerance(s):

Tolerances of 0.25 ppm each have been established for residues of simazine per se in or on corn grain and fresh corn, including sweet corn kernels plus cob with husk removed (K+CWHR) [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for broadcast or banded preplant application at 3-4 lb ai/treated A in the fall preceding planting of corn.

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for broadcast or banded preplant or preemergence application at 2-4 lb ai/treated A. The 80% WP formulation may be applied by aerial equipment. The 80% WP and 4 lb/gal FlC may be tank mixed at lower use rates with other herbicides.

The 2 lb/gal FlC MAI formulation is registered for (i) broadcast preplant or preemergence application at 1-1.5 lb ai/A in 20 to 40 gal of water/A by ground equipment, or in 2 to 4 gal of water/A by aerial equipment; (ii) split preplant application of 1 lb ai/A in the fall followed by 1 lb ai/A in the spring; (iii) early preplant application of 2 lb ai/A in the fall or spring; or (iv) broadcast preplant or preemergence application at 1-1.5 lb ai/A in 20-60 gal of water/A to no-till corn planted directly into a cover crop or established sod crop.

The 34.67% FlC MAI formulation is registered for broadcast preemergence or preplant application at 2-3 lb ai/A in 20-60 gal of water. Application may be tank mixed with atrazine and paraquat and is applied by ground equipment.
Grazing of animals on all areas treated with simazine is prohibited.

Conclusions:

The Simazine Guidance Document dated 3/1/84 required additional data depicting residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on field corn grain and sweet corn K+CWHR and a field corn grain processing study; residue data for sweet corn canny waste were conditionally required. The sweet corn canny waste data will no longer be required because a tolerance has been established for residues in or on sweet corn forage. Data submitted in response to the Guidance Document (MRID 40614449) support the tolerance for residues of simazine per se in or on field corn grain and sweet corn K+CWHR, and indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites in or on these commodities exceeding that established tolerance level. Residue concentration factors for processed corn commodities could not be determined from the submitted processing study (MRID 40614449) because the raw commodities used bore nondetectable residues. The submitted data do not depict residues of simazine hydroxymetabolites in or on field corn grain or sweet corn K+CWHR. Therefore, the following additional data are required:

○ Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on field corn grain and sweet corn K+CWHR following preemergence application of representative WP, DF, or FlC formulations at 4 lb ai/A. Field corn tests must be conducted in IL(17%) or IA(18%), IN(9%) or OH(5%), MN(9%) or WI(5%), and NE(11%), which collectively represent ca. 70% of the 1987 U.S. field corn production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). Sweet Corn tests must be conducted in FL(7%), MN(22%) or WI(20%), NY(7%), and OR(10%) or WA(10%) which collectively account for ca. 70% of the 1985 U.S. commercial sweet corn production (Vegetables 1986 Summary, June 1987, Ag. Statistics Board, NASS, USDA).

○ A processing study depicting the potential for concentration of simazine residues of concern in wet milled products (starch, crude oil, and refined oil), dry milled products (grits, meal, flour, and crude and refined oils), and grain dust processed from field corn grain bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these products, appropriate food/feed additive tolerances must be proposed. The need for a processing study may be waived if field residue tests
using rates exaggerated by the highest theoretical concentration factor for any one of the processed products indicate that no detectable residues of concern occur in or on corn grain.

A Canadian tolerance has been established at 0.1 ppm (negligible residues) for residues of simazine per se in or on corn. No Mexican or Codex MRLs have been established for simazine residues in or on corn grain; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023336*. 00023272*. 00027973*. 40614449*.

References (not used):

[The following reference(s) contain only duplicate or insufficient data pertaining to adequate assessment of the tolerance.]


Discussion of the data:

**Field corn grain.** Ciba-Geigy Corp. (1988; MRID 40614449) submitted data from 18 tests conducted in CA(2), FL, IL, IN, IA, KS, MI, MN, MO, NE, NY(2), NC, OH, TX, WA, and WI depicting combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on field corn grain harvested 134-180 days following preemergence application of a WP formulation at 4.0 lb ai/A (1x the maximum registered seasonal rate). Combined residues in or on 27 treated and 13 control samples were <0.15 ppm (nondetectable, including simazine, G-28279 and G-28273 at <0.05 ppm each).

In the same submission Ciba-Geigy provided data from a field corn grain processing study conducted during 1985. Combined residues in or on the 18 samples representing nine processed products were <0.15 ppm (nondetectable). However, since grain samples exhibited no measurable weathered residues, the potential for concentration of simazine residues of concern cannot be determined from these data.

**Sweet corn kernels plus cobs with husks removed (ears).** Ciba-Geigy Corp. (1988; MRID 40614449) submitted field residue data from five tests conducted in CA, FL, NY, WA, and WI depicting combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on sweet corn ears harvested 74-93 days
following preemergence application of a WP formulation at 4.0 lb ai/A (1x the maximum seasonal rate). Combined residues in or on 10 treated and five control samples were <0.15 ppm (nondetectable, including simazine, G-28279 and G-28273 at <0.05 ppm each).

All data discussed above were collected using GLC Method AG-539. Fortification study data indicate residue recovery percentages that ranged from 67-111% for simazine, 61-105% for G-28279, and 51-93% for G-28273, which resulted from sample fortifications ranging from 0.05-1 ppm of each. Samples were stored frozen for 244-429 days prior to analysis.

Ciba-Geigy Corp. and Monsanto Co. (1971-1974; MRIDS 00023272, 00023336, and 00027973, not reviewed in the interim residue chemistry chapter) submitted data from four tests conducted in NY(2) and KY depicting residues of simazine per se in or on field corn grain and sweet corn K+CWR following application of 4-8 lb ai/A (1-2x). All samples bore negligible residues (<0.05 ppm). Samples were analyzed by the GLC method of PAM Vol. II or a modification of AG-126 method.

Additional residue data concerning simazine residues in or on sweet corn and field corn grain have not been reviewed here because they represent analytical methods considered inadequate for data collection, postemergence tests, or tests receiving less than the maximum exposure potential registered use rate.

Geographic representation of the data is adequate. The test states of CA(<1%), FL(<1%), IL(17%), IN(9%), IA(18%), KS(2%), MI(3%), MN(9%), MO(3%), NE(11%), NY(1%), NC(1%), OH(5%), TX(2%), WA(<1%) and WI(5%) account for >70% of the 1987 U.S. production of field corn grain (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). The test states of CA(2%), FL(7%), NY(7%), WA(10%), and WI(20%) along with neighboring states of MN(22%) and OR(10%) account for ca. 80% of 1986 U.S. sweet corn production (Vegetables, 1986 Summary, Ag. Statistics Board, NASS, USDA, p. 9 & 47). The submitted data support the tolerance for residues of simazine per se in or on corn grain and sweet corn ears (K+CWR). These data would also support a tolerance that included residues of the chloroanabolites in the definition at the same quantitative level. Hydroxymetabolite data are not available; therefore, further data are required.

Forage, Fodder, and Straw of Cereal Grains Group

Conclusions for the Forage, Fodder, and Straw of Cereal Grains Group:

The available data are insufficient to determine if a crop group tolerance is appropriate. If the registrant seeks a crop group tolerance, the following data are required:
Additional residue data are required for forage, fodder, and straw commodities of the representative crop group member corn (see crop section below for details).

Use directions must be proposed and appropriate supporting residue data must be submitted for the additional representative group members wheat and any other cereal grain crop.

Corn forage and fodder

Tolerance(s):

Tolerances of 0.25 ppm have been established for residues of simazine per se in or on corn forage and fodder [40 CFR §180.213].

Use directions and limitations:

See the "Corn grain (field and sweet)" section under the Cereal Grains Group for details of use directions and limitations.

Conclusions:

The Simazine Guidance Document dated 3/1/84 required additional data depicting residues of simazine and its chlorometabolites in or on corn forage and fodder. The data submitted in response to the Guidance Document (MRID 40614449) support the tolerance for residues of simazine per se in or on corn forage and fodder and indicate that the maximum registered use pattern will not result in combined residues of simazine and its chlorometabolites exceeding that same established tolerance level. However, the available data do not depict residues of simazine hydroxymetabolites in or on corn forage and fodder. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on field corn and sweet corn forage and fodder following preemergence application of representative WP, DF, or F1C formulations at 4 lb ai/A. Tests must be conducted in conjunction with those required for field corn grain and sweet corn K+CWH.

A Canadian tolerance has been established at 0.1 ppm (negligible residues) for residues of simazine per se in or on corn. No Mexican or Codex MRLs have been established for simazine residues in or on corn forage and fodder; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodities.
References (used):

MRID(s): 00023272*. 00027972*. 00027973*. 00023336*. 40614449*.

References (not used):

[The following reference(s) were not used because they contain duplicate data or data not useful in assessing the tolerance for simazine]


Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614449) submitted data from 18 tests conducted in CA(2), FL, IL, IN, IA, KS, MT, MN, MO, NE, NY(2), NC, OH, TX, WA, and WI depicting combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on field corn forage and fodder harvested 59-176 days following preemergence application of a WP formulation at 4-8 lb ai/A (1-2x maximum use rate). Combined residues were <0.15 ppm (nondetectable, including simazine, G-28279 and G-28273 at <0.05 ppm each) in or on 23 of 24 forage samples; a single sample bore 0.06 ppm simazine per se. Combined residues in or on 27 corn fodder samples were <0.15(nondetectable)-0.11 ppm, including <0.05 ppm each of simazine and G-28279, and <0.05-0.11 ppm of G-28273. Samples from the TX test having combined residues of 0.19-0.2 ppm may have been contaminated, as a control sample from the same test bore combined residues of 0.16 ppm. One forage sample harvested 176 days following application of a 2x rate bore combined residues of <0.15 ppm (nondetectable), while a fodder sample from the same test bore residues of 0.07 ppm, including <0.05 ppm simazine, <0.05 ppm G-28279, and 0.07 ppm G-28273. Samples were stored at -15 C for 244-459 days prior to analysis by GLC Method AG-539. Recovery efficiencies were 58-119% from samples fortified with 0.20-1.00 ppm of simazine and its metabolites.

Ciba-Geigy Corp. and Monsanto Co. (1971-1974; MRIDS 00023272, 00023336, 00027972, and 00027973, not reviewed in the interim residue chemistry chapter) submitted data from four tests conducted in NY(2), NJ, and KY depicting residues of simazine per se in or on field corn and sweet corn forage or fodder following application of 4-8 lb ai/A (1-2x). Nine samples all bore negligible residues (<0.05 ppm). Samples were analyzed by the GLC method of PAM Vol. II or a modification of AG-126 method.
Additional residue data submitted concerning simazine residues in or on corn forage and fodder were not reviewed here because they do not represent the maximum exposure potential under registered uses. These include tests of postemergence applications, tests receiving less than the maximum use rate, or tests that were analyzed using an inadequate method.

Geographic representation of the data is adequate since the test states of CA(<1%), IL(17%), IN(9%), IA(18%), KS(2%), KY(2%), MI(3%), MN(9%), MO(3%), NE(11%), NJ(<1%), NY(1%), NC(1%), OH(5%), and TX(2%) account for ca. 80% of the 1987 U.S. field corn production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). These data support the tolerances for residues of simazine per se in or on corn forage and fodder and indicate that the maximum registered use pattern would not result in combined residues of simazine and its chlorometabolites exceeding that same tolerance level. However, the data do not depict residues of simazine hydroxymetabolites in or on corn forage and fodder. Therefore, additional data are required.

Miscellaneous Commodities

Artichokes

Tolerance(s):

A tolerance of 0.5 ppm has been established for residues of simazine per se in or on artichokes [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF and 4 lb/gal FlC formulations are registered for a single directed application per year to artichokes at 2-4 lb ai/A in 20-40 gal of water/A following the last fall tillage. Simazine should not be used on gravelly, sand, or loamy sand soils.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on artichokes, but it required additional data on combined residues simazine and its chlorometabolites (G-28279 and G-28273). Data submitted in response to the Guidance Document (MRID 40614444) show that combined residues will not exceed the established tolerance level when harvested 0-7 days following the maximum registered use pattern. The available data do not depict residues of simazine hydroxymetabolites in or on artichokes. Therefore, the following additional data are required:
Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on artichokes harvested following directed spray application of representative WP, DF, or F1C formulations at 4.0 lb ai/A according to label directions. Tests must be conducted in CA.

No Canadian or Mexican tolerances or Codex MRLs exist for simazine residues in or on artichokes; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023918. 40614444*.

References (not used):

[The following reference(s) were not used because they represent duplicate data or data that were not useful in assessing the tolerance.]

MRID(s): 00025883. 00027922.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614444) submitted data from three CA tests depicting combined residues of simazine and its two chlorometabolites (G-28279 and G-28273) in or on artichokes. Samples were harvested at intervals of 0, 1, 3 and 7 days following a single broadcast directed application of a WP formulation of simazine at 4.0 lb ai/A (1 x the maximum use rate) in 20 gal of water using ground equipment. Combined residues were <0.15 ppm (nondetectable including simazine, G-28279 and G-28273 at <0.05 ppm each) in or on 22 of 24 treated samples and six control samples; the other two treated samples harvested 0 and 3 days posttreatment bore combined residues of 0.05-0.07 ppm (including simazine at 0.05-0.07 ppm and nondetectable chlorometabolite residues). Samples were stored at -15 C for 446-534 days prior to analysis by GLC method AG-539. Recoveries were 70-105% from samples fortified with simazine and its metabolites at 0.05-1.00 ppm. The tests were conducted with adequate geographic representation as all domestic artichokes are produced in CA (1982; Census of Agriculture, Vol. 1, Part 51, p. 335).

Additional submitted data are not reviewed because the tests were conducted at less than the maximum registered use pattern. The data discussed above indicate that combined residues of simazine and its chlorometabolites will not exceed support the established tolerance for residues of simazine per se in or on artichokes and would support a tolerance that included residues of the chlorometabolites in the definition at the same level.
Asparagus

Tolerance(s):

A tolerance of 10 ppm has in been established for residues of simazine per se in or on asparagus [40 CFR §180.213].

Use directions and limitations:

The 4% G formulation is registered for preemergence application to established asparagus cutting beds at 2 oz product/100 ft² (2.18 lb ai/A) in the spring. The 80% WP, 90% DF and 4 lb/gal FlC formulations are registered for application to established asparagus (one year or more) at 2-4 lb ai/A in 20-40 gal of water/A. Application is made in the spring at least three days before the first cutting or following harvest. Simazine should not be applied to sand, loamy sand, or gravelly areas of fields in order to avoid crop injury. A 3-day PHI is in effect.

Conclusions:

The Simazine Guidance Document dated 3/1/84 required additional residue data to assess the tolerance for residues of simazine stated per se in or on asparagus, including data on chlorometabolite residues. Data submitted in response to the Guidance Document (MRID 40614445) indicate that combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on asparagus will not exceed the established tolerance level following simazine application according to the maximum registered use pattern. The available data do not depict residues of simazine hydroxy metabolites in or on asparagus. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxy metabolites of concern in or on asparagus harvested 3 days after application of representative WP, DP, FlC formulations at 4 lb ai/A in 20-40 gal of water/A. Tests should be conducted in CA(49%), MI(11%), and WA(35%) which collectively account for >90% of 1986 U.S. asparagus production (Vegetables, 1986 Summary, Ag. Statistics Board, NASS, USDA, p. 18).

We note that Ciba-Geigy Corp. (1988; MRID 40614445) has proposed reducing the tolerance to 0.5 ppm and increasing the PHI from 3 to 7 days. The available residue data (including chlorometabolites) would support these changes.

A Canadian tolerance of 0.1 ppm (negligible residues) has been established for residues of simazine per se in or on asparagus.
No corresponding Mexican tolerance or Codex MRL has been established; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023899. 40614445*.

References (not used):

[The following reference(s) were not used because they represent duplicate data or data that were not useful in assessing the tolerance.]

MRID(s): 00023242. 00023970. 00025884. 00027821. 00113675. 00138259.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614445) submitted data from seven tests conducted in CA, IL, MD, MI, NJ, NC, and WA depicting residues of simazine and its chloromethylates in or on asparagus. Samples were harvested 3, 7 and 10 days following a single application of a WP formulation at 4.0 lb ai/A (1x the maximum registered use rate) in 18-40 gal of water/A. Residues of simazine per se were <0.05(nondetectable)-3.9 ppm in or on 12 samples harvested 3 days posttreatment, and <0.05(nondetectable)-0.44 ppm in or on 28 samples harvested 7-10 days posttreatment. Residues of the two chloromethylates were nondetectable (<0.05 ppm each) in 35 samples, while G-28279 occurred at levels of 0.05-0.09 ppm in or on the remaining five samples. Combined residues of simazine and its chloromethylates ranged from <0.15-3.9 ppm (including <0.05 ppm each for simazine, G-28279 and G-28273). Fourteen control samples bore combined residues of <0.15(nondetectable)-0.20 ppm. Samples were stored at -15 C for 621-748 days prior to analysis by GLC method AG-539, which has a limit of detection of 0.05 ppm. Recoveries were 58-132% from samples fortified with simazine and the metabolites at 0.05-1.00 ppm.

Geographic representation is adequate since the states of CA(49%), MI(11%), NJ(2%) and WA(35%) account for virtually all of the commercial U.S. asparagus production (Vegetables, 1986 Summary, Ag. Statistics Board, NASS, USDA, p. 18). Additional data submitted were not reviewed because they represent less than the maximum registered use pattern. These include tests with samples taken beyond the established PHI or conducted by unspecified methodology, and tests receiving less than the maximum registered use rate or applications of simazine at exaggerated dilutions.
Avocados

Tolerance(s):

A tolerance of 0.25 ppm been established for residues of simazine per se in or on avocados [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FC formulations are registered for directed broadcast or banded application to avocado groves at 2-4 lb ai/A in 20-40 gal of water/A (CA and FL only). Treatment is made after final preparation of groves (unspecified). The 4 lb/gal EC may be tank mixed with other herbicides. The 34.67% EC MAI formulation (formulated with paraquat) may be applied at the same rate with a nonionic surfactant in 50-200 gal of water/A. Simazine should not be applied on gravelly, sand or sandy loam soils. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for residues of simazine per se in or on avocados, but required additional residue data on simazine chlorometabolites (G-28279 and G-28273). Data submitted in response to the Guidance Document (MRID 40614446) indicate that combined residues of simazine and its chlorometabolites in or on avocados will not exceed the established tolerance level following application of simazine according to the maximum registered use pattern. The available data do not depict residues of simazine hydroxymetabolites in or on avocados. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chloromethabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on avocados following directed broadcast application of representative WP, DF, and FL formulations at 4.0 lb ai/A applied in 20-40 gal/A. Tests must be conducted in the state of CA.

No Canadian or Mexican tolerances or Codex MRLs exist for simazine residues in or on avocados; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00092496. 40614446*.
References (not used):

[The following reference(s) were not used because they represent duplicate data or data that were not useful in assessing the tolerance.]

MRID(s): 00023972. 00025885. 00027942.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614446) submitted residue data from nine CA tests depicting combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on avocados. Eighteen samples were harvested 33, 67, or 85 days following a single broadcast application of a WP formulation at 4.0 lb ai/A (1x the maximum registered use rate) in 30 or 100 gal of water/A. Combined residues in or on treated samples and six control samples were all <0.15 ppm (nondetectable, including simazine, G-28279 and G-28273 at <0.05 ppm each). Samples were stored at -15 C for 342-619 days prior to analysis by GLC Method AG-539, which has limits of detection of 0.05 ppm for each compound. Recovery efficiencies were 63-107% from samples fortified with simazine and its metabolites at 0.05-0.2 ppm each. Geographic representation is adequate since the state of CA accounts for 86% of the U.S. commercial avocado production (1982 Census of Agriculture, Vol 1., Part 51, p. 360). Additional avocado residue data have not been reviewed here because they involve tests receiving less than the maximum registered use rate.

Bananas

Tolerance(s):

A tolerance of 0.2 ppm has been established for residues of simazine and its metabolites 2-amino-4-chloro-6-ethylamino-s-triazine and 2,4-diamino-6-chloro-s-triazine in or on bananas [40 CFR §180.213(a)].

Use directions and limitations:

There are no registered uses on bananas in the U.S. for products containing simazine. The tolerance was established for residues occurring on fruit imported into the U.S. after treatment with simazine in the country of origin according to the following use patterns.

A 40% WP MAI formulation is registered for use on bananas in Central America as a preemergence or early postemergence treatment. The single use rate is 1.6 lb ai/A, applied in 20-30 gal of water/A. Repeat applications may be made at 30-day intervals; the maximum annual application rate is 6.4 lb ai/A. A 0-day PHI
is in effect (use directions are taken from Section B of PP#6E1725).

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the tolerance for combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on bananas. No additional data were required, and none have been submitted. However, the available data do not depict residues of simazine hydroxymetabolites in or on bananas. Therefore, the following additional data are required:

- Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on bananas following application of a representative formulation of simazine at the maximum registered use rate.

No Canadian or Mexican tolerances or Codex MRLs exist for simazine residues in or on bananas; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023273. 00023274. 00023275. 00023276. 00023277.

Discussion of the data:

N/A.

Olives

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on olives [40 CFR §180.213].

Use directions and limitations:

The 80% WP, 90% DF, and 4 lb/gal FlC formulations are registered for directed application to olive groves at 2-4 lb ai/A in 20-40 gal of water/A after final preparation of groves. Treatment may be repeated on an annual basis in mid winter. Spray must not contact foliage, stems, or fruit.
Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the established tolerance for simazine per se in or on olives, but additional data were required on residues of simazine chlorometabolites. An olive processing study was conditionally required, depending on the outcome of field residue trials. Data submitted in response to the Guidance Document (MRID 40614447) indicate that combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on olives will not exceed the established tolerance level harvested following simazine application according to the maximum registered use pattern. The submitted processing study did not use fruit bearing measurable weathered residues. The available data do not depict residues of simazine hydroxymetabolites in or on olives nor do they depict residue data resulting from a processing study illustrating the potential for the concentration of residues in olive oil. Therefore, the following additional data are required:

- Data depicting simazine residues of concern, including its hydroxymetabolites, in or on olives following a single application of a representative formulation at 4.0 lb ai/A in 20-40 gal of water in the state of CA.

- A processing study depicting the potential for concentration of simazine residues of concern in oil processed from olives bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in the oil, an appropriate food additive tolerance must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the theoretical concentration factor for oil indicate that no detectable residues of concern occur in or on olives.

No Canadian or Mexican tolerances or Codex MRLs exist for simazine residues in or on olives; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.

References (used):

MRID(s): 00023973. 40614447*.

References (not used):

[The following reference(s) were not used because they represent duplicate data or data collected at less than the maximum registered use pattern.]
MRID(s): 00027942. 00030179.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614447) submitted residue data from two CA tests depicting combined residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on olive fruits harvested 229-234 days after broadcast application of a WP formulation at 4.0 lb ai/A (1x the maximum registered use rate) in 20-30 gal/A of water. Combined residues of simazine and its chlorometabolites in or on four treated samples and two control samples were all <0.15 ppm (nondetectable, including simazine, G-28279, and G-28273 at <0.05 ppm each).

In the same submission Ciba-Geigy provided data from a processing study conducted in 1985 which found combined residues of <0.15 ppm (nondetectable, including simazine, G-28279 and G-28273 at <0.05 ppm each) in or on the three fruit samples and three oil samples. Since the fruit samples exhibited no measurable weathered residues, the potential for concentration of simazine residues of concern cannot be determined from these data.

All of the data discussed above were collected using GLC Method AG-539, which has a limit of detection of 0.05 ppm. Recoveries were 80-110% for simazine and G-28279, and 57-75% for G-28273, from samples fortified at 0.05-0.2 ppm. Samples were stored at -15 C for 503-588 days prior to analysis. Geographic representation of the data is adequate since CA produces 100% of the U.S. commercial olive crop Additional data have not been reviewed here because they represent tests conducted at less than the maximum registered use pattern.

Sugarcane

Tolerance(s):

A tolerance of 0.25 ppm has been established for residues of simazine per se in or on sugarcane [40 CFR §180.213]. Food additive tolerances of 1 ppm each have been established for residues of simazine per se in the sugarcane byproducts, molasses and syrup, resulting from applications of simazine to sugarcane plants [40 CFR §185.5350].

Use directions and limitations:

The 80% WP, 90% DF and 4 lb/gal FL1C formulations are registered for application at planting or following harvest (if ratoon crop is to follow) at 2-4 lb ai/A, and for one postemergence broadcast application or up to two interline-directed applications prior to close-in at the same single use rate. Applications should be made in 20-40 gal of water/A, and the maximum total use rate per
crop cycle should not exceed 10 lb ai/A. Treated forage must not be fed to or grazed by livestock. No PHI has been established.

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the established tolerances for residues of simazine per se in or on sugarcane and sugarcane byproducts (molasses and syrup), but required additional data on residues of simazine and its chlorometabolites in or on sugarcane and sugar-
cane forage. A processing study was conditionally required, depending on the outcome of field residue trials. Data submitted in response to the guidance document (MRID 40614448) show that combined residues of simazine and its chlorometabolites (G-28279 and G-28273), will not exceed the 0.25 ppm tolerance in or on sugarcane. Concentration factors for residues in processed commodities cannot be determined from the submitted processing study studies because the limits of detection claimed for the analytical method have not been validated. A restriction prohi-
biting treated forage to be fed to livestock was added to the label in lieu of submitting a tolerance proposal for sugarcane forage. The available data do not depict residues of simazine hydroxymetabolites in or on sugarcane. The following additional data are required:

- Data depicting residues of simazine, its chlorometabo-
lites (G-28279 and G-28273), and hydroxymetabolites of concern in or on sugarcane harvested at normal crop maturity following three applications of representative WP, 90% DF and 4 lb/gal F1C formulations, including a postemergence broadcast application at 2 lb ai/A, and two interline directed applications prior to close-in at 4 lb ai/A/application in 20-40 gal of water/A (seasonal use rate of 10 lb ai/A) Tests must be performed in FL or LA and HI.

- A processing study depicting the potential for concentra-
tion of simazine residues of concern in molasses, refined sugar, and bagasse processed from sugarcane bearing measurable weathered residues. The established food/feed additive tolerance for molasses will be reassessed following evaluation of these data.

No Canadian or Mexican tolerances or Codex MRLs exist for simazine residues in or on sugarcane; therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for this commodity.
References (used):

MRID(s): 00023911. 00084430. 40614448*.

References (not used):

[The following reference(s) were not used because they represent duplicate data or data not useful in assessing the tolerance.]

MRID(s): 00023926. 00027827. 00084429.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614448) submitted residue data from three tests conducted in FL(2) and LA(1) depicting residues of simazine and its chlorometabolites (G-28279 and G-28273) in or on sugarcane. Tests were conducted in 1985 and 1986, and six samples were harvested 108 and 126 days following three applications of a WP or DF formulation at a total application rate of 10 lb ai/A (1x the maximum registered seasonal use rate). Combined residues of simazine and its chlorometabolites were all nondetectable (<0.15 ppm including simazine, G-28279 and G-28273 at <0.05 ppm each). Three untreated control samples also exhibited nondetectable combined residues (<0.15 ppm).

Also included in this report are data from a sugarcane processing study depicting combined residues of simazine plus chlorometabolites that resulted from a processing study on sugarcane harvested 110 days following total treatments of 10 and 20 lb ai/A (1x and 2x the maximum registered use rates). Combined residues of simazine and its chlorometabolites were 0.05 and 0.06 ppm, and 0.06 and 0.09 ppm in samples from cane receiving the 1x and 2x treatments, respectively, with a limit of detection of 0.01 ppm (see below). Combined residues in or on one sample each of processed samples from each treatment rate are as follows: bagasse, 0.24 and 0.31 ppm; mixed juice, 0.15 and 0.23 ppm; clarified juice, <0.15 (nondetectable) and 0.18 ppm; hydrosol, <0.15 (nondetectable) and 0.16 ppm; syrup, 0.22 and 0.37 ppm; molasses, 0.63 and 0.65 ppm; and sugar, <0.15 ppm (nondetectable) at both rates. These fraction were analyzed with a 0.05 ppm limit of detection.

All of the samples discussed above were stored at -15 C for a period of 458-844 days prior to analysis using GLC Method AG-539, which has limits of detection of 0.05 ppm for each of the three compounds. The limit of detection was claimed to be 0.01 ppm in some of the residue analyses reported in this study; however, this was not verified with adequate fortification data. Recoveries were 69-128% from samples fortified with simazine and its metabolites at 0.05-0.2 ppm.

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Geographic representation is adequate since the states of FL(47%) and LA(22%) account for ca. 70% of the 1987 U.S. sugarcane production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). These data support the tolerance for simazine per se in or on sugarcane and also support the food additive tolerance established for simazine per se in the sugarcane byproducts, molasses and syrup. However, the degree of concentration of residues of concern in processed products could not be adequately assessed because the processing study did not verify the level of residues on the whole sugarcane. Therefore, additional data are required.
MAGNITUDE OF THE RESIDUE IN MEAT, MILK, POULTRY, AND EGGS

Milk, and the Fat, Meat, and Meat Byproducts of Cattle, Goats, Hogs, Horses, and Sheep

Tolerances:

Tolerances of 0.02 ppm (negligible residues) have been established for residues of simazine per se in milk, and the fat, meat, and meat byproducts of cattle, goats, hogs, horses, and sheep [40 CFR §180.213].

Conclusions:

The Simazine Guidance Document dated 3/1/84 concluded that the available data support the established tolerances for residues of simazine per se in milk, and the fat, meat, and meat byproducts of cattle, goats, hogs, horses, and sheep. However, the Guidance Document did require additional ruminant feeding studies involving the chlorometabolites G-28279 and G-28273; this requirement was conditional on the demonstrated absence of these chlorometabolites as metabolites of simazine in ruminant metabolism studies. If the required animal metabolism studies reveal additional metabolites of toxicological concern, additional ruminant feeding studies may be required.

Data submitted (1988; MRID 40614456) in response to the Guidance Document are adequate to support a tolerance for combined residues of simazine and chlorometabolites G-28279 and G-28273 provided the theoretical dietary intake, when calculated, does not exceed feeding levels. Presently, the nature of the residue in animals is not adequately understood, and numerous data gaps exist concerning the magnitude of the hydroxymetabolites in feed items of animals. Therefore, the expected dietary intakes for beef and dairy cattle, and swine will not be calculated. The available data indicate that combined residues of simazine and its chlorometabolites were <0.03 ppm (nondetectable) in milk and tissues from cows fed simazine at 0.5 ppm in the diet. Finite residues of G-28273 were 0.01-0.04 ppm in milk and 0.01 ppm and in tenderloin and kidney samples from cows fed at 5 ppm in the diet.

Hydroxysimazine (G-30414) residues in milk reviewed in the previous Chemistry Chapter (MRID 00025452) were nondetectable (<0.05 ppm) following a feeding study of dairy cows with simazine at 50 ppm.

Note to the PM: We recommend that the phrase "negligible residues" be deleted from the tolerance entries for milk and animal tissues.
No Canadian or Mexican tolerances or Codex MRLs have been established for simazine residues in milk or animal tissues. Therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for these commodities.

References (used):

MRIDs: 00025452. 00026977. 00080629. 40614456*.

References (not used):

[The following references contained only duplicate or irrelevant data concerning simazine residues in milk and ruminant tissues.]

MRIDs: 00025450. 00055681. 00055682. 00080628. 00080630.
00093525. 00111685. 40614430.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614456) submitted data from a ruminant feeding study in which nine lactating dairy cows (three per dose group) received an oral daily dose of technical grade simazine (96.9% purity) via balling gun for 28 consecutive days at 0.5, 2.5, and 5 ppm in the diet; two additional cows served as controls. Milk samples were collected twice per day at 0, 1, 5, 7, 12, 19, and 26 days following the initiation of treatment. One cow from each feeding level was sacrificed 20-21 hours following the daily dosing on test days 14, 21, and 28, and the remaining cows were sacrificed on the 28th day; control cows were sacrificed on days 14 and 28. Residues were determined in blood, liver, kidney, perirenal and omental fat, and muscle tissue samples collected at the time of sacrifice.

Combined residues of simazine and its chlorometabolites G-28279 and G-28273 in milk collected throughout the dosing period from cows dosed at 0.5 ppm were <0.03 ppm; cows dosed at 2.5 ppm yielded milk containing residues of <0.03 ppm (including G-28273 at 0.01 ppm); and cows dosed at 5 ppm yielded milk containing residues ranging from <0.03 to <0.05 ppm (including G-27273 at 0.01-0.04 ppm).

Combined residues of simazine and its chlorometabolites G-28279 and G-28273 were nondetectable (<0.03 ppm) in tissues (blood, round muscle, loin muscle, kidney, liver, omental fat, and perirenal fat) from dairy cows at all sample intervals and dose levels with two exceptions. Residues of G-28273 (0.01 ppm) were found in tenderloin and kidney samples from the cow fed 5 ppm and sacrificed on day 21.

Combined residues of simazine and its chlorometabolites G-28279 and G-28273 were nondetectable (<0.03 ppm each) in ten milk samples and in all tissues (two samples each of blood, round
muscle, loin muscle, kidney, liver, omental fat, and perirenal fat) from control cows. Milk samples were analyzed by the GLC method AG-497. Tissues were analyzed using GLC method AG-540 (modification of method AG-476). The limits of detection were 0.01 ppm for each compound in all tissues. Residue results were corrected for procedural recoveries obtained from fortified controls. Recoveries from 13 milk samples fortified at 0.01-0.2 ppm were 58-101% for simazine, 64-86% for G-28279 and 50-106% for G-28273. Recoveries from six tissue samples fortified at 0.01-0.2 ppm were 74-120% for simazine, 73-99% for G-28279, and 56-92% for G-28273. Milk samples were stored at -15 C for ca. 344-402 days. Tissues were stored at the same temperature for ca. 176-265 days.

Eggs and the Fat, Meat, and Meat Byproducts of Poultry

Tolerance:

Tolerances of 0.02 ppm (negligible residues) have been established for residues of simazine per se in eggs, and the fat, meat, and meat byproducts of poultry [40 CFR §180.213].

Conclusions:

The Simazine Guidance Document dated 3/1/84 required poultry feeding studies involving the chlorometabolites G-28279 and G-28273; this requirement was conditional on the demonstrated absence of these chlorometabolites as metabolites of simazine in poultry metabolism studies.

Data submitted (1988; MRID 40614457) in response to the Guidance Document are adequate to support a tolerance for combined required of simazine and its chlorometabolites G-28279 and G-28273 provided the theoretical dietary intake, when calculated, does not exceed feeding levels. Presently, the nature of the residue in animals is not adequately understood, and numerous data gaps exist concerning the magnitude of the hydroxy-metabolites in feed items of animals. Therefore, the expected dietary intakes for poultry will not be calculated. These data indicate that combined residues of simazine and its chlorometabolites were <0.03 ppm (nondetectable) in eggs and tissues from laying hens fed up to 1 ppm in the diet.

Note to the PM: We recommend that the phrase "negligible residues" be deleted from the tolerance entries for eggs and poultry tissues.

No Canadian or Mexican tolerances or Codex MRLs have been established for simazine residues in eggs or poultry tissues. Therefore, no questions of compatibility exist with respect to U.S. tolerances and Codex MRLs for these commodities.
References (used):
MRIDs: 40614457*.

References (not used):
[The following references contained only duplicate data concerning simazine residues in eggs and poultry.]
MRIDs: 40614442.

Discussion of the data:

Ciba-Geigy Corp. (1988; MRID 40614457) submitted data from a poultry feeding study in which 45 mature Leghorn hens (15 per dose group) were fed technical grade simazine (99.8% purity) ad libitum at levels of 0.1, 0.5, or 1 ppm in the feed for 28 consecutive days; fifteen additional hens served as controls. Feed samples were prepared fresh weekly; simazine concentrations in the chicken feed were regularly analyzed for possible degradation. Egg samples were taken from each treatment group on test days 0 (pretreatment), 1, 3, 7, 14, 21, and 28. Three hens of each treatment group were sacrificed after 7, 14, 21, and 28 days, and samples of skin plus attached fat, liver, fat, and lean muscle (breast plus thigh) were analyzed.

Combined residues were <0.03 ppm (nondetectable, including <0.01 ppm each of simazine, G-28279, and G-28273) in all tissue samples (12 each for skin, fat, liver, and lean muscle) from all feeding levels and sample intervals. Combined residues in 12 samples of eggs were <0.03 ppm (nondetectable); six additional samples yielded combined residues of ≤0.03 ppm (including G-28273 at 0.01 ppm).

Combined residues were <0.03 ppm (nondetectable) in four egg samples and all tissue samples from control hens. Poultry tissue and egg samples were analyzed by the GLC method AG-540 (modification of AG-476) which is adequate for data collection. The reported limits of detection were 0.01 ppm for each compound in egg and all tissues. Residue results were corrected for procedural recoveries obtained from spiked controls. Recoveries from egg and tissue samples fortified at 0.01-0.5 ppm were 60-101% for simazine, 67-109% for G-28279 and 61-127% for G-28273. All samples were stored at -15 C, eggs for 272-333 days and tissues for 314-499 days.
NATURE AND MAGNITUDE OF THE RESIDUE IN FISH AND POTABLE WATER

Tolerances:

A tolerance of 12 ppm has been established for residues of simazine and its metabolites 2-amino-4-chloro-6-ethylamino-s-triazine and 2,4-diamino-6-chloro-s-triazine in fish [40 CFR §180.213(a)].

A food additive tolerance of 0.01 ppm has been established for the combined residues of simazine and its metabolites 2-amino-4-chloro-6-ethylamino-s-triazine and 2,4-diamino-6-chloro-s-triazine in potable water [40 CFR §185.5350 formerly 21 CFR §193.400(a)].

Note to the PM: Under present policy, the Agency does not establish tolerances for pesticides in potable water (47 FR 241:56137; December 1, 1982); therefore, we recommend that this entry be deleted from 40 CFR §185.5350 (formerly 21 CFR §193.400).

Use directions and limitations:

The 80% WP, 90% G and 1% F1C formulations are registered for use on aquatic areas for treatment of standing or drained ponds and fish hatcheries. Refer to Table 9 for specific sites, formulations, and applications rates. Treatment is restricted to ponds with little or no outflow and no more than 8 pounds of active ingredient per acre can be used where striped bass fry or fingerlings are cultivated. In drained ponds, only one application per year may be made to the pond bottom in 20-40 gallons of water followed by a period of 72 hours before refilling the pond; split applications may be made to standing ponds. Spot treatment applications may not be made. Water from treated ponds may not be used for irrigation of agricultural crops, watering of livestock, or human consumption for 1 year following application.
<table>
<thead>
<tr>
<th>Site (drained/undrained)</th>
<th>Formulation</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ponds</td>
<td>90% G, 80% WP</td>
<td>1.35-3.42 lb ai/A-ft</td>
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<tr>
<td></td>
<td></td>
<td>2.7 -6.75 lb ai/A-ft</td>
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<tr>
<td></td>
<td>1% FLC</td>
<td>8-12 lb ai/A³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.17-0.4 lb ai/A-ft</td>
</tr>
<tr>
<td>Fish Hatcheries</td>
<td>90% G, 80% WP</td>
<td>8-12 lb ai/A³</td>
</tr>
<tr>
<td>Utility Cooling Ponds and Waste Water and Treatment Ponds</td>
<td>80% WP</td>
<td>1.4-3.4 lb ai/A-ft</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.7-6.8 lb ai/A-ft</td>
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<tr>
<td></td>
<td></td>
<td>8-12 lb ai/A³</td>
</tr>
</tbody>
</table>

* May be used on drained ponds only.

Conclusions:

Fish: The Simazine Guidance Document dated 3/1/84 concluded that the nature of the residue in fish is adequately understood and that combined residues of simazine and its chlorometabolites G-28279 and G-28273 (plus the hydroxymetabolite G-30414 not included in the current tolerance definition) will not exceed the established tolerance of 12 ppm. No additional data were required at that time, and none have been submitted; however, residue studies on fish and shellfish reflecting analysis for simazine and all metabolites of concern (i.e., chloro- and hydroxymetabolites) are required. The following additional data are required now because hydroxymetabolites have recently been recognized as metabolites of potential toxicological concern and previously accepted studies are no longer considered to be acceptable due to evolving Branch policies and Guidelines:

- Residue studies must be submitted pertaining to fish and freshwater shellfish exposed to simazine applied in the water at the maximum rate according to label directions. Representative samples must be analyzed by adequate analytical methods and all simazine residues of concern must be determined. The registrant must propose a tolerance or an exemption from the requirement of a tolerance for simazine residues of concern in freshwater shellfish. Alternatively, for shellfish, the registrant(s) may propose label restrictions prohibiting use of simazine where commercial shellfishing is practiced.

Data reviewed for the Guidance Document revealed that exposure of bluegill sunfish to water containing 2.5 ppm [¹³C]simazine for 14 days resulted in accumulation of 7.5 ppm total [¹³C]-residues in
the muscle of the fish. Of this radioactivity, 76.6% was identified: simazine per se comprised 51.2%, chlorometabolites G-28279 and G-28273 comprised 19.4% and 4.2%, respectively; and hydroxy-metabolites G-30414, G-17792, and G-17791 comprised 0.1%, 0.6%, and 1.1%, respectively.

No Canadian or Mexican tolerance or Codex MRLs are in effect for simazine residues in fish or shellfish. Therefore, no compatibility questions exist with respect to the Codex MRL.

**Potable water:** The Simazine Guidance Document dated 3/84 concluded the combined residues of simazine and its chlorometabolites G-28279 and G-28273 are nondetectable (<0.03 ppm in potable water following registered use and recommended a tolerance increase from 0.01 ppm to 0.03 ppm to accommodate the nondetectable residue sum of these compounds at <0.01 ppm each.

Additional residue chemistry data were not required in the 1984 Guidance Document; however, additional data to support environmental fate requirements for Guidelines Reference No. 164-2 submitted in response to the 1984 Guidance Document indicate that combined residues of simazine and its chlorometabolite G-28279 may be up to 0.70 in pond water 1 year following registered use; an additional residue contribution of the hydroxy metabolite G-30414 (presently not included in the tolerance definition) may be up to 0.11 ppm. Thus, the following additional data are required:

1. Simazine residues of concern in water sampled 1 year following split application of a G and a WP formulation represented in separate tests to a standing pond at 6.8 lb ai/A-ft/application. Pesticide residue levels in potable water are no longer regulated by the establishment of food additive tolerances, but rather by setting acceptable residue levels in drinking water (ARLDW). The registrant(s) must propose an ARLDW for simazine residues of concern.

No Canadian or Mexican tolerance or Codex MRLs are in effect for simazine residues in potable water. Therefore, no compatibility questions exist with respect to the Codex MRL.

**References (used):**

References (not used):

[The following references were not used because they represent duplicate data or data that were not useful in assessing the tolerance.]

MRIDs: 00163270. 00156010. 00156009. 00155188. 00154892. 00154893. 00154890. 00154870. 00117187. 00023992. 00024009. 00025425. 00025428. 00026303. 00034214.

Discussion of the data:

**Potable water:** Ciba-Geigy Corp. (1988; MRID 40614421 and 1988; MRID 40614422) submitted two pond water dissipation studies regarding the environmental fate of simazine and its metabolites, G-28279 and G-30414, in water following split application of a WP formulation made 4 weeks apart at 6.8 lb ai/A-ft/application (1x) to manmade ponds in IA and GA. Samples of water were taken at various intervals up to 1 year following treatment and analyzed using a capillary gas chromatography method for the parent simazine and its chlorometabolite, G-28279, and by HPLC for the hydroxymetabolite, G-30414 with a reported limit of detection of <0.01 ppm for each. Residues of simazine, G-28279, and G-30414 were 0.01, 0.01, and 0.27 ppm, respectively, in water samples from the IA pond, and were 0.36, 0.34, and 0.11 ppm, respectively, from the GA pond 365-366 days posttreatment. The registrant suggested that marked differences in residue levels from the two tests were due to the presence of cattails and submerged grasses in the IA pond and the back of any vegetation in the GA pond.

These data are insufficient to assess the established 0.01 ppm tolerance for combined residues of simazine and its metabolites G-28273 and G-28279 because the chlorometabolite, G-28273, was not included in the analysis. These data do indicate that the present tolerance of 0.01 ppm may be too low because combined residues of simazine and its chlorometabolite G-28279 were 0.70 ppm in pond water 1 year following registered use. Additional data are required depicting simazine residues of concern in potable water.

**REGULATORY INCIDENTS**

USDA monitored data pertaining to residues of simazine as part of the 1983, 1984, 1985, and 1988 National Residue Monitoring Program. When these data are available, they will be included as an addendum to this chapter.

The FDA Surveillance monitoring data from FY78 through November 11, 1988 reported simazine residues of 0.025 ppm in the single tested sample of domestic milk collected in 1984.
TOLERANCE REASSESSMENT SUMMARY

The qualitative nature of the residues in both plants and animals is not adequately understood; additional metabolism data are required for both topics. The adequacy of residue analytical methods for data collection and tolerance enforcement cannot be assessed until the requested metabolism data have been submitted and evaluated. Development of additional methods is required for simazine hydroxymetabolite residues in or on plant commodities, meat, milk, poultry, eggs, fish, and water; confirmatory trials for those methods must also be conducted. Storage stability data are required for the hydroxymetabolite residues, and storage intervals and conditions must be reported for all sample data used to support tolerances.

Although most established tolerances for residues of simazine per se in or on plant commodities are supported by the available residue data and requirements for chlorometabolite data have generally been met, additional data are required for all commodities on residues of hydroxymetabolites which are now considered to be of potential toxicological significance; only those crops for which data can be translated from other commodities do not require additional residue data. Additional residue data are required specifically for apples, artichokes, asparagus, avocados, bananas, blueberries, corn forage and fodder, field corn grain, grapes, peaches, pecan nutmeats, plums, raspberries, olives, oranges, sweet corn K+CWHR, and sugarcane. Processing studies are required for apples, field corn grain, grapes, olives, oranges, and sugarcane. Label amendments clarifying or modifying use directions are required for apples, avocados, pears, and walnuts.

Tolerances have been established for residues of simazine per se in or on dewberries and currants for which no registered uses exist. We recommend that these tolerances be revoked. We note that Ciba-Geigy Corp. (1988; MRID 40614445) has proposed that the tolerance for residues in asparagus by reduced from 10 ppm to 0.5 ppm, concomitant with an increase in the PHI from 3 to 7 days.

The available residue data for animal commodities support the currently established tolerances for residues of simazine per se in meat milk, poultry, and eggs, assuming that the tolerances for residues in feed commodities are also adequately supported. Following submission and evaluation of the requested animal and plant metabolism data and field residue data for feed commodities, the adequacy of residue data for meat, milk, poultry, and eggs and the need for additional data will be reevaluated.
We recommend that the phrase "negligible residues" be deleted from the tolerance entries for milk, eggs, animal tissues, and poultry tissues. We also recommend that the tolerance for residues in drinking water be deleted from 40 CFR §185.5350, as such tolerances are no longer established under current Agency policy.

Metabolism and residue data for freshwater shellfish and residue data for potable water are also required.
MASTER RECORD IDENTIFICATION NUMBERS

[The following lists are derived from a search of the Pesticide Document Management system conducted 10/5/88.]

MRIDs (used):


00023275 Schenker, M.; Holzhauer, S.; Schnurr, G.; et al. (1975) Simazine ...and Amaryln...Residues in Bananas after Application of Gesatop Z 80 WP at the Normal Use Rate, Costa Rica, 1974: No. RVA 48/75. (Unpublished study received Jan 6, 1976 under GE1725; submitted by Ciba-Geigy Corp., Greensboro, N.C.; CDL:095229-C)

00023276 Schenker, M.; Holzhauer, S.; Schnurr, G.; et al. (1975) Simazine ...and Amaryln...Residues in Bananas after Application of Gesatop Z 80 WP at Double Use Rate, Costa Rica, 1974: No. RVA 50/75. (Unpublished study received Jan 6, 1976 under GE1725; submitted by Ciba-Geigy Corp., Greensboro, N.C.; CDL:095229-D)


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00027818  Geigy Chemical Corporation (19??) Results of Tests on the Amount of Residue Remaining Including Descriptions of the Analytical Methods Used: [Simazine]. (Unpublished study received Dec 1, 1964 under 5F0447; CDL:090487-C)


00027822  Chiesi, A. (1964) [Residue Data: Simazine on Blueberries]: AG-A 900. (Unpublished study received Jan 15, 1966 under 7F0534; submitted by Geigy Chemical Co., Ardsley, N.Y.; CDL:090650-E)

00027823  Geigy Chemical Company (1962) [Simazine Residue Data: Boysenberries]: AG-A 277. (Unpublished study received Jan 15, 1966 under 7F0534; CDL:090650-F)


00027825  Geigy Chemical Company (1964) [Simazine Residue Data: Oranges]. (Unpublished study received Jan 15, 1966 under 7F0534; CDL: 090650-H)

00027828  Geigy Chemical Company (1962) [Simazine Residue Data: Walnuts]. (Unpublished study received Jan 15, 1966 under 7F0534; CDL: 090650-K)


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Geigy Chemical Company (1966) [Residues of Simazine in Avocados]. (Compilation; unpublished study received on unknown date under 7F0534; CDL:090651-G)

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00105759 Elanco Products Co. (1963) General Summary: [Trifluralin Studies]. (Compilation; unpublished study received Oct 10, 1963 under 1471-35; CDL:119190-A; 120368; 119194)

00109475 Chevron Chemical Co. (1981) Results of Analysis of Almond Nut Samples Treated with Orthene 75 S Soluble Powder. (Unpublished study received Apr 20, 1982 under 239-EX-93; CDL:247273-A)

00111689 Ciba-Geigy Corp. (1964) [Study: Propazine Residues in Sorghum Plants—Simazine, Atrazine and Propazine Residues in Sheep & Cattle]. (Compilation; unpublished study received Oct 5, 1964 under 100-455; CDL:101155-A)

00113675 Interregional Research Project No. 4 (1976) The Results of Tests on the Amount of Paraquat Residues Remaining in or on Asparagus, Including a Description of the Analytical Method Used. (Compilation; unpublished study received Jul 3, 1976 under 6E1845; CDL:095940-A)

00114465 Chevron Chemical Co. (1977) Residue Chemistry Data To Support Amendment to Ortho Paraquat CL ... Label To Add Princep as a Tank Mix for Improved Control of Weeds and Grasses in Dormant Alfalfa. (Compilation; unpublished study received Apr 18, 1977 under 239-2186; CDL:230970-A)


Interregional Research Project No. 4 (1977) Results of Tests Concerning the Amount of Residues of Simazine, ... in or on Birdsfoot Trefoil. Unpublished compilation. 10 p.


### TABLE A. GENERIC DATA REQUIREMENTS FOR SIMAZINE.

<table>
<thead>
<tr>
<th>Data Requirement</th>
<th>Test substance(^1)</th>
<th>Does EPA have data?</th>
<th>Bibliographic citation(^2)</th>
<th>Must additional data be submitted?</th>
<th>Time frame for submission(^3)</th>
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<td>171-2. Chemical Identity(^6)</td>
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<td>171-3. Directions for Use(^5)</td>
<td>(See Index)</td>
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<tr>
<td>171-4. Nature of the Residue (Metabolism) - Plants</td>
<td>PAIRA &amp; plant Partially metabolites</td>
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<td>00023913. 00024025.</td>
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<td>171-4. Nature of the Residue (Metabolism) - Livestock</td>
<td>PAIRA &amp; plant Partially metabolites</td>
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<td>171-4. Residue Analytical Methods</td>
<td>TGA &amp; metabolites Partially</td>
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<td>171-4. Storage Stability</td>
<td>TEP &amp; metabolites Partially</td>
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<td>00025458. 40614441*.</td>
<td>Yes(^12)</td>
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<td>171-4. Magnitude of Residue in Plants</td>
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<td>Citrus Fruits</td>
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<td>- Grapefruit</td>
<td>TEP</td>
<td>Partially</td>
<td>see Oranges</td>
<td>Yes\textsuperscript{13}</td>
<td>18 months</td>
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<td>- Lemons</td>
<td>TEP</td>
<td>Partially</td>
<td>00023329*.</td>
<td>Yes\textsuperscript{14}</td>
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<td>- Oranges</td>
<td>TEP</td>
<td>Partially</td>
<td>00023329. 00024033. 00025409. 00032571. 00033035. 00035665. 00087676. 00106691. 00113821.</td>
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<td>Pome Fruits</td>
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<td>- Apples</td>
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<td>00012166*. 00023898. 00024059*. 00106691*. 00132787*. 40614451*.</td>
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<td>- Pears</td>
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<td>00023920.</td>
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<td>Stone Fruits</td>
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<td>- Cherries</td>
<td>TEP</td>
<td>Partially</td>
<td>00023329*. 00023922. 00131376*.</td>
<td>Yes\textsuperscript{20}</td>
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<td>- Peaches</td>
<td>TEP</td>
<td>Partially</td>
<td>00023908. 00131376*. 40614452*.</td>
<td>Yes\textsuperscript{21}</td>
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<td>- Plums (fresh prunes)</td>
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<td>00023329*. 00023910. 00023921.</td>
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<th>Data Requirement</th>
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<th>Must additional data be submitted?</th>
<th>Time frame for submission</th>
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<td>Small Fruits &amp; Berries</td>
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<td>- Blueberries</td>
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<td>00023900. 40614453*.</td>
<td>Yes23</td>
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<td>- Caneberries</td>
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<td>Partially</td>
<td>00023895. 00023901. 00023902. 00023903.</td>
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<td>- Cranberries</td>
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<td>Partially</td>
<td>00023905.</td>
<td>Yes25</td>
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<td>- Grapes</td>
<td>TEP</td>
<td>Partially</td>
<td>00023906. 00027967*. 40614454*.</td>
<td>Yes26</td>
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<td>- Strawberries</td>
<td>TEP</td>
<td>Yes</td>
<td>N/A.</td>
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<td>Tree Nuts</td>
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<td>- Almonds</td>
<td>TEP</td>
<td>Partially</td>
<td>00023917. 00035666.* 00131377.*</td>
<td>Yes28</td>
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<td>- Filberts</td>
<td>TEP</td>
<td>Partially</td>
<td>00023329*. 00023932. 00035666*.</td>
<td>Yes29</td>
<td>18 months</td>
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<td>- Macadamia Nuts</td>
<td>TEP</td>
<td>Partially</td>
<td>00023907.</td>
<td>Yes30</td>
<td>18 months</td>
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<td>- Pecans</td>
<td>TEP</td>
<td>Partially</td>
<td>00013137*. 00023327. 00023329*.</td>
<td>Yes31</td>
<td>13 months</td>
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<td>- Walnuts</td>
<td>TEP</td>
<td>Partially</td>
<td>00023923. 00131377*.</td>
<td>Yes32</td>
<td>18 months</td>
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(continued)
### TABLE A. GENERIC DATA REQUIREMENTS FOR SIMAZINE (Continued).

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<th>Data Requirement</th>
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<th>Bibliographic citation</th>
<th>Must additional data be submitted?</th>
<th>Time frame for submission</th>
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<td>Cereal Grains</td>
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<td>- Corn (field/fresh)</td>
<td>TEP</td>
<td>Partially</td>
<td>00023336*. 00023272*. 00027973*. 40614449*.</td>
<td>Yes$^{33}$ Yes$^{34}$</td>
<td>18 months 24 months</td>
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<td>Forage/Fodder/Straw of Cereal Grains</td>
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<td>- Corn forage/fodder</td>
<td>TEP</td>
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<td>00023272*. 00027972*. 00027973*. 00023336*.</td>
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<td>Miscellaneous Commodities</td>
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<td>- Artichokes</td>
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<td>00023918. 40614444*.</td>
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<td>18 months</td>
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<td>- Asparagus</td>
<td>TEP</td>
<td>Partially</td>
<td>00023899. 40614445*.</td>
<td>Yes$^{37}$</td>
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<td>- Avocados</td>
<td>TEP</td>
<td>Partially</td>
<td>00092496. 40614446*.</td>
<td>Yes$^{38}$</td>
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<td>- Bananas</td>
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<td>00023273. 00023274. 00023275. 00023276. 00023277.</td>
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<td>- Olives</td>
<td>TEP</td>
<td>Partially</td>
<td>00023973. 40614447*.</td>
<td>Yes$^{40}$ Yes$^{41}$</td>
<td>18 months 24 months</td>
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<td>- Sugarcane</td>
<td>TEP</td>
<td>Partially</td>
<td>00023911. 00084430. 40614448*.</td>
<td>Yes$^{42}$ Yes$^{43}$</td>
<td>18 months 24 months</td>
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<th>Data Requirement</th>
<th>Test substance¹</th>
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<th>Bibliographic citation²</th>
<th>Must additional data be submitted?</th>
<th>Time frame for submission³</th>
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<td>171-4. Nature/magnitude of the residue in Fish and Potable Water</td>
<td>PAIRA &amp; plant Partially metabolites</td>
<td>40614421*  40614422*  00025444  00034709  GS650070-73  GS650070-20</td>
<td>Yes⁴</td>
<td>15 months</td>
<td>15 months</td>
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<td>171-4. Magnitude of the residue in Meat, Milk, Poultry, &amp; Eggs</td>
<td>TGI or plant Partially metabolites</td>
<td>00025452  00026977  00080629  40614456*  40614457*</td>
<td>Reserved⁶</td>
<td>18 months</td>
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</tbody>
</table>

1. Test substance: TGI = technical grade of the active ingredient; PAIR = purified active ingredient; PAIRA = purified active ingredient, radiolabeled; TEP = typical end-use product; EP = end-use product.

2. MRID numbers designated by an asterisk (*) contain data that were submitted in response to the initial Simazine Guidance Document dated 3/84 or were otherwise not cited in the previous Residue Chemistry Chapter.

3. Data must be submitted within the indicated time frame, based on the date of this Guidance Document.

4. The same chemical identity data are required as under 40 CFR §158.150-190, with emphasis on impurities that could constitute residue problems. Refer to Product Chemistry Data Requirements tables.

5. The registrant must amend all pertinent labels to specify a maximum single application rate and a maximum seasonal application rate or a limit on the number of applications permitted per season; rates must be expressed in terms of amount of active ingredient per unit area, or the equivalent which can readily be converted to such. In addition, the minimum time interval between repeat applications must be specified.

6. Data depicting the total terminal residue of uniformly ring-labeled [¹⁴C]simazine in corn and two additional dissimilar crops (we recommend asparagus and a representative citrus fruit). A completely characterized test substance representative of technical simazine used in commercial formulations must be applied under conditions representing normal cropping practices and at rates high enough to result in sufficient radiolabeled residues for characterization. The identities and quantities of residues in or on all relevant raw agricultural commodities must be determined in order to elucidate terminal residues. Representative
TABLE A. (Continued).

samples from these studies must also be analyzed by the residue analytical methods developed for data collection and tolerance enforcement to ascertain that the methods are capable of adequately recovering and quantifying all residues of concern.

7. Metabolism studies characterizing the total terminal residue of simazine in ruminants and poultry. Animals must be dosed orally for a minimum of three days with ring-labeled $[^14]C$simazine, at a level sufficient to make residue identification and quantitation possible. Eggs must be collected twice a day during the dosing period, and test animals must be sacrificed within 24 hours of the final dose. The distribution and identity of residues must be determined in eggs, liver, kidney (ruminants only), muscle, and fat. Representative samples from these studies must also be analyzed by the residue analytical methods developed for tolerance enforcement to ascertain that the methods are capable of adequately recovering and identifying all residues of concern. Should the metabolism of simazine or its metabolites in ruminants and/or poultry following oral dosing differ significantly from that in rats, swine metabolism data may also be required.

8. Residue analytical methods must be developed and validated which will quantify residues of the simazine hydroxymetabolites of concern in or on plant commodities, meat, poultry, eggs, fish, and potable water.

9. Successful confirmatory trials of the proposed methods for determination of hydroxymetabolites of concern in plant and animal commodities must be conducted by an independent laboratory. Results of at least one set of samples each for an oily crop, a non-oily crop, and meat and milk (a total of six samples, including two control samples, two control samples fortified at the tolerance level, and two control samples fortified at 2-5 times the tolerance level per commodity) must be submitted. No more than three sets of samples per commodity may be tested to achieve successful recovery rates of 70-120% with negligible interference compared to the established tolerances. For additional details of data requirements, refer to PR Notice 88-5, Tolerance Enforcement Methods - Independent Laboratory Confirmation by Petitioner.

10. Representative plant and animal tissue samples bearing residues of simazine chlorometabolites (G-28273, G-28279) and hydroxymetabolites of concern must be subjected to analysis by multiresidue protocols I and III from PAM Vol. I, Appendix II. Multiresidue protocols I-IV are available from the National Technical Information Service under Order No. PB 203734/AS.

11. The nature of the residue in plants and animals is not adequately understood. If the metabolism studies requested in the sections "Qualitative Nature of the Residue in Plants" and "Qualitative Nature of the Residue in Animals" reveal the presence of additional metabolites of concern, additional validated methods for data collection and tolerance enforcement will be required.
12. The sample storage conditions and intervals must be supplied for all required and previously submitted residue data for plant and animal commodities. Data are also required which depict the decline in levels of simazine residues of concern in commodities stored under the range of conditions and for the range in intervals specified. Crop samples bearing measurable weathered residues or fortified with atrazine residues of concern and fortified meat, milk, and egg samples must be analyzed immediately after harvest or fortification and again after storage intervals that represent actual residue sample storage conditions and allow for reasonable unforeseen delays in sample analysis. In laboratory tests using fortified samples, the pure active ingredient and pure metabolites must be used. However, if field weathered samples are used, the test substance must be a typical end-use product. For additional guidance on conducting storage stability studies, the Registrant is referred to an August 1987 Position Document on the Effects of Storage on Validity of Pesticide Residue Data available from NTIS under order no. PB88112362/AS.

13. The data required for oranges will be translated to fulfill residue data requirements for grapefruit.

14. The data required for oranges will be translated to fulfill residue data requirements for lemons.

15. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on oranges harvested at normal fruit maturity after spring broadcast application of representative WP, DF, or FlC formulations at the following rates: (i) 4 lb ai/A in CA; (ii) 9.6 lb ai/A in FL; and (iii) 4.8 lb ai/A in TX. Granular formulations may be used for the FL and TX tests. Spray formulations must be applied in 20-40 gal of water/A using ground equipment.

16. A processing study depicting the potential for concentration of simazine residues of concern in dried pulp, oil, and molasses processed from oranges bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these commodities, appropriate food/feed additive tolerances must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the highest theoretical concentration factor for any one of the processed products indicate that no detectable residues of concern occur in or on oranges.

17. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on apples harvested at regular intervals following application of representative G, WP, DF, and FlC formulations at 4.0 lb ai/A. Tests must be performed in the states of MI(11%), NY(10%) or PA(5%), and WA(42%), which collectively represent ca. 70% of the U.S. commercial apple production (Crop
18. A processing study depicting the potential for concentration of simazine residues of concern in dry pomace and juice processed from apples bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these commodities, appropriate food/feed additive tolerances must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the highest theoretical concentration factor for any one of the processed products indicate that no detectable residues of concern occur in or on apples.

19. The data required for apples will be translated to fulfill residue data requirements for pears; however, the registrants must propose label amendments specifying a PHI for simazine application to pears that is supported by the translated residue data.

20. The data required for plums will be translated to support residue data requirements for cherries.

21. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on peaches harvested at normal fruit maturity after spring directed broadcast or banded application of representative WP, DF, or F1C formulations at 4 lbs ai/A in GA(7%) or SC(23%) and NJ(5%) or PA(6%) and at 2 lbs ai/A in CA(34%), representing the major U.S. areas of peach production and the geographic limitations on simazine use. Spray formulations must be applied in 20-40 gal of water/A.

22. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on plums harvested at normal fruit maturity after directed broadcast or banded application of representative WP, DF, or F1C formulations at the rates 4 lbs ai/A in MI. Spray formulations must be applied in 20-40 gallons of water/A using ground equipment.

23. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on blueberries harvested at normal fruit maturity after spring application of representative G, WP, DF, or F1C formulations to established blueberry orchards at 4 lb ai/A according to label directions. Tests must be conducted in MI(41%), NJ(34%), NC(5%) or GA(2%), and OR(3%) or WA(5%) which represent ca. 90% of the 1982 U.S. blueberry acreage (1982 Census of Agriculture, Vol.1, Part 51, p. 371).
TABLE A. (Continued).

24. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on raspberries harvested at normal fruit maturity after directed spring application of representative G, WP, DF, or FL1 formulations to established plants at 4 lb ai/A according to established use directions. Tests must be conducted in CA(7%), OR(38%), and WA(44%) which collectively represent ca. 80% of the 1982 U.S. raspberry acreage (Census of Agriculture, 1982, Vol.1, Part 51, p. 372).

25. Data required for blueberries will be translated to fulfill residue data requirements for cranberries.

26. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on grapes harvested at normal fruit maturity following early spring directed application of representative WP, DF, or FL1 formulations to vineyards at 4.8 lb ai/A in 20-40 gal of water/A. Tests must be conducted in CA which accounted for ca. 90% of the 1987 U.S. grape production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA).

27. A processing study depicting the potential for concentration of simazine residues of concern in raisins, raisin waste, dry pomace, and juice processed from grapes bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these products, appropriate food/feed additive tolerance must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the highest theoretical concentration factor for any one of the processed products indicate that no detectable residues of concern occur in or on grapes.

28. The data required for pecans will be translated to support residue data requirements for almonds.

29. The data required for pecans will be translated to support residue data requirements filberts.

30. The data required for pecans will be translated to support residue data requirements for macadamia nuts; however, the registrant must propose a maximum application rate per season and an appropriate PHI which are supported by the available residue data.

31. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on pecan nutmeats harvested at normal maturity after directed application of representative WP, DF, or FL1 formulations at 4 lbs ai/A in 20-40 gal of water/A in the spring before weeds emerge. Tests must be conducted in AL(9%), GA(41%), and NM(11%) or TX(18%) which collectively accounted for ca. 80% of the 1987 U.S. pecan production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA).
TABLE A. (Continued).

32. The data required for pecans will be translated to fulfill residue data requirements for simazine on walnuts, provided that the posttreatment intervals correspond to the PHI that is to be established; therefore, the registrants must propose label amendments that specify a PHI for simazine use on walnuts that is supported by the available field residue data.

33. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on field corn grain and sweet corn K+OHHR following preemergence application of representative WP, DF, or F1C formulations at 4 lb ai/A. Field corn tests must be conducted in IL(17%), IA(18%), IN(9%) or OH(5%), MN(9%) or WI(5%), and NE(11%), which collectively represent ca. 70% of the 1987 U.S. field corn production (Crop Database, Jan. 1988, Ag. Statistics Board, NASS, USDA). Sweet Corn tests must be conducted in FL(7%), MN(22%) or WI(20%), NV(7%), and OR(10%) or WA(10%) which collectively account for ca. 70% of the 1985 U.S. commercial sweet corn production (Vegetables 1986 Summary, June 1987, Ag. Statistics Board, NASS, USDA).

34. A processing study depicting the potential for concentration of simazine residues of concern in wet milled products (starch, crude oil, and refined oil), dry milled products (grits, meal, flour, and crude and refined oils), and grain dust processed from field corn grain bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in any of these products, appropriate food/feed additive tolerances must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the highest theoretical concentration factor for any one of the processed products indicate that no detectable residues of concern occur in or on corn grain.

35. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on field corn and sweet corn forage and fodder following preemergence application of representative WP, DF, or F1C formulations at 4 lb ai/A. Tests must be conducted in conjunction with those required for field corn grain and sweet corn K+OHHR.

36. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on artichokes harvested following directed spray application of representative WP, DF, or F1C formulations at 4.0 lb ai/A according to label directions. Tests must be conducted in CA.

37. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on asparagus harvested 3 days after application of representative WP, DF, F1C formulations at 4 lb ai/A in 20-40 gal of water/A. Tests should be conducted in CA(49%), MI(11%), and WA(35%)
which collectively account for >90% of 1986 U.S. asparagus production (Vegetables, 1986 Summary, Ag. Statistics Board, NASS, USDA, p. 18).

38. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on avocados following directed broadcast application of representative WP, DF, and FL/C formulations at 4.0 lb ai/A applied in 20-40 gal/A. Tests must be conducted in the state of CA.

39. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on bananas following application of a representative formulation of simazine at the maximum registered use rate.

40. Data depicting simazine residues of concern, including its hydroxymetabolites, in or on olives following a single application of a representative formulation at 4.0 lb ai/A in 20-40 gal of water in the state of CA.

41. A processing study depicting the potential for concentration of simazine residues of concern in oil processed from olives bearing measurable weathered residues. Exaggerated field use rates and/or short posttreatment intervals may be required to achieve such residues. If residues concentrate in the oil, an appropriate food additive tolerance must be proposed. The need for a processing study may be waived if field residue tests using rates exaggerated by the theoretical concentration factor for oil indicate that no detectable residues of concern occur in or on olives.

42. Data depicting residues of simazine, its chlorometabolites (G-28279 and G-28273), and hydroxymetabolites of concern in or on sugarcane harvested at normal crop maturity following three applications of representative WP, 90% DF and 4 lb/gal FL/C formulations, including a postemergence broadcast application at 2 lb ai/A, and two interline directed applications prior to close-in at 4 lb ai/A/application in 20-40 gal of water/A (seasonal use rate of 10 lb ai/A) Tests must be performed in FL, or IA and HI.

43. A processing study depicting the potential for concentration of simazine residues of concern in molasses, refined sugar, and bagasse processed from sugarcane bearing measurable weathered residues. The established food/feed additive tolerance for molasses will be reassessed following evaluation of these data.

44. Residue studies must be submitted pertaining to fish and freshwater shellfish exposed to simazine applied in the water at the maximum rate according to label directions. Representative samples must be analyzed by adequate analytical methods and all simazine residues of concern must be determined. The regis-
TABLE A. (Continued).

The registrant must propose a tolerance or an exemption from the requirement of a tolerance for simazine residues of concern in freshwater shellfish. Alternatively, for shellfish, the registrant(s) may propose label restrictions prohibiting use of simazine where commercial shellfishing is practiced.

45. Simazine residues of concern in water sampled 1 year following split application of a G and a WP formulation represented in separate tests to a standing pond at 6.8 lb ai/A-ft/application. Pesticide residue levels in potable water are no longer regulated by the establishment of food additive tolerances, but rather by setting acceptable residue levels in drinking water (ARLDW). The registrant(s) must propose an ARLDW for simazine residues of concern.

46. On receipt of the data requested in the sections entitled "Qualitative Nature of the Residue in Animals", and "Magnitude of the Residue in Plants", appropriate tolerances for residue in animal products will be determined, with considerations for any newly found metabolites of toxicological concern.
SIMAZINE
SECOND ROUND REVIEW
PRODUCT CHEMISTRY
TASK 1
(Final Report)

CONFIDENTIAL APPENDICES

Appendix A: 4 Pages
Appendix B: 2 Pages
Appendix C: 1 Page
Appendix D: 1 Page
Appendix E: 1 Page

Confidential Appendices to RCB's Scientific Review of the Registration Standard for the pesticide simazine [Confidential FIFRA Trade Secret/CBI].
Simazine product and residue chemistry chapter

Page ____ is not included in this copy.
Pages 198 through 206 are not included in this copy.

The material not included contains the following type of information:

— Identity of product inert ingredients
— Identity of product impurities
✓ Description of the product manufacturing process
✓ Description of product quality control procedures
— Identity of the source of product ingredients /
— Sales or other commercial/financial information
— A draft product label
✓ The product confidential statement of formula
— Information about a pending registration action
— FIFRA registration data
— The document is a duplicate of page(s) _________
— The document is not responsive to the request

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.