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Date Out of EFGWB: AUG 28 1991

TO: B. Briscoe
Product Manager #50
Special Review and Reregistration Division (H7508W)

FROM: Henry Nelson, Ph.D., Acting Section Head *H Nelson*
Surface Water Section
Environmental Fate and Groundwater Branch/EFED (H7507C)

THRU: Hank Jacoby, Chief *Hank Jacoby*
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

Attached, please find the EFGWB review of:

Reg./File #(s): 080803-0

Common Names: Atrazine

Type of Product: Herbicide

Company Name: Ciba-Geigy

Purpose: Review of surface water monitoring data

Date Received: 5/8/89 Action Code: 660

EFGWB #(s): 89-0569

Total Reviewing Time: 1 month

Deferrals to: Ecological Effects Branch/EFED
 Science Integration & Policy/EFED
 Non-Dietary Exposure Branch/HED
 Dietary Exposure Branch/HED
 Toxicology Branch I/HED
 Toxicology Branch II/HED

1. CHEMICAL:

Common Name: Atrazine

Chemical Name: 2-Chloro-4-ethylamino-6-isopropylamino-
1,3,5-triazine

Type of Product: Herbicide

Chemical Structure:

Physical/Chemical Properties

Molecular Weight: 354

Physical State : White crystalline solid

Aqueous Solubility: 70 mg/L @ 22°C

Vapor Pressure: 3.0 X 10⁻⁷, mm Hg

Log Octanol/Water Partition Coefficient 2.33 to 2.71

2. TEST MATERIALS:

Not applicable.

3. STUDY/ACTION TYPE:

Review of surface water monitoring data.

4. STUDY IDENTIFICATION:

(1) MRID #410652-05 (Vol. 2)

Balu K. 1989. Summary of surface water monitoring data for atrazine. Completed on March 17, 1989. Performed and submitted by Ciba Geigy Corp., Greensboro, NC. Study No. EIR-89001

Appendix D: Baker D. 1988. Sediment, nutrient and pesticide transport in selected Great Lakes Tributaries. Completed February 1988. Performed by Water Quality Laboratory of Heidelberg College, Tiffin, Ohio for the Great Lakes National Program Office of U.S. EPA (Region 5).

(2) MRID #411352-06

Roux P. 1989. Summary of atrazine surface-water monitoring program. Completed in February 1988. Performed by Roux Associates and submitted by Ciba Geigy Corp., Greensboro, NC. Laboratory Study No. CG-02814

Note: The main text of this study also appears as Appendix B of 411352-05 (Vol. 1)

(3) MRID #410652-05 (Vol. 1)

Balu K. 1989. Summary of surface water monitoring data for atrazine. Completed on March 17, 1989. Performed and submitted by Ciba Geigy Corp., Greensboro, NC. Study No. EIR-89001

Appendix A: Ross R. and Balu K. 1985. Summary of atrazine surface water monitoring data during 1975-1985. Submitted by CIBA-GEIGY.

(4) MRID #410652-05 (Vol. 1)

Balu K. 1989. Summary of surface water monitoring data for atrazine. Completed on March 17, 1989. Performed and submitted by Ciba Geigy Corp., Greensboro, NC. Study No. EIR-89001

Appendix C: Roux P. 1988. Summary of atrazine/metolachlor cross-over in the surface-water monitoring program. Completed in February 1988. Performed by Roux Associates and submitted by Ciba Geigy Corp., Greensboro, NC. Laboratory study #CG-02814.

(5) No MRID # (Not submitted by a registrant)

Goolsby DA and Thurman EM. 1991. Herbicides in rivers and streams of the upper midwestern United States. To be published in: Proc. 46th Ann. Meeting Upper Mississippi River Conservation Committee.

5. REVIEWED BY:

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6. APPROVED BY:

Hank Jacoby, Chief
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AUG 28 1991

7. CONCLUSIONS:

Conclusions with respect to the accuracy and representativeness of the data in studies 1 through 5 are as follows:

(1) The sampling and QA/QC information provided was inadequate for EFGWB to assess the accuracy of the data in Study 1 (Baker 1988). All but one of the 8 Lake Erie tributaries sampled drain relatively high atrazine use areas. Sampling intervals were not provided and do not appear to have been determined by runoff events. However, the large number of samples collected during the April 15 to August 15 sampling period suggests sampling frequencies of several per week.

(2) The accuracy of the Study 2 (MRID #411352-06) data as evidenced by the QA/QC procedures and results appears to be generally good. However, the study was designed to determine somewhat more typical than worst case atrazine concentrations in surface waters draining atrazine use areas. This was done through:

(a) the random selection of rivers and semi-random selection of the sampling location in each river with no regard to the volume of atrazine use/drainage area above each sampling location.

(b) the use of set sampling intervals not dictated by rainfall and runoff events.

(3) The QA/QC and other information provided is inadequate to fully assess the accuracy and representativeness of the data in Study 3 (Ross and Balu 1985).

(4) The analytical and QA/QC procedures described in the 1988 En-Cas report entitled "Analysis of Atrazine Residues in Samples from a Surface Water Monitoring Program: Analytical Phase of Roux Associates Project No. CG-02814" appear to be adequate (see DER for 411352-06, study 2). If the same analytical and QA/QC procedures were used in cross-over study 4 (Roux 1988), they are probably adequate. Nevertheless, EFGWB needs to see the actual QA/QC data (field and lab blanks, recoveries, calibration, etc.) to determine the accuracy of the cross-over data.

(5) EFGWB could not determine the accuracy of the data because no information was provided on QA/QC procedures. This was a multiple pesticide study, so the sampling sites in 10 midwestern states were not selected based specifically upon the drainage of atrazine use areas.

Based upon a review of 5 studies covering numerous locations, EFGWB has developed and/or concurs with the following conclusions concerning the distribution and time dependence of atrazine concentrations in surface waters:

(1) Atrazine is typically applied at or within a few days after corn planting which typically takes place from early April through late May depending upon the location. In surface waters draining high atrazine use areas, peak observed concentrations (frequently > 10 ug/L but rarely greater than 50 ug/L) are typically observed in conjunction with the first major runoff event following corn planting/atrazine application after which atrazine concentrations generally gradually decline over several weeks to 2-3 months to concentrations < 1.0 ug/L (most samples collected from September through March have atrazine concentrations < 1.0 ug/L). In a few locations, peak atrazine concentrations continued to occur in conjunction with additional runoff events occurring within approximately 2 months after application.

(2) A high percentage of the Study 2 and 3 samples collected through out the year from surface waters which drain atrazine use areas had atrazine concentrations > than the detection limit of 0.1 ug/L (Study 2: 88.7% of 336 samples collected during 1986-1987 from 14 locations in 14 surface waters; Study 3: 90.1% of 1407 samples collected during 1975-1981 from 33 locations in 18 surface waters; Study 3: 88.7% of 461 samples collected during 1982-1985 from 6 locations in 3 surface waters). Although the April-August sampling bias (more samples are typically collected during the 3-4 months after atrazine application than at other times of the year)

contributes to the high percentages, the majority of samples collected from September through March also had atrazine concentrations > 0.1 ug/L.

(3) Although a high percentage of the Study 2 and 3 samples have atrazine concentrations > 0.1 ug/L (item 1), the majority of the Study 2 and 3 samples have atrazine concentrations ≤ 1.0 ug/L despite the April-August sampling bias (Study 2: 77.7% of 1986-1987 samples; Study 3: 72.4% of 1975-1981 samples; Study 3: 77.2% of 1982-1985 samples).

(4) A substantial percentage of the Study 2 and 3 samples have atrazine concentrations between 1.0 and 10 ug/L (Study 2: 19.0% of 3/86-11/87 samples; Study 3: 27.1% of 1975-1981 samples; Study 3: 22.3% of 1982-1985 samples).

(5) Only a small percentage of the Study 2 and 3 samples had atrazine concentrations > 10 ug/L (Study 2: 3.3% of 3/86-11/87 samples; Study 3: 0.64% of 1975-1981 samples; Study 3: 0.43% of 1982-1985 samples). Furthermore, the percentages of Study 2 and 3 locations from which at least one sample with an atrazine concentration > 10 ug/L was collected were low. However, neither study was designed to determine peak concentrations. For study 1 (in which relatively large numbers of samples were collected from April 15 to August 15 of 1982-1985), 53.3% of peak observed atrazine concentrations representing 7 of 8 locations sampled were > 10 ug/L. For study 5 (in which one sample per location was collected in conjunction with the first major post-application runoff event), 34.1% of the 1989 post-application samples (one from each of 123 locations sampled) representing 8 of the 10 states sampled had atrazine concentrations > 10 ug/L.

(6) Reported atrazine concentrations rarely exceeded 50 ug/L. The following were the only atrazine concentrations > 50 ug/L reported in studies 1 through 5: 245 ug/L 1984 Lost Creek, OH and 226 ug/L 1985 Rock Creek, OH (study 1); 234 and 56 ug/L 1976 Miss. River 10 miles below Vicksburg (study 2); 108 ug/L in Spoon River at London Mill, IL, 71.6 ug/L in Old Man Creek near Iowa City, IA, 52.2 ug/L in Bonapas Creek at Browns, IL and 52.0 ug/L in Wahoo Creek at Itica, NE (study 5).

(7) The importance of conducting monitoring studies in surface waters which drain areas known to receive applications of the pesticide of interest is illustrated by the results of study 4 which was designed to determine metalochlor in surface waters known to drain metalochlor use areas. Despite large areas of atrazine use within the United States, the atrazine concentrations reported for study 4 samples were much lower than samples collected from the other studies where most of the surface waters sampled were known to drain atrazine use areas.

(8) The highest 1982-1984 average of April 15-August 15 time weighted mean concentrations of atrazine in the 8 Lake Erie tributaries sampled in Study 1 was 5.30 ug/L for Honey Creek, OH. The distribution of the 1982-1984 averages of April 15-August 15 time weighted mean concentrations (TWMCs) for the 8 locations in the 8 tributaries sampled was as follows:

1982-1984 Average of 4/15-8/15 TWMCs \leq 1.0 ug/L (1 tributary)
1.0 ug/L < Average TWMC \leq 2.0 ug/L (1 tributary)
2.0 ug/L < Average TWMC \leq 3.0 ug/L (3 tributaries)
Average TWMC > 3.0 ug/L (3 tributaries)

(9) The highest 3/86-11/87 arithmetic mean atrazine concentration in Study 2 was 8.22 ug/L for Little Crooked Creek, IL. The distribution of 3/86-11/87 arithmetic means for the 14 locations in the 14 surface waters sampled in Study 2 was as follows:

C \leq 1.0 ug/L (11 surface waters)
1.0 ug/L < C \leq 2.0 ug/L (0 surface waters)
2.0 < C \leq 3.0 ug/L (0 surface waters)
C > 3.0 ug/L (3 surface waters)

(10) The highest arithmetic mean atrazine concentration for samples collected from as early as 1975 to as late as December 1981 in Study 3 was 3.87 ug/L. The distribution of arithmetic means for the 33 locations in 18 surface waters sampled within the 1975-1981 interval in Study 3 was as follows:

C \leq 1.0 ug/L (16 locations)
1.0 ug/L < C \leq 2.0 ug/L (12 locations)
2.0 < C \leq 3.0 ug/L (4 locations)
C > 3.0 ug/L (1 location)

(11) Arithmetic mean atrazine concentrations for samples collected 1982-1985 in Study 3 from 6 locations in 3 surface waters were all < 1.7 ug/L. Arithmetic means for samples collected 1982-1985 in Study 3 from 4 surface water source tap waters were all < 1.0 ug/L.

(12) The data were inadequate to determine any year to year or decade to decade trends in atrazine concentrations in surface waters. The data are also inadequate to determine whether (as predicted) atrazine concentrations in surface water source drinking waters are generally comparable to those in the source.

8. RECOMMENDATIONS:

Refer to the EFGWB position paper on atrazine in groundwater and surface water for a comparison of atrazine concentrations in surface waters to potential levels of concern.

9. BACKGROUND:

This is a review of data on atrazine concentrations in surface water (41065205 and 41065206) submitted by CIBA-GEIGY in response to a data call-in. MRID #s 41065207 and 41065208 are also listed on the Data Review Record sheet for package 49311, but were not included in the package EFGWB received for review. In the April 11, 1989 letter from CIBA-GEIGY to J. Andreasen, 41065207 and 41065208 are identified as use data and were therefore probably sent to the BEAD for review.

Also included in this review is a study recently conducted by the U.S. Geological survey. Although it was conducted after the registrant's response to the data call-in, it was included in this review for comparative purposes because it was the only one of the 5 studies reviewed in which sampling times were determined by post-application runoff events.

10. DISCUSSION:

See recommendations and conclusions.

11. COMPLETION OF ONE-LINER

Attached

12. CBI INDEX:

Not applicable.

DATA EVALUATION RECORD
Study 1

SHAUGNESSY No. 080803
COMMON NAME: Atrazine
CHEMICAL NAME: 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine
FORMULATION: Not applicable
DATA REQUIREMENT: Surface Water Monitoring

MRID #410652-05 (Vol. 1)
Balu K. 1989. Summary of surface water monitoring data for atrazine. Completed on March 17, 1989. Performed and submitted by Ciba Geigy Corp., Greensboro, NC. Study No. EIR-89001

Appendix D: Baker D. 1988. Sediment, nutrient and pesticide transport in selected Great Lakes Tributaries. Completed February 1988. Performed by Water Quality Laboratory of Heidelberg College, Tiffin, Ohio for the Great Lakes National Program Office of U.S. EPA (Region 5).

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AUG 28 1991

SIGNATURE: *H Nelson*

DATE: 8/23/91

APPROVED BY: Hank Jacoby
TITLE: Chief, Environmental Fate and Groundwater Branch
ORGANIZATION: Environmental Fate and Effects Division/OPP

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CONCLUSIONS:

- (1) The sampling and QA/QC information provided was inadequate for EFGWB to assess the accuracy of the data in the Baker 1988 study.
- (2) The distribution of the April 15-August 15 TWMCs (one 4/15-8/15 TWMC for each of 3 years and each of 8 tributaries sampled = 24 total TWMCs) was as follows:

TWMCs \leq 1.0 ug/L (6 over 3 tributaries; 25%)
1.0 ug/L < TWMCs \leq 5.0 ug/L (12 over 6 tributaries; 50%)
5.0 ug/L < TWMCs \leq 10 ug/L (6 over 5 tributaries; 25%)
TWMCs > 10 ug/L (0; 0%)

(3) The distribution of the peak observed concentrations (one peak observed concentration for each of 3 or 4 years and each of 8 tributaries sampled = 30 total peak observed concentrations) was as follows:

- $C_{\max} \leq 1.0 \text{ ug/L}$ (1; 3.3%)
- $1.0 \text{ ug/L} < C_{\max} \leq 10 \text{ ug/L}$ (13 over 6 tributaries; 43.3%)
- $10 \text{ ug/L} < C_{\max} \leq 50 \text{ ug/L}$ (14 over 6 tributaries; 46.7%)
- $C_{\max} \geq 50 \text{ ug/L}$ (2, 226.0 and 245.0 ug/L, over 2 tributaries; 6.7%)

METHODS AND MATERIALS:

(1) Sampling Locations:

Eight tributaries of Lake Erie (7 in OH, 1 in MI) were sampled for pesticides, each at one location (Table 1.1 and Figure 1.1).

(2) Sampling Periods/Years:

Samples were collected from April 15-August 15 in 1982 through 1985.

(3) Sampling Methodology:

Grab samples were collected at the Cuyahoga River and River Raisin sites. Automatic samplers housed in USGS gauging stations and capable of collecting samples either twice a day for six consecutive days or 4 times a day for 7 consecutive days were used at the other 6 sampling locations. However, the total number of samples analyzed for pesticides at each location for each year (Surface Water Appendix Table 1.1) was generally less than the total number of days in the April 15 to August 15 sampling period (122) and always much less than 122 times 2 (twice a day sampling) or 4 (four times a day sampling). The reason for the number of samples analyzed for pesticides being much lower than the theoretical maximum possible number of sample collections is unclear.

The times, frequency, and compositing (if any) of sample collection for pesticides were not provided. Based upon the total number of samples collected over the April 15-August 15 sampling periods, there were probably at least 3 samples collected per week at each location. No information was provided on the depth of sampling or on whether samples included the surface film. The use of single automatic samplers at 6 of the 8 locations indicates that samples were not taken at various points across the width of the surface water and composited.

(4) Analytical Procedures:

Samples were analyzed for as many as 18 separate pesticides including atrazine. The pesticides were extracted from the water samples with methylene chloride (extract volume/sample volume and number of extractions not provided), concentrated in the methylene chloride extract by Kuderna-Danish evaporation, and then transferred to iso-octane for analysis by capillary GC using nitrogen thermionic detector. Confirmation of identity was achieved through the use of 2 columns (DB-1 and DB-2). The detection limit for atrazine was 0.05 ug/L. The

linear range of calibration curves was ≥ 0.5 ug/L. The mean percent recovery for atrazine for 1984 and 1985 were 86 and 69%, respectively. The reported concentrations were corrected for recoveries less than 100%.

(5) QA/QC Procedures:

The QC program reportedly included the analysis of blanks, spiked samples, and replicates, but no details were provided in this report other than the mean percent recoveries given above. No information was provided on the shipping and storage of samples, the storage stability of samples, or the elapsed time between sampling and analysis. Therefore, EFGWB could not evaluate the accuracy of the data.

The study author indicates that more detailed information on the QA/QC procedures and analytical methods used can be obtained from the following paper:

Kramer J and Baker D. 1985. An analytical method and quality control program for studies of currently used pesticides in surface waters. IN: Taylor J and Stanley T, eds. Quality assurance for environmental measurements. ASTM STP 867. Amer. Soc. Testing and Materials, Philadelphia, P. 116-132.

RESULTS:

Atrazine time weighted mean concentrations (TWMCs) and maximum observed concentrations of samples collected during April 15 to August 15 of 1982 through 1984 or 1985 were reported for each of the 8 Lake Erie tributaries sampled (Tables 1.2 and 1.3). The results of the analysis of individual samples (other than those with the maximum observed atrazine concentration) were not tabularly reported. However, same page plots of flow and concentrations of 4 of the pesticides (including atrazine) vs. time during the April 15 - August 15 sampling period were presented for each year and the 3 sampled surface waters with the highest pesticide concentrations (Figures 1.2 through 1.13). In addition, based upon pooled results from the April 15-August 16 sampling periods, "concentration exceedency curves" (concentration vs. percent of April 15 - August 15 sampling period concentration is exceeded) were presented for six of the pesticides and all 8 sampled surface waters (Figure 1.14).

Atrazine TWMCs for samples collected from the 8 tributaries during April 15 to August 15 of 1982 through 1984 ranged from 0.254 ug/L (Cuyahoga river 1984) to 7.67 ug/L (Honey Creek 1985). The distribution of the April 15-August 15 TWMCs (one 4/15-8/15 TWMC for each of 3 years and each of 8 tributaries sampled - 24 total TWMCs) was as follows:

TWMCs ≤ 1.0 ug/L (6 over 3 tributaries; 25%)
1.0 ug/L < TWMCs ≤ 5.0 ug/L (12 over 6 tributaries; 50%)
5.0 ug/L < TWMCs ≤ 10 ug/L (6 over 5 tributaries; 25%)
TWMCs > 10 ug/L (0; 0%)

The average April 15-August 15 TMWCs over sampling years 1982-1984 for each of the 8 tributaries sampled were in decreasing order as follows: 5.30±2.32 ug/L (Honey Creek), 3.76±2.62 ug/L (Lost Creek), 3.72±2.40 ug/L (Sandusky River), 2.93±2.09 ug/L (Rock Creek), 2.66±0.86 ug/L (Maumee River), 2.32±2.64 ug/L (U. Honey Creek), 1.60±0.88 ug/L (Raisin River), and 0.417±0.200 ug/L (Cuyahoga River).

Atrazine peak observed concentrations for samples collected from the 8 tributaries during April 15 to August 15 of 1982 or 1983 through 1985 ranged from 0.742 ug/L (Cuyahoga River 1982) to 245. ug/L (Lost Creek 1984). The distribution of the peak observed concentrations (one peak observed concentration for each of 3 or 4 years and each of 8 tributaries sampled = 30 total peak observed concentrations) was as follows:

- $C_{\max} \leq 1.0$ ug/L (1; 3.3%)
- 1.0 ug/L $< C_{\max} \leq 10$ ug/L (13 over 6 tributaries; 43.3%)
- 10 ug/L $< C_{\max} \leq 50$ ug/L (14 over 6 tributaries; 46.7%)
- $C_{\max} \geq 50$ ug/L (2, 226.0 and 245.0 ug/L, over 2 locations; 6.7%)

The highest peak observed concentrations in samples collected from the 8 tributaries during April 15 to August 15 of 1982 or 1983 through 1985 were in decreasing order as follows: 245.0 ug/L (Lost Creek 1984), 226.0 ug/L (U. Honey Creek 1985), 48.41 ug/L (Honey Creek 1982), and 48.09 ug/L (Rock Creek 1985). All other peak observed concentrations were < 40 ug/L.

COMMENTS:

(1) The sampling and QA/QC information provided was inadequate for EFGWB to assess the accuracy of the data in the Baker 1988 study.

(2) Based upon the same page plots of flow and atrazine concentration vs. time within the April 15 - August sampling period of 1983-1985, the study author developed the following conclusions with which EFGWB concurs:

(a) Atrazine concentrations in late April to early May were generally low (< 1 ug/L), reached peak concentrations in late May, June, and July during or shortly after major runoff events and then gradually declined to relatively low levels again toward mid-August even in conjunction with runoff events.

(b) In some locations, atrazine concentrations continued to peak in conjunction with runoff events several times over at least 2 months after application.

(3) Based upon the concentration exceedency curves, the study author indicated that although maximum concentrations of atrazine are frequently less than those of metalochlor and alachlor, atrazine generally occurs at less than peak concentrations for longer periods of time. EFGWB concurs and believes that is also reflected by the fact that atrazine TMWCs are frequently greater than those for metalochlor and alachlor even in surface waters where the maximum observed concentrations for atrazine are less than those for metalochlor and alachlor.

(4) The study author indicates that low pesticide concentrations in the Cuyahoga River are due to the small percentage of agricultural land use within the Cuyahoga watershed.

(5) Although much of the River Raisin watershed drains agricultural use areas, the pesticide concentrations in the River Raisin were generally much lower than those in the 6 other surface waters sampled which also drain high agricultural use areas. The study author indicates the reason may be due to many of the soils in the River Raisin watershed being more permeable than those in the watersheds of the other surface waters sampled.

Page _____ is not included in this copy.

Pages 13 through 25 are not included.

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 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.
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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.

DATA EVALUATION RECORD
Study 2

SHAUGNESSY No. 080803
COMMON NAME: Atrazine
CHEMICAL NAME: 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine
FORMULATION: Not applicable
DATA REQUIREMENT: Surface Water Monitoring

MRID #411352-06
Roux P. 1989. Summary of atrazine surface-water monitoring program. Completed in February 1988. Performed by Roux Associates and submitted by Ciba Geigy Corp., Greensboro, NC. Laboratory Study No. CG-02814

Note: The main text of this study also appears as Appendix B of 411352-05

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DATE: 8/23/91

APPROVED BY: Hank Jacoby
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SIGNATURE:

CONCLUSIONS:

(1) The accuracy of the data as evidenced by the QA/QC procedures and results appears to be generally good. However, the study was designed to determine somewhat more typical than worst case atrazine concentrations in surface waters draining atrazine use areas. This was done through:

(a) the random selection of rivers and semi-random selection of the sampling location in each river with no regard to the volume of atrazine use/drainage area above each sampling location.

(b) the use of set sampling intervals not dictated by rainfall and runoff events.

(2) The overall concentration distribution for the 336 samples collected from 14 locations in 14 surface waters was as follows:

C ≤ 0.1 ug/L (38 samples; 11.3% of total samples)
0.1 ug/L < C ≤ 1.0 ug/L (223 samples; 66.4%)
1.0 ug/L < C ≤ 5.0 ug/L (55 samples; 16.4%)
5.0 ug/L < C ≤ 10 (9 samples over 5 locations; 2.7%)
C > 10 ug/L (11 samples over 3 locations; 3.3%).

(3) The highest reported concentration (30.5 ug/L) and the highest reported arithmetic mean over the 3/86-11/87 sampling period (8.22 ug/L) were for samples collected from Little Crooked Creek, IL.

METHODS AND MATERIALS:

(1) Surface Waters Sampled:

Surface waters sampled included 4 in Indiana, 3 in Illinois, 3 in Michigan, and one each in Iowa, Kansas, and Florida (Table 2.1 and Figure 2.1). The estimated atrazine use in lbs ai/acre for the watershed of each sampled surface water is given in Table 2.2. The 14 surface waters sampled in 6 states were randomly selected from a larger group of 60 surface waters in 19 states whose watersheds included one or more counties in which atrazine is sold (and assumed to be used). Surface waters whose watersheds were sufficiently large such that drainage from any one county would contribute negligibly to the total flow were not included in the 60 candidates for sampling.

(2) Sampling Location Within Each Surface Water

The single sampling site for each surface water was located at the bridge closest to a semi-randomly selected (randomly selected with the restrictions on selection listed below) USGS gauging station on the river. The sampling sites selected were those for which the flow would be adequately represented by the flow determined at the gauging station. Sampling sites were not located close to gauging stations downstream from large reservoirs (where potentially high residence times could substantially decrease pesticide concentrations) or close to gauging stations that were upstream of more than one gauging station receiving drainage from a significant portion of the watershed area in the same county.

(3) Sampling Times:

Surface water samples were collected in 1986 and 1987. Samples were collected every 2 weeks in the peak growing period of April, May, and June and monthly in March, July, August, September, October, and November. Samples were not collected in December, January, or February.

(4) Sampling Methodology:

Bailers suspended from bridges were used to collect water samples from the water surface to a depth of approximately one foot at one or more cross-section points across the width of the surface water. If the computed mixing length was less than the distance to the nearest significant upstream tributary, the surface water was considered well mixed at the sampling location

(theoretically requiring sampling at only one cross-sectional point near the center of the surface water). However, in such cases grab samples were generally collected at 3 evenly spaced cross-section points across the width of the surface water to account for the possibility of incomplete mixing due to direct atrazine runoff to the river at the sampling location. If the computed mixing length was greater than the distance to the nearest significant upstream tributary, grab samples were collect at a number of evenly spaced cross sectional points equal to the smallest integer ≥ 3 and greater than the ratio of the surface water width to the computed mixing width. For each sampling interval, multiple bailings from the same cross-sectional point and from different cross-sectional points across the width of the surface water were composited. Samples were shipped in glass containers packed with ice and stored refrigerated until analysis.

(5) Analytical Procedures:

All samples were analyzed only for atrazine. Samples were filtered through one Reeve-Angel and one Whatman 2V filter paper. Atrazine was adsorbed from the water samples by drawing the samples by suction through pre-conditioned C-8 Bond-Elut reverse phase cartridges. The adsorption of atrazine to the columns was enhanced by the addition of 50 mL of saturated sodium chloride to each 1000 mL of sample prior to drawing the samples through the columns. Adsorbed atrazine was eluted from each column with 6 X 0.5 mL ethyl acetate. The combined ethyl acetate eluates were evaporated to dryness followed by re-dissolving of the resulting residues in methyl ethyl ketone for analysis by isothermal (between 165 and 185°C) GC using a Hall electrolytic conductivity detector operating in the oxidative halogen specific mode. Confirmations of atrazine's identity by GC/MS were generally performed on samples with apparent atrazine levels > 3 ppb. A "screening level" (quantification limit) of 0.1 ug/L atrazine based upon a 1 liter sample was reported.

(6) QA/QC Procedures:

Calibration curves of peak height vs. concentration were developed from injections of various concentrations of standard atrazine solutions (8 solutions ranging from 0.05 ug/L to 10 ug/L) at the beginning and end of each GC run, and after each 3-6 sample injections during each GC run. River water samples with atrazine peak heights exceeding the highest peak height on the calibration curve were diluted to reduce the peak height to within the peak height range of the calibration curve.

One field (bailer) or laboratory blank was analyzed for each 12-15 samples analyzed to check for contamination during sampling and analysis. Atrazine was detected in only 2 of the 88 field (bailer) controls and was not detected in any of the 65 laboratory controls.

One spiked laboratory sample (of de-ionized water) was analyzed for each 12-15 surface water samples analyzed to determine the accuracy of the analytical procedure in determining atrazine in de-ionized water. The mean recovery for 102 laboratory de-ionized water samples spiked at levels ranging from 0.10 to 25 ppb (the approximate range of atrazine detections in the river water) was $98\% \pm 14\%$.

Spiked field surface water samples at 10 or 25 ug/L were used to determine the stability of atrazine during shipping and storage, and the accuracy of the analytical method in determining atrazine in actual river water. The mean recovery for the 55 spiked field surface water samples analyzed at the same time as the (unspiked) river water samples was $90\% \pm 11\%$. In a separate storage stability study, the mean recovery for 17 spiked field surface water samples stored for 6 months under refrigeration was $109\% \pm 9.6\%$.

RESULTS:

The results of the sample analyses for each of the 14 surface waters sampled in the Roux 1989 study are presented in Table 2.3. Same page plots of the atrazine concentration, precipitation, and river flow (discharge) vs. time in 1986 and 1987 are given for each sampling location in Figures 2.2 through 2.15.

The maximum observed concentration, the concentration distribution, and arithmetic-mean concentration of atrazine for each of the 14 surface waters sampled are summarized in Table 2.4. Atrazine was detected at > 0.1 ug/L in 298 (88.7%) of the 336 samples collected from the 14 surface waters. The overall concentration distribution for the 336 samples collected from 14 locations in 14 surface waters was as follows:

- C \leq 0.1 ug/L (38 samples; 11.3% of total samples)
- 0.1 ug/L $<$ C \leq 1.0 ug/L (223 samples; 66.4%)
- 1.0 ug/L $<$ C \leq 5.0 ug/L (55 samples; 16.4%)
- 5.0 ug/L $<$ C \leq 10 (9 samples over 5 locations; 2.7%)
- C $>$ 10 ug/L (11 samples over 3 locations; 3.3%).

The highest peak concentrations reported were 30.5, 30, 29, 28, 18, 14, and 12 ug/L in Little Crooked Creek, IL; 30 and 13.0 ug/L in Clifty Creek, IN; and 14 and 12 ug/L in the Wabash River, IN; All other reported concentrations were < 10 ug/L. The highest arithmetic means over the entire 3/86-11/87 sampling period were 8.22 ug/L in Little Crooked Creek, IL; 3.28 ug/L in Wabash River, IN; and 3.16 ug/L in Clifty Creek, IN. The arithmetic means over the 3/86-11/87 sampling period for the remaining 11 surface waters sampled in the Roux 1989 study were all < 1 ug/L.

COMMENTS:

(1) The accuracy of the data as evidenced by the QA/QC procedures and results appears to be generally good. However, the study was apparently designed more for determining typical rather than peak atrazine concentrations as discussed in items 2 and 3 below.

(2) Although atrazine is applied to at least part of the drainage area of all the surface waters sampled, the volume of atrazine use and the drainage surface area above the sampling locations was apparently not a factor in the selection of the initial 60 candidate surface waters nor in the final random selection of 14 surface waters for sampling.

(3) Although the frequency of sampling was doubled during the peak corn planting/early growing period of April, May, and June, set sampling intervals were used which were not modified to reflect rainfall or runoff events. However, as part of the data analysis, the study author did relate the sampling dates to observed runoff events.

(4) Atrazine is used primarily as a pre-emergent herbicide for corn. It is therefore applied within a few days after planting which occurs between the first part of April and the last part of May in most of the country (Figure 2.16). Most of the atrazine concentrations exceeding 3 ug/L were reported for samples collected in April, May, and June (during corn planting/early growing periods).

(5) At most locations, the peak observed atrazine concentration appeared to occur during or shortly after the first substantial runoff period following estimated corn planting times after which atrazine concentrations generally gradually decreased to background levels < 1 ug/L in July or August.

(6) Other than eliminating some surface waters with large watersheds, the procedure for selecting the initial 60 candidate surface waters for sampling was unclear.

Page _____ is not included in this copy.

Pages 31 through 52 are not included.

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DATA EVALUATION RECORD
Study 3

SHAUGNESSY No. 080803
COMMON NAME: Atrazine
CHEMICAL NAME: 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine
FORMULATION: Not applicable
DATA REQUIREMENT: Surface Water Monitoring

MRID #410652-05 (Vol. 1)
Balu K. 1989. Summary of surface water monitoring data for atrazine. Completed on March 17, 1989. Performed and submitted by Ciba Geigy Corp., Greensboro, NC. Study No. EIR-89001

Appendix A: Ross R. and Balu K. 1985. Summary of atrazine surface water monitoring data during 1975-1985. Submitted by CIBA-GEIGY.

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SIGNATURE: *H Nelson*

DATE: 8/23/91

1661 8 2 90V

APPROVED BY: Hank Jacoby
TITLE: Chief, Environmental Fate and Groundwater Branch
ORGANIZATION: Environmental Fate and Effects Division/OPP

SIGNATURE:

AUG 28 1991

CONCLUSIONS:

(1) The QA/QC and other information provided is inadequate to fully assess the accuracy and representativeness of the data.

(2) The overall atrazine concentration distribution for the 1407 samples collected during 1975-1981 from 33 locations in 18 surface waters was as follows:

$C \leq 0.1$ ug/L (138 samples; 9.8% of the total)
 0.1 ug/L $< C \leq 1.0$ ug/L (881 samples; 62.6%)
 1.0 ug/L $< C \leq 5.0$ ug/L (356 samples over 26 locations; 25.3%)
 5.0 ug/L $< C \leq 10$ ug/L (25 samples over 12 locations; 1.8%)
 $C \geq 10$ ug/L (7 samples over 6 locations; 0.6%).

The highest peak concentrations reported were 234 ug/L on 10/4/76 and 56 ug/L on 10/18/76 in the Mississippi River 10 miles above Vicksburg. The highest arithmetic mean over the 1975-1981 sampling period was 3.87 ug/L in the Missouri River 10 miles below St. Joseph (19 samples 4/75-12/75). Arithmetic means for all other locations were < 3.0 ug/L.

(3) The overall atrazine concentration distribution for the 463 samples collected during 1982-1985 from 6 locations in 3 surface waters was as follows:

- C ≤ 0.1 ug/L (47 samples; 11.2%)
- 0.1 ug/L < C ≤ 1.0 ug/L (309 samples; 66.7%)
- 1.0 ug/L < C ≤ 5.0 ug/L (92 samples over 6 locations; 19.9%)
- 5.0 ug/L < C ≤ 10 ug/L (11 samples over 4 locations; 2.4%)
- C ≥ 10 ug/L (3 samples over 2 locations; 0.6%).

The highest peak concentrations reported were 28.0 ug/L on 11/16/82 in the Mississippi River 1 mile above Vicksburg and 16.0 ug/L on 7/12/82 in the Mississippi River at Greenville, KS. The highest arithmetic mean over the 1982-1985 sampling periods was 1.61 ug/L in the Mississippi River 8 miles above the CIBA GEIGY Plant in St. Gabriel, LA (46 samples 6/82-6/85)

METHODS AND MATERIALS:

(1) Sampling Locations:

Sampling locations included 11 in the Mississippi River (1 in MO, 2 in AR, 2 in TN, 3 in MS, 3 in LA), 4 in the Missouri River (all in MO), 3 in the Des Moines River (all in IA), 17 in other miscellaneous surface freshwaters (2 in IA, 4 in IL, 3 in AL, 1 in FL, 2 in TX, 2 in KS, 2 in CA, 1 in PA), and over 20 in the Gulf of Mexico (Table 3.1 and Figures 3.1, 3.2, 3.3, and 3.4). Samples were also collected of 2 tap water supplies (Baton Rouge, LA and St. Gabriel, LA).

(2) Sampling Years:

The report covers surface water samples collected from 1975 through 1985 by Ciba Geigy. The years in which samples were taken varied depending upon the sampling location (Table 3.2).

(3) Sampling Frequency Within Any Given Year:

(a) 1975-1981: Samples were collected weekly during the peak corn planting/growing season of April to August and biweekly to monthly at other times.

(b) 1982-1985: Samples were collected biweekly except at the Vicksburg, MS site where samples were collected weekly.

(4) Sampling Methodology:

(a) 1975-1981: Permanent sampling sites such as bridges and ferry crossings were used when possible. The locations of sampling sites sampled by boat were marked by identifying or establishing a landmark on the river

bank so that subsequent samples could be collected from the same cross section. For most sampling intervals and locations, ten grab samples were collected at evenly spaced intervals across the width of the stream or river being sampled. The samples were then composited by mixing into a 5 gallon container. Samples were collected at depths of approximately one foot to avoid the inclusion of surface film into the samples. The composite sample was split into 2 one quart samples for shipping to the laboratory.

(b) 1982-1985: River samples were collected from free flowing water near the river bank in metal cans and then shipped to the laboratory. Tap water samples were collected in residences. Sources for the tap water sampled included both well water and river water.

(5) Shipping/Storage Stability:

(a) 1975-1981: Atrazine was reported to be stable at ambient temperatures in storage stability studies run for up to 28 days. Therefore, samples were not refrigerated during shipping and generally not refrigerated during storage except in rare cases where the elapsed time between sampling and analysis exceeded 28 days.

(b) 1982-1985: Samples were not refrigerated during shipping, but were refrigerated during storage. Information was not provided on the storage stability of refrigerated samples or elapsed times between sampling and analysis.

(6) Analytical Procedures:

(a) 1975-1981: Water samples were filtered (filter not specified) to remove silt and debris. All samples were analyzed for atrazine; most of the 1975 samples were also analyzed for major degradates of atrazine (Surface Water Appendix Figure 3.5). Atrazine and its major degradates were adsorbed from the water samples by passing the samples through pre-conditioned columns packed with 20-40 mesh XAD-4 resin. Atrazine and major metabolites G-30033, G-28279, and G-28273 were eluted from the columns with diethyl ether. Major metabolite G-34048 was eluted from the columns with methanol. The diethyl ether eluates were either evaporated to low volume or to dryness followed by residue re-dissolving in benzene prior to analysis by GC with a Colson Conductivity Detector in the nitrogen specific mode. Confirmations were performed using a chloride specific detector and/or GC/MS. The methanol eluates were evaporated to dryness and the residues re-dissolved in 0.1 N HCl prior to analysis by TLC. Detection limits were as follows: atrazine (<0.1 ppb), G-30033 (0.1 ppb), G-28279 (0.1 ppb), and G-34048 (0.5 ppb). "Typical" recoveries for atrazine ranged from 85-100%.

(b) 1982-1985: All samples were analyzed only for atrazine. Samples were filtered through one Reeve-Angel and one Whatman 2V filter paper. Atrazine was adsorbed from the water samples by drawing the samples by suction through pre-conditioned C-18 or C-8 Bond-Elut reverse phase cartridges. The adsorption of atrazine to the columns was enhanced by the addition of

50 mL of saturated sodium chloride to each 1000 mL of sample prior to drawing the samples through the columns. Adsorbed atrazine was eluted from each column with 5 X 0.5 mL ethyl acetate. The combined ethyl acetate eluates were evaporated to dryness followed by re-dissolving of the resulting residues in methanol for analysis by isothermal (170°C) GC using a Hall Electrolytic Conductivity detector. Confirmations were performed with the use of both the nitrogen and reductive chloride modes of the detector or by GC/MS.

A "screening level" (presumably the method detection limit) of 0.1 ug/L atrazine based upon a 1 liter sample was reported. Recoveries based upon fortification levels of 0.1, 0.25, and 0.5 ug/L ranged from 70-90%.

RESULTS:

The results of the sample analyses for atrazine and its degradates (analysis for degradates on 1975 samples only) are presented in Tables 3.5 through 3.43. The results are graphically presented by concentration vs. time plots in Surface Water Figures 3.6 through 3.20.

(1) 1975-1985 Atrazine in Surface Freshwaters:

(a) 1975-1981: The maximum observed concentration, the concentration distribution, and arithmetic mean concentration of atrazine for each of the 33 locations in 18 surface waters sampled are summarized in Table 3.3. Atrazine was detected at > 0.1 ug/L in 1268 of the 1407 samples collected during 1975-1981 from 33 locations in 18 surface waters. The overall atrazine concentration distribution for the 1407 samples was as follows:

$C \leq 0.1$ ug/L (138 samples; 9.8% of the total)
 0.1 ug/L $< C \leq 1.0$ ug/L (881 samples; 62.6%)
 1.0 ug/L $< C \leq 5.0$ ug/L (356 samples over 26 locations; 25.3%)
 5.0 ug/L $< C \leq 10$ ug/L (25 samples over 12 locations; 1.8%)
 $C \geq 10$ ug/L (7 samples over 6 locations; 0.6%).

The highest peak concentrations reported were 234 ug/L on 10/4/76 and 56 ug/L on 10/18/76 in the Mississippi River 10 miles above Vicksburg; 17.8 ug/L on 6/25/75 in the Mississippi River 10 miles below Helena, AR; 16.7 ug/L on 6/25/75 in the Mississippi River 1 mile above Helena, AR; 14.0 ug/L on 6/9/75 in the Missouri River 10 miles below St. Joseph; 13.59 ug/L on 6/30/75 in the Des Moines River at the Mississippi River confluence; and 13.0 ug/L on 5/27/75 in the Wabash River at the Ohio River confluence. All other atrazine concentrations were < 10 ug/L.

The highest arithmetic means over the entire variable sampling periods were 3.87 ug/L in the Missouri River 10 miles below St. Joseph (19 samples 4/75-12/75), 2.42 ug/L in the Republican River at the Miss. River confluence (18 samples 4/75-2/76), 2.25 ug/L in the Wabash River at the Ohio River confluence (19 samples 4/75-3/76), 2.19 ug/L in the Mississippi River 10 miles below Vicksburg (182 samples 3/75-12/79), and 2.14 ug/L in the Des Moines River at the Mississippi River confluence (55 samples 3/75-

12/76). Of the 28 remaining locations 12 had arithmetic means between 1 and 2 ug/L and 16 had arithmetic means below 1 ug/L.

(b) 1982-1985: The maximum observed concentration, the concentration distribution, and arithmetic mean concentration of atrazine for each of the 6 locations in 3 surface waters sampled are summarized in Table 3.4. Atrazine was detected at > 0.1 ug/L in 416 of the 463 samples collected during 1982-1985 from 6 locations in 3 surface waters. The overall atrazine concentration distribution for the 463 samples was as follows :

- $C \leq 0.1$ ug/L (47 samples; 11.2%)
- 0.1 ug/L $< C \leq 1.0$ ug/L (309 samples; 66.7%)
- 1.0 ug/L $< C \leq 5.0$ ug/L (92 samples over 6 locations; 19.9%)
- 5.0 ug/L $< C \leq 10$ ug/L (11 samples over 4 locations; 2.4%)
- $C \geq 10$ ug/L (3 samples over 2 locations; 0.6%).

The highest peak concentrations reported were 28.0 ug/L on 11/16/82 in the Mississippi River 1 mile above Vicksburg and 16.0 ug/L on 7/12/82 in the Mississippi River at Greenville, KS. All other atrazine concentrations were < 10 ug/L.

The highest arithmetic means over the entire variable sampling periods were 1.61 ug/L in the Mississippi River 8 miles above the CIBA GEIGY Plant in St. Gabriel, LA (46 samples 6/82-6/85); 1.08 ug/L in the Mississippi River 1 mile above Vicksburg (165 samples 1/82-6/85); and 1.01 ug/L in the Mississippi River at Greenville, KS (58 samples 5/82-2/85). The arithmetic means of the 3 remaining locations were < 1 ug/L.

The Ohio River at the Miss. River confluence, the Missouri River near St. Charles, the Mississippi River 1 mile above Vicksburg, and the Mississippi River 8 miles above the CIBA-GEIGY Plant in St. Gabriel were the only locations sampled both prior to and after January 1982. The arithmetic means and concentration distributions for the pre and post January 1982 samplings were comparable at the first two locations, but appear to be somewhat higher for the post January 1982 samplings than for the pre January 1982 samplings at the latter 2 locations. However, the differences are not great, and the number of locations available for comparison is too small to develop conclusions concerning overall trends in atrazine concentrations from 1975-1985.

(2) Atrazine Degradates in Surface Freshwaters: Some of the surface freshwater samples collected in 1975 were analyzed for 1 to 4 of the following degradates : 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (G-34048 - hydroxylated atrazine), 2-chloro-4-ethylamino-6-amino-s-triazine (G-28279 - desisopropylated atrazine), 2-chloro-4-amino-6-isopropylamino-s-triazine (G30033 - desethylated atrazine), and 2-chloro-4,6-diamino-s-triazine (G28273 - desalkylated atrazine)(Figure 3.5).

Most of the samples analyzed had atrazine degradate concentrations less than detection limits of 0.5 to 1.0 ug/L. Hydroxylated atrazine was detected at concentrations ≥ 1 ug/L in 5 samples ranging from 1.0 to 1.8 ug/L. Desisopropylated atrazine was detected at concentrations ≥ 1 ug/L in 4 samples ranging from 1.1 to 2.1 ug/L. Desalkylated atrazine was detected at

concentrations ≥ 1 ug/L in 2 samples (1.89 and 1.80 ug/L). Desethylated atrazine was not detected at concentrations ≥ 1 ug/L in any samples. Atrazine degradate concentrations were typically 2X to > 10 X lower than the atrazine concentration, but were occasionally comparable.

(3) 1982-1985 Atrazine in Surface Water Source Tap Water: The results of the surface water source tap water sample analyses for atrazine along with the maximum, arithmetic mean and concentration distribution for each of the 4 surface water source tap water locations covered by the Ross and Balu 1985 summary are presented in Tables 3.12, 3.17, 3.40, and 3.42.

Atrazine was detected at > 0.1 ug/L in 156 of the 221 samples collected during 1982-1985 from 4 surface water source tap waters. The overall atrazine concentration distribution for the 221 samples was as follows: $C \leq 0.1$ ug/L (65 samples; 29.4%), $0.1 < C \leq 1.0$ ug/L (138 samples; 62.4%), $1.0 < C \leq 5.0$ ug/L (17 samples over 2 locations; 9.4%), $5.0 < C \leq 10$ ug/L (1 sample; 0.6%), and $C \geq 10$ ug/L (0 samples; 0.0%).

The highest observed peak concentrations reported were 5.10 ug/L on 7/10/84, 5.0 ug/L on 7/25/84, 3.90 ug/L on 6/15/84, and 3.10 ug/L on 7/21/82 all in Missouri River St. Charles, MO tap water. All other tap water concentrations were < 3.0 ug/L.

The arithmetic means over the entire sampling period for the 4 tap water locations were as follows: 0.89 ug/L in the Missouri River source St. Charles tap water (68 samples 7/82-2/85); 0.39 ug/L in the Ohio River source tap water (51 samples 7/82-2/85); 0.14 ug/L in the Miss. River source Baton Rouge tap water (30 samples 2/83-6/85); and 0.12 ug/L in the Sacramento River source tap water (72 samples 5/82-7/85).

Pesticides (such as atrazine) with relatively low soil or sediment/water partition coefficients are frequently reported at concentrations in tap water that are comparable to concentrations reported in the corresponding surface water source. The reason is that most drinking water plants employ only filtration and/or coagulation/flocculation, and chlorination in treatment none of which effectively remove trace organics with low soil/water partition coefficients. The arithmetic means and concentration distributions of atrazine in the Ohio, Missouri, and Sacramento River source tap waters are comparable to those in their surface water sources (Surface Water Appendix Spreadsheets 3.10, 3.15, and 3.38). The arithmetic means and concentration distribution of atrazine in the Baton Rouge tap water appears to be substantially lower than those generally observed for the lower Mississippi River, but it was unclear from the study report whether the Baton Rouge tap water is derived from groundwater or the Mississippi. In any event, the number of surface water source tap waters sampled is too low to develop conclusions concerning the relative concentrations of atrazine in surface water source tap water versus those in the corresponding surface water source.

(4) Atrazine Concentrations in the Gulf of Mexico: Of 48 samples collected in the Gulf of Mexico at the mouth of the Mississippi River from 1975 to 1985, 5 had atrazine concentrations ≥ 1 ug/L ranging from 1.2 to 2.5 ug/L. The atrazine concentration distribution for 174 samples collected at 11 locations off Venice,

LA in the Gulf of Mexico from 1975 through 1985 was as follows: $C \leq 0.1$ ug/L (51 samples; 29.3%), $0.1 < C \leq 1.0$ ug/L (100 samples; 55.9%), $1.0 < C \leq 5.0$ ug/L (17 samples; 9.5%), $5.0 < C \leq 10$ ug/L (3 samples; 1.7%), and $C > 10$ ug/L (1 sample at 56.4 ug/L; 0.6%). The majority of observed atrazine concentrations > 1 ug/L were in samples collected in 1975 and in 1980. Only 2 samples collected from 1981 through 1985 had atrazine concentrations > 1 ug/L.

COMMENTS:

The QA/QC and other information provided is inadequate to fully assess the accuracy and representativeness of the data for the following reasons:

- (1) The results of field and laboratory blank analyses (if any) were not provided.
- (2) "Typical" recoveries were reported to range from 85 to 100% for the 1975-1981 samples and 70 to 100% for the 1982-1985 samples, but no recovery data were provided. In addition, it was unclear whether reported recoveries were from de-ionized water or river water.
- (3) Although recoveries are frequently a function of the level of spiking, no information was provided on the levels of spiking for the 1975-1981 samples, and the highest level of spiking (0.5 ug/L) for the 1982-1985 samples was well below many of the reported concentrations.
- (4) No information was provided on the development of calibration curves from standard solutions.
- (5) Although storage stability data for unrefrigerated samples over a 28 day period was provided, the maximum time intervals between sampling and analyses for 1982-1985 samples was not provided.
- (6) Samples collected at each sampling time during 1982-1985 were reported to generally be single grab samples collected close to the river banks. Therefore, they were not as representative of the overall river water as the 1975-1981 samples which were generally composited from 10 grab samples collected at equal intervals across the width of the river. None of the samples collected from 1975 to 1985 were time composited such as over 24 hours.
- (7) The criteria used for the selection of sampling locations was not provided.
- (8) Sampling times were at set intervals and neither dictated nor correlated with rainfall and runoff events.

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DATA EVALUATION RECORD
Study 4

SHAUGNESSY No. 080803
COMMON NAME: Atrazine
CHEMICAL NAME: 2-chloro-4-ethylamino-6-isopropyl amino-1,3-5-triazine
FORMULATION: Not applicable
DATA REQUIREMENT: Surface Water Monitoring

MRID #410652-05 (Vol. 1)
Balu K. 1989. Summary of surface water monitoring data for atrazine. Completed on March 17, 1989. Performed and submitted by Ciba Geigy Corp., Greensboro, NC. Study No. EIR-89001

Appendix C: Roux P. 1989. Summary of atrazine/metolachlor cross-over in the surface-water monitoring program. Completed in February 1988. Performed by Roux Associates and submitted by Ciba Geigy Corp., Greensboro, NC. Laboratory study #CG-02814.

REVIEWED BY: Henry Nelson, Ph.D.
TITLE: Chemist
ORGANIZATION: EFGWB/EFED/OPP
TELEPHONE: (703) 557-7356

AUG 28 1991

SIGNATURE: *H. Nelson* DATE: 8/23/91

APPROVED BY: Hank Jacoby
TITLE: Chief, Environmental Fate and Groundwater Branch
ORGANIZATION: Environmental Fate and Effects Division/OPP

SIGNATURE:

CONCLUSIONS:

(1) The analytical and QA/QC procedures described in the 1988 En-Cas report entitled "Analysis of Atrazine Residues in Samples from a Surface Water Monitoring Program: Analytical Phase of Roux Associates Project No. CG-02814" appear to be adequate (see DER for 411352-06, study 2). If the same analytical and QA/QC procedures were used in the cross-over study, they are probably adequate. Nevertheless, EFGWB needs to see the actual QA/QC data (field and lab blanks, recoveries, calibration, etc.) to determine the accuracy of the cross-over data.

(2) Atrazine concentrations in samples collected from the 10 known to drain high metalochlor use areas were generally less than in samples collected in other studies from surface waters known to drain high atrazine use areas. (The highest peak concentrations observed were 4.5 ug/L in the Skunk River, IA.)

METHODS AND MATERIALS:

(1) Surface Waters Sampled:

Surface waters sampled were 3 in Iowa, 2 in Georgia, and one each in Delaware, Louisiana, Michigan, Minnesota, Ohio, and South Dakota (Table 4.1 and Figure 4.1).

(2) Sampling Times:

Surface water samples were collected monthly in September, October, and November of 1986; monthly in March, July, August, September, October, and November 1987; and bimonthly in April, May, and June 1987. Samples were not collected in December, January, or February.

(3) Sampling Methodology:

No information was provided on sampling methodology.

(4) Analytical/OA-QC Methodologies:

The study author refers readers to a En-Cas Laboratories report entitled "Monitoring of Atrazine in Surface Water" dated 1987 for information on analytical and QA/QC procedures.

RESULTS:

The results of the sample analyses are presented in Table 4.2. Same page plots of the atrazine concentration, precipitation, and river flow (discharge) vs. time in 1986 and 1987 are given for each sampling location in Figures 4.2 through 4.8.

The maximum observed concentration, the concentration distribution, and arithmetic mean concentration of atrazine for each of the 11 surface waters sampled are summarized in Table 4.3.

Atrazine was detected at ≥ 0.1 ug/L in 107 of the 163 samples collected from the 14 rivers. The highest peak concentrations observed were 4.5 ug/L in the Skunk River, IA; 4.5 ug/L in the Bayou Tech River, LA; 2.70 ug/L in Skunk Creek, SD; 1.90 ug/L in the Mad River, OH; 1.80 ug/L in the North River, IA; 1.40 ug/L in the Rum River, MN; and 1.20 ug/L in Strockly Branch, DE. However, those were the only observed concentrations > 1.0 ug/L.

COMMENTS:

(1) Atrazine is used primarily as a pre-emergent herbicide for corn. It is therefore applied within a few days after planting which occurs between the first part of April and the last part of May in most of the country (Figure 21). However, 4 of the 7 reported concentrations > 1 ug/l were for samples collected in June 1987, 2 were for samples collected in July 1987, and the remaining one was for a sample collected in early August 1987. That suggests that the

persistence of atrazine may be sufficient to extend its potential for runoff to several months after its application in some locations.

(2) The study author refers readers to a En-Cas Laboratories report entitled "Monitoring of Atrazine in Surface Water" dated 1987 for information on analytical and QA/QC procedures. However, that report was not included for review. The analytical and QA/QC procedures described in the 1988 En-Cas report entitled "Analysis of Atrazine Residues in Samples from a Surface Water Monitoring Program: Analytical Phase of Roux Associates Project No. CG-02814" appear to be adequate (see DER for 411352-06, study 2). If the same analytical and QA/QC procedures were used in the cross-over study, they are probably adequate. Nevertheless, EFGWB needs to see the actual QA/QC data (field and lab blanks, recoveries, calibration, etc.) to determine the accuracy of the cross-over data.

(3) The study was primarily designed for the determination of metolachlor in rivers within metolachlor use areas. Since atrazine is so widely used, samples collected during the second phase of the study were also analyzed for atrazine. However, atrazine concentrations in samples collected from the 10 known to drain high metolachlor use areas were generally less than in samples collected in other studies from surface waters known to drain high atrazine use areas.

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Pages 152 through 162 are not included.

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DATA EVALUATION RECORD
Study 5

SHAUGNESSY No. 080803
COMMON NAME: Atrazine
CHEMICAL NAME: 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine
FORMULATION: Not applicable
DATA REQUIREMENT: Surface Water Monitoring

No MRID # (Not submitted by a registrant)
Goolsby DA and Thurman EM. 1991. Herbicides in rivers and streams of the upper
midwestern United States. To be published in: Proc. 46th Ann. Meeting Upper
Mississippi River Conservation Committee.

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CONCLUSIONS:

(1) EFGWB could not determine the accuracy of the data because no information was provided on QA/QC procedures.

(@) This was a multiple pesticide study, so the sampling sites in 10 midwestern states were not selected based specifically upon the drainage of atrazine use areas.

(2) The distribution of concentrations in samples collected during the first post-application runoff event (one per sampling location - 123 total) over the 10 states from which samples were collected was as follows:

C ≤ 0.1 ug/L (3 of 123 total; 2.4%)
0.1 ug/L < C ≤ 1.0 ug/L (23; 18.7%)
1.0 ug/L < C ≤ 5.0 ug/L (38; 30.9%)
5.0 ug/L < C ≤ 10 ug/L (17; 13.8%)
10 ug/L < C ≤ 50 ug/L (38 over 8 states; 30.9%)
C > 50 ug/L (4 over 3 states; 3.3%)

(3) The highest observed concentrations of atrazine in the post-application samples were 108 ug/L in Spoon River at London Mill, IL

METHODS AND MATERIALS:

(1) Locations Sampled:

Surface water samples were collected at 150 U.S. Geological Survey stream flow gaging stations over 10 midwestern states (IA, IL, IN, KS, MN, MO, NE, OH, SD, and WI)(Figure 5.1). Surface waters sampled had drainage areas ranging from < 100 to > 700,000 sq. miles.

(2) Sampling Times:

Surface waters were sampled prior to pesticide application (March-April), during the first runoff event following pesticide applications (May-June), and during the fall (October-November). However, at some locations only a post-application sample was collected and at a few locations only a pre-application sample was collected.

(3) Analytical Procedures:

All samples were analyzed by immunoassay analysis for 11 herbicides including atrazine and 2 atrazine degradates (desethyl-atrazine and desisopropyl-atrazine). Confirmation of analysis was performed on 35% of the pre-application samples and on most of the post-application and fall samples by GC/MS. No other information on the analytical methods (sample preparation, instrumental operating parameters) was provided.

(4) QA/QC Procedures:

No information was provided on QA/QC procedures.

RESULTS:

The results of the pre-application and post-application sample analyses for atrazine and 2 atrazine degradates are presented in Tables 5.2 through 5.12 for each of the 10 states from which samples were collected. The results of the Fall sample analyses were not yet available.

The state specific pre-application and runoff event post-application concentration distributions of atrazine are presented in Table 5.13. Most of the pre-application samples collected from surface waters in all 10 states had atrazine concentrations < 1 ug/L. The distribution of concentrations in samples collected during the first post-application runoff event (one per sampling location - 123 total) over the 10 states from which samples were collected was as follows:

C ≤ 0.1 ug/L (3 of 123 total; 2.4%)
0.1 ug/L < C ≤ 1.0 ug/L (23; 18.7%)
1.0 ug/L < C ≤ 5.0 ug/L (38; 30.9%)
5.0 ug/L < C ≤ 10 ug/L (17; 13.8%)
10 ug/L < C ≤ 50 ug/L (38 over 8 states; 30.9%)
C > 50 ug/L (4 over 3 states; 3.3%)

The highest observed concentrations of atrazine in the post-application samples were 108 ug/L in Spoon River at London Mill, IL; 71.6 ug/L in Old Man Creek near Iowa City, IA; 52.2 ug/L in Bonapas Creek at Browns, IL; 52.0 ug/L in Wahoo Creek at Itica, NE; 48.4 ug/L in South Skunk River near Oskaloosa, IA; and 42.10 ug/L in North Skunk River near Sigourney, IA. All other post-application samples had atrazine concentrations < 40 ug/L.

Post-atrazine application concentrations of desethyl-atrazine and desisopropyl-atrazine were generally comparable to each other (within a factor of < 2) and are both generally greater than 10X lower than the post-application concentrations of atrazine. The highest observed post-application concentrations of the atrazine degradates were 3.80 ug/L for desethyl-atrazine in Bonpas Creek and 3.20 ug/L for desisopropyl-atrazine in Old Man Creek. The pre-application concentrations of desethyl-atrazine and desisopropyl-atrazine are frequently less than 10X lower than the pre-application concentrations of atrazine, but all pre-application concentrations of the atrazine degradates are < 1 ug/L.

COMMENTS:

(1) The analytical procedure and QA/QC information provided was inadequate for EFGWB to assess the accuracy of the data.

(2) This was the only one of the 5 studies reviewed in which post application sampling times were determined by runoff events instead of by pre-set intervals. The results of this study indicate the importance of sampling in conjunction with runoff events if one of the objectives of the study is to determine maximum atrazine concentrations. The percentage of locations sampled with an atrazine concentration exceeding 10 ug/L is substantially higher than in studies 2, 3, and 4.

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