Appendix B:
Description of Available Atrazine Monitoring Studies

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Appendix B. Description of Available Atrazine Monitoring Studies

B.1 Ecological Monitoring Program Data

The 2003 IRED required the atrazine registrants to conduct watershed monitoring for atrazine as a condition of re-registration. One component of the monitoring program is focused on flowing water bodies, and provides two to three years of monitoring data, accrued over a three-year period (2004-2006), in the most vulnerable watersheds associated with corn and sorghum production. These data are targeted specifically to atrazine use and are designed to represent exposure in the watersheds most prone to atrazine runoff. In this case, vulnerability has been defined using the USGS WARP model. The principal factors influencing WARP predictions of exposure and hence the vulnerability ranking are:

- Atrazine use,
- Rainfall intensity,
- Soil erodibility,
- Watershed area, and
- Dunne overland flow

Surface water data included in this study were collected using a targeted methodology that relied on WARP to identify the upper 20th percentile of vulnerable watersheds and a statistical design to select a subset of 40 watersheds that may be representative of 1,172 vulnerable watersheds. The atrazine use input was derived by calculating the mean annual atrazine concentration (at the 95th percent confidence limit) across all watersheds in the United States where atrazine is used. Given the statistical nature of the sampling design of this study, it is not possible to extrapolate the monitoring data from the 40 watersheds beyond the upper 20th percentile of watersheds (i.e., the 1,172 vulnerable watersheds).

Samples were collected from 20 locations within the designated watersheds every four days during the peak use period for atrazine (April to August) during the 2004-2005 growing season, and a second set of 20 watersheds were sampled during the 2005-2006 growing season (several watersheds from the 2004-2005 sample period were carried over for a third year of monitoring). The strength of this data set is the targeted nature of site selection to areas of high atrazine use, the frequency of the sampling (every four days during peak use season), and the collection of multiple samples on selected days from a number of sites that allows for a statistical description of the variability surrounding the time series data. More detail on the approach, methodology and objectives of the surface water Ecological Monitoring Program for atrazine may be found at:

http://www.epa.gov/oppsrrd1/reregistration/atrazine/

A preliminary analysis of this Ecological Monitoring Program data from 2004 to 2006 has been completed. The data have been statistically evaluated for each site/year combination, including number of non-detections, frequency of detection, maximum concentration, mean concentration, median concentration, and number of scheduled samples that ultimately did not occur or samples that were not subsequently analyzed. These statistics provide a general picture of the level of exposures seen in these data relative to the other data sets described in this assessment.

Overall, the data suggest a similar pattern of atrazine exposure in surface water as in the other data sets evaluated as part of this assessment. Atrazine was detected in a total of 2,979 out of 3,601 samples for an overall frequency of detection of 79%. The frequency of detection ranged across all watersheds and years from a maximum of 100% to a minimum of 11%. The maximum concentration detected from all watersheds was 208.8 µg/L from the Indiana 11 site in 2005. The mean annual concentrations ranged from a maximum of 9.5 µg/L from the Missouri 01 site in 2004 to a low of 0.1 µg/L for the Nebraska 06 site in 2006, while the median values ranged from 4.2 µg/L for the Missouri 02 site in 2004 to 0.1 µg/L for the Ohio 03 site in 2004. It should be noted that a number of watersheds, particularly in Nebraska, experienced dry periods where scheduled sampling did not take place; therefore, the statistics for those watersheds may not represent actual conditions expected in normal or wetter years.

This data set is currently releasable only upon completion and submission of an Affirmation of Non-multinational Status form under section 10(g) of FIFRA. Information on how to submit a request to obtain a copy of the data may be obtained from the following website:

http://www.epa.gov/espp/atrazine_ewm_data.htm

Although the ecological monitoring data set was targeted specifically to high atrazine use areas, very few of the watersheds actually are co-located with the HUC8 watersheds used in this assessment to identify topeka shiner locations. And of these watersheds, none are representative of the species habitat. The Topeka shiner resides in headwater streams with limited to no flow which are generally classified as 1st order stream while the Ecological monitoring watersheds are generally 2nd and 3rd order streams. Because the topeka shiner resides in low flow headwater steams the targeted monitoring data collected from 2nd and 3rd order streams may under-estimate exposures that the species may be exposed to.

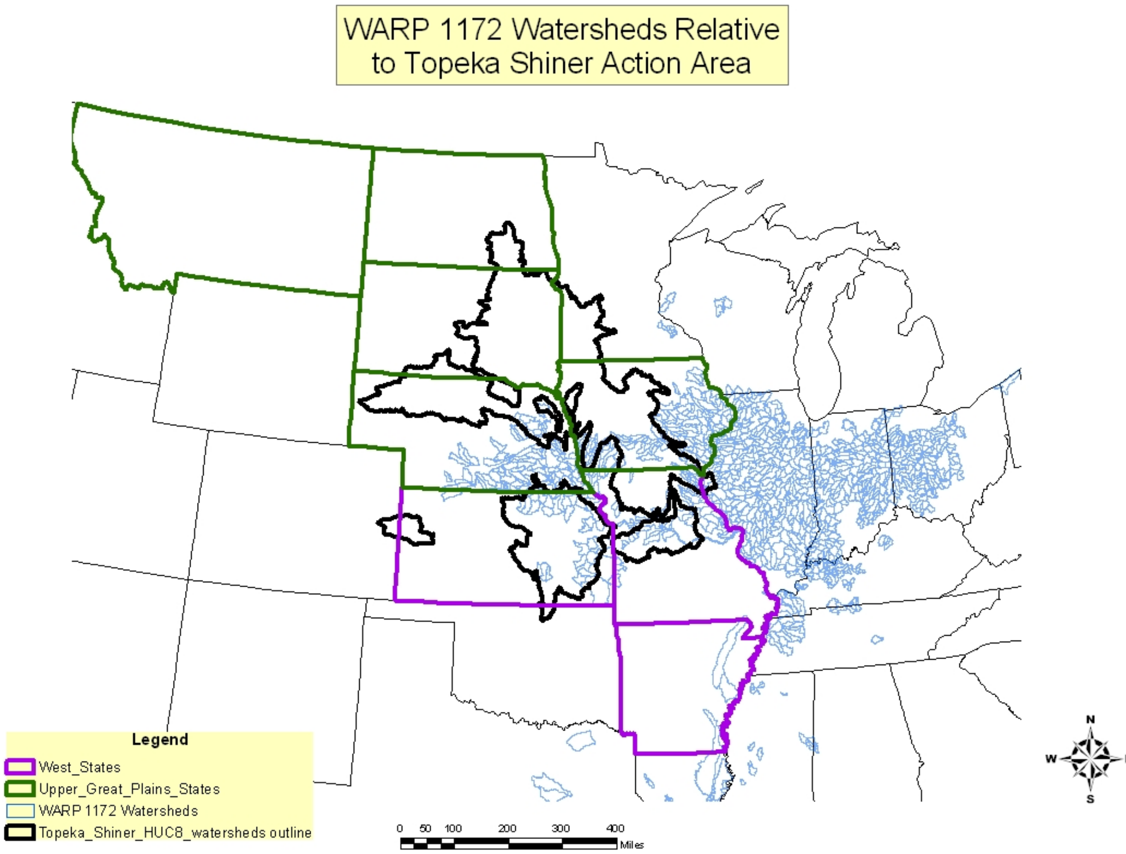

Figure B-1. WARP Vulnerable Watersheds Relative to the Action Area for the Topeka shiner

B.2. USGS NAWQA Data

An analysis was completed of the entire USGS NAWQA data set for atrazine. A data download was conducted from the USGS data warehouse (http://water.usgs.gov/nawqa). Overall, a total of 20,812 samples were analyzed for atrazine. Of these, 16,742 samples had positive detections (including estimated values) yielding a frequency of detection of roughly 80%. The maximum detection from all samples was 201 µg/L from the Bogue Chitto Creek in Alabama near Memphis in 1999. Overall, the average concentration detected was 0.26 µg/L when considering only detections and 0.21 µg/L when considering all detections and non-detections (using the detection limit as the value for estimation). The location of all NAWQA surface water sites relative to the action area and the targeted monitoring data is shown in Figure B-2.

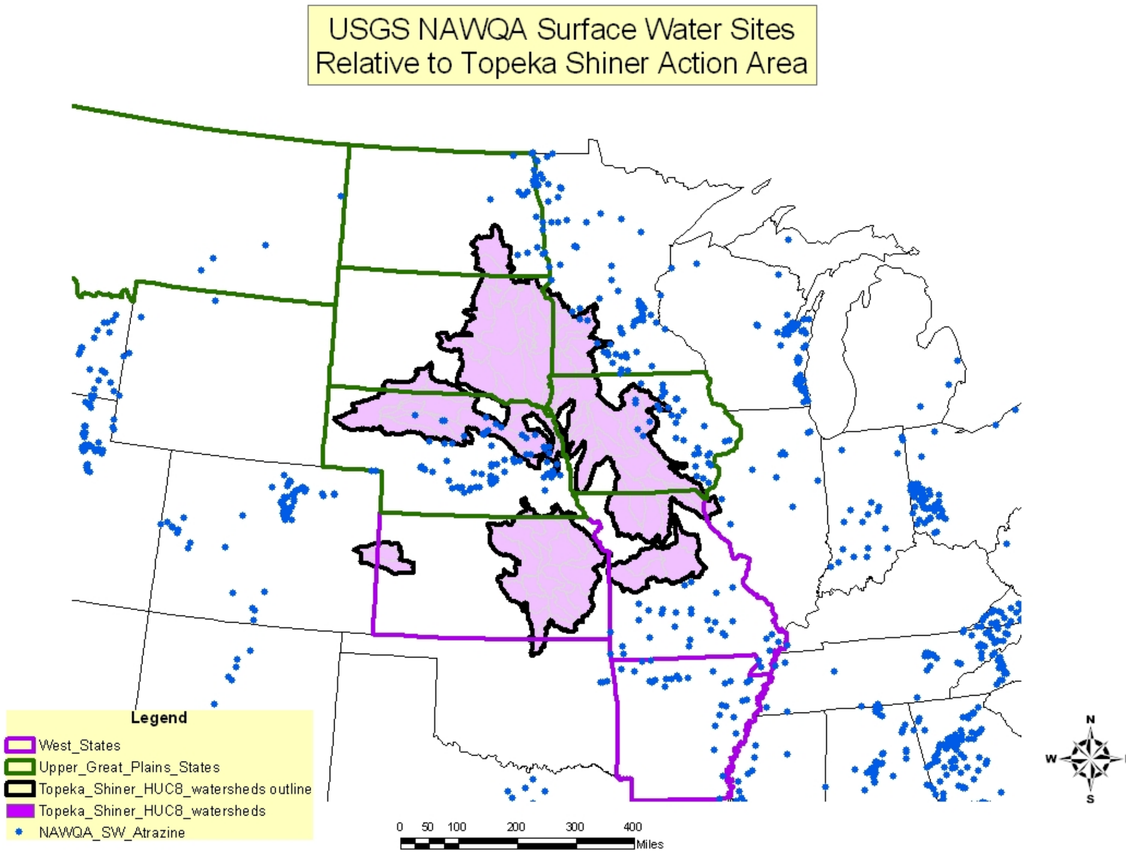

Figure B-2. All USGS NAWQA Sites Relative to Action Area

The top ten sites with the highest atrazine concentrations from the national NAWQA data were selected for refined analysis of the detections. All values from the national data set were ranked and the top ten sites were selected based on maximum concentration. Each location was analyzed separately by year, and the annual maximum and annual time weighted mean concentrations were calculated. The minimum criterion for calculating time-weighted means for each sampling station was at least 4 samples in a single year. The equation used for calculating the time weighted annual mean is as follows:

$$[((T_{0+1}\text{-}T_0) + ((T_{0+2}\text{-}T_{0+1})/2))*C\ t_{0+1})] + (((T_{i+1}\text{-}T_{i\text{-}1})/2)*C_i) + [((T_{end}\text{-}T_{end\text{-}1}) + ((T_{end\text{-}1}\text{-}T_{end\text{-}2})/2)*C_{Tend\text{-}1})]/365$$

where: Ci = Concentration of pesticide at sampling time (Ti)
Ti = Julian time of sample with concentration Ci
T_0 = Julian time at start of year = 0
T_{end} = Julian time at end of year = 365

Generally, the maximum (peak) concentrations from the USGS NAWQA data are consistent with peak concentrations observed from the targeted monitoring data, and roughly two times the values predicted using both the static water body and the flow adjusted approach. The time weighted mean (TWM) values from this analysis are roughly an order of magnitude below the static water body model predictions, two times above those estimated in the refined flow-adjusted EECs, and consistent with the targeted monitoring data. This analysis is somewhat biased because the selected USGS NAWQA data represent those sites with the highest concentrations and the majority of the sampling locations are within the same geographic extent as the targeted data – the 1,172 vulnerable watersheds. In reality, there are many more NAWQA sites within and outside the action area with atrazine detections and these sites would be expected to have lower concentrations (peak and annual average) than those reported for the top ten sites. Also of note is that there appears to be a general downward trend in atrazine exposures over time in these data (e.g. Bogue Chitto Creek), although some exceptions are noted (e.g. Sugar Creek, IL). Downward trends in exposure over time are expected given the label changes that have reduced application rates and implemented setbacks in the 1990's. Comparison of these data with modeled predictions for the intermediate duration exposures (14-day, 30-day, etc.) was not conducted because the NAWQA data generally do not have the frequency needed to conduct a meaningful interpolation between data points. Table B-1 presents a summary of the annual time weighted mean concentrations, and Table B-2 presents a summary of the annual maximum concentrations.

Table B-1. Annualized Time Weighted Mean (TWM) Concentration (µg/L) for the Top Ten NAWQA Surface Water Sites (Ranked by Maximum Concentration Detected)										
	Station Name (ID)									
Year	**Bogue Chitto Creek, near Memphis, TN (02444490)**	**Tributary to S Fork Dry Creek, near Schuyler, NE (06799750)**	**Sugar Creek, New Palestine, IN (394340085524601)**	**Kessinger Ditch, near Monroe City, IN (03360895)**	**LaMoine River @ Colmar, IL (05584500)**	**Sugar Creek @ Milford, IL (05525500)**	**Tensas River @ Tendal, LA (07369500)**	**Maple Creek near Nickerson, NE (06800000)**	**Auglaize River near Ft Jennings, OH (04186500)**
1992			0.98					1.32	
1993			0.77	3.80				1.43	
1994			0.87	2.56					
1995			2.28	0.74					
1996			1.30				4.32		2.18
1997			5.36		3.45		5.55	1.03	2.82
1998			0.82		1.79		2.94	1.21	1.88
1999	9.62		0.28				2.50	0.68	
2000	6.49		0.56			1.26		0.15	
2001	1.20		0.83			0.78		0.22	1.28
2002	2.88		0.51			2.22		1.26	0.80
2003	2.14	4.46	0.70			7.83		2.23	1.42
2004	1.77	68.78[a]	0.67			1.24		3.31	1.93

[a] TWM concentration likely biased because the first sample on May 8 is the peak sample from this year.

Table B-2. Maximum Concentration (µg/L) for the Top Ten NAWQA Surface Water Sites (Ranked by Maximum Concentration Detected)										
	Station Name (ID)									
Year	Bogue Chitto Creek, near Memphis, TN (02444490)	Tributary to S Fork Dry Creek, near Schuyler, NE (06799750)	Sugar Creek, New Palestine, IN (394340085524601)	Kessinger Ditch, near Monroe City, IN (03360895)	LaMoine River @ Colmar, IL (05584500)	Sugar Creek @ Milford, IL (05525500)	Tensas River @ Tendal, LA (07369500)	Maple Creek near Nickerson, NE (06800000)	Auglaize River near Ft Jennings, OH (04186500)
1992			14					25	
1993			8.5	120				11.2	
1994			11	24					
1995			27	2.6					
1996			14.2				30		18
1997			129		108		92.3	10.3	85.2
1998			7.88		27.7		19.3	30	9.96
1999	201		2.39				13.9	10.7	
2000	136		3.84			23		0.87	
2001	4.5		14.4			6.96		1.21	10.4
2002	24.8		4.01			21.3		16.4	2.58
2003	18.8	21.3	10.5			108		34.8	13.4
2004	14.6	191	28.3			10.9		91.9	18.7

B.3. USGS Watershed Regression of Pesticides (WARP) Data

The NAWQA data were then compared against the percentiles used to develop the USGS WARP model. Comparison against WARP percentiles was conducted because the WARP model has been reported to be a valuable tool for site selection and assessing overall vulnerability. More information on the WARP model may be found at:

http://pubs.usgs.gov/wri/wri034047/wrir034047.pdf

The WARP data were developed using a subset of the national data described above (all WARP data are included in the national data analysis described above). Data collected between 1992 and 1999 from a total of 113 sample sites were used to create the model. Sample sites were selected based on the robustness of the data available at a given site. The model yields predicted daily exposures at various percentiles of occurrence. The Agency compared the national NAWQA data and the model predictions against the mean and 95^{th} percentile values from the data used. The maximum 95^{th} percentile value from the WARP data was 20.2 µg/L as compared to a maximum of 201 µg/L from all data. The maximum mean value used in the WARP model development data was 3.82 µg/L, which is consistent with the annual TWM values discussed above.

B.4. Heidelberg College Data

Data from Heidelberg College, which consists of two intensively sampled watersheds (Maumee and Sandusky) in Ohio, were also analyzed. These sample sites are on the extreme northern edge of the action area and are also included in this analysis to provide context to the modeled exposures. It appears that the Sandusky watershed is within the boundary of the vulnerable watersheds included in the targeted monitoring study, while the Maumee watershed is outside this boundary. More information on the water quality monitoring program at Heidelberg College may be found at the following website:

http://wql-data.heidelberg.edu/

The Heidelberg data were collected more frequently than other data included in this assessment. The study design was specifically established to capture peak and longer-term trends in pesticide exposures. Data were collected between 1983 and 1999 and consist of an average of roughly 100 samples per year with several days of multiple sampling.

For the Sandusky watershed, a total of 1,597 samples were collected with 1,444 detections of atrazine (90.4% frequency of detection). The maximum concentration detected in the Sandusky watershed was 52.2 µg/L, and the overall average concentration was 4.5 µg/L. For the Maumee watershed, a total of 1,437 samples were collected with 1,305 detections of atrazine (90.8% frequency of detection). The maximum concentration detected in the Maumee watershed was 38.7 µg/L with an overall average concentration of 3.7 µg/L.

This analysis was further refined by deriving the annual TWM and maximum concentrations by sampled watershed by year. The results of this analysis are presented in Table B-4. The results show a consistent pattern with that seen in other data collected from high atrazine use areas with general TWM concentrations between 1 and 3 µg/L. In addition, these data are generally two times lower than the peak refined flow-adjusted EECs and are generally consistent with the longer-term flow-adjusted average concentrations.

Table B-4 Annual Time Weighted Mean and Maximum Concentrations (µg/L) for Atrazine in Two Ohio Watersheds from the Heidelberg College Data

Year	Sandusky Watershed		Maumee Watershed	
	TWM	Max	TWM	Max
1983	1.34	7.97	0.98	5.42
1984	1.08	8.73	1.27	11.71
1985	1.83	19.46	1.00	6.21
1986	3.32	24.61	1.64	10.01
1987	1.76	16.45	1.80	9.92
1988	0.41	1.53	0.43	2.15
1989	1.30	15.71	1.07	8.49
1990	1.96	19.31	1.69	14.78
1991	1.49	20.59	2.044	21.45
1992	0.39	40.53	0.51	7.35
1993	1.27	26.34	1.21	22.66
1994	0.86	10.10	0.82	4.02
1995	1.39	15.46	1.30	14.06
1996	1.56	23.40	1.19	16.19

Table B-4 Annual Time Weighted Mean and Maximum Concentrations (µg/L) for Atrazine in Two Ohio Watersheds from the Heidelberg College Data				
Year	Sandusky Watershed		Maumee Watershed	
	TWM	Max	TWM	Max
1997[a]	**2.16**	**53.21**	2.09	38.74
1998	1.49	40.03	1.41	27.62
1999	1.57	17.11	1.88	19.37

[a] Sample year 1997 from Sandusky selected for data infilling by interpolation in order to calculate CASM duration exposure values.

As with the ecological monitoring program data and the USGS NAWQA data, these data are not considered to be directly representative of the habitat where the topeka shiner resides and thus are provided herein for context only. No further analysis of these data were conducted

B.5. Summary of Open Literature Sources of Monitoring Data for Atrazine

Atrazine is likely to be persistent in ground water and in surface waters with relatively long hydrologic residence times (such as in some reservoirs) where advective transport (flow) is limited. The reasons for atrazine's persistence are its resistance to abiotic hydrolysis and direct aqueous photolysis, its only moderate susceptibility to biodegradation, and its limited volatilization potential as indicated by a relatively low Henry's Law constant. Atrazine has been observed to remain at elevated concentrations longer in some reservoirs than in flowing surface water or in other reservoirs with presumably much shorter hydrologic residence times in which advective transport (flow) greatly limits its persistence.

A number of open literature studies cited in the 2003 IRED (U.S. EPA, 2003a), document the occurrence of atrazine and its degradates in both surface water and groundwater. These data support the general conclusion that higher exposures tend to occur in the most vulnerable areas in the Midwest and South and that the most vulnerable water bodies tend to be headwater streams and water bodies with little or no flow.

The analysis in the IRED also documents the occurrence of atrazine in the atmosphere. The data indicate that atrazine can enter the atmosphere via volatilization and spray drift. The data also suggest that atrazine is frequently found in rain samples and tends to be seasonal, related to application timing. Finally, the data suggest that although frequently detected, atrazine concentrations detected in rain samples are less than those seen in the monitoring data and modeling conducted as part of this assessment and support the contention that runoff and spray drift are the principal routes of exposure. More details on these data can be found in the 2003 IRED (U.S. EPA, 2003a).

B.6. Miscellaneous Drinking Water Monitoring Data Derived from Surface Water

A number of surface water data sets were evaluated as part of the 2003 IRED. Included in that analysis were data from Acetochlor Registration Partnership (ARP) Monitoring Study, the Novartis Population Linked Exposure (PLEX) Database, the USGS 1992-1993 Study of 76 Mid-Western Reservoirs (USGS Open File Report 96-393), the USGS 1989-1990 Reconnaissance Study of Mid-Western Streams (USGS Open File Report 93-457), the USGS 1994-1995 Reconnaissance Study of Mid-Western Streams (USGS Open File Report 98-181), the USGS 1990-1992 Study of 9 Mid-Western Streams (USGS Open File Report 94-396), USGS NAWQA data available in 2002, as well as numerous open literature studies. In general, these data show a pattern of atrazine exposure in various water body types (streams vs. reservoirs), collected with a variety of study objectives (human health vs. ecological health) consistent with those summarized previously in this assessment. The maximum reported concentration from the studies (excluding open literature) was 108 μg/L from the USGS study (Open File Report 93-457) for Mid-Western Streams sampled between 1989 and 1990. Atrazine exposure in rivers, streams, lakes, and reservoirs documented in the open literature cited in the 2003 IRED were consistent with these results with no concentrations above 100 μg/L (except edge of field runoff concentrations in mg/l range which were reported as diluted to μg/L ranges when reaching surface water bodies). In addition, the 2003 IRED summarized reports from the Agency's 6(a)(2) incident database and found the highest concentration at 62 μg/L.

More detail on the individual studies and analysis of the data may be found in the 2003 IRED at the following website:

http://www.epa.gov/oppsrrd1/reregistration/atrazine/efed_redchap_22apr02.pdf

Subsequent to the completion of the 2003 IRED, additional monitoring data from surface water sources used for drinking water were submitted to the Agency for review. Atrazine monitoring results from 2003 to 2005 were collected as part of the Atrazine Monitoring Program (AMP) for purposes of assessing dietary risk for human health. In this study, data were collected from over 100 community water systems (CWS) in 10 states including many in the action area of this assessment. Monitoring was weekly through the growing season (generally April through July) with biweekly monitoring for the rest of the year. Both raw and finished water were monitored. In general, the results were consistent with those discussed above, with maximum detected concentrations of 33.1 μg/L in 2002, 39.7 μg/L in 2004, and 84.8 μg/L in 2005.

B.7. References

References for this appendix are in Section 8 of the risk assessment.