

REREGISTRATION ELIGIBILITY SCIENCE CHAPTER
FOR
ATRAZINE
ENVIRONMENTAL FATE AND EFFECTS CHAPTER

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I. Executive Summary

The Agency performed a refined assessment on atrazine. It was based on ecotoxicological data as well as microcosm and mesocosm studies submitted to support registration and discovered in publicly available literature. A substantial amount of monitoring data for freshwater streams, lakes, reservoirs, and estuarine areas, as well as reports of incidents of adverse effects on aquatic and terrestrial organisms associated with the use of atrazine were found. In the refined assessment, potential risk is described in terms of the number of aquatic monitoring sites in lakes/reservoirs, streams and estuarine areas with concentrations that equal or exceed concentrations shown to cause adverse effects. Cumulative exceedence curves for monitoring data were constructed in the following way: maximum annual atrazine concentrations were plotted versus the percent of sampling sites in water bodies (streams, rivers, lakes, reservoirs, estuarine areas) with equal or greater annual maximum concentrations. Eco-toxicological endpoint values from both laboratory and simulated field study results as well as 10th [per]centile values¹ for acute and chronic effects for groups of freshwater and estuarine plants and animals, calculated from laboratory data, were plotted on graphs as horizontal lines. Percentage exceedence was calculated where the endpoint lines crossed the concentration curve.

Based on the results of this refined assessment, the Agency finds that in areas of high atrazine use, there is widespread environmental exposure that (1) has resulted in direct acute effects on many terrestrial plant species at both maximum and typical use rates, (2) may have caused direct effects on aquatic non-vascular plants which in turn could have caused reductions in primary productivity, (3) may have caused reductions in populations of aquatic macrophytes, invertebrates and fish, (4) may have caused indirect effects on aquatic communities due to loss of species sensitive to atrazine and resulting in changes in structure and functional characteristics of the affected communities. Potential adverse effects on sensitive aquatic plants and other non-target aquatic organisms as well as their populations and their communities, are likely to be greatest where atrazine concentrations in water equal or exceed approximately 10 to 20 $\mu\text{g/L}$ on a recurrent basis or over a prolonged time period. Based on monitoring data, maximum concentrations at up to 35% of the sites exceeded the atrazine concentration ($>10 \mu\text{g/L}$) at which these adverse effects are found in simulated field studies. Up to 20% of the sites exceeded the atrazine concentration ($>20 \mu\text{g/L}$) at which adverse effects are found in simulated field studies as well as many of the 10th [per]centile values for acute and chronic effects from analyses of laboratory data. The frequency of occurrence and extent of the potential impacts will vary depending upon the type of water bodies and their proximity in time and space to atrazine

¹The 10th [per]centile value is the estimated value in a distribution of species specific toxicity values where 10% of the species are more sensitive to atrazine and 90% are less sensitive. Giddings *et al* 2000 (page 139) describes the calculation of the 10th [per]centile as follows: “The toxicity values (geometric means for each species) were ranked by concentration, and for each species the centile ranking was calculated as $i/(n+1)$, where i is the rank for that species and n is the total number of species...The centiles were plotted against the log transformed concentrations, and a linear regression was conducted to characterize each distribution....From each regression, the 10th centile in sensitivity was estimated.” The actual 10th [per]centile values are found in Tables 5.3 and 5.4 on pages 168 and 169 of the reference.

applications. Recovery from the effects of atrazine and the development of resistance to the effects of atrazine in some vascular and non-vascular aquatic plants is reported and adds uncertainty to these findings. Further research is needed to quantify the impact that these effects would have on these risk conclusions. In addition, atrazine has been reported to cause sub-lethal effects in aquatic organisms and amphibians. These include endocrine effects in frogs at $\sim 0.1 \mu\text{g/L}$ and in largemouth bass at $\sim 50 \mu\text{g/L}$, as well as olfactory effects in salmon at $\sim 0.5 \mu\text{g/L}$. As these data are made available on these and other potential effects of atrazine on the environment and non-target organisms, the Agency will evaluate them and determine their importance and relevance in the risk of atrazine to the environment and non-target organisms.

Atrazine is a triazine herbicide which inhibits photosynthesis in sensitive plants, and thus adversely affects their ability to produce food to meet their energy needs. Detrimental effects on plants are rapid and appear to increase as both the atrazine concentration and the duration of exposure increases. Prolonged exposure results in starvation and ultimately the death of plants. Plant recovery and resistance are two complicating issues which add uncertainty to any risk assessment on atrazine, and there is insufficient information to do more than report that both occur. In the aquatic environment, recovery from the detrimental effects of atrazine exposure could serve to mitigate risk to plants, while the replacement of sensitive species of plants by resistant ones raises ecological questions relating to structural, functional and nutritional changes in communities and ecosystems that are not easily answered without further research.

Atrazine is widely used on major food crops as well as non-crop areas across the U.S. In the environment, atrazine is both persistent and mobile in surface and ground water. Its persistence in water varies from 41 to 237 days, but in lakes such as Lake Michigan which is characterized by cold water temperatures, low productivity, high pH, low nitrates and low organic carbon, atrazine can persist for years. Extensive detections of atrazine in both surface and ground water show that atrazine and its degradates are mobile, persistent and widespread in both surface and ground water. Finally, atrazine has been widely detected in air and rainfall samples in high use areas and also in areas far removed from regions of high use.

The preliminary ecological risk assessment indicated that risk quotients exceeded the levels of concern for direct chronic effects on mammals, birds, fish, aquatic invertebrates and direct acute effects on non-target terrestrial and aquatic plants. The conclusions from this assessment are that potential direct effects on these groups of non-target organisms are possible at maximum and in some cases typical use rates.

Although risk quotients based on EECs from maximum foliar dissipation half-life data (17-days) indicate that levels of concern (LOCs) for chronic risks for birds and mammals are exceeded, the Agency considers that these risk quotients may be over estimates. Due to the conservative nature of the exposure estimates, direct chronic effects on birds and mammals that are exposed from ingestion of soil organisms and on birds and mammals exposed to habitats adjacent to fields that have atrazine levels on plants as a result of drift, are unlikely to occur except in unusual circumstances such as oversprays.

Exposure through spray drift and runoff is likely to result in direct acute effects on many terrestrial plant species at both maximum and typical use rates. Incidents confirming damage to nontarget plants support this conclusion, and 1996-98 data from the American Association of Pest Control Operators (AAPCO) rank atrazine high among 58 pesticides confirmed to be involved in spray drift complaints.

Risk quotients also exceed the LOC (1.0) for direct chronic adverse effects on freshwater fish (<1.0 - 3.1), freshwater invertebrates (<1.0 - 3.4), as well as direct effects on freshwater vascular plants (<1.0 - 5.5) and freshwater algae (<1.0 - 4.2). Tenth centile ecotoxicological toxicity values for these endpoints were also available, and were generally lower than the values for the most sensitive species. When these 10th [per]centile values were used to calculate RQs, the resultant LOC exceedences are similar or greater than those above, which are based on the most sensitive species.

While these LOC exceedences are not great, potential direct chronic effects on fish and aquatic invertebrates suggest the possibility of population effects, and potential direct effects on phytoplankton and macrophytes suggest the possibility of indirect effects on aquatic zooplankton, fish and the aquatic community itself. Following a review of the available ecotoxicological data for atrazine, including laboratory and simulated field data, the Agency identified the endpoints of greatest concern as indirect adverse effects on aquatic communities due to loss of species sensitive to atrazine and resulting in changes in structure and functional characteristics of the affected communities, and reductions in populations of aquatic macrophytes, invertebrates and fish. These potential adverse effects are shown in mesocosm and microcosm studies. Since these microcosm and mesocosm studies as well as extensive monitoring data were available, a refined risk assessment was conducted. The refined assessment was designed to address the endpoints above, but would also include the 10th [per]centile values for direct effects. The refined assessment focuses on the potential risks associated with atrazine concentrations in ponds, freshwater streams, lakes and reservoirs, and estuaries.

In areas of high use, atrazine is likely to be resident in ponds for extended time periods. Tier 2 modeling simulations show that for months **every year**, atrazine concentrations in ponds adjacent to sorghum and sugarcane fields may exceed the levels (10 to 20 $\mu\text{g/L}$) at which some simulated studies have shown reductions in fish and invertebrate populations, macrophytes, and primary production. Similar modeling simulations for corn show that atrazine concentrations in ponds exceed the levels at which studies have shown reductions in fish populations, invertebrate populations, macrophytes, and primary production in 70 to 83% of the years. Monitoring data from lakes and reservoirs that serve as community drinking water supplies also show that a number of reservoirs and lakes have atrazine concentrations at or above 20 $\mu\text{g/L}$. Further, data from monitoring mid-western reservoirs and lakes show that in 1992 and 1993, between 33% and 35% of the 76 reservoirs and lakes sampled exceeded levels where a reduction in primary productivity could occur; and, from 2.5% to 4.5% exceeded levels where invertebrate populations are likely to be reduced. These impacts were more likely to occur during the months of June and July and when the highest concentrations were usually found. Lakes and reservoirs

in the states of Indiana, Illinois and Ohio appeared to be at greatest risk.

Concentrations of atrazine in streams would likely be less of a concern due to the transient nature of the atrazine concentrations inherent in flowing water systems. Yet, in 1989, atrazine levels where reductions in invertebrate populations and primary production are likely to occur were found in 12% to 34%, respectively, of the 129 Mid-Western streams sampled following atrazine applications. In addition, based on simulated field testing and laboratory testing, macrophytes could have been reduced in 52 to 63% of the streams sampled following atrazine applications. Reduction in primary production was also possible at these levels as well. Similar impacts were shown in 1995 monitoring data on 50 Mid-Western streams sampled following atrazine applications. Concentrations where reductions in invertebrate populations and primary production are likely to occur were found in 17% to 35% of these streams, respectively. These results indicate that atrazine concentrations in Mid-Western streams were generally constant between 1989 and 1995. Monitoring data in 1989 also show that by fall, maximum atrazine concentrations in Mid-Western streams are significantly lower, such that primary production and macrophytes may be reduced in only about 1% of the 143 streams sampled.

Monitoring data for 9 Mid-Western streams from 1990 to 1992 show that the highest pulse concentrations (20 to 90 $\mu\text{g/L}$) exceed many of the assessment endpoints for streams. While the duration of these high concentrations of atrazine is not likely to be long since pulses of runoff tend to move quickly downstream, they may last for hours especially during the spring and during runoff events when numerous fields in a watershed are receiving applications of atrazine at similar times. Thus, it is possible that reductions in invertebrate populations and primary production could occur as a result of post-application stream contamination from the spring applications of atrazine. The frequency of such reductions occurring may be low considering that the frequency of the pulses above 10 $\mu\text{g/L}$ are low and depend on the flow volume of each stream. The frequency of similar reductions occurring in rivers is probably lower than for streams since the peaks and average concentrations of atrazine are lower in rivers.

The NAWQA stream monitoring data, though extensive, were not specifically designed to time monitoring to correspond to atrazine applications or specifically oriented to atrazine treatment areas. Thus, they are likely to underestimate the concentrations likely to be present in streams. The magnitude of this underestimate is unknown. NAWQA monitoring data for 40 agricultural sites from 1991 through 1996 show that levels where reductions in invertebrate populations and primary production are likely were found for 11% to 35% of the sites. These levels were the maximum atrazine concentrations for these 40 agricultural sites.

When various USGS stream monitoring surveys from 1989 to 1995 are analyzed by their population percentiles, on average, atrazine concentrations in streams are probably low, less than 6 $\mu\text{g/L}$. Yet, as indicated in both simulated field and laboratory studies, potential reductions in primary productivity and macrophytes are possible at atrazine concentrations in streams above 2.5 $\mu\text{g/L}$. Of greater concern, however, are the 95th and 90th percentile atrazine concentrations for post-applications in 1994 and 1995. These concentrations range from 20 to 45 $\mu\text{g/L}$ and exceed concentrations at which there were reductions in invertebrate populations and primary

productivity in streams.

The maximum concentrations of atrazine in the estuarine Terrebonne basin in Louisiana show that approximately 70 to 80 % of the sites monitored exceeded concentrations at which reductions in primary productivity and macrophytes occur. These percentages fall only slightly to 61 to 75% for the mean concentrations. Also, approximately 30% of the sites based on the maximum atrazine concentrations, and 7% for the mean concentrations, exceeded concentrations at which reductions in fish and invertebrate populations occur.

Weekly sampling shows many levels declining substantially from peak within a week's time, but often rising to nearly previous levels the following week. These sampling peak levels correspond very closely to peak concentrations predicted by modeling for ponds in areas of sugarcane production.

The maximum atrazine concentrations in the Chesapeake Bay are considerably lower than those found in Louisiana. These concentrations by site and year (from 1977 through 1993) still exceed concentrations at which reductions in macrophytes and primary productivity occur for 8 to 12 % of the site and year combinations, respectively. It is uncertain whether atrazine is contributing to reductions in submerged aquatic vegetation and primary productivity at certain sites in the Bay.

The above risk estimates are based on existing monitoring data. As more recent monitoring data becomes available, these estimates will be updated.

II. Introduction

Differences Between Deterministic and Probabilistic Risk Assessments

The standard method used in the EPA Office of Pesticide Programs (OPP) to characterize ecological risk is the ratio or quotient method. "Typically, the ratio (or quotient) is expressed as an exposure concentration divided by an effects concentration" (U.S. EPA 1998, Part A, Section 5.1.3). A risk quotient (RQ) is the ratio of the estimated environmental concentration of a chemical to a toxicity test effect level for a given species. It is calculated by dividing an appropriate exposure estimate (e.g. EEC or estimated environmental concentration) by an appropriate toxicity test effect level (e.g. LC50). Thus, the RQ is an index (an indicator or measure of a condition) of the potential adverse effects. As an index, the risk quotient needs some reference point or bearing to have meaning. Thus, the Agency has established Levels of Concern (LOCs) in order to identify when the potential adverse effects are of concern to the Agency (See Appendix XVI, Table 1). LOCs are criteria used to indicate potential risk to non-target organisms and the need to consider regulatory action. When an LOC is exceeded, it means that a pesticide, when used as directed, has the potential to cause adverse effects on non-target organisms.

The current ecological risk characterization process, which is based on RQs and LOCs, is useful

and can provide the risk managers with a screening method to facilitate the rapid identification of pesticides that are not likely to pose an ecological risk or those that may pose a risk. As noted in the EPA Ecological Risk Assessment Guidelines, “The principal advantages of the quotient method are that it is simple and quick to use and risk assessors and managers are familiar with its application. It provides an efficient, inexpensive means of identifying high- or low-risk situations that can allow risk management decisions to be made without the need for further information” (Ibid, Part A, Section 5.1.3).

While the objective of the Agency is to advance toward probabilistic risk assessment methods for pesticide risk assessment, current deterministic methods such as the quotient have not been dismissed. Rather, they remain an integral component of the current risk assessment for the registration and reregistration of pesticides. This is consistent with current Agency guidance for Ecological Risk Assessment. However, risk assessors and risk managers who use RQs recognize that they contain an unknown degree of conservatism and they tend to obscure uncertainties and variability. Thus, while an RQ can be useful in determining whether risk is likely to be high or low, it may not be helpful to a risk manager who needs to make a decision requiring an incremental quantification of risk (ibid, p. 97). Likewise, an RQ does not provide the risk manager with an indication of uncertainty surrounding the risk estimation (ibid). Further, RQs cannot address some questions raised by risk managers which can be pivotal to major regulatory decision-making on the basis of ecological risk concerns: “What is the magnitude of defined risk -- How big is it?” “What is the probability of the risk -- How likely is it to occur?” “How certain are you that an adverse effect will occur -- How sure are you?” As noted in the US EPA Ecological Risk Assessment Guidelines (ibid, p.92), “If the risks are not sufficiently defined to support a management decision, risk managers may elect to proceed with another iteration of one or more phases of the risk assessment process.”

Ecological risk assessments may be refined in many ways, including deterministic and probabilistic methods. The newest method, and the one receiving widespread attention at the present time, is the probabilistic risk assessment. Probabilistic risk assessment is a general term for a risk assessment that uses probability distributions to characterize variability and/or uncertainty in risk estimates. In these risk assessments, one or more (random) variables in the risk equation are defined mathematically by probability distributions. Similarly, the output of a probabilistic risk assessment is a range or distribution of risks experienced by the various members of the exposed population of non-target organisms of concern.

In ecological risk assessments, risk distributions may reflect variability or uncertainty in exposure or toxicity. Following a deterministic screening level assessment that indicated potential high acute risk, a risk manager may request an answer to the following question: “What is the magnitude and likelihood (i.e., probability) of acute risks to an exposed individual from the use of Pesticide X?” After determining that the time, resources and expertise required to perform a probabilistic risk assessment was justified, the results of such an assessment could provide the following conclusion: *Based on the best available information regarding exposure and toxicity, mortality is expected to be X% or greater in the majority (X% or more) of the scenarios, with a probability of X%.* The above example is based on a situation where the

available data permitted the development of distributions for both the toxicity and exposure variables. Other probabilistic results are possible when only one of the variables can be represented by a distribution.

The primary advantage of probabilistic risk assessment for assessing ecological risks within OPP is that it gives a quantitative description of the probability or likelihood of the impact as well as the magnitude or severity of the effect. The quantitative analysis of uncertainty and variability provides a more comprehensive characterization of risk than is possible in the deterministic RQ or point estimate method. Another significant advantage of probabilistic risk assessment is the additional information and potential flexibility it affords the risk manager. For example, the risk assessor can provide a range of percentile exposures (e.g., 5th, 25th, 50th, 75th, 95th) based on the distribution of these exposures, and the manager can select the percentile at which he/she is comfortable making a decision. Probabilistic risk assessment can also more reliably identify the variables and model parameters that have the greatest influence on the risk estimates through sensitivity analyses. Finally, once the probabilistic model is developed, it is relatively easy to modify the model to run “what-if” scenarios to determine the effect that mitigation measures would have on the risk conclusions.

While a probabilistic risk assessment can provide a useful tool to characterize and quantify variability and uncertainty in risk assessments, it is not appropriate for every site. It generally requires more time, resources, and expertise on the part of the assessor, reviewer, and risk manager than a point estimate risk assessment. In addition, communicating the results of a probabilistic risk assessment may be a challenge. If the additional information is unlikely to affect the risk management decision, then it may not be prudent to proceed with a probabilistic risk assessment. However, if there is a clear value added from performing this assessment, then the use of probabilistic risk assessment as a risk assessment tool generally should be considered despite the additional resources that may be needed. The decision to use probabilistic risk assessment methods is pesticide and use-specific and is based on the complexity of the problems due to the behavior of the pesticide and the quality and extent of site-specific data. EFED recommends a tiered approach to risk assessment so that the scope of the assessment matches the scope of the pesticide and use-specific problems being assessed.

The Agency has developed pilot aquatic and terrestrial animal models as well as a ‘generic case study’ in order to demonstrate the models. The models and the case study were reviewed by the SAP in March 2001, and the Panel described the Agency’s efforts as being at the forefront of conducting an ecological probabilistic risk assessment. The OPP Probabilistic Risk Assessment Implementation Team is currently finalizing the models which will be used for Level 2 Probabilistic Risk Assessments. [Find information for all SAP meetings at <http://www.epa.gov/scipoly/sap/2001/index.htm>] Appendix XVI contains a more complete discussion of deterministic and probabilistic ecological risk assessment methods.

General Description of the Ecological Risk Assessment for Atrazine

The Agency’s reregistration eligibility science chapter for atrazine includes both a preliminary

assessment, based on a deterministic screening level risk quotient analysis, and a refined assessment. The preliminary assessment focuses on the three atrazine uses sites that comprise the greatest percent of national use: corn, sorghum and sugar cane (~ 98% of pounds applied), and is based on the most sensitive eco-toxicological values from studies submitted to the Agency and modeled exposure estimates. The PRZM/EXAMS model, a Tier 2 exposure model, is used instead of the Tier 1 GENEEC model. The refined assessment is based on additional ecotoxicological data as well as microcosm and mesocosm studies discovered in publicly available literature, a substantial amount of monitoring data for freshwater streams, lakes, reservoirs, and estuarine areas, and reports of incidents of adverse effects on aquatic and terrestrial organisms associated with the use of atrazine. In the refined assessment, risk is described in terms of the likelihood that concentrations in water bodies will equal or exceed concentrations shown to cause adverse effects. Cumulative exceedence curves for monitoring data were constructed in the following way: maximum annual atrazine concentrations were plotted versus the percent of sampling sites in water bodies (streams, rivers, lakes, reservoirs, estuarine areas) with equal or greater annual maximum concentrations. Eco-toxicological endpoint values from both laboratory and simulated field study results as well as 10th [per]centile values² for acute and chronic effects for groups of freshwater and estuarine plants and animals, calculated from laboratory data, were plotted on the graph as horizontal lines. Percentage exceedence was calculated where the endpoint lines crossed the concentration curve. In addition, 95th, 90th, 75th and 50th percentile exposure values based on monitoring data were evaluated and compared to the endpoint values in order to estimate the likelihood that adverse effects on aquatic organisms and/or their communities will occur.

Syngenta's Aquatic Ecological Risk Assessment of Atrazine

In January 2001, Syngenta Crop Protection Inc. submitted a document to EPA titled "*Aquatic Ecological Risk Assessment of Atrazine - A Tiered Probabilistic Approach, A Report of an Expert Panel*" dated June 30, 2000 (referenced as Giddings *et al.*, 2000) along with supporting documentation. It was prepared by the Atrazine Ecological Risk Assessment Panel and Ecorisk, Inc. This document was an up-date of a previous ecological risk assessment (Solomon *et al.*, 1996).

Syngenta's aquatic ecological risk assessment of atrazine was designed as a case study of the tiered process recommended by the Ecological Committee on FIFRA Risk Assessment Methods (ECOFRAM), and it is relatively consistent with these recommendations. The tiered process and methods developed by ECOFRAM were recommendations to the Agency. Subsequent to those recommendations, the EPA has developed and proposed a plan for implementing refined risk assessment methods including probabilistic assessment methods [See <http://www.epa.gov/scipoly/sap/2000/index.htm#april> , FIFRA Scientific Advisory Panel Meeting, April 5-7, 2000:Implementing Probabilistic Ecological Assessments: A Consultation; and, <http://www.epa.gov/scipoly/sap/index.htm#march>

²See footnote 1 in the Executive Summary for an explanation.

March 13 - 16, 2001: A Case Study: Advancing Ecological Risk Assessment Methods in the EPA, Office of Pesticide Programs]. While this plan and approach is based on the recommendations from ECOFRAM, it contains methods and approaches that differ from it because EPA recognized limitations in some of the methods and approach and has further refined methodologies to be more reflective of EPA needs for greater transparency and conservancy in underlying assumptions.

Syngenta's Atrazine Ecological Risk Assessment Panel arrived at the following conclusions (Executive Summary, pp.18 and 19): *“The integration of an unusually comprehensive data set including laboratory bioassays, field and microcosm modeling, and environmental monitoring revealed that atrazine does not pose an ecologically significant risk to most aquatic environments in North America. Although direct toxic effects on aquatic animals are very unlikely to occur, some inhibitory effects on algae, phytoplankton, or macrophyte production may occur in certain habitats vulnerable to agricultural runoff. These effects are likely to be transient and recovery would be rapid. The Panel has considered and identified uncertainties associated with this assessment. The Panel considers the Total Risk estimates derived in Tiers 3 and 4 to be conservative - that is, the actual risks are probably lower than these estimates. This judgement is based on the conservative assumptions in the simulation models, the biases inherent in the monitoring data, and the very sensitive benchmark for chronic effects on plants (10th centile of the distribution of No Observed Effect Concentrations). The conservative nature of the risk assessment is corroborated by the community-level No Observed Effect Concentration observed in microcosms and mesocosms (50 µg/L), which is almost never exceeded in surface water measurements or exposure simulations.”*

EPA scientists and risk managers reviewed Syngenta's aquatic risk assessment of atrazine, and convened a workshop in October 2001 with the technical assistance of Syracuse Research Corporation (SRC). The objectives of the workshop were: to discuss the four levels of refinement portrayed in the assessment, the assumptions behind each refinement, the decisions made to transition to higher levels of refinement, and to compare the approach used in this assessment to that proposed by EPA's Environmental Fate and Effects Division's (EFED) Refined Risk Assessment Implementation Team. Comments from risk assessors and risk managers, in the Office of Pesticide Programs, the Office of Water, as well as the contractor were integrated and compiled by the contractor. EFED developed the comments into a document titled, “Review of Atrazine PRA” (see Appendix XVII).

EPA concluded that Syngenta's aquatic ecological risk assessment of atrazine is a well written document, and a good faith effort to conduct a probabilistic ecological risk assessment for atrazine. It includes an expanded data set of laboratory studies, simulated field studies, and analyses of monitoring data (beyond that detailed by the Agency in its January 26, 2001 “Registration Eligibility Science Chapter Atrazine Environmental Fate and Effects Chapter”). During the 60-day comment period, other commenters also submitted comments on the EFED science chapter and for the most part referenced Syngenta's probabilistic risk assessment. The Agency reviewed all documents submitted and has provided responses to comments. Based on this additional information, the Agency was able to further refine its risk assessment and modify

the format of it's science chapter.

The Agency's review of Syngenta's probabilistic risk for Atrazine details the problems and weaknesses that were found. In general, the Agency identified problems in the areas of transparency concerning the information used and the calculations performed, lack of sensitivity analyses, inconsistencies in the Tiered process, and the lack of model availability and documentation.

The Agency noted that the document "*lacks the transparency needed to support the conclusions at each Tier.*" There were "*insufficient rationale explaining what selected data or literature sources were excluded from the risk assessment...[and] calculations [could not] be reproduced because input assumptions or data are incompletely documented.*" Sensitivity analyses were not reported in the atrazine document and should be included because they are a critical component of uncertainty analysis especially when multiple simulations with alternative modeling approaches and assumptions are presented as in this document. In addition, the tiered process in the document did not clearly link the results from lower tiers to the areas of refinement for subsequent analyses in the higher tiers. Neither did the document relate the results from each tier to the original problem formulation. Many of the models used in document, especially in the higher tiers, were new models that have received minimal scientific peer review. Such models cannot be adequately considered by the Agency without undergoing some scientific review. A broad consensus must be built through scientific peer review so that scientists and risk managers can understand and accept the model outputs.

In Tiers 2 and 3, the Expert Panel presented risk in terms of a summary statistic termed "*Total Risk*" which represented the area under selected Joint Probability Curves (JPC)³. This area was given the acronym AUC. The interpretation and meaning of "*Total Risk*" or the AUC is not straightforward, and EPA believes that it is necessary to assess the ecological relevance of any risks that are identified by this index by going back to the JPC itself as well as the exposure and toxicity data from which it was prepared. EPA was not able to do this from the data submitted. In Tier 3, species sensitivity distributions (SSDs) of LC₅₀, EC₅₀ and NOEC values were used to construct the JPCs. The interpretation of non-exceedence to an absence of impact or concern for a particular species is highly dependent upon the slope of the exposure-response curve. This approach results in potential mis-characterizations of risk. EPA believes that JPCs based on SSDs may be more confusing than helpful and recommends an alternative approach. In the Agency's approach, risk characterization is achieved by overlaying the exposure distribution with the exposure-response curves for multiple receptors (e.g., the 5th, 25th, 50th, 75th, 90th, 95th percentile species from an SSD). This approach would permit a quantified determination of both the fraction of species likely to be exposed to concentrations above their respective effects levels as well as the average severity of the response in each of the species. EPA considers this

³A Joint Probability Curve or JPC is a plot of the probability of exceedence versus the magnitude of effect. A probability distribution of exposure concentrations (exceedence curve) is integrated with a concentration-effect curves for acute mortality, species sensitivity distributions, or other effect endpoints. See Giddings *et al* 2000, page 54.

approach much more informative than simply presenting the AUC for each SSD based JPC.

On December 13th, 2001 the Agency met with representatives from Syngenta, the Atrazine Panel and Ecorisk, Inc. The Atrazine Panel presented a summary of the ecological risk assessment document, and EPA presented a summary of its review of the document. The goals of the meeting were to establish dialogue and to facilitate information exchange. All parties agreed that it is an open question on how to use SSDs in regulatory decision making, and that “*Total Risk*” really represents mean risk and is a index or ranking of risk. Total risk estimates based on AUCs are simply a means to summarize a lot of data and how this should be best interpreted and used in regulatory decision making is an another area that needs much discussion. In addition, there was considerable discussion on the use of specific mesocosm and microcosm studies used in both Syngenta’s and the Agency’s risk assessments. The Agency and the Atrazine Panel continued to differ in its conclusions on the utility of certain of these studies in determining the risk of atrazine to aquatic organisms and communities. Consequently, the Agency also disagreed with the Panel’s conclusion that the community-level No Observed Effect Concentration observed in microcosms and mesocosms is 50 $\mu\text{g/L}$. Rather, the Agency would conclude that a community-level NOEC would be less than 10 to 20 $\mu\text{g/L}$.

Following the discussion, the Panel thanked EPA for it’s comments and suggestions, and all agreed to the following: (1) Kimberly Lowe (Special Review and Reregistration Division, SRRD) would be the formal contact person for future communication; (2) the Panel would provide a written response to EFED’s comments which EFED would review; (3) EFED would provide comments on the Panels “Possible Future Work Topics” including our sense of priority. SRRD reminded the attendees that the atrazine RED is on a firm schedule for completion by August 2002, and that EFED’s revised science chapter and response to comments will need to be completed in early spring in order to follow this schedule.

As per the agreement, on February 7, 2002, the Agency identified the following “Possible Future Work Topics” as high priority: (1) Formal sensitivity analysis at Tiers 2, 3 and 4, including an analysis addressing whether inclusion of other data (fate, tox) would alter conclusions; (2) Focal species dose-response approach vs SSDs at Tier 3; (3) Consider additional assessment endpoints, especially effects on aquatic invertebrate populations and communities; (4) Exploration of toxicity, exposure and risk to amphibians, including comments on some recent unpublished work of Tyrone B. Hayes, PhD [Laboratory for Integrative Studies in Amphibian Biology, Department of Integrative Biology, University of California, Berkeley, CA 94720-3140] which indicates that exposures of less than 1 ppb atrazine may result in impaired sexual development in the African clawed frog (*Xenopus laevis*). Comments on the differences between these results and the results from ongoing work being done at Syngenta’s request, as well as implications from the extant work on the effects of atrazine on endocrine systems in amphibians would be welcome.

Subsequently, the Agency met with Syngenta, the Atrazine Panel and Ecorisk, Inc. on March 18, 2002 where the Expert Panel presented a summary of their response to EFED’s comments. Electronic copies of this response titled “*Supplement to ‘Aquatic Ecological Risk Assessment of Atrazine - A Tiered Probabilistic Approach’ Including Responses to EPA Comments*” were

provided at the meeting and paper copies followed a few days later. In addition, the Atrazine Ecological Risk Assessment Panel noted that another Panel had been formed to address the atrazine endocrine issues. Members of this Panel presented details of ongoing and planned laboratory and field research as well as preliminary results from this research.

The supplementary document provided at the March 18th meeting comprised 293 pages of comments and detailed analyses. The following conclusion is found in the summary of the supplement: *“The various sensitivity analyses conducted in preparation of this document have increased the Panel’s confidence in it’s original conclusions. In the vast majority of locations atrazine poses an insignificant risk to aquatic life, However, in certain high-exposure situations, atrazine may reach concentrations that could cause ecologically significant effects on plant productivity and community structure. In cases where the effects are severe (and there are, to our knowledge, no confirmed effects on plant communities in nature), indirect effects on fish and invertebrates are possible. However, direct acute and chronic effects on animals are extremely unlikely based on the data available to the Panel. Emerging issues with atrazine and amphibians are being addressed by another independent scientific Panel commissioned by Syngenta.”* The Agency has yet to review this supplement in detail due to the timing of its receipt. However, some of the general statements are similar to those being made in the Agency’s ecological risk assessment.

After an intensive review of Syngenta’s aquatic probabilistic risk assessment of atrazine, the Agency concluded that some of the additional information found in the assessment would enable the Agency to further refine its risk assessment and modify the format of it’s science chapter. However, the Agency also concluded that it could not totally rely upon Syngenta’s probabilistic risk assessment as the basis of the Agency’s science chapter because: (1) of the major concerns the Agency identified in it’s review of Syngenta’s risk assessment and summarized above; and, (2) the endpoints of major concern were indirect adverse effects on aquatic communities due to loss of species sensitive to atrazine and resulting in changes in structure and functional characteristics of the affected communities, and reductions in populations of aquatic macrophytes, invertebrates and fish. These adverse effects are shown in mesocosm and microcosm studies. A fully probabilistic risk assessment cannot be conducted for the community-level and population-level effects because the available microcosm and mesocosm studies showing effects on aquatic populations and communities only establish thresholds of adverse effects. They do not provide measures of severity of impacts with increasing exposure levels (dose-response relationships) which are needed for conducting a probabilistic risk assessment. In addition, the Agency notes that the results of the Agency’s preliminary risk assessment shows that Levels of Concern (LOCs) are not exceeded for most of the direct acute and chronic effects on aquatic organisms. This would indicate that a probabilistic risk assessment for these endpoints is not needed at this time.

III. Problem Formulation

Chemical and Usage

Atrazine (6-chloro-N-ethyl-N-isopropyl-1, 3, 5-triazine-2, 4-diamine) has the second largest poundage of any herbicide and is widely used to control broadleaf and many other weeds, primarily in corn, sorghum and sugarcane. As a selective herbicide, atrazine is applied pre- and post-emergence.

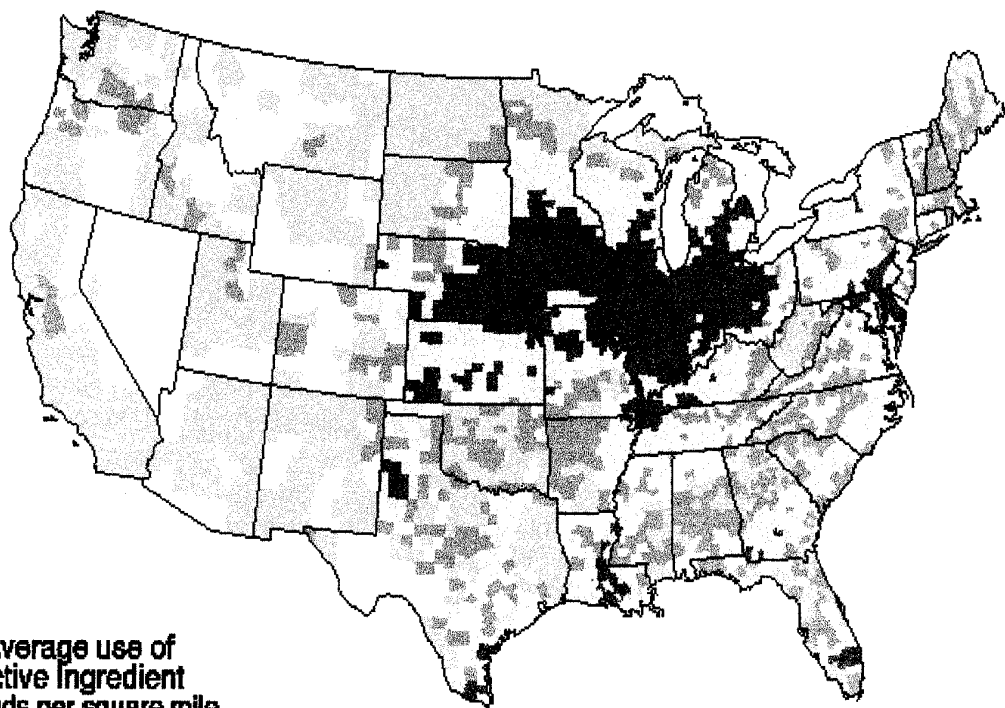
A national map of atrazine use per unit area is provided below. The map was downloaded from a U.S. Geological Survey (USGS), National Water Quality Assessment Program (NAWQA) website. The map is based upon the 1992 Census of Agriculture. The heaviest atrazine uses per unit area (those of > 66 lbs ai/sq mi of county/yr) occur in large portions of DE, IA, IL, IN, OH, and NE and in smaller portions of FL, KS, KY, LA, MD, MI, MN, MO, PA, TN, TX, and WI.

Atrazine is used on a variety of terrestrial food crops, non-food crops, forests, residential/industrial uses, golf course turf, recreational areas and rights-of-way. Atrazine yields season-long weed control in corn, sorghum and certain other crops. The major atrazine uses include: corn (83 percent of total ai produced per year - primarily applied pre-emergence), sorghum (11 percent of total ai produced), sugarcane (4 percent of total ai produced) and others (2 percent ai produced). Atrazine formulations include dry flowable, flowable liquid, liquid, water dispersible granule, wettable powder and coated fertilizer granule. The maximum registered use rate for atrazine is 4 lbs ai/A; and 4 lbs ai/A is the maximum, single application rate for the following uses: sugarcane, forest trees (softwoods, conifers), forest plantings, guava, macadamia nuts, right-of-ways/fence rows/hedges, ornamental sod (turf farms), ornamental and/or shade trees, and Christmas trees.

About 60 million acres of the total corn acres are treated with an average of about 63 up to an estimated maximum of up to 75 million lbs ai per year. The maximum label rates for corn are 0.84 to 3 lbs ai/A. The typical application rates on corn vary depending on the type and use for the corn, and are as follow: fresh sweet corn - 1.5 lbs ai/A (with 1 application on an average of about 50 percent to an estimated maximum of 60 percent of the 220,000 acres), processed sweet corn - 0.9 lbs ai/A (with 1 application on an average of about 58 percent up to an estimated maximum of 65 percent crop treated of the total 464,000 acres grown), and corn - 1.0 lbs ai/A (with an average of 1.1 applications on an average of about 82 percent crop treated up to an estimated 97 percent crop treated of the total 72 million acres grown).

ATRAZINE

ESTIMATED ANNUAL AGRICULTURAL USE



**Average use of Active Ingredient
Pounds per square mile
of county per year**

- No Estimated Use
- < 1.080
- 1.080 - 5.587
- 5.588 - 21.211
- 21.212 - 66.515
- >= 66.516

Crops	Total Pounds Applied	Percent National Use
corn	53,796,206	84.13
sorghum	7,339,963	11.48
sugar cane: sugar & seed	1,711,322	2.68
pasture	518,074	0.81
sweet corn	444,523	0.70
sod	119,182	0.19
proso millet	11,937	0.02
field and grass seed	6,305	0.01

Sorghum is treated with about 8 to 12 million lbs ai per year on an average of about 58 percent and up to an estimated maximum of 74 percent crop treated of the total 11 million US acres. The maximum label rates for sorghum are 1.3 to 3 lbs ai/A with a typical use rate of 1.1 lbs ai/A, averaging 1.1 applications per year for an average of 1.2 lbs ai/A/year.

Sugarcane is treated with about 2.5 to 5 million lbs ai per year on an average of 76 percent and up to an estimated maximum of 95 percent of the total 855 thousand US acres. The maximum, single application rates for sugarcane are 3.4 to 4 lbs ai/A with a typical use rate of 2.6 lbs ai/A, averaging 1.5 applications per year for an average of 3.9 lbs ai/A/year.

Other registered crop uses include: barley, guava, hay, macadamia nuts, oats, pasture, pineapples, rice, rye and winter wheat. Registered non-crop uses include uses on ornamental sod (farms), golf courses (turf), rangeland, residential lawns, Bermudagrass, grasses grown for seed, landscape maintenance, ornamental trees, forests, Christmas trees, recreational areas, rights-of-way, and industrial areas.

Mechanism of Action

Atrazine inhibits photosynthesis by stopping electron flow in Photosystem II. Triazine herbicides associate with a protein complex of the photosystem II in chloroplast photosynthetic membranes (Schulz *et al.*, 1990). The result is an inhibition in the transfer of electrons which in turn inhibits the formation and release of oxygen.

Approach to Risk Assessment

Identification of Assessment Endpoints

One of the most important steps in problem formulation is the selection of the endpoint(s) upon which the ecological risk assessment will be based. The Agency guidelines define assessment endpoints as “explicit expressions of the actual environmental value that is to be protected” which are “operationally defined by an ecological entity and its attributes” (U.S. EPA, 1998, p. 32 and Appendix B). The ecological entity can be a species, a functional group of species, a community, an ecosystem, or an other entity of importance or concern. An attribute is the characteristic of the entity that is important to protect and is potentially at risk. The selection of clearly defined assessment endpoints is crucial because they provide direction and boundaries to the risk assessment so that it addresses management concerns. Each assessment endpoint needs one or more “measures of effect”, which are changes in the attributes of an assessment endpoint itself or changes in some surrogate test in response to exposure to a pesticide. (Ibid, 1998)

The Agency reviewed the available laboratory ecotoxicological and environmental fate data submitted in support of the registration and re-registration of atrazine, additional published laboratory and simulated field data found as a result of literature searches by both the Agency and provided by the primary registrant, Syngenta, and extensive monitoring data from the U.S.

Geological Survey (USGS), the USGS' National Water Quality Assessment Program (NAWQA), the Louisiana Department of Agriculture and Forestry (LDAF), and the Chesapeake Bay Monitoring Data Base. The Agency also reviewed distributions of the ecotoxicological data developed by the Expert Panel in their "Aquatic Ecological Risk Assessment of Atrazine - A Tiered Probabilistic Approach", as well as an analysis of "National Water Quality Assessment Program Datasets for use in Atrazine Ecological Risk Assessments."

The typical assessment endpoints for pesticide ecological risk assessments were identified and included direct acute and chronic adverse effects on mammals, birds, fish, aquatic invertebrates, and non-target plants. The additional laboratory and simulated field data found in the literature were also reviewed. The Agency determined that the most important endpoints for atrazine were: **direct acute effects** on many terrestrial plant species, **direct effects** on aquatic non-vascular plants which in turn can cause reductions in primary productivity, **reductions in populations** of aquatic macrophytes, invertebrates and fish, and especially **indirect effects on aquatic communities** due to loss of species sensitive to atrazine and resulting in changes in structure and functional characteristics of the affected communities. These adverse effects were shown in mesocosm and microcosm studies.

The Conceptual Model

The initial steps of every ecological risk assessment will generally involve a point estimate (deterministic) risk assessment. This preliminary assessment provides both the risk assessor and the risk manager with a familiar a baseline reference point with which to compare the results from any refinement and other similar risk assessments. The results of this preliminary can determine the need for refining the assessment. Thus, the Agency determined that all the direct acute and chronic endpoint values should be compared to modeled exposure estimates using the quotient method to estimate risks. The basic structure of the quotient model can be expressed by the general equation:

$$Risk = f(exposure, toxicity)$$

Since risk is a function of exposure and toxicity, the model is based on the characterization of exposure and effects.

The most sensitive acute and chronic ecotoxicological effects endpoint values for mammals, birds, fish, aquatic invertebrates, terrestrial and aquatic plants were compared to the results from terrestrial and aquatic exposure models designed to provide conservative estimates of pesticide exposure. The terrestrial FATE model and the aquatic tier 2 PRZM/EXAMS models were used to calculate the estimated environmental concentrations (EECs) for atrazine use on corn, sorghum, and sugar cane. The EECs were divided by the endpoint values to calculate risk quotients. In turn, the risk quotients were compared to established regulatory levels of concern (LOCs). If they exceeded the Agency's LOCs, then either a regulatory action could be considered or a refined risk could be conducted.

Based on the preliminary ecological risk assessment, there are potential direct adverse effects on

terrestrial plants, direct adverse chronic effects on mammals, and to lesser extent direct adverse effects on birds. Although risk quotients based on EECs from maximum foliar dissipation half-life data (17-days) indicates that LOCs for chronic risks are exceeded, the Agency considers that these risk quotients are over-estimates for birds and mammals that are exposed from ingestion of soil organisms and for birds and mammals exposed to habitats adjacent to the field that have atrazine levels on plants as a result of drift. There is insufficient available information to refine this assessment. If a refinement is necessary for regulatory decision-making, additional data in the form of field studies would be required. Field studies investigating direct effects on non-target terrestrial plants could show whether atrazine poses a risk to terrestrial plants. Field studies where residues on mammalian and avian food items are measured over time could show whether atrazine poses a chronic risk to mammals.

Potential direct chronic effects on fish and aquatic invertebrates suggest the possibility of population effects. Similarly, direct effects on phytoplankton and macrophytes suggest the possibility of indirect effects on aquatic zooplankton, fish and the aquatic community itself. Since the Agency determined that the most important endpoints for atrazine were shown in simulated field studies, e.g., mesocosm and microcosm studies, and extensive monitoring data on atrazine was available, a refined aquatic assessment was conducted. The refined assessment was designed to address aquatic the direct and indirect aquatic effects as noted, and would also include the 10th centile values based on laboratory studies as calculated by Syngenta. These values are similar to or lower than the toxicity values for the most sensitive species typically used by the Agency in the preliminary assessment.

The monitoring data suggest that atrazine concentrations in surface waters reach levels that could result in the direct and indirect adverse effects on aquatic organisms and their communities as seen in the simulated field studies, particularly in high use areas. The abundance of surface water monitoring data for atrazine was collected from studies designed to assess the water-quality at the monitoring sites, not to establish exposure levels in aquatic habitat for comparison with aquatic ecotoxicity values. As such, it is often difficult to interpret what the distributions of the data are showing concerning exposure to aquatic populations and communities. The Agency chose a conservative approach by using the "available" maximum concentrations. There are some uncertainties with these maximum values. For example, all the monitoring sites were not sampled continuously on a daily basis; the sampling was not specifically designed to correspond to atrazine applications; the sampling was not specifically oriented to atrazine treatment areas. Consequently, if sampling missed a runoff event (i.e., a rainfall event) or if the site was spatially distant from atrazine applications, then the peak value would also have been missed. In effect, then, the conservative selection of the available maximum values is at least partially balanced by the low probability that the available maximum value represents the highest value due to a rainfall event. The use of the maximum concentrations also helps to focus the assessment on the high risk areas where risk mitigation should targeted first.

Syngenta submitted a detailed analysis of the available NAWQA monitoring data covering the 1992 to 1995 stream sampling program ("National Water Quality Assessment Program Datasets for use in Atrazine Ecological Risk Assessments", Appendix 6 in Syngenta's Comments in

Response to the Notice of Availability of Environmental Fate and Effects Assessment on Atrazine to Re-registration Eligibility Decision [OPP-34237A]) Syngenta chose to combine agricultural, urban and integrator sites into a single distribution (5217 samples from 1059 sites), and then further refined it by only considering samples with atrazine residues greater than 0.019 $\mu\text{g/L}$ (2808 samples from 547 sites). While the 99th, 95th and 90th percentile values from the combined distributions do not differ greatly from the those values calculated by the Agency for each of the three groups of sites and found in the table on page 52, the Agency's calculations more clearly show the areas where the atrazine levels may pose the greatest potential risk. Combining the data tends to dilute the information and obscure the areas of potential risk concerns.

In the refined assessment, potential risk is described in terms of the number of aquatic monitoring sites in lakes/reservoirs, streams and estuarine areas with concentrations that equal or exceed concentrations shown to cause adverse effects. Cumulative exceedence curves for monitoring data were constructed in the following way: maximum annual atrazine concentrations were plotted versus the percent of sampling sites in water bodies (streams, rivers, lakes, reservoirs, estuarine areas) with equal or greater annual maximum concentrations. Eco-toxicological endpoint values from both laboratory and simulated field study results as well as 10th [per]centile values for acute and chronic effects for groups of freshwater and estuarine plants and animals, calculated from laboratory data, were plotted on the graph as horizontal lines. Percentage exceedence was calculated where the endpoint lines crossed the concentration curve. In addition to the reasons noted above, the Agency chose to use maximum annual atrazine concentrations from the monitoring data because the data are likely to underestimate the concentrations present in these water bodies since the water sampling was not specifically designed to time monitoring to correspond to atrazine applications nor was it specifically oriented to atrazine treatment areas. As noted above, the use of the maximum concentrations helps to focus the assessment on the high risk areas where risk mitigation should targeted first.

Coordination with EPA's Office of Water (OW)

The EPA's Office of Water (OW) is developing national ambient water quality criteria for protection of aquatic life for atrazine. Aquatic life criteria developed by OW are estimates of concentrations of a chemical in water that should not result in unacceptable adverse effects on aquatic organisms and their uses. When a decision is made that a national criterion is needed for a particular chemical, the Office of Water typically establishes two criteria (for fresh and salt water): a Criterion Continuous Concentration (CCC) and a Criterion Maximum Concentration (CMC). The CCC and CMC are generally estimates of the highest four-day average and one-hour average concentration, respectively, that should not result in unacceptable effects on aquatic organisms or their uses. Additional information related to OW's water quality criteria for atrazine can be found at center.water-resource@epa.gov.

To assess the potential risks to non-target aquatic life from use of pesticides, OPP generally uses the Quotient Method, a screening level assessment, whereby an Estimated Environmental Concentration (EEC) is divided by an effect level that is generally taken from a toxicity study

submitted to EPA in connection with a pesticide's registration or reregistration. The result is a risk quotient (RQ) which is compared to a level of concern (LOC) for acute and chronic effects to non-target aquatic organisms.

Because the two approaches are different, OPP and OW are currently consulting on their respective methodologies. When the consultation is completed, there may be some modifications to these approaches which may result in some revisions to the final OPP and OW products. For additional details concerning the methods used by OW and OPP, refer to Appendix XV.

IV. Characterization of Environmental Exposure

Atrazine is expected to be mobile and persistent in the environment. The main route of dissipation is microbial degradation under aerobic conditions. Because of its persistence and mobility, atrazine is expected to reach surface and ground water. This is confirmed by the widespread detections of atrazine in surface water and ground water.

Atrazine is persistent in soil, with a half-life (time until 50% of the parent atrazine remains) exceeding 1 year under some conditions (Armstrong *et al.*, 1967). Studies on agricultural soils (Sirons *et al.* 1973; Dao *et al.* 1979) indicate that deethylated atrazine could account for extended toxicity in agricultural soils from one year to the next.

Atrazine is a mobile pesticide which can be transported via spray drift and runoff to surface water, and can leach to ground water. Davies *et al.* (1994) found that atrazine residues in ground water following a forest application may seep into adjacent Tasmanian surface waters, resulting in prolonged exposures to low levels of atrazine. Atrazine concentration in the small seepage ranged from 0.8 to 68 $\mu\text{g/L}$ during the two months after spraying. Atrazine concentrations in the Tasmanian stream peaked at 22 $\mu\text{g/L}$ the day of treatment and decreased with time from the day of spraying from a median of 8.1 $\mu\text{g/L}$ to a median of 0.3 $\mu\text{g/L}$ 13 to 15 months after spraying. Peak runoff of pesticides occurs when a severe storm closely follows application on sloping land (Baker *et al.* 1985; Frank *et al.* 1982; Moody and Goolsby 1993; Wauchope, 1978; Wauchope and Leonard, 1980; Wu *et al.* 1983). Maximum bulk concentrations of atrazine in runoff in the low milligrams per liter range have been documented (Hall *et al.* 1972; Kadoum and Mock, 1978; Roberts *et al.* 1979). Once runoff reaches adjacent surface waters, such as streams, rivers, ponds or lakes, the concentrations are diluted and the maximum concentrations of atrazine reported in the literature are typically in the low microgram per liter range (Richard *et al.* 1975, Frank and Sirons, 1979; Wu, 1981). One or more applications closely followed by successive rainfall/runoff events, however, can result in "pulsed" dosing and higher concentrations that are evident in the monitoring data. Maximum atrazine concentrations in runoff and surface waters reported in selected references include: 4,700 $\mu\text{g/L}$ in bulk field runoff at the edge of a treated field (Wauchope 1978), 87.1 $\mu\text{g/L}$ in a survey of 12 streams in northwest Ohio (Baker *et al.* 1981), 32.8 $\mu\text{g/L}$ in a survey of 11 streams in Ontario (Frank and Sirons 1979), 26.0 $\mu\text{g/L}$ in a survey of 92 streams entering Great Lakes (Frank *et al.* 1979), 69.44 $\mu\text{g/L}$ (water) and 95.19

$\mu\text{g/L}$ (bottom sediment) in 5 rivers flowing into Lake Erie (Waldron 1974), 26.9 $\mu\text{g/L}$ in 5 Quebec rivers (Muir *et al.* 1978), 10 $\mu\text{g/L}$ in 9 central European rivers (Hörmann *et al.* 1979), 42 $\mu\text{g/L}$ in rivers and reservoirs in Iowa and Louisiana (Richard *et al.* 1975), and 1.0 $\mu\text{g/L}$ in the estuarine waters of the Rhode River estuary in Maryland (Wu 1981). Frank *et al.* (1979) reported that 77 percent of the samples from Canadian streams entering the Great Lakes were contaminated with atrazine.

Finally, atrazine is quite persistent in a large freshwater body like Lake Michigan, which has cold water, low productivity, high pH (8.2), low nitrate, and low dissolved organic carbon (1.5 mg/l). The estimated half-life is 87 years (based solely on degradation of atrazine in the lake), or 31 years (based on degradation in the lake and mass outflows from the lake with volatilization and mass loading inputs shut off). The two single-most important loads to Lake Michigan include runoff and precipitation, where the precipitation accounts for about 30% of the total load. (Kenneth Rygwelski, 2002, personal communication regarding materials submitted for inclusion in the first draft of the Lake Michigan Lake Wide Management Plan, LaMP 2002).

Atrazine enters the atmosphere via volatilization and spray drift and is aerially deposited (a source of importance to some water bodies). About 25 percent of the atrazine entering Lake Michigan is from aerial deposition (Lake Michigan Mass Balance Study, 1999). Atrazine concentrations in rainfall samples taken in 1996 in the Lake Michigan Study were 2.8 $\mu\text{g/L}$, which are similar to the atrazine concentrations (up to 2.9 $\mu\text{g/L}$) in rainfall reported in Minnesota (Capel *et al.* 1994).

A recent study reports that atrazine was detected in more than 60% of weekly rainfall samples taken in 1995 from agricultural and urban sites in Mississippi, Iowa, and Minnesota (Majewski *et al.*, 2000). Similarly, air samples taken from agricultural sites in 1995 showed positive detections of atrazine in more than 80% of samples from IA, 60% of samples from MS, and in about 50% of samples from MN. Urban sites in MN and IA had a slightly lower frequency of atrazine detections in rainfall compared to agricultural sites, while in MS about 30% of the urban samples had positive detections (Foreman *et al.*, 2000). These studies also reported that atrazine was detected in 35% of rainfall samples and in 76% of air samples taken at a background site in Michigan located far from agricultural and urban areas. These data indicate that atrazine is transported through the atmosphere.

V. Characterization of Ecological Effects

Atrazine is practically non-toxic to birds and mammals on an acute basis. The avian acute oral LD₅₀ value is 940 mg/kg, while the avian dietary LC₅₀ value used in this assessment is >5000 ppm. The mammalian acute toxicity value used in the assessment is based on the rat LD₅₀ (1,869 mg/kg). The mammalian LOAEL (500 ppm) significantly reduced adult rat body weight and adult food consumption (NOAEL 50 ppm). At 50 ppm, second generation rat pups had significantly reduced body weight (NOAEL, 10 ppm). The LOAELs for bobwhite and mallard ducks were 225 ppm, based on 29 and 49% reductions in egg production, respectively (NOAEL,

225 ppm). However, atrazine is toxic to terrestrial plants with the lowest EC25 values for the seedling emergence test equal to 0.003 lbs ai/A, and the lowest EC25 for the vegetative vigor test equal to 0.008 lbs ai/A.

In general, atrazine is not very acutely toxic to aquatic animals. The most sensitive freshwater species tested are the rainbow trout 96-hour LC₅₀ (5.3 mg/L) and the midge (*Chironomus tentans*) 48-hour LC₅₀ 0.72 mg/L. The most sensitive estuarine/marine animals tested are the spot (*Leiostomus xanthurus*) 96-hour LC₅₀ (8.5 mg/L) and the copepod (*Acartia tonsa*) 96-hour LC₅₀ (88 µg/L). With rare exceptions, reported and modeled surface water concentrations of atrazine are considerably lower than these acute toxicity values. Suspended sediments had little effect on moderating the toxicity of atrazine to *Daphnia pulex* (Hartman & Martin 1985).

The most sensitive chronic NOAEC toxicity values for aquatic animals are 65 µg/L for the brook trout, 60 µg/L for the scud (*Gammarus fasciatus*) in freshwater, 1,900 µg/L for sheepshead minnow (*Cyprinodon variegatus*) and 80 µg/L for the mysid shrimp (*Mysidopsis bahia*). The sheepshead minnow acute 96-hour LC₅₀ is greater than 16 mg/L with 30 percent mortality. Estimating the chronic NOAEC toxicity value for the more acutely sensitive spot (*Leiostomus xanthurus*) using acute-to-chronic ratio, the NOAEC for spot would be a slightly less than 1 mg/L.

Syngenta's "Aquatic Ecological Risk Assessment of Atrazine - A Tiered Probabilistic Approach, A Report of an Expert Panel" (Giddings *et al.*, 2000), provided a review of an extensive literature search for atrazine, including laboratory, simulated field, and actual field studies. Some of the data presented in this report were already included in the Agency's science chapter for atrazine. Additional data, beyond that included in the Agency's document, were included in the data analyses conducted by the atrazine expert panel. Of note is the calculation of the 10th [per]centile ecotoxicological values for acute and chronic adverse effects on different groups of aquatic organisms (See Tables 5.3 and 5.4 in Giddings *et al.* 2000). Since these values included an extensive data base of acute and chronic effects, the Agency included them as important assessment endpoints. Specifically, the 10th [per]centile values that were included in this science chapter are: chronic adverse effects on both fish and aquatic invertebrates (freshwater animals: 62 µg/L; saltwater animals: 23 µg/L), acute and chronic effects on aquatic plants (freshwater acute phytoplankton: 32µg/L; freshwater acute macrophyte: 18µg/L; saltwater acute phytoplankton: 27µg/L; freshwater chronic plants: 2.3µg/L; saltwater chronic plants: 9.1µg/L). These values are similar to or lower than the most sensitive endpoint values used by the Agency.

Similarly, many of the available microcosm and mesocosm simulated field studies were referenced in both Syngenta's document as well as that of the Agency; yet, Syngenta's listing was more extensive. The Agency tended to focus on those studies that showed adverse effects of atrazine at low concentrations in the aquatic environment. Some of the results from these studies were identified by the Agency as important endpoints. Syngenta, however, viewed some of these same studies differently. These differences focused on the quality of the studies and the interpretation and utility of the results. A discussion of some of the differences is found in Appendix XVII.

Atrazine inhibits photosynthesis by stopping electron flow in Photosystem II. It has a rapid effect on plants with an equilibrium between the plant and water attained in the vascular aquatic plant *Potamogeton perfoliatus* within one hour. Recovery of oxygen evolution in treated plants (5, 25 and 100 $\mu\text{g/L}$) placed in atrazine-free water is rapid, with no significant differences from controls after two hours, but indications of residual photosynthetic depression persisted after the 77-hour recovery period (Jones *et al.*, 1986). Given the persistent atrazine concentrations in ponds, uncertainty exists about the effect(s) on plant recovery which would occur following chronic energy losses via respiration for sensitive species during prolonged suppression of photosynthesis.

VI. Environmental Risk Characterization

Summary

The Agency finds that in areas of high atrazine use, there is widespread environmental exposure that (1) has resulted in direct acute effects on many terrestrial plant species at both maximum and typical use rates, (2) may have caused direct effects on aquatic non-vascular plants which in turn could have caused reductions in primary productivity, (3) may have caused reductions in populations of aquatic macrophytes, invertebrates and fish, (4) may have caused indirect effects on aquatic communities due to loss of species sensitive to atrazine and resulting in changes in structure and functional characteristics of the affected communities. Potential adverse effects to sensitive aquatic plants and other non-target aquatic organisms as well as their communities, are likely to be greatest where atrazine concentrations equal or exceed approximately 10 to 20 $\mu\text{g/L}$ on a recurrent basis or over a prolonged time period. Based on monitoring data, maximum concentrations at up to 35% of the sites exceeded the atrazine concentration ($>10 \mu\text{g/L}$) at which these adverse effects are found in simulated field studies. Up to 20% of the sites exceeded the atrazine concentration ($>20 \mu\text{g/L}$) at which adverse effects are found in simulated field studies as well as many of the 10th [per]centile values for acute and chronic effects from analyses of laboratory data. The frequency of occurrence and extent of the potential impacts will vary depending upon the type of water bodies and their proximity in time and space to atrazine applications. Recovery from the effects of atrazine and the development of resistance to the effects of atrazine in some vascular and non-vascular aquatic plants is reported and adds uncertainty to the conclusions.

The LOC (1.0) was exceeded for direct chronic adverse effects on freshwater fish ($<1.0 - 3.1$), freshwater invertebrates ($<1.0 - 3.4$), as well as direct effects on freshwater vascular plants ($<1.0 - 5.5$) and freshwater algae ($<1.0 - 4.2$). If the 10th centile values from Tables 5.3 and 5.4 of Syngenta's "Aquatic Ecological Risk Assessment of Atrazine - A Tiered Probabilistic Approach," were used to calculate the RQs, the LOC exceedences would be similar to or greater than those calculated by the Agency, and the greatest exceedences would be for direct adverse effects on aquatic plants.

Terrestrial Risk Characterization (Birds and Mammals)

The results of the preliminary ecological risk assessment indicated that the RQs for direct acute adverse effects on mammals and birds were below the LOCs (0.5). Thus, the Agency considered these potential risks to be low.

LOC (1.0) exceedences for direct chronic effects on mammals and birds ranged from 1.6 - 96, and <1 to 4.3. Syngenta contended that the NOAEC for chronic effects on mammals should be 50 ppm versus 10 ppm selected by the Agency, and they recommended that average initial residue EECs for both mammals and birds should be 343 (190 - 486) ppm and 147 (38 - 286) ppm for 4 pound and 2 pound per acre applications, based on residue studies that they examined (no references provided). When these average initial concentrations are compared to the mammal 50 ppm value for calculating RQs, the LOC (1.0) is still exceeded for mammals (3 - 7), and also for birds (<1 - 1.5), but the exceedences are considerably lower than the Agency's calculations.

Terrestrial environmental concentrations (EECs) of atrazine to which birds and mammals may be exposed, were estimated based on the highest value measured for the foliar dissipation half-life from application of atrazine to turf in several locations throughout the southeastern United States. These foliar dissipation half-lives are most representative of atrazine used as a post-emergent herbicide applied directly to foliage of target plants. Atrazine is, however, used predominantly during crop pre-planting and pre-emergence and is, under these circumstances applied directly to soil rather than to foliage. As a result, EECs based on foliar dissipation half-life data, although indicative of post-emergent applications, may not be truly representative of pre-plant and pre-emergence applications. Acute risks to mammals and birds were qualitatively assessed from EECs that were based on the maximum foliar dissipation half-life of 17-days obtained from foliar dissipation studies conducted in the southeastern United States. The ratio of the peak day-0 EECs to the LC50 values corresponding to the highest toxicities for mammals and birds indicate that the resulting risk quotients (RQs) are far less than Levels of Concern (LOCs), thereby indicating negligible potential for acute risks to birds. The risk quotients for small mammals exceed the LOCs for restricted use (RQ=0.2) and endangered species (RQ=0.1).

Syngenta contended that an average half-life of 4-days would be a better estimate for a foliar half-life value. However, additional data has not been submitted to the Agency to support this value. In addition, even if the 4-day value was used, the peak day-0 EEC's would not change, and thus, neither would the LOC exceedences for small mammals. Rather, the number of days that the LOC would be exceeded would be reduced. The Agency has used the conservative foliar half-life value of 17-days in the terrestrial FATE model for estimating terrestrial exposure.

EFED's screening-level assessment suggests the potential for adverse chronic effects to mammals and birds from atrazine applied at typical and maximum labeled rates. The RQs calculated based on estimated residues on terrestrial food items exceed EFED's levels of concern (LOC=1.0) for chronic effects based on No Adverse Effect Concentrations (NOAECs) of 50 and 10 ppm for rats and 225 ppm NOAECs for birds. The 10 ppm level is the NOAEC for adverse effects on second-generation pup body weights, while the 50 ppm NOAEC is based on reduced body weight and food consumption in adult rats. The chronic LOCs, based on mammalian reproductive NOAECs of 50 and 10 ppm, are exceeded for 54 and 94 days, respectively, for

maximum residue levels (4.0 lbs ai/A for sugarcane) on short grass when foliar dissipation is considered. At the typical use rate for sugarcane (2.6 lbs ai/A), the duration of exceedence is 61 and 100 days, respectively.

As with mammals, the screening-level assessment suggests that there is the potential for adverse impacts on avian reproduction from maximum and typical application rates. At the Lowest Observed Adverse Effect Concentration (LOAEC) of 675 ppm, the following adverse effects were noted for bobwhite quail: 29% reduction in egg production, a 67% increase in defective eggs, a 27% reduction in embryo viability, a 6 to 13% reduction in hatchling body weight, and a 10 to 16% reduction in 14-day old bobwhite body weight; and, for mallard ducks: reductions of 49% in egg production and 61% in egg hatchability (Pedersen and DuCharme, 1992). This concentration is less than the modeled value for the maximum application rate (4.0 lbs ai/A for sugar cane) on short grass - 960 ppm.

It is important to consider, however, that exposure of birds and mammals to atrazine applied as a pre-plant or pre-emergent herbicide is primarily a result of ingestion of earthworms and other soil organisms that can serve as a food source as well as from inadvertent ingestion of soil. The estimated maximum residues for small and large insects from the maximum and typical application rates are: small insects - 540 ppm, and 351 ppm; large insects - 60 ppm and 39 ppm, respectively. These maximum estimated concentrations fall precipitously when average concentrations are considered (small insects - 180 ppm and 117 ppm; large insects - 28 ppm and 18.2 ppm, respectively). These estimated concentrations are peak concentrations expected immediately following application. They will decrease over time based on the foliar half-life, and the average exposure is likely to be less than these estimates. Although risk quotients based on EECs from maximum application rates, maximum expected residue concentrations, and a foliar dissipation half-life of 17-days indicate that LOCs for chronic risks are exceeded, these risk quotients are likely over-estimates for birds and mammals that are exposed from ingestion of soil organisms.

Terrestrial Risk Characterization (Plants)

The LOC (1.0) exceedences for direct effects on terrestrial plants (<1.0 - 280; 8 - 9 test species exceeded the LOC from spray drift and runoff; 2 - 3 test species exceeded the LOC from spray drift alone) indicated potential risk concerns. The incident reports for terrestrial plants appear to confirm the concerns indicated by the preliminary RQ assessment, however, the fact that many of the reported incidents were for effects on corn, which was the least sensitive of the test species, raises uncertainty here.

Atrazine applications to crop and non-crop areas pose a risk to non-target plants in areas adjacent to treated fields via spray drift and runoff. EFED's screening-level assessment for nontarget plants, which uses standard values for runoff and drift and compares exposure values to EC_{25} values for tested species, suggests that atrazine poses risk to a wide range of nontarget species. Although only crop species are tested, the results are assumed to represent a range of wild plants. These plants may serve as habitat and/or a food source for birds, mammals beneficial insects and

other organisms. Non-target terrestrial plants in adjacent fields or habitats are potentially at risk from spray drift and from runoff for all registered uses. The level of concern for endangered terrestrial plant species is exceeded for both monocots and dicots, with greater concern evident for higher application rates. The assessment also indicates concern for endangered plant species growing in areas adjacent to atrazine-treated fields from combined spray drift and runoff.

The assessment resulted in exceedences for ground and aerial applications of atrazine at typical and maximum labeled rates. The assessment suggests that three out of the ten tested crops (cucumber, soybeans, and cabbage) are at risk when spray drift alone is considered. The combination of spray drift and runoff poses risks to eight out of the ten crops if grown in dry habitats and to nine out of ten crops if grown in low-lying, semi-aquatic habitats. The screening-level assessment assumes that wetter habitats are at greater risk because they would receive a greater runoff load than would drier areas.

Preliminary Aquatic Risk Characterization

The results of the preliminary ecological risk assessment indicated that the RQs for direct acute adverse effects on freshwater fish and aquatic invertebrates were below the LOCs (0.5). Thus, the Agency considered these potential risks to be low.

The LOC (1.0) was exceeded for direct chronic adverse effects on freshwater fish (<1.0 - 3.1), freshwater invertebrates (<1.0 - 3.4), as well as direct effects on freshwater vascular plants (<1.0 - 5.5) and freshwater algae (<1.0 - 4.2). If the 10th centile values from Tables 5.3 and 5.4 of Syngenta's "Aquatic Ecological Risk Assessment of Atrazine - A Tiered Probabilistic Approach," were used to calculate the RQs, the LOC exceedences would be similar to or greater than those calculated by the Agency, and the greatest exceedences would be for direct adverse effects on aquatic plants.

Refined Aquatic Risk Characterization

The refined risk assessment that follows is based upon ecotoxicological data as well as microcosm and mesocosm studies submitted to support registration and discovered in publicly available literature, as well as a substantial amount of monitoring data for freshwater streams, lakes, reservoirs, and estuarine areas. It includes cumulative exceedence curves of maximum annual atrazine concentrations from the monitoring data versus the percent of sampling sites in water bodies (streams, rivers, lakes, reservoirs, estuarine areas) with equal or greater annual maximum concentrations. The exceedence curves were constructed with Weibull plot positions, which assign a probability to each ranked concentration value as the rank divided by the sum of total number of samples plus one. Horizontal lines plotted on the graphs of the exceedence curves represent the eco-toxicological endpoint values from both laboratory and simulated field study results as well as 10th centile values calculated from laboratory data. The intersection of a cumulative exceedence curve with one or more horizontal lines representing key assessment endpoints gives the percentage or percentages of the samples, sites, and/or years with an equal or higher concentration than the assessment endpoint.

Endpoints of Concern for the Refined Assessment

The measures of effect and assessment endpoints used in the refined risk assessment are listed below in Tables 1-3 for each of the three aquatic areas being characterized: (1) freshwater ponds, lakes and reservoirs; (2) freshwater streams; and, (3) estuaries and estuarine marshes. When the assessment endpoint relies on a laboratory measurement, the word “estimated” is used to describe the endpoint; when it relies on a simulated field or field measurement, the term “likely” is used.

These measures of effect support the assessment endpoints and provide the basis for the refined aquatic risk assessment. They were taken from a large number of ecotoxicological studies submitted to the Agency and available in the published literature. These measures provide an expanded view of direct and indirect effects of atrazine on aquatic organisms, their populations and communities in the laboratory, in simulated field situations, and in actual field situations. They show effects of atrazine that are often not captured in the data typically generated by the registrant to support registration.. Included are the 10th centile results from distributions of laboratory ecotoxicological data presented in Giddings *et al* 2001. The results from a number of simulated field studies are presented as measures of effect in the following tables or discussed later as showing adverse indirect effects on aquatic organisms or populations: e.g., Lampert *et al.* 1989, Lakshinarayana *et al* 1992, Pearson and Crossland 1996, Kettle *et al* 1987, de Noyelles *et al* 1989. Giddings *et al* 2000 suggested that these and other simulated and actual field studies which showed adverse effects at low atrazine concentrations in water were not representative of the of the majority of studies with atrazine, were poorly documented, and scientifically flawed. The agency disagrees with most of the most points raised by the authors and has presented the Agency’s comments in Appendix XVII. The following tables include measures of effect based on simulated and actual field studies showing adverse effects at low atrazine concentrations in water. A complete listing of the simulated and actual field studies reviewed by the Agency is found in Appendix XI. Ecological Effects Characterization, e. Multi-species Tests (Microcosms, Field Studies). A tabular listing of the simulated field studies reviewed in Giddings *et al* 2001 is found in Table 6.1 of their document. While the Agency’s descriptions identify studies whose results were likely confounded by the addition of other pesticides in addition to atrazine, Table 6.1 in Giddings does not provide this information. Such studies are not included in Tables 1-3.

Table 1. Key Endpoints for the Lentic Freshwater Environment (e.g., reservoirs, lakes). The Endpoints Chosen for Use in the Refined Risk Assessment are Highlighted.

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Fish	Lab	Acute Fish (96-hours) LC50 = 5,300 µg/L	Rainbow trout / Mortality	00024716 Beliles & Scott 1965	Fish Mortality Estimated to Occur at 5,300 µg/L

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
	Lab	Chronic Fish (44-weeks) NOAEC = 65 µg/L; LOAEC= 120 µg/L; MATC= 88 µg/L	Brook trout / [7.2 % red. mean length, 16 % red. mean body weight]	00024377 Macek <i>et al.</i> 1976	Reduction in Fish Growth Estimated to Occur at 88 µg/L
	Distribution of Lab Data	10 th centile value = 62 µg/L	Freshwater Aquatic Animal Chronic Data	Table 5.4 in Giddings <i>et al</i> 2001	Fish Population Reductions Estimated to Occur at 62 µg/L
	Field (mesocosms)	96% Reduction in # of Young Fish Occurred at 20 µg/L (Caused by Loss of Food and Habitat)	Bluegill sunfish	45202912 Kettle, de Noyelles, Jr., Heacock and Kadoum 1987	Fish Populations Likely to be Reduced at 20 µg/L due to Loss of Food and Habitat
Invertebrates	Lab	Acute Invertebrate (48-hour) LC ₅₀ = 720 µg/L	Midge / Mortality	00024377 Macek <i>et al.</i> 1976	Invertebrate Mortality Estimated to Occur at 720 µg/L
	Lab	Chronic Invertebrate (48-hour) NOAEC = 60 µg/L; LOAEC= 140 µg/L; MATC= 92 µg/L	Scud / [25 % red. in development of F ₁ to seventh instar]	00024377 Macek <i>et al.</i> 1976	Reduction in Invertebrate Populations Estimated to Occur at 92 µg/L
	Distribution of Lab Data	10 th centile value = 62 µg/L	Freshwater Aquatic Animal Chronic Data	Table 5.4 in Giddings <i>et al</i> 2001	Reduction in Invertebrate Populations Estimated to Occur at 62 µg/L
	Field	59-65% Reduction in Daphnid population growth occurred at 10 µg/L over 18-days	Daphnids	45087414 Lampert <i>et al.</i> 1989	Invertebrate Populations Likely to be Reduced at 10 µg/L
Non-Vascular Plants	Lab	Acute Algae (1-week) EC ₅₀ = 1 µg/L	Four species [41-93% reduction in chlorophyll production]	00023544 Torres & O'Flaherty 1976	Reduction in Primary Production Estimated to Occur at 1 µg/L
	Distribution of Lab Data	10 th centile value = 32 µg/L for acute effects on phytoplankton, and 2.3 µg/L for chronic effects on plants	Freshwater Aquatic Plant Data	Tables 5.3 & 5.4 in Giddings <i>et al</i> 2001	Acute Effects on Phytoplankton Estimated at 32 µg/L and Reductions in Primary Production Estimated to Occur at 2.3 µg/L
	Microcosm	23% Reduction in gross primary production 10 µg/L (at day 2); recovery by day 7	phytoplankton	45087413 Johnson 1996	Reduction in Primary Production Estimated to Occur at 10 µg/L

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
	Field	42% Reduction in phytoplankton biomass (at days 2-7) occurred at 20 $\mu\text{g/L}$	phytoplankton	45020011 DeNoylles <i>et al.</i> 1982	Reduction in Primary Production Likely to Occur at 20 $\mu\text{g/L}$
Vascular Plants	Lab	Acute (14-days) $\text{EC}_{50} = 37 \mu\text{g/L}$	Duckweed [50% reduction in growth]	43074804 Holberg 1993	Reduction in Macrophytes Estimated to Occur at 37 $\mu\text{g/L}$
	Distribution of Data	10 th centile value = 18 $\mu\text{g/L}$ for acute effects on macrophytes, and 2.3 $\mu\text{g/L}$ for chronic effects on plants	Freshwater Aquatic Plant Data	Tables 5.3 & 5.4 in Giddings <i>et al.</i> 2001]	Acute Effects on Macrophytes Estimated at 18 $\mu\text{g/L}$ and Reductions in Macrophyte Populations Estimated to Occur at 2.3 $\mu\text{g/L}$
	Mesocosm	60% Reduction of macrophyte vegetation occurred at 20 $\mu\text{g/L}$; by May of following year, 95% Reduction of macrophytes	Macrophytes	45202912 Kettle, de Noyelles, Jr., Heacock and Kadoum 1987	Reduction in Macrophytes (number & diversity) Likely to Occur at 20 $\mu\text{g/L}$

Table 2. Key Endpoints for the Lotic Freshwater Environment (e.g., streams). The Endpoints Chosen for Use in the Refined Risk Assessment are Highlighted.

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Fish	Lab	Acute Fish (96-hours) $\text{LC}_{50} = 5,300 \mu\text{g/L}$	Rainbow trout / Mortality	00024716 Beliles & Scott 1965	Fish Mortality Estimated to Occur at 5,300 $\mu\text{g/L}$
	Lab	Chronic Fish (44-weeks) $\text{NOAEC} = 65 \mu\text{g/L}$; $\text{LOAEC} = 120 \mu\text{g/L}$; $\text{MATC} = 88 \mu\text{g/L}$	Brook trout / [7.2 % red. mean length, 16 % red. mean body weight]	00024377 Macek <i>et al.</i> 1976	Reduction in Fish Growth Estimated to Occur at 88 $\mu\text{g/L}$
	Distribution of Lab Data	10 th centile value = 62 $\mu\text{g/L}$	Freshwater Aquatic Animal Chronic Data	Table 5.4 in Giddings <i>et al.</i> 2001	Fish Population Reductions Estimated to Occur at 62 $\mu\text{g/L}$

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Invertebrates	Lab	Acute Invertebrate (48-hour) LC ₅₀ = 720 µg/L	Midge / Mortality	00024377 Macek <i>et al.</i> 1976	Invertebrate Mortality Estimated to Occur at 720 µg/L
	Lab	Chronic Invertebrate (48-hour) NOAEC = 60 µg/L; LOAEC = 140 µg/L; MATC = 92 µg/L	Scud / [25 % red. in development of F ₁ to seventh instar]	00024377 Macek <i>et al.</i> 1976	Reduction in Invertebrate Populations Estimated to Occur at 92 µg/L
	Distribution of Lab Data	10 th centile value = 62 µg/L	Freshwater Aquatic Animal Chronic Data	Table 5.4 in Giddings <i>et al.</i> 2001	Invertebrate Population Reductions Estimated to Occur at 62 µg/L
	Outdoor Stream	Significant Increase in daytime and nighttime invertebrate drift occurred at 22 µg/L due to increased predation	various species of stream dwelling invertebrates	45020003 Davies <i>et al.</i> 1994	Invertebrate Populations Likely to be Reduced at 22 µg/L
Non-Vascular Plants	Lab	Acute Algae (1-week) EC ₅₀ = 1 µg/L	Four species [41-93% reduction in chlorophyll production]	00023544 Torres & O'Flaherty 1976	Reduction in Primary Production Estimated to Occur at 1 µg/L
	Distribution of Lab Data	10 th centile value = 32 µg/L for acute effects on phytoplankton, and 2.3 µg/L for chronic effects on plants	Freshwater Aquatic Plant Data	Tables 5.3 & 5.4 in Giddings <i>et al.</i> 2001	Acute Effects on Phytoplankton Estimated at 32 µg/L and Reductions in Primary Production Estimated to Occur at 2.3 µg/L
	Stream (first order adjacent to corn field in Canada)	79% (mean) Reduction in Total Phytoplankton Counts at 2.62 µg/L (mean; range = 0.211 - 13.9)	phytoplankton	45020008 Lakshinarayana, O'Neill, Johnnavithula, Leger and Milburn, 1992	Reduction in Primary Production Likely to Occur at 2.62 (0.211 - 13.9) µg/L

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
	Outdoor Artificial Streams	Depression of Photosynthesis at 10 µg/L	Various species of stream algae. Photosynthesis reduction measured by open water oxygen methods.	[MRID pending] Kosinski and Merkle, 1984	Reduction in Primary Production Likely to Occur at 10 µg/L
Vascular Plants	Lab	Acute (14-days) EC ₅₀ = 37 µg/L	Duckweed [50% reduction in growth]	43074804 Holberg 1993	Reduction in Macrophytes Estimated to Occur at 37 µg/L
	Distribution of Lab Data	10 th centile value = 18 µg/L for acute effects on macrophytes, and 2.3 µg/L for chronic effects on plants	Freshwater Aquatic Plant Data	Tables 5.3 & 5.4 in Giddings <i>et al</i> 2001	Acute Effects on Macrophytes Estimated at 18 µg/L and Reductions in Macrophytes Estimated to Occur at 2.3 µg/L

Table 3. Key Endpoints for the Estuarine/Marine Environment (e.g., estuaries, tidal , marshes). Endpoints Chosen for Use in the Refined Risk Assessment are Highlighted.

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Fish	Lab	Acute Fish (96-hours) LC50 = 2,000 $\mu\text{g/L}$	Sheepshead minnow / Mortality	45208303 Hall <i>et al.</i> 1994	Fish Mortality Estimated to Occur at 2,000 $\mu\text{g/L}$
	Lab	Chronic Fish NOAEC = 1,900 $\mu\text{g/L}$; LOAEC= 3400 $\mu\text{g/L}$; MATC= 2542 $\mu\text{g/L}$	Sheepshead minnow [89 % red. Juv. survival]	45202920 Ward & Ballantine 1985	Reduction in Fish Populations Estimated to Occur at 2542 $\mu\text{g/L}$
	Distribution of Lab Data	10 th centile value = 23 $\mu\text{g/L}$	Saltwater Aquatic Animal Chronic Data	Table 5.4 in Giddings <i>et al</i> 2001	Fish Population Reductions Estimated to Occur at 23 $\mu\text{g/L}$
Invertebrates	Lab	Acute Invertebrate LC ₅₀ = 94 $\mu\text{g/L}$	Copepod (<i>Acartia tonsa</i>)	45202920 Ward & Ballantine 1985	Invertebrate Mortality Estimated to Occur at 94 $\mu\text{g/L}$
	Distribution of Lab Data	10 th centile value = 23 $\mu\text{g/L}$	Saltwater Aquatic Animal Chronic Data	Table 5.4 in Giddings <i>et al</i> 2001	Invertebrate Population Reductions Estimated to Occur at 23 $\mu\text{g/L}$
	Lab	Chronic Invertebrate NOAEC = 80 $\mu\text{g/L}$; LOAEC= 190 $\mu\text{g/L}$; MATC= 123 $\mu\text{g/L}$	Mysid [37 % red. Adult survival]	45202920 Ward & Ballantine 1985	Reduction in Invertebrate Populations Estimated to Occur at 123 $\mu\text{g/L}$
Non-Vascular Plants	Lab	Acute (120-hours) Algae LC ₅₀ = 22 $\mu\text{g/L}$	Algae (Chrysophyceae; <i>Isochrysis galbana</i>)	41065204 Parrish 1978	Algae Mortality Estimated to Occur at 22 $\mu\text{g/L}$
	Distribution of Lab Data	10 th centile value = 27 $\mu\text{g/L}$ for acute effects on phytoplankton, and 9.1 $\mu\text{g/L}$ for chronic effects on plants	Saltwater Aquatic Plant Data	Tables 5.3 & 5.4 in Giddings <i>et al</i> 2001	Acute Effects on Phytoplankton Estimated at 27 $\mu\text{g/L}$ and Reductions in Primary Production Estimated to Occur at 9.1 $\mu\text{g/L}$

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
	Field	Up to 50% reduction in primary production (days 3-11, 3-13, 3-7, respectively at 0.12, 0.56 and 5.8 $\mu\text{g/L}$) Mean value is 2.16 $\mu\text{g/L}$	phytoplankton	45020021 Bester <i>et al.</i> 1995	Reduction in Primary Production Likely to Occur at 0.12 - 5.8 $\mu\text{g/L}$ with a mean of 2.16 $\mu\text{g/L}$
Vascular Plants	Lab	Significant reduction in dry weight occurred at 10 $\mu\text{g/L}$ (calculated MATC from NOAEC=7.5 and LOAEC=14.3)	Sago Pondweed	[MRID pending] Chesapeake Bay Program 1998	Reduction in Macrophytes Estimated to Occur at 10 $\mu\text{g/L}$
	Distribution of Lab Data	10 th centile value = 9.1 $\mu\text{g/L}$ for chronic effects on plants	Saltwater Aquatic Plant Data	Tables 5.3 & 5.4 in Giddings <i>et al</i> 2001	Reductions in Macrophytes Estimated to Occur at 9.1 $\mu\text{g/L}$
	Microcosm	16% Reduction in Tuber formation; 55% Reduction in Biomass over reproductive season at 4 $\mu\text{g/L}$	Wild Celery (<i>Vallisneria Americana</i>)	45020001 Cohn 1985	Reduction in Macrophytes Likely to Occur at 4 $\mu\text{g/L}$

Atrazine in Ponds

In order to assess aquatic exposure to ponds under both maximum and typical use rate conditions, EFED implemented the refined tier II approach using the PRZM/EXAMS models (A brief description of these models and their input values are presented in Appendix V). The upper tenth percentile concentration values, expressed in ppb ($\mu\text{g/L}$), are summarized below. The results of three uses, corn, sugarcane, and sorghum, were based on the standard scenarios provided by EFED's Water Quality Tech Team (WQTT) to predict reasonable high exposure values, i.e., soils with high runoff potential and heavy rainfall amounts, for both maximum and typical use rates.

Treated Crop	Use Rate (lb ai/A)	Atrazine EEC Values ppb ($\mu\text{g/L}$)				
		Peak Conc.	96-hour Average	21-day Average	60-day Average	90-day Average
Sugarcane	4.0	205	204	202	198	194
	2.6	133	133	131	129	126
Corn	2.0	38.2	38.0	37.2	35.5	34.2
	1.1	21.0	20.9	20.5	17.7	18.8

Sorghum	2.0	72.7	72.3	70.6	67.7	65.9
	1.2	43.6	43.4	42.4	40.6	39.5

The modeling results indicate that atrazine does have the potential to move into surface waters, especially for sugarcane use. Peak EECs for sugarcane, in particular, track very closely with peak levels found in monitoring data in Louisiana streams near sugar cane production areas (See Figure 3 below and compare with Figure 12). Klassen and Kadoum (1979) found atrazine to be persistent in a farm pond ecosystem with estimated half-lives of six to eight months. These data support the persistence of atrazine seen in the gradual reductions in EEC levels produced by the PRZM-EXAMS model presented in the above table. With such stable atrazine concentrations in ponds, only small differences exist between acute and chronic atrazine exposures for ponds. Therefore, the significance of the duration of the toxicity tests conducted becomes less important for assessing risks in ponds.

Data from the PRZM/EXAMS model were used to estimate the chemical contributions of runoff, erosion and spray drift to the standard farm pond. The results, expressed as percentages, are tabulated below:

Percent of Pesticide Loadings from Different Sources to the Standard Pond

Use	Runoff	Erosion	Spray Drift
Corn	55.03%	3.47%	41.50%
Sugarcane	99.15%	0.85%	0.01%
Sorghum	71.80%	5.29%	22.91%

The erosion losses were relatively small for all three simulated uses, with runoff and spray drift accounting for most of the loading for corn and sorghum. For sugarcane, most loading in the model simulations was from runoff.

Syngenta has questioned the Agency’s use of environmental fate data for the model inputs in PRZM/EXAMS simulations. Syngenta claimed that more environmental fate data are available and EFED should not just based on the few submitted studies. Without formal reviews of these additional data, EFED can not determine the validity of Syngenta’s claim. However, the Agency re-ran PRZM/EXAMS based on Syngenta suggested inputs to see the impact to the exposure results. The results are tabulated below. There are three scenarios for corn and sorghum and four for sugarcane. The first one is based on the original values used in the Agency’s Science Chapter, and the second and third scenarios are based on Syngenta’s suggested environmental fate inputs. In the original modeling runs for the Science Chapter, the Agency assumed the values of 75% for the application efficiency and 5% for off-target spray drift into the pond for aerial applications. These assumptions are not as conservative as some of the Spray Drift Task Force (SDTF) results indicate [AGDRIFT model (www.agdrift.com)]. For example, the value of off-target spray drift can be up to 15%. According to the current Agency guidance on modeling

inputs for aerial applications, the application efficiency should be 95% and the off-target spray drift should be 5%. For ground applications, the values are 99% and 1%, respectively. Scenarios 2 and 3 represent the results of different application efficiency values of 75% and 95%, respectively. In addition, Syngenta has claimed that ground applications are the common practices for sugarcane uses in Louisiana. For this reason, the Agency also ran the ground application of 99% efficiency and 1% off-target spray drift for sugarcane use with Syngenta's suggested input values and the results are in scenario 4. Comparing the results of different scenarios for each use, the difference is not significant. This is especially true considering that the drift value is fixed at 5%. This is compared to the default drift value of SDTF's AgDRIFT model which is more than 10%, and can range from 13% to 15% depending on the version of AGDRIFT model. Thus, the Agency chose not to change the exposure characterization for ponds.

Treated Crop	Scenario	Atrazine EEC Values ppb ($\mu\text{g/L}$)				
		Peak Conc.	96-hour Average	21-day Average	60-day Average	90-day Average
Sugarcane (4.0 lb ai/a)	1 ¹	205	204	202	198	194
	2 ²	167.6	166.7	163.8	157.8	152.9
	3 ³	207	206	203	195	189
	4 ⁴	200.6	199.6	196.7	189.8	183.8
Corn (2.0 lb ai/a)	1	38.2	38.0	37.2	35.5	34.2
	2	29.7	29.4	28.4	26.6	25.1
	3	35.3	35.0	33.8	31.6	30.0
Sorghum (2.0 lb ai/a)	1	72.7	72.3	70.6	67.7	65.9
	2	47.9	47.4	46.0	42.7	40.4
	3	58.4	57.8	56.0	52.0	49.2

¹ Original environmental fate inputs found in Agency's Science Chapter;

² Based on Syngenta's suggested environmental fate inputs;

³ Based on Syngenta's suggested environmental fate inputs;

⁴ Ground application of 99% efficiency and 1% off-target spray drift for sugarcane use with Syngenta's suggested input values.

Risk of Atrazine to Aquatic Organisms and Communities in Ponds

The following graphs (Figures 1, 2, and 3) show the PRZM-EXAMS modeled peak, 96-hour, 21-day, 60-day, and 90-day water column dissolved concentrations of atrazine for 36 years

(sorghum and corn) and 20 years (sugarcane) and the percentage (%) of years with equal or greater concentrations. Intersecting these curves are horizontal lines representing the key assessment endpoints for ponds found in Table 1.

Figure 1. PRZM/EXAMS Modeling Atrazine Results of Kansas Sorghum Pond Scenario

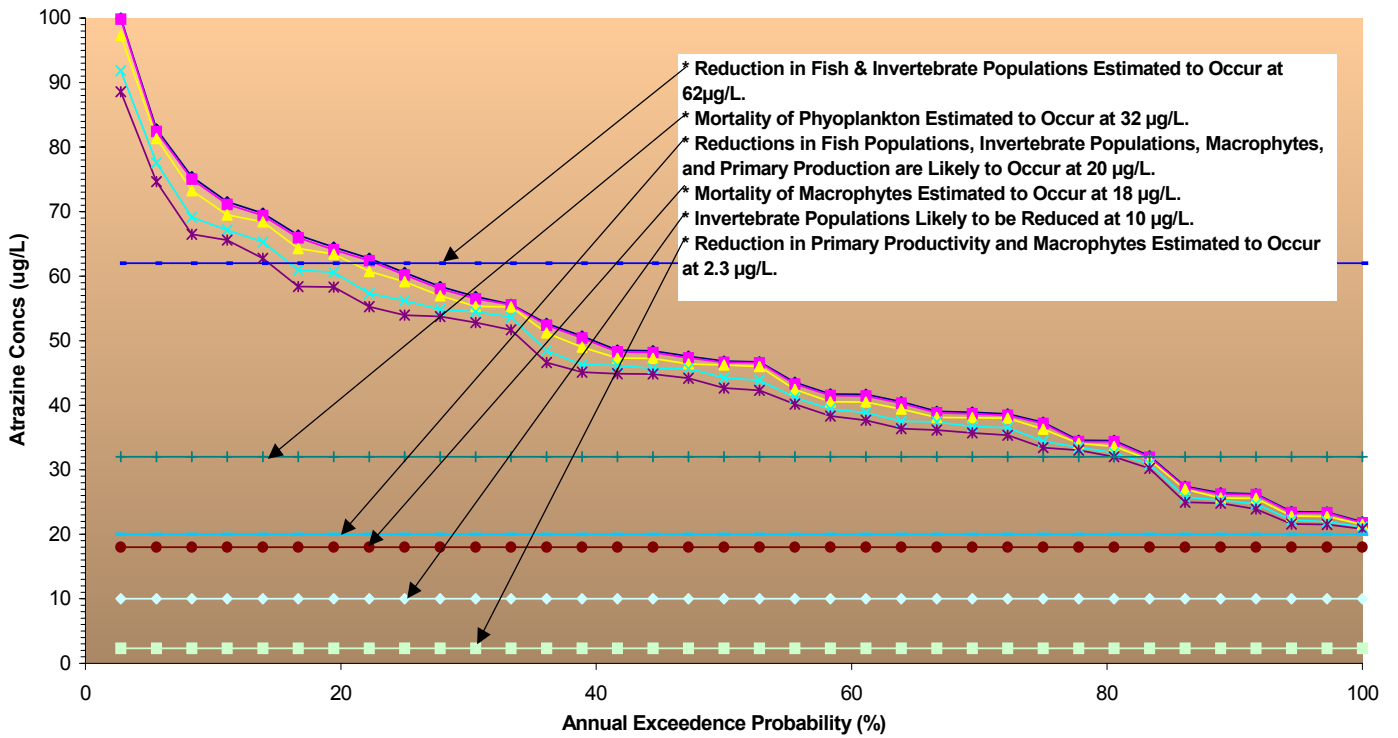


Figure 2. PRZM/EXAMS Modeling Atrazine Results of Ohio Corn Scenario

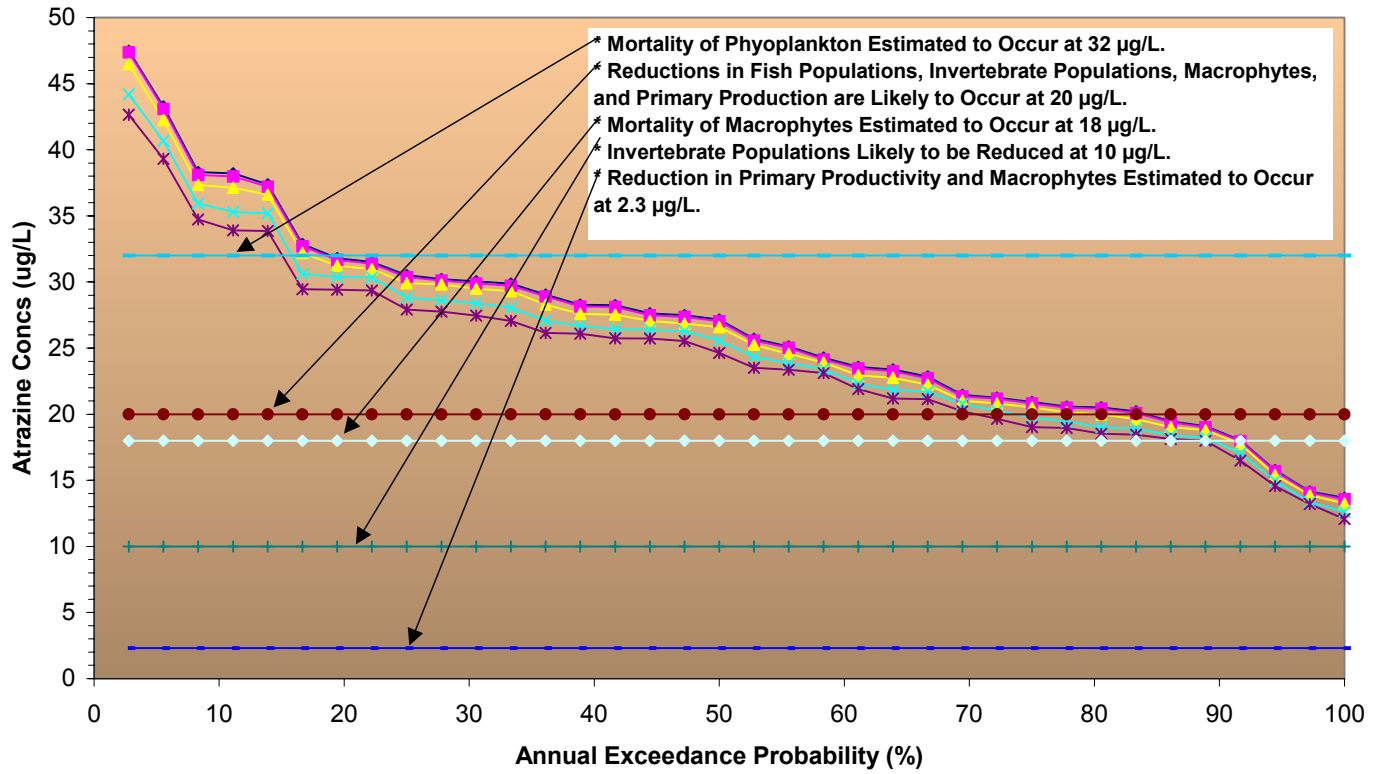
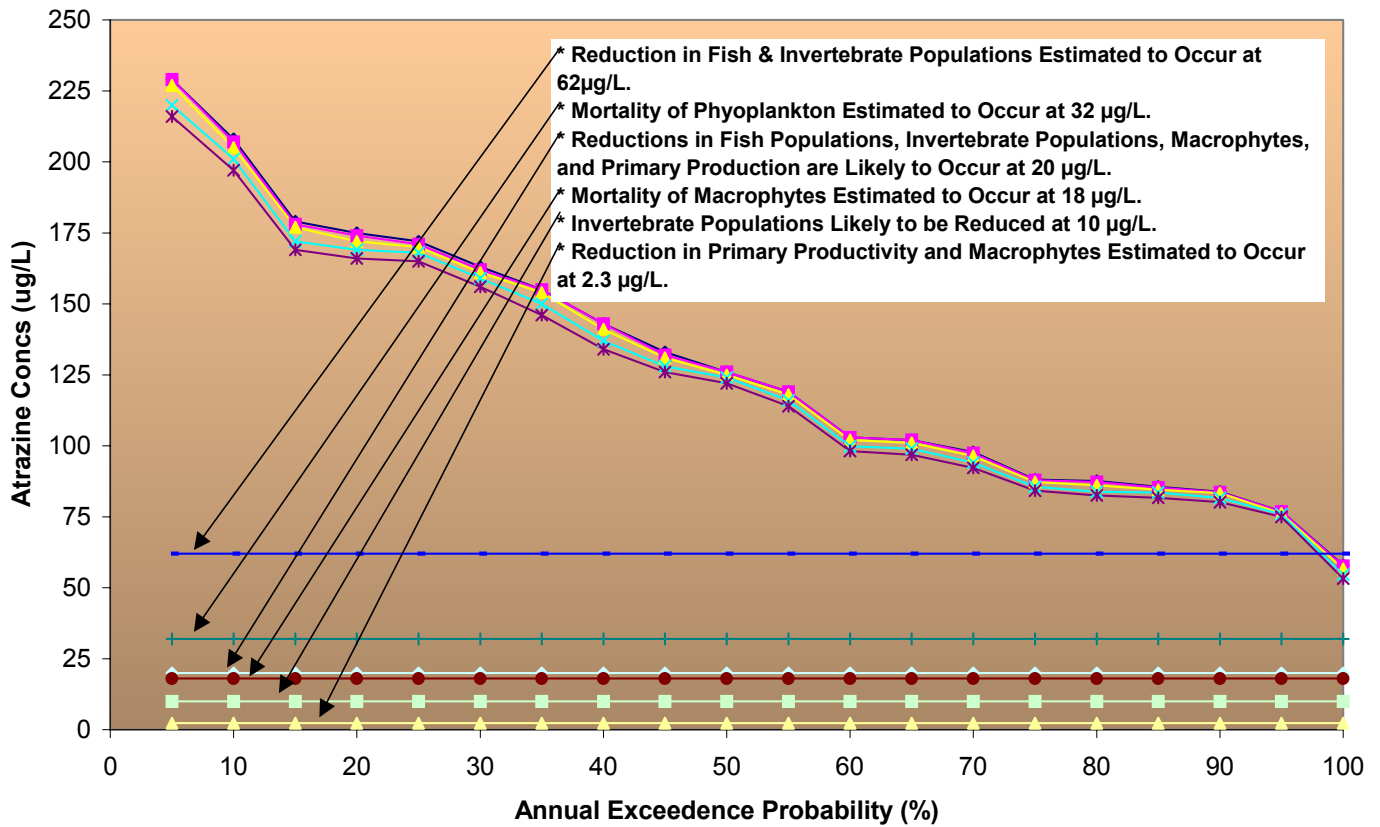


Figure 3. PRZM/EXAMS Modeling Atrazine Results of Louisiana Sugarcane Scenario



Based on modeling simulations, it is possible that for months every year, atrazine concentrations in ponds from use on sorghum and sugarcane exceed the levels ($\geq 20 \mu\text{g/L}$) at which simulated studies have shown reductions in fish and invertebrate populations, macrophytes, and primary production. For corn, modeling simulations indicate that atrazine concentrations in ponds exceed the levels at which studies have shown reductions in fish populations, invertebrate populations, macrophytes, and primary production in 70 to 83% of the years.

While the standard pond scenario assumes instantaneous mixing, it is more likely that the aquatic vegetation in shallow areas around the edge of the pond, particularly the edge nearest the treated field, as well as in the epilimnion in larger static bodies of water, will be exposed to higher atrazine levels than the mean concentration for the whole pond. The loss of rooted aquatic plants along the edge of a water body has several consequences, including: 1) the release of nutrients into the water which is likely to increase phytoplankton growth, which may decrease light penetration to plants in deeper water. If the plants in deeper water die they too release more

nutrients to the phytoplankton. 2) lost rooted vegetation along the shore line does not intercept and hold sediments from runoff. Suspension of sediments in the water column adds to the light blockage from phytoplankton. Sediment deposited on plant leaves further reduces the ability of the plant to photosynthesize. One study reported 27 percent reduction in photosynthesis from sediments on the leaves only (Jones and Estes, 1984). 3) water movements along the shores from wind-generated waves or other sources may stir up sediments into the water column and onto plant leaves. At some point, the stresses on the ability of plants to photosynthesize from atrazine, sediments and light attenuation exceed the capacity of the plants in deeper water to produce sufficient energy to meet their own needs. The plant dies and repeats the cycle releasing more nutrients, providing the conditions for the growth of more phytoplankton and causing further attenuation of light, resulting in adverse effects on an ever increasing number of aquatic plants.

The loss of the submerged vegetation reduces the availability of habitat for small fish and aquatic invertebrates to avoid predators. With increasing losses of vegetation the populations of aquatic invertebrates and small fish decline as the larger predators consume more prey until the numbers of prey decline. With the loss of the vascular plants, the source of food becomes evermore dependent on phytoplankton to sustain the trophic levels for those animals which survive. For those organisms dependent on vascular plants for food their populations will likely decline as the food sources decline.

Kettle *et al.* (1987) observed the decline in vascular vegetation following a single application of 20 $\mu\text{g/L}$ of atrazine to a pond. Within a couple of months the vegetation had declined 60 percent compared to controls. By the following spring, aquatic vegetation was reduced 90 percent. Upon draining the ponds that spring, bluegill young had been reduced 96 percent compared to controls, fish in treated ponds had fewer prey items in their stomachs and some aquatic invertebrate taxa were missing. These indirect community effects on fish and aquatic invertebrate populations were the result of the impact of atrazine on aquatic vegetation.

Atrazine in Lakes and Reservoirs

Baier *et al.* (1985) reported that in the United States atrazine concentrations may reach up to 88.4 $\mu\text{g/L}$ in surface water from drinking water reservoirs. Waldron (1974) reported atrazine concentrations up to 69.4 $\mu\text{g/L}$ from U.S. surface waters. In addition, the most recent 6(a)2 report received by the Agency on December 7, 2001 and provided by Syngenta, showed a total of 221 atrazine detects from lakes and reservoirs in Illinois, Kansas and Louisiana during the period of June 1, 2000 to April 30, 2001 that exceeded the 3.0 $\mu\text{g/L}$ MCL. Of these 221 detects, 45 were for finished tap water with the highest atrazine concentration at 12 $\mu\text{g/L}$. For the remaining raw water samples, the highest atrazine detection was 62 $\mu\text{g/L}$, thus showing that atrazine concentrations can reach up to 62 $\mu\text{g/L}$ in drinking water reservoirs. Finally, the data below show that some high detections ($> 20 \mu\text{g/L}$) of atrazine have been reported for finished drinking water in the States of Illinois, Indiana, Ohio, and Missouri.

Acetochlor Registration Partnership (ARP) Monitoring Study of Atrazine in Surface Water Source CWSs

214-GI-IL	Gillespie	05/29/96	49.48
214-GI-IL	Gillespie	05/15/96	41.00
219-SH-IL	Shipman	05/29/96	34.65
214-GI-IL	Gillespie	06/12/96	28.68
219-SH-IL	Shipman	05/01/96	25.68
340-NV-IN	North Vernon	05/28/96	24.84
219-SH-IL	Shipman	06/12/96	23.71
330-LO-IN	Logansport	05/27/97	23.11
150-FL-IL	Flora	05/29/96	22.69
455-MO-OH	Monroeville	05/27/97	21.32
219-SH-IL	Shipman	06/27/96	20.61
219-SH-IL	Shipman	07/10/96	20.60
219-SH-IL	Shipman	05/15/96	20.58

Novartis Population Linked Exposure (PLEX) Database of Atrazine Concentrations in CWSs in 21 States

1350300-IL		1994	30
	HILLSBORO		
1350150-IL	COFFEEN	1994	30
1350600-IL	SCHRAM CITY	1994	30
1350650-IL	TAYLOR SPRINGS	1994	30
1010225-MO	DREXEL	1994	27
1170400-IL	GILLESPIE	1996	42.00
1170030-IL	KAHO PUBLIC WATER DISTRICT	1996	42.00
1170050-IL	BENLD	1996	42.00
1170250-IL	DORCHESTER	1996	42.00
1170300-IL	EAGERVILLE	1996	42.00
1170650-IL	MOUNT CLARE	1996	42.00
1171200-IL	WILSONVILLE	1996	42.00
1175450-IL	SPRING CREEK WTR ASSN	1996	42.00
0801511-OH	SARDINIA, VILLAGE OF	1996	38.73
3900811-OH	MONROEVILLE, VILLAGE OF	1997	29.58
4502314-OH	NEWARK, CITY OF	1997	20.75

Risk of Atrazine to Aquatic Organisms and Communities in Lakes and Reservoirs that may be used as Community Water Supplies (CWSs)

The tabular data above show that a number of finished drinking water sites have atrazine concentrations (> 20 µg/L) above levels at which reductions in fish populations, invertebrate

populations, macrophytes, and primary production have been observed in simulated field studies and are likely to occur in some lakes and reservoirs that are used as drinking water sources (See Key Endpoints Table 2).

USGS 1992-1993 Study of 76 Mid-Western Reservoirs (USGS Open-File Report 96-393):

The USGS sampled the outflows from 76 midwestern reservoirs 8 times (approximately once every two months) from April 1992 through September 1993 (USGS Open -File Report 96-393; a total of 608 samples). The samples were analyzed for a number of pesticides and pesticide degradates including atrazine, deethyl atrazine (DEA), and deisopropyl atrazine (DIA). The reservoirs were selected from a list of approximately 440 reservoirs in 11 midwestern states.

The sampling frequency was inadequate for the Agency to provide atrazine time series (i.e., the fluctuations of concentrations with time) for the reservoirs. However, in Figures 4 and 5, the Agency generated cumulative exceedence curves of maximum annual atrazine concentrations for each reservoir in 1992 and 1993 versus the percent of lakes and reservoirs with equal or greater annual maximum concentrations. The maximum atrazine concentration sampled for each of the 76 reservoirs was selected for 1992, and ranged from 12.42 to 0.025 $\mu\text{g/L}$. Similarly, the maximum concentrations of atrazine for 1993 ranged from 11.03 to 0.025 $\mu\text{g/L}$; however, there were only 75 samples for 1993 since one reservoir, Coralville Lake in Iowa was not sampled in 1993. The highest concentrations of atrazine were found in lakes and reservoirs in Indiana, Ohio, and Illinois. The horizontal line in Figures 4 and 5 represent the key assessment endpoints found in Table 1.

Figure 4. USGS 1992 Mid-Western Lake/Reservoir Sampling Results
Maximum Atrazine Concentrations

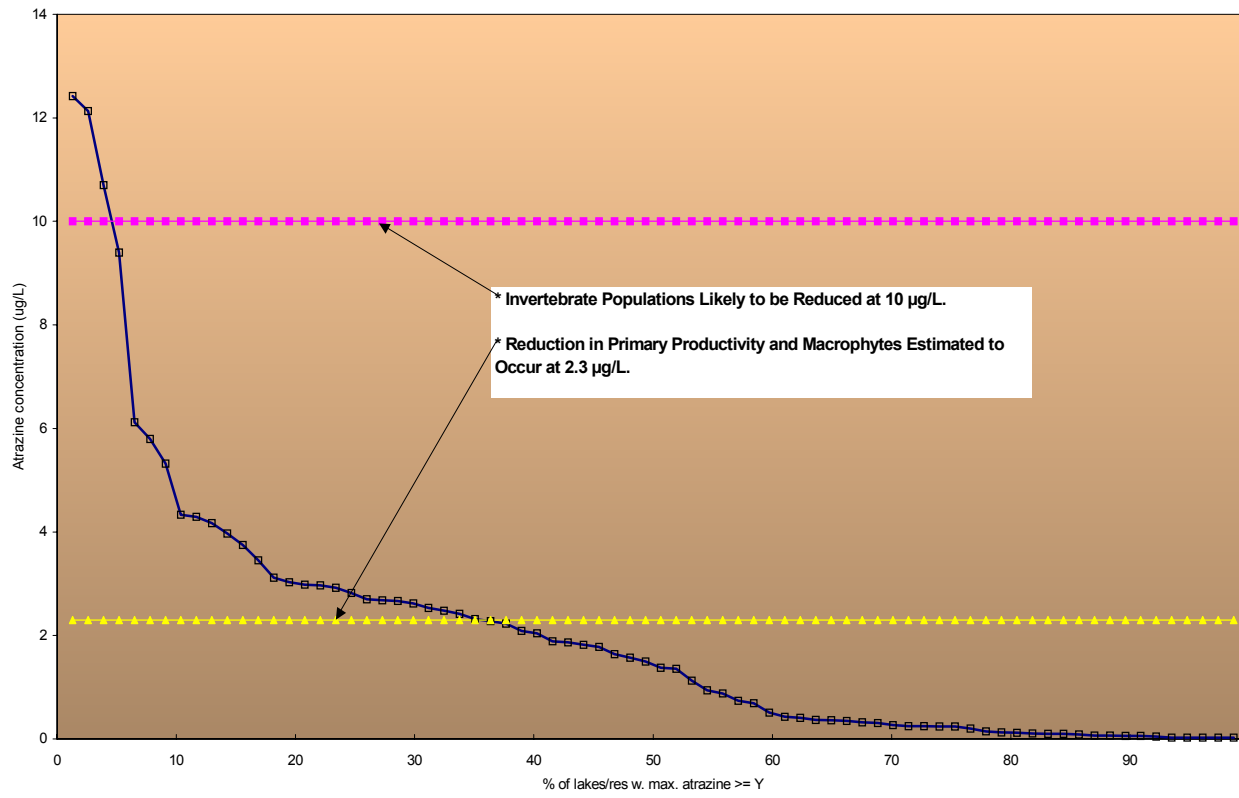
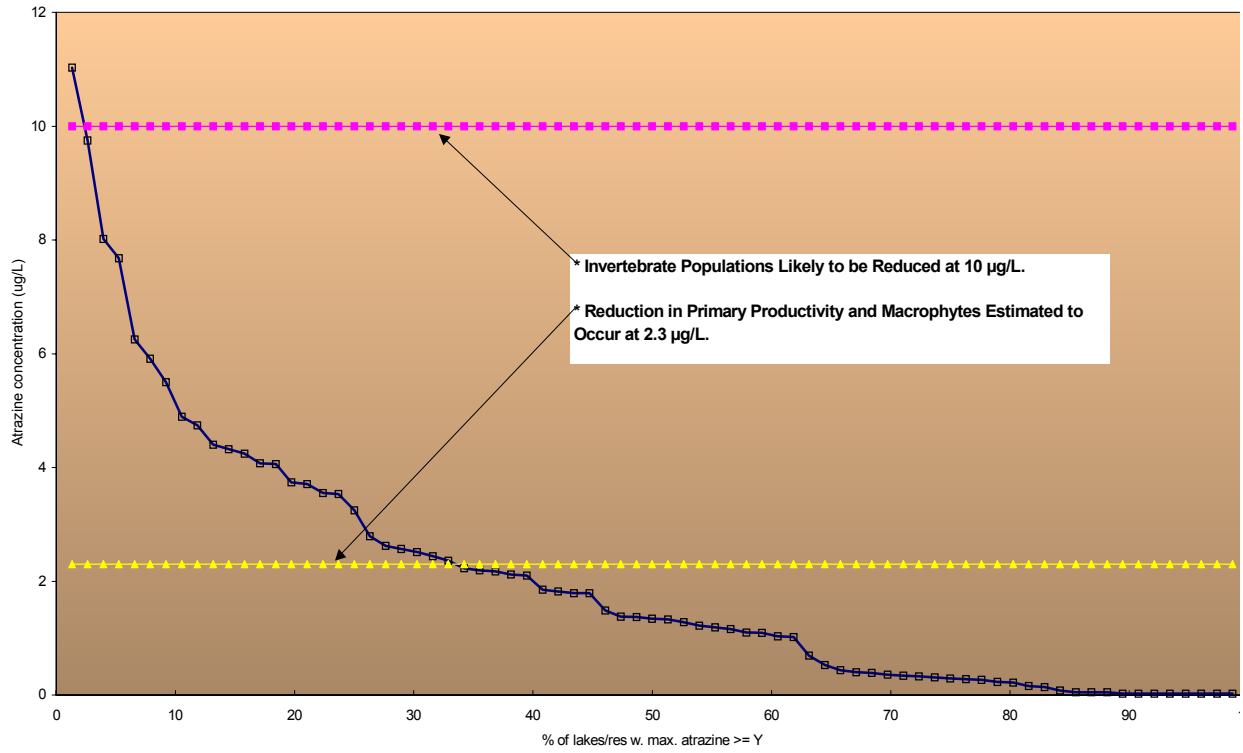


Figure 5. USGS 1993 Mid-Western Lake/Reservoir Sampling Results
Maximum Atrazine Concentrations



Risk of Atrazine to Aquatic Organisms and Communities in 76 Mid-Western Reservoirs/Lakes

Based on Figures 4 and 5 for 1992 and 1993, between 33% and 35% (~25) of the 76 reservoirs and lakes sampled exceed levels where a reduction in primary productivity could occur; and, from 2.5% to 4.5% (1 to 3) exceed levels where invertebrate populations are likely to be reduced. These impacts are more likely to occur during the months of June and July and when the highest concentrations are usually found. Lakes and reservoirs in Indiana, Illinois and Ohio are at greatest risk.

Atrazine in Streams

The highest pesticide concentrations occur in brief pulses following rain events and are usually associated with the storm event soonest after the application. Gilliom *et al.* (1999) have reported that these pulses commonly reach 30 to 40 $\mu\text{g/L}$, with a maximum reported value of 108 $\mu\text{g/L}$. In some years, atrazine concentrations exceed 100 $\mu\text{g/L}$ in small (less than fourth-order) streams when storm runoff occurs within a few weeks following planting (Baker *et al.* 1981; Baker 1987). Dilution and degradation usually reduce atrazine concentrations in streams within a few weeks of the rain event (Thurman *et al.* 1992; Moody and Goolsby 1993; Kolpin and Kalkoff 1993). Atrazine concentrations vary from year to year, depending upon usage and rainfall patterns; from watershed to watershed, depending upon the size of the watershed and the intensity of the agricultural activity in it; and within watersheds, depending upon the flow volume and location in the watershed.

Davies *et al.* (1994) reported that atrazine persisted in Tasmanian streams adjacent to treated forested areas for 12 to 16 months following a single application. Seepage continued to feed atrazine into streams for months, and they estimated that the half-life in streams is of the order of 3 months.

In 1989/1990 and 1994/95 reconnaissance studies of 50 to 123 midwestern streams, the USGS reported maximum atrazine concentrations during post-application runoff events of 108 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$, respectively. In a 1995-98 study of 9 Ohio tributaries to Lake Erie, Heidelberg College reported annual maximum atrazine concentrations ranging from 54.6 $\mu\text{g/L}$ to 80 $\mu\text{g/L}$.

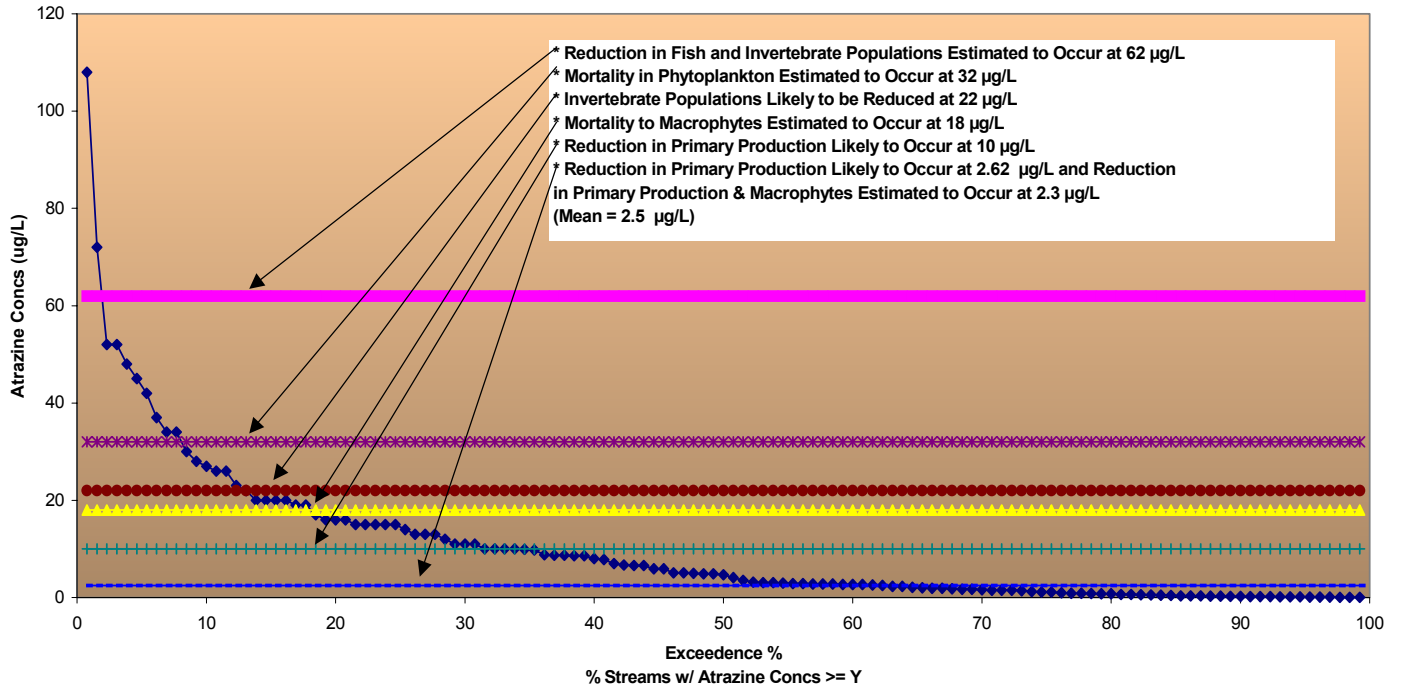
USGS 1989-1990 Reconnaissance Study of Mid-Western Streams (USGS Open-File Report 93-457):

- 1989--one "pre-application" sample, one "post-application" sample and one "Fall" sample from 52, 129, and 143 mid-western streams, respectively, across 10 states.
- 1990--one "pre-application" sample, and one "post-application" sample from 52 and 50 mid-western streams, respectively, across 10 states.
- Samples were analyzed for a number of pesticides including atrazine, DEA, and DIA.
- No time series curves were constructed, but cumulative exceedence curves for post-

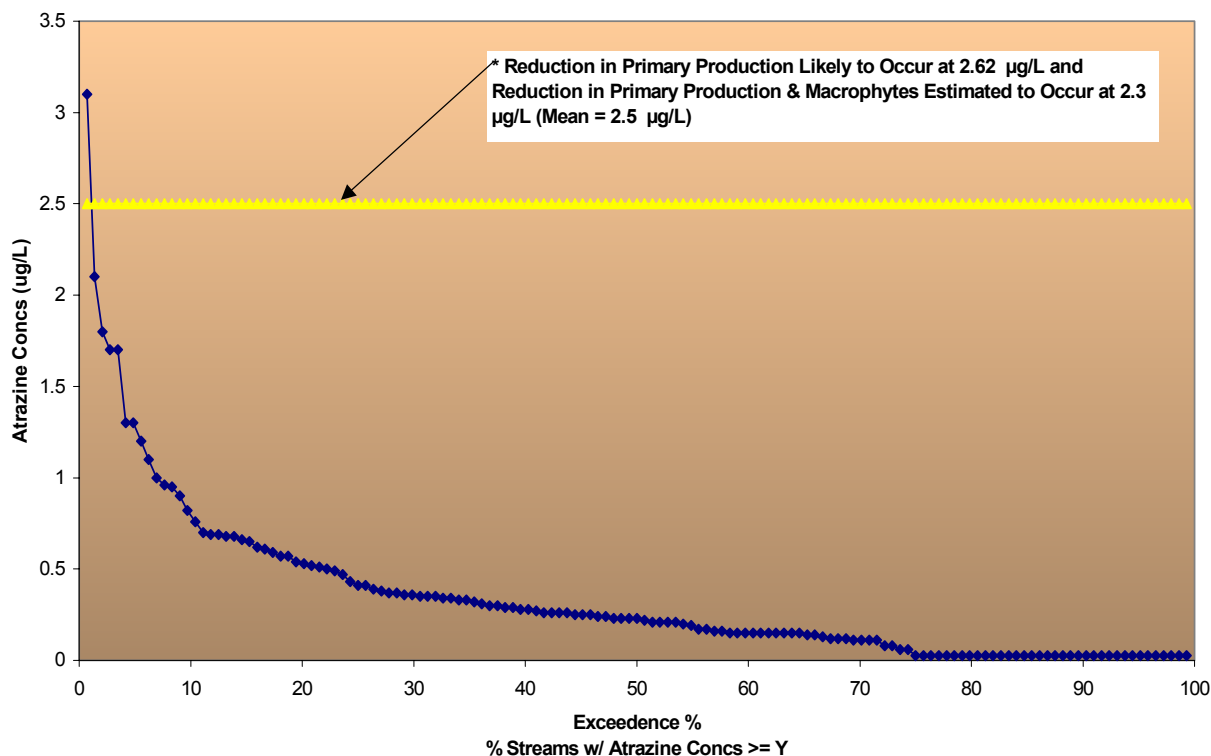
application, and fall concentrations of atrazine in 1989 are provided in Figures 6 and 7 to show that atrazine concentrations are highest after the application of atrazine and drop to much lower levels by the fall. The horizontal lines represent the assessment endpoints for streams found in Table 2.

- Figure 6, showing the exceedence curves for atrazine concentrations in mid-western streams following applications of atrazine in 1989, is based on 129 samples ranging from 108 to 0.025 $\mu\text{g/L}$. These are the maximum concentrations of atrazine measured in each of the 129 streams following applications of atrazine in 1989. Following the highest reading of 108 $\mu\text{g/L}$, the next five highest values appear to continue a trend (72, 52, 52, 48, 45).
- Figure 7, showing the exceedence curves for atrazine concentrations in mid-western streams in the fall in 1989, is based on 143 samples ranging from 3.1 to 0.025 $\mu\text{g/L}$. These are the maximum concentrations of atrazine measured in each of the 143 streams in the fall of 1989.

Figure 6. USGS Mid-Western Streams Sampling Results for 1989
 Post-Application Atrazine Concentrations (from 129 Streams)



**Figure 7. USGS Mid-Western Streams Sampling Results for 1989
Fall Atrazine Concentrations (from 143 Streams)**



Risk of Atrazine to Aquatic Organisms and Communities in Mid-Western Streams in 1989, Post-Application and in the Fall

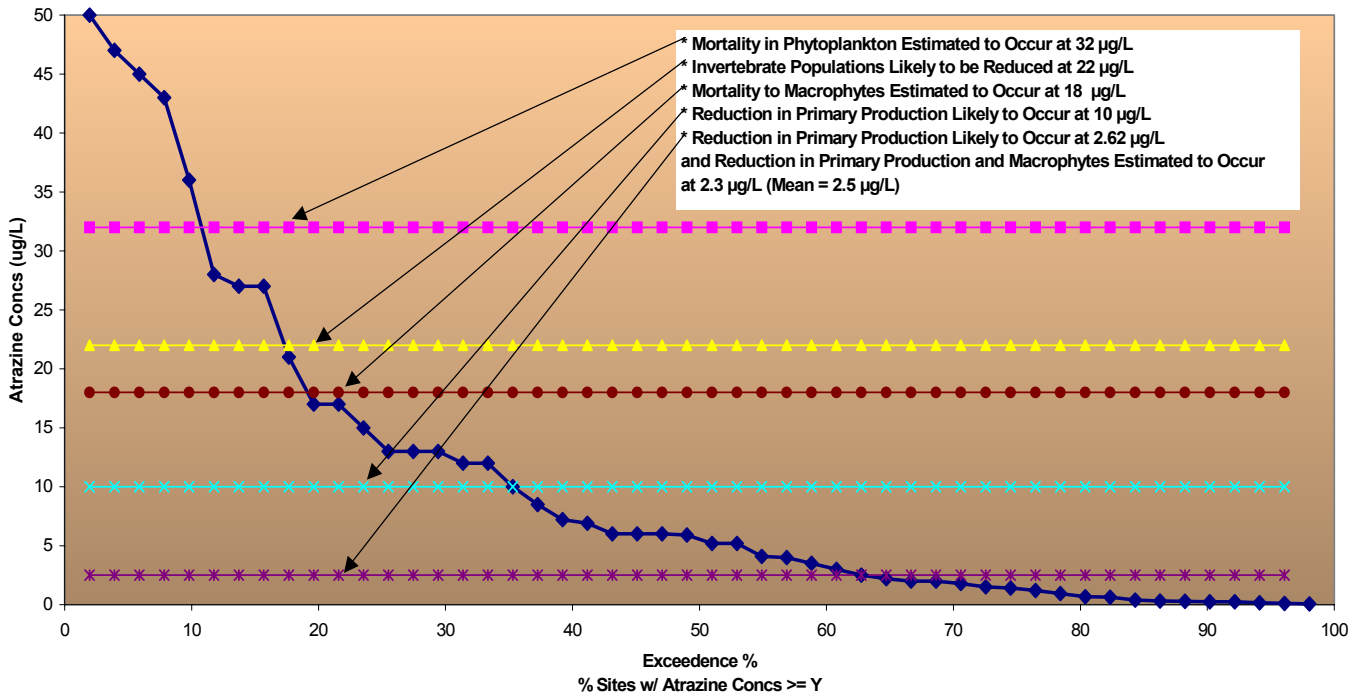
Based on Figure 6, reductions in invertebrate populations and primary production were likely to occur in 12% to 34% (15 to 44), respectively, of the 129 Mid-Western streams sampled following atrazine applications in 1989. In addition, based on simulated field testing and laboratory testing, macrophytes may be reduced in 52 to 63% (67 to 81) of the streams sampled following atrazine applications. Reduction in primary production is also possible at these levels as well. See Figure 8 below for similar results in 1995.

Figure 7 shows that maximum atrazine concentrations in Mid-Western streams are significantly lower by fall of 1989. By fall, primary production and macrophytes may be reduced in only about 1% (~1 to 2) of the 143 streams sampled. The maximum atrazine concentrations did not exceed any other of the endpoints identified in Figure 6.

USGS 1994-1995 Reconnaissance Study of Mid-Western Streams (USGS Open-File Report 98-181):

- 1994--one “pre-application” sample, and one “post-application” sample from 52 and 50 mid-western streams, respectively, across 8 states.
- 1995--one “post-application” sample from 50 mid-western streams across 7 states.
- Samples analyzed for a number of pesticides including atrazine, DEA, and DIA.
- No time series curves were constructed, but Figure 8 shows the 1995 “post-application” cumulative exceedence curve for the maximum stream concentrations in 50 Mid-Western streams. The horizontal lines represent the assessment endpoints for streams found in Table 2.

Figure 8. USGS Mid-Western Stream Sampling Results for 1995 Post-Application Atrazine Concentrations for 50 Streams



1995, Post-Application

Based on Figure 8, reductions in invertebrate populations and primary production are likely to occur in 17% to 35% (9 to 18), respectively, of the 50 Mid-Western streams sampled following atrazine applications in 1995. In addition, based on laboratory testing, macrophytes may be reduced in 64% (32) of the streams sampled following atrazine applications. These results are similar to those in Figure 6 for 1989, and indicates that atrazine concentrations in Mid-Western streams were generally constant over this time period.

USGS 1990-1992 Study of 9 Mid-western Rivers/Streams (USGS Open-File Report 94-396):

- Each of 9 mid-western rivers/streams sampled several hundred times from April 1990 through July 1990.
- Samples were collected 1-2 times per week and automatically collected during runoff events either at several hour intervals or in response to changes in flows. During runoff events, 2-4 samples were typically collected at different times on the same day.
- Samples analyzed for a number of pesticides including atrazine.
- No cumulative exceedence curves were constructed from the data, but two sets of atrazine time series are provided as examples. Multiple samples from a site on the same day are averaged. The two time series graphs are presented in Figures 9 and 10 to show the atrazine concentrations for Robert's Creek Iowa and Silver Creek, Illinois. The maximum concentrations pulse up to 90 $\mu\text{g/L}$ and periodically exceed 10 $\mu\text{g/L}$. The maximum atrazine concentrations for rivers range lower, from 10 to 20 $\mu\text{g/L}$.

Robert's Creek IA (Scribner et al 1994)

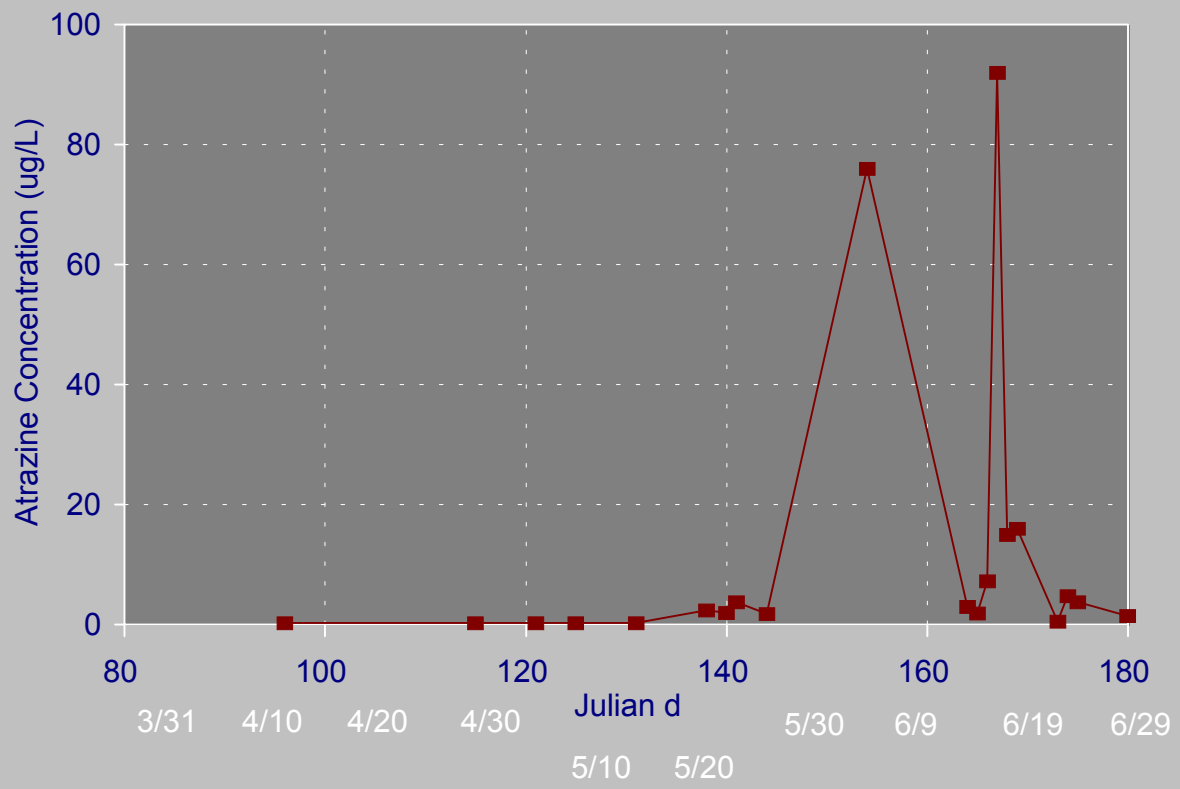
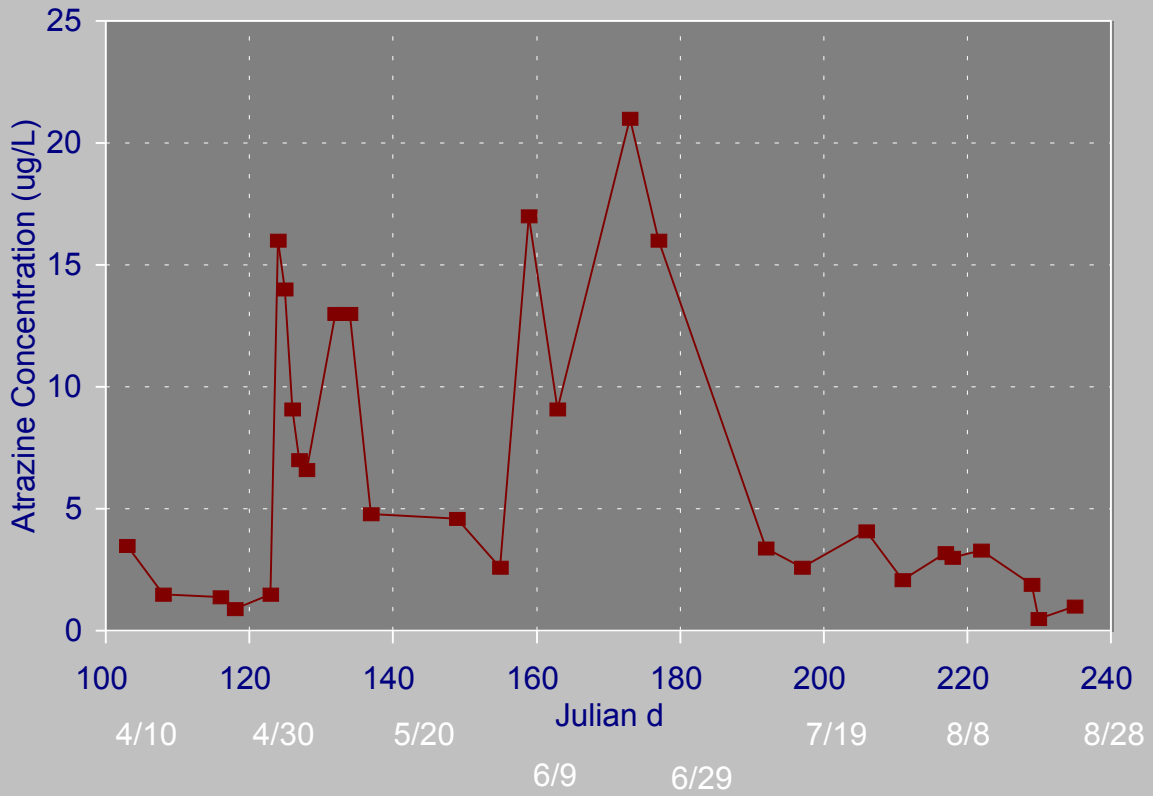


Fig.10 1990 Atrazine Time Series

Silver Creek IL (Scribner etal 1994)



Risk of Atrazine to Aquatic Organisms and Communities in Mid-Western Streams
Sampled from April 1990 through July 1990

The highest pulse concentrations in Figures 9 and 10 exceed many of the assessment endpoints in Table 2 for streams. While the duration of these high concentrations of atrazine is not likely to be long since pulses of runoff tend to move quickly downstream, they may last for hours especially during the spring and during runoff events when numerous fields in a watershed are receiving applications at similar times. Thus, it is possible that reductions in invertebrate populations and primary production could occur as a result of post-application stream contamination from the spring applications of atrazine. The frequency of such reductions occurring may be low considering the frequency of the pulses above 10 $\mu\text{g/L}$ and depending upon the flow volume of each stream. The frequency of similar reductions occurring in rivers is probably lower than for streams since the peaks and average concentrations of atrazine are lower in rivers.

Atrazine in Streams Based on The National Water-Quality Assessment (NAWQA)
Program of the U.S. Geological Survey (USGS).

Additional monitoring data on atrazine concentrations for streams are derived from the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS). The NAWQA program is designed to describe the status of and trends in quality of the nation's ground water and surface water resources and to link assessment of status and trends with an understanding of the natural and human factors that affect the quality of water. The building blocks of this program are Study-Unit Investigations in 60 major hydrologic basins of the nation. The 60 NAWQA Study Units cover about one-half of the conterminous United States, and encompass 60 to 70 percent of national water use. The initial results of 20 Study Units are available through the NAWQA web site covering 1991 through 1996. The program is on-going.

The results from "indicator" and "integrator" sites were analyzed for aquatic atrazine exposure data. Indicator sites usually representing small watersheds with areas in the order of 20 to 100 square miles, were chosen to represent water quality conditions of streams in relatively homogeneous basins associated with specific land use and natural characteristics that were targeted for study. The small watersheds were nested within larger watersheds that represented larger rivers and mixed land uses for the purpose of "integrating" the effects of complex combinations of land-use settings, point sources, and natural influences typical of the region. The size of the "integrator" sites are usually in the order of 500 to greater than 1,000 square miles. Integrator sites are generally sampled downstream from indicator sites and are located at key nodes in the drainage network. Results from the integrator sites provide a general check on the persistence of water quality influences evident at the indicator sites; the results also can be used for water-budget and contaminant transport assessments.

The 65 sites available from the NAWQA web page consist of 40 agricultural indicator sites, 11 urban indicator sites, and 14 integrator sites. In most of the agricultural basins, cropland and

orchard-vineyard land account for more than 40 percent of the basin area and urban land accounts for less than 5 percent. Water quality conditions at urban indicator sites are affected primarily by urban, suburban, commercial, and industrial sources. The number of samples are 1606, 650, and 605, respectively, for the 40 agricultural sites, 11 urban indicator sites, and 14 integrator sites.

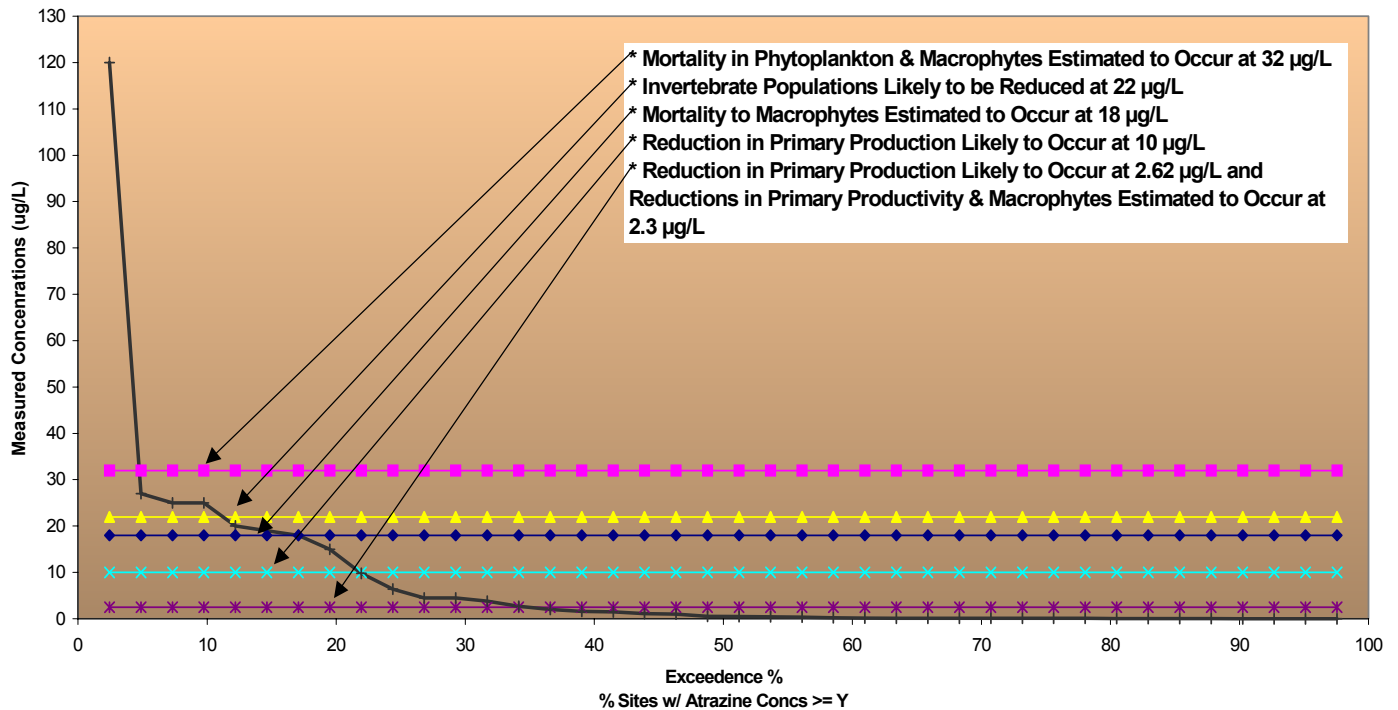
The following 3 figures indicate the distribution of atrazine concentrations found in samples at these 65 sites.

The summaries of concentrations at different percentiles are shown in the following table:

NAWQA DATA Indicator Site (number)	maximum ($\mu\text{g/L}$)	99 th percentile	95 th percentile	90 th percentile	50 th percentile
agriculture (40)	120.0	13.0	3.25	1.2	0.027
urban (11)	14.0	2.75	0.65	0.33	0.041
integrator (14)	27.0	12.5	5.35	1.95	0.062

Since most of the atrazine use is associated with agriculture, the Agency focused further analysis on the agricultural sites. The maximum atrazine concentrations were determined for each of the 40 agricultural sites and cumulative exceedence plots based on these maximum site concentrations were graphed and are presented in Figure 11. The horizontal lines represent the key assessment endpoints for streams as listed in Table 2.

Figure 11. National Water Quality Assessment Program (NAWQA): Maximum Atrazine Concentrations for 40 Agricultural Sites



Risk of Atrazine to Aquatic Organisms and Communities in Streams Based on NAWQA Agricultural Sites

It is important to note that the NAWQA monitoring data were not specifically designed to time monitoring to correspond to atrazine applications or specifically oriented to atrazine treatment areas. Thus, they are likely to underestimate the concentrations likely to be present in streams. The magnitude of this underestimate is unknown.

Assuming that the NAWQA monitoring data for the 40 agricultural sites are generally representative, Figure 11 shows that from 11% to 35% (4 to 14) of the 40 sites exceed atrazine concentrations at which reductions in invertebrate populations and primary production occur. These estimates are based on the maximum atrazine concentrations for these 40 agricultural sites.

A summary table of population percentiles for the various stream surveys is given below: In general the table shows that on average atrazine concentration in streams is probably low, less than 6 $\mu\text{g/L}$. As noted in Table 2 and in Figures 6 through 11, reductions in primary productivity and macrophytes are possible at atrazine concentrations above 2.5 $\mu\text{g/L}$. Of greater concern, however, are the 95th and 90th percentile atrazine concentrations for post-applications in 1994 and 1995 as found in the shaded areas of the table below. These concentrations range from approximately 20 to 45 $\mu\text{g/L}$. Since these are the 95th and 90th percentile concentrations, we conclude that reductions in invertebrate populations and primary productivity are likely to occur 5 to 10 % of the time in streams located in agricultural areas where atrazine is used.

USGS (FR93-457) (sample number)	max val ($\mu\text{g/L}$)	99th percentile	95th percentile	90th percentile	50th percentile
Pre-Appl. 1989 (52)	1.7	---	0.9415	0.666	0.235
Post-Appl. 1989 (129)	108	97.2	43.5	27	4.7
1989 Fall (143)	3.1	2.66	1.28	0.796	0.25
Pre-Appl. 1990 (52)	3.8	---	1.475	0.866	0.24
Post-Appl. 1990 (50)	33	---	29.25	25.4	8.1
All Samples (426)	108	50.92	22.65	15	0.465
USGS (F.R.94-396) (sample number)					
All Samples (215)	92	40.84	17	14	2.7
USGS (F.R.93-657) (sample number)					
All Samples (542)	11	8.257	4.685	2.87	0.36
USGS (F.R.98-181) (sample number)					
Pre-Appl. 1994 (53)	2.3	---	0.355	0.276	0.14
Post-Appl. 1994 (51)	38	---	25.4	20.8	4.2
Post-Appl. 1995 (50)	50	---	45.9	35.2	5.55
All Samples (154)	50	48.35	27.25	18.5	1.35

Risk of Atrazine to Aquatic Organisms and Communities for Streams in General

Herbicides may exert an important impact on stream ecosystem productivity and structure. A number of studies have been conducted on the effects of atrazine applications on phytoplankton and a few tests have addressed the more subtle productivity and/or community-level effects. Lakshminarayana *et al.* (1992) monitored atrazine effects on phytoplankton numbers from 9 June to 16 November 1989 at various points on a natural, first-order stream adjacent to a tiled corn field treated with 4 liters per hectare at concentrations of up to 1.89 $\mu\text{g/L}$ in the stream (no replication for statistical analyses). Artificial streams have been used to assess community level effects of atrazine by several authors. Gruessner and Watzin (1996) monitored effects of atrazine concentrations ($\leq 5 \mu\text{g/L}$) typically found in a Vermont stream and found no significant reduction in chlorophyll a levels of attached algae throughout a 14-day exposure, but found a significant increase in the total number of early, aquatic insect emigrants at $\leq 5 \mu\text{g/L}$. Lynch *et al.* (1985) also reported a significant increase in insect emergence from streams treated at 25 $\mu\text{g/L}$, while no significant or lasting effects were found on the structure of macroinvertebrate populations, periphyton standing biomass or rates of primary production and community respiration. However, the use DMSO as the carrier solvent which accelerates the movement of chemicals across cell membranes, may have affected the results. Carder and Hoagland (1998) found significant ($p \leq 0.05$) reductions in benthic mud algae (ranging from 35 to 58% compared to controls) throughout a 4-week, recirculation study at both 15 and 155 $\mu\text{g/L}$. The lack of atrazine effects at 155 $\mu\text{g/L}$ on any of the six dominant algal species appeared to be because of their ability to tolerate atrazine commonly encountered in agricultural streams such as Wahoo Creek where they were collected. Krieger *et al.* (1988) reported significant ($p < 0.001$) reductions in stream *Aufwuchs* communities exposed to atrazine for 20 days as measured by ash-free dry weight (range 24 to 31% compared to controls) and chlorophyll a levels (30 to 44%) at 24 and 134 $\mu\text{g/L}$ at 25°C and at 10°C. Only the 134 $\mu\text{g/L}$ level reduced ash-free dry weight (47%) and in chlorophyll a levels (40%). At 100 $\mu\text{g/L}$ atrazine (the lowest test concentration), Kosinski and Merle (1984) and Moorehead and Kosinski (1986) reported significantly ($p < 0.5$) inhibited phytoplankton net community productivity, measured as dissolved oxygen for at least 3 days. Kosinski and Merkle (1984) used artificial outdoor streams in Texas stocked with algal communities derived from a spring and an agriculturally impacted stream to assess the impact of atrazine as well as other herbicides on the productivity (photosynthesis and respiration) of stream algae. While treatments with atrazine at 1 and 10 mg/L caused severe inhibition of photosynthesis, even chronic treatments at 10 $\mu\text{g/L}$ caused small but detectable inhibition of photosynthesis. While most of the stream studies were on the effects on phytoplankton, the benthic algae account for the bulk of photosynthesis in all but the largest streams (Wetzel, 1975).

Atrazine in Estuaries - Louisiana

Since 1992 the Louisiana Department of Agriculture and Forestry (LDAF) has collected data on atrazine and other pesticides in surface and ground water. LDAF and the Louisiana Department of Environmental Quality have been collecting surface water data on atrazine in the Upper Terrebonne watershed basin which lies just west of the Mississippi River at Baton Rouge and

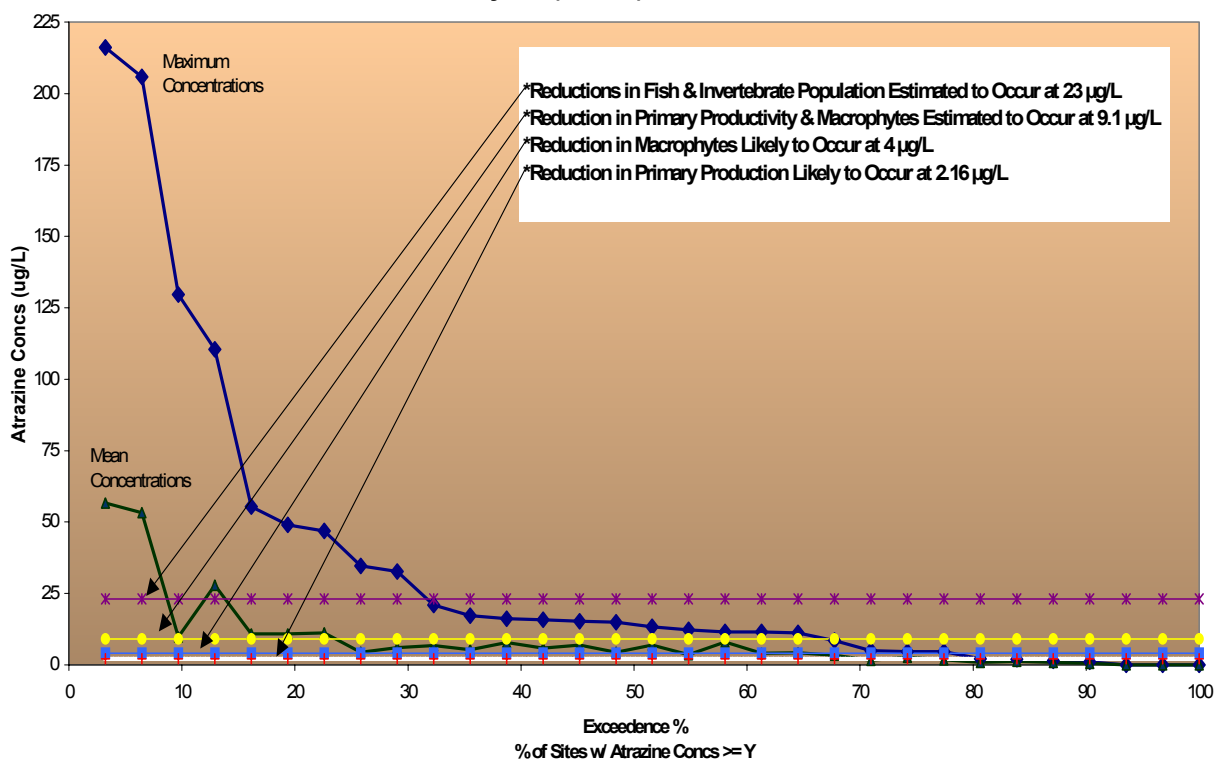
east of the Atchafalaya River Basin. The basin covers an area extending approximately 120 miles from the Mississippi River on the north to the Gulf of Mexico to the south, and varies in width from 18 to 70 miles. It is primarily lowland and is subject to flooding except the natural levees along major waterways. The coastal portion of the basin is prone to tidal flooding and consists of marshes ranging from fresh to saline. Much of the recent Upper Terrebonne data are available on the state internet site at <http://www.deq.state.la.us/surveillance/atrazine/index.htm>. Data from 1998 are summarized below plotted in Figure 12 as a cumulative exceedence curve with the maximum and mean concentrations by site (28 sites) against the percentage of sites with equal or greater concentrations. The horizontal lines represent the key assessment endpoints for estuarine/marine areas as listed in Table 3.

% prob.	peak	95%	90%	75%	50%
Conc. Max (ppb)	216.2	210.0	125.8	34.7	13.3
Conc. Mean (ppb)	56.7	54.7	24.5	8.0	4.5

Thirty-one stations were sampled either weekly or in conjunction with atrazine “events,” i.e., pre-emergent, post emergent, lay-by, or fall applications in areas near bayous, canals and ditches in the Terrebonne watershed. The majority of stations were located downstream on streams that receive runoff from predominantly sugar cane and corn production areas. The data show peak levels over 200 $\mu\text{g/L}$ for more than one station, and over 100 $\mu\text{g/L}$ for at least two more.

Risk of Atrazine to Estuarine Organisms and Communities in Louisiana

Figure 12. Louisiana Max & Mean Atrazine Concentrations
By Site (28 Sites) in 1998



Based on maximum atrazine concentrations, Figure 12 shows that from 70 to 80 % (20 to 22) of the sites exceed concentrations at which reductions in primary productivity and macrophytes occur. This only falls to 61 to 75% (17 to 21) for the mean concentrations. Approximately 30% (8) of the sites based on the maximum atrazine concentrations, and 7% (2) for the mean concentrations exceed concentrations at which reductions in fish and invertebrate populations occur, based on laboratory testing. Although mean levels per station are lower, most are still in a range that could have adverse impact on aquatic life.

Weekly sampling shows many levels declining substantially from peak within a week's time, but often rising to nearly previous levels the following week. As indicated earlier, the Terrebonne sampling peak levels correspond very closely to peak concentrations predicted by PRZM/EXAMS for ponds in areas of sugar cane production (See Figure 3).

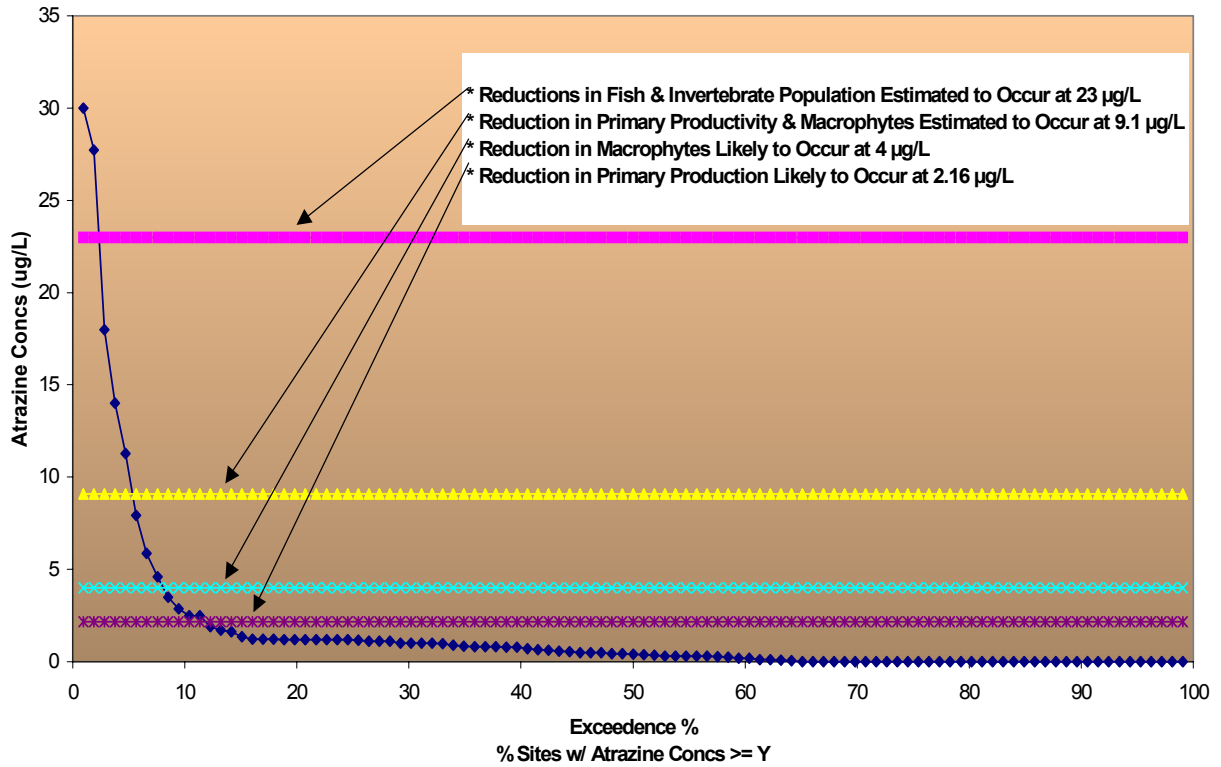
Atrazine in the Chesapeake Estuary

One hundred and six maximum atrazine concentrations from 40 sites in the Chesapeake Bay and its tributaries taken over a period from 1977 through 1993 are plotted in Figure 13. These data

come from “Data Base of the Occurrence and Distribution of Pesticides in Chesapeake Bay” (<http://www.agnic.nal.usda.gov/cbp/pest/atrazine.html>). The summary table below indicates that the maximum atrazine level found was 30 $\mu\text{g/L}$, while the 95th, 90th, and 75th percentile values ranged from 10 to 1.2 $\mu\text{g/L}$. The data are plotted in Figure 13 as a cumulative exceedence curve with the maximum concentrations by site and year against the percentage of sites and years with equal or greater concentrations. The horizontal lines represent the key assessment endpoints for estuarine/marine areas as listed in Table 3.

Chesapeake Bay (105 sites)	max conc ($\mu\text{g/L}$)	95th percentile	90th percentile	75th percentile	50th percentile
	30.0	10.3	2.7	1.2	0.4

Figure 13. Surface Water Monitoring Results for Atrazine in the Chesapeake Bay's Tidal Rivers Maximum Concentrations by Site and Year (1977 - 1993)



Risk of Atrazine to Estuarine Organisms and Communities in the Chesapeake Bay

The maximum atrazine concentrations in the Chesapeake Bay are shown in Figure 13 to exceed concentrations that are likely to reduce macrophytes and primary productivity for 8 to 12 % (8 to 13) of the site and year combinations, respectively. Atrazine could be contributing to reductions in submerged aquatic vegetation and primary productivity at certain sites in the Bay. Additional analyses of the available data are necessary. Specifically, attempts should be made to establish co-occurrence of sites with atrazine concentrations above approximately 4 µg/L with sites in the bay which are still unable to achieve their submerged aquatic vegetation (SAV) goal.

There are insufficient data to determine definitively that atrazine is a significant contributor to the decline in aquatic vegetation in Chesapeake Bay and other estuaries. It is possible, however, that atrazine and other herbicides used in these watersheds are a source of stress to aquatic vegetation. Another important stressor is eroding sediment from development in the watershed

and this, combined with herbicide residues, could negatively affect estuarine ecosystems.

Atrazine has been detected in ground and/or surface waters of the Chesapeake Bay watershed (Stevenson *et al.*, 1978, Wu, 1980; Kemp *et al.*, 1982; Glotfelty *et al.*, 1984; Hall and Anderson, 1991). Herbicides, including atrazine, represent a potential source of stress for estuarine vegetation and have been suggested as a possible cause for the decline of submerged aquatic vegetation in Chesapeake Bay (Correll *et al.* 1978).

Numerous species of submerged vascular plants were important in this estuarine ecosystem until about the mid-1970's when their abundance declined (Bayley *et al.*, 1978; Stevenson and Confer, 1978; Orth and Moore, 1983, 1984; Orth *et al.*, 1991). Prior to the decline of the submerged aquatic vegetation (SAV) in the Chesapeake in the 1970's, these plants were responsible for 40% of the relative primary production in the Chesapeake. After the decline, SAV produced less than 10 % of the primary production (Anderson, 1981). According to surveys by the U.S. Fish and Wildlife Service, 28% of their Chesapeake Bay stations were vegetated in 1971 compared to about 10% of the stations in 1978. Although SAV reductions could be identified in several distinct areas of the Chesapeake, the overall decline appears to have been random (Cohen, 1985).

Atrazine concentrations as low as 4 to 10 $\mu\text{g/L}$ have been shown to reduce plant growth and productivity in 5 SAV species after exposures of 5 or more weeks (Forney and Davis, 1981; Jones and Winchell, 1984; Cohen, 1985; Jones *et al.*, 1986). Atrazine levels of 50 to 150 $\mu\text{g/L}$ inhibit photosynthesis by 50% for various SAV species (Forney & Davis, 1981; Correll and Wu, 1982; Jones *et al.*, 1982; Kemp *et al.*, 1982; Cunningham *et al.*, 1984; Delistraty and Hershner, 1984; Jones and Estes, 1984; Jones and Winchell, 1984; Jones *et al.*, 1986). One to two-hour atrazine exposures resulted in the 50% reductions in photosynthesis in some of the above studies. Jones *et al.* (1986) showed that the uptake of atrazine by vascular aquatic plants occurred within 15 minutes. Plants appeared to recover after 2-hour washing with atrazine-free water, although some indications of depression of photosynthesis remained at the end of the 77-hour recovery period.

Jones and Estes (1984) studied different routes of atrazine toxicity based on measurements of the photosynthetic response of pondweed, *Potamogeton perfoliatus*. Leaves were exposed to atrazine in water (0 and 100 $\mu\text{g/L}$) and to atrazine sorbed soil (0 and 120 $\mu\text{g/kg}$). The effect of shading from untreated soil was also investigated. The results showed that soil sorbed-atrazine was relatively unavailable for uptake by *P. perfoliatus* and the reduction in photosynthesis due to settled soil on the leaves was 27 percent, while the reduction attributable to atrazine was 8%. When atrazine was present in the water alone, in water plus soil without atrazine-sorbed soil, and then in water along with atrazine-sorbed soil, the percent reduction in photosynthesis attributable to atrazine was reported as 69%, 55%, and 52%, respectively. The total reduction in photosynthesis was 69%, 83% and 79% to 83%). These results show that the major source of plant toxicity is from water exposure.

Atrazine concentrations in the upper reaches of shallow estuarine creeks adjacent to atrazine-treated corn are expected to yield the highest atrazine concentrations in the Chesapeake Bay.

Atrazine levels in the upper parts of tidal creeks may persist for days as the atrazine-laden water moves back and forth in the creek with daily tidal flow. In areas like these creeks, Kemp *et al.* (1982) found concentrations as high as 100 $\mu\text{g/L}$ in shallow water close to agricultural fields, which are at least 3 times the highest level cited in the above monitoring data.

Toxicity of Degradates Compared to Parent Atrazine and the Potential Impact on Risk

Listed in the table below are the available toxicity values used for a comparison of atrazine and its four primary degradates.

Toxicity Comparison of Atrazine with its Degradates					
Test Type	Atrazine	Hydroxyatrazine	Deethylatrazine	Deisopropylatrazine	Diaminochloroatrazine
Mammalian Acute Oral LD ₅₀ (mg/kg)	97 % ai	97.1 % ai	95.7% ai	96.7 % ai	98.2 % ai
Female	1,190 ⁴	--	668 (1.78) ⁵	810 (1.47)	--
Male	1,317 ²		1,891 (0.70)	2,290 (0.58)	
Combined Oral LD ₅₀ Male & Female	1,869 ⁶	--	1,111 (1.7)	1,240 (1.5)	--
Mammalian Gestation (Days 6-15) ppm	200 / 1,400 ⁷	500 / 2,500 (0.4)	25 / 100 (10)	5 / 25 (40)	50 / 500 (4.0)
Carcinogenicity 2-Year	10 / 70	10 / 25			
Carcinogenicity 2-Year	70 / 400	25 / 200			
Algae (Cell counts) 12-14-day EC ₅₀ :					
Anabaena inaequalis	30	> 10,000 (< 0.003)	1,000 (0.03)	2,500 (0.012)	7,000 (0.004)
Scenedesmus quadricauda	100	> 10,000 (< 0.01)	1,200 (0.08)	6,900 (0.01)	4,600 (0.02)
Chlorella pyrenoidosa	300	> 10,000 (< 0.03)	3,200 (0.09)	> 10,000 (< 0.03)	> 10,000 (< 0.03)
Anabaena variabilis	4,000	> 10,000 (< 0.4)	3,500 (1.1)	5,000 (0.8)	> 10,000 (< 0.4)
Anabaena cylindrica	1,200	> 10,000 (< 0.12)	8,500 (0.14)	> 10,000 (< 0.12)	> 10,000 (< 0.12)

⁴ Atrazine purity 85.5 %ai

⁵ Atrazine/degrade toxicity ratio

⁶ Most toxic atrazine technical value

⁷ NOAEC / LOAEC values, NOAEC values were used to estimate toxicity ratios

The major atrazine degradates are generally long-lived and appear to be about toxicologically equivalent to atrazine for mammals, but much less toxic to algae than atrazine. Toxicity data for these degradates are unavailable for birds, fish, aquatic invertebrates, and terrestrial plants.

The dealkylatrazine degradates are more acutely toxic to female rats and more chronically toxic to gestating rat pups than the parent atrazine (ratios greater than 1). The acute comparison was made using an atrazine 85.5% WP formulation, the most toxic atrazine form with both male and female toxicity values. Toxicity data for male and female acute toxicity values were not available for technical grade atrazine data. Combined male and female acute toxicity values for dealkylatrazine degradates were similar to the most acutely toxic technical grade atrazine value (i.e., ratios 1.1 and 1.01). The dealkylatrazine degradates were also more toxic to rat pups during gestation than the parent atrazine. However, the dealkylatrazine degradates were generally less toxic (ratios less than 1) to algae than atrazine. Toxicity data are unavailable for birds, fish, aquatic invertebrates and terrestrial plants for comparison. Based on the available degradate toxicity data, all of the atrazine degradates appear to be more acutely and chronically toxic to mammals than the parent atrazine. Hence, the chronic risks to mammals would persist longer than risks from the parent atrazine.

Incidents

The Ecological Incident Information System (EIIS) maintained by EFED has a total of 109 reported incidents for atrazine from 1991 through 1999. Thirteen incidents are classified as “Unlikely”, 50 are listed as “possible” and two are “Unrelated;” with one exception, they are not discussed further. In only one case, a 1996 cotton use in Louisiana, were fish carcasses analyzed for atrazine residues. Shad and carp tested positive for atrazine, but the conclusion was that atrazine was unlikely the cause of mortalities (I004021-004).

Forty incidents are considered “Probable,” and four incidents are listed as “Highly Probable.” The 4 incidents listed as “Highly Probable” include 3 home/lawn use incidents and 1 corn use incident. In the corn use incident report, 100 bass and 100 bream (# B000163-001) were reported to be affected from a registered use of atrazine. The three home/lawn incidents were lawn applications which affected grass; two were concluded to be misuse/accidental (# I005579-001, I005132-001). The third home incident (# I001910) was a registered EC use which affected grass and non-target plants.

The forty “Probable” incidents include: 16 (40 %) cases affecting corn; 11 (27.5 %) affecting grass; 11 (27.5 %) fish kills; 1 bird kill case ; and affects on ornamentals (2 cases), fruit trees (2 cases), berries (1), garden (1), oats (1), runoff killed vegetation around an atrazine/cyanazine-treated field and pond irrigation water killed greenhouse plants. Four “probable” incidents are classified as misuse (accidents): two cases from corn use (I005879-003, pears, raspberry and oats and I007371-013, grass and ornamentals); and two lawn misuse cases: I009445-031, grass; and

I009445-029, bluegrass.

Analysis of 14 corn incidents occurring in 1999 which were submitted by Novartis indicates that in all cases, formulations of Bicep II (a mixture of atrazine and metolachlor) were used. The reported applications rates ranged from 1.4 quarts of atrazine /1.4 quarts of metolachlor to 2.6/2.6 quarts/A. Effects included distorted and cupping leaves, failure to unfurl, uneven height, chlorotic yellowing and necrotic leaves, and killed. Corn acreage affected ranged from 55 to 55 percent of 600 acres.

There were 11 grass incidents resulting from home/lawn uses; three of these cases are considered misuse (accidental).

Given the low toxicity of atrazine to fish, the reason for the frequency of fish kill incidents is uncertain. About 60 percent of the reported fish kills listed under atrazine in the incident record occur during the Spring when atrazine is applied, soils are saturated and heavy rainfall is frequent. Heavy runoff may carry atrazine, other pesticides and organic loads into surface waters. The high volume and wide-spread use of atrazine increases the probability of co-occurrence of fish kills with atrazine applications. There are some other scenarios which may explain atrazine induced fish kills as well as causes unrelated to atrazine use.

Three plausible scenarios could exist in which atrazine applications may be responsible for the fish kills. First, atrazine concentrations in surface waters from runoff and/or spray drift may be much higher in shallow water adjacent to treated fields than estimated by EFED or found in monitoring studies. Second, atrazine in surface water may kill aquatic plants and the decaying process of dead plants may lower dissolved oxygen to levels too low for fish survival. Third, atrazine is known to increase the toxicity of organophosphate insecticides, such as chlorpyrifos, and a number of other pesticides which may have been applied earlier to atrazine-treated crops or applied in other fields upstream in the watershed.

Possibilities also exist that other causes, not atrazine, may be responsible for some or all of the reported atrazine incidents. Heavy organic loads consume oxygen from the water as the organic matter oxidizes, thereby causing low dissolved oxygen levels which may cause fish to suffocate and die. Other pesticides in the watershed may have killed the fish as the water flowed past atrazine-treated fields. Since limited information is available in the atrazine incident records, such as water and tissue analyses, conclusions of responsibility would appear to be uncertain and the result of coincidence with little evidence for cause and effect.

Certainty / Uncertainty

This refined assessment, while providing a greater certainty of adverse effects on aquatic life than that based on modeled exposure and typical laboratory toxicity values, also contains inherent uncertainties. Two important sources of uncertainty can be attributed to the monitoring data and the laboratory (including laboratory data on the major degradates) and field study data themselves. The monitoring data were not collected for the purpose of supporting an ecological

risk assessment. Thus, the spatial and temporal distributions of the monitoring data do not match those for the laboratory toxicity studies or the field studies. Another important uncertainty with regard to using monitoring data for the atrazine ecological risk assessment is that there are little or no monitoring data for some areas that might be most vulnerable. These include prairie potholes, first-order streams, wetlands, ponds, and playa lakes near high-use areas where community-level impacts could be locally significant.

Much of the monitoring data used to assess risks to aquatic organisms in streams and rivers and the Chesapeake Bay can not be interpreted to be the worst case scenario. The data are generally from random sampling sites in a watershed. There is no indication that the samples were collected from areas near atrazine-treated fields or that the samples were collected during the periods of application and the first heavy runoff after application. Also most of the sampling was not on a frequent enough basis to determine the peak numbers nor the duration of atrazine exposures in flowing water. Rather, these monitoring data present a random snapshot of what atrazine levels are present in a number of watersheds.

The laboratory and field study data for the most part are taken from published literature. The EPA scientists did not have access to the raw data necessary to evaluate some of these studies as is typically done for data submitted by registrants to support registration. Also, while a majority of the laboratory and field toxicity data indicated similar effects at similar exposure levels, there were some studies that showed no effects at similar exposure levels. In addition, while the laboratory toxicity data indicate adverse effects to certain species of organisms, we cannot determine with certainty that impacts on these or similar species would result in a loss of ecological function or important changes in community structure in natural systems. However, both community function and structure are important considerations which are addressed to a certain extent by the simulated and actual field studies. In addition, only limited ecotoxicological data is available for the major atrazine degradates. These degradates are generally long-lived and appear to be about toxicologically equivalent to atrazine for mammals, but much less toxic to algae than atrazine. However, toxicity data for these degradates are unavailable for birds, fish, aquatic invertebrates, and terrestrial plants.

Atrazine is a triazine herbicide which inhibits photosynthesis in sensitive plants. Photosynthetic depression inhibits the formation and release of oxygen, and oxygen production is a reflection of a plant's ability to produce food to meet its energy needs. Detrimental effects on plants are rapid and appear to increase as both the atrazine concentration and the duration of exposure increases. Prolonged exposure results in starvation and ultimately the death of plants. Rapid recovery of oxygen evolution (within hours) is observed in aquatic plants if atrazine exposure is removed. Plant recovery and resistance are two complicating issues which add uncertainty to any risk assessment on atrazine, and there is insufficient information to do more than report that both occur. In the aquatic environment, recovery from the detrimental effects of atrazine exposure could serve to mitigate risk to plants, while the replacement of sensitive species of plants by resistant ones raises ecological questions relating to structural and functional changes in communities and ecosystems that are not easily answered without further research.

In spite of the uncertainties listed above, the robust body of surface water monitoring data, combined with extensive effects data for aquatic organisms, enabled EFED to provide quantitative conclusions on the frequency and extent of adverse effects of atrazine in a refined aquatic risk assessment. The extensive databases as well as the refined assessment increase the certainty of the conclusions beyond preliminary risk assessments that are typical for all other herbicides.

VII. Environmental Fate Assessment

Atrazine is expected to be mobile and persistent in the environment. The main route of dissipation is microbial degradation under aerobic conditions. Because of its persistence and mobility, atrazine is expected to get into surface and ground water. This is confirmed by the widespread detections of atrazine in surface water and ground water.

Atrazine can contaminate nearby non-target plants, soil and surface water via spray drift during application. Atrazine is applied directly to target plants during foliar application, but pre-plant and pre-emergent applications are generally far more prevalent.

The resistance of atrazine to abiotic hydrolysis (stable at pHs 5, 7, and 9) and to direct aqueous photolysis (stable under sunlight at pH 7), and its only moderate susceptibility to degradation in soil (aerobic laboratory half-lives of 3-4 months) indicate that atrazine is unlikely to undergo rapid degradation on foliage. Likewise, a relatively low Henry's Law constant (2.6×10^{-9} atm·m³/mol) indicates that atrazine will probably not undergo rapid volatilization from foliage. However, its relatively low octanol/water partition coefficient ($\text{Log } K_{ow} = 2.7$), and its relatively low soil/water partitioning (Freundlich K_{ads} values < 3 and often < 1) may somewhat offset the low Henry's Law constant value thereby possibly resulting in some volatilization from foliage. In addition, its relatively low adsorption characteristics indicate that atrazine may undergo substantial washoff from foliage. It should also be noted that foliar dissipation rates for numerous pesticides have generally been somewhat greater than otherwise indicated by their physical chemical and other fate properties. In terrestrial field dissipation studies performed in Georgia, California, and Minnesota, atrazine dissipated with half lives of 13, 58, and 261 days, respectively. The inconsistency in these reported half-lives could be attributed to the temperature variation between the studies in which atrazine was seen to be more persistent in colder climate. Long term field dissipation studies also indicated that atrazine could persist over a year in such climatic conditions. A forestry field dissipation study in Oregon (aerial application of 4 lb ai/A) estimated an 87 day half-life for atrazine on exposed soil, a 13 day half-life in foliage, and a 66 day half-life on leaf litter.

Atrazine is applied directly to soil during pre-planting and/or pre-emergence applications. Atrazine is transported indirectly to soil due to incomplete interception during foliar application, and due to washoff subsequent to foliar application. The available laboratory and field data are reported above. For aquatic environments reported half-lives were much longer. In an anaerobic aquatic study, atrazine overall, water, and sediment half-lives were given as 608, 578,

and 330 days, respectively.

Deethyl-atrazine (DEA; G-30033) and deisopropyl-atrazine (DIA; G-28279) were detected in all studies (Appendix II), and hydroxy-atrazine (HA; G-34048) and diaminochloro-atrazine (DACT; G-28273) were detected in all but one of the listed studies. Deethylhydroxy-atrazine (DEHA; GS-17794) and deisopropylhydroxy-atrazine (DIHA; GS-17792) were also detected in one of the aerobic studies. All of the chloro-triazine and hydroxy-triazine degradates detected in the laboratory metabolism studies were present at much less than the 10% of applied that the EFED uses to classify degradates as “major degradates”.

For studies limited to several months, the relative concentrations of the degradates in soil were generally DEA>DIA>DACT~HA. However, for an aerobic soil metabolism study and an anaerobic aquatic metabolism study both lasting a year, the concentration of HA was comparable to that of DEA over the last few months of the studies. In addition, some literature indicates that higher quantities of HA can be formed in soil and in sediment under acidic conditions. Other hydroxy-triazine degradates have only rarely been detected in lab studies.

The structures of atrazine, DEA, DIA, DACT, HA, DEHA, DIHA, and diaminohydroxy-atrazine (DAHA) are provided in Appendix I. Note that DIA and DACT are also degradates of simazine. In addition, DACT is also a degradate of cyanazine.

The soil/water partitioning of atrazine, DEA, DIA, and DACT are relatively low as shown by Freundlich adsorption coefficients of < 3 and often < 1 for 4 different soils. The Freundlich adsorption constants for HA are substantially greater, being approximately 2 for sand, but 6.5, 12.1, and 390 for a sandy loam, loam, and clay soil, respectively. No adsorption/desorption data are available for other hydroxy-triazine degradates. However, the higher soil/water partitioning exhibited by HA compared to atrazine suggests that the other hydroxy-triazines are likely to exhibit higher soil/water partitioning than corresponding chloro-triazine degradates.

In a limited study on atrazine and its chloro-degradates in surface water source CWSs, the detection of all was relatively widespread. However, atrazine predominated with the relative order of concentrations generally being atrazine >>DEA>DIA~DACT.

In the Novartis Rural Well Survey (Tierney, et al., 1999), which also included four hydroxy-triazine degradates as analytes, the four hydroxy-triazine degradates were all detected. Of the hydroxy-triazine degradates, hydroxy-atrazine was detected the most frequently and generally at the highest level, but not to the same extent as atrazine or the chloro-triazine degradates. The percentages of detection above a LOD of 0.1 $\mu\text{g/L}$ in the Rural Well Survey for atrazine, DEA, DIA, DACT, HA, DEHA, DIHA, and DAHA were 26.8%, 32.0%, 16.7%, 25.9%, 6.11%, 2.99%, 0.27%, and 0.33%, respectively. Unlike in the surface water study on degradates where atrazine concentrations were generally much greater than chloro-triazine degradate concentrations, the DEA, and DACT chloro-triazine degradate concentrations in the Rural Well Survey were often comparable to those of atrazine. The relative order of concentrations in the Rural Well Survey was generally atrazine~DEA~DACT>DIA>HA .

The relatively widespread detection of atrazine and various chloro-triazine degradates in the surface water study on degradates and in the Rural Well Survey is consistent with the widespread use of atrazine, the persistence of atrazine and the mobility of atrazine and its chloro-triazine degradates. The lower frequency of detection and generally lower levels of the HA in the Rural Well Survey is consistent with its higher soil/water partitioning than atrazine and the chloro-triazine degradates.

The available fate and ground water data indicate that hydroxy-triazine degradates other than possibly HA are unlikely to significantly contaminate surface water. They are not appreciably formed in soil, and they are likely to exhibit higher soil/water partitioning than corresponding chloro-triazine degradates. In addition, they were detected much less frequently and at much lower levels than hydroxy-atrazine in the Rural Well Survey.

The substantially higher soil/water partitioning and generally slower rate of formation in soil exhibited by HA compared to atrazine and some of the chloro-triazine degradates indicate that it is likely to have a lower potential for surface water contamination. However, HA was detected in 6.1% of the samples in the Rural Well Survey at concentrations up to 6.5 $\mu\text{g/L}$. Also, there have been reported concentrations of HA in soil sometimes approaching and possibly in some cases (e.g., acidic soils) exceeding that of DEA. Therefore, occasional significant contamination of surface water by HA cannot be ruled out by the EFED without at least some screening data.

Atrazine should be somewhat persistent in ground water and in surface waters with relatively long hydrologic residence times (such as in some reservoirs) where advective transport is limited. The reasons for this are the resistance of atrazine to abiotic hydrolysis and to direct aqueous photolysis, its only moderate susceptibility to biodegradation, and its limited volatilization potential as indicated by a relatively low Henry's Law constant. As will be discussed later, 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 greatly limits its persistence.

The relatively low soil/water partitioning of atrazine and chloro-triazine degradates indicates that their concentrations in/on suspended and bottom sediment in equilibrium with the water column will be somewhat comparable. However, despite relatively low soil/water partitioning, limited data indicated that activated carbon can be effective in reducing atrazine and its triazine degradate concentrations by several fold to over an order of magnitude depending upon the frequency and conditions of its use.

Atrazine has been widely detected in rainfall. A USGS study (reference 16) showed that the highest concentrations of atrazine occur in the high use, midwestern corn belt during the application season (mid-April through mid- July). Volume-weighted concentrations ranging from 0.2 to 0.9 $\mu\text{g/L}^{-1}$ were reported in the late spring and summer of 1990 and 1991. In addition, the chloro-degradates DEA and DIA were also detected in rainfall together with atrazine. Moreover, high ratios of DEA to atrazine (approximately 0.5) were attributed to atmospheric degradation. Mass deposition of atrazine and degradates have been found to be higher in the

midwestern corn belt, but to decrease with distance away from the corn belt. The USGS study estimated that approximately 0.6% of applied atrazine was annually deposited in rainfall over the study area.

VIII. Drinking Water Assessment

A separate document titled *Drinking Water Exposure Assessment for Atrazine and Various Chloro-triazine and Hydroxy-triazine Degradates* is attached as a separate document. The following is the Executive Summary taken from the drinking water assessment.

Executive Summary

The Office of Pesticide Programs' Environmental Fate and Effects Division (EFED) has analyzed the data from four major surveys of surface and ground water to assess the contribution of atrazine and its major chloro- and hydroxy- degradates to drinking water. This drinking water exposure assessment was used by OPP's Health Effects Division (HED) in its dietary risk assessment for atrazine.

Results from the largest database indicated an overall level of approximately 10% detection of atrazine residues in samples and community water systems (CWSs) in states with major atrazine use. The occurrence of atrazine in surface water sourced CWSs appeared to be much more common than in ground water sourced CWSs (37.2% compared with 3.5%). In a survey of targeted rural wells, however, the occurrence was much higher, close to 24% detection for atrazine and 34% for atrazine or its chloro- degradates. This is probably due to the relative depths of the wells on average, and their proximity to fields to which atrazine was applied.

Data from these surveys do not indicate short-term exposure exceedences for atrazine and its degradates when compared to EPA Health Advisory Levels (HALs) or Drinking Water Levels of Comparison (DWLOCs) provided by HED for acute effects. A number of systems were identified, however, where sustained levels of total chloro-triazines were at or above HED's levels of concern for chronic and subchronic effects. Some data were presented on the effectiveness of water treatment for atrazine, and it was shown that a number of systems were able to reduce their average levels with activated carbon.

Sources of Data Analyzed

The exposure assessment of atrazine in Community Water Supplies (CWSs) was based primarily on an analysis of the Novartis Population Linked Exposure (PLEX) database (Section 4 of the Drinking Water Report). The database included atrazine concentrations in thousands of CWSs in 21 major atrazine use states over the 1993-1998 period, and also included the populations served by the CWSs. The CWSs with data in the PLEX database included those with ground water, surface water, and combination (blend) of ground and surface water sources. The data were collected quarterly by CWSs to comply with the monitoring requirements of the Safe

Drinking Water Act (SDWA).

The exposure assessment of atrazine and its chloro- and hydroxy-triazine degradates in non-CWS rural well ground water was based upon an analysis of results from the Novartis/States Rural Well Survey (Section 5) and data on atrazine concentrations in 177 wells from the Acetochlor Registration Partnership (ARP) Monitoring Study (reference 10; see Section 8).

In addition, data on atrazine concentrations in surface water sourced CWSs from the Novartis Voluntary Monitoring Study (VMS) and the ARP Surface Water Monitoring Study were statistically analyzed (See Sections 6 and 7, respectively). Those studies on surface water sourced CWSs included fewer than 100 CWSs and 175 CWSs, respectively, compared with the thousands of CWSs included in the PLEX database. However, because samples were taken more frequently than for the PLEX database, the VMS and ARP studies provided far more time series data per CWS than the Novartis PLEX database which has just one data point per quarter per CWS.

Additional data on atrazine concentrations in OH CWSs (reference 13), in IL CWSs (reference 14), in TX CWSs (reference 15), and in CWSs in several states (reference 16) were also briefly discussed (see Section 9).

Estimating Concentrations of Chloro-triazine Degradates

Limited data on the concentrations of chloro-triazine degradates in surface water sourced CWSs (reference 11) were used to develop regression equations relating the sum of chloro-triazine degradate (DEA, DIA, and DACT) concentrations to atrazine concentrations (see Section 3.1). The regression equations were applied to other PLEX, VMS, and ARP data on atrazine concentrations in surface water sourced CWSs to estimate the sum of atrazine and its major chloro-triazine degradate concentrations (see Section 3.1).

General Results

Because the chloro-triazine degradates are judged to be of toxicological concern, results were presented for both parent atrazine and for total chloro-triazines (TCT) in ground or surface water sourced finished drinking water. General findings were as follows:

Of the 21,241 CWSs in 21 states with atrazine data in the CWS PLEX database through 1998, 2,386 CWSs (11.2%) had one or more atrazine detections above limits of quantification (LOQs). Of a total of 88,766 samples in the database, 8,685 (9.8%) had detections above the LOQs. The LOQs varied from 0.01 to 0.5 $\mu\text{g/L}$, but were typically at 0.1 $\mu\text{g/L}$. Results for later years changed somewhat, such that the % detect increased as the LOQs decreased. These data apply to the CWSs in the PLEX database for states in the atrazine use area.

Individual Values and Acute Levels of Concern

No systems exceeded HED's drinking water level of comparison (DWLOC) for acute effects of 298 parts per billion during the five-year period (1993-1998) of quarterly monitoring in the PLEX database. The peak total chloro-triazine (TCT) level for any system was 60 $\mu\text{g/L}$, while the highest individual level of parent atrazine in PLEX during the five-year period was 42 $\mu\text{g/L}$. Levels of parent atrazine did not exceed the Office of Water's Health Advisory Level (HAL) of 100 $\mu\text{g/L}$, either.

For the subsample of systems included in the Voluntary Monitoring Study (VMS), the Acetochlor Registration Partnership (ARP) Study, and the Rural Well Survey (RWS), concentrations were sometimes higher than those in the PLEX database, but again no systems exceeded the HED acute DWLOC and only one system exceeded the OW HAL. Individual peak TCT levels ranged from 18 $\mu\text{g/L}$ in shallow ground water (RWS) to 89 $\mu\text{g/L}$ in surface water systems (VMS). Maximum levels of parent atrazine ranged generally from 12 $\mu\text{g/L}$ (RWS) to 64 $\mu\text{g/L}$ (VMS), although one sample in the ARP Ground Water study had a concentration of 132 $\mu\text{g/L}$ atrazine.

Annual and Seasonal Means

For annual and quarterly mean concentrations that represent longer-term exposure, a number of systems serving a substantial number of people had sustained levels of the analytes at or above levels of concern for chronic and subchronic effects. Quarterly mean TCT levels were as high as 42-62 $\mu\text{g/L}$ in systems sampled in the VMS. Data from the ARP showed quarterly mean levels as high as 34 $\mu\text{g/L}$. Annual mean TCT values ranged as high as 24 $\mu\text{g/L}$ (ARP) and 25 $\mu\text{g/L}$ (VMS).

EFED noted systems from the PLEX, the VMS, and the ARP databases whose TCT levels approached or exceeded HED's DWLOC of 12.5 $\mu\text{g/L}$. Because only one sample per quarter was analyzed for each CWS in PLEX, that sample may underestimate the quarterly mean for the system or may overestimate it. The drinking water assessment performed by HED will employ a probabilistic approach that goes beyond individual comparisons with a pre-determined level.

For the parent chemical, the maximum annual mean atrazine concentration for individual years from 1993 to 1998 ranged from 4.30 $\mu\text{g/L}$ to 12.0 $\mu\text{g/L}$ in the PLEX database. Of the 21,241 CWSs with atrazine data in the database, 182 CWSs had one or more annual mean parent atrazine concentration \geq the MCL of 3 $\mu\text{g/L}$ during the 1993-1998 period. Most of these were in the 3-6 $\mu\text{g/L}$ range.

Of the 182 CWSs mentioned above for potential "multiple exceedence," 81 were actual independent suppliers. Of these, 33 are in Illinois, 16 are in Missouri, 12 are in Kansas, 12 are in Ohio, 4 are in Kentucky, 2 are in Indiana, and one each are in North Carolina and Texas.

Water Treatment Effects

There were limited data from which to determine whether treatment was effective in removing

atrazine residues from drinking water. However, such a comparison was possible for part of the VMS data. A comparison of a limited number of raw and treated samples from the VMS indicated that of the 15 CWSs having one or more finished atrazine annual means $\geq 3 \mu\text{g/L}$, 10 of these systems would have had one or more additional finished annual means $\geq 3 \mu\text{g/L}$ without activated carbon treatment.

Time series are also provided in the Appendix B-4 for 15 CWSs which (based upon raw water data) would have had one or more annual means $\geq 3 \mu\text{g/L}$ without activated carbon treatment. As before, the substantial (several fold) reduction in atrazine concentrations in those systems with the use of activated carbon treatment can be seen from a comparison of the raw and finished water time series for each CWS.

Other studies examined by EFED have looked at the effectiveness of a variety of treatment processes on the removal of various chemicals from the drinking water of systems of different sizes, types and locations. Powdered activated carbon treatment has been shown to be effective in reducing atrazine residues in raw water. In addition, reverse osmosis methods have demonstrated significant reduction in triazine levels where employed under certain circumstances (reference 17). EFED is in the process of a continuing evaluation of current methodology available for these and other pesticides.

IX. Preliminary Environmental Risk Assessment

The fate, drinking water, and ecological effects assessments are found in the appendices. The risk assessment is presented with the fate characteristics for both maximum and typical application rates for the major uses (i.e., corn, sorghum, and sugarcane) and some select minor uses.

a. Summary of Risk Assumptions

The basic process used by EFED integrates the results of the exposure and ecotoxicity data to evaluate the likelihood of adverse ecological effects. The means of integrating the results of exposure and ecotoxicity data is called the quotient method. For this method, risk quotients (RQs) are calculated by dividing exposure estimates by ecotoxicity values, both acute and chronic.

$$\text{RQ} = \text{EXPOSURE}/\text{TOXICITY}$$

RQs are then compared to OPP's levels of concern (LOCs). These LOCs are criteria used by OPP to indicate potential risk to nontarget organisms and the need to consider regulatory action. The criteria indicate that a pesticide used as directed has the potential to cause adverse effects on nontarget organisms. LOCs currently address the following risk presumption categories: (1) acute - potential for acute risk and regulatory action may be warranted in addition to restricted use classification (2) acute restricted use - the potential for acute risk exists, but may be

mitigated through restricted use classification (3) acute endangered species - the potential for acute risk to endangered species exists and regulatory action may be warranted, and (4) chronic risk - the potential for chronic risk exists and regulatory action may be warranted. Currently, EFED does not perform assessments for chronic risk to plants, acute or chronic risks to nontarget insects, or chronic risk from granular/bait formulations to mammalian or avian species.

The ecotoxicity test values (i.e., measurement endpoints) used in the acute and chronic risk quotients are derived from the results of required studies. Examples of ecotoxicity values derived from the results of short-term laboratory studies that assess acute effects are: (1) LC50 (fish and birds) (2) LD50 (birds and mammals) (3) EC50 and EC05 or NOEC (aquatic plants and aquatic invertebrates) and (4) EC25 and EC05 or NOEC (terrestrial plants). Toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are NOAEL and LOAEL for birds and mammals and NOAEC and LOAEC for fish and aquatic invertebrates. The NOAEL or NOAEC values are used as the ecotoxicity test value in assessing chronic effects.

There is a large body of atrazine toxicity data on aquatic plants that assess many different endpoints (e.g., O₂ production, nutrient uptake, chlorophyll and carotenoid levels, and growth). However, to be consistent with other risk assessments, only the standard registrant-submitted data are used to calculate risk quotients.

Risk presumptions, along with the corresponding RQs and LOCs are tabulated below.

Risk Presumptions for Terrestrial Animals

Risk Presumption	RQ	LOC
Birds and Mammals		
Acute High Risk	$EEC^1/LC50$ or $LD50/sqft^2$ or $LD50/day^3$	0.5
Acute Restricted Use	$EEC/LC50$ or $LD50/sqft$ or $LD50/day$ (or $LD50 < 50$ mg/kg)	0.2
Acute Endangered Species	$EEC/LC50$ or $LD50/sqft$ or $LD50/day$	0.1
Chronic Risk	$EEC/NOAEC$	1

¹ abbreviation for Estimated Environmental Concentration (ppm) on avian/mammalian food items

² $\frac{mg/ft^2}{LD50 * wt. of bird}$ ³ $\frac{mg \text{ of toxicant consumed/day}}{LD50 * wt. of bird}$

Risk Presumptions for Aquatic Animals

Risk Presumption	RQ	LOC
Acute High Risk	$EEC^1/LC50$ or $EC50$	0.5
Acute Restricted Use	$EEC/LC50$ or $EC50$	0.1
Acute Endangered Species	$EEC/LC50$ or $EC50$	0.05
Chronic Risk	$EEC/NOAEL$	1

¹ EEC = (ppm or ppb) in water

Risk Presumptions for Plants

Risk Presumption	RQ	LOC
Terrestrial and Semi-Aquatic Plants		
Acute High Risk	EEC ¹ /EC25	1
Acute Endangered Species	EEC/EC05 or NOAEC	1
Aquatic Plants		
Acute High Risk	EEC ² /EC50	1
Acute Endangered Species	EEC/EC05 or NOAEC	1

¹ EEC = lbs ai/A

² EEC = (ppm or ppb) in water

b. Aquatic Exposure and Risk Assessment

The atrazine aquatic risk assessment focuses mainly on aquatic plants and invertebrates and the potential for effects on sensitive plant species to result in community-level impacts which affect a range of aquatic organisms. The assessment is broken down by the type of water body (i.e., small static fresh water bodies such as ponds, flowing fresh water such as streams and rivers, larger bodies of fresh water such as lakes and reservoirs, and estuarine and marine habitats). Exposure for these three types of aquatic environments was estimated using PRZM-EXAMS modeling simulations (ponds) and monitoring data (streams, lakes and reservoirs, and estuarine/marine environments). Details on exposure are outlined for each type of aquatic environment.

EFED's initial assessment of aquatic risk, i.e., dividing modeled exposure concentrations by toxicity values from standard tests to generate risk quotients (RQs) which are then compared to levels of concern, will be confined to a standard pond scenario. The process used to assess risk for flowing fresh water, lakes and reservoirs, and estuarine and marine habitats will consider surface water monitoring data to estimate exposure and will use toxicity data taken principally from the open scientific literature.

1. Pond Risk Assessment

Pond Exposures

No monitoring data were available for atrazine in ponds, therefore the assessment of risks to aquatic organisms in ponds is limited to the refined tier II approach with PRZM/EXAMS. The upper tenth percentile concentration values, expressed in $\mu\text{g/L}$ (ppb), are summarized below. The results of three uses, corn, sugarcane, and sorghum, were based on the standard scenarios in the Environmental Fate and Effects Division to predict reasonable high exposure values, i.e.,

soils with high runoff potential and heavy rainfall amounts for maximum and typical use rates for aerial pre-plant, spray applications. The Annual Exceedence Probability graphs and data tables for maximum use rates can be found in Appendix V.

Information on maximum use rates are based on the Atrazine use reports and labels. Data on acres treated, percent of crop treated and average application (typical) use rates are from Biological and Economic Analysis Division's Quantitative Usage Analysis (dated May 10,1999). The maximum and typical use rates applied as an aerial spray applications of atrazine on Louisiana sugarcane are 4 and 2.6 lbs ai/A, respectively. Ohio corn are 2.0 and 1.1 lbs ai/A and Kansas sorghum are 2.0 and 1.2 lbs ai/A. The EECs used for the atrazine risk assessment for aquatic species in ponds are summarized in the following table.

Treated Crop	Maximum & Typical Use Rates (lb ai/A)	Atrazine EEC Values ppb ($\mu\text{g/L}$)				
		Peak Conc.	96-hour Average	21-day Average	60-day Average	90-day Average
Sugarcane	4.0	205	204	202	198	194
	2.6	133	133	131	129	126
Corn	2.0	38.2	38.0	37.2	35.5	34.2
	1.1	21.0	20.9	20.5	17.7	18.8
Sorghum	2.0	72.7	72.3	70.6	67.7	65.9
	1.2	43.6	43.4	42.4	40.6	39.5

The modeling results indicate that atrazine does have the potential to move into surface waters, especially for sugarcane use. Klassen and Kadoum (1979) found atrazine to be persistent in a farm pond ecosystem with estimated half-lives of six to eight months. These data are consistent with the persistence of atrazine seen in the gradual reductions in EEC levels produced by the PRZM-EXAMS model presented in the above table. With relatively stable atrazine concentrations in ponds, only small differences exist between simulated acute and chronic atrazine exposures for ponds, and the duration of the toxicity tests has little significance for assessing risks.

Monitoring data in the Upper Terrebonne watershed of Louisiana, an area with high sugarcane acreage, shows some atrazine levels in surface waters as high as 216 $\mu\text{g/L}$. This atrazine level supports and is consistent with the pond EECs (205 $\mu\text{g/L}$) derived from the maximum use rate of 4.0 lbs ai/A on sugarcane.

The post-processor, LOAD.EXE, was used to estimate the chemical contributions of runoff, erosion and spray drift to the standard farm pond. The results expressed as percentages are tabulated below:

Percent of Pesticide Loadings from Different Sources to the Standard Pond

Use	Runoff	Erosion	Spray Drift
Corn	55.03%	3.47%	41.50%
Sugarcane	99.15%	0.85%	0.01%
Sorghum	71.80%	5.29%	22.91%

The erosion losses were the smallest among the three components, except for the sugarcane use scenario. Most of the atrazine losses to aquatic environments are from runoff, although spray drift also appears to have a large contribution in the corn scenario.

Pond Risk Quotients

The toxicity values used in the 1-hectare, 2-meter deep, pond risk assessments are limited to submitted studies using the standard toxicity endpoints. Normally, chronic risks are estimated using 96-hour and 21- to 90-day EECs, corresponding to the duration of the test, because it is uncertain when during the exposure the toxic effects are triggered. For atrazine, 21-day EECs were generally used for chronic exposures, because the difference in EEC values are so small. However, chronic risks to fish were estimated using 21-day and 90-day EECs, because the toxicity to fish in the full-life test increased at some later time compared to the results from the 28-day fish early-life stage test. The toxicity endpoints used in the pond risk assessment are included in Appendix XI: rainbow trout (*Onchorhynchus mykiss*) - acute, brook trout (*Salvelinus fontinalis*) - chronic, midge (*Chironomus tentans*) - acute, scud (*Gammarus fasciatus*) - chronic, duckweed (*Lemna gibba*) - 14 days (Hoberg 1993) and the algae (*Kirchneria subcapitata*) - acute (Hoberg 1993). Community-level atrazine effects on vascular plants, aquatic invertebrates populations and fish recruitment found in literature studies yield more sensitive endpoints and are discussed after the risk quotient assessment.

Risk Quotients for Sugarcane (Maximum Use Rate) (1 Pre-plant Aerial Application at 4.0 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)			
Species	Exposure	Toxicity	Risk Quotient
Freshwater Fish Acute LC ₅₀	205 ppb	5,300 ppb	0.039
Fish Reproduction NOAEC	194 - 202 ppb	65 ppb	2.9 - 3.1
Aquatic Invertebrate Acute LC ₅₀	205 ppb	720 ppb	0.28
Freshwater Invertebrate Reproduction NOAEC	202 ppb	60 ppb	3.4
Freshwater Vascular Plant EC ₅₀	205 ppb	37 ppb	5.5
Freshwater Algae EC ₅₀	205 ppb	49 ppb	4.2

Risk Summary for a Maximum Pre-emergent Aerial Spray on Sugarcane: Atrazine aerially sprayed pre-emergence at 4.0 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity to aquatic plants (RQ = 1), restricted use for aquatic invertebrates (RQ = 0.1), and endangered species for aquatic invertebrates (RQ = 0.05) and aquatic vascular plants (RQ = 1.0 for the EC_{NOEC}).

The levels of concern for chronic effects (**RQ = 1.0**) are exceeded by risk quotients for aquatic plants, fish and aquatic invertebrates based on the chronic EECs resulting from both the maximum use rate and the typical use rate for sugarcane and the NOAEC values for both fish and aquatic invertebrates. Chronic 21- to 90-day EECs (**194 - 202 µg/L**) for the maximum use rates for sugarcane exceed the LOAECs for brook trout (120 µg/L which reduced mean length by 7.2% and body weight by 16%), fathead minnow (150 µg/L which reduced F₁ length by 6.7% and body weight by 22%), *Gammarus fasciatus* (140 µg/L) which reduced the development of F₁ to the seventh instar by 25%), and exceed the NOAEC values for *Chironomus tentans* (110 µg/L) and *Daphnia magna* (140 µg/L).

Risk Quotients for Sugarcane (Typical Use Rate) (1 Pre-plant Aerial Application at 2.6 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)			
Species	Exposure	Toxicity	Risk Quotient
Freshwater Fish Acute LC ₅₀	133 ppb	5,300 ppb	0.025
Fish Reproduction NOAEC	126 - 133 ppb	65 ppb	1.9 - 2.0
Aquatic Invertebrate Acute LC ₅₀	133 ppb	720 ppb	0.18
Freshwater Invertebrate Reproduction NOAEC	131 ppb	60 ppb	2.2
Freshwater Vascular Plant EC ₅₀	133 ppb	37 ppb	3.6
Freshwater Algae EC ₅₀	133 ppb	49 ppb	2.7

Risk Summary for a Typical Pre-emergent Aerial Spray on Sugarcane: Atrazine aerially sprayed pre-emergence at 2.6 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity for aquatic plants (RQ = 1), restricted use for aquatic invertebrates (RQ = 0.2), and endangered species for aquatic invertebrates (RQ = 0.05) and for aquatic vascular plants (RQ = 1.0 for the EC_{NOAEC}).

The levels of concern for chronic effects (**RQ = 1.0**) are exceeded by risk quotients for aquatic plants, fish and aquatic invertebrates based on the chronic EECs resulting from both the maximum use rate and the typical use rate for sugarcane and the NOAEC values for both fish and aquatic invertebrates. Chronic 21- to 90-day EECs (**131 - 126 µg/L**) for the typical use rates for sugarcane exceed the LOAECs for brook trout (120 µg/L which reduced mean length by 7.2% and body weight by 16%) and exceed the NOAEC values for bluegill sunfish (95 µg/L), *Gammarus fasciatus* (60 µg/L) and *Chironomus tentans* (110 µg/L).

Risk Quotients for Corn (Maximum Use Rate) (1 Pre-plant Aerial Application at 2.0 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)			
Species	Exposure	Toxicity	Risk Quotient
Freshwater Fish Acute LC ₅₀	38.2 ppb	5,300 ppb	0.0072
Fish Reproduction NOAEC	34.2 - 37.2 ppb	65 ppb	0.53 - 0.58
Aquatic Invertebrate Acute LC ₅₀	38.2 ppb	720 ppb	0.053
Freshwater Invertebrate Reproduction NOAEC	37.2 ppb	60 ppb	0.63
Freshwater Vascular Plant EC ₅₀	37.2 ppb	37 ppb	1.0
Freshwater Vascular Plant EC _{NOEC}	37.2 ppb	< 3.4 ppb	> 11
Freshwater Algae EC ₅₀	38.2 ppb	49 ppb	0.78

Risk Summary for a Maximum Pre-emergent Aerial Spray on Corn: Atrazine aerially sprayed pre-emergence at 2.0 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity for aquatic plants (RQ = 1.0) and for endangered species for aquatic invertebrates (RQ = 0.05) and aquatic vascular plants (RQ = 1.0 for the EC_{NOEC}). The risk quotients are freshwater fish acute (0.0072) and reproduction NOAEC (0.53-0.58), and aquatic invertebrate reproduction NOAEC (0.63) do not exceed levels of concern.

Risk Quotients for Corn (Typical Use Rate) (1 Pre-plant Aerial Application at 1.1 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)			
Species	Exposure	Toxicity	Risk Quotient
Freshwater Fish Acute LC ₅₀	21.0 ppb	5,300 ppb	0.0040
Fish Reproduction NOAEC	18.8 - 20.5 ppb	65 ppb	0.29 - 0.32
Aquatic Invertebrate Acute LC ₅₀	21.0 ppb	720 ppb	0.029
Freshwater Invertebrate Reproduction NOAEC	20.5 ppb	60 ppb	0.34
Freshwater Vascular Plant EC ₅₀	20.5 ppb	37 ppb	0.56
Freshwater Vascular Plant EC _{NOEC}	20.5 ppb	< 3.4 ppb	> 6.0
Freshwater Algae EC ₅₀	21.0 ppb	49 ppb	0.43

Risk Summary for a Typical Pre-emergent Aerial Spray on Corn: Atrazine aerially sprayed pre-emergence at 1.1 lbs ai/A yields a risk quotient that exceeds the level of concern for endangered species for aquatic vascular plants (RQ = 1 for the EC_{NOEC}). The risk quotients are freshwater fish acute (0.0040) and reproduction NOAEC (0.29-0.32), aquatic invertebrate acute (0.029) and reproduction NOAEC (0.34) do not exceed levels of concern.

Risk Quotients for Sorghum (Maximum Use Rate) (1 Pre-plant Aerial Application at 2.0 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)			
Species	Exposure	Toxicity	Risk Quotient
Freshwater Fish Acute LC ₅₀	72.7 ppb	5,300 ppb	0.014
Fish Reproduction NOAEC	65.9 - 70.6 ppb	65 ppb	1.0 - 1.1
Aquatic Invertebrate Acute LC ₅₀	72.7 ppb	720 ppb	0.10
Freshwater Invertebrate Reproduction NOAEC	70.6 ppb	60 ppb	1.2
Freshwater Vascular Plant EC ₅₀	72.7 ppb	37 ppb	2.0
Freshwater Vascular Plant EC _{NOEC}	72.7 ppb	< 3.4 ppb	> 21
Freshwater Algae EC ₅₀	72.7 ppb	49 ppb	1.5

Risk Summary for a Maximum Pre-emergent Aerial Spray on Sorghum: Atrazine aerially sprayed pre-emergence at 2.0 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity for aquatic plants (RQ = 1.0), restricted use for aquatic invertebrates (RQ = 0.1), and endangered species for aquatic invertebrates (RQ = 0.05) and aquatic vascular plant species (RQ = 1.0 for EC_{NOEC}).

The levels of concern for chronic effects (RQ = 1.0) are exceeded by risk quotients for aquatic plants, fish and aquatic invertebrates based on the chronic EECs resulting from the maximum use rate for sorghum and the NOAEC values for both fish and aquatic invertebrates.

Risk Quotients for Sorghum (Typical Use Rate) (1 Pre-plant Aerial Application at 1.2 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)			
Species	Exposure	Toxicity	Risk Quotient
Freshwater Fish Acute LC ₅₀	43.6 ppb	5,300 ppb	0.0082
Fish Reproduction NOAEC	39.5 - 42.4 ppb	65 ppb	0.61 - 0.65
Aquatic Invertebrate Acute LC ₅₀	43.6 ppb	720 ppb	0.061
Freshwater Invertebrate Reproduction NOAEC	42.4 ppb	60 ppb	0.71
Freshwater Vascular Plant EC ₅₀	43.6 ppb	37 ppb	1.2
Freshwater Vascular Plant EC _{NOEC}	43.6 ppb	< 3.4 ppb	> 13
Freshwater Algae EC ₅₀	43.6 ppb	49 ppb	0.89

Risk Summary for a Typical Pre-emergent Aerial Spray on Sorghum: Atrazine aerially sprayed pre-emergence at 1.2 lbs ai/A yields risk quotients that exceed the levels of concern for acute toxicity for vascular plants (RQ = 1) and endangered species for aquatic invertebrates (RQ

= 0.05) and for aquatic vascular plants (RQ = 1 for EC_{NOEC}). The risk quotients for freshwater fish acute (0.0082) and reproduction NOAEC (0.61-0.65), aquatic invertebrate acute (0.061) and reproduction NOAEC (0.71) do not exceed levels of concern.

Evidence of Community-Level Pond Effects from Field Data

Results from artificial ponds in Kansas (Kettle *et al.*, 1987) treated with atrazine at 20 µg/L provide evidence of significant community effects on aquatic organisms at concentrations substantially lower than the EECs for all of the above pond scenarios. The atrazine effects on the aquatic community included significant impacts on vascular plants (60 and 90% reductions in vegetation and the virtual loss of 3 plant species), aquatic invertebrates (reduced numbers and loss of some species as indicated by stomach contents), and fish (96% reduction in the number of young bluegills).

Atrazine Effects on Aquatic Plants

Many algal studies show 50% reductions in photosynthesis in 24 hours, 50% and higher reductions in chlorophyll production in one week, and 50% reductions in cell growth at water concentrations less than the peak EECs for **corn**, (maximum use rate and effects on a number of algal species below the typical, corn use, EECs (**20 µg/L**) and all peak EECs for sorghum and sugarcane (Hoberg, 1991; Hughes, 1986; Parrish, 1978; Stratton and Corke, 1981; Torres and O'Flaherty, 1976). See Appendix XI for aquatic plant toxicity data.

Peak and chronic model-simulated EECs (**189 - 205 µg/L**) from atrazine use on **sugarcane** also exceed the EC₅₀ for growth on the vascular plants including duckweed (37, 43, 170, and 170 µg/L), *Elodea canadensis* (80 µg/L), Eurasian water-milfoil (91 µg/L), and 50% reduction in oxygen production in *Potamogeton perfoliatus* at 30 µg/L (Hoberg, 1993; Hoffman and Winkler, 1990; Kemp *et al.*, 1985). Sugarcane EECs exceed acute effects on 14 algal species and chronic effects on an additional 2 algal species and 36 algal strains reported by Butler *et al.* (1975).

For **sorghum**, the peak and chronic model-generated EECs (**39.5 - 72.7 µg/L**) exceed the EC₅₀ for growth on the vascular plants including duckweed (37 µg/L; Hoberg, 1993) and non-growth effects on *Potamogeton perfoliatus* (30 µg/L, 50% reduction in oxygen production; Kemp *et al.*, 1985). Sorghum EECs exceed acute effects on 9 to 11 algal species, respectively and chronic effects on one additional algal species and 36 algal strains reported by Butler *et al.* (1975).

For the maximum use rate on **corn**, the peak and chronic modeled EECs (**34.2- 38.2 µg/L**) exceed the EC₅₀ for growth on the vascular duckweed (37 µg/L), for non-growth effects on *Potamogeton perfoliatus* (30 µg/L, 50% reduction in oxygen production), and exceed acute effects on 9 algal species and 2-week, chronic effects on 36 algal strains at 10 µg/L reported by Butler *et al.* (1975). The typical use rate on corn yields peak and chronic EECs (**18.8 - 20 µg/L**) exceed only the 2-week, chronic effects on 36 algal strains at 10 g/L reported by Butler *et al.* (1975).

Results from some freshwater microcosm studies at 5 $\mu\text{g/L}$ atrazine show slight, non-significant changes in the range or physical parameters such as reduced D.O. levels and pH levels and increased conductivity and alkalinity, but no significant effects on phytoplankton, zooplankton, or macro-invertebrates. Adverse effects on vascular plant primary productivity first appeared at about 10 $\mu\text{g/L}$ and at 15 $\mu\text{g/L}$ reductions occurred in copepod and rotifer densities after 7 days. Similar effects were reported for mesocosm studies: transient effects on water chemistry first appeared at < 0.1 to 10 $\mu\text{g/L}$; at 1 $\mu\text{g/L}$ reductions in primary production and zooplankton numbers, and increases in bacterial numbers; at 10 to 68 $\mu\text{g/L}$, reductions occurred in zooplankton populations, and 20 $\mu\text{g/L}$, 60% reduction in macrophyte vegetation and elimination of 3 vascular species (Hoagland et al., 1993; Kettle et al., 1987)

Conclusion: Based on standard acute and chronic toxicity and the standard 2-meter deep pond adjacent to treated-sorghum and sugarcane fields, atrazine EECs exceed levels of concern for direct effects on fish and aquatic invertebrate reproduction and freshwater vascular plants and algae. Atrazine EECs from applications to corn do not exceed levels of concern for fish or aquatic invertebrates, but corn EECs do exceed levels of concern for some algal species.

Atrazine use on the above crops is estimated to yield surface water concentrations which exceed a number of non-standard, sublethal toxicity levels reported in the literature for a number of fish species and exceed concentrations which have indirect community effects on aquatic species. Indirect effects on fish and aquatic invertebrates are severe due to the loss of 60 to 95 percent of the vegetative cover, which provides habitat to conceal young fish and aquatic invertebrates from predators.

Direct effects of atrazine to nontarget aquatic plants indicate high risk. Numerous reports attest to atrazine's ability to inhibit photosynthesis, change community structure, and cause the mortality of aquatic flora at concentrations between 20 and 500 $\mu\text{g/L}$ (deNoyelles and Kettle 1980; deNoyelles *et al.* 1982; Dewey 1986; Kettle *et al.* 1987).

2. Lake and Reservoir, Stream, and Estuarine Risk Assessments

See Section VI, Environmental Risk Characterization above.

c. Terrestrial Risk Assessment

1. Animal Risk Assessment

Acutely, atrazine is practically non-toxic to birds and mammals. Risks from atrazine uses on sugarcane, corn and sorghum are assessed for maximum and typical use rates using the typical risk assessment methodology. Given the maximum use rate of 4 lbs ai per acre on sugarcane, the upper limit atrazine exposure levels would be about **960 ppm** on short grass and **540 ppm** on foliage in the treated field and along the field edges. The residue levels on insects are assumed to be **15 and 135 ppm per lb ai/acre** for large and small insects, respectively. The mammalian

acute toxicity value used in the assessment is based on the rat LD₅₀ (**1,869 mg/kg**). A dose equal to the mammalian LOAEL (500 ppm) significantly reduced adult rat body weight and adult food consumption (**NOAEL 50 ppm**). At 50 ppm, second generation rat pups had significantly reduced body weight (**NOAEL, 10 ppm**). The LOAELs for bobwhite and mallard ducks were 675 ppm, based on 29 and 49% reductions in egg production, respectively (**NOAEL, 225 ppm**). Risk quotients are provided for a range of appropriate food items for each animal group in the following tables for atrazine applications on sugarcane, corn and sorghum.

In order to determine the length of time that levels of concern would be exceeded following applications, a conservative foliar half-life was estimated from the following atrazine residue data. Based on transferable residue data from atrazine-treated turf, the atrazine half-lives for sprays are 5.2 (± 0.22), 15.6 (± 0.86) and 17 (± 0.18) days in Georgia, 3.2 (± 0.81), 3.3 (± 0.80) and 3.8 (± 0.87) days in North Carolina. For granular applications, the atrazine half-lives are 4.9 (± 4.9) days (no irrigation) and 6.0 (± 0.69) days (after irrigation) in Florida and 6.8 (± 0.91) days (no irrigation) and 10.5 (± 0.41) days (after irrigation) in Georgia. These data indicate fairly high variation in atrazine half-lives (i.e., from 3.2 to 17 days). An atrazine, foliar half-life of 17 days will be used as a conservative estimate for dietary assessment of risks for avian and small mammals. The Terrestrial Fate Residue model was used to estimate the daily residue levels. Appendix IX contains the documentation of the method, the equation and examples for atrazine.

Risk Quotients for Maximum Use Rate on Sugarcane (Pre-plant, Aerial Spray; 1 Application at 4.0 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)			
Surrogate Species	Exposure	Toxicity	Risk Quotient
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	60 - 960 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.031 - 0.49 0.021 - 0.34 0.0048 - 0.077
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	60 - 540 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.031 - 0.27 0.021 - 0.19 0.0048 - 0.043
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	60 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0067 0.0048 0.00096
Mammalian Reproduction NOAEL	60 - 960 ppm	10 ppm	6.0 - 96
Avian Subacute Dietary LC ₅₀	60 - 960 ppm	> 5,000 ppm	< 0.012 < 0.19
Avian Reproduction NOAEL	60 - 960 ppm	225 ppm	0.27 - 4.3

Risk Summary for the Maximum Sugarcane Spray Use: Risk quotients derived for a single application at the typical use rate of 4.0 lbs ai/A on sugarcane exceed the levels of concern for restricted use (**RQ = 0.2**) for small and medium-sized herbivores and small insectivores, and endangered species (**RQ = 0.1**) for small and medium-sized herbivores and insectivores.

Chronic level of concern (**RQ = 1.0**) is exceeded for mammalian and avian reproduction. The maximum atrazine level on short grass (**960 ppm**) exceeds the chronic LOAEL values for both bobwhite and mallards and the mammalian LOAEL for rats. At 675 ppm, adverse effects on bobwhite included: 29% reduction in egg production, a 67% increase in defective eggs, a 27% reduction in embryo viability, a 6 to 13% reduction in hatchling body weight, and a 10 to 16% reduction in 14-day old bobwhite body weight (Pedersen and DuCharme, 1992). At 675 ppm, adverse effects on mallards included reductions of 49% in egg production, 61% in egg hatchability and 12 to 17% in adult food consumption (Pedersen and DuCharme, 1992). The mammalian reproductive **NOAELs (50 ppm**, for reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded.

Based on a conservative, foliar half-life of 17 days and maximum atrazine levels on short grass and broadleaf foliage, atrazine residues would exceed the avian reproductive **NOAELs (225 ppm)** for **35 and 21** days, respectively. The mammalian reproductive **NOAELs (50 ppm)**, reduction in adult body weight and food consumption) and (**10 ppm**), reduction in second generation pup body weights) are exceeded on grass for **72 and 111 days**, respectively and on broadleaf foliage for **58 and 97 days**, respectively.

Spray drift onto vegetation in areas surrounding a treated field (i.e., field borders and riparian areas next to streams) using the standard, 5 percent spray drift value for aerial applications would appear to yield atrazine levels which do not pose a reproductive risk to birds and pose low chronic risks to small mammals. At 4 lbs ai/A, maximum atrazine levels on grass are 48 ppm and 27 ppm on broadleaf foliage; at 2 lbs ai/A, atrazine levels are 24 ppm on grass and 13.5 ppm on broadleaf foliage. Based on these spray drift exposures, atrazine would exceed only the NOAEC of 10 ppm for rat pup body weight reductions for 21 days. These risks to wildlife will be reassessed when peer review of the Ag Drift Model is completed and approved.

Risk Quotients for Typical Use Rate on Sugarcane (Pre-plant, Aerial Spray; 1 Application at 2.6 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)			
Surrogate Species	Exposure	Toxicity	Risk Quotient
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	39 - 624 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.020 - 0.32 0.014 - 0.22 0.0031 - 0.050
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	39 - 151 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.020 - 0.08 0.014 - 0.053 0.0031 - 0.012
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	39 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0044 0.0031 0.00063
Mammalian Reproduction NOAEL	39 - 624 ppm	10 ppm	3.9 - 62
Avian Subacute Dietary LC ₅₀	39 - 624 ppm	> 5,000 ppm	< 0.0078 < 0.12

Avian Reproduction NOAEL	39 - 624 ppm	225 ppm	0.17 - 2.8
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Risk Summary for Typical Sugarcane Spray Use: Risk quotients derived for a single application at the typical use rate of 2.6 lbs ai/A on sugarcane exceed the levels of concern for restricted use (**RQ = 0.2**) for small and medium-sized herbivores and for endangered species (**RQ = 0.1**) for small and medium-sized herbivores.

Chronic level of concern (**RQ = 1.0**) is exceeded for mammalian and avian reproduction NOAECs. Typical atrazine levels on short grass (**624**) exceeds the chronic NOAEL values for both bobwhite and mallards and the mammalian NOAEL for rats.

Risk Quotients for Maximum Use Rate on Corn and/or Sorghum (Pre-plant, Aerial Spray; 1 Application at 2.0 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)			
Surrogate Species	Exposure	Toxicity	Risk Quotient
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	30 - 480 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.015 - 0.24 0.010 - 0.17 0.0024 - 0.039
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	30 - 270 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.015 - 0.14 0.010 - 0.095 0.024 - 0.022
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	30 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.034 0.0024 0.00048
Mammalian Reproduction NOAEL	30 - 480 ppm	10 ppm	3.0 - 48
Avian Subacute Dietary LC ₅₀	30 - 480 ppm	> 5,000 ppm	< 0.0060 < 0.096
Avian Reproduction NOAEL	30 - 480 ppm	225 ppm	0.13 - 2.1

Risk Summary for Maximum Corn and Sorghum Spray Use: Risk quotients derived for a single application at the maximum use rate of 2.0 lbs ai/A on corn or sorghum exceed the levels of concern for restricted use (**RQ = 0.2**) for small mammalian herbivores and for endangered species (**RQ = 0.1**) for small mammalian herbivores and insectivores.

Chronic level of concern (**RQ = 1.0**) is exceeded for mammalian and avian reproduction. Maximum atrazine levels on short grass (**480 ppm**) exceed the chronic LOAEL value for bobwhite chicks and the NOAECs (225 ppm) for bobwhite and mallard ducks for 35 days. The mammalian reproductive **NOAELs (50 ppm**, reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded for 54 and 94 days, respectively for maximum residue levels on short grass.

Based on these spray drift exposures, atrazine would exceed only the NOAEC of 10 ppm for rat

pup body weight reductions for 7 days. These risks to wildlife will be reassessed when peer review of the Ag Drift Model is completed and approved.

Risk Quotients for the Typical Use Rate on Corn (Pre-plant, Aerial Spray; 1 Application at 1.1 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i>, 1994)			
Surrogate Species	Exposure	Toxicity	Risk Quotient
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	16.5 - 264 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0084 - 0.13 0.0058 - 0.093 0.0013 - 0.021
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	16.5 - 148.5 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0084 - 0.075 0.0058 - 0.052 0.0013 - 0.012
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	16.5 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0019 0.0013 0.00026
Mammalian Reproduction NOAEL	16.5 - 264 ppm	10 ppm	1.6 - 26
Avian Subacute Dietary LC ₅₀	16.5 - 264 ppm	> 5,000 ppm	< 0.0033 < 0.053
Avian Reproduction NOAEL	16.5 - 264 ppm	225 ppm	0.73 - 1.2

Risk Summary for Typical Corn Spray Use: Risk quotients derived for a single application at the typical use rate of 1.1 lbs ai/A on corn exceed the levels of concern for restricted use (**RQ = 0.2**) and for endangered species (**RQ = 0.1**) for small mammalian herbivores.

Chronic level of concern (**RQ = 1.0**) is exceeded for mammalian and avian reproduction. Maximum atrazine levels on short grass (**264 ppm**) exceed the chronic LOAEL value for bobwhite and the NOAECs (225 ppm) for bobwhite and mallard ducks for about 4 days. The mammalian reproductive **NOAELs (50 ppm**, reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded for about 40 and 80 days, respectively, based on maximum residue levels on short grass.

Risk Quotients for the Typical Use Rate on Sorghum (Pre-plant, Aerial Spray; 1 Application at 1.2 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i>, 1994)			
Surrogate Species	Exposure	Toxicity	Risk Quotient
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	18 - 288 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0092 - 0.15 0.0064 - 0.10 0.0014 - 0.023
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	18 - 162 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0092 - 0.082 0.0064 - 0.057 0.0014 - 0.013

Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	18 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0020 0.0014 0.00029
Mammalian Reproduction NOAEL	18 - 288 ppm	10 ppm	1.8 - 29
Avian Subacute Dietary LC ₅₀	18 - 288 ppm	> 5,000 ppm	< 0.0036 < 0.058
Avian Reproduction NOAEL	18 - 288 ppm	225 ppm	0.08 - 1.1

Risk Summary for Typical Sorghum Spray Use: Risk quotients derived for a single application at the typical use rate of 1.2 lbs ai/A on sorghum exceed the levels of concern for endangered species (**RQ = 0.1**) for small and medium-sized mammalian herbivores.

Chronic level of concern (**RQ = 1.0**) is exceeded for mammalian and avian reproduction. Atrazine residue levels on short grass (**288 ppm**) exceed the chronic NOAECs for bobwhite and mallard ducks for about 5 days. The mammalian reproductive **NOAELs (50 ppm**, reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded for 42 and 90 days, respectively for maximum residue levels on short grass.

2. Plant Risk Assessment

a. Spray Drift and Runoff Assessments

Atrazine applications to crop and non-crop areas pose an exposure to non-target plants in areas adjacent to treated fields via spray drift and runoff. Standard EFED values were used for spray drift and runoff levels. Spray drift levels for ground and aerial applications are 1 and 5 percent, respectively. Atrazine is highly mobile in soils and has a low soil-water partitioning coefficient and a water solubility value of about 33 ppm. Its runoff is estimated at 2 percent. The scenario for plants growing in dry areas receive runoff from 1 hectare to 1 hectare, while a 1-hectare wet area receives runoff from 10 hectares. All plant toxicity values are present as pounds active ingredient per acre (lbs ai/A). The EC₂₅ values are used to calculate risk quotients for the typical non-target plants and the NOAEC values are used for endangered and threatened plant species. The formulae for deriving EECs for plants are given in Appendix X. The following tables present risk quotients for non-target terrestrial plants following at-plant, aerial and ground applications of 4 lbs ai/A, which is the maximum application rate for atrazine (i.e., sugarcane). Assuming a 60 percent aerial spray efficiency, the exposure values used to assess risks for 4 lbs ai/A are 0.2 lbs ai/A for aerial spray drift, 0.248 lbs ai/A for both spray drift and runoff to dry areas, and 0.68 lbs ai/A for spray drift and runoff to wet areas. All risk quotients are rounded off to two significant digits.

Atrazine Risk Quotients for Terrestrial Plants (4 lbs ai./A; Aerial Application)
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Crop	Spray Drift (5%)		Spray Drift + Runoff to Dry and Wet Areas		
	Vegetative Vigor EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species	Seedling Emergence EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species in Dry Areas	Risk Quotients Typical/Endangered Species in Wet Areas
Carrot	1.7 / 2.0	0.12 / 0.10	0.003 / 0.0025	83 / 99	230 / 270
Oats	2.4 / 2.0	0.083 / 0.10	0.004 / 0.0025	62 / 99	170 / 270
Ryegrass	>4.0 / >4.0	<0.05 / <0.05	0.004 / 0.005	62 / 50	170 / 140
Lettuce	0.33 / 0.25	0.61 / 0.80	0.005 / 0.005	50 / 50	140 / 140
Onion	0.61 / 0.5	0.33 / 0.40	0.009 / 0.005	28 / 50	76 / 140
Cucumber	0.008 / 0.005	25 / 40	0.013 / 0.005	19 / 50	52 / 140
Soybean	0.026 / 0.02	7.7 / 10	0.19 / 0.025	1.3 / 9.9	3.5 / 27
Cabbage	0.014 / 0.005	14 / 40	0.014 / 0.01	18 / 25	49 / 68
Tomato	0.72 / 0.5	0.28 / 0.40	0.034 / 0.01	7.3 / 25	20 / 68
Corn	>4.0 / >4.0	< 0.05 / <0.05	> 4.0 / > 4.0	<0.062 / <0.062	<0.17 / <0.17

The levels of concern for terrestrial plants are exceeded for acute risk (RQ = 1.0) and endangered plant species (RQ = 1.0). Three out of the ten crops (i.e., cucumber, soybeans, and cabbage) are at risk from spray drift, if planted adjacent to atrazine-treated sugarcane. Of the ten crops, only corn is not at risk from combined spray drift and runoff exposures.

Assuming 100 percent ground spray, application efficiency, the exposure values used to assess risks for 4 lbs ai/A are 0.04 lbs ai/A for aerial spray drift, 0.12 lbs ai/A for both spray drift and runoff to dry areas, and 0.84 lbs ai/A for spray drift and runoff to wet areas. All risk quotients are rounded off to two significant digits.

Atrazine Risk Quotients for Terrestrial Plants (4 lbs ai./A; Ground Application)					
Crop	Spray Drift (1%)		Spray Drift + Runoff to Dry and Wet Areas		
	Vegetative Vigor EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species	Seedling Emergence EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species in Dry Areas	Risk Quotients Typical/Endangered Species in Wet Areas
Carrot	1.7 / 2.0	0.024 / 0.02	0.003 / 0.0025	40 / 48	280 / 340
Oats	2.4 / 2.0	0.017 / 0.02	0.004 / 0.0025	30 / 48	210 / 340
Ryegrass	>4.0 / >4.0	<0.01 / <0.01	0.004 / 0.005	30 / 24	210 / 170
Lettuce	0.33 / 0.25	0.12 / 0.16	0.005 / 0.005	24 / 24	170 / 170
Onion	0.61 / 0.5	0.066 / 0.08	0.009 / 0.005	13 / 24	93 / 170
Cucumber	0.008 / 0.005	5.0 / 8.0	0.013 / 0.005	9.2 / 24	65 / 170
Soybean	0.026 / 0.02	1.5 / 2.0	0.19 / 0.025	0.63 / 4.8	4.4 / 34
Cabbage	0.014 / 0.005	2.9 / 8.0	0.014 / 0.01	8.6 / 12	60 / 84

Tomato	0.72 / 0.5	0.056/ 0.08	0.034 / 0.01	3.5 / 12	25 / 84
Corn	>4.0 / >4.0	<0.01/<0.01	> 4.0 / > 4.0	<0.03 /<0.03	<0.21 /<0.21

Three out of the ten non-target crop species (i.e., cucumbers, soybeans and cabbage, which are all dicots) are at risk from spray drift alone, if grown adjacent to atrazine-treated sugarcane ground sprayed with 4 lbs ai/A, the maximum registered use rate.. The combination of spray drift and runoff poses risks to eight out of the ten crops if grown in dry habitats and to nine out of ten crops if grown in low-lying, semi-aquatic habitats.

A ground application of 2 lbs ai/A to corn and/or sorghum poses a diminished risk to adjacent crops compared to 4-lb ai/A applications to sugarcane, but only one of these species (i.e., soybeans from spray drift) would no longer exceed the acute level of concern. At the typical corn use rate of 1.1 lbs ai/A, the non-target crops at risk are cucumbers from spray drift (RQ = 1.4), 7 out of 9 non-target species growing in dry habitats, and all 9 non-target species, if grown in semi-aquatic habitats. Risk quotients for endangered plant species indicate concern for endangered species growing in areas adjacent to atrazine-treated fields from combined spray drift and runoff.

Non-target terrestrial plants in adjacent fields or habitats are potentially at risk from spray drift and from runoff for all registered uses. The level of concern for endangered terrestrial plant species is exceeded for both monocots and dicots.

b. Atmospheric Deposition Assessment

Volatility as a route of field dissipation raises concerns about the atmospheric fate of atrazine, its aerial transport and whether aerial deposition poses the potential for risks to non-target terrestrial plants. The Lake Michigan Mass Balance study monitors all sources of inputs into Lake Michigan, including atmospheric inputs. In the 1970's and 1980's, atmospheric inputs were reported to be 24 percent of the total atrazine input into Lake Michigan and in the 1990's the atmospheric contribution was 29 percent (Russell Kreis, US EPA, Great Lakes National Program Office, Region 5; personal communication, dated 11/07/2000). The potential for adverse effects on sensitive, non-target crops and plants from atmospheric deposition is uncertain.

Atrazine concentrations in rainfall have been measured up to 3.5 $\mu\text{g/L}$ in Germany (Braun *et al.*, 1987). In 1990-1991, the 95th and 99th percentile atrazine levels in rainfall in the mid-west were reported to be 0.42 and 1.0 $\mu\text{g/L}$, respectively (USGS Fact Sheet FS-181-97). Capel *et al.* (1994) reported the frequency of detections and pesticide levels in rainfall from 1991 to 1993 in Minnesota; in 1991, atrazine was detected in 2 % of the samples with a maximum concentration of 0.82 $\mu\text{g/L}$, in 1992 it was 18 percent and 2.2 $\mu\text{g/L}$, and in 1993 it was 71 % and 2.9 $\mu\text{g/L}$. Subsequent 1994 monitoring data from 6 Minnesota sites around the state found detections in 93% of the samples (range: 86 - 100%) and a maximum level of 2.8 $\mu\text{g/L}$ (range of maximum levels: 0.74 - 2.8 $\mu\text{g/L}$). Atrazine concentrations in rainfall monitored in the Lake Michigan study ranged from ND to about 400 ng/L. At one Lake site, much higher atrazine levels were

believed to be an outlier (Russell Kreis, e-mail on 11/07/2000). Logic would suggest that atrazine concentrations in rainfall near Lake Michigan would be higher than the rainfall levels in Minnesota. Higher atrazine levels in rainfall would be consistent with the lake's proximity to and the prevailing winds from the corn belt just to the west and south, where USGS (Fact Sheet FS-181-97) has indicated the highest US poundage use of atrazine per square kilometer in the northern parts of Illinois and Indiana.

The Minnesota data for atrazine between 1991 and 1994 indicate a gradual increase in both the frequency of detection and the maximum concentration. Lake Michigan rainfall data also indicate increasing atrazine levels in rainfall from the 1970's through the 1980's and 1990's. Latest available data on atrazine concentrations in rainfall is from Lake Michigan in 1996.

d. Incident Reports

A number of incidents have been reported in which atrazine has been associated with some type of environmental effect with variable levels of certainty ranging from unlikely to highly probable. As of October 26, 2000, 109 incidents were listed in the Ecological Incident Information System (EIIS) files under atrazine: 4 cases are listed as highly probable, 40 as probable, 50 as possible, 13 as unlikely, and 2 as unrelated. Atrazine alone is not very toxic to the birds, mammals, and aquatic animals cited in most of these incidents. In none of these cases has evidence been provided that firmly demonstrate that atrazine has produced the reported effects. In only one incident (# I004021-004) was analytic analyses of the fish made for atrazine; many chemicals were identified and high profenofos levels were found in the fish and the organophosphate was determined to be responsible for the large fish kill. In many cases, the inference of these reported incidents to atrazine effects is likely due to the wide spread use of atrazine and the proximity of the atrazine application and timing to the occurrence to the incident. Having said this, synergism and indirect effects could explain how atrazine could have caused some of these incidents.

The majority of the incidents (about 40 percent of the "probable" cases) are listed as effects on corn mostly from corn applications. A number of the crop losses are large (50, 55, 56, 75 percent and a few "All" cases); other incidents cited acres lost: (3, 8, 12, 15, 17, 18, 18, 20, 50, 50, 50, 55, 60, 65, 65, 71, 80, 80, 82, 90, 100, 155, 240, 596, and 631 acres).

Forty incidents are considered "Probable," and four incidents are listed as "Highly Probable." The 4 incidents listed as "Highly Probable" include 3 home/lawn use incidents and 1 corn use incident. The corn use incident reported affecting 100 bass and 100 bream (# B000163-001) resulting from registered use. The three home/lawn incidents were lawn applications which affected grass; two were concluded to be misuse/accidental (# I005579-001, I005132-001). The third home incident (# I001910) was a registered EC use which affected grass and non-target plants.

The forty "Probable" incidents include: 16 (40 %) cases affecting corn; 11 (27.5 %) affecting grass; 11 (27.5 %) fish kills; 1 bird kill case ; and affects on ornamentals (2 cases), fruit trees (2

cases), berries (1), garden (1), oats (1), runoff killed vegetation around an atrazine/cyanazine-treated field and pond irrigation water killed greenhouse plants. Four “probable” incidents are classified as misuse (accidents): two cases from corn use (I005879-003, pears, raspberry and oats and I007371-013, grass and ornamentals); and two lawn misuse cases: I009445-031, grass; and I009445-029, bluegrass.

Analysis of 14 corn incidents occurring in 1999 which were submitted by Novartis indicates that in all cases, formulations of Bicep II (a mixture of atrazine and metolachlor) were used. The reported applications rates ranged from 1.4 quarts of atrazine /1.4 quarts of metolachlor to 2.6/2.6 quarts/A. Effects included distorted and cupping leaves, failure to unfurl, uneven height, chlorotic yellowing and necrotic leaves, and killed. Corn acreage affected was approximately 55 percent of 600 acres. There were 11 grass incidents resulting from home/lawn uses; three of these cases are considered to misuse (accidental).

Many fish species have been killed in these atrazine incident reports, including: bluegills, largemouth bass, catfish, quillback carpsucker, carp, redhorse, shad, bream, garfish, perch, minnows and crappie. In some incidents very large numbers of fish have been killed. Among the fish kill incidents classified as possible to highly probable, the following large fish kills and the state have been reported: a thousand bluegill and a thousand largemouth bass (DE: # I000116-002), 300 largemouth bass and 300 bluegill (DE: # B0000-300-28), 600 catfish (IL: # I001081-001), a thousand quillback carpsucker, a thousand carp and a thousand redhorse suckers (IL: # I005002-006), 100 bass and 100 bream (SC: # B000163-001), 2,000 perch (WA: #I010274-002), and a number of incidents cite “All” killed for bass, bluegill, catfish, crappie, etc. The frequency and magnitude of these fish kills are would not appear to be the result of direct toxic effects due to atrazine alone.

Given the low toxicity of atrazine to fish, the reason for the frequency of fish kill incidents is uncertain. About 60 percent of the reported fish kills listed under atrazine in the incident record occur during the Spring when atrazine is applied, soils are saturated and heavy rainfall is frequent. Heavy runoff may carry atrazine, other pesticides and organic loads into surface waters. The high volume and wide-spread use of atrazine increases the probability of co-occurrence of fish kills with atrazine applications. There are some other scenarios which may explain atrazine induced fish kills as well as causes unrelated to atrazine use.

Three plausible scenarios could exist in which atrazine applications may be responsible for the fish kills. First, atrazine concentrations in surface waters from runoff and/or spray drift may be much higher in shallow water adjacent to treated fields than estimated by EFED or found in monitoring studies. Second, atrazine in surface water may kill aquatic plants and the decaying process of dead plants may lower dissolved oxygen to levels too low for fish survival. Third, atrazine is known to increase the toxicity of organophosphate insecticides, such as chlorpyrifos, and a number of other pesticides which may have been applied earlier to atrazine-treated crops or applied in other fields upstream in the watershed.

Possibilities also exist that other causes, not atrazine, may be responsible for some or all of the

reported atrazine incidents. Heavy organic loads consume oxygen from the water as the organic matter oxidizes, thereby causing low dissolved oxygen levels which may cause fish to suffocate and die. Other pesticides in the watershed killed the fish as the water flowed past atrazine-treated fields. Since limited information is available in the atrazine incident records, such as water and tissue analyses, conclusions of responsibility would appear to be uncertain and the result of coincidence with little evidence for cause and effect.

The deaths of five Canada geese following an atrazine spray treatment on corn (# I008168-001) is also difficult to understand, unless atrazine was synergistic with or another corn pesticide was present, such as chlorpyrifos.

X. Reported Sub-Lethal Effects

Atrazine has been reported to cause sub-lethal effects in aquatic organisms and amphibians. These include endocrine effects in frogs at $\sim 0.1 \mu\text{g/L}$ and in largemouth bass at $\sim 50 \mu\text{g/L}$, as well as olfactory effects in salmon at $\sim 0.5 \mu\text{g/L}$. In addition, some studies have been conducted where these effects were not demonstrated. Following is brief summary of these reports.

Endocrine Effects

Frogs (Hayes *et al.* 2002)

Three replicates of thirty, 4-day old African clawed frog tadpoles (*Xenopus laevis*) were exposed to nominal atrazine concentrations of 0.01, 0.1, 1.0, 10.0 and 25 parts per billion (ppb) through metamorphosis (Hayes *et al.* in press) into adult frogs. Atrazine exposures had no effect on mortality, time to metamorphosis, length or weight at metamorphosis. Up to 20 percent (16 to 20%) of the male frogs exposed to ≥ 0.1 ppb atrazine had gonadal abnormalities including multiple testes and/or ovarian tissues within testes (hermaphroditism); no gonadal abnormalities occurred in controls.

Hayes *et al.* conducted a second experiment with atrazine tested at nominal concentrations of 0.1, 0.4, 0.8, 1.0, 25 and 200 ppb. Atrazine concentrations were confirmed in both experiments. No analytical results for either study were included in the pre-publication. Control males had larger laryngeal muscles than females at metamorphosis. In both studies, treated males had a threshold effect on reducing laryngeal muscle diameters (demasculinized) at ≥ 1.0 ppb compared to controls. Kendall's rank coefficient suggested a dose effect with increasing atrazine concentrations ($p < 0.01$). In addition, adult male and female *Xenopus* exposed to 25 ppb atrazine for 46 days suffered a 10-fold decrease in plasma testosterone. No raw data were available for statistical analyses.

Hayes *et al.* hypothesized that atrazine induces aromatase and promotes the conversion of testosterone to estrogen. This disruption in steroidogenesis via induction of aromatase is hypothesized as a likely explanation for the 10-fold decrease in plasma testosterone, demasculinization of the male larynx and the production of hermaphrodites.

Hayes reported collection and analyses of leopard frogs (*Rana pipins*) at 7 sites in the west and mid-west states. One hundred frogs were collected at each site with about 50 percent males. In atrazine-treated areas in the mid-west states, 100 percent of the male leopard frogs had gonadal abnormalities. At the two western sites, no gonadal abnormalities were found in leopard frogs (Hayes, T. B., A. Collins, M.Lee, M. Mendoza, N. Noriega, A. Ali Stuart, and A. Vonk. 2002. National Academy of Science USA 99(8): 5476-5480, and personal communication Hayes, 2002).

Frogs (Syngenta)

Syngenta in an oral presentation to EPA staff also provided test results from atrazine studies on the African clawed frog. There were no effects on the sex ratio of frogs exposed to atrazine concentrations of 0.01, 0.1, 1.0, 10 and 25 ppb during critical phases of development (undefined periods). The results of their study were reported as follows: “The ethanol solvent control exhibited significant activity on the frogs including effects on mortality, length, and development time. The possible confounding effect of ethanol within all treatments including atrazine is not known. There was no convincing evidence that atrazine increased the larynx cross-section area, although statistically significant differences were noted, especially in the 25 ppb group, and at high doses in various *ad hoc* tests performed. Unequal group sizes and other potential confounding study design elements further complicate interpretation. In addition, variability in the time course of frog ontogeny and potential tank effects, coupled with the lack of an ‘estrogen’ positive control group, prevented clear conclusions to be drawn from this preliminary study. Additional statistical analyses and studies are planned to further investigate these questions.”

Thirty larval frogs per replicate and 3 replicates per treatment were exposed via test vessel solutions for approximately 60 days until metamorphosis was complete. Atrazine concentrations in the ethanol solution were 0.01, 0.1, 1.0 10.0 and 25 ppb and test solutions were renewed every three days. Analytical measurements of atrazine indicated recoveries ranging from 69 to 117 percent of nominal concentrations (no details were provided on the recoveries for each replicate at the beginning and end of the three day periods).

The information on the Syngenta study did not provide any raw data. It is obvious that the level of ethanol in the Syngenta study was too high because it caused mortality and growth effects. The ethanol concentration was not reported and the number of mortalities were not reported. When the solvent controls demonstrate effects, the results of the study are compromised and the study is invalid. The ANOVA test should not have been used to test for enlarged laryngeal diameters, when smaller laryngeal diameters were the probable test result for treated male frogs.

Atrazine effects on tadpoles are a concern because atrazine use coincides with spring rains and the breeding season for amphibians. While these gonadal abnormalities and laryngeal alterations raise concerns about adverse effects on amphibian reproduction, there is no conclusive evidence that these changes have an adverse effect on amphibian reproduction. Additional testing with atrazine-treated tadpoles and adult frogs should be conducted to determine what, if any, effects

occur on reproduction.

Largemouth Bass (Syngenta - Wieser & Gross, 2002)

Adult largemouth bass (*Micropterus salmoides*) were exposed to nominal concentrations of technical grade atrazine (purity 97.1%) at 0, 25, 35, 50, 75, and 100 $\mu\text{g/L}$ for 20 days to determine the potential effects on endocrine function. Additionally, bass were exposed to commercial grade (purity 42.1%) atrazine at 100 $\mu\text{g/L}$. After 20 days, plasma concentrations of estradiol, 11-ketotestosterone, testosterone, and vitellogenin (a protein that serves in yolk formation) were measured.

Although the study concluded that atrazine treatment did not affect plasma steroid or vitellogenin levels, EFED believes that the study is confounded by the high level of variability in the test results. However, the results show that in spite of high levels of variability, atrazine treatment significantly increased plasma estradiol in females and significantly decreased plasma 11-ketotestosterone in males. Additionally, although not statistically significant, vitellogenin levels in atrazine-treated female fish appeared to be elevated relative to controls. The presence of quantitative levels of plasma vitellogenin in male bass is of particular concern since the protein is normally only expressed in females; males can be induced to synthesize vitellogenin if exposed to an estrogenic compound. Furthermore, the formulated endproduct appeared to have enhanced effects on plasma steroids and vitellogenin levels relative to technical grade atrazine. These data further substantiate EFED's concerns regarding the endocrine disrupting potential of both technical grade atrazine and its formulated endproduct.

Previous studies examining the endocrine disrupting potential of both technical and commercial grade atrazine have shown that atrazine exposure increased plasma estradiol. Additionally, treatment with commercial atrazine increased plasma vitellogenin levels and decreased plasma testosterone levels at concentrations greater than 50 $\mu\text{g/ml}$ (Gross *et al.* 1997; Grady *et al.* 1998). The current study was undertaken to examine more environmentally relevant doses and exposure routes. To that end, reproductively mature (approximately 2 year old) Florida strain largemouth bass were exposed to technical grade atrazine using a static renewal, no flow system at concentrations ranging from 0 to 100 $\mu\text{g/L}$ and to commercial grade atrazine at 100 $\mu\text{g/L}$. After 20 days, plasma steroid and vitellogenin levels were measured. Vitellogenin has been recommended as a biomarker for measuring exposure to environmental estrogens since it is a sex-specific protein that is normally synthesized in yolk-producing females following its induction by estrogen; males fish do not typically synthesize vitellogenin unless exposed to an environmental estrogen.

In the current study, female bass treated with 100 $\mu\text{g/L}$ formulated atrazine contained significantly higher plasma estradiol and exhibited plasma vitellogenin roughly 37 times greater (260 $\mu\text{g/ml}$) than controls (7 $\mu\text{g/ml}$). Male bass treated with 100 $\mu\text{g/L}$ formulated atrazine contained significantly lower plasma 11-ketotestosterone. While not statistically significant, plasma testosterone (286 pg/ml) was lower than controls (433 pg/ml) and plasma vitellogenin (42 $\mu\text{g/ml}$) was 7 times greater than controls (6 $\mu\text{g/ml}$). Male plasma estradiol in atrazine-

treated fish was not significantly different than controls; however, levels of estradiol in male fish were surprisingly high. Although there was considerable variability in plasma vitellogenin levels, atrazine-treated fish appeared to have elevated plasma vitellogenin relative to controls at 50 and 100 $\mu\text{g/L}$ of atrazine. Plasma 11-ketotestosterone was significantly lower in fish exposed to atrazine concentrations greater than 35 $\mu\text{g/L}$. Treatment of fish with commercial grade atrazine resulted in a significant increase in plasma estradiol in female fish and a significant decrease in 11-ketotestosterone in male fish. Although not statistically significant, plasma vitellogenin in both female and male fish appeared to be increased in fish treated with technical and commercial grade atrazine.

Although high variability confounds this study's ability to resolve the effects of atrazine on plasma steroids and vitellogenesis, the study has demonstrated that technical grade atrazine affects plasma 11-ketotestosterone in males and that the formulated product affects plasma estradiol in females. The non-guideline study is classified as supplemental and provides useful information on the potential effects of atrazine on endocrine-mediated pathways. (MRID 45622304).

Mammals (tabulated HED studies)

Based on mammalian chronic studies, the Human Health Effects Division (HED) has concluded there is evidence that atrazine is associated with endocrine disruption. Direct measurements of norepinephrine, dopamine, and GnRH, and of serum hormones such as certain steroid hormones and luteinizing hormone, as well as changes in estrous cycling and histomorphologic changes in hormone responsive tissues, indicate neuroendocrine disruption.

Daphnia Pulicaria

In a *Daphnia pulicaria* study, the females did not yield males at any atrazine level (i.e., 0, 0.93, 4.1, 8.7, 444, 87 $\mu\text{g/L}$). This study indicates that atrazine does not produce endocrine effects in offspring of female *Daphnia pulicaria* exposed to likely atrazine concentrations for up to 12-days.

Turtles and Alligators

Atrazine was tested on eggs of the red-eared slider turtle (*Pseudemys elegans*) and the American alligator (*Alligator mississippiensis*) to determine if atrazine produced endocrine effects on the sex of the young. The turtle and alligator eggs were placed in nests constructed of sphagnum moss treated with 0, 10, 50 100 and 500 $\mu\text{g/L}$ for 10 days shortly after being laid. The test temperatures, 27.3°C for the turtle and 32.8° for alligators, were temperatures which normally yield all male young. No adverse effects were found. Analysis of the embryonic fluids indicated that no atrazine was present in the eggs at detection limit (0.5 $\mu\text{g/L}$). Under these conditions, atrazine does not appear to be an endocrine disruptor. The two non-guideline studies are classified as supplemental and provide useful information on the potential effects of atrazine on endocrine-mediated pathways (MRID 455453-03 and 455453-02).

Olfactory Effects

Salmon

Moore and Waring (1998) report atrazine effects on reproductive endocrine function in mature male Atlantic salmon (*Salmo salar* L.) parr exposed to nominal concentrations of 0.5, 5, 10, and 20 $\mu\text{g/L}$, which were collected and measured at the end of the test. The measured levels are reported as 0.04, 3.6, 6.0 and 14.0 $\mu\text{g/L}$ which are 8, 72, 60, and 70 percent of nominal, respectively. There appears to be uncertainty about the test concentrations, since the water samples were collected only after the test period and the authors concluded that atrazine in the water samples suffered rapid degradation as the result of an unavoidable delay in being analyzed. The male parr exposed to nominal atrazine levels of $\geq 0.5 \mu\text{g/L}$ responded to female hormones in urine with reduced priming effect on milt and the plasma 17,20 β -dihydroxy-4-pregnen-3-one levels. The priming effect of urine on plasma testosterone and 11-ketotestosterone concentrations was found at $\geq 3.6 \mu\text{g/L}$ and $\geq 6.0 \mu\text{g/L}$, respectively. Atrazine affected the accumulation of steroids in bile and directly impacted upon the testes, modifying 17,20 β -dihydroxy-4-pregnen-3-one and androgen secretion. The guideline requirement (72-5) is fulfilled by the brook trout study (MRID 00024377).

XI. Endangered Species Concerns

The Agency has developed a program (the “Endangered Species Protection Program”) to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that will eliminate the adverse impacts. At present, the program is being implemented on an interim basis as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989), and is providing information to pesticide users to help them protect these species on a voluntary basis. As currently planned, but subject to change as the program is developed, the final program will call for label modifications referring to required limitations on pesticide uses, typically as depicted in county-specific bulletins or by other site-specific mechanisms as specified by state partners. A final program, which may be altered from the interim program, will be described in a future Federal Register notice. The Agency is not imposing label modifications at this time through the RED. Rather, any requirements for product use modifications will occur in the future under the Endangered Species Protection Program.

Levels of Concern for Endangered species are exceeded for terrestrial plants and vascular aquatic plants. Risk quotients exceed the levels of concern for endangered terrestrial plant species from spray drift and from runoff into both terrestrial and semi-aquatic plants.

In general, risks to birds, mammals, and beneficial insects are not anticipated from direct effects of atrazine use. However, the use of atrazine or any herbicide could have adverse chronic effects on terrestrial and aquatic plants in areas adjacent to treated fields that would have indirect effects on these animals from the loss of food sources and the loss of vegetative habitat for cover, reproduction and the survival of offspring (Freeman and Boutin, 1994).

Acute levels of concern for endangered species are exceeded for aquatic invertebrates for all crop uses, except for the typical use rate on corn (1.1 lbs ai/A). Chronic levels of concern for endangered species are exceeded for fish and aquatic invertebrate reproduction for all use rates, except for corn and the typical use rate on sorghum. However, Kettle et al. (1987) demonstrated severe effects on aquatic vegetation and indirect effects on fish reproduction and invertebrate populations exposed to 20 $\mu\text{g/L}$ of atrazine in artificial Kansas ponds. Atrazine effects in the ponds included 60 to 90 percent reduction in vascular pond vegetation and the loss of three plant species, significant reductions in aquatic macro-invertebrate populations, a significant reduction in food consumption by adult bluegills, and a 96 percent reduction in the number of young bluegill. It is likely that reductions in the number of macro-invertebrates are due to the loss of vegetative cover to avoid predators and that bluegill young were eaten due to limited vegetative cover and the reduced availability of food (i.e., aquatic invertebrates) for adult fish species. Atrazine levels of 20 $\mu\text{g/L}$ found in streams and rivers are not unlikely to occur in ponds, marshes and lakes which may adversely affect aquatic vegetation, such that the loss of the vegetative habitat could affect populations of endangered aquatic invertebrates and the recruitment of young endangered fish species.

The potential adverse effects of atrazine effects on homing and reproduction in endangered salmon and other anadromous fish species is currently uncertain. The laboratory study of olfactory function in mature Atlantic salmon parr and the effect of atrazine in the range of 0.5 $\mu\text{g/L}$ for sensing female hormones in urine and behavior to ground salmon skin is notable. This is so especially if the effects are significant on salmon reproduction at such a low atrazine concentration, because existing concentrations in streams inhabited by endangered salmonids may exceed this level for prolonged periods. Atrazine concentrations are likely to be their highest in the late spring and early summer following applications, at a time when salmon are returning from the ocean to spawn. It is unclear from the results of the test by Moore and Waring (1998) whether the effect on olfactory function is manifested in mature adult salmon and what effect it might have on reproduction and recruitment. These data are preliminary and additional studies are necessary to determine if there are adverse atrazine effects on adult salmon homing and adult male milt production responses to female hormones in ovulating female urine. Further study is also needed on whether those effects could be significant to reproduction and recruitment.