Atrazine Ecological Monitoring Program Subgroup: Recommendations for Monitoring Design

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The ideas and recommendations of the Atrazine Ecological Monotoring Program Subgroup members listed below have been used to design a monitoring program for evaluating the impacts of atrazine on aquatic communities. EPA has integrated the concepts and recommendations from the subgroup into this summary report.

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Recommendations

The Atrazine Ecological Monitoring Subgroup used the USGS Watershed Regression on Pesticides (WARP) model to identify those watersheds (at a HUC-10/11 scale) with flowing water bodies that are predicted to be most potentially vulnerable to atrazine surface water loading. These vulnerable watersheds reflect atrazine use on corn and sorghum. The subgroup then identified 40 watersheds that give a statistical representation of a tier of 1172 most potentially vulnerable watersheds. As described in the guidelines below, monitoring sites will be located in flowing water bodies within these 40 watersheds. Two years of monitoring results from these sites will be compared to the four screening trigger values identified by the Atrazine MOA Ecological Subgroup. Based on this comparison, the Agency will evaluate the need for additional monitoring and/or mitigation actions in the 40 HUC-10/11 watersheds and the implications for the larger set of 1172 watersheds. The subgroup will identify additional monitoring locations in sugarcane areas by the spring of 2004. In addition, the subgroup is evaluating existing information to develop a strategy on how to approach monitoring in static water bodies and estuaries.

Introduction

This document briefly describes the goals, scope, and methods for selecting and monitoring vulnerable watersheds and water bodies, as well as the supporting rationale that the subgroup used in reaching recommendations for an atrazine ecological monitoring program. This work reflects a joint effort lead by the Office of Pesticide Programs (OPP) in coordination with the following EPA offices and groups:

- EPA Office of Water's (OW) Office of Wetlands, Oceans, and Waterways (OWOW) and Office of Science and Technology (OST);

- EPA Office of Research and Development (ORD) research groups from Corvalis, OR and Duluth MN;
- and Syngenta Crop Protection, Inc.

The group worked together to identify watersheds that are most likely to be vulnerable to atrazine impacts in flowing water bodies, and to select a subset of those watersheds for monitoring that will allow EPA to make inferences to the larger population of watersheds vulnerable to atrazine runoff. The steps taken in developing this monitoring program were approved by those in OW who administer the Total Maximum Daily Load (TMDL) program under the Clean Water Act as well as those in OPP who administer FIFRA. The outputs from the subgroup reflect a coordinated and consistent approach to the issues for these two program offices.

The purpose of this atrazine monitoring program is to identify the percentage of water bodies located in the most potentially vulnerable watersheds (based on use intensity and runoff vulnerability) that exceed a designated effects-based trigger. The trigger, which reflects both magnitude and duration of exposure, is based on impacts to the primary producers in the aquatic plant community and the subsequent impacts to the community structure. The monitoring program will also gather additional information on atrazine use and practices, watershed and water body characteristics, and other factors to facilitate identifying water bodies beyond the initial sampling pool that have the potential for atrazine loadings that exceed effects-based thresholds. A water body that exceeds the trigger(s) will be considered a candidate for load reduction. Anticipated actions include continued monitoring and analysis of loading source(s), contact with states and other Federal agencies, such as USDA, to determine if practices or programs exist that will reduce the atrazine load, and implementation of best management practices or other regulatory options to bring the water body into compliance with the effects-based atrazine thresholds. Additional monitoring will also be required to evaluate the effectiveness of the mitigation actions. The initial focus of this monitoring program is on flowing water bodies in the most vulnerable watersheds. The results of this survey and evaluation of other information will determine the extent to which additional water bodies may need to be surveyed.

Goals for Monitoring Sub-Group

At the beginning of the monitoring study design process, OW and OPP worked with EPA's regional monitoring coordinators to identify the critical management questions that need to be addressed in the atrazine monitoring program. The subgroup was charged with designing a monitoring program that could answer these management questions:

(1) To what extent are waters exceeding effects-based thresholds for atrazine?

The program will initially focus on flowing waters in vulnerable watersheds. The extent of exceedances will be quantified in terms of X% of watersheds having flowing water bodies that exceed the trigger with Y% confidence.

(2) Where are the waters that are exceeding effects-based atrazine thresholds?

Based on results of monitoring study, EPA will be able to identify other watersheds of likely concern. The focus is to develop criteria that will help states identify water bodies in which atrazine loads exceed effects-based thresholds.

(3) Once waters with atrazine levels that exceed effects-based thresholds are identified, mitigation will be pursued through registrant actions or the TMDL process. What level of

reduction in atrazine loading is necessary to meet effects-based thresholds? What activities, implemented when, will achieve necessary reductions?

Results of the monitoring program will assist in identifying the nature of exceedance and the types of activities that will be needed to reduce atrazine loads. Over the period of the study, the subgroup will determine an appropriate time frame to allow for the remediation measures to positively impact the watershed.

Scope of Eco-Monitoring Program

Given the complexity of the task and the tools used to achieve the outcome of the effort, the monitoring subgroup focused the initial program on flowing water bodies representing potentially vulnerable watersheds in the corn- and sorghum-producing areas. Besides the 40 sites representing these watersheds, the subgroup has agreed to continue its work in several other areas listed below:

1. **Static Water Bodies** - EPA and Syngenta have agreed to review the raw water data on atrazine concentrations collected from the approximately 140 Community Water Systems that are being monitored for human health concerns. In addition, Syngenta will provide historical data from the Novartis Voluntary Monitoring Program (VMP) sites. The CASM model which was used for flowing water is amenable to use in static water bodies, and the subgroup must determine on a statistical and ecosystem basis how these CWS monitoring data represent other static water bodies. This information will provide the basis for developing a monitoring strategy for static water bodies.

2. **Sugarcane Use Area and Estuaries** - The sugarcane use area is a unique situation which has clear freshwater and estuarine issues. Syngenta and EPA will work to develop a strategy to select the most appropriate locations and number of sites for monitoring atrazine in sugarcane growing areas. The selection of sites and protocol for monitoring in the sugarcane areas will be completed by March 15, 2004. Before recommending a monitoring program for estuaries, OPP will discuss this issue with the Oceans and Coastal Protection Division in OWOW, and the subgroup will review all relevant data such as the Louisiana monitoring data to confirm whether it reflects estuarine residue patterns. The subgroup will need to determine the role of dilution and transport in estuaries and gather information on these parameters by looking at nitrate concentrations or some other chemical marker to determine how to approach an estuary monitoring program. This analysis will be completed by March 15, 2004.

Identification of Vulnerable Watersheds

This section provides a brief synopsis of the steps used to identify those watersheds that are expected to be most potentially vulnerable to atrazine loading. Details and documentation will be provided in future reports prepared by Syngenta and Waterborne Environmental.

Watershed Vulnerability Assessment: The workgroup identified the 5th level of the hydrologic unit boundary scale – commonly referred to as HUC10 or HUC11 – as the workable scale for evaluating the vulnerability of watersheds to atrazine loading. Hydrologic unit boundaries define the areal extent of surface water drainage to a point, and may be mapped at different scales. On a broad scale, the Mississippi River Basin represents a hydrologic unit boundary. Hydrologic unit boundaries can be delineated for each river that flows into the Mississippi, and for increasingly smaller tributaries farther upstream. The hierarchical system of mapping

watersheds established by the USGS now includes six levels, with national maps available for the fiirst four levels. An in-depth description of the classification system can be found at the USDA NRCS Watershed Boundary Dataset website [http://www.ftw.nrcs.usda.gov/huc_data.html]. The HUC-10/11 watershed (5th level) level used for this assessment represents watersheds that are typically 40,000 to 250,000 acres in size. Because the mapping at this level is not available for all states, the workgroup collected the best available coverages for the states in which atrazine is used.

The initial analyses identified three tiers of watersheds relevant to atrazine use in corn and sorghum. The first tier consisted of approximately 10,000 HUC-10/11 watersheds in which atrazine was used on corn and sorghum. The subgroup calculated atrazine use intensity on a county basis using the average of the last 5 years (1998-2002) from Doane's Agricultural Services. The subgroup generated a second tier of 5,860 HUC10/11 watersheds that intersected counties with use intensities of 0.25 lb ai/county acre or higher. The vulnerability to atrazine loading in this tier of high-use watersheds was evaluated using USGS' WARP (Watershed Regression for Pesticides) model. The WARP model integrates use intensity, watershed area, soil susceptibility to runoff and rainfall intensity with available water monitoring data. Based on a comparison of available surface water monitoring data with WARP estimates, the subgroup determined that the highest 20% of vulnerable watersheds identified using WARP provided a meaningful distinction of vulnerable watersheds for monitoring site selection. This resulted in a third tier of 1,172 watersheds identified as the most potentially vulnerable to atrazine loading.

Representative Sampling of Vulnerable Watersheds: From the tier of most potentially vulnerable watersheds, the subgroup selected a representative sample for monitoring. After evaluating several options for selecting a representative sample of watersheds from this tier, the subgroup decided on an approach that would result in a set of geographically dispersed sites that were stratified in a manner that would optimize the chance of finding sites with the highest atrazine concentrations to monitor. The 1,172 HUC-10/11 watersheds were stratified into two WARP categories and 40 were selected with a probability proportional to atrazine use. Watersheds that were selected were also spatially balanced across the corn and sorghum use area. The selection process is adapted from ORD's generalized random tessellation stratified (GRTS) process. This was developed as part of EPA's EMAP program; more information is available at the ORD/NHEERL Aquatic Resource Monitoring web site, http://www.epa.gov/nheerl/arm. Since this departure from simple random sampling has some sampling variability built into the process, survey "error" will be an important component of the uncertainty analysis in evaluating the results of this study. This is addressed briefly in a later section.

***General Information on the 40 Watersheds Selected*:** The subgroup selected 40 watersheds in 10 states: Ohio, Indiana, Kentucky, Illinois, Iowa, Missouri, Nebraska, Minnesota, Tennessee, and Louisiana. The selected watersheds averaged 129 square miles in size, with a median size of 121 square miles and a 75th percentile size of 186 square miles. The smallest watershed was 8.2 square miles, while the largest was 333.9 square miles. Twenty-seven watersheds were headwater watersheds with no upstream surface flow contribution from the main stream channel from outside the watershed. Five watersheds have existing monitoring data: two from USGS NAWQA and two from previous Syngenta monitoring programs. Twelve watersheds are in current NAWQA units; none of the watersheds include Community Water Systems in the current Atrazine Monitoring Program for surface water sources of drinking water.

Selection of Water Bodies for Sampling

After identifying the watersheds to be sampled, the workgroup developed criteria for identifying an index monitoring within the watershed. Details of the selection process will be available in Syngenta's study protocols documents. This section briefly summarizes the major steps used to identify water bodies for sampling within the watershed.

The cumulative flow accumulation along the stream drainage network was derived from the National Elevation Dataset, NED (USGS has created several nationwide coverages of elevational derivatives, available through the EROS Data Center web page). The flow direction grid describes the direction of the flow of water across a landscape and can be used to estimate the cumulative area above any point in a drainage network (flow accumulation) through a procedure that sums the number of grid cells "upstream" of each point. Stream networks of sufficient size to support perennial flow were identified by this method.

This process also accounted for the number of flow cells that intersected with row crop area (as identified by the National Land Cover Dataset). Thus, the cumulative flow accumulation and the percentage of that flow accumulation under row crop was calculated for each stream segment.

The criteria for selecting stream segments for monitoring focused on stream segments relevant to study goals, e.g., sub-watersheds with higher row-crop densities (and, thus, higher likelihood of atrazine use) and sub-watersheds with minimal urban influences. The selection process also avoided sub-watersheds that may be subject to major annual variation in atrazine load as a result of crop rotation or highly "flashy" hydrology which may minimize longer atrazine exposures.

The subgroup's final eligible stream selection criteria were as follows:

- Minimum drainage area of 9 sq miles
- Maximum drainage area of ½ the HUC11 watershed, unless total watershed area is less than 50 sq. miles. If total HUC11 area is less than 50 sq. miles, tributaries of larger streams will be manually identified
- Percent Urban Accumulation less than 10%
- Upper 50th percentile of Percent Crop Accumulation

The subgroup selected stream segments with maximum drainage areas that would (1) exclude major river stems running through the interbasin HUC10/11 watersheds, (2) avoid larger streams/rivers (5th and 6th order) within larger HUCs, and (3) allow for a sufficient watershed size to minimize the likelihood of monitoring data distortion due to annual crop rotation changes.

All eligible stream segments were ordered randomly for field evaluation. The field crew will begin at the most downstream point of the first randomly-ordered segment and work upstream until a suitable sampling site is located. If no suitable location is found for the first segment, the process will be repeated for the next randomly selected segment until a suitable site is located. The site and associated watershed will be characterized using field information and the site selection report will be submitted to EPA for approval.

The key element in evaluating the sites is to get a quick read on any site characteristics which could render a site ineligible. Field verification is necessary since the base data for identifying candidate sites is not at such a detailed local scale. The field evaluators will screen out areas with low corn agriculture, a prevalence of herbicide-tolerant corn or other use of herbicides other than atrazine, point sources such as pesticide distributors, or other anomalies.

Monitoring Study Design

Characteristics of the monitoring study design are described below:

- **Timing**: The monitoring study will begin at the first 20 sites in 2004 and for the second 20 sites in 2005. Each site will be monitored for two years. The sampling will start early enough to capture the first runoff events, and continue until the end of the growing season.

- **Sampling Frequency**: A fixed 4-day interval will be followed for sampling at all sites. Twenty-five percent of the sites (5 for each 20) will also be monitored daily during the first 2 or 3 runoff events after 50% of corn and/or sorghum has been planted in the specific watershed.

- **Data Collected**: The study will collect and analyze the atrazine concentrations and daily flow rates. In addition, Syngenta will survey and obtain current and historical environmental and agronomic data, including planting, harvesting dates and atrazine application information for each sampling watershed.

The study protocol with detailed study design information will be provided by Syngenta and reviewed by EPA.

Laboratory Analysis, Data Reporting, and Quality Assurance

The atrazine residues in water will be analyzed using an immunoassay method to determine the parent concentrations with a level of detection (LOD) of 0.05 ppb. While the immunoassay method will be validated with the traditional GC/MS method for the CWS monitoring program, Syngenta does not plan to conduct additional validations with the ecological monitoring program.

As with all monitoring programs, quality assurance and quality control (QA/QC) processes will be implemented and documented to assure the validity of the data collected. The scope of data is not limited to the water analyses and will include the GIS data and metadata sets used in the design of the monitoring sites selection.

In addition to submitting the data in report form, Syngenta will also provide the data in electronic form. After the data have been reviewed and approved by EPA, it will be stored in EPA's STORET database.

Analysis of Monitoring Results

Monitoring results from each of the two years of sampling at the initial 40 sites will be compared to the concentration and duration triggers derived by the Ecological MOA Subgroup, and will also be used to run the CASM model to improve the confidence that the triggers have been met. Three outcomes are possible for any individual year of sampling at a site. The results may clearly indicate that the 5% CASM Community Sensitivity Index (CSI) trigger was or was not exceeded. However, given the uncertainty inherent in periodic sampling described below, it is also possible that the results do not clearly indicate whether or not the 5% CSI level was reached. That is, the uncertainty bounds around the concentration and duration of atrazine in the chemograph straddle the 5% CSI regression line.

The combination of these results from two years of sampling will determine the need for further action at each of the 40 sites. If both years of data indicate that the 5% CSI has been reached, the sampled water body representing its HUC11 is considered to have exceeded the effects-based atrazine thresholds. If both years indicate that the 5 % CSI was not attained, Syngenta can conclude its sampling in that HUC11. If the two years of sampling result in mixed, or uncertain results, then further monitoring and possibly other watershed management activities would be appropriate.

As described below, the uncertainty introduced by year-to-year differences in use and rainfall will be considered when analyzing data from the 40 initial HUC11 watersheds. This will allow Syngenta and the Agency to put sampling results in context, whether or not they indicate that the level of concern has been reached. If the confidence in monitoring results are rendered less certain by climatic and use conditions during the two sampling years, further monitoring in effected sites may be necessary.

Discussion of Uncertainty

Any analysis of the results must characterize and properly account for the following sources of uncertainty:

- **Frequency of sampling (magnitude/duration of atrazine in waters)**
  Because sampling at 4-day intervals has a 75% probability of missing the peak concentration on any particular day, nearly any calculated time-weighted concentration will likely be less than the actual time-weighted concentration by some unknown amount. The subgroup will need to determine the best way to calculate the rolling averages. Linear extrapolation (connecting the dots) between intervals is not the appropriate model in this instance. Results from the daily monitoring during runoff events (for the 5 sites in each starting year) will help the subgroup determine the extent of uncertainty around the fixed-interval estimates, and how they may differ for the 14, 30, 60, and 90-day periods. Any model used to estimate concentrations between intervals, however, must be peer-reviewed and receive a favorable recommendation before it can be used.

- **Year-to-year variations in rainfall, use, and other factors**
  There is also an element of temporal variability involved in any sampling program that occurs over a period of time, especially one that spans a period of more than one year. In order to account for this temporal variability (e.g., rainfall, drought, runoff, use), it is desirable to collect samples over a range of seasons, weather, and environmental conditions. One year of drought may result in atrazine levels in surface water that greatly underestimate a given local average, while a very wet year may show levels that greatly exceed the same level. For these reasons samples will be collected for at least two years in order to determine the natural variability inherent in the monitored chemical levels. This variation will be considered in establishing the overall characterization of the watershed.

- **Sampling and analysis error**
  Another major type of variability in a monitoring project is associated with the variability from sample collection and analysis. Standard QA/QC procedures and Good Laboratory Practices (GLP) protocols will apply to all aspects of this project, and in particular to the collection, chain-of-custody, laboratory and reporting phases. These will address and characterize uncertainty in those areas of the study.

- **Survey error**
  In this survey a sample of 40 watersheds have been selected to make statistical inferences about a larger population of vulnerable watersheds. In any survey which employs a "statistical sample" to represent a larger population, there are procedures for calculating an 'unbiased estimator' of the characteristic of interest (e.g., for the mean CSI of the larger population, or for what percent of the larger population has a CSI greater than 5%). These calculations also provide a 'variance' around the estimator that is part of the uncertainty involved in making statements about the larger population. The uncertainty inherent in these calculations does not depend on the relative sizes of the sample and the population it is representing, but rather on the sample size only. A larger sample will have more precise (tighter) 'confidence' intervals around its estimates of the population than a smaller one, where the upper and lower bounds on these estimates can encompass a wide range of the population. These calculations and those inherent in 'drawing' the sample will be used to provide population estimates and to report the precision associated with them.