



Protocol for Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds

June 2007

Enclosed is the protocol for the following study:

**Atrazine Ecological Exposure Flowing Water Chemical
Monitoring Study in Vulnerable Watersheds**

The enclosed protocol was signed at the initiation of the study. Some of the study information and study procedures have since been added or altered through formal Protocol Amendments, which have been issued in adherence to the rules of Good Laboratory Practices.

STUDY PROTOCOL

Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in
Vulnerable Watersheds

Data Requirement

Atrazine Interim Registration Eligibility Decision – January 31, 2003

Sponsor/Testing Facility

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Conducted By

Waterborne Environmental, Inc.

Study Identification Numbers

Syngenta Study No.: 1508-03
Contractor Study No.: 242.71

PRINCIPAL STUDY PERSONNEL -

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PROTOCOL SIGNATURES

Title: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds

Syngenta Study No.: 1508-03

Contractor Study No: 242.71

Proposed Experimental Start Date: November 5, 2003

Proposed Experimental Termination Date: May 1, 2004

Principal Field Investigator, Waterborne Environmental, Inc.:

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11/20/03
Date

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Quality Assurance, Quality Associates, Inc.:

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11/25/03
Date

Study Director, Syngenta Crop Protection:

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November 6, 2003
Date

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Management, Syngenta Crop Protection:

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11/12/2003
Date

[Redacted Line]
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ATRAZINE ECOLOGICAL EXPOSURE FLOWING WATER CHEMICAL MONITORING STUDY IN VULNERABLE WATERSHEDS

1.0 INTRODUCTION/OBJECTIVE

The objective of this study is to select, characterize, and measure atrazine concentrations in flowing water bodies at forty locations representative of 1172 watersheds highly vulnerable to agrochemical runoff from corn and sorghum agriculture arising from non-point sources. In addition to the residue concentration, the corresponding duration of each atrazine exposure event is a key endpoint of this study. The resulting atrazine runoff concentration and event duration data will be compared against Ecological Levels of Concern (LOC).

The forty corn and sorghum watersheds are representative of a population of 1172 watersheds (largely delineated at the HUC10/11 level) identified to be in the upper 20th percentile of vulnerability for agrochemical runoff as defined by watershed specific calculations using the Watershed Regression for Pesticides (WARP) algorithm developed to represent the 95th percentile annual atrazine concentration in flowing water bodies. The 1172 watersheds were selected from a pool of 5860 watersheds totally included within or intersecting with eleven "core" atrazine use states as well as those watersheds included or intersecting counties in a further 26 atrazine use states that fall into the upper 45th percentile of counties ranked by atrazine cropped area use intensity across the USA.

Within each watershed eligible river segments were identified using USEPA approved criteria related to watershed size, crop density, and urban percentage. If there was more than one eligible segment, one was chosen at random from that watershed's pool of eligible segments to represent the HUC10/11.

Additionally, four sites (two in Florida and two in Louisiana which will be selected by a process different from the one described above) will be selected according to this protocol except that the crop of interest will be sugarcane.

Single grab samples will be taken every four days from all sites and additionally, at ten of the sites, more frequent additional daily composite samples will be taken automatically during periods of high flow resulting from runoff within the watershed. These water samples will be analyzed for parent atrazine using US EPA approved immunoassay procedures with a level of determination of around 0.05 ppb. Flow measurements (or estimates in the absence of suitable channels and/or flumes) will be taken at suitable sites and a proportion of samples will be analyzed for total suspended solids.

Half of the monitoring sites will be monitored in the 2004 and 2005 seasons while the other half will be monitored in the 2005 and 2006 seasons. Monitoring at each site will start well in advance of the first application of atrazine to the watershed and will

continue until approximately 120 days after local estimates suggest that approximately half of the corn fields in the watershed have been treated with herbicides. At sites with additional flow driven sampling, the additional sampling will be continued for 60 days or until the first 2 or 3 major runoff events have been sampled after the same time point.

Tillage, cropping, maintenance, mitigation and chemical application in the watersheds will be performed by landowners, farmers and tenants following typical local practice. This study design call for careful observation and consultation with farmers, landowners and other stakeholders on a voluntary basis to develop the best available understanding of the management of the watershed during, and in the years preceding, the study.. Of particular importance will be efforts to estimate the amount of atrazine applied in the watershed and the timing of its application. Where necessary and feasible, particular attention will be paid to the sub-watershed(s) contributing most significantly to the flow at the sampling point. In addition, a detailed watershed map will be created using the best available data sources and combined with detailed soil, cropping and mitigation data in a geographic information system (GIS). In addition, local weather station data and, where necessary, data from automated weather stations installed as part of the study will be used to help interpret study findings.

This study design calls for careful consultation with agricultural chemical dealers and salespeople on a voluntary basis to develop the best available understanding of the management of the watershed during, and in the years preceding, the study. Of particular importance will be efforts to estimate the amount of atrazine applied in the watershed and a verification of the percent of row crop that is corn and sorghum. Where necessary and feasible, particular attention will be paid to the sub-watershed contributing the flow at the selected sampling point

The atrazine residue data generated in the study will be recorded in the STORET database. The results from each site will be reported annually by December 15th of each year.

Since the information about atrazine use and corn/sorghum cropping density will be collected from local contacts and may often be anecdotal and these raw data may be used to develop “best available” databases, this aspect of the program along with the associated mapping will not be considered to be under the requirements of EPA FIFRA Good Laboratory Practice Standards (GLP), 40 CFR Part 160 [1].

2.0 JUSTIFICATION

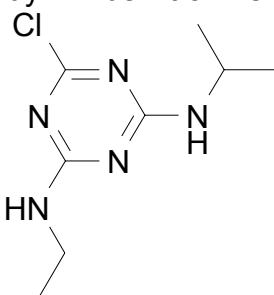
The selection process used to identify the highly vulnerable watersheds, that form the pool represented by the watersheds used for the study, was approved by US EPA Office of Pesticide Programs (OPP) and Office of Water (OW) staff. Similarly, the initial selection of forty HUC10/11 watersheds identified by the vulnerability assessment and from 1172 was assessed using the office of water procedure This procedure also included additional site characterization process was approved by EPA representatives.

A list of substitute index sites established by EPA representatives to substitute for sites deemed ineligible during the detailed site selection will be used as needed to maintain a forty site total for the corn and sorghum component of the field study.

Finally, the collection of supporting ancillary data from the watersheds associated with the study to accompany the residue and flow measurements will permit the evaluation of higher resolution watershed scale models that may provide an improved approach for assessing the intrinsic potential vulnerability of a watershed as well as providing a more finely resolved mechanism for comparing relative watershed vulnerabilities.

3.0 TEST SUBSTANCE IDENTIFICATION

The test substance for this study will be Atrazine.



Atrazine

CAS Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-N'-(1-methylethyl)-
CAS Number: 1912-24-9

Since Atrazine will be applied as commercial formulations according to local practices (by a range of farmers and landowners) in each watershed beyond the control of the Study Director and his delegates, there will be no formal protocol descriptions of test substance characterization or handling and safety

4.0 STUDY TIMING AND REPORTING SCHEDULE

The atrazine ecological exposure monitoring study will have a delivery schedule as shown in the table below. The delivery dates, beyond the table below, will be identified by amendment.

Deliverable Schedule	Due Dates
Site search protocol approval	Nov., 6 2003
Site search progress report 1 due	Nov. 17, 2003
Site location approvals in batches (corn/sorghum and sugarcane)	Nov. '03 – Jan. '04
Experimental Start – Field Group 2004/2005	Feb. 1, 2004
Site search and characterization report due	May 1, 2004
Interim report – Field Group 2004/2005	Dec. 15, 2004
Experimental Start – Field Group 2005/2006	Feb. 1, 2005
Interim reports– Field Group 2004/2005 & 2005/2006	Dec. 15, 2005
Interim report – Field Group 2005/2006	Dec. 15, 2006
Final Summary and Overview report – Entire study	June 30, 2007

5.0 SITE SELECTION

Publicly accessible sites will be identified working upstream along a USEPA approved segment until a suitable sampling location is identified. If a site is not identified along the first eligible segment, another is selected from the pool of eligible segments and the identification process continues. The process will continue until all possible locations are exhausted or a suitable site is identified.

5.1 Data Available for Site Selection

Each HUC10/11 watershed and the provided raw GIS data will be analyzed based on a set of criteria listed below to make high resolution GIS-based selection evaluations regarding the most likely sampling locations along eligible river reaches in the selected HUC10/11 watersheds. This GIS process will employ raw data supplied to Waterborne from documented sources. The GIS evaluation criteria are:

- Accessibility
- Channel Characteristics
 - Confluence Complexity
 - Channelization/Stability
- Land Cover Analysis
 - Urban Channel Environment
 - Managed Channel Environment
 - Forrest Complexity

Sampling locations with applicability/safety issues that seriously influence the suitability as defined in the above list, will be documented but not carried forward to the field based site selection step.

Spatial information in the form of detailed maps will be shared with local agricultural chemical dealers or Syngenta sales resources to identify any anomalies involving atrazine use patterns or shifts in crop production. Recommendations that suggest

significant deviation from the conditions sought in the project objective will be evaluated and approved. Alternate watersheds may be supplemented.

5.2 Field Based Site Selection

Field teams will visit the sites identified from the available GIS information. A detailed photographic record of each watershed will be prepared. This will include, at a minimum, the prospective location of the sampling and flow monitoring stations, and key features of the sampling location. One meter resolution aerial photographs of the potential sampling locations, as available and necessary, will also be prepared.

The river reaches at all suitable sampling locations will be assessed to describe the following:

- River Depth Profile
- Channel and Bank Geometry
- Flood Plain Characteristics
- Potential Safety/Security Issues
- Flow Regime
- Sediment Loading
- Bed Composition
- Bank Stability/Vegetation
- Local (Within Visual Range of the Monitoring Site) Land Use
- Proximity to Land Based Sources of Pesticide Contamination
- Possible Monitoring/Sampling Equipment Locations
- Suitability for Flow Measurement

Watersheds identified by available GIS information and field visits will be assessed. The most downstream suitable location on the first suitable randomly ordered segment will be selected. This location will define the watershed. When a watershed is selected as one of the forty sampled watersheds, the watershed information will be checked against 1:24,000 scale USGS topographic map data and Digital Elevation Model (DEM) layers (USGS, 2003). This review of the watershed boundaries will identify any delineation complications. The hydrography and land use information will also be reviewed and compared with recent aerial imagery to ensure that the site is suitable for the purposes of the study.

6.0 SITE CHARACTERIZATION

When a specific sampling point is chosen based on the GIS and field components of site selection and approved by USEPA, a more detailed characterization of the watershed defined by that sampling point, will be performed. Maps will be prepared that include the best available information for these watersheds. This information will include aerial images, classified images related to land cover, and surface features like roads, lakes, and urban/suburban areas.

7.0 SITE APPROVAL

Each site will be characterized and the information summarized in a short report for approval by EPA. If a watershed is found to have a significant potential point source (e.g. mixer/loader wash pad, or storage facility) upstream of the sampling point, or other significant divergence from the study objective, the summary report will contain supporting information for that potential rejection. Where a candidate site proves unacceptable to EPA or relative to the stated study objectives, the agreed process will be used to select another watershed (or location within the same watershed if multiple potential sampling points exist).

Once EPA has approved a set of sampling sites the contributing watershed to that site will be numbered by a State Designation and a number. Numbers will be assigned by starting in the Upper Northwest “corner” of a state and numbering the sites starting at 01 on the basis of “reading order” – i.e. moving west to east at the same latitude and then down to repeat the process such that the last numbered site is the one nearest the south eastern “corner” of the state (e.g. IA04).

8.0 TEST SITE INSTRUMENTATION

The test site instrumentation will be identified by amendment.

9.0 DOCUMENTATION OF ONGOING WATERSHED AGRONOMY AND ENVIRONMENTAL FACTORS

The documentation of ongoing watershed agronomy and environmental factors will be identified by amendment.

10.0 TEST SUBSTANCE APPLICATION

There is no test substance applied in this study.

10.0 SAMPLING

Sampling and related activities will be identified by amendment.

12.0 ANALYTICAL METHODOLOGY

Analytical methodology will be identified by amendment.

13.0 DATA REPORTING

Reporting schedules are set out in section 4.0 and apply to the detailed site selection and characterization, but not to the tasks related to the preliminary site selection.

Waterborne Environmental Inc. (Waterborne) will deliver a detailed report of the site selection and characterization aspects of this study in advance of the final reporting due date.

14.0 DATA RETENTION

Laboratory and field data will be recorded in notebooks. All raw data must be retained in the study file. Raw data are work sheets, records, memoranda, notes of telephone conversations, written and emailed correspondence, or verified copies thereof, which are the results of original observations and activities of the study, and are necessary for the reconstruction and evaluation of the report of that study. Raw data may include but are not limited to photographs, computer printouts, magnetic media, written notes, recorded media, or optical media.

All original raw data generated except for facility raw data, such as equipment maintenance logs, will be archived upon completion of the study. This data will be subsequently transferred to the study sponsor as a separate final raw data package for archival. Facility raw data will be archived at the respective facility. Certified copies of facility raw data necessary for reconstruction of the study will be provided to the sponsor for archive as requested. A verified copy of the final study report and site selection and characterization raw data package will be archived by Waterborne.

15.0 PROTOCOL CHANGES

If modifications to this protocol are deemed necessary, an amendment/ deviation will be written. The amendment/deviation will include a description of the change, the reason for the change, the effect of the change on the study, and the effective date of the change. The protocol amendment/deviation will be signed and dated by the Principal Field Investigator and Study Director.

16.0 STUDY DIRECTOR AUTHORIZATIONS

The Study Director or his designate will be informed as soon as possible (verbally within 12 hours with email follow up) of issues that arise during the site selection and characterization that compromise adherence to the protocol. Other issues that require Study Director involvement will be communicated by email within 24 hours (ideally faster than this).

Field Investigator(s) are authorized to proceed with necessary protocol modification upon the verbal authorization of the Study Director (with email and paper follow-up within 24 hours). All study issues will be documented in the raw data and in a protocol amendment/deviation.

17.0 QUALITY ASSURANCE

As a commitment to conduct research studies in compliance with GLP, Waterborne has contracted Quality Associates Inc. (QAI), Columbia, Maryland to serve as the independent Quality Assurance Unit for this project. Waterborne Standard Operating Procedures (SOPs) related to this study will be made available to QAI, who will conduct periodic inspection of field and/or laboratory procedures to assure that Waterborne SOPs and GLP are being followed. The results of these inspections will be reported to the Principal Field Investigator, Study Director, and the Study Director's management. The final report will be reviewed for protocol and GLP compliance. A signed statement will be included with the final report specifying when inspections were made and when inspections were reported to the Field Principal Investigator, Study Director, and the Study Director's management.

18.0 STATISTICAL METHODS

Averages, standard deviations, and rankings may be performed on the data collected during this study. Statistical inferences and interpretations will also be discussed in the final report.

19.0 REFERENCES

USGS Digital Raster Graphics (DRGs). Geocommunity, GIS Data Depot website.
<http://data.geocomm.com/drg/index.html>. Accessed October 6, 2003.