VOLUME ___ OF ___ OF SUBMISSION

ATRAZINE: INTERIM REPORT

TITLE

Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds Interim Report: Watershed Selection Process

DATA REQUIREMENT

October 31, 2003 Amended Interim Registration Eligibility Decision for Atrazine

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COMPLETION DATE

March 30, 2004

PERFORMING LABORATORY

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LABORATORY STUDY IDENTIFICATION

Syngenta Number T001509-03
Waterborne Number WEI 936.32

SUBMITTER/SPONSOR

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VOLUME 1 OF 1 OF STUDY

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STATEMENT OF <u>NO</u> DATA CONFIDENTIALITY CLAIM

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Company: Syngenta Crop Protection, Inc.

Company Representative: Tom Parshley

Title: Senior Regulatory Product Manager

Signature: Tom Parshley Date: 4-1-04

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GOOD LABORATORY PRACTICE STATEMENT

This report Atrazine Ecological Exposure Monitoring Program Interim Report:-Watershed Selection Process presents approaches used to identify watersheds for ecological monitoring in the United States and is not a study as defined by the US EPA Good Laboratory Practice (GLP) Standards (40 CFR 160).

Study Director: There is no GLP Study Director for this volume

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30 March 2004

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Project Officer, Author
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Date

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Representative of Submitter/Sponsor

Date

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GENERAL INFORMATION

Study Title:	Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds Interim Report: Watershed Selection Process
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WEI Project No.:	936.32
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Chemical Name:	Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (CAS#1912-24-9)
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Data transmittal:	Data will also be transferred to EPA EFED via DVD disk

EXECUTIVE SUMMARY

The Atrazine Interim Reregistration Eligibility Decision (IRED) issued by the USEPA on January 31, 2003 discussed the revised human health and environmental risk assessments for atrazine uses and included an assessment of ecological risks and related actions, which the registrants (including Syngenta Crop Protection Inc) are required to address. EPA stated in the IRED executive summary that

"The environmental risk assessment suggests that exposure to atrazine could result in community-level and population-level effects in aquatic communities at concentrations of 10-20 ppb atrazine.

To address these risks, the Agency has determined that an ecological assessment process (is needed) to identify waterbodies at risk and monitor these waterbodies for atrazine concentrations."

In order to achieve this, discussions between Syngenta and USEPA led to a decision to investigate water bodies via a framework of pre-defined watersheds throughout areas of the United States with significant agricultural uses of atrazine. This report focuses on the collation and processing of spatial information that would be used to help identify watersheds within the United States that may be candidates for monitoring.

A watershed-based approach was agreed to be most appropriate and the key tool for the primary identification of watersheds of interest was agreed to be a series of government spatial data sets examined, combined and otherwise processed in a geographic information system (GIS). Accordingly, a large GIS consisting of many basic layers and 14 layers of particular interest summarized on a watershed basis ("watershed metrics") was developed for a 37 state area encompassing all significant agricultural use of atrazine. The watershed scale was either HUC10/11 or, if data of that quality were not available, the best USGS defined watershed designation available (typically HUC8) within a particular state was used. The details of the generation of these spatial datasets in the GIS are provided in an accompanying document "Atrazine Ecological Exposure Monitoring Program Interim Report – Supporting

Spatial Data" (Harbourt et al., 2004a). The use of these spatial datasets to refine a list of watersheds follows in this second Interim report.

Watersheds of potential interest were identified based on atrazine use intensity on corn and sorghum (site selection appropriate to the sugarcane use-pattern will be handled by a separate process). By selecting counties in the upper 45th percentile of the atrazine corn-sorghum cropped area use intensity and identifying watersheds that intersected with these, the pool of watersheds was reduced from an initial total of 9513 in the 37 states of the contiguous US with reported atrazine use to 5860.

A series of potential watershed selection criteria were developed after careful analysis of many combinations of watershed metrics for these higher atrazine corn-sorghum cropped area use intensity areas. Using these criteria, the resulting pool of 5860 selected watersheds was ground truthed against atrazine surface water monitoring information (where any data were available for any of the watersheds). From this analysis, it was agreed that the optimum technique for identifying a further subset of watersheds with the maximum potential for higher annual non-point source atrazine residues to occur in streams and rivers was the selection of watersheds that fell in the upper 20th percentile of the distribution of Watershed Regression for Pesticides (WARP) values calculated using the 95th percentile annual mean predictive algorithm. This step reduced the pool to 1172 watersheds of further interest (1155 HUC10/11 and 17 HUC8).

The final step in the identification of watersheds for the selection of sampling sites for the monitoring program was to select 40 watersheds from the pool of 1172 representing the highest potential for non-point atrazine transport. In order to select a spatially representative statistical subsample of 40 from this pool of 1172 watersheds, USEPA adopted the Generalized Random Tessellation Stratified (GRTS) method. A specific GRTS method termed "WARP (2,4], Use PPS, (4,14] Use PPS: Spatially Balanced on Points" was used to select 40 primary and 10 oversample watersheds. These 50 watersheds were then each spatially analyzed in a GIS to select synthetic stream segments meeting a set of criteria that were agreed by USEPA and Syngenta to qualify them as eligible to become sampling points for the surface water monitoring study. This final set of eligible synthetic stream segments provided a series of target locations for site search teams to visit in the watersheds in order to identify sites that also meet certain practical criteria. The latter effort is reported in a site search progress report (Harbourt, 2003) as well as a series of 47 site specific reports (Harbourt et al., 2004b-vv). These sampling locations are each characterized by unique subwatersheds within each of the finally selected HUC10/11 watersheds and will serve as the atrazine eco-monitoring study areas.

1.0 INTRODUCTION

The Atrazine Interim Reregistration Eligibility Decision (IRED) issued by USEPA on January 31, 2003 (US EPA, 2003) discussed revised human health and environmental risk assessments for atrazine uses and included an assessment of ecological risks and related actions, which the registrants (including Syngenta Crop Protection Inc) are required to address. EPA stated in the IRED executive summary that:

"The environmental risk assessment suggests that exposure to atrazine could result in community-level and population-level effects in aquatic communities at concentrations of 10-20 ppb atrazine.

To address these risks, the Agency has determined that an ecological assessment process (is needed) to identify waterbodies at risk and monitor these waterbodies for atrazine concentrations."

In order to achieve this, discussions between Syngenta and USEPA led to a decision to investigate water bodies via a framework of pre-defined watersheds throughout areas of the United States with significant agricultural uses of atrazine. Waterborne Environmental, Inc. was contracted by Syngenta Crop Protection, Inc. to help identify water bodies within the U.S. that might be suitable candidates for the atrazine ecological exposure monitoring specified under this IRED. This report outlines the methods used to determine suitable candidate watersheds for the ensuing field monitoring effort and then for making a spatially balanced statistical selection from the resulting pool of 1172 watersheds shown to have higher potential for atrazine exposure. In addition, the report describes the approach used to select a specific candidate sampling sites within a selected potentially vulnerable HUC 10/11 watershed.

A watershed-based approach was agreed to be most appropriate and the key tool for the primary identification of watersheds of interest was agreed to be geographic information systems (GIS). Accordingly, a large GIS consisting of many basic layers and 14 layers of particular interest summarized on a watershed basis ("watershed metrics") was developed for a 37 state area encompassing all significant agricultural use of atrazine. The watershed scale was either HUC10/11 or, if data of that quality were not available, the best USGS defined watershed designation available (typically HUC8) within a particular state was used. The details of the generation of the layers in this GIS are provided in an accompanying document "Atrazine Ecological Exposure Monitoring Program Interim Report – Supporting Spatial Data" (Harbourt et al., 2004a). This report describes the use of these GIS layers to refine the list of watersheds and then to select specific eligible stream segments suitable for investigation to locate specific candidate sampling sites from within selected potentially vulnerable watersheds.

1.1 Report Objectives

The primary objective of this report is to present a record of decisions on the approaches agreed to identify the (largely) HUC10/11 watersheds with the greatest potential for higher atrazine exposures in streams and rivers arising from agricultural non-point source runoff from agricultural use patterns. Secondly, the report examines approaches to identify from that subset of watersheds a statistically representative group suitable for inclusion in the atrazine ecological exposure monitoring study. Finally, the report records the approach agreed to select specific candidate sampling sites from within selected potentially vulnerable watersheds. In order to achieve these overall objectives, the following steps were completed:

- Narrowed the search to high atrazine cropped area use intensity counties and the watersheds that contain them;
- Utilized the GIS watershed based metric data collected and presented in the accompanying report to rank these watersheds;
- Compared several sets of indicators (combinations of metrics) to atrazine surface water monitoring results
- Agreed upon the most appropriate indicators;
- Evaluated the resulting set of potentially vulnerable watersheds for their spatial distribution and similarities;
- Examined approaches for selecting a subset of HUC's that are representative of the potentially vulnerable set and that are selected on the basis of either maximum spatial diversity, known ecological/agronomic and climatic variations across the subset, or by randomization techniques.

- Selected 40 watersheds plus 10 “spares” using the Generalized Random Tessellation Stratified (GRTS) method using two sets of criteria to incorporate aspects of high atrazine use as well as a higher potential for runoff.

- Examined approaches for selecting specific eligible stream segments suitable as candidate sampling sites within a selected HUC10/11 watershed in order to provide a series of target locations for site search teams to visit the watershed to identify candidate sampling sites that also met certain practical criteria (the latter effort is reported in a site search progress report (Harbourt, 2003) as well as a series of 47 site specific reports (Harbourt et al., 2004b-vv)).

2.0 BACKGROUND

The process described in this report focuses on the subset of approaches agreed upon by USEPA and Syngenta for selecting the watersheds with the greatest potential for atrazine runoff to surface waters from among the entire pool of watersheds associated with the 37 states with the highest atrazine cropped area use intensity for corn and sorghum. In the course of this work, several additional approaches were investigated in considerable detail but since they did not produce the desired EPA goal, it was agreed that they would not be reported here.

3.0 IDENTIFICATION OF MORE VULNERABLE WATERSHEDS

A Geographical Information System (GIS) was used to process spatial data sets in order to represent various parameters expected to be of potential value in the identification of water bodies more vulnerable to non-point source transport of agrochemicals via rainfall-induced runoff. These data layers include derived metrics, hydrology, land cover, agricultural census data, elevation, soils, precipitation and rainfall intensity. The details of the generation and metadata for these GIS layers are provided in the accompanying document "Atrazine Ecological Exposure Monitoring Program Interim Report – Supporting Spatial Data" (Harbourt et al., 2004a).

3.1 Watershed Scale Metrics

For consistency among the state HUC levels and the resulting watershed metrics, in states where the most detailed USGS delineated watershed data available was at the HUC-12/14 level, these were aggregated up to the HUC10/11 level in order to ensure that watershed boundaries would meet a common (maximum) resolution. Those states providing only HUC8 information were also included in the set referred to as HUC10/11 metrics. For these HUC8-only states, the processing steps were the same as those used for HUC10/11 scale watersheds, except the information was applied to larger HUC8 areas resulting in a certain degree of smoothing of inhomogeneities. In addition, these HUC8 watersheds had lower resolution boundaries than those derived via aggregation. Figure 1 shows the seven states within the 37 state set where the HUC8 level was the best available spatial resolution.

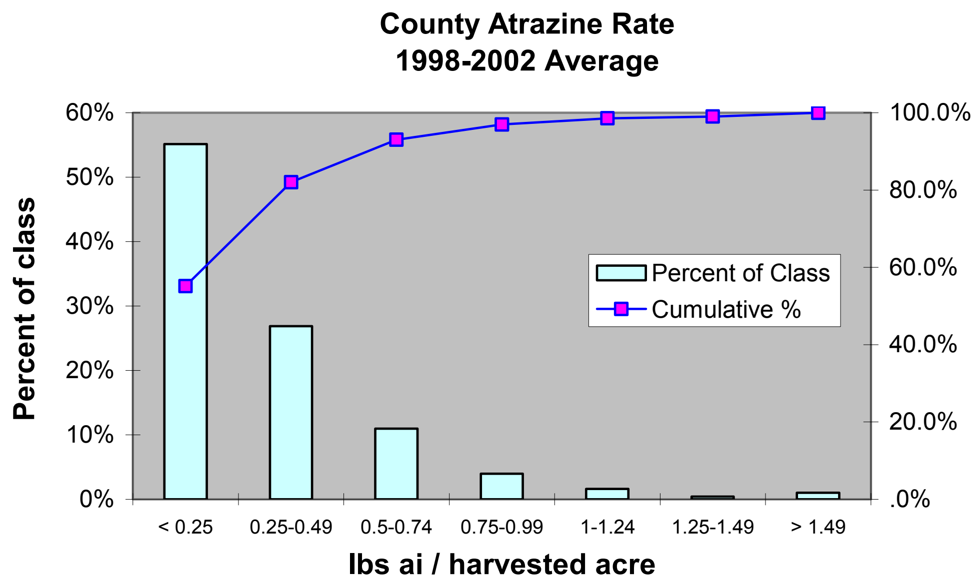
3.2 Atrazine Cropped Area Use Intensity: County and Watershed

Atrazine cropped area use intensity information is believed to be the most significant single factor for differentiating between the potential of watersheds to generate atrazine runoff. The most reliable source of information on atrazine use is data at a county level of resolution from a commercial survey organization (Doane's). It has been found that the best information is obtained by averaging several years of Doane's data and therefore the data layer used for this study represents the average values for atrazine cropped area use intensity (pounds applied per harvested county acre) across a 5 year period from 1998 to 2002. Figure 2 shows the distribution of atrazine cropped area use intensity for all the counties with any atrazine usage in the USA and the inset graph below provides the numeric distributions. After evaluation, an atrazine cropped area use intensity cutoff criterion of 0.25 lb active ingredient per harvested acre was selected since it represents the upper 45th percentile of the distribution and is judged to be fully inclusive of the more vulnerable use areas. Figure 3 shows the counties in the upper 45th percentile of the atrazine cropped area use intensity distribution. The green outline shows the group of 37 states that served to define the areas included in the compilation of GIS data layers (Harbourt et al., 2004a). The blue outline shows the subset of 11 states representing the "core" group of 11 mid-western states that were also used for comparison with the data from the 37 sites.

The figure below shows the watersheds that were considered to meet this criteria for "higher atrazine cropped area use intensity; they included:

A) The HUC10/11 watersheds that were associated with the 11 "core" states. Note that all watersheds in this area were included even where the atrazine use intensity was NOT in the upper 45th percentile of cropped area use intensity counties (e.g. Northern Minnesota, Southern Missouri and south western New York). This resulted from an early request from EPA to include 100 percent of these states in the later steps of the analysis

B) All the HUC10/11 units (or HUC8 watersheds in states for which no higher resolution watershed were available – see Harbourt et al., 2004a) that touched or were contained within any of the counties outside the group of 11 "core" states



The HUC based cropped area use intensity values could be less than the cropped area use intensities of the counties. This is largely because the watershed area weighted calculations included areas outside of the 0.25 lb ai/harvested acre use intensity county, which had much lower use intensities than the adjacent county.

3.3 Analysis of High Atrazine Cropped Area Use Intensity Watersheds

EPA and Syngenta examined many different and potentially runoff transport related metrics (calculated on a watershed basis) for this subset of high atrazine cropped area use intensity watersheds in considerable depth in order to explore all feasible options that could help identify the landforms and other characteristics that might correlate with a potential for higher non-point source transport potential for agrochemicals. After this evaluation, the most relevant three metrics were identified to be:

- USGS Watershed regression for Pesticides (WARP) Predicted 95th Percentile Atrazine Concentration,
- Percent Flow Accumulation Under Crop, and
- Minnesota Runoff Index Classified as Severe.

Correlation analysis and principal components analysis were tools used (*inter alia*) to identify inter-relationships between the various metrics; these are presented in the accompanying "Atrazine Ecological Exposure Monitoring Program Interim Report – Supporting Spatial Data" report (Harbourt et al., 2004a). The correlation tables and Principle Components Analysis (PCA) analyses showed that the WARP, Flow Accumulation Under Crop, and Minnesota Runoff Index–Severe were largely independent. The PCA vector plots showed different magnitudes and directions for the three metrics in n-dimensional space where n was fourteen. This variability in vector properties is an indicator of independence and minimal repeat variability attributed to the three metrics. The variability in each metric, which can be explained by a single PCA component, is a result of the influence of row crop on the metrics derived from the high quality NLCD land cover data. Because only one component accounts for the majority of variability, row crop alone is a sufficient indicator of variability.

3.3.1 USGS WARP Predicted 95th Percentile Atrazine Concentration

The Watershed Regression for Pesticides (WARP) was calculated for each watershed. WARP is a regression-based tool designed and validated for atrazine by the USGS (USGS, 2002). Data from watersheds across the USA were included in the regression if either a U.S. Geological Survey National Water-Quality Assessment (NAWQA) or National Stream Quality Accounting Network (NASQAN) program monitored pesticides at the watershed's pour point. Separate regression equations were derived for 9 percentile values extracted from each sampling stations historic sample record. The following equation is the WARP model with coefficients predicting the 95th percentile concentration:

$$WARP = 10\text{^}\left(-4.60 + \left(0.67U^{0.25}\right) + \left(1.12 LogR\right) + \left(3.59K\right) + \left(0.0006A^{0.5}\right) - \left(0.11 * D\right)\right)$$

where, U is watershed cropped area use intensity in kg/km^2, R is the USLE rainfall erosivity factor (100 ft-tons/acre)(in/h), K is the USLE soil erodibility (tons/acre), A is area (km^2), and D is Dunne overland flow (USGS, 2002).

WARP was calculated for each watershed using metrics calculated at the HUC 10/11 level. The benefit of the WARP metric is that it integrates information about cropped area use intensity, soil erodibility, rainfall, and a small correction for watershed basin scale. Thus it combines the factor (watershed load) considered most critical by EPA with landscape factors that modify potential soil transport; moreover, the fact that the WARP 95th percentile equation was calibrated on the basis of atrazine use and measured flowing water residues demonstrates its relevance. Figure 5 shows the resulting ranges of WARP results for the set of HUC10/11 units intersecting the set of higher atrazine cropped area use intensity counties.

3.3.2 Percent Flow Accumulation Under Crop

Flow accumulation under crop is a raster-based measure of the concentration of flow within cropped areas. This metric provides watershed scale information sufficient to determine that a concentrating flow is likely on a cropped field. A concentrating flow has the potential to carry sediment and pesticides from agricultural areas. National Elevation Data (NED) tiles at 30-meter resolution, and NLCD land cover data at 30-meter resolution were used to create flow accumulation under crop. Flow accumulation under crop is an potentially highly relevant metric because it brings together the potential for slopes to cause significant amounts of water to flow across land with row crops (and therefore potentially treated).

Significant flow accumulation was determined to be where the metric exceeded a cutoff level of nine pixels (each 30 by 30 m) that equates to a delivery area of approximately 2 acres. The percent of the total row crop pixels meeting this criterion in a watershed constituted the metric for watershed Percent Flow Accumulation under crop. For further description of the Percent Flow Accumulation Under Crop metric, see Harbourt et al. (2004a). Flow Accumulation is strongly correlated with crop and thought beneficial for this analysis. This is logical since the metric is a measure of a property that by definition only occurs in cropped areas. Figure 6 shows the resulting values of flow accumulation under crop for the set of HUC10/11 units intersecting the set of higher cropped area use intensity counties. The upper 10th percentile color band in this figure has a spatial coverage slightly different from WARP in Figure 5. This difference was one of the reasons why Flow Accumulation was carried forward from the 11 state-included HUC area to the 37 state analysis.

3.3.3 Minnesota Runoff Index Classified as Severe

Minnesota Runoff Index Classified as Severe appeared to be a very relevant metric since it was not correlated with the other two key metrics and it focused on factors known to drive runoff transport in the Midwest. For details related to the calculation and background for this metric, see Harbourt et al. (2004a). Despite the apparent applicability of this method, inherent problems with STATSGO analysis limited the application to watershed wide analyses. Therefore limiting the metric to purely cropped areas was not an option because of the uncertainty about the exact location of specific soils within STATSGO polygons that are nearly the same spatial scale as the HUC10/11 units. It also does not build in atrazine use rate (via cropping) since higher values of runoff are indicated even where there is no agricultural cropping.

Minnesota Runoff Index Classified as Severe is largely based on soil hydrologic group. Although there were other important factors like ponding and slope allowances, the majority of the information conveyed from this index relates to the percent hydrologic group C and D soils. Figure 7 shows the resulting values of the Minnesota Runoff Index Classified as Severe for the set of HUC10/11 units intersecting the set of higher use intensity counties (the upper 45th percentile of atrazine cropped area use intensity counties)

3.4 Atrazine Surface Water Monitoring Data: Preparation of Calibration / Validation Data Sets

Atrazine surface water monitoring data from the 37 state region along with sources and references are presented in Harbourt et al. (2004a). These were used as a validation/calibration data set to help evaluate the performance of the three metrics described above both individually as well as in various combinations. Monitoring data from USGS, state programs, and universities were evaluated on a station-by-station basis. Sampling stations were assigned the HUC10/11 identifier of the HUC unit in which they were located. This allowed the association of HUC10/11 metrics with atrazine surface water monitoring data for the subset of the HUC units with available monitoring data. Figure 8 shows the watersheds with atrazine surface water analytical data superimposed upon a map of the watersheds in the pool representing higher atrazine cropped area use intensity areas; it is clear that the watersheds with atrazine data provide a broad spatial representation of the range of cropping and climatic conditions across the 37 state region. Figure 9 is a histogram of all the reported sample concentrations (45994 samples) from the sample locations within the higher atrazine cropped area use intensity areas used for calibration / validation.

To enable the use of this surface water monitoring data to ground truth the vulnerability predictions, two subsets of sampling stations (and hence HUC's) were selected. The first was the pool of stations that had never had a single detection of atrazine above 0.1 ppb in their sampling record. As shown in figure 9, an atrazine concentration of 0.1 ppb represents the **lower** 21^{st} percentile concentration for the atrazine surface water samples obtained in the HUC10/11 units intersecting or contained within the eleven states or higher atrazine cropped area use intensity counties in the remaining 26 states. The second group was the pool of stations that had at least one detection of atrazine above 3.0 ppb in their sampling record. An atrazine concentration of 3.0 ppb represents the **upper** 18^{th} percentile concentration from the atrazine surface water monitoring data. Of the 45994 samples collected from 1581 sample stations, 487 were in the upper 18^{th} percentile and 526 in the lower 21^{st} percentile.

This simple approach provided a set of watersheds whose records indicate that they have no history of vulnerability to atrazine runoff to surface water and another set that does show indications of such vulnerability. When compared with groups of watersheds predicted via the spatial metrics to be vulnerable to atrazine non-point source transport to streams and rivers, the inclusion of a watershed in the former (no detects) group qualifies as a "false positive" result while the inclusion of a watershed in the second group (at least one significant detect) qualifies as "positive agreement".

3.5 Comparison of Predictions with Calibration / Validation Data Set

Various combinations of the three preferred metrics were examined in detail at both the 11 and the 37 state levels of processing. Figures 10 – 12 show maps of the watersheds selected using some combinations of the metrics at the 11 state level, which served as the initial dataset used for testing hypotheses. The maps show that while there is a certain amount of overlap in the heartland of the corn belt, the watersheds selected by the upper 10th percentile of the Flow Accumulation under Crop metric are complementary to the watersheds selected by WARP alone and tend to extend to the North West of the region. Similarly, the watersheds, which are unique to the upper 10th percentile of the Minnesota runoff index severity ranking, show a tendency to be in the South East of the 11 state region (Figure 10). The complementary nature of the watersheds selected by these three metrics suggested that combinations of upper percentiles would yield an optimized predictive tool for watershed vulnerability. As a result, several candidate combinations were selected for calibration/validation against the selected "upper" and "lower" pools of the atrazine surface water monitoring data.

The table below summarizes the comparison of watersheds selected via combinations of the three metrics with the two populations of atrazine surface water monitoring data. The table should be read as follows:

"When the upper 10th percentile of WARP, Flow accumulation under crop and Minnesota runoff index classified as severe are selected independently using the 11 state compilation of HUC10/11 watersheds, 930 watersheds are selected from a total population of 3440. Of these watersheds, 126 have some atrazine surface water monitoring data available and, of these, 77 are in the upper pool and 17 are "false positives"

By examining the table, several patterns emerged and the following conclusions were drawn:

- The use of the Minnesota runoff index severe rating tended to introduce substantial numbers of watersheds but a relatively high number of false positives were obtained. This metric was not pursued further when the 37 state watershed population was examined
- Flow accumulation under crop proved a reasonably effective selection tool at the 11 state processing level since, of the 32 watersheds which had atrazine surface water monitoring data among the 287 unique watersheds "added" by consideration of this metric, only 7 were false positives while 15 were new sites with a history of at least one significant detection.

- WARP at the upper 10^{th} percentile gave a strong indication of watershed vulnerability with NO false positives at the 11 state processing level. The population of upper 20^{th} percentile watersheds provided an even stronger signal with no false positives out of 632 watersheds selected. It was clear that the use of the upper 20^{th} percentile of the WARP metric gave a more satisfactory set of watersheds than the combination of the upper 10^{th} percentiles of WARP and Flow Accumulation under Crop.
- When the analysis was extended to the 37 state processing level, it became clear that the upper 20^{th} percentile of WARP was the most powerful tool; of the 195 watersheds with atrazine surface water monitoring data included in the 1172 sites selected by this criterion, 156 had experienced at least one significant atrazine detection, while only 2 watersheds were false positives.
- Given the broader set of WARP selected watersheds in the 37 state population, the additional value offered by a combination with the upper 10^{th} percentile of the Flow Accumulation under Crop metric decreased. Of the 26 watersheds with atrazine monitoring data added to those already selected via WARP, only 5 had a history of significant atrazine detections while 16 were “false positives”.

Metric Combination[1]	# States	Pool of included HUC's	Total #. HUC's Selected	# Sampled[2] HUC's	# "Upper" Pool HUC's	# "Lower" Pool HUC's
WARP90+FA90 + MN90	11	3440	930	126	77	17
WARP90+FA90	11	3440	626	83	60	7
WARP90	11	3440	339	51	45	0
FA90 (unique)	11	3440	287	32	15	7
MN90 (unique)	11	3440	304	43	17	10
WARP95+FA95+MN95	11	3440	493	59	39	8
WARP80[3]	11	3440	632	102	85	0
WARP80[4]	37	5860	1172	195	156	2
FA90	37	5860	526	57	29	47
FA90 (unique)	37	5860	263	26	5	16
W80+FA90	37	5860	1435	221	161	18

[1] Metric abbreviations are as follows:

MN = Minnesota Severe Runoff Index rating;

FA = Flow Accumulation under Crop

WARP = Watershed Regression for Pesticides 95th percentile annual residue prediction algorithm

*80 = Upper 20th percentile of metric

*90 = Upper 10th percentile of metric

*95 = Upper 5th percentile of metric

[2]Pool of sampled HUC's for the 11 state group was 574 (295 in the "upper" group and 87 in the "lower" group). For the 37 state group was 797 (333 in the "upper" group and 198 in the "lower" group).

[3]WARP80 for 11 states was calculated before variable Dunne overland flow was available, so an average value of 2.57 was applied.

[4]Variable Dunne overland flow was used to calculate WARP80 for the 37 state watersheds.

3.6 Selection of Watersheds for Further Consideration Via the WARP Metric

As a result of the ground truthing comparisons, it was agreed that the upper 20th percentile of the WARP metrics for the watersheds in the 37 state level processing group should be selected as a pool for further investigation. These 1172 watersheds are shown in Figure 13 while Figure 14 shows the HUC8 watersheds (commonly known as Cataloging Units or Basins) that include one or more of the selected HUC10/11 watersheds. The pool of HUC8 watersheds is mostly contiguous, with only a few outliers and this has implications for the final sampling site location selection process.

Figures 15 – 17 are views of this selected set highlighting the spatial differences across the set of 1172 HUC10/11 watersheds in area, percent corn/sorghum, and atrazine watershed cropped area use intensity. Figure 15 shows the area distribution with the general trend east to west of increasing watershed size. Figure 16 shows a relatively diverse cross-section of watershed percent corn/sorghum values ranging from one to 74 percent. The lower end of this range is an artifact of including all counties from the core 11 states (Harbourt et al., 2004a). In Figure 17, atrazine cropped area use intensity is generally higher than for the 3440 HUC10/11 watersheds because the set of 1172 HUC10/11 watersheds are selected from the top set of WARP watersheds and cropped area use intensity is a driving variable within WARP.

4.0 STATISTICAL SELECTION OF 40 SITES

The set of 1172 HUC10/11 watersheds selected by means of the upper 20th percentile of the WARP metric is still much too large a population for a detailed monitoring study such as is the one required for the Atrazine Ecological Exposure Monitoring Program. Accordingly, further selection processes were needed to identify a subset of 40 watersheds that were representative of key aspects of the selected highly vulnerable watersheds.

4.1 The General Random Tessellation Stratified (GRTS) Method

Various approaches were examined to select a statistically based sample spatially representative of key watershed parameters driving potential atrazine runoff. After some evaluation, the method of Stevens and Olsen (2003), from USEPA was identified as the best available; this is termed the generalized random tessellation stratified (GRTS) approach. Many alternate GRTS statistical survey design examples were reviewed. These designs were variations of the spatially balanced survey design methodology. The basic principle in GRTS designs is that all potential samples selected should have a spatial distribution that is similar to the population from which they are selected. It is also possible to select HUC10/11s with probability proportional to another variable, e.g., WARP predicted value, when selecting a GRTS sample. Additionally the population may be stratified and then a GRTS calculation performed within each stratum. This provided the best flexibility in capturing different aspects of the potentially vulnerable fraction of watersheds defined by WARP that EPA desired to emphasize.

4.2 WARP (2,4], Use PPS, (4,14] Use PPS: Spatially Balanced on Points

The USEPA selected the GRTS method that was spatially balanced on points with WARP values stratified using two categories: (2,4] and (4,14]. Category (2,4] is stratum group “a”, and category (4,14] is stratum group “b”. Within each stratum, HUC10/11s with probabilities proportional to the Atrazine Use value were selected. The samples were spatially balanced across the HUC10/11s to reflect the geographic dispersion of the 1172 watershed population. The result of this method meets the goal that the 40 selected HUC10/11s were to be (1) geographically dispersed and (2) distributed across the range of WARP predicted values, and distributed across the range of Atrazine use. 10 oversample, or alternate, watersheds were also selected in the GRTS design (5 in each stratum) for inevitable substitution dependant on actual field conditions.

Figure 18 illustrates the spatial distribution of the 1172 HUC10/11s and the 40 selected (plus 10 oversamples) HUC10/11s from the design. Figure 19 is a scatter plot of the same two sets of HUC10/11s illustrating the distribution over WARP predicted values and Atrazine Use (kg/km^2).

5.0 SELECTING ELIGIBLE SEGMENTS IN SELECTED WATERSHEDS

The set of 50 HUC10/11 watersheds selected by the GRTS methodology provided a starting point for determining eligible segments for the sampling suitability analysis. The U.S. Geological Survey provided hydrologically conditioned flow direction grids for HUC8 watersheds encompassing the 50 HUC10/11 watersheds (Detenbeck, 2003a; Detenbeck, 2003b). These 30-m resolution flow direction grids are a product of the Elevation Derivatives for National Applications (EDNA) database (USGS, 2004). EDNA is a multi-layered database derived from a version of the National Elevation Dataset (NED), which has been hydrologically conditioned for improved hydrologic flow representation.

5.1 Processing HUC8 Flow Direction

Each pixel value in a flow direction grid defines the direction water will flow from that pixel (Figure 20). When the flow direction grids were processed using the flow accumulation command in ESRI ArcMap Spatial Analyst, the accumulated flow product showed areas of concentrated flow that correspond to stream channels (Figure 21). Flow accumulation sums the number of pixels that flow into each downslope pixel (Figure 22).

To determine the number of crop pixels that flow into a given downslope pixel, the flow accumulation command was weighted by NLCD crop pixels overlaid on the flow direction grid. Downslope pixels only sum the pixels coincident with crop to produce this output grid. For each pixel in the output crop accumulation grid, the result was the number of crop pixels that flowed into it (Figure 23). NLCD urban land cover was processed using the same methodology to produce "urban accumulation" grids (i.e. the extent to which urban pixels flowed to a point). Percent crop accumulation and percent urban accumulation grids were produced by dividing the crop accumulation and urban accumulation grids by their flow accumulation grids.

5.2 Criteria for Eligibility

After examination of alternatives, it was agreed that the following criteria were most appropriate to determine eligible synthetic stream segments in each HUC10/11 watershed:

1. Minimum drainage area of 9 square miles
2. Maximum drainage area of half the HUC10/11 watershed, unless the total area is less than 50 square miles
    a. If total HUC10/11 area is less than 50 square miles, tributaries of larger streams will be manually identified to ensure small drainage areas (that meet the minimum area requirement) are not arbitrarily eliminated by the imprecision of the synthetic streams
3. Percent Urban Accumulation less than 10%
4. Upper 50th percentile of Percent Crop Accumulation

Flow accumulation pixels represent the amount of drainage area contributing to a given point. Thus, the flow accumulation grid was used to process and ultimately select pixels within the eligible drainage area requirements. These pixels defined a first criteria for eligible synthetic streams. Percent urban accumulation was next used to screen out synthetic streams that were unduly influenced by urban areas. Lastly, the percent crop accumulation values for the remaining synthetic stream segments were divided into upper and lower 50th percentiles. The upper 50th percentile of percent crop accumulation was the final selection criteria applied and the resulting set defined the eligible synthetic streams. The identification of the eligible synthetic streams within the 40 original and 10 oversample HUC10/11 watersheds was the final product from this work that moved forward into the site selection portion of this overall project.

6.0 SUMMARY

The spatial datasets and watershed analysis approaches developed for the identification of potential watershed vulnerability have provided new insights into monitoring site selection. The WARP model, calibrated for atrazine at the 95th percentile, performed well at the HUC10/11 scale. The upper 20th percent of the watersheds (1172) in high atrazine use areas when ranked using the WARP 95th percentile predicted concentrations were selected as a potentially vulnerable subset representing the pool of high atrazine use watersheds. In order to select a spatially representative statistical subsample from this pool of 1172 watersheds, USEPA adopted the Generalized Random Tessellation Stratified (GRTS) method and a specific GRTS method termed "WARP (2,4], Use PPS, (4,14] Use PPS: Spatially Balanced on Points" was used to select 40 primary and 10 oversample watersheds. These 50 watersheds were then each spatially analyzed in a GIS to select synthetic stream segments meeting a set of criteria that were agreed by USEPA and Syngenta to qualify them as eligible to become sampling points for the surface water monitoring study. This final set of eligible synthetic stream segments provided a series of target locations for site search teams to visit in the watersheds in order to identify sites that also meet certain practical criteria. The latter effort is reported in a site search progress report (Harbourt, 2003) as well as a series of 47 site specific reports (Harbourt et al., 2004b-vv). These sampling locations are each characterized by unique subwatersheds within each of the finally selected HUC10/11 watersheds and will serve as the atrazine eco-monitoring study areas.

7.0 REFERENCES

Detenbeck, N. E., 2003a. Personal communication. EDNA flow direction grids. ftp://edcftp.cr.usgs.gov/pub/edcuser/kverdin/epa. Site accessed September 12, 2003.

Detenbeck, N. E., 2003b. Personal communication. EDNA flow direction grids. ftp://edcftp.cr.usgs.gov/pub/edcuser/kverdin/efed. Site accessed October 27, 2003.

Harbourt, C.M., 2003. Progress Report: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., M.H. Ball, J.R. Trask, M.K. Matella, J.R. Trask, N.J. Snyder, and W.M. Williams, 2004a. Atrazine Ecological Exposure Monitoring Program Interim Report – Supporting Spatial Data. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004b. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Wolf Creek, IA (IA01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004c. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Nishnabotna River, IA (IA02). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004d. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Pecatonica River, IL (IL01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004e. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Pine Creek, IL (IL02). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004f. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Spring Creek, IL (IL03). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004g. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in

Vulnerable Watersheds- Iroquois River, IL (IL04). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004h. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Panther Creek, IL (IL05). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004I. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Sugar Creek West Fork, IL (IL06). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004j. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Grindstone Creek, IL (IL07). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004k. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Horse Creek, IL (IL08). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004l. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Muddy Creek, Illinois, IL (IL09). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004m. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Pecatonica River, IL. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004n. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Mill Creek, IN (IN01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004o. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Eel River, IN (IN02). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004p. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in

Vulnerable Watersheds- Eightmile Creek, IN (IN03). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004q. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Rock Creek, IN (IN04). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004r. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Limber Lost Creek, IN (IN05). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004s. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Vermilion River, North, IN (IN06). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004t. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- White River, IN (IN07). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004u. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Whitewater, Nolans Fork, IN (IN08). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004v. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Raccoon Creek, IN (IN09). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004w. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Brandywine Creek, IN (IN10). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004x. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Little Pigeon Creek, IN (IN11). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004y. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in

Vulnerable Watersheds- Wabash River, Clark, IN. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004z. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Wabash River, Crawford, IN. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004aa. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Brashears Creek, KY (KY01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004bb. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Two mile Creek, KY (KY02). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004cc. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Rough River, KY. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004dd. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Saline Bayou, LA. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004ee. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Whitewater North Fork, MN (MN01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004ff. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- South Fabius River, MO (MO01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004gg. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Youngs Creek, MO (MO02). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004hh. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in

Vulnerable Watersheds- Little Sni-a-Bar Creek, MO (MO03). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004ii. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Contrary Creek, MO. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004jj. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Wahoo Creek, NE (NE01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004kk. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Middle Loup River, NE (NE02). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004ll. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Platte River, NE (NE03). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004mm. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Big Blue River, Upper Gage, NE (NE04). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004nn. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Muddy Creek, Nebraska, NE (NE05). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004oo. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Crooked Creek, NE (NE06). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004pp. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Big Blue River, Lower Gage, NE (NE07). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004qq. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in

Vulnerable Watersheds- Big Blue West Fork, NE. Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004rr. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Kokosing River, OH (OH01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004ss. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Licking River, North Fork, OH (OH02). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004tt. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Mad River, OH (OH03). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004uu. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Deer Creek, OH (OH04). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Harbourt, C.M., J.R. Trask, M.K. Matella, M.H. Ball and J.M. Cheplick, 2004vv. Sampling Site Selection: Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds- Obion Middle Fork, TN (TN01). Prepared by Waterborne Environmental, Inc., Leesburg, VA for Syngenta Crop Protection, Inc., Greensboro, NC.

Olsen, A. R. 2003. Personal communication. Generalized Random Tessellation Stratified (GRTS) Spatially-Balanced Survey Designs for Aquatic Resources. USEPA, NHEERL. September 3, 2003.

Pierce, C. Robert; Anderson, J. 1992. Minnesota Rating for Potential Leaching and Surface Runoff of Pesticides, University of Minnesota Extension Service publication FO-05758 (online availability: http://www.extension.umn.edu/distribution/cropsystems/DC5758.html, 8/5/2003).

U. S. Department of Agriculture, Natural Resources Conservation Service (USDA-NRCS), National Soil Survey Center. 1991, revised 1994. State Soil Geographic (STATSGO) Data Base, Miscellaneous Publication Number 1492.

U. S. Department of Agriculture, Natural Resources Conservation Service (USDA-NRCS). 1997. MLRA metadata and data. http://www.nrcs.usda.gov/technical/land/meta/m2147.html.

U.S. Geological Survey (USGS), 2002. Development and application of watershed regression for pesticides (WARP) methods to estimate atrazine concentration distributions in streams. Draft 11/5/02.

U.S. Geological Survey (USGS), 2004. Elevation Derivatives for National Applications (EDNA). http://edna.usgs.gov/.

U.S. Environmental Protection Agency (USEPA). 2003a. Memorandum of Agreement Between the U.S. Environmental Protection Agency and Syngenta Crop Protection, Agan Chemical Manufacturing, Dow AgroSciences, Drexel Chemical, and Oxon Italia S.P.A., Platte Chemical Concerning the Registration of Pesticide Products Containing Atrazine.

U.S. Environmental Protection Agency (USEPA). 2003b. Interim Reregistration Eligibility Decision for Atrazine. Case No. 0062. www.epa.gov/oppsrrd1/REDs/atrazine_ired.pdf.

Wauchope, R. D. 1978. The pesticide content of surface water draining from agricultural fields--a review. Journal of Environmental Quality. 7:459-472.

Wauchope, R. D., and R. A. Leonard. 1980. Maximum pesticide concentrations in agricultural runoff: A semi-empirical prediction formula. Journal of Environmental Quality. 9:665-672.

8.0 FIGURES

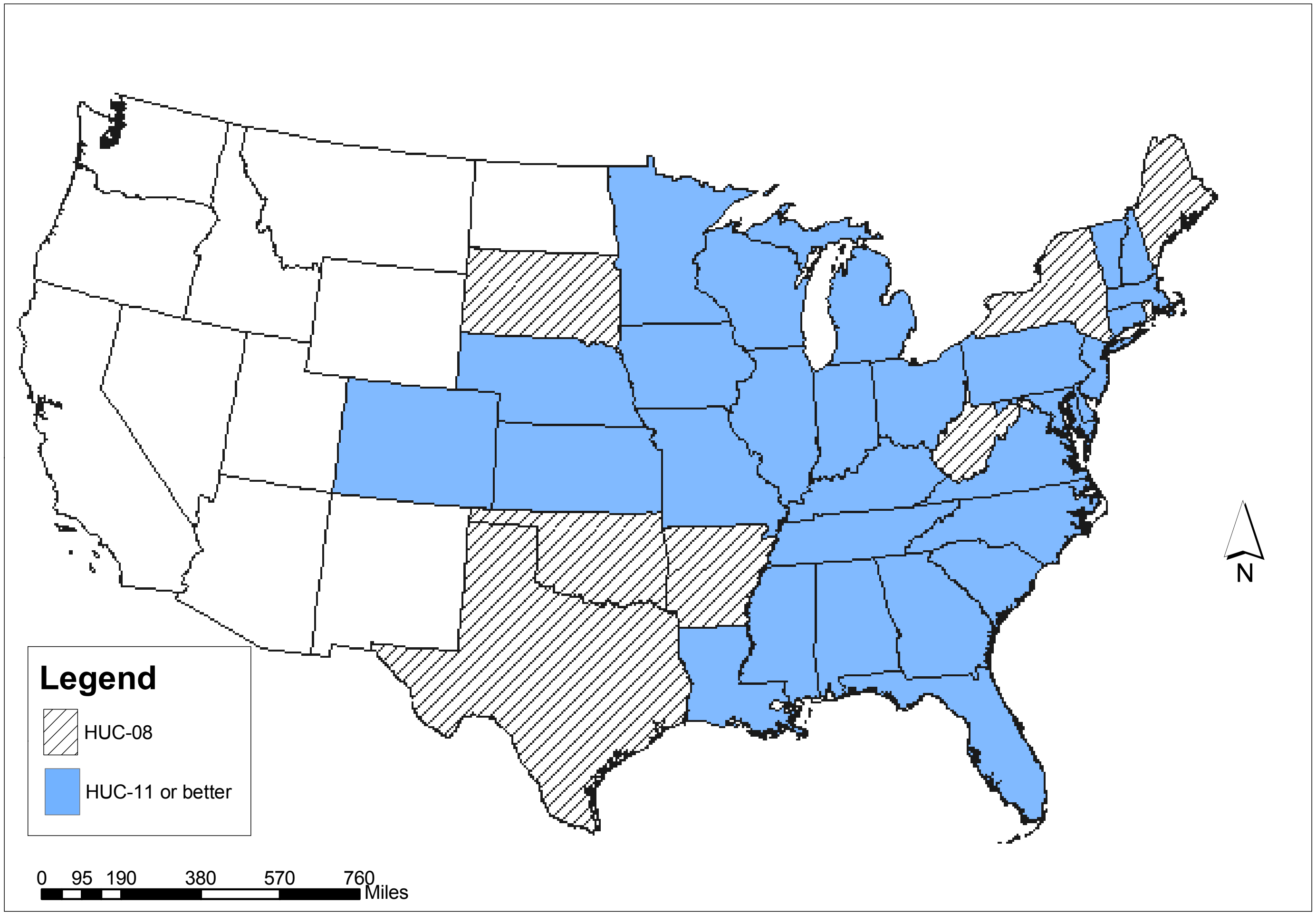


Figure 1: Finest resolution HUC level information available for the 37 high atrazine use states

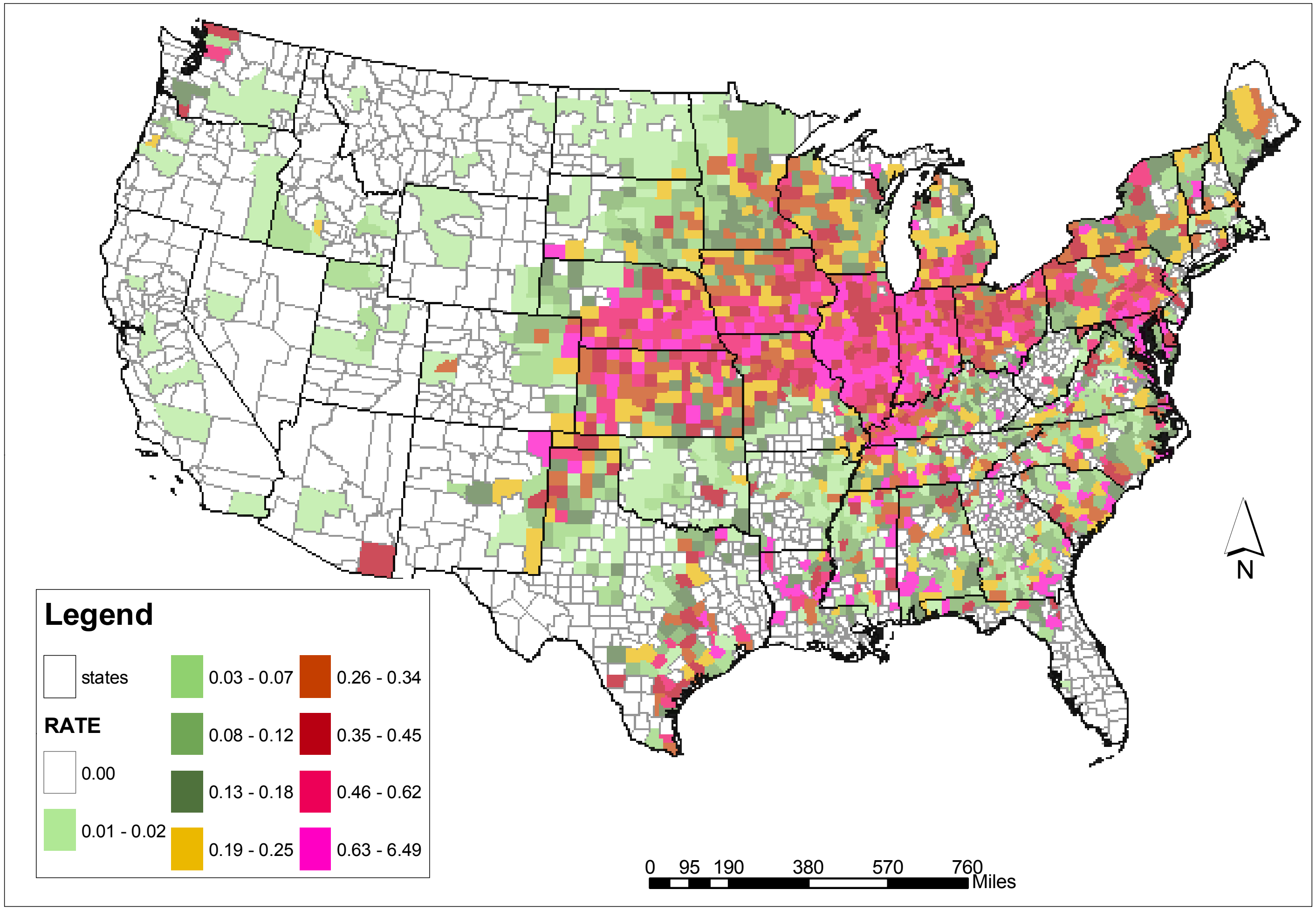


Figure 2: The distribution of cropped area use intensity for all counties with any atrazine usage (lb per harvested acre)

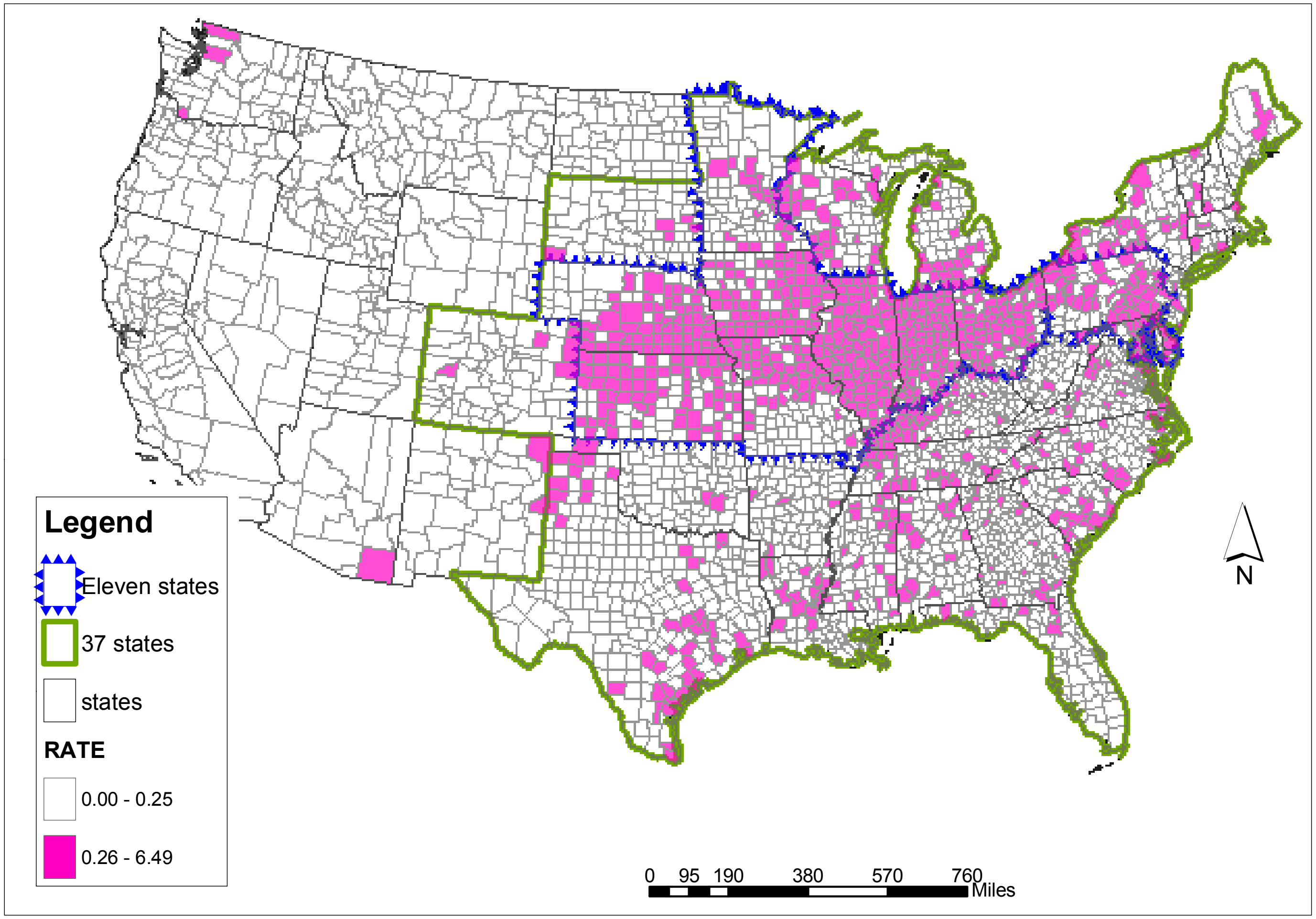


Figure 3: Counties with atrazine cropped area use intensity greater than 0.25 lb per harvested acre and outlines of the 11 and 37 state processing stages.

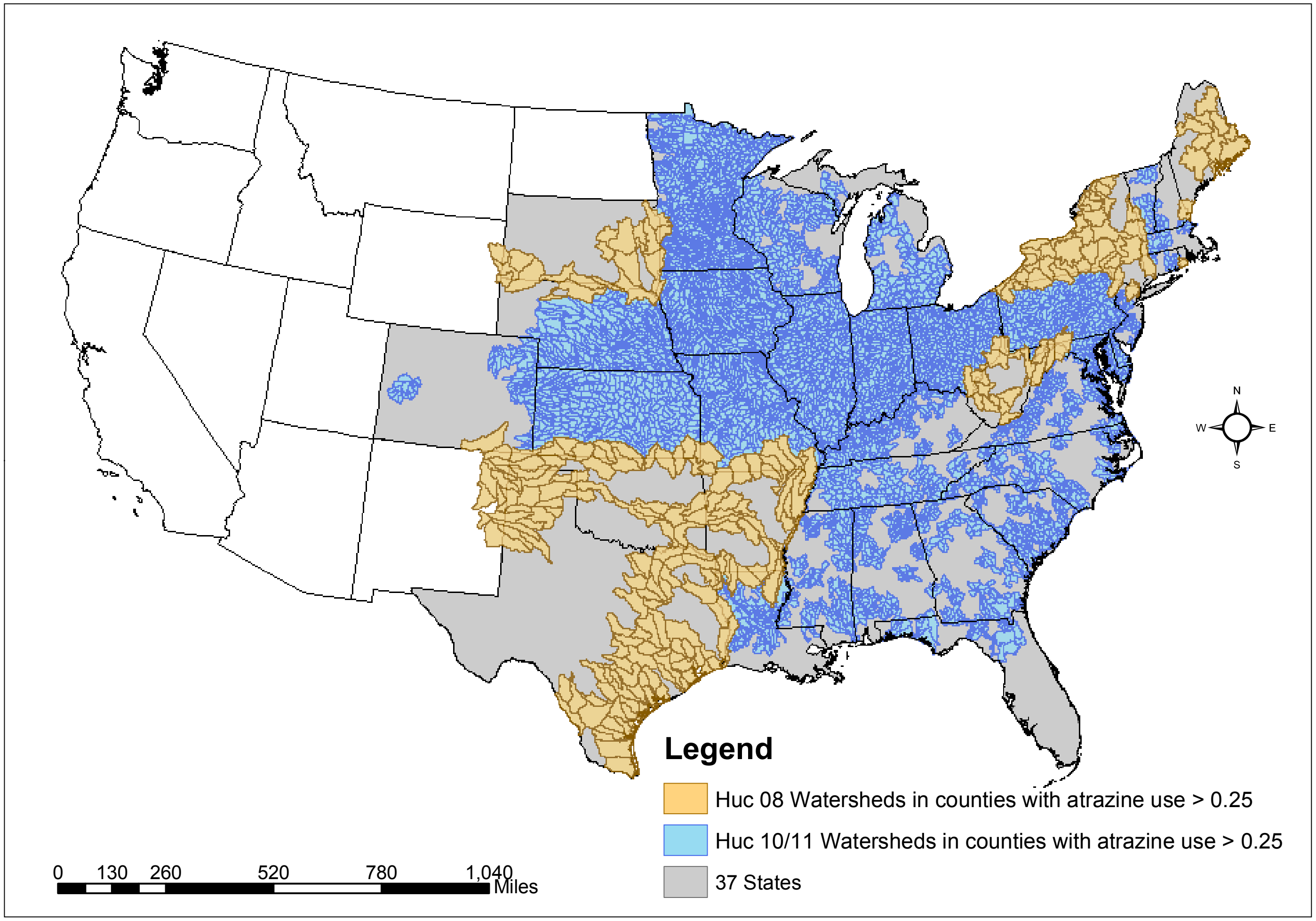


Figure 4: HUC 10/11or HUC 08 units contained within or intersecting higher use counties

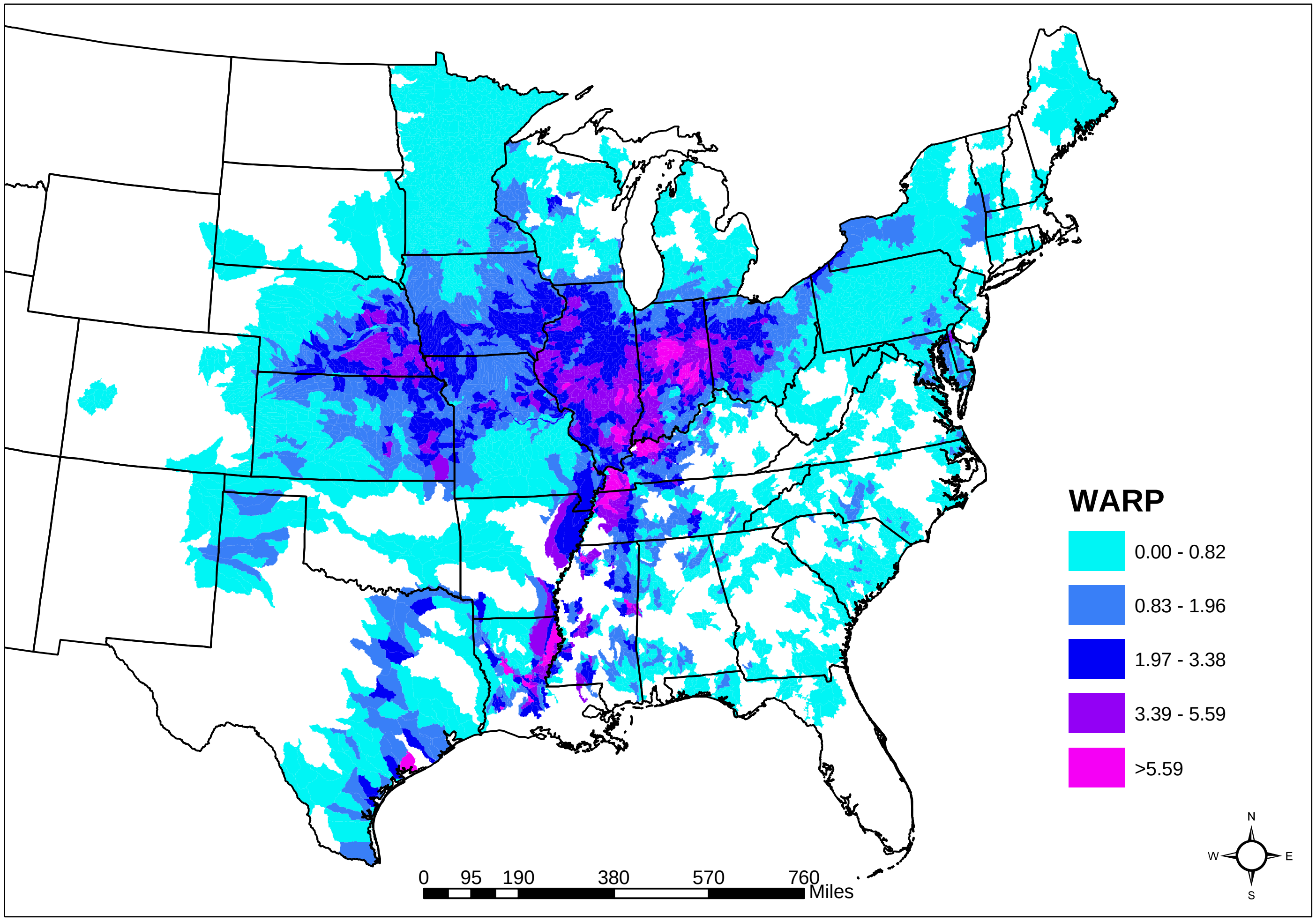


Figure 5: WARP metric predicted concentrations by higher potential risk watersheds

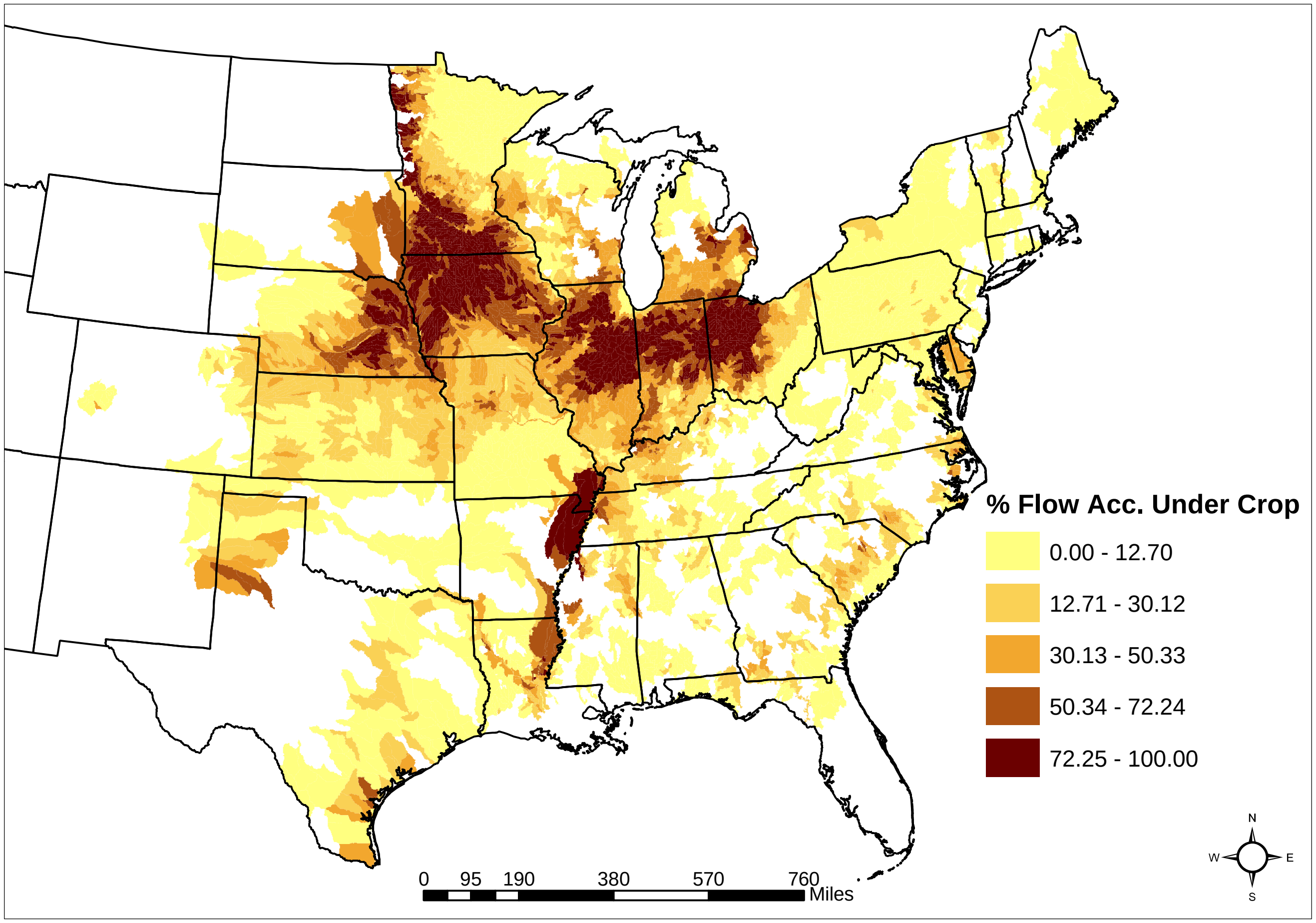


Figure 6: Percent Flow Accumulation Under Crop by HUC10/11 unit

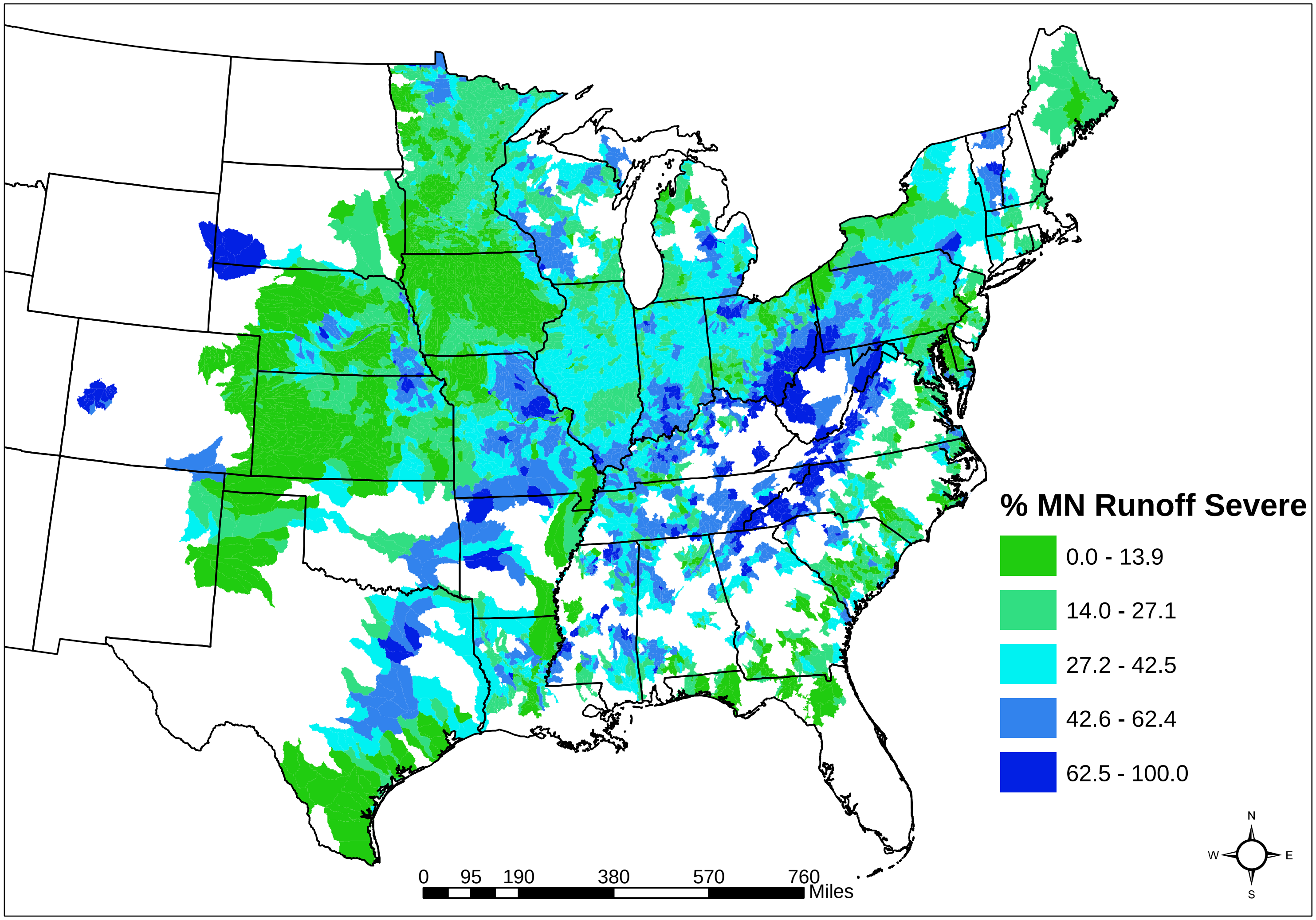


Figure 7: Minnesota Runoff Index Classified as Severe by HUC10/11 unit

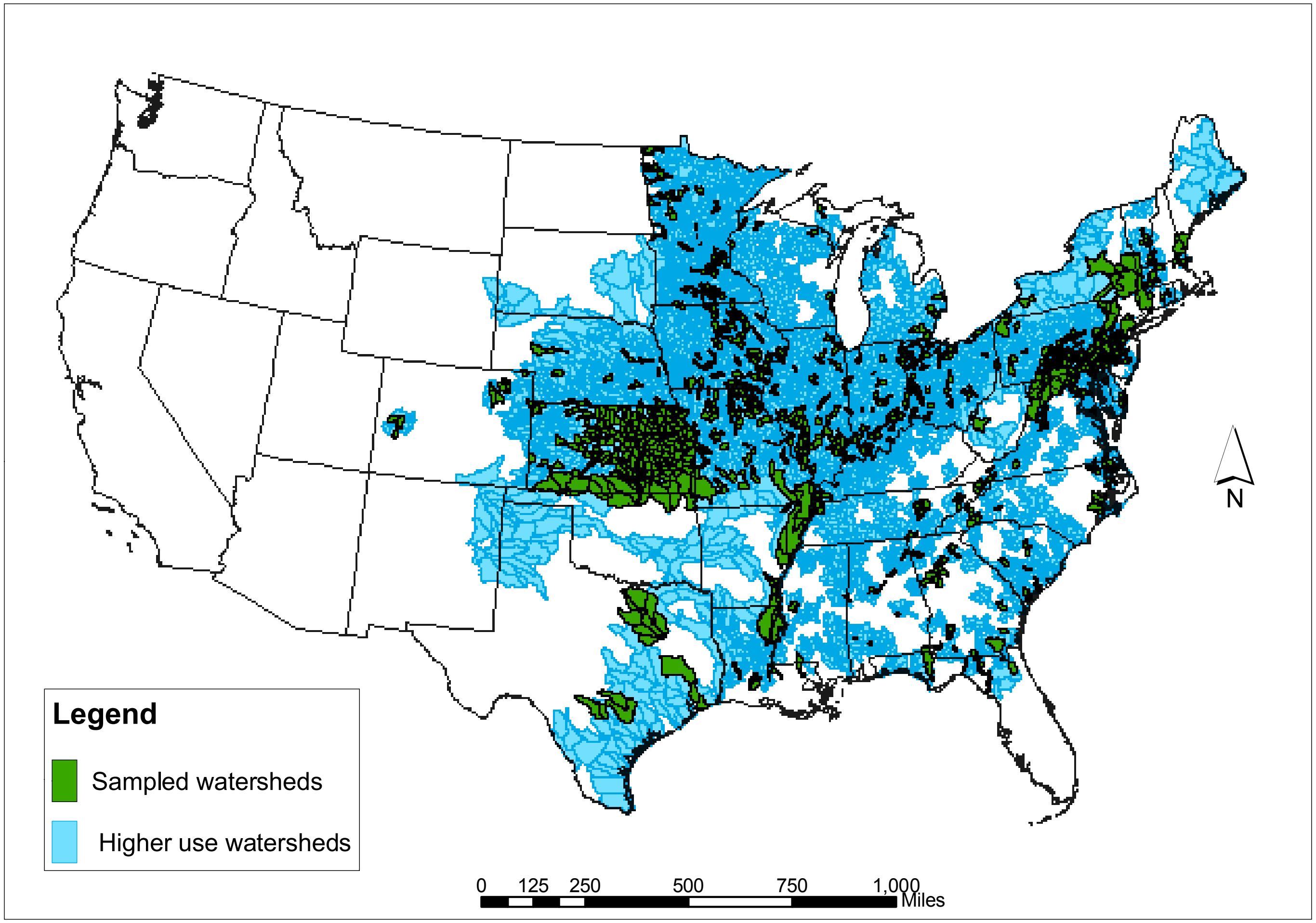


Figure 8: Watersheds with atrazine surface water monitoring data that also intersect or are contained within higher atrazine use rate counties

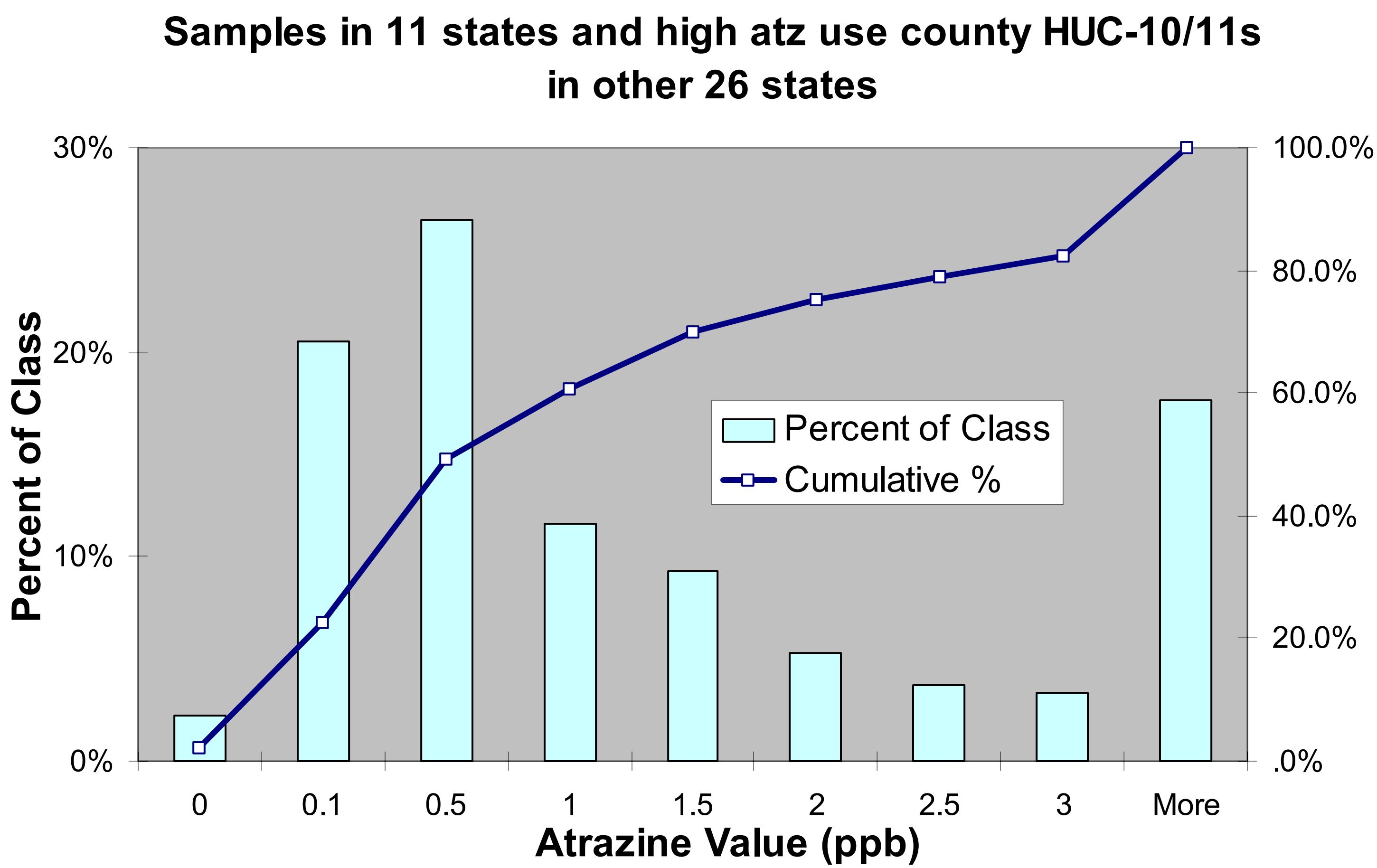


Figure 9: Histogram of sample concentrations from the full set of sampling stations located within the watersheds in the upper 45th percentile of atrazine cropped area use intensity

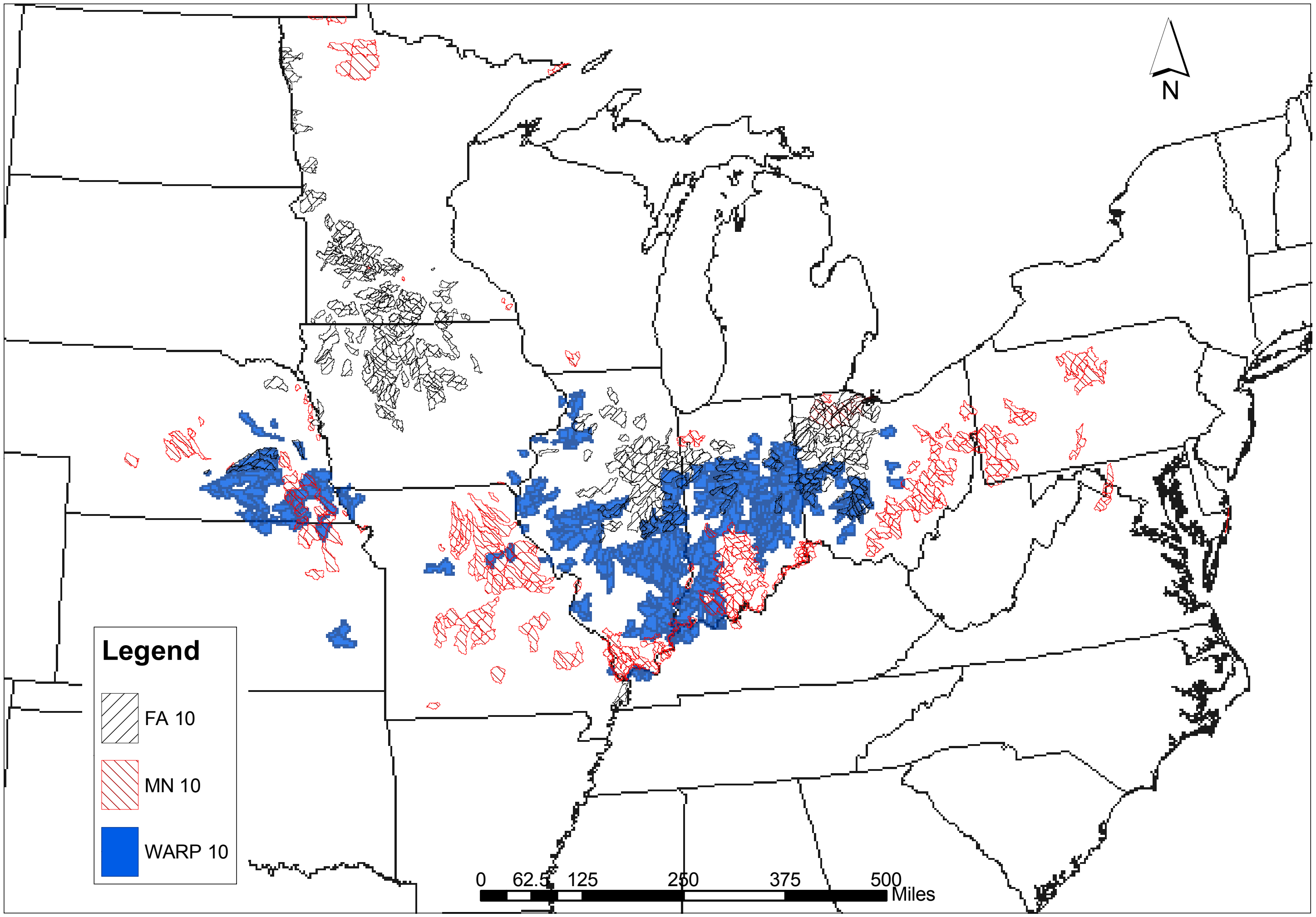


Figure 10: 11 state level WARP upper 10th Percentile, Flow Accumulation upper 10th Percentile, and Minnesota Runoff upper 10th Percentile

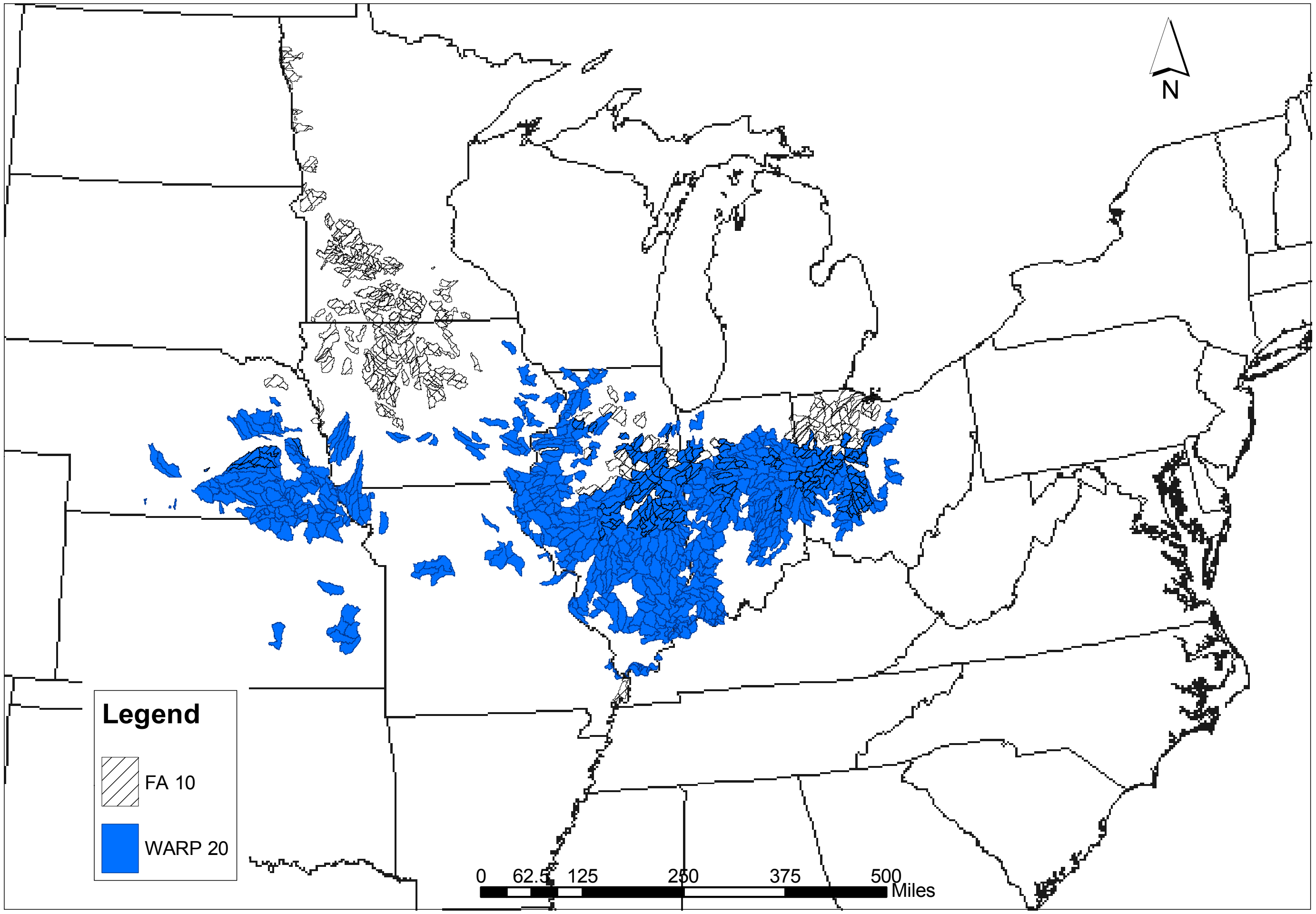


Figure 11: 11 state level WARP upper 20th Percentile and Flow Accumulation upper 10th Percentile

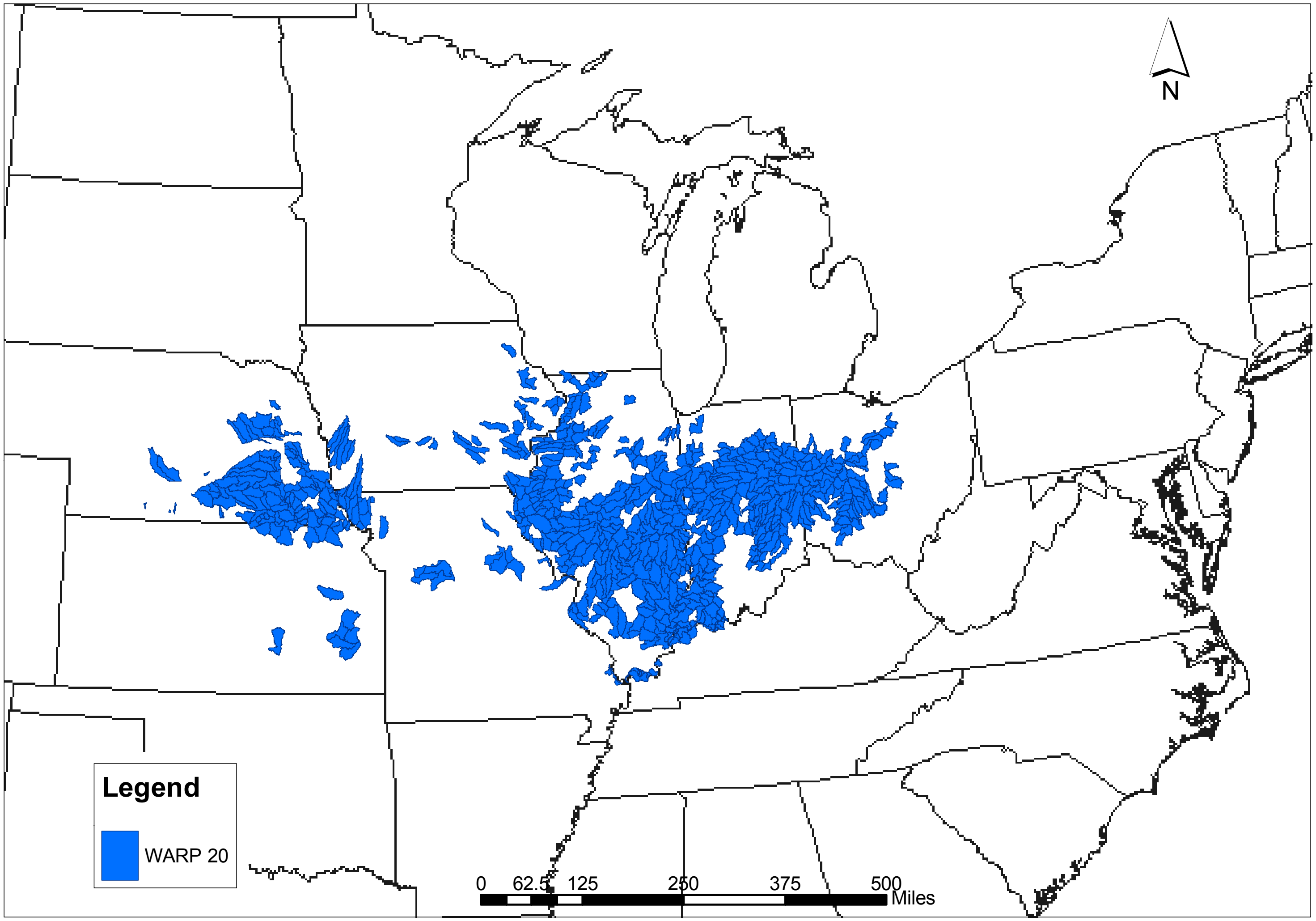


Figure 12: 11 state level WARP upper 20th Percentile

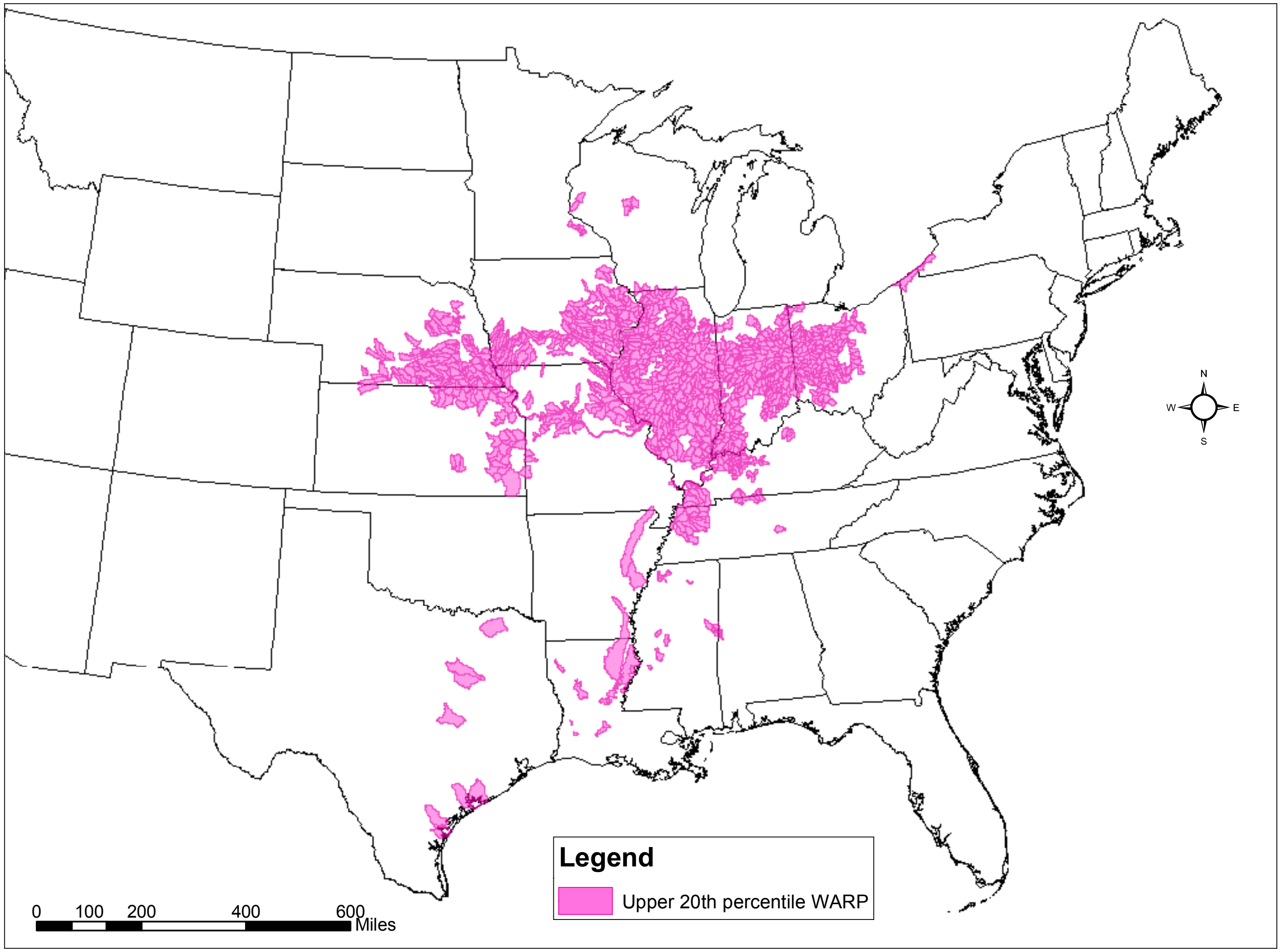


Figure 13: HUC10/11 Selected watersheds selected using the upper 20th percentile WARP model result

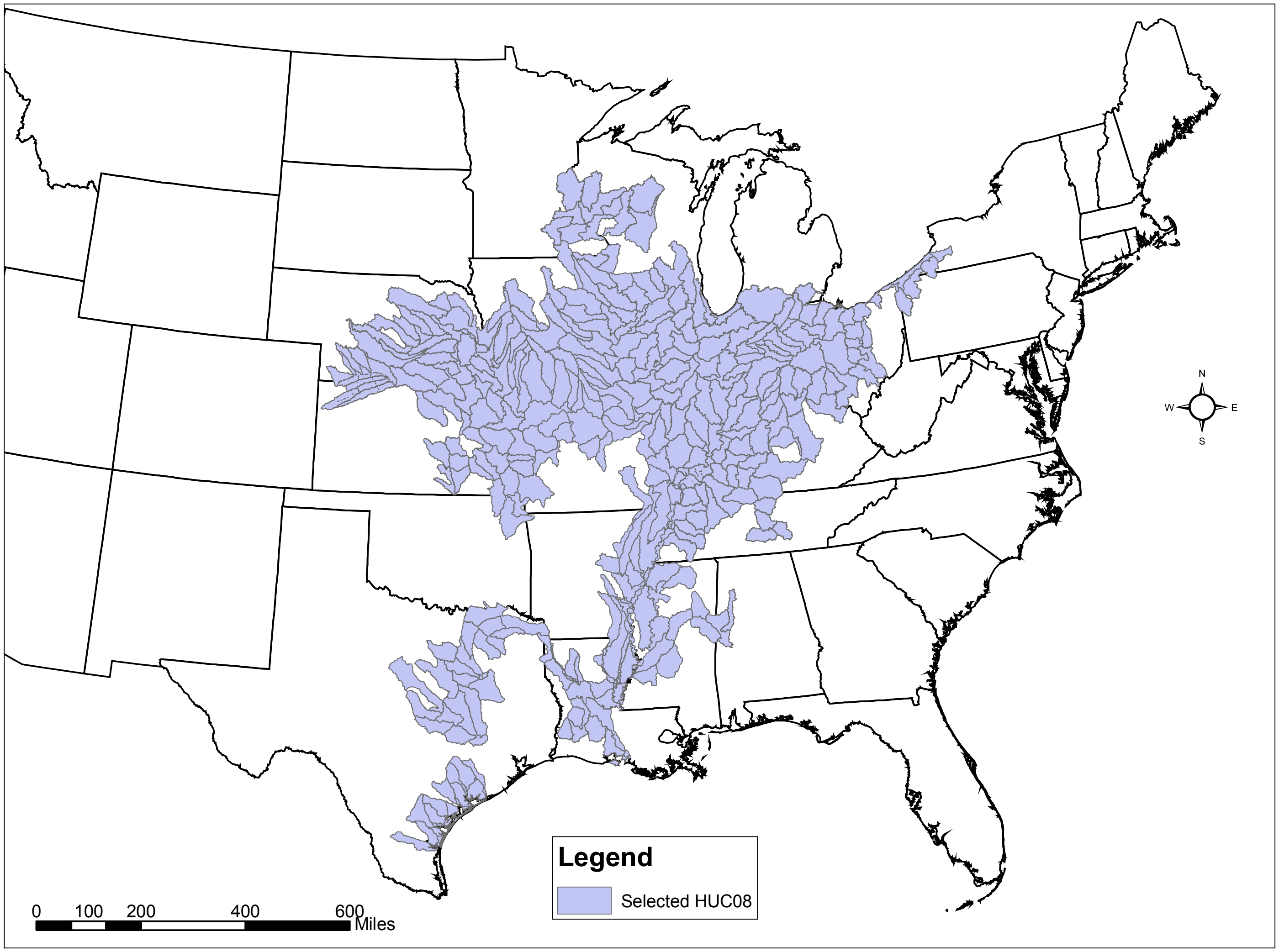


Figure 14: HUC8 basins containing at least one selected HUC10/11 watershed

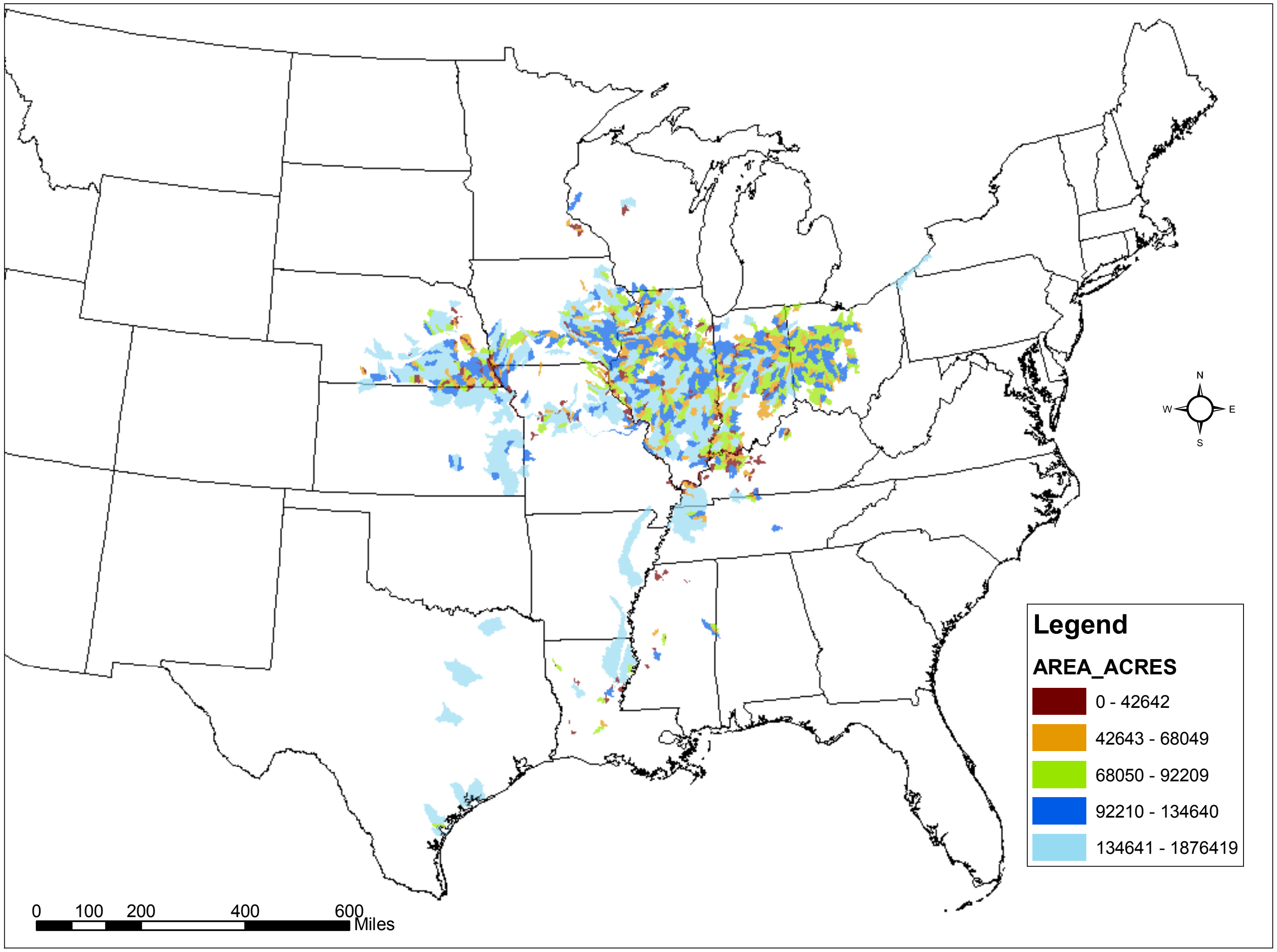


Figure 15: Watershed area for the selected set of HUC10/11 watersheds

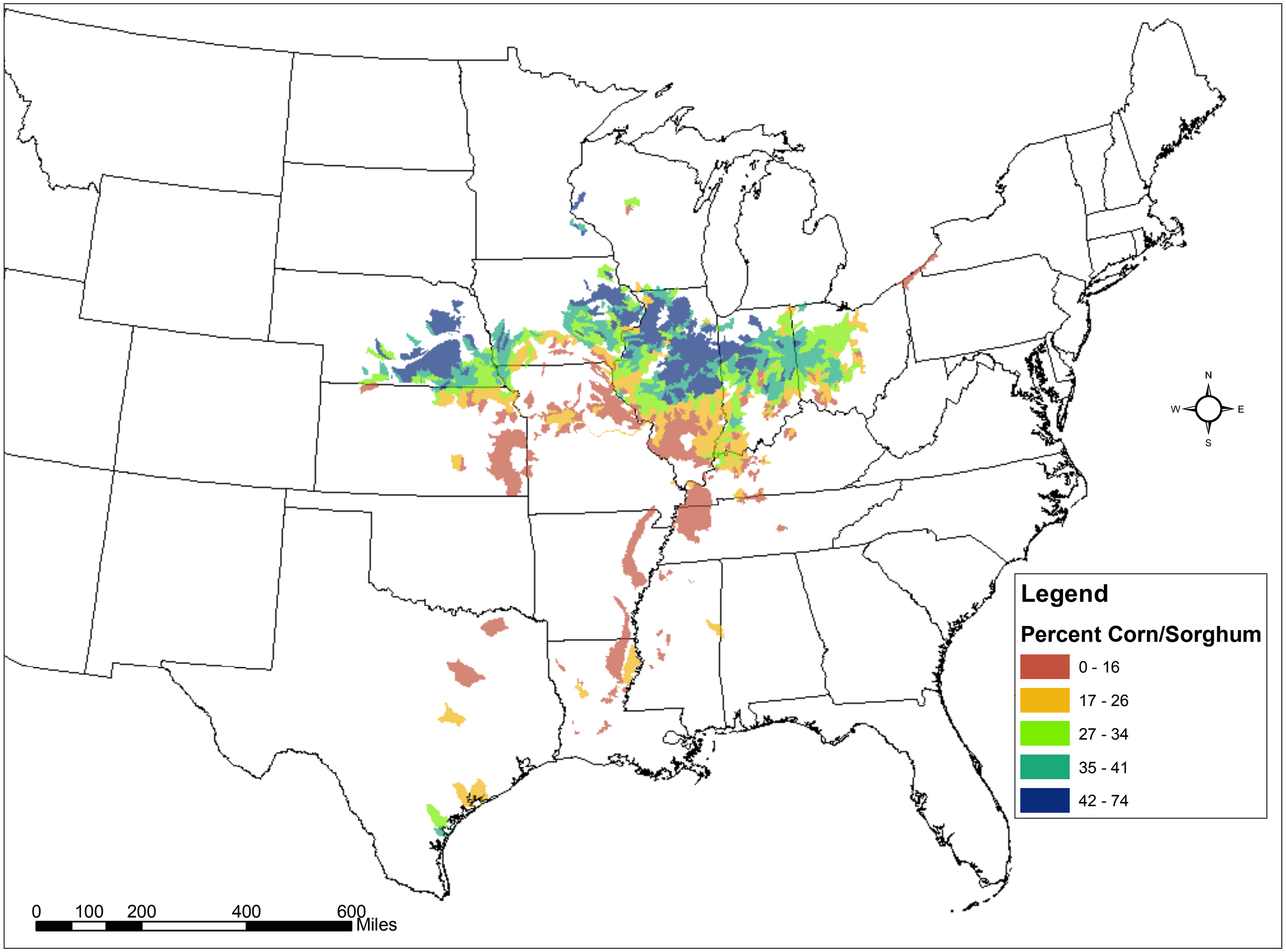


Figure 16: Watershed percent corn/sorghum land use for the selected set of HUC10/11 watersheds

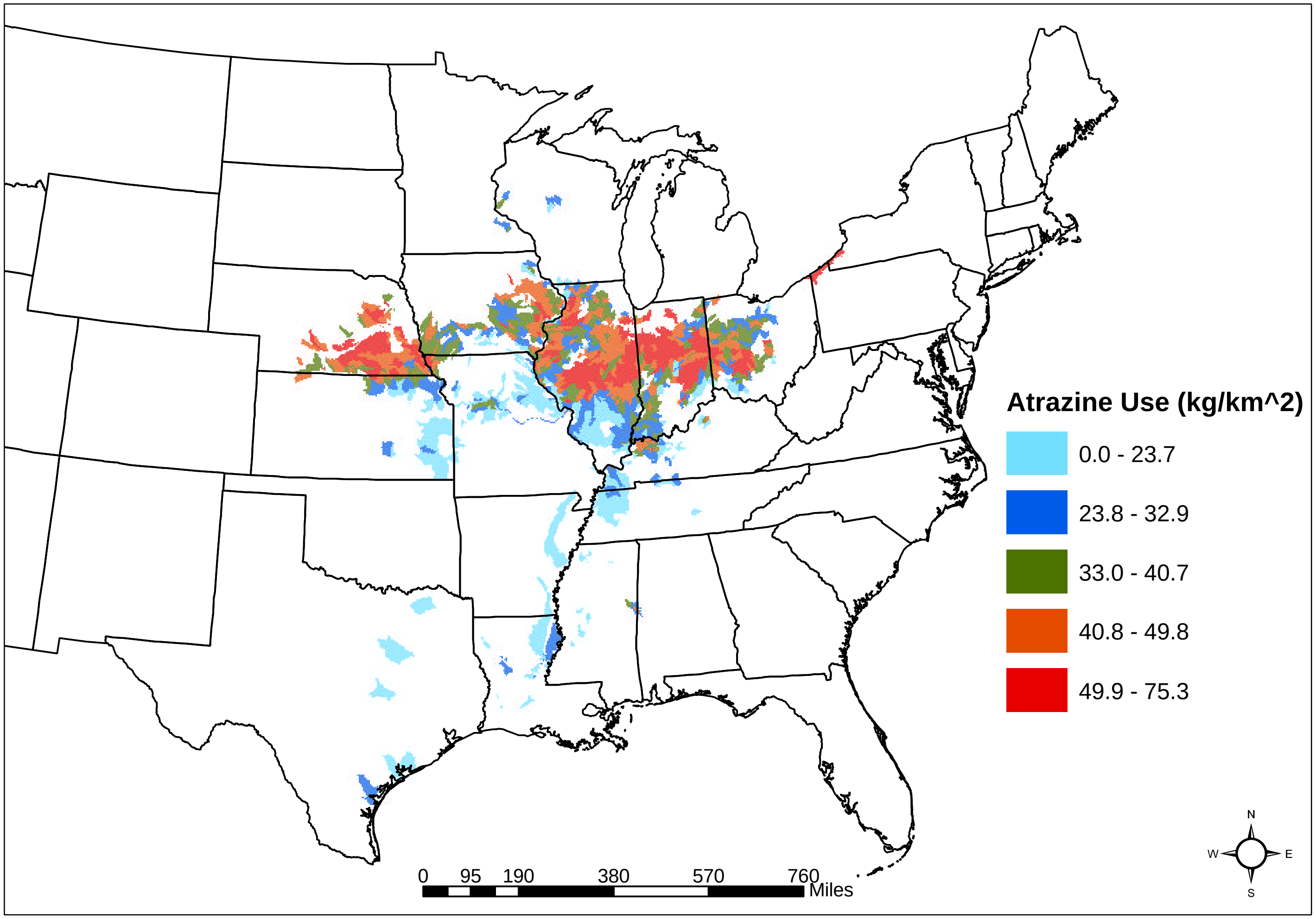


Figure 17: Watershed atrazine use for the selected set of HUC10/11 watersheds (kg per harvested km^2)

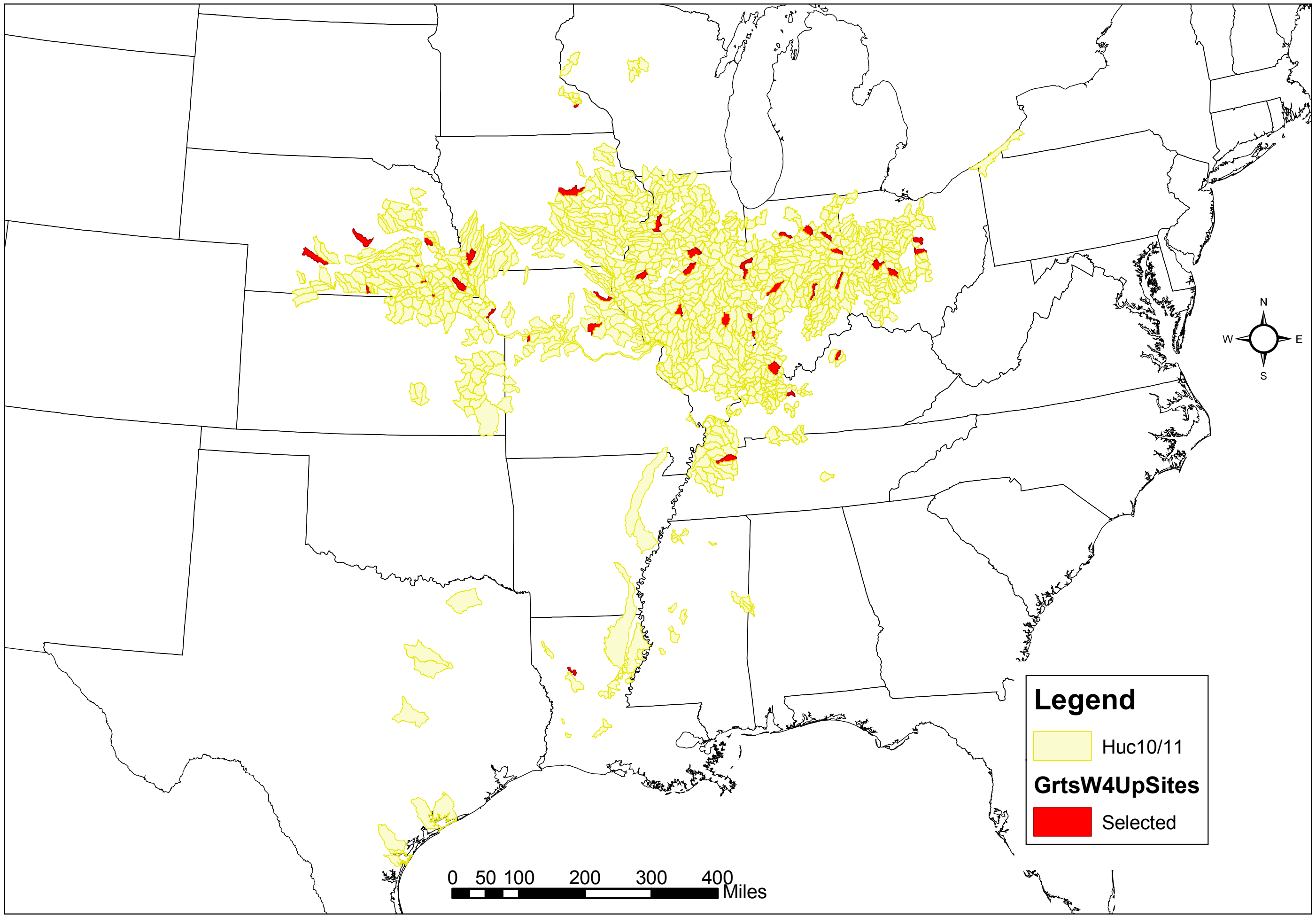


Figure 18: Spatial distribution of 1172 HUC10/11s and 40 selected HUC10/11s from GRTS design

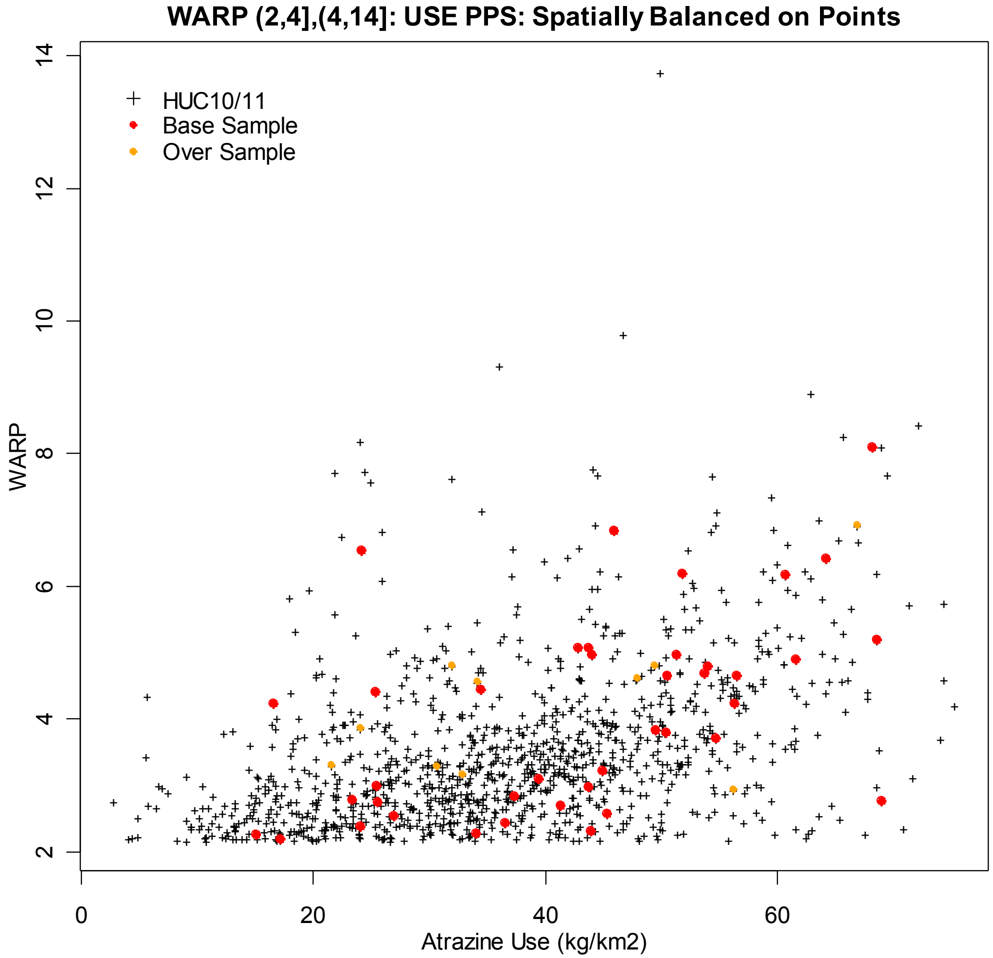


Figure 19: GRTS scatter plot of distribution of WARP predicted values and atrazine use (kg/km2)

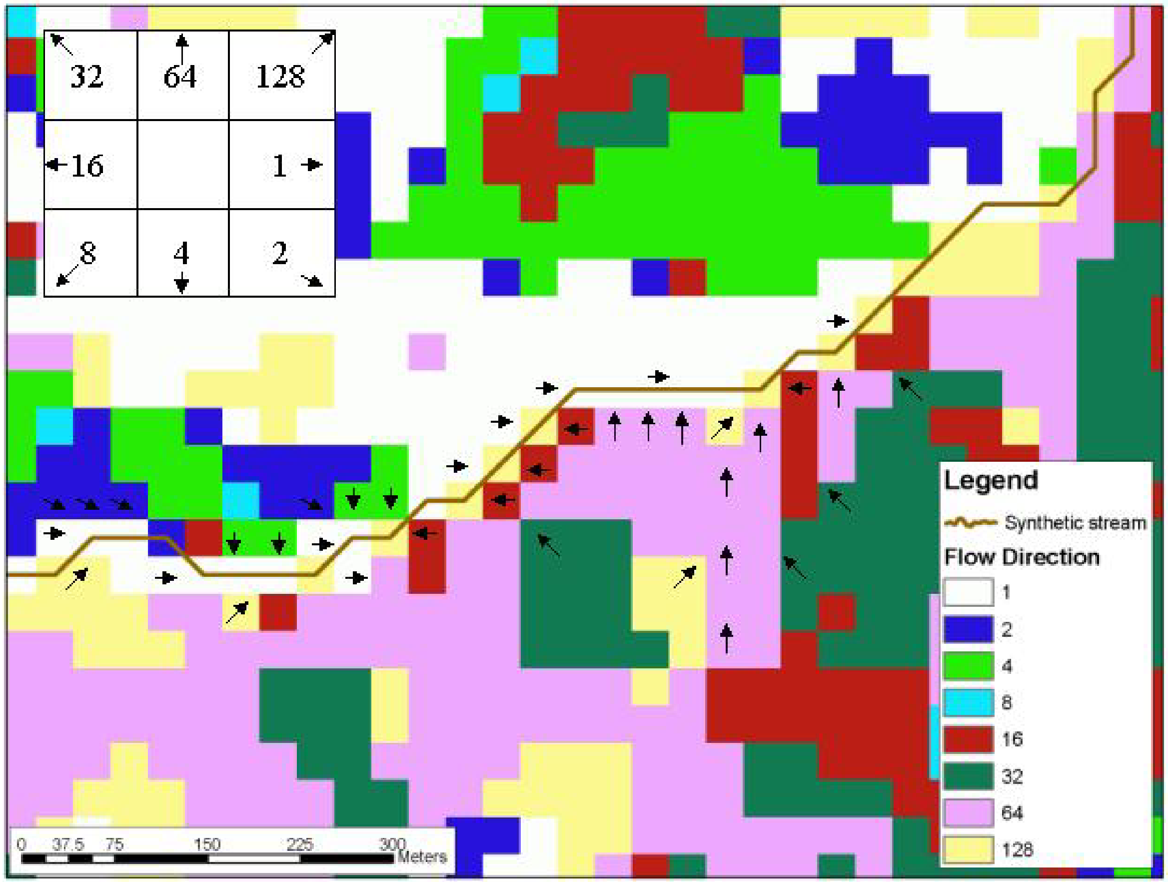


Figure 20: Flow direction grid overlaid with synthetic stream

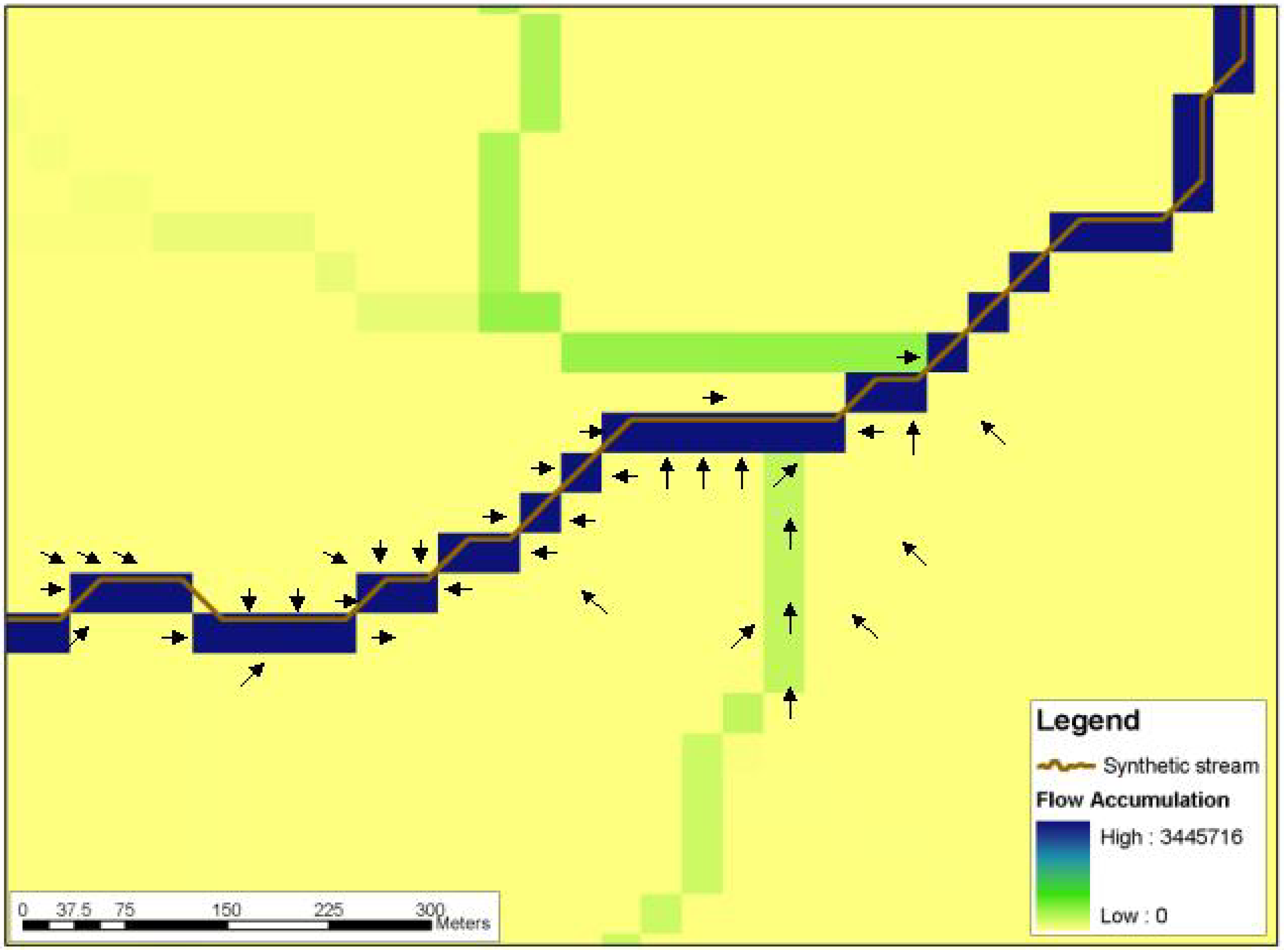


Figure 21: Flow accumulation grid

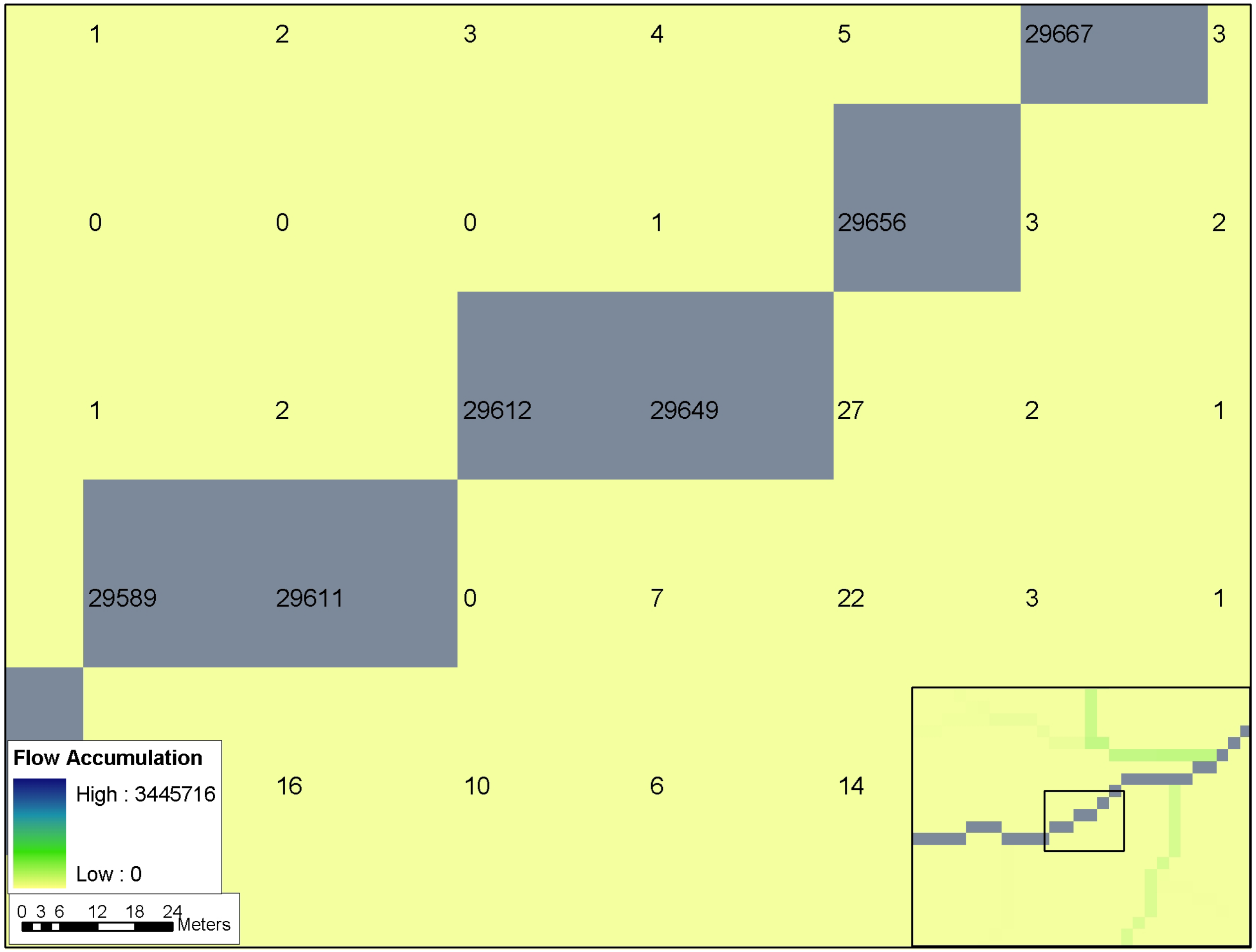


Figure 22: Flow accumulation sum values displayed on flow accumulation grid

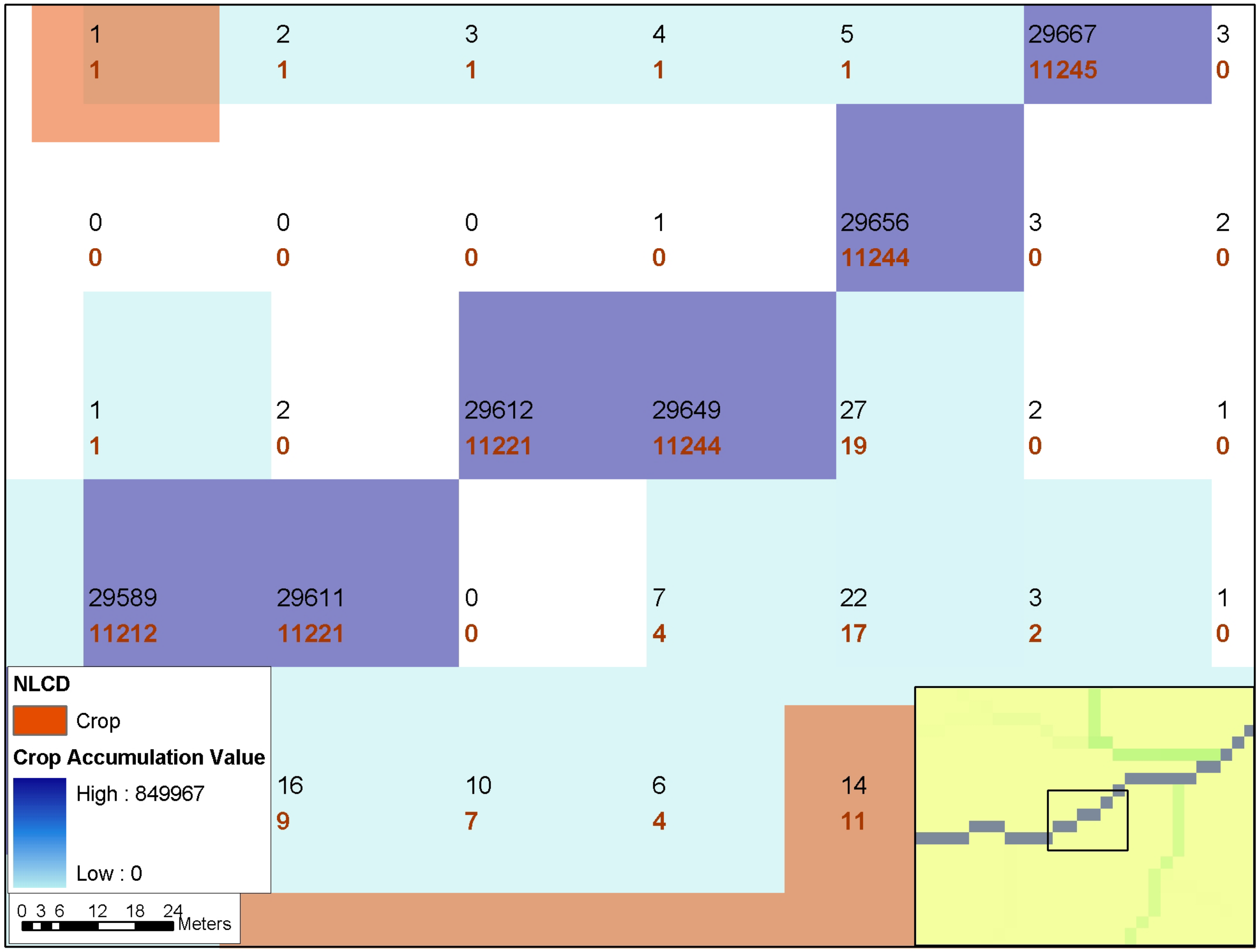


Figure 23: Crop accumulation sum values displayed underneath flow accumulation sum values