

## Le Sueur River and Little Beauford Ditch Acetochlor Impairment Response Report

---



10/23/2013

Minnesota Department of Agriculture  
625 Robert Street North  
Saint Paul, Minnesota 55155-4194

<http://www.mda.state.mn.us>

651-201-6000 or 800-967-2474  
TTY: 1-800-627-3529

### **Authors and Contributors**

Pesticide Management Unit,  
Pesticide and Fertilizer Management Division:

*Larry Van Lieshout, Ron Struss and Joseph Zachmann*

Monitoring and Assessment Unit,  
Pesticide and Fertilizer Management Division:

*Bill VanRyswyk, Matt Ribikawskis and Dave Tollefson*

### **Acknowledgements**

The following cooperating organizations were critical to the collection, analysis and interpretation of much of the data presented in this report:

Acetochlor Impairment Report Plan Advisory Committee (listed in Appendix 1)

Acetochlor Registration Partnership

Crystal Valley Cooperative

Department of Soil, Water, and Climate, University of Minnesota  
Minnesota Department of Agriculture Laboratory Services Division

Minnesota Pollution Control Agency

Southern Research and Outreach Center, University of Minnesota

Stone Environmental, Inc.

WFS Cooperative

Water and Environmental Analysis Laboratory, University of Wisconsin Stevens Point

### **Cover Photo**

The Little Beauford Ditch at high flow on September 9, 2005.

# Table of Contents

INTRODUCTION .....	5
UNITS USED IN THIS REPORT .....	6
BACKGROUND .....	6
The Le Sueur River and Little Beauford Ditch Watersheds .....	6
Acetochlor’s role and use in the watershed.....	7
Acetochlor fate and transport.....	8
RESULTS .....	9
Activity 1: Establish and coordinate a technical advisory group and stakeholder group.....	9
Activity 2: Computer modeling of acetochlor runoff and Best Management Practice effectiveness... 11	
Acetochlor BMPs in the Little Beauford Ditch subwatershed.....	11
Acetochlor BMPs in the for Le Sueur River watershed.....	13
Activity 3: Develop acetochlor management recommendations from computer modeling results.....	14
Activity 4: Watershed scale water monitoring. ....	14
Activity 5: Subwatershed scale water monitoring .....	20
Sampling methods.....	21
Analytical methods.....	22
ELISA Monitoring Conclusions.....	26
Activity 6: Collect farming system information on acetochlor use in the watersheds. ....	27
Activity 7: Collect voluntary acetochlor BMP use information in the watershed.....	29
Activity 8: Evaluate effectiveness of reduced rates Best Management Practice on loss to tile water..	30
Activity 9: Evaluate effectiveness of filter strip BMP on acetochlor loss to surface water. ....	32
Activity 10. Develop an “Acetochlor Impairment Response Report” by March 2013. ....	33
A NATIONAL CONTEXT FOR MINNESOTA’S ACETOCHLOR IMPAIRMENTS .....	34
CONCLUSIONS.....	37
RECOMMENDATIONS .....	39
REFERENCES .....	40
APPENDIX 1 (Advisory committee for Acetochlor Impairment Response Plan) .....	41
APPENDIX 2 (Units and scientific terms used in this report).....	42
APPENDIX 3 (Acetochlor report submitted by the Acetochlor Registration Partnership).....	43

## List of Tables

Table 1. Herbicide products containing acetochlor registered for use in Minnesota – 2012.....	7
Table 2. Chemical properties of acetochlor, other common corn herbicides.....	9
Table 3. Meeting summary of Acetochlor Impairment Response Plan Advisory Committee.....	10
Table 4. Number of samples with concentrations above 10% and 50% of the acetochlor standard.....	15
Table 5. Concentrations statistics for the Le Sueur River and Little Beauford Ditch monitoring sites.....	15
Table 6. Storm analysis for Little Beauford Ditch pesticide samples.....	19
Table 7. The Le Sueur River watershed sampling locations for ELISA analysis.....	21
Table 8. Summary statistics from acetochlor ELISA analysis in the Le Sueur River watershed .....	24
Table 9. Survey responses of awareness and use of acetochlor BMPs in the Le Sueur River watershed...	30
Table 10. Detections of acetochlor (and breakdown products) in tile water.....	31
Table 11. Water body impairments listed in the EPA database for the herbicide atrazine .....	34

## List of Figures

Figure 1. Le Sueur River Watershed.....	6
Figure 2: Pathways for pesticide fate and transport in the environment.....	8
Figure 3. Effect of various management practices on acetochlor loss in the Le Sueur River watershed....	13
Figure 4. Little Beauford Ditch hydrograph with acetochlor concentrations for May and June, 2011. ....	16
Figure 5. Acetochlor concentration plot for the period of record at Little Beauford Ditch .....	17
Figure 6. Acetochlor concentration plot for the period of record at Le Sueur River .....	17
Figure 7. Le Sueur River subwatersheds and sampling locations.....	21
Figure 8. Acetochlor ELISA vs acetochlor GC/MS concentrations.. ..	23
Figure 9. Acetochlor ELISA vs combined acetochlor and metolachlor GC/MS concentrations.....	23
Figure 10. Median acetochlor concentrations from the ELISA analysis 2009-2012. ....	24
Figure 11. Acetochlor concentrations measured by ELISA and GC/MS on May 7 and May 11, 2012 .....	25
Figure 12. Location of dealerships included in acetochlor use survey of agronomists.....	27
Figure 13. Percentage of acetochlor acres incorporated within the Le Sueur River Watershed, 2010.....	28
Figure 14. Pounds of acetochlor active ingredient (a.i.) applied per acre.....	29
Figure 15. Tile drainage study plots at University of Minnesota Southern Research Center .....	31
Figure 16. Vegetative filter strip study site subwatershed map .....	32
Figure 17. Vegetative filter strip study site photos. ....	33

# INTRODUCTION

In 2008, the Minnesota Pollution Control Agency (MPCA) included two water bodies, the Le Sueur River and Little Beauford Ditch, on the state's 303(d) Total Maximum Daily Load (TMDL) list of impaired waters<sup>1</sup> for violations of the acetochlor water quality standard. Acetochlor is a corn and soybean herbicide whose use is regulated by the Minnesota Department of Agriculture (MDA).

This report describes specific activities completed and evaluated in response to these water quality impairments. The activities are outlined in the Acetochlor Impairment Response Plan developed by the MDA in cooperation with the MPCA in 2009. Some of the activities are in direct response to the acetochlor water quality impairments; others are in response to MDA's on-going responsibility to assure pesticides are used in a manner that does not cause unreasonable adverse effects on the environment.

To assist in implementing the Acetochlor Impairment Response Plan, the MDA convened an Acetochlor Impairment Response Plan Advisory Committee made up of local representatives from the affected counties, interest groups, and farmers. This group has provided local input and helped direct the activities of the MDA to fine tune Acetochlor Impairment Response Plan activities.

This report is organized around the ten activities identified in the Acetochlor Impairment Response Plan:

1. Establish and coordinate a Technical advisory group and stakeholder group;
2. Computer modeling of acetochlor runoff and Best Management Practice effectiveness;
3. Develop recommendations from computer modeling results;
4. Watershed scale water monitoring;
5. Subwatershed scale water monitoring;
6. Collect farming system information in watersheds;
7. Track Best Management Practice use and adoption;
8. Evaluate effectiveness of reduced rates Best Management Practice on loss to tile water;
9. Evaluate effectiveness of filter strips Best Management Practice on loss to surface water;
10. Develop an "Acetochlor Impairment Response Report" by March 2013.

This report summarizes the findings from these activities and provides the conclusions and recommendations of MDA staff.

---

<sup>1</sup> Minnesota's Impaired Waters and TMDLs: <http://www.pca.state.mn.us/index.php/water/water-types-and-programs/minnesotas-impaired-waters-and-tmdls/minnesotas-impaired-waters-and-total-maximum-daily-loads-tmdls.html>

# UNITS USED IN THIS REPORT

The Minnesota Department of Agriculture laboratory reports acetochlor concentration in water using the unit *micrograms per liter*, or  $\mu\text{g/L}$ . For substances dissolved in water, micrograms per liter is equivalent to the unit *parts per billion*, or ppb. Since parts per billion is the more familiar unit, it is used in this report to report acetochlor concentration. More information on units used in this report is in Appendix 2.

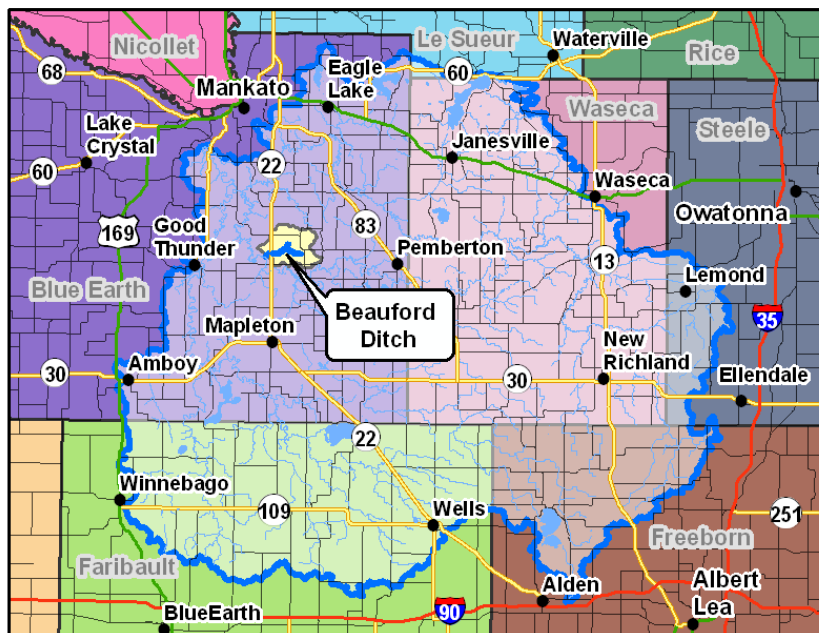
## BACKGROUND

### The Le Sueur River and Little Beauford Ditch Watersheds

The Le Sueur River watershed is one of the twelve major watersheds of the Minnesota River Basin. It is located in south central Minnesota within Blue Earth, Faribault, Freeborn, Le Sueur, Steele, and Waseca counties. The Le Sueur River watershed spans 45 miles from the city of Mankato in the northwest to the city of Albert Lea in the southeast and is 706,252 acres in area. Agriculture is the predominant land use within the watershed with corn and soybeans being major crops grown (USDA 2008).

The Le Sueur River watershed is divided into three main subwatersheds, the Upper Le Sueur, Big Cobb and Maple. These subwatersheds are described further in the “Activity 5” section later in this report.

The Little Beauford Ditch, also known simply as Beauford Ditch, is a smaller subwatershed of the Le Sueur River watershed. It is 5,500 acres in size and located entirely in Blue Earth County, just south of the city of Mankato. Figure 1 presents the Le Sueur River and Little Beauford Ditch watersheds.



*Figure 1. Le Sueur River Watershed (The Little Beauford Ditch is a subwatershed of the Le Sueur).*

## Acetochlor's role and use in the watershed

Acetochlor herbicide is widely used in Minnesota for field corn production, as well as the production of sweet corn, seed corn, and popcorn. It was introduced on the market in 1994 and is now sold under several trade names and as a component of numerous of herbicide premixes, see Table 1.

*Table 1. Herbicide products containing acetochlor registered for use in Minnesota – 2012.*

Breakfree products	Harness products	Staunch	Tremor products
Cadence products	Imperium	Surestart	TripleFlex
Confidence products	Keystone products	Surpass	Volley products
Degree products	Overtime products	Topnotch	Warrant
Fultime			

Reference to commercial products or trade names does not imply endorsement by the Minnesota Department of Agriculture. List may not include all products. Always check the label or consult MDA's product registration database at <http://state.ceris.purdue.edu/doc/mn/statemn.html>.

Normally, acetochlor would adversely impact soybeans. However, an encapsulated formulation of acetochlor, called Warrant, was introduced in 2011 that is labeled for use on soybeans, as well as corn.

Between 2001 and 2010, an average of 3.8 million pounds per year of acetochlor was sold in Minnesota<sup>2</sup>. It was applied to 31 percent of state's corn acres in 2009, making it the second most commonly used corn herbicide in terms of area covered<sup>3</sup>. Based on dealership interviews, 26 percent of corn acreage in the Le Sueur River and Little Beauford Ditch watersheds received an acetochlor application in 2009<sup>4</sup>.

Acetochlor is a preemergence herbicide which means it is applied before weeds germinate and emerge from the soil. It can also be applied early preplant and preplant incorporated. Most acetochlor product labels also allow early postemergence applications on up to 11-inch corn. Recommended application rates are dependent on soil type. Higher application rates are recommended on fine texture (high clay content) or high organic matter soils.

Acetochlor controls many annual grass weeds, yellow nutsedge, and a limited number of annual broadleaf weeds such as pigweed and black nightshade. To improve control of broadleaf weeds, acetochlor is generally used in conjunction with other pre- or postemergence herbicides. A number of corn weed control products are on the market that are mixtures of acetochlor with other herbicides, usually atrazine.

Acetochlor is in the chloroacetamide herbicide family which also includes the herbicides alachlor (Micro-Tech), metolachlor (Dual II Magnum, Charger, Clinch), and dimethenamid (Outlook). It controls weeds by inhibiting growth of seedling shoots (Herbicide Site of Action: Group 15 (WSSA) / Group K<sub>3</sub> (HRAC)). Specifically, it inhibits the formation of very-long-chain fatty acids which are an important component of the cell membrane. Blocking their production results in abnormal cell membrane formation and inhibits cell division.

---

<sup>2</sup> Minnesota Department of Agriculture Pesticide Sales Information. 2010.

<http://www.mda.state.mn.us/chemicals/pesticides/useandsales.aspx>

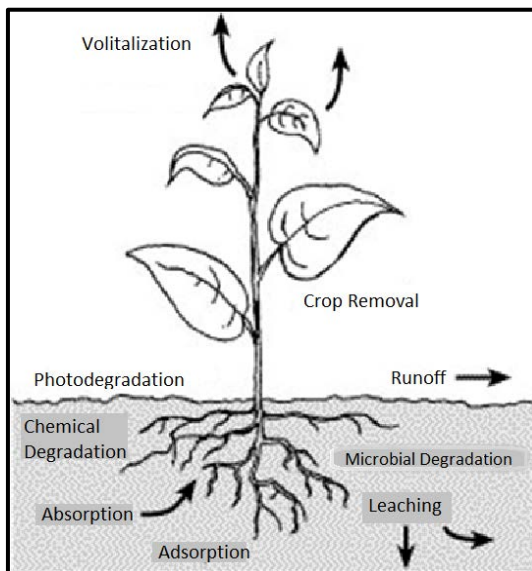
<sup>3</sup> Minnesota Department of Agriculture. 8/11. 2009 Pesticide usage on four major crops in Minnesota.

<sup>4</sup> Minnesota Department of Agriculture. 2010. Dealer agronomist survey of acetochlor use in the Le Sueur River watershed.

## Acetochlor fate and transport

When a pesticide is introduced into the environment, a number of processes interact and affect its movement and fate. These are summarized in Figure 2. Properties that affect the fate and transport of herbicides such as acetochlor in the environment include soil adsorption, soil persistence, solubility in water, and vapor pressure.

Soil adsorption,  $K_{OC}$ , measures a pesticide's tendency to bind to soil which affects its movement from the application site. Low  $K_{OC}$  values indicate weak soil adsorption or bonding of the pesticide molecules to soil particles. This can increase pesticide loss by runoff and leaching especially if rainfall is heavy. High  $K_{OC}$  values indicate strong bonding of the pesticide molecules to soil particles. This results in less pesticide loss through runoff or leaching, but more loss while associated with eroding soil particles. However, loss through eroding soil particles is only considered the main loss pathway for pesticides with  $K_{OC}$  greater than 1000 mL/g. The  $K_{OC}$  for acetochlor is 150 mL/g.



**Figure 2:** Pathways for pesticide fate and transport in the environment.

Soil persistence is a pesticide's resistance to degradation in the soil and is often expressed as its half-life. Half-life is the time it takes for the pesticide to degrade to half its previous amount through biological, chemical or photo- degradation. A larger half-life indicates that it takes a longer time for the pesticide to degrade. More persistent pesticides remain in the soil longer subjecting them to leaching and surface runoff. For residual herbicides used in annual crops, the desired persistence is long enough to provide season-long weed control, but short enough that it does not carry-over and harm the crop planted the following year. The half-life for acetochlor is 14 days. The primary means of acetochlor degradation in the soil is metabolism by soil microorganisms.

Pesticide solubility in water also has an impact on its mobility. A pesticide with low solubility is less likely to leach into the soil or runoff while dissolved in surface water. However, pesticides with high water solubility do not necessarily leach more since it still depends greatly on their soil adsorption. The water solubility for acetochlor is 223 mg/L.

Acetochlor has a high vapor pressure ( $3.3 \times 10^{-8}$  mm Hg) indicating that volatility is not an important environmental fate or transport process.

Adsorption, half-life, and solubility values for acetochlor and other commonly used corn herbicides are given in Table 2. The table also contains values that the U.S. Environmental Protection Agency (EPA) uses to indicate higher runoff or leaching potential. The low soil adsorption and high solubility of acetochlor both suggest that it has potential to leave fields as surface runoff. This is more likely if weather and field conditions result in surface water runoff soon after application. Surface runoff can be reduced by shallow soil incorporating the herbicide which increases pesticide-soil contact. Acetochlor's properties



also suggest that it has potential to leach from fields but this loss is less than surface runoff on most Minnesota soils.

**Table 2.** Chemical properties of acetochlor, other common corn herbicides <sup>a</sup>, and levels of these parameters that EPA uses to indicate higher potential for pesticide runoff and leaching <sup>bc</sup>.

Property	Acetochlor	Atrazine	Glyphosate	Metolachlor	EPA Level
Soil Adsorption, K <sub>oc</sub> (mL/g)	150	100	24,000	170	< 500
Half-life (days)	14	60	47	24	> 21
Solubility (mg/L)	223	33	900,000	530	> 30

<sup>a</sup> www.wsi.nrcs.usda.gov and pmep.cce.cornell.edu

<sup>b</sup> Metolachlor is the active ingredient in Dual II Magnum, Cinch, Brawl, Me-Too-Lachlor, and Stalwart herbicides, and a number of premixes. Dimethenamid is the active ingredient in Outlook herbicide.

<sup>c</sup> Minnesota Department of Agriculture. 2007.

<http://www.mda.state.mn.us/chemicals/pesticides/~~/media/Files/chemicals/swqdesigndoc.ashx>

When acetochlor breaks down in the environment, some of its degradation products are more soluble and mobile than the parent compound and therefore have greater potential to be detected in surface and groundwater. The most common acetochlor degradates detected are acetochlor ESA (ethanesulfonic acid) and acetochlor OXA (oxanilic acid). MDA has monitored the concentration of these degradates and results indicate they are well below the guidelines for aquatic life and human health.

The Acetochlor Registration Partnership, representing the principal registrants of acetochlor products with the EPA, has submitted to the MDA its interpretation of fate and transport considerations relative to the listing of the Le Sueur River and Beauford Ditch as impaired waters (Appendix 3).

## RESULTS

The Acetochlor Impairment Response Plan included ten activities designed to provide information on and insight into the acetochlor water quality impairment in the Le Sueur River and Little Beauford Ditch. The final activity is the development of this Acetochlor Impairment Response Report. Results and findings from the activities are reported in this section.

### **Activity 1: Establish and coordinate a technical advisory group and stakeholder group.**

Due to a significant overlap of membership that would occur, it was decided to establish one advisory group that would combine the functions of both the technical advisory group and stakeholder group. Membership of the Acetochlor Impairment Response Plan Advisory Committee, as it was named, is provided in Appendix 1.

The advisory committee met three times. A summary of the meetings is provided in Table 3. The advisory committee will meet one more time to review the final draft of this report. The Minnesota Department of Agriculture appreciates the dedication of advisory committee members and the contributions they provided.

**Table 3. Meeting summary of Acetochlor Impairment Response Plan Advisory Committee**

Date and venue	Agenda items and decisions
<p>September 15, 2010 Community Room Snell Motors Mankato, MN</p>	<p><u>Agenda items:</u></p> <ol style="list-style-type: none"> <li>1. Introduction of committee members</li> <li>2. Review of acetochlor impairment and need for response</li> <li>3. Role of advisory committee and proposed meeting schedule</li> <li>4. Review and comment on proposed “Acetochlor Impairment Response Plan”</li> <li>5. Review and comment on proposed survey of pesticide dealers</li> </ol> <p><u>Actions:</u></p> <ul style="list-style-type: none"> <li>• The committee thought the group’s make-up was adequate. No additional committee members were suggested.</li> <li>• The committee thought the activities proposed in the Acetochlor Impairment Response Plan were adequate.</li> <li>• The committee thought the types of questions proposed for the pesticide dealer survey were adequate.</li> </ul>
<p>April 7, 2011 Community Room Snell Motors Mankato, MN</p>	<p><u>Agenda items:</u></p> <ol style="list-style-type: none"> <li>1. Preliminary acetochlor water monitoring results from 2010.</li> <li>2. Summary of 2010 Saint Clair acetochlor runoff study.</li> <li>3. Sharing and discussing results of Le Sueur watershed agronomist survey.</li> <li>4. Review of fact sheet on acetochlor water quality standard and label requirements.</li> <li>5. Other clean water activities happening in the Le Sueur watershed.</li> <li>6. 2011 planned acetochlor impairment response activities.</li> <li>7. Closing ideas and suggestions.</li> </ol> <p><u>Actions:</u></p> <ul style="list-style-type: none"> <li>• The committee appreciated project updates.</li> <li>• The committee found the results of the agronomist survey to “ring true”.</li> <li>• The committee thought the project was overall on track.</li> </ul>
<p>September 4, 2012 Conference Room Ziegler Equipment Mankato, MN</p>	<p><u>Agenda items:</u></p> <ol style="list-style-type: none"> <li>1. Results of grower survey on acetochlor best management practice use.</li> <li>2. Acetochlor water monitoring results.</li> <li>3. “Listing” and “delisting” pesticide water quality impairments.</li> <li>4. What have we learned about the acetochlor impairment so far?</li> <li>5. Committee guidance on developing the Acetochlor Impairment Response Report.</li> </ol> <p><u>Actions:</u></p> <ul style="list-style-type: none"> <li>• The committee appreciated project updates.</li> <li>• The committee found the results of the grower survey on BMP use to “ring true”.</li> <li>• The recommendation of one committee member to advocate for delisting acetochlor received general support.</li> </ul>
<p>June 6, 2013 Conference Room Minnesota Pollution Control Agency Mankato, MN</p>	<p><u>Agenda items:</u></p> <ol style="list-style-type: none"> <li>1. Review and comment on draft Acetochlor Impairment Response Report.</li> </ol> <p><u>Actions:</u></p> <ul style="list-style-type: none"> <li>• The committee offered several recommendations for improving report clarity.</li> <li>• The committee suggested ways of sharing the report to communicate the conservation measures farmers are using.</li> </ul>

- |  |                                                                                                                                                                                       |
|--|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <ul style="list-style-type: none"><li>• The committee indicated that although the process was a long one, MDA-MPCA partnership used to address this impairment worked well.</li></ul> |
|--|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

## **Activity 2: Computer modeling of acetochlor runoff and Best Management Practice effectiveness.**

The effectiveness of different management practices on pesticide runoff can be determined by conducting field experiments that measure losses under various conditions. However this process requires a great deal of information making it impractical and expensive to determine runoff for every combination of soils, pesticides, weather conditions, and management practices. For this reason, pesticide runoff potential is typically assessed by computer models that are based on studies that relate various factors to pesticide runoff.

The Minnesota Department of Agriculture contracted with the University of Minnesota to evaluate the effectiveness of acetochlor best management practices (BMPs) in the Le Sueur River watershed using computer modeling. Dr. David Mulla and PhD graduate student Solomon Folle from the Department of Soil, Water and Climate conducted the study (Folle 2010). The acetochlor study was part of a larger study which also evaluated the effectiveness of nutrient and sediment BMPs within the Le Sueur River watershed. The study report was completed June 30, 2009. More information and a full copy of the report are available at: <http://www.mda.state.mn.us/protecting/cleanwaterfund/research/swatmodel.aspx>. Also, Solomon Folle's dissertation is available at: [http://conservancy.umn.edu/bitstream/59212/1/Folle\\_umn\\_0130E\\_10935.pdf](http://conservancy.umn.edu/bitstream/59212/1/Folle_umn_0130E_10935.pdf).

After evaluating different models, the Soil and Water Assessment Tool (SWAT) model was selected for evaluating acetochlor BMP effectiveness in the Le Sueur River watershed (Folle et al., 2007; Folle et al., 2009). Despite the strengths of the SWAT model, it is important to note model weaknesses with respect to acetochlor fate and transport:

- There is no routing of flow and pollutants within a subwatershed
- Targeted placement of BMPs like filter strips, grassed water ways, riparian buffer zones, wetlands, grassland or other land use within a given subwatershed is not possible.
- The tile drainage routines in SWAT are based on empirical parameters related to timing of field drainage and they do not explicitly account for the spacing of tile drains or depth of shallow water table.

The extent of pesticide loss from agricultural fields can vary with application rate, pesticide properties, soil cover, soil type, topography, and weather conditions following application. Efforts to reduce pesticide pollution of water resources can be improved by understanding pesticide transport processes. Three pesticides, including acetochlor, were studied. Analysis of predicted and observed monthly average acetochlor losses indicated the SWAT model predicted the losses with great accuracy.

**Acetochlor BMPs in the Little Beauford Ditch subwatershed:** Calibration of the SWAT model for pesticide loss utilized the 2005 the Beauford Ditch subwatershed monitoring data. Acetochlor loss was predominately (93 percent) in solution form. Approximately 4.1 percent of the applied acetochlor was predicted to have reached the mouth of the Little Beauford Ditch subwatershed.

The acetochlor BMPs evaluated with the SWAT Model for the Little Beauford Ditch sub-watershed included: 1) acetochlor rate of application; 2) watershed area of application; 3) timing of application; 4) incorporation of acetochlor; and 5) effects of buffer strips. The following scenarios were compared:

1. Acetochlor was evaluated at a baseline rate of 1.6 lb/A and at low/high label rates of 1.3 and 2.2 lb/A.
2. Watershed area of application investigated the effect reducing application to critical contributing areas and the effect of limiting the portion of the land treated.
3. The date of application was varied from April 29 to May 3.
4. Incorporation of acetochlor was compared to surface application.
5. The effects of buffer strip width and location were examined.

Acetochlor rate simulation showed that application rate had a significant effect on acetochlor loss. In comparison with the baseline rate, applying 1.3 lb/A reduced acetochlor loss by 17 percent. Applying 2.2 lb/A increased acetochlor loss over the baseline rate by 37 percent. The 1.3 lb/A application rate resulted in a maximum acetochlor concentration of 4.39 ppb, whereas a 2.2 lb/A rate resulted in a maximum concentration of 7.23 ppb.

The second set of scenarios for the Little Beauford Ditch subwatershed involved the area receiving acetochlor and looked at applications to “critical contributing areas” (CCA) versus non-CCAs. CCAs are portions of the landscape that accumulate overland water flow and are hydrologically connected to surface waters (lakes, ponds, rivers, streams ditches, etc.) by surface runoff or subsurface drainage (Galzki, et al. 2011). Watershed area receiving acetochlor was studied by applying acetochlor at 1.3 lb/A to CCAs and 1.6 lb/A to non-CCAs which resulted in an 11 percent reduction of acetochlor loss relative to the baseline scenario. Applying 1.3 lb/A to CCAs and 2.2 lb/A to non-CCAs resulted in a 3 percent reduction of acetochlor loss relative to the baseline scenario. Application of acetochlor at a rate of 1.6 lb/A to 20 percent of the land planted to corn reduced acetochlor losses by 56 percent relative to the default application on 35 percent of the corn land. Increasing the area receiving acetochlor to 50 percent of the corn land increased acetochlor loss by 117 percent relative to the baseline scenario.

The third BMP involved date of application which was varied from April 29 to May 3. Application date had a significant effect on acetochlor loss. Delaying acetochlor application from April 29 to May 3 increased the loss by 31 percent with an application rate of 1.6 lb/A, and increased loss by 8 percent with an application rate of 1.3 lb/A. This increase is due to the occurrence of storms shortly after May 3, indicating acetochlor should not be applied shortly before rainstorms to avoid losses. In general, maximum acetochlor concentrations in the Little Beauford Ditch were reached in the month of May.

The fourth set of scenarios involved incorporation of acetochlor. Incorporation of acetochlor significantly reduced acetochlor loss relative to the baseline scenario with no incorporation. At the lowest acetochlor application rate (1.3 lb/A), incorporation reduced acetochlor loss by 95 percent relative to the baseline application rate of 1.6 lb/A.

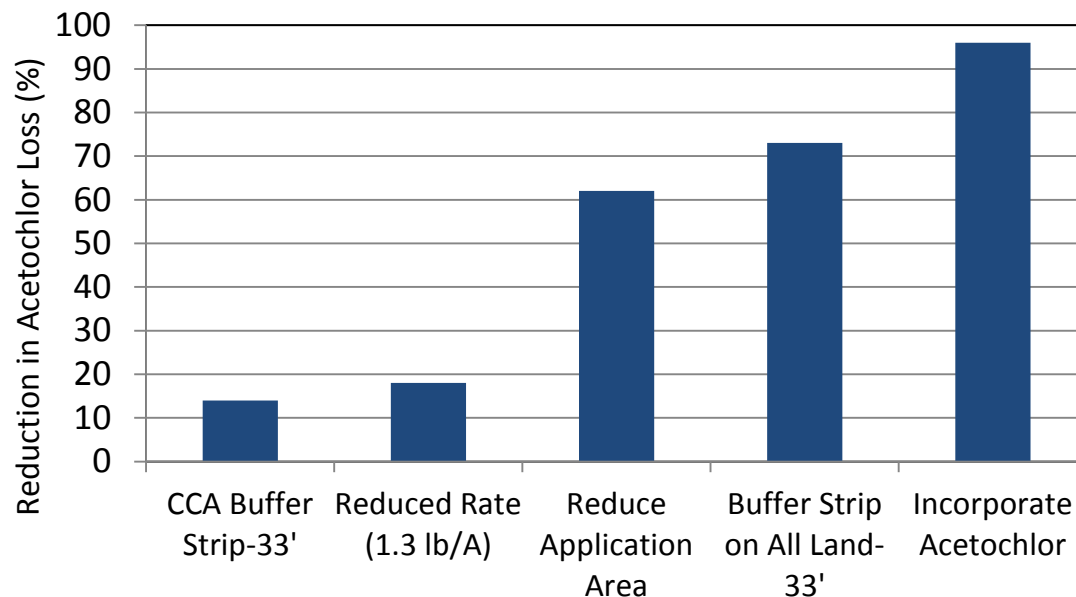
The fifth set of scenarios involved field buffer strips. Buffer strips of various widths applied to entire fields or only at CCAs were investigated with different rates of acetochlor. The presence of field buffer strips had a significant effect on acetochlor losses, and buffer width was somewhat important. A 33 foot wide buffer applied throughout the watershed, reduced acetochlor loss 68 percent relative to without buffers. A 66 foot wide buffer reduced losses 89 percent. Buffers were more effective at lower rates of acetochlor application. Installing buffer strips only in CCAs reduced acetochlor loss by roughly 50 percent, relative to the baseline scenario.

**Acetochlor BMPs in the for Le Sueur River watershed:** The calibrated SWAT model was then used to estimate pesticide runoff and the impact of BMPs to reduce offsite movement in the Le Sueur River watershed. Maximum acetochlor losses were calculated to have occurred in the years 2000, 2005 and 2006, with an average loss of 1.63 percent of applied product. The average acetochlor loss for years 1994-2006 was approximately 0.47 percent of applied product. Of this loss, 94 percent was in solution rather than soil-bound. The months of April, May, and June are the critical period for most acetochlor loss occurs due to the limited time for degradation and high rainfall.

Based on the results from the Little Beauford Ditch subwatershed, six acetochlor best management practices were selected and applied to the entire Le Sueur River watershed for simulation modeling:

1. Reduced rate of application, 1.3 lb/A;
2. Reducing application area from 35 percent of the watershed to 20 percent;
3. Change in application time, post emergence on May 3<sup>rd</sup>;
4. Incorporation of acetochlor;
5. 33 foot buffer strips on all corn and soybean fields; and,
6. 33 foot buffer strips on CCAs.

The simulation results, Figure 3, showed incorporation of acetochlor reduces losses by over 95 percent. This practice may not be feasible for adoption by farmers if it requires significant changes in tillage, manure management, or erosion control. Reducing application rate from 1.6 to 1.3 lb/A reduces the loss by 18 percent. Reducing application area to 20 percent of the corn land and establishing 33 foot buffer strips on all corn-soybean fields reduces the loss by 62 and 73 percent, respectively. Buffer strip establishment exclusively on CCAs reduced the loss by 14 percent. Changing postemergence application time to May 3 reduces losses by 9 percent. This practice also may not be feasible since application timing depends greatly on weather conditions.



**Figure 3.** Effect of various management practices on acetochlor loss in the Le Sueur River watershed. Reduction in loss is relative to a baseline 1.6 lb/A preemergence acetochlor application.

### **Activity 3: Develop acetochlor management recommendations from computer modeling results.**

This activity was a direct continuation of Activity 2. Computer modeling results from Activity 2 were used to develop the following acetochlor management observations and recommendations:

- Acetochlor is primarily lost in the soluble phase through surface runoff and tile drainage.
- Soil incorporation of acetochlor had the greatest impact on reducing runoff losses by removing the herbicide from the soil surface. The adoption of this practice has to be considered in the context of associated nitrogen fertilizer, tillage practices, and erosion concerns.
- Buffer strips installed in CCAs are very effective at reducing acetochlor losses.
- Reduction in the area receiving acetochlor is also very effective at reducing acetochlor losses.
- Reductions in application rate are somewhat effective at reducing acetochlor losses, especially if practiced in critical areas.
- It is important to apply acetochlor well in advance of spring rainstorms to reduce losses. There is no systematic benefit of delaying pre-plant acetochlor application from late April to early May due to the high frequency of spring rainstorms.
- Growers have a wide range of acetochlor BMPs to choose from depending on their specific management approach and availability of money, time, and equipment.

### **Activity 4: Watershed scale water monitoring.**

Concentrations of acetochlor in the Le Sueur River and the Little Beauford Ditch violated the MPCA Chronic Water Quality Standard for acetochlor, resulting in their placement on the state's 303(d) TMDL list of impaired waters in 2008. The Chronic Water Quality Standard for acetochlor is a 3.6 ppb average concentration over four days and was established for the protection of aquatic life. The standard needs to be exceeded twice during a three-year period to support an impairment listing. The MPCA determined that this occurred early in the 2001 growing season for the Le Sueur River (four-day average acetochlor concentrations of 5.67 ppb and 4.81 ppb) and early in the 2005 growing season for Little Beauford Ditch (four-day average acetochlor concentrations of 5.43 ppb and 4.90 ppb). The Le Sueur River exceeded the standard again in 2005 (a four-day average acetochlor concentration of 4.19 ppb). No subsequent standard exceedance has been documented in either stream reach since 2005.

Pesticide monitoring has continued at both the Le Sueur River outlet and Little Beauford Ditch sites since the impairment determination in 2008. Table 4 presents the number of samples above 10 and 50 percent of the aquatic life standard. Since the last standard exceedance in 2005, 50 percent of the standard concentration has only been measured twice from either site. Statistics including maximum concentration measured for each year that monitoring has occurred are presented in Table 5.

Since 2005, the concentration of acetochlor in samples collected from these two sites has only exceeded the 3.6 ppb standard once. The sample was collected during a storm event from the Little Beauford Ditch site that had an acetochlor concentration of 4.13 ppb in an equal-flow increment (EFI) composite sample. It occurred on June 14-15, 2011, during the rising leg and peak flow periods of the hydrograph that represented approximately 11.5 hours. This sample was collected following a storm event that delivered approximately 1.58 inches of total rainfall to the Little Beauford Ditch site. The rainfall occurred during two separate periods. The first period began at approximately 14:00 CST and ended

**Table 4.** Number of samples with concentrations above 10 % and 50% of the 3.6 ppb acetochlor standard concentration, 1999 - 2012, for the Le Sueur River and Little Beauford Ditch monitoring sites.

Site	Standard of 3.6 ppb	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Little Beauford Ditch	Total Detections	--	--	--	--	--	--	26/34	7/11	8/14	13/20	10/13	17/29	12/23	12/14
	# > 10% Standard	--	--	--	--	--	--	9	1	0	3	1	3	5	3
	# > 50% Standard	--	--	--	--	--	--	5	0	0	0	0	0	1	0
Le Sueur River	Total Detections	19/26	22/33	27/37	18/26	17/28	26/34	14/27	11/15	17/24	15/23	16/20	16/20	17/21	9/15
	# > 10% Standard	5	9	10	5	5	10	3	3	4	3	5	1	3	3
	# > 50% Standard	2	4	7	1	1	0	2	0	0	1	0	0	0	0

Gray shading indicates change in sampling beginning in 2006 from equal-flow increment composite sampling to equal-time increment based composite sampling. For further discussion, refer to the MDA's Surface Water Design Document.

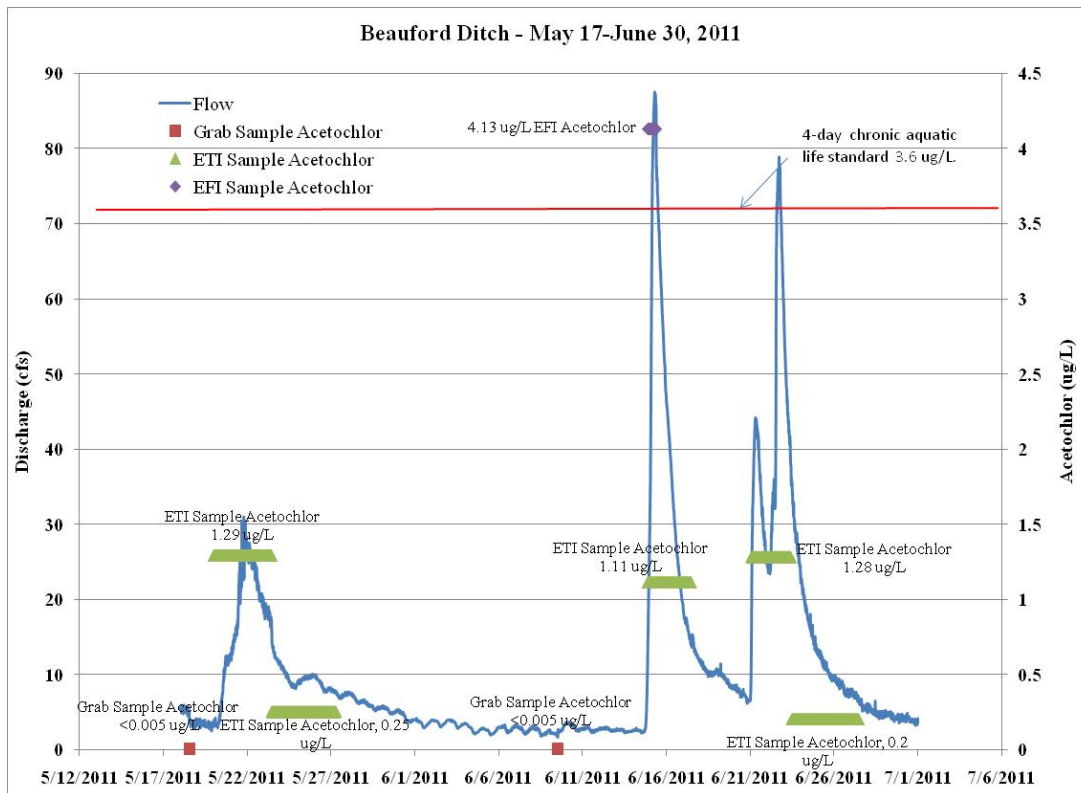
**Table 5.** Concentrations statistics for the Le Sueur River and Little Beauford Ditch monitoring sites. Yellow shaded rows indicate years in which violations of the acetochlor standard (3.6 ppb) occurred.

Le Sueur River			
Year	Acetochlor (ppb)		
	Median	90 <sup>th</sup> %-tile	Maximum
1999	0.09	1.08	3.63
2000	0.11	1.90	3.55
2001	0.13	2.67	9.00
2002	0.08	0.91	7.10
2003	0.09	1.42	2.38
2004	0.06	0.82	1.52
2005	P	0.42	5.30
2006	0.13	0.58	1.24
2007	P	0.85	1.5
2008	P	0.91	2.05
2009	0.06	0.40	0.47
2010	0.10	0.24	0.40
2011	0.06	0.71	0.98
2012	P	0.99	1.63

Little Beauford Ditch						
Year	Acetochlor (ppb)					
	Median	90 <sup>th</sup> %-tile	Maximum			
1999	Pesticide monitoring of the Little Beauford Ditch began in 2005					
2000						
2001						
2002						
2003						
2004	Pesticide monitoring of the Little Beauford Ditch began in 2005					
2005				P	3.88	12.1
2006				0.06	0.21	1.58
2007				0.04	0.14	0.19
2008				P	0.70	1.46
2009	P	0.16	0.43			
2010	P	0.31	0.51			
2011	P	1.25	4.13			
2012	0.07	0.51	1.74			

at 19:00 CST on June 14<sup>th</sup>, totaling 0.89 inches. The second rainfall period started at approximately 22:00 CST on June 14<sup>th</sup>, ended at 4:30 CST on the 15<sup>th</sup>, and totaled 0.67 inches. Maximum rainfall intensity was similar for both events with 0.14 inches in 15 minutes for the first event and 0.12 inches in 15 minutes for the second event. From the onset of rainfall to peak flow was approximately 17 hours in this small relatively flat watershed. The total duration of this event was approximately 70 hours using a start and stop associated with a flow of approximately 10 cubic feet per second (cfs) (approximately when the sampler activated). The storm was sufficient to produce a combination of overland and subsurface tile flow but was not unusual for the season or watershed.

An equal-time increment (ETI) composite sample for pesticides was also collected during this storm event. The ETI composite started at 21:52 CST on June 14<sup>th</sup> and ended at 11:52 CST on June 17<sup>th</sup>, 2011. The sample represented approximately 62 hours. The acetochlor concentration in this sample was 1.11 ppb. This data suggests the 4-day standard was not exceeded during this storm event. Additional pesticide samples were collected during May and June events at the site. Figure 4 presents the hydrograph and pesticide samples collected from mid-May through June, 2011.

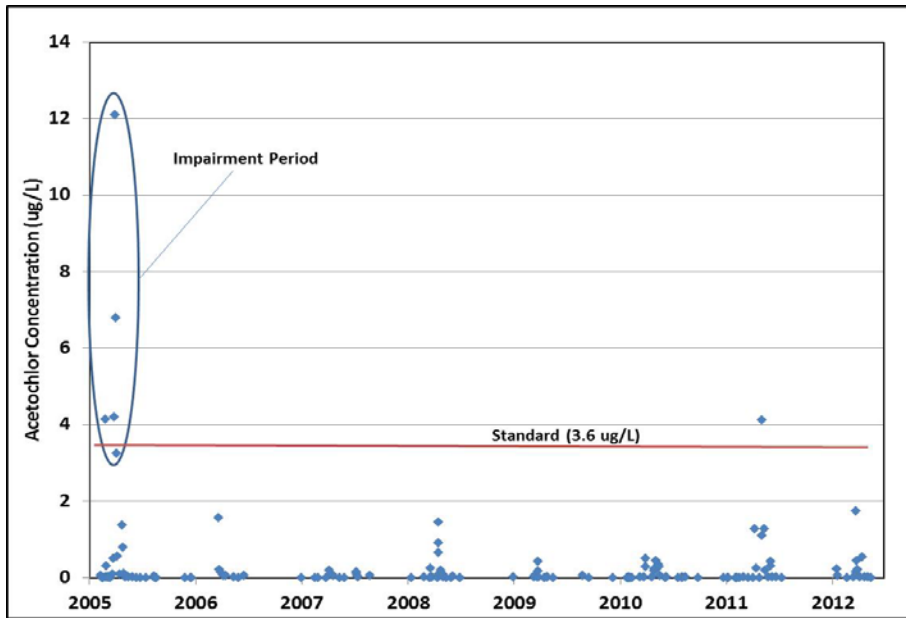


**Figure 4.** Little Beauford Ditch hydrograph with acetochlor concentrations for May and June, 2011. Acetochlor concentration is expressed as  $\mu\text{g/L}$ , which is equivalent to parts per billion (ppb).

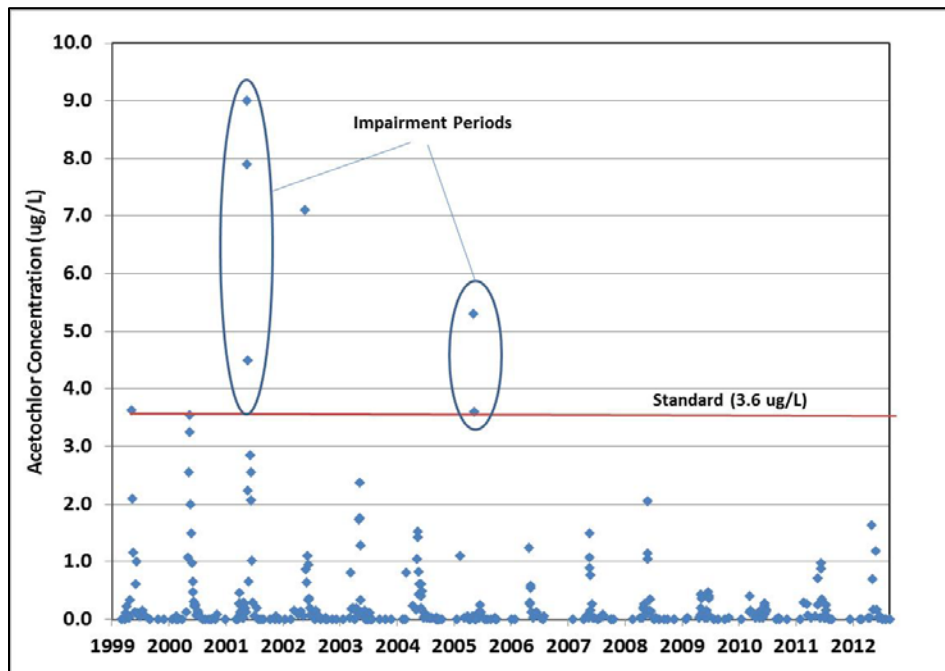
This period represents the only occasion during which a concentration in excess of the acetochlor chronic (4-day) aquatic life standard was measured since 2005. The elevated concentration was measured in an equal-time increment composite sample that represented 11.5 hours during the rising and peak flow periods. A corresponding equal-time increment sample representing most of the storm flow period (62 hours) had an acetochlor concentration of 1.11 ppb.

Long-term grab concentration plots for the Little Beauford Ditch and Le Sueur River sites are presented in Figures 5 and 6, respectively. During the period of record, approximately 334 pesticide samples were collected from the Le Sueur River site and 155 samples from the Little Beauford Ditch site. As discussed above and indicated in Figure 5, acetochlor concentrations were measured above the 3.6 ppb standard concentration only once at either site since the impairments occurred in 2005.





**Figure 5.** Acetochlor concentration plot for the period of record at Little Beauford Ditch. Approximately 155 pesticide samples have been collected at this site since 2005. Acetochlor concentration is expressed as  $\mu\text{g/L}$ , which is equivalent to parts per billion (ppb).



**Figure 6.** Acetochlor concentration plot for the period of record at Le Sueur River representing approximately 334 samples. Acetochlor concentration is expressed as  $\mu\text{g/L}$ , which is equivalent to parts per billion (ppb).

Most acetochlor applications in the Le Sueur watershed occur during the months of April and May. An analysis of all samples with detections over 1.0 ppb acetochlor from the Le Sueur River and its tributaries indicated that 77 percent of the detections occurred during the month of May and 20 percent occurred during the month of June. It is important to point out that the MDA sampling methods did change in 2006 moving from a flow-based compositing (equal-flow increment, EFI) to primarily a time-based composite (equal-time increment, ETI) protocol, as indicated in the shaded portion of Table 4 above. Time-based compositing is regarded as a better method for the collection of samples to be compared with duration-based standards like the 4-day chronic aquatic life standard for acetochlor that was used in the determination of the impairment violations. This change in protocol was implemented after extensive discussion with the MPCA.

Starting in 2005, the characteristics of all storm events that exceeded 0.5 inch total rainfall and where samples were collected for acetochlor in the Little Beauford Ditch during April, May and June were recorded. These records are compiled in Table 6. Storm event characterization was limited to the Little Beauford Ditch site because the single rain gauge located at the monitoring site was thought to be more representative of the broader watershed than would be the case for the much larger Le Sueur River.

Table 6 indicates that 25 storm events in excess of 0.5 inch of total precipitation occurred during this period with 44 acetochlor samples collected. Samples were collected during storm flow periods between April 11, 2005 and May 28, 2012. Total rainfall amounts ranged from 0.57 to 3.12 inches, with the maximum (3.12 inches) occurring during the 2005 event that resulted in the impairment. Peak flows also occurred during this period.

Table 6 also indicates that all detections in excess of the standard were measured in flow-based composites or grab samples. No exceedances were measured in time-based composite samples. Statewide corn planting progress percentage is also presented in the Table 6. The use of statewide data here may not exactly represent watershed with respect to corn planting but is a good reference to indicate that for most of the events the majority of the corn had been planted when the events occurred. Indeed, 75 percent of the pesticide samples were collected after approximately 60 percent of the corn had been planted on a statewide basis. These data suggest that changes in acetochlor management and use have reduced the likelihood of acetochlor concentrations exceeding the standard in the Little Beauford Ditch.

**Table 6. Storm analysis for Little Beauford Ditch pesticide samples. Shaded cells represent samples collected that were above the acetochlor standard of 3.6 ppb.**

Event	Begin	End	Total Rain (inches)	Max Hourly Intensity (in)	Max Stage (feet)	Max Flow (cfs**)	Planting Progress %	Acetochlor Concentration (ppb)
1	4/11/05 7:45	4/12/05 5:45	2.04	0.29	15.89	129	0	4.15
2	5/8/05 18:30	5/8/05 21:15	0.68	0.56	12.92	11	78	0.51
3	5/12/05 4:30	5/13/05 7:15	3.12	0.56	18.50	287	78	12.1
3			3.12	0.56	18.50	287	78	4.2
3			3.12	0.56	18.50	287	78	6.8
4	5/17/05 5:30	5/18/05 21:00	0.67	0.14	13.66	32	89	3.25
5	6/8/05 3:30	6/8/05 8:15	1.29	0.79	14.00	44	92	0.79
5			1.29	0.79	14.00	44	92	1.38
6	4/30/06 0:30	5/1/06 2:15	0.76	0.12	15.34	109	48	1.58
7	3/29/07 21:00	4/1/07 2:15	1.66	0.17	15.16	92	98	0.00
8	5/19/07 17:45	5/20/07 4:00	0.83	0.43	12.54	4	88	0.19
9	5/31/07 14:09	6/4/07 13:09	0.77*	0.26*	12.82	9	99	0.07
10	5/2/08 19:02	5/9/08 4:30	0.94	0.20	13.49	27	1	0.25
10			0.94	0.20	13.49	27	1	0.025
10			0.94	0.20	13.49	27	1	0.025
11	5/29/08 23:41	5/30/08 19:00	0.99	0.58	14.15	49	95	1.46
11			0.99	0.58	14.15	49	95	0.92
11			0.99	0.58	14.15	49	95	0.67
11			0.99	0.58	14.15	49	95	0.11
12	6/5/08 15:12	6/16/08 14:58	1.34	0.35	13.69	32	98	0.08
12			1.34	0.35	13.69	32	98	0.19
12			1.34	0.35	13.69	32	98	0.11
12			1.34	0.35	13.69	32	98	0.025
13	5/6/09 11:20	5/6/09 12:30	1.64	1.14	13.21	19	59	0.43
13			1.64	1.14	13.21	19	59	0.18
14	5/6/10 19:45	5/7/10 23:00	0.57	0.10	12.40	2	87	0.025
15	6/3/10 21:45	6/4/10 23:15	0.77	0.31	12.65	6	100	0.025
16	6/10/10 8:30	6/11/10 8:45	0.91	0.32	13.69	33	100	0.18
16			0.91	0.32	13.69	33	100	0.24
17	6/17/10 16:00	6/18/10 4:00	1.05	0.46	14.96	83	100	0.25
18			1.05	0.46	14.96	83	100	0.44
18	4/10/11 0:30	4/10/11 2:15	0.88	0.76	13.94	48	100	0.025
19	4/25/11 21:00	4/26/11 20:30	0.86	0.14	14.35	57	100	0.00
20	5/20/11 3:45	5/22/11 20:00	1.6	0.31	13.62	31	47	1.29
20			1.6	0.31	13.62	31	47	0.25
21	6/14/11 14:00	6/15/11 21:30	1.58	0.41	14.88	80	99	1.11
21			1.58	0.41	14.88	80	99	4.13
22	6/21/11 0:00	6/23/11 0:30	1.83	0.57	14.86	79	99	1.28
22			1.83	0.57	14.86	79	99	0.20
23	5/1/12 22:00	5/2/12 5:00	0.76	0.67	12.66	6	48	0.16
24	5/4/12 16:15	5/9/12 13:40	2.23	0.77	14.08	47	48	1.74
24			2.23	0.77	14.08	47	48	0.44
24			2.23	0.77	14.08	47	48	0.22
25	5/26/12 8:30	5/28/12 4:45	1.04	0.65	14.02	45	98	0.54

\* A portion of this event (5/31/07 04:30 – 6/1/07 18:45) had no rain data due to equipment malfunction. The values indicated for this event likely underrepresent the actual rain total and storm intensity. \*\* cfs = cubic feet per second, a measure of flow.

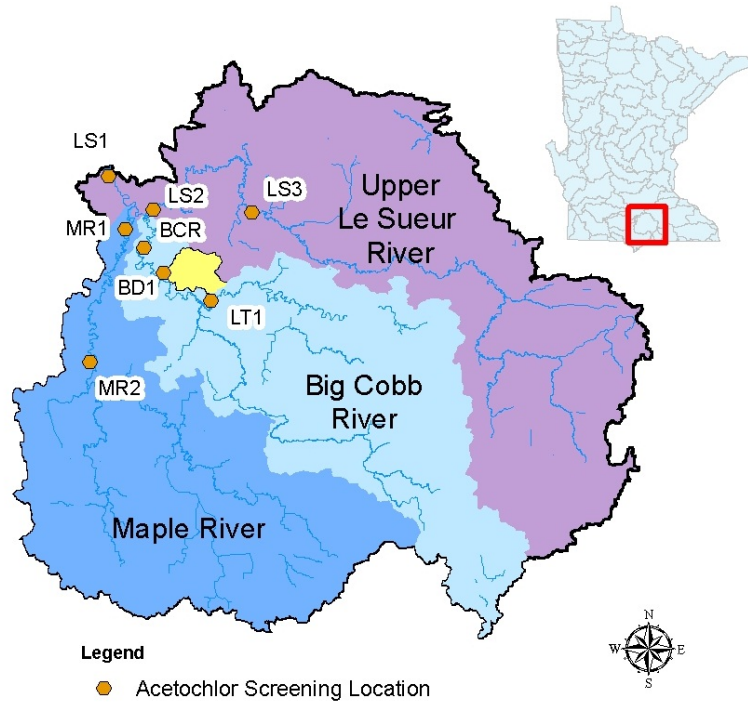
### **Activity 5: Subwatershed scale water monitoring.**

In 2009 the MDA, with support from the MPCA, began a study to evaluate the use of an enzyme-linked immunosorbent assays (ELISA) method and to enhance our understanding of the spatial and temporal distribution of acetochlor presence in the Le Sueur River and its tributaries. ELISA was evaluated as a surrogate method for acetochlor due to the high cost of conventional laboratory analysis. Several published studies have verified the utility of ELISA or immunoassay type of analysis for screening water samples and many have compared ELISA analysis with more conventional techniques, such as gas chromatography mass spectrometry (GC/MS), with good results (Casino et al., 2001, Holman et al., 2000).

A report summarizing the first year of data and evaluating the ELISA method was published by MDA in 2010 (MDA, 2010). Based on those results and in consultation with the MPCA, the MDA continued the ELISA monitoring for the duration of the project. Throughout the project (2009-2012) acetochlor ELISA samples were compared with conventional GC/MS methods on a limited basis to provide a meaningful evaluation as to the reliability of the acetochlor ELISA method and the relationship between the two methods.

A primary concern in the use of ELISA for evaluating acetochlor concentrations is the potential for cross-reactivity with other herbicides in the chloroacetanilide family of chemicals to which acetochlor belongs, or to degradates of those herbicides. Based on a review of the acetochlor ELISA information provided by the manufacturer, Abraxis, the herbicide metolachlor represented the greatest potential for cross-reactivity. MDA pesticide data obtained for the Le Sueur River and Little Beauford Ditch through GC/MS analysis in recent years indicated metolachlor concentrations ranged from non-detect to 76 ppb. Concentrations in excess of 1 ppb represented less than five percent of the samples collected. In instances where metolachlor concentrations exceeded 1 ppb, acetochlor concentration also typically exceeded 1 ppb. The exception to this pattern were samples collected in February, March and early April that can exhibit elevated metolachlor concentrations without a corresponding elevated acetochlor concentration. The presence of metolachlor in these samples was generally attributed to fall application of the product. Although registered for fall application in Minnesota, acetochlor is typically not applied in the fall. Due to these issues, the experimental design for this project considered the timing and anticipated concentrations of the two chemicals. In addition, analytical laboratory GC/MS confirmation was conducted on all ELISA samples that exceeded 2 ppb acetochlor.

The eight locations in the Le Sueur River watershed sampled for this study are presented in Figure 7 and Table 7. The drainage areas for the sample locations included in this study range in size from approximately 5,100 acres to over 700,000 acres. The Upper Le Sueur, Big Cobb Outlet and Maple River Outlet represent the three major tributaries to the Le Sueur River. The channels of all of the major tributaries become more deeply incised and the landscape changes to include many deep ravines and gullies as they approach the mainstem of the Le Sueur River. The Le Sueur River near St. Clair, Little Cobb River, Little Beauford Ditch and Upper Maple River represent areas typical of the upper portions of the Le Sueur River watershed. These subwatersheds consist of flatter landscapes where the channels are not as deeply incised and networks of agricultural drainage ditches and subsurface tile facilitate water movement and enhance agricultural productivity.



**Figure 7.** Le Sueur River watershed with the three major subwatersheds and the Little Beauford Ditch watershed (highlighted in yellow) identified along with the sampling locations.

**Table 7.** The Le Sueur River watershed sampling locations for ELISA analysis.

Site Name (Road Crossing)	Location Code	Drainage Area (Acres)
Le Sueur River Outlet (Hwy 66)	LS1	710,041
Upper Le Sueur River (CR 8)	LS2	285,189
Le Sueur River near St. Clair (CR 28)	LS3	225,078
Big Cobb River Outlet (CR 16)	BCR	195,145
Little Cobb River (CR 16)	LT1	82,868
Little Beauford Ditch (Hwy 22)	BD1	5,111
Maple River Outlet (CR 35)	MR1	216,879
Upper Maple River (CR 18)	MR2	197,362

### Sampling methods

Samples collected as part of this study consisted of grab, equal-time increment and equal-flow increment composites. Grab samples were collected at the majority of the sites either by using extension poles with the sample bottle attached to the end, weighted samplers lowered from a bridge deck, or wading out and simply lowering the sample bottles into a representative portion of the stream.

Composite samples were collected at the Le Sueur River Outlet (LS1) and Little Beauford Ditch (BD1) sites. The composite samples were collected by ISCO autosamplers activated by increased stream stage. Composite samples were collected for an equal-time increment (ETI), every hour or every two hours, or on an equal-flow increment (EFI) basis. Composite samples were collected in glass jars under refrigerated conditions. Grab samples were also collected at these two locations. Samples were not simultaneously collected from all locations. Samples were collected during the same storm events and an effort was made to collect samples from all major storm events during the growing season.

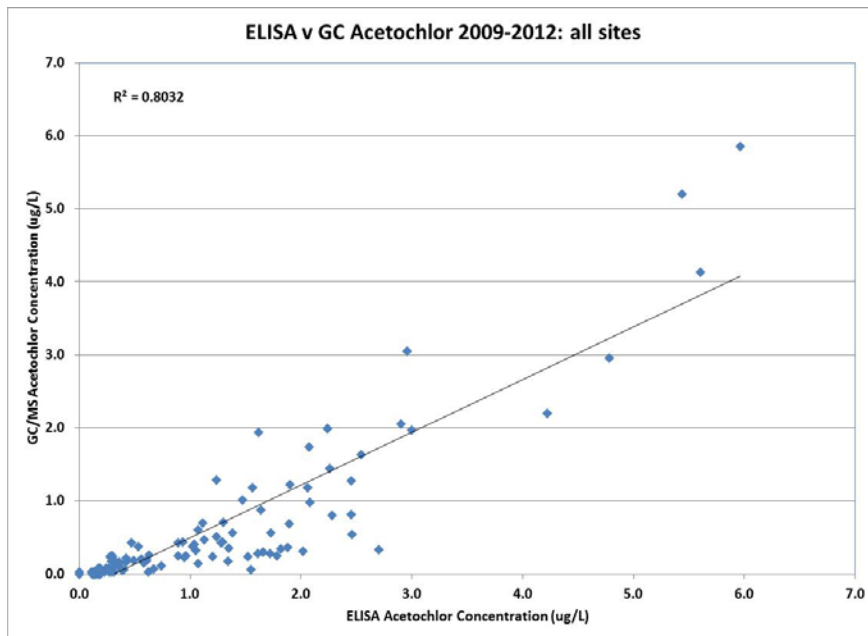
Sampled water was placed in 950 mL glass amber bottles, from which the 50 mL ELISA aliquot was removed for pesticide analysis. Grab and composite samples were stored in coolers with ice or in a refrigerator until analysis. Because the ELISA analysis was used to screen samples for concentrations greater than 2 ppb for eventual analysis by GC/MS, it was necessary to hold and refrigerate the remaining 900 mL portion of the sample pending analysis results. ELISA samples were frozen and sent to the University of Wisconsin, Steven Point Water and Environmental Analysis Laboratory (WEAL) in batches.

### **Analytical methods**

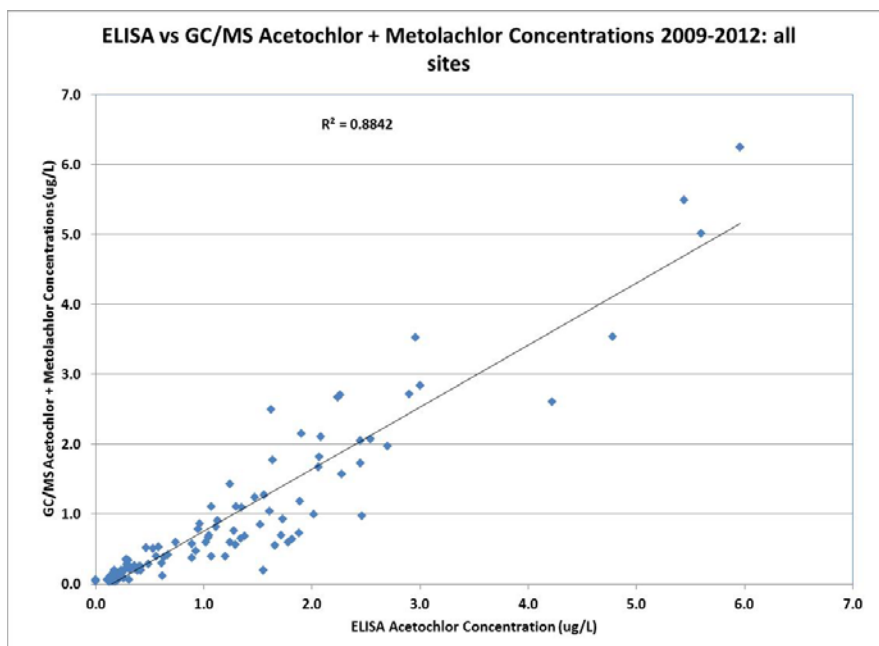
Acetochlor ELISA analysis was conducted at the WEAL using acetochlor ELISA kits manufactured by Abraxis. These kits have a reported acetochlor detection range of 0.10 to 2.5 ppb. Abraxis reports cross-reactivity with other chloroacetanilide herbicides and their degradates. ELISA information from Abraxis and previous Le Sueur River pesticide monitoring data indicate that metolachlor has the greatest potential for cross-reactivity.

To evaluate acetochlor and metolachlor cross-reactivity and general ELISA performance, select samples were split and submitted to the MDA laboratory for GC/MS analysis for pesticide analytes including acetochlor and metolachlor. A smaller subset of samples were analyzed using liquid chromatography mass spectrometry (LC/MS-MS) for eight chloroacetanilide degradates including those of acetochlor and metolachlor. Samples submitted to the MDA laboratory for verification included all ELISA samples having acetochlor concentrations in excess of 2 ppb. Because there was a delay pending the ELISA results, some GC/MS samples exceeded the three week holding time.

Approximately 130 samples were submitted for both ELISA and GC/MS acetochlor analysis over the duration of the project. Figure 8 presents a comparison of those results and suggests a strong relationship between the two methods ( $R^2 = 0.80$ ). Figure 9 presents the acetochlor ELISA concentration compared to the cumulative pesticide concentration for acetochlor and metolachlor from the GS/MS analysis. Combining the two compounds indicates a stronger correlation than acetochlor alone ( $R^2 = 0.88$ ), suggesting some cross-reactivity with metolachlor may be occurring in the ELISA analysis.



**Figure 8.** Relationship between the acetochlor ELISA analysis and acetochlor GC/MS concentrations. Note the coefficient of determination,  $R^2$ , equals 0.80. Acetochlor concentration is expressed as  $\mu\text{g/L}$ , which is equivalent to parts per billion (ppb).

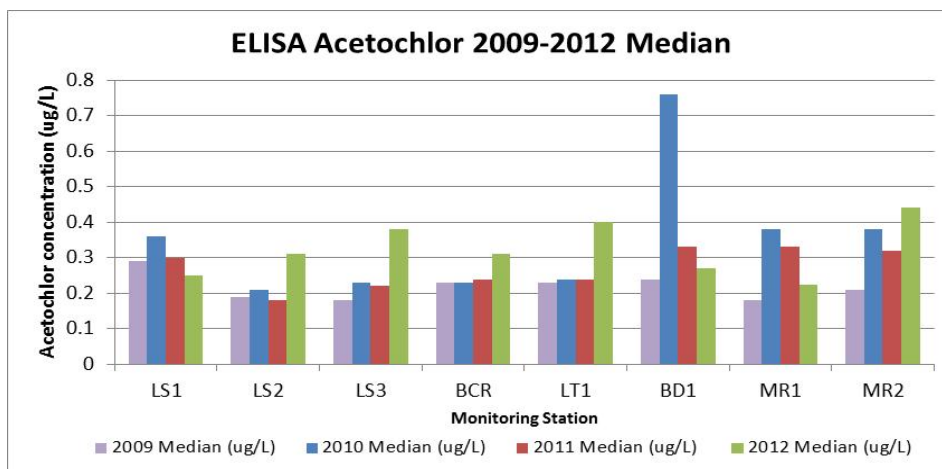


**Figure 9.** Relationship between the acetochlor ELISA analysis and the combined acetochlor and metolachlor GC/MS concentrations. Note the coefficient of determination,  $R^2$ , equals 0.88. Acetochlor concentration is expressed as  $\mu\text{g/L}$ , which is equivalent to parts per billion (ppb).

Acetochlor ELISA results for the eight sampling locations are presented in Table 8. Median concentrations ranged from 0.18 to 0.76 ppb over the duration of the project. All sites had relatively similar median concentrations as presented in Figure 10. This likely relates to a large percentage of the Le Sueur River watershed having similar land use, agronomic systems, and hydrology. Without information on acetochlor use by subwatershed, it is difficult to ascertain if the variability observed is related to product use, climatic factors, or other characteristics of the watersheds. There does not appear to be a clear relationship between watershed size and acetochlor concentration. The data shows samples collected at LS1 (Le Sueur Outlet) are fairly consistent with acetochlor concentrations in contributing subwatersheds.

**Table 8.** Summary statistics from acetochlor ELISA analysis in the Le Sueur River watershed for each sampling location. See Table 7 for sampling location codes and Figure 7 for sampling locations.

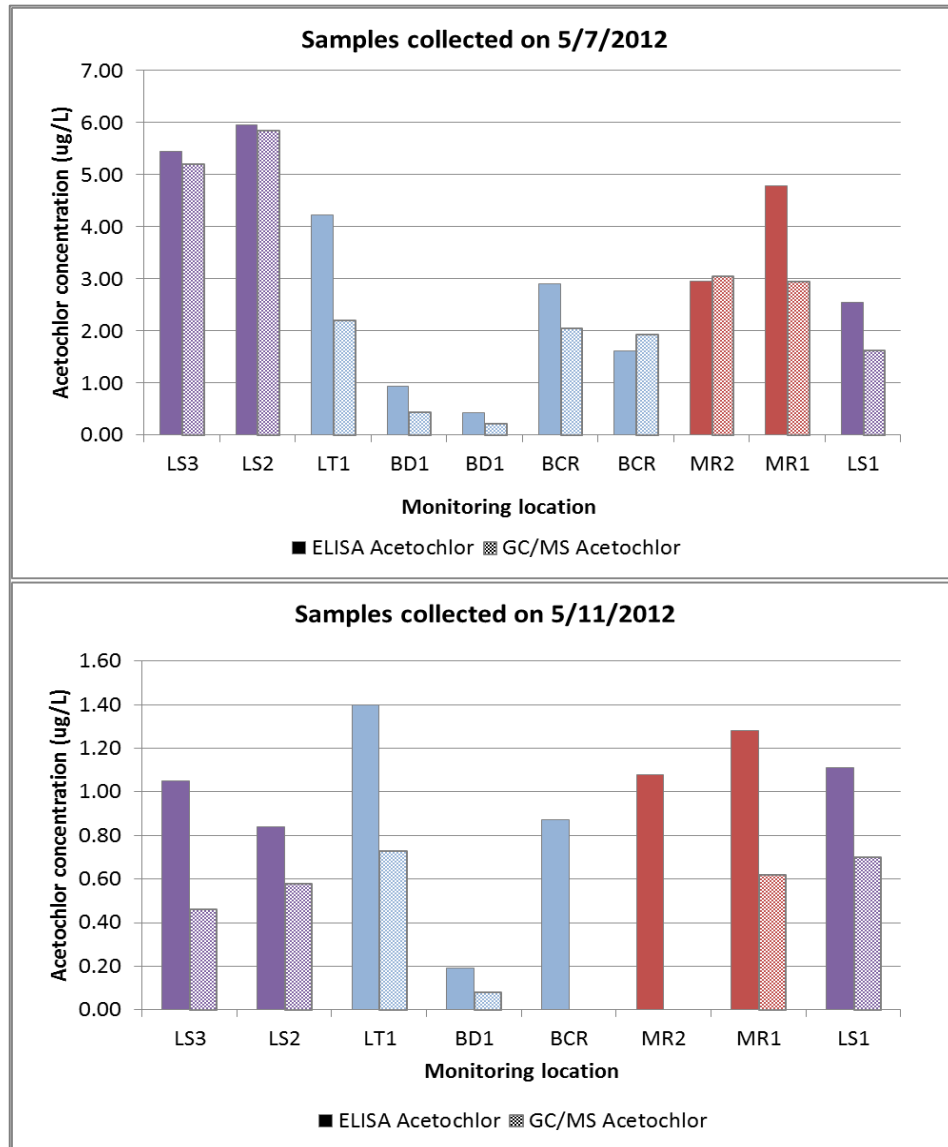
Sampling locations:	LS1	LS2	LS3	BCR	LT1	BD1	MR1	MR2
Watershed acres	710,041	285,189	225,078	195,145	82,868	5,111	216,879	197,362
2009 Sample #	14	8	10	9	9	10	11	9
2010 Sample #	15	16	16	17	15	14	19	19
2011 Sample #	17	18	17	17	13	15	16	15
2012 Sample #	16	13	10	13	10	13	12	8
2009 Median (ppb)	0.29	0.19	0.18	0.23	0.23	0.24	0.18	0.21
2010 Median (ppb)	0.36	0.21	0.23	0.23	0.24	0.76	0.38	0.38
2011 Median (ppb)	0.30	0.18	0.22	0.24	0.24	0.33	0.33	0.32
2012 Median (ppb)	0.25	0.31	0.38	0.31	0.40	0.27	0.23	0.44
2009 Max (ppb)	1.13	0.74	1.56	1.38	1.07	0.89	1.89	2.28
2010 Max (ppb)	1.61	1.34	2.45	1.36	1.82	1.88	2.02	1.78
2011 Max (ppb)	2.08	2.49	2.59	2.26	2.70	5.60	3.00	2.24
2012 Max (ppb)	2.54	5.96	5.44	2.90	4.22	2.46	4.78	2.96



**Figure 10.** Median acetochlor concentrations from the ELISA analysis conducted in the Le Sueur River watershed from 2009-2012. Acetochlor concentration is expressed as  $\mu\text{g/L}$ , which is equivalent to parts per billion (ppb).



As indicated in Table 8, the acetochlor ELISA monitoring conducted during the 2012 season included several maximum concentrations in excess of the 3.6 ppb acetochlor standard concentration. These detections include the highest concentrations of acetochlor measured since ELISA monitoring began in 2009. The samples with the elevated concentrations were collected on May 7, 2012. Consistent with the verification protocol, split samples collected at the same time were submitted to the MDA laboratory for GC/MS confirmation. The ELISA and GC/MS concentrations from May 7, 2012, are presented in Figure 11. Figure 11 also presents ELISA and GC confirmation concentration from samples collected approximately four days later, on May 11, 2012.



**Figure 11.** Acetochlor concentrations measured by ELISA and GC/MS on May 7 and May 11, 2012 in the Le Sueur River watershed. Different bar colors represent the three subwatersheds of the Le Sueur River. Acetochlor concentration is expressed as  $\mu\text{g/L}$ , which is equivalent to parts per billion (ppb).

The GC/MS data from May 7, 2012 confirmed two sites did experience acetochlor concentrations above the 3.6 ppb acetochlor standard. However, the May 11, 2012 data indicates concentrations had fallen well below the standard prior to four days. The two sites with confirmed concentrations above the standard were both upper Le Sueur River sites (LS2 and LS3) representing the same subwatershed of the Le Sueur River. The elevated concentrations did not appear to have resulted in concentrations in excess of the standard at the Le Sueur Outlet site (LS1), presumably due to lower concentration water from the Big Cobb and Maple Rivers. It is not anticipated these acetochlor concentrations in the upper Le Sueur River sites (LS2 and LS3) from May 7 to May 11, 2012 will constitute a violation of the acetochlor water quality standard. Further assessment will be completed by MDA and MPCA staff to determine if a violation had occurred once the flow data is available for the LS2 and LS3 sites. In order for a violation to have occurred the average acetochlor concentration would need to exceed the 3.6 ppb standard concentration for a four-day period.

### **ELISA Monitoring Conclusions**

The acetochlor ELISA method produced comparable results to the GC/MS method ( $R^2 = 0.80$ ). In general, the acetochlor ELISA method tended to over-predict the acetochlor concentration when compared to the acetochlor concentration measured by GC/MS. There may have been cross-reactivity with metolachlor, as the total concentration (acetochlor and metolachlor summed) from the GC/MS method showed a stronger correlation with the acetochlor ELISA concentration ( $R^2 = 0.88$ ).

This study indicates that the acetochlor ELISA method is a reasonable screening tool for evaluating acetochlor concentrations in surface water. When combined with GC/MS verification for split samples above a pre-determined critical concentration, ELISA is a reasonable surrogate for high-cost, conventional laboratory analysis.

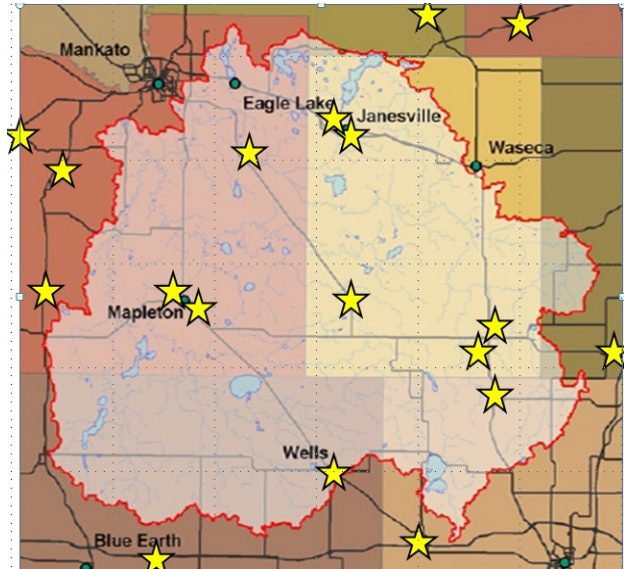
Acetochlor median concentrations from the eight sites in the Le Sueur River watershed yielded similar results. These similar concentrations are likely a function similar watershed characteristics, hydrology, acetochlor usage and management, and climate throughout the watershed. The data does not suggest any of the three major Le Sueur River subwatersheds are contributing disproportionately to acetochlor concentrations at the Le Sueur outlet.

**Activity 6: Collect farming system information on acetochlor use in the watersheds.**

Eighteen agronomists working with crop supply dealerships servicing the Le Sueur River watershed were surveyed about acetochlor sales and application practices during the 2010 crop year (Figure 12). These agronomists supplied herbicides for 276,350 acres which accounted for 80% of estimated 2010 corn acres in the watershed.

The surveys were in the form of in-person interviews by Denton Bruening and Ron Struss of the MDA and took place during February 2011.

Among the 18 agronomists interviewed, 17 had sold acetochlor in the past and 16 were currently selling acetochlor. Thirteen had over 15 years of experience in the watershed. All agronomists surveyed were aware of the acetochlor impairment.



**Figure 12.** Location of dealerships included in acetochlor use survey of agronomists.

The following are survey results concerning past, present and future acetochlor use in the Le Sueur River watershed based on the responses from the 18 agronomists:

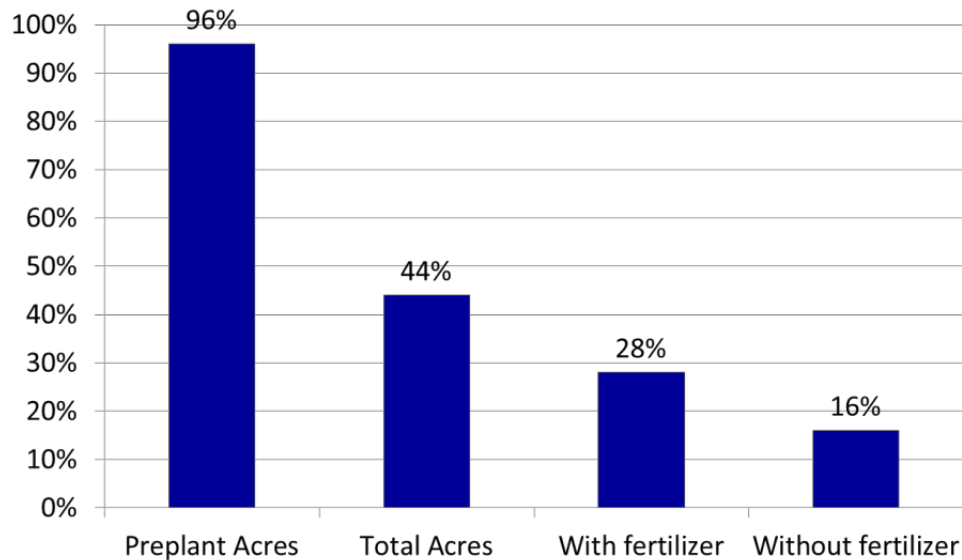
- 67 percent of watershed corn acres received some type of preplant or preemergence herbicide application.
- 26 percent of watershed corn acres received acetochlor. Other herbicides commonly used for grass control were metolachlor (Dual), 16 percent of acres, and dimethenamid (Outlook), 13 percent of acres.
- Acetochlor application timing was 46 percent preplant, 50 percent preemergence, and 3 percent postemergence.
- Less than 0.1 percent of acetochlor was fall applied compared to 50 percent for metolachlor and 28 percent for dimethenamid.
- On watershed acres receiving acetochlor, 99 percent were applied with the reduced “Roundup Ready” rate. Use of the reduced rate was expected to remain steady for the next five years.
- A majority (57 percent) of watershed agronomists reported a downward trend in the amount of acetochlor used the past 5 years due to the use of the reduced rate and the use of alternative herbicides.
- There was a variety of opinions concerning the future five-year trends, with 53 percent of agronomists expecting the acres treated with acetochlor to remain flat and 35 percent expecting the acreage to decrease due to the use of alternative herbicides. The remainder expected use to increase due to the availability of more premixes containing acetochlor.
- Incorporation of applied acetochlor was fairly common and was used on 96 percent of preplant acres and 44 percent of total acres (Figure 13). Agronomist felt the trend in incorporation was down or flat due to inconvenience and timing leading to more pre- and postemergence applications. Most predicted the acres of acetochlor being incorporation will remain flat.

Other herbicide use and application information obtained through the survey:

- 43 percent of corn herbicides sold by dealers were custom applied.
- Autosteer was used in 61 percent of acetochlor applications.
- Individual boom control was used in 73 percent of acetochlor applications.
- Expanded use of acetochlor on soybeans is not expected.

A summary of this information is:

- Acetochlor used on 26 percent of Le Sueur watershed corn acres in 2010.
  - Represents a downward trend from 2005.
  - Future trend in acres applied to is flat or down.
- Reduced rates used on 99 percent of acetochlor acres in 2010.
  - Represents a downward trend in rate applied from 2005.
  - Future trend in rate applied is flat.
- 44 percent of acetochlor was incorporated in 2010.
  - Represents a downward or flat trend from 2005.
  - Future trend in incorporation is flat.
- Since 2005, acetochlor use has gone down both in acres applied and rate applied.
  - Acetochlor use is not expected to increase from 2010 levels in the next five years.



**Figure 13. Acetochlor use practices** (percentage of acetochlor acres) utilized within the Le Sueur River Watershed during 2010.

**Activity 7: Collect voluntary acetochlor BMP use information in the watershed.**

Twenty-one crop growers in the LeSueur River watershed were surveyed during June and July of 2012 to determine the awareness and use of acetochlor BMPs. As a group, these growers applied acetochlor to approximately 9,730 acres which represents 8 percent of the corn acres in the watershed that received acetochlor. Of the surveyed growers, 46 percent owned their land and 54 percent rented their land.

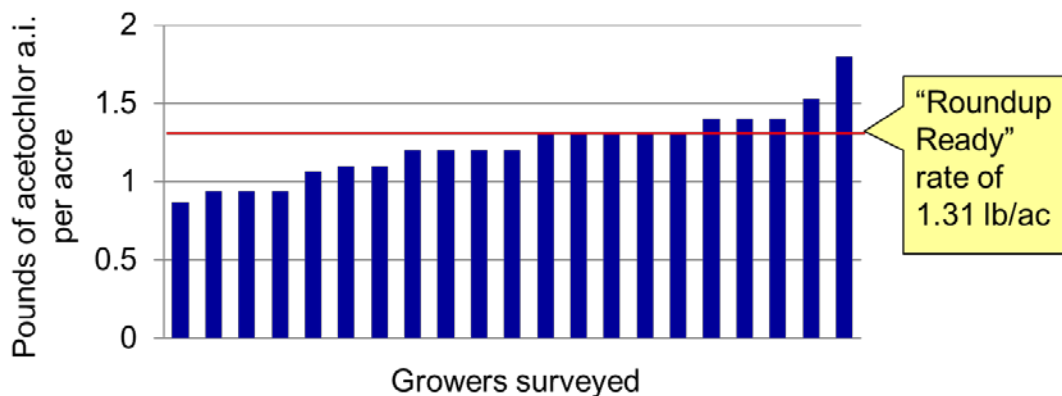
The surveys were conducted as in-person interviews by Denton Bruening and Jim Freilinger of the Minnesota Department of Agriculture (MDA). They received assistance from the Watonwan Farm Service dealerships in New Richland and Mapleton and the Crystal Valley Cooperative dealerships in Waldorf and Janesville. The dealerships provided the names of 2010 acetochlor customers and provided introductory calls to growers advising them to expect an interview invitation from the MDA.

The survey was based on three main questions: 1) What acetochlor BMPs are being used?, 2) What acetochlor BMPs might be used?, and 3) What are barriers to BMP use?

The questions asked and a summary of the responses are given in Table 9. Responses are listed both as percent of the growers responding and a percent of the acres they farm. Figure 14 provides detail on the acetochlor rates utilized by growers.

Widely used BMPs include scouting, reduced rates, setbacks and filter strips from water, precision application, and soil incorporation. Less used BMPs include alternative herbicides, conservation tillage, mechanical cultivation, application setbacks from tile inlets and filter strips around tile inlets. An Advisory Committee member familiar with conservation practices in the two watersheds commented that the survey under-reported the amount of conservation tillage actually being used. It was thought this could have been caused by miscommunication during the survey on the level of residue cover that qualifies as conservation tillage.

The two BMPs which showed the most potential for increased use were 1) the use of alternative herbicides, and 2) the use of precision application. BMPs that show low potential for increased use were soil incorporation, application setbacks from tile inlets, filter strips around tile inlets, mechanical cultivation, and conservation tillage.



**Figure 14.** Pounds of acetochlor active ingredient (a.i.) applied per acre reported by surveyed Le Sueur River Watershed corn growers.

The survey results indicate that although many growers are not aware of the acetochlor impairment and the formal acetochlor BMPs, many of the BMPs are being used. This indicates that growers may be obtaining this information through other sources such as, crop supply agronomist, production magazines and articles, and University of Minnesota Extension.

**Table 9. Survey responses concerning grower awareness and use of acetochlor BMPs in the Le Sueur River watershed. For questions 10-13, percentages are based only on growers that have fields with these circumstances.**

Question	% of Growers	% of Acres
1. Are you aware of the acetochlor impairment?	24	9
2. Are you aware of acetochlor BMPs?	33	33
3. Is your weed control program same on rented and owned land?	95	96
4. Do you use field scouting BMP?	95	97
5. Do you use reduced acetochlor rates?	95	96
6. Do you use alternative herbicides instead of acetochlor?	38	
7. Do you use cultivation to reduce herbicide use?	14	7
8. Do you use application setback from water?	92	
9. Do you use of vegetative filter strips at water runoff points?	100	
10. Do you use setbacks at surface tile inlets?	7	
11. Do you use surface tile inlet filter strips?	0	
12. Do you use of conservation tillage? *	29	35
13. Do you incorporate acetochlor applications?	71	56
14. Is auto-steer or auto-boom shutoff utilized?	81	91

\* An Advisory Committee member commented that use of conservation tillage is under-reported. See text for details.

**Activity 8: Evaluate effectiveness of reduced rates Best Management Practice on loss to tile water.**

A potential path for acetochlor to leave fields and enter surface water is to leach to tile drainage lines which outlet to surface streams and ditches. This potential loss was studied by University of Minnesota using small field research plots at the Southern Research and Outreach Center in Waseca, Minnesota (Figure 15; Randall and Vetsch 2011). Funding was provided by the Minnesota Department of Agriculture utilizing state Clean Water Legacy Act funding. Gyles Randall, Jeff Vetsch and Dave Groh conducted the research.

The effect of broadcast acetochlor rates (0, 1.3, and 2.2 lb/A) applied in mid-May on the acetochlor concentration in tile water drainage was tested for three years. Low precipitation in in 2008 and 2009 resulted in little to no water flowing through tile drainage lines which limited data collection. Some acetochlor was detected in the tile water during these years, but at very low concentrations.

In 2010, heavy rain in June (June 11 = 1.24 inches, June 18 = 3.93 inches, June 27 = 1.11 inches) resulted in abundant tile water flow. A summary of the acetochlor detects in tile water is given in Table 10. Average acetochlor concentration in tile water under plots receiving the reduced 1.3 lb/A acetochlor rate were lower (0.073 ppb) than those from plots receiving the 2.2 lb/A acetochlor rate (0.443 ppb). For

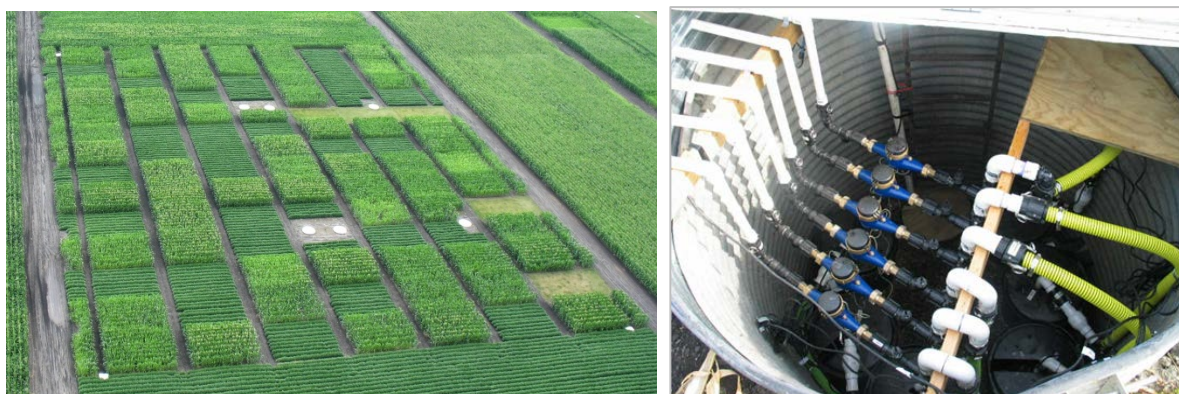
reference, the acetochlor chronic water quality standard established for the aquatic life protection is an average concentration of 3.6 ppb over four days.

Although almost one-half of the total 2010 tile drainage occurred after July 1, no acetochlor was detected in tile water collected more than six weeks after application. This is true even though over 8 inches of rainfall were received in late September.

It should be noted that 5 of the 39 samples collected prior to acetochlor application contained detectable levels of acetochlor which ranged from 0.03-0.07 ppb.

Using basic assumptions, the researchers calculated the acetochlor loss for the 1.3 and 2.2 lb/A rates to be  $4.4 \times 10^{-6}$  and  $51.0 \times 10^{-6}$  lb acetochlor/A.

Results in Table 10 indicate that although there is acetochlor loss through tile lines, it is at concentrations that will not contribute to surface water exceeding the water quality standard concentration of 3.6 ppb.



**Figure 15.** (Left) Overview of tile drainage study plots at University of Minnesota Southern Research Center. (Right) Sump where tile drainage plots outlet and drainage volume is measured and water quality samples are collected.

**Table 10. Detections of acetochlor (and breakdown products) in tile water at University of Minnesota Southern Research Center, Waseca, Minnesota in 2010.**

Acetochlor (lb/A)	# detections	% detections	Avg conc. of detection (ppb) <sup>a</sup>	Acetochlor loss (lb/A)
0	1 of 47	2.1	** b	**
1.3	3 of 59	5.1	0.073	$4.4 \times 10^{-6}$
2.2	4 of 37	10.8	0.443	$51.0 \times 10^{-6}$

<sup>a</sup> Acetochlor chronic water quality standard = 3.6 ppb for four days. Established for the protection of aquatic life.

<sup>b\*\*</sup> = just detectable.

**Activity 9: Evaluate effectiveness of filter strip Best Management Practice on acetochlor loss to surface water.**

The effectiveness of 30-foot grass filter strips in reducing acetochlor in field runoff is being studied on a corn-soybean field near Saint Clair, Minnesota. Stone Environmental is conducting the study under contract by the Acetochlor Registration Partnership with technical assistance by the Minnesota Department of Agriculture.

Three watersheds have been delineated in the field, each of which drains into an adjoining ditch via a “side inlet” culvert (Figure 16). Semi-circular filter strips have been established at the outlet of two of the watersheds; the third watershed has no filter strip and serves as a control (Figure 17). Fiberglass flumes are installed at the outlet of each watershed to measure and record runoff volume and rate. Monitoring equipment is installed in conjunction with each flume to measure rainfall and collect water samples for later analysis for acetochlor content.



*Figure 16. Map showing relative size and relationship of subwatersheds, A (6.6 A), B (15.6 A), and C (10.0 A).*

The purpose of the filter strips is to increase the infiltration of acetochlor into the soil where it can be adsorbed to the soil particles. Fields were treated with post-planting / preemergence applications of acetochlor at 1.3 lb/A.

Although similar, the three watersheds do vary in size and slope. Runoff from the three watersheds were monitored in 2010 before filter strips were established to mathematically model the relationship between the areas; a process referred to as calibration. Once calibrated, runoff results from the three watersheds can be mathematically adjusted so that differences in treatments, and not differences in watershed size and slope, can be assessed.

Rainfall events in 2010 were adequate to calibrate the watersheds. In September 2010, vegetative filter strips were established in front of flumes in watersheds A and B. Watershed C did not have a filter strip installed and serves as the control.

Unfortunately, subsequent to the successful establishment of the filter strips, there have been inadequate runoff events to assess filter strip effectiveness. The Acetochlor Registration Partnerships plans to continue the study until adequate data is collected.





**Figure 17.** (Top Left) Surface water monitoring station located behind a 30-foot grass filter strip. (Top Right) Surface water monitoring station on control watershed with no filter strip. (Bottom Left) Surface water monitoring station with flume for runoff rate measurement and instrument cabinet containing sampling equipment. (Bottom Right) Pondered water in front of flume following a larger rainfall event in September 2010.

**Activity 10. Develop an “Acetochlor Impairment Response Report” by March 2013.**

Activity 10 is this report. Report conclusions and recommendation follow in the next two sections.

# A NATIONAL CONTEXT FOR MINNESOTA'S ACETOCHLOR IMPAIRMENTS

The U.S. Environmental Protection Agency (EPA) has assembled in a database the assessment, impairment and TMDL implementation information reported by states under Sections 305(b) and 303(d) of the Clean Water Act. The database is current as of 2010 and includes state reporting of pesticide impairments for 17,097 miles of rivers and streams (of 971,156 total miles assessed), and 652,495 acres of lakes, reservoirs and ponds (of 18,944,731 total acres assessed).<sup>5</sup>

Great Lakes open waters (29,661 square miles) have also been reported for pesticide impairments, with most due to the impacts of legacy pesticides no longer registered for use. A much smaller number of bays and estuaries, coastal and Great Lakes shorelines, and wetlands have also been reported as impaired by pesticides.

Because of an apparent reporting or posting inconsistency, Minnesota's acetochlor listings do not appear in the database category of "Pesticides," and instead are listed under the "Toxic Organics" category. This appears to be unique to Minnesota's listing, as there are no other chemicals used exclusively as pesticides reported in the "Toxic Organics" category.

Regardless, the Le Sueur River (6.15 impaired miles) and Little Beauford Ditch (3.09 impaired miles) are the only water bodies nationally reported for acetochlor impairments. Therefore, there are no opportunities to compare the nature of similar acetochlor assessments, listings, probable causes, or approaches to delisting.

For comparison, select reported impairments were identified from the EPA database for Corn Belt states where pesticides used in corn production are identified as the cause of water body impairment. Of the available pesticide impairments, only atrazine impairments are comparable to Minnesota's acetochlor impairments. As such, atrazine is listed as the cause of impairment for 223 water bodies. Table 11 shows the distribution of impaired rivers and streams (4,714 miles) and impaired lakes, reservoirs and ponds (43,387 acres) among Corn Belt states.

**Table 11. Water body impairments listed in the EPA database for the herbicide atrazine in Corn Belt states through 2010.**

State	Number of atrazine impairments
Iowa	2
Illinois	19
Kansas	175
Missouri	1
Nebraska	24
Ohio	2
TOTAL	223

<sup>5</sup> All impairment data summarized in this section was obtained from [http://ofmpub.epa.gov/tmdl\\_waters10/attains\\_nation\\_cy.control](http://ofmpub.epa.gov/tmdl_waters10/attains_nation_cy.control) accessed on September 27, 2012.

Because the causes of lake, reservoir and pond impairments—and the associated responses to address such impairments—likely differ from those for river and stream impairments, only river and stream impairments for atrazine are further discussed below.

The EPA database indicates that the majority of reported atrazine river and stream impairments are in need of a Total Maximum Daily Load (TMDL) determination. In Kansas, many water bodies originally listed as atrazine-impaired are now in “compliance with applicable standards” (sometimes because the “original basis for listing was incorrect”). Nevertheless, there are a few examples of TMDL documents describing the implementation of mitigation measures, or concluding that atrazine-impaired waters eventually attained required water quality uses through adjustment to assessment methodologies or the absence of impacts verified through monitoring. They are summarized below.

### **Kansas atrazine TMDLs**

*Tuttle Lake:* The Kansas-Lower Republican Basin TMDL,<sup>6</sup> although structured around Tuttle Lake, included priority tributary rivers and streams within the Lower Little Blue Subbasin. While the TMDL included attainment of drinking water standards for atrazine, the same standard (3 ppb) was used for assessment of support for chronic aquatic life support. Seasonal variation was incorporated in the TMDL through the documentation of the seasonal (May-June) occurrence of elevated atrazine levels.

The following endpoints were identified to define achievement of the water quality standards:

1. Average monthly atrazine exceedances over 3 ppb will not occur more frequently than once every three years in Tuttle Creek Lake or the streams within its watershed.
2. Average annual concentrations of atrazine will be below 3 ppb in Tuttle Creek Lake, its outlet and the streams comprising its watershed.
3. No individual sample of atrazine will exceed 170 ppb.

The TMDL established milestones in order to judge progress in the interim, including no atrazine concentration digressions over 3 ppb in Tuttle Creek Lake nor the streams of the Blue River Drainage in any month other than May or June, and no digressions of atrazine concentrations over 3 ppb in streamflow throughout the Tuttle Creek basin during flows less than the long term mean daily flow of the Big Blue, Little Blue and Black Vermillion Rivers and Mill and Rose Creeks. These milestones and TMDL endpoints were considered reachable through implementation of best management practices (BMPs) for atrazine as outlined by Kansas State University. The Kansas BMPs are similar to Minnesota’s general herbicide BMPs and those specific to atrazine.

*Turkey Creek:* A TMDL for Turkey Creek was established in 2006, based on atrazine concentration exceedances of 3 ppb as the assessment threshold for attainment of chronic aquatic life support. Desired implementation activities included the monitoring of atrazine levels in the streams during the planting seasons for corn and sorghum and employing BMPs on cropland to minimize atrazine runoff. Implementation tools included providing technical assistance to growers on the BMPs, revising atrazine criteria into the Kansas Surface Water Quality Standards once EPA finalizes national criteria, and conducting an educational program along with the state of Nebraska on atrazine reduction and usage targeted to row crop producers.

---

<sup>6</sup> [http://www.epa.gov/region07/water/pdf/tuttle\\_lake\\_tmdl.pdf](http://www.epa.gov/region07/water/pdf/tuttle_lake_tmdl.pdf) accessed September 28, 2012.

## Nebraska atrazine TMDLs

For an atrazine impairment first identified in 1998 for the Big Blue River (50 miles), applicable water quality standards were determined to be attained in 2003 due to new assessment methods that recognized seasonality (e.g., May-June peak concentrations). The current assessment procedures for chemical water quality data and information to support aquatic life beneficial uses indicate that such uses are supported when  $\leq 10\%$  of samples exceed acute or chronic water quality criteria.<sup>7</sup>

Other atrazine impairments in Nebraska have been similarly assessed or reassessed according to the same assessment procedures (e.g., Middle Creek, June 2007 TMDL; Mud Creek – Loup River Basin, May 2012). Leadership for implementation of any necessary attainment measures is delegated to the Nebraska Department of Agriculture.

## Ohio atrazine TMDLs

For an atrazine impairment in the White Oak Creek Watershed (90 miles),<sup>8</sup> the applicable water quality standard of 3 ppb was for surface water intakes at community water supplies, and the TMDL seasonal target (May-June) was set at 35 ppb as the daily maximum, representing a target necessary to ensure that atrazine concentrations would not exceed a 90-day rolling average of 3 ppb. While this approach was developed to protect a drinking water source, the Ohio example is noted because the concept of seasonality is similar to that used in Nebraska's Big Blue River atrazine TMDL for aquatic life.

## Illinois atrazine TMDL

Illinois developed a TMDL for the Little Wabash River Watershed and submitted a draft final report in June 2008. The conclusions reached included development of a load-duration curve to address the impairment, though it concluded that runoff from agricultural lands should be addressed through implementation of voluntary controls. The eventual Implementation Plan will recommend BMPs for reducing the amount of atrazine in the watershed.

In the cases reviewed above, beneficial use attainment and, it seems, delistings (removal from the impaired water body list) are linked to at least one or more of the following factors:

1. *The assessment methods used:* Some impairments and responses include an acknowledgment of seasonality to the “digressions” or exceedances of a row-crop (corn) herbicide concentrations in the assessed water body, and recognition that exceedances during specific seasons are expected or allowable to a certain degree, but should not occur outside of specific applications seasons;
2. *Lack of recurring exceedances:* Specified amounts of time are needed to demonstrate that exceedances are not routine (at least outside of certain seasons or by employing periods of rolling averages); and,
3. *Availability of Best Management Practices (BMPs):* Information dissemination and outreach, as managed by those closest to pesticide regulation and education, is the preferred tool to minimize anticipated losses of herbicide to water bodies.

---

<sup>7</sup> Nebraska methodologies available at [http://www.deq.state.ne.us/Publications/0/17ddb685e0238e1d862571320063a1e2/\\$FILE/2006%20IR%20Assessment%20Methodology.pdf](http://www.deq.state.ne.us/Publications/0/17ddb685e0238e1d862571320063a1e2/$FILE/2006%20IR%20Assessment%20Methodology.pdf) accessed September 28, 2012

<sup>8</sup> [http://www.epa.gov/waters/tmdl/docs/38282\\_WOC\\_TMDL\\_Final.pdf](http://www.epa.gov/waters/tmdl/docs/38282_WOC_TMDL_Final.pdf) accessed September 28, 2012

Because impairment response efforts—including follow-up monitoring and full-scale TMDL development—are extremely resource intensive, the different approaches to listing and delisting atrazine-impaired waters in other Corn Belt states (and impairments nationwide for other toxics) should be carefully reviewed by Minnesota state agencies for ways in which pesticide impacts might be assessed in the future to ensure that water bodies are appropriately listed or delisted.

## CONCLUSIONS

No violations of the acetochlor water quality standard have been detected in either the Le Sueur River or the Little Beauford Ditch since the impairments in 2005. This could be the result of a change in acetochlor management since 2005 which has reduced acetochlor runoff, or an absence of rainfall events large enough to produce runoff during the critical acetochlor runoff time period following corn planting.

Changes in acetochlor management were investigated in Activity 6, collection of farming system information on acetochlor usage, and in Activity 7, collection of voluntary acetochlor BMP use. In Activity 6 pesticide dealer agronomists were interviewed about past, present (2010) and future acetochlor management by their customers, and in Activity 7 corn growers who use acetochlor were interviewed about their current and anticipated future use of water quality best management practices for acetochlor. Most notable from both the agronomist and corn grower interviews is the increased use of acetochlor at reduced application rates following the wide-spread introduction of glyphosate tolerant corn to the watershed in 2005. The 1.3 lb/A reduced application rate is 40 percent less than the 2.2 lb/A full application rate and 20 percent less than the 1.6 lb/A application rate that typically was previously used. Agronomists reported 99 percent of acetochlor acres were applied at reduced rates and corn growers reported 96 percent of acetochlor acres were applied at reduced rates. Agronomist predicted that the use of reduced application rates would continue at their present level for the next five years, the time period used in the interview as the foreseeable future.

In addition to using the reduced application rate best management practice, interviewed corn growers reported wide use of scouting, application setbacks and filter strips adjacent to water, precision application, and soil incorporation. However, the interviews focused on current and future best management practice use, so it cannot be determined whether use of the practices has increased since 2005.

In Activity 2, the University of Minnesota evaluated the effectiveness of water quality best management practices for acetochlor using the Soil and Water Assessment Tool (SWAT). This computer model predicted an 18% reduction in acetochlor loss to surface water in the Le Sueur River watershed by reducing acetochlor application rates from 1.6 lb/A (pre-2005 baseline rate) to 1.3 lb/A (post-2005 reduced rate). The model also predicted a 62% reduction in acetochlor loss to surface water by establishing buffer strips on all corn and soybean fields and a 95% reduction in acetochlor loss to surface water by soil incorporating all applied acetochlor.

The University of Minnesota evaluated the effectiveness of the reduced rate water quality best management practices for acetochlor on loss to tile water in Activity 8. Measured average acetochlor concentration in tile water under plots receiving the 1.3 lb/A reduced rate was 0.073 ppb, two orders of magnitude lower than the 3.6 ppb concentration of the acetochlor standard. This indicates that an expansion of tile drained acres in the Le Sueur River watershed is unlikely to contribute to future

violations of the acetochlor water quality standard. It should be noted the average acetochlor concentration in tile water from plots receiving the reduced 1.3 lb/A acetochlor application rate was six times less than the average acetochlor concentration from plots receiving the full 2.2 lb/A acetochlor application rate (0.073 ppb vs. 0443 ppb).

The conclusion from the above activities is that there have been changes in acetochlor management since 2005; that being the almost universal use of reduced application rates following the introduction of glyphosate tolerate corn. Computer modeling by the University of Minnesota predicts an 18 percent reduction in acetochlor loss to surface water in the Le Sueur River watershed from use of that practice.

The question remains whether there have been rainfall events since 2005 large enough to produce runoff during the critical acetochlor runoff time period following corn planting. Activity 4, watershed scale water monitoring, indicates that there have been. From 4/11/2005 to 5/28/2012, 25 storm events in excess of 0.5 inch of total precipitation occurred in the Little Beauford Ditch watershed and 44 acetochlor samples were collected. Seventy-five percent of the pesticide samples were collected after approximately 60 percent of the corn had been planted on a statewide basis. No violations of the acetochlor water quality standard were measured during this time period. As expected, elevated acetochlor concentrations were typically measured during storm flow events occurring in May and June following the primary acetochlor application period. Activity 5, Subwatershed scale water monitoring, found that expanded monitoring of the major subwatersheds of the Le Sueur River did not indicate that any of the watersheds were contributing disproportionately to acetochlor concentrations measured at the river's mouth. It also found the lower cost enzyme-linked immunosorbant assay (ELISA) water quality screening method provides a reasonable measure of acetochlor concentration.

The final conclusion is there have been rainfall events since 2005 large enough to produce runoff during the critical acetochlor runoff time period following corn planting, and that changes in acetochlor management, mainly the almost universal use of reduced application rates, have contributed to decreased acetochlor concentrations in impaired reaches of the Le Sueur River and Little Beauford Ditch. Information collected during interviews with Le Sueur River watershed agronomists and corn growers did not indicate any future changes in acetochlor management that will reverse this trend.

In preparation of this report, the Minnesota Department of Agriculture conducted a review of how pesticide impairments have been addressed in other states. Since no other state beside Minnesota has had a water body impairment due to acetochlor, impairments caused by the corn herbicide atrazine in Corn Belt states were reviewed. The review noted that delisting (removal from the impaired water body list) of water bodies impaired by atrazine is apparently linked to at least one of three factors:

1. Recognition that exceedances during specific seasons are expected or allowable to a certain degree, but should not occur outside of specific application seasons;
2. Lack of recurring exceedances and the need for specified amounts of time to demonstrate that exceedances are not routine; and,
3. Availability of best management practices (BMPs) and their dissemination by those closest to pesticide regulation and education.

## RECOMMENDATIONS

Based on information collected through the activities of the Acetochlor Impairment Response Plan, it is the conclusion of this report that changes in acetochlor management have significantly reduced the likelihood of acetochlor water quality standard violations in the impaired reaches of the Le Sueur River and Little Beauford Ditch. There is an effort currently underway at the Minnesota Pollution Control Agency (MPCA) to further clarify criteria for listing and de-listing water bodies potentially impacted by toxic pollutants such as acetochlor.

With these two considerations in mind, the Minnesota Department of Agriculture (MDA) makes the following recommendations to the MPCA:

1. MDA continue to monitor for acetochlor in at the Le Sueur River outlet and Little Beauford Ditch sites for the foreseeable future;
2. MDA track acetochlor use in the Le Sueur River watershed making use of county-based pesticide sales data;
3. MDA and partners continue to promote use of acetochlor water quality best management practices in the Le Sueur River watershed;
4. The Acetochlor Registration Partnership, MDA and other partners continue to assess the effectiveness of vegetated filter strips in reducing acetochlor loss to surface water and provide a report on their effectiveness once sufficient runoff data is collected;
5. Assuming no violations of the acetochlor standard are identified in the two impaired reaches during the 2013 water quality assessment, MPCA should consider removing them from the impaired waters list during the 2014 listing cycle; and,
6. MDA continue to assist efforts by MPCA to clarify and potentially modify guidance criteria used to list and delist water bodies for this and potential future pesticide impairments so that the probability of exceeding a water quality standard over time is factored into listing and de-listing decisions.

END

## REFERENCES

- Casino P., S. Morais, R. Puchades, and Á. Maquieira. Evaluation of Enzyme-Linked Immunoassays for the Determination of Chloroacetanilides in Water and Soils. *Environ. Sci. Technol.*, 2001, 35(20), pp 4111–4119.
- Folle, S. 2010. SWAT Modeling of Sediment, Nutrients and Pesticides in the Le Sueur River Watershed, South-Central Minnesota. Ph.D dissertation, University of Minnesota.
- Folle, S., Dalzell, B., and Mulla, D.J. 2007. Comparison of the WIN-PST and SWAT Models for Pesticide Losses in Surface Runoff of the Le Sueur River Watershed. University of Minnesota. A report submitted to the Minnesota Department of Agriculture.
- Folle, S., Dalzell, B., and Mulla, D.J. 2009. Evaluation of Best Management Practices (BMPs) in Impaired Watersheds Using the SWAT Model. University of Minnesota. A report submitted to the Minnesota Department of Agriculture.
- Galzki, J.A., A.S. Birr, and D.J. Mulla. 2011. Identifying Critical Agricultural Areas with Three-Meter Lidar Elevation Data for Precision Conservation. *J. Soil Water Conserv.* 66:423-430.
- Holman R. E., R. Leidy, A.Walker. 2000. Evaluation of Selected Pesticides in North Carolina Surface Water Supplies: Intake Study. Paper No. 98148. *J. American Water Resources Assoc.*
- Minnesota Department of Agriculture and Minnesota Pollution Control Agency. 2009. Le Sueur River and Little Beauford Ditch Acetochlor Impairment Response Work Plan. Retrieved from: <http://www.mda.state.mn.us/en/chemicals/pesticides/acetochlor1/~media/Files/chemicals/pesticides/acetochlorworkplan.ashx>
- Randall, G.W. and J. Vetsch. 2011. Effect of Acetochlor Application Rate on Acetochlor Concentration and Loss in Tile Drainage. <http://www.mda.state.mn.us/protecting/cleanwaterfund/research/~media/Files/protecting/cwf/reducedacet6.ashx>.
- USDA, N.M. 2008. Rapid Watershed Assessment Resource Profile for the Le Sueur Watershed (MN) HUC 7020011. <http://www.mn.nrcs.usda.gov/technical/rwa/Assessments/07020011.html>. USDA, NRCS Minnesota.



# APPENDIX 1

## Advisory Committee for Acetochlor Impairment Response Plan (8-22-12)

Company or Organization	First Name	Last Name
<b>GROWERS &amp; GROWER ASSOCIATIONS</b>		
Grower, SWCD Supervisor, Corn & Soybean Associations	Allen	Marble
Grower, Farm Bureau representative	Scott	Schweer
MN Soybean Grower Association	Steve	Commerford
MN Agricultural Water Resources Coalition	Warren	Formo
<b>DEALERS, APPLICATORS &amp; ADVISORS</b>		
Crystal Valley – Waldorf	Mark	Meyer
McPherson Crop Management - Janesville	Bernie	Paulson
Watonwan Farm Service - New Richland	Chris	Beyer
<b>LOCAL GOVERNMENT</b>		
Local Water Planner, Blue Earth County	Julie	Conrad
Alternate Water Planner, Waseca County	Mark	Leiferman
Alternate Water Planner, Waseca County	Lenny	Hulburt
SWCD, Waseca County	Marla	Watje (way-gee)
Alternate SWCD, Faribault County	Michele	Stindtman
Alternate SWCD, Blue Earth County	Jerad	Bach
<b>CHEMICAL COMPANIES</b>		
Dow AgroScience, Sales Representative	Neil	Trygestad
Monsanto, Technology Development Representative	Bruce	Drager
<b>AGENCIES</b>		
NRCS-USDA, Soil Conservationist	Ryan	Braulick
MPCA, Watershed Project Manager	Scott	MacLean
MDA, Pesticide Management Unit Supervisor	Gregg	Regimbal
MDA, Pesticide Management Unit	Ron	Struss
<b>ACADEMIC</b>		
South Central College, Farm Business Mgt. (also grower)	Todd	Stencel
University of Minnesota Extension, County Educator	Diane	DeWitte
University of Minnesota Extension, Regional Educator	Ryan	Miller

## APPENDIX 2

### Units and scientific terms used in this report:

A	Acre, British unit of land area.
cfs	Cubic feet per second, British measure of flow.
CST	Central standard time
EFI	Equal flow increment
ETI	Equal time increment
g	Gram, metric unit of weight.
L	Liter, metric unit of volume.
lb	Pound, British unit of weight.
µg	Micrograms, metric unit of weight. Equivalent to 0.000,001 gram.
µg/L	Micrograms per liter, metric unit of concentration. In water solutions equivalent to parts per billion (ppb).
mg	Milligram, metric unit of weight. Equivalent to 0.001 gram.
mg/L	Milligrams per liter, metric unit of concentration. In water solution equivalent to parts per million (ppm).
mL	Milliliter, metric unit of volume. Equivalent to 0.001 liter.
mL/g	Milliliter per gram, metric unit of concentration.
mm	Millimeter, metric unit of length. Equivalent to 0.001 meter.
mm Hg	Millimeters of mercury, metric unit of pressure. 1 atmosphere of pressure = 760 mm Hg.
ppb	Parts per billion. In water solutions equivalent to micrograms per liter (µg/L).
R <sup>2</sup>	R squared, statistical coefficient which indicates how well data points fit a line or curve.

## **APPENDIX 3**

### **“Rational for Delisting of Impaired Watersheds due to Acetochlor in the State of Minnesota”**

Submitted to the Minnesota Department of Agriculture by  
the Acetochlor Registration Partnership on 12-19-12.

(Report contained in the following attached pages.)