Surface Water Quality Monitoring Design Document

June 2007

MINNESOTA DEPARTMENT OF AGRICULTURE

MONITORING UNIT
ENVIRONMENTAL SECTION
PESTICIDE & FERTILIZER MANAGEMENT DIVISION

Table of Contents

Minnesota Department of Agriculture

The Minnesota Department of Agriculture (MDA) Monitoring Unit has developed this Surface Water Monitoring Design Document as a framework for surface water pesticide monitoring over the next several years. While the strategy is necessarily long-term, this document will be periodically updated as necessary. In addition, on an annual basis the Monitoring Unit will develop a Surface Water Monitoring Work Plan that details monitoring efforts for the coming monitoring season. The MDA is the lead state agency involved in the monitoring of agricultural chemicals in surface and ground waters of the state.

1.0 Introduction

Agriculture remains a dominant industry within Minnesota and a major factor in the economy of the State. Farming practices are dynamic and respond quickly to changes in market factors, climatic and pest variability, and various other production constraints. Among these constraints, farmers make decisions as to the level and intensity of various management practices, including decisions regarding agricultural chemicals. MDA's Monitoring Unit seeks to provide information on impacts to the State's water resources, including surface water in agricultural and urban areas, from the routine use of agricultural chemicals. A companion document addresses the MDA's ground water monitoring efforts. Information collected by the Monitoring Units is made available to policy makers and the general public so that management decisions may be appropriately made to minimize, reduce or eliminate impacts from agricultural chemicals.

Because of the large and complex nature of modern agriculture and the vastness of surface water resources in the state, it is not practical for the MDA (or any other state agency) to achieve a comprehensive evaluation of all water resources in the state every year. This document provides a conceptual design for identifying and selecting representative agricultural watersheds within different "Pesticide Monitoring Regions" (PMRs) for assessment. The level of assessment for any given region will vary depending upon agricultural activity and chemical usage, environmental sensitivity and historical water quality data with a few watersheds receiving very detailed assessments and many watersheds receiving more limited evaluation during periods of peak pesticide detection probability. Although designed primarily as a pesticide monitoring program, the MDA will collect and analyze nutrient and sediment data whenever possible to continue to expand the body of information that relates to the potential impact associated with agricultural activities in the state. In an effort to optimize limited resources, the

MDA will seek the development of cooperative relationships with existing monitoring programs at the local, state or national level whenever possible.

1.1 Program Goal and Objectives

The primary goal of the MDA's surface water monitoring activities is to provide detailed information on the impact of pesticides on Minnesota's surface waters as directed by the Minnesota Pesticide Control Law (Minn. Stat. § 18B) and the state Pesticide Management Plan (PMP). Protection of Minnesota's citizens and water resources from agricultural chemicals is the fundamental purpose of this goal. To achieve this goal the following objectives have been identified:

1. Measure the pesticide concentrations in representative streams and rivers in agricultural areas of Minnesota;
2. Provide analysis of pesticide concentration dynamics (magnitude, duration and frequency of detections) at locations that have demonstrated the potential to exceed surface water standards or other relevant numeric criteria;
3. Collect other relevant information related to pesticide fate and transport such as stream flow, persistence and use data compiled by other sources;
4. Evaluate pesticides in agricultural drainage systems, springs, lakes and urban water resources;
5. Compile, analyze and disseminate the information developed through the monitoring program to policy makers, scientists, and citizens; and
6. Document and evaluate the effectiveness of actions taken to prevent or minimize the impacts associated with pesticides and nutrients and verify that water body impacts are, indeed, minimized or do not lead to impairments of use.

With these objectives in mind, this document lays out a strategy that will be implemented and evaluated over the next several years in Minnesota. This document describes changes to the MDA's existing monitoring that come as part of an on-going effort to optimize limited monitoring resources and/or methods that maximize information and resource protection. Some of these changes are the direct result of experience gained while collecting and analyzing data from Minnesota streams and rivers over several years. Other modifications were made in response to suggestions from the Minnesota Pollution Control Agency (MPCA) to more closely match the monitoring recommendations of MPCA's 2005 Total Maximum Daily Load Assessment Guidance.

The MDA and MPCA each conduct surface water quality monitoring activities to meet their individual authorities and responsibilities. Whenever possible, monitoring activities are coordinated to optimize efficiency. The details of the relationship are discussed in a July 5, 2004, Cooperative Surface Water Quality Monitoring System Agreement signed by the commissioners of each agency and available at http://www.mda.state.mn.us/appd/ace/swagreement.pdf. The Cooperative Agreement identifies the MPCA's primary monitoring goal as assessment of the chemical, physical and biological integrity of lakes, streams and wetlands in the state. This design, if properly implemented, should provide scientifically rigorous and legally defensible data that will allow the MDA and the MPCA as well as other regulators and policy makers to effectively evaluate and protect water resources in the state.

In recognition that the surface water resources of the state are at risk from pesticides and fertilizers (nutrients) from both agricultural and urban sources, the surface water monitoring efforts of the MDA will include representative sampling from both locations (agricultural and urban) for pesticides and nutrients whenever feasible. The collection of nutrient data along with pesticide data is considered critical because it provides insight into the overall condition of the aquatic system along with providing a better indication as to the level of impact agricultural activities may be having on an aquatic system. There are also studies that suggest the presence of elevated concentrations of nutrients such as nitrate may influence the impacts associated with pesticides although these relationships are not well understood.

1.2 Statutory Authority

The MDA has broad authority to take action to prevent any unreasonable adverse effects on the environment (as defined in statute) including impacts to surface waters from pesticides. The MDA also has the authority and responsibility to develop and promote pesticide voluntary best management practices.

Information on pesticide detections in Minnesota's surface water resources will be collected and analyzed by the MDA's Monitoring Unit with the assistance of other state agencies and cooperators. Those detections determined to be the result of non-point source contamination will be evaluated relative to a surface water standard or other relevant surface water reference value.

Following review of surface water monitoring data, the commissioner of the MDA may, as outlined in the PMP, determine that a pesticide has been found at a "concentration of concern" relative to a water quality standard, water quality criterion or water quality advisory value (i.e., a "reference value), and that the concentration of concern is not the result of misuse or unusual or unique circumstances.

If the concentration of a pesticide in a surface water body exceeds a numerical standard, the water body may be subject to formal listing as "impaired" on the Clean Water Act's 303(d) list assembled by the MPCA (see the MPCA website at http://www.pca.state.mn.us/water/index.html for additional information on MPCA surface water standards and the impaired waters process). This may result in initiating a Total Maximum Daily Load (TMDL) study under the federal Clean Water Act section 303(d). For the purposes of this design document, the source of surface water quality reference values in Minnesota is the MPCA. If a pesticide does not have an MPCA reference value, then reference values from the EPA or other states will be considered. While the MDA is the lead state agency for pesticide environmental and regulatory functions, it works closely with the MPCA in its role as the lead agency for regulating the TMDL process and for managing pollution in surface water bodies under Minn. Rules Chapters 7050.

To provide flexibility in evaluating and responding to concentrations that might lead to future impairment listings of water bodies, and in recognition of the complex variables that can contribute to peak concentrations, there is no single value or percentage of a reference value that will trigger the development of preventive actions such as voluntary pesticide-specific BMPs or educational campaigns. Instead, preventive actions will be considered when surface water monitoring results for a pesticide exceed 10 to 50% of its reference value. The commissioner will consider a number of factors in determining if an exceedance means that the pesticide is a surface water pesticide of concern requiring initiation of specific preventive actions. The most important factors will be monitoring and use trends. For example, if the use of a pesticide is stable or increasing, and the concentration is at 10 to 50% of its reference value and exhibits an increasing trend, then preventive actions may be taken to ensure that the water body does not become impaired.

A determination that a pesticide is a surface water pesticide of concern will initiate the development of preventive actions including voluntary pesticide-specific BMPs to protect surface waters from further contamination. Such actions will be taken prior to, and in an effort to prevent, the impairment of a surface water body.

In summary, "surface water pesticide of concern," as it is used in this design document, means the detection of a pesticide in surface water at concentrations of concern relative to a water quality standard, water quality criterion or water quality advisory value (i.e., a "reference value"), not due to misuse or unusual or unique circumstances, but likely to be the result of normal use of product or practice.

Surface water pesticide of concern status, as determined through the analysis of scientifically valid information, allows the state and all involved parties to take a proactive approach to focus limited resources on pesticides which are adversely impacting Minnesota's water resources. Inclusion in concentration of concern status is a useful tool to communicate to all involved parties that there is a scientific basis for concern about the use of a specific pesticide and its impact on water quality. Surface water pesticide of concern status does not regulate the use of a pesticide in Minnesota. Rather it triggers development of voluntary BMPs for those pesticides.

With regard to pesticides in surface water, regulatory authority for the MDA is provided through the Pesticide Control Law as stated in Minn. Stat. § 18B.26, subd. 5.,

> *The commissioner shall review each application and may approve, deny or cancel the registration of any pesticide. The commissioner may impose state use and distribution restrictions on a pesticide as part of the registration to prevent unreasonable adverse effects on the environment.*

Surface water pesticide of concern status may not be appropriate in a number of cases where a pesticide has been detected in surface water in Minnesota. Detections which are low relative to a surface water reference value or which are sporadic and not indicative of widespread presence as a result of use in accordance with label directions will need to be evaluated by the committee and the commissioner. It may not be appropriate for determining a surface water pesticide of concern and developing BMPs for a product which is being phased out or likely will have its use significantly reduced. The commissioner may promote generic (core) BMPs, and the MDA and the registrant may coordinate additional prevention efforts (MDA, 2005a).

1.3 Background

The seasonal presence of pesticides in the rivers and streams of the agricultural areas of the U.S. is well established. Most pesticides products applied to fields and crops are quickly adsorbed by plants or transformed (degraded) in the soil. However, under some circumstances small amounts of the applied product are lost to surface water via overland flow, subsurface drainage or by other means (Battaglin et al., 2003). A significant source for adverse effects from pesticides is through contamination of the hydrologic system, which supports aquatic life and is used for recreation, drinking water and many other purposes. There are a combination of factors including environmental conditions, agricultural management practices and pesticide properties which will determine if, when and how a pesticide will move from the field to the broader environment, including surface waters (Larson et al., 1997).

In 1987 the Minnesota Legislature revised the Minnesota Pesticide Control Law which requires: "The commissioner (of Agriculture) shall: (1) determine the impact of pesticides on the environment, including the impacts on surface water and groundwater in this state; (2) develop best management practices involving pesticide distribution, storage, handling, use, and disposal; and (3) cooperate with and assist other state agencies and local governments to protect public health and the environment from harmful exposure to pesticides" (Minnesota Statute § 18B.04). This legislation along with the Minnesota Comprehensive Ground Water Protection Act (1989) expanded protection responsibilities of the MDA, including specific direction regarding monitoring for agricultural chemicals and the management of those chemicals when found to impact ground water. The Ground Water Protection Act mandated development of a State Pesticide Management Plan (PMP) with monitoring to act as the primary support to management decisions within that Plan. The PMP includes provisions for the protection of surface as well as ground water.

In response to these two pieces of legislation, the MDA initiated a Ground Water Monitoring Program in 1987 and a Surface Water Monitoring Program in late 1990. Specifically, in 1991 the MDA, in cooperation with the MPCA, began seasonal monitoring for pesticides in the surface waters of Minnesota. This initial statewide sampling was conducted for three years at MPCA-established long-term surface water monitoring stations. The results of this study (MDA 1996 Common Detection Advisory Committee Report) provided MDA with a general indication of which of the more commonly used pesticides were present in the rivers and streams and in which regions of Minnesota contamination was occurring.

In 1992, the MDA began a program that focused on continuous flow-based automated monitoring at select locations. This new monitoring strategy was adopted to allow for accurate quantification of pesticide and nutrient concentration dynamics coupled with water volume to allow for the estimate of chemical load. This monitoring strategy also provides for the determination of pesticide concentration magnitude, the frequency of detection and the approximate duration that the pesticide is present. These three variables (frequency of detection, magnitude of concentration and duration of concentration) are considered critical to assessing pesticide impact to surface waters and implementing the Minnesota PMP.

The locations where continuous automated monitoring has occurred have changed over the years and included small streams as well as large rivers. The number and location of sites has varied depending upon available funding and changing programmatic requirements. In general, continuous flow-based automated monitoring has occurred at locations where there was a special interest or concern and/or where an existing monitoring effort was underway that allowed for cooperative collection of data.

As part of this monitoring design, the process by which continuous flow-based automated monitoring stations are selected and prioritized will be more formalized. Currently the MDA is involved in the operation of five stream sites where continuous flow-based automated monitoring is occurring. Specific information on the operation of these sites and all of the other surface water locations where the MDA has operated intensive pesticide monitoring is presented in Table 1.

MDA's intensive long-term monitoring efforts have focused on two primary areas of the state: southeastern Minnesota and the Minnesota River Basin. Surface water monitoring at most of the intensively monitored sites has utilized equal flow increment (EFI) composite sample collection during storm flow periods. Baseflow periods were typically characterized by grab samples collected between storm events. Although storm based EFI sampling is more complicated and labor intensive, if properly conducted it generally provides better resolution of chemical concentration and presence over the course of a storm flow period when compared to an equivalent grab sampling protocol.

In 2002, the MDA Surface Water Monitoring Program expanded to include pesticide and nutrient sampling from 25 "Statewide Survey Sites." One sample was collected from 25 rivers in different agricultural areas of the state to give a general indication of whether the pesticide data being collected at the more intensively sampled "long-term intensive monitoring sites" was representative of other rivers and streams in the state. The results of this sampling were inconclusive relative to the effort's goals, but reinforced the need to sample rivers during storm flow periods following peak pesticide application periods (May, June and July).

Table 1. Locations where the Minnesota Department of Agriculture has conducted intensive monitoring since beginning surface water monitoring in the early 1990's.

Site Location	County	Watershed Acres	Years Monitored	# of Pesticide Samples Collected
Middle Branch Whitewater River	Winona	16,100	1993-Present	600+
South Branch Whitewater River	Winona	49,200	1993-2000	213
East Branch Blue Earth River	Fairbault	122,300	1992-1996	146
Cascade Creek	Olmsted	15,400	1998-2000	76
Chaska Creek	Carver	9,600	1999-2002	102
Bent Creek	Carver	9,600	1997-2002	151
Bevins Creek	Carver	83,800	1995-2002	157
Sand Creek	Scott	163,100	1995-2002	187
Minnesota River at Jordan	Scott	10,389,800	1996-2002	42
Minnesota River at Judson	Nicolett	7,186,900	1999-2004	161
Blue Earth River at Rapidan Dam	Blue Earth	155,300	1999-2004	163
Le Sueur River	Blue Earth	710,400	1999-Present	217
Seven Mile Creek	Nicolett	23,600	2004-Present	45
North Branch of the Root River	Fillmore	361,600	2004-Present	59
Beauford Watershed	Blue Earth	4,500	2005-Present	35
Lake Harriet	Hennepin	142	1992-1995	88

In 2003 the MDA sought cooperators and identified a different group of "Statewide Survey Sites," selecting one or two watersheds from each Pesticide Monitoring Region (PMR) of the state. Each of the 15 sites selected was sampled approximately four times during peak pesticide detection periods (May, June and July) with an emphasis on collecting samples during stormflow periods. In 2004, the "Statewide Survey" site sampling was continued although some of the sites were changed slightly because of the availability of cooperators. In 2004, 16 sites were sampled by MDA staff and cooperators for a total of 64 pesticide samples.

In 2005 the "Statewide Survey" included approximately 51 sites due primarily to a general recognition that sampling from more Minnesota streams was valuable. An effort was made to include both large and small watersheds from each of the PMRs. All 51 sites were sampled, most four times each during peak detection periods (May, June and July), for a total of over 200 pesticide samples of which approximately 34 sample sites were collected by cooperators. Most of these sites were also sampled in 2006 as Tier 1 and Tier 2 sites (the Tier structure is introduced below). In addition six urban stream sites were selected for Survey type monitoring during the 2006 season.

Figure 1. Monitoring station on the Le Sueur River showing refrigerated autosampler for the collection of composite samples.

2.0 Statewide Agricultural Surface Water Pesticide Monitoring

The following monitoring design has been developed to provide for spatial representation of the different Pesticide Monitoring Regions (PMRs) within in Minnesota. The level or "Tier" of monitoring within the PMRs will be contingent upon historical pesticide data with sampling frequency increasing when historical data indicate the potential for pesticide concentrations to exceed available water quality reference values. Watersheds that exhibit greater potential for pesticide movement to surface water will move from a lower to higher Tier as resources permit. Each spring an annual Surface Water Monitoring Workplan will be developed prior to the sampling season detailing site locations, cooperator information, sampling protocol, analyte list and the respective Tier or intensity of sampling anticipated at each location.

The MDA has established ten PMRs to organize water quality monitoring strategies in watersheds that have similar hydrologic and agricultural characteristics (Figure 2). Pesticide Monitoring Regions borders follow county boundaries, but also generally represent different hydrologic regions of Minnesota. These distinct hydrologic regions include parts of: 1) the Red River of the North Basin, 2) the Rainy River Basin, 3) Lake Superior Basin, 4) the Upper Mississippi River Basin, 5) the St. Croix River Basin, 6) the Upper Minnesota River Basin, 7) the Missouri and Des Moines River Basins, 8) the Middle and Lower Minnesota River Basin, 9) the Lower Mississippi River Basin, and 10) the Twin Cities Metropolitan Region.

The Statewide monitoring conducted by the MDA has indicated that the south central and south eastern Minnesota PMRs (Region 8 and 9, respectively) have generally exhibited higher pesticide concentrations in monitored streams and rivers then in other regions of the state. As such, the MDA's intensive long-term monitoring has focused on these two regions. These regions tend to exhibit higher concentrations for a variety of reasons including climate, soils, geology, slopes, agricultural practices and intensity as well as pesticide use patterns. With the expanded monitoring proposed in this document, it is quite possible that intensive monitoring may be necessary in other PMRs if elevated concentrations of pesticides are confirmed. It is also worth noting that PMRs 2 and 3 will have very minimal if any pesticide samples collected due to the limited use of pesticides in those areas.

2.1 Tier 1 - Statewide Pesticide Survey Sampling

Minnesota is blessed with an abundance of surface water resources. This abundance, while being an asset in many respects, complicates monitoring and assessment by presenting literally thousands of miles of rivers and streams to evaluate. As discussed above, the MDA has established PMRs throughout the state that exhibit similar pesticide use practices and hydrologic/geologic characteristics. Within each of these PMRs (except Regions Two and Three) stream monitoring locations will be identified in agricultural or urban watersheds and will be sampled during peak pesticide detection periods. The objective of the Tier 1 sites will be to identify and assess the occurrence and general magnitude of pesticides in river systems representing different agricultural/urban areas of the state. A total of four samples will be collected from each agricultural Tier 1 site during peak pesticide detection periods of May, June and July. Select Tier 1 sites may also be sampled during the late fall and/or early spring to assess the movement of fall applied products such as metolachlor. Urban sampling locations may have a slightly different time period for sample collection which will extend later into the summer to better reflect urban pesticide use patterns. Pesticide Monitoring Regions that have historically indicated a higher potential for pesticide occurrence in surface water will likely have more monitoring sites then other lower priority PMRs.

The primary limiting factor for Tier 1 sampling will be laboratory capacity and the availability of MDA staff or cooperators to collect samples. In an effort to assess as many watersheds as practical from representative PMRs while distributing the sample load to the MDA laboratory in a reasonable fashion, the following guidance has been developed for the MDA's Tier 1 statewide pesticide sampling:

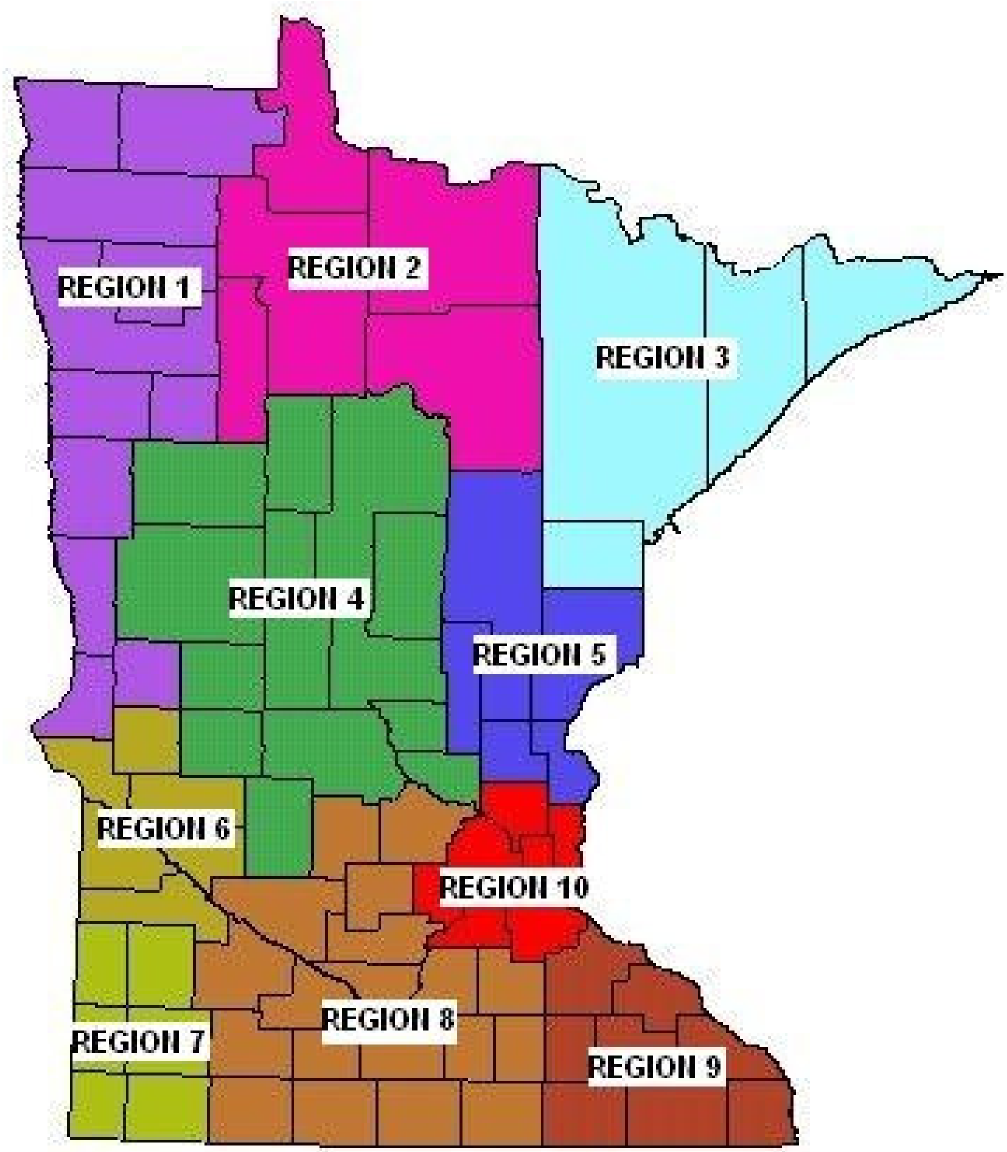

Figure 2. Pesticide Monitoring Regions (PMRs) Developed by the Minnesota Department of Agriculture.

2.1.1 Tier 1 Sampling Guidelines

1. An annual Statewide Sampling Workplan will be developed each year prior to the sampling season detailing Tier 1 site locations, cooperator information and sampling protocol;

2. Sites will be selected for pesticide and nutrient sampling from throughout the agricultural areas of the state with a preference for a mixture of both small and large watersheds representative of each PMR whenever feasible;

3. Sampling protocol will be generally consistent with the previous Statewide Survey sampling conducted by the MDA and will target storm flow periods when possible. The annual workplan will specify the Tier 1 sampling protocol;

4. Locations with existing flow or stage gaging information (continuous, preferably real-time) will be the sought out and given priority;

5. Four base neutral pesticide and nutrient samples will be collected during May, June, and July from each agricultural location. Urban locations will be sampled six times with similar 15 day sampling periods extending later into the summer. Additional sampling may occur at select Tier 1 sites for assessment of fall applied products or for winter baseflow assessments in January if feasible;

6. An effort will be made to maintain consistency in site locations for a minimum of three years. The purpose of this is to account for climatic and pesticide use variability that may not be apparent in any given year;

7. Samples will be collected by MDA staff and cooperators and submitted to the MDA or Minnesota Department of Health laboratories in St. Paul for pesticide analysis;

8. The data will be compiled in MDA's annual report and compared to appropriate reference values. Sites with individual pesticides concentrations above 50 percent of reference values will be recommended for Tier 2 sampling the following year.

9. As sites move from Tier 1 to Tier 2, replacement sites will be identified for Tier 1 monitoring and will be prioritized as resources permit.

2.2 Tier 2 - Duration Assessment Sampling

Tier 2 Sites will be selected based upon pesticide sampling within the last five years that indicates the potential for concentrations at levels of concern (i.e. above 50% of the appropriate reference values). The objective of the Tier 2 sampling will be to collect sufficient concentration data to allow for comparison with duration based aquatic life or human health reference values. The Data Analysis section below provides greater detail on the requirements necessary for comparing concentration based reference values to stream data. In general the Tier 2 sampling guidelines will be the same as the Tier 1 with the following additions:

2.2.1 Tier 2 Sampling Guidelines

1. Sampling frequency will be increased at Tier 2 locations to allow for the collection of at least one additional sample for duration assessment as indicated below. Under certain circumstances (constant flow regime) a single concentration sample may be representative of the entire duration period but under most circumstance (dynamic flow regime) at least two samples should be collected during the assessment duration period (4 or 30 day). Continuous flow/stage gaging is critical at the Tier 2 sites. When possible, sampling will continue for a minimum of 5 years at Tier 2 sites;

2. Assessment Protocol - Chronic standards or advisory values based on aquatic toxicity (animal or plant) are compared to 4-day average concentrations, whereas chronic standards based on human health are compared to 30-day average concentrations. The following protocols are recommended:
    - Four-Day Assessment Protocol- a second sample should be collected only when the first sample (any of the Tier 1 samples above) is collected during a storm event (defined here as a minimum of a five fold increase in streamflow as a result of a precipitation event) thereby allowing time-weighted averaging during the duration period. The second sample should be collected within 96 hours of the first but there should be at least 24 hours between the samples.

    - Thirty Day Assessment – In general, 30 day assessments will be necessary for Class 2A and Class 2Bd waters. Under the Tier 1 sampling guidance above, most 30 day periods will have a minimum of two samples. In addition, following the Four-Day Assessment Protocol (#2 above), if a sample is collected during a storm event at least three samples will be available for averaging. No additional sampling is recommended for 30 day assessments unless site specific conditions warrant.

3. The data from Tier 2 sites will be compiled in MDA's annual report and compared to appropriate standards or criteria. Sites with concentrations or time-weighted average concentrations (discussed in the Data Analysis and Assessment section below) of pesticides at levels above existing water quality reference values will be recommended for Tier 3 evaluation and monitoring the following year.

2.3 Tier 3 - Enhanced Duration Assessment Sampling

Tier 3 sites will include intensive equal time increment (ETI) pesticide monitoring designed to provide concentration data ideally suited for comparison with a duration based water quality reference values, such as the Four-day aquatic life standard. Automated samplers will be deployed at most Tier 3 sites to facilitate the collection of these samples. The frequency of sample collection will be dependent upon the specific characteristics of the reach or watershed being evaluated and the availability of automated monitoring equipment. Monitoring stations with access to AC power and refrigerated autosamplers will be ideally suited for the collection of single samples composited over four day periods. Under these circumstances, a typical sample will be collected over a 96 hour period with equivalent pulses of water being collected on an hourly or more frequent basis. Tier 3 sites that do not have access to AC power or refrigeration may require shorter duration composite samples or grab samples. Grab samples between composite periods will also be collected along with limited comparative samples collected on a equal flow increment (EFI) basis when available. Data from the ETI composite samples will not only be useful for comparison with duration based standards but also provide context for assessing Tier 1 and Tier 2 data. New Tier 3 stations will be established as resources permit.

2.3.1 Tier 3 Sampling Guidelines

1. Surface water monitoring at Tier 3 sites will utilize stage activated equal-time increment (ETI) composite sample collection for 48 or 96 hour durations. Autosamplers will be stage or manually activated during stormflow periods following pesticide application. Autosamplers will be allowed to run for the duration of the established period (48 or 96 hours) regardless of flow condition. Refrigerated autosamplers will target 96 hour duration periods to minimize the number of samples collected. Under certain circumstances where sampler based sampling is not practical, grab samples may be used to assess the respective time periods. Baseflow periods will be characterized by grab samples as necessary.

2. Tier 3 sites will be sampled during the anticipated peak pesticide concentration periods. Those periods may include late fall and/or early spring sampling to characterize fall applied products as well as post application May, June and July samples as well as mid winter samples to characterize true baseflow conditions. The number of samples will vary from watershed to watershed and from year to year but a general number of 16 samples will be targeted.

3. Data from Tier 3 sites will be analyzed for comparison with appropriate stream standards as specified in the Data and Analysis section below.

2.4 Tier 3 - Equal Flow Increment (EFI)

Tier 3 EFI sites will include intensive monitoring designed to completely characterize pesticide behavior and loading dynamics for the monitored watershed. In addition to the intensive data collection, frequent sampling will allow for the assessment of new pesticides and/or degradates that may not be detected in the statewide sampling due to different climatic, seasonality, travel pathway or use patterns. The intensive data collection will also provide essential information about peak pesticide detection concentration, duration and timing that may also be useful for interpreting data collected from the Tier 1, 2 and 3 monitoring efforts. Tier 4 sites may be established at locations where accurate estimates of pesticide loads are important i.e. where specific BMP implementation activities are being evaluated or where impairments have been determined and load estimates are deemed necessary.

2.4.1 Tier 3 EFI Sampling Guidelines

1. Surface water monitoring at the most intensively monitored sites will utilize equal flow increment (EFI) composite sample collection during storm flow periods if possible. However it is anticipated that new sites may not have established stage-discharge relationships and therefore EFI sampling may not be possible for the first year. In addition, technical issues may at times preclude the collection of composite samples. Under these circumstances grab samples during stormflow periods will be collected. Although storm based EFI sampling is more complicated and labor intensive, if properly conducted it generally provides better resolution of chemical concentration and presence over the course of a storm hydrograph and should provide reasonable concentration values for comparison with water quality reference values. Baseflow periods will be characterized by grab samples.

2. Tier 3 EFI sites will be sampled the minimum number of samples required to adequately characterize pesticide behavior over the monitoring period. The number of samples normally falls in the range of 25 to 40 during a typical runoff year. The stratified sampling protocol discussed above (stormflow composites, baseflow grabs) will be implemented to provide greater sampling frequency during dynamic flow periods. In a typical year most of the Tier 4 samples will be collected during the period of April, May, June and July and at least half will typically be collected during stormflow periods.

3. Data from Tier3 EFI sites will be analyzed for the computation of annual load as well as comparison to water quality reference values as described in the data analysis section below.

3.0 Lake Pesticide Monitoring

In recent years the MDA has not routinely monitored lake water quality for pesticides in Minnesota. During the years 1992 through 1995, pesticide monitoring was conducted by the MDA and USGS on Lake Harriet, an urban lake located in the City of Minneapolis. The results of that study were published in the Sixteenth Annual North American Lake Management Society Special Session Proceedings (Wotzka et.al., 1998). The study showed that several common urban turf pesticides were present in Lake Harriet as well as low levels of common agricultural pesticides. The source of the agricultural pesticides was determined to be atmospheric in nature. As part of the development of this design document, the MDA has determined that lake monitoring for pesticides is appropriate and should be integrated into the annual surface water monitoring workplan as resources permit.

In 2007 and every five years thereafter, the MDA expects to be participating in EPA's National Lakes Assessment (NLA) Program which will include sampling from 40 to 50 lakes in Minnesota. This will be a cooperative effort with the EPA, Minnesota Pollution Control Agency and the Minnesota Department of Natural Resources. The goal of the project is to look at national as well as regional lake conditions and make statements about overall lake health and condition. The lakes for the study will be statistically selected by EPA and MPCA to represent geographic areas of the country. Over 1000 lakes will be sampled during this effort nationally. EPA is laying out a detailed list of parameters and metrics that will be collected in the course of this study. However pesticide data will not be available from all lakes sampled from other states. Pesticide samples collected in Minnesota as part of the NLA will be sent to the MDA Laboratory in St. Paul for analysis.

The details of the lake sampling program including locations, timing and specific analytes will be presented in the annual surface water work plan. Based on the results of this study, the MDA may also initiate an annual lake sampling survey to be presented in the annual Surface Water Monitoring Work Plan as well.

4.0 Urban Stream Pesticide Monitoring

Previous data collected by the MDA have indicated that streams from urban watersheds have different pesticides detected as compared to the streams where row crop agriculture dominates the land use. This is a result of unique pesticide use patterns associated with the urban landscape. Because of these differences and uncertainties associated with the potential impact of these pesticides on urban streams, a sampling program is also recommended to collect pesticide samples from urban streams. These samples should be analyzed for the base neutral as well as the acid herbicide analytes. Several of the larger Twin City Metropolitan Area streams are currently monitored for conventional pollutants by the Metropolitan Council Environmental Services (MCES). Opportunities for cooperative sample collection from some of these locations will be explored and an urban stream monitoring program will be included in the annual workplan as resources permit.

Urban pesticide monitoring efforts will follow the same Tiered protocols as the agricultural PMR survey sites. Urban sampling locations may have a slightly different time period for sample collection which will extend later into the summer to better reflect urban pesticide use patterns.

5.0 Precipitation Pesticide Monitoring

The MDA has been collecting precipitation samples for pesticide analysis since 19__. Atmospheric contamination by pesticides occurs primarily from agricultural use. Pesticides can enter the atmosphere during application, through volatilization, and through wind erosion of soil particles to which pesticides are sorbed (Capel et. al. 1998). Precipitation monitoring is important because atmospheric transport of pesticides can result in surface water contamination many miles from the point of application. For surface water that is remote from agricultural or urban areas, such as much of northern Minnesota, atmospheric deposition may be the primary source of pesticides.

Continued monitoring of precipitation for pesticides is recommended to assess potential trends in concentrations and account for in atmospheric deposition as it relates to other pesticide monitoring activities conducted by the MDA. The specifics of the locations and collection protocols for the precipitation monitoring will be presented in the annual Surface Water Monitoring Work Plan.

6.0 Special Monitoring Studies

1. Drain Tile Monitoring - The Monitoring Unit is currently provides technical support at two different locations in south central Minnesota where field scale subsurface agricultural drainage systems are being monitored. Water quality responses to different nutrient and pesticide BMPs are evaluated at these locations. New pesticide products may also be evaluated for leaching rates and relative persistence. Detailed information about agricultural inputs, cropping systems and yields are collected and compared to water quality data. Because of the significant role that agricultural drainage plays in the hydrology in much of southern and western Minnesota, field and small scale watershed evaluation and monitoring is an important element of this Design Document.

2. SE Minnesota Spring Monitoring – Select springs in SE Minnesota are also monitored for pesticides as part of a MDA's ground water monitoring system. The springs are monitored in cooperation with the Minnesota Department of Natural Resources as well as other regional cooperators. Additional details on spring monitoring are presented in the Ground Water Monitoring Design Document and the annual Ground Water Monitoring Work Plans.

7.0 Surface Water Nutrient and Sediment Monitoring

Although the focus of the MDA's surface water monitoring efforts have historically been oriented towards the collection of pesticide data, nutrients including nitrate-N, orthophosphorus and total phosphorus and more recently sediment data such as total suspended solids (TSS) have also been collected along with pesticides. There are two primary reasons for the collection of these additional analytes. First, surface water quality problems associated with agricultural activities are not limited to pesticides but extend to other agricultural chemicals (fertilizers) and practices. Coupled with this is t that the additional expense associated with the collection of nutrients and TSS are minimal when placed in the context of the overall cost of implementing a pesticide monitoring program.

The second justification for the collection of nutrient and TSS data involves the corollary or interpretive value that these additional parameters provide. For instance, the relative concentration of nitrate-N in a particular sample may provide evidence as to the primary source of the water in a stream at a given point in time. Nitrate-N is a conservative constituent for which peak concentrations typically occur in water that has percolated through an agricultural soil. If peak concentrations for a particular pesticide occur in the same sample that a peak nitrate-N concentration was found, it provides additional evidence that the pesticide probably had a similar transport pathway or mechanism. In similar fashion, peak pesticide concentrations occurring when TSS was also high would suggest an overland transport mechanism. The relative concentration of these constituents along with the flow and precipitation record provide valuable insight into the fate and transport mechanisms associated with pesticide movement in an agricultural landscape and are critical to understanding and assessing the potential effectiveness of BMPs designed to limit surface water impacts.

All nutrient and sediment data collected by the MDA is given to the MPCA and our cooperators to help aid in various projects around the state.

8.0 Data Analysis and Assessment

The Monitoring Unit has developed the following approach for evaluating pesticide surface water monitoring data. The data collected from the rivers and streams as part of the tiered sampling process will be evaluated each winter and the results and associated recommendations for changes presented in the annual surface water monitoring workplan or annual program report. In addition, pesticide and flow data will be provided to the Minnesota Pollution Control Agency for analysis and assessment.

The primary objective of this section is to provide a consistent protocol for estimating river concentration data for comparison to existing water quality standards and/or criteria to assess the potential impact to the waterbody. Because most of the “chronic” water quality standards and criteria are duration based (4-day or 30-day periods) it is necessary to integrate time into the assessment process and thereby “average” concentration data over given periods. Although storm based equal-time increment sampling is more complicated and labor intensive, if properly conducted it generally provides better resolution of chemical concentration and presence over the course of a storm hydrograph and should provide excellent concentration values for comparison with standards and/or criteria. This section also provides guidance on the calculation of pollutant load and flow-weighted mean concentration utilizing grab and composite sample data.

8.1 Assessment of a Water Body for Pesticides

In most instances a minimum of two samples (grab, composite or a combination of the two) is preferred to calculate an average concentration over the exposure period being evaluated (i.e. 4- or 30-day). Automated sampling during flow events with grab samples collected between flow events to evaluate base flow is the preferred approach for sampling for pesticides in river and streams. Concentrations may then be applied or “weighted” for their respective flow periods to characterize water quality during the exposure period under consideration. Greater detail on calculating “weighted” concentrations is provided below.

Grab samples from gaged and ungaged locations such as Tier 1 or 2 sampling discussed above, may be used to characterize a river or stream for assessment purposes if appropriate supporting flow data is available (preferably continuous data). In general, grab samples should be collected with consideration for the flow condition of the river and with consideration for the relevant exposure period(s) being evaluated. If dynamic flow conditions exist during the exposure period(s) being characterized, additional sampling, above the minimum, may be warranted. Time weighted mean concentrations will also be calculated for these samples whenever appropriate.

The atrazine and alachlor chronic standards for 2A and 2Bd waters are human health-based, requiring comparison to 30-day average concentrations. Outstanding resource value waters or trout streams also have class 2 classifications (2A, 2Bd, or 2B) that would dictate what chronic standard applies and if it is compared against 30-day or 4-day time periods.

8.2 Estimating Time and Flow-Weighted Mean Concentrations

This section describes the procedures utilized for integrating and assigning appropriate time periods and associated flow volumes for surface water composite and grab samples when estimating time-weighted mean concentrations (TWMC), chemical load and flow-weighted mean concentrations (FWMC). The purpose of this section is to ensure that consistent procedures are utilized when determining the appropriate time periods, and associated volumes, to integrate with chemical concentrations for the purpose of calculating chemical load and FWMC. Because the MDA surface water samples are collected utilizing different methods (grab and composite samples) and at varying time intervals as dictated by changing flow conditions, it is recognized that professional judgment sometimes plays a part in assigning concentration duration and associated volume to collected samples.

For comparison with water quality standards and or criteria sample concentrations should be weighted for their respective time/flow period. For instance, if a grab sample and a composite sample are collected during a four day period, the grab representing base-flow concentrations before or after the stormflow period and the composite sample representing concentrations during the stormflow, the samples will be "time weighted" on an hourly basis for their respective flow period and a mean value determined.

The following procedures should be used for assigning times and/or flows to samples:

a. During all relatively static flow periods grab samples should be assigned a time (flow period) equal to half that between it and the previous sample, plus half that between it and the next sample.
b. The assigned time for grab samples that are collected immediately before or after a composite sample, should extend to the beginning or end of the hydrograph event or to the beginning or end of the composite sample collection whichever is most appropriate.
c. The assigned time for grab samples collected between two composite samples should extend from the end of the composite sample collection time to the beginning of the next composite sample collection time
d. In some instances, composite sample collection periods should be extended in order to better represent the event period, such as when a composite sample collection time ends half way down the descending leg of the hydrograph. The time assigned to that composite sample should be extended to the end of that hydrograph.
e. In rare instances where samples are not collected during a hydrograph it may be appropriate to assign concentrations from the nearest collection period, be it a base-flow grab or storm-flow composite in order to adequately characterize that flow period or to use statistical methods such as regression analysis of flow and concentration to predict concentrations. This method will be used primarily when determining annual pollutant loads and FWMC and is generally not appropriate for the determination of TWMC for comparison with standards.

The calculation of a TWMC involves weighting individual samples in relation to the time they are used to characterize the stream system (Baker and Richards, 1990). Time-weighted mean concentrations are calculated as follows:

$$\mathbf{TWMC} = \frac{(\Sigma\, C_i T_i)}{(\Sigma\, T_i)}$$

Where $\mathbf{C_i}$ is the observed concentration for the *i* th time period,
$\mathbf{T_i}$ is the time represented by each sample.

A flow weighted mean concentration is simply mass or load normalized for volume. A properly collected equal flow increment composite sample submitted to the laboratory will produce an analytical result that is a FWMC that is referred to as a sample event mean concentration (EMC). To calculate a FWMC for a period of time that is longer than that represented by individual EMC (monthly or annual for instance) it is necessary to combine concentration and flow data from multiple samples. This is achieved by first calculating the individual mass of chemical that each sample period represents (sample concentration multiplied by flow period volume), then the masses for all of the respective sample periods are summed to give total load and then divided by the total flow volume for the period of interest.

Flow-Weighted Mean Concentration Equation :

$$\mathbf{FWMC} = \frac{(\Sigma\, C_i Q_i T_i)}{(\Sigma\, Q_i T_i)}$$

Where $\mathbf{C_i}$ is the concentration for the *i* th time period,
______$\mathbf{Q_i}$ is the flow during the time period,
$\mathbf{T_i}$ is the time characterized by that concentration.

9.0 Pesticide Analyte Evaluation Protocol

This section of the Design Document provides a framework for consistent evaluation of pesticide compounds and their associated degradates that are selected for surface water monitoring conducted by the MDA Monitoring Unit. The goal is to provide a systematic approach for prioritizing which pesticide compounds and associated degradates to include in laboratory analytical suites for surface water monitoring in Minnesota. Because of the wide range of agricultural chemicals routinely used in the state it is only practical to sample and test for those chemicals which pose the greatest risk to surface water. Pesticides considered to be of greatest risk will be determined using available information on the amount of the chemical used statewide and regionally, the available human health and ecological risk information, the potential to reach water resources once applied, and laboratory capability and associated costs. These criteria are used to rank potential analytes from which a target list is developed for surface water monitoring. Each of these factors is considered and weighted accordingly. Although still under development the qualitative total calculated would be used in the selection of target analytes. This weighting and selection method has the advantage that a number of key factors can be considered simultaneously in selection of analytes.

The Six (6) major criteria are:

1. <u>Pesticide Use & Patterns of Use</u> – Pesticide analyte selection is based largely on pesticide use within Minnesota. Use information is obtained from the Minnesota Agricultural Statistics Service, and other use surveys conducted by the Minnesota Department of Agriculture, or other entities. Information regarding the registration of new pesticide active ingredients is also considered. Pesticides that are used, or anticipated to be used, on significant crop acreage (define high, medium, low usage regionally) in the State are given the highest priority. Additional pesticides granted special registration to address new or emerging pest control problems may also be considered for analyte development. Often pesticide usage is urban or regional in nature as such monitoring for specific chemicals may also occur or be focused in specific regions.

2. <u>Human Health and Ecological Risk</u> – Chemicals with established water quality standards and /or guidelines will be ranked according to their relative risk. In general chemicals with very low standards and/or guidelines will be of greater concern/priority.

3. <u>Environmental Fate and Transport Properties</u> – Environmental fate and transport properties of a pesticide determines if there is the potential for that pesticide to be transported via surface runoff to surface water, or via leaching to groundwater. Key pesticide environmental fate properties affecting runoff or leaching potential include: water solubility, acid-base dis-association constants, ionic properties, soil/sediment sorption coefficients, and environmental stability or persistence. The US-EPA has established the following values for these properties when determining which pesticides may be of concern for groundwater:

a. ▪ Mobility: Kd <= 5ml/g; Koc <= 500 ml/g; or detection at > 75 cm in the soil profile
b. ▪ Persistence: Soil half life > 21 days; degradation < 10% in 30 days
c. ▪ Water solubility: > 20 mg/L

US-EPA has no equivalent values for surface water and the MDA uses water solubility and persistence as key determinants for potential surface water analytes.

4. Analytical Method/ Capability Based – Pesticides and degradation products with validated analytical methodologies of acceptable precision and accuracy are considered for inclusion. MDA laboratory resources are limited, therefore, careful decisions are made regarding which analyte screens and detection limits are appropriate for the MDA Monitoring Unit goals and objectives. Some factors considered in association with the MDA Laboratory are:
    a. Equipment needs and availability
    b. Method development requirements
    c. Staff resources
    d. Technical limitations (holding times, sample preservation, detection limits)

5. Previous Pesticide Detections – The decision on the inclusion of specific pesticide analytes may also be based on detections in water samples collected by other programs or laboratories within the state or elsewhere. Or that the MDA laboratory has alerted the Monitoring Unit about based upon the GCMS screening.

6. Costs – The analysis of water samples for pesticides is a major contributor to the costs of monitoring pesticide impacts to water resources. One way to maximize the information obtained while minimizing analytical costs is to use multi-chemical analytical methods which provide analyses for a large number of pesticides through one pass or analytical screen. Pesticides that require a unique single analytical method such as Glyphosate may have an analytical or sample collection cost that outweighs the benefit of analysis. In such instances, the analyte may not be included in the final suite unless other characteristics such as Environmental Fate and/or Environmental Risk warrant inclusion.

9.1 Annual Evaluation of Existing and New Chemicals of Concern

Each winter the MDA monitoring program will review available pesticide use information to determine the changes in use patterns and amounts for currently registered compounds. The program further checks on new or changing registrations that may have water quality concerns. In addition, work from other federal, state or local agencies, and the University of Minnesota or other research organizations is reviewed. The comments of the Pesticide Management Plan Committee (PMPC, see the PMP for details) and any comments arising from public comment related to PMPC deliberations on the MDA's annual monitoring report may also be considered. Any new information regarding environmental fate characteristics of presently registered products is also reviewed. This new use data along with existing monitoring data will be reviewed to determine what if any modifications are necessary. When reviews dictate a need, the analytical suite or suites will be changed accordingly. If the MDA Laboratory Services cannot provide analytical capability, outside laboratories will be evaluated.

10.0 References

Battaglin, W.A., Thurman, E. M., Kalkhoff, S .J., and Porter, S. D., 2003. Herbicides and transformation products in surface waters of the Midwestern United States. Journal of the American Water Resources Association, vol. 39, no. 4, p. 743-756.

Birr, A. S. and Mulla, D. J., 2002. Relationship between lake and ground water quality patterns and Minnesota agroecoregions. Hydrological Sci. Tech. 18(1-4):31-41.

Capel, P. D., Lin, M., and Wotzka, P. J., 1998. Wet atmospheric deposition of pesticides in Minnesota, 1989-94. U.S. Geological Survey Water Resources Investigation Report 97-4026.

Larson, S. J., Capel, P. D. and Majewski, M. S., 1997. Pesticides in Surface Waters. Ann Arbor Press. 373 pp.

Mulla D. J. and S. Folle, 2005. Target Agroecoregions for Pesticide BMP Promotion, Evaluation and Future Monitoring. Final Report for MDA Contract Number A61809:

Minnesota Department of Agriculture/Minnesota Pollution Control Agency Cooperative Agreement For Surface Water Quality Monitoring in Minnesota. July 5, 2004

Minnesota Department of Agriculture., 2005. 2003 pesticide usage on four major Minnesota crops. Minnesota Department of Agriculture and Minnesota Agricultural Statistics Service, St. Paul, MN.

Minnesota Department of Agriculture, 2007. Ground Water Monitoring Design Document.

Minnesota Department of Agriculture, 2005a. Pesticide Management Plan.

Minnesota Department of Agriculture, 2003. Ground Water Monitoring Program Design Document.

Minnesota Department of Agriculture, 1996. Common Detection Advisory Committee Report.

Wotzka P. J., Capel, P. D., Ma, L., and Lee, J. T, 1998. Pesticide transport and cycling in the Lake Harriet Watershed, Minneapolis, Minnesota. Sixteenth Annual North American Lake Management Society International Symposium. Minneapolis Lakes and Parks – Special Proceeding.