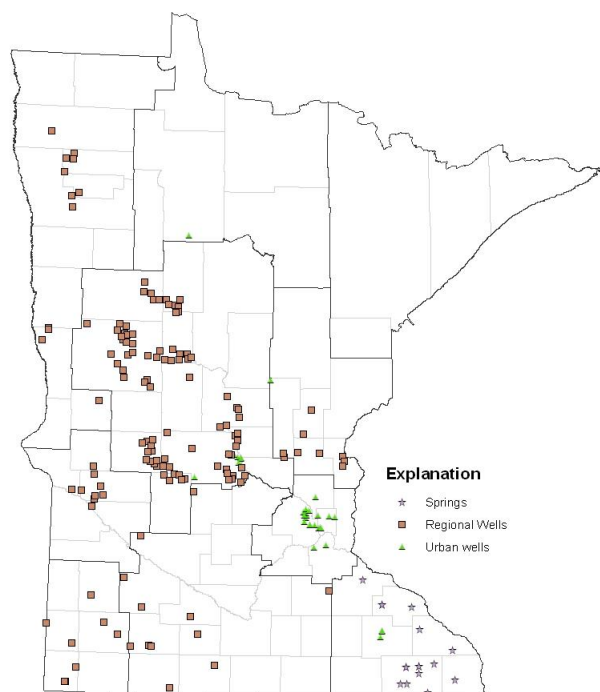


GROUNDWATER MONITORING NETWORK DESIGN (Revised)



July 2011

*MINNESOTA DEPARTMENT
OF AGRICULTURE*

*MONITORING & ASSESSMENT UNIT
ENVIRONMENTAL SECTION
PESTICIDE & FERTILIZER MANAGEMENT DIVISION*

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SECTION 1 - INTRODUCTION

Agriculture remains an important industry within Minnesota and a major factor in the economy of the State. In Minnesota, farming is an intense undertaking with a relatively short growing season. As a result, the State's farming practices are dynamic, responding quickly to changes in market factors, climate, pest variability, and other production constraints. Within the context of these conditions, farmers make decisions as to the level and intensity of various management practices, including decisions regarding the use of agricultural chemicals.

Minnesota Department of Agriculture's (MDA's) Monitoring and Assessment Unit (MAU) seeks to provide information on impacts to the State's groundwater from the routine application of agricultural chemicals. This document describes the design of the MDA groundwater monitoring program, while a companion document addresses similar efforts in surface water monitoring. Information collected by the MAU is made available to the public so appropriate management decisions may be made to minimize, reduce or eliminate water quality impacts from agricultural chemicals.

Because of the large and complex nature of modern agriculture and the vastness of Minnesota's groundwater resources, it is not practical for the MDA (or any other entity) to achieve a comprehensive evaluation of all the groundwater resources in the State. It is also highly unlikely that the routine use of pesticides would significantly impact all of Minnesota's groundwater systems. However, there are areas in the State where shallow groundwater may be highly sensitive to the application of pesticides at the ground surface. This document provides a conceptual design for monitoring groundwater throughout the State. Aspects of monitoring for any specific area of the State will vary depending upon agricultural activity and chemical usage, environmental sensitivity, and historic water quality data. Accordingly, some areas will receive very detailed assessments while other locations are served adequately with a more limited evaluation. Although designed as a pesticide monitoring program, the MDA collects and analyzes nitrate-nitrogen samples to add to 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 seeks 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 overall goal of the MDA groundwater monitoring program is to determine the impacts of pesticides on vulnerable groundwater within each of the MDA pesticide monitoring regions (as discussed later on, in Section 3) where agriculture is a primary land use.

MDA Information Expectations. Management needs with respect to groundwater monitoring are based on information expectations articulated in the following three categories and guide the design of the program:

1. Water quality concerns
2. Information goals
3. Monitoring objectives

1. Water Quality Concerns. MDA water quality concerns are simply stated as the impact of pesticides on groundwater. A pesticide impact means the occurrence of any pesticide in groundwater regardless of concentration. Any pesticide is a possible target for analysis. Acetochlor, alachlor, atrazine, metolachlor, and metribuzin are of particular concern due to detections in previous years. Changes in concentration of pesticides over time are also of concern.

2. Information Goals. Monitoring groundwater in sensitive areas of each region of the State provides the MDA with the ability to interpret the collected data on a regional and State-wide basis. In so doing, the evaluation of the effectiveness of pesticide management practices, as either impacting or protecting the groundwater in individual regions of the State, is made possible.

3. Monitoring Objectives. Based on the above water quality concerns and information goals, project objectives are straight forward, although difficult, time consuming and expensive to meet. The MDA monitoring program provides data and information on the following items:

- total number of wells sampled
- total number of wells with detectable levels of pesticides
- total number of samples collected
- total number of samples with detectable pesticide residues
- concentration of pesticides detected
- changes in pesticide concentration over time
- differences in concentration from one region of the State to another
- changes over time in number of wells containing measurable levels of pesticides
- range in pesticide concentration detected
- detected concentrations in relation to available reference values

Consequently, the overall objectives of this monitoring program are: to collect samples from vulnerable groundwater in different regions of the State; to analyze those samples for pesticide concentrations; to statistically analyze these laboratory sample analysis results in order to extract the maximum amount of information; to disseminate the information gathered to interested parties; and to provide the information required to managers for evaluation of the impact on the State's groundwater from the use of agricultural chemicals. Assessment of the effectiveness of MDA's pesticide management plan and best management practices (BMP's) are also facilitated with this data.

1.2 - Historical Perspective

In 1985 the MDA and Minnesota Department of Health (MDH) undertook a cooperative survey of groundwater for pesticides and nitrate-nitrogen in areas of agricultural land use in the State that were considered susceptible to contamination, such as outwash sands and karst bedrock areas (Klaseus, et.al., 1989). This survey found that pesticides commonly applied to fields in agricultural production through normal use were appearing in groundwater at detectable concentrations. The most frequently detected pesticides were atrazine and alachlor, which are both herbicides. A second survey by the MDH in 1986, targeted primarily toward private drinking water wells in rural areas, produced similar results (Klaseus and Hines, 1990).

In 1987 Minnesota enacted the Minnesota Pesticide Control Law (Chapter 18B of Minnesota State Statutes), which included a requirement for the evaluation of pesticide impacts on the environment and, through subsequent legislation, development of a State pesticide management plan (see insets). In response to this charge, the MDA initiated a groundwater monitoring program in 1987 and a surface water monitoring program in 1990.

Minnesota Statutes 18B.04 PESTICIDE IMPACT ON THE ENVIRONMENT.

“The commissioner shall:

- (1) determine the impact of pesticides on the environment, including the impacts on surface water and groundwater in the 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.”

18B.045 Pesticide management plan.

Subdivision 1. **Development.** The commissioner shall develop a pesticide management plan for the prevention, evaluation, and mitigation of occurrences of pesticides or pesticide breakdown products in groundwater and surface waters of the State. The pesticide management plan must include components promoting prevention, developing appropriate responses to the detection of pesticides or pesticide breakdown products in groundwater and surface waters, and providing responses to reduce or eliminate continued pesticide movement to groundwater and surface water. By September 1 of each even-numbered year, the commissioner must submit a status report on the plan to the environmental quality board for review and then to the house of representatives and senate committees with jurisdiction over the environment, natural resources, and agriculture.

In 1989 the Minnesota Comprehensive Groundwater Protection Act (Minnesota Statutes 103H) expanded groundwater protection responsibilities of the MDA, including specific direction regarding detection and trend monitoring following detection of agricultural chemicals (see inset). The Groundwater Protection Act mandated the development of BMPs for chemicals commonly found in groundwater. Monitoring of the State’s groundwater was to serve as the primary support for management decisions made as part of the Pesticide Management Plan.

103H.251 Evaluation of detection of pollutants.

Subdivision 1. **Methods.** (a) The commissioner of agriculture for pollution resulting from agricultural chemicals and practices and the pollution control agency for other pollutants shall evaluate the detection of pollutants in groundwater of the State. Evaluation of the detection may include collection technique, sample handling technique, laboratory practices, other quality control practices, climatological conditions, and potential pollutant sources.

(b) If conditions indicate a likelihood of the detection of the pollutant or pollutant breakdown product to be a common detection, the commissioner of agriculture or the pollution control agency must begin development of best management practices and continue to monitor for the pollutant or pollutant breakdown products.

Subdivision 2. **Analysis of pollution trend.** The commissioner of agriculture for pollution resulting from agricultural chemicals and practices and the pollution control agency for other pollutants shall develop and implement groundwater monitoring and hydrogeologic evaluation following pollution detection to evaluate pollution frequency and concentration trend. Assessment of the site-specific and pollutant-specific conditions and the likelihood of common detection must include applicable monitoring, pollutant use information, physical and chemical properties of the pollutant, hydrogeologic information, and review of information and data from other local, state, or federal monitoring databases.

In 1990 the MDA expanded the scope and scale of the groundwater monitoring program, leading to the eventual sampling of more than 400 shallow monitoring wells. By 1996 the MDA had collected more than 10 years of groundwater monitoring data from various locations in the State. At this point the MDA completed a formal evaluation of the monitoring system currently in place and determined the network had provided all the information it was capable of providing. It was further concluded that many of the network wells were becoming old and were already, or would soon be, past their useful life span. The decision, therefore, was made to design a new State-wide network capable of detecting pesticide presence and changes over time in groundwater. The network was envisioned as the broadest element in determining the effectiveness of BMPs implemented as part of pesticide management plans. Since water quality monitoring is expensive, time consuming, and difficult to undertake, the MDA needed to phase in the plan over several years. In 1998, in response to previous groundwater contamination, the MDA began a cooperative effort with twelve individual counties in the Central Sand Plains of the State. Wells at eighty-six sites, containing multiple wells at different depths, were installed (see Figure 1). The monitoring well network in the Central Sands was completed, and sampling commenced, by early 2000. Specific design considerations for this network are described in a subsequent section.

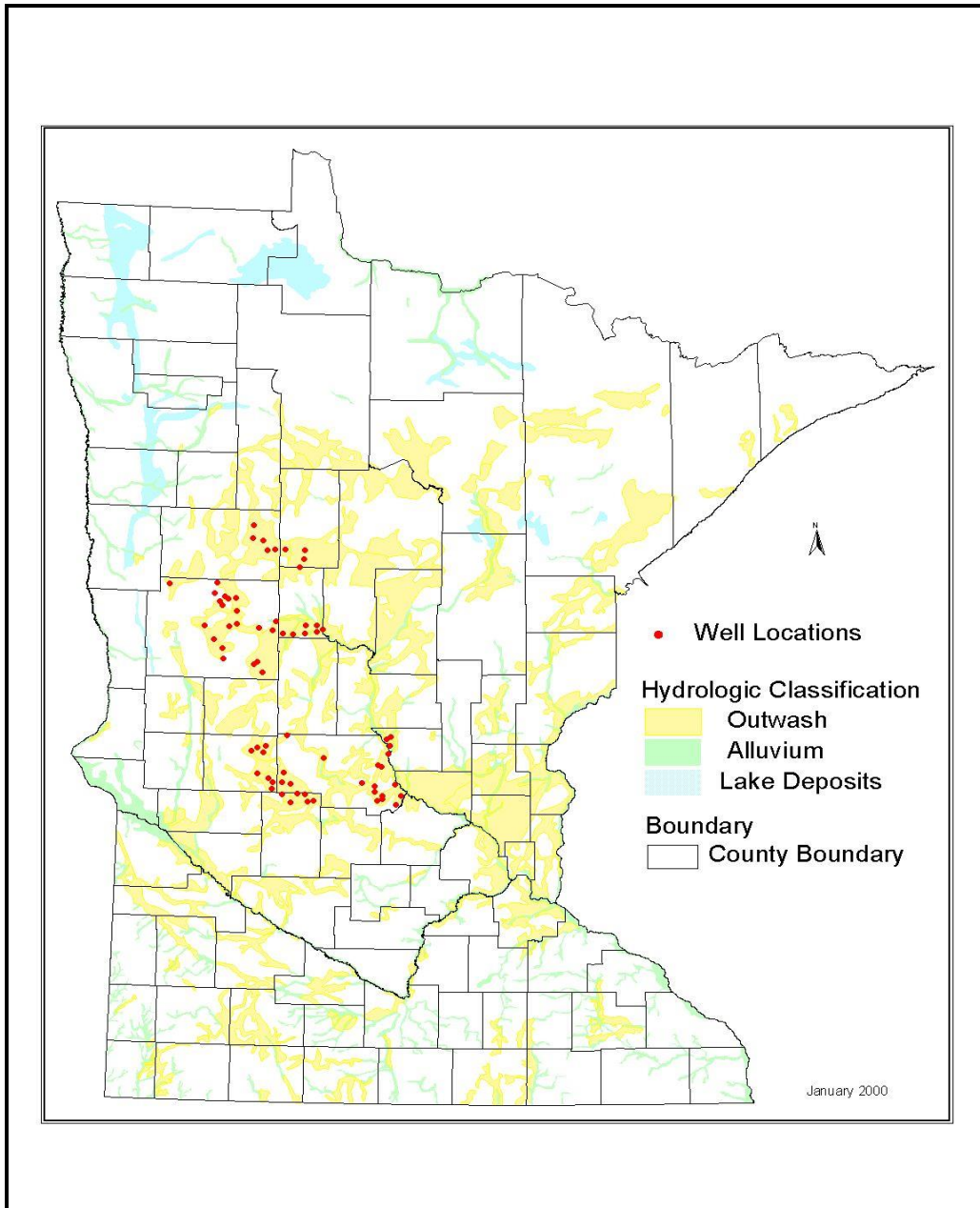


Figure 1 - Locations of MDA Central Sands monitoring wells installed in 2000.

As part of the groundwater monitoring program reevaluation, a reconnaissance sampling was conducted in southeastern Minnesota streams during low flow periods in mid-winter 1997. Nearly 100 sample points were carefully chosen to include likely locations where groundwater was emerging into the bed of the streams via springs. This reconnaissance was attempted in order to determine the likelihood of the ability to successfully continue such an effort. Access to the streams proved to be exceptionally difficult and reaching the sampling locations placed personnel in extremely hazardous situations that could result in injury or death. MDA

abandoned this plan and searched for other means to collect representative groundwater samples from southeast Minnesota.

In 1993, as part of the surface water monitoring program, two springs located at a Minnesota Department of Natural Resources (MDNR) fish hatchery in southeastern Minnesota were sampled. The number of springs being monitored was expanded by four at two other MDNR fish hatcheries in the region in 2003. These springs are now considered part of the groundwater monitoring program.

Expansion of the groundwater monitoring program also included installation of monitoring wells in the more sensitive aquifers of western Minnesota, coupled with the sampling of pre-existing wells in those areas. The final piece in the MDA's vision for a complete State-wide network in areas of row crop agriculture included the sampling of existing, and newly installed, monitoring wells located in sand and gravel deposits within the till plains of south central Minnesota and in the outwash sands north of the Twin Cities.

In response to a need for up to date information on pesticide impacts to drinking water, the MDA designed and implemented a survey of public non-community and private drinking water wells in early 2004. With the assistance of the MDH and the Minnesota Pollution Control Agency (MPCA), the MDA selected drinking water wells throughout the agricultural regions of the State. A randomly generated grid was structured to locate 100 points across the State's primary agricultural regions. Wells nearest to the grid line intersections were located and sampled during January, February and March of 2004. Seventy-one of the 100 available locations were able to be sampled. Figure 2 shows the locations that were able to be sampled and each site's pesticide detection status. Table 1 summarizes the results of the survey. Three wells contained a pesticide parent compound and 14 contained pesticide degradates. In total, 14 wells were found to have a positive detection for a parent or a degradate.

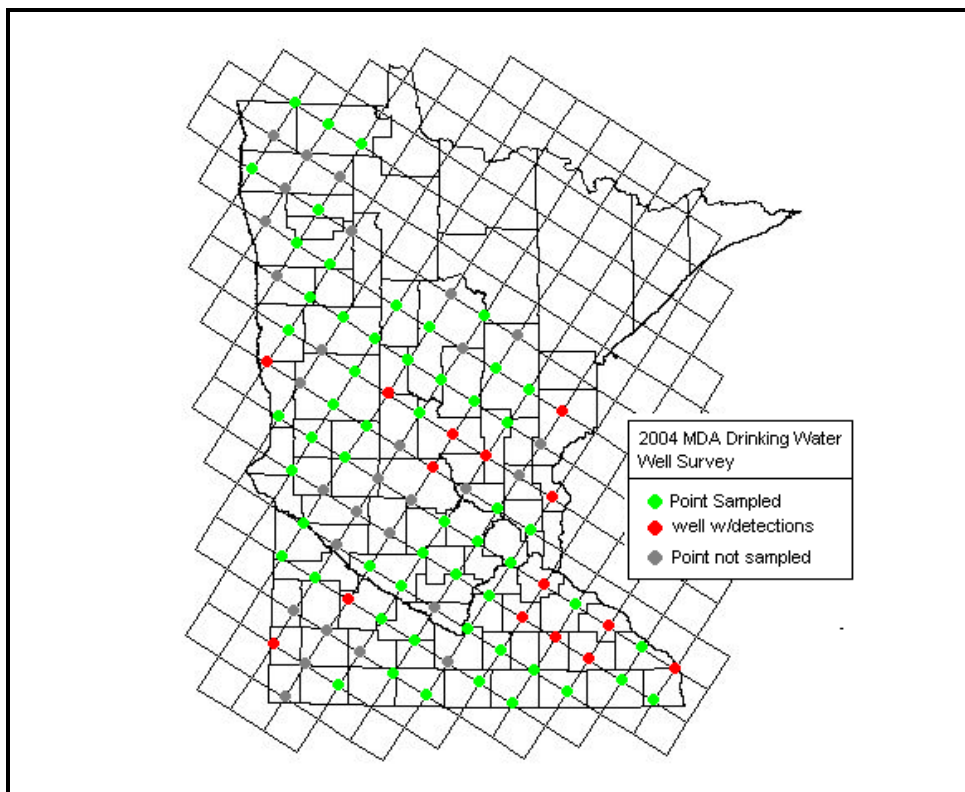


Figure 2 - MDA 2004 drinking water well survey grid points, with pesticide detection status.

Table 1 - Results of 2004 drinking water survey for pesticide presence.

Analyte Detected	Number of Wells Positive	Percent Positive (%)	Median of Detections (µg/L)	Maximum Detected Concentration (µg/L)
acetochlor ESA	5	7.0	0.34	3.68
acetochlor OXA	1	1.4	0.12	0.12
alachlor ESA	11	15.5	0.60	3.46
alachlor OXA	1	1.4	0.35	0.35
Atrazine	4	5.6	0.08	1.52
deisopropylatrazine	2	2.8	0.17	0.35
desethylatrazine	10	14.1	0.09	0.65
Metolachlor	3	4.2	P*	P*
metolachlor ESA	9	12.6	1.71	6.74
metolachlor OXA	5	7.0	0.22	0.45

* P means the compound was detected, but at levels below that required for quantification.

SECTION 2 - ANALYTE SELECTION

Water samples from groundwater monitoring wells are collected and analyzed for commonly used agricultural chemicals. Many pesticides are highly unlikely to leach to groundwater, and the analysis of water samples for pesticides is extremely expensive. As a result, the MDA carefully selects which pesticides to include in water sample analysis. To be included, the pesticide must be used in the State, it must have environmental fate characteristics that could result in groundwater impacts (see Table 2), and it must have a laboratory analytical method that is possible to undertake considering physical, chemical or financial constraints (MDA, 2006).

The list of agricultural chemicals for which water samples will be analyzed is dynamic and will change as the program progresses due to pesticide use changes or alterations in laboratory methods. For example, in 2008 the MDA was awarded a Legislative-Citizen Commission on Minnesota Resources (LCCMR) grant for the purposes of developing additional analytical capabilities. Previous laboratory analyses consisted of one base-neutral pesticide analysis, one analytical procedure for chloroacetanilide degradates, and one for detecting chlorophenoxy acid herbicides. In an attempt to increase laboratory efficiency and capacity, the MDA utilized the LCCMR grant to develop a liquid chromatography-tandem mass spectrometry (LC-MS/MS) analytical method capable of analyzing for a much broader suite of chemicals and at potentially lower concentrations. Basic development of the method was completed in January 2010. The two methods now used by the MDA monitoring program are termed GC and LC for gas chromatography and liquid chromatography, respectively. The current list of chemical analytes for 2011 is located in Table 3.

Table 2. Physical and chemical criteria for selection of a pesticide for inclusion in the MDA groundwater monitoring analytical suite.

Parameter	Criteria for Selection
Solubility in water	> 3 ppm
Soil octanol/water partition coefficient	< 1900 cm ³ /gm
Hydrolysis half-life	> 14 days
Anaerobic half-life	> 9 days
Aerobic half-life	> 9 days

Table 3 - List of pesticide analytes, inorganic analytes, and method reporting limits for groundwater monitoring during 2011.

GCMS Method			Reporting Limit			EAW LCMSMS (-)			Reporting Limit			EAW LCMSMS (+)			Reporting Limit		
Acetochlor	0.05	ppb	2,4,5-T	50	ppt	Acetamiprid	15	ppt	Alachlor	0.05	ppb	2,4,5-TP	50	ppt	Aldicarb sulfone	15	ppt
Atrazine	0.05	ppb	2,4-D	8.3	ppt	Aldicarb sulfoxide	50	ppt	Boscalid	0.3	ppb	2,4-DB	13.3	ppt	Azoxystrobin	10	ppt
Chlorothalonil	0.12	ppb	Acetochlor ESA	30	ppt	Bensulfuron Methyl	16.7	ppt	Chlorpyrifos	0.04	ppb	Acetochlor OXA	33.3	ppt	Bromacil	20	ppt
Clomazone	0.1	ppb	Alachlor ESA	41.6	ppt	Carbaryl	25	ppt	Cyanazine	0.2	ppb	Alachlor OXA	33.3	ppt	Carbofuran	13.3	ppt
Cyfluthrin	0.5	ppb	Bentazon	0.8	ppt	Chlorimuron Ethyl	20	ppt	Deisopropylatrazine	0.2	ppb	Clopyralid	41.6	ppt	DEDI Atrazine	50	ppt
Desethylatrazine	0.05	ppb	Dicamba	50	ppt	Disulfoton Sulfone	20	ppt	Desethylatrazine	0.05	ppb	Dicamba	50	ppt	Diuron	13.3	ppt
Diazinon	0.12	ppb	Dichlorprop	50	ppt	Halosulfuron Methyl	30	ppt	Diazinon	0.12	ppb	Dichlorprop	50	ppt	Hexazinone	10	ppt
Dimethenamid	0.05	ppb	Dimethenamid ESA	6.7	ppt	Imazamethabenz Acid	10	ppt	Dimethenamid	0.05	ppb	Dimethenamid ESA	6.7	ppt	Imazamethabenz Methyl	5	ppt
Dimethoate	0.22	ppb	Dimethenamid OXA	10	ppt	Imazamox	13.3	ppt	Dimethoate	0.22	ppb	Dimethenamid OXA	10	ppt	Imazapic	10	ppt
Disulfoton	0.15	ppb	Flufenacet OXA	8.3	ppt	Imazapyr	8.3	ppt	Disulfoton	0.15	ppb	Flufenacet OXA	8.3	ppt	Imazapyr	8.3	ppt
EPTC	0.23	ppb	Isoxaflutole Deg	50	ppt	Imazaquin	16.7	ppt	EPTC	0.23	ppb	Isoxaflutole Deg	50	ppt	Imazethapyr	6.7	ppt
Esfenvalerate	0.2	ppb	MCPA	5	ppt	Imidacloprid	20	ppt	Esfenvalerate	0.2	ppb	MCPA	5	ppt	Isoxaflutole	25	ppt
Ethafuralin	0.15	ppb	MCPB	10	ppt	Linuron	20	ppt	Ethafuralin	0.15	ppb	MCPB	10	ppt	Metalaxyl	8.3	ppt
Fonofos	0.1	ppb	MCPP	50	ppt	Metsulfuron methyl	23.3	ppt	Fonofos	0.1	ppb	MCPP	50	ppt	Neburon	10	ppt
Lambda Cyhalothrin	0.2	ppb	Mesotrione	50	ppt	Nicosulfuron	26.6	ppt	Lambda Cyhalothrin	0.2	ppb	Mesotrione	50	ppt	Norflurazon	20	ppt
Malathion	0.09	ppb	Metolachlor ESA	10	ppt	Prometryn	3.3	ppt	Malathion	0.09	ppb	Metolachlor ESA	10	ppt	Propoxur	10	ppt
Metolachlor	0.07	ppb	Metolachlor OXA	10	ppt	Saflufenacil	15	ppt	Metolachlor	0.07	ppb	Metolachlor OXA	10	ppt	Siduron	6.7	ppt
Metribuzin	0.1	ppb	Picloram	41.6	ppt	Sulfometuron methyl	8.3	ppt	Metribuzin	0.1	ppb	Picloram	41.6	ppt	Thiamethoxam	25	ppt
Metribuzin DA	1	ppb	Propachlor ESA	30	ppt	Thifensulfuron Methyl	16.7	ppt	Metribuzin DA	1	ppb	Propachlor ESA	30	ppt	Thiobencarb	8.3	ppt
Metribuzin DADK	1	ppb	Propachlor OXA	10	ppt	Triasulfuron	23.3	ppt	Metribuzin DADK	1	ppb	Propachlor OXA	10	ppt			
Metribuzin DK	1	ppb	Tembotrione	50	ppt				Metribuzin DK	1	ppb	Tembotrione	50	ppt			
Myclobutanil	0.2	ppb	Triclopyr	50	ppt				Myclobutanil	0.2	ppb	Triclopyr	50	ppt			
Oxadiazon	0.05	ppb							Oxadiazon	0.05	ppb						
Parathion, Methyl	0.12	ppb							Parathion, Methyl	0.12	ppb						
Pendimethalin	0.08	ppb							Pendimethalin	0.08	ppb						
Phorate	0.12	ppb							Phorate	0.12	ppb						
Prometon	0.1	ppb							Prometon	0.1	ppb						
Propachlor	0.1	ppb							Propachlor	0.1	ppb						
Propazine	0.1	ppb							Propazine	0.1	ppb						
Propiconazole	0.2	ppb							Propiconazole	0.2	ppb						
Pyraclostrobin	0.23	ppb							Pyraclostrobin	0.23	ppb						
Simazine	0.1	ppb							Simazine	0.1	ppb						
Tebuconazole	0.2	ppb							Tebuconazole	0.2	ppb						
Tebuprimiphos	0.1	ppb							Tebuprimiphos	0.1	ppb						
Terbufos	0.19	ppb							Terbufos	0.19	ppb						
Tetraconazole	0.15	ppb							Tetraconazole	0.15	ppb						
Triallate	0.1	ppb							Triallate	0.1	ppb						
Trifluralin	0.17	ppb							Trifluralin	0.17	ppb						
Zeta Cypermethrin	0.5	ppb							Zeta Cypermethrin	0.5	ppb						

Inorganic analyte

Analyte Name	Type	MRL (mg/L)
Nitrate-nitrite nitrogen	Nutrient	0.50

SECTION 3 - MONITORING DESIGNS

Geographic Considerations. In 2004, to facilitate water quality monitoring, pesticide management and BMP promotion, the MDA, with assistance of the University of Minnesota, divided the State into the 10 pesticide monitoring regions (PMRs), as shown in Figure 3.

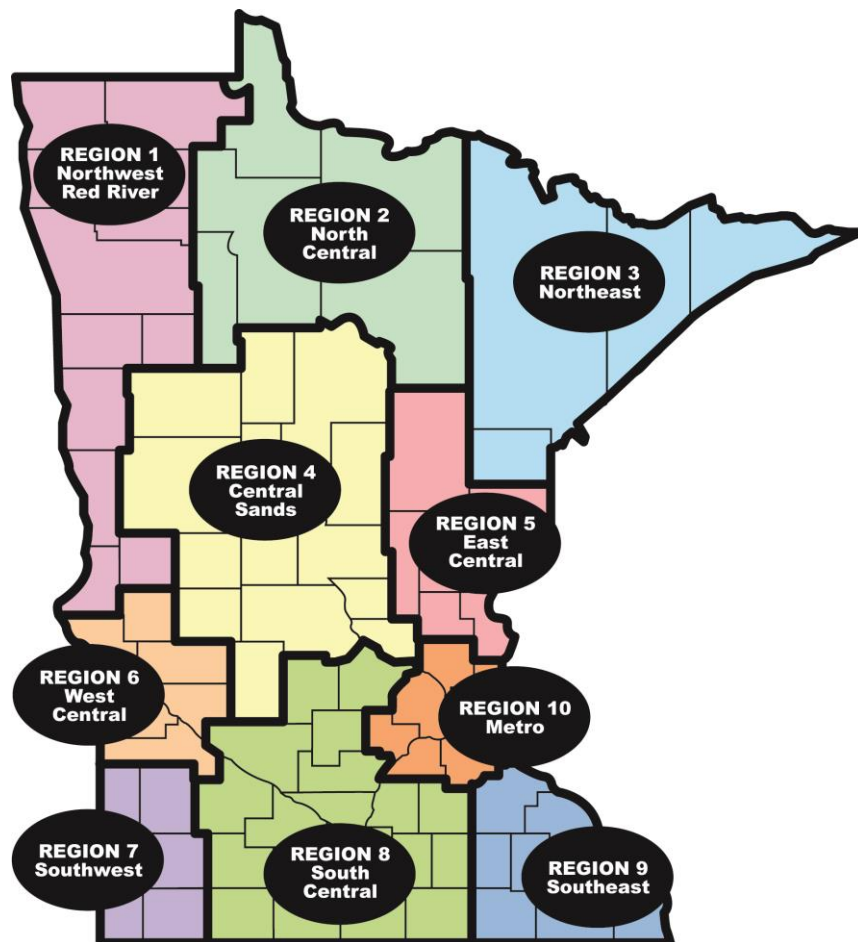


Figure 3 - Map of MDA pesticide monitoring regions (PMRs).

These PMRs are based on areas with similar cropping practices, soil, hydrogeologic conditions, rainfall, and agro-ecosystem characteristics.

PMR boundaries are based on county lines in order to facilitate implementation and reporting of results. Characteristics of the various PMRs can be found in Table 4. Specific monitoring designs for each region are based on their individual characteristics. Water quality monitoring data is collected and analyzed to facilitate evaluation of conditions within each region and between the regions.

It is unlikely that PMRs 2 and 3 will ever be included in the monitoring program due to very small amounts of agricultural production in these heavily forested areas. Five PMRs (1, 5, 6, 7, and 8) are included in a common design described below. Three other PMRs (4, 9, and 10) have unique monitoring designs based on their distinctive land use, hydrogeologic, or other important characteristics.

Table 4 - MDA pesticide monitoring region (PMR) descriptions and characteristics.

PMR	Counties Included	Physical Characteristics
1 Northwest Red River	Kittson, Roseau, Marshall, Pennington, Red Lake, Polk, Norman, Mahnomen, Clay, Wilkin, Traverse, Grant	Glacial lake bed w/ high clay content soils 150 to 250 ft thick; gravel aquifers buried under clay; beach ridge deposits of sand and gravel; high value agriculture of sugar beets and small grains
2 North Central	Lake of the Woods, Koochiching, Beltrami, Clearwater, Itasca	Mostly forested and bog; little agriculture in discontinuous areas; groundwater resources quite variable
3 Northeast	St. Louis, Lake, Cook, Carlton	Forested with shallow bedrock; agriculture nearly non-existent
4 Central Sands	Becker, Hubbard, Cass, Crow Wing, Morrison, Wadena, Otter Tail, Todd, Douglas, Pope, Stearns, Benton, Sherburne, Kandiyohi	Large glacial outwash sand plains that are highly sensitive to surface activities; high value potatoes and other crops; irrigated fields are common
5 East Central	Aitkin, Pine, Mille Lacs, Kanabec, Chisago, Isanti	Glacial outwash and lacustrine sands; low pH soils; generally poor cropping conditions; some irrigation; some potato production
6 West Central	Stevens, Big Stone, Swift, Chippewa, Lac Qui Parle, Yellow Medicine	Some areas of glacial outwash sand; thin and narrow alluvial aquifers; many buried sand aquifers; mix of corn and soybeans; thick glacial tills in some areas
7 Southwest	Lincoln, Lyon, Pipestone, Murray, Rock, Nobles	Aquifers consist of highly sensitive alluvial river valley deposits; fractured quartzite formations and well protected deep cretaceous sediments; sufficient water supply is hard to come by; rural water systems are large and growing
8 South Central	Wright, Meeker, Renville, McLeod, Sibley, Nicollet, Le Sueur, Rice, Steele, Waseca, Blue Earth, Brown, Redwood, Cottonwood, Watonwan, Jackson, Martin, Faribault, Freeborn	A mix of glacial outwash sands; deep glacial tills, glacial lacustrine deposits; wind blown silts, river valley deposits; and deep bedrock aquifers; sensitivity varies accordingly; corn and soybeans; intensive ag production; most productive land in the state
9 Southeast Karst	Goodhue, Wabasha, Winona, Olmsted, Dodge, Mower, Fillmore, Houston	Karst geology that is highly sensitive to surface activities; shallow wind blown silt and glacial till soils; springs, sinkholes and disappearing streams; high value trout streams; extremely shallow to very deep bedrock aquifers; some river valley alluvial deposits
10 Metro	Anoka, Ramsey, Washington, Dakota, Scott, Carver, Hennepin	Urban, suburban and transitional areas; some irrigated farming; hobby farms; much farming conducted on leased land by relatively large farm operations; outwash sand and gravel to deep bedrock aquifers

General Considerations. The groundwater monitoring program is designed to satisfy the following three primary goals:

- Evaluate the impacts of pesticides to the most vulnerable groundwater within the MDA PMRs that contain significant amounts of agricultural land.
- Determine the frequency of detections, the concentration of detections, and changes in detections and concentration over space and time.
- Evaluate the need for pesticide best management practices and other pesticide management plan activities in the various regions of the State.

Rather than a-priori inclusion of all program objectives during the design phase, several are satisfied via post-priori analysis of pesticide sample results and associated data and information.

Well and Site Selection. As a priority, the MDA is interested in monitoring the groundwater that is most sensitive to surface activities, is therefore relatively shallow, and lies within agricultural production areas. Quaternary water table aquifer (QWTA) wells that are part of the MDNR observation well network were initially utilized. Although expensive, the installation of new wells for the program was also accomplished.

Several design options were considered for conducting the monitoring program's site selection process. Cluster sampling was considered and was deemed inappropriate due to the likelihood of poor geographic coverage. Geospatial random sampling was evaluated and determined to have the poorest cost/benefit ratio for all regions except PMR 4. Simple random sampling from a list of wells for each region was considered and determined to be insufficient due to small numbers of appropriate wells available and the ensuing likelihood of poor geographic coverage. Grid-based and judgmental sampling methods, with well locations based on established well and site selection criteria, were ultimately selected as the best approach, depending on characteristics of the specific monitoring region. In this scenario, the selected or installed well serves as the access point to groundwater for evaluating each region's sensitive groundwater conditions. The resulting data are, therefore, utilized as a first step reconnaissance in evaluation of potential impacts from pesticides on the State's groundwater (see Figure 4 for MDA's sampling site locations).

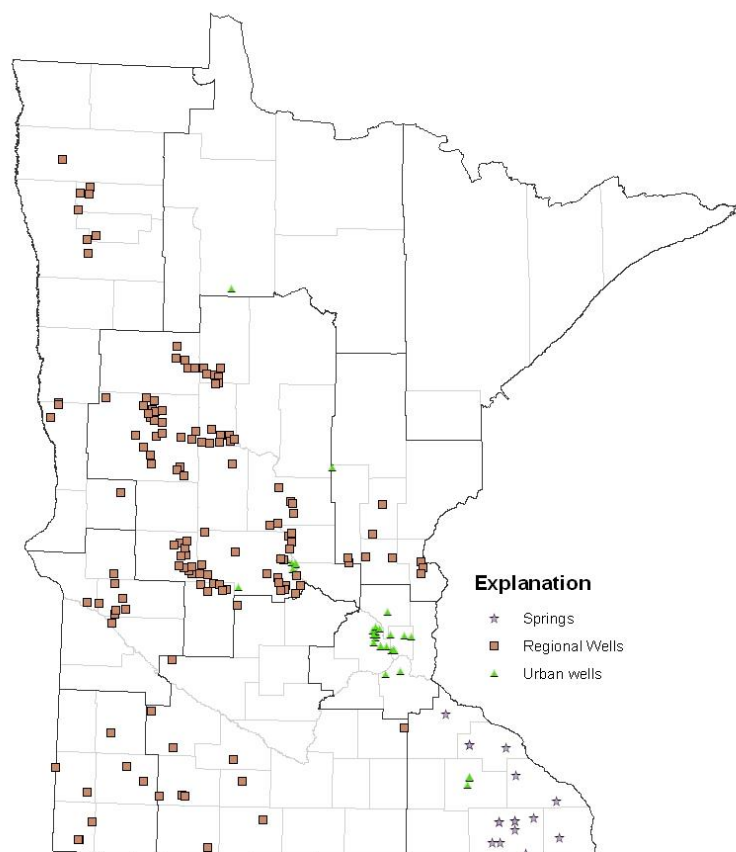


Figure 4 - Map of PMRs and approximate sampling locations.

Sampling Frequency. Based on various resource limitations and logistical considerations, networks for PMRs 1, 5, 6, 7 and 8 are generally limited to seven to ten wells per PMR. One sample is collected from each well in these regions during April, and again in October, of every year. Four total samples during the months of May, June and September, are collected from springs in PMR 9; MDNR springs are sampled quarterly. Residential wells in PMR 9 are sampled once in the fall. PMR 4 samples are collected from a randomly selected group of wells for sampling in the spring and fall, while making sure each of the sites get sampled at least once during the year. Sites with deep wells in PMR 4 are sampled in the spring and fall, with samples collected from the shallow and deep well at each site. Urban well samples are collected once a year during the summer. The number of samples the program is capable of collecting is evaluated on an annual basis and adjustments are made as needed. All details concerning sample numbers are in annual work plans, which are made available on the monitoring program's web page every year.

3.1 - PMRs 1, 5, 6, 7, and 8

Characteristics of These Individual PMRs

Although similar in many respects, each of these currently monitored regions has characteristics that require consideration during well site selection and installation. Characteristics of each PMR that significantly influence the distribution of wells and sites, or the installation of new wells, are detailed as follows.

PMR 1

PMR 1 is dominated by features developed as a result of the presence of glacial Lake Agassiz. Along the periphery of this ancient lake, wave action deposited beach ridges consisting of sand and gravel. As the lake receded in steps, each beach ridge was interspersed with finer sediments resulting in the development of wetland areas sitting atop clay rich sediment between successions of several discontinuous beach ridges. West of the final beach ridge, the major basin portion of the lake resulted in the calm water deposition of ten to over one-hundred feet of fine lake clays. In the beach ridge areas, discontinuous sand and gravel aquifers of varying thickness and aerial extent occur along a more than 100 mile stretch. These beach ridges contain the most sensitive aquifer formations in PMR 1 and, as a consequence, are the targeted areas for this monitoring program. Most water bearing formations in the lake bed area are buried beneath significant amounts of lake clays and, as such, are generally protected from activities at the ground surface. A few areas also exist where coarser soil materials provide a relatively rapid link between the ground surface and Buffalo aquifer. These areas are of great interest to the program, as well.

Agricultural production in PMR 1 varies from intensive growth of high value crops in the lake plain areas to lower value row crops, animal agriculture, hay and pasture in the beach ridge areas. Many areas within the beach ridge deposits of sand and gravel have limited agricultural production, having been converted to various set-aside programs or purchased to restore native prairie. Locating existing wells or sites for installing new wells has proven difficult in some areas of PMR 1.

PMR 5

PMR 5 was initially ranked as a lower priority due to its limited agricultural production. The region was brought into the program in 2006 following development and implementation of monitoring in the other higher priority areas.

Outwash sands with overlying sandy, low pH soils are the primary areas of interest for monitoring in PMR 5. Locally, lake and river derived sands are also sensitive to land based activities. These sandy deposits occur intermittently and are often of limited aerial extent. Many of the sandier areas are forested rather than cropped and contain layers of dense Superior lobe till. The northerly portion of this PMR is more heavily forested, with agriculture being sparse and irregular. Historically this region has shown pesticide detections in drinking water wells and monitoring wells underscoring the sensitivity of the region's groundwater to pesticide use. Due to the limited extent of agricultural production in the

region, well locations tend to be clustered together as defined by the presence of larger areas of row crop agriculture on sandy outwash or lake derived soils.

PMR 6

The most sensitive groundwater conditions in PMR 6 are alluvial river valley deposits of sand and gravel. A large outwash plain in the vicinity of Appleton is also of concern. The river valley deposits tend to be narrow, and relatively thin, with sandy surface soils and are highly valued where they exist. These areas display rapid infiltration of water from the soil surface to underlying groundwater and contain little capacity to limit the downward movement of dissolved or suspended chemicals. Agricultural chemicals have been detected in these areas in reconnaissance sampling previously completed.

Irrigated fields of corn and soybeans are prevalent in the areas of interest in PMR 6. Soils in the area typically have higher pH and low organic matter. Animal agriculture is increasing in the area, although it is somewhat limited by the availability of adequate supplies of water.

PMR 7

Conditions in PMR 7 are similar to conditions in PMR 6 in that the most sensitive groundwater appears as alluvial river valley sand and gravel deposits. Missing from PMR 7 are large areas of glacial outwash sand and gravel. Accordingly, wells tend to follow distinct lines where alluvial river valley channels are present. Many of the alluvial aquifers are so narrow that locating a suitable point for drilling is difficult. In other cases locations that, based on available information, should have an aquifer near the surface are either permanently de-watered or contain water on an ephemeral or intermittent basis only.

PMR 7 is another area of corn and soybean production on medium to large fields. Animal agriculture is expanding similar to PMR 6. Production of ethanol in PMR 7 is expanding but may be severely limited by inadequate supplies of groundwater needed for processing.

PMR 8

The majority of the shallow groundwater in PMR 8 is located in thin bands of sand and gravel within the silt and clay rich glacial tills of the region. PMR 8 also contains shallow groundwater in a small number of lake derived sandy deposits, limited sandy outwash areas and, as in PMRs 6 and 7, along rivers as alluvial systems. Each of these aquifer types are consequently represented with either existing or newly drilled wells. Some of the wells in PMR 8 are completed under leaky confining units where, even though the location is considered sensitive, water quality changes may be relatively slow to occur. PMR 8 contains the largest land area and greatest number of counties out of all the regions in the program. As such, it was determined that additional wells were needed to adequately represent this region.

Well Site Selection

The groundwater and wells of primary interest for PMRs 1, 5, 6, 7 and 8 are completed in shallow "water table" conditions classified as QWTA. Quaternary water table aquifers are

typically made up of sand and gravel deposited in large sand plain areas from glacial outwash, or they can be found in narrow bands along rivers or glacial lake beach-ridges as water deposited sediments.

Initially, a list of wells for consideration was generated from the MDNR observation-well data web page (http://climate.umn.edu/ground_water_level). Well selection priority was accomplished through a simple random ranking. Every QWTA well within each PMR was assigned a number. Wells were ranked via a list of random numbers generated with statistical software. No qualification criteria were included in the ranking process. A site visit to each selected well was made by MDA staff to review the well site location for suitability for inclusion in the network. If a well was disqualified due to location issues, the next highest ranked site was selected.

Well qualification criteria for inclusion in the network were established to facilitate the assessment of site-specific conditions necessary to achieve the stated goals and objectives of the program. To capture these conditions, qualification criteria were set such that qualifying wells sites must:

- Be completed in the QWTA aquifer of interest.
- Have row crop agriculture immediately up-gradient of the site.
- Lie outside of flood prone areas so water cannot pond around the well head.
- Have a readily available and accessible location.
- Have a well log, or other construction information, available.
- Be geographically remote from potential point sources of pesticides.
- Be capable of providing sufficient volumes of water for the required sample size.

Replacement Well Installation

When utilizing existing wells for a water quality monitoring program, it is inevitable that some of the wells will have problems with their construction, integrity or other reasons that limit their functioning as a water quality monitoring well. In cases where this occurs, rather than selecting an alternative well, the site will be listed for well replacement. Wells on the list will be replaced as resources permit. In many situations, and for various reasons, an alternative site for replacement well installation will need to be chosen. In such cases professional judgment will be used to determine the most suitable location and will be based on the aforementioned well selection criteria and specific subsurface qualifications.

Having identified a site that meets the site characterization conditions on the land surface does not ensure that the subsurface conditions will be adequate for inclusion of the site in the network. The following criteria are applied to either existing wells, or during drilling of new wells, for the evaluation of the subsurface conditions of the site for inclusion in the network:

- First water bearing formation is less than 40 feet below the ground surface.
- First water bearing formation is in an unconfined condition.
- No more than 10 cumulative feet of clay is present from the ground surface to the top of the first water-bearing formation.

The depth of a well at a given site is determined primarily by the water table elevation. Well screens are placed to intersect the water table with allowance for its fluctuation over time. Screened intervals of wells are placed intersecting the water table to capture the uppermost layer of water. The purpose of this placement is to effectively sample water recharging the aquifer from the nearby land surface. This is a conservative approach for rapid measurement of potential impacts of pesticide management practices occurring at the land surface up-gradient of the monitoring site. The general range of total depth for wells at these sites is from a few feet to approximately fifty feet in depth. Sites with water table depths greater than forty feet are rejected due to the relative uncertainty of sample water origin from the land surface and high costs associated with installation (there is a significant change in construction requirements in the Minnesota Well Code for well depths greater than 50 feet).

New wells are constructed of two inch flush threaded PVC pipe. Borings are generally completed using a truck-mounted hollow stem auger to drill to the appropriate depth for setting the well screen. Upon setting the screen and pipe into the bore hole, the annular space around the screen is filled with gravel pack material, made up of a gravel size suitable for a #10 slot screen opening, to a level two feet above the screened interval. Well borings are completed in glacial outwash or sand lenses within glacial till materials. Thus, screens are all #10 slot opening (0.01 inch or 0.25 mm). The majority of screens are of ten-foot length. This screen length is selected to ensure the source of sample water is from the shallowest groundwater as. Occasionally other screen intervals are utilized when either existing wells meet other network criteria or special circumstances regarding setting or construction call for such a variation.

Annular space around the pipe above the gravel pack is grouted with bentonite grout or other suitable grout material (according to Well Code) to the base of the protective outer casing. A protective steel casing (Schedule 80) with locking cover is placed with neat cement grout filling the annular space to ground level. Steel or wooden posts are installed to protect and mark the well head after construction is completed. Details of well installation can be found in the MDA monitoring program document "Specifications for Installation of Water Quality Monitoring Wells in Unconsolidated Geologic Material", which can be found as Appendix A1.

3.2 - PMR 4

Characteristics of PMR 4

In 1996 PMR 4, or the Central Sands area, was determined to be an area of specific concern for groundwater pesticide impacts. This decision was based on results from the previous ten year monitoring effort in comparison to the other regions, as shown in Table 5 (Hines and Juenemann, 1996).

Table 5 - Results from the original MDA groundwater monitoring network for 1985 through 1996.

PMR	Wells Sampled	Samples Collected	Percent of Wells Containing Pesticides (%)	Percent of Samples Containing Pesticides (%)
1	10	31	10	6
4	290	1615	34	37
5	22	70	23	20
6	35	81	6	5
7	11	37	18	5
8	38	86	16	9
9	118	344	27	44
10	42	78	14	9

The PMR 4 monitoring network targets areas that are highly susceptible to the use of agricultural chemicals. Site selection criteria provide that sandy soils overlying sandy or gravelly materials be included. These criteria are generally applicable to what constitutes the Central Sand Plain areas of Minnesota. Specific areas included in the network are:

- **Park Rapids – Staples Outwash Plain** (Becker, Hubbard, Otter Tail, Wadena, Todd Counties)
- **Detroit Lakes Pitted Outwash Plain** (Otter Tail, Becker Counties)
- **Mississippi Valley Outwash** (Stearns, Morrison, Benton, Sherburne, Wright Counties)
- **Anoka Sand Plain** (Benton, Sherburne Counties)
- **Crow Wing Outwash Plain** (Morrison County)
- **Belgrade-Glenwood Outwash Plain** (Pope, Kandiyohi, Stearns Counties)

Characteristics of these areas include sandy to loamy soil materials overlying relatively thick deposits of glacial outwash sand. The soils tend to be neutral to acidic, with low organic matter and low cation exchange capacity, providing limited opportunity for the binding or degradation of pesticide compounds. Irrigation practices on corn, soybeans, potatoes and other specialty crops are common in the sand plain areas due to the low water holding capacity of the soils. Hydraulic conductivity tends to be high within both the unsaturated and saturated zones within the outwash. These characteristics, coupled with the previously described findings of groundwater contamination in similar geologic settings, have led to the high priority assigned to these sand plain areas.

Network Design

The network design was developed over a two year time span in a collaborative effort with the United States Geological Survey, the Minnesota Pollution Control Agency (MPCA), the MDNR, the MDH, the University of Minnesota, St. Cloud State University, Soil and Water Conservation Districts for the region's counties, and other local agencies. To help guard against a spatial bias, a randomly started, unaligned grid was used to establish the network. Grid nodes were set at four-mile intervals yielding a regular grid pattern of square plots. Each plot was then characterized against project criteria and were included or excluded from consideration for the network based on meeting the specific criteria. For plots meeting the criteria, a randomizing procedure was used to identify a point as a potential monitoring site. Areas around the identified point were further characterized against specific program criteria for inclusion or exclusion. Landowners are contacted after completion of site selection seeking their participation in the project. The final well location was selected with landowner input and concurrence. Following the extensive design period, nests of two or more wells were installed. Nests of multiple wells were used to enable sampling the top of the water table as it raises and lowers in response to pumping and climatic conditions.

Plot Characterization and Selection

Plot qualification criteria for inclusion in the network were determined to address the probability of geologic sensitivity to pollution and agricultural management. To capture these conditions, plot qualification criteria were set such that qualifying plots must contain:

- Greater than 50% sandy soils.
Sandy soils are determined to be those soils that have sand texture classification for all soil horizons in the top four feet of the soil profile.
- Greater than 25% of land area in the plot under active agricultural management.
Active agricultural management means that land is managed for production of row crops or row crops in rotation (primarily targeting areas receiving pesticide and/or nutrient inputs).
- Greater than 33% upland sandy soils.
Upland sandy soils are determined to be sandy soils with water table or seasonal high water at a depth of six feet or greater.
- Greater than 50% of soils identified as sandy under active agricultural management.

Well Site Characterization and Selection

A target site was randomly chosen within each plot. When a potential site target point occurred within the appropriate soils and land use, further evaluation was performed for field criteria. If no suitable site was found within sandy soils and agricultural land use, a new random number pair was generated and the process was followed repeatedly until a suitable site was found. If all possible areas within a plot were exhausted through this process, with no suitable site being found, the plot was eliminated from consideration for the network.

Site qualification criteria for inclusion in the network were determined to assess the local conditions necessary to achieve the stated purpose and objectives of the program. To capture these conditions, site qualification criteria were set such that qualifying sites must:

- Have land under active agricultural management within 0.1 mile up gradient of site.
- Lie up gradient of potential point sources or areas where spills may occur (such as roads).
- Lie at least 0.3 mile from potential up gradient point sources (such as farmsteads).
- Lie at least 1.0 mile from up gradient agricultural chemical dealership facilities.
- Lie outside of flood prone areas.

2008 Changes in PMR 4 Sampling Frequency

During June 2008 the number of samples the MDA laboratory was able to process was reduced, which required a change in the sampling regime for PMR 4. Prior to 2008 there had been randomized quarterly sampling of 29 sites per quarter for all four quarters of the year. Following the second sampling quarter of 2008, the design changed to the collection of one sample from each well every year. The wells were randomly distributed between quarters 2 and 4 (spring and fall) for sampling.

To determine possible impacts to network data as a result of switching from a quarterly to a bi-annual sampling scheme, data for atrazine and its degradates (the design compound) was analyzed for differences across seasons. Upon analysis it became clear that, for the design compound, there was no significant seasonality in the data. Probability and box plots of atrazine data for each season of sampling were constructed (Figure 5) and display remarkable similarity between the different seasons. To test the hypothesis that seasonality is not present in the data, a Kruskal-Wallis non-parametric analysis of variance across seasons was conducted. Results indicated that there was no significant difference between the seasons.

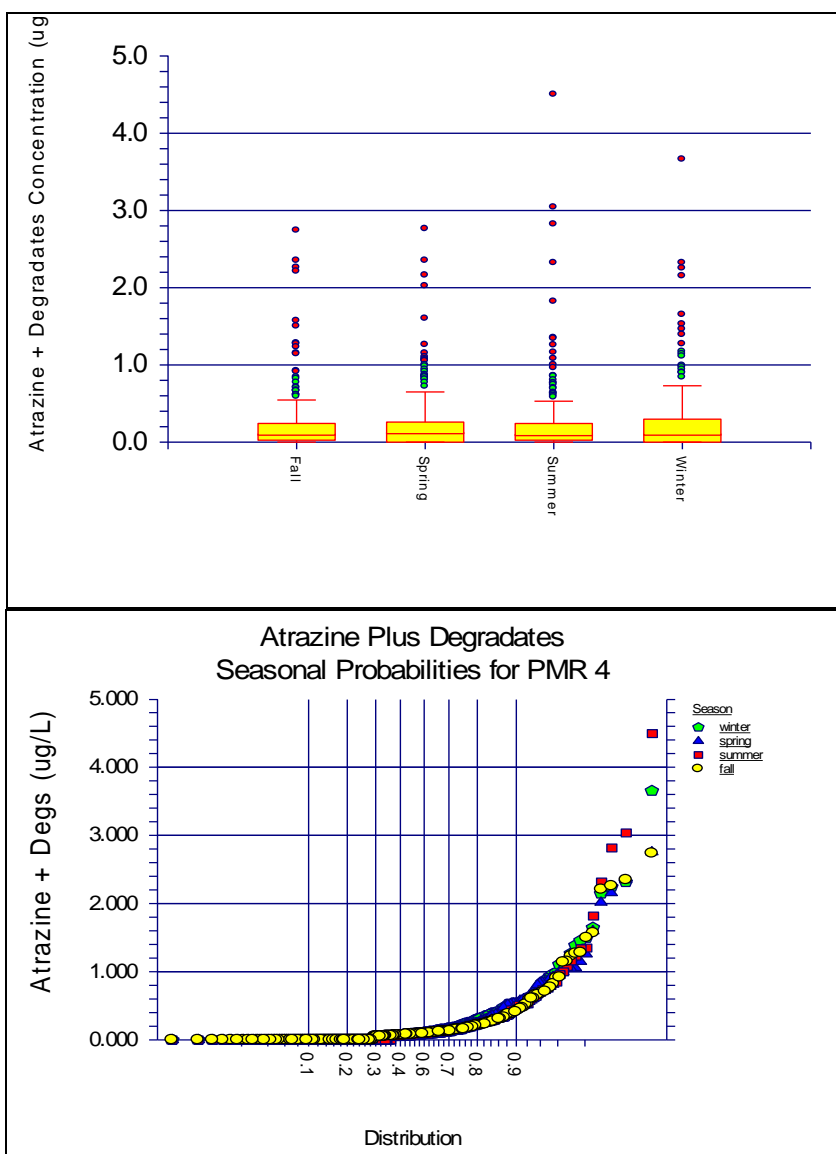


Figure 5. Box and probability plot comparisons of total atrazine results by season for MDA PMR 4.

Although atrazine does not display any seasonality, there is concern that the changes will impact other pesticide compounds of interest for the monitoring program. Seasonal probability plots of acetochlor and its degradates, alachlor and its degradates, metolachlor and its degradates, and metribuzin and its degradates (Figure 6) were also produced as a check on seasonal differences for those compounds. These plots convincingly show that any differences are small and are unlikely to impact forthcoming decisions by the MDA.

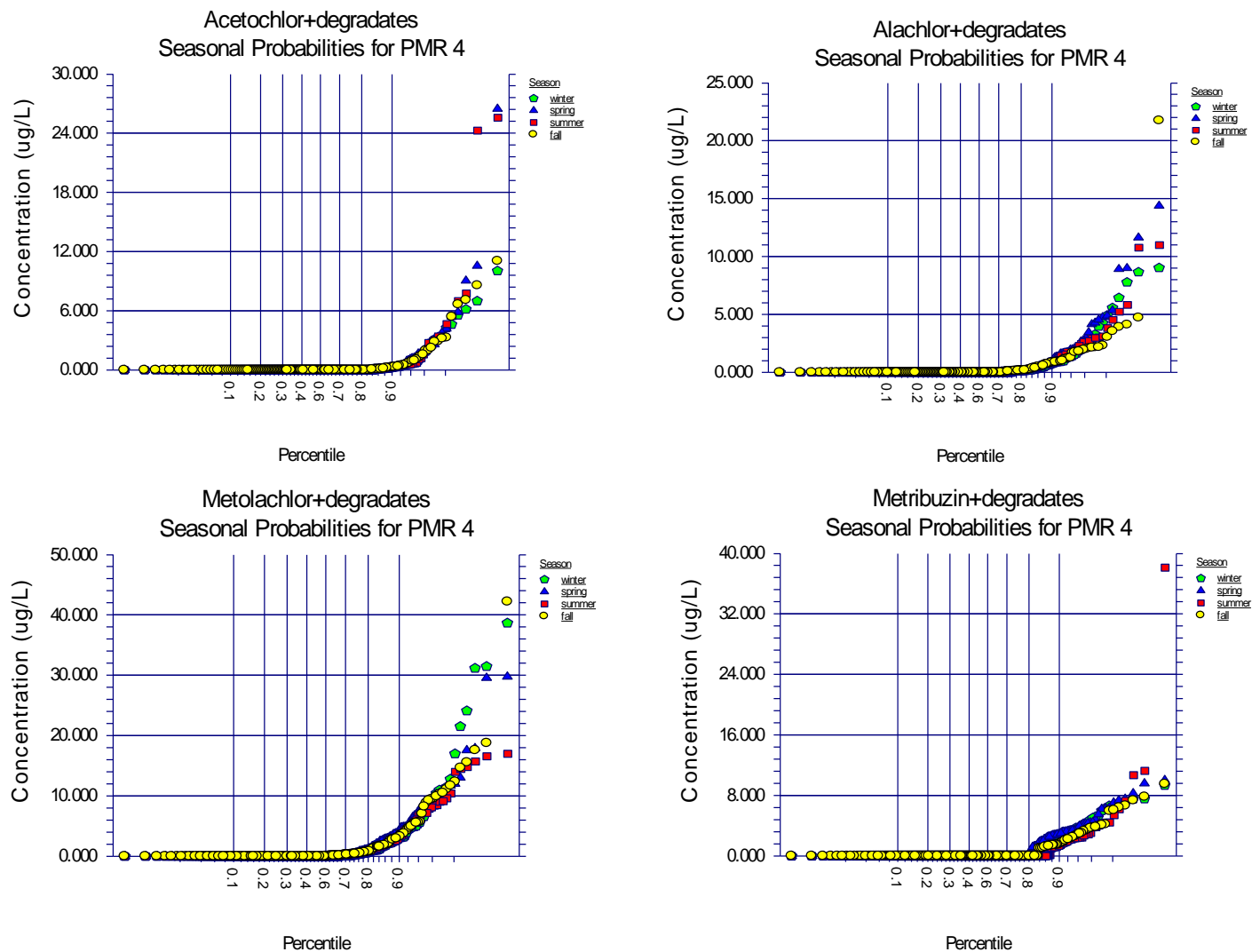


Figure 6. Probability charts by season for total acetochlor, alachlor, metolachlor and metribuzin by season for MDA PMR 4.

One of the primary goals of the program is to determine long term trends in the data. Significant changes to sampling schedules has the potential impact of causing serious alterations to conclusions regarding trends and was carefully evaluated before any permanent changes were implemented. Long term trends in atrazine concentrations and detections were evaluated using data from all four quarters versus quarters 2 and 4 only, as well as quarters 1 and 3 only. Results of the analysis show no significant difference in calculated trends between the full data set versus the truncated data sets (see Figure 7).

This lack of difference implies that any conclusions based on either data set would be similar. The greatest difficulty in changing the sampling scheme is in the affect on the power of statistical tests conducted on the data, and the concomitant increase in uncertainty. This uncertainty is evident upon visual inspection of the edited data sets compared to the complete data set. Any increase in uncertainty serves to increase the amount of time required to evaluate trends in the data and to attain the desired level of power in statistical tests. Although impossible to determine the actual power of statistical tests on MDA monitoring data (due to censored data and the resultant truncated data frequency distributions), the calculated power from the two available sets does show a decrease when sampling is limited to two quarters versus four. Decreases in power, as indicated here, are primarily due to a reduction in the number of samples available for analysis. The MDA has concluded that the practical significance of this decrease in power is of minimal consequence for the types of decisions that will be made based on this set of data.

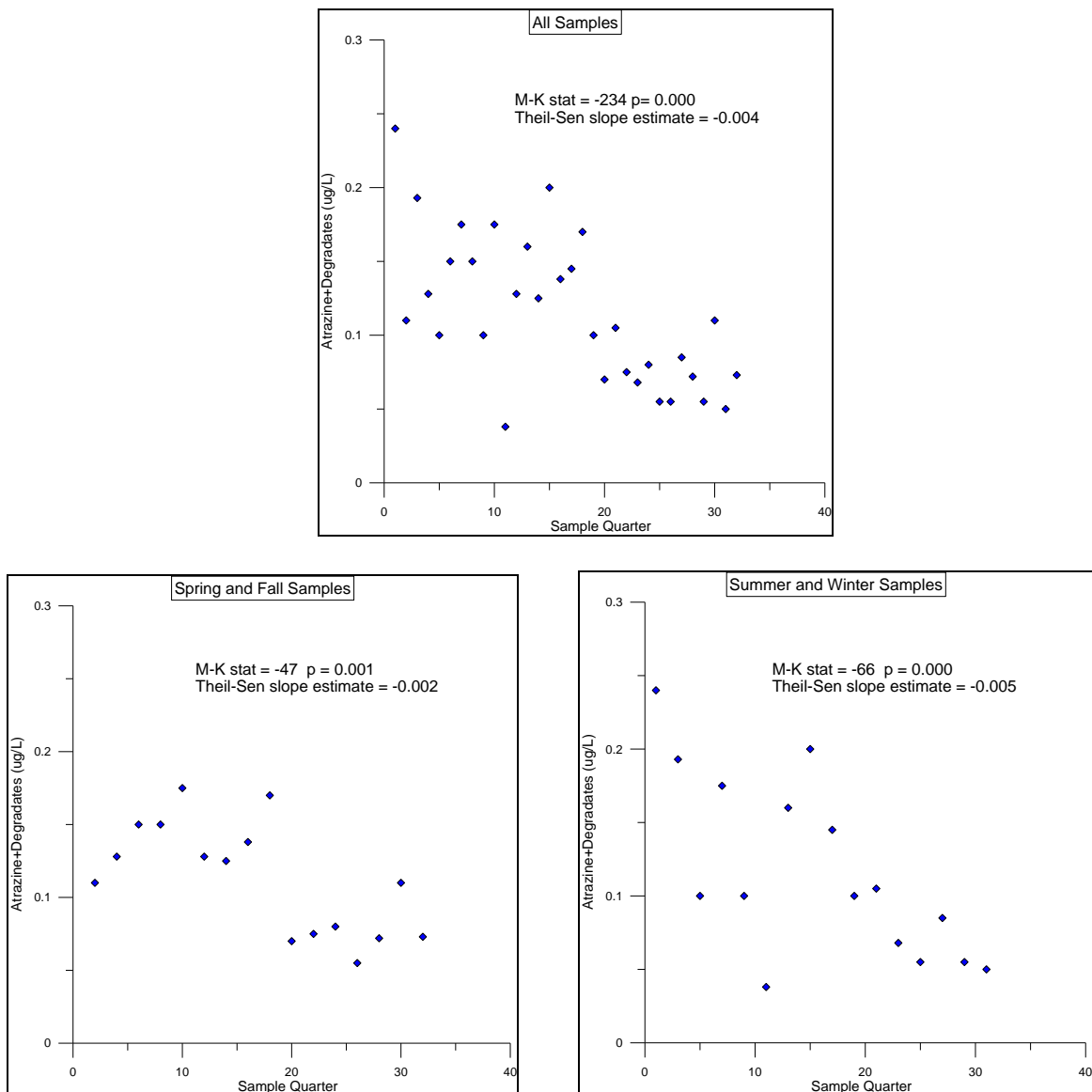


Figure 7. Total atrazine median results for samples collected from MDA PMR 4 wells from 2000 through 2007.

3.3 - PMR 9

Characteristics of PMR 9

PMR 9 encompasses the State's karst geology. Karst geology is characterized as an area containing near-surface carbonate bedrock that is fractured and relatively soluble. Obvious features of karst areas include sinkholes, caves, disappearing streams, springs, deeply incised valleys, and thin layers of erodible soils. These conditions all serve to make shallow groundwater in the area highly susceptible to contamination from activities at the ground surface. Naturally occurring springs and domestic drinking water wells provide the two primary means of access to groundwater for sampling in the region.

Spring Selection Criteria

The MDA is interested in monitoring groundwater that is sensitive to surface activities, is therefore shallow, and lies within agricultural production areas. Through utilization of MDNR springshed mapping and available geologic information, the MDA was capable of selecting those springs that represent the shallowest groundwater in the region. To be selected for consideration, a spring had to meet the initial selection criteria:

- Mapped springshed, or assumed contributing area, contains at least 50% agriculture land use.
- Spring must be perennially flowing.
- Land owner(s) is willing to provide long-term access to sampling site.
- Spring and sampling location is safely accessible at all times of the year.

Spring Selection

The population of springs from which selection was made was a list of springs developed in cooperation with the MDNR. Springs emerging from the following geologic formations (see Figure 8 for stratigraphy) were considered:

- The Upper Carbonate Group
 - Cedar Valley, Wapsipinicon, Maquoketa, Dubuque and Galena Formations
- The Platteville Formation (if not overlain by the Decorah confining unit)
- The St. Peter Formation (if not overlain by the Glenwood confining unit)
- The Prairie DuChien Group
 - Shakopee Limestone and Oneota Dolomite Formations
- The Jordan Sandstone

The list of springs generated by MDNR hydrologists and MDA staff was followed up by a site visit to each selected spring by MDA staff. MDA staff reviewed the location of the spring for suitability for inclusion in the network. In 2011 the MDA began to eliminate previously sampled springs that are intimately connected to sinkholes and upstream rivers. Through sampling for turbidity, total suspended solids, and phosphorus it became clear that a number of springs in the program had very close connections to surface features. These close connections overwhelm more diffuse flow patterns resulting in the sampling of sinkhole and upstream river water. The program concluded that replacing those sites over time with springs that primarily represent diffuse flow would allow results that were more in line with

agency goals of monitoring general groundwater conditions in the area. See Appendix A2 for results of the inorganic analyses on samples from the springs.

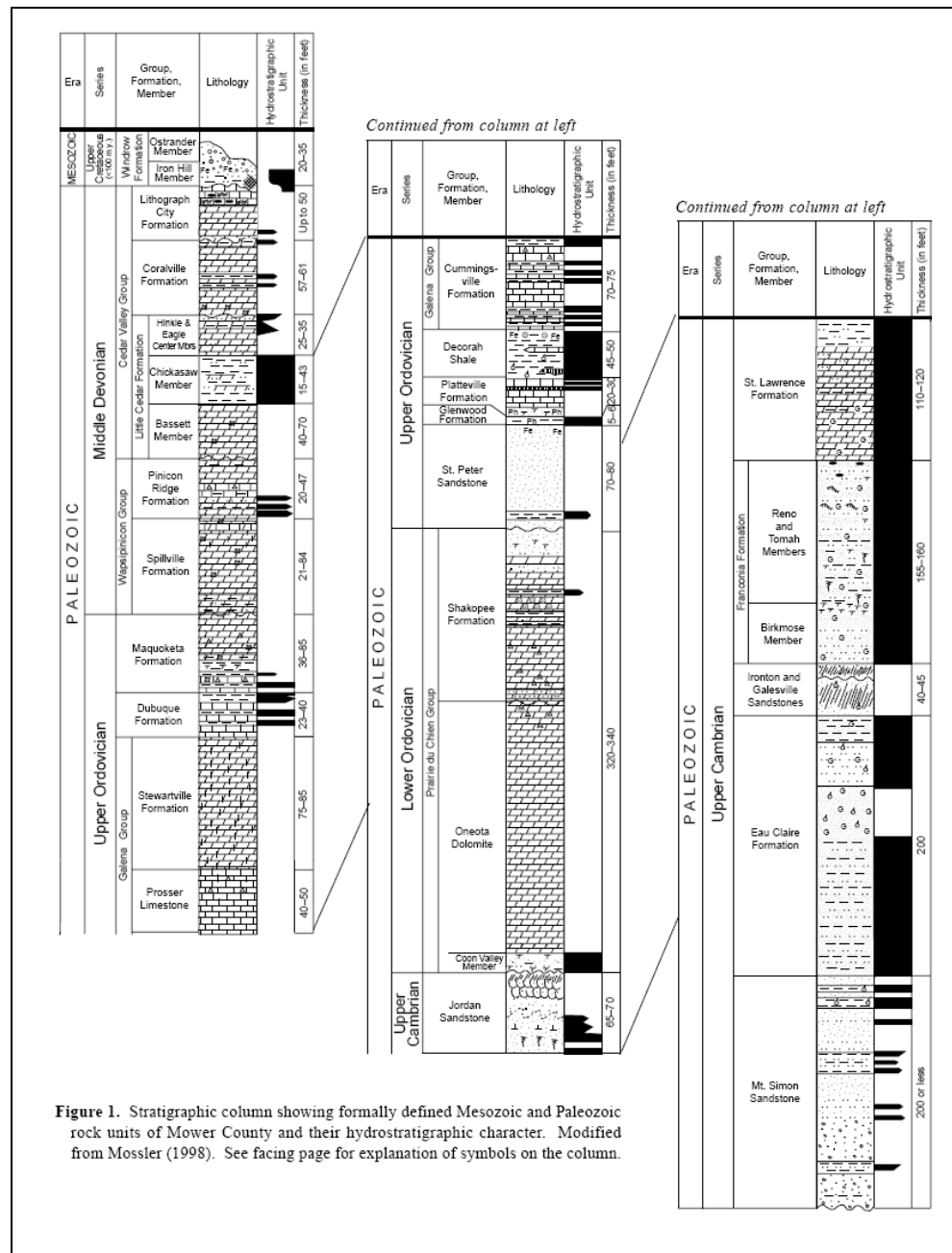


Figure 8 - Southeast Minnesota bedrock stratigraphy (from Mower County Geologic Atlas).

Alternate Spring Selection

When utilizing a finite list of sample points for a water quality monitoring program, it is inevitable that some of the locations will have or will develop land use changes, problems with access, or some other reason that limits their function as a useful long-term sample point. In cases where this occurs, an alternative spring will be selected from those remaining on the list of eligible springs. The same final selection criteria will be applied to the alternate springs.

Sample Collection at Springs

Samples are collected four times each year. Samples are collected on two week intervals during the period beginning May 15 and ending June 30 near the middle of the sampling interval. No more than one sample gets collected during any two week interval. One additional sample is collected during a low flow period in September or October.

Domestic Well Sampling in PMR 9

To complete the design for monitoring in PMR 9 the MDA selected a group of private drinking water wells for sampling, which began in 2009. Domestic well qualification criteria for inclusion in the network were established to facilitate the assessment of site-specific conditions necessary to achieve the stated goals and objectives of the program. To capture these conditions, well qualification criteria were set such that qualifying wells must:

- Be completed in the aquifer of interest.
- Have a well owner willing to participate.
- Lie outside of flood prone areas so water cannot pond around the well head.
- Be up-gradient of point sources of agricultural chemicals, or at least ¼ mile from such sources if the well is down-gradient.
- Have a readily available and accessible location, not inside a building of any kind, from which to collect the water sample.
- A well log or other construction information available, such as owner reported depth.

Newer drinking water wells in PMR 9 are constructed to standards mandated in the Minnesota Water Well Code and are finished in deeper, less sensitive aquifers. Many wells that are completed in the shallower, more susceptible conditions are old, poorly constructed, or located in close proximity to potential point sources of contamination, which renders them unusable for this program. As a result, selection of suitable wells for inclusion in the monitoring program was difficult.

3.4 - Urban Groundwater Monitoring

As stated in the MDA/MPCA groundwater monitoring memorandum of agreement (MOA), the urban sampling program is operated in cooperation with the MPCA. Based on MDA site selection criteria, the MPCA chooses from wells scheduled for sampling by their program and an additional sample is collected for pesticides analysis. Many urban areas may also contain significant agricultural land, much of which is in the process of conversion to suburban

development. Long-term monitoring in such settings is quite difficult and remains a future consideration for the program.

Samples collected from urban settings undergo analyses for pesticides commonly used in urban and suburban environments. Sampling for urban use pesticides is conducted in urban centers within the geographic bounds of several PMRs, but primarily within PMR 10.

SECTION 4 - DATA ANALYSIS

Information needs of the MDA require that data from the network undergoes well thought out statistical analyses. Both parametric and non-parametric analytical procedures may be used for analysis of water quality variables in MDA monitoring. Unlike parametric procedures, non-parametric analytical methods do not use the data values but use the ordered ranks of the data instead. The best use of a given statistical test or procedure is dependent on the type of frequency distribution the data follows. Determination of the frequency distribution can be quite difficult, particularly if the data distribution is truncated. Truncation of a data distribution is the result of pesticide analytical methods having mass limits beneath which sample concentrations are unable to be reliably determined. It is at this point that the data is censored and results are reported as “not detected”, resulting in the truncation of the data distribution as in Figure 9. Use of rank order statistics requires no assumption as to the shape of the water quality variable frequency distribution. Therefore, data from MDA water quality monitoring will primarily be analyzed by non-parametric procedures. Parametric procedures will be utilized if conclusive proof is available that the data follows a normal distribution or if the data can be transformed to a normal distribution. Parametric methods may also be used in cases where violations of test assumptions are small, for tests that are known to be robust with respect to violations of pertinent assumptions, or in cases where parametric results may be helpful in making decisions regardless of the violation of assumptions.

Statistical Tests. Prior to formal statistical analysis of the data, a graphical inspection of the data will be conducted. Determination of which statistical methods are appropriate usually requires the use of tests to determine how well the data distribution fits a hypothesized distribution. Historic data from the monitoring program show that MDA water quality data are unlikely to be normally distributed (see Figure 9).

Pesticide occurrence in wells will be calculated as a simple ratio of total number of wells sampled to the total number of wells with pesticides present. Occurrence ratios will also be calculated for each pesticide compound and sampling region.

As previously stated, MDA water quality monitoring data is generally quite skewed and contains a large percentage of censored results which may render the determination of the shape of the data distribution inconclusive. In such cases, non-parametric measures are utilized; however, this does not preclude the use of the mean as a measure of central tendency. In many situations where toxic chemicals are a concern, the mean concentration may be a valuable tool as it accounts for extreme values in the sample population (which may be important for risk assessment), while the median does not.

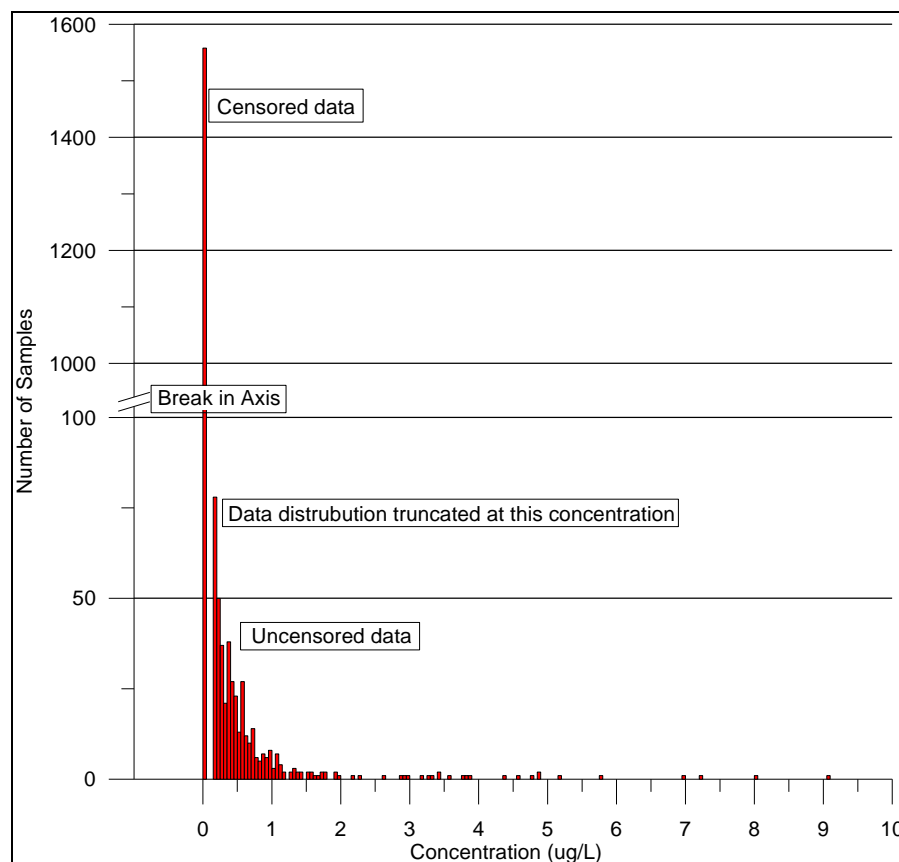


Figure 9. Atrazine frequency distribution of laboratory results from original monitoring network (1985 – 1996).

For MDA's groundwater monitoring, however, the central tendency of pesticide concentrations will be accepted as the median. Seventy-fifth percentiles and ninetieth percentiles will also be calculated for each analyte of concern for all networks.

Sample results for this state-wide, regional network will likely contain relatively large spatial and temporal variability. The network will not have equivalent spatial coverage of sites in each region and will undoubtedly have different data variances among regions. These circumstances violate the assumptions upon which many comparative statistical tests are based. Such conditions decrease the power of many statistical tests, resulting in the need for a large amount of data over many years for test results to be mathematically conclusive. As a consequence, small magnitude trend analysis conducted on sample results from the network as a whole (across all regions) will most likely be inconclusive for many years. This may or may not be true for trend analysis within individual regions or on specific wells. Trend analysis on network data will also be completed utilizing step trend procedures such as the student's t-test and its non-parametric analog. Step trend analysis is geared toward the assessment of relatively large changes in conditions that a network such as this may be capable of revealing. Large magnitude

changes will likely be evident upon graphical inspection of the data long before statistical tests are conclusive. In addition, analysis of small magnitude trends will be conducted on data from individual wells and on data within a single PMR. After many years of sampling it is possible that statistical tests will return a statistically significant result simply due to large sample numbers, while having no practical meaning. Data will be interpreted accounting for this potentiality.

4.1 - Trend Analysis Considerations

Analyzing MDA monitoring data for trends in pesticide contamination of groundwater is the single most important aspect following detection. Unfortunately, analyzing data for trends is somewhat troublesome due to the multitude of agents which can cause a change in contamination status, such as changes in crops grown, the use of pesticides, and weather patterns. Analytical detection limits resulting in censored, or truncated, data limits the usefulness of most common statistical analysis tools. Seasonal, spatial, analytical, and sampling variability can serve to render data insufficient for conclusive results. It is therefore important to view analytical data generated from water well samples as only one component of the trend monitoring question. Ancillary data, such as that mentioned above, must also be collected if the results of the monitoring are to be interpreted and transformed into information from which sound decisions may be made. This document focuses on the water quality data analysis, leaving discussion of linkages with ancillary data for further consideration.

A critical aspect of trend analysis is the power and significance of the test and is governed, to a large extent, by the frequency of sample collection. The characteristics of the data, in relation to the statistical analysis techniques, establish the power and significance of any test utilized and can vary from one point in time to another. The numerical value representing the power of the test is the probability of concluding a trend is present when one actually does exist. The significance level of the test is the probability of concluding a trend exists when a trend is actually not present. Power and significance, therefore, correspond to Type II and Type I error, respectively. Type II error is the error associated with accepting the null hypothesis when it should be rejected, while a Type I error occurs when the null hypothesis is rejected when it should be accepted.

When deciding on the levels of significance and power to accept for a given test and thereby define data acceptability or design parameters, it is critical to consider which type of error it is most important to minimize. Minimization of Type I errors results in two predicaments. First, a small risk of Type I error results in a decrease in the sensitivity of the test for detecting trends, in other words significance decreases. Second, with small sample numbers a small level of significance decreases the power of the test tremendously. Generally Type I errors in MDA water quality monitoring would result in implementation of additional monitoring and management activities when actual conditions may not warrant it. Type I errors may, therefore, be considered conservative (i.e. precautionary) in nature and afford an additional measure of protection to the resource of concern. The consequence of accepting low power is an increase in Type II errors and the need for a more extensive data set for trend analysis to be

conclusive. The increase in Type II errors could result in no implementation of related protective activities although real conditions would demand action. Type II errors could result in an increase in pollution to the resource of concern. Therefore, because of the implications of delayed detection of trends associated with Type II error, trend analysis on MDA monitoring data will strive to keep the power of the statistical tests as close to 1.00 as possible. Correspondingly, decision errors of 20 percent for Type I errors and 10 percent for Type II errors has been established as tolerable for MDA pesticide management programs. In holding the associated power this close to 1.00, it is recognized that the level of significance will vary as the sampling program continues.

Based on the above, analyzing data for trends must take into account the attributes of the data that have been collected. Most important is the level of trend and the variability that can be expected in the data that will be analyzed. Loftis et. al. (1987) describe a procedure for determining the power of statistical trend analysis in water quality monitoring data. A key component of this power determination is the trend versus standard deviation ratio of the data. The initial monitoring design in PMR 4 was developed around the criteria to be able to determine an atrazine trend that, if left untreated, would result in exceedence of a recommended allowable drinking water level within 10 years. This level of trend would allow the MDA to take action long before the threat to groundwater became severe. As an example, consider atrazine as a compound of particular interest because of its frequency of occurrence in Minnesota groundwater. Atrazine has a maximum contaminant level (MCL) of three parts per billion in public drinking water. Pesticide data from monitoring conducted by the MDA during the period 1985 through 1996 had standard deviations between 0.4 and 0.6, resulting in a trend to standard deviation ratio of 0.5 to 0.75. Differences in data variability have a significant impact on the ability to determine a trend in a given time period. The upper portion of Table 6 is data collected from a subset of Central Sand Plain wells from the original network that had a standard deviation of 1.71, while the lower portion of the table is for data that had a standard deviation of 0.52. Notice the extremely large difference in the period of time required to achieve a power of one for these two data sets.

Following these procedures the MDA will determine the power of monotonic trend tests on the program's monitoring results. Because of the inclusion of censored data in MDA data sets, the true power of the test will be uncalculable. It is therefore necessary for users of MDA data to use power calculations only as a relative rather than absolute value.

Table 6. Example of the power of a monotonic trend test for pesticide data. Data are atrazine results from the 1985 to 1996 monitoring of wells in the Central Sand Plains setting within Minnesota.

Power of a monotonic trend test. MDA Old Network															
std	per	per units	base trn	freq	mltpl	T	s	T/s	n	Nt	T*	F	P	LY	LM
annual sample															
3	10	years	0.3	1	10	0.3	1.71	0.18	12	2.2982	1.372184	0.19	0.81	12.00	144
3	10	years	0.3	1	10	0.3	1.71	0.18	19	4.5883	1.333379	0.00	1.00	19.00	228
Twice a year															
3	10	years	0.3	2	20	0.15	1.71	0.09	24	2.3042	1.321237	0.17	0.83	12.00	144
3	10	years	0.3	2	20	0.15	1.71	0.09	35	4.0598	1.307737	0.00	1.00	17.50	210
quarterly sample															
3	10	years	0.3	4	40	0.075	1.71	0.04	48	2.3057	1.300228	0.16	0.84	12.00	144
3	10	years	0.3	4	40	0.075	1.71	0.04	69	3.9743	1.294315	0.00	1.00	17.25	207
every other month															
3	10	years	0.3	6	60	0.05	1.71	0.03	69	2.1633	1.294315	0.19	0.81	11.50	138
3	10	years	0.3	6	60	0.05	1.71	0.03	103	3.9458	1.289990	0.00	1.00	17.17	206
every month															
3	10	years	0.3	12	120	0.025	1.71	0.01	136	2.1167	1.287901	0.20	0.80	11.33	136
3	10	years	0.3	12	120	0.025	1.71	0.01	204	3.8886	1.285757	0.00	1.00	17.00	204
annual sample															
3	10	years	0.3	1	10	0.3	0.52	0.58	6	2.6438	1.533206	0.16	0.84	6.00	72
3	10	years	0.3	1	10	0.3	0.52	0.58	10	5.7403	1.396815	0.00	1.00	10.00	120
twice a year															
3	10	years	0.3	2	20	0.15	0.52	0.29	11	2.3435	1.383029	0.18	0.82	5.50	66
3	10	years	0.3	2	20	0.15	0.52	0.29	17	4.5133	1.340606	0.00	1.00	8.50	102
quarterly sample															
3	10	years	0.3	4	40	0.075	0.52	0.14	21	2.1921	1.327728	0.20	0.80	5.25	63
3	10	years	0.3	4	40	0.075	0.52	0.14	32	4.1261	1.310415	0.00	1.00	8.00	96
every other month															
3	10	years	0.3	6	60	0.05	0.52	0.10	32	2.2460	1.310415	0.18	0.82	5.33	64
3	10	years	0.3	6	60	0.05	0.52	0.10	47	3.9989	1.300649	0.00	1.00	7.83	94
every month															
3	10	years	0.3	12	120	0.025	0.52	0.05	62	2.1423	1.295821	0.20	0.80	5.17	62
3	10	years	0.3	12	120	0.025	0.52	0.05	93	3.9359	1.290924	0.00	1.00	7.75	93
std = health or other standard per = period of interest per units = period unit base trn = base trend value freq = samples per year (1 = annual; 4 = quarterly, etc) mltpl = samples over period of interest T = trend of interest s = standard deviation of samples already collected T/s = trend to standard deviation ratio n = number of samples collected Nt = dimensionless trend number T* = t-stat F = t distribution probability P = power LY= years of sampling needed LM= months of sampling needed															
These calculations are based on the student's t test on the slope of a regression analysis. As regression is a parametric test, violation of the normality assumption will affect the actual power of the test.															

4.2 - Reporting

A written report of findings from groundwater monitoring will be completed on an annual basis. These reports will cover the previous calendar year and will include a summary of analytical results, including statistical analysis when or where sufficient data exists. All reports from the program will be placed on the department's web site (www.mda.state.mn.us/monitoring).

For management decision making purposes, the minimal data elements and information discussed under "Monitoring Objectives" in Section 1 will be reported on an annual basis for both regional and state-wide scales.

Written reports will be submitted to MDA regulatory personnel involved in pesticide management decision making. Reports may be sent to other interested parties including, but not limited to, the following:

- MPCA
- MDH
- Minnesota Department of Administration - EQB

4.3 - Performance Reviews

Periodic formal evaluations of the groundwater monitoring program will be conducted in order to determine whether the design is meeting the goals established. Continuous informal evaluation of the program is mandatory and will aid in determining when a formal review is necessary. In the event that expectations are not being met, the MDA will be obligated to take corrective action through modification of the network design. Any modifications adopted must be thoroughly documented with justification and reasoning clearly stated. The changes will be captured as a re-written design, attached to this original document as supplements, or be placed within the annual work plan. The specific means of documentation will depend on the magnitude and permanence of the changes to the design.

4.4 - Standard Operating Procedures (SOPs)

Sampling will be conducted following procedures described in the program's Quality Assurance Project Plan (QAPP) for PMR 4. Field quality control procedures are also described in this document. Laboratory analytical procedures developed for previous monitoring will be maintained. Laboratory quality control procedures, as outlined in the PMR 4 QAPP, will also be maintained for all facets of groundwater monitoring. Work plans, which include number of samples and the frequency of sampling, for any given year will be posted on the program web page at the beginning of each calendar year. All sampling sites will be located utilizing available Geographic Positioning Systems (GPS) technology.

Manipulation and analysis of laboratory analytical data will be conducted with Microsoft Excel, NCSS, Statistica, and/or SYSTAT software. Mapping of environmental components and well site locations will be accomplished by using Geographic Information Systems (GIS) software.

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APPENDICES

Appendix A1: Specifications for Installation of Water Quality Monitoring Wells In Unconsolidated Geologic Material

A. General Specifications.

1. **Drilling method.** Wells installed in unconsolidated geological material for the MDA Monitoring and Assessment Unit will, under all circumstances covered by this document, be drilled using a hollow-stem auger.
2. **Borehole Size and quality.** Hollow-stem augers must have a minimum inside working diameter of at least 4 inches larger than the outside diameter of the well casing or screen. In nearly all circumstances the MDA will be installing 2" diameter well screens and casing necessitating the use of a nominal inside diameter of 6 inches for all auger flights utilized. This specification is required to ensure that there is sufficient space available to insert a tremie for placing filter pack material into the well or so that filter pack material may be poured into the annulus without causing bridging or auger flight binding during removal. All boreholes must be installed straight and plumb to permit geophysical logging and installation of casing.
3. **Well construction materials and practices.**
 - a. General. Well screens, casings, annular sealants, and all other monitoring well components must be new material capable of lasting for the design life of the well installation. All construction materials and installation procedures must comply with the Minnesota Water well Construction Code.
 - b. Well screen. Well screens must be factory fabricated slotted or wire wound PVC. Hand cut screens are unacceptable and may not be used. The maximum screen length for MDA wells is 10 feet. Five and three foot screens may also be used depending on the needs of the specific location or project. Well screen slot size will be 0.010" (commonly referred to as #10 slotted screen) unless conditions of the site are known ahead of time (e.g. grain size analysis) or other design considerations dictates otherwise. Deviations from this specification must be adequately documented and approved by the MDA project supervisor or senior hydrologist prior to installation. Well screens should be installed with the water table inundating approximately 70 percent of the screen.
 - c. Filter pack. The standard filter pack material for MDA monitoring wells is #30 Red Flint sand. Other filter pack materials may be used if there are sound technical reasons for such and if approved prior to use by the project supervisor or senior hydrologist. Under no circumstance may filter fabrics be utilized in construction of MDA monitoring wells. For wells greater than 50 feet in depth a tremie pipe must be used for placement of filter pack material in the well. In wells less than 50 feet in depth filter pack material may be poured (slowly and carefully) into the annular space between the well screen, casing and auger. When pouring extreme care must be taken to avoid filter pack bridging between the auger and well casing or screen. If bridging begins to occur pouring must be stopped, bridging alleviated if possible, and a tremie used for

any further filter pack placement. The filter pack must be extended to two feet above the top of the well screen.

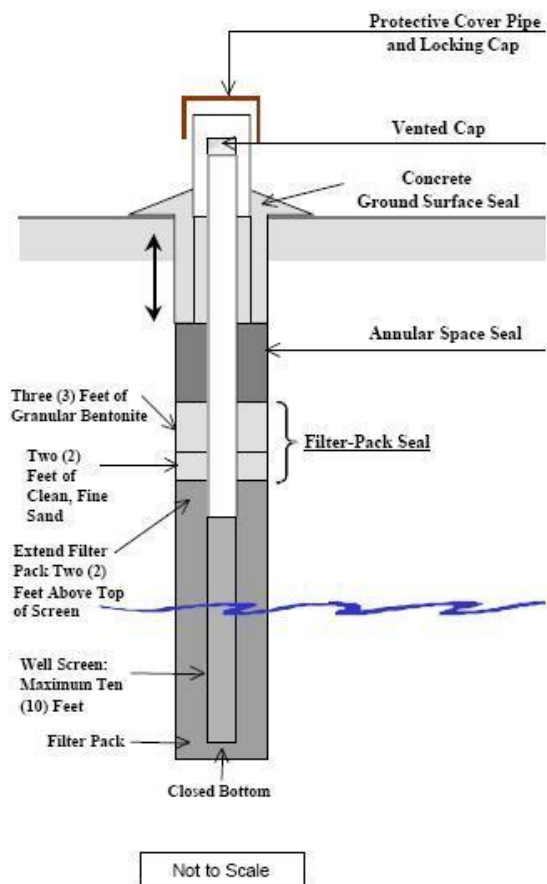
- d. Filter pack seal. To guard against the grout slurry entering the filter pack and screened interval, a filter pack seal consisting of two feet of fine sand overlain by two feet of bentonite must be placed above the filter pack. The bentonite chips or pellets must be hydrated with the addition of enough fresh water to accomplish the task.
- e. Surface seal. The entire annular space from the top of the bentonite seal to the surface of the ground must be filled with grout as required in the Minnesota Water Well Construction Code. These wells will be used to sample water and determine the water level, therefore it is imperative that each well be tightly and effectively grouted and cased to prevent interaquifer movement of groundwater and vertical leakage of surface water runoff to the screen of the well.
- f. Protective top casing. Each well must be completed with a steel protective casing as required in the Minnesota Water Well Construction Code. The outer protective casing shall be installed to a height of no more than three feet above the ground surface (MN Well Code requires at least two feet of protective casing above the ground surface). The inner well casing should be no more than 6 inches lower than the top of the outer casing. A locking cap must be installed on each outer protective casing and locked with a four tumbler combination padlock provided by the MDA.
- g. Geologic Log. The contractor shall carefully and accurately keep a log with descriptive notes made of everything encountered by the drill and of all difficulties or unusual conditions met in drilling. Within 10 working days after the completion of the well a typewritten log shall be prepared and delivered to the MDA. The contractor shall follow all applicable state codes and regulations pertaining to the completion and submittal of well log reports.
- h. Well Development. The contractor will furnish the necessary pump and other needed equipment and shall develop the wells by such approved methods as shall be necessary to the satisfaction of the MDA. At the conclusion of the development the well shall be cleared of all accumulations of sand and other materials that have entered the open hole to the full depth of the well.
- i. Abandonment of well. Any hole in which the contractor voluntarily stops work and /or fails to complete in accordance with these specifications, shall be considered abandoned. If any hole is declared abandoned, no payment for that hole shall be made by the MDA for any part of the drilling or casing used. All abandoned wells shall be filled by the contractor at his own expense.
- j. Marker posts and reflective markings. Each well must have three posts at least four inches in diameter (or square) around the well at equal distances from each other and two feet from the casing. The posts must extend at least four feet below and four feet above the established ground surface. Reflective

markers, paint or tape must be applied to the well and fence post so the location may be seen when approached from any direction.

- k. Site Restoration. The contractor will take steps to minimize disturbance of the drilling sites. These steps include, but are not limited to, entering and leaving the site by the same route, landscaping of debris and cuttings produced as a result of drilling operations to original site conditions, and general clean up of the site after completion of the well installations.
 - l. MDA inspection. Inspection and acceptance will be made by the MDA after completion of the work described in the above specifications. Successful completion will be determined by mutual agreement of the MDA and the contractor.
4. **Specifications for well drilling contracts.** The following specifications are to be used as the basis for structuring Requests for Proposals for well drilling bids. All well construction materials and drilling practices must comply with the Minnesota Water Well Construction Code. The unit product for which the MDA will pay invoices is per foot of finished well depth for a functioning monitoring well.
- a. Bid items. Bids will be sought for the price per foot of monitoring wells completed up to 25 feet deep and also for wells completed at depths from 25 feet to 50 feet. No wells will be installed where the finished depth is greater than 50 feet. The cost for augering of the borehole, casing and grouting installation, and stand-by time should be included in this item. Other bid items should include the price per foot for drilling a dry or otherwise unused borehole (including drilling and sealing of unused borehole).
 - b. Narrative specifications.
 - i. The contractor will be responsible for obtaining utility clearance for each well site prior to drilling as well as obtaining at his own cost any and all necessary state and local permits and licenses which may be required by law to perform the work defined in these specifications. The MDA will be responsible for acquiring permission for well installation from land-owners.
 - ii. Wells to be constructed of new 2" Schedule 40 PVC flush thread well casing with new factory fabricated 10 feet long flush threaded #10 slotted PVC screens (materials to be provided by the contractor).
 - iii. Wells to be drilled by hollow stem auger with minimum inside auger diameter of 6".
 - iv. Auger end plugs must be used when drilling any well to prevent movement of geologic material up into auger.
 - v. Well screens to be placed where 70 percent of screen is inundated with water at time of drilling. It will be the responsibility of the contractor to obtain an accurate water level reading to accomplish this specification.
 - vi. A filter pack of #30 sand to be installed around the well screen to two feet above the screen.

- vii. Two feet of fine silica sand followed by three feet of bentonite is to be placed over the filter pack as a seal to prevent grout leakage to the screened interval.
- viii. The remaining annular space between the filter pack seal and the ground surface is to be grouted with neat cement.
- ix. Wells to be completed with 6 inch diameter protective steel casing installed with at least four feet below and two feet above the established ground surface.
- x. The contractor will be responsible for keeping a complete and accurate well log of the boreholes drilled.
- xi. Wells are to be developed to acceptable clarity by well driller following installation.
- xii. Inner well casing is to be capped with expansion J-plugs provided by the contractor.
- xiii. Suitable locking caps for the outer casing are to be provided and installed by the contractor. The MDA will provide the locks.
- xiv. Installing three reflective posts around each completed well will be the responsibility of the contractor. These markers must be at least four inches square and extend four feet above the ground surface.
- xv. Dry or otherwise unused boreholes are to be sealed by the contractor according to the Minnesota Well Code.
- xvi. The contractor will be responsible for submitting all paperwork required by the Minnesota Department of Health following the installation of each monitoring well.
- xvii. Restoring the site to the conditions previous to the well installation shall be the responsibility of the contractor.
- xviii. Between-site decontamination of all pertinent well drilling equipment is required and is the responsibility of the contractor.
- c. Diagrammatic representation of well drilling specifications
 - i. The following diagram is to be used only in conjunction with the associated written specifications.
 - ii. Where a discrepancy exists, the written specifications shall take precedence over the diagrammatic specifications

Diagram for well construction specifications for wells drilled in unconsolidated geologic material. Adopted from State of Oregon DEQ Guidance Document.



Appendix A2: Results of inorganic analyses on water samples from springs in PMR 9.

Inorganic Analyte	County	# of Samples	Minimum (mg/L)	Median (mg/L)	75% (mg/L)	90% (mg/L)	Maximum (mg/L)
Nitrate/Nitrite-nitrogen (mg/L)	Fillmore	56	2.95	9.46	11.50	13.17	16.00
	Houston	8	6.38	6.73	6.97	7.07	7.08
	Winona	8	3.22	4.02	4.07	4.11	4.12
	Wabasha	16	4.26	4.58	4.79	4.93	5.01
	Goodhue	8	5.75	6.62	7.68	7.85	7.90
Orthophosphorus (mg/L)	Fillmore	40	0.009	0.028	0.047	0.058	0.112
	Houston	8	0.008	0.018	0.023	0.025	0.025
	Winona	0	-	-	-	-	-
	Wabasha	16	0.010	0.021	0.030	0.035	0.036
	Goodhue	8	0.009	0.019	0.023	0.026	0.027
Total Phosphorus (mg/L)	Fillmore	40	0.036	0.061	0.078	0.251	9.450
	Houston	8	0.024	0.031	0.033	0.036	0.037
	Winona	0	-	-	-	-	-
	Wabasha	16	0.024	0.036	0.043	0.047	0.050
	Goodhue	8	0.023	0.031	0.033	0.035	0.035
Total Suspended Solids (mg/L)	Fillmore	40	nd	0.75	9.70	210.50	16,000.00
	Houston	8	nd	nd	0.20	0.27	0.30
	Winona	0	-	-	-	-	-
	Wabasha	16	nd	nd	0.30	0.89	3.00
	Goodhue	8	nd	0.55	3.80	4.91	5.30
Turbidity (NTU)	Fillmore	40	0.276	0.909	8.04	166.9	4,640.0
	Houston	8	nd	0.149	0.323	0.399	0.405
	Winona	0	-	-	-	-	-
	Wabasha	16	nd	nd	0.150	0.650	0.662
	Goodhue	8	nd	0.381	0.615	0.960	1.030