



2014-2015 Private Well Pesticide Sampling Project Report

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1. Introduction/Project Purpose

This report is intended to summarize the sampling events conducted by the Minnesota Department of Agriculture (MDA) as part of the Private Well Pesticide Sampling (PWPS) Project for the 2014 and 2015 sampling seasons. At the direction of the Minnesota Legislature (HF1183 Article 2, Sec. 3, part b), the MDA initiated the PWPS Project to evaluate pesticide presence and magnitude in private residential drinking water wells when nitrate nitrogen (nitrate) is detected in a water quality samples as part of the [MDA Township Testing Program \(TTP\)](#).

The primary goal of the PWPS Project is to provide information to homeowners and the general public related to the presence of pesticides in private drinking water wells located in geologically sensitive areas with row crop agriculture. The study was in part motivated by the report [“Analysis of Co-occurrence of Nitrate Nitrogen and Pesticides in Minnesota Groundwater”](#) which investigated the link between nitrate and pesticides in wells from around the state (MDA, 2006). Results suggested that mobile pesticides are more likely to be detected in a well when nitrate concentrations increase beyond natural background levels. The PWPS Project will provide additional data for the evaluation of the relationship that exists between nitrate and pesticide concentrations in private drinking water wells.

As part of the PWPS Project, groundwater samples were analyzed at environmentally relevant concentrations for pesticides and their breakdown products from wells previously sampled for nitrate as part of the TTP. Wells were selected from townships with at least 30 percent of the area characterized with vulnerable groundwater and at least 20 percent of the area in row crop production. All homeowners with a previous nitrate detection had the opportunity to have their well tested for nitrate and pesticides by MDA staff, as part of the PWPS Project. As such, the population of wells sampled as part of the PWPS Project was voluntary and not randomized.

The MDA began sampling for the PWPS Project in Dakota County in September of 2014. This was referred to as the PWPS Pilot Project and was intended to serve as a model for the implementation of the full scale PWPS Project in 2015. The results from the PWPS Pilot Project are included in this report. The sampling techniques used during the PWPS Pilot Project were refined and fully implemented in eight counties during the monitoring season (May-October) of 2015 (see [2016 work plan](#)). The 2015 sampling included additional sampling in Dakota County as well as sampling in Benton, Morrison, Olmsted, Stearns, Sherburne, Wadena and Washington Counties. The PWPS Project will continue to be implemented in phases over the next several years assuming continued funding. Each phase will include an evaluation of selected private wells that were previously sampled for nitrate as part of MDA TTP. Figure 1 identifies townships that were sampled and that will be sampled over the next several years.

This report will focus on the pesticide sampling portion of the PWPS Project. A more comprehensive review of the nitrate results along with specific county geologic conditions and well characteristics will be summarized in county based TTP Summary Reports that will be completed by the MDA.

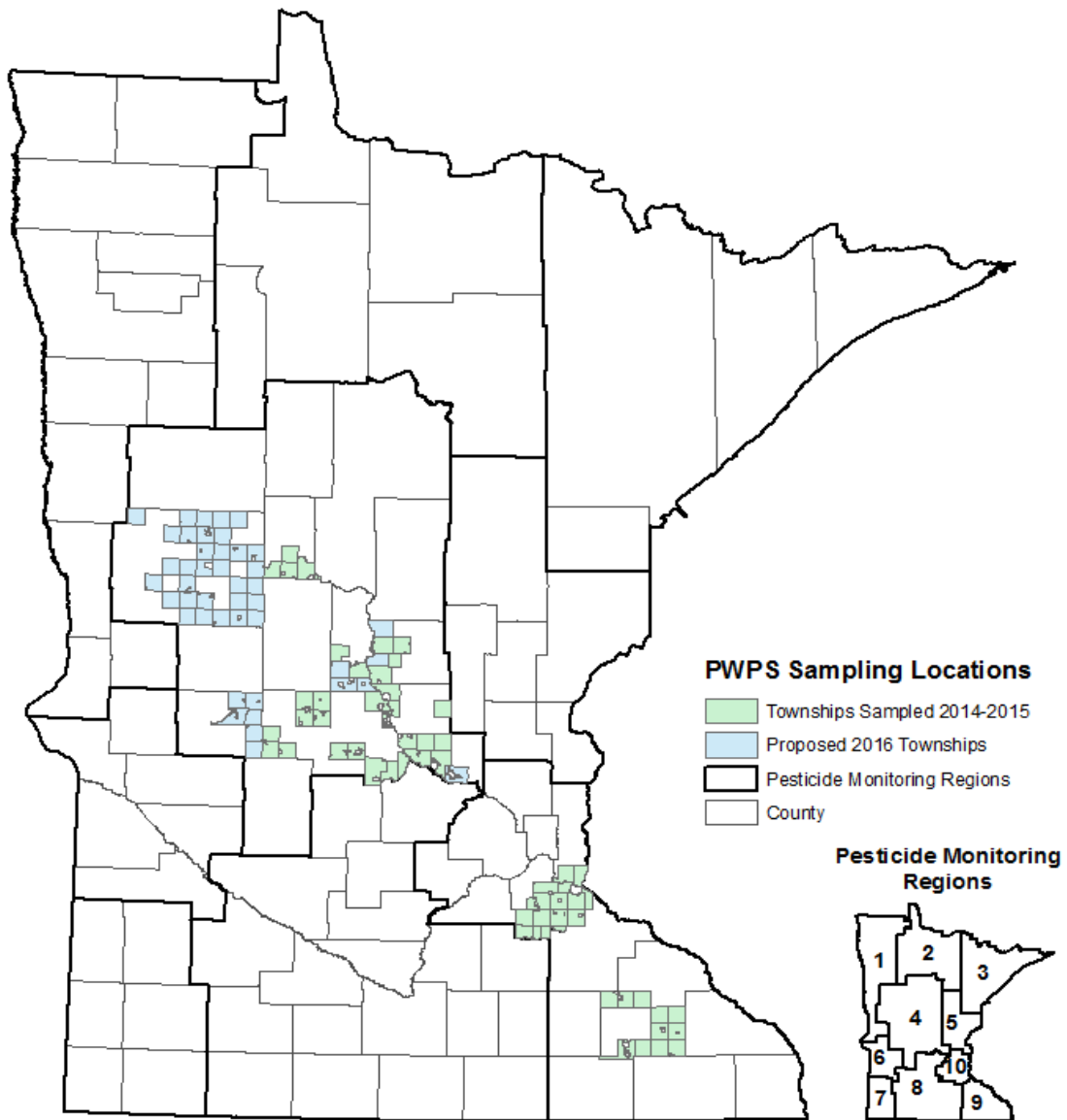


Figure 1. PWPS Project townships sampled through 2015 (green) and townships slated for sampling in 2016 (blue).

2. Project Methods

Wells were selected from townships that have at least 30 percent of the area classified as vulnerable to groundwater contamination and have a minimum of 20 percent row crop production. All homeowners with private wells were offered the opportunity to sample their wells for nitrate as part of the TTP.

In an effort to stay consistent with the legislative intent, which specified “monitoring for pesticides when nitrates are detected,” the MDA elected to offer pesticide sampling to all private residential well owners who had participated in the TTP and had detectable concentrations of nitrate in their well water. Homeowners were sent a letter from the MDA explaining the PWPS Project and were required to return a Consent Form. The MDA staff then called the homeowners that responded to the letter to schedule a time for sample collection from an outside water faucet. With homeowner permission, samples were collected whether the homeowners were present or not.

Laboratory Selection and Contracting

The MDA Laboratory Services Division (MDA laboratory) indicated they were not able to accommodate the anticipated sample load from the PWPS Project due to other obligations and commitments. In addition, other Minnesota State agency labs (Minnesota Department of Health (MDH), Minnesota Pollution Control Agency (MPCA), and Minnesota Department of Natural Resources (DNR) were contacted prior to solicitation of outside contractors for the pesticide analysis, and those laboratories also indicated they were not able to perform the analyses required.

In May of 2014, a Request for Proposals (RFP) was generated and posted to the State Register to solicit outside laboratory contractors to perform the pesticide analyses in the PWPS Project. Minnesota Valley Testing Laboratories (MVTL) from New Ulm, Minnesota was the only laboratory to bid on the RFP posted by the MDA.

The MVTL analytical list was limited in comparison to the MDA laboratory routine analysis of 137 pesticide compounds. It was comprised of 22 pesticide related compounds (Table 1). The MVTL analysis included two of the primary atrazine degradates that would most likely contribute to drinking water risk in Minnesota. The MVTL analysis did not include all of the compounds requested in the RFP and had higher method reporting limits. In particular, the MVTL proposal did not include degradates of acetochlor, alachlor, metolachlor or metribuzin. After a review of historical monitoring data from the MDA ambient monitoring program, the MDA determined that the presence of a parent pesticide compound at the MVTL reporting level (0.5 ppb) would be a useful screen for the presence of pesticides and their degradates at concentrations of potential drinking water concern. MVTL was awarded the contract based on this evaluation.

Table 1. MVTL analytes and method reporting limits (MRLs) for the PWPS Project.

Pesticide Analyte	MRL (µg/L)	Reference Value (µg/L)	Pesticide Analyte	MRL (µg/L)	Reference Value (µg/L)
Acetochlor	0.5	9.0*	Metolachlor	0.5	300*
Alachlor	0.5	5.0*	Metribuzin	0.5	10*
Atrazine	0.5	3.0*	Pendimethalin	0.5	40.0***
Deisopropylatrazine	0.5	3.0*	Phorate	0.3	1.0***
Desethylatrazine	0.5	3.0*	Propachlor	0.5	15.0***
Chlorpyrifos	0.5	0.6**	Prometon	0.5	10.0***
Cyanazine	0.2	1.0*	Propazine	0.5	10.0**
Dimethenamid	0.5	300*	Simazine	0.5	4.0*
EPTC	0.5	40**	Terbufos	0.2	0.1***
Ethalfuralin	0.5	10***	Triallate	0.5	10.0***
Fonofos	0.5	0.5***	Trifluralin	0.5	9.0***

*Health Risk Limit

**Health Based Values

***Risk Assessment Advice/Rapid Assessment

Sampling Methods

All wells sampled as part of the PWPS Project included analysis for pesticides and nitrate. In addition, wells in Morrison, Dakota and Sherburne Counties were sampled for redox parameters (total dissolved iron, total dissolved manganese and sulfate) as part of a related project investigating the geochemical conditions and denitrification potential within the sampled aquifers. This redox project was initiated in cooperation with the United States Geological Survey (USGS).

MDA staff collected all of the samples for the PWPS Project in Dakota County in 2014. The MDA hired four temporary Hydrologists (PWPS Hydrologists) to collect the majority of the groundwater samples during the 2015 sampling season.

The PWPS Hydrologists also conducted the following activities:

- Contacted the participating homeowners and schedule the sampling event,
- Coordinated the drop off of sampling supplies and the pick-up of samples with MVTL,
- Maintained and decontaminated the sampling equipment and vehicle; and,
- Recorded, stored and maintained any pertinent sampling records.

A Standard Operating Procedure (SOP) was developed to standardize sample collection protocols. It was utilized for the 2015 PWPS Project sampling. This SOP was modified to include the redox parameters sampled in Morrison, Dakota and Sherburne Counties as part of the possible denitrification project with USGS. Samples were collected from outside water faucets after allowing the water to run for a minimum of 15 minutes. Stabilization parameters (pH, temperature, dissolved oxygen and conductivity) were measured during well purging and recorded on field log forms. A MVTL courier dropped off supplies and picked up samples from MDA satellite offices following chain of custody procedures. The number of

weekly deliveries and pick-ups was determined based on the sampling schedule and coordinated with the PWPS Hydrologist. All samples were cooled after collection. When ready for transport, they were placed on ice in coolers and submitted to MVTL by courier, usually within a few days of collection.

The Highly Pathogenic Avian Influenza (HPAI) virus, which can harm poultry, was present in several Minnesota counties in 2015. To prevent the potential spread of HPAI, the MDA asked well owners if there were poultry present at their property and implemented biosecurity measures outlined in the Modified 2015 Avian Flu MDA Field Staff Biosecurity Guidance Private Well Water Sampling Protocol if poultry were present. The MDA did not sample locations where HPAI had been detected. Overall, 93 wells were sampled at locations where poultry were present.

In addition to collecting the sample, the homeowners were asked survey questions outlined in the Well Information and Potential Nitrate Source Inventory Form. These questions were asked over the phone or in person. If the homeowner was not present, the form was completed as thoroughly as possible by the PWPS Hydrologist. This data was recorded and was entered into the PWPS Project database.

Data Management

Letters documenting the analytical results from the 2014 and 2015 PWPS Project were sent to the participating homeowners. The letters included a cover letter briefly explaining the results, the laboratory analytical reports and a fact sheet that described the sampling process and potential health effects. Homeowners who had pesticides detected in their water sample were contacted prior to the letter being sent and were sent a table that compared their analytical results to the Health Risk Limit (HRL) or other health-based drinking water reference values.

Sample results from the PWPS Project are currently being stored as hard copies, pdfs and in Excel spreadsheets. The MDA is developing other options for long-term data storage, including possible migration to the statewide water quality data management system (EQuIS) administered by MPCA. A data management plan is currently being developed for the PWPS Project. It should be noted that the land owner and well location information will be protected as private data by the MDA at locations where pesticides were collected as required by Minnesota statute 18B.10.

Analysis and Reporting

Data generated from self-selection (volunteer) surveys are generally not conducive to analysis with common advanced statistical methods as the inclusion probability of each sample is undeterminable. Therefore, data analysis was limited to basic statistical summaries. Basic summary information computed and reported included: number of samples collected, the chemicals detected, range of measured concentrations, comparison with health-based standards and the frequency of detection.

This report will focus on the pesticide sampling portion of the PWPS Project. A more comprehensive review of the nitrate results along with specific county geologic conditions and well characteristics will be summarized in County based [Township Testing Summary Reports](#). Because of limited detection of pesticides, co-occurrence between nitrate and pesticides was not evaluated as part of this report.

3. PWPS Project Sampling Results

Groundwater samples analyzed in the PWPS Project were collected from locations where nitrate was detected as part of the MDA TTP. 3,709 homeowners in Benton, Dakota, Morrison, Olmsted, Sherburne, Stearns, Wadena and Washington counties had nitrate detections in samples collected as part of the initial TTP as presented in Table 2. Invitation letters were sent to all of these homeowners, beginning

with locations in Dakota County, in August of 2014. The letter from the MDA explained the PWPS Project and required homeowners to return a Consent Form to be included in the project.

Fifty-two percent (1,946) of the homeowners contacted requested pesticide sampling (Table 2). Participation varied depending on the county. Metro area counties such as Dakota County (58 percent) and Washington County (57 percent) appeared to have a higher participation rate than rural counties like Wadena (37 percent) and Morrison (49 percent).

Table 2. Homeowner participation by county for the 2014 through 2015 sampling season.

County	Letters Mailed	Response	Percent Response	Wells Sampled 2014/2015	Percent Wells Sampled
Benton	307	153	50%	145	47%
2014 Dakota Pilot Project	410	267	65%	267	65%
Dakota	461	268	58%	248	54%
Morrison	191	94	49%	91	48%
Olmsted	414	182	44%	183	44%
Sherburne	596	320	54%	301	50%
Stearns	905	443	49%	394	44%
Wadena	112	42	37%	39	35%
Washington	313	177	57%	173	55%
Totals	3,709	1,946	52%	1,841	47%

A total of 1,841 wells or 47 percent of the 3,709 homeowners with nitrate detections were sampled from 2014 through 2015. Approximately 99 of the homeowners that initially agreed to have their well sampled later chose not to. In addition, the MDA was unable to sample 24 wells that were scheduled to be sampled in 2015 due to time constraints. These wells were to be sampled by the MDA in 2016.

A total of 151 Quality Assurance and Quality Control (QA/QC) groundwater samples were collected and submitted to MVTL for their internal QA/QC program during the 2014 and 2015 sampling seasons. This represents approximately eight percent of the total samples collected from private drinking water wells (1,841 samples).

Pesticides were detected above the MVTL MRL's reporting limits in six of the private drinking water wells sampled (0.3 percent). The wells with pesticide detections were located in a single well from Benton, Olmsted, Sherburne, Stearns County and two wells in Washington County. When pesticides were detected in a well, a pesticide confirmation sample was collected and sent to MVTL and a duplicate was sent to the MDA laboratory for low level pesticide analysis. In addition to lower reporting limits, the MDA laboratory has the ability to analyze for a larger list of pesticides and degradates than MVTL.

The MVTL analysis indicated the presence of metolachlor in four of the wells, atrazine in one well and atrazine and desethylatrazine in the remaining well (Tables 3 and 4). Confirmation samples analyzed by the MDA laboratory generally confirmed MVTLs initial analytical results. Samples analyzed by the MDA laboratory identified a total of 17 different pesticides and/or pesticide degradates in the wells sampled. No samples exceeded drinking water standards for any of the detected pesticides or degradates. However, nitrate concentrations exceeded the 10 mg/L HRL in five of the six wells where pesticides were detected.

A review of MDA files indicates that there are no potential point sources and agricultural chemical spills located within one mile of any of the pesticide detections. Two abandoned agricultural chemical sites and an active agricultural chemical facility were located within approximately 1.3 miles of the Benton County well. However, it is unlikely that these locations were the cause of the pesticide detections based on the distance to the potential source areas, a possible groundwater boundary (Platte River) between the active facility and a clean well between the impacted well and abandoned facilities. The Sherburne County well is located approximately 1.4 miles north of an active agricultural chemical facility in MDA's Comprehensive Site Investigation Program. However, the well is likely up gradient from the facility and groundwater is also separated by a groundwater boundary (St. Francis River).

There does not appear to be a correlation between the depth of the wells and pesticide detections. The wells with pesticide detections varied from a shallow (< 30 foot) sand point well set in glacial outwash in Sherburne County, a 50 foot deep well set directly above bedrock in Benton County to a 200 foot deep well, finished in bedrock, in Washington County. The MDA was unable to obtain well information from the County Well Index or from the homeowner for the Olmsted County, Stearns County and one of the Washington County wells.

In addition, 577 wells in Morrison, Dakota and Sherburne Counties were sampled for redox parameters (total dissolved iron, total dissolved manganese and sulfate) as part of a related project investigating the geochemical conditions and denitrification potential within the sampled aquifers. Approximately 18 percent of the 577 redox samples collected exceeded the 100 ug/L MDH risk assessment advice for manganese (Table 5). None of the sulfate samples exceeded the health standard for sulfate and there currently is no standard for iron.

Table 3. Pesticide Analytical Results for detected pesticides and related degradates in Benton, Olmsted and Sherburne Counties. *The reference value presented represents the lowest applicable drinking water human health based standard or benchmark available.*

Analytes	Reference Value	Benton County			Olmsted County			Sherburne County		
		MVTL Sample 1 (ug/L)	MVTL Sample 2 (ug/L)	MDA Sample 3 (ug/L)	MVTL Sample 1 (ug/L)	MVTL Sample 2 (ug/L)	MDA Sample 3 (ug/L)	MVTL Sample 1 (ug/L)	MVTL Sample 2 (ug/L)	MDA Sample 3 (ug/L)
Acetochlor ESA	300	---	---	0.592	--	--	0.412	--	--	0.0388
Acetochlor OXA	100	--	--	<0.0333	--	--	<0.0333	--	--	<0.0333
Alachlor ESA	70	--	--	0.64	--	--	0.588	--	--	<0.0416
Alachlor OXA	70	--	--	<0.0333	--	--	<0.0333	--	--	<0.0333
Atrazine	3	0.7	0.8	0.727	0.6	<0.5	0.533	<0.5	<0.5	0.0319
Desethylatrazine	3	0.5	<0.5	0.559	<0.5	<0.5	0.354	<0.5	<0.5	<0.050
Deisopropylatrazine	3	<0.5	<0.5	<0.150	<0.5	<0.5	0.274	<0.5	<0.5	<0.150
DEDI Atrazine	3	--	--	0.125	--	--	0.485	--	--	<0.05
Hydroxyatrazine	20	--	--	0.0126	--	--	0.0079	--	--	<0.0067
Bentazon	30	--	--	<0.005	--	--	<0.005	--	--	<0.005
Dimethenamid ESA	300	--	--	<0.0067	--	--	0.0079	--	--	<0.0067
Metalaxyl	20	--	--	0.083	--	--	<0.0083	--	--	<0.0083
Metolachlor	300	<0.5	<0.5	<0.025	<0.5	<0.5	0.128	0.6	0.6	0.553
Metolachlor ESA	800	--	--	2.58	--	--	1.13	--	--	0.173
Metolachlor OXA	800	--	--	0.975	--	--	0.115	--	--	0.133
Metribuzin	10	<0.5	<0.5	0.128	<0.5	<0.5	<0.075	<0.5	<0.5	<0.075
Metribuzin DADK	10	--	--	1.85	--	--	<0.5	--	--	<0.5

*-- = not sampled

Table 4. Pesticide Analytical Results for detected pesticides and related degradates in Stearns and Washington Counties. *The reference value presented represents the lowest applicable drinking water human health based standard or benchmark available.*

Analytes	Reference Value	Stearns County			Washington County #1			Washington County #2		
		MVTL Sample 1 (ug/L)	MVTL Sample 2 (ug/L)	MDA Sample 3 (ug/L)	MVTL Sample 1 (ug/L)	MVTL Sample 2 (ug/L)	MDA Sample 3 (ug/L)	MVTL Sample 1 (ug/L)	MVTL Sample 2 (ug/L)	MDA Sample 3 (ug/L)
Acetochlor ESA	300	-	-	<0.03	-	-	0.104	-	-	0.166
Acetochlor OXA	100	-	-	<0.0333	-	-	0.0746	-	-	0.117
Alachlor ESA	70	-	-	0.776	-	-	0.301	-	-	0.245
Alachlor OXA	70	-	-	<0.0333	-	-	0.109	-	-	0.0689
Atrazine	3	<0.5	<0.5	<0.030	<0.5	<0.5	0.0637	<0.5	<0.5	0.0484
Desethylatrazine	3	<0.5	<0.5	<0.050	<0.5	<0.5	0.0706	<0.5	<0.5	0.0576
Deisopropylatrazine	3	<0.5	<0.5	<0.150	<0.5	<0.5	<0.150	<0.5	<0.5	<0.150
DEDI Atrazine	3	-	-	<0.05	-	-	<0.05	-	-	<0.05
Hydroxyatrazine	20	-	-	0.0236	-	-	<0.0067	-	-	<0.0067
Bentazon	30	-	-	<0.005	-	-	0.0057	-	-	0.0051
Dimethenamid ESA	300	-	-	<0.0067	-	-	<0.0067	-	-	<0.0067
Metalaxyl	20	-	-	<0.0083	-	-	<0.0083	-	-	<0.0083
Metolachlor	300	0.7	0.6	0.478	1.7	1.1	2.27	2.9	2.9	2.56
Metolachlor ESA	800	-	-	1.61	-	-	3.03	-	-	4.7
Metolachlor OXA	800	-	-	0.165	-	-	1.68	-	-	2.57
Metribuzin	10	<0.5	<0.5	<0.075	<0.5	<0.5	<0.075	<0.5	<0.5	<0.075
Metribuzin DADK	10	-	-	<0.5	-	-	<0.5	-	-	<0.5

*- = not sampled

Table 5. Manganese Results from Dakota, Morrison and Sherburne Counties.

County	Wells Sampled Redox Parameters	Manganese Detections	Percent Detected	Manganese Exceedances	Percent Exceeded
Dakota	248	54	21.8	12	4.9
Morrison	28	9	32.1	3	10.7
Sherburne	301	153	50.8	89	29.4
Totals	577	216	37.4	104	18

4. Recommendations

After the 2015 sampling season was complete, the MDA reviewed the analytical results and determined that additional pesticide analysis and lower reporting limits would be desirable to further the understanding of pesticide presence in private drinking water wells. As such, the MDA posted an RFP with the intent of expanding the analytical list and achieving lower reporting limits for the 2016 through 2017 sampling seasons. The MDA identified a list of 52 potential pesticides that were either detected during the last five years as part of the routine ambient monitoring program as well as several neonicotinoid insecticides to include in the 2016 RFP. The 2016 RFP list was subsequently expanded to include 127 pesticide analytes currently evaluated by the MDA laboratory. Laboratories were evaluated based on their experience and qualifications as well as their ability to achieve the laboratory analytical criteria listed in the RFP. A laboratory in California was selected and a contract for the 2016 and spring 2017 season has been executed.

MDA plans to sample wells in Morrison, Ottertail, Sherburne and Pope Counties during the 2016 sampling season. It is anticipated that approximately 935 wells will be sampled in these locations. The locations of samples collected beyond 2016 will be determined by the areas that are sampled for nitrate as part of the TTP. MDA also plans to re-sample many of the wells sampled in 2014 and 2015 using the new pesticide analytical method.

5. References

Minnesota Department of Agriculture, 2006. Analysis of the Co-occurrence of Nitrate-Nitrogen and Pesticides in Minnesota Groundwater, online PDF file accessed on 6/1/2016, <http://www.mda.state.mn.us/Global/MDADocs/chemfert/reports/co-occur-rev-05-10-06.aspx>