DEPARTMENT OF AGRICULTURE

2018 Private Well Pesticide Sampling Work Plan

3/22/2018

Funding Acknowledgement

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Section 1: Project Organization

Table 1: Project Organization Chart

Name	Title/Responsibility
Bill VanRyswyk	Monitoring and Assessment Unit Supervisor
Larry Gunderson	Fertilizer Technical Unit Supervisor
Jeff Paddock	Hydrologist: Project Lead & Technical Management
Kim Kaiser	Hydrologist: Technical Management
Brennon Schaefer	Hydrologist: Data Analysis & Technical Assistance
Nikol Ross	Hydrologist: Field Management & Technical Assistance
Dylan Timm, Adam McCollough	Hydrologists: Data Management & Assistance
Jaime Nielsen – St. Paul, Ryan Meyer – Staples/St. Cloud, Ben Bruening – Rochester, Lauren Bammert – Mankato	Field Hydrologists: Sampling, Data Entry &Technical Support
Leo Raab	Weck Laboratories: Lab Project Supervisor
Augustin Pierri	Weck Laboratories: Lab Analyst
Chris Samatmanakit	Weck Laboratories: Lab Coordination
Kathy Reynolds	MDA Laboratory Services Division Supervisor, Technical Assistance
Kris Gronfor, Brian Miller	MDA Laboratory Services, QA/QC Technical Assistance

Section 2: Project Purpose

At the direction of the Minnesota Legislature (Minn. Stat.; 2013 Minn. Laws Chap. 137 Art. 2 Sec. 3(b)), the Minnesota Department of Agriculture (MDA) began evaluating pesticide presence and magnitude in private residential drinking water wells in Dakota County in September of 2014 as part of the Private Well Pesticide Sampling (PWPS) Pilot Project. The PWPS Pilot Project served as a model for the implementation of the PWPS

Project throughout the state. This Work Plan will outline the steps and procedures that will be taken to implement the PWPS Project during the 2018 sampling season.

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. The sampled wells are located in areas that are geologically sensitive and have significant row crop agriculture. This will be achieved by analyzing water samples at environmentally relevant concentrations for commonly used pesticides and their primary metabolites (degradates).

The PWPS Project is funded primarily with Clean Water Land and Legacy Act funding, with supplemental funding from MDA's dedicated pesticide funds collected from the sale of pesticides. The PWPS Project is currently funded through June 30, 2019, and will continue through 2020 if funding beyond that date is procured. Each phase will include an evaluation of selected private wells that were previously sampled for nitrate-nitrogen (nitrate) as part of the MDA Township Testing Program (TTP).

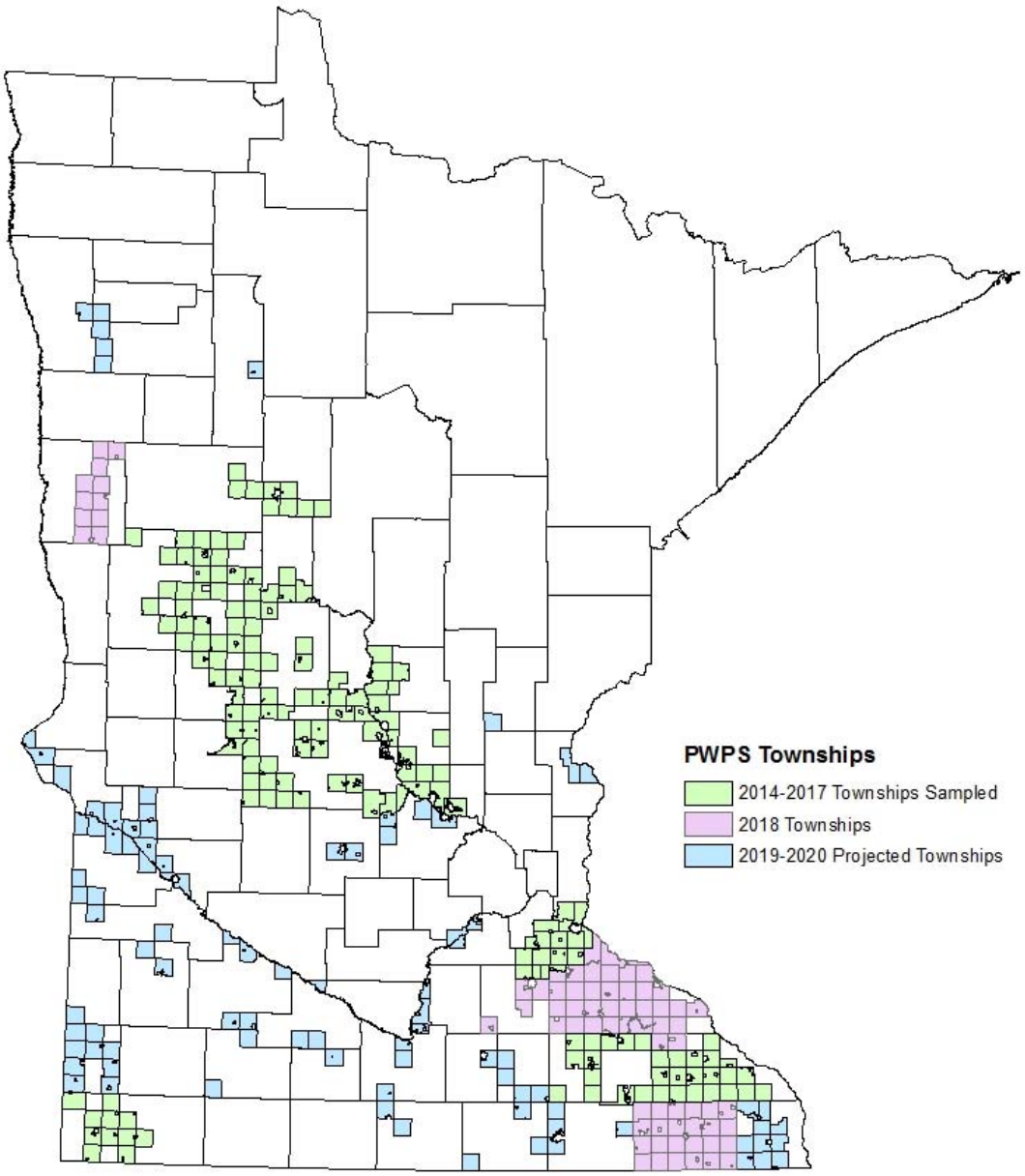
Objectives for the water quality data generated by the PWPS Project include:

- Provide useful public health information to homeowners participating in the TTP that had nitrate detected in their wells.
- Evaluate the relationship between pesticide and nitrate presence in private wells (co-occurrence). This may prove useful for determining if there are nitrate concentration thresholds at which pesticide sampling would be advised.
- The PWPS Project will provide the MDA with additional information related to the extent and magnitude of pesticide contamination in deeper aquifers and allow for a comparison and assessment with shallow groundwater pesticide data collected from the MDA's ambient monitoring well network. This may prove useful for estimating pesticide degradation rates over time.

Section 3: Project Scope Description & Methods

The MDA will continue to evaluate commonly used pesticide presence and magnitude in private residential drinking water wells throughout the state in 2018. The MDA intends to sample wells in five new counties in 2018 (Clay, Fillmore, Goodhue, Rice and Wabasha) and will complete well sampling in two counties (Becker and Dodge) that were not completed in 2017 due to time constraints (Figure 1). The MDA will continue to resample wells that had been previously sampled for pesticides during the 2014 and 2015 seasons using the updated analytical method. Wells initially sampled in 2014 and 2015 were analyzed for a list of twenty two pesticides and will be reanalyzed for at least 125 pesticides as time and budget allow. The MDA intends to resample Wadena County in 2018 and additional counties may be resampled depending on budget and time constraints.

Figure 1: Townships that have been sampled and townships that are projected to be sampled as part of the PWPS Project.



Participation from well owners will be solicited from a population of wells where nitrate has been detected in samples analyzed as part of the TTP. Further discussion of the TTP project can be found at the following link: (http://www.mda.state.mn.us/protecting/cleanwaterfund/gwdwprotection/townshiptesting.aspx).

The specific tasks associated with this Work Plan include:

- **Well Selection** – Identify wells to be targeted for sampling based on initial TTP nitrate results and homeowner interest;
- **Laboratory Contracting** – The current laboratory contract with Weck Laboratories expires on December 31, 2018. Ensure the laboratory is capable of analyzing for the appropriate pesticides and achieving the target reporting limit concentrations similar to the MDA Laboratory Services Division (MDA Laboratory);
- **Laboratory QA/QC Protocols** – Develop and follow appropriate laboratory QA/QC procedures for evaluating the contract laboratory and ensuring sample collection and handling integrity;
- **Well Sampling Locations and Methods** – Description of when wells will be resampled and circumstances when confirmation samples will be collected;
- **Collect samples and submit to contract laboratory** – Collect samples from private wells following appropriate sample collection methods;
- **Data Management** – Coordinate data management of the pesticide results, location, and well information generated during the project;
- **Homeowner Reporting** – Coordinate reporting and response letters to homeowners;
- **Data Analysis** – Identify and coordinate appropriate analyses of the pesticide data, and associated information, generated during this project; and,
- **Project Reporting** – Report on the results of the project annually to the legislature, as well as upon the completion of the project.

This Work Plan will present the specific actions associated with these tasks in the following sections.

Section 3.1: Well Selection

In an effort to stay consistent with the legislative intent, which specified "monitoring for pesticides when nitrates are detected," the MDA will offer pesticide sampling to all private residential well owners who had participated in the initial TTP sampling and had any amount of nitrate detected in their well water.

The MDA conducted the PWPS Project in nineteen counties in 2014 through 2017. During the 2014 through 2017 sampling seasons, approximately 7,400 homeowners who had nitrate detected in their wells were sent a letter from the MDA explaining the PWPS Project and asking if they would like to participate. Homeowners who chose to participate were required to return a consent form. This consent form must be signed and returned to the MDA by the participant. The consent form also explains how the land owner information will be protected as private data by the MDA.

The well selection protocol used during the 2014 through 2017 sampling seasons will continue to be used during the 2018 sampling season. Approximately 4,100 wells were sampled in the 2014 through 2017 sampling seasons. The MDA estimates that approximately 1,622 new wells will be sampled in the 2018 sampling season. In addition, the MDA will resample approximately 27 wells in Wadena County that were previously sampled for

MDA List 1 pesticides in 2015. Additional counties that had previously been sampled for MDA List 1 pesticides may be reanalyzed in 2018 as time and budget allow.

Section 3.2: Laboratory Contracting

The MDA laboratory indicated they were not able to accommodate the anticipated sample load from the PWPS Project due to other obligations and commitments. 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 initial RFP posted by the MDA. The MVTL proposal was limited to the MDA List 1 pesticides, which was comprised of 22 pesticides and pesticide degradates. All of the pesticides analyzed during the 2014 and 2015 sampling season were analyzed for MDA List 1 pesticides.

Due, in part, to the limited pesticide detections measured during 2014 and 2015 sampling seasons, the MDA elected to advertise another RFP in an attempt to find a laboratory capable of analyzing additional pesticides and pesticide degradates at lower reporting limits similar to the MDA Laboratory. Four laboratories responded to the RFP and Weck Laboratories was chosen to perform the analysis during the 2016 through 2018 sampling seasons.

Weck Laboratories (Weck) is capable of analyzing for the majority of the pesticides on the current MDA Laboratory target analyte list at similar reporting levels. The final list of 125 pesticides that will be analyzed by Weck is presented in Appendix A. All of the samples collected during the 2018 sampling season will be analyzed by Weck. As discussed in Section C below, the MDA Laboratory will be utilized to evaluate the performance of Weck through the evaluation of fortified samples and split samples to confirm pesticide concentrations in the initial round of testing by Weck.

Section 3.3: Laboratory Quality Assurance & Quality Control (QA/QC)

Five percent of the total samples collected will be submitted as field duplicates and five percent will be submitted as field blanks. The field duplicates and blanks collectively will be referred to as QA/QC samples and will be submitted to Weck as blind samples. Quality Control Reports, including surrogate recovery, Laboratory Control Sample (LCS) and matrix spike recovery and QA/QC narratives, will be included with all of the analytical results received from Weck Laboratories. The MDA will review the QA/QC information from Weck using methods documented in the MDA's *Laboratory Data Review Guidance: Guidance Document 29* and identify any irregularities.

If the analytical results indicate irregularities, or if the MDA determines it is necessary, the MDA Laboratory will be utilized to provide QA/QC review of quality control information provided by Weck, including an evaluation of the following:

- Calibration curve (to include a minimum of 5 points);
- Lab blanks (including method blank);
- Surrogates;

- LCS and a LCS Duplicate; and,
- Confirmation criteria of detected analytes.

The MDA Laboratory will also be used to prepare fortified samples for submission to Weck. The fortified samples will contain known quantities of pesticides that will be submitted to Weck as blind routine samples. The MDA Laboratory will also be used to analyze confirmation split samples if initial Weck sample results indicate abnormally high or unusual pesticide detections. Confirmation samples are discussed in greater detail in Section 3.5 below.

Section 3.4: Well Sampling Locations & Methods

Private well groundwater samples will be collected in 2018 from locations where nitrate was detected as part of the TTP. Based on previous responses, the MDA estimates that approximately 49.5 percent of the homeowners that receive invitation letters will accept the offer to have their wells sampled as part of the PWPS Project. There were 3,249 nitrate detections in the five counties sampled as part of the Township Testing Program in 2017. With an anticipated 49.5 percent response rate, the MDA anticipates that there will be approximately 1,608 new locations sampled for pesticides (Table 2).

In addition, the MDA will sample approximately 11 wells in Becker and Dodge Counties that were not sampled in 2017 and will resample approximately 29 wells in Wadena County that were sampled by the MDA in 2015. This will bring the estimated total to approximately 1,649 wells sampled in 2018; with QA/QC samples included, the total sample number rises to 1,813 samples as presented in Table 2.

Table 2- Projected Samples Table.

County	TTP Nitrate Detections	2015 Pesticide Samples	Expected Response Rate	Projected Wells	QA/QC Samples	Total Samples
Becker Carryovers	--	--	--	2	0	2
Dodge Carryovers	--	--	--	9	0	9
Clay	67	--	49.5%	33	3	36
Fillmore	920	--	49.5%	455	46	501
Goodhue	1,212	--	49.5%	600	60	660
Rice	160	--	49.5%	79	8	87
Wabasha	890	--	49.5%	441	44	485
Wadena Resamples	--	39	75.0%	30	3	33
Total	**3,249**	**39**	**--**	**1,649**	**164**	**1,813**

All of the samples will be collected by MDA field hydrologists. The field hydrologists will be based in St. Paul and MDA satellite offices in Staples/St.Cloud, Mankato and Rochester. The proximity of the MDA office to the county to be sampled will determine which field hydrologist will sample individual counties. The counties will be sampled individually and at a township level by the hydrologists, if possible, to avoid confusion and increase efficiency.

The field hydrologists will also conduct the following activities:

- Contact the participating homeowners and schedule the sampling event;
- Coordinate the shipping of samples with the laboratory;
- Maintain and decontaminate the sampling equipment and vehicle;
- Record, store and maintain any pertinent sampling records; and,
- Stay in close contact with the MDA project team.

A Standard Operating Procedure (SOP) was developed to standardize sample collection protocols and will be utilized for the 2018 PWPS Project sampling season. Samples will be 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) will be measured during purging and recorded along with sample information. All field data will be recorded in electronic on field data acquisition log forms. The samples will then be placed in an iced cooler during each day's sampling activity, transported back to the respective MDA office at the end of each day, and stored in MDA refrigerators until they are shipped to Weck Laboratories in California.

In addition to collecting water samples, the field hydrologists will ask the homeowner survey questions. This data will be recorded and entered into the project database. If the homeowner is not present or cannot be contacted, the form will be completed as thoroughly as possible by the MDA field hydrologist.

Section 3.5: Well Resampling/Confirmation Samples

The MDA will collect confirmation resamples from wells with elevated pesticide concentrations. A split sample will also be collected and submitted to the MDA Laboratory for confirmation. Private wells will be considered for pesticide resampling when the initial pesticide results indicate the following:

- **Elevated Concentrations**
  - Pesticide concentrations in the initial sample that exceed 50 percent of the health reference value (HRL, RAA, HBV, RA, MCL, etc.) for any pesticide(s).

- **Unique Detections**
  - When pesticides are detected that are considered unusual or unique with respect to results previously observed in samples analyzed as part of the PWPS project or MDA's ambient monitoring program. For example, the MDA may resample if a pesticide(s) or pesticide degradate(s) is detected in a pattern or frequency that is unexpected and may be indicative of a release or a localized problem. This sampling may occur even if concentrations are below 50 percent of the health reference value.

The MDA will also review records to determine if there may be a release associated with the elevated concentration(s). The presence of a release and the confirmation sample results will determine whether the MDA continues sampling the well or whether additional action is required. All elevated or unique detections as defined above will be discussed with the MDA Incident Response Unit (IRU) and/or the Minnesota Department of Health (MDH).

Section 3.6: Data Management

Sample results from the 2014 through 2017 PWPS Project are currently being stored in Excel spreadsheets. However, data migration to the statewide Environmental Quality Information System (EQuIS) database has started and will continue through the 2018 monitoring season. It is anticipated that all project water quality data will be in EQuIS by the end of 2018. It should be noted that the land owner personal information will be protected as private data by the MDA for all pesticide results, although the water quality results are considered public data. In general, location-based pesticide data will be aggregated at the township scale and made available as requested.

However MDA is currently evaluating modification of the consent form to include "consent" to release well location data with the pesticide water quality data. This would allow MDA to manage the pesticide and nitrate data in a similar fashion. Without "consent" from the property owner, well location information (MDA measured coordinates) is considered private or non-public data as it relates to the release of the pesticide water quality data.

Section 3.7: Homeowner Reporting

Letters documenting the analytical results from the 2018 PWPS Project sampling will be sent to the participating homeowners after results have been received and reviewed. The letters will include the analytical results from the nitrate and pesticide analyses, a copy of the laboratory analytical report, a copy of the *Nitrate in Groundwater* pamphlet (which provides information on the risks associated with nitrate in drinking water) and a factsheet that explains the results and provides additional information on water treatment systems and cumulative risk.

Section 3.8: Data Analysis

Data analysis will be limited to basic statistical summaries. Basic summary information to be computed and reported will include:

- Aggregate (at township scale to protect privacy);
- Basic statistic (median, 75th percentile, and 90th percentile concentration, and detection frequency) will be computed for the MDA's Pesticide Monitoring Regions or at the county scale;
- Pesticide co-occurrence with nitrate;
- Comparison with MDA ambient network pesticide results (shallow wells) at PMR scale; and
- Risk assessment (in coordination with the MDH).

Section 3.9: Project Reporting

The MDA will complete a report that discusses and characterizes the 2018 PWPS Project results. The report will focus on the pesticide presence, detection frequency and concentration magnitude for the counties evaluated. In addition, factsheets that describe the results will be developed for each county sampled in 2018.

2018 Private Well Pesticide Sampling Work Plan

Appendix 1

2018 Laboratory Analyte List

Weck Analysis		
Target Compound	Reporting Limit (ng/L)	Method
2,4,5-T	50	538
2,4,5-TP	50	538
2,4-D	10	538
2,4-DB	20	538
Acetamiprid	25	538
Acetochlor	30	538
Acetochlor ESA	30	538
Acetochlor OXA	33.3	538
Alachlor	30	538
Alachlor ESA	41.6	538
Alachlor OXA	33.3	538
Aldicarb Sulfone	15	538
Aldicarb Sulfoxide	50	538
AMPA	1000	547M
Atrazine	30	538
Azoxystrobin	10	538
Bensulfuron-methyl	16.7	538
Bensulide	250	538
Bentazon	10	538
Boscalid	50	538
Bromacil	30	538
Bromoxynil	25	538
Carbaryl	25	538
Carbendazim	10	538
Carbofuran	13.3	538
Chlorantraniliprole	50	538
Chlorimuron-ethyl	20	538
Chlorpyrifos	40	538
Chlorpyrifos Oxon	40	538
Clomazone	15	538
Clopyralid	41.6	538
Clothianidin	25	538
Cyanazine	25	538
Cyantraniliprole	100	538
Cyfluthrin	100	538
DEDI Atrazine	50	538
Deisopropylatrazine	25	538
Desethylatrazine	50	538
Diazinon	30	538
Diazinon Oxon	75	538
Dicamba	50	538
Dichlorprop	50	538

Weck Analysis		
Target Compound	Reporting Limit (ng/L)	Method
Dicrotophos	25	538
Difenoconazole	25	538
Dimethenamid	15	538
Dimethenamid ESA	6.7	538
Dimethenamid OXA	10	538
Dimethoate	50	538
Dinotefuran	25	538
Disulfoton Sulfone	20	538
Diuron	13.3	538
Ethofumesate	50	538
Flufenacet OXA	8.3	538
Flumetsulam	50	538
Flutriafol	10	538
Fluxapyroxad	10	538
Fonofos	15	538
Glyphosate	1000	547M
Halosulfuron-methyl	30	538
Hexazinone	10	538
Hydroxyatrazine	6.7	538
Imazamethabenz-acid	10	538
Imazamethabenz-methyl	5	538
Imazamox	13.3	538
Imazapic	10	538
Imazapyr	8.3	538
Imazaquin	16.7	538
Imazethapyr	6.7	538
Imidacloprid	20	538
Isoxaflutole	40	538
Linuron	20	538
Malathion	50	538
MCPA	5	538
MCPB	20	538
MCPP	50	538
Mesotrione	50	538
Metalaxyl	8.3	538
Metolachlor	25	538
Metolachlor ESA	10	538
Metolachlor OXA	10	538
Metribuzin	75	538
Metribuzin DA	25	538
Metribuzin DADK	500	538
Metribuzin DK	1000	538

Weck Analysis		
Target Compound	Reporting Limit (ng/L)	Method
Metsulfuron-methyl	23.3	538
Myclobutanil	10	538
Nicosulfuron	26.6	538
Norflurazon	20	538
Norflurazon-desmethyl	50	538
Oxadiazon	75	538
Oxydemeton-methyl	20	538
Parathion-methyl	100	538
Parathion-methyl Oxon	25	538
Pendimethalin	75	538
Phorate	25	538
Picloram	41.6	538
Picoxystrobin	50	538
Prometon	100	538
Prometryn	5	538
Propachlor	30	538
Propachlor ESA	30	538
Propachlor OXA	10	538
Propazine	25	538
Propiconazole	10	538
Pyraclostrobin	25	538
Pyroxasulfone	50	538
Saflufenacil	15	538
Sedaxane	75	538
Siduron	6.7	538
Simazine	75	538
Sulfometuron-methyl	8.3	538
Tebuconazole	10	538
Tebuprimiphos	30	538
Tembotrione	50	538
Terbufos	30	538
Tetraconazole	10	538
Thiacloprid	50	538
Thiamethoxam	25	538
Thifensulfuron-methyl	16.7	538
Thiobencarb	8.3	538
Tolfenpyrad	100	538
Triallate	50	538
Triasulfurpn	23.3	538
Triclopyr	50	538
zeta-Cypermethrin	500	538