



2016 Private Well Pesticide Sampling
Work Plan

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Minnesota Department of Agriculture

Monitoring and Assessment Unit

Environmental Section

Pesticide and Fertilizer Management Division



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1. Project Organization

Table 1. Project Organization

Name	Project Title/Responsibility
Jeff Paddock	Hydrologist 2, Project Lead
Bill VanRyswyk	Supervisor, Project Oversight
Brennon Schaefer	Hydrologist 2, Technical Assistance
Larry Gunderson	Supervisor, Project Oversight
Kim Kaiser	Hydrologist 3, Project Coordination
Nikol Ross	Hydrologist 1, Project Coordination & Technical Assistance
Dylan Timm	Hydrologist 1, Data Management
Adam McCullough, Jaime Nielsen, Ryan Meyer	Sampling Hydrologists /Sampling, Data Entry and Technical Assistance
Chris Samatmanakit	Weck Laboratories/Lab Coordination
Vacant	State Program Administrator Principal, MDA Laboratory Services Division (Pesticide QC)/Technical Assistance

2. Project Purpose

At the direction of the Minnesota Legislature (HF1183 Article 2, Sec. 3, part b), **Cite: [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 in 2015. This Work Plan will outline the steps and procedures that will be taken to implement the 2016 PWPS Project.

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 high agricultural production. This will be achieved by analyzing water samples at environmentally relevant concentrations for commonly used pesticides and their primary metabolites. 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, 2017, and will continue in phases 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:

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

3. Project Scope Description and Methods

The MDA will continue to evaluate commonly used pesticide presence and magnitude in private residential drinking water wells throughout the state. The MDA intends to sample wells in four additional counties in 2016 (Ottertail, Pope, Sherburne and Morrison) and will begin to resample wells in Dakota County that had previously been sampled. The MDA is resampling the wells previously sampled for pesticides during the 2014 and 2015 seasons because additional pesticides have been added to the target analyte list and reporting limit concentrations have been lowered. Additional counties will likely be re-sampled beginning in the spring of 2017.

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 TTP webpage](#).

The specific tasks associated with this Work Plan include:

- A. **Well Selection** – Identify wells to be targeted for sampling based on first round TTP nitrate results and homeowner interest;
- B. **Laboratory Selection and Contracting** – Identify and contract a laboratory capable of analyzing for the appropriate pesticides *and* achieving the target reporting limit concentrations similar to the MDA Laboratory Services Division (MDA laboratory);
- C. **Laboratory QA/QC Protocols** – Develop and follow appropriate laboratory QA/QC procedures for evaluating the contract laboratory and ensuring sample collection and handling integrity;
- D. **Sampling Methods and Procedures** – Identify and follow appropriate sample collection methods from the private drinking water wells;
- E. **Data Management** – Coordinate data management of the pesticide results, location, and well information generated during the project and designate data management system;
- F. **Homeowner Reporting** – Coordinate reporting and response letters to homeowners;
- G. **Data Analysis** – Identify and coordinate appropriate analyses of the pesticide data, and associated information, generated during this project; and,

- H. **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.

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 first round of the TTP and had any amount of nitrate detected in their well water.

As previously discussed, the MDA conducted the PWPS Project in eight counties in 2014 and 2015. During the 2014 and 2015 sampling seasons approximately 3,709 homeowners who had nitrate detected in their wells were sent a letter from the MDA explaining the PWPS Project asking if they would like to participate in the PWPS Project. Homeowners who chose to participate were required to return a consent form. This consent form will be utilized for 2016 and revised as appropriate. The consent form must be signed and returned to the MDA. As indicated in the consent form, the land owner and well location information will be protected as private data by the MDA in regard to the pesticide sample result. However, the well location is considered public with respect to the nitrate result.

The well selection protocol used during the 2014 and 2015 sampling seasons will continue to be used during the 2016 sampling season. Approximately 1,841 wells were sampled in the 2014 and 2015 sampling seasons. The MDA estimates that approximately 940 wells will be sampled in 2016 sampling season. As time and resources permit, an additional 500 wells that were previously sampled for pesticides in 2014 and 2015 will be targeted for re-sampling in Dakota County during the 2016 season.

Laboratory Selection and 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 RFP posted by the MDA. The MVTL proposal was limited to the MDA List 1 Pesticides, which is comprised of 22 pesticide-related compounds and includes the five groundwater common detection parent compounds. All of the pesticides analyzed during the 2014 and 2015 sampling season were analyzed for MDA List 1 pesticides.

In part due 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 pesticide compounds 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 season. Weck Laboratories is capable of analyzing for the vast majority of the pesticides on the current MDA laboratory target analyte list at similar reporting levels. The final list of 127

pesticides that will be analyzed by Weck is located in Table 2. All of the samples collected during the 2016 sampling season will be analyzed by Weck Laboratories.

Laboratory Quality Assurance and Quality Control (QA/QC)

Five percent of the total samples collected will be submitted as replicates and five percent will be submitted as field blanks. Quality Control Reports, including surrogate recovery, Laboratory Control Sample and matrix spike recovery and QA/QC narratives, will be included with all of the analytical results. 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 indicated irregularities, or if the MDA determines it is necessary, the MDA laboratory will be utilized to provide QA/QC review of laboratory 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;
- Laboratory control sample (LCS) and a LCS Duplicate; and,
- Confirmation criteria of detected analytes.

The MDA laboratory will also be used to prepare fortified, spiked samples for submission to Weck, as well as analysis of split samples if determined necessary. The MDA Laboratory may also be used as confirmation of the Weck sample results if abnormally high or unusual detections occur.

Table 2. Pesticide Analyte List for 2016 sampling for the PWPS Project, Weck Laboratory.

Pesticide	MRL (ng/L)	Pesticide	MRL (ng/L)	Pesticide	MRL (ng/L)
2,4,5-T	50	Dichlorvos	15	Metribuzin	75
2,4,5-TP (Silvex)	50	Dicrotophos	25	Metribuzin DA	500
2,4-D	8.3	Difenoconazole	25	Metribuzin DADK	500
2,4-DB	20	Dimethenamid	15	Metribuzin DK	5,000
Acetamiprid	25	Dimethenamid ESA	6.7	Metsulfuron Methyl	23.3
Acetochlor	30	Dimethenamid OXA	10	Myclobutanil	10
Acetochlor ESA	30	Dimethoate	100	Nicosulfuron	26.6
Acetochlor OXA	33.3	Dinotefuran	25	Norflurazon	20
Alachlor	30	Disulfoton sulfone	20	Norflurazon-Desmethyl	50
Alachlor ESA	41.6	Diuron	13.3	Oxadiazon	75
Alachlor OXA	33.3	Ethalfuralin	50	Oxydementon-Methyl	20
Aldicarb sulfone	15	Ethofumesate	50	Pendimethalin	75
Aldicarb sulfoxide	50	Flufenacet OXA	8.3	Phorate	25
Atrazine	30	Flumetsulam	50	Picloram	41.6
Deisopropylatrazine	150	Flutriafol	10	Picoxystrobin	50
Desethylatrazine	50	Fluxapyroxad	10	Prometon	100
DEDI Atrazine	50	Fonofos	15	Prometryn	3.3
Hydroxyatrazine	6.7	Glyphosate	1,000	Propachlor	30
Azoxystrobin	10	AMPA	1,000	Propachlor ESA	30
Bensulfuron-methyl	16.7	Halosulfuron-Methyl	30	Propachlor OXA	10
Bensulide	250	Hexazinone	10	Propazine	25
Bentazon	5	Imazamethabenz Methyl	5	Propiconazole	10
Boscalid	50	Imazamethabenz acid	10	Pyraclostrobin	25
Bromacil	30	Imazamox	13.3	Pyroxasulfone	50
Bromoxynil	25	Imazapic	10	Saflufenacil	15
Carbaryl	25	Imazapyr	8.3	Sedaxane	75
Carbendazim	10	Imazaquin	16.7	Siduron	6.7
Carbofuran	13.3	Imazethapyr	6.7	Simazine	75
Chlorantraniliprole	50	Imidacloprid	20	Sulfometuron Methyl	8.3
Chlorimuron-ethyl	20	Isoxaflutole	40	Tebuconazole	10
Chlorpyrifos	40	Linuron	20	Tebuprimiphos	30
Chlorpyrifos-oxon	40	Malathion	50	Tembotrione	50
Clomazone	15	MCPA	5	Terbufos	30
Clopyralid	50	MCPB	20	Tetraconazole	10
Clothianidin	25	MCPB	50	Thiacloprid	50
Cyanazine	25	Mesotrione	50	Thiamethoxam	25
Cyantraniliprole	100	Metalaxyl	8.3	Thifensulfuron Methyl	16.7
Cyfluthrin	100	Methyl parathion	100	Thiobencarb	8.3
Cypermethrin	100	Methyl paraoxon	25	Tolfenpyrad	100
Diazinon	30	Metolachlor	25	Triallate	50
Diazinon-O analog	10	Metolachlor ESA	10	Triasulfuron	23.3
Dicamba	50	Metolachlor OXA	10	Triclopyr	50
Dichlorprop	50				

Sampling Methods and Procedures

As previously discussed, groundwater samples in 2016 will be collected from locations where nitrate was detected as part of the TTP. Approximately 52 percent of the homeowners that received invitation letters returned invitation letters stating that they would like to have their wells sampled as part of the PWPS Project. Current nitrate detection numbers from the four selected counties in the TTP that will be sampled in 2016 are estimated at 1,848 and the MDA anticipates that there will be approximately 937 new locations sampled for pesticides (Table 3). In addition, the MDA will resample approximately 500 wells in Dakota County in 2016. This will bring the estimated total to approximately 1,400 samples in 2016.

Table 3. 2015 Estimated Sample Numbers and Participating Counties.

County	Estimated number of initial nitrate detections	Estimated number of PWPS Samples
Ottertail	1,066	522
Pope	66	32
Sherburne	246	133
Morrison	470	230
Total	1,848	937

All of the samples will be collected by the MDA hydrologists. The hydrologists will be based in MDA satellite offices in Staples, St. Cloud and Detroit Lakes. The proximity of the satellite office to the county to be sampled will determine which hydrologist will sample that county. The counties will be sampled individually and at a township level by the hydrologists, if possible, to avoid confusion and increase efficiency. The re-samples in Dakota County will be collected by MDA hydrologist based in St. Paul.

The hydrologists will also conduct the following activities:

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

A Standard Operating Procedure (SOP) was developed to standardize sample collection protocols and will be utilized for the 2016 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 on field log forms. The samples will then be placed in an iced cooler during each day's sampling activity, transported back to the 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 the sample, the hydrologists will ask the homeowner survey questions outlined in the Well Information and Potential Nitrate Source Inventory Form. 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 hydrologist or county employee.

Letters documenting the analytical results from the 2016 PWPS Project sampling will be sent to the participating homeowners after all of the results have been received. The letters will include the analytical results from the nitrate and pesticide analyses, a copy of the laboratory analytical report, and a copy of the *Nitrate in Groundwater* pamphlet (which provides information on the risks associated with nitrate in drinking water).

Data Management

Sample results from the 2014-2015 PWPS Project are currently being stored in Excel spreadsheets. The MDA is currently working with the Minnesota Pollution Control Agency (MPCA) to secure long-term data storage in the statewide water quality database Environmental Quality Information System (EQUS). 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 for all pesticide results, although the results are considered public data. Location based pesticide data will be aggregated at the township scale and made available as requested.

Homeowner Reporting

Results will be reported back to each individual well owner in a timely basis. This report will include all the analytical results along with a letter explaining what was detected.

Data Analysis

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. As a result, statistical inference from this type of data may be inappropriate. Therefore, 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 concentration, 75th and 90th percentile concentration, detection frequency) will be computed for MDAs 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 Minnesota Department of Health.

Project Reporting

The MDA will complete a report that discusses and characterizes the 2016 PWPS Project results. The report will focus on the pesticide presence, detection frequency and concentration magnitude for the counties evaluated. If sufficient data is available MDA will also evaluate the co-occurrence of pesticides and nitrate in private wells.