

## Private Well Pesticide Sampling Project Phase 2 Monitoring Plan, 2023

### Purpose

This monitoring plan has been developed in consideration with respect to the detection of cyanazine degradates above the established Health Risk Limit (HRL) in some private drinking water wells in Minnesota. In 2023, the Minnesota Department of Agriculture (MDA) will continue to target geologically vulnerable private wells in agricultural areas as part of the Private Well Pesticide Sampling (PWPS) Project. The PWPS Project Phase 2 sampling efforts will continue to focus specifically on two herbicides, cyanazine and atrazine, as well as their known degradates. The degradates of cyanazine were identified as the pesticide-related compounds that posed the greatest risk to drinking water, based on sampling performed in the first phase of the PWPS Project (2016 to 2020). The primary purpose of the PWPS Project Phase 2 monitoring effort is to provide information to well owners regarding the presence of total cyanazine (cyanazine + degradates) in their drinking water. The MDA will continue to utilize the previously selected contract laboratory, Eurofins Eaton Analytical LLC, for most of the pesticide analytical work.

The PWPS Project is primarily funded through the Clean Water Fund, with additional supporting funds provided through the MDA Pesticide Regulatory Account and a Multipurpose Grant provided by the US Environmental Protection Agency.

### Monitoring Objectives

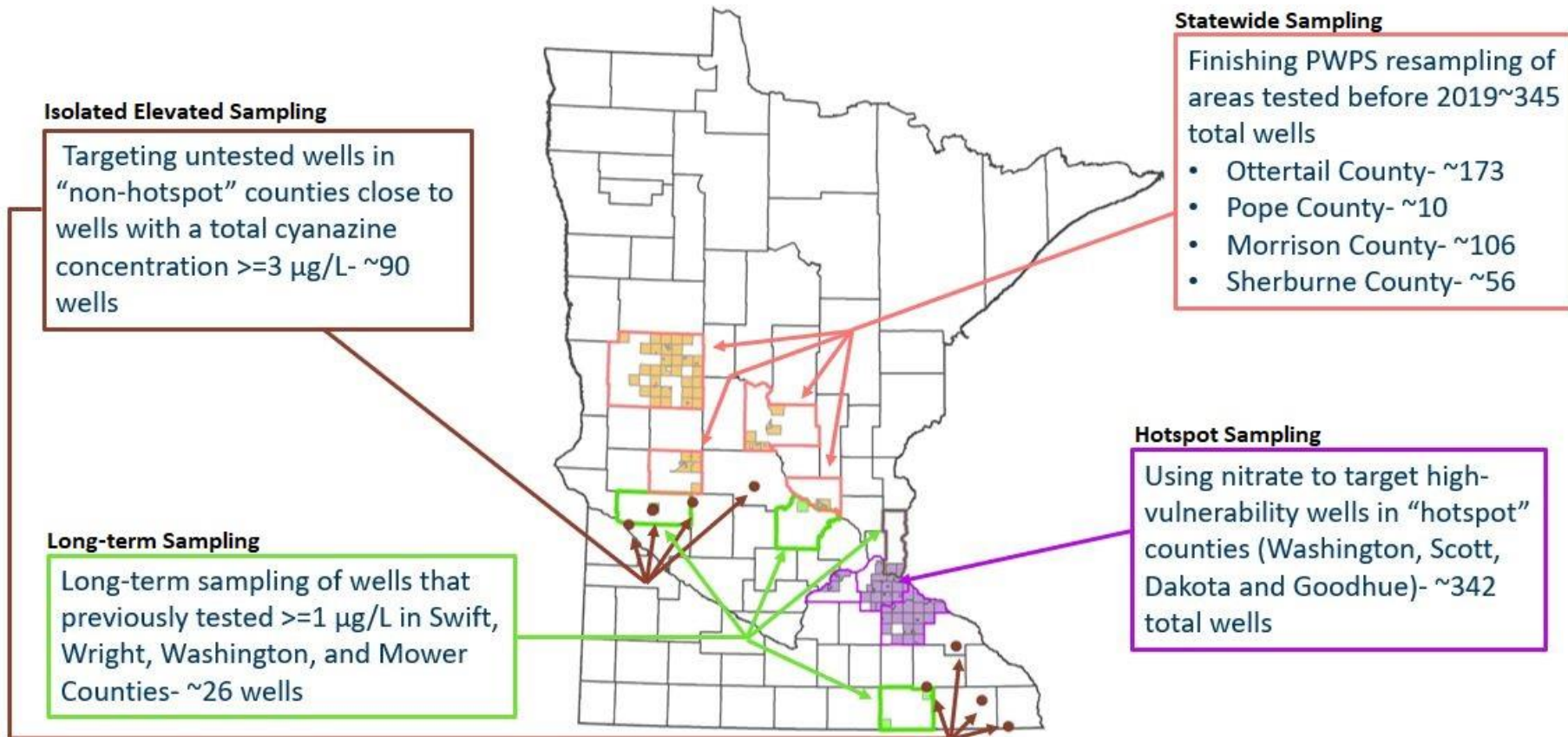
Using a targeted approach, based on previous sample results and geologic conditions as discussed in the 2022 PWPS Project Phase 2 Monitoring Plan (<https://www.mda.state.mn.us/private-well-pesticide-sampling-project-results-work-plans>), the MDA will target wells assessed to be at greatest risk for the presence of cyanazine degradates (Figure 1). Specific monitoring objectives for 2023 include the following main items (additional sampling may be added as resources allow):

1. **Statewide Sampling** - To better define statewide extent and magnitude, the MDA will continue to target wells from the PWPS Project counties that have not been evaluated for total cyanazine. Wells will be selected through risk-based evaluation, as determined from regional co-occurrence and the sensitivity of geologic conditions.
2. **Hotspot Sampling** - To better define local extent and magnitude in areas with known clusters of wells exceeding the total cyanazine HRL of 1 µg/L, the MDA will target untested wells in Washington, Dakota, Goodhue, and Scott Counties. Wells will be selected based on previous nitrate concentrations in comparison to a select threshold for each county.
3. **Isolated Elevated Sampling** - In several counties, where isolated detections of total cyanazine above the acute HRL of 3 µg/L have been detected, the MDA will target untested wells that are in close proximity to wells with an elevated concentration.
4. **Long-term Sampling** - The MDA will target wells that previously indicated a total cyanazine concentration over 1 µg/L, on a three-year reoccurring basis, to assess how concentrations are changing over time.

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In accordance with the Americans with Disabilities Act, this information is available in alternative forms of communication upon request by calling 651-201-6000. TTY users can call the Minnesota Relay Service at 711. The MDA is an equal opportunity employer and provider

Figure 1. PWPS Project Phase 2 sample plan allocation for specific objectives in 2023.



### Specific sample allocations for 2023:

- 1) Statewide Sampling - Counties/areas previously untested for cyanazine degradates: *(assumes a 60% response rate)*
  - Morrison County ~ 106 samples.
  - Otter Tail County ~ 173 samples.
  - Pope County ~ 10 samples.
  - Sherburne County ~ 56 samples.
- 2) Hotspot Sampling - Cyanazine-vulnerable wells in “hotspot” counties/areas:
  - Scott County ( $\geq 1$  mg/L nitrate) ~ 17 samples.
  - Washington County ( $\geq 3$  mg/L nitrate) ~ 57 samples.
  - Dakota County ( $\geq 5$  mg/L nitrate) ~ 147 samples.
  - Goodhue County ( $\geq 5$  mg/L nitrate) ~ 121 samples.
- 3) Isolated Elevated Sampling - Targeting untested wells that are nearby previously tested wells have been found to have a concentration equal to or above the acute level ~ 90 samples.
- 4) Long-term Sampling – Wells, sampled approximately 3 years prior, that were over the total cyanazine chronic HRL ~ 30 samples.

#### Additional sampling needs:

- Remaining areas to prioritize (e.g., wells outside of the original TTP population or well owners that did not respond to previous requests for participation in the PWPS Project Phase 1) ~ 240 wells.
- Holdovers from 2022 ~ 3 samples (1 in Hubbard, 1 in Dakota, 1 in Fillmore).
- Verification samples ~ 40 samples.
- Post treatment samples ~ 10 samples.
- QA/QC (10% of regular samples collected) ~ 104 samples.

This plan prioritizes areas of the state thought to be at greatest risk for cyanazine presence based on available data. As additional data is collected and assessed, the prioritization strategy may be modified. Sample collection is not planned to exceed 1,200 total samples in 2023.

### Sampling Methods and Procedures

The following activities associated with sampling will be performed:

- Contact the participating homeowners and schedule the sampling events.
- Collect samples.
- Coordinate the delivery of sampling supplies and shipping of samples with laboratories.
- Maintain and decontaminate the sampling equipment and vehicle.
- Record, store and maintain any pertinent sampling records and manage sample results/data.

A Standard Operating Procedure (SOP) was developed to standardize sample collection protocols and will be utilized for the 2023 PWPS Project Phase 2 sampling season. All samples will be collected by MDA hydrologists.

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, ORP, and conductivity) will be measured during purging and recorded on field log forms in Survey 123. The samples will then be placed in an iced cooler during each day's sampling activity, transported back to the respective office at the end of each day, and stored in controlled refrigerators until they are shipped or delivered to the appropriate laboratory.

In addition to collecting the samples, the hydrologists will ask the homeowner survey questions outlined in the field log form in Survey 123. 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 hydrologists. Due to the detection of Highly Pathogenic Avian Influenza (HPAI) in Minnesota, homeowners will be asked if there are poultry or waterfowl on the premises where sampling will be performed. The hydrologists will follow established biosecurity protocols as necessary and delay sampling any property where poultry or waterfowl are present until later in the sampling season, when the risk of avian influenza is likely to have diminished.

Letters documenting the analytical results from the PWPS Project Phase 2 sampling will be sent to participating homeowners after all the results have been received. Homeowners with total cyanazine results above 1 µg/L (the chronic health level) will receive notification of this issue, via phone call and/or email, as soon as possible after the results are received from the lab, as well.

### **Analyte list and bottles**

Pesticide analysis through the contract laboratory will include the parent compounds of cyanazine and atrazine, as well as some of their known degradates. Cyanazine-specific degradates include: cyanazine acid, cyanazine amide, deethylcyanazine, deethylcyanazine acid, and deethylcyanazine amide. Cyanazine and atrazine share two similar degradates: deisopropylatrazine and didealkylatrazine. Desethylatrazine and hydroxyatrazine, which are only degradates of atrazine, will also be analyzed (Table 1). The pesticide samples will be collected in 40 mL amber vials, preserved with ammonium acetate and sodium omadine, and sent to the contract laboratory. Nitrate samples will also be collected during the same sample collection event as the pesticide samples. They will be collected in 125 mL HDPE bottles preserved with sulfuric acid, and will be analyzed by the MDA Laboratory. Finally, at select locations, major cations (calcium, magnesium, sodium, potassium, iron, manganese, strontium, and arsenic) and major anions (bromide, chloride, fluoride, and sulfate) may be collected, in two 250 mL bottles (Table 2). The bottle for anions analysis would be unpreserved, while the bottle for cations analysis would be preserved with nitric acid. Any major cations and anions samples collected would be analyzed by the Minnesota Department of Health (MDH) Public Health Laboratory.

**Table 1. List of pesticides to be run by contract laboratory for the PWPS Project Phase 2.**

Analyte	CAS#	MRL (ng/L)
Cyanazine	21725-46-2	5
Cyanazine acid	36576-43-9	5
Cyanazine amide	36576-42-8	5
Deethylcyanazine	21725-40-6	5
Deethylcyanazine acid	36749-35-6	5
Deethylcyanazine amide	36556-77-1	5
Atrazine	1912-24-9	5
Deisopropylatrazine	1007-28-9	5
Desethylatrazine	6190-65-4	5
Didealkylatrazine	3397-62-4	25
Hydroxyatrazine	2163-68-0	5

**Table 2. List of cation and anion inorganic analytes for the PWPS Project Phase 2.**

Analyte	MRL	Laboratory
<u>Cations</u>		MDH Public Health Lab
arsenic	1.0 µg/L	
calcium	2.0 mg/L	
iron	20.0 µg/L	
magnesium	2.0 mg/L	
manganese	10.0 µg/L	
potassium	0.50 mg/L	
sodium	0.50 mg/L	
strontium	2.0 µg/L	
<u>Anions</u>		MDH Public Health Lab
bromide	0.0050 mg/L	
chloride	0.50 mg/L	
fluoride	0.20 mg/L	
sulfate	0.50 mg/L	
nitrate	0.20	MDA Lab

### Quality Assurance and Quality Control

In addition to the routine samples, the MDA will collect approximately 10% Quality Assurance/Quality Control (QA/QC) samples consisting of field blanks and duplicate samples. Verification samples will also be collected as soon as possible (approximately two months after initial sampling) from wells with total cyanazine or total atrazine concentrations greater than or equal the respective health reference values. The actual number of verification samples collected will depend upon results from sampling and laboratory resources. Verification samples will be split between the contract lab and the MDA Laboratory, which provides validation of the previously detected analytes and adds supplemental evaluation of the contract lab analytical method.

### **Post-treatment samples**

During the PWPS Project Phase 1 sampling, homeowners with water treatment systems were offered the opportunity for a pre- (water taken before treatment) and post- (water taken after treatment) treatment sample to be collected, most often where verification sampling was performed. Some post-treatment samples have also been taken at the homeowner's request non-verification sampling. Similar to previous years, limited post-treatment samples will again be collected, upon homeowner request, as resources allow.

### **Post-treatment resources**

- "Assessment of in-home reverse osmosis systems for removing pesticides and nitrate-nitrogen from private well water": [www.mda.state.mn.us/pesticide-monitoring-reports](http://www.mda.state.mn.us/pesticide-monitoring-reports).
- MDH home water treatment guidance: <https://www.health.state.mn.us/communities/environment/water/docs/factsheet/hometreatment.pdf>

### **Other Considerations & Factors**

#### **Public drinking water sampling**

As shown by prior sampling performed by the MDA in conjunction with the MDH, there is potential for public water supplies to be impacted by total cyanazine. In 2023, the MDH is planning to continue to sample for cyanazine and atrazine related compounds at public drinking water supply wells that are located near private wells with elevated detections of total cyanazine. The MDA will provide private well sampling results to the MDH, so they can perform a public well vulnerability assessment and at-risk public wells can be targeted for sampling.