



Pesticides of Concern in the Pineland Sands Region, Minnesota: Current and Historical Concentrations Above Ecological and Human-Health Screening Benchmarks

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Abstract

The Pineland Sands region of central Minnesota is a sandy, irrigated landscape in which shallow groundwater can interact with springs, streams, wetlands, and lakes. These connections create potential pathways for mobile agricultural chemicals to move from recharge areas toward surface-water habitats. This study screened October 2025 pesticide samples and historical pesticide records accessed through EPA TADA/EQuIS to identify concentrations above selected ecological and human-health benchmarks. Current samples represented lakes, streams, groundwater springs, groundwater wells, and piezometers hyporheic-riparian zone wells. Current and historical results were standardized to micrograms per liter and compared with EPA aquatic-life benchmarks, EPA Human Health Benchmarks for Pesticides, federal drinking-water maximum contaminant levels, and Minnesota Department of Health human health-based water guidance values. The 2023 USDA National Agricultural Statistics Service Cropland Data Layer provided land-cover context for the project area. Two current groundwater and groundwater-connected samples were above EPA aquatic-life benchmark values: clothianidin at Site 10 DNR a 33 ft groundwater well near the Straight River, and metribuzin at 18/CR115 Straight River Spring, an in-channel groundwater spring. No current results were above EPA HHBP, federal MCL, or Minnesota guidance values. Historical records showed a broader screening pattern for alachlor, atrazine, clothianidin, imidacloprid, metolachlor, metribuzin, metribuzin DADK, and thiamethoxam. Neonicotinoid insecticides were the most frequent historical pesticide group above aquatic-life benchmark values, primarily relative to freshwater invertebrate chronic endpoints. Human-health findings were limited to historical imidacloprid and metribuzin DADK concentrations above Minnesota guidance values. Because most of the benchmark-above records were groundwater samples, the findings are best interpreted as screening-level indicators in groundwater-connected settings rather than evidence of biological impairment or regulatory noncompliance.

Keywords: Pesticides, Groundwater, Aquatic-life benchmarks, Neonicotinoids, Cropland data layer, Pineland sands, Minnesota, Sandy aquifers

Introduction

Pesticides detected in groundwater, springs, streams, and lakes can serve as indicators of agricultural chemical occurrence, mobility, and potential exposure pathways in shallow hydrogeologic settings. Pesticide mobility is influenced by fate properties such as sorption, solubility, and persistence.¹ Sandy soils and leaching through the soil profile are especially relevant to groundwater transport.² In the Pineland Sands region, shallow sandy aquifers and permeable outwash deposits provide a setting where groundwater detections are important to screen.³ Where groundwater discharges to streams, springs, wetlands, or lakes, those detections may also be relevant to potential surface-water exposure.⁴

The aquatic and wetland portions of this landscape also provide ecological context for interpreting benchmark results. Wild rice (*Zizania palustris*), where present, is relevant because it grows in shallow lakes, marshes, and streams, is sensitive to water-level and water-quality conditions, and provides food, cover, and habitat for waterfowl, pollinators, mammals, and other wetland wildlife.^{5,6} Other potentially relevant receptor groups in groundwater-connected streams, springs, wetlands, and lakes include algae, aquatic vascular plants, aquatic insects, other freshwater invertebrates, fish, amphibians, and wetland birds. These groups are discussed as ecological receptors represented by the screening benchmarks, not as organisms for which biological effects were directly measured in this study.

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Pesticide groups considered

The analysis focused on selected herbicides, neonicotinoid insecticides, and pesticide degradates that were detected in the current and/or historical records and had applicable ecological or human-health screening values. Detailed selection logic and pesticide class information are provided later in the manuscript under Pesticides reviewed and screening selection. These compounds are important in the Pineland Sands because agricultural land use and irrigated sandy soils can influence pesticide movement.⁷ Soil-profile leaching and chemical fate properties also affect whether pesticides or degradates remain in groundwater.² Groundwater-surface-water connections are important because groundwater may be discharged to streams, springs, wetlands, or lakes.⁴

Benchmark screening and study objectives

Environmental Protection Agency (EPA) aquatic-life benchmarks are screening tools used to compare pesticide concentrations with ecological toxicity endpoints.⁸ Concentrations above aquatic-life benchmark values do not prove biological impairment, and groundwater concentrations above aquatic-life benchmark values should not be described as direct surface-water benchmark exceedances. EPA Human Health Benchmarks for Pesticides provide human-health screening context.⁹ Federal drinking-water values provide regulatory drinking-water context where maximum concentration levels (MCLs) are available.¹⁰ Minnesota Department of Health guidance values provide state health-based context for water-quality interpretation.¹¹ These human-health comparisons do not by themselves establish regulatory noncompliance unless an enforceable standard applies to the sampled water source.

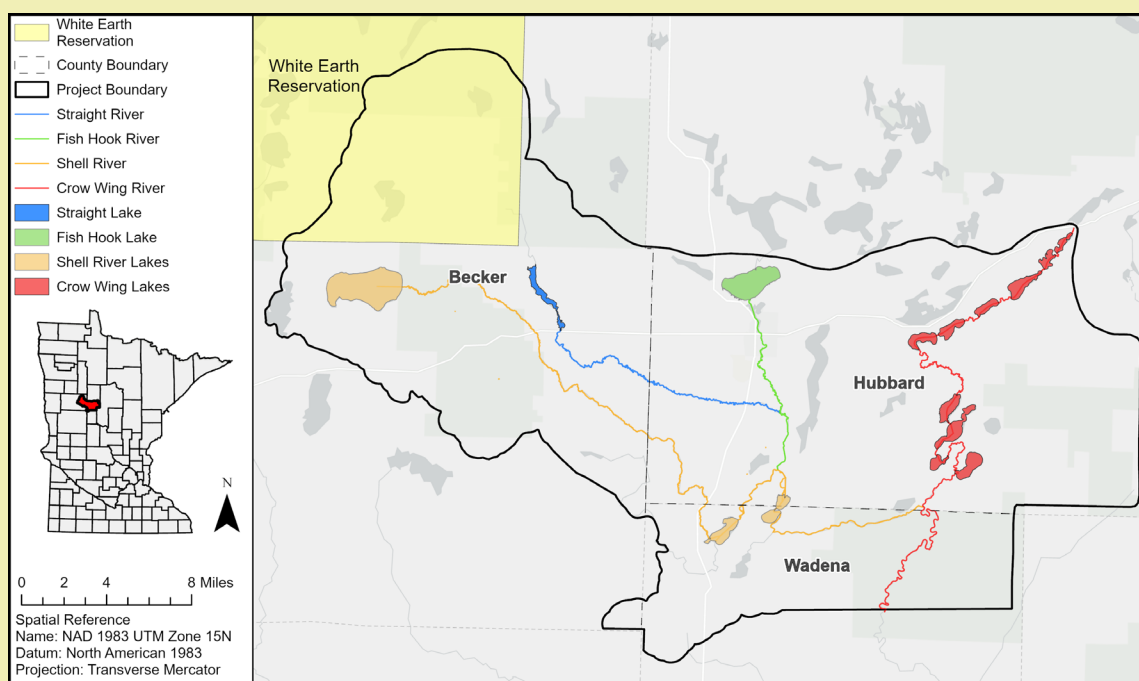
The objectives of this study were to: (1) summarize current pesticide sampling results above selected benchmark values; (2) summarize historical pesticide records accessed through Tools for Automated Data Analysis (TADA)/Environmental Quality Information System (EQuIS) above selected benchmark values; (3) distinguish aquatic-life, federal drinking-water, EPA human health benchmarks for pesticides (HHBP), and Minnesota state guidance comparisons; and (4) identify historical sites and pesticide groups that may warrant closer review in hydrologically connected settings.

Materials and Methods

Study area and land-cover processing

The Pineland Sands region of Minnesota contains hydrogeologic and land-use conditions that make pesticide occurrence relevant to water-quality screening. The region includes extensive surficial glacial outwash deposits and aquifer materials commonly ranging from very fine sand to fine gravel.³ Groundwater systems in the Straight River area can discharge to streams and lakes, and United States Geological Survey (USGS) work identified agricultural chemicals transported through groundwater flow or runoff as a potential concern for the stream system.⁴ The Minnesota Department of Agriculture (MDA) identifies the Central Sands/PMR 4 region as a large glacial outwash sand-plain setting with high sensitivity to surface activities, high-value crops, and common irrigation.⁷ The Central Sands Private Well Network has been monitoring the area for pesticides and nitrate since 2011 in this vulnerable groundwater setting (Figure 1).¹²

Figure 1: Pineland sands project area counties with major rivers and connected lakes



The 2023 USDA National Agricultural Statistics Service Cropland Data Layer (CDL) was used to summarize crop and land-cover composition within the project boundary. The 2023 Minnesota CDL is a 30-meter, raster, geo-referenced, crop-specific land cover dataset produced using satellite imagery and extensive agriculture ground reference data collected during the growing season.¹³ The CDL raster was clipped to the project boundary in ArcGIS Pro and reclassified into 12 broader crop and land-cover classes to simplify interpretation of agricultural and non-agricultural cover types (Table 1). Pixel counts or mapped-area summaries for each reclassified class were converted to percent of total project area. The land-cover summary was used as study-area context and was not used to assign individual pesticide detections to specific source areas.

The land-cover composition (Figure 2) was summarized to provide study area context for the current and historical pesticide results. The reclassified 2023 U.S. Department of Agriculture (USDA) National Agricultural Statistics Service CDL showed that the project area was dominated by forest and wetland cover rather than continuous cropland.¹³ Forest represented 43.92% of the mapped project area, followed by wetlands at 15.65%, grassland/pasture/shrubland at 12.10%, open water at 6.71%, and developed/barren/other cover at 5.05%. Agricultural classes were present but spatially discontinuous, with corn at 5.63%, other row crops at 3.64%, potatoes at 2.21%, hay/forage at 2.14%, soybeans at 1.51%, small grains at 1.44%, and fallow/idle cropland at less than 0.01%. These proportions place the pesticide detections within a mixed forest-wetland-agricultural landscape rather than a uniformly cultivated setting.

Table 1: Reclassification of original 2023 USDA NASS cropland data layer classes

Reclassified Class	Original CDL Classes Combined
Corn	Corn; Sweet Corn
Soybeans	Soybeans
Potatoes	Potatoes
Small Grains	Barley; Spring Wheat; Winter Wheat; Rye; Oats; Millet; Speltz; Buckwheat
Other Row Crops	Sorghum; Sunflower; Canola; Flaxseed; Mustard; Sugarbeets; Dry Beans; Other Crops; Peas; Carrots
Hay/Forage	Alfalfa; Other Hay/Non-Alfalfa; Clover/Wildflowers; Sod/Grass Seed
Fallow/Idle Cropland	Fallow/Idle Cropland
Grassland/Pasture/Shrubland	Switchgrass; Shrubland; Grassland/Pasture
Forest	Deciduous Forest; Evergreen Forest; Mixed Forest
Wetlands	Woody Wetlands; Herbaceous Wetlands
Open Water	Open Water
Developed/Barren/Other	Developed/Open Space; Developed/Low Intensity; Developed/Medium Intensity; Developed/High Intensity; Barren

Note: CDL = Cropland Data Layer. The reclassification grouped detailed crop-specific and non-agricultural CDL values into broader analysis classes for study-area context. Non-agricultural classes were used as broad land-cover categories rather than detailed habitat classifications.

Current sampling design

Current pesticide sampling was conducted in October 2025 within the Pineland Sands study area. (Figures 3 and Figure 4) Pesticide samples were collected to determine pesticide presence/absence and concentration in project-area waters. Sites represented lakes, streams, groundwater springs, groundwater wells, and piezometers or hyporheic-riparian zones. Sites were selected primarily around agricultural land and locations where previous water-quality information suggested possible agricultural influence. Nitrate-nitrogen ($\text{NO}_3\text{-N}$), potassium (K), chloride (Cl), and sodium (Na) were used as supporting water-quality indicators during site selection. $\text{NO}_3\text{-N}$ was used as the strongest indicator of possible agricultural influence because MDA groundwater monitoring has evaluated $\text{NO}_3\text{-N}$ and pesticide occurrence together and found that detections became more likely as $\text{NO}_3\text{-N}$ increased above background, although nitrate alone did not reliably predict pesticide concentrations.⁷ K was included as a supporting nutrient indicator because applied K fertilizers can increase K concentrations in the soil solution of sandy, low-buffer-capacity soils, especially where rainfall, recharge, or irrigation moves water through the soil profile.¹⁴ Cl was included because fertilization and other human activities can add chloride to soils, and Cl is mobile in soil water.¹⁵ Na was included to help evaluate whether elevated Cl may partly reflect road-salt influence from sodium chloride (NaCl); MDA identifies road salt, fertilizer use, livestock excretion, and household water softeners as major contributors to elevated Cl in the environment.⁷ These ions were used to help interpret land-use and recharge influence, not as direct predictors of pesticide occurrence.

Figure 2: 2023 Crop and Land-Cover Composition Within the Project Boundary. Panel A shows the reclassified 2023 USDA NASS Cropland Data Layer within the project boundary. Panel B shows the percent of total project area represented by each reclassified crop or land-cover class

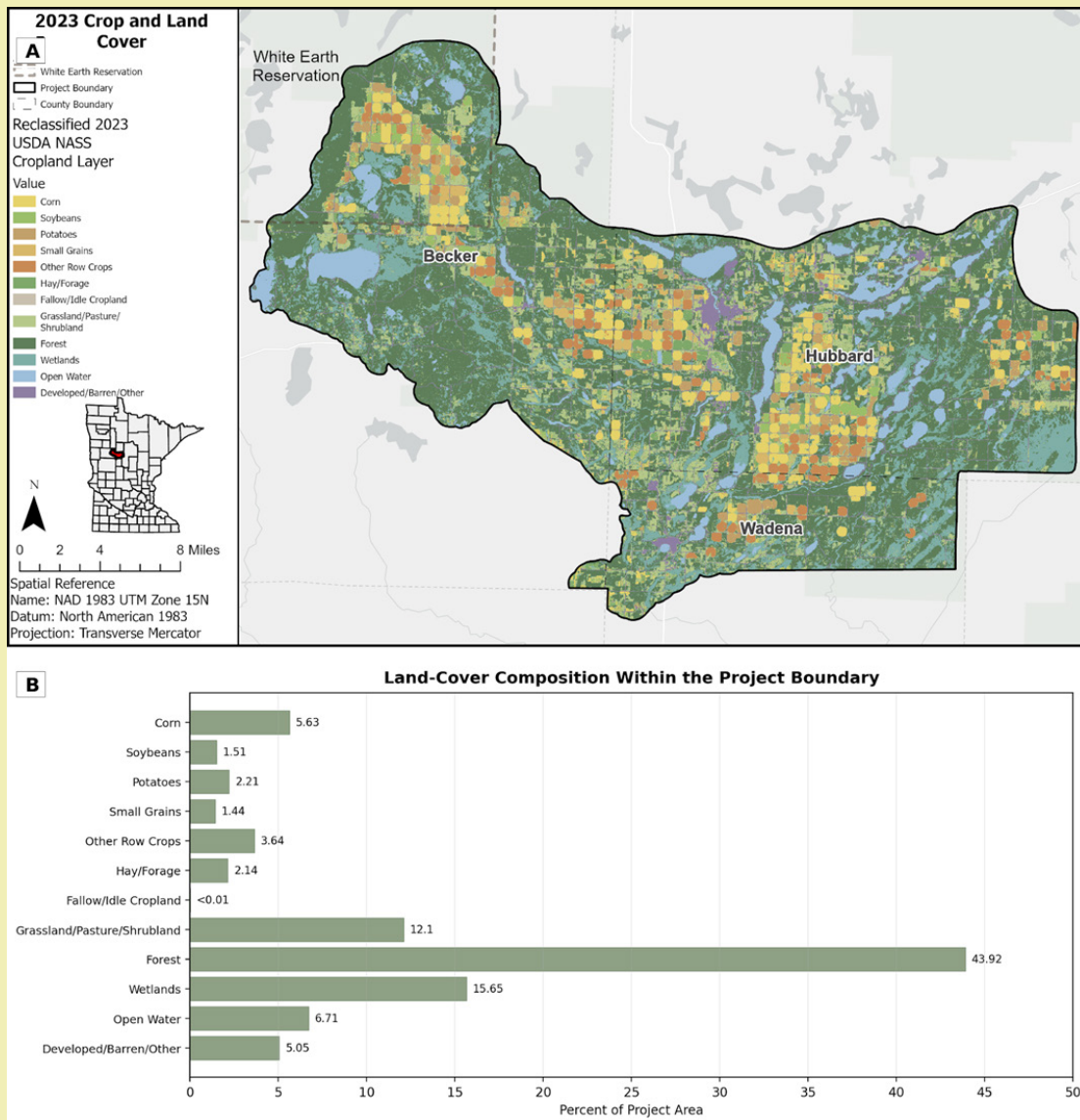


Figure 3: October 2025 Pesticide sampling locations for lakes, springs and streams

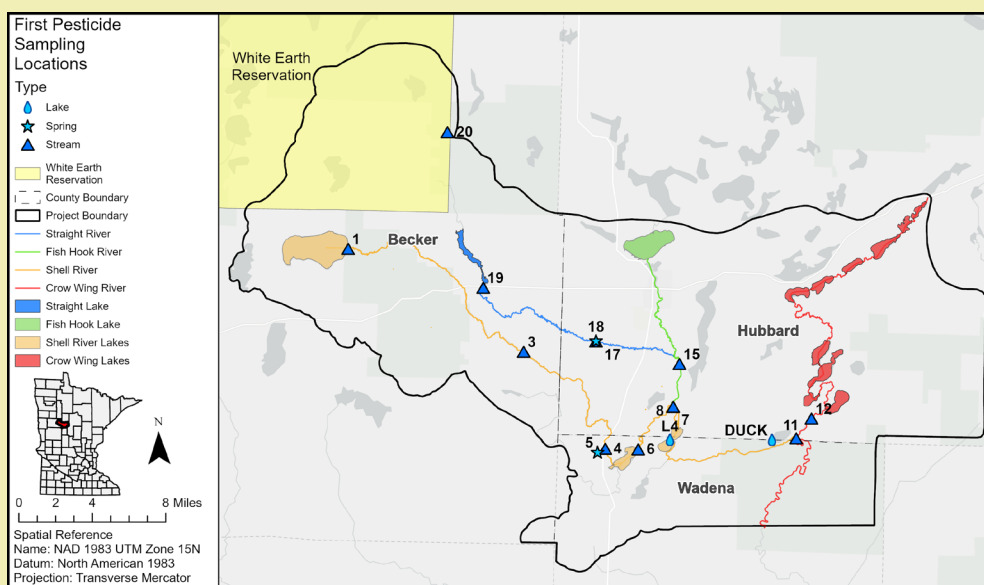
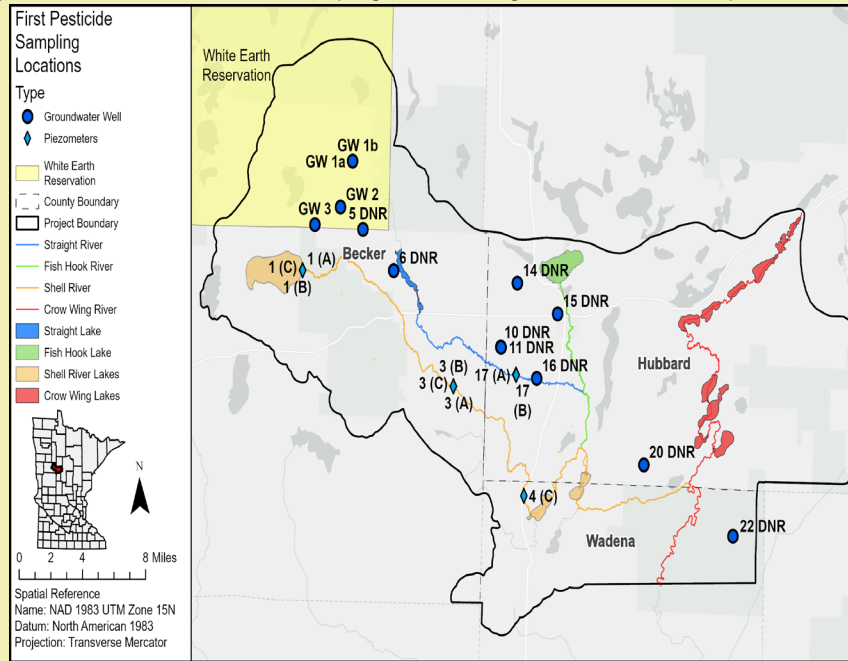


Figure 4: October 2025 Pesticide sampling locations for groundwater wells and piezometers.



Note: GW1a and GW1b represent a groundwater well nest with wells located approximately 5 ft apart. Sites 1, 3, 4, and 17, suffixes A, B, and C identify riparian and hyporheic zone wells nest positions: A = Riparian zone piezometer closest to the stream; B = Riparian zone piezometer farthest from the stream; and C = Streambed piezometer. Site labels ending in DNR indicate Minnesota Department of Natural Resources (DNR) observa-

Seasonal timing was considered because pesticide movement can be affected by pesticide application periods, precipitation timing, and recharge. MDA notes that pesticide movement is often related to pesticide properties and the timing and magnitude of precipitation relative to application periods.⁷ MDA groundwater monitoring design includes spring/fall sampling in pesticide management region (PMR) 4, April and October sampling in several pesticide monitoring regions, and May-June plus low-flow sampling for some springs.¹⁶ MDA surface-water monitoring also emphasizes the growing-season period, with pesticide detections above numeric reference values reported across May through August and rainfall-related pesticide movement discussed in relation to spring and early-summer precipitation.⁷ The October 2025 sampling event therefore provides a fall snapshot rather than a complete seasonal trend.

As summarized in (Table 2), the October 2025 sampling event included 38 water samples plus four quality-assurance and quality-control samples. The 38 water samples included 2 lake samples, 11 stream samples, 2 groundwater spring samples, 13 groundwater well samples, and 10 piezometer or hyporheic-riparian zone

samples. Quality-assurance/quality-control samples included three field duplicates and one deionized water field blank. Duplicate samples included two stream duplicates, collected at Site 1 and Site 17, and one groundwater-well duplicate collected at GW 3.

Sample handling and laboratory analysis

Pesticide samples were collected to determine presence/absence and concentration in project-area waters. During collection, pesticide samples were transferred to amber bottles to limit light exposure and were kept cold on ice until analysis. Samples were sent to the University of Wisconsin-Stevens Point Water and Environmental Analysis Laboratory because of its water-quality analytical capacity and pesticide scope for this project.¹⁷ Samples were not filtered in the field. Before analysis, the laboratory filtered samples using a vacuum filtration setup that included Whatman glass microfiber Grade 934-AH filter discs with 1.5 µm pore size and 0.45 µm membrane filters, 47 mm diameter. Laboratory reports listed liquid chromatography-mass spectrometry (LC/MS) and liquid chromatography electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) methods for pesticide analysis.

Table 2: Current sampling design and quality-assurance/quality-control samples

Sample Category	Count	Description
Lakes	2	Surface-water lake samples
Streams	11	Surface-water stream and river samples
Groundwater springs	2	Spring or groundwater-discharge settings
Groundwater wells	13	Groundwater well samples
Piezometers / streambed or riparian wells	10	Shallow groundwater or groundwater-surface-water interface samples
Field duplicates	3	Two stream duplicates and one groundwater-well duplicate
Deionized water field blank	1	Deionized water blank exposed to field conditions

The current pesticide laboratory analysis included three pesticide packages: neonicotinoid insecticides, nitrogen- and phosphorus-containing pesticides, and chloroacetanilide herbicide metabolites (Table 3a). For interpretation, the same analytes were also organized into five broader chemical or reporting groups used in the benchmark-screening discussion (Table 3b).

Table 3a: Current pesticide laboratory packages included in the October 2025 sampling event

Pesticide Package	Analytes Included	Reporting Notes
Neonicotinoid insecticides	Acetamiprid; Clothianidin; Dinotefuran; Imidacloprid; Thiamethoxam	Reported in ng/L; converted to µg/L for benchmark screening.
Nitrogen- and phosphorus-containing pesticides	Acetochlor; Alachlor; Atrazine; Cyanazine; Deethylatrazine; Deisopropylatrazine; Dimethenamid; Dyfonate; Eptam/EPTC; Ethalfuralin; Metolachlor; Metribuzin; Pendimethalin; Phorate; Prometon; Propachlor; Propazine; Simazine; Triallate; Trifluralin	Reported in µg/L. This package included parent herbicides and other pesticide analytes used for occurrence screening.
Chloroacetanilide herbicide metabolites	Alachlor ESA; Alachlor OA; Metolachlor ESA; Metolachlor OA	Reported in µg/L; included as occurrence context.

Note: Table 3a lists the three pesticide laboratory packages analyzed for the current October 2025 samples. Benchmark comparisons were made only for detected analytes with applicable benchmark or guidance values.

Table 3b: Pesticide analyte groups included in current laboratory analysis

Analyte Group	Analytes Included	Reporting Notes
Neonicotinoid Insecticides	Acetamiprid; Clothianidin; Dinotefuran; Imidacloprid; Thiamethoxam	Reported in ng/L; converted to µg/L for benchmark screening.
Triazine and Triazinone Herbicides and Related Compounds	Atrazine; Cyanazine; Deethylatrazine; Deisopropylatrazine; Metribuzin; Prometon; Propazine; Simazine	Reported in µg/L.
Chloroacetanilide Herbicides	Acetochlor; Alachlor; Metolachlor; Propachlor	Reported in µg/L.
Chloroacetanilide Herbicide Metabolites	Alachlor ESA; Alachlor OA; Metolachlor ESA; Metolachlor OA	Reported in µg/L; included as occurrence context.
Other Pesticides in Analytical Package	Dimethenamid; Dyfonate; Eptam/EPTC; Ethalfuralin; Pendimethalin; Phorate; Triallate; Trifluralin	Reported in µg/L.

Note: Table 3b organizes the current laboratory analytes into broader chemical or reporting groups used for interpretation. Benchmark comparisons were made only for detected analytes with applicable benchmark or guidance values.

Pesticides reviewed and screening selection

The pesticides and degradates included in this section were selected because each had at least one current or historical concentration above a reviewed benchmark or guidance value. These included alachlor, atrazine, clothianidin, imidacloprid, metolachlor, metribuzin, metribuzin desaminodiketometribuzin (DADK), and thiamethoxam. The current laboratory packages included additional analytes, but those compounds were not emphasized unless they had benchmark-above results. This selection approach is consistent with MDA analyte-selection logic, which considers pesticide use, environmental fate, occurrence information, analytical capability, and available reference values.⁷

The herbicides and herbicide-related degradates included in the screening were alachlor, atrazine, metolachlor, metribuzin, and metribuzin DADK. Alachlor is a chloroacetanilide/chloroacetamide herbicide associated with agricultural weed control.¹⁸ Metolachlor is a chloroacetanilide/chloroacetamide herbicide used for agricultural weed control and has drinking-water context in Minnesota.¹⁹ Atrazine is a chlorotriazine herbicide with federal drinking-water and aquatic-life benchmark context.²⁰ Metribuzin is a triazinone herbicide used to control broadleaf weeds and some grasses.²¹ Metribuzin DADK is an environmental degradate of metribuzin and was evaluated separately where Minnesota human-health guidance applied.²²

The insecticides included in the screening were clothianidin, imidacloprid, and thiamethoxam. These compounds are systemic neonicotinoid insecticides used in agricultural and non-agricultural settings.²³ Clothianidin has Minnesota drinking-water and occurrence context.²⁴ Imidacloprid has Minnesota groundwater and health-based guidance context.²⁵ Thiamethoxam has Minnesota drinking-water and occurrence context.²⁶ Recent MDA monitoring provides additional Minnesota context for neonicotinoid detections in groundwater and surface water.⁷ EPA freshwater invertebrate benchmarks were used to evaluate aquatic-life screening relevance for detected neonicotinoids.⁸ Thiamethoxam can also break down to clothianidin, so the two compounds were interpreted together where occurrence and fate information overlapped.²³

The environmental relevance of these pesticides depends partly on fate and transport properties, including soil organic carbon partitioning, soil-water partitioning, soil half-life, water solubility, and relative leaching potential. The pesticide properties database (PPDB) provides pesticide property information that supports comparison of sorption, persistence, and other fate characteristics.¹ The Groundwater Ubiquity Score combines organic carbon partition coefficient (K_{oc}) and soil half-life to estimate relative leaching potential.²⁷ In sandy soils with low organic matter, compounds with lower sorption, higher solubility, and moderate to high persistence are generally more likely to move with infiltrating water toward shallow groundwater.²

Historical data review and benchmark screening

Historical pesticide records were accessed through TADA/EQuIS and related environmental data access sources for the Pineland Sands study area.²⁸ The historical records included data submitted by multiple monitoring organizations, including Minnesota Department of Agriculture - Pesticide Monitoring, Minnesota Pollution Control Agency (MPCA) - Ambient Groundwater, USGS Minnesota Water Science Center, and EPA National Aquatic Resources Survey (NARS). Current samples were collected during the October 2025 project sampling event; historical records were prior monitoring records reviewed for the study area. Records were reviewed by analyte, date, site, county, media type, source organization, result value, and detection-condition information where available. Current and historical concentrations were standardized to $\mu\text{g/L}$ before benchmark screening.²⁹ Neonicotinoid results reported in nanograms per liter were divided by 1,000 before comparison with benchmark values expressed in $\mu\text{g/L}$.

Only numeric detected concentrations were counted as benchmark-above results. Non-detects, reporting-limit-only values, and results identified as below detection or below reporting limits were excluded from benchmark-above counts. This rule was important because some apparent benchmark-above rows represented non-detect or reporting-limit records rather than confirmed detections.

Benchmark screening used EPA aquatic-life benchmarks,⁸ EPA 2021 Human Health Benchmarks for Pesticides,⁹ federal drinking-water MCL/MCLG values where available,¹⁰ and Minnesota Department of Health human health-based water guidance values.¹¹ Aquatic-life benchmarks were the primary basis for the observed benchmark-above pattern. Human-health, federal MCL, and Minnesota state values were reviewed as supporting context for detected pesticides.

Historical pesticide time-series figures were created using numeric historical concentration records for each pesticide after data cleaning. Reported zero values were retained, while non-detect records and negative values were excluded. For each pesticide, results were grouped by sample month and year in ArcGIS Pro Charts. When more than one numeric result for the same pesticide occurred within the same month-year period, ArcGIS Charts calculated the mean concentration for that pesticide during that period. The plotted historical time-series values therefore represent monthly mean concentrations across the historical sites included for each pesticide, rather than individual sample results or maximum concentrations (Table 4).

Results

Current pesticide results above aquatic-life benchmark values

As shown in (Table 5), current sampling identified two groundwater or groundwater-connected results above EPA aquatic-life benchmark values. Clothianidin was detected at 78.5 ng/L at Site 10 DNR, equivalent to 0.0785 $\mu\text{g/L}$, which was above the EPA freshwater invertebrate chronic benchmark value of 0.05 $\mu\text{g/L}$. Metribuzin was detected at 3.14 $\mu\text{g/L}$ at 18/CR115 Straight River Spring, which was above the EPA nonvascular plant NOAEC benchmark value of 2.3 $\mu\text{g/L}$. No current lake or stream result was above the aquatic-life benchmark values reviewed, and no current result was above an EPA HHBP, federal MCL, or Minnesota state health-based water guidance value.

Historical pesticide results above selected screening benchmarks

Together, (Table 6) and (Figure 5) show that historical records contained a broader set of benchmark-above concentrations than the current sampling event. The most consistent pattern involved neonicotinoid insecticides, especially clothianidin, imidacloprid, and thiamethoxam relative to freshwater invertebrate chronic benchmarks. Herbicide-related benchmark-above results were less frequent but included alachlor, atrazine, metolachlor, and metribuzin relative to aquatic plant endpoints. One metribuzin DADK result was above Minnesota state health-based guidance. Two imidacloprid results were above the lowest Minnesota state health-based value, and those results occurred at a site already represented in the aquatic-life benchmark screening.

Table 4: Benchmark endpoints crossed in the current and historical screening

Pesticide	Benchmark Category	Endpoint and Benchmark Value	Screening Context
Alachlor	EPA Aquatic Life	Nonvascular Plant NOAEC = 0.035 µg/L; Vascular Plant NOAEC = 0.339 µg/L	Historical herbicide results above plant-based aquatic-life benchmarks
Atrazine	EPA Aquatic Life	Nonvascular Plant IC50E = <1 µg/L	Historical NARS lake/lacustrine wetland result above plant benchmark; interpreted cautiously because the benchmark is listed with a less-than qualifier
Clothianidin	EPA Aquatic Life	Freshwater Invertebrate Chronic (ChronicD) = 0.05 µg/L	Current and historical neonicotinoid results above freshwater invertebrate chronic benchmark
Imidacloprid	EPA Aquatic Life; Minnesota State Guidance	Freshwater Invertebrate Chronic (ChronicD) = 0.01 µg/L; Freshwater Invertebrate Acute (AcuteC) = 0.385 µg/L; Lowest MDH Health-Based Value = 2.0 µg/L	Historical neonicotinoid results above aquatic-life benchmarks; two historical results were above the lowest MDH value
Metolachlor	EPA Aquatic Life	Nonvascular Plant NOAEC = 1.5 µg/L; Vascular Plant NOAEC = 4.4 µg/L; Nonvascular Plant IC50E = 8 µg/L; Vascular Plant IC50F = 14 µg/L; Freshwater Vertebrate Chronic (ChronicB) = 30 µg/L	Historical herbicide results above plant-based aquatic-life benchmarks
Metribuzin	EPA Aquatic Life	Nonvascular Plant NOAEC = 2.3 µg/L	Current and historical herbicide results above plant-based aquatic-life benchmark
Metribuzin DADK	Minnesota State Guidance	Lowest MDH Health-Based Value = 10.0 µg/L	One historical degradate result above Minnesota state health-based guidance
Thiamethoxam	EPA Aquatic Life	Freshwater Invertebrate Chronic (ChronicD) = 0.74 µg/L	Historical neonicotinoid results above freshwater invertebrate chronic benchmark

Note. Endpoint abbreviations are EPA aquatic-life screening endpoints. AcuteA = short-term freshwater vertebrate endpoint; ChronicB = long-term freshwater vertebrate endpoint; AcuteC = short-term freshwater invertebrate endpoint; ChronicD = long-term freshwater invertebrate endpoint; IC50E = nonvascular plant 50% inhibition endpoint; IC50F = vascular plant 50% inhibition endpoint; NOAEC = no-observed-adverse-effects concentration. Values with "<" or ">" are qualified benchmark values and should be interpreted cautiously.

Table 5: Current pesticide sample results above aquatic-life benchmark values

Site	Medium	Analyte	Result (µg/L)	Benchmark Endpoint	Benchmark Value (µg/L)
10 DNR	Groundwater	Clothianidin	0.0785	Freshwater invertebrate chronic (ChronicD)	0.05
18/CR115 Straight River Spring	Groundwater spring	Metribuzin	3.14	Nonvascular plant NOAEC	2.3

Note. ChronicD = long-term freshwater invertebrate endpoint. NOAEC = no-observed-adverse-effects concentration. These comparisons are screening-level results and do not demonstrate biological impairment or regulatory noncompliance

Pesticide groups of concern and human-health context

Neonicotinoid insecticides were the clearest benchmark-above group in the historical dataset. Clothianidin and imidacloprid each had more than 100 historical groundwater results above freshwater invertebrate chronic benchmark values, and thiamethoxam also had multiple historical results above its freshwater invertebrate chronic benchmark. Recent MDA monitoring provides a useful comparison, as clothianidin was among the most frequently detected parent pesticides in 2024 groundwater samples.⁷ MDA

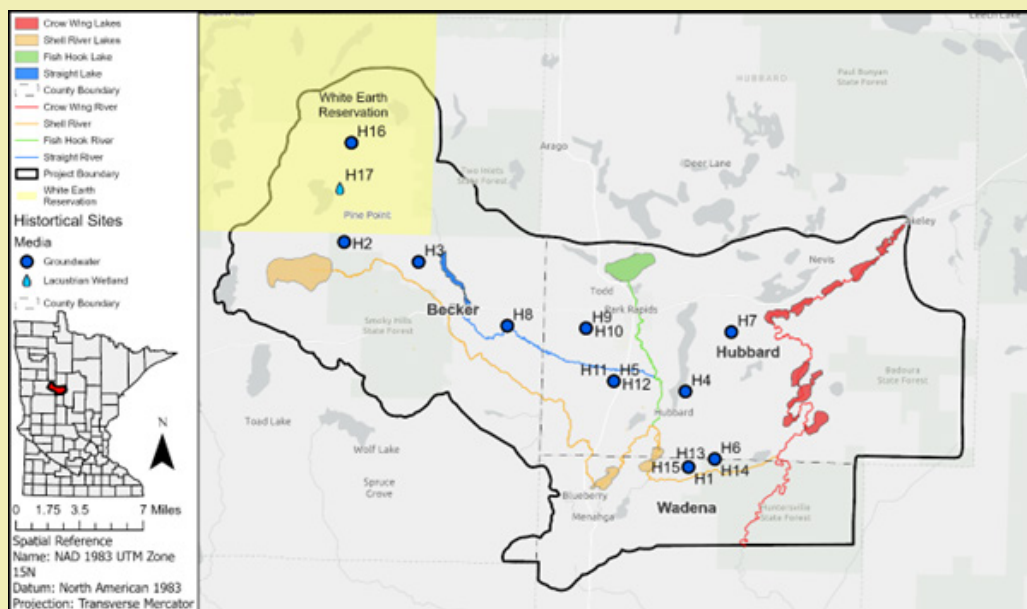
also found that clothianidin and imidacloprid accounted for most pesticide detections above aquatic-life/reference values in 2024 river and stream monitoring.⁷ The low chronic freshwater invertebrate benchmarks for these neonicotinoids make them especially important in screening.⁸ This is particularly relevant where mobile compounds may move through sandy groundwater settings, because chemical sorption, persistence, and soil-profile conditions influence leaching potential.^{1,2}

Table 6: Historical pesticide results above selected benchmark values

Analyte	Results Above Benchmark	Date Range	Site/County Distribution	Maximum Result (µg/L)	Benchmark Endpoint(s) Crossed
Alachlor	3	11/13/2000-05/13/2002	1 site in Becker County	0.72	EPA Aquatic Life: Nonvascular Plant NOAEC; Vascular Plant NOAEC
Atrazine	1	8/2/2017	1 site in Becker County	1.133	EPA Aquatic Life: Nonvascular Plant IC50E (<1 µg/L)
Clothianidin	102	10/13/2011-10/12/2022	3 Becker; 8 Hubbard; 3 Wadena sites	1.46	EPA Aquatic Life: Freshwater Invertebrate Chronic (ChronicD)
Imidacloprid	101 aquatic-life; 2 MDH state-guidance results	05/14/2010-10/13/2022	2 Becker; 6 Hubbard; 3 Wadena sites	2.26	EPA Aquatic Life: Freshwater Invertebrate Chronic (ChronicD) and Acute (AcuteC); Minnesota state guidance: lowest MDH value (2.0 µg/L)
Metolachlor	6	03/28/2000-05/18/2001	1 Becker; 1 Wadena site	31.2	EPA Aquatic Life: Nonvascular Plant NOAEC; Vascular Plant NOAEC; Nonvascular Plant IC50E; Vascular Plant IC50F; Freshwater Vertebrate Chronic (ChronicB)
Metribuzin	2	03/28/2000-05/13/2015	1 Becker; 1 Wadena site	7.84	EPA Aquatic Life: Nonvascular Plant NOAEC
Metribuzin DADK	1	8/17/2000	1 Becker County site	38	Minnesota state guidance: lowest MDH value (10.0 µg/L)
Thiamethoxam	22	10/29/2014-10/21/2021	4 Hubbard; 3 Wadena sites	6.34	EPA Aquatic Life: Freshwater Invertebrate Chronic (ChronicD)

Note. Counts are individual detected results above at least one reviewed benchmark or guidance value, not unique sites. One result may cross multiple endpoints. Endpoint abbreviations are defined in Table 4 note; Minnesota state guidance values are human-health values and should be interpreted separately from aquatic-life benchmarks. Source-organization details are best shown in the supplementary historical site table.

Figure 5: Historical sites with concentrations above selected benchmark values



The benchmark endpoints also help identify the ecological receptor groups most relevant to the screening results. For clothianidin, imidacloprid, and thiamethoxam, the most sensitive aquatic-life comparisons in this study were associated with freshwater invertebrate endpoints.⁸ In groundwater-connected streams, springs, wetlands, or lakes, those receptors may include aquatic insects, midges, amphipods, daphnids, and other small invertebrates that support fish, amphibians, and wetland birds. For alachlor, atrazine, metolachlor, and metribuzin, the most relevant benchmark endpoints were associated with aquatic plants and algae, including nonvascular plants, aquatic vascular plants, duckweed, and algal growth endpoints.⁸ Wild rice, where present in the study-area landscape, is also relevant as a culturally and ecologically important wetland plant that provides food and habitat for waterfowl, pollinators, mammals, and other wildlife.^{5,6} These organisms should be viewed as potentially sensitive ecological receptors represented by the screening values, not as evidence of observed biological effects.

Herbicide-related benchmark-above concentrations were less frequent but still important. Alachlor, metolachlor, and metribuzin crossed plant-based aquatic-life benchmark values in the historical dataset, and the current metribuzin result at 18/CR115 Straight River Spring shows that herbicide concentrations above aquatic-life screening values can also occur in groundwater-discharge settings. Atrazine was represented by one historical NARS lake/lacustrine wetland result above the aquatic plant benchmark used in this screening.

Metribuzin DADK was evaluated separately from parent metribuzin because the DADK result was compared with Minnesota human-health guidance, while parent metribuzin was mainly compared with EPA aquatic-life plant benchmarks. MDA's 2024 groundwater results show that Metribuzin DADK was detected in PMR 4, but at a lower frequency than major chloroacetanilide degradates such as metolachlor ethane sulfonic acid (ESA), metolachlor oxanilic acid (OA), and alachlor ESA.⁷ The historical DADK result above Minnesota guidance shows why the degradate remained part of the screening, even though broader degradate patterns may be better evaluated using more frequently detected degradates.

Human-health benchmark findings were more limited than aquatic-life findings. EPA HHBP values, federal MCLs, and Minnesota state health-based water guidance values were reviewed for the relevant pesticides, but no current detections were above an EPA HHBP, federal MCL, or Minnesota state guidance value. In the historical dataset, two imidacloprid results and one metribuzin DADK result were above Minnesota state health-based guidance values. These human-health findings are presented separately from aquatic-life benchmark findings because they reflect different receptors, exposure assumptions, and interpretive meaning.

Historical pesticide time-series figures

Historical time-series (Figures 6-12) summarize numeric historical concentration records after data cleaning. Reported zero values were retained, while non-detect records and negative values were excluded. The figures show monthly average concentrations across available historical sites for each pesticide and are intended to provide temporal context rather than site-specific trends. When multiple results for the same pesticide occurred within a month-year period, the plotted value represents the mean concentration for that month-year group. A time-series figure is not shown for alachlor because only three total alachlor detections were available after data cleaning. Alachlor is retained in Tables 4 and 6 because those detections were still relevant to plant-based aquatic-life screening. Media descriptions below refer to the benchmark-above records summarized in Table 6, not every plotted historical value.

Average historical atrazine concentrations were generally low across the record, except for one increase tied to the 2017 EPA NARS lake/lacustrine wetland record. Because the relevant atrazine aquatic plant benchmark is listed with a less-than qualifier for the nonvascular plant IC50E endpoint, the result is included in the screening but interpreted cautiously.

Clothianidin showed repeated historical detections from 2011 through 2022, with several elevated monthly averages later in the record. The benchmark-above clothianidin records summarized here were groundwater records from Becker, Hubbard, and Wadena counties. Because clothianidin is a neonicotinoid insecticide with a low freshwater invertebrate chronic benchmark relative to many herbicide benchmarks, the recurring groundwater detections are important for screening (Figure 8).

Imidacloprid average concentrations were higher during the earlier and middle portions of the historical record and generally decreased after about 2017-2018, although detections continued. The benchmark-above imidacloprid records summarized here were groundwater records. The pattern remains important because imidacloprid has a very low freshwater invertebrate chronic benchmark of 0.01 ($\mu\text{g/L}$), and two historical results also exceeded the lowest Minnesota state guidance value (Figure 9).

Metolachlor showed a high early historical peak and several smaller early detections, followed by mostly low or near-zero monthly averages. The benchmark-above metolachlor records summarized here were groundwater records from Becker and Wadena counties. This pattern suggests episodic historical occurrence rather than a consistent long-term regional signal, but the early concentrations were high enough to cross multiple aquatic-life plant endpoints and the freshwater vertebrate chronic endpoint (Figure 10).

Figure 6: Time series of average historical atrazine concentrations

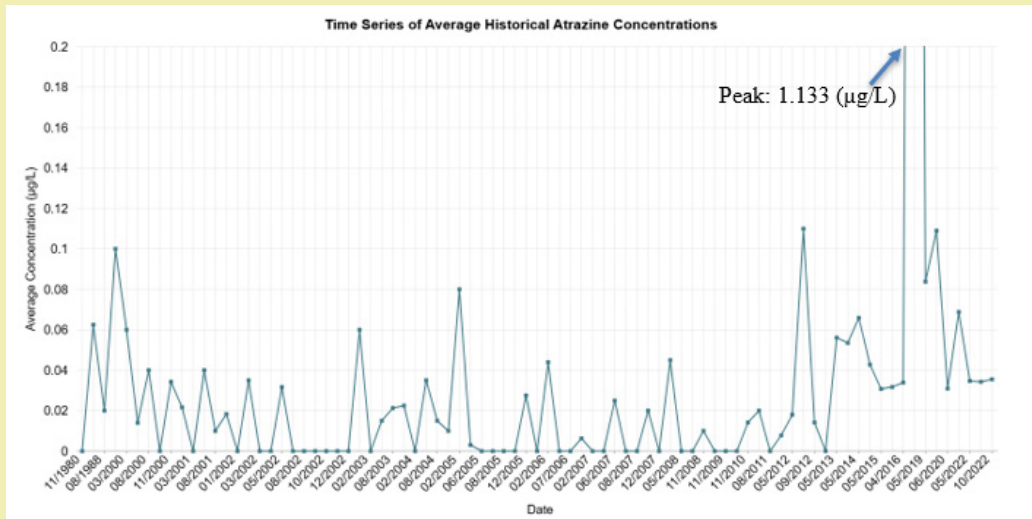


Figure 7: Time series of average historical clothianidin concentrations

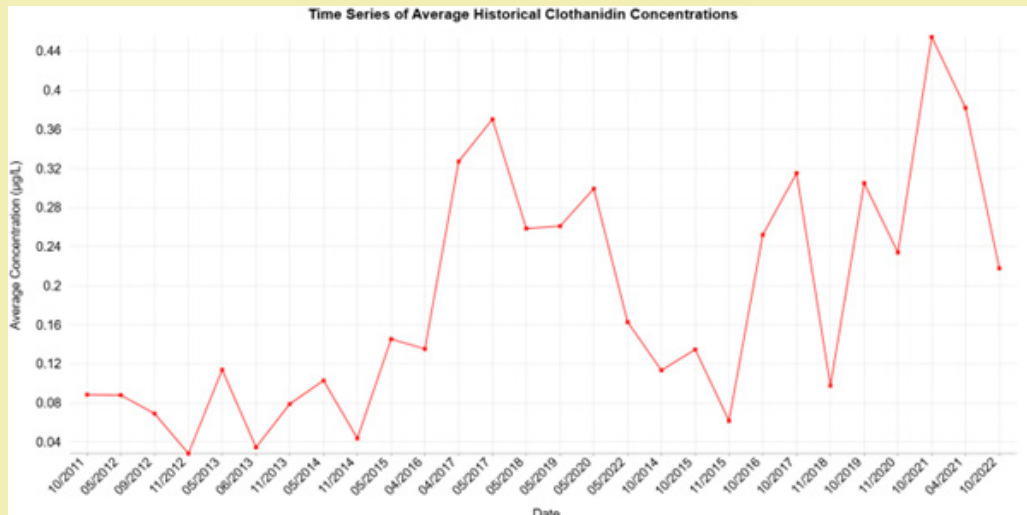


Figure 8: Time series of average historical imidacloprid concentrations

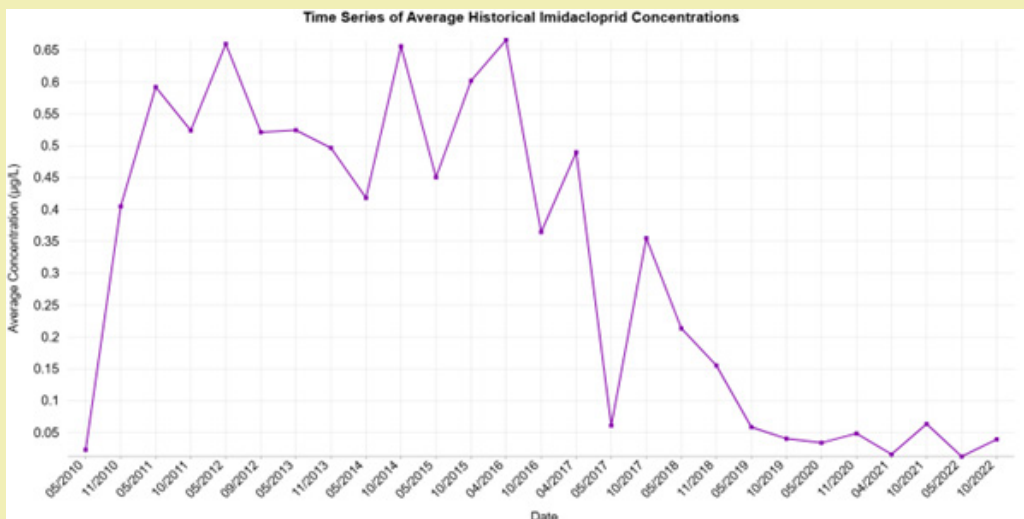
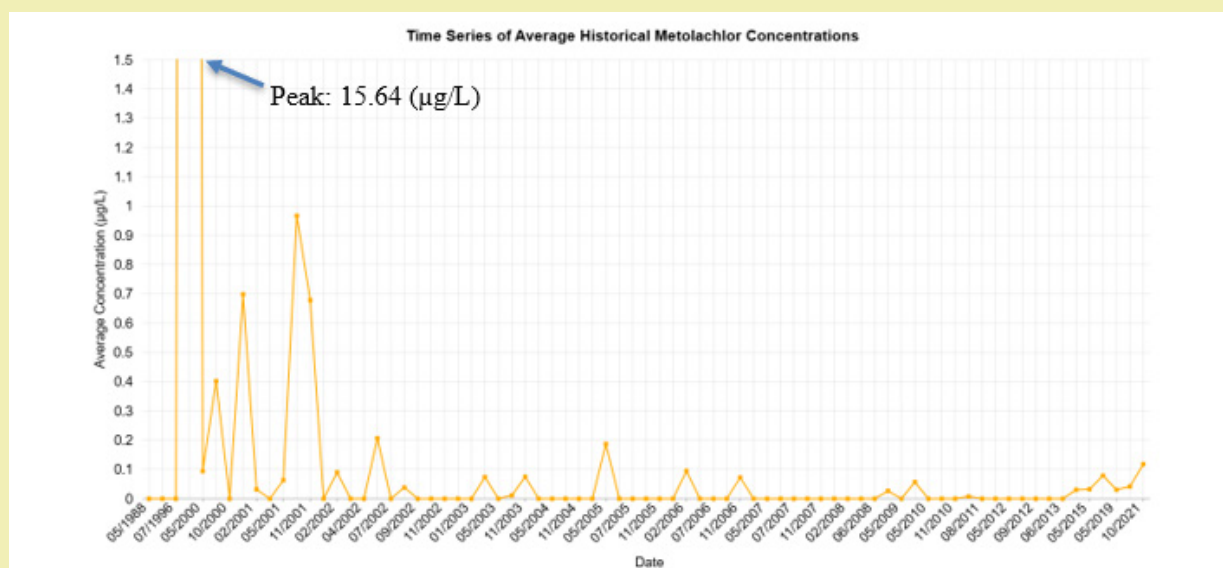
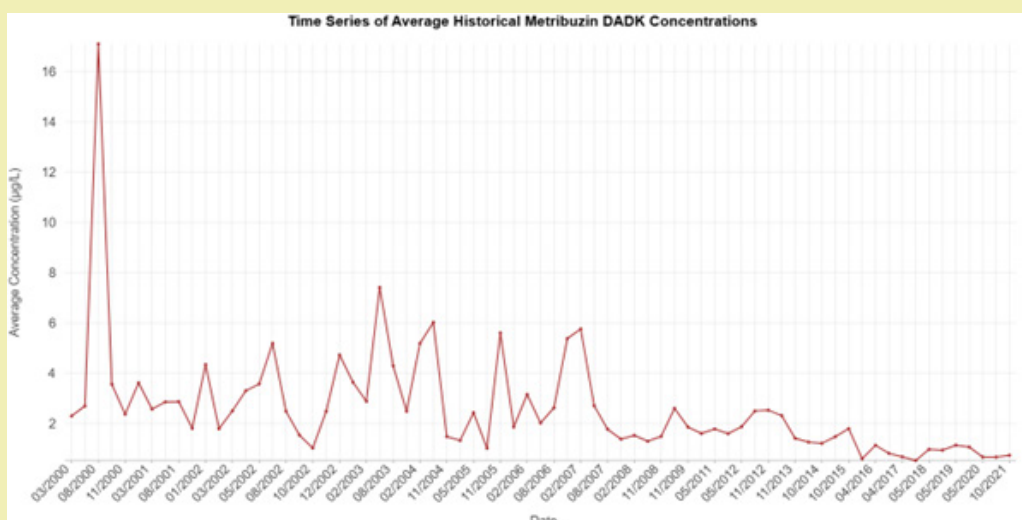


Figure 9: Time series of average historical metolachlor concentrations**Figure 10:** Time series of average historical metribuzin DADK concentrations

Metribuzin DADK had its largest average concentration near the beginning of the historical record, followed by lower but recurring concentrations. The benchmark-above DADK result summarized here was a groundwater record. Metribuzin DADK was reviewed separately from parent metribuzin because the DADK result was compared with Minnesota human-health guidance, while parent metribuzin was mainly compared with EPA aquatic-life plant benchmarks (Figure 11).

Parent metribuzin concentrations were generally low for much of the record but became more variable in the later historical period, including a distinct mid-2010s peak. The benchmark-above metribuzin records summarized here were groundwater or groundwater-connected records. The screening concern for parent metribuzin is mainly tied to the EPA nonvascular plant NOAEC, making this figure most relevant to herbicide occurrence for algae and similar nonvascular aquatic plants.

Thiamethoxam concentrations increased after the early 2010s, reached their highest monthly averages during the mid-2010s, and remained detectable with variable concentrations later in the record. The benchmark-above thiamethoxam records summarized here were groundwater records from Hubbard and Wadena counties. Together with clothianidin and imidacloprid, this pattern supports the conclusion that neonicotinoid insecticides were the most consistent historical pesticide group of concern for freshwater invertebrate benchmark screening (Figure 12).

Discussion

Interpretation of groundwater concentrations above aquatic-life benchmark values

Most results above aquatic-life benchmark values were measured in groundwater rather than surface water, so the sampled medium is central to interpretation. Groundwater concentrations

above aquatic-life screening values should not be described as direct surface-water aquatic-life benchmark exceedances. Instead, they identify locations where groundwater concentrations may be relevant to potential aquatic exposure if groundwater discharges to streams, springs, wetlands, or lakes. This interpretation is consistent with the sandy aquifer setting of the Pineland Sands³ and with the documented stream-aquifer connection in the Straight River area.⁴

The distinction matters because the organisms represented by the aquatic-life benchmarks, including aquatic plants, algae, aquatic insects, other freshwater invertebrates, fish, and amphibian prey resources, would only be directly exposed if groundwater carrying these compounds reaches biologically active surface-water or wetland habitats.⁸

The current metribuzin result at 18/CR115 Straight River Spring deserves particular attention because the sample was collected in a spring setting. Although it is not a direct surface-water sample, it

is more directly relevant to potential surface-water input than an upland groundwater well with less direct evidence of connection to a stream channel. Paired groundwater-discharge and receiving-water samples would be needed to evaluate the concentration entering surface-water habitat.

Land cover, water-quality indicators, and pesticide mobility context

The land-cover summary places the pesticide results within the actual project landscape. The project boundary was dominated by forest, wetlands, grassland/pasture/shrubland, and open water, while agricultural classes occurred in more localized areas. Pesticide detections therefore should not be interpreted as representing uniform agricultural influence across the entire project boundary. Instead, they likely reflect the interaction of local land use, recharge, soil texture, water-table position, pesticide properties, and groundwater flow paths.

Figure 11: Time series of average historical metribuzin concentrations

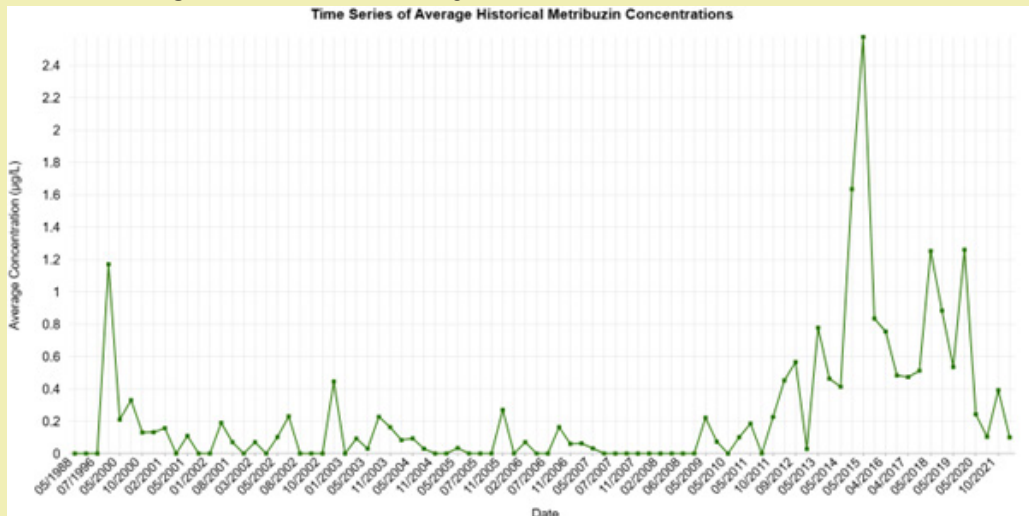
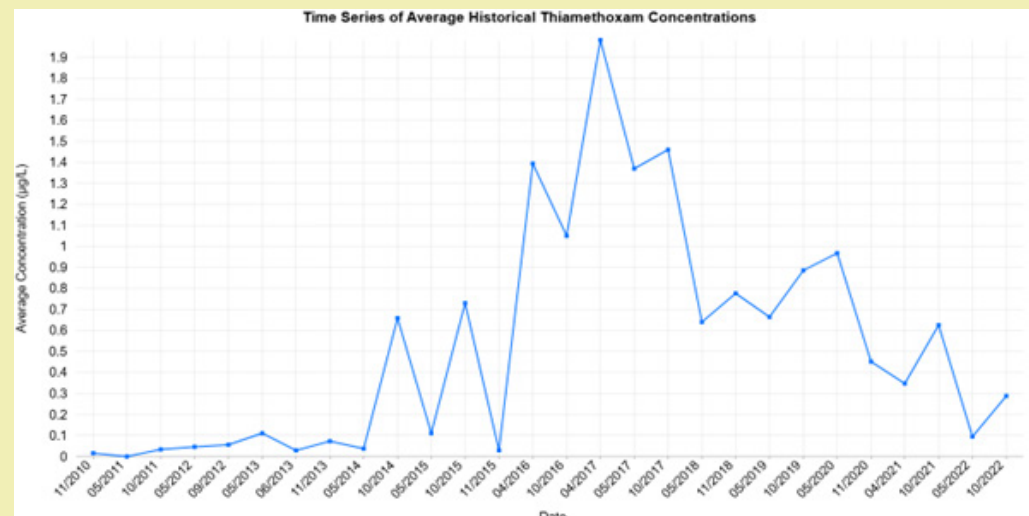


Figure 12: Time series of average historical thiamethoxam concentrations



Nitrate, potassium, chloride, and sodium were used as supporting site-selection indicators rather than direct evidence of pesticide occurrence. Nitrate is the strongest of these indicators for agricultural influence in groundwater because it is commonly associated with fertilizer inputs and recharge through agricultural soils. The MDA 2024 groundwater analysis found a weak positive relationship between nitrate and total pesticide concentrations and reported that pesticide detections became more likely when nitrate concentrations were above background, although pesticides were still detected in many samples with lower nitrate concentrations.⁷ Potassium helped characterize possible nutrient inputs because applied K can be displaced and leached through sandy soils, but it was interpreted cautiously because K can also reflect soil mineral weathering, irrigation-water chemistry, and cation-exchange processes and should not be used alone as a pesticide or fertilizer tracer.¹⁴ Chloride can reflect several land-use sources, including fertilization and other human activities, and it is mobile in soil water.¹⁵ Sodium helped provide context for possible road-salt influence because sodium chloride is a common road-salt compound; MDA identifies road salt, fertilizer use, livestock excretion, and household water softeners as major contributors to elevated chloride in the environment.⁷ Together, these ions helped characterize land-use and recharge influence, but none should be interpreted alone as a pesticide tracer.

Pesticide leaching potential is influenced by both site conditions and chemical properties. Lower K_{oc} or soil-water distribution coefficient (K_d) values generally indicate weaker sorption to soil or organic carbon and greater potential mobility in soil water.¹ Higher water solubility and longer soil half-life can also increase the likelihood that a pesticide or its degradate persists long enough to move below the root zone.² The Groundwater Ubiquity Score combines K_{oc} and soil half-life to estimate relative leaching potential toward groundwater.²⁷ In sandy soils with low organic matter and high permeability, compounds with low sorption and moderate to high persistence can be especially relevant to groundwater screening.³⁰

The present screening did not fully evaluate degradate timing or land-use change, but both questions are important future steps. Future analysis of metolachlor ESA/OA and alachlor ESA/OA may help evaluate whether groundwater detections reflect seasonal recharge, historical use, or longer groundwater travel times. Future work should also compare older agricultural land-cover conditions with the 2023 cropland data layer CDL summary to evaluate whether changes in cropland distribution, crop type, or agricultural intensity correspond with changes in pesticide detections. If the 2006 CDL is available and comparable for the study area, it should be considered; otherwise, the earliest comparable CDL year should be used. National CDL documentation notes that full continental U.S. CDL coverage began in 2008, so pre-2008 comparisons should be checked carefully for availability and consistency.³¹

Additional mobility-focused work should include soil organic carbon and depth-to-water information. Soil organic carbon affects pesticide sorption and can help explain why some compounds remain more mobile in sandy settings. Depth to water should also be evaluated because a shallow water table can shorten the travel distance from the land surface to groundwater and may increase the relevance of pesticide detections in recharge or groundwater-discharge areas. Pairing land cover, soil organic carbon, depth to water, pesticide fate properties, and non-detect/censored-data methods would provide a stronger basis for future trend and transport interpretation.

Limitations and uncertainty

This screening approach has several limitations. Benchmark comparisons do not demonstrate biological effects, toxicity in the field, or regulatory noncompliance. Historical records may differ in sampling design, monitoring objectives, analytical methods, reporting limits, and detection-condition fields. Some historical records required careful interpretation because negative values, non-detects, or reporting-limit values may represent limits rather than measured concentrations. To avoid overcounting benchmark-above results, this review counted only numeric detected concentrations as results above benchmarks. For future trend analysis, however, non-detect records should not simply be discarded; censored-data methods or consistent substitution approaches could help retain more information about concentration patterns over time.

Another limitation is that aquatic-life benchmarks were applied mainly to groundwater results. This is useful as a screening approach where groundwater may discharge to surface water, but the results should not be treated as direct evidence that aquatic organisms were exposed to the same concentrations. The historical time-series figures also show monthly mean concentrations across available historical sites for each pesticide; they are useful for broad temporal context but should not be interpreted as site-specific trends or complete seasonal analyses. Paired groundwater and surface-water sampling, along with soil organic carbon, depth-to-water, and land-use-change analysis, would be needed to evaluate actual transport from groundwater to surface-water habitats.

Conclusions

This study identified two current groundwater or groundwater-connected pesticide concentrations above EPA aquatic-life benchmark values, along with a broader historical pattern of benchmark-above concentrations in the Pineland Sands study area. October 2025 sampling identified clothianidin above the freshwater invertebrate chronic benchmark at Site 10 DNR and metribuzin above the nonvascular plant NOAEC at 18/CR115 Straight River Spring. No current detections were above EPA Human Health Benchmarks for Pesticides, federal drinking-water MCLs, or Minnesota Department of Health human health-based water guidance values.

Historical pesticide records accessed through TADA/EQuIS identified concentrations above selected benchmark or guidance values for alachlor, atrazine, clothianidin, imidacloprid, metolachlor, metribuzin, metribuzin DADK, and thiamethoxam. Neonicotinoid insecticides dominated the historical pattern relative to freshwater invertebrate chronic benchmark values, while herbicide-related benchmark-above concentrations were less frequent and were mainly associated with plant-based aquatic-life endpoints. Human-health findings were limited to historical imidacloprid and metribuzin DADK concentrations above Minnesota state guidance values.

Because most benchmark-above concentrations were measured in groundwater, these results should be interpreted as screening-level indicators of potential concern rather than direct evidence of surface-water aquatic-life impairment, human-health effects, or regulatory noncompliance. The current metribuzin result from a spring or groundwater-discharge setting is especially important because it represents groundwater near a likely discharge point to a stream channel. Future work should prioritize paired groundwater and surface-water sampling at springs, streambed wells, riparian wells, and gaining stream reaches; incorporate non-detect/censored-data methods for trend analysis; compare older and current land-cover conditions; and evaluate soil organic carbon and depth to water to better understand pesticide mobility in sandy groundwater settings.

Artificial Intelligence Acknowledgment

Generative AI tools, including Microsoft Copilot and Google Gemini Pro, were used in a limited support role during manuscript preparation. AI assistance included:

- a. Explaining and troubleshooting ArcGIS Pro workflows, map layout issues, and chart formatting.
- b. Revising wording in manuscript sections that were initially drafted by the author.
- c. Organizing benchmark information and tables for manual review.
- d. Assisting with reference organization and citation-management checks.
- e. Identifying possible source-search directions for author review.

AI was not used to originate the scientific conclusions, interpretations, results, benchmark determinations, or final citations in this manuscript.

All AI-assisted wording was reviewed by the author to confirm meaning, numerical values, benchmark comparisons, and citation accuracy. Sources suggested during AI-assisted work were independently checked before use. University of Minnesota and

project guidance on appropriate use of generative AI tools was followed.

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Conflict of Interest

Regarding the publication of this article, the authors declare that they have no conflict of interest.

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