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Examination of Soil Water Nitrate-N Concentrations from Common Land Covers and Cropping Systems in Southeast Minnesota Karst

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Abstract

The purpose of this study was to identify the range of soil water nitrate-nitrogen (nitrate) concentrations measured at a four-foot depth from nine different land covers and cropping systems in southeast Minnesota. Results from the five-year study (2011-2015) found low concentrations of soil water nitrate, generally less than 2 mg/L, from prairie, forest and low maintenance homeowner lawn sites. Cattle pasture sites and a golf course averaged 5.1 and 3.7 mg/L, respectively. A grass field border and grassed waterway had similar concentrations and averaged between 5.9 mg/L (non-fertilized) and 8.9 mg/L (fertilized). Concentrations from the grass strips were higher than expected and likely explained by subsurface mixing of soil water between adjacent land covers. Nitrate concentrations collected from lysimeters in cultivated row crop settings were comparable to tile drained sites in Minnesota, but were highly variable and averaged 22.3 mg/L with a typical range of 8.0 to 28.0 mg/L. Corn fields with alfalfa in the rotation had nitrate concentrations averaging 6.6 mg/L which were 70% lower when compared to sites without perennials. When considered within the context of this study's limitations, data collected from the Southeast Lysimeter Network could serve as a useful educational tool for farmers, crop advisors, rural homeowners and groundwater advisory groups.

Background and Purpose

The geology of southeastern Minnesota's Driftless Area is comprised of carbonate bedrock (limestone and dolostone), sandstone and shale. Over millennia, naturally acidic rain and soil water has interacted with carbonate bedrock to form karst features including dissolutionally-enlarged fractures, subterranean conduits, sinkholes, and springs. Most of the bedrock formations in this area are covered by less than 50 feet of surficial deposits (Mossler, 1995) and in many areas, moderate to well-drained soils are less than ten feet thick (Dogwiler, 2013). This can result in direct hydrologic connections between the land surface and underlying bedrock and can facilitate the rapid movement of water and potential contaminants from the land surface into bedrock aquifers used for drinking water (Green et al, 2014; Runkel et al, 2014), and ultimately groundwater return flow to springs, streams and rivers. One of the most common nutrients found in southeast Minnesota groundwater is nitrate-nitrogen (NO₃-N, from this point forward referred simply as nitrate). Nitrate is a common form of plant-available nitrogen that is water soluble and can primarily come from nitrogen fertilizer, manure, sewage, or the breakdown of soil organic matter. If not utilized by plants or retained in soil organic material, nitrate can move rapidly by water and leach through the soil and into groundwater.

The loss of nitrogen from agricultural lands has both local and regional impacts. Regionally, excess nitrogen lost from agricultural applications, primarily from the upper Midwest, are one of the main contributors to the hypoxic zone in the Gulf of Mexico (Alexander et al, 2008, Robertson et al, 2019). A 2013 report estimated that about 89% of the nitrogen measured in surface water in southeast Minnesota watersheds was derived from cropland, primarily through groundwater pathways (MPCA, 2013). More locally, results from private drinking water testing in Houston, Fillmore and Winona Counties have shown 15.3% to 19.1% of the sampled wells were at or above the drinking water health standard of 10 mg/L for nitrate (MDA, 2017).

Understanding the source of nitrate and how it moves into groundwater is a key step in helping manage the region's water resources. A common question raised during nitrate reduction planning discussions is how do nitrates compare between different crops or landcovers? The objective of this five-year study was to identify the range of nitrate concentrations present in soil water infiltrating from the unsaturated root zone across common land covers and cropping systems in southeast Minnesota. Land use in this region mainly consists of cultivated row crops so much of this investigation focused on agricultural land covers, but other non-agricultural land covers including prairies, forests, pastures and turf were also studied. Although this investigation does not attempt to fully quantify the magnitude of the nitrate flux or loading to aquifers, our results provide insight to the potential risk of loss to groundwater associated with various land covers. These data will help inform farmers, their advisors and other stakeholders as they work toward reducing nitrate in drinking water and surface water.

Information presented in this report were collected as part of an initiative known as the Southeast Minnesota Lysimeter Network (SLN). This undertaking represented a collaboration among several partners, including the Fillmore Soil and Water Conservation District (SWCD), Winona SWCD, Winona State University-Southeastern Minnesota Water Resources Center (SMWRC), Minnesota Pollution Control Agency (MPCA) and Minnesota Department of Agriculture (MDA). Funding for this work was provided in-part by Minnesota's Clean Water Fund from MPCA and through MDA's Root River Field to Stream Partnership (RRFSP).

Methods

The study took place across four counties and 23 sites in southeast Minnesota from 2011-2015 (Figure 1). Table 1 summarizes the 2015 land use across the four-county study area. On average, land managed for corn-soybean production, forest, and grass/pasture was over 80% while landcovers in alfalfa, turf and golf courses were less than 10%. Sampling sites were located on private property and cooperators were identified by staff from the Fillmore SWCD, Winona SWCD and MDA. The most common agricultural practices in southeast

Figure 1. Lysimeter network locations across a four County area in southeast Minnesota.

Minnesota were sampled, as well as several other common non-agricultural land cover types (Table 2). Land covers were grouped into three categories: non-agriculture, ag pasture/grass strips and ag rowcrop. Crop and nitrogen management information were collected for each agricultural site and consisted of nitrogen application rates, timing, source and placement (Table 3). Nitrogen application rates included the actual amount of nitrogen from commercially applied fertilizers, first and second year manure credits and credits from alfalfa. Total nitrogen rates also included incidental nitrogen sources from starter, ammonium thiosulfate (AMS), diammonium phosphate (DAP) and monoammonium phosphate (MAP) fertilizers containing nitrogen. Tables 1 and 2 provide additional management details about each site. Soils at the monitoring locations consisted of well drained to moderately well drained silt-loam soil types. The typical range of organic matter in these soils is 2.7% to 3.9% with an average of 3.3%.

County	Corn and Soybeans	Alfalfa	Forest	Grass/Pasture	Turf/Homeowner Lawns 1	Golf Course 2	
	-% of county area-						
Fillmore	45%	6%	22%	21%	3%	$< 0.1\%$	
Olmsted	43%	4%	15%	23%	6%	0.1%	
Winona	22%	6%	39%	21%	4%	0.1%	
Wabasha	33%	5%	24%	23%	3%	< 0.1%	
Overall Avg.	36%	5%	25%	22%	4%	< 0.1%	

Table 1. Land use as a percentage of county area. (Source: 2015 Cropscape Cropland Data Layer-Center for Spatial Information and Science Systems)

¹Uses the developed open space classification in CropScape and likely overestimates the area managed for turf. ²Digitized from the MNGEO 2015 aerial photography.

Equipment

Soil water samples were collected using 50 porous cup tensiometers (Figure 2), more commonly called suction cup lysimeters. Lysimeters consisted of a 24-inch long piece of PVC pipe, sampling and suction lines and porous ceramic tip. The basic construction involved attaching and sealing a ceramic tip to one end of a 1.5 inch diameter PVC pipe with epoxy and attaching a rubber stopper to the other end. The rubber stoppers were secured with electrical tape and special adhesive to ensure complete sealing. Two, 0.25 inch diameter plastic tubes were passed through the rubber stopper to ensure an air tight seal. One tube was used as the sample line. It extended to the bottom of the porous ceramic tip and was used for sampling water from the lysimeter. The other line, the suction line, was used to create a vacuum within the lysimeter.

At cultivated row crop sites, lysimeters were installed to a depth of four feet within the vadose zone and placed a minimum of 40 feet into the field. This distance was used to minimize edge of field variability caused by compaction, non-uniform fertilizer applications, and help avoid other factors that can be common in the headland areas of row-crop fields. At most locations, at least two lysimeters were paired together at each site to better understand variability. Having two lysimeters also provided redundancy in the event one lysimeter failed. Typically, paired lysimeters were installed 20 feet apart. To prevent damage from tillage equipment, a trenching machine was used to create a 2.5 foot deep trench to route the sample and suction lines from lysimeters to the field edge. The sample and suction line tubing was routed through PVC conduit to protect it from being crushed by the soil during reburial and terminated in a single sampling port. At the desired lysimeter location within the field, an additional 1.5 foot deep hole was excavated within the bottom of the trench using a four-inch diameter soil auger. To minimize soil disturbance directly above the lysimeters, the hole was hand augered at an approximate 20-degree angle from the bottom and long axis of the machined trench. This ensured that the sampling tip was beneath undisturbed soil and not directly under the

Figure 2. A) Installation of lysimeter sample and vacuum lines in a field managed for continuous corn silage and dairy manure. Sample lines were trenched 2.5 feet below the surface while lysimeters were placed four feet below the soil surface. **B)** Porous tension ceramic cup lysimeter with vacuum and sampling lines. Pen in lower right corner of photograph used for scale and is pointing at the ceramic tip.

excavated trench. A distilled water and silica slurry mixture was placed in the augered hole around the ceramic tip to ensure adequate hydraulic contact and movement of water to the lysimeter. Bentonite clay was packed above the ceramic tip during backfill to prevent drainage along the side of the lysimeter. At the golf course and homeowner lawn sites, lysimeters were installed using a hand auger to a depth of about two feet. At two row-crop sites, the full four-foot depth was not achieved because of refusal due to shallow bedrock. In all cases the lysimeters were installed a minimum of 4 to 6 inches above the bedrock at least two feet below the surface. At all sites the depth of the lysimeter sampling tip was below the rooting depth of the associated land cover vegetation. Lysimeters were permanently installed at each location and not removed during the study period. Lysimeter construction, installation and training was provided by MDA and SMWRC with assistance from Fillmore SWCD and MPCA.

Sampling and Analysis

A 30-40 centibar vacuum was applied to the lysimeters between sampling periods. Sampling intervals were consistent throughout the study period and were collected every two weeks during the frost-free period, typically from April through October (Figure 3). In some years it was possible to start sampling in March and extend sampling through November due to above normal temperatures. Samples were collected using a hand operated vacuum pump and one-liter Erlenmeyer flask. In most cases 300-600 mL of water was available for sampling of which 100 mL was used for nitrate analysis. Samples were placed on ice in a cooler and kept refrigerated until analysis. Water samples were analyzed using a Hach® DR6000 UV spectrophotometer (pour-through method 357-10049, DOC 316.53.01072) located in the MDA Preston field office within a week of sample collection. The detection limit using this method is 0.1 mg/L. Samples were analyzed using standardized quality assurance and control (QA/QC) procedures. As part of the QA/QC, a duplicate of no less than 10% of the water samples were selected randomly and analyzed by the Minnesota Department of Agriculture (MDA Lab) certified laboratory located in St. Paul. It should be noted that the MDA lab method includes both nitrite and nitrate ($NO₂-N+ NO₃-N$) while the DR6000 method does not report nitrite(NO₂-N). Nitrite is seldom present in groundwater and if detected is typically less than 0.3 mg/L, transforms quickly to the more stable nitrate form (USEPA, 1987), and therefore is not considered to be a significant factor when comparing the two methods. Additional details regarding the duplicate sample results are included in Appendix C of this report. Statistical group tests were used to identify significant differences between the various land covers. If *p* values were less than or equal to 0.05 when using non-parametric tests on the nitrate median, the groups were considered statistically different. The Mann-Whitney test was used when comparing individual pairs while the Kruskal-Wallis multiple comparison test was used across all land covers. Statistical analysis was conducted using R and Minitab® statistical software.

Figure 3. Soil water nitrate collection from a continuous corn grain site (OM70/90). The sampling port was located in a grassed waterway.

Table 2. Land cover and farming practices evaluated during the five-year soil water nitrate study.

Table 3. Land cover and nitrogen management details by site and year. Total nitrogen rates in pounds per acre (lb/ac) from manure or commercial fertilizers is displayed in parenthesis. Total nitrogen includes first and second year manure nitrogen credits and credits associated with alfalfa and other incidental nitrogen sources from starter, AMS, DAP and MAP fertilizers.

¹ Some or all nitrogen fertilizer records were not available

Abbreviation key: C-C = corn following corn rotation, C-S = Corn following soybean rotation, bdcst-inc. = broadcast-incorporate, DAP = diammonium phosphate, MAP = monoammonium phosphate, AMS = ammonium sulfate, UAN = urea ammonium nitrate, ESN = environmentally stable nitrogen, pp = preplant

Study Considerations and Limitations

Lysimeters are one of the most basic and economical ways to collect soil water samples for nitrate monitoring. See Appendix A for additional discussion: *Considerations when Interpreting Soil Water Nitrate Concentrations from Lysimeters.* This study's interpretations were constrained by several factors. The main objective was to assess the relative range of nitrate concentrations across a wide range of land covers. As such, there was limited ability to replicate some of the land cover categories at multiple sites. About two-thirds of the land cover categories had less than three replications. In the case of the golf course or homeowner lawns, only one or two sites were monitored and there were no turf sites with high nitrogen fertilizer inputs. As a percentage of the county land use, however, turf represents less than 5% of the county area and golf courses less than 0.1% (Table 2). Due to time and labor constraints and the practicality of retrieving samples, usually fewer than three lysimeters were installed within the row crop field sites. Other studies have preferred to use sub-surface pattern tile research plots to better control for other variables. (Randall and Goss, 2008 and Brouder et al, 2005). Monitoring nitrate

concentrations and loss from tile drainage systems are preferred since drainage water measured at the tile outlet represents an integrated average across the entire field rather than a few point locations. However, this study was motivated to specifically assess nitrate concentration ranges associated with non-tile drained karst landscapes. The relatively steep topography and moderate to well-drained silt loam soils that are characteristic of the Driftless Area of southeastern Minnesota are generally not suitable for intensive, patterned subsurface tile drainage systems and, as such, the practice is not common within the region.

This experimental design attempted to address the cautions (described in Appendix A) that must be taken when interpreting results collected from lysimeters. Primarily, the inclusion of at least a pair of lysimeters located a minimum of 20 feet apart at each field site provides an opportunity to compare the results for each sampling event and assess if the nitrate concentrations of the paired samples were consistent, and therefore likely representative of the larger site.

Precipitation During the Study Period

Precipitation can influence the range of nitrate concentrations measured in soil water. Small soil water sample volumes collected during dry conditions tend to have higher concentrations while during very wet conditions nitrates can be reduced due to dilution. Additionally, nitrate can be 'stored' in the soil profile during unusually dry periods and then be flushed out during subsequent wet periods (Kaushal et al, 2010). This has been well documented in several studies in southeast Minnesota, northeast Iowa and Midwest streams (Schilling et al, 2019, Van Metre et al, 2016, Barry et al, 2020).

Annual precipitation totals were summarized from the National Weather Service station at Preston during the study period (Table 4). The weather station at the City of Preston was selected because it is centrally located within the study area and has a long-term precipitation record. The 30-year (1981- 2010) normal or average for Preston was 35.6 inches per year. Annual precipitation totals ranged from a low 28.1 inches in 2012 to a high of 47.6 inches in 2013 with a five-year average of 34.9 inches. When compared to the percent departure from normal, values ranged from 21% below normal to 34% above normal in 2012 and 2013, respectively. When the departure from normal was within 10%, precipitation was considered near normal. If precipitation was below normal by more than 10% it was considered dry and when 10% above normal it was considered wet. Years 2011 and 2012 were both dry while years 2014 and 2015 were near normal. Figure 4 shows that 2013 was very wet with most precipitation occurring from April through June and October.

Table 4. Annual precipitation totals, departure from normal and classification during the study period. The 30-year (1981-2010) normal or average for Preston is 35.6 inches.

Figure 4. Cumulative daily precipitation at Preston during the study period (2011-2015). The study period contained a mixture of wet, dry and normal conditions.

Interpreting Nitrate Concentrations from Row-Crop Fields

General guidelines for interpreting nitrate concentrations measured in sub-surface tile drainage water were summarized in a 2005 report from Purdue University Extension (Brouder et al, 2005). A modified table from this report is provided as Table 5 and includes data from the Midwest corn-belt. Although soil water samples collected during this study may not be a direct comparison to tile drainage water, Table 5 is a useful reference for helping interpret soil water nitrate concentrations. Brouder et al. (2005) indicates that concentrations between 10 to 20 mg/L would be typical for Midwestern corn belt row crop systems with nitrogen applied at economically optimum nitrogen rates. It should be noted these concentrations can vary considerably by site and weather conditions.

Table 5. General guidelines for interpreting nitrate-N concentrations in tile drainage water. The interpretation is derived from numerous studies conducted throughout the Midwest corn belt and highlights land management strategies commonly found in association with a concentration measured in tile water leaving the field (modified from Brouder et al, 2005).

Lysimeter Comparison Values

Northcentral Lysimeters

For the past several decades the MDA's Fertilizer Field unit has initiated groundwater protection demonstration projects using lysimeters. These sites have been used to help foster partnerships among farmers, their crop advisors, citizens and local, state and university staff. Some of the longest running demonstration sites are located on coarse textured irrigated soils in northcentral Minnesota (Figure 5).

Soil water nitrate collected from a wide range of cropping systems and weather conditions provide a useful comparison with the SLN. It should be noted that all the northcentral sites contain coarse textured sandy loam or loamy sand soil textures and many sites were irrigated. Table 6 provides the summary statistics and reflect sampling conducted between years 2000-2019.

Figure 5. MDA northcentral water quality demonstrations sites. Project counties outlined in black.

Table 6. Soil water nitrate-N summary statistics across various cropping systems in northcentral Minnesota. Data reflect years from 2000-2019.

Table 7 displays the summary statistics of soil water nitrate measured from turf sites located in Otter Tail and Stearns county. Data collected from the Otter Tail county site reflect years 2000-2004 and the Stearns site reflect years 2014-2019. Lysimeter depth was about 16 to 20 inches at these sites. The Stearns site is a long-term study to evaluate the relationship between soil water nitrate and lawn nitrogen fertilizer application rates. Replicated and randomized treatments included a zero-rate check, a low rate of 3 lb N/1,000 ft², a medium rate of 6 lb N/1,000 ft² and a high rate of 9 lb N/1,000 ft². These data provide a very useful reference for nitrate concentrations measured from fertilized and nonfertilized turf sites in Minnesota.

Table 7. Soil water nitrate-N summary statistics from the two turf sites in northcentral Minnesota. Data reflects years from 2000-2019.

Lysimeter Comparison Values

MDA and Discovery Farms Minnesota On-Farm Drainage Tile Monitoring

Another source of information that can be used for comparison with the SLN is from a network of on-farm sub-surface tile drainage monitoring sites associated with the MDA and Discovery Farms Minnesota. Table 8 summarizes the annual flow weighted mean concentrations (FWMC) and yield (lb/ac) from 2011-2015. Samples were collected across nine counties (Figure 6) using automated equal flow increment composite sampling methods. Crops grown included corn, soybean and corn with alfalfa rotations. It also included sites that received dairy and hog manure and sites with only commercial fertilizer. The FWMC across all sites was 21.4 mg/L with a typical range (i.e. interquartile range) of 15.6 mg/L to 25.6 mg/L. The average nitrate loss was 17.0 lb/ac with an interquartile range of 5.5 lb/ac to 31.1 lb/ac.

Figure 6. On-farm drainage tile monitoring locations associated with the MDA and Discovery Farms Minnesota. Project counties are outlined in black.

Table 8. Annual FWMC's and loss from sub-surface tile drainage across in nine counties from 2011-2015. Data from Discovery Farms Minnesota and Minnesota Department of Agriculture.

Results and Discussion

Soil water nitrate concentrations measured across nine different types of land covers in the SLN are summarized in Figure 7 and Table 9. Nearly 3,000 individual nitrate tests were analyzed from 50 different lysimeters across 23 different sites during the five-year study. In Figure 7, land cover types were grouped into three different categories and the averages were sorted from lowest to highest N concentration within each category. The box plot represents the middle 50% of the data or the interquartile range. Although soil water sampled from lysimeters is not used directly for drinking water, the Environmental Protection Agency (EPA) maximum contaminant level of 10 mg/L for drinking water is provided for reference and shown as a dashed horizontal line. The length of each box indicates variability. Figure 7 clearly shows that the non-agriculture sites have much less variability and lower soil water nitrate while the agricultural sites have both higher nitrate and higher variably. Results from the group statistical tests are also provided in Figure 7 and last row of Table 9. Time-series charts showing

the average monthly nitrate concentrations by individual site can be found in Appendix B. Table 10 provides the statistical analysis results between the various paired land cover types. When significant, the value in parenthesis below the *p* value represents the median point difference in mg/L between the respective pairs. For instance, when comparing the prairie versus forest land covers there were no significant differences (*p* value = 0.718). However, when comparing the prairie to the golf course, the golf course had significantly higher concentrations (*p* <0.01) and this difference was estimated to be 2.4 mg/L.

Non-Agriculture

The lowest nitrate concentrations were found in the 'non-agriculture' group which included grassland prairie (CRP), deciduous forest, low maintenance homeowner lawns and a golf course. Soil water nitrate concentrations within this category averaged between 0.1 mg/L to 3.7 mg/L with a typical range (i.e. interquartile range) of <0.1 to 5.3 mg/L. Standard deviations for the prairie and forest were very small and ranged from 0.3 mg/L to 0.9 mg/L. For comparison, Randall et al, (1997) found flow weighted average nitrate concentrations of 2 mg/L from a drainage tile research plot managed for CRP in southcentral Minnesota. The highest concentration observed at one of the lysimeter network prairie sites was 3.1 mg/L. This high reading is likely related to a millipede infestation within one of the lysimeter sampling ports. This particular species, a yellow-spotted millipede (Apheloria tigana), produces cyanide to fend off potential predators. Under aerobic conditions, the biodegradation of cyanide compounds produces ammonia which is then converted to nitrite and nitrate in the presence of nitrifying bacteria (Richards and Shieh, 1989).

For the lawn and golf course sites the average concentrations ranged from 1.1 to 3.3 mg/L. For comparison, average soil water nitrate concentrations from the northcentral Minnesota turf sites were similar and averaged 2.3 mg/L (Table 7) . A maximum concentration of 26 mg/L was observed at the homeowner lawn site in 2011. This was the result of a one-time over-application of nitrogen to the lawn by the homeowner. The golf course represented samples collected from the fairway and tee box. The fairway received minimal nitrogen fertilizer applications while the tee box received scheduled applications throughout the growing season. Fertilizer application records were not available, but conversations with the course manager indicated that low rates (less than 1.0 lb/1000ft² or ~40 lb/ac) were applied typically three times a year on the tee and only one time on the fairway. A 2015 and 2016 study sampled nitrate from shallow monitoring wells across six golf courses in Iowa (Schilling et al, 2018). The average nitrogen rate applied to the tee box, fairway and rough was estimated at less than 40 lb N/ac. Results from that study found that nitrate was not detected above 1.0 mg/L at half of the six courses and the overall mean concentration was 2.2 mg/l. Schilling et al. (2018) also approximated the mass of nitrate recharge to groundwater. This was estimated to be less than 10% of the commercial fertilizer nitrogen that was applied.

Statistically, the prairie and forest sites had the same concentrations. The homeowner lawn sites had higher concentrations when compared to the prairie and forest while the golf course had the highest average concentrations of 3.7 mg/L. When comparing the golf course site to the row crop sites, the row crop sites had significantly higher concentrations (*p* = <0.01) and this median point difference was estimated to be 14.0 mg/L.

Figure 7. Typical range of soil water nitrate concentrations measured across nine different types of land covers in southeast Minnesota from 2011-2015. This chart represents nearly 3,000 individual samples collected from suction-cup lysimeters, typically from a depth of four feet. The boxes represent the interquartile range or middle 50% of the data. Average values as black dots are displayed next to each box while the median is represented by the horizontal line. Sites that do not share the same letter (displayed above the average value) are significantly different at the 0.05 level when using a Kruskal-Wallis multiple comparison test on the median. Although soil water is not used directly for drinking water, the dashed horizontal line is included as a reference and represents the 10 mg/L drinking water standard. For the grass strip sites, NF is non-fertilized, and F is fertilized. For the Ag row crops, alfalfa with corn had at least three years of alfalfa in the rotation and one year of corn during the sampling period. C/S were fields managed for corn-soybean rotations while C/C were sites managed for corn following corn or continuous corn. These two rotations were grouped together.

Table 9. Soil water nitrate-N summary statistics by land cover type from 2011-2015.

*(NF) = non-fertilized, (F) = fertilized, C-S = corn following soybeans and C-C = corn following corn *Sites that do not share the same letter were considered significantly different at the 0.05 level when using a Kruskal-Wallis multiple comparison test between medians.*

Table 10. Statistical analysis results between paired land cover types. The top value represents the *p* value. Cells shaded gray were considered statistically different at the 0.05 level when using the Mann-Whitney paired test between medians. Shaded cells with an asterisk are significant at the <0.01 level. When significant, the median point nitrate-nitrogen concentration (mg/L) difference between respective pairs is displayed in parentheses. For instance, when comparing the prairie versus the forest there were no significant differences (*p* value = 0.718). However, when comparing the prairie (column) to the golf course (row), the golf course had significantly higher concentrations (*p* < 0.01) and this difference was estimated to be 2.4 mg/L.

Ag Pasture and Grass Strips

The average soil water nitrate concentrations in the 'ag pasture and grass strip' category averaged between 5.1 to 8.9 mg/L with an interquartile range 0.5 mg/L to 11.0 mg/L. Nitrate concentrations from pasture sites averaged 5.1 mg/L and were significantly lower than the ag grass strips (*p* < 0.01), but were not significantly different from the golf course (*p* = 0.123). Pasture sites were seeded to perennial cool season forage grasses and grazed by cow/calf beef operations. Nitrogen inputs were limited to that supplied by manure and low amounts of commercial fertilizer. Some sites were rotationally grazed with no additional commercial fertilizer applied during the study while other sites received up to 60 lb N/ac/year of nitrogen fertilizer. At some sites, nitrogen inputs from manure were underestimated due to limited grazing records. At pasture site GW/GY it was observed in 2015 that cattle were loafing near the lysimeter sampling port. This presumably resulted in concentrated manure and urine input directly above the lysimeter, resulting in atypical nitrate transport to the lysimeter. Six months of samples ranging in nitrate-N concentrations of 66 to 360 mg/L were considered outliers and not used in the analysis.

In addition to the three pasture sites, two grass strips were monitored. One was managed as a grass field border while the other was a grassed waterway. The field border did not receive nitrogen while the grassed waterway received the same amount of fertilizer as the adjacent corn field. At the field border site, the 50-foot wide strip of grass ran parallel with the field slope and was located between two rowcrop fields. This site was managed for cool-season grasses and was mowed occasionally for forage. At a second site, a grass strip was managed as a grassed waterway within a concentrated flow area within a field managed for continuous corn. Typical of most commercial fertilizer applications, the grassed waterway received the same rate of fertilizer as the adjacent corn field. Even though the field border didn't receive fertilizer while the grassed waterway did, statistically both grass strip sites had similar concentrations (*p*=0.187). It's possible that in some years, some of the nitrogen fertilizer applied to the field could have been broadcast beyond the target application area and incidentally fertilized the field border as well. Another contributing factor could be related to shallow sub-surface soil water flow from an adjacent crop field. Lateral flow and mixing of shallow soil water from adjacent corn fields likely occurred at both the fertilized and non-fertilized grass strip sites. Adjacent fields near the non-fertilized field border site have slopes of 4-6%, therefore, soil water sampled from the lysimeter could have been a mix of water that infiltrated through both the grass strip and an adjacent crop field that received nitrogen fertilizer. Piezometers were not installed to measure groundwater flow direction, but visual evidence during lysimeter installation suggested that subsurface groundwater flow direction was consistent with surface slope of the field. With that said, nitrate concentrations were significantly lower in both the fertilized and non-fertilized grass strips when compared to continuous corn or corn-soybean rotations (*p*<0.01). When comparing the ag grass strips to average nitrate concentrations found in cornsoybean land covers, the non-fertilized and fertilized grass strips had 60-74% less nitrate in soil water. Grass strips placed at the field edge were likely helping reduce concentrations contained in shallow, lateral flow from adjacent cropland. This reduction could be caused by a variety of factors including lower nutrient inputs within the grass strip, dilution from rainwater infiltrating within the grass strip, nitrogen uptake by the cool-season grass over a longer growing season when compared to the adjacent row crops, landscape position, immobilization and denitrification.

Ag Row Crop

The third category, 'Ag Row Crop', represented row crop fields managed for corn and soybean rotations (C-S) and continuous corn (C-C) and corn rotations with alfalfa. The 'Alfalfa with corn' classification had at least three years of alfalfa in the rotation and one year of corn during the sampling period. Row crop sites without alfalfa received a mix of both manure and commercial fertilizers and one site was organic. Soil water nitrate averaged 6.6 mg/L under row crop sites with alfalfa which equated to 70% less nitrate when compared to row crop fields without alfalfa in the rotation. Randal et al (1997) found that nitrate loss in subsurface drainage water from continuous corn and corn-soybean systems were about 37 and 35 times higher, respectively, than from alfalfa and CRP systems primarily due to greater evapotranspiration. This results in less drainage and greater uptake and/or immobilization of nitrogen by perennial crops.

Sites managed for continuous corn and corn-soybean rotations without perennials had the highest concentrations in the lysimeter network and averaged 22.3 mg/L with an interquartile range between 8 mg/L to 28 mg/L. This range indicates a high degree of variability and likely reflects the wide range of nitrogen management on the selected farms, diverse weather conditions and inherent variability associated with lysimeters. The standard deviation for the corn and soybean row-crop sites was 21.8 mg/L. For comparison, the standard deviations from the non-agriculture sites ranged from just 0.3 to 3.2 mg/L.

Results from a row-crop field in Fillmore County, site B70/90, were interesting. It was expected that this site would have concentrations between a typical range of 10-20 mg/L. However, in four of the five study years, concentrations remained at or below 10 mg/L and during the first two years nitrate concentrations were typically below 2.0 mg/L. This field was previously in CRP for ten years and did not receive nitrogen fertilizer. This resulted in less residual soil nitrate stored within the soil profile and less nitrate available for leaching in subsequent years. A legacy effect caused by the CRP grassland combined with dry conditions in 2011 and 2012 likely explain why concentrations remained very low during the first two years of row crop production. This farmer also applied lower rates of nitrogen because less nitrogen was expected to be lost through volatilization and leaching with a split nitrogen application program. Although the effectiveness of split applications can be mixed and weather dependent, this practice generally results in higher nitrogen use efficiencies and about 7% less nitrate loss when compared to a pre-plant nitrogen fertilizer application program (Iowa State University, 2013).

Nitrate loss calculation estimates

Nitrate loading was approximated from the SLN row crop sites. Nitrate loss expressed in traditional farm scale units (pounds per acre) was estimated by multiplying the volume of recharge passing through the soil by the nitrate concentration when using the following equation:

Nitrate loss (lb/ac) = 27,154 gal/ac. in. *8.34 lb/gal / 1,000,000 * nitrate concentration (mg/L) * drainage (in.) This equation results in a conversion factor of 0.226 and the following simplified equation:

 $0.226 *$ nitrate (mg/l) $*$ drainage (in.) = lb/ac nitrate

For example, assuming a nitrate concentration of 10.0 mg/L and 5-acre inches of drainage water, the amount of nitrate loss equates to 0.226 * 10.0 * 5.0 = 11.3 lb/ac. In this study, drainage volumes were not measured directly from the lysimeters, but were estimated from a nearby long-term tile monitoring site and applied to the row crop sites in the lysimeter network. This comparison assumes that drainage and evapotranspiration rates were similar across the lysimeter network. Where accurate weather data

exist, nitrate loading estimates from the lysimeter network could be improved by using a water balance method and applying an evapotranspiration model that is specific to each site. At a tile drainage monitoring site located about 30 miles west of the Lysimeter Network study area (station SRT, MDA-Root River Field to Stream Partnership) in Mower county, Minnesota an average 24% of the annual precipitation or 8.0 inches of drainage per acre was measured from 2011-2015 (Table 8). This equated to a FWMC of 15.7 mg/L or when 25.3 lb/ac nitrate loss. This field was managed for a corn-soybean rotation and the corn crop typically received a total of 170 lb/ac of pre-plant nitrogen.

Table 11. Annual sub-surface drainage, and nitrate FWMC's and loss from a 59-acre field managed for corn and soybeans in Mower County. This long-term monitoring site is located about 30 miles west of the Lysimeter Network and is one of several edge of field demonstration sites associated with the Root River Field to Stream Partnership.

*Values are underestimated and represent a partial season. Data were not available from January 1, 2011 through May 17, 2011.

With the assumption that 8-acre inches of drainage water also occurred on the lysimeter network fields, the average nitrate loss was estimated to be 40.3 lb/ac with an interquartile range of 14.5 lb/ac to 50.6 lb/ac. For comparison, the average nitrate loss from the Mower site was 25.3 lb/ac. This was about 60% lower than the SLN. These differences can be partly explained by the following factors: (1) Lower permeability of the glacial till soils at the Mower county site could result in higher rates of denitrification under certain years and conditions and therefore less nitrate measured in drainage leachate (Rodvang and Simpkins, 2001) (2) Nitrate losses from 2011 reflect a partial year at the Mower county site and are underestimated due to a partial year of sampling (3) lysimeter loss estimates may not represent the entire field when compared to tile drainage samples, and (4) the SLN contains a greater diversity of nitrogen management practices including rotations with continuous corn and manure that had higher nitrogen fertilizer inputs.

Row-crop Nitrate Comparisons

To aid interpretation, results from the SLN were compared to other lysimeter and tile drainage sites in Minnesota and Midwest corn belt.

Generally, nitrates measured from the corn-soybean and continuous corn sites in the SLN were within the range of concentrations found in sub-surface drainage tile across Minnesota (Table 8). Nitrate concentrations were not significantly different (p=0.212) and both data sets averaged between 21.4 to 22.3 mg/L. Although the averages were very similar, the standard deviation from the lysimeter network was 12.9 mg/L higher. The likely reason for this difference is because lysimeters represent small point measurements within the field and therefore subject to more variation. In contrast, pattern tiled drainage sites have less variation since the concentration measured at the tile outlet represents a composite mixture of drainage water that is representative of the entire area of the drained field. When concentrations were compared to tile drainage sites across the Midwest corn belt (Table 5), the SLN concentrations were about 12% higher than the 20 mg/L row crop reference value contained in that report.

When the SLN corn-soybean and continuous corn sites were compared to a irrigated northcentral cornsoybean site (Table 6) during the same monitoring period of 2011-2015, the northcentral site had significantly higher concentrations (P<0.05) and the median point difference was estimated to be 6.6 mg/L. Higher nitrate concentrations are to be expected in this region of the state because the sandy soils that are common in this area can result in greater nitrate loss below the crop root zone. Furthermore, row crops grown on coarse textured soils require higher rates of nitrogen fertilizer, therefore, soil pore water can contain higher nitrate in solution.

Suggestions for Further Study

Where appropriate weather data are available, nitrate loss estimates could be refined using a water balance method and evapotranspiration model for each site. In future studies, performance monitoring of septic system drain fields in areas with low and high density housing, cover crops and alternative crops such as hemp should be explored. For site B70/B90, concentrations were much lower than expected and additional investigation could be warranted regarding the effect of no-till and split nitrogen applications in a corn-soybean rotation. Additional monitoring of grassed waterways and edge of field grass strips would also be beneficial. Grassed waterways are one of the most widely used conservation practices by farmers in southeast Minnesota and quantifying the effect of these practices would be beneficial as an input for groundwater modeling. For best management practice (BMP) comparison sites, additional statistical analysis should be conducted to estimate how many samples would be needed to detect a given percent change in nitrate concentration at the 0.10 and 0.05 confidence levels. This could help lower labor and analytical costs in future monitoring efforts.

Summary and Conclusions

Low levels of soil water nitrate, generally less than 0.5 mg/L, were consistent across the prairie and forest sites. In these land covers, nitrate concentrations are very low because nitrogen is mineralized from soil organic sources and the nitrogen supplied is in equilibrium with plant nitrogen needs. A fertilized golf course site averaged less than 4 mg/L and had similar concentrations when compared to cattle pasture sites. Fertilized and non-fertilized grass strips (grassed waterway and field border) were higher than expected but averaged less than 9.0 mg/L. Elevated concentrations, especially in the nonfertilized grass field border, are likely explained by subsurface mixing of soil water between adjacent land covers. Nitrate concentrations in row crop settings averaged 22.3 mg/L and were spread across a large range of values as depicted by a standard deviation of 21.8 mg/L. This high degree of variability can be explained by the wide range of cropping systems and management systems sampled, diverse weather conditions and variability that is inherent with lysimeter sampling. Although highly variable, average row crop nitrate levels from the lysimeter network were similar to flow weighted concentrations collected from sub-surface drainage tile sites across Minnesota during the same monitoring period.

Any nitrate not used by row crops is susceptible to leaching from the rooting zone and can increase the risk for transport to groundwater, especially in karst landscapes. The use of BMPs, especially proper rate and timing of nitrogen, are key practices to help reduce nitrate concentrations in groundwater. Though, it's important to recognize that these practices alone may not consistently obtain levels below the drinking water standard of 10 mg/L. Integrating perennials into row crop systems can be a key practice for reducing nitrate in groundwater. The use of perennials is used by many livestock farmers in southeast Minnesota and the performance of this practice was measured. In corn rotations with alfalfa, soil water nitrate averaged 6.6 mg/L which was 70% lower when compared to row crop sites without perennials. This reduction can be explained by lower nitrogen inputs, increased nitrogen uptake and/or immobilization and higher rates of evapotranspiration by perennial covers over a longer growing season when compared to row crops (Randal et al, 2008).

The use of lysimeters proved to be a cost-effective tool to estimate the relative range of concentrations and nitrate risk to groundwater between various types of land covers. When shared within the context of this study's limitations, data collected from the Southeast Lysimeter Network serves as a useful educational tool for farmers, crop advisors, rural homeowners and groundwater advisory groups.

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Literature Cited

Alexander, Richard B., Smith, Richard A., Schwarz, Gregory E., Boyer, Elizabeth W., Nolan, Jacquelin V. and Brakebill, John W. (2008). Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. Environmental Science and Technology. 42, 822-830, pg. 828.

Barry, John D., Miller, Tom, P.,Steenberg, Julia R., Runkel, Anthony C, Kuehner, Kevin J, Alexander, Calvin E. Jr. (2020). Combining high resolution spring monitoring, dye tracing, watershed analysis, and outcrop and borehole observations to characterize the Galena Karst, Southeast Minnesota, USA. 16th Sinkhole Conference, NCKRI symposium 8.

Brouder, S., Hofmann, B., Kladivko, E., Turco, R., Bongen, A. and Frankenberger, J., (2005). Interpreting nitrate concentration in tile drainage water. Purdue University Extension.

Cropscape. Year 2015 Cropland Data Layer. Center for Spatial Information and Science Systems, George Mason University. [https://nassgeodata.gmu.edu/CropScape/.](https://nassgeodata.gmu.edu/CropScape/)

Dogwiler, Toby. (2013). Southeastern Minnesota Soil Water Lysimeter Network Project Final Report. Winona State University Department of Geosciences.

Faaga, J. and Selker, J. (2004). Field Measurements of Nitrate Leaching Below Willamette Valley Row and Mint Crops. Oregon State University Extension Service.

Green, Jeffrey A., John D. Barry and E. Calvin Alexander, Jr., (2014). Springshed Assessment Methods for Paleozoic Bedrock Springs of Southeastern Minnesota. Report to the LCCMR. Sept. 2014, 48 pp.

Haarder, E.B, M.C, Looms, Johnson, K.H and L. Nielsen. (2011). Vadose Zone J. 10:84-97.

Iowa State University, (2013). Nutrient Reduction Strategy. Reducing Nutrient Loss: Science shows what works. Retrieved from [https://store.extension.iastate.edu/product/Reducing-Nutrient-Loss-Science-Shows-What-Works.](https://store.extension.iastate.edu/product/Reducing-Nutrient-Loss-Science-Shows-What-Works)

Kaushal, S.S., Pace, M.L., Groffman, P.M., Band, L.E., Belt, K.T., Meyer, P.M., and Welty, C., (2010), Land Use and Climate Variability Amplify Contaminant Pulses: Eos, Transactions, American Geophysical Union, v. 91, p. 221–222, doi[:10.1029/2010EO250001.](https://doi.org/10.1029/2010EO250001)

Minnesota Department of Agriculture Township Testing Program. Various reports retrieved from [https://www.mda.state.mn.us/township-testing-program.](https://www.mda.state.mn.us/township-testing-program)

Mossler, J.H., (1995). C-08 Geologic atlas of Fillmore County, Minnesota [Parts A and C]. Minnesota Geological Survey. Retrieved from the University of Minnesota Digital Conservancy, http://hdl.handle.net/11299/58513.

Nitrogen in Minnesota Surface Waters, (2013). Minnesota Pollution Control Agency. Report, wq-s6-26a, Minnesota Pollution Control Agency, 2013. Retrieved fro[m https://www.pca.state.mn.us/sites/default/files/wq-s6-26a.pdf.](https://www.pca.state.mn.us/sites/default/files/wq-s6-26a.pdf)

Randall, G. W. and M.J. Goss. (2008). Nitrate Losses to Surface Water through Subsurface, Tile Drainage. In Nitrogen in the Environment: Sources, Problems, and Management, ed. J.L. Hatfield, and R.F. Follett. P. 145- 175. Elsevier Sciences B.V.

Randall, G.W., Huggins, D.R., Russelle, M.P., Fuchs, D.J., Nelson, W.W. and Anderson, J.L., (1997). Nitrate Losses through Subsurface Tile Drainage in Conservation Reserve Program, Alfalfa, and Row Crop Systems. Journal of Environmental Quality, 26: 1240-1247. doi[:10.2134/jeq1997.00472425002600050007x.](https://doi.org/10.2134/jeq1997.00472425002600050007x)

Richards DJ, Shieh WK. (1989). Anoxic activated-sludge treatment of cyanides and phenols. Biotechnology Bioengineering. 33:32-38. Referenced in chapter 6 of Agency for Toxic Substances and Disease Registry (ATSDR). 2006. Toxicological profile for Cyanide. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Robertson, D.M., and Saad, D.A. (2019), Spatially referenced models of streamflow and nitrogen, phosphorus, and suspended-sediment loads in streams of the Midwestern United States: U.S. Geological Survey Scientific Investigations Report 2019–5114, 74 p. including 5 appendixes, https://doi.org/10.3133/sir20195114.

Rodvang, S.J. & Simpkins, William.(2001). Agricultural Contaminants in Quaternary Aquitards: A Review of Occurrence and Fate in North America. Hydrogeology Journal. 9. 44-59. 10.1007/s100400000114.

Runkel, Anthony C.; Steenberg, Julia R.; Tipping, Robert G.; Retzler, Andrew J. (2014). OFR14-02, Geologic controls on groundwater and surface water flow in southeastern Minnesota and its impact on nitrate concentrations in streams. Minnesota Geological Survey. Retrieved from the University of Minnesota Digital Conservancy, http://hdl.handle.net/11299/162612.

Schilling, K. E. and Streeter, M.T. (2018). Groundwater Nutrient Concentrations and Mass Loading Rates at Iowa Golf Courses. Journal of the American Water Resources Association (JAWRA) 54(1): 211-224[. https://doi.org/10.1111/1752-1688.12604.](https://doi.org/10.1111/1752-1688.12604)

Schilling, K.E., Jones, C.S., Clark, R.J. et al (2019). Contrasting NO3-N concentration patterns at two karst springs in Iowa (USA): insights on aquifer nitrogen storage and delivery. Hydrogeology Journal 27, 1389-1400. https://doi.org/10.1007/s10040-019-01935-y.

USEPA, (1987). Estimated national occurrence and exposure to nitrate and nitrite in public drinking water supplies. Washington, DC, United States Environmental Protection Agency, Office of Drinking Water.

Van Metre, P.C., Frey, J.W., Musgrove, M., Nakagaki, N., Qi, S., Mahler, B.J., Wieczorek, M.E. and Button, D.T. (2016). High Nitrate Concentrations in Some Midwest United States Streams in 2013 after the 2012 Drought. J. Environ. Qual., 45: 1696-1704. doi[:10.2134/jeq2015.12.0591.](https://doi.org/10.2134/jeq2015.12.0591)

APPENDIX A

Considerations when interpreting soil water nitrate-nitrogen concentrations collected from lysimeters

Lysimeters are one of the most basic, versatile and economical ways to collect samples for measuring nitrate-nitrogen (nitrate) concentrations in soil water. Measuring nitrate concentrations in the unsaturated vadose zone and lowermost depth of the crop rooting zone of cultivated crops can provide important insights and feedback regarding nitrogen management practices. However, results can be highly variable. For instance, nitrate results collected two lysimeters separated only a few feet apart can vary considerably. The following is a brief list of factors to consider when interpreting results collected from lysimeters.

Soils are complex systems with various chemical, physical and biological interactions, and measuring the

movement of nitrate through soil is controlled by the complex interaction of these properties combined with variations in precipitation. Consider the complex movement of water through the soil. Water moves in an irregular manner through the soil profile along a path of least resistance. During dry conditions, water moves between the small pore spaces between the soil particles very slowly. This slow form of water movement is called matrix flow. During wet conditions, such as during a large rain event when the soil is approaching saturation, flow through larger pores such as worm holes or old root channels occurs. This is a fast form of water movement called preferential flow. Nitrate concentrations vary between matrix flow and preferential flow which helps explain why soil water nitrate concentrations from lysimeters located only a few feet apart can be substantially different. These concepts are best illustrated

Figure 1. This photograph shows the cross section of a soil profile with blue dye poured at the soil surface. The wetting front and irregular preferential flow pattern are clearly shown as the blue dye percolates through the soil. This can help explain why soil water nitrate concentrations from one lysimeter can have markedly different concentrations when compared to another lysimeter only a few feet away. Figure adapted from Haarder et al, 2011.

in Figure 1 (adapted from Haarder et al., 2011) showing the cross section of a soil profile after infiltrating four inches of water-soluble blue dye on a sandy textured soil. The wetting front and irregular preferential flow pattern are clearly shown as the blue dye percolates through the soil. In this case, if a lysimeter had been placed on the left side of the soil profile, nitrate concentrations could have been much different when compared to the right side.

Another factor to consider is that nitrate measured by lysimeters within the crop root zone represents the amount of nitrate present at that specific point in the soil profile and may not always correspond to what is observed in deeper groundwater. At common lysimeter install depths, usually about four feet, the fate and movement of nitrate can take several pathways. Some of those include: (i) percolate to deeper bedrock layers where it can mix with older groundwater that has been diluted from non-crop land covers (ii) migrate back to the root zone through capillary rise or (iii) be converted into nitrogen gas $(N₂)$ by denitrification or other reduction processes deeper in the soil profile or aquifer. Despite these factors, nitrate concentrations measured in coarse-textured/sandy aquifers or shallow, unconfined karst aquifers in southeast Minnesota can have nitrates that are consistent with the range of concentrations measured in soil water beneath row-crop fields.

Due to sample and labor constraints involved with lysimeter sampling, typically only a few lysimeters are installed within a small area of a crop field. Lysimeters in effect become point measurements that may not capture the high level of spatial variability represented within the field. This makes it difficult to discern if nitrate concentrations are an accurate representation of the entire field and management system or just that particular point within the field. That is why sub-surface pattern tile drainage sites or groundwater springs are preferred monitoring locations for nitrate, since concentrations represent a composite mixture that is averaged across the drained field area or springshed contributing area. To reduce uncertainty, pairs or groups of lysimeters are typically installed and a mean concentration is applied to the lysimeter group.

Additional factors to consider:

- Typically, a vacuum is paced on the lysimeter to allow collection of a soil water sample. This vacuum could bias preferential flow to the lysimeter within the soil column, causing the sample to not fully represent the water moving through the soil profile.
- Ideally, drainage volume from lysimeters should also be measured to help normalize for differences in sample size between sites and lysimeters by calculating a flow weighted mean concentration (FWMC). A FWMC is defined as the total mass load divided by the total water volume. This normalization process allows comparison among different sites based on the total volume of water rather than the concentration itself. Flow weighted averaging is an appropriate method to represent the average nitrate concentration over multiple sampling events and are much better than simply averaging the individual concentrations since sampling events with low volumes can bias results with sample events that collect small volumes with very high concentrations. Accurately measuring drainage volume from lysimeters is challenging so FWMCs are typically not calculated.
- The soil immediately surrounding lysimeters is disturbed during installation. It may take at least a year for the soil to fully settle around the lysimeters resulting in higher uncertainty in the measurements during that period.
- Samples can be influenced by adjacent, upgradient land use due to lateral movement of shallow groundwater flow paths. This can be a factor for some locations with steeper field slopes.

With these considerations in mind, the use of lysimeters can be a cost-effective tool for evaluating nitrate concentrations and can serve as an important educational tool for farmers, crop advisors, rural homeowners and groundwater advisory groups.

APPENDIX B- Average monthly nitrate by lysimeter site

APPENDIX C Quality assurance report: duplicate RPD results

Water samples were analyzed using a Hach® DR6000 UV spectrophotometer (pour-through method 357-10049, DOC 316.53.01072) located in the MDA Preston field office within a week of sample collection. Samples were analyzed using standardized quality assurance and control (QA/QC) procedures. To evaluate the performance of the machine during this study, a minimum of 10% of the nitrate samples were split in the field and sent to the Minnesota Department of Agriculture certified laboratory (MDA Lab) located in St. Paul. Field duplicate samples were used as a part of the quality assurance plan to evaluate the performance and precision of the DR6000 and determine the extent of any analytical problems. Due to budget constraints, duplicate samples were sent in two out of the five years during the study. The MDA lab method (SM 4500-No3 F) using flow injection includes both nitrite and nitrate (NO₂ + NO₃-N) while the DR6000 method does not report nitrite. Nitrite (NO₂-N) is seldom elevated in groundwater because it is typically transformed quickly to nitrate, therefore, it is not considered to be a significant factor when comparing the two methods.

The Relative Percent Difference (RPD) calculation method was used to evaluate the precision of duplicate samples when comparing the DR6000 to the MDH certified lab for years 2014 and 2015. The RPD is the difference between the MDH certified lab and samples analyzed by the DR6000 machine divided by their average and expressed as a percent. The RPD calculation is:

$$
RPD = \frac{|X1 - X2|}{(X1 + X2)/2} * 100
$$

X1 = sample concentration determined by Hach DR6000 X2= sample concentration determined by MDA certified lab

A goal of this testing program was to have 90% of the duplicate samples within 10% of the RPD. Table 1 and Figure 1 summarize the RPD results. For 2014, 61 field duplicate pairs were analyzed representing 17% of the total samples analyzed on the DR6000. Of the 61 pairs, 87% of the DR6000 duplicate samples were within the 10% RPD goal and 95% were within 20% RPD. In 2015, 114 sample pairs were analyzed representing 31% of the total samples. Of the 114 sample pairs, 89% of the DR6000 samples were within 10% of the RPD and 95% of the duplicate samples were within the 20% RPD. Across both years, 88% of the samples were within 10% of the RPD. Across both years, 90% of the samples were within a RPD of 11%. The overall difference between

the DR6000 samples and those

Table 1. Relative Percent Difference (RPD) results between Hach DR6000 and MDA certified lab.

Figure 1. Time series chart of RPD results

analyzed by the MDH lab ranged from -0.3 mg/L to 0.6 mg/L (IQR). The median difference between the DR6000 method and the MDH certified lab was 0.3 mg/L. The method report limit is 0.1 mg/L for the DR6000.