NITRATE CONTAMINATION IN SOUTHEAST MINNESOTA'S KARST LANDSCAPE: IMPACTS OF LAND USE AND PRECIPITATION

by

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of the requirements for the degree

of

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in

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DEDICATION

I dedicate this document to my wife, Sabrie, for her endless support, encouragement, and patience throughout the completion of this degree. Her willingness to be a sounding board for project ideas and provide constructive criticism was pivotal to my success within this program.

To my parents, thank you for instilling in me a deep love for the natural world. Whether it be deer hunting in the woods or road trip vacations, the foundation for pursuing this degree and a career in natural resources was built on those memories and experiences.

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I would like to express my gratitude to Dr. Adam Sigler for his commitment to my success within the Land Resources and Environmental Science program and with the completion of this paper. His meticulous reviews and subject expertise allowed me to navigate this project efficiently. I would also like to acknowledge the Minnesota Caving Society for providing me a private dataset that includes years of field collected data. Lastly, to Dodge County, for partially funding my pursuit of this degree.

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ABSTRACT

Minnesota's karst landscape is highly susceptible to elevated concentrations of nitrate due to land use practices and precipitation patterns. Minnesota's karst landscape covers the southeast portion of the state that is drained by the Root and Zumbro River Watersheds and is home to Niagara Cave. Karst topography is characterized by porous limestone and sandstone which promotes the interaction between surface and groundwater through landscape features such as sinkholes, springs, and caves. However, this rapid water movement makes water resources of the region vulnerable to contamination from non-point sources like fertilizers used on dominant crops such as corn [*Zea mays* L.] and soybean [*Glycine max* (L.) Merr.]. Therefore, to understand the interaction between land use and fertilizers, I compiled data from the Minnesota Caving Club, the National Water Quality Portal, CropScape, and the Minnesota Department of Natural Resources. Nitrate concentrations were analyzed temporally using scatter plots and linear regression. I mapped the data using ArcGIS Pro to evaluate spatial patterns. There was little variation in nitrate concentration in surface water over time, with 24.8% of samples exceeding the health risk limit of 10 mg/L. Concentrations of nitrate in groundwater samples were more consistently above 10 mg/L (50.7% of samples) and exhibited larger seasonal variability. Concentrations often decreased after large rainfall events, such as the 2019 flood year, and increased during years with lower precipitation. On average, 47.8% of land use in the study area is classified as either in corn or soybean production. My results highlight karst landscape's sensitivity to surface inputs and precipitation patterns, thus emphasizing the importance of expansion of subsurface monitoring and agricultural best management practices.

INTRODUCTION

Sources and Forms of Nitrogen

Since the global expansion of traditional row-crop agriculture, farmers have taken every opportunity to increase crop yields. It began with simple mechanisms like flood control or irrigation, but technological advancements, like the Haber-Bosch process, allowed fertilizers to increase crop production (Liu, 2021). Fritz Haber discovered that ammonia could be synthesized by reacting atmospheric dinitrogen with hydrogen in the presence of iron at high pressures and temperatures. Carl Bosch later developed a way to synthesize ammonia at an industrial scale, earning him the Nobel Prize in 1931 (Erisman et al., 2008).

By the mid-1900s, United States ammonia plants were producing 662 million kilograms (730,000 tons) of ammonia per year, beginning the modern age of fertilization. By the year 2014, 18 billion kilograms (20 million tons) of fertilizer per year were being supplemented into seasonal farming practices (University of Nebraska-Lincoln, 2015).

Issues with Nitrate-N Pollution

Nuisance Algae

With the expansion of nitrogen fertilizers and increasing population densities, nitrate contamination in surface waters has become a global issue. Discharge from point sources, like industrial and domestic wastewater and failing septic systems, introduce concentrated amounts of nitrate to ground and surface water. Surface water under natural conditions typically has nitrate concentration below 1 mg/L, but the effluent from wastewater treatment plants can range up to 30mg/L, which is three times the drinking water standard of 10 mg/L set by the USEPA (US

EPA, n.d.). For non-point sources like agricultural fertilizer, overland flow caused by precipitation leads to elevated nitrate-N in surface waterbodies. Excessive nutrient loading of nitrogen and phosphorus promotes algal growth, which consumes the available oxygen in the water column. The lack of oxygen creates a hypoxic environment, which results in fish kills (Romanelli et al., 2020).

Human Health

The U.S. Environmental Protection Agency states that 15% (43 million) of the U.S. population relies on private drinking water (DeSimone et al., 2009). Private drinking water wells and many municipal systems across the country are drawing water from subsurface aquifers. Typically, municipal systems drill wells that are deep enough to avoid human-introduced nitrate-N in upper aquifers. However, private drinking water wells are often shallow enough to be influenced by nitrate-N pollution from land use on the surface. The EPA has determined 10 mg/L to be the health risk limit for human consumption of nitrate-N in drinking water. Infants that consume formula with nitrate-N above 10 mg/L have been linked to methemoglobinemia (Knobeloch, 2000).

Landscape Controls

Karst geography is made up of predominantly limestone and sandstone bedrocks. An active karst region has less than 15 m (50 ft) of depth to bedrock, with many instances of bedrock exposure. The highly erosive and porous composition of the bedrock leads to frequent mixings of surface and groundwater. Landscape features that contribute to irregular movement of

water include sinkholes, caves, and springs. This landscape offers a unique relationship between land use, surface, and groundwater.

Hydraulic Controls

Fertilization of traditional crops like corn and soybeans mainly happens in the spring during early plant growth. Nitrate-N contamination is highly seasonal and weather-dependent. Varying frequencies and intensities of wet-dry seasons will cause dilutions and concentrations within aquifers. A drought event will cause immediate nitrate increases in groundwater, with springs showing quicker but weaker responses than wells (Jutglar 2021). Karst aquifers responded more often to seasonal shifts than aquifers with smaller pores or fractured bedrocks (Jutglar, 2021). Although climate outlooks vary based on region, a warmer and wetter environmental outlook would cause greater seasonal fluctuations for nitrate in groundwater.

Research Focus

Objectives

To address the challenges posed by nitrate contamination in southeast Minnesota's karst landscape, this study aims to explore the specific relationships between land use, precipitation, and nitrate levels in surface and groundwater. Human activities, particularly modifications to agriculture, have increased the application of chemical fertilizers in the environment. Seasonal precipitation plays a significant role in this process as heavy rainfalls can dilute nitrate within bedrock aquifers by introducing more water, while drought conditions can lead to higher nitrate-N concentrations due to reduced water volume. I aim to identify trends, or the absence of trends,

in nitrate levels, providing insights that can assist local officials and state agencies in addressing water contamination.

METHODS

Study Area

Southeast Minnesota is located within the upper Mississippi River basin. The largest city in the region, Rochester, sits at 312 m (1,024 ft) above sea level and experiences 82.3 cm (32.4 in) of precipitation on average per year. The regional geology transitions from glacial till plains in the west to rolling bluffs of karst to the east. The data used in this study were collected in two of southeast Minnesota's HUC 8 watersheds, the Root and Zumbro River. Both watersheds flow west to east and have a majority of land cover as agriculture. These watersheds outlet into the Mississippi River along Minnesota's eastern boundary.

Root River Watershed

The Root River encompasses 400,000 ha (1 million ac), beginning as a drainage ditch in Mower County and meandering 130 km (81 miles) through heavily farmed lands before transitioning into wooded, rolling terrain (Figure 1). It eventually flows into the Mississippi River south of La Crosse, Wisconsin. Near Forestville State Park, the river vanishes underground, reemerging at Mystery Cave near Preston. Sandy glacial till plains make up the western portion of the watershed, which is dominated by row crop agriculture. The watershed transitions to a karst landscape in eastern Fillmore County, which is characterized on the surface by the presence of rolling bluff lands. The eastern edge of the watershed has mixed land use

where row crop agriculture occurs in flat bluff tops or valleys with larger patches of forest on steeper slopes (Figure 3).

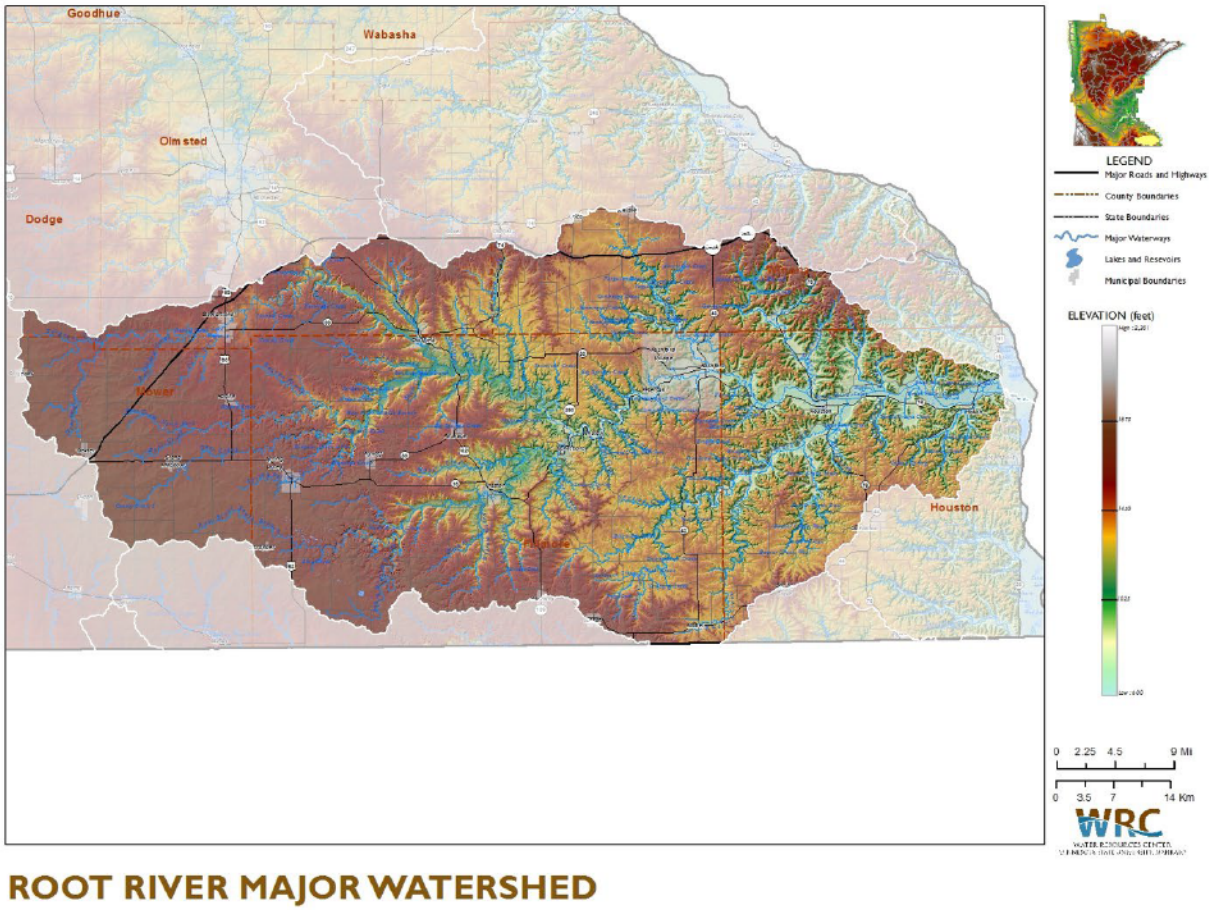


Figure 1: Root River Basin in Minnesota (Minnesota River Basin Data Center, n.d.).

Zumbro River Watershed

The Zumbro River watershed is the northern neighbor to most of the Root River Watershed. The Zumbro River watershed spans over 360,000 ha (900,000 ac), covering portions of six southeast Minnesota counties which include Olmsted, Dodge, Steele, Rice, Goodhue, and Wabasha (Figure 2). One of Minnesota's largest cities, Rochester, lies in the in the southeastern

quadrant and upper reaches of the watershed. The landscape within the watershed features glacial till plains, steep bluffs with sandy soils, and karst topography in the eastern region. This karst landscape is marked by exposed bedrock, sinkholes, caves, and spring-fed streams (Figure 3). To the west at the headwaters, the terrain transitions to lake plains, drumlin fields, and rolling moraines from the most recent glaciation. Row crop agriculture dominates the watershed's land use, particularly in the western half. In the eastern portion, small, cold-water streams fed by groundwater support healthy trout populations.

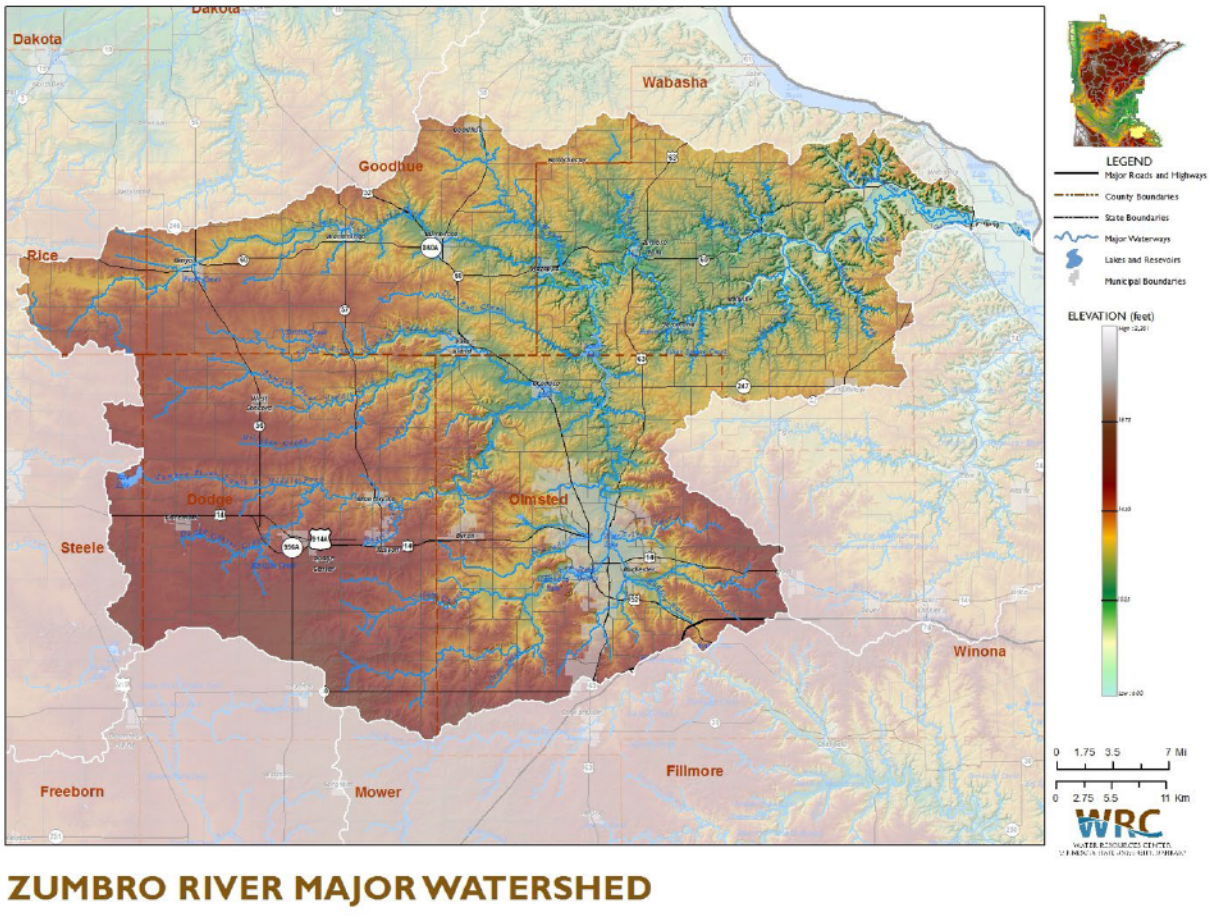


Figure 2: Zumbro River Basin in Minnesota (Minnesota River Basin Data Center, n.d.).

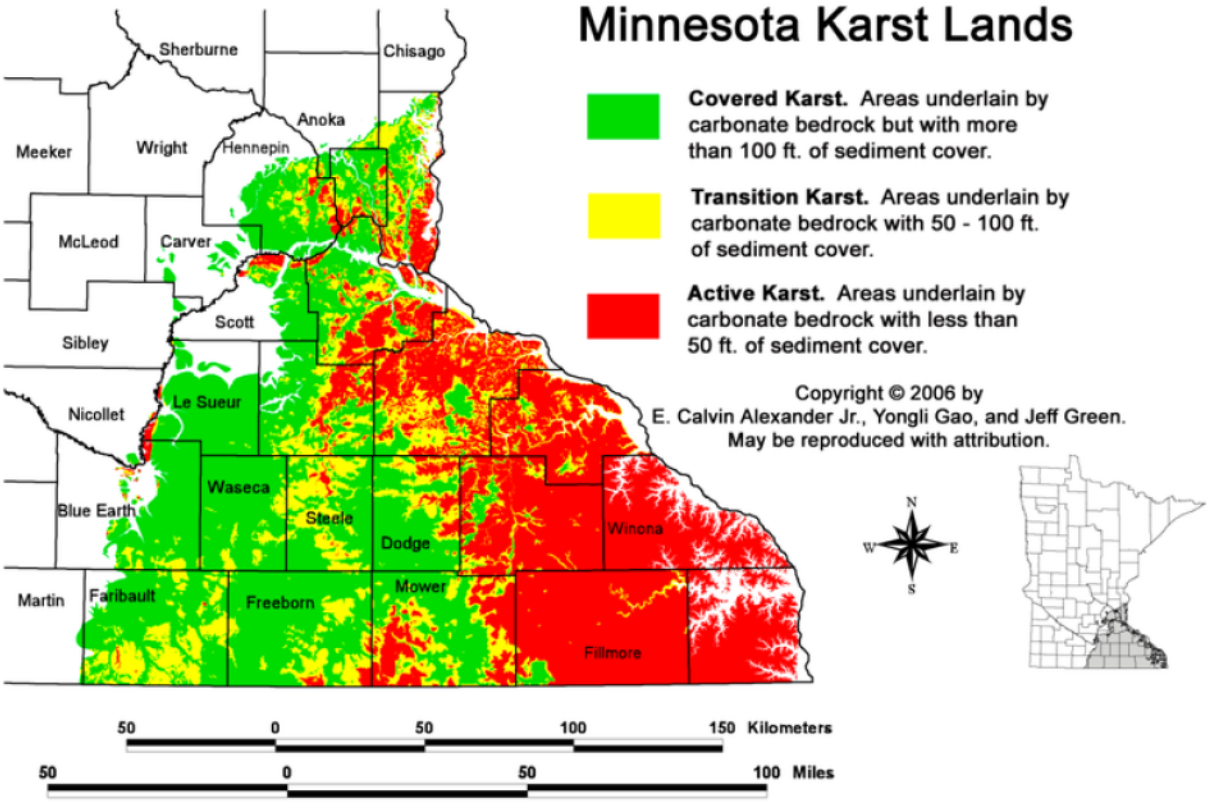


Figure 3: Coverage of karst landscape in southeastern Minnesota (Minnesota Pollution Control Agency, n.d.).

Niagara Cave

Niagara Cave is a unique limestone cave located near Harmony in southeastern Minnesota and within the Root River Watershed. It is one of the largest caves in the Midwest and is known for cave formations like an 18 m (60 ft) underground waterfall, towering ceilings, and intricate stalactites and stalagmites (Figure 4). Niagara Cave is part of the region's karst landscape, with its passageways carved by water moving through the soluble limestone. The cave maintains a cool temperature of around 8 °C (48 °F) year-round and has been meticulously explored, mapped, and sampled for decades.



Figure 4: Underground waterfall in Niagara Cave (Bishop, 2025).

Data Sources

Minnesota Caving Club

The Minnesota Caving Club (MCC) provided exclusive access to two datasets that included surface and groundwater data. Both datasets were collected by an MCC board member to track the long-term relationship between surface and groundwater.

The first dataset, labeled "Springs & Caves," contains temporal nitrate-N data from springs and cave drips throughout the Zumbro and Root River watersheds. It includes 123

nitrate-N lab results from 2014 to 2022. Since MCC is a volunteer group, sample collection occurred randomly each year but followed a seasonal trend, as caving is safer in the winter months. All samples in this dataset were analyzed by the Southeast Minnesota Water Analysis Laboratory (SEMWAL) using a Dionex ICS-1600 Ion Chromatograph, with a laboratory reporting limit of 0.5 mg/L and the lowest calibration standard of 0.47 mg/L.

The second dataset consists of sites located within the Niagara Cave complex, where sample locations are named after specific cave formations designated by MCC members. It includes 41 nitrate-N samples collected from 2015 to 2024 at 15 cave formations. Sampling was opportunistic, occurring during MCC caving trips, with the fewest samples collected in 2024 (one) and the most in 2023 (nine). Cave formations with the highest number of sample collections include Wishing Well (cave stream), Bridal Veil (cave drip), and End of Cave (ephemeral shower). The data were compiled to show slope, R^2, p-value, sample size, and percentage of samples ≥10 mg/L. The p-value was calculated using a two-tailed paired t-test.

Samples were analyzed using a Thermo Scientific Genesys UV-Visible Spectrophotometer, which has a nitrate-N range of 0.01 to 35 mg/L. These accuracy values are the manufacturer values, which constitute the best-case scenario for instrument performance, but other work has indicated much lower accuracy for volunteer collected/analyzed data (MSU Extension Water Quality, 2022). Because benchtop meters, including the spectrophotometer, can produce nitrate-N values that vary from lab-certified tests, this dataset is less accurate than the Dionex system used for the first dataset.

National Water Quality Portal

Nitrogen data from the National Water Quality Portal (NWQP) provide access to water-quality data stored in WQX, which combines data from previously separate databases such as USGS NWIS and BioData, EPA STORET, and USDA-ARS STEWARDS (Water Quality Portal, 2021). Data were downloaded from the NWQP for Olmsted and Filmore County and transferred into an excel file and streamlined for ease of quantitative analysis. The data were filtered for nitrogen data in surface and groundwater within Olmsted and Fillmore Counties. The search yielded 2,992 samples of which 113 were identified as groundwater, and 2,879 were surface waters. Each data point with associated coordinates was spatially represented using ArcPro (Figure 11). The samples were analyzed for nitrate-N at an accredited laboratory.

Minnesota Department of Natural Resources

Precipitation data were accessed through the Minnesota DNR's Climate Trend tool which uses publicly sourced data from the National Oceanic and Atmospheric Administration (National Centers for Environmental Information, 2025). The database provides precipitation data organized by HUC-8 watersheds ranging from 1895 to 2025 (Figure 5). The available precipitation data are aggregated at timesteps ranging from daily to annual, with monthly and annual totals providing context for this study.

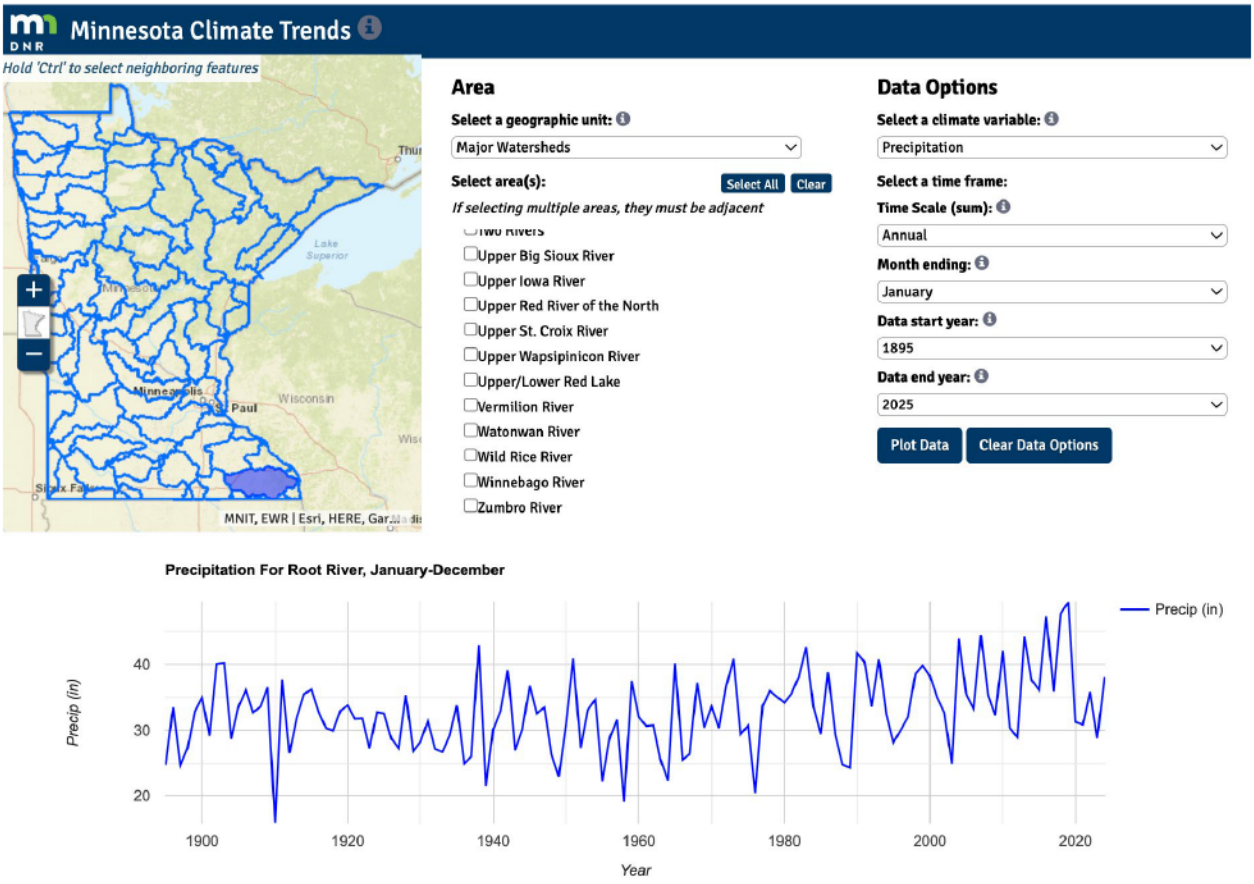


Figure 5: MN DNR Climate Trend tool for the Root River watershed by annual total precipitation (in).

CropScape

Land cover data were obtained through the CropScape Cropland Data Layer from the United States Department of Agriculture (USDA). The area of interest (AOE) was searchable by county within Minnesota. Fillmore and Olmsted County had spatial and statical data for acreages of agricultural and non-agricultural land uses. CropScape produced percentage cover graphs and spatial cover maps through a built-in function.

Synthesis of Data

Spatial Mapping

Each of these three datasets, Springs & Caves, Niagara Cave, and USGS Water Quality Data had assigned UTM coordinates denoting the specific location of sample collection. These coordinates were converted to a table and mapped using ESRI's ArcGIS Pro 3.3.1 software and QGIS. Each dataset's symbology was mapped with symbology to show ranges of nitrate results (0.0-0.99 mg/L, 1.0-9.99 mg/L, and ≥10 mg/L). The lowest range is considered background levels of nitrate naturally occurring in the environment (Dubrovsky et al., 2010). The middle range to account for nitrate values above natural occurrence but below the designated health risk limit. The upper range, ≥10 mg/L, was chosen because it is the recognized health risk limit from the Environmental Protection Agency (US EPA, 2024) for the consumption of nitrate in water by humans.

Temporal Analysis

Three datasets, Springs & Caves, Niagara Cave, and USGS Water Quality Data were compiled into pivot tables and charts, which depicted fluctuations in nitrogen values over time. The Springs & Caves data were formatted into excel spreadsheets organized in rows for individual samples, and columns for variables such as unique name, UTM coordinates, nitrate-N concentration (mg/L), sampling date, type of cave formation, and either surface or groundwater collection. Average nitrate-N concentration was plotted versus time for different combinations of surface and groundwater data aggregated by year and month.

The second dataset was collected in the Niagara Cave complex and entered into an Excel spreadsheet featuring 19 unique columns with primary information like location, cave formation name, cave formation type, and nitrate-N concentrations accompanied by date in each row. Not

all sites were sampled on every sampling event, so the result is a sparce table (blank values for nitrate-N concentration for many location/date combinations). Nitrate-N concentrations were plotted versus time for varying combinations of surface and groundwater data collected by year and month. The dilution effect was analyzed by subdividing Niagara Cave temporal nitrate data in two ways, the average of the years before 2019 (2015-2018) and after 2019 (2019-2024). Then again and average of the two years before 2019 (2017 and 2018) and after 2019 (2019 and 2020).

RESULTS

Nitrate-N Changes Over Time

Surface Water

When plotted as a complete dataset, the 2,992 surface water collection points from the USGS data in Fillmore and Olmsted County yielded significant change ($p = <0.01$) in average nitrate-N from 1992 to 2023 (Figure 6). The health risk limit (≥10 mg/L) was exceeded in 744 (24.8%) samples, 2202 (73.5%) samples tested between 1.0 and 9.99 mg/L, and 46 (1.5%) tested below 1.0 mg/L.

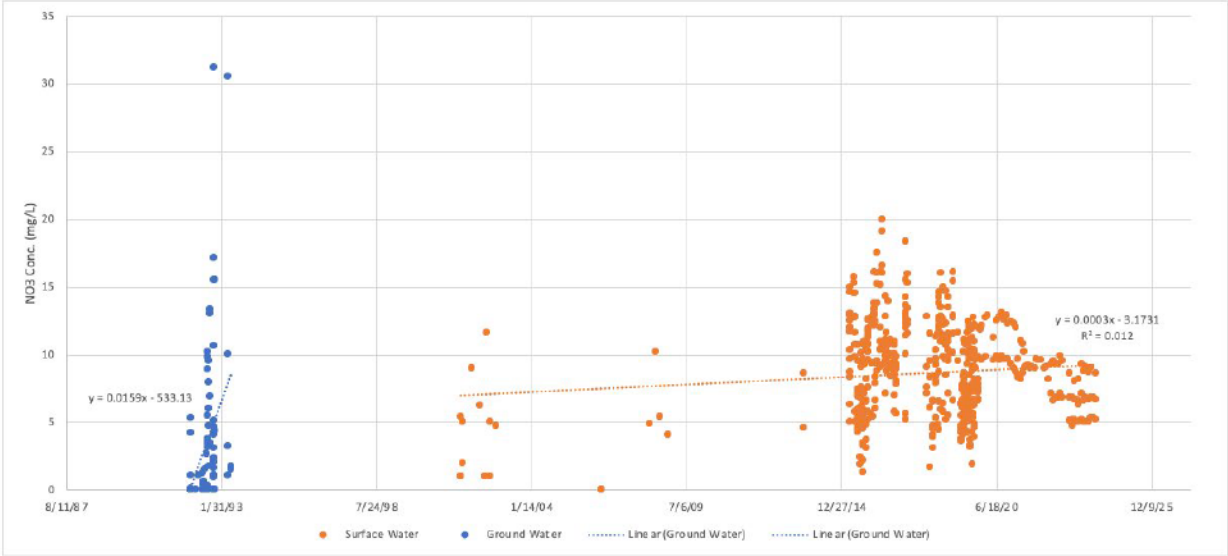


Figure 6: Fillmore and Olmsted Counties' USGS nitrate concentration (mg/L) for surface and groundwater collection points.

Nitrate-N concentration for the 25 samples collected from surface water sites in the Springs and Caves dataset did not change over time ($p = 0.97$; $R^2 = 0.007$; Figure 7).

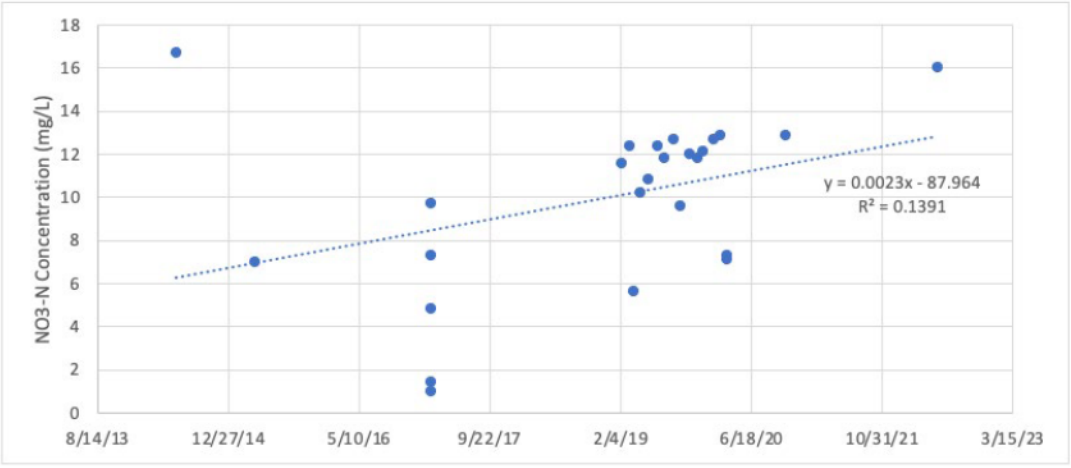


Figure 7: Nitrate concentration (mg/L) for surface and groundwater collection points for the Springs and Caves dataset.

<u>Groundwater</u>

The 113 USGS groundwater data points display a scatter of nitrate-N concentrations over a short span from 1991-1993. Two outlying points above 30 mg/L are present, one in October of 1992 and one in May of 1993. Nitrate-N concentration for the 113 samples collected from groundwater sites in the USGS dataset did not change over time ($p = 0.99$; $R^2 = 0.0002$; Figure 8).

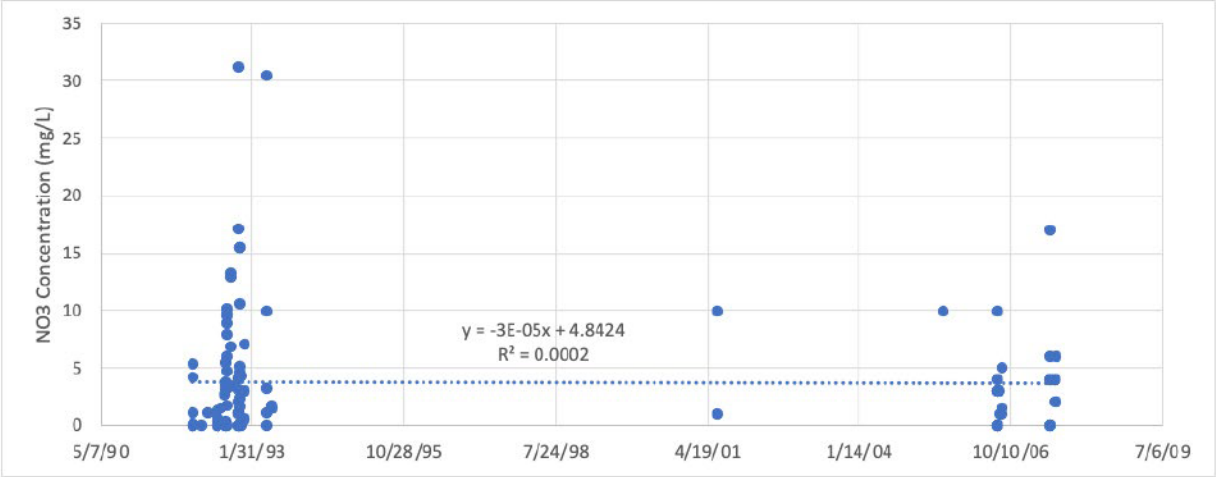


Figure 8: Nitrate results from the USGS dataset filtered by groundwater with a linear trendline.

The groundwater samples collected in the Springs & Caves dataset includes collection results from springs, caves, and wells. A total of 52 samples were collected from 2014 to 2021. The linear regression trendline fit to the data resulting in a non-significant slope over time ($p = 0.45$; $R^2 = 0.106$; Figure 9).

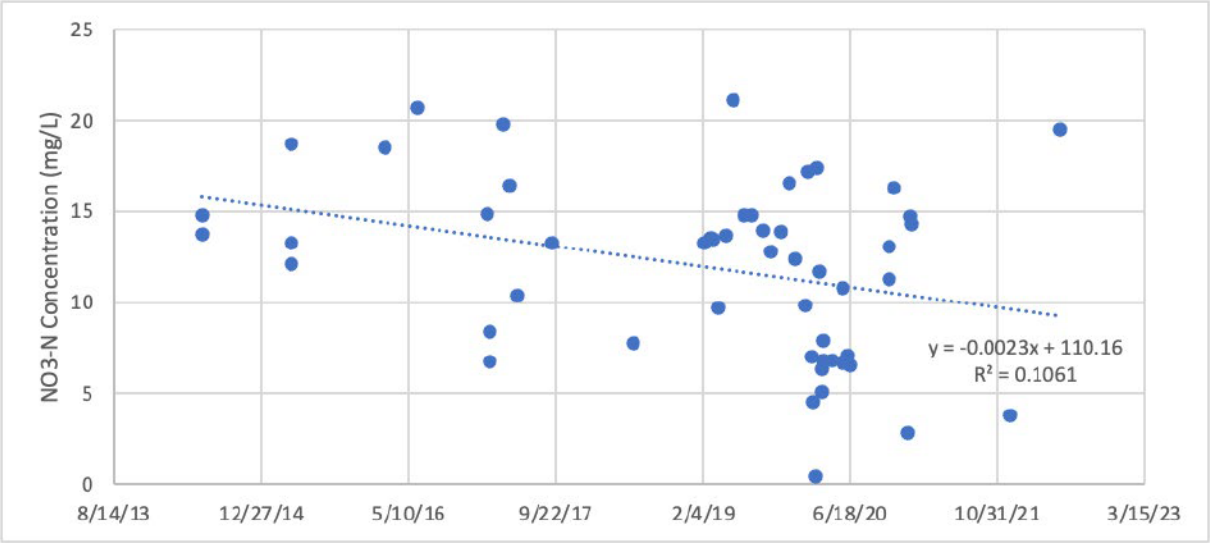


Figure 9: Nitrate results in the Springs & Caves dataset filtered by wells, cave drips, and springs.

Niagara Cave has nitrate data available at 12 formations within the complex. These 12 formations all have samples from at least two years. Other than the Kitchen Sink/Well remaining near zero throughout time, every formation exceeds 10 mg/L at some point (Figure 10).

For the years included in this study, a greater than annual average rainfall occurred in 2019 which resulted in 126 cm (49.7 in) of total precipitation. The lowest annual precipitation within this timeframe occurred in 2021 at 71.8 cm (28.3 in), which falls below the long-term mean annual precipitation of 82.3 cm (32.4 in; Figure 10).

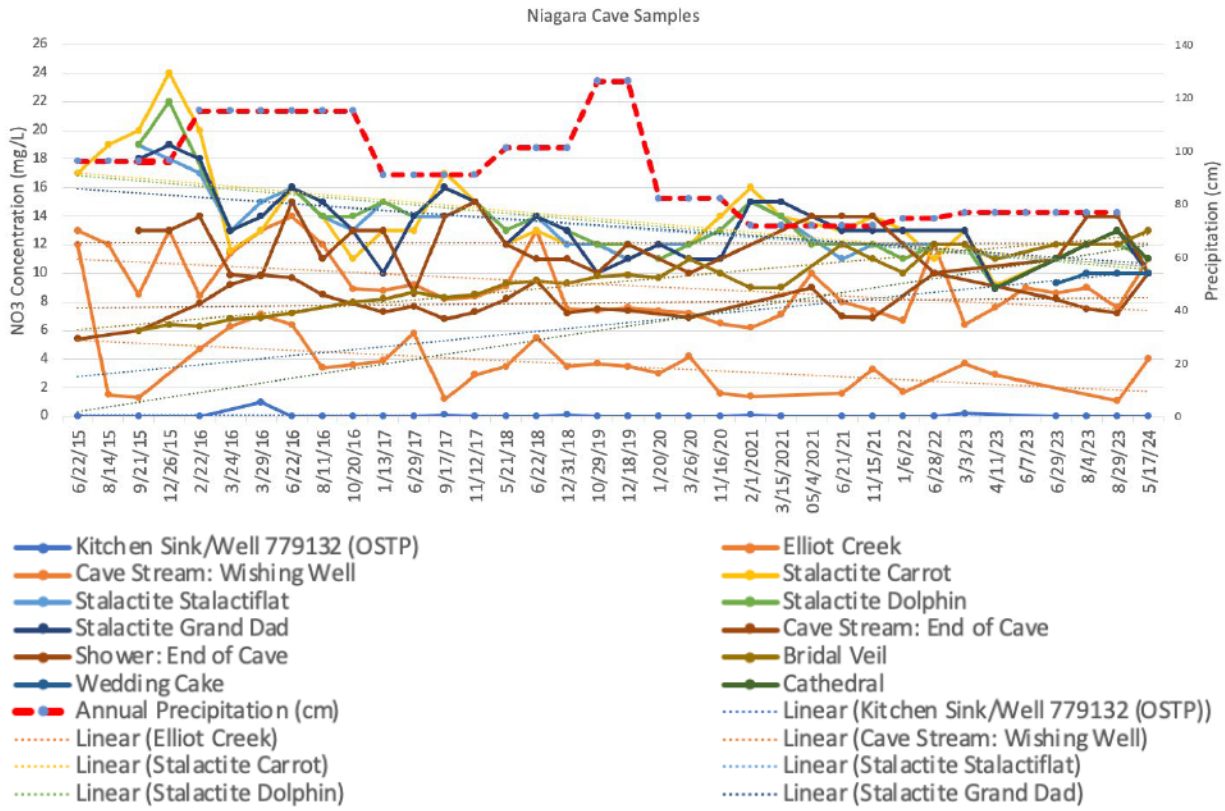


Figure 10: Nitrate concentration (mg/L) at cave formations in Niagara Cave with linear trendlines. Annual precipitation (in) plotted on the secondary y-axis. The red dashed line is the average annual rainfall from the Rochester International Airport.

Of the 12 cave formations, 10 formations had more than five unique data points, allowing further assessment of slope, r-squared test, and p-value (exclusions includes Wedding Cake and Cathedral formations; Table 1). The formations that had statistically significant trends over time have p-values highlighted in green in Table 1. Of the five formations highlighted, four have a downward slope (Stalactite Carrot, Stalactite Stalactiflat, Stalactite Dolphin, and Stalactite Grand Dad), and one (Bridal Veil) has a positive slope. Four sites (Stalactite Carrot, Stalactite Stalactiflat, Stalactite Dolphin, and Stalactite Grand Dad) have all but 1 sample result ≥10 mg/L.

Table 1: Summary of Niagara Cave data for each cave formation.

Cave Formation	Slope (mg/L/yr)	R-Squared	P-Value	Sample Size	% ≥10 mg/L
Kitchen Sink/Well 779132 (OSTP)	-1.3	0.04	0.87	30	0%
Elliot Creek	-37.5	0.16	0.44	29	3%
Cave Stream: Wishing Well	-37.9	0.23	0.98	36	28%
Stalactite Carrot	-68.6	0.37	0.03	34	97%
Stalactite Stalactiflat	-56.4	0.55	0.00	31	97%
Stalactite Dolphin	-68.6	0.55	0.00	32	97%
Stalactite Grand Dad	-54.6	0.40	0.03	31	97%
Cave Stream: End of Cave	7.3	0.01	1.00	26	8%
Shower: End of Cave	-0.4	0.00	1.00	26	88%
Bridal Veil	69.1	0.91	0.00	30	37%
Wedding Cake	76.7	0.23	0.77	4	75%
Cathedral	121.1	0.08	0.90	5	80%

Spatial Distribution

A qualitative assessment of nitrate concentrations across space did not reveal any clear patterns. Fillmore County (Figure 12) and Olmsted County (Figure 13) have a few clusters of elevated nitrate concentrations, but without pattern. The values that are above the health risk limit of 10 mg/L are widely distributed.

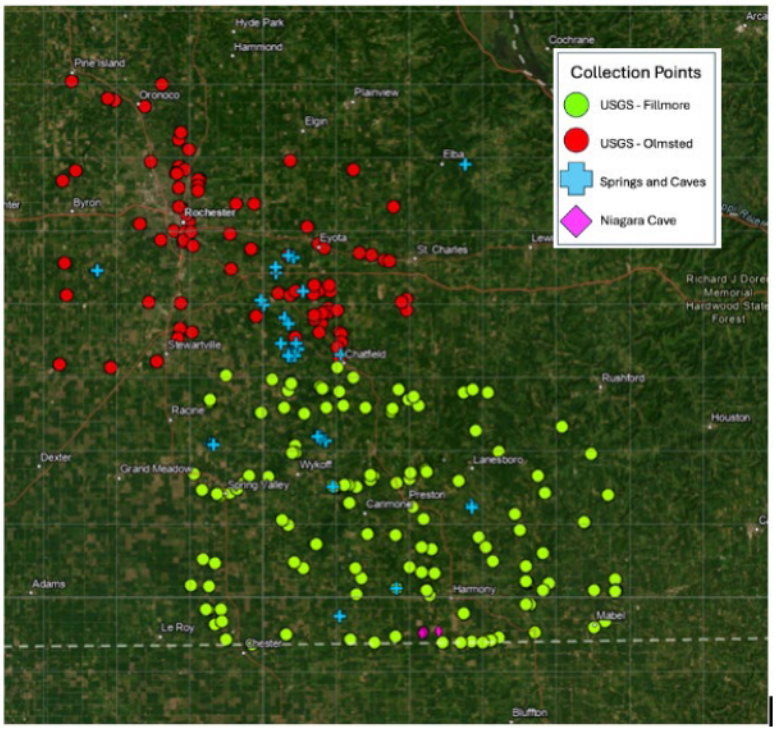


Figure 11: Surface and ground water collection points from Minnesota Caving Club and USGS. Red and green circles are USGS data, the blue crosses are from the Springs & Caves dataset, and the pink diamonds are for Niagara Cave.

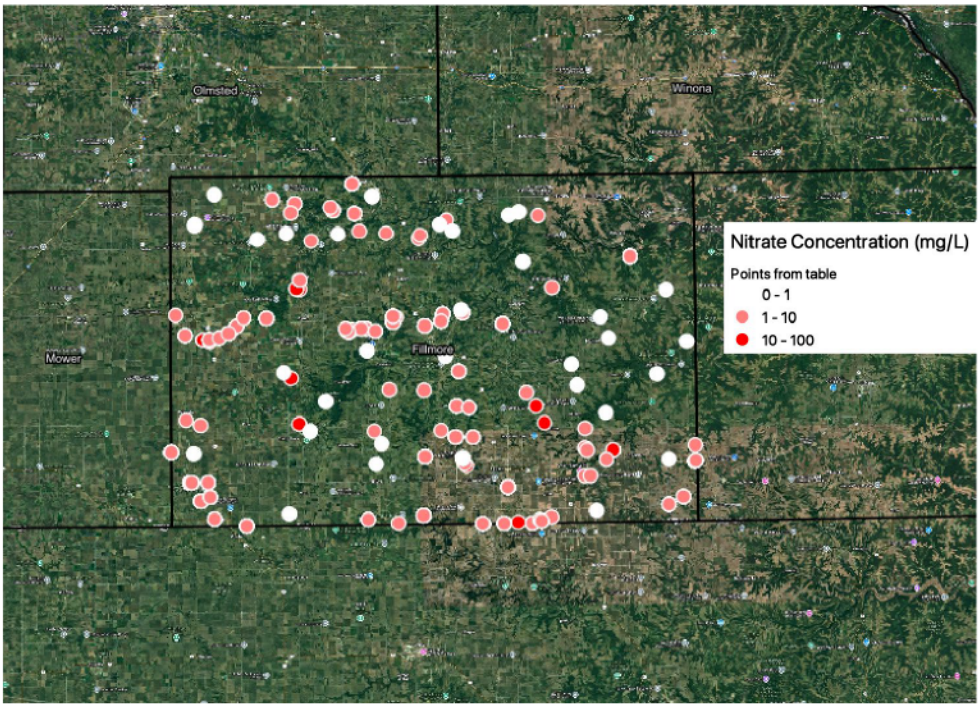


Figure 12: Fillmore County USGS data with nitrate concentrations (mg/L) with points symbolized by concentration range according to the legend.

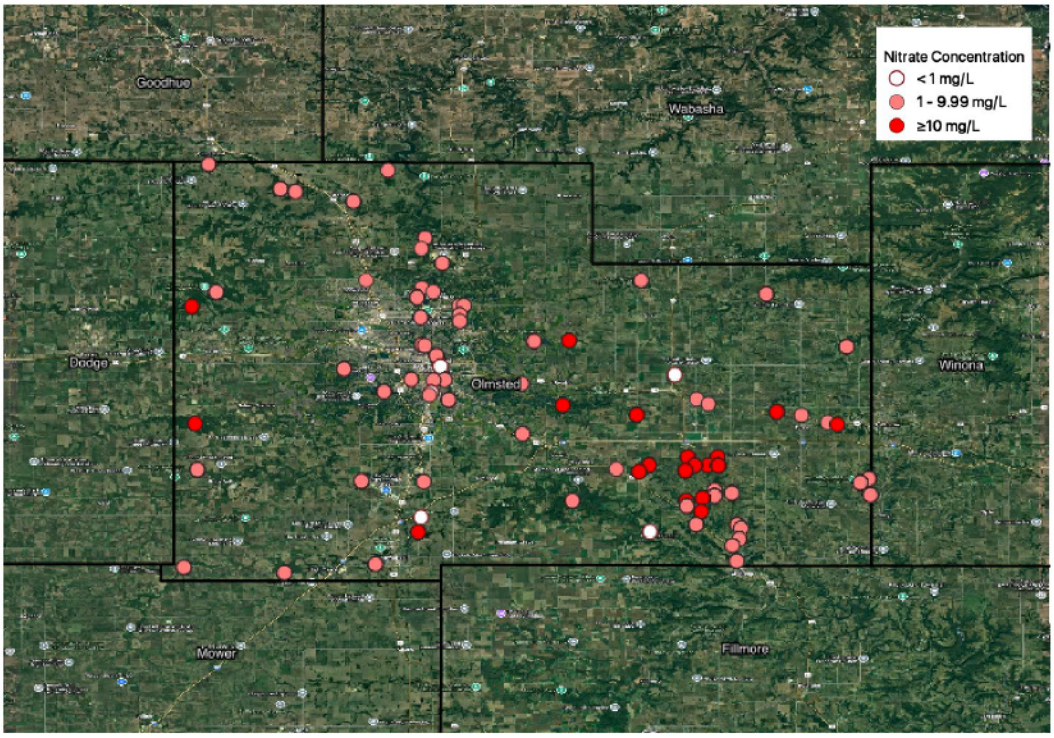


Figure 13: Olmsted County USGS data with nitrate concentrations (mg/L) with points symbolized by concentration range according to the legend.

The Springs & Caves dataset produced a cluster of high value nitrate levels in southeastern Olmsted County. Many of these results were at or above the health risk limit, with two surpassing 20 mg/L. Of the 123 nitrate readings, one was recorded below 1 mg/L (Figure 14).

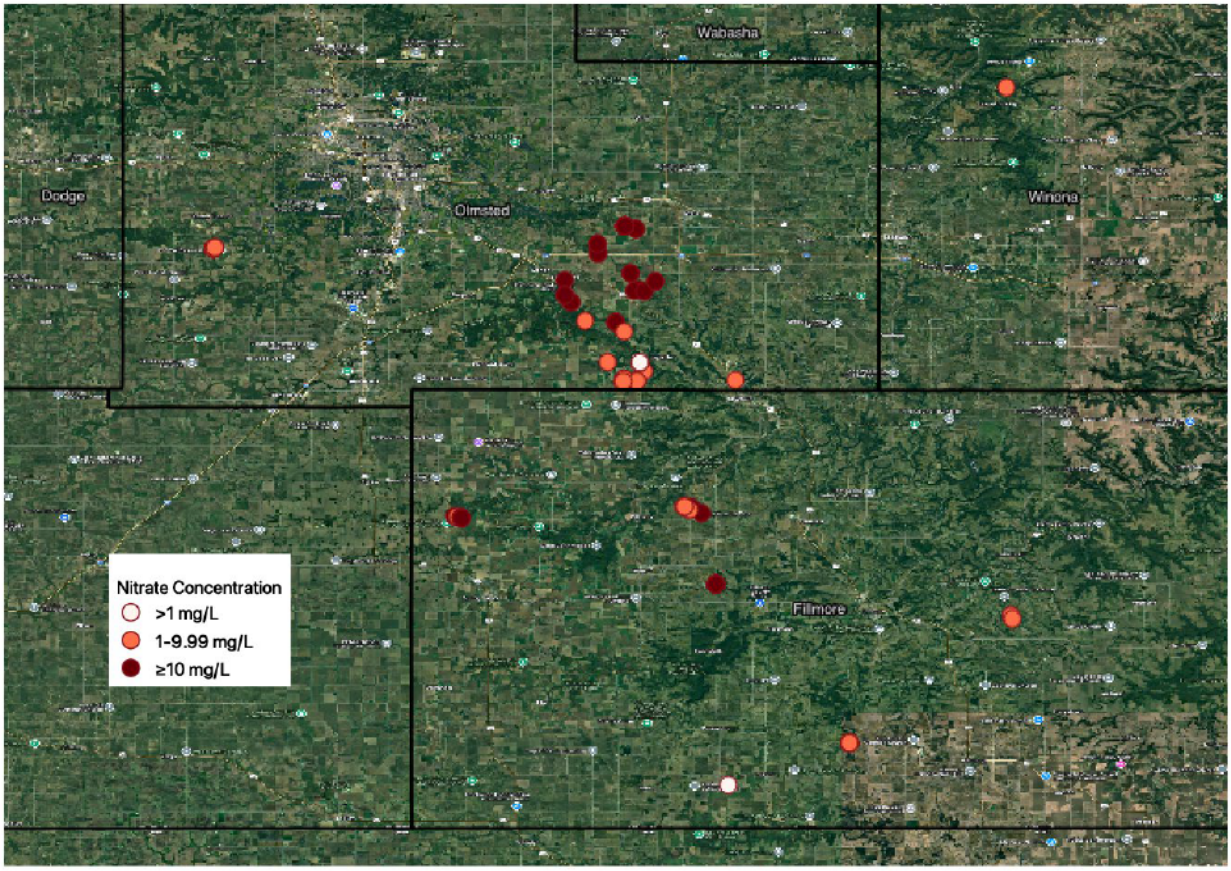


Figure 14: Springs & Caves data with nitrate concentrations (mg/L) with points symbolized by concentration range according to the legend.

Niagara Cave has 12 cave formations collection points with each having a unique sample size. Each cave formation occupies one point on the map in Figure 15. Due to sample collection occurring at the exact same place over time, each single point is represented as long-term average nitrate-N. The data yielded seven (58%) sites over the health risk limit of 10 mg/L, four sites between 1-9.99 mg/L, and one below 1 mg/L. The one site below 1 mg/L is a nearby private drinking water well #779132 (Figure 15).



Figure 15: Niagara Cave data with nitrate concentrations (mg/L) with points symbolized by concentration range according to the legend.

Land Use

According to the United States Department of Agriculture, Olmsted and Fillmore County are heavily dominated by agricultural land uses (Figure 16 and 18). Agricultural land use includes any cash crop or pasture and does not include developed areas or forests. The top three land uses in Olmsted County are corn at 48,500 ha (120,000 ac, 27.30% of land area), pasture (21.51%), and soybeans (18.18%; Figure 17). Land use in Fillmore County is similar with corn as the number one land use with over 72,000 ha (180,000 ac, 31.92% of land area), followed by pasture (19.78%), and soybeans (18.26%) (Figure 19).

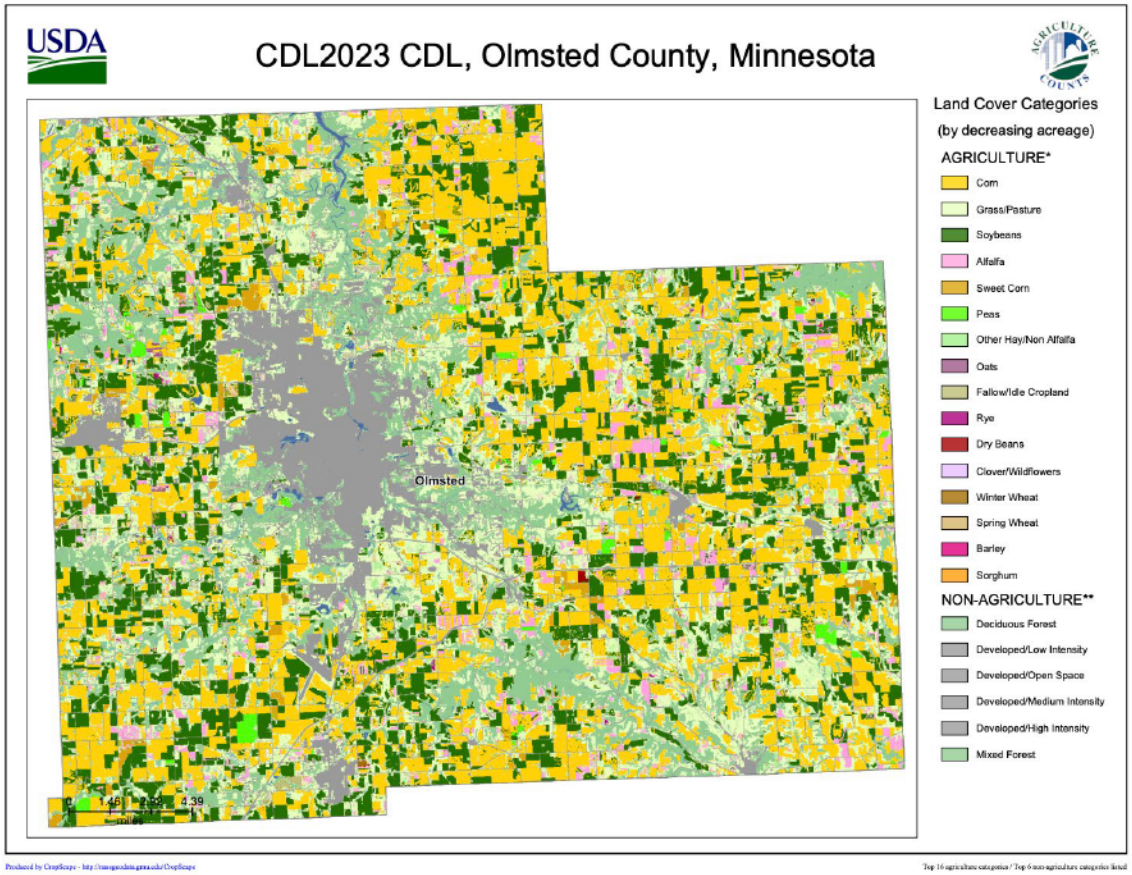


Figure 16: Map of top land uses in Olmsted County, Minnesota from CropScape (USDA, n.d.).

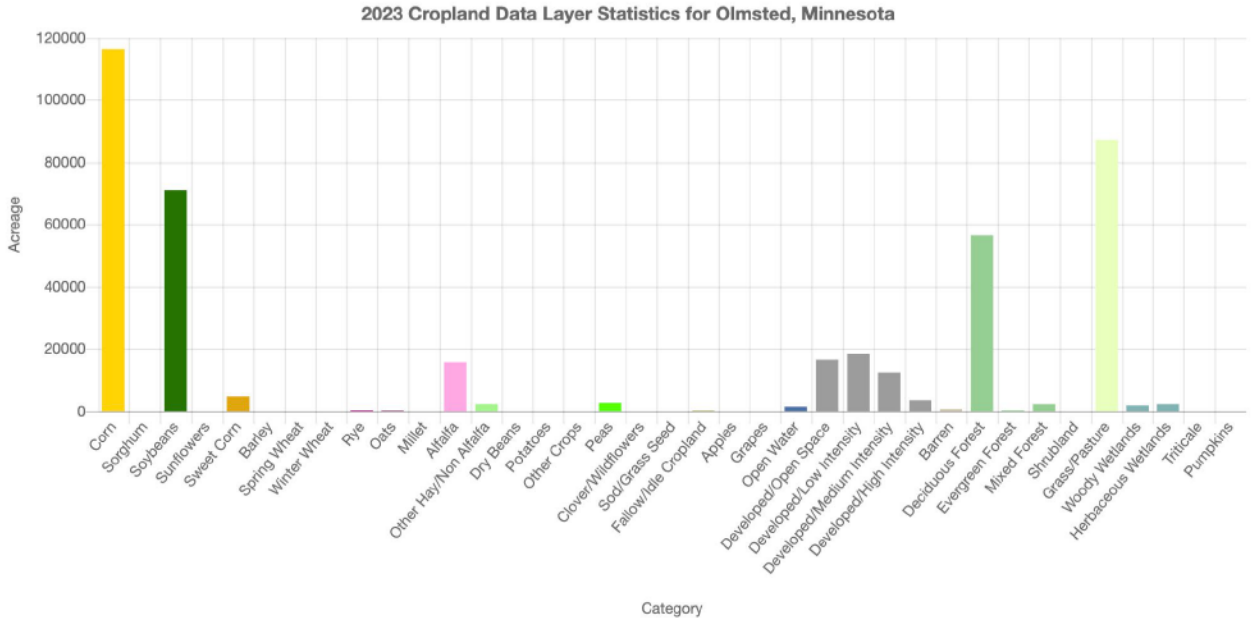


Figure 17: Statistics of land uses in Olmsted County, Minnesota from CropScape (USDA, n.d.).

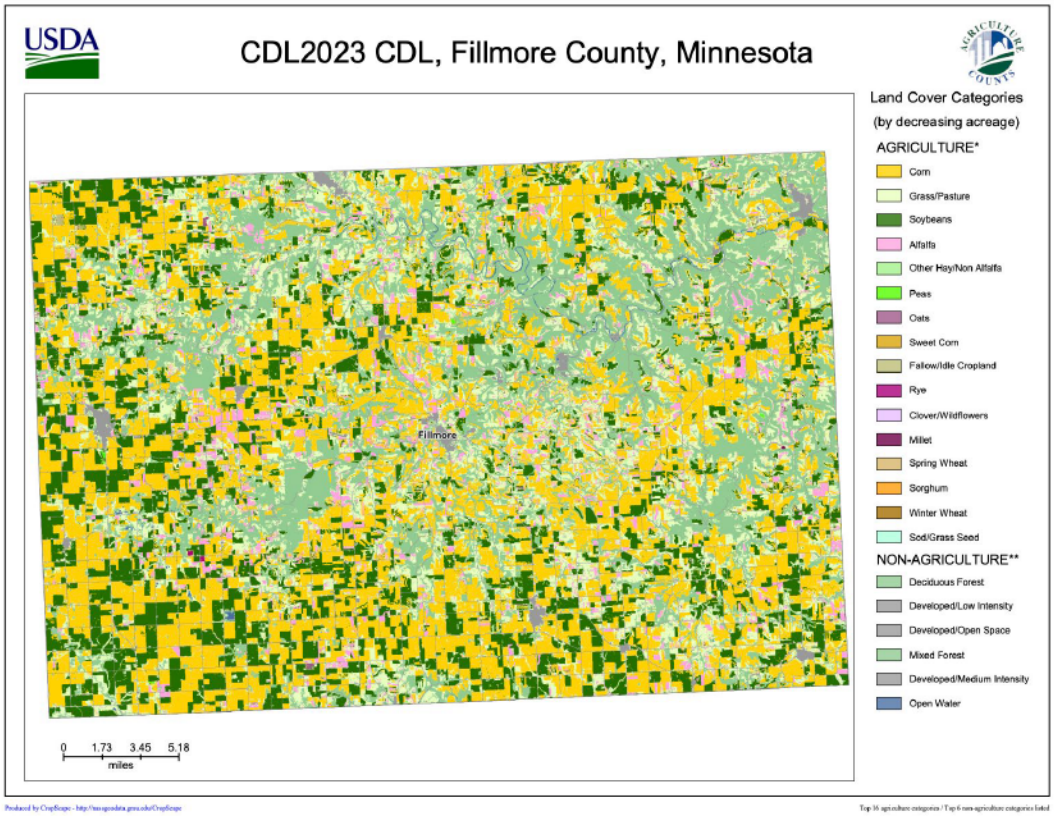


Figure 18: Map of top land uses in Fillmore County, Minnesota from CropScape (USDA, n.d.).

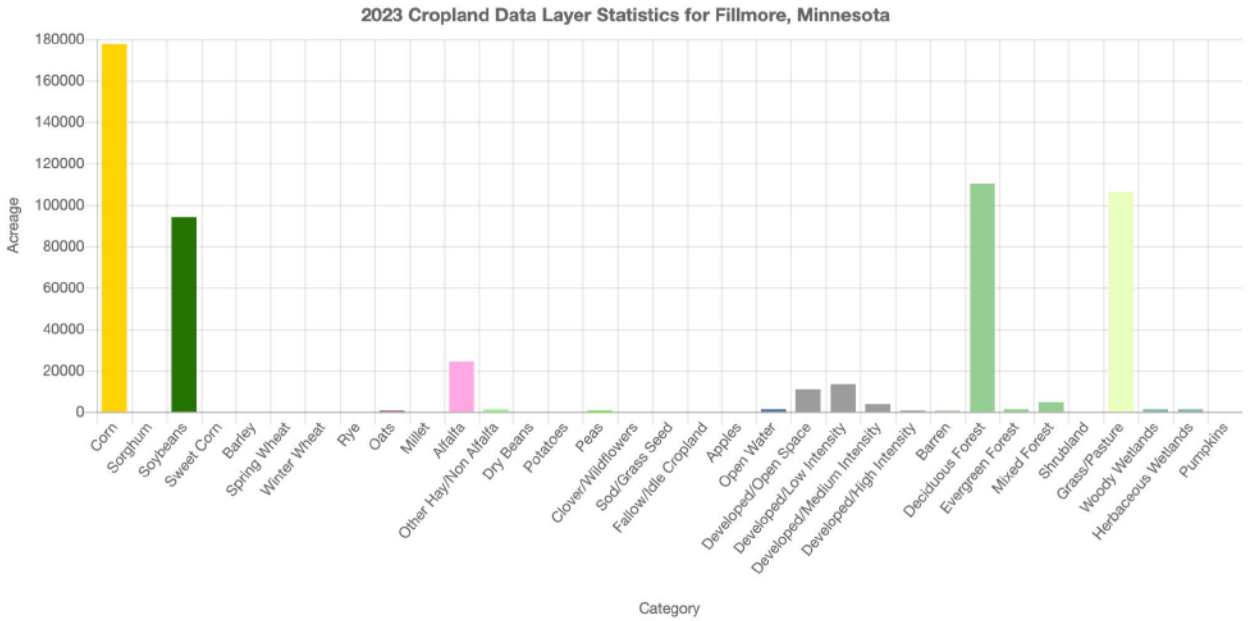


Figure 19: Statistics of top land uses in Fillmore County, Minnesota from CropScape (USDA, n.d.).

Dilution Effect

During the years where the annual precipitation greatly deviates from the mean, shallow aquifers experience a surplus, or shortage, of available water. Seven of nine formations and the well completed in the St. Peter sandstone (#779132) experienced decreases in nitrate post-2019. Two formations saw increases in nitrate post 2019, and two formations did not have pre 2019 available data for analysis (Table 2). Average nitrate-N concentration for a two-year timeline pre-2019 (2017+2018) and post-2019 (2019+2020) yielded seven formations and one well with decreasing nitrate-N concentrations, and one formation with increasing nitrate-N concentration.

Table 2: Average nitrate at each cave formation pre- (2015-2018) and post- (2019-2024) 2019 flood year of 126 cm (49.7 in) of annual precipitation.

Cave Formation	Concentration: Pre 2019	Concentration: Post 2019	Change	NO3-N Average 2017+2018	NO3-N Average 2019+2020	Change
Kitchen Sink/Well 779132 (O	0.09	0.02	-0.07	0.03	0.00	-0.03
Elliot Creek	4.38	2.75	-1.63	3.51	3.20	-0.31
Cave Stream: Wishing Well	10.36	8.04	-2.32	9.03	7.22	-1.81
Stalactite Carrot	15.48	12.36	-3.11	14.13	12.20	-1.93
Stalactite Stalactiflat	14.73	11.94	-2.79	14.25	12.00	-2.25
Stalactite Dolphin	15.20	11.94	-3.26	14.50	12.00	-2.50
Stalactite Grand Dad	14.81	11.99	-2.82	13.88	11.00	-2.88
Cave Stream: End of Cave	7.90	7.96	0.06	7.71	7.27	-0.45
Shower: End of Cave	12.22	12.09	-0.13	12.09	10.67	-1.42
Bridal Veil	7.81	10.84	3.02	8.83	10.08	1.25
Wedding Cake		9.83				
Cathedral		11.2				



Figure 20: Average long-term nitrate concentration pre-2019 flood year.



Figure 21: Average long-term nitrate concentration post-2019 flood year (includes 2019).



Figure 22: Change in nitrate concentration represented as "Rise" or "Fall" in nitrate concentration from Pre 2019 to Post 2019.

DISCUSSION

Nitrate-N Trends

The analysis of nitrate-N concentrations in southeast Minnesota's karst landscape reveals complex temporal and spatial patterns influenced by land use, precipitation, and the unique hydrogeology of the region. Long-term trends in surface water in the USGS dataset spanning from 1993 to 2023 does indicate a significant increasing change in average nitrate-N concentrations. In addition, 24.8% of samples from the USGS dataset exceeds the EPA's health risk limit of 10 mg/L, suggesting that surface water nitrate levels are influenced by consistent

anthropogenic inputs, primarily from runoff the of the dominant land use, agriculture. Groundwater data from both the USGS (1992–2007) and Springs & Caves datasets (2014–2022) exhibit greater variability, with no statistically significant trends ($p < 0.05$). The Niagara Cave sites with statistical significance showed four of five having a negative slope, suggesting nitrate concentrations are decreasing over time. However, it is difficult to pinpoint what led to these statistically significant trends without meticulous knowledge of the farmed fields above and adjacent to the cave complex. Further communication with the producers farming this land may provide context to topographic slopes, karst features, depth to bedrock, etc. which would aid in understanding the surface and groundwater interaction at each collection point. The USGS groundwater data also yielded fewer collections that exceeded the HRL (12.3%). This variability in groundwater nitrate concentration is likely due to the complexities of subsurface flow in a karst system, reacting quickly to surface inputs and precipitation.

The divergence between surface and groundwater trends can be attributed to their differing hydrological controls. Surface waters, such as those in the Root and Zumbro River watersheds, are directly exposed to overland flow and point-source discharges, leading to more immediate and uniform nitrate loading. Groundwater, however, interacts with the karst aquifer's porous limestone and sandstone, where nitrate can be transported quickly through conduits, retained, or travel laterally along aquitards. These landscape features can result in delayed or amplified groundwater responses from surface conditions. In addition, these karst features can introduce variability in subsurface nitrate values from one precipitation event to the next because surface water will not flow into the ground in the same way each event. Niagara Cave data support the variability of surface and groundwater interaction as most of the cave formations

exceed 10 mg/L at some point, with significant fluctuations tied to precipitation events, such as the 2019 flood year (Figure 10).

Agricultural Influence

Agriculture, the dominant land use in Olmsted and Fillmore Counties, is a primary driver of nitrate contamination. CropScape data indicate that corn and soybeans, which together account for over 45% of land area in both counties, require substantial nitrogen fertilizer inputs. These crops, coupled with pasture lands, make up 66% of land cover in Olmsted County, and 69% of land use in Fillmore County (according to 2023 Cropscape data). Agriculture related inputs on the majority land use are likely driving increases in surface nitrates over time. The datasets for groundwater were not nearly as robust and yielded no statistically significant trends, other than the five formations within Niagara Cave. Clear spatial patterns in nitrate concentration were not discernable, suggesting that agricultural influence is pervasive across the study area, with notable regions of higher nitrate concentration (Figure 12 and 13). A lack of clear spatial nitrate concentration patterns in a landscape with evenly distributed agricultural land use is consistent with non-point source pollution, where fertilizer and manure spreading results in nitrate leaching through the region's sandy glacial plains or porous bedrock.

Mitigating agricultural nitrate inputs requires balancing cropland productivity with human health. Through the combination of fate and transport modeling and best management practices (BMPs), such as precision agriculture (See & Spray technologies), could reduce over-application of fertilizers (Almasri and Kaluarachchi (2007). Large scale adoption of technological advances comes as a hurdle because producers must be able to afford the product,

and also see meaningful changes in annual budget. Specifically, southeast Minnesota may face challenges due to the region's karst topography, where rapid infiltration could hinder effectiveness. More practical and affordable BMPs are contracted in-the-field. Secchi et al. (2007) monitored 13 major subbasins with conservation practices that included conservation tillage, terraces, land set-aside, grassed waterways, contouring, and simple nutrient reduction strategies; surface nitrate was reduced by 6 to 20% relative to the baseline when nitrogen fertilizer spraying was reduced (Secchi et al., 2007).

Dilution Effect with a Changing Climate

The dilution effect, where increased precipitation reduces nitrate concentrations in aquifers, is evident in the Niagara Cave data pre- and post-2019 flood year (126 cm; 49.7 in of precipitation). Seven of nine cave formations experienced decreased nitrate levels post-2019, supporting the hypothesis that heavy rainfall dilutes nitrate in shallow karst aquifers (Table 2). Conversely, drought years like 2021 (71.8 cm; 28.3 in) reduce the subsurface water supply which leads to concentration of existing nitrate. These dilution effect results align with Jutglar et al. (2021), who noted rapid nitrate spikes in springs during droughts, with more sustained responses in wells due to slower filtration times.

Southeast Minnesota's climate is trending warmer and wetter, with an estimated 4.8 cm (1.9 in) increase in annual rainfall since 1895 (Coffman et al., 2024). This shift could amplify the dilution effect, potentially lowering average nitrate concentrations in drinking water aquifers during wet years. However, it also raises concerns about the potential of legacy nitrate contamination from previous decades filtering through deeper aquifers. This may complicate

long-term nitrate trends and would be extremely difficult to track. A wetter climate may also increase runoff and leaching events. Monitoring groundwater at a variety of depths over time would be the most effective approach to understanding nitrate responses. Shallow groundwater monitoring could identify trends for faster moving and younger flows, whereas deeper aquifer sampling may allow for the tracking of older water. Agroecosystems are tied for the highest potential to transfer nitrogen, so consistent monitoring at varying depths is critical (Shukla and Saxena, 2020). It also reinforces the strong relationship between surface inputs and potential for groundwater contamination.

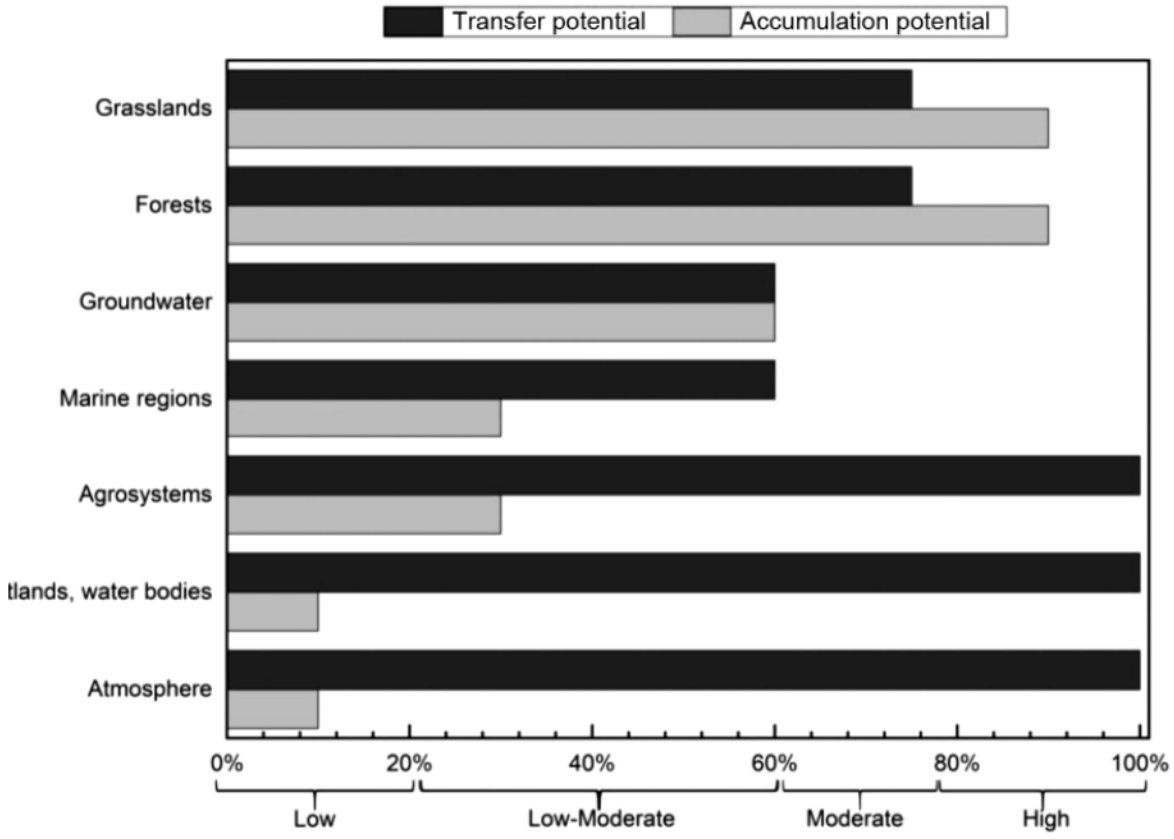


Figure 23: Nitrogen accumulation potential and transfer potential of different ecosystems (Shukla and Saxena, 2020)

Importance of Subsurface Sample Collection

Subsurface sampling like that in the Niagara Cave and Springs & Caves datasets provides critical insights into nitrate dynamics not seen with just surface water data. The ability to sample cave drips, streams, and springs within the same karst system reveals the direct interaction between surface inputs and groundwater responses. For example, nitrate concentrations at cave formations like Bridal Veil follow precipitation inputs (Fig. 10), reinforcing the need for site specific subsurface monitoring. The data collected in this study were fairly limited even though analysis was performed on three datasets. The data from the Minnesota Caving Club would benefit from more frequent and consistent collections, rather than being limited to two or three collections a year in some cases. Ideally MCC volunteers would collect nitrate concentrations at every identified cave formation once or twice a month. After three years of collection, a fairly robust dataset would start to take shape. This level of detail is essential in karst landscapes due to the irregularity of water movement from sinkholes, caves, and conduits. A traditional well sample may miss localized contamination, especially closer to the surface.

Scaling up subsurface sampling efforts could enhance our understanding of nitrate transport and inform policy to protect water quality. The Minnesota Caving Club's volunteer-collected data give insight into the importance of small initiatives, and how they can have a broad impact. Funding and coordination with agencies like the Minnesota Department of Natural Resources or the EPA could allocate money to support increasing sample sizes and frequencies of existing subsurface collection. It could also lead to the creation of new volunteer groups that help to expand the network. Southeast Minnesota's rural population is heavily reliant on groundwater for human and livestock consumption. Expanding approaches to monitoring nitrate will provide more insight into managing contamination and validating the dilution effect.

CONCLUSION

The findings from this research highlight the complex linkages between land use, climate, and geology in shaping nitrate contamination in southeast Minnesota. Nitrate-N concentrations in surface water have statistically significant upward trends. Even the relatively coarse timestep datasets analyzed here suggest decreases in nitrate concentration after precipitation events, reinforcing the theory of a dilution effect. The dilution effect offers a natural buffer against high nitrate levels, but a changing climate may intensify seasonal extremes. Subsurface sampling emerges as a powerful tool, warranting further investment to protect drinking water and aquatic ecosystems in this vulnerable landscape. Future research should explore lag times in nitrate transport and the efficacy of precision agriculture in reducing inputs, building on this study's foundation to address one of Minnesota's most pressing environmental challenges.

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