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CONCENTRATION-STREAMFLOW RELATIONSHIP IN THE RED RIVER TO NORTH NEAR GRAND FORKS, NORTH DAKOTA

By

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Bachelor of Art, University of Minnesota 2016

A Thesis

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of the

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for the degree of

Master of Science Energy Systems Engineering

Grand Forks, North Dakota

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Name: KABAMBA NGOYI

Degree: Master of Science

This document, submitted in partial fulfillment of the requirements for the degree from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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Chris Nelson
Dean of the School of Graduate Studies

7/21/2021

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PERMISSION

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Department Institute of Energy System studies

Degree Master of Science

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Kabamba N Ngoyi
July 21, 2021

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DEDICATION

I am dedicating my thesis work to my family. A special feeling of gratitude to my loving parents, Ngoyi Mutanda and Tshibola Ngalula whose prayers, words of encouragement and push for tenacity ring in my ears. My sister Deborah, and Brothers: Patrick, Joel and Ben have never left my side and are very special.

I am dedicating this work to four beloved people who have mean and continue to mean so much to me. Although they are no longer of this world, their memories continue to regulate my life. To my paternal Grandmother Kabamba Helene, my maternal Grand Mother Angeline Tuseku, maternal Grand Father Patrice Mubiayi, and my Uncles Willy Balowayi and Jules Kabasubabo may you find peace and love in Paradise.

ABSTRACT

For the last 15 years, the nutrient concentrations have fluctuated in both particulate and dissolved forms. The increasing concentration of sulfate and chloride in the North Great Plain Basin impose threats to water quality in the Basin. During this spring snowmelt season of 2021, water samples were collected three times daily in the Red River at Grand Forks, North Dakota to develop a concentration streamflow relationship for sulfate, nitrate, chloride, and fluoride. The 2020-2021 winter was very dry as a result the snowmelt streamflow was very low, the rising limb period was short, but the streamflow increased rapidly from 75 m^3/sec to 180 m^3/sec in five days then started to decrease. Sulfate concentration showed a response to streamflow during the study period, fluoride concentration was low and fluctuated very little, nitrate concentration was very low during the melt period then started to change over the course study. Chloride concentration remains very high during the rest of the study period. The C-Q relationship indicates a counterclockwise direction for sulfate. The nitrate concentration was highly variable to discharge which may be attributed to flushing from organic soil. Chloride C-Q relationship showed a counterclockwise hysteresis relationship. Discharge showed a little influence on fluoride concentration which can be explain by chemostatic behavior.

INTRODUCTION

Water Quality

Water is an essential indicator to human health determinant and plays a substantial role in life sustenance (Somani et al., 2014). Poor water quality causes a major threat to health and it is the cause of 80 percent of disease in developing countries (Somani et al., 2014). Every year, 1.8 million people die globally due to water quality related disease (Somani et al., 2014). Water quality is defined as the chemical, physical and biological property of water depending on its suitability for a designated use (Roy, 2019). It can be used for different purposes such as agriculture, drinking, fisheries, or industries (Roy, 2019). Each of these different areas has a different chemical, physical, and biological standard to support the use (Roy, 2019). As an instance, there are different regulations for water to be used in agriculture compared to drinking (Roy, 2019). For the last century, water quality assessment standard has been put in place to verify that each area follows the standard (Roy, 2019).

Anthropogenic activities and climate change can deteriorate the quality of fresh water (Jeannote et al., 2020). Water security has been rated by the world Economic Forum as one of the top concerns for social well-being (stets et al., 2020). Pollution and dynamic change in water availability is a major cause of water insecurity (Stets et al., 2020). The Clean Water Act was implemented in US to focus on upgrading wastewater treatment plants to decrease point discharge of nutrients and organic material (stets et al., 2020). In some locations, best management practice has been implemented to address nonpoint source pollution arising from agricultural land (Stets et al., 2020).

United States Geological Survey

United States Geological Survey (USGS) collects data to study the quality of water, how water has been changed temporally and give the opportunity to investigate why water quality change over time (U.S. Geological Survey, 2018). The USGS personnel used the National Field Manual for the Collection of Water-Quality Data (NFM) because it is a guideline and protocol for USGS field personnel who collect water quality data (U.S. Geological Survey, 2018). This manual provides a detailed, comprehensive procedure for tracking the surface and groundwater quality water (U.S. Geological Survey, 2018). It contains methods and protocols for sampling water resources, how to process samples for water quality analysis, a method to use for measuring field parameters, how to sample water for the low level of mercury and organic wastewater chemical, sampling sediment for chemistry (U.S. Geological Survey, 2018). The manual provides a guide to ensure that data collected are accurate, high quality, and can be proved scientifically (U.S. Geological Survey, 2018). The USGS provides information on temperature, dissolved oxygen, specific conductance, pH measurement, and turbidity (U.S. Geological Survey, 2018). The data collected by USGS help us to understand how groundwater moves through the earth and evaluate how biogeochemical processes affect the water quality (U.S. Geological Survey, 2018). The USGS has a multipurpose network containing more than 10,000 stream gages.

During the cold season, ice affects streamflow (U.S. Geological survey, 2018). The ice formation on the rivers causes discharge data to be very high, and these incorrect data may cause improper interpretation of flow condition and application of the data (U.S. Geological survey, 2018). This is one of the reasons the discharge data values for the stream are disabled for the view and resume when ice conditions start melting (U.S. Geological survey, 2018). However, if the ice affected the streams minimally; discharge data will continue to display, and the streamflow seems to increase in the night and decrease during midday near-baseline (U.S. Geological survey,2018).

USGS does not sample water daily in the Red River for the State of ND because it is expensive (Galloway et al., 2013). As a result, USGS did a statical analysis to determine an efficient sample design allowing them to analyze for the trends and load by minimizing the sampling number (Galloway et al., 2013). The Red River at Grand Forks North Dakota is a first level 1 design site, so samples are collected for major ions, trace metals, nutrients, bacteria, and sediment (Galloway et al., 2013). USGS does collect eight samples a year: January, April (2 samples), May, June, July, August, and October (Galloway et al., 2013). Since 2012, a few extra samples have been collected for another sampling program with a different sampling purpose (Galloway et al., 2013). However, USGS does have daily estimates of sulfate, nitrate plus nitrite and a few other constituents that are based on a regression equation from their continuous water-quality monitor which have error (Galloway et al., 2013).

Concentration-Discharge Relationship

Water and solutes movement are naturally coupled through the landscape by hydrosphere-lithosphere-atmosphere interactions (Knapp et al., 2020). The response of stream water chemistry to changes in discharge provides an understanding on the mechanism of the release of water and solutes by the watersheds and their storage (Knapp et al., 2020). Even though Concentration-Discharge (*C*-*Q*) has been studied for more than decade, the scientists still has pending questions on what *C*-*Q* relationships inform us about catchment behavior (Godsey et al., 2009). The data availability and simple analysis make it easy for the catchment hydrologist to study *C*-*Q* relationships (Godsey et al., 2009). The *C*-*Q* analysis have been recently focusing on mixing models from different sources of water such as old and new water, groundwater, melting snow and precipitation (Godsey et al., 2009). The mixing model are "inferred from the shape of the concentration-discharge relationship for different solute" (Godsey et al., 2009). The *C-Q* relationship can be used as an indicator of biogeochemical process and hydrologic (Knapp et al., 2020).

During spring snowmelt season three different behaviors of the C-Q relationships can emerge: dilution, flushing and chemostatic. Dilution occurs when the *C* decreases with increasing river discharge (Knapp et al., 2020). This behavior has been associated with source limitation meaning that the limited solutes have been mixed with more waters resulting dilution (Knapp et al., 2020). However, when there is mobilization behavior; there is a pattern of increasing solute concentration with increasing discharge resulting flushing (Knapp et al., 2020). This might be because of some source area contribution and other nutrients that demonstrate a buffered response (Diamond 2013). Lastly, in a chemostatic behavior, the concentration remains constant as streamflow fluctuates (Knapp et al., 2020). During a base flow, the composition of water is determined largely by point-source and groundwater inputs and the diffuse inputs are small to the river (House et Al., 1998). However, during flood events the inflows diffusion of water become more important because it can lead to dilution of solutes in the base flow, or it can increase the solute concentration depending on the source water history and how it interacts with soil components (House et Al., 1998).

A hysteresis loop is often observed when a plotting stream solute concentration-discharge is made (Davies and Evans 1999). It occurs when the solute concentration at given discharge on the rising limb of the hydrograph differs from the same discharge on the falling limb (Davies and Evans 1999). Some studies suggested that hysteresis is assigned to the flushing behavior during the early part of the storm flow causing increasing concentration on the rising limb (Davies and Evans 1999). Contributions from different flow sources peak at different times can make simple components to mix and causing hysteresis (Davies and Evans 1999). Hysteresis concentration-discharge happens anytime there is a difference in the timing or different form of solute and discharge responses (Davies and Evans 1998). Hysteresis loops are tested with the data collected at the study area (Davies and Evans 1998).

PURPOSE

For the last ten years, many lakes in the Northern Great Plain (NGP) have experienced the frequent algae blooms. This phenomenon can be attributed to the higher concentration of nitrogen and phosphorus which is partly due to intense land management practice. The export of nutrients to streams and lakes leads to eutrophication and degradation of surface water quality. In addition, elevated concentration of sulfate and chloride impose threats to water quality across the NGP. Degradation of water quality reduced its quality for drinking and aquatic life. The cold climate and snowmelt hydrology play an essential role by controlling phosphorous concentration, exporting, and supplying in the river. This study will develop a concentration-streamflow relationship for nitrate, sulfate, chloride, and fluoride during the 2021 spring snowmelt season. Since the 2020-2021 winter was very dry, the snowmelt streamflow was low. However, a mid-spring blizzard across the Red River Basin caused substantial streamflow and we anticipated an interesting scientific insight from the concentration-streamflow relationship. The mid-spring extreme event followed by a hydrologically dry winter is frequently occurring under the changing climate in the NGP (Mahmood et al., 2017). Furthermore, the concentration-streamflow relationship is also sensitive to recent wetting and warming situation in the NGP region. Thus, the findings of this study have enormous the scientific impacts on *C*-*Q* relationships and solute export to the downstream of the Red River Basin. In addition, the study will help to gain a better understanding on the relationship between concentration-streamflow due to the influence of hydroclimatic variation from the soil condition and origin of the species.

Preliminary samples were collected during the late fall and early winter of the year 2020 and the other samples were collected before spring snowmelt and the start of streamflow in 2021. In the beginning of streamflow, the sample was collected three times a day for two weeks and the remaining samples collected once a day. During each visit in the Red River, temperature of water in degree Celsius, specific conductance, dissolved oxygen, pH concentration was collected. The United States Geological Survey (USGS) stream gauging network provided streamflow data discharge (05082500) for the collection. The data provided by USGS network is seasonal in the cold region because of the amount of ice in the streams. The chemistry analysis was done at the laboratory to know the concentration of nutrients. Preliminary results indicate that the nutrient concentration in both particulate and dissolved forms have fluctuated over last 15 years.

The objective is to use a water-quality trend analysis to determine the amount of natural water quality variability and to determine if the water quality change in the Red River occurred in response to hydroclimatic variability or possible human activities. The study's focus will be to analyze the streamflow and nutrients concentration data (USGS and field sampling during the 2021 spring season) for a 2004-today period in the Red River Valley in North Dakota/Minnesota.

STUDY AREA

The study area (known as the southern Red River to North Basin draining at USGS gauge, ID: 05082500, near Grand Forks, North Dakota) is an agricultural watershed (~30,100 square miles or 77959 km^2) situated in the southern of the Red River Basin (RRB) (~47.85°N, 97.02°W) (Figure 1). The Red River forms most of the border between MN and ND (MN dept of natural resources, 2020). It flows northward 550 miles from its source in Breckenridge, MN to Lake Winnipeg in Canada (MN dept of natural resources, 2020). It is located on the eastern edge of the Great Plains and it is not considered a valley from the geological point of view (MN dept of natural resources, 2020). Seventy-two percent of the basin is used for agricultural production such as crop (wheat, soybeans, corns, sugar beets) (Nustad and Vecchia 2020). The remaining land covers are pasture, forests, open water, and wetlands (Stoner, et Al., 1993). The dark appearance of soil is due to high clay content in soils (MN dept of natural resources, 2020). The soils are fertile and suitable for agriculture (Nustad and Vecchia 2020). The western part of the Red River of the North Basin has a dry semiarid climate and subhumid for the eastern part (Nustad and Vecchia 2020). Seventy-five percent of its annual flow comes from eastern tributaries (Nustad and Vecchia 2020). Runoff occurs during spring and early summer. This is due to rains falling on melting snow and heavy rains fallings on saturated soil (Nustad and Vecchia 2020). The abundance of lakes, wetlands, prairies potholes in the most physiographic area outside the Red River Valley changes the residence time of water. As a result, it affected the amount of biota, dissolved constituents carried by water (Nustad and Vecchia 2020).

Water quality is a big concern for federal, state, and provincial governments because of the increasing concentration of sulfate and total dissolved solids (Nustad 2020). Sulfate and total dissolved have been exceeded frequently for the past 10-15 years (Nustad 2020). The Red River contributes 68% of the total phosphorus and 34 percent of total nitrogen to the lake Winnipeg even though 16% of the Red River flow to Lake Winnipeg (Nustad 2020). During spring runoff and after thunderstorms, the concentration of dissolved chemical constituents is normally low in surface water (Nustad and Vecchia 2020). Along the Red River of the North, calcium and magnesium are the principal cations and bicarbonate is the principal anion (Nustad and Vecchia 2020). The use of fertilizer such as nitrogen and phosphorous and nitrogen from manure can contribute to nutrients to lakes, streams, and reservoirs (Nustad and Vecchia 2020). Nitrate and other nitrogen species have not been detected regionally as a widespread problem in the basin (Tornes and Brigham 1994).

The water quality in surficial in the southeast subregion is very different from that in the West and Central subregions (stoner et al., 1993). Eastern tributaries have lower dissolved-solid concentrations than the tributaries draining in the western part of The Basin (Nustad and Vecchia 2020). As an example, sodium, sulfate, silica, potassium are higher in the west and central subregions and radium is higher in the east region (stoner et al., 1993). The difference in soil, geology, climate, and the persistence of nutrients in each region is an indicator in the distributions of water quality in the Red River Basin (stoner et al., 1993).

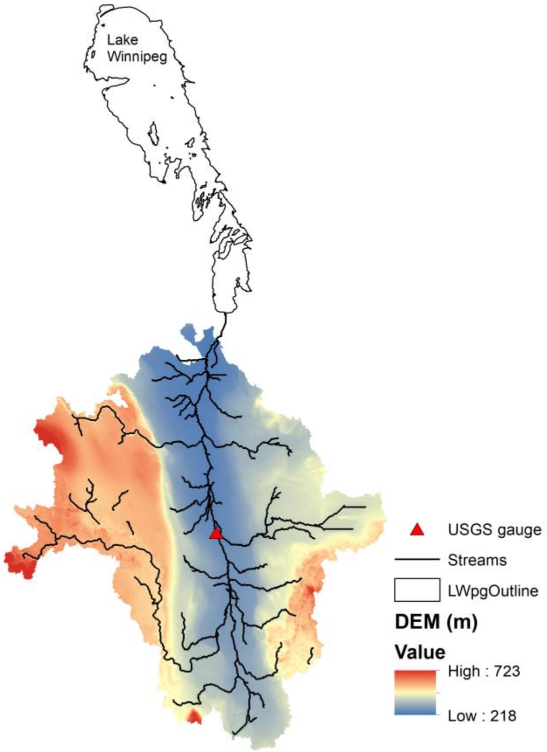


Figure 1: Topography of Red River Basin Study Area

Topography derived from Shuttle Radar Topographic Mission (SRTM) digital elevation model (DEM) and locations of streamflow gauge (USGS gauge). Concentrations were also measured from the USGS gauge location.

METHODS AND MATERIAL

Sampling

According to the National Water Quality laboratory, all sites should be at or near streamflow gaging stations not more than 100 feet from the gage site because stream discharge is associated with chemical constituent concentration. Both data are needed to evaluate the relationship between discharge and water quality characteristics and compute the constituent's transportation (Shelton 1994). Sampling sites should be where there is a uniform flow and avoiding upstream sites or points of sources to reduce issues caused by poorly mixed flows or backwater effects (Shelton 1994). For example, collecting samples directly downstream from a bridge may be contaminated from the bridge structure or runoff from the road surface (Shelton 1994).

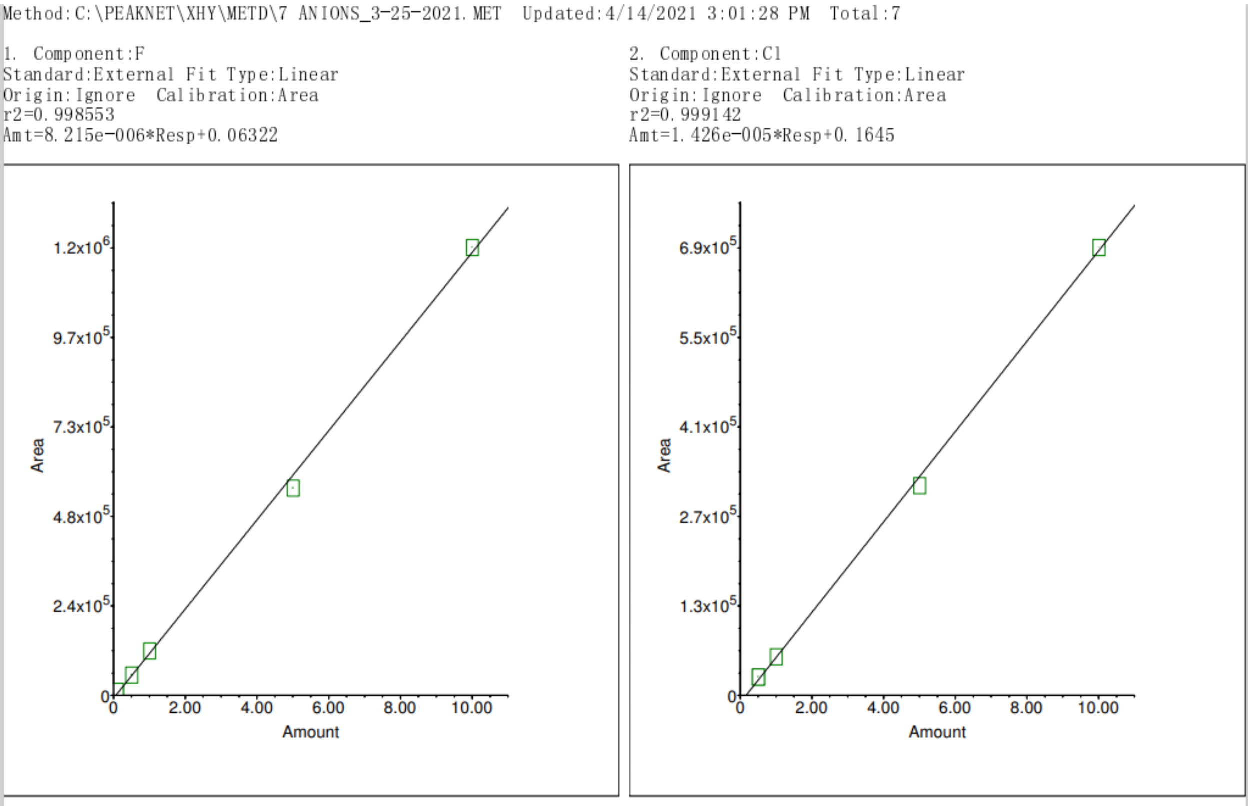
For this project, water sampling was collected during the 2021 spring snowmelt runoff event from the Red River Grand Forks, North Dakota. The samples were collected three times daily in the beginning of high flow (04/02-04/07) (04/19-04/30), twice a day when the flow started to decrease (03/21-04/01) (04/08-04/18), one time daily during low flow (05/01-05/09), and one time a week (05/10-05/31). The samples were collected to test some nutrients including Chloride, nitrate, sulfate, fluoride, phosphate. The water sampling was collected using Nasco brand sampling pole. During each collection, sampled water was filtered in an effective size pore (0.45 micron) and put in 250ml polyethylene bottles to store water. Filtered water was preserved immediately using another clean 250 ml polyethylene bottle. The collected and filtered sample was stored in a refrigerator at a 4 degree Celsius for a maximum of 28 days. The USGS stream gauging provided stream discharge or streamflow data for the Red River of the North at Grand Forks, ND (ID:05082500) with a Latitude of 47°55'37", longitude of 97°01'44", the drainage area of 26,300 square miles. Due to the amounts of ice in streams, the streamflow gauges are seasonal in the cold regions. Streamflow starts when ice inside the stream starts to melt and break up during the spring season and stops in the late fall because the stream water freezes.

Data Review

The reported concentration of nutrients in the Red River depends on sampling methods and varies over time and between agencies (Tornes and Brigham 1994). For instance, water sampling collected near the surface at the stream center may not have the concentration of the same nutrient as water sampling collected using advanced sample collection methods (Tornes and Brigham 1994). Different methods used to analyze water sampling data change over time between agencies (Tornes and Brigham 1994). A different method can be used by a different agency or by the same agency over time (Tornes and Brigham 1994). Improving analytical methods and sampling can result in lower detection limits causing lower reports limits (Tornes and Brigham 1994). The difficulty in determining the proper reporting limits for each solute's concentration analysis in each laboratory make it complicated to interpreted nutrients concentration because of the unknown method the agency used (Tornes and Brigham 1994). Through this report, phosphate was not reported by the Ion Chromatograph (DX -120) because it was under the detection limit. The USGS website was used in this report for data discharge.

LABORATORY EXERIMENT

Anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO43-, and SO_4^{-2}) were analyzed on Dionex DX- 120 Ion Chromatograph (IC) equipped with AS50 Autosampler using IonPac™ AS14 Analytical Column. For anion measurement, eluent (also called mobile phase) carrying samples flow-through separation column (filled with OH^- type anion-exchange resin) and then suppression system (also acts as ion-exchanging). During flowing through the separation column, the analytes (anions like Cl^-, F^-, Br^-, NO_3^-, NO_2^-, SO_4^{-2} etc.) in the sample will be separated from each other and then get in suppression system. In the suppression system, eluent ($NaCO_3$ and $NaHCO_3$) will be converted into H_2CO_3 (weakly conductive acid) and analytes will be converted into HX (X: Cl^-, F^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-} etc.) highly conductive acid, which can be measured using the conductive detector. All the samples were filtered through 0.45 mm filter paper and refrigerated before measurement. Before running the sample, the standards were prepared with the 7 anions in 5 levels (mg/L): 0.1, 0.5,1.0,5.0, and 10.0. As shown in figure 2, the calibration curve is only linear in some range. The concentrations of Cl and SO_4 are much higher than the standards range (e.g. Cl: 20-40 mg/L, SO4: 250-500 mg/L), which may introduce some error.



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Method:C:\PEAKNET\XHY\METD\7 ANIONS_3-25-2021.MET  Updated:4/14/2021 3:01:28 PM  Total:7

1. Component:F                              2. Component:Cl
Standard:External Fit Type:Linear           Standard:External Fit Type:Linear
Origin:Ignore  Calibration:Area             Origin:Ignore  Calibration:Area
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Amt=8.215e-006*Resp+0.06322                 Amt=1.426e-005*Resp+0.1645
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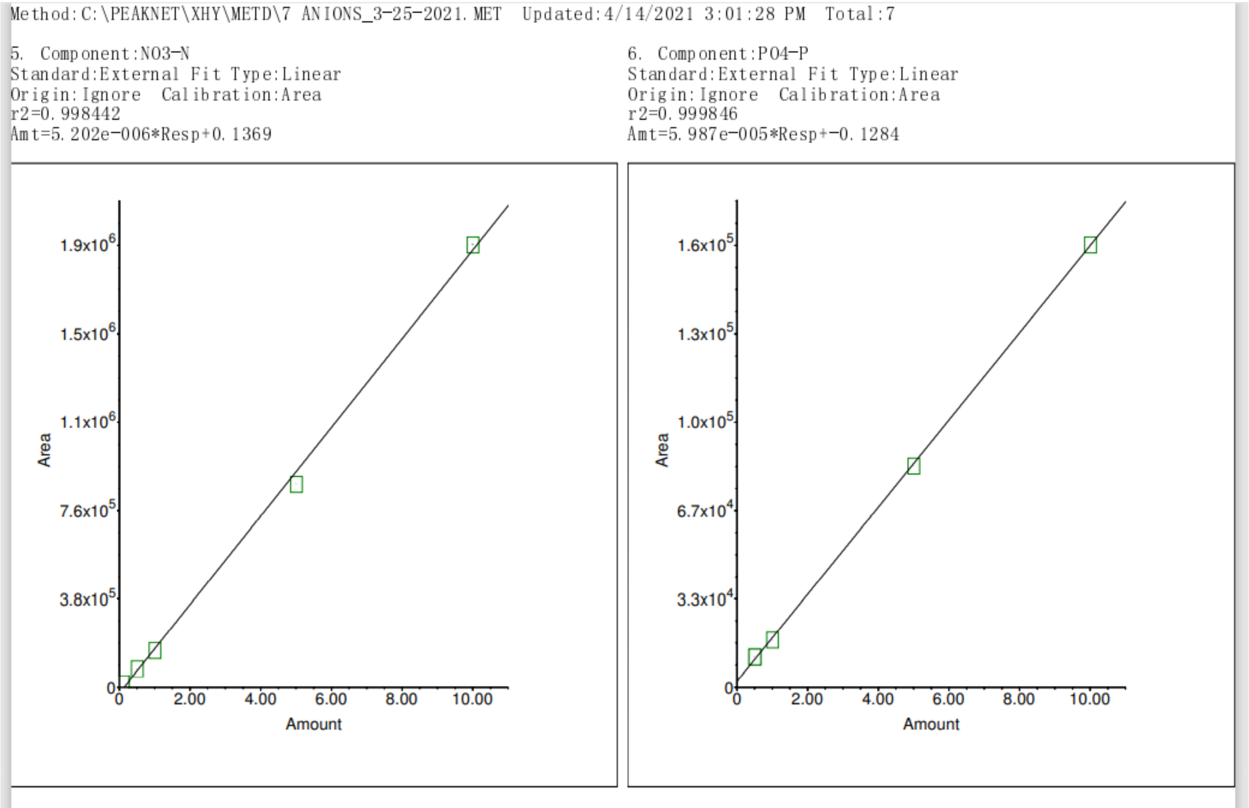

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Method:C:\PEAKNET\XHY\METD\7 ANIONS_3-25-2021.MET  Updated:4/14/2021 3:01:28 PM  Total:7

5. Component:NO3-N                          6. Component:PO4-P
Standard:External Fit Type:Linear           Standard:External Fit Type:Linear
Origin:Ignore  Calibration:Area             Origin:Ignore  Calibration:Area
r2=0.998442                                 r2=0.999846
Amt=5.202e-006*Resp+0.1369                  Amt=5.987e-005*Resp+-0.1284
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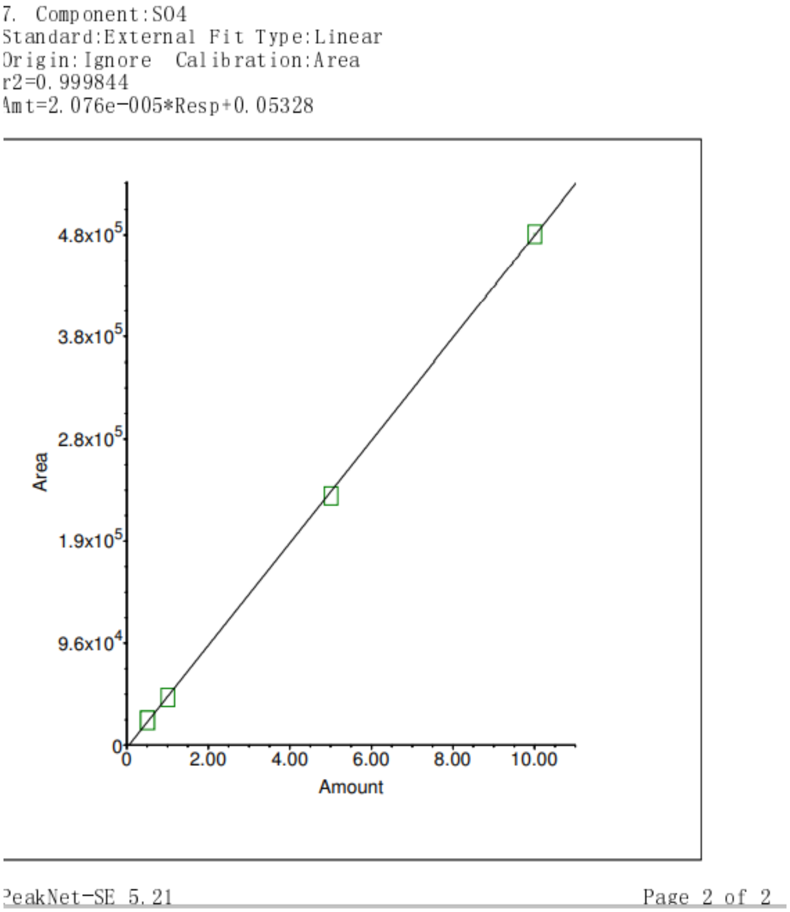

```
7.  Component:SO4
Standard:External Fit Type:Linear
Origin:Ignore  Calibration:Area
r2=0.999844
Amt=2.076e-005*Resp+0.05328
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PeakNet-SE 5.21                                   Page 2 of 2
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Figure 2: IC calibrations curves for Sulfate, Nitrate, phosphate, Chloride, and Fluoride

DISCUSSIONS AND RESULT

Water Chemistry and Hydrology

A very dry winter that began in late 2020 continued into the winter 2021, and the snowfall in North Dakota was slightly low or about average. The annual average snowfall in Grand Forks, North Dakota is 47.8 inches. The total snowfall for the year of 2020-2021 was 35.7 inches which is 11.4 inches below normal. Most of the snowfall occurred from January through April. October through December was the driest side to end the year compared to the year of 2019. The 2020-2021 winter had low snow accumulation at the Red River study site resulting to low discharge compared to the previous year. The streamflow discharge began on March 26, 2021 and it experiences high seasonality each year making the daily discharge to change consistently in the Red River Valley (Figure 3). Based on the fluctuation of streamflow discharge, three distinct periods are identified: initial thaw and melt runoff (Mar 26-Apr 08), rising limb (Apr 09 - Apr 14) and recession limb (Apr 15 – May 18). Since, the 2020-2021 winter was very dry, the thaw and melt resulted very little streamflow as seen in initial thaw and melt runoff (Mar 26-Apr 08), period. The rising limb (Apr 09 - Apr 14) resulted from snowmelt water from a mid-spring blizzard (Apr 7-8). The rising limb period was short, but the streamflow increased rapidly from 75 m3/s to 180 m3/sec within the span of five days. The streamflow peaked at the end of the rising limb period and then it started to decrease during recession limb. The streamflow volume continued to recess since Apr 15 during the recession limb period. In summary, the streamflow varied in three phases during the study period.

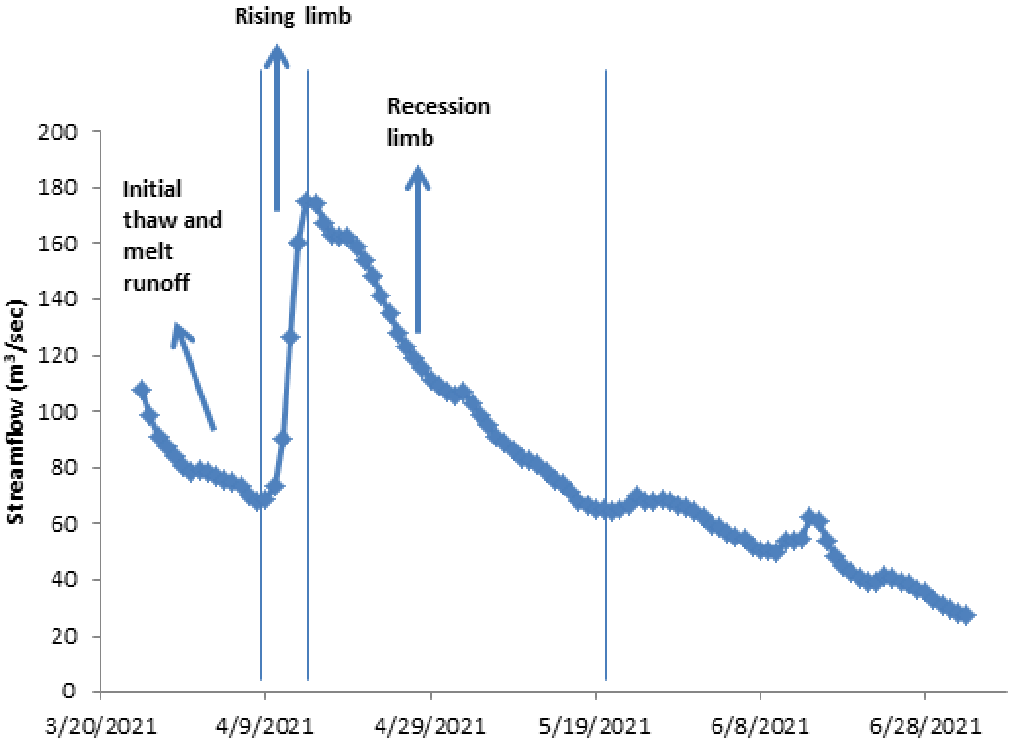

Figure 3: streamflow time series during the study period

Water chemistry showed variation in solute (sulfate, nitrate, phosphate, chloride, and fluoride) concentration (table 1). Water chemistry showed considerable variation in sulfate concentrations during the study period (Figure 4). During the initial thaw and melt runoff (Mar 26-Apr 08), the sulfate concentration fluctuated very little. However, the concentration rapidly increased since Apr 11 and continued to increase until Apr 16. Between Apr 16 and Apr 30, high sulfate concentration was observed. Since early May, the concentration gradually decreased. Clearly, the rapid increase since Apr 11 was lagged by two days from the increase of streamflow during the rising limb period.

Table 1: Red River water sampling concentrations

Red River mean and standard deviation concentration (mg/L) Grand Forks, North Dakota, from (March 2021- May 2021)

	Fluoride	Chloride	Nitrate	Sulfate
Baseflow(mg/l)	0.22±0.02	20.8±1.13	0.31±0.17	197.6±21.89
Rising limb (mg/l)	0.21±0.05	20.6±4.56	0.38±1.23	204.1±80.00
Recession limbs (mg/l)	0.2±0.4	28.1±2.48	1.12±1.21	434.2±54.68
Study period	0.21±0.29	22.4±4.44	0.56±1.08	228±120

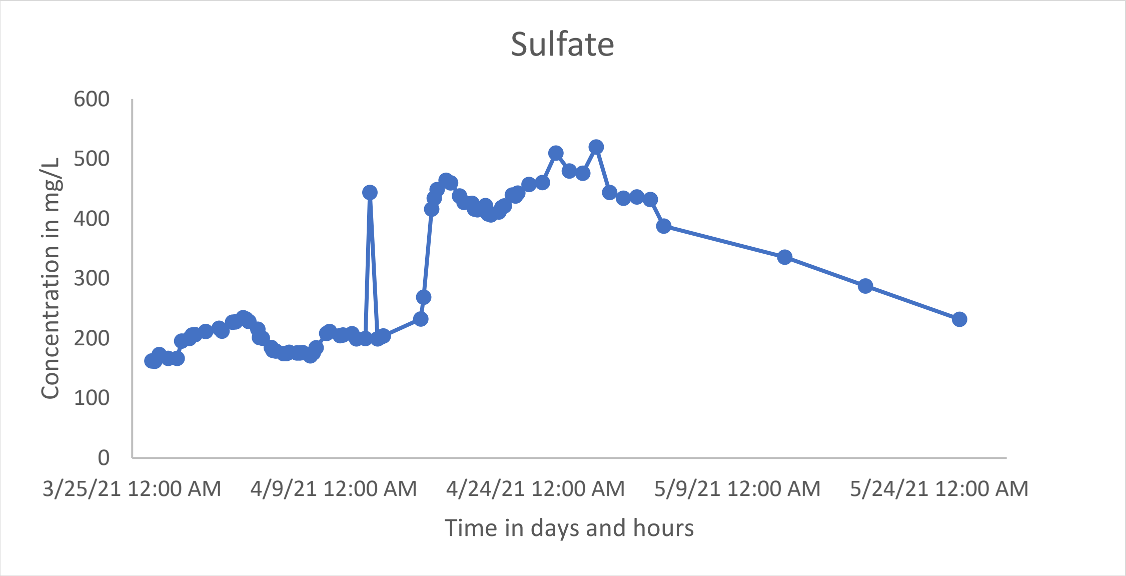

Figure 4: Sulfate concentration time series during study period

Time (Day and hour) to Concentration (c) (mg/L) Relationship for Red River Valley Grand Forks, ND during the spring snowmelt of 2021.

Like sulfate, the nitrate concentration time series showed substantial variation over the study period (Figure 5). The nitrate concentration also was invariant during initial thaw and melts period and increased precipitously from Apr 9. The rise of concentration was continued until Apr 16 followed by a quick recession during Apr 17-May 9 period. Figure 6 shows the temporal dynamics of chloride concentration with time in the study period. Since Apr 9, the concentration rose rapidly until Apr 16 and remained very high during the rest of the study period. Unlike other ions, fluoride concentration was low and fluctuated very little during the study period (Figure 7).

Our time series observations of solute concentration varied from that of USGS operation at this location. Our detailed sampling provided interesting scientific insight. The sampling frequency in the Red River was higher (3 times daily during the spring snowmelt, twice daily when discharge started to decrease and once a week during low flow) during the study area compared to USGS which sample 8 times a year January, April (2 samples), May, June, July, August, and October (Galloway et al., 2013). The soil permeability and solute source availability play an essential role in nutrient concentration. During a dry year, the low solute concentration can be attributed to dilution due to high runoff volume. It can be assigned to not enough interaction between snowmelt water and soil due to frozen soil or some nutrients was not diluted enough due to limited runoff volume. The water quality in the Red River during low flow events reflects the chemistry of the glacial-drift aquifer system (Christensen 2007). The rise of concentration (sulfate, nitrate and chloride) during rising limb (streamflow increases, Apr 9-Apr 16) clearly indicates substantial flushing in the Red River Basin during that mid-spring blizzard event.

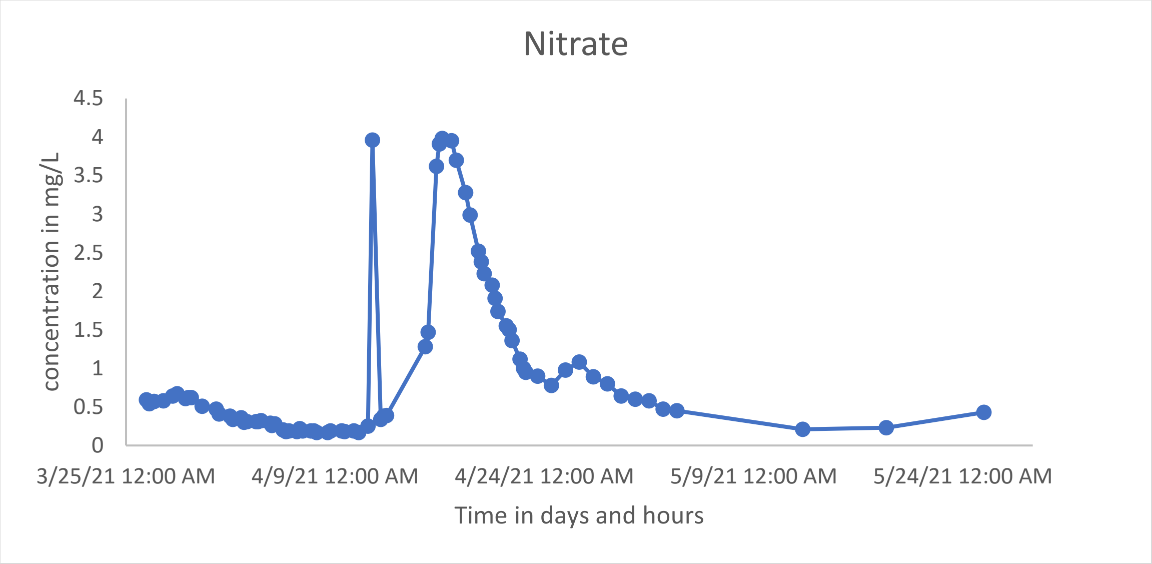

Figure 5: Nitrate Concentration during the study period

Time (Day and hour) to Concentration (c) (mg/L) Relationship for Red River Valley Grand Forks, ND during the spring snowmelt of 2021.

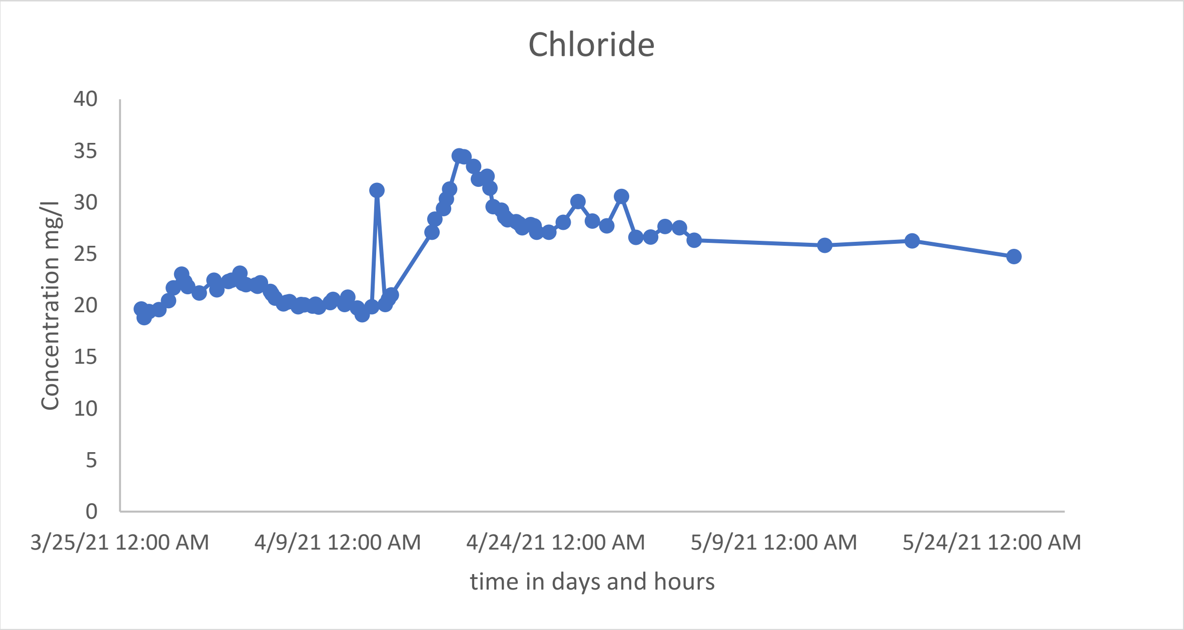

Figure 6: Chloride times series during the study period

Time (Day and hour) to Concentration (c) (mg/L) Relationship for Red River Valley Grand Forks, ND during the spring snowmelt of 2021.

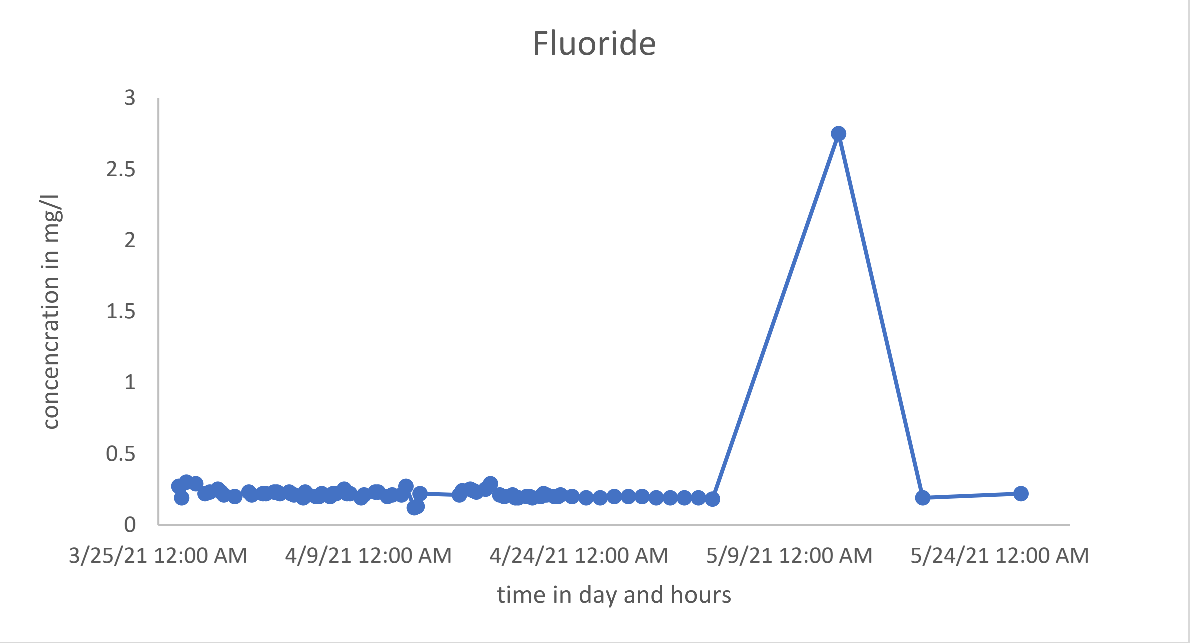

Figure 7: Fluoride time series during the study period

Time (Day and hour) to Concentration (c) (mg/L) Relationship for Red River Valley Grand Forks, ND during the spring snowmelt of 2021.

An assessing trend was used to understand how water quality conditions have changed in the Red River Basin, particularly the one that describes streamflow change (Nustad and Vecchia 2020). Discharge conditions reflect hydroclimatic variability (Nustad and Vecchia 2020). A shift from wet climate to dry climate resulted in a decrease in streamflow in the basin in 2021. A dry climate led to decreasing soil moisture and surface water storage. To understand how water quality conditions are changing, it is important to consider the more recent (2004-2020) state of soil moisture and water storage thought the Red River Basin and to understand how the contributions of groundwater and surface runoff affect nutrient transport and concentrations (Nustad and Vecchia 2020). It is important to select a certain period for trend analysis because the result will varies based on trend period select (Nustad and Vecchia 2020). The trend period choosen for this study is selected because of the data availability for most site and constituents which allow result comparison between sites. The use of different data to develop trend models for the same site and period can lead to slightly different results but the result will not be contradicte each other (Nustad and Vecchia 2020).

Sulfur is abundant in the soil of Red River basin but especially in the saline soil of the western part of the North Dakota Basin. North Dakota saline soil contains a mixture of salts and sulfates is the most dominant form (Nustad and Vecchia 2020). The high concentration of sulfate in North Dakota streams is due to the high solubility and abundance of sulfate, some studies have linked it to urbanizations (Nustad and Vecchia 2020). However, the trends in sulfate concentration may result from climate change, land use or atmospheric deposition (Nustad and Vecchia 2020). During the year of 2000-2015, the highest median concentration was in the Sheyenne River and other North Dakota tributaries (Nustad and Vecchia 2020). A change in annual flow played an important role in median sulfate concentration (Nustad and Vecchia 2020). The median ranges from 510 mg/L at North Dakota tributary site to 14.0 mg/L at Manitoba Tributary site (Nustad and Vecchia 2020). During 2000-2015, the streams in North Dakota and the Red River Basin have seen an increasing sulfate concentration (Nustad and Vecchia 2020). Many sites had an increasing sulfate concentration of forty percent or greater and 50mg/L or more including all three Manitoba main -stem sites (Nustad and Vecchia 2020). Only two Manitoba tributaries had significant decreasing sulfate concentration (Boyne river in Carman and Cooks Creeks at Boundary-St Clements and Springfield) (Nustad and Vecchia 2020). The largest sulfate increase was more than 200 mg/L for Bis De Sioux River near Doran in Minnesota (Nustad and Vecchia 2020). For the Red River of the North Dakota at Grand Forks the median concentration was 138 mg/L from 2000-2015 comparing to the result from spring snowmelt (03/26/21-05/25/21) which was 228 mg/L. The result is different because different trend models were used, and few sampling collections were collected during the 2021-time frame.

Human activities such as urbanization and road deicing have been a cause of increasing chloride concentration (Nustad and Vecchia 2020). Urban activities are concentrated in the major cities of Grand Forks and Fargo in North Dakota, Winnipeg in Manitoba (Nustad and Vecchia 2020). Chloride is natural in Red River soils and highly soluble (Nustad and Vecchia 2020). In sedimentary bedrock, chloride is the dominant ion resulting in high chloride concentration in groundwater (Nustad and Vecchia 2020). Chloride median concentration varies from 5.69 mg/L in the Roseau River at Dominion City, Manitoba to 75.0 mg/L in the La Salle River at La Barriere Park, Manitoba (Nustad and Vecchia 2020). During the trend period (2000-2015), the chloride concentration increased for most study sites (Nustad and Vecchia 2020). A significant increase in chloride concentration were observe in Main-Stem sites ranging from eighteen to sixty-five percent (Nustad and Vecchia 2020). Even though chloride increased from the beginning, the chloride concentration was less than 50 mg/L across the basin by the end of the trend period (Nustad and Vecchia 2020). The median chloride concentration for 2000-2015 in Red River Grand Forks was 16.9 mg/L comparing to 22.4 mg/L for spring snowmelt (03/26/21-05/25/21). Increasing concentration of chloride in the Red River Basin are linked to changes in the landscape, but changes of natural hydroclimatic are increasing the salts amount to reach streams through surface and subsurface runoff (Nustad and Vecchia 2020).

Nitrate is the primary form of dissolved nitrogen in streams and ground water (Nustad and Vecchia 2020). The origin of nitrate in the river can be linked to a point source pollution such as fertilizer application, industrial or municipal effluent (Nustad and Vecchia 2020). The exportation of nitrogen streams with subsurface drainage can be more than three times comparing to other agricultural streams (Nustad and Vecchia 2020). During 2001-2003, the nitrate concentration in water from the Red River were less than 1 mg/L. The increasing concentration of nitrate for the main-stern Red River sites may have been caused by Human activities (Nustad and Vecchia 2020). The concentration of nitrate in groundwater for 1990-2004 in Grand Forks Counties ranged from less than 0.023 to 1.13 mg/L (Christensen 2007). Sheridan county had the highest groundwater nitrate concentration comparing to other North Dakota well sites on the North Dakota side of the basin (Christensen 2007). The Nitrate concentration from Minnesota counties in groundwater ranges from less than 0.005 mg/L to 1.33 mg/L. In the Lake-Washed Till Plain and Moraine physiographic areas. Marshall and Otter Tail Counties in Minnesota did have the higher concentration of nitrate, which can be explained by high fertilizer applications comparing to other Minnesota counties in 2002 (Christensen 2007). In 2002, Sheridan County in North Dakota did not have high fertilizer application comparing to other North Dakota and Minnesota counties (Christensen 2007). Even though there is correlation between ground water nitrate concentration and fertilizer application in Minnesota counties, North Dakota counties had little correlation between fertilizer applications and nitrate concentrations in groundwater (Christensen 2007). Generally, the concentration of nitrate is low during spring runoff and after rain events.

Concentration -Discharge Relationships

Figure 8 shows show the *C-Q* relationships for the snowmelt streamflow for sulfate. Here, I observed a set of *c–q* responses contrasting to the *C-Q* relationships resulting in a hysteresis loop. The counterclockwise rotational direction of the sulfate hysteresis loop clearly indicates higher concentrations in the recession limb samples than the rising limb samples (Figure 9). Such a cyclic *c–q* relationship may be due to mixing of groundwater (high concentration) and surface water (snowmelt water, low concentration). It is clear that the *c–q* slope for the recession limb is higher than the rising limb, suggesting the dominance of intense flushing after the streamflow approaches peak-flow; in contrast, the lower slope for the rising limb is indicative of subdued flushing or dilution. This indicates the groundwater contribution is higher in the recession limb streamflow compared to rising limb streamflow.

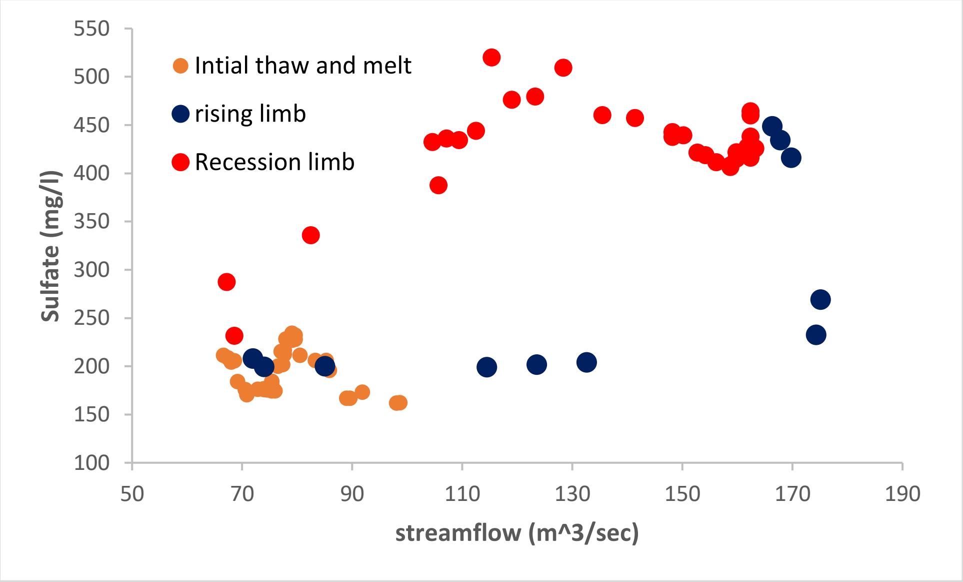

Figure 8: Streamflow vs Sulfate Concentration relationship

Daily streamflow and Sulfate concentration from March 26, 2021 to May 25, 2021 in the Red River Grand Forks, North Dakota. Snowmelt induced streamflow began on 03/24/21 and declined on 04/16/21. Lower discharge decreases the sulfate concentration and high discharge increase the concentration.

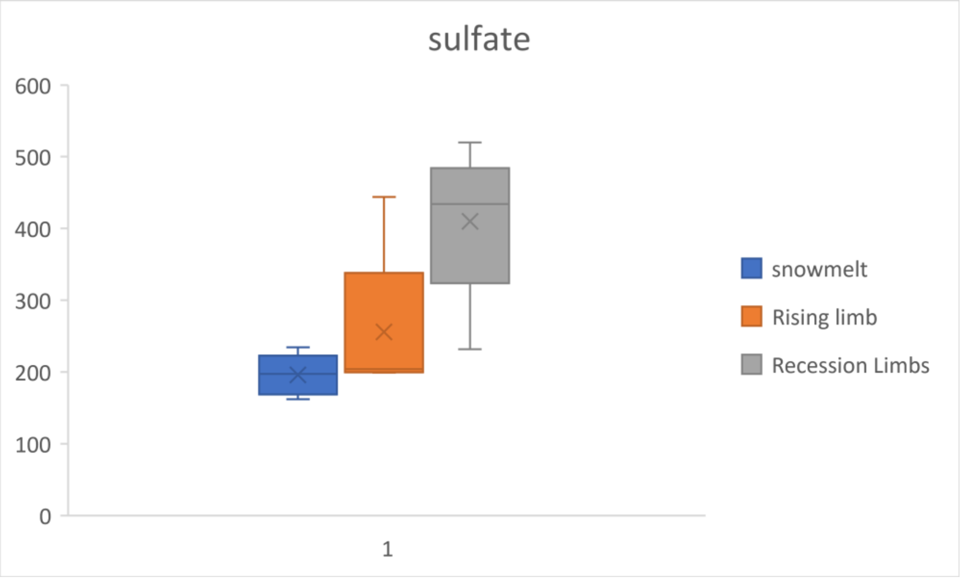

Figure 9: Box Plot of Sulfate Concentration in rising limb, recession limb and initial snowmelt

Variability of sulfate (mg/L) concentrations during the spring open water season (March-May), spring snowmelt for the Red River Valley East Grand Forks/Grand Forks. Each box has line at the lower quartile, median, and upper quartiles values. The concentration ranges from 161.92 mg/L to 519.98 mg/L

Nitrate concentration showed a strong positive response to increasing discharge (Figure 10). Overall, nitrate concentrations were low during the study period. The concentration increased with increasing discharge in the rising limb. The concentration was highly variable relative to discharge. The increased concentrations may be attributed to flushing from organic soil during high flow. Flushing was the dominant process in this agricultural catchment. The concentration in the recession limb is slightly lower than the rising limb (Figure 11).

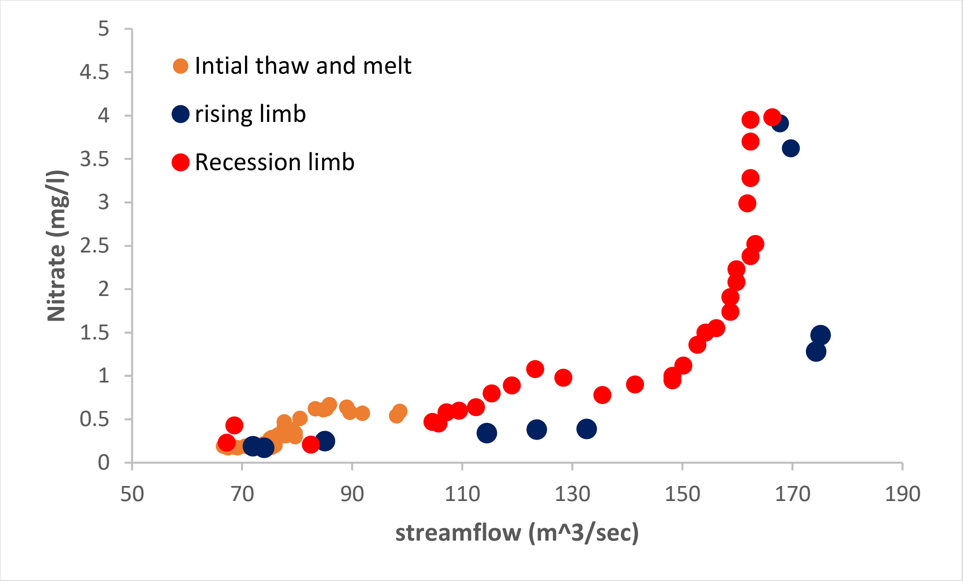

Figure 10: Streamflow vs Nitrate Concentration relationship

Daily streamflow and nitrate concentration from March 26, 2021 to May 25, 2021 in the Red River Grand Forks, North Dakota. Snowmelt induced streamflow which began on 03/24/21 and decline on 04/16/21. Raising in streamflow lead to increasing nitrate concentration and decreasing in streamflow lead to decrease in nitrate concentration.

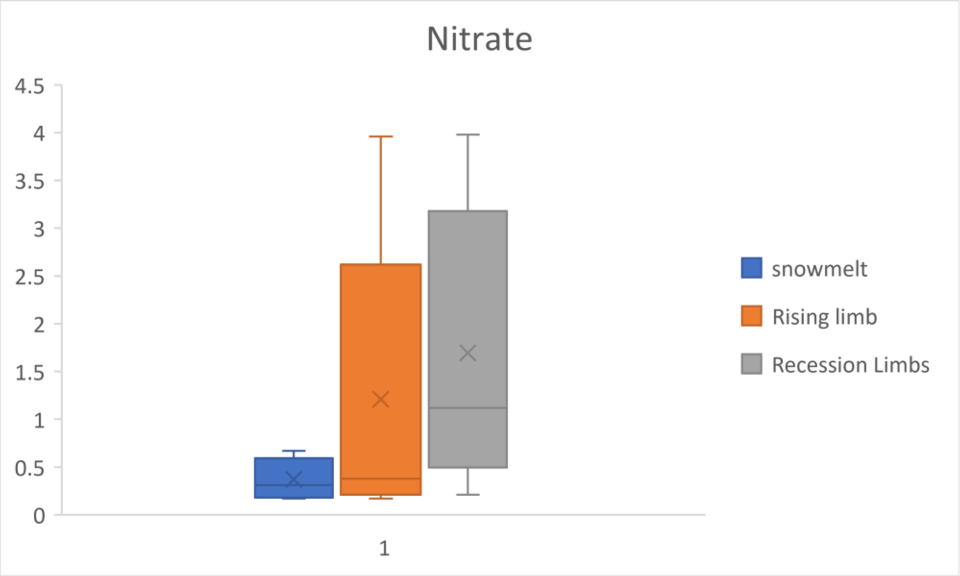

Figure 11: Box Plot of Nitrate Concentration in rising limb, recession limb and initial snowmelt

Variability of nitrate (mg/L) concentrations during the spring open water season (March-May), spring snowmelt for the Red River Valley East Grand Forks/Grand Forks. Each box has line at the lower quartile, median, and upper quartiles values. The concentration ranges from 0.17 mg/L to 3.98 mg/L.

Like the sulfate C-Q relationship, the chloride C-Q relationship a counterclockwise a hysteresis relationship (Figure 12). The slope in the rising limb is slightly higher than that of sulfate. I believe the sources of chloride are both rainwater and base flow from Inyan Kara formation. The mixing of surface and groundwater caused the hysteresis loop. The concentration in the recession limb is higher than rising limb (Figure 13).

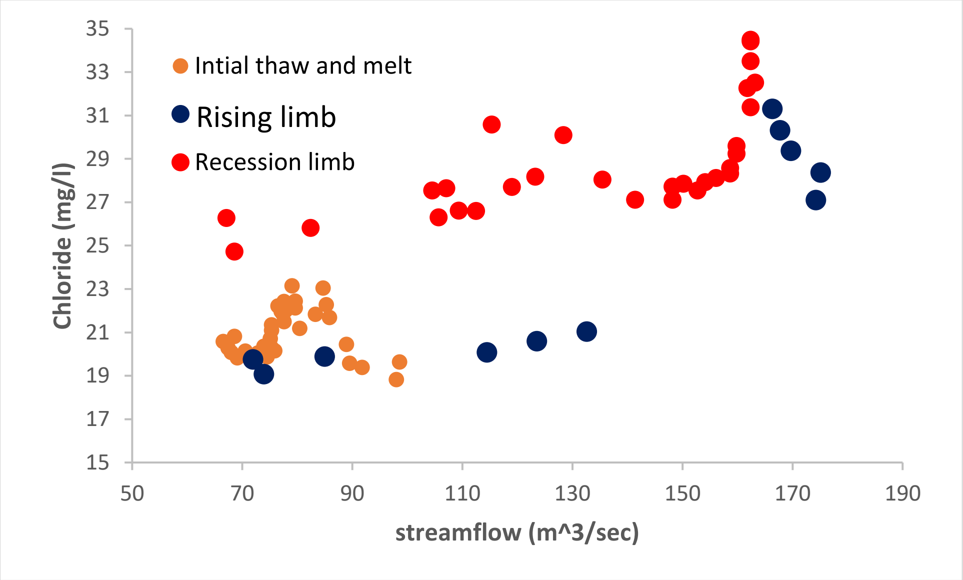

Figure 12: Streamflow vs Chloride Concentration relationship

Daily streamflow and chloride concentration from March 26, 2021 to May 25, 2021 in the Red River Grand Forks, North Dakota. Snowmelt induced streamflow began on 03/24/21 and declined on 04/16/21. Lower discharge decreases the chloride concentration and high discharge increase the chlorideconcentration.

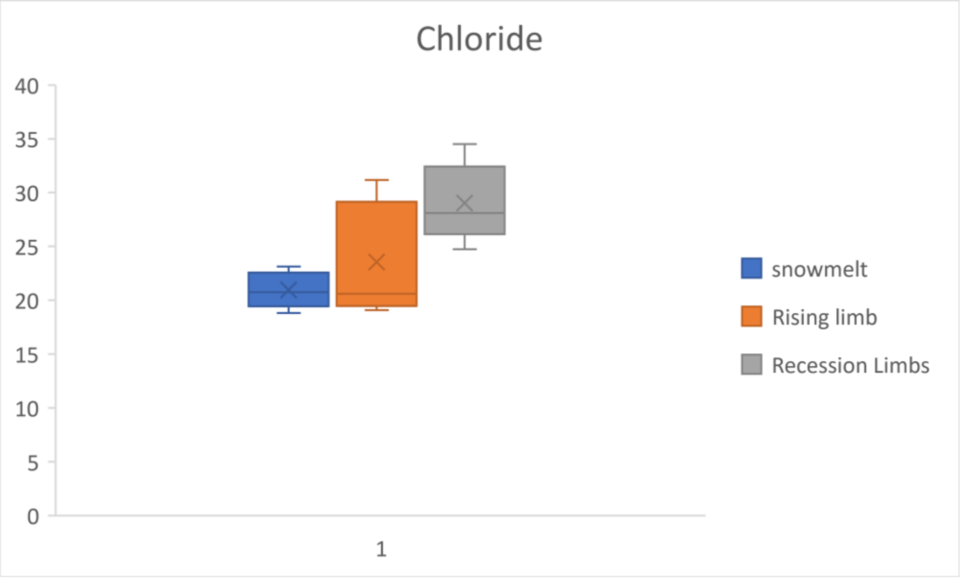

Figure 13: Box Plot of Chloride concentration in rising, recession and initial snowmelt.

Variability of Chloride (mg/L) concentrations during the spring open water season (March-May), spring snowmelt for the red river valley East grand Forks/Grand Forks. Each box has line at the lower quartile, median, and upper quartiles values. The concentration ranges from 18.82 mg/L to 34.5mg/L

The C-Q relationship of fluoride is considered as slight flushing behavior (Figure 14). The result showed little influence of discharge on fluoride concentration. This is confirmed by the low variability in fluoride concentration. This might be because the volume of water stored in a catchment is much larger than the amount of discharge during the spring snowmelt event. Chemostatic process was the dominant process in the catchment. The concentration in the recession limb is higher than rising limb (Figure 15).

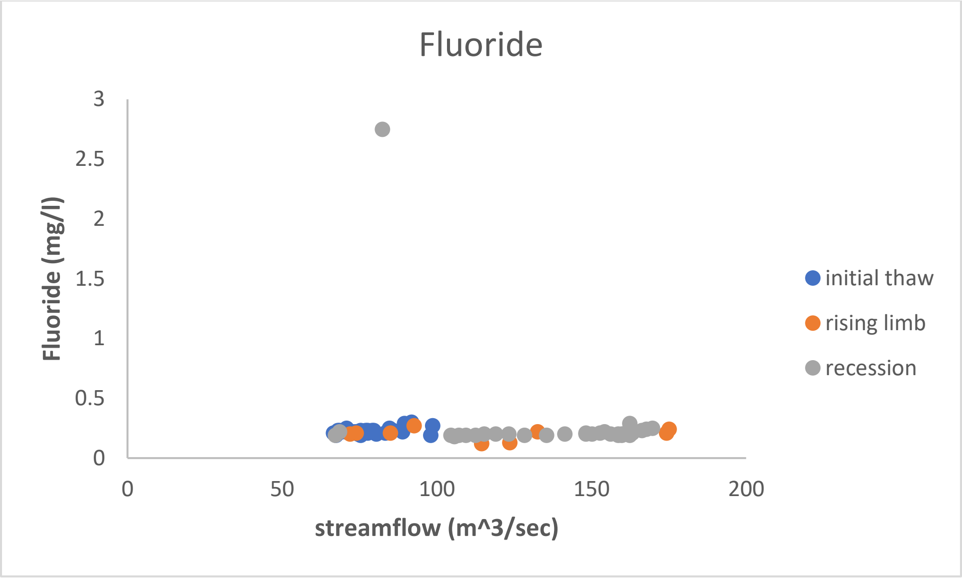

Figure 14: Streamflow Vs Fluoride Concentration relationship during the study period

Daily streamflow and fluoride concentration from March 26, 2021 to May 25, 2021 in the Red River Grand Forks, North Dakota. Snowmelt induced streamflow which began on 03/24/21 and decline on 04/16/21. Fluoride concentrations were not affected by the streamflow change.

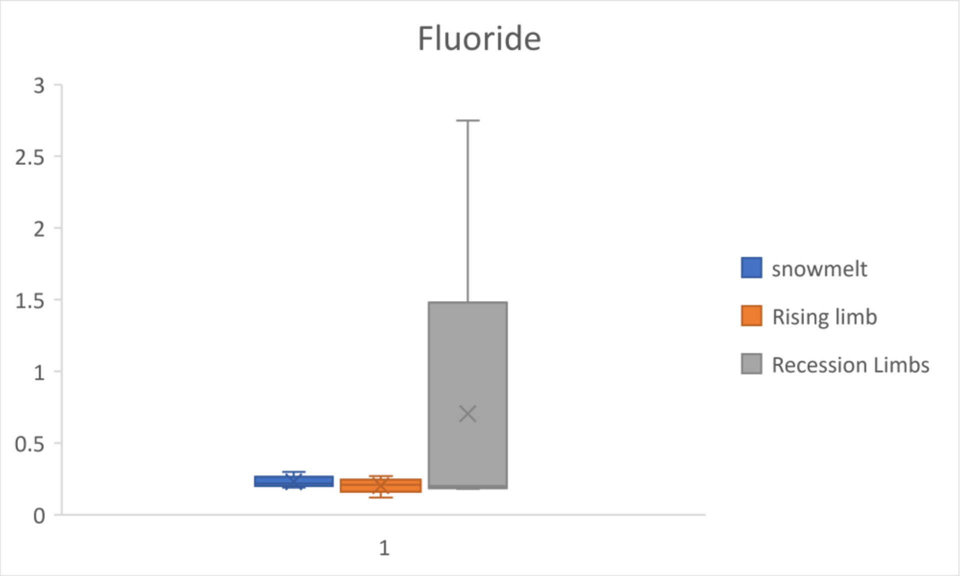

Figure 15: Box Plot of Fluoride concentration in rising limb, recession limb and initial snowmelt

Variability of Fluoride (mg/L) concentrations during the spring open water season (March-May), spring snowmelt for the Red River Valley East Grand Forks/Grand Forks. Each box has line at the lower quartile, median, and upper quartiles values. The concentration ranges from 0.19mg/L to 0.3mg/L

Annual Export

Between 1985 and 2015, the annual flow average of sulfate tripled from 376,000 to 1 million metric ton per year comparing to 178,175 metric ton (2285 kg/km^2) in the Red River Basin during the spring snowmelt of 2021 by the current study. The nitrate export for the spring season of 2021 at Red River Grand Forks, North Dakota were 6 kg/km^2 (600 kg/ha). The Total export of Chloride and Fluoride during the spring season of 2021 were 173 kg/km^2 (172,90 kg/ha) and 2.62 kg/km^2 (262 kg/ha) respectively.

The annual export varied with hydrological conditions and as a function of land management practice. The annual export represents the estimated amount of a nutrient transported by the Red River flowing across the boundary each year (Nustad and Vecchia 2020). The annual export varies yearly because of the change of streamflow variation (Nustad and Vecchia 2020). The concentration-discharge relationship is primary driven by the primary source and transport mechanism (Nustad and Vecchia 2020). During dry years, the annual export is small comparing to wet years. Nitrate is more soluble in water. During spring snowmelt event, a higher proportion of nitrate is lost as compared to the fall (Almen et al., 2021). When the second highest drainage occurred in 2014, the highest total nitrogen load lost were 10.9 kg/ha/year (Almen et al., 2021). The current study shows the nitrogen load is 135 kg/ha. This correlation showed that a greater streamflow has a greater impact on the annual export nutrient concentration (Almen et al., 2021). The lowest annual export in 2012 was low (0.08kg/ha/year) due to low amount of streamflow (Almen et al., 2021). In 2013, the nitrate export was approximately 7 kg/ha/year near Manitoba (Almen et al., 2021) compared to 600 kg/ha during the spring snowmelt season in the Red River Grand Forks, North Dakota.

Chloride concentrations were the lowest in 2009-2011 but the annual load was the largest of the period (Nustad and Vecchia 2020). Even though annual loads were larger, they were 25 percent larger than the flow average when compared to 1988-1992 with chloride loads being the smallest (Nustad and Vecchia 2020). Between 1985 and 2015 the annual flow average increased about 1.5 times from 145,000 to 239,000 metric tons per year compared to the annual total export for the spring snowmelt event of 2021 at Red River Grand Forks, North Dakota were 13,500 metric tons.

CONCLUSIONS

It is important to monitor water quality and streamflow to understand changes in water quality and load. This can be done by frequent sampling, daily streamflow data from different stream gages with water quality sampling sites, and previous data (decade). Water quality is affected by many factors such as climatic variability, agricultural activities, and population growth which make it difficult to know the driven change. The change could be because of hydrologic flow path, soils, and geology. The current study explored the water quality and solute export by conducting high resolution sampling (2-3 times/day, a total of 66 samples), whereas the operational water sampling by USGS is limited 8-10 samples per year. The results from the current show remarkable improvement in the detail of C-Q relationships for sulfate, chloride, nitrate and fluoride and their scientific insights for process-based modeling.

The current study shows a unique hysteresis C-Q relationship for sulfate and chloride. The high-resolution sampling was able to decipher the hysteresis relationship while conventional operational sampling is not be able to detect the hysteresis relationship. The C-Q relationship for nitrate show intense flushing in both rising and recession limb which was not observed in recent studies. Such intense flushing also indicates basin wide agricultural activities, fertilizer usage and livestock farming. However, the current study was not able to detect any significant phosphate concertation in the study site. The current findings also report a large nitrate load export in the study area compared to other reported load estimates from other parts of the Red River Basin.

In the current study of spring snowmelt 2021 (Red River Grand Forks), historical data from 34 sites (2000-2015) were used to compared current data to understand how water quality has changed over time in the Red River Basin. During the winter season 2020-2021, the winter conditions were very dry resulting in low snow accumulation and low amount of spring snowmelt runoff comparing to previous year. As climate continues to change snow accumulation and snowmelt runoff, some uncertainty on hydrologic fluxes and land surfaces conditions which include the freeze and thaw cycle of stubble will be observed. As a result, the hydroclimatic conditions observed in the North Great Plain played an important role in controlling solute exports.

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