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IMPACTS OF COLD REGION HYDROCLIMATIC VARIABILITY ON
PHOSPHORUS EXPORTS: INSIGHTS FROM CONCENTRATION-DISCHARGE
RELATIONSHIP

By

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Bachelor of Science, University of North Dakota 2015

A Thesis

Submitted to the Graduate Faculty

of the

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in partial fulfillment of the requirements

for the degree of

Master of Science Geological Engineering

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This thesis, submitted by Tyson L. Jeannotte in partial fulfillment of the requirements for the Degree of Master of Science 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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Title: Impacts of Cold Region Hydroclimatic Variability on Phosphorus Export: Insights from
Concentration-Discharge Relationship

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Degree Master of Science

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Tyson L. Jeannotte
May 11, 2019

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ABSTRACT

In Devils Lake ND, a terminal lake in the Northern Great Plains, algae blooms are of great concern due to the recent increase of streamflow and subsequent elevated concentrations of nutrients, particularly phosphorus. To date, very few studies explore P concentration to streamflow relationship in cold region agricultural basins, specially the headwater catchments of the Devils Lake basin. This study gains a better understanding of the impacts of hydroclimatic variation on concentration to streamflow relationships between two headwater catchments (Mauvais Coulee: 1032 km² and Tributary 3: 160 km²) draining to Devils Lake during the 2016-2018 period. This study presents high-resolution *P* observation data during the first flush of snowmelt runoff while identifying the controlling factors of P exports using both field-based observations and hydroclimatic variability detected by physically based hydrologic simulations. United States Geological Survey provided the streamflow measurements, and I collected water samples (filtered and unfiltered) three times daily during the spring snowmelt seasons of 2017 and 2018 and analyzed for P. Based on P concentration in soil and accumulated snow, the soil is the most likely source of observed P in the stream waters. Total P is dominated by dissolved P, with little contribution from particulate P, which is presumed to be locked in an ice matrix in frozen soils. The Mauvais Coulee basin (2016-17 and 2017-18) expresses near chemostatic concentration to streamflow relationships in the rising limb of the hydrograph, while concentration to streamflow relationship correlate positively in the descending limb. The poor correlation in the rising limb of the hydrograph suggests that the excessive amount of snow water equivalent and the existence of basal ice limit the contact time between meltwater and soil

resulting in inconsistent P export. In 2018, Tributary 3 basin showed a linear and positive concentration to streamflow relationship in both rising and descending limbs suggesting extensive flushing of P from soil. Frozen soil conditions simulated by a physically based model show strong correlations with the observed concentration to streamflow relationships suggesting that the extent of frozen soil conditions can partly explain the extent of chemostatic behavior. Higher annual export loads per unit basin area were observed in Tributary 3 in both field seasons partially due to the heavily cultivated and tilled soil of agricultural lands. Tillage indexes suggest that there are more exposed soil and less crop residues in Tributary 3 basin, while the Mauvais Coulee basin has more crop residue and less exposed soil. This suggests that the volume of runoff and the land management practices are contributing factor in total load export.

INTRODUCTION

Water quality is a critical indicator of the health of the overall environment; specifically, it is driven by anthropogenic activities and hydroclimatic variation (U.S Environmental Protection Agency 1994; Williamson et al., 2009; Read et al., 2015). Phosphorus export to streams and lakes can lead to eutrophication and degradation of surface water quality and impose a risk to water uses such as drinking, recreation, and support of aquatic life (Dodds & Welch 2000). Nutrient enrichment in surface water bodies and resulting decline in water quality are of great concern for lakes and streams across North America (U.S Environmental Protection Agency 1994; Beaver et al., 2014; Read et al., 2015). Frequent occurrences of algae blooms over the last few decades in many lakes of the Northern Great Plains (NGP) region can be attributed to elevated phosphorus concentration partly due to land management practices in agricultural and livestock farms (Cordeiro et al., 2017; Ryberg 2017). For example, the Red River Basin (RRB) watershed has been identified as the major contributor of nutrients to Lake Winnipeg, the 10th largest freshwater lake on Earth in terms of surface area (24,500 km²) (Lake Winnipeg Stewardship Board, 2006; McCullough et al., 2012; Schindler et al., 2012; Ryberg 2017). In addition to land management practices, cold region hydrologic responses via snow accumulation and consequent streamflow with land surface conditions such as frozen soil will influence nutrient exports to major channels and wetlands. However, our knowledge of the connections between streamflow responses and nutrient exports is quite limited and based on few, field observations. Thus, a comprehensive well-coordinated and high-resolution field-based observation on cold region hydroclimatology, in-stream phosphorus concentration along with land management practices and properties is needed to improve our understanding and develop a realistic robust quantitative framework to simulate nutrient exports.

Phosphorus (P) does not occur freely in nature, but it forms compounds with other elements and is mainly obtained from calcium phosphates and apatite ores. Found in Earth's crust, P is one of the major contributors to eutrophication, is a naturally occurring nutrient that is essential for plant growth (Schindler 1977; Carpenter et al., 1998; Amarawansa et al., 2015). In the past, point source P was the largest source of P pollution. However, point source pollutions are easier to monitor and regulate. Recently observed elevated amounts of P are likely coming from agricultural practices, which are considered non-point source pollutants (Carpenter et al., 1998). Non-point sources of P include dead biomass, minerals, rocks, and a variety of fertilizers which can enter streams through natural erosion, surface runoff, and leaching (Sharpley et al., 1994; Ryberg 2017). Non-point source pollution is a serious issue because it is difficult to manage and model since it can be distributed over quite a large area. Further, it is more inconsistent than point source pollution, largely due to the role that changing climate and weather play in exporting P (Carpenter et al., 1998; Corriveau et al., 2013). Nevertheless, to reduce agriculture's portion of P export into our streams, it is critical to understand how P is related to topography, local climate, soil characteristics, crop cover, tillage and water management practices in the watershed (Baulch et al., 2019).

Modeling P export from agricultural landscapes has made significant progress, but it remains a major scientific challenge, especially in cold regions with semiarid continental climates (e.g. Johnes, 1996; Johnes et al., 1996; Johnes and Heathwaite, 1997; McGunkin et al., 1999). Determination of nutrient exports in cold region agricultural basins are particularly difficult using traditional models such as SWAT, HSPF, MIKE SHE, SPARROW, AGNPS, and DWSM. Model failures are expected due to inadequate representation of cold region processes, such as redistribution of snow and frozen soil infiltration, poor understanding of the connection

between streamflow and nutrient concentration at the basin scale, and lack of information about the land management practices and their influence on hydrology and nutrient export. In addition, climatic extremes resulting in highly variable precipitation and subsequent streamflow fluctuations, rain on snow events, and freeze and thaw cycling/basal ice layer presence exert a strong impact on nutrient exports to the stream (Baulch et al., 2019). In the NGP, snowmelt is the major contributor to annual streamflow and often accounts for ~80% of the annual runoff (Hansen et al., 2000; Liu et al., 2012; Dumanski et al., 2015; Ali et al., 2016). Snowmelt runoff is also a major exporter of nutrients and the mechanism of nutrient export is complex, partly due to the frozen state of the soils, dead or dormant vegetation, and the low kinetic energy associated with snowmelt compared to falling rain (Flaten, 2016; Baulch et al., 2019). Initially, the snowpack is the primary source of nutrients, but soil and surface plant debris become more important as snowmelt progresses due to thawing of soils and basal ice, resulting in more direct contact between overland flow and soil matrix (Quinton, 2006). Koiter et al. (2013) suggested three major sources (topsoil, streambanks and shale bedrock) of in-stream suspended sediments across the South Tobacco Creek (STC) watershed in southern Manitoba, CA, based on geochemical and radionuclide fingerprinting. While the topsoil contribution from the agricultural field is very high (64%–85%) at upstream headwater basins, the suspended sediments at the basin outlet are coming from streambank (32%–51%) and shale bedrock (29%–40%) sources (Koiter et al., 2013). To date, there are no model or quantitative frameworks available representing adequate cold region processes and soil nutrient-snowmelt water interactions adequately. Thus, an insight from a comprehensive study using high-resolution concentration to streamflow relationship, adequate hydro climatological data, and cold region hydrologic

simulation assist in better understanding of P export and its dependency on climate and land management practices.

Understanding of the concentration to streamflow relationship is very useful to decipher the mechanism of P export. The use of concentration to streamflow relationship is also convenient as both c and q data are readily available via scientific agencies and can be measured in the field. Several studies have observed the different concentration to streamflow relationships and provided a mechanistic explanation of them (Stamm et al., 1998; Preedy et al., 2001; Sinaj et al., 2002). Three possible concentration to streamflow relationships that have been identified during the spring snowmelt season: 1. dilution, 2. flushing, and 3. chemostatic. Dilution occurs when the P concentrations display a strong and negative correlation with the streamflow. It is normally observed during rainfall events as water stored in a catchment is diluted by less concentrated atmospheric waters (Godsey et al., 2009; Herndon et al., 2015). On the contrary, flushing represents the enrichment of nutrients with streamflow (a strong positive correlation) that depends entirely on the stream water velocity (Mahmood et al., 2019). During this relationship, there will be a constant increase of P concentration as the level of streamflow increases, indicating that phosphorus is supplied within the basin (Johnson et al., 1969). Both flushing and dilutions represent a dependent relationship between c and q . The dependent concentration to streamflow relationship occasionally also exhibits a cyclical association where the concentration to streamflow relationship for the rising limb of the hydrograph differs noticeably from that of the recession limb of the hydrograph, resulting in a hysteresis behavior (Evans & Davies 1998). Finally, chemostatic response displays little correlation between concentration and streamflow where concentration remains invariable or constant as streamflow fluctuates (Godsey et al., 2009; Basu et al., 2010; Hunsaker et al., 2017). The chemostatic

relationship may arise from a steady-state condition between the dissolution kinetics of nutrients in a homogeneous source such as soil and the stream water velocity (Haygarth et al., 2004). In this case, the very slow draining of soil water (source water) prevent exchange of nutrient between soil and solution (Haygarth et al., 2004). This relationship also can be attributed to release and subsequent transport of nutrients due to low flow velocities. Chemostatic characteristics of catchments (Godsey et al., 2009; Basu et al., 2010) with emergent biogeochemical stationarity at the annual scale (Basu et al., 2010) are also reflected in independent relationships.

To date, there are no studies that identify the critical factors of nutrient export in cold regions using well-coordinated high-resolution field observations of P concentration and physically based numerical simulation. Moreover, the impacts of extreme spring hydroclimatic responses on P export in the headwater catchments of the Devils Lake Basin (DLB) are seldom investigated. The objective of this study is to gain a better understanding of the impacts of hydroclimatic variation on P concentration, export and concentration to streamflow relationships in the headwaters of the DLB during the 2016-2018 period. Specifically, the current study aims to advance the knowledge about the mechanism of P export by investigating hydrological processes such as snow accumulations and streamflow generations. This study presents high-quality P observation data during summer low flow events and more importantly, during the first flush of snowmelt runoff the most critical event for nutrient export (Han et al., 2010; Liu et al., 2013). The current study identifies the controlling factors of P exports using both field-based observations and hydroclimatic variation detected by physically based hydrologic simulations (e.g. soil conditions, increased and decrease streamflow volumes). Additionally, this study

demonstrates the significance of seasonal climatic variation as well as land management practices in space and time on hydrology and in-stream nutrients.

STUDY AREA

The study was conducted in two sub-catchments in the headwaters of the Devils Lake basin, North Dakota, located in the eastern part of the Great Plains of North America (Figure 1). Note that the Devils Lake basin is a sub-basin of the Red River of the North Basin, which is a transboundary watershed in the eastern part of the Northern Great Plains. In addition, the DLB is a closed basin, which means there is no natural outlet resulting in all the coulees and streams draining into a terminal lake. The Devils Lake basin is classified as a cold dry continental climate in accordance with the Thornthwaite climate classification system (Todhunter & Fietzek-DeVries 2016; Van Hoy et al., 2017). The study area is vital for agriculture production, high-latitude, semiarid, low relief, and it endures cold winters. For nutrient export, hydrology is the most crucial element. Streamflow and precipitation are often, but not always strongly correlated; fluctuate from year to year; and are highly seasonal. Mean annual precipitation varied highly over last few decades. Mean annual precipitation during 1951-1980, 1881-2010, 2010-2017 were 466, 579, and 518 mm, respectively (Todhunter & Fietzek-DeVries 2016; Van Hoy et al., 2017). Figure 2 and 3 present the fluctuation of streamflow for last two decades. Average annual peak streamflow from the gage (USGS ID: 05056100) is 43.1 m and is usually dominated by spring snowmelt from late March to mid-April. Base flow contribution is very small in this region due to low permeability of the soils (Wiche & Pusc 1994; Vecchia 2002, 2008).

Over the last two decades, observed streamflow at USGS gages was highly variable from year to year in both basins (Figures 2 and 3). At Mauvais Coulee Basin there have been 8 years of peak discharge values $> 40 \text{ m}^3/\text{s}$, which are spatially and temporally consistent with peak discharge values ($> 15 \text{ m}^3/\text{s}$) in Tributary 3. Figures 2 and 3 show three major hydrologic regimes (1998-2004, 2005-2011 and 2012-16) based on streamflow fluctuations. During the

1998-2004 period, annual and peak stream flows were very low due to drought (Mahmood et al., 2017) while streamflow volumes and peaks were very high during the 2005-2011 period due to an increase in precipitation (Mahmood et al., 2017, Van Hoy et al., 2018). However, the streamflow amount recessed again during the 2012-2016 period due to lack of snowfall and high evaporation (Van Hoy et al., 2018). Interestingly, streamflow is not often correlated with annual precipitation; instead, the association is very high with annual snowfall, while poor correlation exists with rainfall (Van Hoy et al., 2018).

The Mauvais Coulee basin (1032 km²) (Figure 1B) is in north-central North Dakota covering parts of Rolette, Towner, and Cavalier counties and originates, on the eastern edge of the Turtle Mountains and drains south into Lake Alice. The highest point in the Mauvais Coulee basin is 672 m in the northwest corner of the basin while the lowest point is 436 m near the outlet of the Mauvais Coulee (Figure 1B). The Tributary 3 (Tributary 3) (160 km²) is located just west of the Mauvais Coulee basin covering a small portion of Rolette County and almost entirely in Towner County. The highest elevation in Tributary 3 is 536 m while the lowest elevation is 436 m near the outlet of the basin prior to connecting to the Mauvais Coulee and entering Lake Alice (Figure 1). In general, most of the region is relatively flat or gently sloped.

The study sites lie entirely in the Northern Glaciated Plains. The modern landscape was formed by the Wisconsin glacier with contributions from other small streams carrying melt water to the glacial Lake Cando (Bluemle 2005). This glacier left moraines, eskers, kames, and a myriad of potholes (Pusc 1993). This area has a smooth to gently rolling topography known as the prairie pothole region and is composed of glacial till surface deposits consisting of Pleistocene sediments laying on top of earlier glacial sediments or bedrock. The bedrock is comprised of Cretaceous Pierre Shale and small portions of the Fox Hills, Hell Creek, and

Cannonball Formations (Bluemle 2003). Primary soil types in the northern portion of the Mauvais Coulee basin are mixture of dark brown fine loam, clay and sand. In the southern portion of the basin, soils are rich in clays, fine silt, and coarser loam with an abundance of gypsum crystals (Bluemle 1984; Soil Conservation Service 2016).

The Mauvais Coulee basin area includes a wide range of land cover types: cultivated crops/agricultural fields, forest, grasslands, wetlands, and developed land (Resolution Land Characteristic 2006) (Figure 1C). Grasslands and slightly wooded areas are primarily located in the low valleys of the basin surrounding channels and open water. The majority of agricultural fields in the area produce a variety of crops including wheat, barley, canola, sunflower, corn, beans, and soybeans (Bryce et al., 1998; Natural Resources Conservation Services 2007; Van Hoy et al., 2017). Throughout the study site, small wetlands are surrounded by a mixture of grass and cattails, and are increasing in size and number during the recent wet periods (Todhunter & Rundquist 2008). In the Northern Great Plains, tillage practices vary due to differences in climate, traditions and policy, and are gradually changing with time. Recently in the Canadian prairies, direct seeding is increasingly replacing conventional tillage (Clearwater & Ranjan 2016). Conventional tillage practices occur in the fall of the year loosening soils and limiting stubble resulting with less snow accumulation and lowering the soil moisture (Clearwater & Ranjan 2016; Baulch et al., 2019). However, conservation tillage is highly recommended in the NGP, because it helps to protect the soils from wind and water erosion, and supports the conservation of soil moisture, and wildlife habitat (Baulch et al., 2019).

Land cover and tillage practices are directly correlated with ecoregions. The Mauvais Coulee basin overlies several ecoregions which include the Northern Black Prairie, a glacial lake basin, and Turtle Mountain ecoregions, while Tributary 3 covers two ecoregions: Northern Black

Prairie and a Drift Plain (U.S Environmental Protection Agency 1998; Bryce et al., 1998; Vandeberg et al., 2015;) (Figure 1D). The Northern Black Prairie covers most of the catchment, extending just east of the Turtle Mountains and extending nearly to the Red River of the North. This ecoregion consists of wooded areas, grasslands, sloughs, and rolling hills (U.S Environmental Protection Agency 1998; Bryce et al., 1998). The former glacial lake basin of Lake Cando extends north to south roughly in the center of Towner County. This ecoregion has a flat topography and delta-like formations that represent a location where streams dumped into a lake. The area is rich in deep soils, which are intensively cultivated via agricultural practices (U.S Environmental Protection Agency 1998; Bryce et al., 1998). The Turtle Mountains are glacial till deposits containing gravel, large boulders in areas, and soils poorly suited for cropland. This ecoregion is heavily forested with an abundance of fresh lakes that are recharged with underlying aquifers. The drift plain has a smooth topography with drained wetlands and a thick layer of glacial till. The drift plain is almost entirely cultivated with areas of mixed tallgrass and shortgrass prairies (U.S Environmental Protection Agency 1998; Bryce et al., 1998).

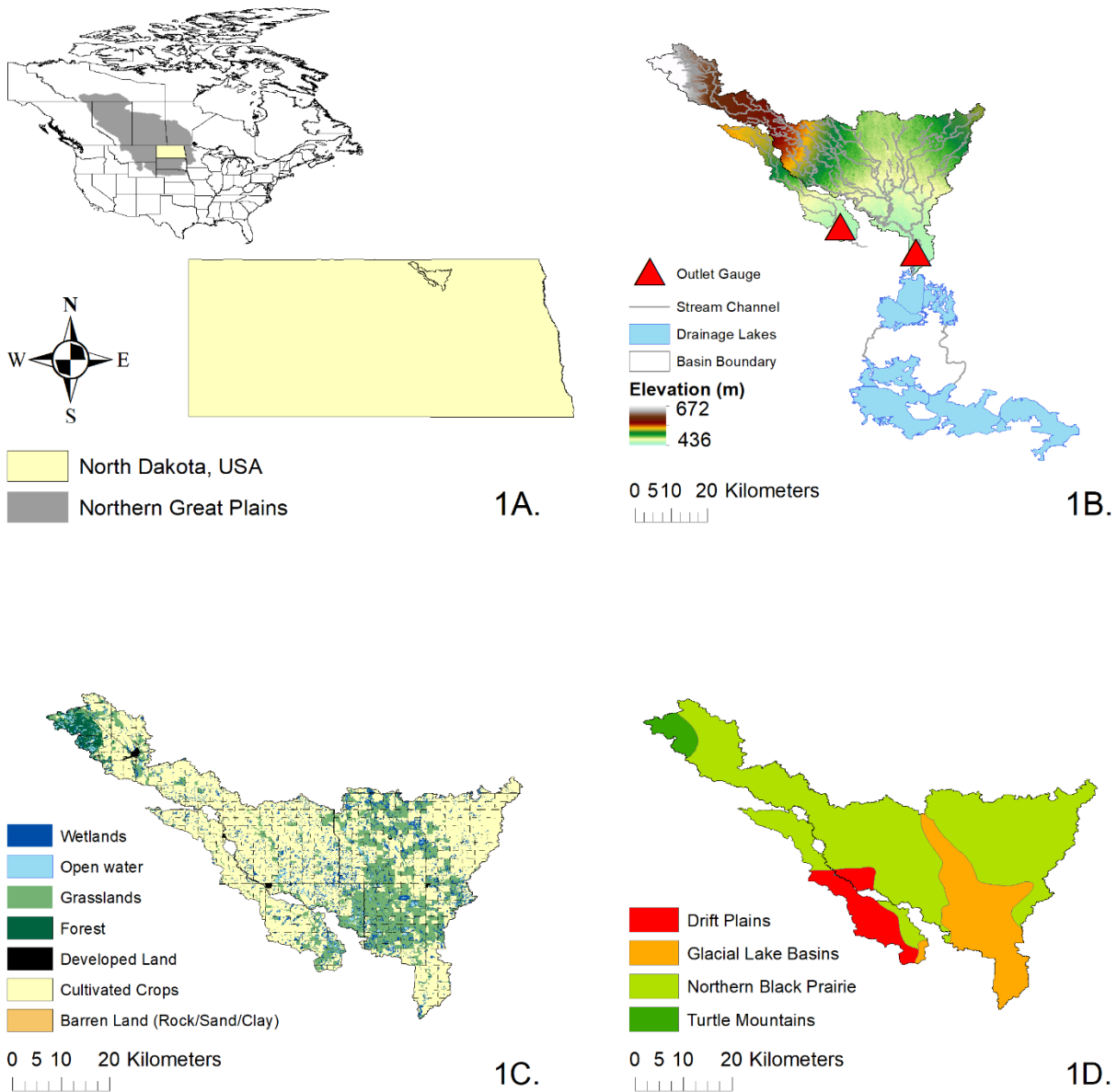


Figure 1. Study Site

Location of the study site, water quality observatories and land surface properties: (A) location of study site in the Northern Great Plains and in North Dakota, USA. (B) Topography derived from a digital elevation model (DEM), locations of United States Geological Survey (USGS) outlet gauges for streamflow, nutrient concentration (c) measurements, and sub-basin boundaries including the Mauvais Coulee Basin (1032 km²) and Tributary 3 (160 km²). (C) Land cover/uses based on National Land Cover Database Map from the Multi-Resolution Land Characteristics Consortium. (D) Environmental Protection Agency (EPA) ecoregion map that identifying ecosystems based on geology, landforms, soils, vegetation, climate, land use, wildlife, and hydrology.

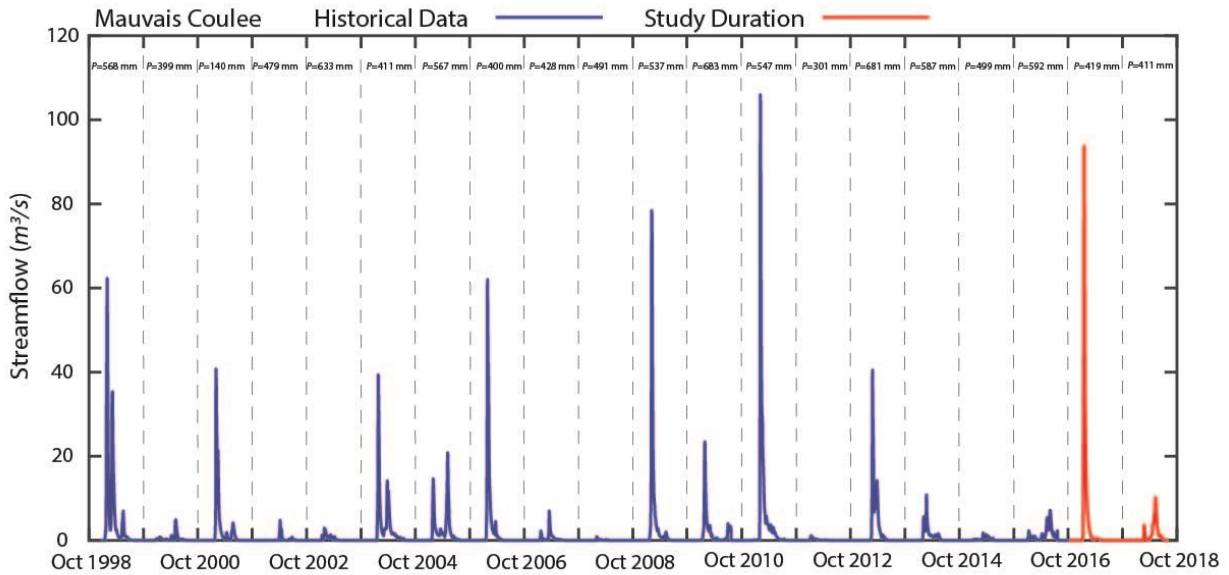


Figure 2. Mauvais Coulee Streamflow Data 1998-2018

Historical streamflow data captured by USGS gage ID: 05056100 from 1998-2018. There are 8 years of peak discharge values $> 40 \text{ m}^3/\text{s}$. From 1998-2004, peak streamflows were very low due to prairie drought. From 2005-2011, the streamflow was very high due to increased precipitation. From 2012-2016 streamflow recessed due to lack of snowfall and high evaporation. Note precipitation data was collected from a climate station south of Cando.

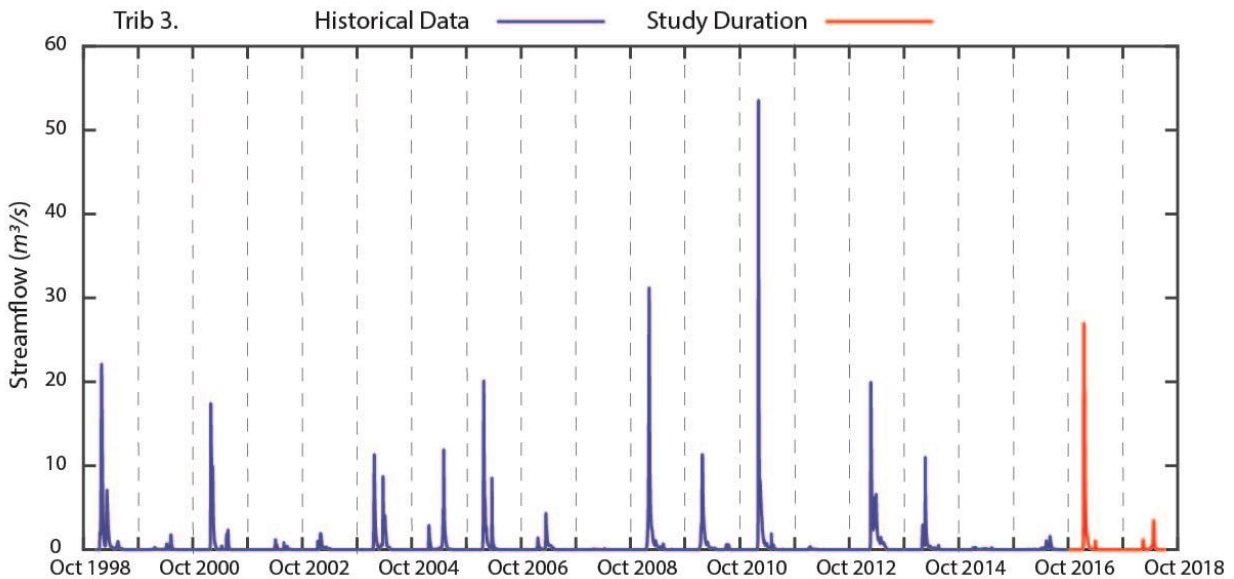


Figure 3. Tributary 3 Streamflow Data 1998-2018

Historical streamflow data captured by USGS gage ID: 05056060 from 1998-2018. There are 8 years of peak discharge values $> 15 \text{ m}^3/\text{s}$. From 1998-2004, peak streamflows were very low due

to prairie drought. From 2005-2011, streamflow was very high due to increased precipitation. From 2012-2016 streamflow recessed due to lack of snowfall and high evaporation.

MATERIALS AND METHODS

Hydrology, Water Quality, and Soil Data Collection

Snow surveys were conducted at ten locations across the basin during the early winter months of the years for 2016-17 and 2017-18. Surveys were conducted three to four times a season, with the final survey being conducted just before spring snowmelt and the start of streamflow (March 26th for 2017 and March 29th for 2018). Most sites were chosen at random to try to create an even distribution over the entire basin (Van Hoy et al., 2018). In the Turtle Mountain area, two sites were identified because it was believed that this area would have different accumulations due to the greater elevation differences (Figure 1B). During each site visit, a Metric Prairie Snow Sampler, designed after the Environment Canada ESC 30, was used to measure depth and a calibrated Snow Water Equivalent (SWE) scale to measure SWE (Geo Scientific Ltd.). Additionally, to check SWE scale accuracy, SWE was also calculated using a gravimetric approach (Sturm et al., 2010; Van Hoy et al., 2018). This SWE was in good agreement with the scale; therefore, more numerous scale measurements were used for model evaluation.

The United States Geological Survey (USGS) stream gauging network provided stream discharge data for this study (Mauvais Coulee ID: 05056100 and Tributary 3 ID: 05056060). The USGS estimates streamflow using hydrometric gauging (D. Thomas, personal communication 2017). The latitude and longitude coordinates for the Mauvais Coulee gage are 48.44298611 and 99.09944444 while Tributary 3's gage is located at 48.45770833 and 99.22416667. Normally, streamflow gauging commences when ice in the stream begins to melt and break up during the spring, and ceases in the late fall when winter begins. Having unknown amounts of ice and snow

in the stream during this time leads to major uncertainties in when the spring flow initially begins. During times of high flow, discharge was measured using an Acoustic Doppler Current Profiler attached to a floating platform, which measured width, depth, and velocity across the channel simultaneously (D. Thomas, personal communication, 2017). Throughout the year, discharge measurements were taken approximately every seven weeks (D Thomas, personal communication, 2017).

Water sampling was conducted primarily at the outlets of the two watersheds (Mauvais Coulee basin and Tributary 3) during the 2017 (March 31st – April 16th) and 2018 (April 24th- May 7th) spring snowmelt runoff events. Water samples were collected three times daily. During low flow months (May-October), water samples were collected twice a month. Each site was sampled for both forms of phosphorus (P): Total P (TP) and Total Dissolved P (TDP). TDP is a portion that is filtered, removing the particulate P. In the lab, particulate P is calculated by subtracting the amount of TDP from TP. Particulate P is absorbed in sediments, plants, and animals. Water samples were collected using a Nasco Swing Sampler. During each sampling time, two samples of 250 ml of water were collected in acid washed bottles. DP concentration samples were filtered using a 0.45-micron water filter and peristaltic pump. Filtered water samples were preserved immediately using 2 ml per liter of sulfuric acid (H₂ SO₄). Once collected, all samples were then stored in a refrigerator at a temperature of 4°C and preserved for a maximum of 28 days (Total Phosphorus Method 8190, Hach Water Analysis Handbook 2017).

The collection of a representative and reliable soil sample for P analysis requires a predetermination of sampling depth, sampling intensity and locations of relative nutrient applications in agricultural fields. Throughout the Mauvais Coulee basin, soil cores were collected from the same locations where snow surveys were conducted. These sites were selected

because these areas gave proper representation of the land cover/uses of the basin. In Tributary 3, sites were selected based on the division of the ecoregions, which also reflect the land cover/uses. Soil cores were collected using a soil core sampler (Grainer, INC) at the depth of 15 cm after agricultural harvest when fields are more accessible (AGVISE Laboratories). Sampling depths should include soils collected from a depth within the tillage zone while excluding soils from below the tillage zone (Coale 2000). However, a study in the Canadian prairies showed strong correlations between P concentrations in runoff from agricultural lands using a depth of 15 cm (Little 2007). Once the soils were removed from the subsurface, they were placed in an air limited soil sample bag provided by AGVISE Laboratories and stored in a cooler until delivered to Northwood, North Dakota AGVISE laboratory for analysis (J Breker Personal communication 2017).

Laboratory Analyses

In the lab, TP and TDP were determined as orthophosphate using the Total Phosphorus Hach Method 8190 (Hach Water Analysis Handbook 2017). This method uses a mixture of sulfuric acid and persulfate to convert organic phosphates to orthophosphates. A sample of 25 ml of water along with 2 ml of sulfuric acid and powder pillow of Potassium Persulfate was measured into an acid resistant glass. Once the proper ingredients were added, the sample was then gently boiled at 150°C for 30 minutes on a hot plate for digestion to occur. Immediately after 30 minutes, the sample was removed from the hot plate and allowed to cool for at least 5 minutes. The Total Phosphorus method was followed by the reactive phosphorus (orthophosphates) method to determine the amount of phosphorus concentration within the sample. 2ml of 1.54 N sodium hydroxide was added to complete oxidation. 10ml of the sample along with a PhosVer 3 powder pillow were added to the measuring vial and stirred for at least 5

minutes to ensure oxidation (Hach Water Analysis Handbook 2017). Samples were then inserted into the colorimeter and results were determined. Three samples along with a blank to zero the colorimeter were analyzed at a time and all results were expressed in milligrams per liter (mg/l).

Soils were analyzed for Olsen Phosphorus by AGVISE Laboratories in Northwood North Dakota using the Olsen P Test developed by Dr. Sterling Olsen in 1954 (Frank et al., 2011). This method used Sodium Bicarbonate to extract soil P which was a result of a search for an extract that would correlate crop response to fertilizers (Olsen et al., 1954; Frank et al., 2011). This method used 2 g of soil mixed with 40 ml of extracting solution (0.5 M NaHCO₃) and shaken at 200 rpm (excursions per minute), for 30 minutes. The sample was then filtered through No.2 filter paper. Once the solution is clear, 5ml of the solution was diluted with 15 ml of distilled water. 5 ml of the diluted solution was mixed with an acid molybdate stock solution and was allowed 10 minutes to process for color development. After the color stabilizes for at least 2 hours, they were inserted into the colorimeter and results were presented in ppm (Olsen et al., 1954; Frank et al., 2011).

Remote Sensing: North Dakota Tillage Practices and Crop Residue

Land cover and tillage practices are strongly correlated with water chemistry, particularly nutrient concentrations (Hunsaker et al., 1995; Dodds & Oakes, 2008). Tillage practices or conservation tillage practices vary from region to region throughout North America. Conservation tillage refers to any practice that leaves at least 33% of crop residue atop of an agricultural field (OmniSTAR Inc, 2006). Tillage practices include minimum-till, ridge-till, strip-till, no-till, and zero-till. Typically, tillage intensity is characterized by the fraction of crop residue on exposed soils in the early spring.

Crop residue cover is vital for tillage practice identification and evaluating the effectiveness of the land management practices across large geographical areas (Beeson et al., 2016). The amount of crop residue left after agricultural harvest is a direct response of tillage practices, crop rotations, and harvesting methods. Crop residue, sometimes referred to as plant waste accumulates on the surface of agricultural fields after fall harvest. Crop residue has an important role in soil conservation by helping to reduce water and wind erosion (Delgado, 2010; Hively et al., 2018). Further, crop residue maintains soil moisture, stores organic carbons, reduces evaporation and improves soil structures (Aase & Tanaka 1991; Magdoff & Weil 2004; Palm et al., 2014; Hively et al., 2018). Increasing crop residue while reducing tillage intensity and the amount of exposed soils can increase soil water retention and help control soil erosion by diminishing nutrient losses in runoff during snowmelt or rainfall events (Mulkey et al., 2017).

Numerous studies have used a remote sensing approach to calculate and accurately estimate crop residue cover. This method may provide an efficient, timelier, objective method of obtaining information on soil tillage intensity over an extended geographical area where mapping and monitoring may be inaccessible (Gould 2006; Beeson et al., 2016). However, the multispectral sensors of soils and crop residues are very similar making it difficult to determine which layer is which (Serbin et al., 2009). Although, depending on the residue type, age, soil type, and moisture content, crop residue may be brighter than the underlying soil (Nagler et al., 2000).

Various satellites with broadband multispectral sensors are currently orbiting Earth collecting Landsat images of agricultural land. Over the years, several methods of classifying multispectral data were developed to identify agricultural practices. The current study utilizes the Normalized Difference Tillage Index (NDTI) to identify the crop residue cover compared to exposed soils.

NDTI extracts time series values from Landsat images, which reliably track changes in tillage intensity (Galloza et al., 2013; Zheng et al., 2013; Beeson et al., 2016). Currently, image availability is one of the most important factors that constrains accuracy when estimating crop residue cover. Landsat images downloaded from October 14, 2016 helped identify tillage intensity throughout this study area. Note: this date was chosen since it was after fall harvest and prior to the soil freezing and any snow accumulations. However, cloud cover may cause some uncertainties.

The NDTI for Landsat Thematic Mapper (TM) data is defined as:

$$NDTI = \frac{TM5 - TM7}{TM5 + TM7}$$

Where TM5 and TM7 are reflectance values from Landsat TM band 5 (1550-1750 nm) and Landsat TM band 7 (2090-2350 nm) (Galloza et al., 2013).

Cold Region Hydrology Model

The Cold Region Hydrology Model (CRHM) is a physically-based model that was specifically created to have the ability to represent cold region hydrological processes through experimentally-based time tested equations. CRHM has a flexible modular design and is spatially-distributed based on hydrological response units (HRUs) allowing for fine scale resolution and parameterization. A HRU is a basin that is classified and/or grouped together by a certain characteristic (i.e. agricultural field, prairie, forested area, wetland, open water, developed land, etc.) and is a basic unit of calculation. CRHM is sensitive to the impacts of land use and climate change, which is why it was used for this current study. Additionally, it has been tested in the Canadian Prairies in many recent studies to examine drought conditions (Fang & Pomeroy

2007; Fang & Pomeroy 2008), areas with a high concentration of wetlands (Fang et al., 2010; Van Hoy et al., 2018), and areas dominated by agricultural land (Cordeiro et al., 2017; Mahmood et al., 2017).

Table 1 presents a complete set of CRHM modules used to create a highly effective model. The infiltration and soil modules are very important for the current study given they are present in the study's soil conditions and they affect nutrient export as explained in more detail in the results and discussion section. The soil module approximates moisture balance, slough storage, overland flow, and subsurface flow (Pomeroy et al., 2007; Domes 2008; Fang 2010, 2013; Van Hoy et al., 2018). This module used a three-layered approach where the third layer is ground water reservoir that outputs water to stream as base flow. The top layer collects water from wetlands, snowmelt, and rainfall and outputs it to crops through transpiration. The middle layer receives water from the overlying layer while allowing outputs through transpiration and/or percolation to the underlying layer. This module ensures that evapotranspiration (ET) does not exceed the interception of wetland storage and soil withdrawal characteristics (Mahmood et al., 2017; Van Hoy et al., 2018).

The infiltration module presents soil conditions year-round. During the non-winter months, this module interprets unfrozen soil infiltration for rainfall based on soil thickness, texture and agricultural tillage (Ayers 1959). During the winter months, this module interprets soils conditions based on three types of soil infiltration into frozen soil: restricted, limited, and unlimited. The frozen soil restricted class is an impermeable layer that has minimal infiltration resulting in meltwater going to ET or runoff (Pomeroy et al., 2007). If SWE values are under 5 mm, the model will use unfrozen soil parameters (Pomeroy et al., 2007; Van Hoy et al., 2018). Limited infiltration depends highly on snow-cover water equivalent and amounts of frozen water

in the first 30 cm of soil (Gray et al., 1986; Pomeroy et al., 2007; Van Hoy et al., 2018). CHRM only allows for six winter snowmelt events over > 5 mm, before changing to restricted infiltration and the melt becomes runoff (Pomeroy et al., 2007; Van Hoy et al., 2018). When melt amounts are < 5 mm, water infiltrates using unfrozen soil conditions. After the occurrence of a large melt event, if the temperature is $< 10^{\circ}\text{C}$, infiltration will automatically change to restricted because the model assumes ice lens formation will occur, restricting infiltration. Unlimited soil infiltrations occur when snowmelt ends resulting with the remaining runoff infiltrating (Pomeroy et al., 2007; Van Hoy et al., 2018). This module is necessary given it is designed to handle conditions that are specific to cold regions and it identifies the infiltration capacity during wet and dry years (Van Hoy et al., 2018).

Table 1. Cold Region Hydrology Model Module Description

Cold Region Hydrology Model Module Descriptions (2017)	
Observation	Reads climate and precipitation data at an hourly time step. Used to set the precipitation, wind speed, relative humidity, air temperature, incoming longwave radiation, and incoming shortwave radiation for each HRU.
Annandale	Determines the amount of radiation that is transmitted through the atmosphere based on temperature utilizing the Annandale Method from Annandale, Jovanic, Benade, and Allen (2002) as modified by Shook & Pomeroy (2012).
Longwave Radiation	Uses hourly average temperature, relative humidity, and incoming shortwave radiation to estimate the incoming longwave radiation (Sicart et al., 2006).
Radiation	Direct and diffuse incoming shortwave radiation in the absence of cloud cover based on latitude, elevation, slope, and azimuth (Garnier & Ohmura, 1970).
Albedo	Determines surface albedo depending on snow cover during the winter and spring while utilizing groundcover in the summer (Verseghy, 1991).
All-wave Radiation	Determines the net radiation during periods that are lacking snowcover using shortwave radiation, which is used to find ET (Granger & Gray, 1990).
Canopy	Estimates snow and rain intercepted by vegetation while dealing with the unloading, sublimation, and melting of intercepted snow, and the evaporation and drip of collected rain.
Energy-Balance	Utilizes incoming and outgoing shortwave and longwave radiation to estimate the radiative, advective, convective, and internal thermal snowpack energy that is available to melt snow.
Infiltration	Monitors unfrozen soil infiltration for rainfall based on soil properties i.e. soil thickness, soil texture, and agricultural practices, such as tillage and tile drainage (Ayers, 1959).
Evaporation	Utilizes the Penman-Monteith (Monteith, 1965) combination method along with surface resistance (Jarvis, 1976) and available energy to calculate ET for most HRUs.
Volumetric	Determines the volumetric soil moisture based on soil properties and sets the parameter fallstat, which is the percentage of soil pore space occupied by water (Centre for Hydrology et al., 2016).
Soil	Approximates moisture balance, slough storage, overland flow, and subsurface flow (Pomeroy et al., 2007; Dornes et al., 2008; Fang et al., 2010, 2013).
Prairie Blowing Snow	Calculates sublimation and blowing snow transport across HRUs using wind speed, air temperature, and relative humidity from the observation module.
Routing	Routes water using the Muskingum routing method from HRUs to down gradient HRUs or to the sub-basin outlets and then from the sub-basin outlets to the basin outlet at the lowest elevation in the model (Mahmood et al., 2017).

RESULTS AND DISCUSSION

Hydrology

Snow surveys were conducted during the winter of 2017 (January 8th, 29th, February 26th, and March 26th) and 2018 (January 7th, March 4th, and 29th). SWE observations for 2017 were recently reported in Van Hoy et al. (2018). Overall, SWE observations had higher snow accumulations, density, and depth in the northwestern part of study site along the area of the Turtle Mountains. Originally, it was thought that it was due to the difference of elevation (550-672 m) from the rest of the study site; however, the northeastern part of the basin is also at higher elevations (475-500 m) and showed very little snow accumulations. The Turtle Mountain part of the basin is heavily forested and has more herbaceous area than the northeast corner, which is almost entirely cultivated (Van Hoy et al., 2018). Taller vegetation tends to trap a greater accumulation of snow that is less vulnerable to midseason melting and blowing snow redistributions. Additionally, the Turtle Mountains also present an area with a high density of depressions, which often traps snow. In the north central part of the basin, snow accumulations are low to above average where vegetation height and density are the dominant factors impacting snow accumulation factors. In the south central portion of the study site, snow accumulations are moderate to high, due to being predominantly herbaceous with very little relief. The most southern portion of the study site consist almost entirely of agricultural fields and likely has low snow accumulations, but could be variable due to the different land management practices varying the size of stubble.

Over the duration of the current study, 2017 winter had more snow accumulations throughout the study site with peak SWE in the northwest corner of 240 mm resulting with higher streamflow when compared to 2018, as discussed later in this section. Figure 4 presents

the averaged peak SWE across the study site prior to spring snowmelt. Note that a spatially averaged SWE (observed prior to the onset of streamflow) provides an estimate regarding the amount of streamflow. In spite of having spatially averaged SWE (52.6 mm) on March 27 2017, streamflow began on March 31 2017 with slightly lower snowmelt streamflow (47 mm) in MAUVAIS COULEE BASIN . These spatially disturbed observations are scientifically acceptable considering the spatiotemporal uncertainty in both streamflow and SWE measurements. In 2017, infiltration during spring snowmelt was restricted due to frozen soil conditions and the presence of a basal ice layer suggesting that the consumption of the snowpack by evaporation (simulated Van Hoy et al., 2018) was limited. In contrast, 2018 had 41.4 mm of SWE prior to spring snowmelt, which resulted in only 4 mm snowmelt streamflow in the Mauvais Coulee basin. It is believed that the snowmelt water was infiltrated due lack of frozen soil area/basal ice layer resulting higher infiltration rate in soil. In addition, the duration between the study's final snow survey (March 29, 2018) and commencement of streamflow (April 24) was ~ three weeks, allowing some sublimation and subsequent snow erosion and bare soil exposures to occur.

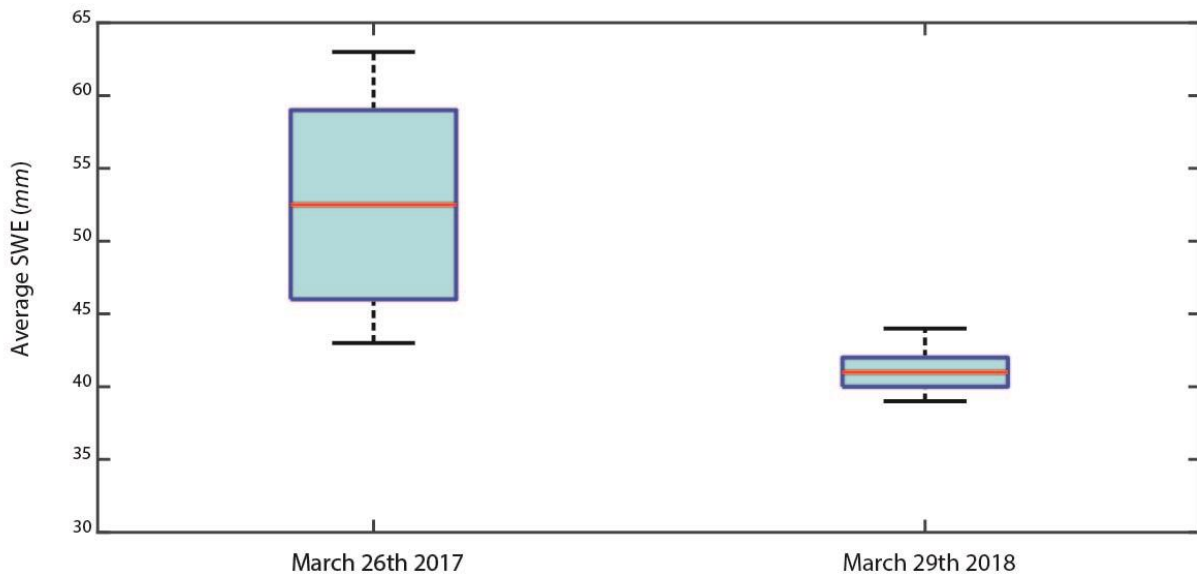


Figure 4. Snow Water Equivalent

Average peak snow water equivalent (SWE) across the study site prior to spring snowmelt. March 26, 2017 average SWE was 52.6 mm, which resulted in 56 mm of streamflow on March 31, 2017. On March 29, 2018, average SWE was much lower, 41.4 mm, and resulted with 4mm of streamflow on April 24, 2018.

Daily discharge at each site varied consistently among the years with the overall seasonal patterns similar at both locations. The Mauvais Coulee basin produces more discharge volume and is the main contributor to Devils Lake rather than Tributary 3. Typically, the spring snowmelt period is associated with a peak in absolute daily discharge while the low flow characterizes summer and fall months whose streamflow is occasionally driven by rainfall events. However, this current study is presented with two different hydroclimatic extremes including a wet winter while having a dry summer (2017) (Figure 5) and a dry winter with a relatively wet summer (2018) (Figure 6). Snowmelt in 2017 produced larger discharge peaks in the Mauvais Coulee basin (73 m³/s) and Tributary 3 (26 m³/s) compared to mean peak discharge (37.65 and 9.09 for Mauvais Coulee basin and Tributary 3) which generally caused larger spring runoffs and

seasonal flooding throughout the study area (Table 2). Large amounts of discharge are a result of the mean snow water equivalent (SWE) measured prior to the initial beginning of streamflow (52.6 cm); after which, streamflow declined and remained nearly constant for the rest of the hydrological year. In 2018, snowmelt produced 95% less discharge than in 2017. In the Mauvais Coulee basin, a wet summer produced higher discharge peaks (12.12 m³/s) than the dry winter (2.66 m³/s) and mean discharges (1.52 and 1.80 for spring and summer). In Tributary 3 consistency among the sites was observed with a wet summer (3.42 m³/s) producing a higher peak discharge than that of the dry winter (1.06 m³/s). However, mean discharge rates were lower in the summer (0.37 m³/s) and higher in the winter (0.71 m³/s), suggesting that in late summer and early fall, rivers are becoming disconnected up stream, decreasing the discharge supply (Table 2).

Table 2. Mean Discharge

Annual, spring snowmelt and summer low flow mean discharge. Higher mean discharges were present during spring snowmelt compared to summer low flows.

Mean Discharge (m³/s)				
Location	Year	Spring (snowmelt)	Summer (low flow)	Annual
Mauvais	2017	37.65	0.89	4.32
	2018	1.52	1.80	1.77
Tributary 3	2017	9.09	0.31	1.53
	2018	0.71	0.37	0.41

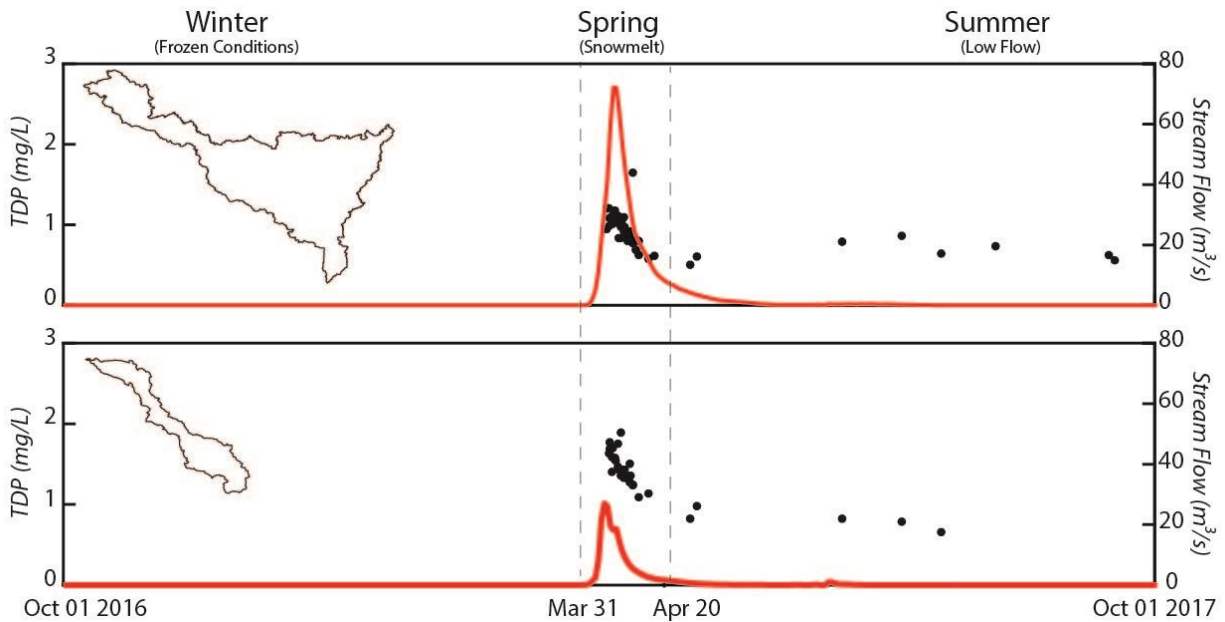


Figure 5. 2017 Water Quality Data

Daily streamflow (q) and TDP concentrations (c) from October 1, 2016 to October 1, 2017 (Top) Mauvais Coulee (Bottom) Tributary 3. Snowmelt induced stream flow began March 31, 2017 and recessed to low flow April 20, 2017. High peak discharge of 73 m^3/s in Mauvais Coulee basin and 26 m^3/s in Tributary 3 indicated a wet winter while a low flows near 0.0 m^3/s suggested a dry summer. TDP Concentrations ranged from 0.5-2 mg/L .

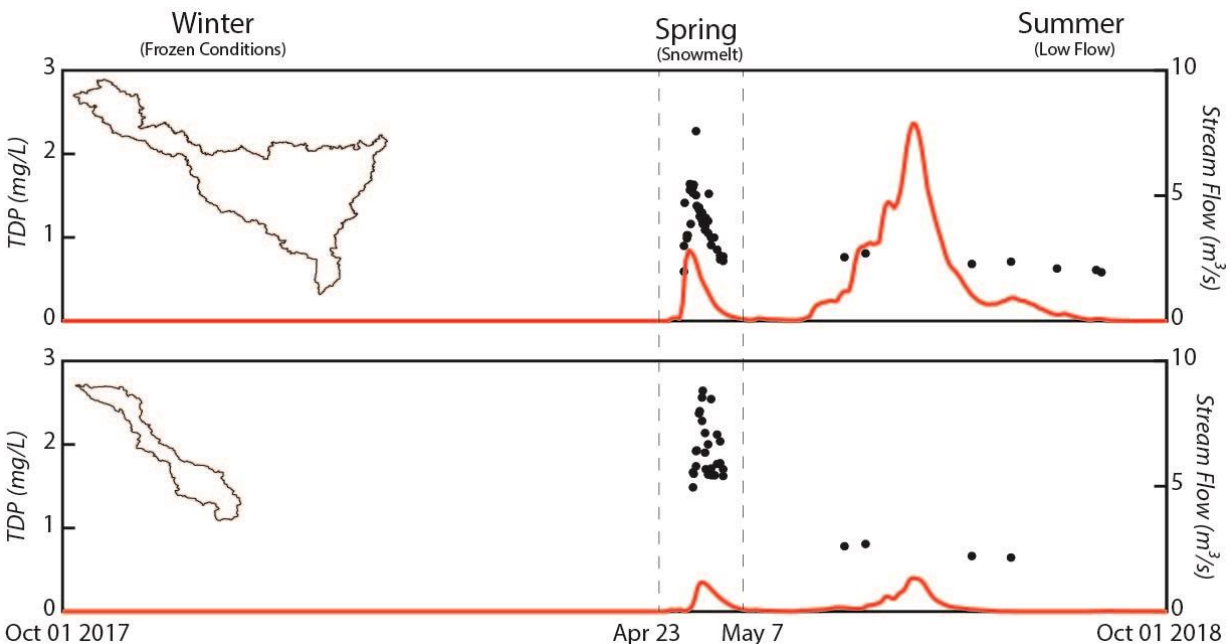


Figure 6. 2018 Water Quality Data

Daily streamflow (q) and TDP concentrations (c) from October 1, 2017 to October 1, 2018 (Top) Mauvais Coulee (Bottom) Tributary 3. Stream flow began April 23, 2018 and recessed to low flow May 7, 2017. A wet summer produced peak discharge of 12.12 m^3/s in Mauvais Coulee

basin while a dry winter peaked at 2.66 m³/s. Tributary 3 showed consistency with a wet summer peak discharge of 3.42 m³/s and a dry winter peak discharge of 1.06 m²/s. TDP concentrations ranged from 0.5-3 mg/L.

Water Chemistry

Water chemistry showed considerable variation in P concentrations among the two rivers (Mauvais Coulee basin and Tributary 3) and hydrological years (2016-17 and 2017-18) (Figure 7). In addition, during a hydrological year, P concentrations of spring season were noticeably different from that of summer, exhibiting the elevated concentration during the spring snowmelt event and low concentration throughout the summer season. Interestingly, the results indicated a significant amount of dissolved P (~95%±5) and very little particulate P contribution to Total P from the two basins in both spring and summer similar to Jensen et al. (2011). The sampling frequency of this study is higher (3 times daily during the spring snowmelt and 2 times monthly during low flow) compared to other studies in the NGP which sampled more during rain events (Corriveau et al., 2013). Note that the sites examined in this study experienced only one basin wide rainfall event (July, 2018) (Figure 6). Nevertheless, dissolved P contribution to total P was greater than that of particulate P in the NGP. During the spring snowmelt event, the importance of dissolved P becomes evident given 95% of the nutrient is in the dissolved form. Conversely, other studies conducted in the Prairie Pothole Region of southwestern Manitoba showed a less dissolved P contribution (< 53%) and more particulate P (Ali et al., 2016; Mahmood et al., 2019). This may be due to the impact of the steeper slope of the Pembina Escarpment (known as Manitoba Escarpment in Canada), allowing sediments to be more easily eroded during the snowmelt runoff event.

Mean concentrations of TDP were typically higher for the Tributary 3 (1.41 and 1.93 for 2017 and 2018) while having the highest peak concentration of 2.64 mg/L; whereas, the highest

peak concentrations for the Mauvais Coulee basin were 2.27 mg/L, with both measurements taken from the 2018 field season (Figure 7). The maximum and mean values of Mauvais Coulee basin and Tributary 3 are much higher than other studies in the Northern Great Plains during the snowmelt event (Liu et al., 2013; Mahmood et al., 2019). Comparing Tributary 3 basin, whose area is similar in size to South Tobacco Creek (75 km²) basin of Southern Manitoba, mean values vary greatly. Mahmood et al., (2019) reported TDP values of < 1.0 mg/L during the spring event of 2009; whereas, TPP values were not comparable to the TPP values of the current study, suggesting the effect of the Pembina Escarpment has more of an impact than originally inferred (Mahmood et al., 2019). However, there was a significant difference in mean concentrations for both basins among the hydrological years. Mean concentrations were considerably lower during the hydrologically wet year of 2017 but increased dramatically during the hydrologically dry year of 2018 (21% and 52% for Mauvais Coulee basin and Tributary 3), suggesting nutrient sources availability and the permeability of the soils have a greater effect on nutrient concentrations (Baulch et al., 2019). Low concentration during wet years can be also attributed to dilution due to high runoff volume while during dry years TDP concentration is not diluted due to limited runoff volume. This can be also attributed to limited interactions between snowmelt waters and soil due to frozen soil/basal ice during wet spring (2017) while the adequate interaction was allowed between soil and snowmelt during the 2018 spring season.

In contrast to spring snowmelt, basins showed relatively low TDP concentrations with an occasional small nutrient increase during the summer low flow season, possibly due to a rainfall event (Corriveau et al., 2013; Yates et al., 2014; Mahmood et al., 2019), suggesting, the source of major P during the low flow season is coming from the groundwater. There is no significant difference in TDP mean concentrations during the low flow months from hydrological year-to-

year measurements ranging from 0.60 to 70 mg/L in both basins. However, in the Mauvais Coulee basin, TP concentrations had a strong agreement with Vandenberg et al. (2014), whose study reported TP concentrations during the low flow seasons (2007-2011) from the surrounding basins including the Mauvais Coulee basin. The Vandenberg et al. (2014) study analyzed samples from three different locations within the Mauvais Coulee basin, resulting with similar TP annual mean concentrations of 0.31, 0.31, 0.36 mg/L, while in the current study we reported 0.31 and 0.30 mg/L, were reported annually.

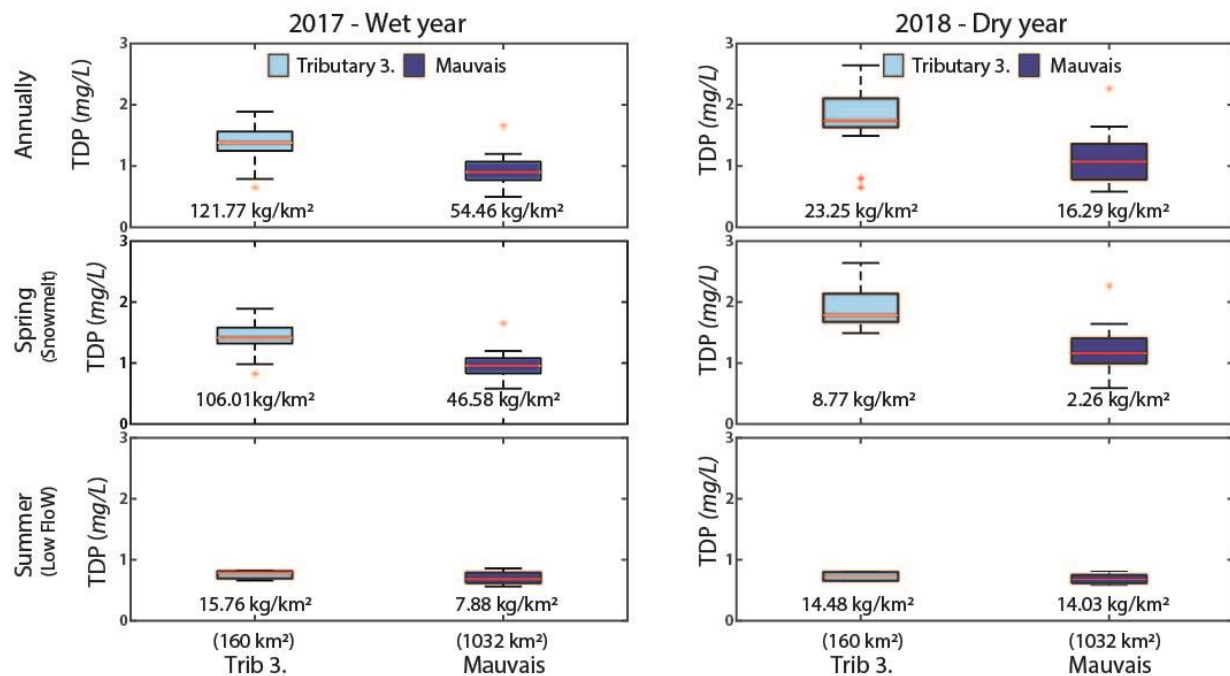


Figure 7: Water Chemistry

Variability of TDP (mg/L) concentrations and total export (kg/km²) for the entire open water season, spring snowmelt and summer low flow for the studied watersheds Mauvais Coulee basin (dark blue) and Tributary 3 (light blue) from 2016-17 (wet year) and 2017-18 (dry year). Each box has lines at the lower quartile, median, and upper quartile values, while the whiskers beyond the box show the extent of the rest of the data with outliers indicated by the red plus (+) signs. TDP concentrations ranged from 0.0-2 mg/L during 2017 and 0.0-3 mg/L for 2018 while observing higher mean concentrations for Tributary 3 (1.14 and 1.93 mg/L for 2017 and 2018) compared to Mauvais Coulee basin. Maximum peak TDP concentrations observed in 2018, 2.27 mg/L (Mauvais Coulee basin) and 2.64 mg/L (Tributary 3). Highest total export was observed in

Tributary 3 for both years with spring snowmelt being the major contributor during 2017, and summer rainfall in 2018.

Table 3 shows spatial mean, maximum and minimum Olson P values for the Mauvais Coulee basin and Tributary 3 basin. Olson P concentrations from Johnston (2006) for North Dakota soil samples collected during 2001 and 2005 have also been included. Estimates of the soil P concentration agree well with other reported soil P concentration in other studies in the NGP (Barica 1987; Johnston et al., 2006; Baulch et al., 2019) and the NGP soil samples have naturally high concentrations in soil P (Barica 1987; Johnston et al., 2006; Baulch et al., 2019). Olsen P concentrations exhibited uneven spatial distribution throughout two study basins with higher concentrations observed in downslope landscapes (Wilson 2016). Highest concentrations (95 and 75 mg/L) were observed in the northwest corner of the Mauvais Coulee basin on the eastern slope of the Turtle Mountains. The lowest concentrations (6 mg/L) were observed in the most eastern portion of the Mauvais Coulee basin where the landscape is flat and predominantly grasslands. Low median concentrations of P (10 and 11 mg/L for 2001 and 2005) reported in Johnston (2006) were compared to the current study (33 and 32.5 mg/L for Mauvais Coulee basin and Tributary 3) and the differing results can be due to large number of samples collected over a large area by Johnston (2006) (38,450 and 66,887 for 2001 and 2005); whereas, this study analyzed only ten samples in the Mauvais Coulee basin and four in Tributary 3. To rule out an atmospheric contribution of P, snow samples were collected from various locations and analyzed for both 2017 and 2018. Lab results showed a minor atmospheric contribution with a TDP mean concentration of 0.045 mg/L, respectively. Thus, based on P concentration in soil and accumulated snow, the soil is the most likely the source of P in the streamflow water as soil P concentration is two order magnitudes greater than snow P concentration. Note that soil P in the top 15 cm is a mixture of soil particles and organic matter from crop residues.

Table 3. Soil Olsen Phosphorus Concentrations

Olsen Phosphorus concentration analyzed by Agvise, Northwood, North Dakota, from fall of 2018 compared with Johnston (2006) *.

Soil Olsen Phosphorus Concentrations			
Location/ year	Median P, mg/L	Max P, mg/L	Min P, mg/L
Mauvais '18	33	95	6
Tributary 3 '18	32.5	62	22
North Dakota '01*	10	> 50	0-5
North Dakota '05*	11	> 50	0-5

Annual Export

The magnitude of the annual P export varied as a function of land use and hydrological conditions. Comparisons of the P load amongst both basins and the two hydrological years, in general show great differences between the spring snowmelt and summer low flow season. In 2017, P export during the spring snowmelt event for both basins was associated with higher sediment loads (46.58 kg/km² and 106.01 kg/km² for Mauvais Coulee basin and Tributary 3) and contributed most to the annual P load (54.46 kg/km² and 121.77 kg/km² for Mauvais Coulee basin and Tributary 3). However, during the 2018 hydrological year, the summer P load (14.03 kg/km² and 14.48 kg/km² for Mauvais Coulee basin and Tributary 3) contributed most to the annual P load (16.29 kg/km² and 23.25 kg/km² for Mauvais Coulee basin and Tributary 3). It's not uncommon to observe years when snowmelt delivered low portions of total runoff or nutrients to also have unusually high summer and fall precipitation; however, sediment load was usually higher during periods of unusually high snowmelt discharge (Corriveau et al., 2013). The P export per unit area for Tributary 3 (106.01 kg/km² in 2017, 121.77 kg/km² in 2018) was greater than the Mauvais Coulee basin (46.58 in 2017 ,54.46 kg/km² in 2018).

In the NGP, watersheds are mainly dominated by agricultural fields with areas of forest cover and grasslands suggesting we would expect similar total P loads. P loads in the Mauvais Coulee basin are consistent in loads observed in the LaSalle watershed in southern Manitoba, which exported 57 kg/km² that drained 1800 km² (Corriveau et al., 2013). However, loads are smaller than those measured in two agriculturally dominated watersheds of Kansas and Missouri (136-288 kg/km²) that drained into 1,300 km² (Chambers et al., 2005). Like the current study, Mahmood et al., (2019) working in a smaller basin, reported twice the amount of total P export than Corriveau et al., (2013), similar to the comparison of Mauvais Coulee basin and Tributary 3, respectively. Considering the dynamics of the hydrology in the NGP, the total P export resulted in seasonal variability between the headwaters and the floodplains region. However, observations from previous studies indicated an increase in nutrients load across the NGP and may be attributable to recent climatic wetting and increased agricultural activities.

Concentration – Streamflow Relationships

Concentration to streamflow relationships for dissolved phosphorus were interpreted separately for each basin to inform scaling and land management influences with streamflow being the dominate driver of these simple nutrient relationships. However, the significance and strength of the concentration to streamflow relationship varied considerably depending on the streamflow. Therefore, R^2 values were used to assess the significance of the relationship. R^2 is a statistical measure of how close data are fitted to a regression line while, R^2 values range anywhere from -1 to 1. In general, a higher R^2 value indicates a stronger and more significant correlation between nutrients and streamflow. Slope values from linear regression between c and q were used to describe the relationship observed in the rising limb. A slope of -1 would suggest that concentrations varied inversely, with discharge and dilution being the dominate processes

controlling concentrations (Hunsaker et al., 2017). The slopes of zero suggested chemostatic behavior in a watershed, indicating invariable concentrations as discharge fluctuates (Godsey et al., 2009). However, limits of chemostatic behavior are defined as $-0.1 < m < 0$ by Herndon et al. (2015).

Figure 8 presents concentration to streamflow relationships for the two basins monitored in this study during the spring snowmelt season of 2017 and 2018, with streamflow measured in cubic meters per second (m^3/s).

Rising Limbs: In each rising limb, the data shows little change in concentrations of dissolved P as streamflow increased up until peak discharge, after which concentrations began to decline. In the Mauvais Coulee basin, no significant relationship was found between dissolved P and streamflow as indicated by low R^2 values of the regressions (< 0.30) during the 2017 and 2018 period. However, at Tributary 3 a high R^2 value (0.93) and slope (1.00) from linear regression during the 2018 snowmelt event showed a strong association between streamflow and dissolved P, indicating intense flushing. In Mauvais Coulee basin, slopes of the regressions in the rising limbs were close to zero for both years, exhibiting nearly chemostatic behavior (Godsey et al., 2009) (Figure 8). However, regression slope in the Mauvais Coulee basin during 2017 (0.00001) were much closer to zero than that of 2018 (0.0043) suggesting that Mauvais Coulee basin was less chemostatic in 2018 (Godsey et al., 2009; Herndon et al., 2015) due to basal ice layers restricting contact time between soil and meltwater affecting nutrient transport (Amarawansa et al., 2015; Baulch et al., 2019).

Recession Limbs: In contrast to the rising limb, after the onset of peak discharge, concentration of dissolved P began to decline. Among all the basins and in both hydrological years, positive linear relationships were observed. In the Mauvais Coulee basin, both high R^2 values (0.36 in

2017 and 0.73 in 2018) indicate strong flushing. However, Tributary 3 showed the contrasting concentration to streamflow relationship between the years. The weakest correlation was observed during the 2018 snowmelt event (0.0214) while the concentration to streamflow relationship exhibited far greater R^2 in 2017 (0.591). Although, slope regressions were steeper in 2018 (0.17) when soil flushing was more predominate, in 2017 (0.02) the soil flushing occurred later effecting nutrient transport.

The weak concentration to streamflow relationships were previously discussed at the catchment scale (Godsey et al., 2009; Mahmood et al., 2019) and the field scale (Roste 2015). Interestingly, Roste (2015) reported a regression slope of -0.03 suggesting chemostatic behavior for dissolved P in the Tobacco Creek Basin. Like Godsey et al., (2009), a log – log plot approach of the concentration to streamflow data was used to verify the absence of a concentration to streamflow relationship through a small range of concentrations and a wide range of flows. Similar ranges of chemistry and flows were observed and suggested that chemistry varied nearly as much as the flows did (Roste 2015). However, relevant to this study concentration to streamflow observations at the headwater, mid-basin, and larger basin scale presented a clearer relationship while the invariant chemical supply become apparent (Mahmood et al., 2019). In the current study, two obvious relationships were observed, one in the rising limb (chemostatic) and one in the recession limb (flushing). Haygarth et al., (2004) reported that a weak concentration to streamflow correlation for P may emerge from a steady-state condition between the dissolution kinetics of P in a homogeneous sources such as soil and snowpack and in-stream water velocity (Haygarth et al., 2004). In this scenario, the sluggish draining of soil water (source water) inhibited any exchange of P between soil and solution (Haygarth et al., 2004). The weaker

concentration to streamflow relationship also could have been due to the release and subsequent export of nutrients driven by low flow velocities.

The concentration to streamflow relationships the during spring snowmelt have been investigated at several sites across the cold region prairies. Liu et al. (2014) reported a strong and inverse relationship of flow weighed mean nutrients concentrations (FWMNC) with average flow rate and SWE utilizing a long term (1993-2010) dataset in a small (0.03 km²) basin within the Tobacco Creek Basin. Additionally, Liu et al., (2014) found a strong and positive correlation between FWMNC and cumulative snowfall. Mahmood et al. (2019), also in the Tobacco Creek Basin, reported a strong and positive correlation of particulate FWMNC while observing a weak correlation for dissolved FWMNC with streamflow and cumulative snowfall. Whereas, this current study shows a strong correlation for dissolved FWMNC with streamflow and cumulative snowfall. Although Corriveau et al. (2013) did not report any type of concentration to streamflow relationship; her study suggests that more variability in total nutrients concentrations occurs during the spring snowmelt event.

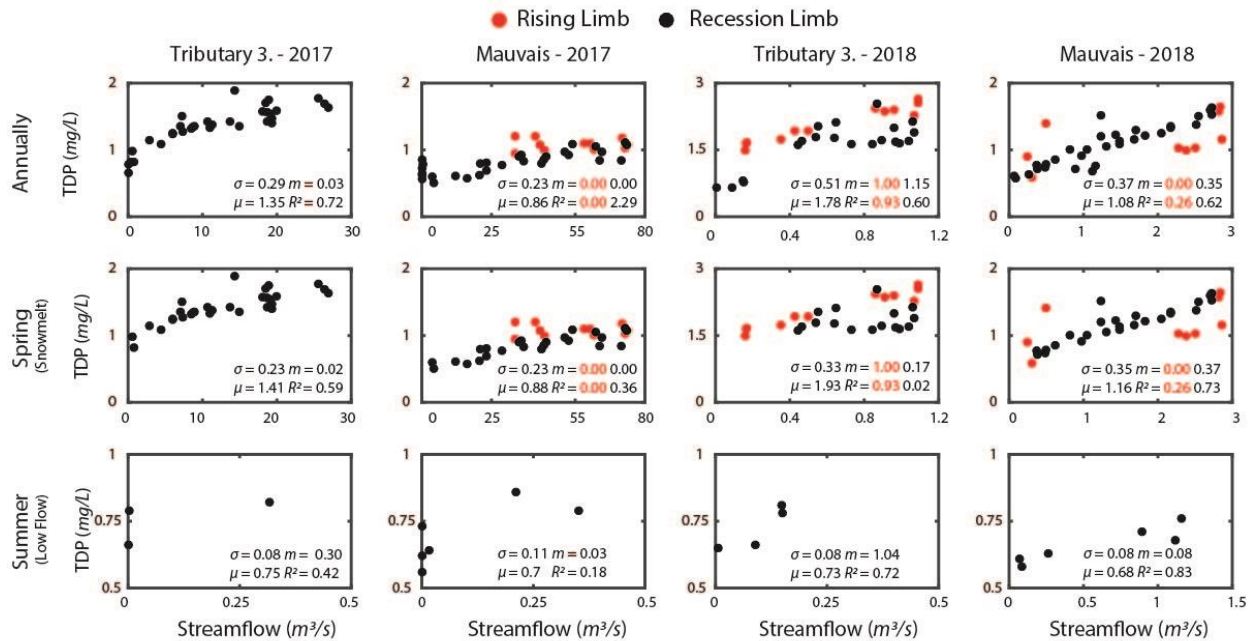


Figure 8. Concentration – Streamflow Relationships

Concentration (c) (mg/L) to Streamflow (q) (m^3/s) relationships for both Mauvais Coulee basin and Tributary 3 during the entire open water season (top), spring snowmelt (middle), and summer low flow (bottom). TDP in the rising limb indicated by the red dots while the black dots represent TDP in the recession limb. In Mauvais Coulee basin, the rising limb displays chemostatic relationships indicated by their slope (m) near zero, while in 2018, Tributary 3 presented intense flushing with a slope of 1.0. In the recession limbs, a positive linear relationship was observed in both basins as streamflow declined into low flow conditions. High R^2 suggested intense soil flushing in the basins for both years while steeper slopes in 2018 indicated higher TDP concentrations exported.

Impacts of Hydroclimatic Conditions

The two water years during the current study showed contrasting hydroclimatological responses. As noted previously in the hydrology section, the water year 2016-17 is characterized by high snow accumulation, subsequent snowmelt streamflow, and very little summer streamflow. In contrast, during the 2017-18 water year, very dry conditions during the winter season resulted in low snow accumulation and negligible amounts of spring snowmelt runoff. However, there was a rainfall runoff during the 2018 summer, which is uncommon in the study

area. In the Mauvais Coulee basin, annual streamflow for 2016-17 was 64 mm while it was only 21 mm during the 2017-18 season. Likewise, in Tributary 3, annual streamflow during 2016-17 and 2017-18 were 121 mm and 23 mm respectively. To gain further insight into hydroclimatological responses, two watersheds were simulated using a physically based cold region hydrologic model. The simulations for both basin were simultaneously compared against SWE observations and basin outlet streamflow (Table 4). The Nash-Sutcliffe Efficiency (NSEs) (Nash & Sutcliffe, 1970) between observed and simulated SWE are 0.7 and 0.8 during 2017 and 2018 respectively. Note that the observations days of this study were limited to four (2017) and three (2018) days that included both peak SWE and SWE prior to snowmelt streamflow. The basin averaged simulated SWE and outlet annual streamflow volumes agreed well with observations in both basins (Table 4). Figure 9 shows the frozen soil or basal ice layer status in the Mauvais Coulee basin and Tributary 3 during the spring streamflow period for each simulation year. The y-axis represents the ratio of frozen soil or basal ice area to total basin area.

Table 4. Cold Region Hydrology Model Performance Evaluation

Note SWE were not measured in Tributary 3 over the duration of this study.

Cold Region Hydrology Model Performance Evaluation				
		Streamflow (mm)		SWE
Location	Year	Observation	Model	$NSE_{obs,mod}$
Mauvais	2017	64	70	0.75
	2018	21	28	0.82
Tributary 3	2017	121	117	No Observation available
	2018	23	19	No Observation available

As climate continues to fluctuate via precipitation and temperature resulting in highly variable snow accumulations and snowmelt runoff, this imposes uncertainty on different aspects of hydrologic fluxes and land surface conditions including the freeze and thaw cycle of stubble (crop residue) and soil columns. Therefore, the hydroclimatic condition observed throughout the

NGP plays an important role in controlling nutrient exports (Haque et al., 2018). Observations during both years exhibited peak maxima concentrations (2017: 1.65 mg/L and 1.89 mg/L; 2018: 2.27 mg/L and 2.64 mg/L for Mauvais Coulee basin and Tributary 3) during the snowmelt discharge event while minimal concentrations were recorded during the summer low flows (2017: 0.58 mg/L and 0.82 mg/L; 2018: 0.59 mg/L and 1.37 mg/L for Mauvais Coulee basin and Tributary 3). Such intra-annual variability is consistent with the observations in other basin across the world (Aubert et al., 2013; Dupas et al., 2016) (Figure 7). Figure 7 shows the median concentration for a dry year (2017-2018), and is consistently higher than that of a wet year (2016-17) in both basins studied during the spring snowmelt seasons. However, annual TDP export per unit basin area for a wet year is also substantially higher than a dry as the annual streamflow volume for wet year exceed greatly compared to that of a dry year (Figure 7). Nutrient losses and concentrations in surface runoff depend on magnitude and contact of sources and transport. Generally, runoff volume has more of an impact on nutrient loads while nutrient sources availability has a greater impact on nutrient concentrations (Baulch et al., 2019). During 2017, thick SWE accumulations before the onset of discharge resulted in high volumes of streamflow and subsequently carried greater total loads of P while smaller snowmelt runoff exported little P during a dry year. Extreme P export during wet years is not uncommon. In the case of the NGP, generally during the first part of the 2000's (2000-2004), the annual load was low with invariant streamflow and nutrient contributions; whereas, nutrient exports were much higher in 2006-2007 and 2010-2011 during wet hydrologic years (Mahmood, 2019). This study's results on the impacts of wet and dry years on P concentration and annual export also agree with a study recently conducted in Broughton's Creek, Manitoba that assessed the impacts of hydroclimatic conditions (i.e, wet: 2013 or dry: 2014) on P concentrations of downstream

water bodies (Haque et al., 2018). Haque et al. (2018) reported low P concentrations during the wet year (2013) and relatively higher P concentration during a dry year that are consistent with the findings of this study.

The following is an explanation and hypothesis for contrasting P concentration and export between wet and dry years:

High snowmelt and subsequent streamflow: Lower mean and median concentration during wet years can be attributed to high SWE accumulation and snowmelt runoff. This study concludes that higher overland snowmelt water slightly dilutes the P concentration before being exported to the stream. In the streams, large volumes of streamflow from the melting of snow in agricultural fields and stream banks further dilutes the P concentration, ultimately resulting in lower P concentration during wet years. In contrast, during dry years, thinner and temporally discontinuous snow accumulations and subsequent very little runoff allow very little opportunity for dilution.

Soil and snowmelt water contact opportunity: Figure 9 shows the frozen soil or basal ice layer status in the Mauvais Coulee basin and Tributary 3 during the spring streamflow period for each simulation year. The y-axis represents the ratio of frozen soil or basal ice area to total basin area. During the wet year in both basins, the entire basin was frozen due to frozen soil or the presence of basal ice layer prior to start of spring snowmelt runoff, while both the soils of the basins were exposed well before the start of spring snowmelt runoff. Such contrasting frozen status between the wet and dry years is due to very high snow accumulation (basin wide 52.2 mm prior to streamflow start) and less erosion during the wet year while the dry year has little snow accumulation and relatively small snow erosion. This study indicates that, prior to discharge, the completely frozen/presence of basal ice layer limits the contact time and interaction opportunity

between soils and meltwaters, resulting with considerably higher total loads and medians concentrations (Quinton and Pomeroy 2006; Costa et al., 2017; Baulch et al., 2019). However, in 2018, due to the absence of a frozen soil/basal ice layer (Figure 9) aided by small snow accumulation (less SWE) and thinner snow cover, gradual release of snowmelt water allowed plenty of contact time and interaction opportunity with soils, resulting in a higher P concentration in stream water (Lilbaek and Pomeroy 2010). The influence of contact time between snowmelt water and soil on stream water P concentration was also demonstrated in a field-scale study conducted in Alberta, CA monitoring the relationship among soil- test P (STP) with runoff TP from 8 small watershed over three years (Little et al., 2007). The small watersheds were uniformly managed and had no farmland or agricultural influences. Soil samples were recovered during the fall and measured against spring snowmelt water chemistry, while soil samples from the late spring were measured with water chemistry of the summer low flow. A strong linear relationship was observed between STP and TP, concluding the interaction of soil to runoff meltwaters (Little et al., 2007).

Further, soil conditions and relative SWE cover throughout the study site showed a significant impact on the concentration to streamflow relationships during spring snowmelt in both hydrological years. Note that during spring snowmelt, atmospheric temperatures fluctuated, causing meltwater to flow during the day while slowing or ceasing in evening when temperatures dropped below freezing. This freeze – thaw cycle created a “pulsing” effect, where nutrients were being released during the day and transport was slower in the morning when the initial thaw began slowly releasing nutrients into the stream. However, as temperatures began to rise, nutrient release became more frequent until temperatures declined in the evening ceasing nutrient export. The high-volume snowmelt runoff and discharge observed in 2017 and the low- volume of 2018,

would lead one to think of either a flushing or dilution relationship to occur during spring snowmelt. However, the freeze-thaw cycle of the soils affect water chemistry while limiting the cycling and exporting of nutrients (Groffman et al., 2001; Bechmann et al., 2005; Matzner and Borken 2008; Messiga et al., 2010) based on the pulsing criteria previously described, resulting with a nearly chemostatic behavior. The extent of chemostatic behavior can be explained by the frozen conditions of the soils (Figure 9). In Mauvais Coulee basin, 2017 soils were completely frozen and presented a near chemostatic behavior, which was stronger than that of 2018 where soils were partly thawed, almost displaying a flushing relationship as seen in Tributary 3 This suggested that soils (frozen or thawed), in fact, were the dominate controllers of how nutrients were exported during spring snowmelt.

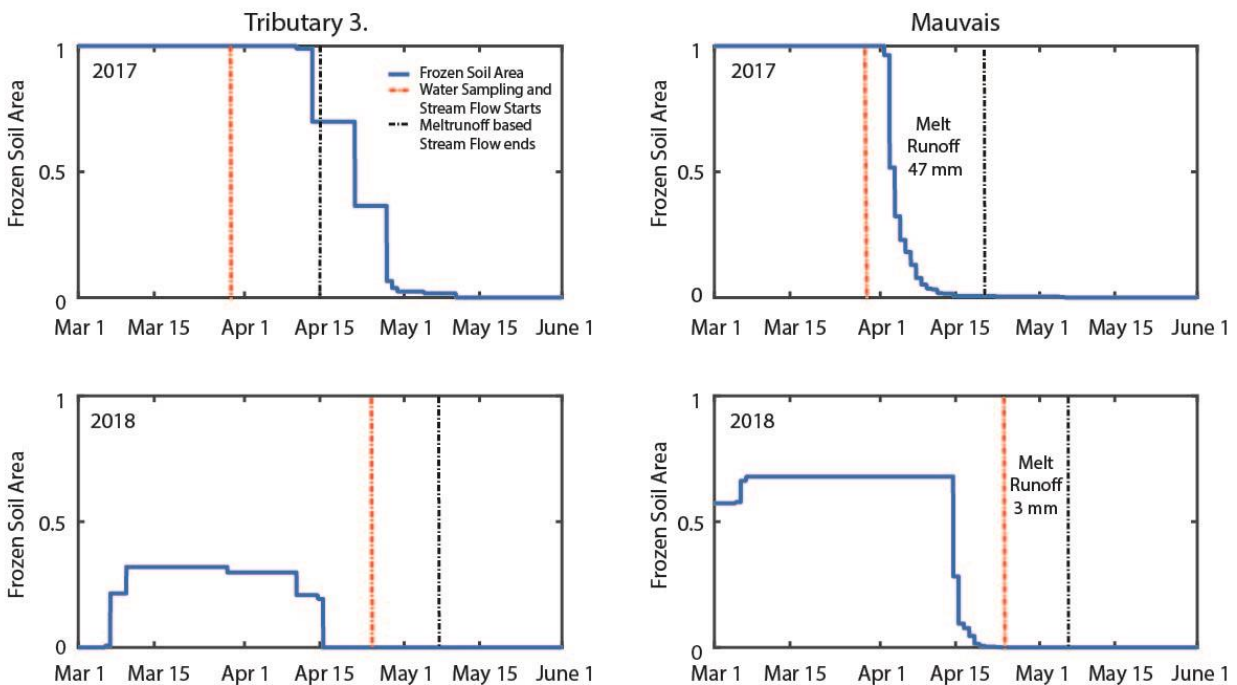


Figure 9: Cold Region Hydrology Model Soil Conditions

Soil conditions in the Mauvais Coulee basin and Tributary 3 during the spring streamflow period for each simulated year 2017 and 2018. The Y-axis presents the ratio of frozen soil to total basin area. The blue line indicates the frozen soil area; the dashed red line presents when water data

collection took place and when streamflow commenced, while the black dash line presents the end of melt runoff based streamflow. In 2017, basin soil conditions were completely frozen when streamflow began and remained frozen partially through the water sampling period. In 2018, soil conditions were completely thawed for the onset of spring streamflow.

Impacts of Land management

In Figure 10, a Landsat series image was utilized to detect the crop residue, which is an indicator to tillage practices and remaining biomass in various agricultural fields (Beeson et al., 2016; Hively et. al., 2018). The top rows of figure 10 show a false color composite of infrared, red and green band for Tributary 3 and Mauvais Coulee basin respectively. In the bottom row of Figure 10, a tillage index is utilized to estimate the amount of crop residue compared to exposed soils. Tillage indexes suggest that Mauvais Coulee basin has more crop residue, suggesting there are less exposed soils; whereas, Tributary 3 has relatively less crop residue suggesting more exposed soils (Figure 11). The results show a correlation with a 2004 roadside survey conducted by the North Dakota NRSC which reported a 0.0 % no-till per acre for Towner County, where the Mauvais Coulee basin resides, and a 0.6% no-till per acre for Rolette county, where a portion of Tributary 3 (Alme T., personal communication, November 2018; Franzen D., personal communication, January 2013) is located. Interestingly, heavy tillage practices indicated by less crop residue in Tributary 3 is associated with the high observed annual total P exports, while higher crop residue in the Mauvais Coulee basin is linked with less annual P (Timmons & Holt 1977). This study indicates that heavily tilled soils in Tributary 3 allow more opportunity and time for snowmelt and soil interaction, resulting in higher export, while high crop residue and prairie grassland permit very little snowmelt and soil interaction in the Mauvais Coulee basin (Timmons & Holt 1977; Jeje 2006; Amarawansha et al., 2015; Donald et al., 2015). This also

suggests that ecoregion landcover explains the greater variances of nutrient export observed in this study compared to the size of basin area (Dodds et al., 2008).

In addition to influencing the total P export, tillage indexes also show a strong correlation with elevated nutrient concentrations and concentration to streamflow relationships observed during spring snowmelt for both of the 2017 and 2018 hydrological years. For example, Tributary 3 has higher TDP mean concentrations (1.93 mg/L), suggesting the significant relationship between having less crop residue and more intense tillage practices (Amarawansa et al., 2015; Donald et al., 2015). Furthermore, observed in all recession limbs of the hydrographs of both basins among the duration of the study, are the variances between the steepness of the regressions. Tributary 3 presents a fast and steady decline, suggesting heavy nutrient export; whereas; in the Mauvais Coulee basin, there is a slow gradual decrease in the recession limbs suggesting less export is occurring, correlating with having more crop residue.

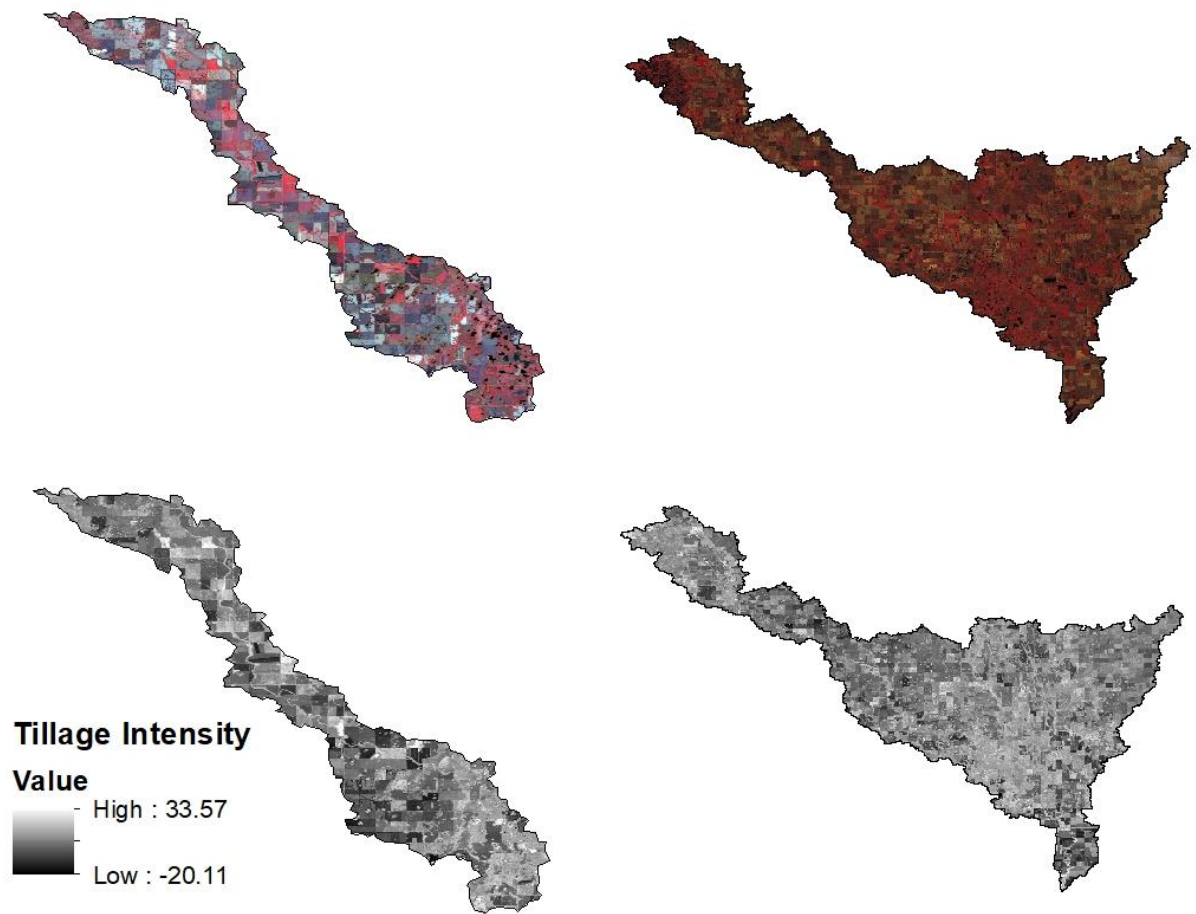


Figure 10. Landsat Series Imagery

Landsat Series Imagery to detect crop residue and tillage intensity for both Mauvais Coulee basin and Tributary 3 Landsat image was download from October 14, 2016 that presents land cover conditions prior to water data collection of 2017. The top row presents a false color of composite of infrared, red, and greens band for Tributary 3 and Mauvais Coulee basin. The bottom row presents the tillage indexes to estimate the amount of crop residue compared to exposed soils. Higher tillage intensity is indicated by the light gray to white areas compared to the low tillage intensity areas indicated by darker areas.

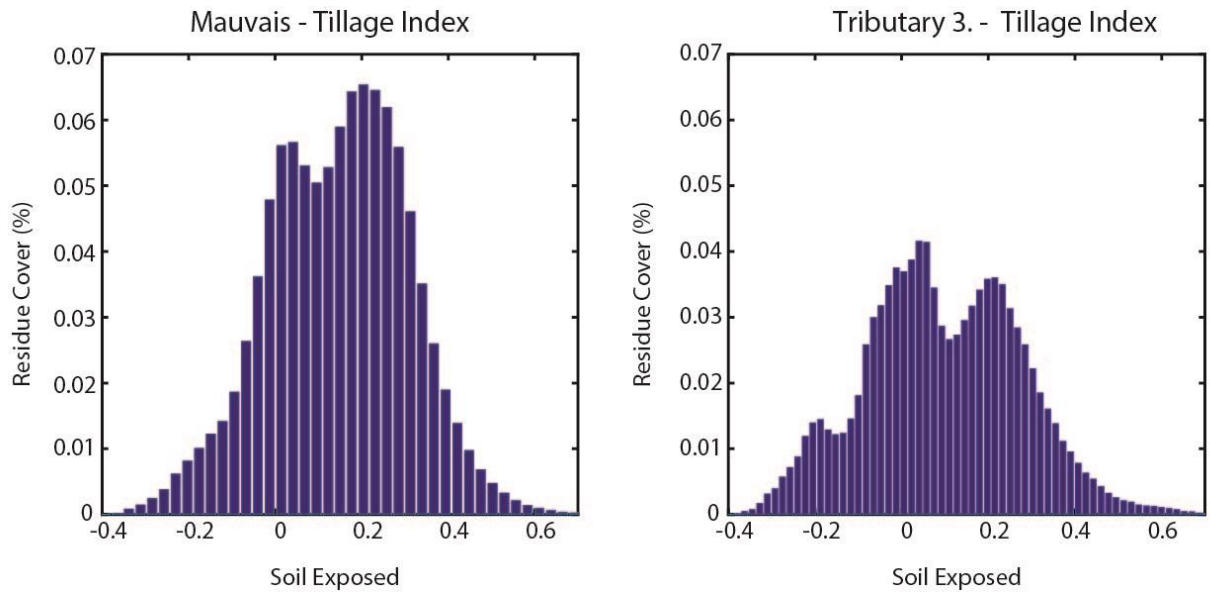


Figure 11. Tillage Indexes

Tillage Indexes of Mauvais Coulee basin and Tributary 3 for October 14, 2016. The y-axis shows crop residue while the x-axis shows soil exposure. The Mauvais Coulee basin presents more crop residue than exposed soil suggesting low tillage practices. Tributary 3 shows less crop residue and more exposed soils indicating more intense tillage practices.

CONCLUSIONS

The contribution of concentration to streamflow relationships to simulating nutrients were previously discussed in other studies around the world. However, very few studies mention nutrient export in cold regions agricultural basins. The objective of this study was to gain a better understanding of the impacts of hydroclimatic variation on concentration to streamflow relationships in the head of waters of the DLB while identifying the controlling factors of P exports using both field-based observations and hydroclimatic variability detected by physically based hydrologic simulations. Data suggests that hydroclimatic variations have strong correlations with nutrient export concentrations and total loads, but remains highly variable and inclusive for concentration to streamflow relationships.

- In-stream mean water chemistry showed considerable variation of TDP concentration between the Mauvais Coulee basin (0.92 and 1.16 mg/L for 2017 and 2018) and Tributary 3 (1.41 and 1.93 mg/L for 2017 and 2017). Across the Mauvais Coulee basin, the snowpack presented a low mean concentration of P (0.045 mg/L). Mean soil P concentration through the study sites were 38.07 mg/L while the maximum concentration can from the Mauvais Coulee basin of 95 mg/L and the minimum concentration of 6 mg/L. Thus, this study concludes that the soils are most likely the source of P observed in streamflow waters during major runoff events.
- This study presents the impacts of two years having contrasting hydroclimatic responses on P concentration and subsequent export. One year (2016-17) experienced high SWE, snowfall, maximum frozen soil conditions and thick basal ice layer. This wet year has low mean concentrations (0.92 and 1.41 mg/L for Mauvais Coulee basin and Tributary

3). However, these hydroclimatic conditions presented high total loads of P (106.01 and 46.58 kg/km² for Tributary 3 and Mauvais Coulee basin) during the spring snowmelt event. In contrast, a dry year (2017-18) had high concentrations (1.16 and 1.93 mg/L for Mauvais Coulee basin and Tributary 3) and low total export loads (8.77 and 2.26 kg/km² for Tributary 3 and Mauvais Coulee basin). This suggests that volume of meltwater runoff influences the load of nutrients, while the contact and opportunity of interaction time between meltwaters and thawed soils are crucial for concentration values (Figure 12).

- The impacts of hydroclimatic responses on concentration to streamflow relationships are inconclusive and are highly variable. During the wet year (2016-17), Mauvais Coulee basin presented a chemostatic relationship in rising limb and a strong soil flushing relationship in the recession limb. Tributary 3 recession limb had a consistent relationship. During the dry year (2017-18), Mauvais Coulee basin had a chemostatic relationship in rising limb and a soil flushing relationship in recession limb. In Tributary 3, a soil flushing relationship were observed in both the rising and recession limbs. This study suggests that the concentration to streamflow relationships observed in the rising limbs are highly influenced by the state of the soil conditions (frozen or thawed). Interestingly, between both years (2016-17 and 2017-18) we observe an extent of chemostatic behavior, where the dry year appeared to be less chemostatic than the wet year.
- Identification of tillage practices were presented in this study to serve as an alternate hypothesis. Tillage indexes identified more crop residue and less loosely exposed soils in Mauvais Coulee basin, while Tributary 3 had less crop residue and more loosely exposed

soils. Based on the loosely exposed soil and the source of in-stream P, these results correlate with having higher total loads and concentrations in Tributary 3 when compared to Mauvais Coulee basin. Although, some studies suggest that dissolved nutrients are derived from plant (crop residue) tissues, which would contradict this hypothesis. However, crop residues are not actually removed, but tilled in the surface of the agricultural fields, which would result with having a mixture of crop residue and loosely exposed soils at the surface readily available for meltwater erosion to transport nutrients during the spring snowmelt event.

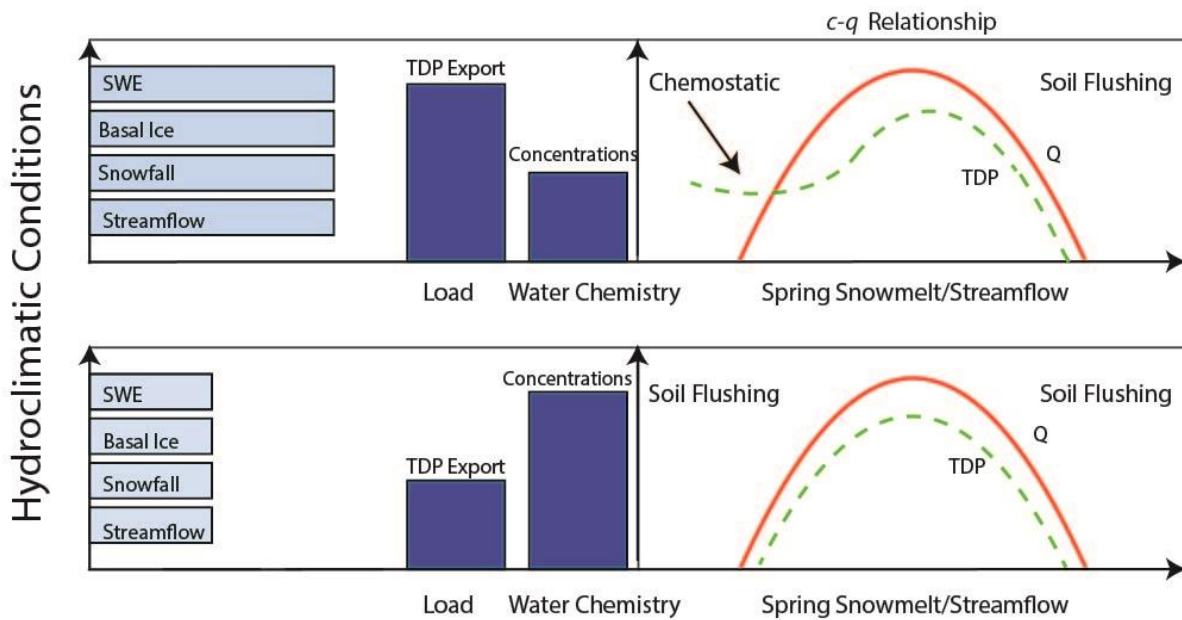


Figure 12. Hydroclimatic Nutrient Export Conclusions

Hydroclimatic responses on nutrient export during spring snow melt. (Top Row) High SWE, snowfall, streamflow, and the existence of a thick basal ice layer, results with high total TDP export loads, but low concentration values. These hydroclimatic responses present a chemostatic relationship in the rising limb and as melt continues and the existence of a basal layer decreases a soil flushing relationship appears in the recession limb. (Bottom Row) Low SWE, snowfall, streamflow, and the minimum existence of a basal ice layer results with a low total TDP load, but a high concentration value. These hydroclimatic responses with the lack of a basal ice layer create more contact and interaction opportunity time between meltwaters and soil, resulting in a soil flushing concentration to streamflow relationship.

FUTURE WORK

The insights to the concentration to streamflow relationship described in this study can be used for a variety of future projects. Although we believe we've done a good job with capturing nutrient export during spring snowmelt, we suggest that a higher-resolution of P data can be achieved using an automatic water sampler. An automatic sampler would help capture the nutrient export during the unpredictable summer rainfall events. Automatic samplers can also assist in providing multiple water sampling sites which can help identify the portions of the study area contributing the most P. These insights can forecast nutrient responses to future climate changes or land use scenarios. Observation data can be used to facilitate simple models that can predict how nutrients exports and enters the water system during spring snowmelt. It can also be used to develop a more complex numerical model that can estimate total load with anticipated performances. This study can be used to assist in the design and implication of new best land management practices while informing and educating the public.

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