SPATIOTEMPORAL DYNAMICS OF WATER QUALITY ANALYTES WITHIN AN INTENSELY MANAGED PRAIRIE WATERSHED

by

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ABSTRACT

A greater understanding of hydrological processes is needed to interpret spatial and temporal water quality dynamics, specifically within intensely managed prairie watersheds. This M.Sc. thesis looks at two years (2013 and 2014) of water quality and water level data, collected from 12 sub-watersheds outlets within the Catfish Creek Watershed (CCW). The CCW is located in southeastern Manitoba, is a tributary of Lake Winnipeg, and spans 642 km^2, with a near-even mix of forest and agricultural land.

The first data chapter (i.e., Chapter 2) analyzes correlations between each sub-watershed's weekly water quality parameters (electrical conductivity, nitrate and phosphate concentrations) and their characteristics (e.g., topography and morphology, land use and land cover, and geology). The second research chapter (i.e., Chapter 4) conducts concentration-discharge (c-q) analyses using daily water quality measurements from four sub-watersheds. Findings indicate that the water quality dynamics within the CCW are both spatially and temporally diverse.

Keywords: prairie watersheds, water quality, spatiotemporal variability, hysteresis, biogeochemical stationarity, antecedent moisture conditions, watershed characteristics, timescale effects.

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water quality analyte (i.e., EC, nitrate and phosphate).

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watershed and each water quality analyte (EC, nitrate, and phosphate). Each box has lines at the lower quartile (blue line), median (red line), and upper quartile (blue line) values, while the whiskers extend from each end of the box to show the extent of the rest of the data (minimum and maximum values). Outliers are shown as red plus signs.

CHAPTER 1
INTRODUCTION

1.1　GENERAL INTRODUCTION

Hydrology is a geoscience aiming to monitor and predict the occurrence, movement, and distribution of water from past to future timescales; these dynamics are determined by the interaction between water, the land and atmosphere (Dingman, 2002).   Hydrological understanding and models can be utilized for flood prediction and to mitigate water quality issues. Floods are caused when regional water storage is exceeded by precipitation or soil-water contributions (L. Li & Simonovic, 2002). Flooding in cold regions can be further intensified when rainfall or snowmelt events occur over a dense snowpack and frozen ground, i.e. impervious surfaces causing overland runoff (Gray, Toth, Zhao, Pomeroy, & Granger, 2001). Runoff can transport nutrients from land into surface waters, causing a change to a region's biogeochemistry in general, and water quality in particular (Cooper & Thomsen, 1988). While agricultural land practices involve the application of nutrients (e.g., fertilizers) to soil and crops to promote increased productivity, nutrients from the land can be transferred to water during rainfall and snowmelt events through overland and subsurface flow. Rainfall can fall directly in-stream, or can reach the stream by falling on land and flowing as overland, subsurface, or groundwater flow (Figure 1.1) (Daughtry et al., 2001; Garen & Moore, 2005); flow paths of special reference for nutrient transport will be further defined in Chapter 2. Hydrobiogeochemical processes – which control both water transport and contaminant transport – are highly spatially and temporally variable and therefore require comprehensive analysis in different regions around the world. Specifically, spatial control factors, temporal control factors, nonlinearity in hydrobiogeochemical dynamics, and data scarcity are the greatest challenges in predicting water quality within a watershed.
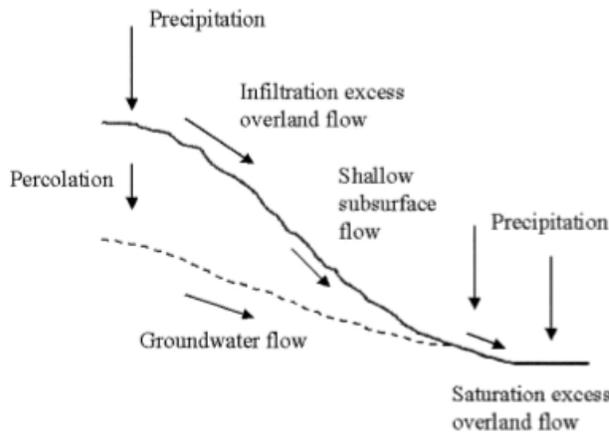
Figure 1.1: Generalized flow paths of precipitation from an input site to a stream (Garen & Moore, 2005).

There is generally a strong correlation between spatial watershed characteristics and water quality (i.e., nutrient concentrations, electrical conductivity, etc.); due to complex interactions between control factors, however, predicting hydrological and biogeochemical responses based on these characteristics is not easy (Bracken et al., 2013). For instance, adjacent land use practices are known to have a strong control on the hydrologic response of a waterbody; for example, if agriculture practices occur very close to the edge of a drain, additional erosion may occur due to the clear-cut removal of vegetation in the riparian zone (Dosskey et al., 2010; Schlosser & Karr, 1981). Vegetation within the riparian zone adds a buffer against erosion, and it also tends to decrease the downstream flow of water, thus increasing sediment and nutrient settling time (Dosskey et al., 2010; Schlosser & Karr, 1981), which can be valuable in linear, man-made drainage networks. An intensely managed watershed, as defined in the context of the current thesis, is a watershed that includes significant agricultural land as well linear, man-made stormwater-control infrastructure (e.g., surface drains and ditches, culverts, etc.). It has been commonly noted that agricultural and urban catchments experience high nutrient export, in comparison with forested catchments (Heathwaite, 1995; Johnson, Richards, Host, & Arthur,

1997; Lee, Hwang, Lee, Hwang, & Sung, 2009; Lenat & Crawford, 1994). Agriculture-intensive regions also generally have tile-drains installed within their fields, which allow soil water to drain faster into nearby drainage networks (Zaimes & Schultz, 2002). Topography also acts as an important driver for hydrological response within a watershed (Bracken et al., 2013) as it determines the flow path of water to the stream, and within the stream.

The temporal factors that influence water quality are also critically important. Indeed, hydrologic responses within a watershed are strongly determined by seasonality, storm characteristics (e.g., duration and magnitude), and antecedent moisture levels (Bracken et al., 2013). Those temporal influences are however complex and somewhat less understood than spatial influences. According to Liu et al. (2011), water quality in cold regions is most strongly influenced by factors related to snowmelt runoff volume (e.g., snow water equivalent, flow rate, and runoff duration), as opposed to land management practices, weather variables, and hydrologic variables. Liu et al. (2011) drew their conclusions from a study in the Canadian prairies where snowmelt-driven runoff dynamics are predominant due to the impenetrability of frozen soils that decrease infiltration and promote overland flow. In general, nutrient concentrations are highest during snowmelt (Bieroza & Heathwaite, 2015; Corriveau, Chambers, & Culp, 2013); however, snow accumulation is spatially dependent on surface roughness and buffers from wind, thus complicating the evaluation of temporal control factors (e.g., forests accumulate greater snowpacks than agricultural lands because the wind only minimally redistributes snow) (Buttle et al., 2016; Fang et al., 2007). The fact that water quality within a watershed does not always fluctuate simultaneously with flow (or water level) can, however, be relied on to infer hydrobiogeochemical processes. Indeed, there is generally a lag-time

associated with hydrological input (precipitation) and the biogeochemical response (Evans & Davies, 1998). Plotting water quality concentrations against time, although useful, cannot thoroughly explain how a watershed reacts to hydrological inputs. A hysteresis curve can be used to compare flow fluctuations with the concentrations of various chemical analytes: the shape and direction of the curve can indicate the source of stream water as either groundwater, soil water, or recent overland flow water; riparian water or hillslope water (Bieroza & Heathwaite, 2015; Bowes, House, Hodgkinson, & Leach, 2005; Evans & Davies, 1998). The concept of hysteresis is further defined in Chapter 4. It is often believed that dissolved in-stream nutrients follow an annual, seasonal, and event-based response curve to flow, that is predictable if watershed characteristics (e.g., topography, antecedent moisture conditions, etc.) are similar (Bond, 1979). In reality, however, it is unknown if hysteretic concentration-discharge behaviours are controlled by temporal factors, spatial factors, or a combination of both. As similar precipitation inputs and soil moisture conditions do not necessarily lead to a similar hydrological response (Bracken et al., 2013), it can be hypothesized that the prediction of biogeochemical response and water dynamics is not straightforward either.

By monitoring a watershed for at least a year, according to Blume, Zehe, & Bronstert (2007), a general sense of a watershed's reaction to hydrological inputs (e.g., rainfall and snowfall events) can be obtained. Event-based (temporal) and regional characteristic (spatial) monitoring will increase the understanding of their reaction. A weakness in many hydrobiogeochemical research studies is that generally only one of two sampling strategies are employed: i) high-frequency, single-year sampling at one site, or ii) low-frequency, multi-year sampling across multiple sites. As well, generally either i) event dynamics, or ii) seasonal and annual dynamics are studied. The

main reason for research being divided up in these ways is the cost (time, money) associated with water quality research, and therefore the choice of a given sampling strategy is based on research objectives, but also (and sometimes mainly) on functionality. High-frequency and long-term data are, however, important for a few reasons, namely that: i) a watershed is not a stationary and uniform entity, but rather undergoes continuous change (due to natural and anthropogenic factors), and ii) climate change has, and will continue, to alter watersheds throughout the world, and high-frequency data is vital for monitoring hydrologic responses to climate changes (Kirchner, 2006). Spatially diverse data is also necessary because no two sites are identical (Beven & Freer, 2001); processes that occur at a small scale are not necessarily transferable to a large scale by means of upscaling; as scale increases, homogeneity generally decreases (Kirchner, 2006). Lastly, it is worth mentioning that prairie landscapes and their low relief make quantifying runoff, discharge, and water quality fluctuations difficult. Fang et al. (2007) characterize the climate in the prairies with long periods of winter (approximately 4 to 5 months), large spring runoff events due to the frozen ground beneath melting snow, high antecedent moisture conditions due to deep soils, the largest rainfall events occurring in spring and early summer, dry mid-summer and fall conditions (e.g., decreased soil moisture, plant growth, evaporation, and runoff), and stream networks with poor drainage (e.g., stagnant water not contributing to major downstream river systems). More than 80% of the total annual runoff is traditionally assumed to occur during spring snowmelt (Corriveau et al., 2013; Gray & Landine, 1988). Intensively managed prairie watersheds are, however, characterized by flashy flows in all seasons due to engineered stormwater-control infrastructure (surface drains), which increase connectivity between riparian areas and the stream, as well as the connectivity between the upstream and downstream ends of a watershed. The extent to which those water management

practices determine short-term, medium-term, and long-term water quality dynamics prevailing in prairie watersheds remains unclear. As previously mentioned, the ecological and hydrological dynamics of a watershed can be greatly impacted by its land use (Dodds & Oakes, 2006; Poor & McDonnell, 2007; Sobonn, Paringit, & Nadaoka, 2007) and topography (Burt & Pinay, 2005; Fang et al., 2007; Ou & Wang, 2011), and this may be especially true in prairie landscapes due to the low relief (e.g., vegetation types and placement, surface water flow patterns, etc.) (Schlosser & Karr, 1981), particularly in relation to spring melt overland flow. Indeed, in addition to general watershed characteristics, snow and snowmelt have a dominant spatial control on the water quality in this region. Snow distribution is controlled mainly by wind and surface roughness (e.g., field stubble, trees, etc.). Land cover types with higher surface roughness will have greater amounts of snow accumulation (Fang et al., 2007); therefore, a forested region will have greater amounts of snow accumulation and simultaneously greater seasonal-spring melt runoff generation, than an agricultural region with fallow fields. Additionally, snowmelt atop frozen soils and nutrient loading are strongly correlated due to crop and other plant residues in contact with snowpacks. This explains why traditionally, spring melt-runoff dominated regions of the prairies have been associated with increased levels of nitrogen and phosphorus in their surface water bodies (Shrestha, Dibike, & Prowse, 2012), but those levels are achieved in a way that is not easily predictable.

1.2   RESEARCH OBJECTIVES AND ANTICIPATED SIGNIFICANCE

The main goal of this M.Sc. thesis was to conduct concurrent spatial and temporal studies of surface water quality along a network of nested prairie sub-watersheds, as a means to address

gaps found in previously mentioned studies. In 2013, Manitoba Infrastructure (MI) paired with the University of Manitoba (U of M) Geological Sciences department to monitor the Catfish Creek Watershed (CCW), an intensively managed prairie landscape where engineered stormwater-control infrastructure (surface drains) is prevalent and high nutrient loading from proximal agricultural practices was suspected. A current "hot" topic in Manitoba is the vulnerability of Lake Winnipeg, a large freshwater lake, which is experiencing blue-green algae blooms as a response to nutrient enrichment. Nutrients, such as nitrogen (N) and phosphorous (P) are examples of water quality analytes analyzed when the degradation of freshwater is suspected (Bieroza & Heathwaite, 2015; Buda & DeWalle, 2009; Heathwaite, 1995). Due to this degradation, Lake Winnipeg and its contributing waterbodies would benefit from the close monitoring of nutrient levels. Increasing nutrient levels can lead to eutrophication, which can cause permanent changes in the biodiversity and general structure of the region's ecosystem (e.g., oxygen depletion within the waterbody) (Harker, 1998; Shrestha et al., 2012). As the CCW is a tributary to Lake Winnipeg, its nutrient loading dynamics are of great significance in this region.

To further the understanding of spatial and temporal water quality analytes within prairie watersheds, the specific research objectives of this M.Sc. thesis were to examine a nested system of prairie watersheds in order to:

(1) Quantify the spatiotemporal variability of water quality parameters and identify any watershed characteristics that may control that variability, and

(2) Determine if water quality is influenced by different runoff processes at various temporal scales (seasonal, annual, rainfall events).

1.3 THESIS STRUCTURE

Two field seasons allowed the compilation of a comprehensive dataset, used to support the analyses presented in two original data chapters (i.e., Chapters 2 and 4) in this M.Sc. thesis. Chapter 2 addresses the spatiotemporal variability of water quality dynamics within the Catfish Creek Watershed (CCW). Chapter 3 is a synthesis that aims to preliminarily summarize Chapter 2, while also indicating the rationale behind Chapter 4 – the latter focusing on the temporal variability of water quality dynamics within the CCW. Both data chapters focus on three water quality analytes, namely electrical conductivity – which is a quasi-conservative tracer useful to infer dominant water flow paths – and nitrate and orthophosphate – which are two dissolved forms of the nutrients nitrogen and phosphorus, often associated with eutrophication issues. Finally, Chapter 5 is the synthesis and concluding section, aiming to bring together the conclusions issued at the end of the two data chapters, highlight the most significant findings, and identify potential areas of future investigation and research.

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CHAPTER 2
SPATIOTEMPORAL DYNAMICS WITHIN A PRAIRIE WATERSHED

2.1   ABSTRACT

Improving our understanding of how spatiotemporal characteristics control hydrological processes is required in order to reduce the cost (i.e., time, money) associated with routine monitoring efforts. This is especially true for intensively managed prairie watersheds, which are vulnerable to flashy flows due to engineered stormwater-control infrastructure (i.e., surface drains) and high nutrient loading from adjacent land use practices (i.e., agricultural fields). However, there have been very few studies of the spatiotemporal variability of water quality dynamics within intensively managed prairie watersheds. This study partially fills that gap, by comparing weekly water quality measurements obtained over a two-year period to regional watershed characteristics with a Spearman's rank correlation analysis. Water quality parameters included electrical conductivity (EC), nitrate and orthophosphate collected across 12 different surface water sites, while watershed characteristics were related to watershed topography and morphology (e.g., area, drainage density, mean elevation, elevation range, and mean slope), land use and land cover (e.g., percent of crop land, exposed land, forest land, shrub land, and wetland), and geology (e.g., percent of metamorphic or plutonic bedrock, percent of fine surficial materials, organic surficial materials, and plain surficial materials).   Various watershed characteristics appeared to control the spatial variability of water quality, although the nature and strength of those controls (i.e., correlations coefficients) were highly temporally variable. There was no single sub-watershed within the CCW, in either or both study years, that was a stable surrogate of average water quality dynamics. Multiple sites could, however, be identified as a hotspot or anti-hotspot, thus providing some guidance as to where, spatially, to sample in order to capture extreme conditions.

2.2 INTRODUCTION

Eutrophication is the nutrient enrichment of a waterbody that promotes the growth of plants and consequently depletes dissolved oxygen in the water (Harker 1998); hence it is a critical problem related to declining water quality in freshwater systems. Blue-green algae blooms can be caused by natural lake processes, but their presence is often attributable to an abundance of nitrogen (N) and phosphorous (P) (Buda & DeWalle, 2009; Haygarth, 2005; McCullough et al., 2012). While both N and P are considered the main nutrients responsible for the health (or lack thereof) of freshwater bodies (Bieroza & Heathwaite, 2015; Heathwaite, 1995), P is considered the most limiting nutrient (Fuchs, Fox, Storm, Penn, & Brown, 2009; Heathwaite, 1995). Both N and P can also occur naturally, but they are typically problematic when they are added in excessive quantities to aquatic systems by human activities, both at point sources (e.g., wastewater treatment facilities) as well as nonpoint sources (NPS) (e.g., diffuse surface runoff and subsurface leachate from agricultural fields) (Heathwaite, 1995; Jarvie et al., 2008; Munn, Frey, & Tesoriero, 2010).

Downstream water quality issues are likely to persist until the depletion of legacy nutrient stores diminish (Basu et al., 2010); even in low intensity NPS agricultural systems, N and P are thought to be key suppliers of the total nutrient loading to downstream water bodies and the main cause of eutrophication in many lakes and rivers (Buda & DeWalle, 2009; Heathwaite, 1995; Heathwaite & Dils, 2000; Poor & McDonnell, 2007; Untereiner, Ali, & Stadnyk, 2015). One reason why P loss from agricultural lands is so strongly related to eutrophication is that the critical concentration required for crop growth is 200-300 μg P L^{-1}, which is an order of

magnitude higher than the critical concentration for eutrophication control (10-20 µg P L^{-1}) (Heathwaite & Dils, 2000). As N and P nutrient concentrations increase within a waterbody, the following adverse effects can occur: the growth and abundance of potentially toxic algal blooms; the deoxygenation of waters leading to increased morbidity in fish and invertebrates; and the loss of biodiversity within the impacted waters (Heathwaite & Dils, 2000). While nutrient loading to waterways from point sources can generally be easily mitigated using engineering measures (Heathwaite, 1995), such is not the case for NPS; hence the importance of considering multiple runoff generation mechanisms – and travel pathways – via which water and nutrients move from land to streams.

Runoff is a broad hydrological term that is used to describe the downslope movement of water above or below the soil surface (Haygarth & Sharpley, 2000). Daughtry et al. (2001) states five important factors controlling runoff: (1) initial soil water content (i.e., antecedent moisture conditions (AMCs)), (2) physical properties of soil, (3) intensity and duration of precipitation events, (4) hydrologic properties of surface soil, and (5) subsurface stratigraphy. It is based on these five factors that travel time of water within a watershed can be inferred. Runoff can transport contaminants from land to surface waters, causing a change to a region's biogeochemistry. This biogeochemical change requires nutrient presence within the flow path, nutrient contact with runoff, and nutrient transport from land to stream (Heathwaite, 1995). According to Haygarth and Sharpley (2000), there are four main natural and human-driven runoff pathways transporting N and P from land to stream within, and above, the unsaturated zone: (1) natural matrix flow, (2) natural preferential flow, (3) natural overland flow, and (4) man-made land drainage. Under saturated conditions, however, groundwater flow is the major

pathway moving water from land to stream (Zaimes & Schultz, 2002). Flow paths are dependent on climatic conditions, soil and vegetation, and/or spatial and temporal scales. For instance, *overland flow* is the lateral movement of water atop the surface of the soil following rainfall (Haygarth & Sharpley, 2000) or snowmelt. When precipitation exceeds the soil's infiltration capacity, *infiltration excess overland flow* (or *Hortonian overland flow*) occurs (Garen & Moore, 2005). When precipitation falls on saturated soil, however, the water that immediately runs off is termed *saturation excess overland flow* (Garen & Moore, 2005). Near-surface soil moisture is an important control for determining runoff flow paths and nutrient movement potential (Grayson & Western, 1998). Overland flow is important for nutrients attached to sediment particles (Heathwaite, 1995), and it has been traditionally believed to be the most important runoff mechanism for P transport in particular (McDowell, Sharpley, & Folmar, 2001). However, recent studies (Allaire et al., 2011; Fernald & Guldan, 2006; Fuchs et al., 2009; Heathwaite, 1995) have shown that N and P losses in subsurface flow can be significant, especially when legacy nutrients are present in both shallow and deeper soil layers (Basu et al., 2010). *Matrix flow* is one example of such subsurface flow mechanism involving the uniform lateral soil water movement that is common in subsoil with higher porosity (e.g., sandy soils) (Haygarth & Sharpley, 2000). *Preferential flow* is rather the lateral or vertical soil water movement that increases the transport of nutrient-enriched water through soil macropores and cracks (Allaire et al., 2011; Haygarth & Sharpley, 2000). *Land drainage* is the lateral movement of water resulting from anthropogenic landscape alterations (Haygarth & Sharpley, 2000), especially surface ditches or tile drains in the subsurface (Zaimes & Schultz, 2002), and these stormwater control infrastructures have been shown to allow the movement of significantly larger amounts of nutrients than natural systems (King et al., 2015; Lam et al., 2016; Untereiner et al., 2015). As for *groundwater flow,* it

includes deep aquifer water movements to the stream (Garen & Moore, 2005) and is usually not important for nutrient transport over short timescales unless said nutrients can bypass the unsaturated zone and reach the water table. The contribution of N and P to streams due to groundwater flow is based on the dilution of the pre-event ground waters and the flow path (Maulé & Stein, 1990; Peterjohn & Correll, 1984).

Land and stream conditions are extremely temporally and spatially dynamic, making the understanding of a watershed's hydrological processes challenging (Heathwaite & Dils, 2000; Ou & Wang, 2011). Hydrobiogeochemical processes – namely runoff generation mechanisms and biogeochemical transformations that control the mobilization and transport of nutrients – are also spatially and temporally dynamic, and therefore require comprehensive analysis in different regions around the world. Particular factors, such as topographic characteristics (e.g., watershed size (drainage area) and shape, elevation, and slope), geological characteristics (e.g., soil types and properties), and land use and land cover types (e.g., crop, forests, and wetlands) have been identified as key controls on runoff and water quality dynamics, together with precipitation amount, intensity, and duration (Fang et al., 2007; Heathwaite, 1995; Y. Li, Wang, & Tang, 2006; Poor & McDonnell, 2007). For instance, high-elevation, steep slope areas tend to be sources of runoff, while low-elevation, low-slope areas (such as valleys) tend to be runoff receptors and have the potential to act as sources or sinks of nutrients (Burt & Pinay, 2005; Untereiner et al., 2015). Another example of critical property is drainage density, which is the total stream length per basin unit area (Townsend, Dolédec, Norris, Peacock, & Arbuckle, 2003): it is determined by elevation and slope patterns and has a strong impact on the timing of water delivery to the watershed outlet (Fang et al., 2007; Ou & Wang, 2011). Streamflow and

streamwater quality are also linked to land use and land cover patterns (Dodds & Oakes, 2006; Poor & McDonnell, 2007; Sobonn et al., 2007), which help differentiate the effects of natural vegetation from those of human activities on hydrological and biogeochemical dynamics (Lee et al., 2009). The majority of the research concludes that nutrient concentrations are highest in streams draining agricultural (crop) land, likely due to runoff events mobilizing previously applied fertilizers (Heathwaite, 1995; Lenat & Crawford, 1994), and/or altering soil conditions (Lee et al., 2009). Tong and Chen (2002) indicated that the proportion of crop land within a watershed is strongly positively correlated with electrical conductivity, and moderately positively correlated with nitrate and phosphate concentrations, while forest land is negatively correlated with nitrate and phosphate concentrations. Studies noted in Poor and McDonnell (2007) showed that nitrate concentration is positively correlated with streamflow rates. However, such correlations are not present everywhere and are sometimes difficult to identify due to the simultaneous influence of land use and other watershed characteristics on hydrological and biogeochemical dynamics, an issue that is particularly present in the Canadian prairies.

In comparison to other systems around the World, the prairies are not a well-studied area (Dodds & Oakes, 2006), making it difficult to identify spatial controls on water quality dynamics (Untereiner et al., 2015). This ecozone extends through parts of central Canada and the United States, and faces unique challenges regarding water quantity management and water quality mitigation due to its generally flat topography, colder climate, and the presence of artificial drainage (Boland-Brien, Basu, & Schilling, 2014). The Canadian prairie landscape, in particular, is characterized by formerly glaciated depressions (Fang et al., 2007) but has a generally low relief, making the quantification of runoff, discharge, and water quality fluctuations difficult.

Snowmelt and event runoff in intensively managed prairie landscapes are probably dependent on land use type, micro-scale topography (e.g., sloughs and wetlands), soil characteristics (e.g., sandy versus clay-rich soils) and man-made infrastructure (e.g., man-made drains), but the relative importance of those factors remains unknown (Zaimes & Schultz, 2002). Indeed, the Canadian prairies are characterized by long and cold winters (approximately four to five months), fast spring runoff rates atop frozen ground, and highly variable moisture conditions due to deep soils and recurrent floods and droughts. The largest rainfall events typically occur in spring and early summer while dry mid-summer and dry fall conditions prevail (i.e. decreased soil moisture, plant growth, evaporation, and runoff). Previous studies have argued that more than 80 percent of the total annual prairie runoff occurs during spring snowmelt (Corriveau et al., 2013; Gray & Landine, 1988), but a more recent study has put forward a decreased number of ~50% for the past few years due to climate change (Dumanski, Pomeroy, & Westbrook, 2015). Because of the relatively flat regional topography, stream networks with poor drainage are common, with significant amounts of stagnant water not contributing to major downstream river systems (Fang et al., 2007; Gray et al., 2001; Grayson & Western, 1998). In addition to the excess moisture problems and delayed land seeding associated with this situation, slow-draining fields are more likely to mobilize nutrients from crop residues or shallow soils and enhance nutrient loss (Dodds & Oakes, 2006; Zaimes & Schultz, 2002). To remedy that situation, engineered stormwater-control infrastructure in the form of artificial surface drainage ditches and sub-surface tile drains has been added in the last century to increase connectivity between in-lands, riparian areas and streams, as well as the connectivity between the upstream and downstream ends of watersheds (Boland-Brien et al., 2014). As a result, intensively managed (or engineered) prairie watersheds are characterized by fast flows through artificial drainage

channels in all seasons, and the extent to which the role of natural watershed characteristics on NPS pollution can still be discerned despite how unclear the uniform artificial drainage of the landscape is (Boland-Brien et al., 2014; Heathwaite, 1995). The current study therefore aimed to advance our understanding of how watershed characteristics control nutrient concentration variability across highly anthropogenically-impacted prairie watersheds. In addition to the fact that both natural landscape factors and human factors might impact water quality dynamics, there is also a lot of temporal variability in runoff generation processes, thus raising the question of whether the same spatial factors are the most important for water quantity and quality dynamics all year long as runoff processes change seasonally. Three specific research objectives were addressed, namely:

(1) Quantify the spatiotemporal variability of water quality across a system of nested prairie watersheds,

(2) Assess if it is possible to find Catchment Average Water Quality Monitoring (CAWQM) sites that exhibit behaviour representative of entire watersheds, and,

(3) Identify the watershed characteristics that control the spatial variability of water quality and the temporal persistence of these controls.

2.3   METHODS

2.3.1 Study Area

The 642 km² Catfish Creek Watershed (CCW) is located approximately 100 km northeast of the city of Winnipeg (Manitoba, Canada) (Figure 2.1a). This region of the Canadian prairies is characterized by a relatively short open water season from approximately late-April (spring thaw) to early-November (fall freeze-up). The Manitoba Conservation Fire Program (MCFP, 2014) was the only agency collecting weather data in the CCW prior to 2013. Average January temperature was -13.7°C and average July temperature was 24.3°C (temperature measured daily at 1300 hrs local time).
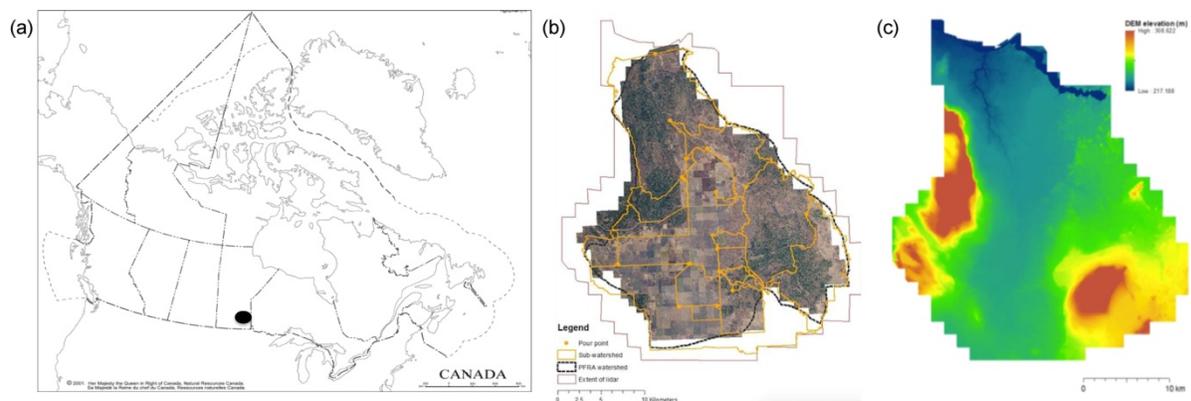
Figure 2.1:   The Catfish Creek Watershed's (CCW) (a) location within Canada, (b) sub-watershed boundaries, and (c) topographic relief map.

Seasonality plays a large role in this watershed, as most precipitation occurs as rainfall during the spring to fall period (with the majority of rainfall occurring from May to early-July), and a lesser amount of precipitation occurs as snowfall during the winter months.   The Manitoba

Conservation Fire Program calculated an average annual rainfall of 459 mm (from 1999-2013), with approximately 25% of this precipitation occurring in June. Furthermore, using the same dataset, the minimum annual rainfall recorded was 271 mm, and the maximum was 669 mm (MCFP, 2014). No historic snowfall data were available from MCFP. During the spring, when melt initiates, infiltration allows snow to recharge soil moisture and groundwater storage, and surface runoff replenishes surface water bodies (Shanley & Chalmers, 1999). Spring flooding is also commonplace, as available melt water often exceeds the infiltration capacity of frozen soils and overland flow occurs (Shook, Pomeroy, & van der Kamp, 2014). The CCW includes a near-even mix of forest and agriculture (crop) land (Figure 2.1b); it has a heterogeneous topography (e.g., flat, hilly) and contains a number of man-made surface drains in both its agricultural and forested portions (Figure 2.1b). This region is representative of many agricultural landscapes in the prairie ecozone, with a maximum topographic relief of 91.4 m and an average slope of 2.5% (Figure 2.1c). The agricultural regions are primarily planted with row and small grain crops. The two main man-made drainage channels are referred to as Main Drain 1 and Main Drain 2, while other smaller order drains include Side Drain, Heckert Drain, and Stead Drain (Figure 2.1b).

In 2013, 12 sites corresponding to the outlets of 12 sub-watersheds within the larger CCW were chosen for gauging and water sampling (Figure 2.2). Those 12 sites were chosen not only to span a range of drainage areas, but also to offer the opportunity to contrast water quality in sub-watersheds that had either a predominantly forested or agricultural land cover, as well as different distributions of elevation, soil types, etc. See Appendix B, Figures 1-4 for photos of four of the twelve sub-watershed outlets. The Catfish Creek is a tributary of Lake Winnipeg, as it drains directly into Traverse Bay at sub-watershed 1 (Figure 2.2). Sub-watershed 1 is the

outlet for the overall CCW (Appendix B-Figure 1) that also experiences backflow from Traverse Bay, thus complicating water quality prediction. The CCW has mostly organic surficial materials (Figure 2.2, Appendix A): the northern region of the watershed, near the outlet, has poorly draining shallow peat and gleyed dark grey clay soils, while the more southern extents of the CCW include poorly draining deep peat complexes and shallow peat soils, as well as a mixture of imperfect to poorly draining clays, tills, and organic soils in the southeast (CanSIS, 1967). The underlying bedrock in the CCW is mostly metamorphic (Appendix A) (AAFC, 2014). Further details about the 12 sub-watersheds can be found in Figure 2.2 and Appendix A.

Table 2.1 (Summary): Topographic characteristics for each of the 12 monitored sub-watersheds within the CCW (modified from Petzold, 2015).

Sub-Watershed #	Site Sample Collection Intensity	Sub-Watershed Topographic Characteristics				
		Area	Drainage Density	Elevation Mean	Elevation Range	Slope Mean
		km^2	m/m^2	m	m	%
1	High	642	0.000570	238	91.4	2.50
2	Low	293	0.000638	238	86.0	1.88
3	Low	175	0.000413	243	83.8	2.95
4	Low	251	0.000664	241	85.6	2.05
5	Moderate	145	0.000390	246	80.9	2.93
6	Moderate	22.6	0.000674	240	83.3	1.92
7	Low	126	0.000602	249	38.2	2.04
8	Low	595	0.000984	235	36.5	1.70
9	Low	107	0.000488	245	80.8	2.02
10	Low	345	0.000940	249	72.7	2.80
11	Low	327	0.000783	250	76.5	2.50
12	Low	0.560	0.000000	238	11.7	3.51
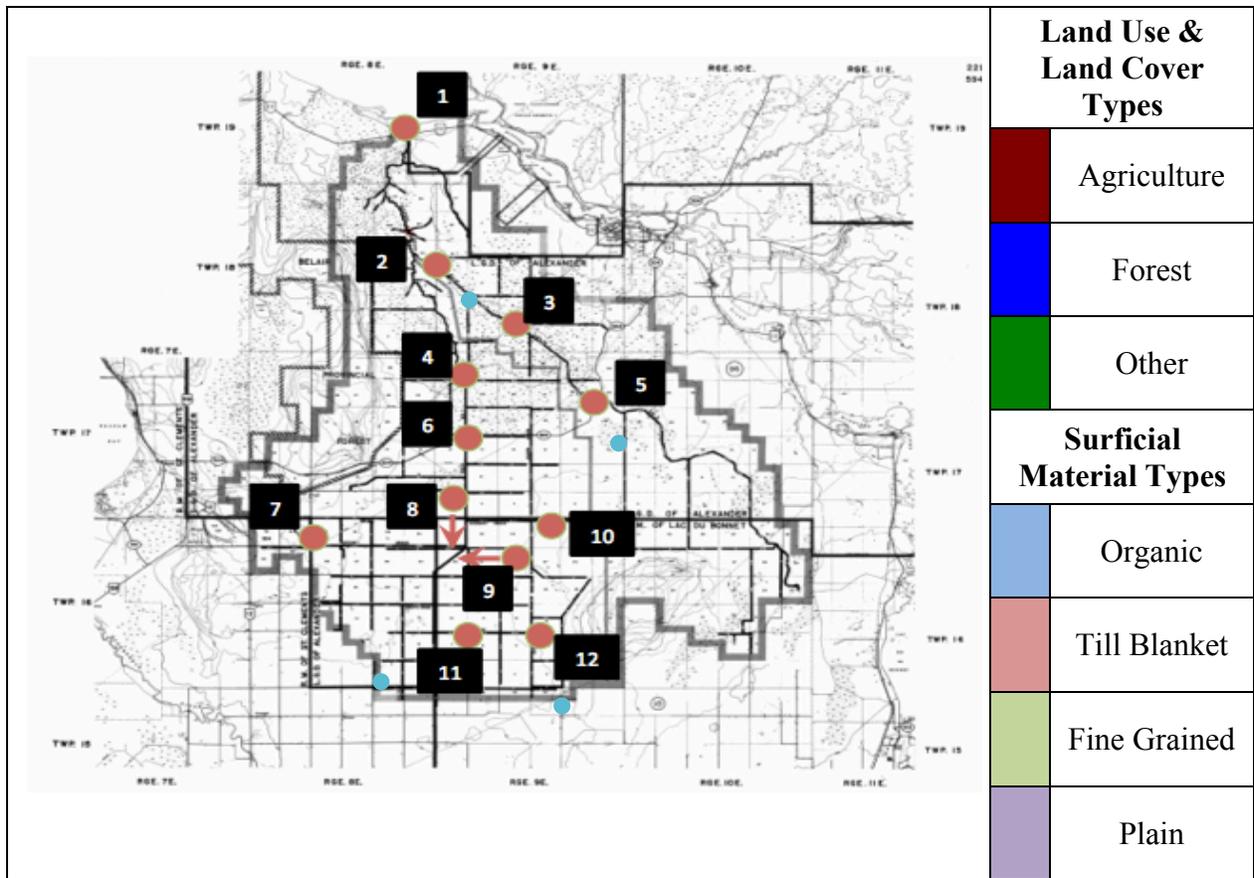
Site	Land Use & Land Cover Types	Surficial Material Types	Site	Land Use & Land Cover Types	Surficial Material Types
1			2		
3			4		

Site	Land Use & Land Cover Types	Surficial Material Types	Site	Land Use & Land Cover Types	Surficial Material Types
5			6		
8			8		
9			10		
11			12		
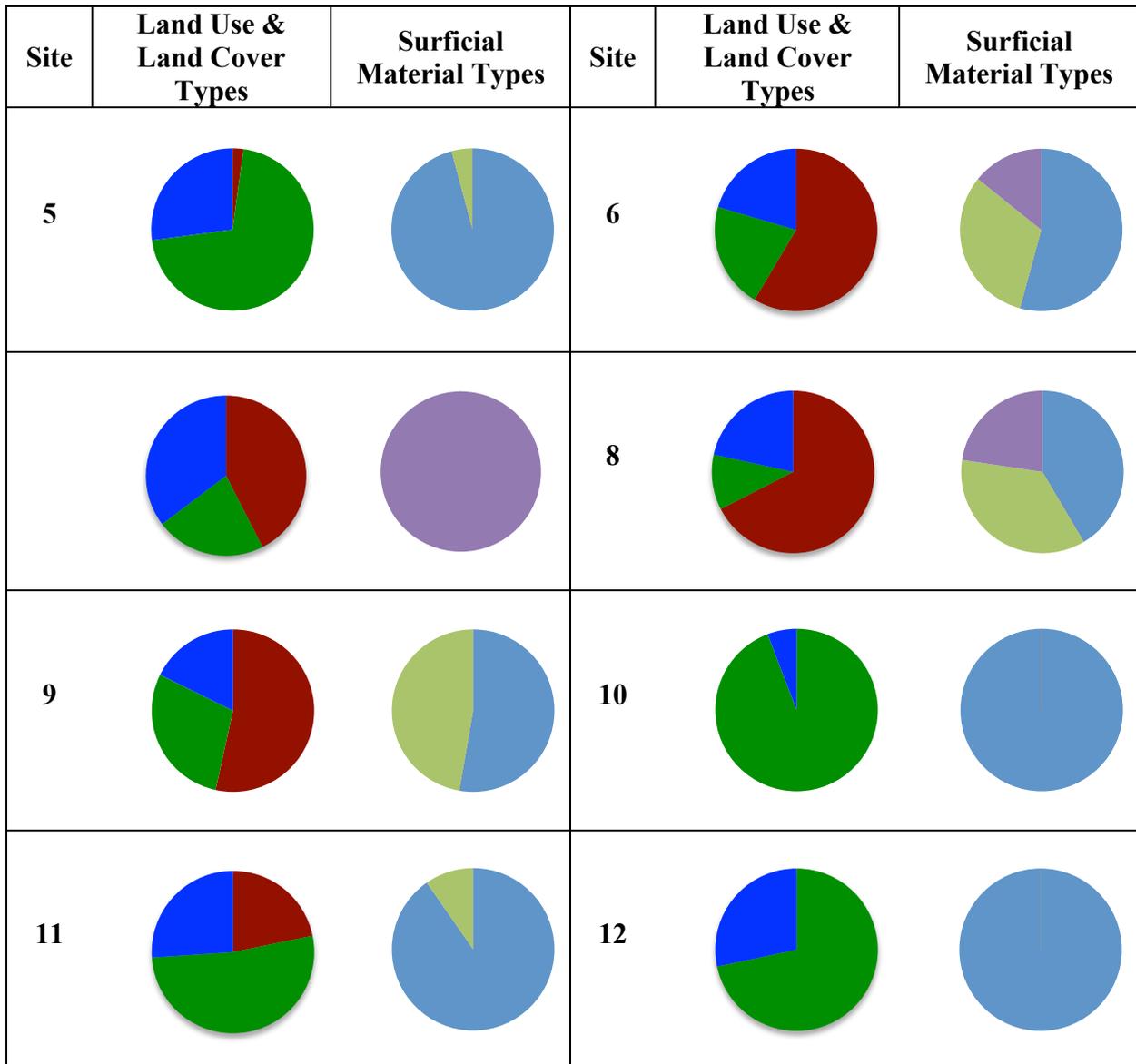
Figure 2.2: Study sub-watershed characteristics (n = 12). Each sub-watershed has a pie chart indicating the percentage of land use that is agricultural (crop), forested, or other (including exposed land, developed land, water, wetland, and shrub land), and a pie graph indicating the percentage of soil that is made of organic, till blanket, fine grain and/or plain materials. The base map is a Water Resources Branch map of the CCW constructed drains (MIT, 2012). On the top map, the location of each sub-watershed outlet is marked with a red dot, and the location of each weather station is marked with a blue dot.

2.3.2 Data Collection, Laboratory Analysis, and Data Analysis

Weather, water level and water quality data were collected through the 2013 and 2014 open water seasons. Throughout the CCW, four weather stations (HOBO U30/NRC Weather) were deployed in 2013 (Figure 2.2): they rely on HOBOlink technology to monitor, record, and upload data from temperature, wind speed, wind direction, and precipitation smart sensors at a 1-minute frequency. At the 12 outlet sites selected across the watershed, Odyssey Capacitive Water Level Loggers calibrated in the laboratory were placed within stilling wells in the drainage channels to monitor surface water level fluctuations at a 15-minute frequency. Surface water samples were collected from spring thaw to winter freeze-up at three different types of outlet sites, namely: (a) high-intensity sites (n = 1, 7-hour frequency), (b) moderate-intensity sites (n = 2, 1-day frequency), and (c) low-intensity sites (n = 9, ~7-14-day frequency) (see Table 2.1 and Appendix A for details pertaining to each sub-watershed and its sampling regime). While grab samples (collected around mid-day on Wednesdays) were used for the nine low-intensity sites, the three high- and moderate-intensity outlet sites were equipped with Hach Sigma^{TM} electronically-controlled, battery-operated automatic samplers (autosamplers): those samplers feature 24 polyethylene bottles (500 mL), a battery that lasts a minimum of 30 days, programmable timing and volume for sample collection, and a rinse cycle to allow for the flushing of the intake line between samples. The autosampler at the high-intensity outlet site was programmed to collect one sample every 7 hours, whereas the autosamplers at the two moderate intensity outlet sites collected a daily composite sample in each bottle, with half of the bottle being filled at 6:00 am and the other half at 6:00 pm. On a weekly basis, the automatic water samplers were visited and sample bottles were collected and replaced with clean bottles. Water

level data collection was delayed in 2013 until April 28, due to loss of water level loggers to ice jamming experienced during the spring freshet.

All collected surface water samples were tested in the field, right upon collection or retrieval, for electrical conductivity (EC) using a Eutech Instruments Multi-Parameter PCSTestr 35. Samples were then kept cool during transport back to the laboratory located at the University of Manitoba where they were filtered using a 0.45 μm membrane within 24 hours of collection. An U.S. Environmental Protection Agency (EPA)-compliant colorimeter (LaMotte Smart3) and associated reagents were used to test each filtered sample for orthophosphate (hereafter referred to as phosphate) and nitrate concentrations. Laboratory quality assurance and quality control procedures, heavily inspired by the United States Environment Protection Agency Water Chemistry Laboratory Manual (USEPA, 2004), were followed to ensure accuracy. Throughout the 2013 and 2014 field seasons, 1657 samples were collected and analyzed for EC, nitrate, and phosphate concentrations. In accordance with the USEPA, for every 100 samples, one filter blank was created by passing deionized water through a syringe filter, and for every 20 samples, one field blank was also produced by testing unfiltered deionized water as a test sample. In total, 18 filter blanks and 83 field blanks were created, and no phosphate and nitrate concentrations were measured in the deionized water pre- or post-filtering. Additionally, for every 20 samples, one field duplicate (i.e., two samples taken from the same site at the same time to be tested separately) and one lab replicate (i.e., a single field sample divided into two aliquots to be tested as two samples) were created. Eighty-five field duplicates were used to evaluate the analysis process, and an average percent difference between EC, nitrate, and phosphate duplicates was 1.52%, 15.09%, and 15.85% respectively. Eighty-seven field samples were split to obtain 174 lab replicates, and an average percent difference between EC, nitrate, and phosphate replicates

was 2.49%, 15.45%, and 11.91%, respectively. Due to the high number of samples considered, these reported average percent differences do not demonstrate significant errors in sample collection or within the analysis process.

To address the first research objective outlined in this chapter's introduction (i.e., quantify the spatiotemporal variability of water quality across a system of nested prairie watersheds), water quality analytes (e.g., EC and nutrient concentrations) were compared at each site for samples taken at approximately the same time every week. Descriptive statistics (i.e., minimum, maximum, mean, median and standard deviation) of EC and nutrient concentrations were also computed and boxplots were built to look at the differences in the statistical distribution of water quality concentrations. To assess the presence of consistent hotspots (i.e., sites with water quality concentrations consistently higher than the CCW mean) or anti-hotspots (i.e., sites with water quality concentrations consistently lower than the CCW mean), the percent difference between site-specific water quality concentrations and the CCW mean water quality concentrations (i.e., average across all 12 sub-watershed sites) was computed on a weekly basis. Below find the two equations utilized to compute percent difference, where C_x is the concentration of a given chemical analyte at sub-watershed x:

$$\text{Mean Concentration (C) across the CCW} = \frac{1}{n}(C_1 + C_2 + ... + C_n)$$

$$\text{Percent Difference} = \frac{\text{Site Specific Concentration}}{\text{Mean Concentration (C) across the CCW}} \times 100$$

Percent differences were also useful to assess whether one, or multiple sites, could be considered as average characteristic long-term monitoring site for water quality (second research objective), (i.e., sites that are always reflective of the average dynamics of the CCW, and hence their percent difference from the CCW mean is always close zero). Indeed, percent differences provided a way to look at the relative variability of water quality analytes, in addition to the absolute variability characterized in a more traditional manner using descriptive statistics. Sites with consistently null, or close to null, percent differences from the CCW mean were identified as Catchment Average Water Quality Monitoring (CAWQM) sites.

To address the third research objective outlined in the introduction (i.e., identify the watershed characteristics that control the spatial variability of water quality and their persistence in time), a correlation analysis was performed to assess the relationship between the water quality parameters (EC, nitrate and phosphate concentrations) measured at the 12 outlet sites and the characteristics of the sub-watersheds upstream of the 12 outlet sites. This correlation analysis was performed on a weekly basis to detect potential changes, in time, in the controls exerted by watershed characteristics on water quality. Here the decision was made to focus on weekly dynamics in order to use all data collected at low-intensity outlet sites; as a result, the samples from the high- and moderate-intensity sites included in the present analysis were taken on the same day as the low-intensity sites' samples. The Spearman's rank correlation coefficient rather than the Pearson correlation coefficient was used since it does not assume normal distribution of the data, and does not presume the presence of linear relationships between pairs of variables (Sokal & Rohlf, 1997). The watershed characteristics considered for that correlation analysis were related to watershed topography and morphology (e.g., area, drainage density, mean

elevation, elevation range, and mean slope), land use and land cover (e.g., percent of crop land, exposed land, forest land, shrub land, and wetland), and geology (e.g., percent of metamorphic or plutonic bedrock, percent of fine surficial materials, organic surficial materials, and plain surficial materials) (Table 2.1, Figure 2.2). The correlation coefficients that were statistically significant at the 95% level (p-value<0.05) were the only ones retained for interpretation. Maps, descriptive statistics, boxplots, percent differences and correlations were built or computed for 2013 and 2014 separately to assess potentially different dynamics between a normal year (2013) and a wetter-than-average year (2014).

2.4   RESULTS

2.4.1 Absolute and Relative Variability of Water Quality Analytes

Distinct weather patterns were experienced in each of the study years: the CCW received 271 mm of rainfall in 2013 (MCFP, 2013) and 530 mm of rainfall in 2014 (MCFP, 2014). In 2013, short-lived convective storms that are typical of the prairies were predominant while 2014 was a flood year associated with successive frontal systems that led to multiple days of heavy rainfall, particularly in June and July. Due to more precipitation in 2014, all drainage channels had a larger range in water levels and a higher average water level, compared to 2013 (Table 2.2). The concentrations of each water quality analyte were highly variable over the study period, not only spatially, but also temporally (Table 2.2, Figure 2.3).

EC concentrations were higher in 2013 compared to 2014 across the majority of the sub-watersheds, as opposed to nitrate and phosphate concentrations that were generally lower in 2013 compared to 2014. In 2013, very few EC outliers were seen, with the vast majority of values falling within the interquartile range (Figure 2.4); however outliers were present for EC concentrations in 2014, as well as for nitrate and phosphate concentrations in both 2013 and 2014. For all sub-watersheds, a greater range in nitrate and phosphate concentrations were experienced in 2014, compared to 2013 (Table 2.2, Figure 2.4). Sub-watershed 5, a moderate-intensity monitoring site, experienced a significantly greater range of water level fluctuation in 2013 (inverse to the rainfall inputs to the watershed), while sub-watershed 1, a high-intensity outlet monitoring site, experienced a significantly greater range in water level fluctuation in 2014 (concurrent with the higher rainfall inputs to the watershed).

The range of nitrate concentrations observed at sub-watershed 5 were also greater in 2013 than in 2014, although the average was lower in 2013. For phosphate, however, the concentration range and average were very similar in both monitoring years (2013 and 2014). As for sub-watershed 1, its nitrate and phosphate range and average concentrations were much higher in 2014 than in 2013, thus highlighting that the impact of a normal versus a wet year was not reflected in a uniform fashion in the behaviour of all sub-watersheds within the CCW.

Figure 2.5 shows the percent difference from the weekly CCW mean concentration for each sub-watershed and each water quality analyte (i.e., EC, and nitrate and phosphate concentration). Towards the identification of CAWQM sites, the ideal boxplots – demonstrating that a sub-

watershed outlet has a response illustrative of average watershed conditions – would be those which have a small box (indicative of small intra-annual variability), and a median (red line on Figure 2.5) that is close to the 0 percent difference line (black horizontal line on Figure 2.5). For EC, potential CAWQM sites for 2013 and 2014 were the outlets of sub-watersheds 4 and 10, respectively. For nitrate, the best candidates for CAWQM sites for 2013 and 2014 were the outlets of sub-watersheds 1 and 12, respectively. However, while sites 1 and 12 had a median nitrate value that was close to the watershed mean, they showcased rather high intra-annual variability. For phosphate, the best candidates for CAWQM sites for 2013 and 2014 were the outlets of sub-watersheds 11 and 7, respectively, although those also showed a considerable amount of intra-annual variability.

Table 2.2: Descriptive statistics for water quality and surface water level based on weekly data for all sub-watersheds in 2013 and 2014.

Sub-Watershed #	# of Weeks	EC (µS)	Nitrate (ppm)	Phosphate (ppm)	Water Level (m)	Water Level /Channel Depth	Statistics	EC(µS)	Nitrate (ppm)	Phosphate (ppm)	Water Level (m)	Water Level /Channel Depth	# of Weeks
		119.50	0.01	0.01	208.00	0.15	**Min**	118.10	0.01	0.01	257.00	0.18	
		309.00	5.72	0.20	1458.00	1.02	**Max**	339.00	6.25	0.47	4230.00	2.95	
1	24	191.93	0.51	0.04	784.46	0.55	**Mean**	247.75	0.68	0.11	1106.73	0.77	21
		152.15	0.13	0.01	784.00	0.55	**Median**	260.00	0.14	0.05	1182.00	0.83	
		72.34	1.25	0.05	203.24	0.14	**STD**	64.16	1.47	0.14	397.29	0.28	
		314.00	0.01	0.01	93.00	0.07	**Min**	435.00	0.01	0.01	0.00	0.16	
		1040.0	9.37	0.39	1056.00	0.80	**Max**	556.00	1.67	0.75	273.00	0.21	
2	17	694.76	0.87	0.07	269.72	0.20	**Mean**	486.00	0.80	0.43	0.00	0.05	5
		681.00	0.04	0.03	243.00	0.18	**Median**	472.00	1.14	0.54	0.00	0.07	
		226.02	2.27	0.10	126.05	0.10	**STD**	49.86	1.47	0.35	110.11	0.08	
		215.00	0.01	0.01	224.00	0.19	**Min**	234.00	0.01	0.01	0.00	0.00	
		557.00	1.50	0.40	815.00	0.69	**Max**	264.00	0.75	0.11	1548.00	1.32	
3	7	389.29	0.26	0.12	624.23	0.53	**Mean**	247.00	0.26	0.04	611.02	0.52	3
		408.00	0.01	0.01	680.00	0.58	**Median**	243.00	0.01	0.01	663.00	0.56	
		150.28	0.61	0.18	164.89	0.14	**STD**	15.39	0.43	0.06	348.35	0.30	
		298.00	0.01	0.01	353.40	n/a	**Min**	160.00	0.01	0.01	0.00	n/a	
		556.00	0.26	0.13	3312.90	n/a	**Max**	602.00	3.74	0.95	2704.00	n/a	
4	11	460.64	0.06	0.05	738.33	n/a	**Mean**	505.89	0.66	0.26	345.75	n/a	19
		487.00	0.01	0.03	646.00	n/a	**Median**	530.00	0.09	0.15	93.00	n/a	
		85.71	0.09	0.04	518.20	n/a	**STD**	121.35	1.11	0.27	581.23	n/a	
		174.00	0.01	0.01	338.30	0.20	**Min**	188.70	0.01	0.01	175.00	0.10	
		561.00	3.96	0.18	2553.20	1.49	**Max**	305.00	3.39	0.20	1951.00	1.13	
5	22	325.11	0.34	0.05	620.17	0.36	**Mean**	235.91	0.75	0.07	781.01	0.45	20
		307.00	0.04	0.03	494.10	0.29	**Median**	229.00	0.33	0.04	663.00	0.39	
		117.50	0.85	0.05	385.04	0.22	**STD**	30.18	0.96	0.07	446.19	0.26	
		448.00	0.01	0.01	284.90	0.09	**Min**	198.60	0.01	0.01	165.00	0.05	
		1642.00	2.16	0.11	809.00	0.26	**Max**	756.00	4.27	1.00	5156.00	1.67	
6	19	628.57	0.16	0.03	412.42	0.13	**Mean**	535.68	0.67	0.27	677.97	0.22	20
		605.00	0.03	0.02	374.70	0.12	**Median**	539.50	0.18	0.22	516.00	0.17	
		245.53	0.45	0.03	107.38	0.03	**STD**	133.65	1.08	0.28	517.25	0.17	
		306.00	0.01	0.19	6.00	0.01	**Min**	144.10	0.01	0.01	17.00	0.02	
		440.00	4.49	0.27	785.00	0.88	**Max**	406.00	2.16	0.38	947.00	1.06	
7	3	389.67	1.60	0.23	87.99	0.10	**Mean**	332.15	0.21	0.15	115.90	0.13	13
		423.00	0.31	0.22	61.00	0.07	**Median**	353.00	0.01	0.1	84.00	0.09	
		72.95	2.50	0.04	76.99	0.09	**STD**	77.01	0.62	0.14	119.71	0.13	
		400.00	0.01	0.01	0.00	n/a	**Min**	178.30	0.01	0.01	53.00	n/a	
		1014.00	0.22	0.09	382.30	n/a	**Max**	1489.0	3.04	0.94	5287.00	n/a	
8	6	738.00	0.06	0.03	11.63	n/a	**Mean**	657.01	0.42	0.41	681.87	n/a	22
		699.50	0.03	0.01	0.00	n/a	**Median**	594.50	0.01	0.29	203.00	n/a	
		230.92	0.08	0.03	77.72	n/a	**STD**	319.24	0.88	0.31	1306.42	n/a	

Sub-Watershed #	# of Weeks	2013 Weekly Samples					Statistics	2014 Weekly Samples					# of Weeks
		EC (µS)	Nitrate (ppm)	Phosphate (ppm)	Water Level (m)	Water Level /Channel Depth		EC(µS)	Nitrate (ppm)	Phosphate (ppm)	Water Level (m)	Water Level /Channel Depth	
9	10	453.00	0.01	0.01	12.00	0.01	Min	198.20	0.01	0.01	13.00	0.01	22
		750.00	0.44	0.17	3790.60	1.91	Max	679.00	4.93	1.48	2208.00	1.11	
		567.40	0.10	0.05	426.24	0.21	Mean	545.96	0.70	0.39	311.81	0.16	
		541.00	0.05	0.03	293.00	0.15	Median	570.00	0.09	0.31	46.00	0.02	
		108.10	0.13	0.06	530.88	0.27	STD	124.86	1.28	0.36	492.71	0.25	
10	4	306.00	0.01	0.01	23.00	0.03	Min	190.40	0.01	0.01	28.80	0.04	16
		637.00	0.44	0.02	1039.00	1.40	Max	637.00	1.23	0.61	277.40	0.37	
		510.75	0.19	0.01	86.58	0.12	Mean	461.03	0.16	0.11	91.84	0.12	
		550.00	0.16	0.01	51.00	0.07	Median	463.00	0.09	0.08	63.20	0.09	
		144.76	0.22	0.01	116.28	0.16	STD	120.87	0.30	0.15	59.86	0.08	
11	6	572.00	0.01	0.01	47.00	n/a	Min	439.00	0.04	0.01	209.00	n/a	13
		948.00	3.12	0.22	2275.00	n/a	Max	1025	10.56	1.30	1440.00	n/a	
		753.00	0.58	0.08	199.09	n/a	Mean	661.69	1.35	0.24	511.97	n/a	
		735.50	0.07	0.06	160.00	n/a	Median	651.00	0.18	0.12	487.00	n/a	
		128.03	1.25	0.08	190.79	n/a	STD	166.50	2.98	0.37	193.08	n/a	
12	6	404.00	0.01	0.01	0.00	0.00	Min	256.00	0.01	0.01	38.00	0.03	16
		1092.00	2.02	0.13	556.00	0.43	Max	878.00	4.58	0.13	1086.00	0.85	
		698.17	0.69	0.05	90.42	0.07	Mean	604.81	0.75	0.04	149.87	0.12	
		691.50	0.03	0.05	60.00	0.05	Median	604.00	0.18	0.03	100.00	0.08	
		266.97	1.03	0.05	68.86	0.05	STD	177.71	1.30	0.04	142.80	0.11	
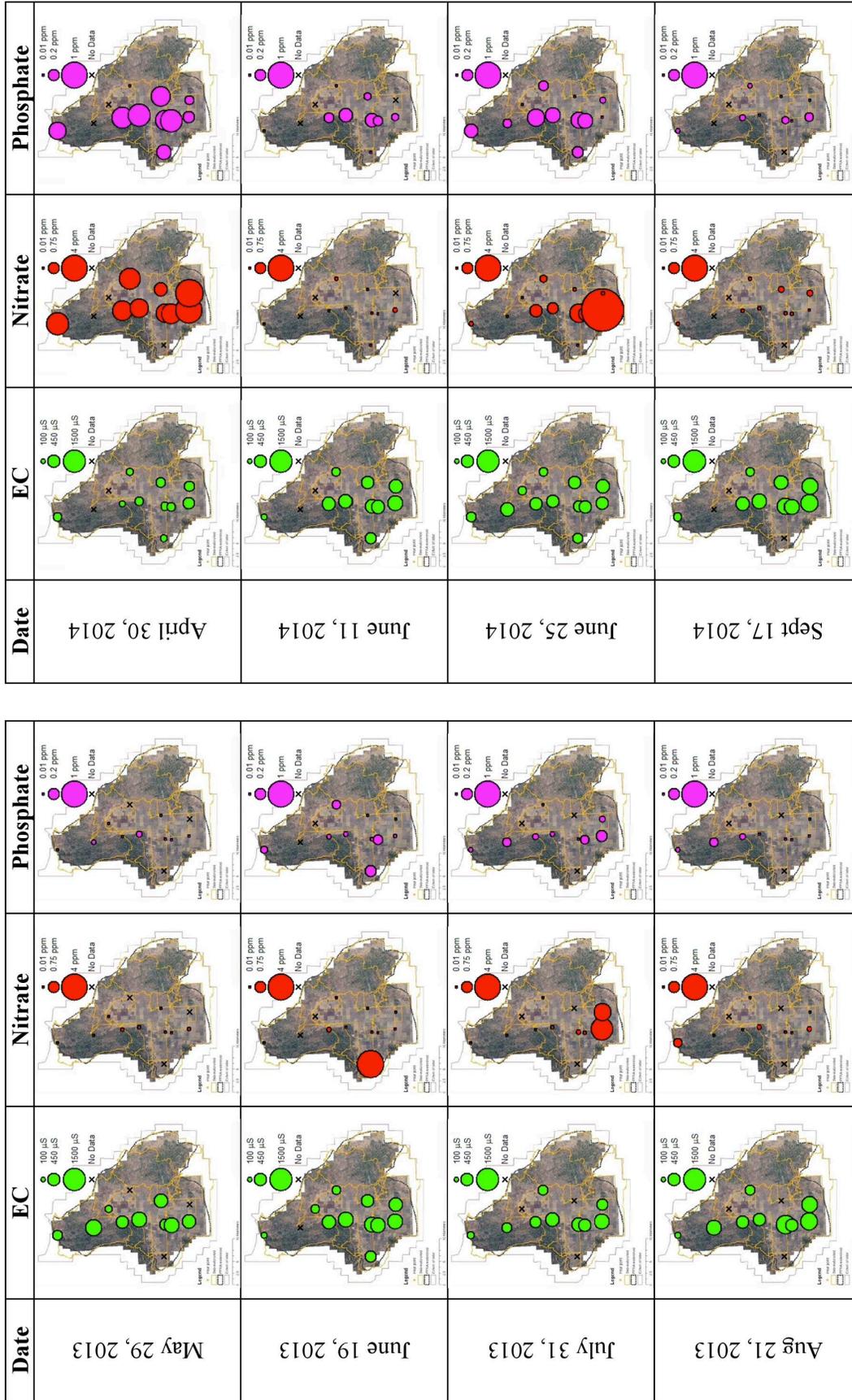
Figure 2.3: Spatiotemporal variability of water quality determinants (EC, nitrate, and phosphate concentrations) across the CCW for eight selected dates.

47
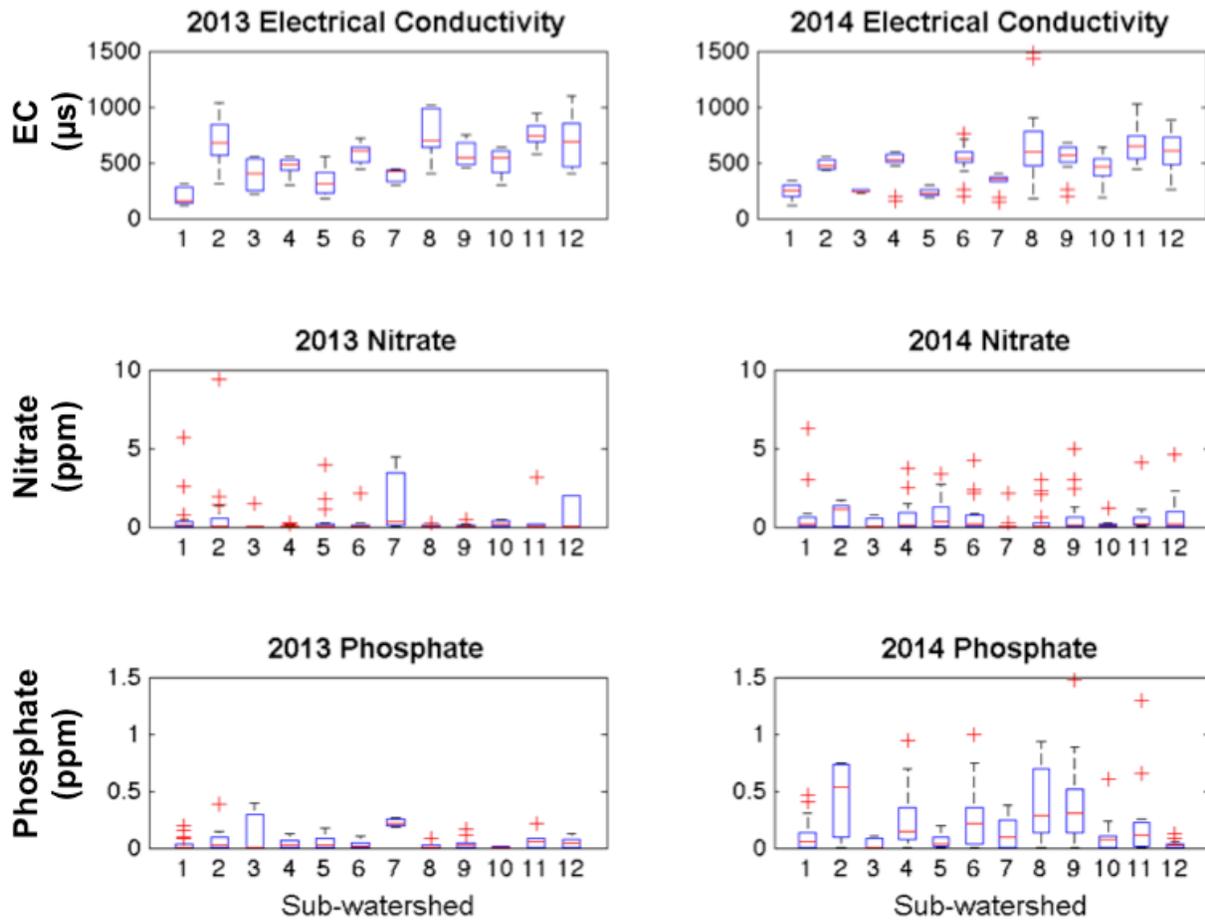
Figure 2.4: Temporal variability of EC, nitrate and phosphate concentrations in each sub-watershed in 2013 and 2014. Each box has lines at the lower quartile (blue line), median (red line), and upper quartile (blue line) values, while the whiskers extend from each end of the box to show the extent of the rest of the data (minimum and maximum values). Outliers are shown as red plus signs.
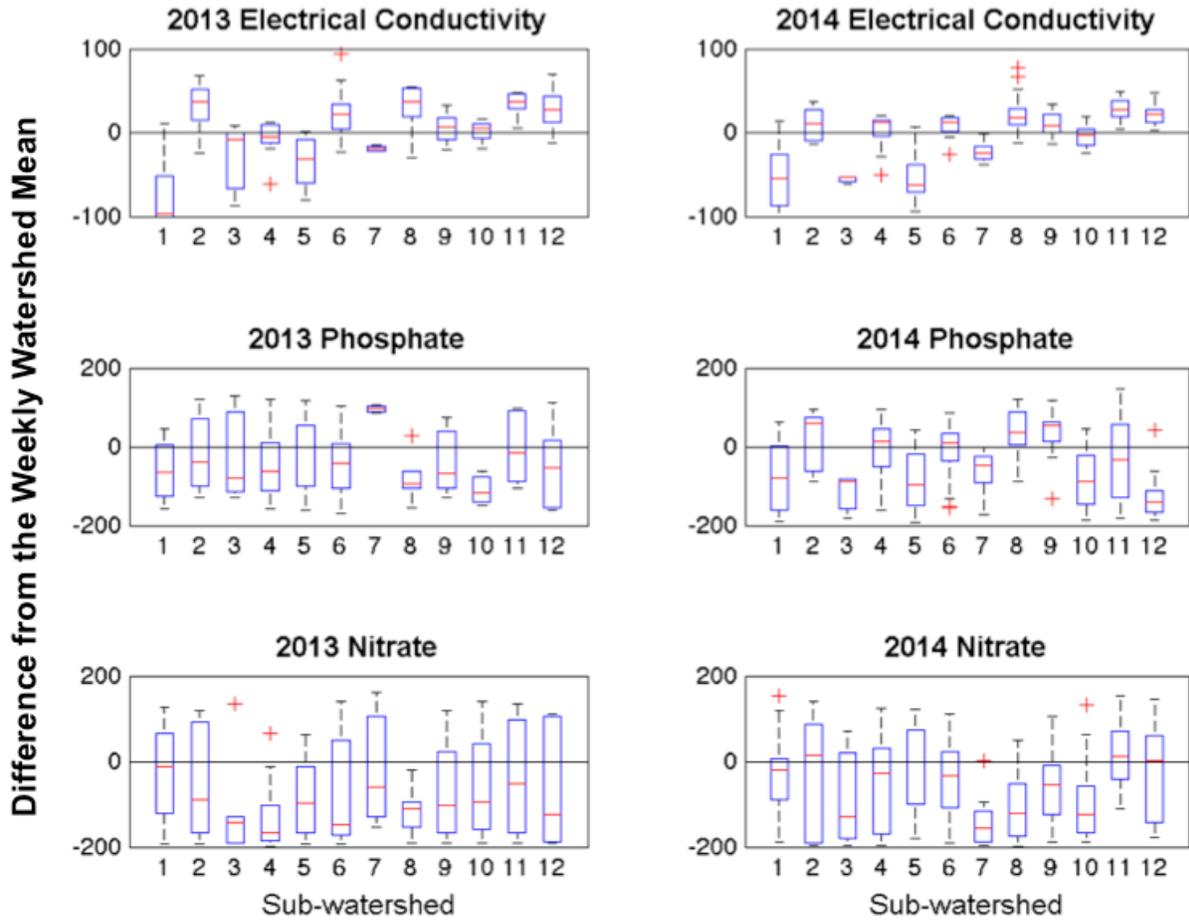
Figure 2.5: Percent difference from the weekly watershed mean for each sub-watershed and each water quality analyte (EC, nitrate, and phosphate). Each box has lines at the lower quartile (blue line), median (red line), and upper quartile (blue line) values, while the whiskers extend from each end of the box to show the extent of the rest of the data (minimum and maximum values). Outliers are shown as red plus signs.

2.4.2 Correlation of Water Quality and Sub-Watershed Characteristics

Figures 2.6, 2.7 and 2.8 show Spearman's rank correlation coefficients (noted as RHO) between weekly water quality concentrations and sub-watershed characteristics. The majority of correlation coefficients computed were, however, not statistically significant, with p-values greater than 0.05. For instance, there were few statistically significant correlation coefficients between EC, nitrate and phosphate concentrations and the topographic characteristics of the sub-watersheds (Figure 2.6). In 2014, significant p-values and strong negative correlations were found between sub-watershed area and EC concentrations, sub-watershed elevation range and EC concentrations, and sub-watershed mean slope and phosphate concentrations (Figure 2.6). The weeks for which phosphate concentrations correlated strongly, and in a statistically significant manner, with sub-watershed mean slope were relatively wet weeks, especially between June 11 and July 9, 2014, when heavy rainfall created consistently wet conditions.

Figure 2.7 shows the correlation of EC, nitrate and phosphate concentrations and the proportion of each land use and land cover (LULC) type present within each sub-watershed. Since the CCW has a near-even mix of crop and forest land (Figure 2.2), the RHO time series associated with forest land and crop land are mirror images to each other. Overall, most of the areal LULC proportions were not correlated with water quality concentrations at the 95% significance level. In both field seasons, EC concentrations were strongly and negatively correlated ($p < 0.05$) with the percent wetland present in the sub-watersheds. For the first 8 weeks of the 2014 spring season, nitrate concentrations were positively correlated ($p < 0.05$) with percent forest land.

(a)

2013

RHO between Electrical Conductivity and Watershed Characteristics

RHO between Nitrate Concentration and Watershed Characteristics

RHO between Phosphate Concentration and Watershed Characteristics

Weeks

— ○ — Sub-Watershed Area
— ○ — Sub-Watershed Drainage Density
— ○ — Sub-Watershed Elevation Mean
— ○ — Sub-Watershed Elevation Range
— ○ — Sub-Watershed Slope Mean
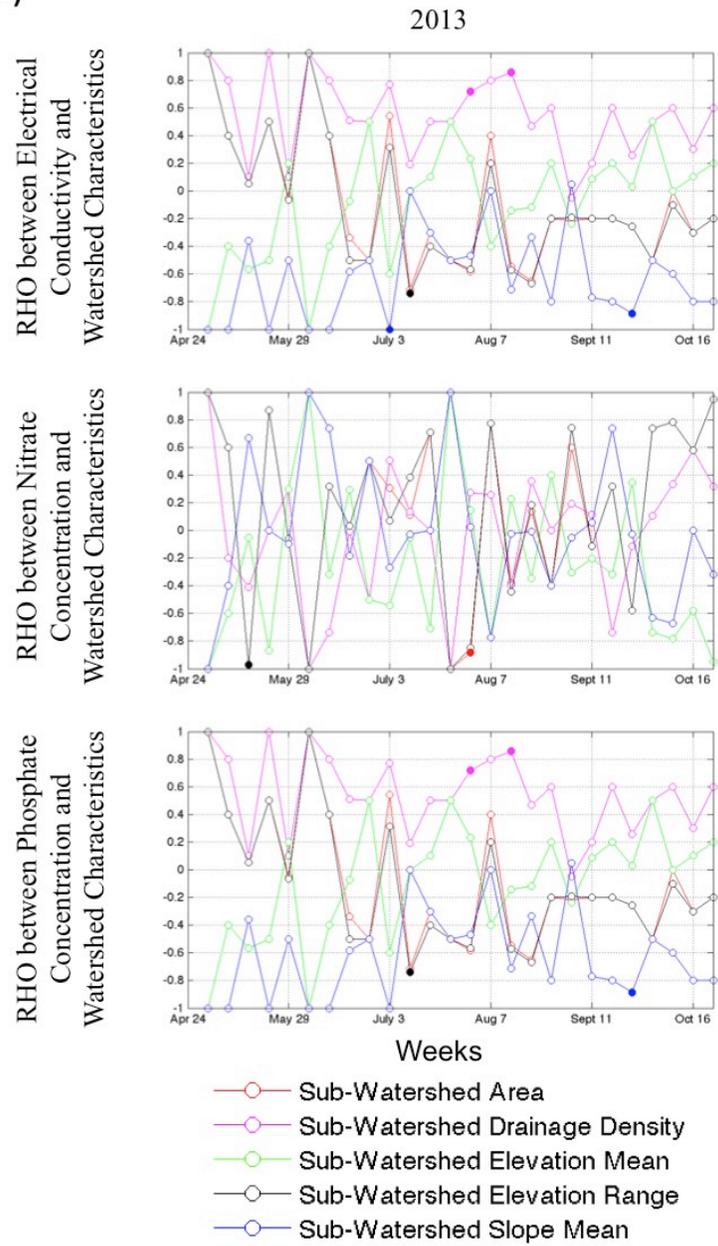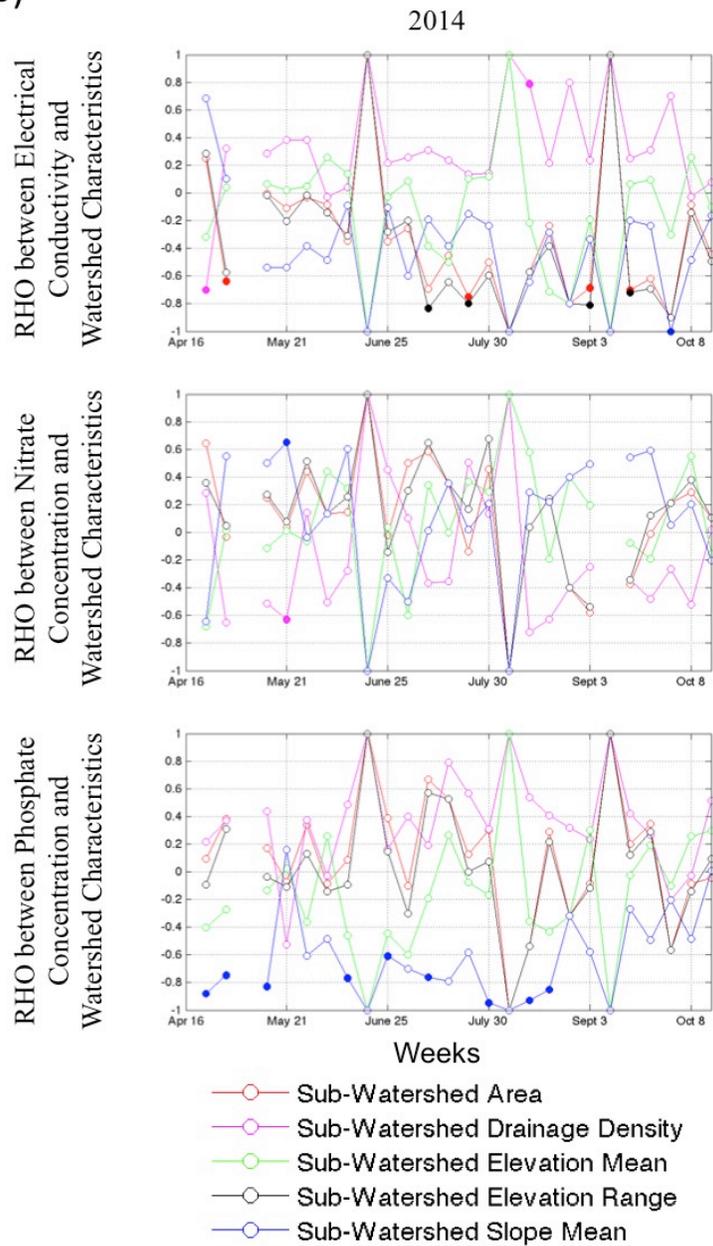
Figure 2.6: (a) 2013 timeseries data and (b) 2014 timeseries data for weekly Spearman's rank correlation coefficients (RHO values) between topographic characteristics and water quality analytes (EC, nitrate, and phosphate concentrations). Weeks with statistically significant RHO values (p-value < 0.05) are indicated with filled-in circles

(a)

2013

RHO between Electrical Conductivity and Watershed Characteristics

RHO between Nitrate Concentration and Watershed Characteristics

RHO between Phosphate Concentration and Watershed Characteristics

Weeks

— ○ — Sub-Watershed % Crop Land
— ○ — Sub-Watershed % Exposed Land
— ○ — Sub-Watershed % Forest Land
— ○ — Sub-Watershed % Shrub Land
— ○ — Sub-Watershed % Wetland

53
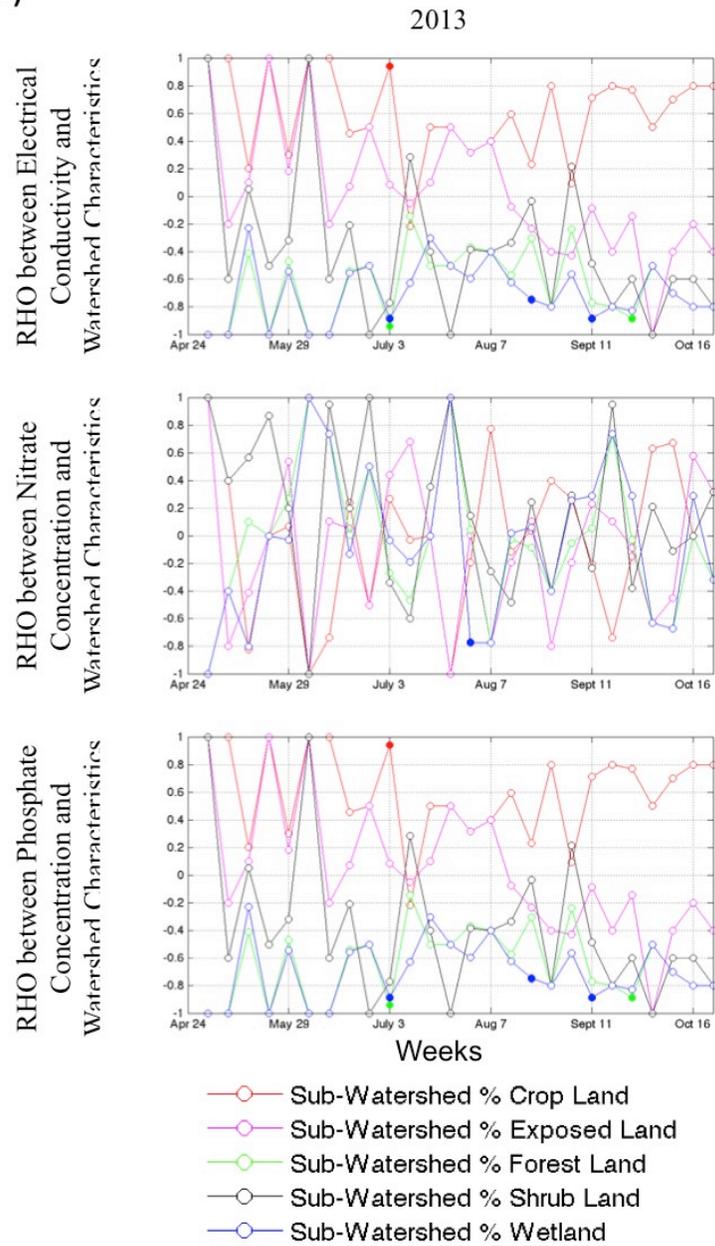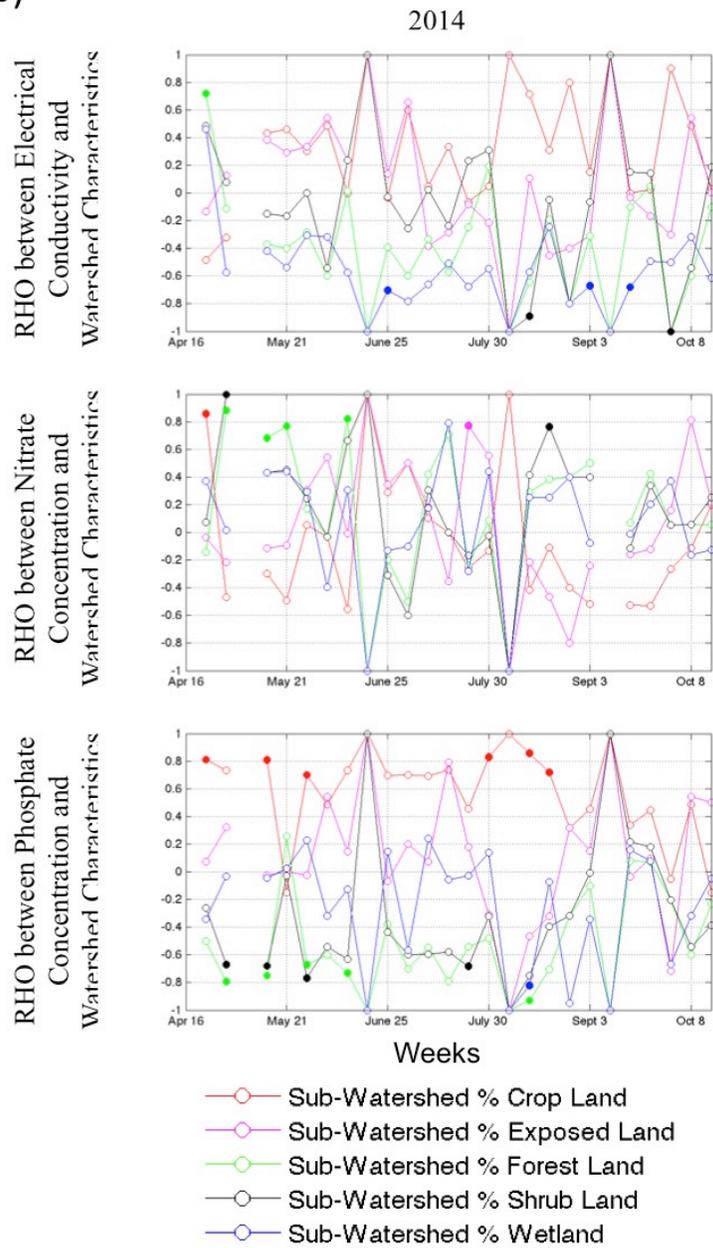
Figure 2.7: (a) 2013 timeseries data and (b) 2014 timeseries data for weekly Spearman's rank correlation coefficients (RHO values) between land use and land cover characteristics and water quality analytes (EC, nitrate, and phosphate concentrations). Weeks with statistically significant RHO values (p-value < 0.05) are indicated with filled-in circles.

(a)

2013

Sub-Watershed % Metamorphic Bed Material
Sub-Watershed % Plutonic Bed Material
Sub-Watershed % Fine Surficial Material
Sub-Watershed % Organic Surficial Material
Sub-Watershed % Plain Surficial Material
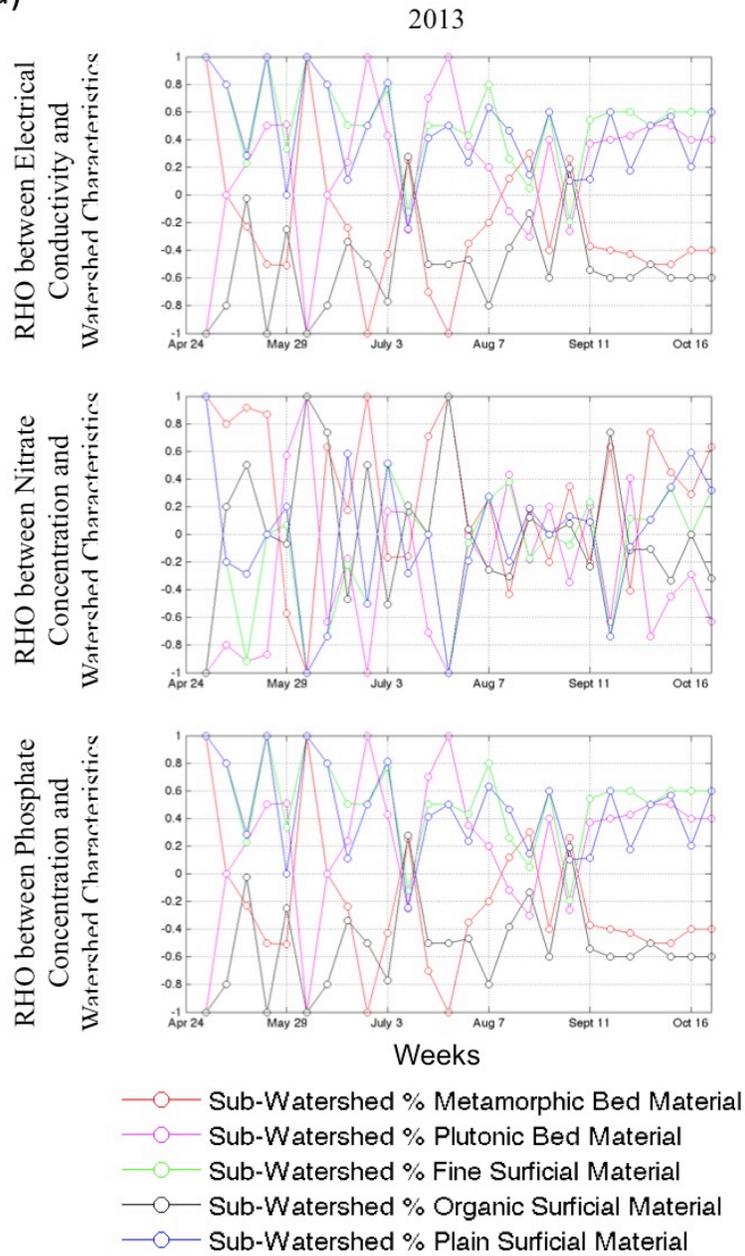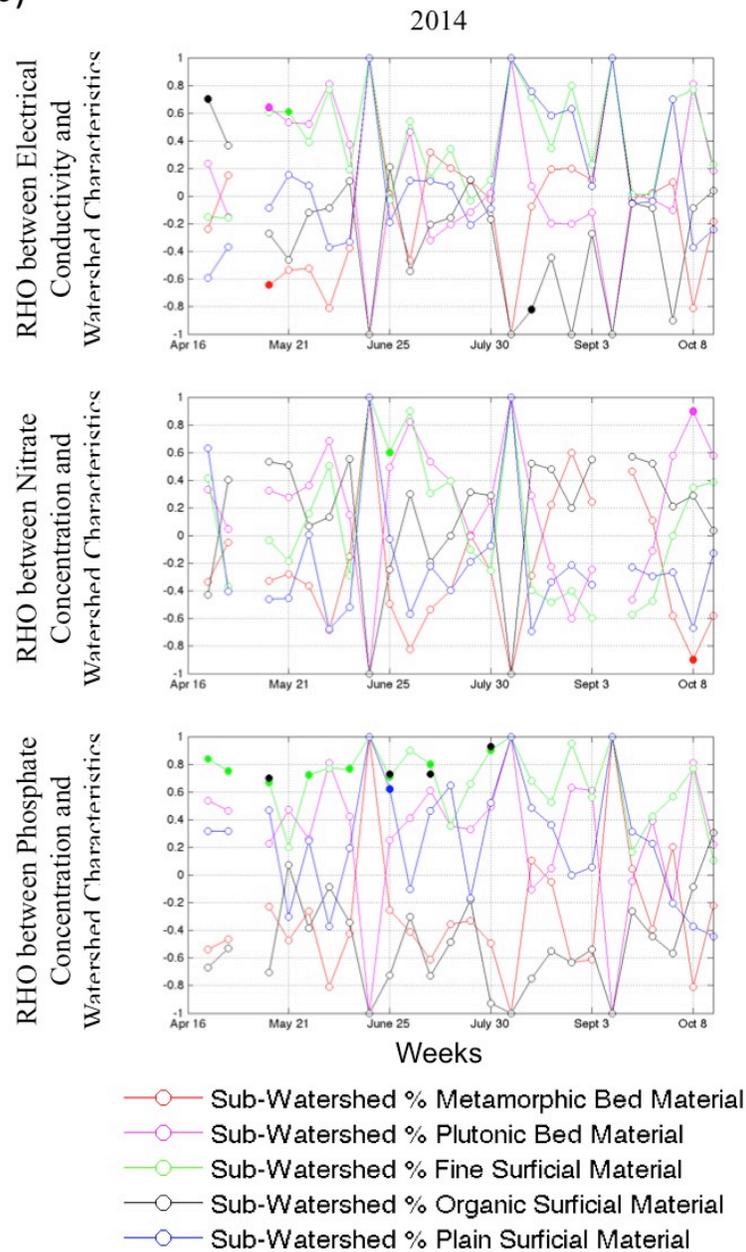
Figure 2.8: (a) 2013 timeseries data and (b) 2014 timeseries data for weekly Spearman's rank correlation coefficients (RHO values) between geological characteristics and water quality analytes (EC, nitrate, and phosphate concentrations). Weeks with statistically significant RHO values (p-value < 0.05) are indicated with filled-in circles.

In 2014, strong associations were observed, such as: a strongly positive correlation between percent crop land and phosphate concentrations; a strongly negative correlation between percent forest land and phosphate concentrations; and a strongly negative correlation between percent shrub land and phosphate concentrations. Similar to what was observed with nitrate, the weeks for which phosphate concentrations correlated strongly ($p < 0.05$) with LULC characteristics were relatively wet weeks in June and early July 2014. It should also be noted that when forest and shrub land percentages were combined, there was little change in the correlation coefficient values and their statistical significance, regardless of the water quality analytes and the year considered.

In 2013, no statistically significant correlations were observed between the proportion of different geologic materials present in the sub-watersheds and water quality concentrations (Figure 2.8). In 2014, however, phosphate concentrations were strongly and positively correlated with both the proportion of fine and organic surficial materials in the first 16 weeks of sampling (spring and summer seasons). The weeks for which phosphate concentrations correlated strongly ($p < 0.05$) with the presence of certain geologic material types were also the wet weeks spanning the June 11 to July 9, 2014 period. Overall, throughout Figures 2.6, 2.7, and 2.8, phosphate concentrations were those that appeared to be the most influenced by sub-watershed characteristics, particularly during the wet weeks of 2014.

2.5 DISCUSSION

The identification of CAWQM sites would be highly beneficial given that monitoring entire watersheds, with ever-changing characteristics and precipitation inputs, is a difficult task that requires a large supply of personnel (time) and financial resources (Grayson & Western, 1998; Thierfelder, Grayson, Von Rosen, & Western, 2003; Zaimes & Schultz, 2002). A study done in 1985 showed that when monitoring soil moisture, some sites in the study area always demonstrated temporal behaviour representative of the field average, while other sites always displayed field extremes (Grayson & Western, 1998; Vachaud, Passerat De Silans, Balabanis, & Vauclin, 1985). In the current study, likely CAWQM sites were identified for each water quality analyte and each monitoring year as summarized below:

- Based on EC in 2013: sub-watershed 4 (majority crop land)

- Based on EC in 2014: sub-watershed 10 (majority developed land)

- Based on nitrate in 2013: sub-watershed 1 (with high intra-annual variability and outliers; even mix of crop and forest land)

- Based on nitrate in 2014: sub-watershed 5 (with high intra-annual variability and outliers; even mix of forest and shrub land)

- Based on phosphate in 2013: sub-watershed 11 (with high intra-annual variability and outliers; majority forest land)

- Based on phosphate in 2014: sub-watershed 7 (with high intra-annual variability and outliers; majority crop land)

EC, with the exception of sub-watershed 1 in 2013, had the smallest range of differences from the mean. For both 2013 and 2014, sub-watersheds 4, 7, 9, and 10 were all relatively

representative of mean EC: the first three are all predominantly crop land while sub-watershed 10 is predominantly developed land. Sub-watershed 1, in 2013 and 2014, experienced nitrate concentrations very close to the watershed mean while sub-watershed 3, in contrast, experienced nitrate concentrations very different from the watershed mean. The CCW experienced large ranges in water quality analytes within the individual sub-watersheds, but a small fluctuation within the CCW as a whole (Figures 2.4 and 2.5); this supports Kirchner (2006), who stated that small-scale processes are not necessarily transferable to large-scale. Although this analysis only relies on a limited number of sites and sampling dates, it demonstrates that there is no single sub-watershed in either or both study years that is a stable spatiotemporal representative of average conditions across the entire CCW. However, sub-watershed 6, a predominantly crop land site, may be the sub-watershed that best represents the CCW: it experienced water quality analyte averages near the overall mean in 2013 for phosphate, and in 2014 for all three analytes (EC, nitrate, and phosphate).

Hotspots, as they pertain to this study, were defined as sub-watersheds experiencing disproportionately high water quality concentrations relative to other sites within the CCW (McClain et al., 2003). Hotspots can occur at the confluence of different flow paths that combine to form a downstream biogeochemical reaction. Single flow paths may also create hotspots by the introduction of reaction catalysts from substrate, groundwater, vegetation, or other riparian inputs (McClain et al., 2003). In contrast, anti-hotspots in the current study were defined as sub-watersheds that experienced disproportionately low water quality concentrations relative to other sites within the CCW. The following sites within the CCW were identified as 2013 and 2014 hotspots and anti-hotspots for each water quality analyte:

- Hotspots:

  - Based on EC 2013: sub-watersheds 2, 8, and 12 (majority crop land)

  - Based on EC 2014: sub-watersheds 8, 11, and 12 (both crop and forest land)

  - Based on nitrate 2013: sub-watersheds 2 and 7 (with high intra-annual variability (outliers); mostly crop land)

  - Based on nitrate 2014: sub-watersheds 1, 11, and 12 (with high intra-annual variability (outliers); mostly forest and shrub land)

  - Based on phosphate 2013: sub-watersheds 2, 3, and 7 (with high intra-annual variability (outliers); both crop and forest land; relatively small areas; sub-watershed have large topographical elevation ranges)

  - Based on phosphate 2014: sub-watersheds 6, 9, and 11 (with high intra-annual variability (outliers); majority crop land; mid-topographical elevation ranges)

- Anti-hotspots:

  - Based on EC in 2013: sub-watersheds 1 and 5 (low intra-annual variability with no outliers; sub-watershed 1 and 5 are high and moderate-intensity sampling sites, respectively; both have relatively large EC ranges)

  - Based on EC in 2014: sub-watersheds 1, 3 and 5 (low intra-annual variability with very few outliers; sub-watershed 1 and 5 are high and moderate-intensity sampling sites, respectively; all three have relatively large EC ranges)

  - Based on nitrate in 2013: sub-watersheds 4 and 8 (low intra-annual variability with very few outliers; mostly crop land)

- Based on nitrate in 2014: sub-watersheds 3, 7 and 10 (relatively low intra-annual variability; only sub-watershed 7 experienced outliers; varied land use and land cover types)

- Based on phosphate in 2013: sub-watersheds 1, 6, and 10 (sub-watershed 1 had high intra-annual variability with outliers; varied land use and land cover types)

- Based on phosphate in 2014: sub-watersheds 3, 5, and 12 (low intra-annual variability with very few; majority forest land)

Overall, nitrate and phosphate both had higher average concentrations, and greater ranges in concentration values in the high rainfall year (2014), which is akin to dynamics also observed by Sharpley et al. (2008) and Zaimes & Schultz (2002) (Table 2). Higher concentrations in a wet year (2014), versus a drier year (2013), is typically due to enhanced contributions and transport of nutrients from soil to stream (Aubert, Gascuel-Odoux, & Merot, 2013).

Land use and land cover controls on EC were present within the Catfish Creek sub-watersheds (Figure 2.7). High EC usually means high magnitude of groundwater flow, while low EC usually indicates higher surface water contributions (Pilgrim, Huff, & Steele, 1979). In 2013 (drier year), electrical conductivity was higher; therefore it is likely that most of the sub-watershed monitoring sites experienced baseflow conditions, with major contributions from groundwater flow (Table 2.2). In 2014 (wetter year), electrical conductivity was lower, therefore suggesting the sub-watershed monitoring sites were mainly fed by surface water from overland flow (Table 2.2). There were also some land use and land cover controls on nitrate and phosphate dynamics detected in the CCW, specifically in relation to forest and crop land (Figure 2.7).

Forest and crop land correlations were inverse of each other for both nitrate and phosphate concentrations, which was in agreement with other studies which reported correlation with degrading water quality in waterbodies adjacent to agricultural land use (Johnson et al., 1997; Lee et al., 2009; Tong & Chen, 2002; Xiao & Ji, 2007). Phosphate concentration correlated positively with % crop land in a statistically significant manner for both the study years (wet and dry). Nitrate correlated positively with % forest land during the wet year, while no statistically significant correlation could be found for the dry year or with % crop land. This finding is consistent with other studies (e.g., Hill et al. 1999; Buda and DeWalle 2009) where an event-driven rise of the water table (due to rain or snowmelt inputs) was found to flush nitrates from the upper soil horizons. Upper soil horizons are indeed susceptible to rapid throughflow and flushing due to large macropores found in forest soils, caused by root channels (Hill et al., 1999). Electrical conductivity was found to be negatively correlated, in both study years, with % wetland cover type; therefore as wetland cover increases, electrical conductivity decreases, implying that the wetlands are mainly fed by surface water.

There were minor surficial geology controls detected within the Catfish Creek Watershed, but some might strongly relate to nutrient loading due to infiltration-excess overland flow (Figure 2.8). Indeed, infiltration-excess overland flow tends to occur when considerable rain falls atop fine surficial materials (small pores) and exceeds the soil maximum infiltration rate, causing water to flow downslope to enter streams and waterbodies (Haygarth & Sharpley, 2000; Horton & Hawkins, 1965). Fine surficial material correlated strongly with phosphate concentration in 2014 (heavy rainfall year), suggested that phosphorus, in the form of plant residues, might have been mobilized by overland flow during the wet conditions experienced in that year. Organic

surficial material was also strongly correlated with phosphate concentrations in the high-rainfall year (2014), which might indicate the mobilization of near-surface soil phosphorus by shallow subsurface flow – which tends to occur in wet organic horizons that have high lateral hydraulic conductivities. No bedrock geology material type, however, was involved in strong and statistically significant correlations with water quality analytes, thus highlighting that it is surface and near-subsurface (and not deep subsurface) landscape characteristics that exert the strongest controls on water quality dynamics (Figure 2.8).

Lastly, there were minimal topographic controls on water quality dynamics (Figure 2.6), likely due to the minor changes in topography (e.g., elevation and slope) across the sub-watersheds, as is typical of the majority of the prairie region. Micro-topography controls may be present, but this study did not include topographic characterizations at a smaller scale. In the high–rainfall year (2014), sub-watershed area and elevation range occasionally correlated negatively with electrical conductivity; hence, as area and elevation range increased, the electrical conductivity at these sub-watershed outlets decreased. Based on the associated relationship between high EC and groundwater contributions (Pilgrim et al., 1979), it can be inferred that decreased area and elevation range in these sub-watersheds are associated with slower flow paths (e.g., groundwater) as opposed to increased area and elevation range being associated with faster flow paths (e.g., surface runoff). Also, in the wet year, slope correlated negatively with phosphate, hinting that as slope increases, phosphate concentration decreases; this is in contrast to other studies (Dosskey et al., 2010; Heathwaite & Dils, 2000; Zaimes & Schultz, 2002) where overland flow during heavy rainfall events was found to increase phosphate loss due to eroding banks. It is likely that this erosion-driven phosphate loss phenomenon was less important in the

CCW due to the absence of significant topographic relief, and the efficiency of riparian buffers within the sub-watersheds (Burt & Pinay, 2005; Dodds & Oakes, 2006; Dosskey et al., 2010; Fuchs et al., 2009; Heathwaite, 1995; Schlosser & Karr, 1981; Zaimes & Schultz, 2002), or the existence of a very short contact time between water and sediment that might not allow nutrients attached to sediment particles to be effectively mobilized (Heathwaite, 1995). Besides, the steepest slopes in the CCW are found on channel banks which are not as phosphate-rich as flatter agricultural lands, which might explain the negative correlation.

2.6   CONCLUSION

The goal of this study was to examine water quality analytes within prairie sub-watersheds in order to: (1) quantify the spatiotemporal variability of water quality across a system of nested prairie watersheds, (2) identify potential CAWQM sites that exhibits behaviour representative of an entire region, and (3) identify the watershed characteristics that control the spatial variability of water quality and the persistence of those controls in time. Regarding the spatiotemporal variability aspect, EC concentrations were higher in 2013 compared to 2014 across the majority of the sub-watersheds, as opposed to nitrate and phosphate concentrations that were generally lower in 2013, compared to 2014. There was no single sub-watershed in either or both study years that was a good (i.e., stable) illustration of average watershed conditions. Multiple sites could, however, be identified as hotspots or anti-hotspots, thus providing some guidance as to where, spatially, to sample in order to capture extreme conditions.

Various watershed characteristics appeared to control the spatial variability of water quality, although those controls were not persistent in time, i.e., they were highly temporally variable. Regarding the influence of geology, some surficial controls on water quality dynamics seemed to exist but such was not the case for bedrock geology characteristics. Very few topographic controls on water quality dynamics were observed, likely due to the minor changes in topography (e.g., elevation and slope) across the sub-watersheds, as is typical of a prairie landscape. Land use and land cover controls on electrical conductivity, phosphate, and nitrate water quality dynamics were present within the Catfish Creek sub-watersheds, with the strongest correlations occurring during the high rainfall year (2014).

To better understand the intricacies of prairie sub-watersheds, where limited macro-topographic changes occur, micro-topographic controls should be investigated. In addition to this, greater analysis of riparian area conditions and soil profiles could help better understand why phosphate concentrations decreased as watershed slope increased. Further investigation of runoff mechanisms within the CCW is also warranted, notably to determine why sub-watersheds with apparently similar characteristics did not correlate similarly with water quality concentrations.

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CHAPTER 3
PRELIMINARY SYNTHESIS AND TRANSITION

3.1 Preliminary Synthesis and Transition

The findings reported in Chapter 2 not only indicated that water quality dynamics within the Catfish Creek Watershed (CCW) are highly variable across space, but it also emphasized the need for multi-site monitoring due to the complex interaction of several sub-watershed characteristics (e.g., topography, geology, and land cover and land use types). Chapter 2 did not, however, address the issue of temporal variability in detail, which is crucial to better understand the water quality dynamics prevailing in prairie sub-watersheds. Indeed, rainfall amounts varied significantly between the two study years: the CCW received 271 mm of rainfall in 2013 (MCFP, 2013) and 530 mm of rainfall in 2014 (MCFP, 2014). The complexity associated with temporal variability assessment was strongly highlighted when the correlations between land use and land cover types and electrical conductivity, phosphate, and nitrate concentrations were found to be time-dependent, with the strongest correlations occurring during the wet year (2014).

The study of temporal watershed dynamics can provide a greater understanding of the drivers of hydrologic change. This is especially true for water quality dynamics that are known to vary annually, seasonally (spring, summer, fall), or as a function of antecedent moisture conditions (wet, intermediate, dry) and specific hydrological events (rainfall-triggered or snowmelt-triggered). The literature reveals that prairie regions are subject to high seasonality as well as high inter-annual variability in hydrological processes (Buttle et al., 2016; Dumanski et al., 2015; Fang et al., 2007; Outram, Cooper, Sünnenberg, Hiscock, & Lovett, 2016; Untereiner et al., 2015). The extent to which water quality dynamics are predictable on the basis of weather

variables in intensively managed prairie landscapes is unknown, as these watersheds are prone to both natural and artificial flow routing mechanisms due to engineered stormwater-control infrastructure (surface drains). They are also especially vulnerable to high nutrient loading from agricultural fields. One goal of Chapter 4 was, therefore, to characterize the temporal variation of water quality dynamics at the seasonal scale in a typical prairie watershed. It is worth noting that some of the results reported in Chapter 2 highlighted the fact that significant controls on water quality can be more or less temporally persistent, with some correlations being detected in isolated weeks while others were detected for several consecutive weeks. Consequently, Chapter 4 was built in such a way that it would not focus on seasonal dynamics only but would rather rely on a range of methods to capture water quality variability across three different time scales (i.e., the annual, seasonal, and rainfall event scales).

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CHAPTER 4
TEMPORAL DYNAMICS WITHIN A PRAIRIE WATERSHED

4.1 ABSTRACT

Recent biogeochemical stationarity studies have shown that intensively managed watersheds in the United States and Europe demonstrate chemostatic behaviour, meaning that nutrient concentrations do not vary much from year to year despite highly variable temperature, precipitation and flow conditions. In contrast, pristine watersheds have been shown to exhibit episodic behaviour, with a higher variability in nutrient concentrations than in flow. Chemostatic behaviours have been associated with legacy nutrient sources deep in soils while episodic behaviours are rather indicative of contemporary sources in shallower soil layers. The existence of chemostatic behaviours in cold and intensively managed Canadian prairie watersheds, however, remains to be verified. The focus was therefore on the 642 km^2 Catfish Creek Watershed (Manitoba, Canada) that includes forest and agriculture land and contains numerous man-made drainage channels. In 2013 and 2014, daily water levels and water quality parameters (electrical conductivity (EC), nitrate, and phosphate) were monitored at four sub-watersheds, and known metrics of chemostatic behaviour were computed. Overall, the biogeochemical stationarity assessment revealed that all four sub-watersheds experienced mostly episodic behaviour. Additionally hysteresis loops were created for sub-watershed rainfall events, and the rotational direction of each loop (i.e., clockwise, anti-clockwise, complex) was used to infer nutrient source. The majority of EC and phosphate hysteresis loops were anti-clockwise, indicating delayed inputs to drainage channels. In contrast, the majority of nitrate hysteresis loops were clockwise, indicating quick mobilization to drainage channels. Antecedent moisture conditions prior to rainfall events were also considered. Results show that the variability of EC, nitrate and phosphate concentrations transcended daily, seasonal, and event scales.

4.2 INTRODUCTION

The anthropogenic modification of watersheds (e.g., through nutrient inputs, channel modification, artificial land drainage) strongly impacts environmental processes in general, as well as water quality in particular in affected regions (Basu, Thompson, & Rao, 2011; Bieroza, Heathwaite, Mullinger, & Keenan, 2014; Daughtry et al., 2001; Heathwaite, 1995). As such, an understanding of the relationship between watershed hydrology and biogeochemistry is required to better circumscribe resultant regional and downstream water quality, and to best predict its response to the spatial and temporal variability of its drivers. Indeed, stream water quality is not annually, seasonally, monthly, daily, or even diurnally invariant (Neal & Heathwaite, 2005). Variability of stream water quality analytes can be influenced by complex biological and hydrological processes, which themselves are highly variable in space and time (Basu et al., 2010; Bieroza & Heathwaite, 2015; Buda & DeWalle, 2009; Fučík, Kaplická, Kvítek, & Peterková, 2012; Heathwaite & Dils, 2000). Nutrients such as nitrogen (N) and phosphorus (P) are examples of water quality analytes examined when the degradation of freshwater is suspected (Bieroza & Heathwaite, 2015; Buda & DeWalle, 2009; Heathwaite, 1995; Y. Li et al., 2006), with P being considered the most limiting nutrient (Fuchs et al., 2009; Heathwaite, 1995). An overabundance of N and/or P within a waterbody can promote the growth of plants to the point of dissolved oxygen depletion (Harker, 1998); this problem is called eutrophication and can lead to problems, such as blue-green algae blooms (Fučík et al., 2012).

Land and stream conditions that control the release and transport of nutrients are extremely dynamic temporally and spatially, making the understanding of a watershed's

hydrobiogeochemical processes highly challenging (Heathwaite & Dils, 2000; Ou & Wang, 2011; Zaimes & Schultz, 2002). N is not easily absorbed in soil particles, making it typically more mobile than phosphorous, and therefore less easy to control within agricultural areas (Zaimes & Schultz, 2002). Agricultural practices are considered a large nonpoint source (NPS) of N and P (Heathwaite, 1995; Jarvie et al., 2008; Munn et al., 2010), and anthropogenic application of nutrients to crops in excess of the crops' nutritional requirements can lead to surface and subsurface nutrient mobilization transport to adjacent waterbodies (Daughtry et al., 2001). Even in low intensity NPS agricultural systems, N and P are thought to be key suppliers of the total nutrient loading to downstream waterbodies and the main cause of eutrophication in many lakes and rivers (Buda & DeWalle, 2009; Heathwaite, 1995; Heathwaite & Dils, 2000; Poor & McDonnell, 2007; Untereiner et al., 2015). N and P can be present during baseflow conditions (Buda & DeWalle, 2009; Zaimes & Schultz, 2002), but fluctuations in seasonal temperatures and event-driven water inputs can mobilize non-baseflow sources of nutrients in a significant manner (Ali & Roy, 2010; Bieroza & Heathwaite, 2015; Buda & DeWalle, 2009; Outram et al., 2016). Therefore, it is important to develop an understanding of temporal water quality fluctuations within a watershed in order to predict and mitigate associated environmental impacts (Basu et al., 2010).

It has been commonly noted that nutrient concentration dynamics are linked to fluctuations in stream discharge, which occur on an event basis as well as a seasonal and annual basis (Clark, Greer, Zipper, & Hester, 2016; Evans & Davies, 1998; Godsey, Kirchner, & Clow, 2009; McDiffett, Beidler, Dominick, & McCrea, 1989). The relationship between concentration and discharge, however, "*rarely takes a simple linear or curvilinear form*" where concentration

increase is proportional to discharge increase (Evans & Davies, 1998). As a result, several types of concentration-discharge analyses have been proposed in the literature to examine that relationship, including: (1) the analysis of concentration-discharge (*c-q*) hysteresis loops at the scale of individual precipitation and hydrological events, and (2) the assessment of biogeochemical stationarity at the monthly, seasonal, annual or multi-annual scale. Firstly, hysteresis loops are revealed by plotting concentration against discharge (*c-q*) during times of increased discharge (i.e., storm events) (Bowes et al., 2005; Evans & Davies, 1998; Fučík et al., 2012; House & Warwick, 1998; McDiffett et al., 1989). The presence of a "loop" rather than a linear or curvilinear relationship signals that concentration and discharge do not peak simultaneously but rather that one variable peaks before the other, hence the term "hysteresis". When a loop is revealed, the *c-q* relationship can be classified based on its rotational pattern (e.g., clockwise, anti-clockwise) (Bowes et al., 2005; Evans & Davies, 1998). Clockwise (CW) *c-q* hysteresis is present when the highest concentrations are observed on the rising limb of the storm hydrograph. Conversely, an anti-clockwise (ACW) loop has the highest concentrations on the falling limb of the storm hydrograph (Bieroza & Heathwaite, 2015; Bowes et al., 2005; Bowes, Smith, & Neal, 2009). Clockwise loops have typically been associated with immediate flushing ("first flush") (Fučík et al., 2012) of readily available solutes or nutrients, implying the mobilization of sources from within or near the stream channel, whereas anti-clockwise loops are associated with delayed inputs, potentially from distant or slow-moving nutrient sources and pathways located either at large distances from the stream channel or in the subsurface (Bieroza & Heathwaite, 2015; Bowes et al., 2005, 2009; Fučík et al., 2012). Secondly, considering *c-q* data over timescales longer than a storm event to analyze biogeochemical stationarity (also known as chemostatic behaviour) was also found by Basu et al. (2010) to be a powerful method

for predicting nutrient exports within anthropogenically modified watersheds. Chemostatic behaviour is deemed present when nutrient concentrations are largely invariant despite varying stream discharge values; within anthropogenically-impacted watersheds, chemostatic behaviour is common, as continual nutrient applications are likely to contribute to legacy stores, which are desorbed slowly from soil over many years (Basu et al., 2011). The opposite of chemostatic behaviour is episodic behaviour, deemed present when nutrient concentrations vary with discharge. Most of the literature on that topic suggests that anthropogenically impacted watersheds exhibit chemostatic behaviour, as these areas are nutrient transport-limited, contrary to forested areas that exhibit episodic behaviour because they are nutrient supply-limited (Thompson et al. 2011).

Studies that combine a biogeochemical stationarity assessment with a hysteresis assessment are rare, even though they have the potential to explain water quality dynamics across a wide range of temporal scales. Indeed, both hysteretic effects and chemostatic or episodic behaviour can be seen as a result of land use and land cover, geological, surficial, antecedent moisture, and rainfall characteristics that interact at different temporal scales (Fučík et al., 2012; House & Warwick, 1998; McDiffett et al., 1989). Currently published literature does not report on biogeochemical stationarity assessments done over different years and different seasons for comparison purposes. With specific reference to nitrate and phosphate hysteresis, most previous studies have observed CW c-q hysteresis (Bieroza & Heathwaite, 2015; Bowes et al., 2005; House & Warwick, 1998), while most ACW c-q hysteresis were associated with rainfall events occurring following dry antecedent conditions (Bowes et al. 2009). The prevalence of nitrate and phosphate CW hysteresis implies that nutrient sources are readily available near stream channels and rapidly

flushed from the system (Ali & Roy, 2010; Bieroza & Heathwaite, 2015; Bowes et al., 2005, 2009; Outram et al., 2016; Poor & McDonnell, 2007). Temporal variability in hydrological processes are mostly driven by antecedent moisture conditions (AMCs) (Bieroza & Heathwaite, 2015; Elsenbeer, West, & Bonell, 1994; Grayson & Western, 1998; James & Roulet, 2009; Outram et al., 2016; Shanley & Chalmers, 1999) and rainfall storm characteristics (Ali, Tetzlaff, Soulsby, & McDonnell, 2012; James & Roulet, 2009; Sharpley et al., 2008); it is, therefore, critical to evaluate as it determines the main mechanisms via which nutrients are mobilized from source to stream (Daughtry et al., 2001). For instance, if the ground is frozen or saturated (wet AMCs), rainwater and meltwater inputs are unlikely to infiltrate the soil, promoting overland flow towards the stream. In contrast, during dry AMCs, rainwater and meltwater inputs are likely to infiltrate, and can potentially reach the stream via slower-moving subsurface flow pathways (Heathwaite, 1995; Hill et al., 1999; James & Roulet, 2009; Shanley & Chalmers, 1999). Storm characteristics (e.g., magnitude and duration) also impact the likelihood of infiltration and/or overland flow (Y. Li et al., 2006; Sharpley et al., 2008), and influence nutrient loss through soil erosion. Seasonality also provides temporal variability in watersheds that experience ranges in climactic conditions (e.g., wet versus dry, cold versus hot) (Bieroza & Heathwaite, 2015; James & Roulet, 2009; Y. Li et al., 2006; Outram et al., 2016; Ross, Petzold, Penner, & Ali, 2015; Thompson, Basu, Lascurain, Aubeneau, & Rao, 2011); dry conditions can create disconnected flow pathways, limiting the ability of nutrients to reach nearby waterways, whereas wet conditions promote continuously connected flow paths, readily contributing nutrients. The literature also suggests that a large rainfall event following a dry period is likely to result in a large nutrient release (Ali & Roy, 2010; Bieroza & Heathwaite, 2015; Outram et al., 2016).

In light of the literature reviewed above, the overall goal of the current study was therefore to characterize the temporal dynamics of water quality in a typical prairie watershed, using a range of methods so as to capture water quality variability across three different time scales, namely the annual, seasonal and event scales. This goal is especially relevant in prairie regions which are known to be subject to high seasonality, as well as high inter-annual variability in hydrological processes (Buttle et al., 2016; Dumanski et al., 2015; Fang et al., 2007; Outram et al., 2016; Untereiner et al., 2015). The focus was on three chemical analytes, namely electrical conductivity, nitrate and phosphate concentrations, with the former being a good universal tracer of overland and subsurface flow pathways in watersheds, while the two latter are key to characterizing dissolved nutrient export. This study was guided by four specific research questions, which are:

(1) Is water quality temporally variable across time scales?

(2) Do prairie watersheds conform to the literature consensus regarding chemostatic behaviour in agricultural areas and episodic behaviour in forested areas?

(3) What do hysteresis loops reveal about nutrient export at the scale of individual rainfall events?, and,

(4) Are antecedent moisture conditions (AMCs) good predictors of water quality dynamics in prairie systems?

4.3 METHODS

4.3.1 Study Area

Located in southeastern Manitoba, the Catfish Creek Watershed (CCW) is situated southeast of Lake Winnipeg, approximately 100 km northeast of the city of Winnipeg (Manitoba, Canada) (Figure 4.1a). The Catfish Creek is a tributary of Lake Winnipeg, flowing directly into Traverse Bay (Figure 4.1b, sub-watershed 1). The CCW covers an area of 642 km^2 in a region of the Canadian prairies with a near-even mix of forest and agricultural (crop) land (4.1b). The topography of this area is relatively heterogeneous (e.g., flat, hilly), maximum relief of 70 m, which makes it representative of many agricultural landscapes in the prairie region. Due to the region's near-flat topography, the majority of its drainage occurs in man-made surface drains. The two major man-made drainage channels are referred to as Main Drain 1 and Main Drain 2, while the watershed also includes other smaller order drainage channels (e.g., Side Drain, Heckert Drain, Stead Drain) (Figure 4.1b).

This region of the Canadian prairies experiences a relatively short open water period; spring thaw normally occurs in late April, while fall freeze-up tends to occur in early November. Average temperatures within the CCW, as observed by the Manitoba Conservation Fire Program (MCFP, 2014) at the Stead, MB weather station from 1999 to 2013, range from -13.7°C in January to +24.3°C in July. Seasonality also pertains to regional precipitation: most of it occurs as rainfall during the spring to fall period, and a lesser amount of precipitation occurs as snowfall during the winter season. The Manitoba Conservation Fire Program also monitored rainfall from

1999-2013, and observed an average annual rainfall amount of 459 mm, with the majority occurring in June. Annual rainfall ranged from 271 mm and 669 mm between 1999 and 2013 (MCFP, 2014).
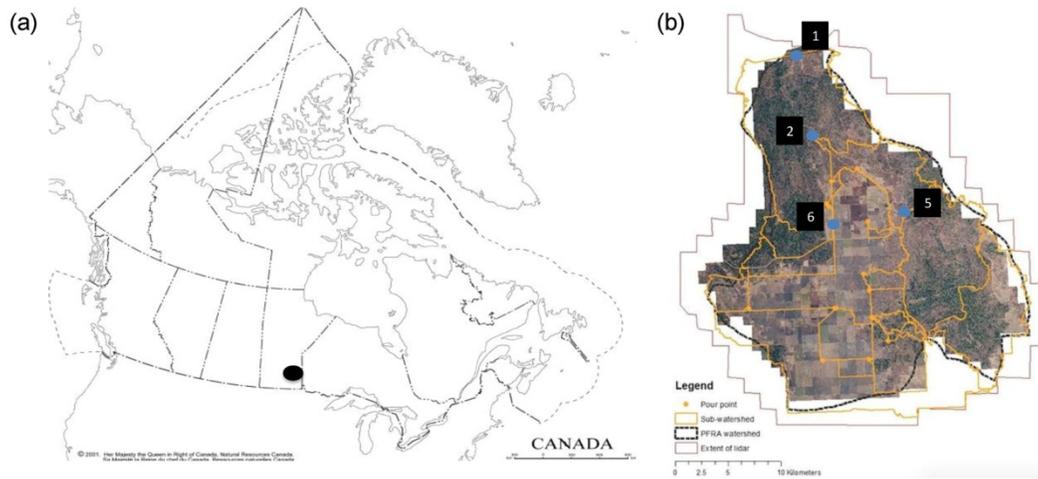
Figure 4.1: The Catfish Creek Watershed's (CCW) (a) location within Canada and (b) sub-watershed boundaries with the location of outlets for sub-watersheds 1, 2, 5, and 6 marked with a blue dot.

During spring, when the freshet initiates, snowmelt infiltration recharges soil moisture and groundwater storage, and surface runoff replenishes surface waterbodies (Shanley & Chalmers, 1999). This process makes snowmelt a critical hydrological process in this Canadian prairie watershed. Spring flooding is commonplace when meltwater exceeds the infiltration capacity of frozen soils, causing overland flow (Buttle et al., 2016; Fang et al., 2007; Gray et al., 2001; Shook et al., 2014). The MCFP database does not include historical snowfall data for the Stead, MB monitoring station (MCFP, 2014).

In 2013, four sub-watersheds within the larger CCW were chosen for gauging and water sampling (Figure 4.1b). These sub-watersheds were chosen to span a range of drainage areas, land cover and land use types, and to represent water quality distributions across both Main Drain 1 and 2. The four sub-watersheds chosen were: sub-watershed 1 at the outlet for the entire CCW, sub-watershed 2 at the confluence of Main Drain 2 and Side Drain, sub-watershed 5 on Main Drain 2 at Provincial Road (PR) 304, and sub-watershed 6 on Main Drain 1 at PR 304.

- Sub-watershed 1 (Appendix B – Figure 1) has an elevation range of 91.4 m, with an average slope of 2.5%. It includes mostly forest land, crop land, shrub land, and wetland in proportions of 35.2%, 31.3%, 18.1%, and 13.5%, respectively. The bedrock material is mostly metamorphic (90.6%) and the surficial material is mostly organic (74.1%).

- Sub-watershed 2 has an elevation range of 86.0 m, with an average slope of 1.9%. This sub-watershed has mostly crop land, forest land, and shrub land cover types, in proportions of 63.5%, 19.5%, and 12.3%, respectively. The bedrock material in this sub-watershed is mostly metamorphic (86.5%) and the surficial material is a mix of organic deposits (65.8%) and fine silt, clay and local stones (23.6%). The outlet of this sub-watershed is relatively remote and inaccessible; hence sampling was dependent on available resources (e.g., all-terrain vehicles) and weather.

- Sub-watershed 5 has an elevation range of 80.9 m, with an average slope of 2.9%. This sub-watershed includes 51.4% of forest land, 32.3% of wetland, and 14.0% of shrub land. The bedrock material in this sub-watershed is mostly metamorphic (86.2%) and the surficial material is mostly organic (95.8%).

- Lastly, sub-watershed 6 (Appendix B – Figure 3) has an elevation range of 83.3 m, with an average slope of 1.9%. This sub-watershed includes mostly crop land, with some

forest and shrub land (proportions of 63.3%, 20.0%, and 11.4%, respectively). The bedrock material is mostly metamorphic (82.3%) and the surficial material is a mix of organic (54.2%), fine silt, clay and local stones (31.6%), and plain sand and gravel outwash (14.2%).

4.3.2 Data Collection, Laboratory Analysis, and Data Analysis

Throughout the CCW, four weather stations (HOBO U30/NRC Weather) were deployed in 2013 (Figure 2.2): they rely on HOBOlink technology to monitor, record, and upload data from temperature, wind speed, wind direction, and precipitation smart sensors at a 1-minute frequency. Water level and water quality data were collected through the 2013 and 2014 open water periods. At the four sub-watershed outlet sites selected across the CCW, Odyssey Capacitive Water Level loggers calibrated in the laboratory were placed within stilling wells in the drainage channels to monitor surface water level fluctuations at a 15-minute frequency. Surface water samples were collected from spring thaw to winter freeze-up at three different intervals, namely: (a) sub-watershed 1 was a high-intensity monitoring site (n = 1, 7-hour frequency), (b) sub-watersheds 2 and 5 were moderate-intensity monitoring sites (n = 2, 1-day frequency), and (c) sub-watershed 6 was a low-intensity monitoring site (n = 1, ~7-14-day frequency). While grab samples (collected around mid-day on Wednesdays) were used for the low-intensity outlet site, the three high- and moderate-intensity outlet sites were equipped with Hach Sigma[TM] electronically controlled, battery operated automatic samplers (autosamplers). Those samplers feature 24 polyethylene bottles (500 mL), a battery that lasts a minimum of 30 days, programmable timing and volume for sample collection, and a rinse cycle to allow for the

flushing of the intake line between samples. The autosampler at the high-intensity outlet site was programmed to collect one sample every 7 hours, whereas the autosamplers at the two moderate intensity outlet sites collected a daily composite sample in each bottle, with half of the bottle being filled at 6:00 am and the other half at 6:00 pm. On a weekly basis, the automatic water samplers were visited and sample containers were collected and replaced with clean bottles.

All collected surface water samples were tested in the field (right upon collection or retrieval) for electrical conductivity (EC), using a Eutech Instruments Multi-Parameter PCSTestr 35. Samples were then kept cool during transport back to the laboratory located at the University of Manitoba where they were filtered using a 0.45 μm membrane within 24 hours of collection. A U.S. Environmental Protection Agency (EPA)-compliant colorimeter (LaMotte Smart3) and associated reagents were used to test each sample for orthophosphate (hereafter referred to as phosphate) and nitrate concentrations. Chapter 2 outlines the laboratory quality assurance and quality control procedures.

To complete the first research objective, descriptive statistics (e.g., minimum, maximum, mean, median, and standard deviation) of EC and nutrient concentrations were calculated. Temporal variability was assessed by building boxplots to look at the seasonal differences in the statistical distribution of water quality concentrations. The open-water period was divided into spring (April 29 – June 30), summer (July 1 – August 31), and fall (September 1 – October 31). Scatterplots were also built to illustrate how water quality analytes correlated with changes in water level.

The second research objective, aimed at assessing chemostatic versus episodic behaviour, was met by computing, for each sub-watershed, the coefficient of variation (CV_C) of each water quality analyte (electrical conductivity, and nitrate and phosphate concentrations) and the coefficient of variation of stream water level values (CV_Q). The existence of chemostatic or episodic behaviour was then determined by the strength of the CV_C/CV_Q ratio in each sub-watershed: a CV_C/CV_Q ratio near zero indicates chemostatic behaviour, while a CV_C/CV_Q ratio closer to, or above 1, indicates episodic behaviour. CV_C/CV_Q ratios were computed for all 2013/2014 samples, and then on a seasonal basis for spring samples only, summer samples only, and fall samples only.

The third research objective, targeting the characterization of concentration-discharge hysteresis, was addressed by evaluating rain events within sub-watersheds 1, 2, and 5 for which high- to moderate-intensity sampling was achieved. Across the 2013 and 2014 open water periods, 40 rainfall-runoff events were manually delineated for sub-watershed 1, nine for sub-watershed 2, and nine for sub-watershed 5. Those events were delineated by manually reviewing each sub-watershed's water levels, examining rainfall records (based on data collected from installed weather stations proximal to each sub-watershed of interest), and matching rain events to water level responses. Hysteresis loops were then developed by plotting event-specific water quality analytes against water levels. Each hysteresis loop was classified as clockwise (CW), anti-clockwise (ACW), or complex (complex classification based on being neither CW or ACW). Events simultaneously occurring at all three sub-watersheds were compared to determine if the hysteresis type was the same or different for each water quality analyte (i.e., EC, nitrate and phosphate concentrations).

In relation to the fourth research objective, two different analyses were performed. Firstly, each sub-watershed's water quality analyte concentrations were correlated with surrogate measures of antecedent moisture conditions (AMCs).   Antecedent moisture conditions were estimated by summing the rain inputs at a given sub-watershed sampling site for different time periods (i.e., 1 hour, 3 hours, 6 hours, 12 hours, 1 day, 2 days, 3 days, 6 days, 12 days or 24 days before each streamwater sample was collected). Spearman's rank correlation coefficients were computed between daily water quality analyte concentrations and surrogate measures of AMCs. Only correlation coefficients that were statistically significant at the 95% level (p-value < 0.05) were retained for interpretation. Secondly, the relation (or lack thereof) between hysteresis type and antecedent moisture conditions (AMCs) was examined using Kruskal-Wallis tests. Those nonparametric tests were performed, considering that the null hypothesis was that the distribution of AMCs be similar for each hysteresis loop type (CW, ACW, or complex). The alternative hypothesis was that the distribution of AMCs be significantly different for at least one type of hysteresis loop, and which would then indicate a potential relationship between AMCs and hysteresis type. This alternative hypothesis was supported if the p-value associated with a Kruskal-Wallis test was below 0.05.

4.4   RESULTS

4.4.1   Temporal Variability of Water Quality Analytes

Rainfall amounts varied significantly between the two study years: the CCW received 271 mm of rainfall in 2013 (MCFP, 2013) and 530 mm of rainfall in 2014 (MCFP, 2014). As a consequence

of the additional rainfall inputs in 2014, all drainage channels had a greater range in water levels, and a higher average water level, compared to 2013 (Table 4.1). Average channel water level was highest in spring at the upstream sub-watershed outlets (5 and 6), but it was highest in summer at the most downstream sub-watershed outlets (1 and 2) (Table 4.1). The concentrations of each water quality analyte were highly variable throughout the study period (Table 4.1, Figure 4.2-4.9).

The dynamics prevailing at each of the four sub-watershed outlets were examined for both study years combined, as well as for each study years' seasons; a summary of these results can be found in Table 4.2. At the outlet of sub-watershed 1, when water level was at its lowest, water quality analyte concentrations were at their highest (Table 4.1, Figure 4.2, and Figure 4.6). In 2013 (lower rainfall input year), sub-watershed 1 experienced the largest range of EC, while in 2014 (higher rainfall input year), this sub-watershed experienced the smallest range of EC (Table 4.1 and Figure 4.2). Conversely, sub-watershed 1 experienced a small range in phosphate concentrations in 2013 and a larger range in 2014, especially during the spring and summer seasons (Table 4.1 and Figure 4.2).

There were not enough samples taken at the outlet of sub-watershed 2 in 2014 to be representative of the full-year dynamics or season-specific dynamics. In 2013, however, very similar electrical conductivity averages were observed in spring and fall, while a large EC range was experienced in the summer season (Table 4.1 and Figure 4.3).

Table 4.1: Descriptive statistics for water quality and surface water level based on combined 2013 and 2014 daily data for sub-watersheds 1, 2, 5, and 6.

Season	Sub-Watershed #	# of Samples	Statistic	EC (µS)	Nitrate (ppm)	Phosphate (ppm)	Water Level (m)	Water Level /Channel Depth
2013/2014 Daily Samples	1	275	Min	105.00	0.01	0.01	228.00	0.16
			Max	368.00	6.25	0.99	1925.00	1.34
			Mean	207.06	0.34	0.07	950.36	0.66
			Median	184.80	0.13	0.03	923.50	0.64
			STD	73.11	0.80	0.11	320.39	0.22
	2	113	Min	314.00	0.01	0.01	194.10	0.15
			Max	1065.00	9.90	1.77	791.20	0.60
			Mean	643.23	0.90	0.18	104.49	0.08
			Median	601.00	0.26	0.04	157.00	0.12
			STD	216.24	1.58	0.30	154.28	0.12
	5	347	Min	157.00	0.01	0.01	93.00	0.05
			Max	569.00	22.48	0.72	2165.00	1.26
			Mean	282.65	0.93	0.08	820.60	0.48
			Median	242.00	0.13	0.06	563.30	0.33
			STD	101.63	2.45	0.08	498.05	0.29
	6	52	Min	198.60	0.01	0.01	63.00	0.02
			Max	1642.00	4.27	1.00	152.00	0.05
			Mean	585.94	0.34	0.14	500.14	0.16
			Median	572.00	0.07	0.05	358.70	0.12
			STD	182.37	0.77	0.22	376.51	0.12
2013/2014 Spring	1	85	Min	232.00	0.01	0.01	294.00	0.21
			Max	347.00	6.25	0.99	1191.00	0.83
			Mean	295.17	0.59	0.12	742.25	0.52
			Median	298.00	0.09	0.07	691.00	0.48
			STD	25.80	1.28	0.16	218.46	0.15
	2	5	Min	314.00	0.01	0.01	588.00	0.44
			Max	811.00	9.37	0.39	791.20	0.60
			Mean	587.00	1.88	0.11	292.33	0.22
			Median	556.00	0.01	0.04	296.00	0.22
			STD	210.31	4.19	0.16	66.58	0.05
	5	165	Min	157.00	0.01	0.01	236.00	0.14
			Max	508.00	22.48	0.38	2165.00	1.26
			Mean	224.69	1.64	0.06	892.74	0.52
			Median	214.00	0.35	0.02	811.00	0.47
			STD	66.28	3.30	0.07	421.16	0.25
	6	15	Min	198.60	0.01	0.01	63.00	0.02
			Max	730.00	4.27	0.75	123.00	0.04
			Mean	563.11	0.60	0.20	585.80	0.19
			Median	608.00	0.04	0.10	497.20	0.16
			STD	156.48	1.17	0.25	362.88	0.12

Season	Sub-Watershed #	# of Samples	Statistic	EC (μS)	Nitrate (ppm)	Phosphate (ppm)	Water Level (m)	Water Level /Channel Depth
2013/2014 Summer	1	91	Min	105.00	0.01	0.01	588.00	0.41
			Max	325.00	1.28	0.38	1925.00	1.34
			Mean	179.84	0.23	0.07	1106.68	0.77
			Median	156.80	0.13	0.03	1060.00	0.74
			STD	57.26	0.28	0.09	282.21	0.20
	2	54	Min	355.00	0.01	0.01	194.10	0.15
			Max	964.00	9.90	1.77	747.10	0.57
			Mean	498.59	1.40	0.32	370.08	0.28
			Median	449.50	1.10	0.11	380.75	0.29
			STD	127.78	1.64	0.38	88.51	0.07
	5	105	Min	220.00	0.01	0.01	93.00	0.05
			Max	421.00	8.23	0.72	1281.00	0.75
			Mean	291.67	0.33	0.10	306.67	0.18
			Median	284.00	0.04	0.07	223.00	0.13
			STD	44.78	0.93	0.09	190.59	0.11
	6	23	Min	420.00	0.01	0.01	70.00	0.02
			Max	1642.00	2.16	1.00	147.00	0.05
			Mean	589.13	0.19	0.15	510.16	0.17
			Median	542.00	0.04	0.03	358.70	0.12
			STD	238.32	0.46	0.25	469.22	0.15
2013/2014 Fall	1	99	Min	109.40	0.01	0.01	228.00	0.16
			Max	368.00	0.92	0.15	1859.00	1.30
			Mean	182.22	0.21	0.04	955.65	0.67
			Median	154.30	0.18	0.02	874.00	0.61
			STD	65.90	0.19	0.03	350.72	0.24
	2	53	Min	540.00	0.01	0.01	379.00	0.29
			Max	1065.00	4.18	0.15	468.00	0.35
			Mean	795.75	0.30	0.04	169.58	0.13
			Median	791.00	0.04	0.02	178.00	0.13
			STD	186.89	0.77	0.04	44.75	0.03
	5	77	Min	207.00	0.01	0.01	191.00	0.11
			Max	569.00	1.45	0.32	785.00	0.46
			Mean	394.56	0.16	0.09	663.45	0.39
			Median	420.00	0.03	0.08	417.00	0.24
			STD	121.26	0.27	0.07	427.36	0.25
	6	13	Min	508.00	0.01	0.01	133.00	0.04
			Max	756.00	2.38	0.28	152.00	0.05
			Mean	597.58	0.34	0.05	423.58	0.14
			Median	571.00	0.13	0.02	325.00	0.11
			STD	81.74	0.63	0.07	165.45	0.05
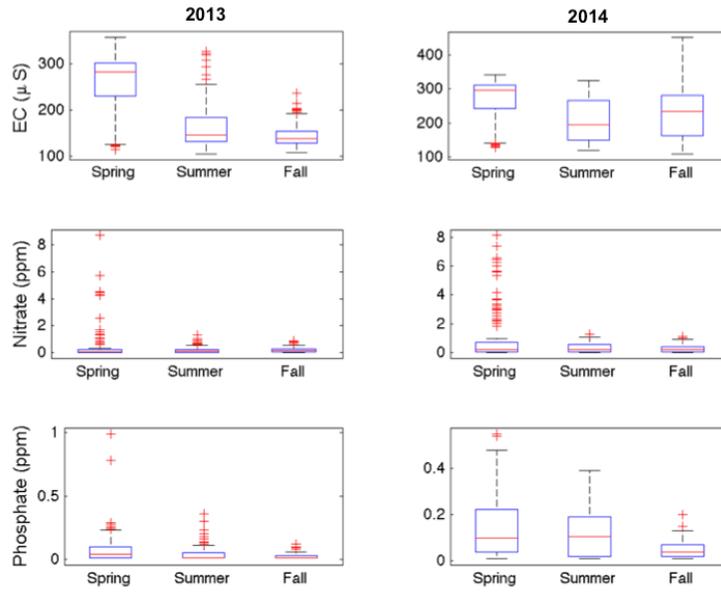
Figure 4.2: Seasonal boxplots for sub-watershed 1's daily electrical conductivity, nitrate concentrations, and phosphate concentrations in 2013 and 2014. Each box has lines at the lower quartile (blue line), median (red line), and upper quartile (blue line) values, while the whiskers extend from each end of the box to show the extent of the rest of the data (minimum and maximum values). Outliers are shown as red plus signs.
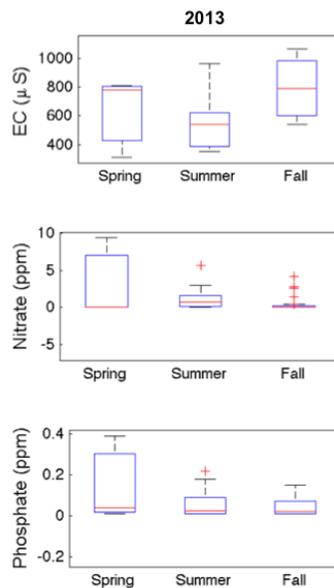
Figure 4.3: Seasonal boxplots for sub-watershed 2's daily electrical conductivity, nitrate concentrations, and phosphate concentrations in 2013 and 2014. Symbology is the same as the one used in Figure 4.2.

Nitrate concentrations were most variable in the spring, while phosphate concentrations were highly variable (i.e., large range in value) throughout all of 2013 (Table 4.1). At the outlet of sub-watershed 5, when water level was at its highest, nitrate concentrations were also at their highest, and EC and phosphate concentrations were at their lowest (Table 4.1 and Figure 4.4). EC in fall of 2013 had a large range (Table 4.1 and Figure 4.4). Phosphate range was larger in 2013 than in 2014, but the range was still relatively low in comparison to the three other sub-watersheds (Table 4.1 and Figures 4.2-4.5). At the outlet of sub-watershed 6, nitrate and phosphate concentrations were highest in spring for the combined study years, while EC was the lowest in spring for both combined study years (Table 4.1 and Figure 4.5). In 2013, sub-watersheds 1 and 6 experienced their highest EC in spring, while sub-watersheds 2 and 5 experienced their highest EC in fall (Table 4.2). Conversely, sub-watersheds 1 and 6 experienced their lowest EC in fall, while sub-watershed 5 experienced its lowest EC in spring. Across sub-watersheds 1, 5, and 6, nitrate concentrations were the highest in the spring of 2014, but lower in the spring of 2013. Across sub-watersheds 1, 2, and 6, phosphate concentrations were generally highest in spring for both combined study years, while they were lower in spring at the outlet of sub-watershed 5 (Table 4.2).
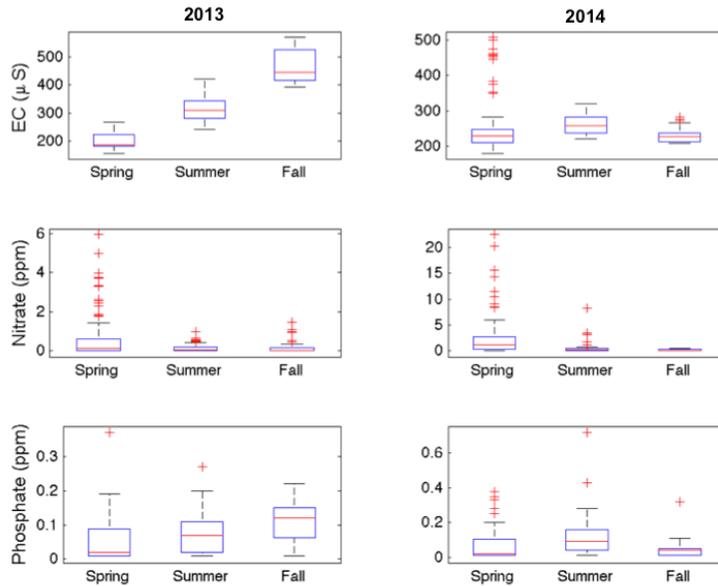
Figure 4.4: Seasonal boxplots for sub-watershed 5's daily electrical conductivity, nitrate concentrations, and phosphate concentrations in 2013 and 2014. Symbology is the same as the one used in Figure 4.2.
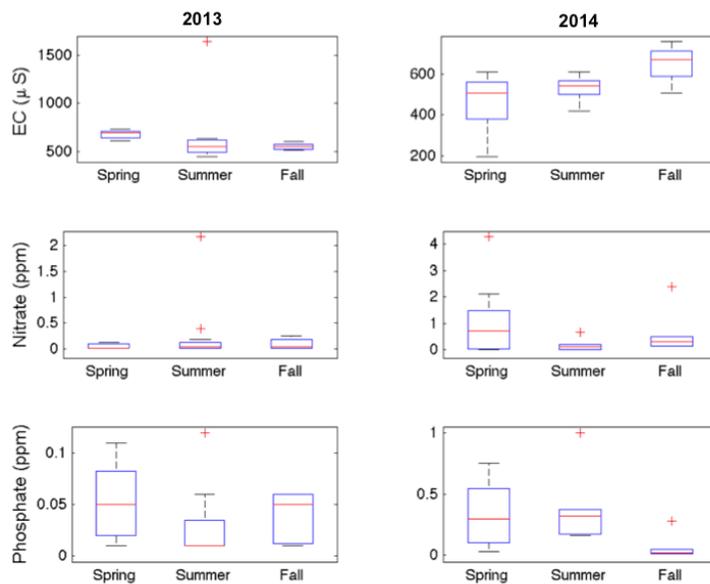

Figure 4.5: Seasonal boxplots for sub-watershed 6's daily electrical conductivity, nitrate concentrations, and phosphate concentrations in 2013 and 2014. Symbology is the same as the one used in Figure 4.2.

Table 4.2: Seasons demonstrating the highest and lowest water quality analytes concentrations based on individual and combined study years for sub-watersheds 1, 2, 5, and 6. When a sub-watershed's water quality analyte is highest or lowest in the same season throughout all three time frames (2013, 2014 and both), this is noted with red. When the water quality analyte is highest or lowest in the same season from two of the three time frames, this is noted with yellow.

Sub-Watershed Statistics		EC			Nitrate			Phosphate		
		2013	2014	Both	2013	2014	Both	2013	2014	Both
1	Highest	Spring	Spring	Spring	Fall	Spring	Spring	Spring	Spring	Spring
	Lowest	Fall	Summer	Summer	Spring	Fall	Fall	Fall	Fall	Fall
2	Highest	Fall	n/a	n/a	Summer	n/a	n/a	Spring	n/a	n/a
	Lowest	Summer	n/a	n/a	Spring	n/a	n/a	Fall	n/a	n/a
5	Highest	Fall	Summer	Fall	Spring	Spring	Spring	Fall	Summer	Summer
	Lowest	Spring	Fall	Spring	Fall	Fall	Fall	Spring	Spring	Spring
6	Highest	Spring	Fall	Fall	Summer	Spring	Spring	Spring	Summer	Spring
	Lowest	Fall	Spring	Spring	Spring	Summer	Summer	Summer	Fall	Fall

4.4.2 Chemostatic or Episodic Behaviour of Individual Sub-Watersheds

The existence of chemostatic or episodic behaviour was determined by the strength of the CV_C/CV_Q ratio in each sub-watershed. The calculated values of CV_C/CV_Q for each of the four sub-watersheds are shown in Table 4.3; chemostatic (<0.30), quasi-chemostatic (0.31-0.65), and episodic (>0.66) behaviours were found throughout the CCW. There was no strong correlation found between nitrate concentrations and water level, or between phosphate concentrations and WL for sub-watersheds 1, 2, 5, and 6 (Figures 4.6-4.9). Nitrate and phosphate, across all sub-watersheds and seasons, demonstrated strong episodic behaviour, with the exception of the

spring season at the outlet of sub-watershed 1, where perfect chemostatic behaviour was observed (Table 4.3).

Electrical conductivity (EC) had the greatest variation throughout the seasons and within each sub-watershed. There was no strong correlation found between EC and WL at the outlet of sub-watersheds 1, 2, and 6 (Figures 4.6, 4.7, and 4.9).   EC at the outlet of sub-watershed 1 experienced episodic behaviour throughout the two years, with the exception of the spring season, when the behaviour was quasi-chemostatic (Table 4.3). EC at sub-watershed 2 was chemostatic throughout all daily samples, but was episodic in spring and summer, and quasi-chemostatic in fall (Table 4.3).   At the outlet of sub-watershed 5, a strong correlation exists between EC and WL in all three seasons (Figure 4.8); EC in this sub-watershed fluctuated between quasi-chemostatic in spring, chemostatic in summer, and quasi-chemostatic again in the fall (Table 4.3).   EC at the outlet of sub-watershed 6 was quasi-chemostatic throughout all seasons (Table 4.3).

Table 4.3: CV_C/CV_Q values obtained for sub-watersheds 1, 2, 5, and 6 for EC, nitrate, and phosphate using all 2013 and 2014 samples, spring-only 2013 and 2014 samples, summer-only 2013 and 2014 samples, and fall-only 2013 and 2014 samples. Episodic (>0.66), quasi-chemostatic (0.31-0.65), and chemostatic (<0.30) are represented by the following colours, respectively, purple, blue, and green.

Season 2013 and 2014	Sub-Watershed #	CV_C/CV_Q		
		EC	Nitrate	Phosphate
All Daily Samples	1	1.04	7.24	3.94
	2	0.23	1.2	1.16
	5	0.59	4.34	1.7
	6	0.41	2.97	2.08
Spring	1	0.89	0	0
	2	1.57	9.77	6.19
	5	0.63	4.27	2.55
	6	0.45	3.14	1.95
Summer	1	1.02	3.96	3.96
	2	1.07	4.9	5.01
	5	0.25	4.58	1.58
	6	0.44	2.57	1.81
Fall	1	1.03	2.72	2.71
	2	0.89	9.72	3.7
	5	0.48	2.59	1.16
	6	0.35	4.79	3.63

Table 4.4: Number of rainfall events in sub-watersheds 1, 2, and 5 that experienced clockwise (CW), anti-clockwise (ACW), and complex hysteresis for each water quality analyte (i.e., EC, nitrate and phosphate).

Sub-Watershed #	Water Quality Analyte	Hysteresis Loop Direction			Total # of Events
		Clockwise (CW)	Anti-Clockwise (ACW)	Complex	
1	EC	5	28	7	40
	Nitrate	22	13	5	
	Phosphate	14	19	7	
2	EC	4	4	1	9
	Nitrate	2	4	3	
	Phosphate	5	2	2	
5	EC	4	5	0	9
	Nitrate	4	1	4	
	Phosphate	1	6	2	
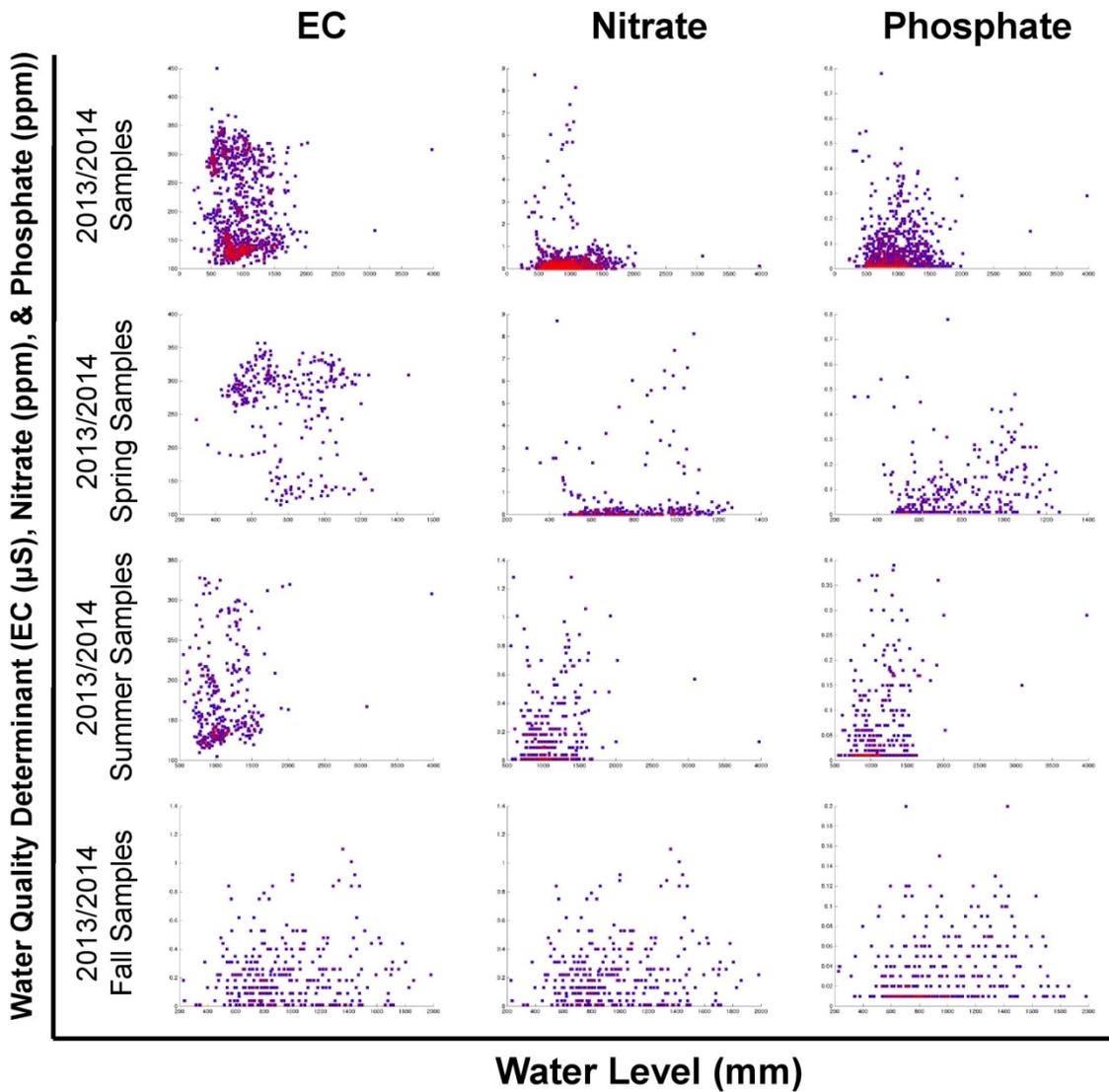
Figure 4.6: Daily electrical conductivity, nitrate concentrations, and phosphate   concentrations in 2013 and 2014, plotted against the water level (mm) at the time the   water   sample   was taken for sub-watershed 1.
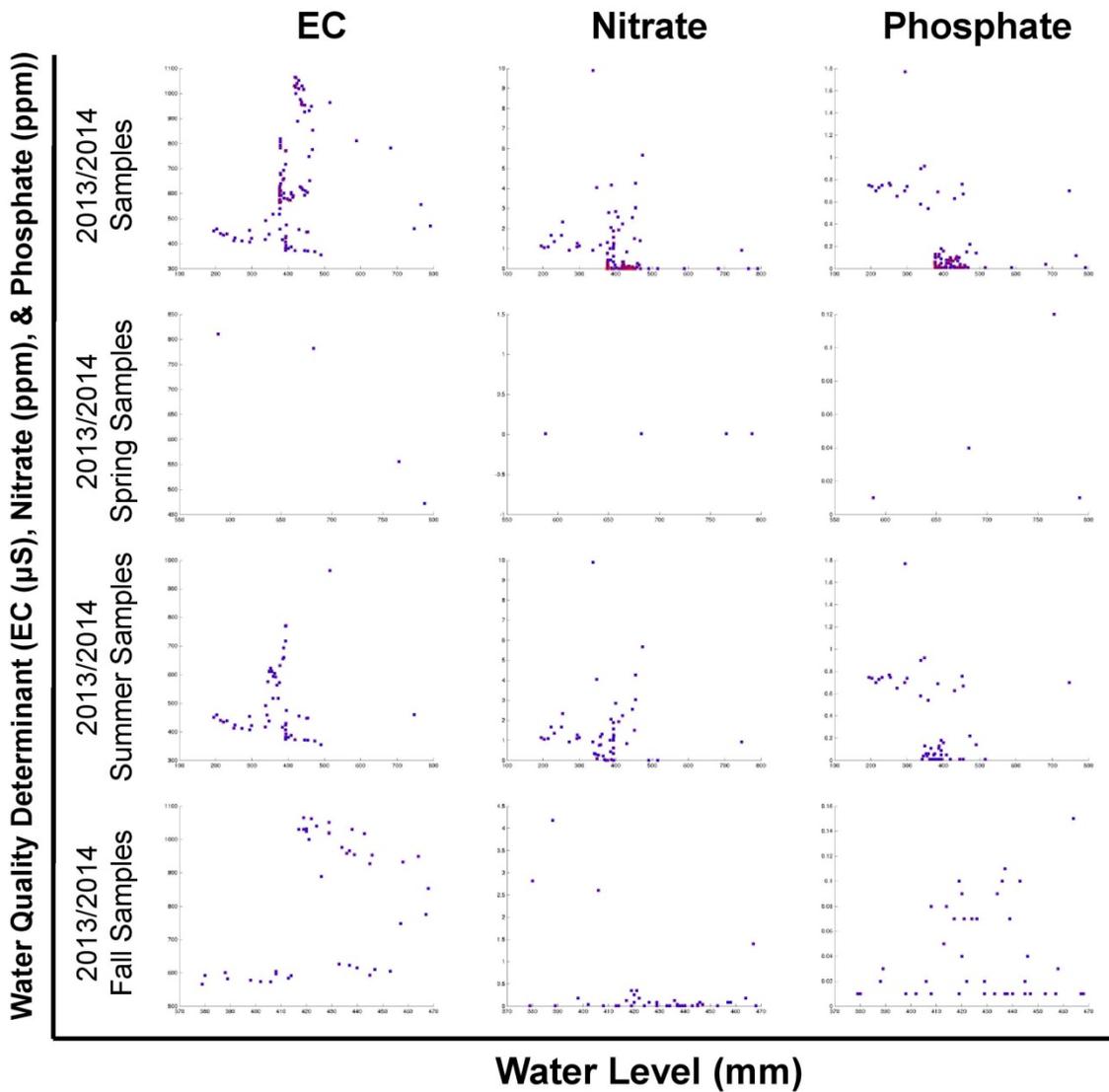
Figure 4.7: Daily electrical conductivity, nitrate concentrations, and phosphate   concentrations in 2013 and 2014, plotted against the water level (mm) at the time the   water   sample   was taken for sub-watershed 2.
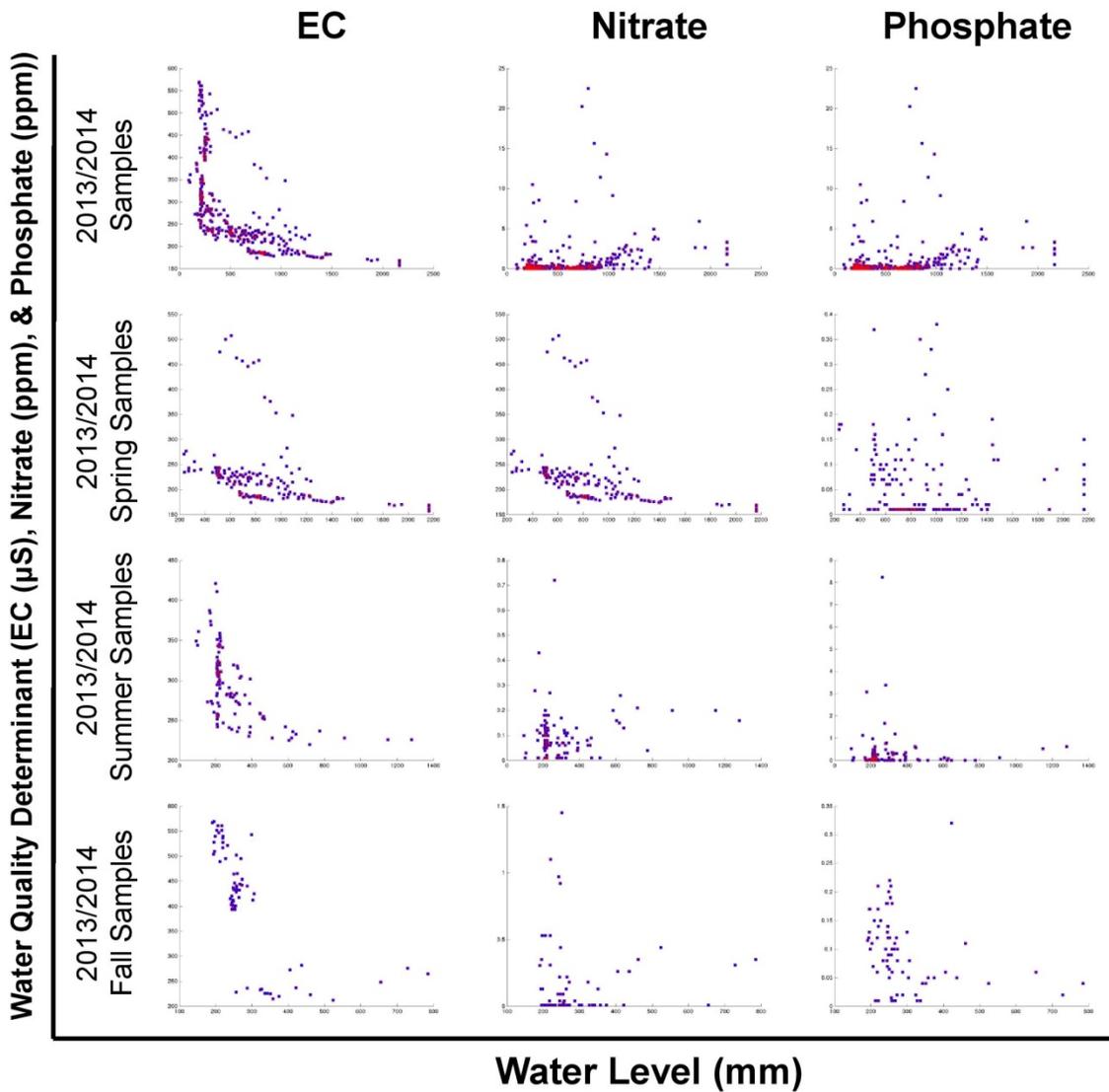
Figure 4.8: Daily electrical conductivity, nitrate concentrations, and phosphate   concentrations in 2013 and 2014, plotted against the water level (mm) at the time the   water   sample   was taken for sub-watershed 5.
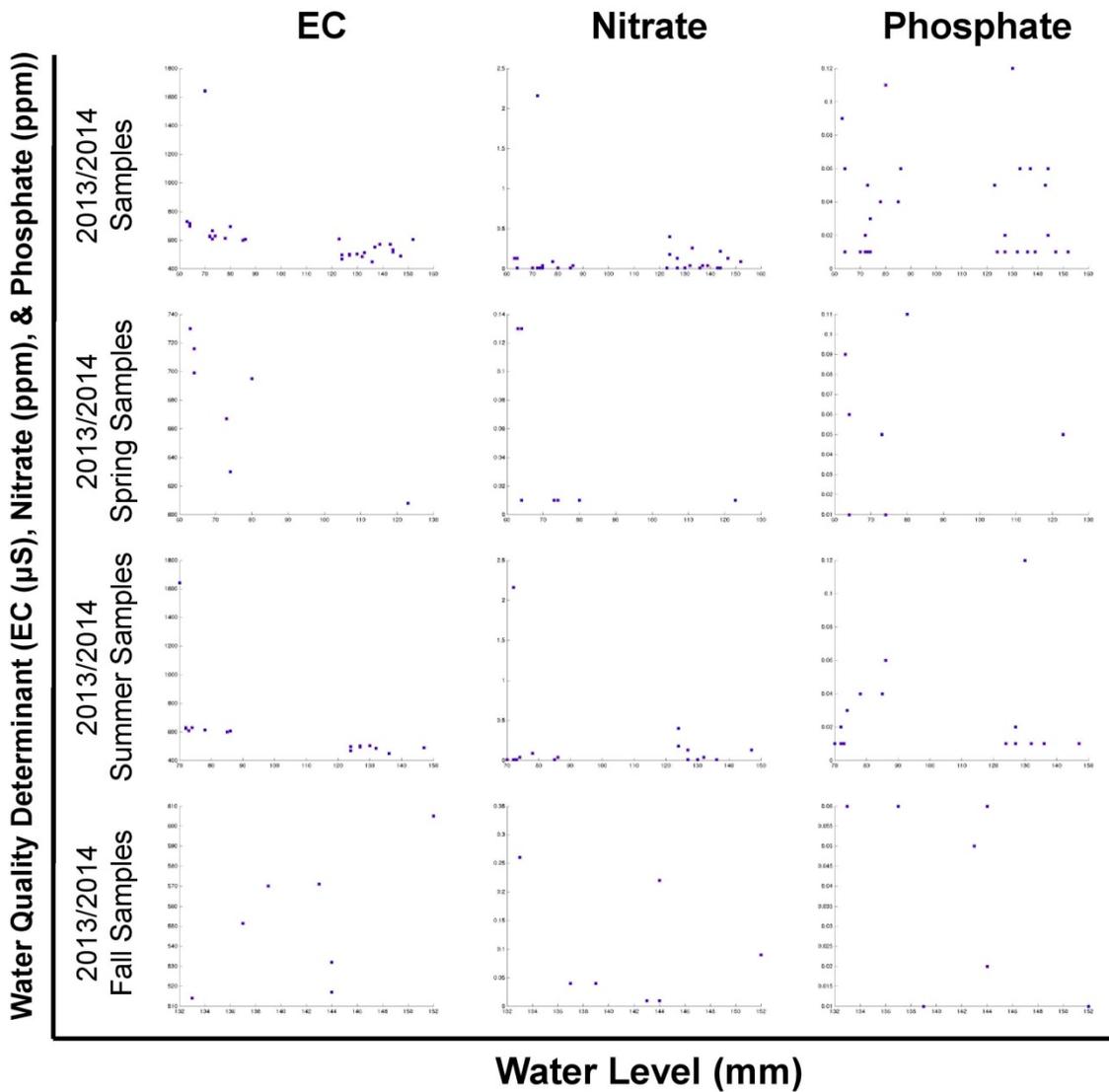
Figure 4.9: Daily electrical conductivity, nitrate concentrations, and phosphate   concentrations in 2013 and 2014, plotted against the water level (mm) at the time the   water   sample   was taken for sub-watershed 9.

4.4.3   Event Scale Hysteresis Loops

The wetter year (2014) experienced a larger number of rainfall events that could be manually delineated. Examples of hysteretic responses for sub-watersheds 1, 2 and 5 in relation to a single rainfall event can be found in Figure 4.10. For sub-watershed 1, the majority of electrical conductivity (EC) and phosphate loops were anti-clockwise (ACW), while the majority of nitrate loops were clockwise (CW) (Table 4.4). Sub-watershed 2 did not demonstrate any consistent hysteresis loop behaviour, with the only dominant loop direction being CW for phosphate (Table 4.4). Similar to sub-watershed 2, sub-watershed 5 did not demonstrate any consistent hysteresis loop behaviour, with the only dominant loop direction being ACW for phosphate (Table 4.4). Figure 4.10 shows that there is great variation between each sub-watershed's loop directions across all three water quality analytes. The percentage of events for which all three water quality analytes (i.e., EC, phosphate and nitrate) led to the same hysteresis type (i.e., loop direction) was: 23.1% for sub-watershed 1, 11.1% for sub-watershed 2, and 12.5% for sub-watershed 5. Hysteresis loops were, however, not always straightforward to interpret. For instance, for sub-watershed 1, complex or unclear hysteresis patterns were observed for 17.9% of the studied events for EC, 12.8% of the studied events for nitrate, and 17.9% of the studied events for phosphate. For sub-watershed 2, complex or unclear hysteresis patterns were observed for 11.1%, 33.3%, and 22.2% of the studied events for EC, nitrate and phosphate, respectively. As for sub-watershed 5, complex or unclear hysteresis pattern were only encountered for nitrate and phosphate, 50% and 25% of the studied events, respectively.
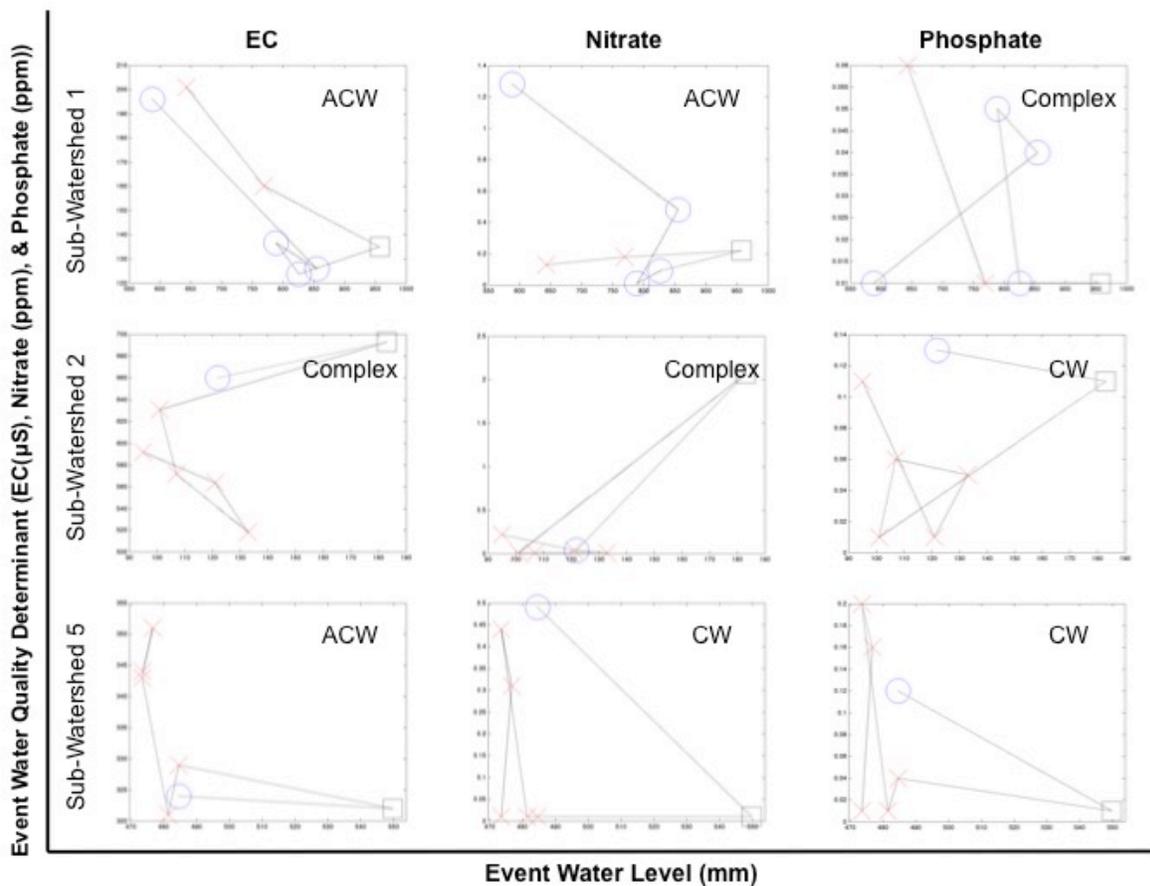
Figure 4.10: Hysteresis loop examples for a single event occurring on the same day (August 17, 2013) across sub-watersheds 1, 2, and 5. Hysteresis loops show event water quality analyte concentrations (EC, nitrate and phosphate) plotted against event water level. Event hysteresis types include clockwise (CW), anti-clockwise (ACW), and complex loops.

4.4.4   Influence of Antecedent Moisture Conditions on Water Quality Analytes

As shown in Table 4.5, less than half of the correlations between each sub-watershed's (1, 2, 5 and 6) water quality analyte concentrations (EC, nitrate, and phosphate) and surrogate measures of antecedent moisture conditions (AMCs) (AMC_{1HOUR}, AMC_{3HOUR}, AMC_{6HOUR}, AMC_{12HOUR}, AMC_{1DAY}, AMC_{2DAY}, AMC_{4DAY}, AMC_{6DAY}, AMC_{12DAY}, AMC_{24DAY}), were statistically

significant (p-value < 0.05).   The largest number of statistically significant correlation coefficients were found for sub-watersheds 1 and 5.   For sub-watershed 1, in particular, a statistically significant correlation was found between electrical conductivity values and AMC_{1DAY}, between nitrate and various AMCs surrogate measures, and between phosphate and AMC_{2DAY} (Table 4.5).   None of the correlation coefficients associated with sub-watershed 1, however, were greater than 0.31, with the average statistically significant correlation coefficient being 0.13 (Table 4.5). Only one statistically significant correlation coefficient was found for sub-watershed 2 (Table 4.5).   For sub-watershed 5, statistically significant correlation coefficients were found between electrical conductivity and AMC_{12DAY}, between nitrate and almost all AMCs surrogate measurements for temporal windows longer than three hours, and between phosphate and AMC surrogate measurements for temporal windows between AMC_{12HOUR} to AMC_{6DAY} (Table 4.5).   However, even though they were statistically significant, none of the correlation coefficients associated with sub-watershed 5 were greater than 0.19, with the average statistically significant correlation coefficient being only 0.12 (Table 4.5).

Lastly, while the correlation analysis described above aimed to examine the link between individual daily concentrations and AMCs, Kruskal-Wallis tests were performed to examine the potential relationship between hysteresis dynamics (i.e., loop direction) and AMCs. Kruskal-Wallis p-values ranged from 0.02 to 1.000, averaging to 0.47 (Table 4.6). The only p-values that were less than 0.05 were related to: the impact of AMC_{24DAY} on nitrate-WL hysteresis within sub-watershed 1, the impact of AMC_{2DAY} on phosphate-WL hysteresis within sub-watershed 2, and the impact of AMC_{2DAY} on both electrical conductivity-WL and phosphate-WL hysteresis loops within sub-watershed 5. Based on the boxplots produced by plotting AMC_s measures as a

function of hysteresis loop direction (not shown) the following was determined: in sub-watershed 1, AMC_{24DAY} values for both CW and ACW nitrate-WL loops are similar, but they are lower for complex nitrate-WL loops. In sub-watershed 2, AMC_{2DAY} values are typically higher when ACW phosphate-WL loops were present, as opposed to CW phosphate-WL loops. In sub-watershed 5, complex phosphate-WL loops were associated with higher AMC_{2DAY} values than CW and ACW phosphate-WL loops. Finally, in sub-watershed 5, CW EC-WL loops were also more common than ACW EC-WL loops when AMC_{2DAY} values were higher.

Table 4.5: Spearman's rank correlation coefficients (RHO values) between surrogate measures of antecedent moisture conditions (AMCs) and daily water quality analyte concentrations for sub-watersheds 1, 2, 5 and 6. Only statistically significant correlation coefficient results (p-value < 0.05) are shown.

Sub-Watershed #		1			2			5			6		
Water Quality Analyte		EC	Nitrate	Phosphate	EC	Nitrate	Phosphate	EC	Nitrate	Phosphate	EC	Nitrate	Phosphate
AMC_{TIME}	AMC_{1HOUR}												
	AMC_{3HOUR}		0.0759						0.1264				
	AMC_{6HOUR}		0.0800						0.1444				
	AMC_{12HOUR}								0.1696	0.1109			
	AMC_{1DAY}	-0.1241							0.1502	0.1899			
	AMC_{2DAY}			0.0716					0.1725	0.1776			
	AMC_{4DAY}	0.0878		0.2024					0.1936	0.1507			
	AMC_{6DAY}	0.1851	0.0426	0.2652					0.1460	0.1427			
	AMC_{12DAY}	0.2567	0.1311	0.3097				-0.1162			-0.3427		
	AMC_{24DAY}	0.2005	0.0097	0.2208			-0.3824	-0.1068			-0.4116		

Table 4.6: P-values associated with the Kruskal-Wallis tests comparing the occurrence of different event hysteresis types (i.e., clockwise, anti-clockwise, and complex) as a function of antecedent moisture conditions (AMCs) for sub-watersheds 1, 2, and 5. P-values lower than 0.05 are noted with yellow.

Sub-Watershed #	Water Quality Analyte	AMC_{TIME}					
		AMC_{1DAY}	AMC_{2DAY}	AMC_{3DAY}	AMC_{6DAY}	AMC_{12DAY}	AMC_{24DAY}
1	EC	0.5930	0.9686	0.8532	0.1871	0.9187	0.1521
	Nitrate	0.4649	0.1961	0.1490	0.1350	0.3846	0.0372
	Phosphate	0.8422	0.7701	0.5523	0.3047	0.2585	0.7961
2	EC	0.2451	0.6210	0.6703	0.2474	0.7408	1.0000
	Nitrate	0.5188	0.9825	0.9544	1.0000	0.1700	0.1178
	Phosphate	0.4328	0.0483	0.0643	0.3272	0.9355	0.9355
5	EC	0.1306	0.0472	0.2482	0.2482	0.5637	0.5637
	Nitrate	0.3189	0.6945	0.1316	0.2125	0.2564	0.1431
	Phosphate	0.2752	0.0219	0.7389	0.3173	0.7389	1.0000

4.5 DISCUSSION

Antecedent moisture conditions and channel water level values had a large impact on water quality concentrations. Average water levels (Table 4.1) were highest in spring in the upstream sub-watersheds (5 and 6), and rather highest in the summer in the further downstream sub-watersheds (1 and 2). This makes sense in a watershed the size of the CCW where water slowly moves longitudinally downstream to the outlet. The concentrations of each water quality analyte were highly temporally variable over the study period. Sub-watershed 1 experienced higher nutrient concentrations during the spring period when water level was lowest (Figure 4.2). Literature suggests that nutrient stores accumulate in soils during dry periods; drier conditions are characterized as times of low precipitation inputs and very few active flow paths, which limits the mobilization of nutrients from land to stream (Ali & Roy, 2010; Bieroza & Heathwaite, 2015; Evans & Davies, 1998; Outram et al., 2016; Thompson et al., 2011). Within

the CCW, the driest seasons are the late-summer and fall (typically), and the latter is followed by frozen winter conditions with snow packs from November until March. This suggests that accumulated nutrient stores within the soil would not be mobilized until the spring freshet and wet spring/summer conditions (Buttle et al., 2016; Fang et al., 2007). High nitrate and phosphate concentrations in spring might also be due to the input of nutrients absorbed into snow and released during snowmelt runoff (Fang et al., 2007; Gray, Granger, & Landine, 1986; Untereiner et al., 2015). Phosphate was highest in spring in sub-watershed 1 (Figure 4.2) and 6 (Figure 4.5), while it was highest in summer for sub-watershed 2 (Figure 4.3) and 5 (Figure 4.4); land use type does not explain that difference in behaviour, as sub-watershed 2 is dominated by agricultural land use, and sub-watershed 5 by forest. Sub-watersheds 1 and 6, however, are both part of Main Drain 1, and sub-watershed 2 and 5 are both part of Main Drain 2: the difference in behaviour between those two groups of sites may therefore be attributable to differing inputs and reactions along each man-made channel.

Overall, the biogeochemical stationarity assessment performed here revealed that all four sub-watersheds experienced mostly episodic behaviour in 2013 and 2014 (Table 4.3), regardless of the chemical analyte considered. This conclusion is in contrast to many previous studies of intensively managed watersheds in the United States and Europe, which have generally demonstrated chemostatic, low inter-annual nutrient variability (Basu et al., 2010, 2011; Thompson et al., 2011). It is reasonable to assume that an anthropogenically-impacted watershed would exhibit chemostatic behaviour, as nutrients build up in soils and are then released slowly (Basu et al., 2010; Thompson et al., 2011). The episodic behaviour, however, of the CCW's sub-watersheds is more comparable to the behaviour demonstrated by pristine or

forested watersheds (Basu et al., 2011; Thompson et al., 2011), experiencing significant inter-annual nutrient variability. Other than sub-watershed 1 in spring (Table 4.3), nitrate and phosphate are strongly episodic for all four sub-watersheds; this indicates that each sub-watershed is linked with nutrient mobilization dependent on proximity to the source. This finding is in harmony with the generally higher spring concentrations of phosphate and nitrate (Table 4.1 and 4.2), hinting that the freshet rapidly mobilizes shallowly and proximally stored nutrients (Bieroza & Heathwaite, 2015; Corriveau et al., 2013; Outram et al., 2016). The behaviour of electrical conductivity was variable among sub-watersheds and seasons; sub-watersheds 1 and 2 are mostly episodic, while sub-watersheds 5 and 6 are mostly quasi-chemostatic (Table 4.3). This indicated that sub-watersheds 1 and 2, which are the two most northern (downstream) sites on Main Drain 1 have switching hydrological dynamics with high EC sources and lower EC sources being dominant at different times. In contrast, sub-watershed 5 (on Main Drain 2) and sub-watershed 6 (further south, upstream, on Main Drain 1) have EC behaviours that are more or less constant, as they do not seem to vary from year to year (Basu et al., 2010, 2011). The episodic behaviour of EC within sub-watersheds 1 and 2 therefore suggests that these sub-watersheds are experiencing periods of overland flow (i.e., low-EC source) and periods of groundwater flow (i.e., higher-EC source) (Garen & Moore, 2005; Haygarth & Sharpley, 2000; Heathwaite, 1995), while the more chemostatic sub-watersheds 5 and 6 are likely experiencing one-single dominant runoff process at the timescale of the analyses (Haygarth & Sharpley, 2000). Sub-watershed 5 is likely experiencing mostly overland flow, as its EC values are consistently moderate, while sub-watershed 6 is likely experiencing mostly groundwater flow, as its EC values are consistently high.

The presence of hysteresis loops during rainfall events indicates that concentration and discharge do not peak simultaneously (Bowes et al., 2005; Evans & Davies, 1998; McDiffett et al., 1989; Outram et al., 2016; Zuecco, Penna, Borga, & van Meerveld, 2016). It should, however, be noted that in this study, hysteresis patterns were analyzed manually, and therefore subject to the analyzer's interpretation. Also, for simplification purposes, only three types of patterns were considered for this study (e.g., CW, ACW, and complex). Other loop types, such as "figure-eight" shapes and others, were bunched together into a single, "complex pattern" category (Zuecco et al., 2016). The majority of EC and phosphate loops were anti-clockwise (ACW) (Table 4.4), which indicates that the highest conductivity and phosphate concentrations occurred on the falling limb of the storm hydrograph and represent delayed inputs to the drainage channels (Bieroza & Heathwaite, 2015; Bowes et al., 2005, 2009; Fučík et al., 2012; Outram et al., 2016; Zuecco et al., 2016). Conversely, the majority of nitrate loops were clockwise (CW) (Table 4.4), indicating that the highest nitrate concentrations occurred on the rising limb of the storm hydrograph. As high EC implies subsurface water sources associated with longer travel times to drainage channels (Pilgrim et al., 1979), the generally ACW EC-WL hysteresis (Table 4.4) within the CCW is plausible. As for the nutrients, Bowes et al. (2005 and 2009) almost always observed CW phosphate-WL hysteresis, as this nutrient is expected to mobilize quickly. While this has been corroborated by other literature (Bieroza & Heathwaite, 2015; Outram et al., 2016), it is contrary to the hysteresis exhibited by phosphate within the CCW's sub-watersheds. The ACW hysteresis behaviour of the CCW's phosphate is potentially due to relatively slow subsurface flow mobilizing soil phosphorus.

In the current study, less than half of the correlations between water quality concentrations and surrogate measures of AMCs were statistically significant, and the magnitude of the correlation coefficients was generally small (Table 4.5). From this it can be assumed that AMCs were not the only drivers of water quality dynamics within the CCW, which is similar to the findings of Bieroza et al. (2014), but dissimilar to the findings of others (Bowes et al., 2005; McDiffett et al., 1989). Of the correlations that were statistically significant, the majority were associated with sub-watersheds 1 and 5 (Table 4.5), which may be related to the higher frequency of water quality sampling at the outlets of those sub-watersheds during the study period. AMCs were not good predictors of event hysteresis type either, as only four statistically significant p-values ($<$ 0.05) were obtained for the Kruskal-Wallis tests described in Table 4.6. The literature states that under wet antecedent moisture conditions, nutrient exports via overland flow and shallow subsurface flow are anticipated, while under dry (low) antecedent moisture conditions, infiltration and deeper (as well as slower) groundwater delays nutrient export to streams (Ali et al., 2012; James & Roulet, 2009). Dry conditions reduce the amount of water reaching the stream, as flow paths are disconnected (Ali & Roy, 2010; Bieroza & Heathwaite, 2015; Outram et al., 2016). In sub-watershed 1 both CW and ACW nitrate-WL loops are equally common when longer-term antecedent moisture conditions (AMC_{24DAY}) are high, therefore no dominant nitrate sources can be inferred based on proximity to the drainage channels for this sub-watershed. The literature states that ACW loops indicate delayed, distant, or slow moving nutrient inputs (Bieroza & Heathwaite, 2015; Bowes et al., 2005, 2009; Fučík et al., 2012); in the current study, Kruskal-Wallis test results therefore imply that in sub-watershed 2, distant phosphate sources are mobilized when short-term (AMC_{2DAY}) antecedent moisture conditions are high (Table 4.6). Conversely, the literature states that CW loops are associated with proximal sources (Fučík et al.,

2012); in the current study, Kruskal-Wallis test results imply that in sub-watershed 5, proximal or near-surface sources of electrical conductivity are mobilized when short-term (AMC_{2DAY}) antecedent moisture conditions are high.

4.6 CONCLUSION

The goal of this study was to examine water quality analytes within prairie sub-watersheds in order to: (1) examine if water quality is temporally variable across different time scales, (2) determine if prairie watersheds conform to the literature consensus regarding chemostatic behaviour in agricultural areas and episodic behaviour in forested areas, (3) utilize hysteresis loops to reveal nutrient export dynamics at the scale of individual rainfall events, and (4) determine if antecedent moisture conditions (AMCs) are good predictors of water quality dynamics in prairie systems. Water quality analyte values were highly dynamic throughout the study period; variability of nitrate, phosphate, and electrical conductivity patterns transcended multi-annual, seasonal and rainfall event scales. The findings regarding chemostatic and episodic behaviour within the four prairie sub-watersheds were surprising: these watersheds were found to be strongly episodic, while the literature suggests that agriculturally dominant areas should rather demonstrate chemostatic behaviour. Event-based hysteresis loops for phosphate were ACW, and therefore representative of a delayed (or slower) export to streams, while event-based hysteresis loops for nitrate were CW, indicating that nitrate sources were proximal to the drainage channels. Also contrary to the literature, antecedent moisture conditions (AMCs) considered in isolation were not sufficient to predict water quality dynamics within the studied prairie sub-watersheds. Chemostatic behaviour (seasonal and multi-annual scale) and ACW hysteresis (rainfall event

scale) are both associated with delayed inputs of nutrients to streams (Basu et al., 2010, 2011; Bieroza & Heathwaite, 2015; Bowes et al., 2005, 2009; Fučík et al., 2012; Thompson et al., 2011), and inversely episodic behaviour and CW hysteresis are associated with shallow or near-surface nutrient sources. The findings within this chapter show that the studied sub-watersheds do not have consistent nutrient sources across the seasonal/multi-annual scale and event scale, implying that water quality analyte's origins fluctuate across scales. Due to the contrast between the findings of the current study and those of previous studies, further analysis is required to determine if this temporal behaviour is potentially influenced by regional practices (e.g., man-made water management, regional tillage, annual crop types and subsequent root types, etc.). Additional analysis of riparian area conditions and soil profiles could also help to better understand the mechanisms responsible for the mobilization of shallow-soil nutrients.

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CHAPTER 5
FINAL SYNTHESIS AND CONCLUSIONS

5.1   Summary of Conclusions and Research Significance

The Catfish Creek Watershed (CCW) is fairly representative of intensively managed prairie watersheds throughout North America. It is characterized by heterogeneous topography (e.g., flat, hilly) and could be broken into twelve nested sub-watersheds representing, on average, a near-even mix of forest and agricultural land. The research objectives for this thesis were to fill some of the knowledge gaps related the spatial and temporal hydrological dynamics associated with prairie landscapes and related water quality dynamics. The current thesis was able to provide answers to some "old" questions, but also led to the generation of new questions based on the multi-faceted analysis of an extensive dataset. Relevant findings, as well as new questions, that should guide future research are briefly highlighted in this chapter.

In relation to the first thesis research objective (i.e., spatiotemporal dynamics of water quality; Chapter 2), some of the physiographic characteristics of the studied sub-watersheds could be correlated with the three studied water quality analytes (electrical conductivity, nitrate and phosphate concentrations). Overall, no statistically significant correlations were observed between geologic material proportions present in the sub-watersheds and water quality concentrations. However, a few statistically significant correlation coefficients between EC, nitrate and phosphate concentrations and macro-topographic characteristics were found. More importantly, a number of statistically significant correlations were found between land use and land cover proportions and water quality analytes, specifically in relation to forest and crop land and nutrient concentrations. No single sub-watershed, in either or both study years, was found to be a stable exemplar of average CCW conditions, but multiple sites were found to consistently

capture extreme conditions, thus making them consistent spatial hotspots or anti-hotspots within the CCW. As notable within Figure 2.3, the sub-watersheds located in the southern portion of the CCW (agricultural, crop land region) seem to behave similarly to each other; this indicates that although statistical analysis suggested otherwise, these sites are likely transport-limited, and therefore managing water in these sub-watersheds is critical in mitigating water quality analytes reaching the stream.

The second research objective (i.e., temporal dynamics of water quality; Chapter 4) delved further into temporal factors that drive water quality analyte fluctuations. One overall conclusion stood out at the end of Chapter 4, namely that water quality analyte values were highly dynamic throughout the study period. This variability (of EC, nitrate and phosphate concentrations) could also be detected at several temporal scales, notably the seasonal, multi-annual, and rainfall event scales. The analysis of concentration-discharge relationships was particularly useful for inferring dominant runoff generation processes and flow paths, and for inferring dominant sources of water (via EC data) and nutrients (via nitrate and phosphate data). Indeed:

- The study of chemostatic versus episodic dynamics was key to assessing water quality dynamics from daily to seasonal scales. The behaviour of EC was variable across sub-watersheds, with downstream sub-watershed outlets (i.e., sub-watersheds 1 and 2) mostly behaving in an episodic manner and likely reflecting water sources that are shallow or proximal to the drainage channels. In contrast, the most upstream sub-watershed outlets (i.e., sub-watersheds 5 and 6) did not showcase significant EC variations from year to year, which is aligned with the definition of chemostatic and quasi-chemostatic behaviour

and likely reflects delayed inputs to the drainage channel. Nitrate dynamics were mostly episodic, suggesting that the nitrate found in the drainage channels is likely sourced shallowly or in riparian areas for all sub-watershed outlets, except that of sub-watershed 1. Similar conclusions were reached about phosphate dynamics (i.e., episodic behaviour).

- – Although the CV_C/CV_Q results are not in compliance with literature, this may be because previous chemostatic and episodic dynamic classification was based on sites that are significantly different from the prairies (e.g., in terms of topography).

- The study of hysteresis loops was also key to assess water quality dynamics at the scale of individual rainfall event. Electrical conductivity was shown to have an ACW hysteresis loop, which likely reflects a delayed input and is consistent with the chemostatic/quasi-chemostatic behaviour observed for some of the targeted sub-watersheds at the daily to seasonal scales. Nitrate was mostly shown to have a CW hysteresis loop, which suggests that stream nitrate is likely sourced shallowly or from riparian areas, and which is consistent with the episodic behaviours highlighted in Chapter 4 at the daily to seasonal scales in relation to nitrate. The fact that nitrate exhibited CW hysteresis can be explained by the typically high nitrate concentration present within this watershed's riparian areas (as measured during additional field work targeting the sampling of perched water table water; data not included in this thesis). This is also in agreement with the literature that often identify riparian areas as nitrogen hotspots (ADD REFERENCE(S)). Conversely, phosphate was shown to have, mostly, an ACW hysteresis loop, which typically illustrates a delayed input and may or may not be fully consistent with the episodic behaviours seen at the seasonal scale in Chapter 4

(depending on the dominant runoff generation mechanisms that primarily mobilize phosphorus from land to stream). Those apparent inconsistencies of hydrobiogeochemical behaviour, not only across temporal scales but also across spatial scales (i.e., sub-watersheds of different sizes), highlight the complex interactions between temporal factors and spatial factors on hydrological processes and water quality dynamics in the CCW.

5.2 FOCUS FOR FUTURE RESEARCH

There is great value in being able to deduce and predict water quality dynamics at various spatial and temporal scales. Moreover, there is a greater value in being able to predict these fluctuations within prairie watersheds that are vulnerable to nutrient runoff linked with agricultural activities proximal to the stream, such as in the CCW. The current thesis was initated with the aim of progressing towards making such predictions. However, upon the conclusion of Chapters 2 and 4, it was clear that to thoroughly understand the spatiotemporal and temporal dynamics of water quality analytes within the Catfish Creek Watershed, additional research would be required. Future research should incorporate regional practices (e.g., man-made water management, regional tillage, annual crop types and subsequent root types, etc.), as well as further information on the characteristics of the area immediately adjacent to each drainage channel (i.e., riparian area). It is believed that land management practices, in particular, might have such a strong impact on water quality dynamics that their "signal" in the landscape is stronger than that of natural or traditional control factors, such as topography, land use and land cover and geology. This would then explain the generally low correlations coefficients reported in this thesis when

addressing the relationships between nutrient concentration dynamics and physiographic and land use watershed characteristics: those correlations showed that the effect of physiography and land use was important – but not sufficient – to consider in order to fully understand prairie water quality. As far as scale and scaling effects are concerned, it is worth mentioning that the specific space and time scales considered in this thesis did not capture the full spectrum of scales at which water quality is known to vary, and control factors on water quality dynamics are known to be important. From a spatial standpoint, for instance, the influence of macro-topography only was considered in Chapter 2, while that of micro-topographic features was not assessed. Along the same lines, the variation of soil properties with depth was not considered either. From a temporal standpoint, the timescales of interest in Chapter 4 were mainly the annual, seasonal and rainfall event scales, meaning that sub-daily dynamics, including diurnal dynamics, were neglected. These temporal scales, although small, can bear significant impact on overall water quality dynamics, especially when it comes to biological influences on nutrient cycling. The dynamics of water quality analytes at these fine-spatial and -temporal scales should be investigated further.

APPENDIX A

Sub-Watershed #	Approximate Location	Site Sample Collection Intensity	Sub-Watershed Topographic Characteristics					Sub-Watershed Land Use and Land Cover					Sub-Watershed Geologic Materials				
			Area	Drainage Density	Elevation Mean	Elevation Range	Slope Mean	Crop Land	Exposed Land	Forest Land	Shrub Land	Wetland	Metamorphic Bed Material	Plutonic Bed Material	Fine (silt, clay & local stones) Surficial Material	Organic Surficial Material	Plain (sand and gravel outwash sheets) Surficial Material
			km²	m/m²	m	m	%	%	%	%	%	%	%	%	%	%	%
1	14 U 685812 5610634	High	642.43	0.000570	237.80	91.44	2.50	31.34	0.10	35.24	18.11	13.50	90.64	9.36	18.18	74.14	5.02
2	14 U 687947 5602513	Low	293.14	0.000638	238.22	85.97	1.88	63.45	0.05	19.48	12.29	1.98	86.45	13.55	23.59	65.78	10.63
3	14 U 691670 5599832	Low	174.94	0.000413	243.14	83.79	2.95	1.88	0.07	47.92	19.48	30.16	88.51	11.49	7.02	92.98	0.00
4	14 U 688861 5596570	Moderate	251.18	0.000664	241.33	85.63	2.05	57.86	0.16	24.87	12.05	2.22	84.11	15.89	28.74	58.30	12.96
5	14 U 696138 5595389	Moderate	145.36	0.000390	245.75	80.93	2.93	1.84	0.07	51.35	13.97	32.29	86.18	13.82	4.20	95.80	0.00
6	14 U 689520 5593072	Moderate	225.91	0.000674	240.36	83.32	1.92	63.27	0.14	19.96	11.37	2.24	82.29	17.71	31.56	54.22	14.22
7	14 U 681921 5586310	Low	125.68	0.000602	249.30	38.24	2.04	48.99	0.08	26.95	20.18	0.00	100.00	0.00	0.00	0.00	100.00
8	14 U 689698 5586591	Low	594.61	0.000984	234.95	36.49	1.70	74.97	0.01	11.63	9.25	0.99	100.00	0.00	35.85	41.51	22.64
9	14 U 689740 5586492	Low	106.67	0.000488	245.16	80.79	2.02	56.71	0.12	24.86	11.44	0.00	64.21	35.79	47.27	52.73	0.00
10	14 U 693050 5588312	Low	344.57	0.000940	248.98	72.69	2.80	1.54	20.60	13.63	0.00	0.00	100.00	0.00	0.00	100.00	0.00
11	14 U 690015 5581649	Low	326.63	0.000783	250.00	76.52	2.50	28.16	0.28	41.78	27.06	0.00	83.33	16.67	9.68	90.32	0.00
12	14 U 693343 5581763	Low	0.56	0.000000	238.29	11.74	3.51	1.51	0.04	47.26	43.03	0.00	100.00	0.00	0.00	100.00	0.00

APPENDIX B

Appendix B – Figure 1: Photo of sub-watershed 1, a mostly forest sub-watershed, taken in July 2013; looking downstream at the outlet of both the sub-watershed and the entire Catfish Creek Watershed.

Appendix B – Figure 2: Photo of sub-watershed 2, a mostly agricultural sub-watershed, taken in August 2013; looking upstream at Side Drain.

Appendix B – Figure 3: Photo of sub-watershed 6, a mostly agricultural sub-watershed, taken in June 2013; looking downstream at Main Drain 2.

Appendix B – Figure 4: Photo of sub-watershed 10, a forested sub-watershed, taken in July 2013; looking downstream at an unnamed small order drain.