THE CONTROLS AND DRIVERS OF DISSOLVED ORGANIC CARBON QUANTITY AND DISSOLVED ORGANIC MATTER QUALITY IN AN IMPACTED GREAT LAKES WATERSHED

THE CONTROLS AND DRIVERS OF DISSOLVED ORGANIC CARBON QUANTITY AND DISSOLVED ORGANIC MATTER QUALITY IN AN IMPACTED GREAT LAKES WATERSHED

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TITLE: The controls and drivers of dissolved organic carbon quantity and dissolved organic matter quality in an impacted Great Lakes Watershed

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ABSTRACT

Intensely managed and modified catchments in the Great Lakes are linked to eutrophication and hypoxia of receiving water bodies downstream, resulting in water quality impairment, and adverse impacts on aquatic ecology. While much focus has been on the role of phosphorous and nitrogen, dissolved organic carbon (DOC) plays a complex and critical role in lake biogeochemical cycles, as it influences the interations between nutrients and contaminants in water and soil through processes of mobilization, transport, biological uptake, and deposition. Human-dominated landscapes have a range of consequences on DOC dynamics as catchment hydrology, plant cover, and nutrient inputs are altered in these environments. As such, the objectives of this study were to identify the controls and drivers of DOC quantity and DOM quality in the Spencer Creek watershed, which is the largest contributor of water to Cootes Paradise that ultimately drains into Lake Ontario. The 159 km^2 study area of the catchment is complex, as the present landscape is composed of a mosaic of various land uses including agriculture, forest, wetland, urban, and industrial regions. Flow alterations contribute to the complexity of the watershed as there are managed reservoirs and alterations in water courses. From 2016- 2018, hydrometric data was collected across 9 monitoring sites, along with surface water samples that were analyzed for DOC concentration and optical properties. Results indicate differences in flow magnitudes and stream DOC between dry and wet conditions, where concentrations during wet conditions were significantly higher compared to dry. Additionally, there was substantial variation in DOC concentration and quality across the Spencer Creek watershed. DOC concentrations were found to be the lowest at groundwater influenced sites in the headwaters of the watershed, and the highest in the mid-catchment region where DOC quality was strongly influenced by wetland sources. The reservoir-influenced sites showed relatively intermediate concentrations of DOC, with quality that exhibited strong microbial signatures. At the outlet, DOC concentrations were attenuated and DOC quality was intermediate between allochthonous and autochthonous end members, reflecting upstream mixing processes. These processes were presented as a conceptual model of water and DOC movement through the Spencer Creek watershed. The implications of this research suggest that with anticipated wetter and warmer conditions DOC concentrations would increase in the watershed. The repercussions of increased DOC concentrations overall imply a decrease of terrestrial carbon storage, and greater input into more reactive and susceptible pools, which may result in further water quality degradation. Overall, the findings from this research provide insight into the fate and transport of water and DOC in a complex, managed catchment in the Great Lakes region, with the aims of providing key information for local stakeholders.

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CHAPTER 1: INTRODUCTION

1.1 Context

Freshwater systems are vulnerable to human influences and activities such as land cover changes, industrialization, urbanization, and agriculture (Basu et al., 2011; Vörösmarty et al., 2010). These activities maximize human access to water and are essential for economic growth, however such modifications to the natural landscape often result in ecosystem impairment and water quality degradation. In the Great Lakes Watershed, extensive changes in land cover first occurred during European settlement two centuries ago, when land resources were needed for economic growth and agricultural purposes (Copeland et al., 1996; Mao and Cherkauer, 1996). Resultantly, there is currently 40% less forest cover surrounding the Great Lakes region compared to pre-settlement conditions, as substantial deforestation occurred to convert land use into cropland (Cole et al., 1998; Copeland et al., 1996).

As growth in this region continues, there are initiatives in place to improve water quality in the Great Lakes region, such as The Great Lakes Water Quality Agreement (GLWQA) between the United States and Canada, which was initially signed in 1972 in response to controlling eutrophication processes due to elevated phosphorus levels (Depinto et al., 1986). In Ontario, the Ontario Water Resources Act (1990) governs the conservation and management of Ontario's waters with the goal of sustainable water use, and long-term environmental well-being of the waters (Government of Ontario, 2018), and the more recent Great Lakes Protection Act (2015) aims to restore the ecological health of the Great Lakes Basin (Government of Ontario, 2015).

On a watershed scale, water management is governed by Conservation Ontario under the Conservation Authorities Act initiated in 1946 (Government of Ontario, 1990). Ontario's 36 conservation authorities aim to mandate conservation, restoration, and management of Ontario's water on a community level (Conservation Ontario, 2018). To achieve their goals, Conservation Ontario implements an Integrated Watershed Management Approach which considers economic, societal, and environmental factors. However, the success of this strategy is highly dependent on achieving a balance between human activities and resource use, and ecosystem conservation (Vörösmarty et al., 2010). Overall, the need for such acts and best watershed management practices is critical as water quality issues in this region are becoming increasingly important due to climate change (Government of Ontario, 2015).

Water quality impairment is an integrated problem with various causes and consequences. However, efforts for management and restoration only focus on a subset of variables that are of immediate concern generally including nitrogen, phosphorous, sediment, or flow (Stanley et al., 2012). Understanding the concentration and quality of organic carbon exported in streams and rivers rarely motivates management practices, despite organic carbon's critical role in biogeochemical cycles (Wilson and Xenopoulos, 2009). Dissolved organic carbon (DOC), which represents the major organic carbon pool in most aquatic ecosystems, is a "modulator" of lake and stream processes (Prairie, 2008; Wetzel, 2001). DOC modifies the influence of other chemicals apparent in waters, and resultantly affects ecosystem structure and function in these environments (Prairie, 2008). As such, understanding DOC regimes in terms of concentration and quality is important, especially in human-impacted and modified environments that differ from natural conditions, as DOC regimes may be altered with greater pools of bioavailable DOM.

1.2 Thesis Objectives

Human influenced catchments with altered land use from natural regimes affect DOC quantities and quality. However, the relationship between hydrological and biogeochemical processes, and their interactions in these complex, managed systems are not well understood. As such, the objective of this work is to identify the controls and drivers of DOC concentration and DOM quality variability in a Great Lakes Watershed using hydrogeochemical and hydrometric data. Specifically, this work will identify if there is a relationship between seasonal and catchment-specific hydrological patterns and DOC variation in concentration and quality. This will test the hypotheses that DOC is (1) temporally variable during the study period and (2) DOC quantity and quality varies across the watershed due to landscape variability and hydrological differences. Overall, this work aims to provide insight into the fate and transport of water and DOC in a complex, managed catchment.

CHAPTER 2: BACKGROUND

2.1 Urbanization in the Great Lakes

Urbanization in Great Lakes regions has resulted in complex landscapes composed of various land use types, hydrological responses, and biogeochemical processes (O'Driscoll et al., 2010; Wang and Kanehl, 2003; Wilcox, 2010). The effects of expanding urbanization in these regions alters drainage networks, catchment flow regimes, and hydrological connectivity (Taniguchi, 1997). Overall physical water storage dynamics within these managed and urbanizing watersheds are poorly understood. These underlying hydrological controls not only characterize flow regimes, but also influence geochemistry processes and patterns (Morrice et al., 1997).

In human-impacted watersheds, hydrologic and biogeochemical responses reflect the features of the natural landscape, as well as the catchment modifications (Basu et al., 2011). Land use type also affects hydrology, as agricultural, ubran, and forested landscapes export distinct nutrient types and amounts, directly affecting downstream water quality (Crosbie and Chow-Fraser, 1999; Peterjohn and Correll, 1984; Steedman, 1988; Wang and Kanehl, 2003). With all these factors considered, intensely managed and modified catchements in the Great Lakes are linked to eutrophication and hypoxia of receiving water bodies downstream (Diaz and Rosenberg, 2008; Kemp et al., 2009). This results in degraded water quality, and adverse impacts on aquatic ecology in the Great Lakes. It is critical to understand the interplay between hydrological and biogeochemical processes, and their interactions in these complex managed systems, as they provide insight into the fate and transport of water and solutes. While much focus has been on the role of nitrogen and phosphorous (Conley et al., 2009; Ryther and Dunstan, 1971), dissolved organic matter (DOM) plays a complex and critical role in lake biogeochemical cycles as the presence of organic matter has the potential to both modify the effect and consequences of other chemical constituents and processes in lake and river systems (Prairie, 2008; Stanley et al., 2012; Wilson and Xenopoulos, 2009).

2.2 Dissolved Organic Matter (DOM) and Dissolved Organic Carbon (DOC)

Dissolved organic matter (DOM) is a complex mixture of organic material including organic acids, macromolecules, and fulvic or humic substances that pass through a 0.45 μm filter in solution (Gergel et al., 1999; Khan et al., 2013; Moore et al., 1998). Despite DOM representing a small fraction of total organic matter, it is the most mobile and active portion as it has a range of implications in terrestrial and aquatic environments (Bolan et al., 2011).

DOM fractions within freshwater systems originate from autochthonous (microbial) or allochthonous (terrestrial) sources. Microbially produced DOM is formed in lakes through microbial respiration by organisms including phytoplankton and other photosynthetic bacteria, whereas terrestrially produced DOM forms through the decomposition and degradation of plant matter and detritus (Khan et al., 2013; Spence et al., 2011). Terrestrially derived DOM primarily enters aquatic systems through the leaching of the surrounding environment into the lakes or streams.

DOM plays a critical role in the global biogeochemical cycle as it influences the interations between nutrients and contaminants in water and soil through processes of mobilization, transport, biological uptake, and deposition (Bolan et al., 2011; Pokrovsky and Shirokova, 2017).

DOM attenuates light due to its yellow-like colour, limiting primary productivity due to a lack of sufficient sunlight required for photosynthesis (Gergel et al., 1999; Khan et al., 2013). Additionally, DOM binds to environmentally harmful trace metals such as copper, mercury, and aluminum forming complexes, and this overall enhances metal solubility and bioavailability (Guo et al., 2001; McKnight et al., 2001; Shafer et al., 1997). The availability of DOM also supports bacterial secondary production, in turn promoting the accessibility of phosphorus to phytoplankton (Gergel et al., 1999).

As carbon composes bulk compostion of organic matter, DOM is quantified through measuring dissoved organic carbon (DOC) concentration (Khan et al., 2013). DOC production is based on the partial decomposition of microbial, terrestrial, or anthropogenically derived organic matter accompanied by its dissolution in pore water. Over the past two decades, an increase in DOC concentrations has been observed throughout Europe and North America (Evans, 2006). With global climate change and increasing temperatures, DOC concentrations in freshwater systems are expected to increase in the future due to higher input of flow from catchments to lake (Thrane et al., 2014). The repercussions of increased DOC concentrations overall implies a decrease of terrestrial carbon storage, and greater input into more reactive and susceptible pools that have greater negative implications (Evans, 2006).

2.3 Biologically Labile and Recalcitrant Dissolved Organic Matter

From a biological perspective, DOM can be classified into labile or recalcitrant pools. Labile DOM primarily originates from microbial (autochthonous) sources, and is bioavailable (Lindell et al., 1995). Resultantly, labile pools of DOM are more easily consumed by bacteria as the structure of this DOM is composed of lower molecular weight compounds, and is less complex in structure. Terrestrially derived (allochthonous) DOM is relatively more refractory or recalcitrant, as the structure of recalcitrant DOM is more complex and is composed of high molecular weight compounds (Münster and Chróst, 1990). Recalcitrant DOM undergoes phases of microbial degradation and transformations prior to reaching aquatic environments (Lindell et al., 1995).

2.4 Controls on Stream DOC

Surface water DOC concentrations vary spatially and temporally as a result of processes occurring in the surrounding terrestrial environment and in-stream (Dawson et al., 2008; Winterdahl et al., 2016). The "base case" scenario describes the drivers and controls of river and stream DOC, which views stream and river DOC as a sequence of terrestrial accumulation, transfer of this DOC into the channel, and in-stream processing (Stanley et al., 2012). DOC in lotic ecosystems, which are characterized by flowing waters, such as streams, creeks and rivers, are typically dominated by terrestrial sources (Aitkenhead-Peterson et al., 2003). Generally, land cover and landscape attributes also be used as predictors for the terrestrial accumulation of DOC as soil type, wetland cover, and topography all play a role (Mulholland and Hill, 1997). The transfer of terrestrial DOC into surrounding channels can be explained by climate variables, as it occurs either hydrologically through connectivity between the surrounding environment and stream, or through atmospheric inputs seasonally from throughfall. In-stream processing affects the quantity and quality of DOC once transferred due to numerous processes including photooxidation, photolysis, biodegradation, microbial processing, respiration, and adsorption/desorption of DOC. Previous studies have determined that the fraction of DOC subject to degradation is < 5- 30% which is moderately small (Stanley et al., 2012).

In-stream processing of DOC is complex, as processes occur simultaneously and affect the analysis of DOC quality. For instance, photolysis, the process in which UV light from the sun separates molecules, can break down the larger components of DOM structure, to smaller, labile, lower molecular weight DOM (Hansen et al., 2016; Laurion and Mladenov, 2013; Moran and Covert, 2007). Resultantly, photolysis of DOC is a sink of DOM in surface layers of lakes, and may ultimately stimulate microbial activity and promote bacterial production (Hansen et al., 2016; Lindell et al., 1995). However, photolysis may also transform labile, lower weight compounds to higher molecular weight recalcitrant material through subsequent reactions. Biodegradation, another in-stream process that affects DOC concentration and quality, is the process of decomposition of organic material by microorganisms. This results in loss of labile, low molecular weight DOM material (including proteins and organic acids), and may be accompanied by the production of high molecular weight material (e.g. fulvic and humic acids), through processes of transforming existing DOM components (Hansen et al., 2016). Considering these two processes alone, and how they alter DOM structure, it is evident that there are several factors and processes at play that affect the end product observed within a single water sample.

2.5 Effects of Human Land Use on DOC

Wetlands are a key source of DOC into streams and rivers (Creed et al., 2003; Eckhardt and Moore, 1990; Gergel et al., 1999; Mulholland, 1997). Greater wetland cover is associated with higher DOC concentrations and loads, and subsequently, percent wetland is a strong predictor for increases in DOC concentration (Eckhardt and Moore, 1990). In human-modified landscapes containing small wetland coverage, modifications to the landscape influence DOC loads and concentration in stream and river systems, however there is a need to better understand these processes (Mulholland and Hill, 1997). Human-modified catchments typically have changes in land use (e.g. plant cover, soil, nutrients) and catchment hydrology (altered channels, reservoirs, dams), which differ from natural conditions prior to disturbance. With the "base case" model of terrestrial accumulation, transfer, and in-stream processing, any change in the terrestrial environment compared to natural or "base" conditions, may consequently change DOC concentration or quality in streams and rivers. Previous studies have been able to determine land use effects on DOC in streams, however, others have not. For instance, agricultural land use has been found to increase (Chow et al., 2007; Molinero and Burke, 2009), decrease (Cronan et al., 1999), or have no effect (Aitkenhead-Peterson et al., 2007) on stream DOC. However, this may be a result of various management practices across study sites, diversity in crop types, and other characteristics unique to each individual agricultural site. Despite the magnitude of DOC concentrations and loads yielding a variety of results across agricultural sites, the composition of DOC between undisturbed and human-impacted catchments displays consistent observations across various land use types and locations. Compositional changes observed from undisturbed to human impacted DOC include changes from high-to-low molecular weight DOC, reduced aromaticity, and increased lability of DOC (Wilson and Xenopoulos, 2009). Land use cover changes due to urbanization is associated with degraded water quality, primarily due to the effects of increased impervious surfaces and drainage channel modifications. Stormwater runoff is also of concern as storm events provide a transport mechanism due to the flushing of non-point source pollutants and contaminants (Goonetilleke et al., 2005). The "first flush phenomenon" describes the observed increase in pollutant concentrations for urban runoff during the rising limb, preceding peak flow on the hydrograph (Deletic, 1998). Similar to the influence of agriculture on DOC, studies looking at the influence of urbanized landscapes on stream DOC concentration suggest mixed results of both an observed increase (Aitkenhead-Peterson et al., 2009; Goonetilleke et al., 2005) and decrease (Maloney et al., 2005) in stream DOC.

2.6 DOM Quality and Fluorescence

The structure and quality of DOM is complex as its composition varies spatially and temporally within freshwater ecosystems (Aiken, 2014). Characterising DOM compostition provides information on its chemical composition, providing insight into how DOM reacts in the envrionment (Hansen et al., 2016). Fluorescence spectrometry has provided a straightforward technique in characterising the nature and quality of DOM across a range of different aquatic environments. Effectively, fluorescence spectrometry techniques are used to "fingerprint" DOM sources and origins, through determining the absorbance and emission properties of DOM structures (Aiken, 2014; Cory and McKnight, 2005; Spencer et al., 2007).

Absorption of light in the UV-visible spectrum (190-780 nm) occurs when the excitation of electrons in a chemical bond jump from a ground energy state to an exctited one (Valeur, 2001). The molecular complexicty of the structure reflects the wavelength absorbed. Molecules with greater complexity such as aromatics absorb light at longer wavelengths (lower energy) and absorb light more easily, whereas simpler single-bonded molecules such as alkanes and carbohydrates absorb shorter wavelengths outside the UV-visible light spectrum as greater energy is required to reach a higher state (Aiken, 2014). Light is emitted when excited electrons return to their ground state after absorption, displaying the phenomenon of fluorescence (Valeur, 2001). Similar to absorption, the molecular structure reflects the intensity of fluorescence with complex structures fluorescing at a greater instensity compared to simpler structures.

Fluorescence spectrometry techniques assume that the molecules composing the structure of DOM behave similarly to pure compounds in solution. Resultantly, any change in fluorescence paramater such as intensity, absorbance, or peak width reflects the variation in DOM strurcture and constituents (Aiken, 2014).

2.7 DOM Quality Indices

Fluorescence data is presented in several ways including excitation-emission matricies (EEMs) and fluorescence indices. EEMs are the most common way of displaying fluorescence data as EEM spectra contain a vast amount of information, and graphically display where peak intensities are occuring (Aiken, 2014) . Fluorescence indices are commonly used to characterize DOM quality in terms of precursor material and processes (Cory and McKnight, 2005; Wilson and Xenopoulos, 2009), humification (Ohno, 2002), and composition and moluecular structure (Peuravuori and Pihlaja, 1997; Weishaar et al., 2003). Indices and their general use are summarized in Table 2.1.

2.7.1 Fluorescence Index (FI)

The fluoresence index (FI) is a qualitative way of measuring the relative proportion of terrestrial and microbial source of the fluorphores, that are asoccisiated with humic DOM fractions (Cory et al., 2011; Cory and McKnight, 2005). A FI values of ~1.8 suggest DOM precursor material is more microbial in nature, where as values of FI ~1.2 display a more terrestrial signature.

2.7.2 Freshness Index (β/α)

The freshness index (β/α) is used to differentiate microbial and terrestial sources of DOM, where β represents more recently derived DOM which is likely to be microbial in source, and α represents highly decomposed DOM (Coble et al., 2014; Wilson and Xenopoulos, 2009). Overall, the ratio of β/α is qualitiative, and its interpretation provides an indication of the relative contribution of recently produced DOM, as increasing values suggest microbial inputs (Parlanti et al., 2000).

2.7.3 Humification Index (HIX)

Humification is the process through which organic matter is formed through microbial synthesis (Ohno, 2002). During the humification process, lower molecular weight compounds undergo polycondensation where the smaller molecules are split out, resulting in condensed, higher molecular weight polymers. The humification index (HIX) describes the degree of humification, where higher values suggest a greater degree of humification, more structurally complex DOM, and a lower H/C ratio (Coble et al., 2014; Dong et al., 2017).

2.7.4 Specific Ultraviolet Absorbance ($SUVA_{254}$)

Specific ultraviolet absorbance ($SUVA_{254}$) is one of the most commonly used indices in freshwater studies (Cory et al., 2011), and is calculated as the absorbance of the water sample at 254nm divided by the DOC concentration in (mg/L), reported in units of L/mg-M (Coble et al., 2014). SUVA has a strong, positive correlation with aromatic carbon content, making it a reliable proxy (Cory et al., 2011; Weishaar et al., 2003). Typical $SUVA_{254}$ values range from 1-6 L/mg-M (Cory et al., 2011; Hansen et al., 2016), however higher values have been reported in the literature observed in interstitial waters (Jaffé et al., 2008). Typically, $SUVA_{254}$ values greater than 6 L/mg-M indicate there may be interference at the absorbance of 254 nm with dissolved iron species (Cory et al., 2011; Hansen et al., 2016; Poulin et al., 2014; Weishaar et al., 2003). The typical surface water concentration range of ferric iron (Fe^{3+}) is 0-0.5 mg/L, which adds 0-0.04 cm^{-1} absorbance to samples at 254 nm, therefore not interfering with SUVA measurements (Cory et al., 2011; Weishaar et al., 2003). However, with waters displaying iron levels greater than this, there may be some interference with iron species.

2.7.5 E2/E3

The E2/E3 ratio is negatively correlated with DOM molecular weight (Ågren et al., 2008; Helms et al., 2008; Peuravuori and Pihlaja, 1997; Wong and Williams, 2010). The ratio is calculated as the absorbance of 250 nm to absorbance at 365 nm (Peuravuori and Pihlaja, 1997). Previous studies have determined that the E2/E3 ratio increases with photolysis as the process breaks down larger components of DOM, decreasing its molecular weight (Dalzell et al., 2009; Moran and Covert, 2003).

2.8 Stable Isotopes of Water

Stable isotopes of water (^{18}O and ^{2}H) are used as conservative tracers to determine sources of water and provide insight into the movement of water throughout the hydrological cycle (Clark and Fritz, 1997). Variation of isotopic composition occurs as a result of isotopic fractionation, where lighter isotopes preferentially evaporate leading to enrichment of the heavier isotope in the remaining water, and as a result of mixing of waters with varying isotopic composition (Hoefs, 2009). These variations in isotopic composition are temperature-dependent, resulting in seasonal shifts of isotopic composition with isotopically heavy summer rain, and lighter snow during the winter (Dansgaard, 1964).

On a global scale Craig (1961) developed a global meteoric water line (GMWL) based on $\delta^{18}O$ and $\delta^{2}H$ values of precipitation samples across the world. This relationship yields the equation $\delta^{2}H = 8.0(\delta^{18}O) + 10‰$ with an R^2 value of 0.95, suggesting that $\delta^{18}O$ and $\delta^{2}H$ are highly correlated. On a local scale, local meteoric water lines (LMWL) are similarly developed using precipitation samples with slopes of the equation ranging from 5 to 9 (Kendall, 2004). In the Great Lakes region, the local meteoric water line yields the equation $\delta^{2}H = 7.18 (\delta^{18}O) + 1‰$ (Longstaffe et al., 2013). Generally, precipitation and groundwater samples plot along the MWL. However, waters that have undergone evaporation plot below the LMWL along a local evaporation line (LEL) with a slope less than that of the LMWL, typically within the range of 4 to 6 (Gibson et al., 1993). The intersection of the LMWL and LEL represent an estimate of weighted mean isotopic composition of annual precipitation of the catchment (Gibson et al., 1993).

CHAPTER 3: SITE DESCRIPTION, MATERIALS, METHODS

3.1 Study Area

The Great Lakes catchment of interest for this study is the Spencer Creek watershed in Hamilton, ON which connects into Hamilton Harbour, and drains into Lake Ontario (Figure 3.1). The study area is 159 km^2, and encompasses the Fletcher Creek, Upper Spencer Creek, Flamborough Creek, Westover Creek, West Spencer Creek, Middle Spencer Creek, Logie's Creek, Borer's Creek, Sydenham Creek, and Lower Spencer Creek subwatersheds which are mandated under Ontario Regulation 161/06, and fall into the boundaries of the Hamilton Regional Conservation Authority.

3.1.1 Geology of the Spencer Creek Watershed

The Spencer Creek Watershed consists of middle and lower Silurian and upper Ordovician sediments such as limestone, siltstone, shale, and dolostone (Ontario Geologic Survey, 1991). The landscape is characterized by processes that occurred during the Wisconsinan glaciation, as quaternary sediments and glacial deposits overly the regional geology, providing ideal conditions for agriculture such as thick nutrient rich soils (Government of Ontario, 2016).

The Niagara Escarpment is a dominant geological feature in the watershed that faces east with the elevation of its crest rising above the town of Dundas (Karrow, 1959). The escarpment is developed on Silurian-aged dolomite, with the area below the escarpment representing the red Queenston shale (Upper Ordovician age), and the bedrock surface above the escarpment is composed of the grey Lockport dolomite (Middle Silurian age) (Karrow, 1959). The escarpment itself is as high as 30.5 m and is composed of dolomite. The Westover Drumlin Field located near Safari Rd at Westover (43° 21' 48.7074 N, 80° 3' 14.4714W") is another prominent geological feature in the watershed. The drumlins are composed of Pleistocene deposits of glacial, glaciofluvial, and glaciolacustrine sediments of the Wentworth Till (Karrow, 1959).

The region has medium to small-scale drift thickness, with most of the watershed representing dolomite with less than 7.6 m of drift (Ontario Geological Survey, 1969). Deeper drift in the watershed occurs in buried valleys, moraines, and drumlins, and these values reach as high as 39 m (Karrow, 1959).

3.1.2 Hydrology of the Spencer Creek Watershed

The headwaters of Spencer Creek are located in Galt Moraine in Puslinch Township, Ontario (Duval et al., 2009). The flow of water is oriented at a southeast direction and moves down from areas with higher elevations to lower elevations moving through Cootes Paradise, Hamilton Harbour, and ultimately into the west end of Lake Ontario. The Spencer Creek is a 6th order stream, and its watercourse is sustained by a network of smaller tributaries and streams flowing into the main stream (Hamilton Conservation Authority, 2009). There are several factors affecting the hydrological conditions within the Spencer Creek watershed. The hydrology varies seasonally due to the humid continental climate within Hamilton, ON with cold winters and hot summers (Woo and Valverde, 1986). Beverly Swamp, located in the northern region of the watershed (43° 220 N, 80 °070 W), plays a role influencing regional hydrology as it reduces flooding during high flow events, and recharges groundwater during periods of low flow (Woo and Valverde, 1986). There are two large reservoirs within the watershed altering the natural regime to avert downstream flooding and for recreational purposes: Valens Reservoir and Christie Dam and Reservoir (Sultana, 2009). Valens Reservoir was constructed in 1966 to prevent downstream flooding and for low flow augmentation (Hamilton Conservation Authority, 2012a). The reservoir is 0.76 km^2, receives drainage water from a 10.9 km^2 area, and has a maximum depth of 4.6 m. Flow in the reservoir is retained during spring and augmented during the summer during times of low flow and the rest is released in autumn (Hamilton Conservation Authority, 2012a). The Christie Dam was constructed by the Hamilton Conservation Authority in 1971 as a flood control structure for the town of Dundas. (Hamilton Conservation Authority, 2012a). There are additionally smaller, privately managed reservoirs in the watershed such as the one located at LaFarge Quarry in Dundas, which influence stream hydrology as a result of storing and releasing water.

3.1.3 Land Use of the Spencer Creek Watershed

The heterogeneity of land use within the Spencer Creek Watershed contributes to its complexity as a watershed. A land use analysis on ArcGIS was performed merging the Southern Ontario Land Use Information System 2.0 (2016) layer and the Agriculture Canada Annual Crop Inventory (2016) layer. The analysis determined that Spencer Creek is 49% agriculture, 21% wetland, 11% forest, 8% urban, 2% extraction, 1% open water, and 10% undefined (Figure 3.2). Site specific land use statistics are summarized in Table 3.1.

3.2 Materials and Field Methods

3.2.1 Site Identification

The sites selected in this study are distributed across smaller tributaries and stream networks that merge into the main Spencer Creek. In 2016, initially 24 potential sampling sites were identified through Arc GIS 10.2.2 using the Ontario Integrated Hydrology Enhanced

Watercourse layer (2012) and the Ontario Road Network Segment with Address (2010). Intersections of the road and stream networks were identified to confine potential sample sites to those accessible by road. The sites were further narrowed down based on areas of interest within different land use types such as sites in wetland, agricultural, and urban dominated regions. Other areas of interest included where streams transitioned from one land use type to another, or where streams of different land use types merged. The three Water Survey of Canada sites in the watershed were also incorporated into the study (WSC stations 2HB007, 2HB023, 2HB015). The 24 potential sites were all initially visited to assess their viability as research sites. Overall, the sites were narrowed down to a final total of 16 sampling sites within the watershed in 2016. Sites that displayed weak stage-discharge relationships in 2016 were removed in 2017, and replaced in order to incorporate reservoirs into the study, more agricultural locations, and to obtain reliable stream-discharge relationships. Therefore, the sites attenuated down to 14 sites in 2017, and remained consistent into 2018. Overall, 9 sites overlap between the 2016-2018 field seasons, which are the main focus of this study (Figure 3.1) (Table 3.1). Almost all sites in this study are along the main Spencer Creek, except for Gore 2 (a tributary of Fletchers Creek) and Harvest (a tributary of Sydenham Creek). Waters draining from Gore 2 later merge with the main Spencer Creek upstream of the Safari site, and Harvest merges with the main Spencer Creek upstream of Dundas (the outlet).

3.2.2 Hydrometric Measurements

Stilling wells were installed at the sampling sites to measure continuous stage. Wells were constructed from 1 m PVC pipes with drilled holes, and with nylon coverings to prevent potential clogging of the well. Solinist Leveloggers (pressure transducers) were placed into the stilling wells to measure water level, conductivity (at select sites), and water temperature. The

Leveloggers were calibrated with 1413 µs/cm calibration solution prior to installation, and were programmed to record measurements every 15 minutes during each field season. Corresponding Solinst Barrologgers were installed at a site upstream (Gore 2) and downstream (Con4WE), recording measurements every 15 minutes, to be later compensated. The stilling wells were hammered down at the selected sampling sites, with the Leveloggers placed at an ideal sampling depth. A metal ruler was also clamped to the well for manual measurements of water level. A Sontek FlowTracker was used to measure manual discharge at all 9 sites, with the exception of Gore 3 and Crooks in 2016 as loggers were not installed at these two sites until 2017. Low flow and high flow measurements were taken approximately 10 times a year to develop yearly rating curves for each site.

3.2.3 Water Sampling

Over 2016-2018, water sampling occurred during the summer months on a biweekly-weekly basis. The field season spanned June-August in 2016, May-November in 2017, and March-October in 2018. A YSI probe was used measure water temperature, conductivity, and pH. Surface water samples were collected for DOC, fDOM, alkalinity, and isotope measurements. In collecting the water samples for DOC, FDOM and alkalinity, a 150 mL plastic syringe was used to collect surface water in a pooled area, with a 0.45 µm polyethersulfone filter placed on the tip of the syringe afterwards. The bottles were environmentalised three times with the filtered stream water prior to filling them up. Once collected, bottles were stored in a refrigerator for future analysis. Isotope samples were directly collected in the stream after environmentalising the bottles three times, ensuring there was no headspace in the bottle for potential evaporation to occur, and were stored at room temperature in the laboratory. DOC and alkalinity samples were collected in 30 mL amber HPE bottles, fDOM samples were collected in 40 mL glass amber bottles, and lastly isotope samples were collected into to 20 mL scintillation vials. A total of 233 surface water samples were collected in 2016, 130 in 2017, and 300 in 2018, for each bottle type (DOC, fDOM, alkalinity, and stable isotopes of water). Precipitation isotopes were collected at the site Valens and near McMaster University using an IAEA style sampler for rain (Gröning et al., 2012) and select snow samples were melted for analysis to construct a local isotopic meteoric water line. In total, there were 117 precipitation samples taken (113 rain, 4 snow).

DOC samples were analysed by The Biogeochemical Analytical Service Laboratory at the University of Alberta. DOC concentrations were determined using a Shimadzu 5000 TOC analyser. Concentrations were reported back in units of mg/L. Stable isotope ratios for hydrogen and oxygen were determined using a Los Gatos Research DTL-100 Water Isotope Analyzer at the University of Toronto. Data was reported back as $\delta\ ^{2}H$ (‰) and $\delta^{18}O$ (‰). The Biogeochemistry Laboratory at the University of Waterloo analysed alkalinity samples. Concentrations were reported back in units of g/L of Na_2CO_3.

3.2.4 Fluorescence Spectroscopy Analysis

The Horiba-Jobin Yvon Aqualog Machine (Aqualog), was used to analyse fluorescence dissolved organic carbon (fDOM) samples using a procedure adapted from Rastelli (2016). Surface water samples were stored in a refrigerator to prior to run, and were then pipetted into quartz cuvettes that were bathed in a 50% nitric acid solution for at least 24 hours prior to use. In order to compare changes in fluorescence parameters, instrumental inefficiences and variablities were accounted for through intrumental calibrartion of Quinine Sulfate (QS) , Raman Signal (RS), and corrections for Rayleigh Scattering, and inner filter effects (IFE). QS and RS standards were run prior to a sample run, as QS applies spectraction corrections in light source output variation and records instrument drift across runs, and RS normalizes data for Raman Scattering, and determines the integration time normalization factors for 0.1, 0.25, 0.5, 0.75, and 1 second.

Water samples were all ran at 5 nm increments at an excitation range of 240 to 600 nm, and an emission range of 212.5 nm to 621.38 nm at 3.27 nm increments. Raman Scattering, IFE, and Rayleigh Masking settings were set at 1st and 2nd order, CCD gain settings were set to medium, and the sum of slit widths was set at 12. All samples were initially run at an integration time of 0.1s to determine if absorbance values at 255 nm were in the correct range and to establish whether samples might need to be diluted. Samples with an absorbance value greater 1.5 were diluted to achieve sample counts in the range of 20,000-45,0000, where values closer to the upper range were ideal. After each run, individual EEMs for each run were visually checked for irregularities. IFE and Rayleigh scattering were corrected for during sample runs and post processing steps. The absorbance and emission data files from each successful run were then imported into RStudio to be processed and analysed.

3.2.4.1 Fluorescence Indices

Characterizing and the sourcing of DOC were dependent on excitation and emission datasets obtained from the EEM of each sample. The five indices used to interpret DOC were: the fluorescence index (FI), freshness index (β/ α), humification index (HIX), $SUVA_{254}$, and E2/E3 (Table 2.1). These indices were calculated within R Studio using a modified code provided by Dr. Claire Oswald of Ryerson University.

The fluorescence index (Cory and McKnight, 2005) is calculated as the ratio of emission at 450 nm/500 nm at an excitation of 370 nm. The freshness index (Wilson and Xenopoulos, 2009) is calculated at an of excitation 310 nm, and is the ratio (β /α) where β is the emission intensity at

380nm, and α is the maximum emission intensity between 420 nm and 435 nm. The humification index (Ohno, 2002) is calculated as the area of peak under an emission of 435 nm to 480 nm divided by the peak area under emission 300 nm to 345 nm at an excitation of 254 nm. However, with the Aqualog settings, an excitation of 255 was used. $SUVA_{254}$ (Karanfil et al., 2002) is calculated as the ratio of UV absorbance at 254 nm to the DOC concentration in mg/L. E2/E3 (Peuravuori and Pihlaja, 1997) is calculated as the ratio between absorbance at 250 nm to absorbance at 365 nm.

3.3 Data and Statistical Analysis

3.3.1 Statistical Tests

Data processing, QA/QC procedures, and statistical analyses were undertaken in MATLAB R2018a and R language for statstical computing (R Core Team, 2018). Prior to analysis, all variables were tested for normality using the Shapiro-Wilks test using the R function shapiro.wilk. The Spearman rho correlation test (non-parametric) was used to determine signifcant correlations among land use cover and DOC and indices data using the cor.test function. A non-parametric statistical approach was also taken to determine significant differences in the mean ranks of all DOC and indices data. First, the Kruskal-Wallis test (kruskal.test in R) was used to determine significant differences in mean ranks for DOC and indices data between all 9 sites, and over the three years of the study period. The Dunn's Test of Multiple Comparisons (non-parametric) was used as a post-hoc to indentify which groups were significantly different. A 95% confidence interval ($p \leq 0.05$) was used to determine significance for all tests. Due to differences in the timing of field seasons (June-August in 2016, May-November in 2017, and March-October in 2018), data from only the overlapping months of the study period (June-August) for each year were considered for all statistical tests to determine significant differences between years. However, all boxplots and scatter plots of the data consider all data points collected from each field season, regardless of the month the data was collected. Results from all statistical tests are included in the Appendix.

3.3.2 Concentration-Discharge Analysis

The relationship between concentration-discharge is often described by a power-law relationship between concentration C, and discharge Q, where the equation describing the relationship is the following,

$$C = aQ^b \qquad [1]$$

where a is a constant representing the intercept, and b is a constant representing the slope of the equation on a logarthicmic axis (Godsey et al., 2009). Using this equation, concentration-discharge relationships within the Spencer Creek Watershed were assessed on a spatial scale. A slope of zero indicates that a catchment behaves chemostatically (an increase in discharge has no effect on chemistry), a slope of -1 indicates that the catchment is diluting solutes whereas a slope of 1 indicates that a catchment is mobilizing solutes. Slopes that are significantly different from zero suggest that catchments do not behave chemostatically (Godsey et al., 2009). Slopes were tested for significance differences (from zero) using an F test with a 95% confidence interval ($p \leq 0.05$).

3.3.3 Principle Component Analysis

A principle component analysis (PCA) using 262 samples from 2016-2018 was completed in R studio using the prcomp () function, to asess the relationship between landscape controls on DOC concentrations and indices data. The fluoresence index (FI) was ommitted from the PCA to minimize bias, as the fluorescence index and freshness index are highly correlated variables. All variables loaded into the PCA were centered (means were subtracted), and scaled (divided by standard deviations) to standardize the variables. Principle components 1 and 2 (PC1 and PC2) were selected for analysis based off a screeplot. The remaining principle components were not explored as there were only 5 variables loaded, and the PC1 and PC2 explained 79.1% of the variation in the dataset. PC1 was further explored and correlated to other variables using the Spearman rho correlation test for categorical data, and the Pearson correlation test for continous data.

3.3.4 Landscape Analysis

Sites were grouped into 4 landscape units based off of site characteristics: headwater sites (Gore 2 and Gore 3), reservoir-influenced sites which are downstream of Valens, Christie, and Lafarge Quarry reservoir (Valens, Crooks, and Harvest), mid-catchment sites that are located in the middle of the catchment (Safari, Valens, Harvest), and the catchment-outlet site (Dundas).

3.3.5 Stable Isotope Analysis

Stable isotopes of water , $\delta^{18}O$ and $\delta\ ^{2}H$, were analysed for the purpose of determining sources of water. A local meteoric water line (LMWL) was established through plotting a regression line through 117 precipitation and snow samples of $\delta\ ^{18}O$ and $\delta\ ^{2}H$ (‰). A local evaporation line (LEL) was established through plotting a regression line through 284 surface water samples of $\delta\ ^{18}O$ and $\delta\ ^{2}H$ (‰) as the slope of the regression line represents the slope of the LEL. All surface water samples for $\delta\ ^{18}O$ and $\delta\ ^{2}H$ (‰) were plotted against the LMWL and LEL.

CHAPTER 4: RESULTS

4.1 Climate

Results from this study include data collected during summer and fall months. Over 2016-2018, total annual precipitation recorded at the Hamilton RBG Weather Station (43.28 N, 79.88 W) was greatest in 2017 (887 mm), followed by 2018 (797 mm), and 2016 (717 mm), with 2016 falling below the 30-year climate normal of 780 mm (Environment and Climate Change Canada, 2019). For the months spanning the field season (March-November), total precipitation was once again greatest in 2017 (746 mm), followed by 2018 (626 mm), and lowest in 2016 (524 mm) (Figure 4.1). Conditions were extremely dry in 2016, such that rainfall in August 2016 (96 mm) accounted for 44% of the total precipitation over the summer months alone. Mean air temperatures over the field season were 13 °C, 14 °C, 12 °C respectively with 2016 averaged at the climate normal (13 °C), whereas 2017 was slightly warmer and 2018 was slightly below.

4.2 Hydrology

4.2.1 Discharge and Total Runoff

To establish terminology, discharge is the volumetric outflow of water and describes how much water flows through a cross sectional area in a given time, with units typically expressed in m^3/s. Runoff represents the total amount of water leaving a region normalized per unit area, and is typically expressed in units of length such as mm (Dingman, 1994).

In 2016, weather conditions were extremely dry during the field season, and resultantly discharge was lowest in 2016 across all sites (Figure 4.2). The continuous lack of rainfall and warm weather resulted in two of mid-catchment sites (Con4WE and HWY5) drying up late summer, until a 60 mm storm event had replenished the streams. In 2017 and 2018, discharge values were overall higher and comparable between the years, except at Crooks where the 2017 hydrograph has a lower magnitude with almost no variation in flow. Total runoff values followed a similar pattern as values were lower in the dry year (2016) compared to 2017 and 2018 (Figure 4.3). For instance, at the outlet of the watershed, Dundas, there was a total of 16 mm of runoff during June to October in 2016, whereas in 2017 and 2018, the total runoff for the same time period were respectively 60 mm and 43 mm.

Hydrographs and total monthly runoff plots over the study period at most sites had typical seasonal patterns of flow across the watershed (Figure 4.2, 4.3). Discharge values were highest at all sites during spring months, when total rainfall contributions were highest and soils were presumed wet from winter snowmelt. During the spring months captured in 2017 and 2018, values were as high as 20 m^3/s at the outlet in Dundas. Peaks in discharge were observed during summer storm events, exhibiting a response to precipitation occurring during summer to early fall. These events were particularly notable in 2016, as summer conditions were prior to the storm events in August. During the summer months, discharge and runoff were considerably lower at most sites excluding the headwater sites and Harvest.

The magnitude of flow and hydrograph shape were variable across all sites due to watershed characteristics and contributing area. The sites Safari, HWY5, Crooks, and Dundas all had larger contributing areas with the greatest range of discharge values, with maximum discharge values of 4.0 m^3/s, 12 m^3/s, 16 m^3/s, and 20 m^3/s respectively. The headwater sites, Gore 2 and Gore 3, had the smallest range of discharge values with a maximum discharge of 0.175 m^3/s and 0.1 m^3/s

respectively throughout the study period. The headwater sites additionally had higher runoff per unit area values. During the dry conditions of 2016, Gore 2 sustained its flow compared to the other 8 sites and had the highest total runoff for the study season from June to October (118 mm) which is 7 times higher than the runoff per unit area at the outlet. At the headwater sites, differences between total runoff during a dry and wet year did not vary as greatly compared to sites downstream. For example, total runoff at Gore 2 during the summer months (June to August) in 2016 was 76 mm, compared to 186 mm and 88 mm in the following two years respectively. The difference between runoff per unit area in during a dry year (2016) a wet year (2017) at Gore 2 represents a 145% increase, whereas a 380% increase in total runoff was observed at Dundas for the same time period and years.

Sites downstream of reservoirs (Valens and Crooks) and downstream of a quarry's reservoir (Harvest) had "flashier" hydrographs with pulses indicating when water was released and stored. In 2017, when flows were high, it is apparent that flow was heavily regulated upstream of Harvest and Crooks, as the hydrographs lack variability that a natural flow regime would exhibit.

4.3 Dissolved Organic Carbon (DOC)

4.3.1 Temporal and Spatial DOC Patterns

DOC patterns were spatially and temporally dynamic as concentrations (mg/L) were variable among sampling sites, annually, and seasonally. DOC concentrations ranged between 1.0- 39.3 mg/L over the study period (Figure 4.4), (Table 4.1). In 2016, DOC concentrations were relatively low where all sites averaged at 6.2 $\pm$ 3.7 mg/L, with a maximum concentration of 17 mg/L. In 2017 and 2018, DOC increased across all sites to averages of 12.3 $\pm$ 9.6 mg/L and

9.2 ± 5.9 mg/L respectively, with concentrations reaching maximums double those observed in 2016 (39.1 mg/L in 2017, and 39.3 mg/L in 2018). DOC concentrations in 2016 were significantly lower than those in 2017 and 2018 across all sites except HWY5 ($p<0.05$) whereas 2017 and 2018 concentrations were comparable and not significantly different (Table 4.2). DOC concentrations varied spatially across the river continuum in the watershed. The headwaters (Gore 2 and Gore 3) exhibited the some of the lowest DOC concentrations, with values averaging at 5.0 ± 6.9 mg/L and 3.1 ± 1.9 mg/L respectively for each site, over the three-year study period (Table 4.3). Moving downstream of the headwaters, concentrations gradually increased from Valens to HWY5, with the highest DOC concentrations at Safari, Con4WE, and HWY5 (all mid-watershed) with concentrations over the three years averaging 11.6 ± 5.2 mg/L, 13.4 ± 7.2 mg/L, and 12.6 ± 5.2 mg/L respectively. Crooks, which is downstream of Christie reservoir and the mid-catchment sites, had a similar three-year average of DOC concentrations averaging at 12.2 ±6.5 mg/L. Water discharging from Crooks towards Dundas is joined with waters discharging from Harvest, a tributary that runs through Lafarge Quarry and that connects to the main Spencer Creek. Harvest had relatively low DOC concentrations comparable to those of the headwater sites with concentrations over the three years averaging at 5.3 ± 5.3 mg/L. At the outlet of the watershed, Dundas, DOC concentrations averaged at 8.7 ± 6.6 mg/L, exhibiting intermediate DOC concentrations compared to the headwater and mid-catchment sites. Across land use types, DOC concentrations were found to be positively correlated to percent wetland cover in the study area (Figure 4.5) (Table 4.4) ($p<0.05$), whereas the correlations between DOC and percent agriculture and urban were negative ($p<0.05$) (Figure 4.6, 4.7).

Seasonal patterns in DOC concentration were relatively weak in 2016, as variability in concentrations were low (Figure 4.8). Prominent peaks in DOC concentration during 2016 were in response to rain events that occurred. In 2017 and 2018, there were no apparent peaks in DOC concentration immediately following individual rain events. However, DOC concentrations gradually increased at the end of summer to early fall and exhibited some peaks during the period (August- November) (Figure 4.8).

4.3.2 DOC Concentration-Discharge

The slopes of the concentration-discharge relationships were used to assess whether catchments were behaving chemostatically (slope of zero), diluting (negative slope significantly different from zero), or were mobilizing chemicals (positive slope significantly different from zero) (Godsey et al., 2009). The relationship between DOC concentration and discharge varied spatially throughout Spencer Creek (Figure 4.9). On a watershed scale, there was general increasing trend between log DOC concentration and log discharge, with a positive slope of 0.16 and an R^2 value of 0.15 ($p < 0.05$) indicating a weakly explained power relationship (Figure 4.10). Spatially, slopes varied from site to-site, exhibiting both positive and negative slopes. At the headwaters, Gore 2 (tributary of Fletcher's Creek) had the greatest slope among all sites (0.57) ($p<0.05$), whereas Gore 3 had a slightly negative slope (slope of -0.07) that was not significant. Moving downstream, slopes gradually increased from 0.07 to 0.08 across Valens, Safari ($p<0.05$), Con4WE ($p<0.05$), until HWY5, where slopes became negative (-0.03, not significant). Downstream of HWY5, Crooks also had a negative slope (-0.09, not significant), whereas the Harvest's tributary had a positive, not significant slope of 0.11. Waters leaving Crooks and Harvest merge and discharge at Dundas, where a positive slope of 0.18 was exhibited ($p<0.05$). Overall, slopes of log DOC concentration- log discharge were significantly different from zero ($p<0.05$) at 4 of the 9 study sites including Gore 2, Safari, Con4WE, and Dundas (Table 4.5).

4.4 DOC Quality

4.4.1 Fluorescence Index (FI)

Over the three-year study period, FI ranged from 1.44 - 1.72 and averaged at 1.54 ± 0.05 (Figure 4.11) (Table 4.3). FI values showed little change between the two wet years (2017 and 2018) at each sampling site. However, in the dry year of 2016, FI was both higher and lower compared to 2017 and 2018 values. Overall, FI values at each site showed little variability over study period as Safari and Crooks were the only sites to exhibit significant differences over the three years ($p<0.05$) (Table 4.2). However, there was strong spatial variability of FI among land use types and sampling sites. FI had a positive correlation with increasing percent agriculture and percent urban land cover ($p<0.05$) (Figure 4.6, 4.7), whereas a negative correlation was observed with increasing % wetland cover (Figure 4.5) (Table 4.4). Along the Spencer Creek watercourse, the headwaters sites had differing FI values as Gore 2 had relatively lower FI values compared to Gore 3, with three-year averages of 1.54 ± 0.03 and 1.58 ± 0.04 respectively. FI decreased downstream of the headwater sites reaching the lowest three-year averaged values at the mid-catchment sites (Safari, Con4WE, and HWY5), with averages of 1.48 ± 0.02, 1.51 ± 0.02, and 1.53 ± 0.03 respectively over the three years. Further downstream, FI gradually increased until Crooks (1.53 ± 0.02), until a sudden increase in FI was observed from the waters of Harvest's contributing tributary, as the highest values of FI in the watershed (1.65 ± 0.04) were at this site. At the outlet, intermediate FI values were observed similar to those at Gore 2 and HWY5 (1.55 ± 0.02).

4.4.2 Freshness Index (β/α)

β/α ranged from 0.51- 0.87 with an average value of 0.64 ± 0.07 over the 3 years (Figure 4.12) (Table 4.3), and had similar spatial trends compared to FI. Temporally, β/α in 2016 was significantly higher ($p < 0.05$) compared to both 2017 and 2018, at all sites expect Gore 2 (Table 4.2). Similar to FI, β/α showed little variability between the two wet years (2017 and 2018) at each sampling site, as these years were statistically from the same group. Spatial variation of β/α mimicked FI variability, as the patterns across the Spencer Creek watercourse were similar, and as highest and lowest β/α occurred at the same sites that had the highest and lowest values for FI. Harvest had the highest β/α, with an average of 0.75 ± 0.06 and the lowest β/α values were at Safari, Con4WE, and HWY5 with averages of 0.56 ± 0.02, 0.58 ± 0.03, and 0.61 ± 0.04 respectively. Across land use types, β/α was negatively correlated with increasing percent wetland cover ($p<0.05$) (Figure 4.5) whereas a positive correlation was observed with increasing percent agriculture and urban cover ($p<0.05$) (Figure 4.6) (Figure 4.7).

4.4.3 Humification Index (HIX)

HIX varied both temporally and spatially over the study period, with values that ranged from 0.63- 0.95 with an average value of 0.88 ± 0.05 (Figure 4.13) (Table 4.3). Similar to both β/α, HIX exhibited strong temporal trends as HIX in 2016 was significantly lower ($p < 0.05$) in the dry year (2016) compared to the wet years (2017 and 2018) at all sites except for Gore 2 and Gore 3, the two headwater sites (Table 4.2). Over the two wet years, there was little variation in HIX, similar to results observed with β/α and FI as these two years were statistically from the same group (Table 4.2).

Across land use types, HIX was positively correlated with increasing percent wetland cover (Figure 4.5) (Table 4.4), whereas increasing percent agriculture exhibited a negative correlation ($p<0.05$) (Figure 4.6). Across landscape units, the opposite spatial trend was observed for HIX compared to β/α and FI. At the headwaters of the Spencer Creek watershed, HIX values at Gore 2 were lower than Gore 3, as the three-year averages were 0.89 ± 0.05 and 0.91 ± 0.03 respectively. A decrease in HIX was observed downstream of Valens Reservoir at Valens (0.84 ± 0.03). Moving further down the watercourse, HIX increased across mid-catchment sites, with the highest values observed across the watershed at Safari, Con4WE, and HWY5 with averages of 0.93 ± 0.01, 0.93 ± 0.02, and 0.92 ± 0.02 over 2016-2018 respectively. These mid-catchment sites had similar enough HIX values that they exhibited no significant differences from another spatially (Table A4). A slight decrease of HIX was observed downstream of the mid-catchment sites at Crooks, with values over the three years averaging at 0.91 ± 0.02. However, further along the watercourse, Harvest had the largest decline in HIX, with values averaging at 0.85 ± 0.06 which are similar to those of Valens. At the outlet, Dundas, the three-year HIX average (0.91 ± 0.02) was intermediate in magnitude compared to the other sites.

4.4.4 Specific Ultraviolet Absorbance ($SUVA_{254}$)

$SUVA_{254}$ ranged from 0.17- 5.74 L/mg-M with an average of 2.98 ± 1.05 L/mg-M over the study period (Figure 4.14) (Table 4.3). Similar to results of FI, $SUVA_{254}$ had strong spatial variation among land use types and sampling sites. However, annual variability of $SUVA_{254}$ between dry and wet years was weak, as there were no temporal significant differences found for $SUVA_{254}$ across sites over the study period, except at Gore 2 between 2016 and 2018 values ($p<0.05$).

$SUVA_{254}$ was found to be positively correlated with increasing percent wetland cover ($p < 0.05$) (Figure 4.5) (Table 4.4), and negatively correlated with increasing percent agriculture cover ($p < 0.05$) (Figure 4.6). Additionally, spatial variation of $SUVA_{254}$ across the Spencer Creek watercourse mirrored patterns seen with HIX, as highest and lowest $SUVA_{254}$ averages were observed at the same sites where highs and lows were observed for HIX. Similar to HIX, the headwater sites had variability between $SUVA_{254}$ with lower three-year averages exhibited at Gore 2 compared to Gore 3 (3.02 ± 2.05 L/mg-M and 2.77 ± 1.15 L/mg-M respectively). The highest values were observed mid-catchment at Safari, Con4WE, and HWY5 with averages of 3.78 $\pm$ 0.77 L/mg-M, 3.87 $\pm$ 0.80 L/mg-M, and 3.57 $\pm$ 0.74 L/mg-M over 2016-2018 respectively. Harvest and Valens had the lowest $SUVA_{254}$ values with averages of 2.10 $\pm$ 0.94 L/mg-M, and 2.25 $\pm$ 0.75 L/mg-M respectively. Similar to the spatial trends of the other indices, the outlet had intermediate $SUVA_{254}$ values compared to the other sites, with a three-year average of 2.89 $\pm$ 0.79 L/mg-M.

4.4.5 E2/E3

E2/E3 had prominent temporal and spatial trends over the study period, with values that ranged from 2.49 –13.41 with an average value of 6.03 ± 1.13 over the three years (Figure 4.15) (Table 4.3). During the two wet years (2017 and 2018), E2/E3 exhibited similar values within each sampling site, showing very little variation in values, similar to trends seen with FI, β/α , and HIX. However, during the dry year in 2016, E2/E3 showed both an increase and decrease in E2/E3 compared to the two wet years.

Spatial variations of E2/E3 were similar to those observed with FI and β/α across the watershed. At the headwaters, average E2/E3 over the study period was lower at Gore 2 (5.05 $\pm$ 0.65) compared to Gore 3 (5.71 $\pm$ 1.64). Moving downstream, E2/E3 values reached their highest across the watershed at Valens, with a three-year average of 7.34 $\pm$ 0.58. Further along the watercourse, E2/E3 decreased past Valens and at Safari, Con4WE, and HWY5 with averages over the study of 5.31 $\pm$ 0.16, 5.36 $\pm$ 0.22, 5.65 $\pm$ 0.33 respectively, where these sites were statistically similar. Past the mid-catchment sites, E2/E3 increased at Crooks (6.33$\pm$ 0.66) and Harvest (6.99 $\pm$ 1.68), exhibiting some of the highest values across the watershed in addition to Valens. At the outlet of the watershed, E2/E3 averages over the study period were intermediate compared to the rest of the watershed (6.20 $\pm$ 0.57). In terms of land use, E2/E3 was found to be negatively correlated with increasing percent wetland cover ($p<0.05$) (Figure 4.5) (Table 4.4), and to be positively correlated with increasing percent agriculture and urban cover ($p < 0.05$) (Figure 4.6, 4.7).

4.5 Landscape and DOC Concentration and Quality

4.5.1 Principle Component Analysis and Landscape Variability

A principle component analysis (PCA) was used to assess the relationship between landscape controls on DOC concentrations and indices data (Figure 4.16). The fluoresence index (FI) was ommitted from the PCA to minimize bias, as the fluorescence index and freshness index are highly correlated variables. All variables loaded into the PCA were centered (means were subtracted), and scaled (divided by standard deviations) to standardize the variables.

The first principle component (PC1) explained 54.7% of the variation in the data set, and was highly correlated with all DOM indices (Figure 4.17) (Table 4.6). $SUVA_{254}$ and HIX had a positive correlation with PC1, whereas β/α, and E2/E3 had negative correlations. DOC concentration exhibited a weak positive correlation with PC1 (Figure 4.17). The second principle component (PC2), which explained 24.4% of the variation, had a strong negative correlation with DOC concentration, however it exhibited a weak correlation with the indices data (Figure 4.18) (Table 4.6). Further PCs were not explored as scree plots determined that PC1 and PC2 explained 79.1% of the variation in the data set, and only 5 variables were loaded.

Reservoir-influenced sites had a wide distribution on the biplot with the largest ellipse (Figure 4.16). The points plot across almost the entire PC1 axis, due to great variability in DOM quality. Mid-catchment points clustered furthest away from reservoir-influenced points, plotting to the right of the zero line with a tighter ellipse. Headwater and catchment-outlet sites clustered in similar regions on the biplot, with overlapping ellipses. Regression plots of PC1 and PC2 against DOC concentration and indices highlight the landscape variability observed in the Spencer Creek watershed (Figure 4.17, 4.18). DOC concentrations, $SUVA_{254}$, and HIX plotted highest at mid-catchment sites, and lowest at reservoir- influenced sites. The opposite trend is observed for β/α, and E2/E3, as these values plot lowest at mid-catchment sites, and highest at reservoir-influenced sites.

4.6 Source Waters from Stable Isotopes Analysis

Stable isotopes of water samples from all sampling sites were plotted against a LMWL developed by plotting 117 samples of both snow and precipitation collected during the 2016-2018 study period (Figure 4.19). The equation of the LMWL for the Spencer Creek watershed was $\delta^2H = 7.9\ (\delta^{18}O) + 12.8‰$ ($R^2 = 0.98$). Compared to the global meteoric water line (GMWL) with the equation $\delta^2H = 8.0\ (\delta^{18}O) + 10‰$, the slopes of the LMWL is comparable, however the deuterium-excess (intercept) varies (Craig, 1961). Additionally, a local evaporation line (LEL) was developed by plotting a regression line through 284 surface water samples, and the equation was $\delta^2H = 4.0\ (\delta^{18}O) - 24.5‰$ ($R^2 = 0.84$), with its slope falling into the range of 4-7 which is commonly reported (Kendall and McDonnell, 1998).

The headwater sites were most isotopically depleted and plotted along the LWML, with most samples plotting below the intersection of the LMWL and LEL (Figure 4.19). The isotopic signature for mid-catchment surface water samples were widely distributed had had the greatest isotopic enrichment, as these samples plotted closely along the LEL. Reservoir-influenced and catchment-outlet samples were isotopically similar, and plotted closer along the LEL. Overall, the isotopically depleted headwater sites corresponded with the lowest DOC concentration in the watershed, whereas the more isotopically enriched sites (mid-catchment, reservoir-influenced, and catchment-outlet) had greater DOC concentrations. Moving downstream in the watershed from the headwater sites to the catchment-outlet, increased evaporation was observed as waters became more isotopically enriched.

4.7 Stream Temperature (°C)

Stream temperatures in 2016 and 2018 were generally higher at all sites compared to 2017 (Figure 4.20). Most sites in 2016 and 2018 (with the exception of Gore 2 and Gore 3), had warm stream temperatures with values ranging from 20 °C to 35 °C. In 2017, the same sites had temperatures with values ranging from 14 °C to 25 °C. Gore 2 and Gore 3 had low stream temperatures consistently over the 3 years. These sites had stream temperatures as low as 10.3 °C to as high as 18.3 °C. The remaining sites display values that are consistently higher over the three-year study period.

CHAPTER 5: DISCUSSION

Water quality impairment is a prominent issue in the Great Lakes region with an increasing need to protect, conserve, and restore the health of upstream tributaries and waters that drain into the Great Lakes. DOC plays an integral role in stream and river dynamics, as it affects a suite of processes that alter ecosystem health and can result in water quality degradation. It is important to understand the various factors that affect and control DOC in the Great Lakes, specifically in regions with strong human-influences in the watershed. Human-dominated landscapes have a range of consequences on DOC dynamics as catchment hydrology, plant cover, and nutrient inputs are altered in these environments. The objectives of this study were to identify the controls and drivers of DOC quantity and quality in the Spencer Creek watershed, which is the largest contributor of water to Cootes Paradise that ultimately drains into Lake Ontario. The 158 km^2 study area of the catchment is complex, as the present landscape is composed of a mosaic of various land uses including agriculture, forest, wetland, urban, and industrial regions. Flow alterations contribute to the complexity of the watershed as there are managed reservoirs and alterations in water courses. Overall, the findings from this research provide insight into the fate and transport of water and DOC in a complex, managed catchment in the Great Lakes region, with the aims of providing key information for local stakeholders.

The results of the 2016-2018 study period showed differences in flow magnitudes and stream DOC between dry and wet years, as well as substantial variation in DOC concentration and DOM quality across the Spencer Creek watershed. DOC concentrations were found to be the lowest at groundwater influenced sites in the headwaters of the watershed, and the highest in the mid-catchment region where DOM quality was strongly influenced by wetland sources. The reservoir-influenced sites showed relatively intermediate concentrations of DOC with DOM quality that exhibited strong microbial signatures. At the outlet, DOC concentrations were attenuated and DOM quality was intermediate between allochthonous and autochthonous end members, reflecting upstream mixing processes. These processes are presented as a conceptual model of the Spencer Creek watershed during wet and dry conditions (Figure 5.1).

5.1 Conceptual Model of Water and DOC Movement in the Spencer Creek Watershed

5.1.1 Drivers of Hydrological Variability

Identifying the drivers of hydrological variability in the study area is essential for developing a conceptual framework between regional hydrology and DOC transport. Flow in the Spencer Creek watershed varied on a temporal scale with changing hydrological conditions over the three-year study period including a dry year (2016) where annual precipitation fell below the 30-year climate normal for the region and two wet years (2017 and 2018) where precipitation exceeded the climate normal (Figure 4.1, 4.2). Flow also varied spatially among monitoring sites, as stream size increased moving from the headwaters to the outlet. Largely, the temporal and spatial patterns of runoff and flow revealed that precipitation is a major driver of flow variability in the mid-catchment region of the Spencer Creek watershed whereas the upper reaches of the watershed yield and generate more runoff per unit area at a more stable rate.

The headwater sites, Gore 2 and Gore 3, were strongly influenced by groundwater as the ability to sustain runoff during dry periods an indicator of groundwater contributions (Sear et al., 1999). Gore 2 yielded the greatest total runoff per unit area during the dry year (data not available for Gore 3) whereas sites downstream exhibited drought-like conditions during the prolonged dry period when there was a lack of precipitation. Both Gore 2 and Gore 3 had little to no variation in total runoff per unit area from month to month (Figure 4.3), whereas most other sites (excluding Harvest's tributary which had heavily regulated flow) had strong seasonal patterns in runoff with lows in the summer and highs during spring and fall. There was additionally little change in annual runoff between the headwater sites during a dry year compared to two wet years, whereas substantial differences in runoff were observed for sites downstream between these varying hydrological conditions (Figure 4.3). This suggests that runoff was sustained by groundwater upwelling in the headwaters as a source, whereas runoff generation from sites downstream was more ephemeral in nature and dependent upon precipitation-driven processes to sustain flows.

Stream temperature results also indicate that the headwater sites are groundwater influenced (Figure 4.20). Over the three-year study period, Gore 2 and Gore 3 consistently had low stream temperatures, even during the warmest months of the summer. Stream temperatures at the headwaters sites never exceeded 20 °C whereas at the remaining sites, stream temperatures were generally greater than 20 °C. Isotopic data provided further insight into groundwater signatures using δ^{18} O ‰ and δ^{2}H ‰ data. The headwater sites consistently had lower $\delta^{18}O$ - δ^{2}H over the study period (Figure 4.19). Furthermore, the headwater samples cluster mostly below the point that the LMWL and LEL intersect, where this intersection represents the location of original un-evaporated composition of water (Kendall and McDonnell, 1998). As the stable isotopic composition of groundwater mirrors that of precipitation in recharge areas that connects to the water table (Kendall and McDonnell, 1998), and Gore 2 and Gore 3 plot along the LMWL whose line is derived from precipitation and snow samples, this suggests that Gore 2 and Gore 3 had a stronger precipitation-influenced signature due to groundwater upwelling. Isotopic data also reveals a trend of increased evaporation of waters moving downstream into the watershed, as samples plot below the LMWL and closer along the LEL, confirming a stronger surface water signature at these sites (Figure 4.19).

Resultantly, in the proposed conceptual model, the hydrogeochemical conditions experienced during the study period of the dry year (2016) are considered “dry conditions” whereas “wet conditions” represent hydrogeochemical conditions experienced during high flows as seen in 2017 and 2018. In this model, the headwater sites provide a constant source of water downstream in both wet and dry conditions, whereas precipitation controls flow variability from catchment areas downstream of the headwaters. Of course, Spencer Creek is also managed heavily at two sites, so the impact of human actions on flows is notable.

5.1.2 DOC Movement and Transfer During Wet and Dry Years

5.1.2.1 Proposed Transfer Mechanism of DOC during Wet and Dry Conditions

In the proposed conceptual model, DOC movement and transfer in the Spencer Creek watershed integrates the effects of hydrology, seasonality, and spatial variation in DOC concentrations (mg/L) observed over the study period. The concentrations of stream DOC measured in the Spencer Creek watershed (1.0- 39.3 mg/L, Figure 4.4) were similar to concentrations observed by Mulholland (1997) in streams across North America (0.1 – 36.6 mg/L). When hydrological conditions were dry in 2016, the lowest DOC concentrations were observed across the watershed. For the same months monitored in the following two years (June to August), concentrations were significantly higher across all sites except HWY5 (Table 4.2), displaying both higher and greater ranges of DOC concentrations. The watershed scale DOC concentration–discharge relationship revealed a significant positive slope indicating there is mobilization of DOC with increasing flows (Figure 4.10) (Godsey et al., 2009). The proposed conceptual model of DOC movement and transfer in the Spencer Creek aligns with studies establishing hydrology as a driver of allochthonous DOC transport from landscape into stream (Ågren et al., 2007; Fasching et al., 2016; Laudon et al., 2011; Mulholland, 1997; Stanley et al., 2012; Tate and Meyer, 1983). In terrestrial environments such as those in forests and grasslands, a large pool of water-soluble DOM is present in the upper soil horizons, whereas, in lower soil horizons, sorption processes take place with iron and aluminum oxides ultimately immobilizing DOM (Kalbitz et al., 2000; McDowell and Wood, 1984; Mulholland, 1997). During low flow conditions, dominant flow paths occur in lower soil horizons which are mineral-rich and have lower DOC concentrations. As flow begins to increase and water tables rise due to precipitation or snowmelt, these flowpaths shift to organic-rich shallow subsurface or surface pathways, flushing large pools of DOM in upper soil horizons into streams (Laudon et al., 2011; Mulholland, 1997; Pacific et al., 2010). This shift from dry to wet conditions essentially rewets soils that store DOC during dry conditions, and increases the hydrological transfer of DOC into streams in the Spencer Creek watershed. Similar results have been found for sulphate dynamics in Beverly Swamp, in the Spencer Creek watershed (Warren et al., 2001).

As the Spencer Creek watershed is 49% agriculture, it is important to consider the relationship between hydrological DOC transfer in agriculture influenced watersheds. Previous studies in agricultural settings have yielded similar conclusions. Stedmon et al., (2006) determined that fundamental shifts in hydrologic flowpaths released DOC from soils in response to precipitation events in an agriculturally dominated region in Horsens, Denmark. Similarly, studies in the midwestern United states have reported increases in stream DOC concentrations in agricultural watersheds during storms due to shifts in DOC sources form mineral soil layers at baseflow to subsurface soil layers during storms (Dalzell et al., 2006; Vidon et al., 2008). While there is a lack of studies analysing DOC-flow dynamics in agricultural sites in Ontario, considerable research has determined increased concentrations of other nutrients that are often associated with high DOC such as soluble reactive phosphorus (SRP) and nitrate (NO_3-) with peaks in discharge (King et al., 2015; Macrae et al., 2007; Williams et al., 2015). The majority of the soils in the Spencer Creek watershed are organic rich and sandy loams (Hamilton Conservation Authority, 2011), therefore this concept of shifts in flowpaths determined in grassland, forested, and agriculture landscapes applies to the conceptual model of DOC movement in the study area.

5.1.2.2 Effect of Wet and Dry Conditions on DOM Quality

Stream DOM quality was more allochthonous during the wet years (2017 and 2018) compared to the dry year (2016), as indicated by results from the freshness index (β/α) and the humification index (HIX) (Figure 4.12, 4.13) (Table 4.2). Both β/α and the HIX had significant differences between wet and dry conditions, at all sites except the headwaters (Table 4.2). This is likely due to drier conditions resulting in shallower streams with higher stream temperatures, greater photodegradation, and limited transfer of terrestrial DOM into streams from a lack of rainfall. Previous studies indicate water temperature is a controlling factor on stream DOM as warmer temperatures increase microbial activity and influence DOM mobilization (Kalbitz et al., 2000; Winterdahl et al., 2016). The warm temperatures and shallow, slow moving waters in 2016 may have stimulated greater microbial production compared to subsequent years. β/α was likely lower in 2017 and 2018 due to increased flows and greater hydrologic connectivity, as greater mixing of water with soils led to greater transfer of terrestrially derived DOM.

5.1.3 Processes Resulting in Spatial Variability of DOC Concentration and DOM Quality in the Proposed Conceptual Model

DOC concentration variability across a watershed is reflective of changes in land use and landscape, as well as in-stream processing of DOC as a secondary control (Dawson et al., 2008). These processes are discussed by landscape unit within the Spencer Creek watershed, and all tie into the proposed conceptual model (Figure 5.1). Within the conceptual model (1) runoff from the headwater sites are treated as providing consistent flows during wet or dry conditions with the lowest DOC concentrations, (2) the greatest DOC concentrations are observed in the mid-catchment region, exporting allochthonous and recalcitrant DOM downstream, (3) reservoirs are sites of DOM processing as the sites downstream of the reservoirs in this study (reservoir-influenced) have strong autochthonous sourced DOM that is labile in nature, and (4) the outlet had intermediate concentrations due to mixing and processing upstream.

5.1.3.1 Headwaters

Despite Gore 2 and Gore 3 having similar land use statistics compared to the mid-catchment sites (Table 3.1), DOC concentrations were lowest because of the groundwater influence. DOC concentrations typically decrease with depth within the soil profile, as the contribution of organic matter from plants decreases (Boyer et al., 1997; McDowell and Wood, 1984). Resultantly, groundwater typically has lower DOC concentrations relative to rivers or streams (Tate and Meyer, 1983), explaining why Gore 2 and Gore 3 consistently had the lowest DOC concentrations in the watershed over the three years. Site- to- site variability in DOC concentration can additionally be investigated using log DOC concentration– log discharge relationships, as they describe if chemicals are mobilizing, diluting, or are at a chemostatic equilibrium with increasing flows (Godsey et al., 2009). Gore 2 and Gore 3 have contrasting trends in concentration– discharge relations despite similar topographic and geographic locations within the watershed (Figure 4.9). These results align with previous research that determined there is high spatial heterogeneity between DOC concentration and discharge relationships in headwater streams due to the heterogeneity of DOM sources (Creed et al., 2015). Gore 2 had a strong positive mobilization relationship ($p<0.05$) indicating that high flows play a role in observed increases in DOC concentrations at this site, whereas Gore 3 had a non-significant trend (Table 4.5). The Fletcher Creek Ecological Preserve is located upstream of Gore 2 and is a calcareous fen with alkaline waters that are typically higher in dissolved inorganic carbon (DIC) (Duval and Waddington, 2018). Resultantly, the wetland is likely low in DOC and is not a major contributor downstream. Instead, DOC is likely flushing from organic rich soils along the banks of Gore 2 during flow events, rather than sourced upstream.

As determined by the PCA, DOM quality and structure in the headwaters had a mixed signature of allochthonous and autochthonous inputs, as values for all indices were intermediate (Figure 4.17) (Table 4.1). A mixed signature is observed likely due to groundwater – surface water interactions at these sites. DOM quality in groundwater samples has been found to have lower molecular weight, indicating a greater allochthonous signature (Inamdar et al., 2012; Shen et al., 2015). However, as water at these sites are a mixture of both groundwater and surface water, the allochthonous signature is attenuated.

5.1.3.2 Mid-catchment

DOC concentrations were highest in the mid-catchment region of the watershed (Figure 4.4) (Table 4.1). Land use in the mid-catchment sites is mixed, with more than half the land use consisting of wetland and agriculture (Table 3.1). The mid-catchment sites combined account for

82% of total wetland cover of the study area in the Spencer Creek watershed, and therefore have the strongest wetland signature among all the landscape units. Beverly swamp, a large (10 km^2) wetland complex is within the mid-catchment region, and is located downstream of Valens and upstream of Safari. Within the swamp, peat depth averages at a depth of 70-80 cm, with an average surface layer organic content averaging 50% (Warren et al., 2001; Woo and Valverde, 1981). In terms of agricultural land use, the mid-catchment sites account for 70% of total agriculture land cover in the watershed. Resultantly, the mid-catchment sites are strongly influenced by both land use types.

With the large contributions of wetlands to this part of the watershed, higher stream DOC concentrations observed support findings of previous studies indicating wetlands as a rich source of DOC into stream and rivers (Creed et al., 2003; Eckhardt and Moore, 1990; Gergel et al., 1999; Mulholland, 1997) as a positive relationship between DOC concentration and increasing percent wetland cover was observed ($p< 0.05$) (Figure 4.5). Previous studies in Beverly Swamp have determined that during high flow periods, flow paths were dominantly from wetland to stream, strongly affecting surface water chemistry whereas during low flow conditions, flow paths were reversed from stream to wetland (Galloway and Branfireun, 2004; Warren et al., 2001). The DOC concentrations and log DOC concentration – log discharge data supports previous work in the region, as concentrations were both significantly higher during wet years ($p<0.05$) (Table 4.2), and log DOC concentration – log discharge relationships had positive slopes at Safari and Con4WE suggesting mobilization of DOC at higher flows (Table 4.5). HWY5 is an outlier from this trend as neither DOC concentrations significantly increased during wet years, nor was a positive slope for log DOC concentration – log discharge observed (Figure

4.9) (Table 4.2). HWY5 is likely at chemostasis, as flows do not significantly alter DOC concentrations.

Indices data supports the strong wetland influence on stream DOC as DOM quality reflects DOC sourced from wetlands rather than agricultural DOC. The mid-catchment sites consistently cluster together on the regression plots of PC1 versus indices determined by the PCA (Figure 4.17). The plots reveal that the mid-catchments sites had the lowest β/α and E2/E3, and the highest HIX and $SUVA_{254}$ suggesting DOM was terrestrially-derived, and had higher molecular weight, humification, and aromatic carbon content at these sites. DOM structure and sources at these sites are indicative of a wetland source, as wetlands accumulate recalcitrant DOM that is more complex in structure and less bioavailable (Tulonen, 2004). Agricultural DOM quality is typically more autochthonous in source and labile in structure, which is a consistent finding among studies (Dalzell et al., 2011; Kelton et al., 2007; Stanley et al., 2012; Williams et al., 2010; Wilson and Xenopoulos, 2009). In this study, FI had a significant positive correlation with increasing agriculture cover ($p<0.05$) (Figure 4.6) (Table 4.4), which again is consistent with the findings from previous studies. Kelton et al (2007) analysed 16 streams across central and southern Ontario in varying land uses and found FI to highest in agricultural and urban streams, whereas boreal streams influenced by wetlands had the lowest FI values. In agricultural watersheds in Ontario, Wilson and Xenopoulos (2009) determined that with increasing agriculture cover, DOM quality indicated a more microbially derived source, and composition changed from high to low molecular weight with reduced aromaticity. Another study in southern Ontario looking at 43 streams in mixed land uses found DOM sources from agricultural streams to be more labile in structure and bioavailable compared to DOM sourced from wetland streams

(Williams et al., 2010). Despite the mixed land use within this region of the watershed, DOM quality results suggest stream DOC is wetland dominated, and that the wetlands within the region influence stream DOC quality more than agricultural sources.

5.1.3.3 Reservoir-Influenced

DOC concentrations were significantly different among the reservoir-influenced sites (Valens, Crooks, and Harvest) (Table A4). Valens and Crooks are both downstream of two large reservoirs operated by the Hamilton Conservation Authority, whereas Harvest is downstream of Lafarge Quarry (a limestone mine) that manages a relatively smaller reservoir. Despite significant differences among the three sites, DOC concentrations between Crooks and Valens had similar three-year averages (Table 4.3), while DOC concentrations at Harvest were more similar to those of the headwater sites. The low DOC concentrations observed are likely a result of little to no sources of organic material within the quarry.

The most striking similarity between the reservoir-influenced sites is reflected in DOM quality, as these sites consistently cluster together on the regression plots of PC1 versus indices determined by the PCA (Figure 4.17). Reservoir influenced sites had the highest β/α and E2/E3, and the lowest HIX and $SUVA_{254}$, implying that DOM had a greater autochthonous signature, and DOM composition had the lowest molecular weight, degree of humification and complexity in reservoirs and standing waters within the Spencer Creek watershed. Previous studies have determined lakes and reservoirs to be sources of autochthonous DOC due to increased microbial activity and photodegradation processes stimulated by solar radiation and warmer waters (Kalbitz et al., 2000; Stedmon et al., 2006; Winterdahl et al., 2016). Comparing sites upstream and downstream of Valens Reservoir (Gore 2 vs Valens) and Christie Reservoir (HWY5 vs

Crooks), an increase in water temperature was observed downstream of the reservoirs compared to upstream inputs (Figure 4.20). Additionally, the Hamilton Conservation Authority has previously determined water leaving Valens and Christie reservoirs are warmer compared to upstream inputs (Hamilton Conservation Authority, 2012b, 2011). Along with enhanced autochthonous production as a result of increased microbial activity, increased water residence times in lakes and reservoirs result in higher DOM photodegradation rates (Stedmon et al., 2006). Photodegradation breaks down larger components of DOM into lower molecular weight structures (Tulonen, 2004). This results in more labile, reactive, and bioavailable DOM as smaller structures are more easily up taken by organisms and therefore have a shorter turnover time compared to larger DOM structures (Jiao, 2010; Sinsabaugh and Foreman, 2003). The high E2/E3 values, and low HIX and SUVA confirm that photodegradation processes are transforming DOM in reservoir-influenced sites. Overall, a combination of both enhanced microbial activity and photodegradation processes are likely responsible for the microbial signature observed.

5.1.3.4 Outlet

The outlet of the study area, Dundas, represents the most urbanized sampling site (Table 3.1) although it represents 7.7% of the urban cover in the total drainage area and therefore not truly reflective of an urban signal. Concentration-discharge patterns at the outlet show that DOC mobilized with increasing flows (Figure 4.9), suggesting that as water outlets into Cootes Paradise, it flushes out greater amounts of DOC with increases in flows. However, the DOC concentrations observed at the outlet were intermediate in concentration in compared to other regions of the watershed (Figure 4.4), likely due to mixing and processing upstream attenuating concentrations, and due to lower overall wetland fractional cover at the outlet (Table 3.1). Creed et al., (2015) suggested that along the river continuum, the greatest variability in DOC concentrations and DOM composition occurs in the headwaters due to heterogeneity of DOM sources and the variable patterns of hysteresis during runoff events. However, as flows accumulate downstream, there is both reduced concentration variability and compositional variability. Concentration variability is reduced due to averaging of allochthonous source areas via hydrological mixing, and this results in DOM inputs having smaller impacts on total stream DOM. Composition variability is reduced due to biogeochemical processing such as degradation leading to preferential losses of aromatic DOM and gains of aliphatic (simple-chained) DOM (Creed et al., 2015; Montgomery, 1999). This concept supports and explains the relative decrease in DOC concentration, as well as the intermediate values for all indices observed at the outlet indicating a mixed signature of allochthonous and autochthonous inputs.

Urban land use was also found to have significant correlations with FI, β/α, and E2/E3 with increasing percent urban land cover (Table 4.4) indicating a greater autochthonous source for DOM that is freshly produced and lower in molecular weight. These findings support those of Williams et al., (2010), indicating that as more land is converted for urban use, greater autochthonous and labile DOM will be produced or transformed from allochthonous sources, further stimulating microbial activity. While DOM quality did not have a strong autochthonous signature at the outlet relative to the other regions of the watershed (such as reservoir-influenced), this relationship does highlight the tendency of DOM composition to change with urban land use.

5.1.4 Processes Resulting in Seasonal Variability of DOC Concentrations in the Proposed Conceptual Model

DOC concentrations in streams and soil vary seasonally, with greater concentrations during the summer months compared to winter (Kalbitz et al., 2000; Stedmon et al., 2006).This study spanned June-August in 2016, May-November in 2017, and March-October in 2018. Resultantly, winter DOC dynamics were not reflected in this study, however seasonal trends between spring and late summer/early fall were observed. Specifically, in 2017 and 2018, DOC concentrations increased around October at almost all sites (Figure 4.8). The timing of peak DOC observed supports previous conclusions made about the seasonality of DOC. Dawson et al (2008) determined that autumn and summer are a peak time for DOC export as a result of greater soil temperatures and moisture during midsummer, which enhances the turnover of organic matter. Leaf litter stored in the stream channel additionally explains increased concentrations observed as it is a source of DOC during the autumn and winter (Meyer et al., 1998). Lastly, manure application during the fall may also increase immediate observed concentrations of DOC (Chantigny, 2003).

5.1.5 PCA in the Context of the Proposed Conceptual Model

PC1 was found to be highly correlated with all indices (Figure 4.17), while PC2 explained the variation in DOC concentration (Figure 4.18) (Table 5.1). Resultantly, PC1 is a DOM quality signal, and may be treated as a "master index" describing how all indices change in response to environmental variables. When PC1 is high, HIX and SUVA are high, whereas β/α and E2/E3 are low, as determined by the loadings (Table 4.6). Consequently, greater PC1 values can be interpreted as a terrestrial signature whereas lower values represent a more microbial signature.

In the context of the proposed conceptual model, the results from the PCA further confirm that DOM quality is influenced by discharge, land use and resultantly landscape unit, along with seasonality (Table 5.1). A greater terrestrial signature was observed along with increased flows (log discharge) and wetland cover, as PC1 was found to be positively correlated with these variables (Figure 5.2) (Table 5.1). A greater microbial signature was found with increased agriculture cover and stream temperature, as they were negatively correlated to PC1. The findings from the PCA further validate the patterns and processes incorporated into the conceptual model of water and DOC movement in the Spencer Creek watershed. While it was established that DOC quantity was influenced by hydrology, land use, and seasonality, the PCA results highlight that DOM quality is additionally influenced by these factors.

5.2 Challenges, Implications, and Management

5.2.1 Challenges and Limitations for Working in Human Impacted Watersheds

Working in large, non-pristine environments, with several stakeholders presents many challenges in conducting research. With an environment such as the Spencer Creek watershed, there are considerable human alterations to the environment that are difficult to account for. For example, permits to take water (PTTW) affect the water balance of the watershed. While these permits are posted online as public information, it is difficult to determine the establish the quantity of water pumped each day for each permit holder. Ultimately, losses of water were unaccounted for, which in turn affects how flow and runoff data are interpreted. Most application of pesticide and manure application within watershed, which likely influence DOC, also went unaccounted for unless there was a sign posted. Spills are also an issue, as not all spills are reported to the Spills Action Centre. For instance, in 2016, individuals were observed dumping

Roundup ® (an herbicide) from a truck, directly into the stream south of Beverly Swamp. While this occurrence was reported to the Hamilton Conservation Authority, the occurrence would not have been public information otherwise and this type of behaviour could be relatively common Another incident took place in July 2016 where a cross connection overflow occurred near the outlet of the watershed, where sewage water was flowing through Chegwin Park. This is another example of how water chemistry was altered due to a human-influenced event. The large size of the watershed additionally poses limitations on this study. While we had 9 monitoring sites across the watershed, there are many tributaries of Spencer Creek we did not monitor or consider for this study.

5.2.2 Implications and Management

There is a projected 11.9% to 16.3% increase in precipitation, and 2.2°C - 2.3°C increase in air temperatures as a result of cli8mate change in the Spencer Creek watershed (Grillakis et al., 2011; Sultana and Coulibaly, 2011). Based on the findings of this study, with anticipated wetter and warmer conditions DOC concentrations would increase in the watershed. Previous studies have determined that DOC concentrations in freshwater systems are expected to increase globally in the future due to higher input of flow from catchments to lake (Thrane et al., 2014). The repercussions of increased DOC concentrations overall implies a decrease of terrestrial carbon storage, and greater input into more reactive and susceptible pools (Evans, 2006). This research found (1) during dry conditions, a greater autochthonous signature of DOC was seen across all sites, (2) increasing agriculture and urban land use was associated with increases in autochthonous DOM quality and (3) reservoir-influenced sites were a source of bioavailable DOC regardless of wet or dry conditions. Labile pools of DOC are of concern as they are easily consumed and promote bacterial activity and biomass production (Moran and Zepp, 1997), and in turn promote the accessibility of phosphorus to phytoplankton (Gergel et al., 1999). This has negative implications for streams and lakes in the Great Lakes region where eutrophication is already a prominent issue (Diaz and Rosenberg, 2008; Kemp et al., 2009), and may result in further water quality degradation.

Management and monitoring strategies in the Great Lakes region typically only focus on the role of nitrogen, phosphorous, sediment and flow (Conley et al., 2009; Stanley et al., 2012) as these variables are of immediate concern. However, water quality degradation is an integrated issue with various causes and consequences, and these variables alone do not explain water quality impairment. DOC plays a prominent role in lakes and streams, as it is the major organic carbon pool in most aquatic ecosystems, and DOC modifies the influence of other chemicals, resultantly influencing ecosystem structure and function (Prairie, 2008; Wetzel, 2001). Sampling for DOC concentration and DOM quality needs to be a part of an integrative approach to long-term water quality monitoring in the Great Lakes region, especially in human dominated landscapes where DOC regimes may be altered. Suggestions for watershed scale monitoring include: (1) selecting sites with varying land use statistics, (2) sampling at various times during the year to obtain seasonality within the data set, and (3) targeting sampling during varying hydrological conditions to capture high flow and low flow events. Using this monitoring strategy, DOC concentrations and DOM quality regimes can be better understood in other watersheds in the Great Lakes region, and incorporated into existing water monitoring programs run by Conservation Authorities.

CHAPTER 6: CONCLUSION

Water quality impairment is a prominent issue in the Great Lakes watershed, as industrialization, urbanization, and agricultural activity have modified the landscape in this region (Cole et al., 1998; Copeland et al., 1996). While water quality is an integrated problem with various causes and consequences, it is critical to consider the role of DOC in the environment as it represents the major organic carbon pool in most aquatic ecosystems, is a "modulator" of lake and stream processes (Prairie, 2008; Wetzel, 2001). Previous studies have determined changes in land use from pre-disturbance landscapes affect DOC quantities and quality (Stanley et al., 2012). However, the relationship between hydrological and biogeochemical processes, and their interactions in these complex, managed systems are not well understood. The objective of this work was to use hydrogeochemical and hydrometric data to identify the controls and drivers of DOC concentration and DOM quality variability in the Spencer Creek watershed. The findings of this research have accepted the hypotheses that DOC is (1) temporally variable during the study period and (2) DOC quantity and quality vary across the watershed due to landscape variability and hydrological differences. Based on the results from this study, a conceptual model of water and DOC movement in the Spencer Creek watershed was proposed with the following key findings and conclusions:

1) Precipitation conditions varied over the three-year study period where 2016 was a dry year and 2017 and 2018 were both wet years based on the 30-year climate normal for the region. This allowed for comparison of DOC between wet and dry conditions, as there was substantial variation in flow magnitudes, which resulted in DOC concentration and DOM quality to vary across the Spencer Creek watershed. In the proposed conceptual

model, DOC significantly increases during wet conditions due to shifts in hydrological pathways from dry conditions.

2) DOC concentrations were lowest at groundwater influenced sites in the headwaters of the watershed due to groundwater influences. DOM quality was found to be intermediate.
3) DOC concentrations were highest in the mid-catchment region where the area is dominated by wetland and agricultural land cover. DOC concentration was found to increase with greater percent wetland cover and decrease with percent agricultural and urban cover. Results in the mid-catchment indicate both concentration and quality were strongly influenced by wetland sources rather than agriculture as concentrations were the highest, and quality was the most allochthonous and recalcitrant relative to the other regions of the watershed.
4) The reservoir-influenced sites had relatively intermediate concentrations of DOC. However, DOM quality was the most autochthonous and labile relative to the other regions of the watershed due to increased microbial activity and photodegradation processes in reservoirs stimulated by solar radiation and warmer waters.
5) At the outlet, DOC concentrations were attenuated and DOM quality was intermediate between allochthonous and autochthonous end members, reflecting upstream mixing processes and biogeochemical processing of DOM occurring along the river continuum.
6) Seasonal increases in DOC concentrations were observed during the later summer and early fall as a result of greater soil temperatures and moisture during midsummer which enhances the turnover of organic matter.

These findings highlight the importance of continued study of DOC dynamics and the complex interconnections between hydrology and geochemistry at the watershed scale in the Great Lakes region. With anticipated wetter and warmer conditions as a result of climate change DOC concentrations would increase in the watershed, and likely in other watersheds in the Great Lakes region as well. The repercussions of increased DOC concentrations overall implies a decrease of terrestrial carbon storage, and greater input into more reactive and susceptible pools (Evans, 2006). Resultantly, monitoring for DOC concentration and DOM quality should be integrated into long term water quality monitoring programs in the Great Lakes region, as the role of carbon in aquatic ecosystems contributes to the greater understanding of water quality degradation.

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TABLES

Table 2.1: Summary of fluorescence indices used in this study, the information each index provides on DOM quality, and its associated calculation.

Fluorescence Index	Purpose	Calculation	Interpretation with increasing allochthonous inputs
Freshness Index (β/α)	Describes the proportion of recently produced DOM. The β peak represents microbial derived organic matter whereas α describes older decomposed matter.	β peak: is the maximum intensity with its excitation at 310-320nm and its emission at 380-420nm. α peak: is the maximum intensity with its excitation at 420-480nm and its emission at 380-420nm.	Decreases
Fluorescence Index (FI)	Indicates whether the source of DOM is of microbial (FI ~ 1.8) or terrestrial (FI~ 1.2) origins.	Ratio of emission at 450nm/ 500nm at an excitation at 370 nm (if using a non-instrument corrected spectra). It is modified to the ratio of emission at 470nm/520nm at an excitation of 370nm.	Decreases
Humification Index (HIX)	Describes the degree of humification of soils (how decomposed the organic material is). High HIX_{EM} values indicate lower H/C ratios, associated with a greater degree of humification.	The area of peak under an emission of 435 to 480 nm divided by the peak area under emission 300 to 345 nm at an excitation of 254 nm.	Increases
Specific Ultraviolet Absorbance at 254nm ($SUVA_{254}$)	Infers aromatic carbon content. A high $SUVA_{254}$ is associated with higher aromatic carbon and molecular weight.	Calculated as the ratio of UV absorbance at 254 nm to the DOC concentration in L $mg^{-1}m^{-1}$	Increases
E2/ E3	Infers the molecular weight of carbon content. High E2/E3 ratios are correlated with low molecular weight.	Calculated as the ratio of absorbance at 250nm to absorbance at 380 nm.	Decreases

Table 3.1: Characteristics of the sampling sites in the Spencer Creek Watershed 2016-2018. The total area contributing to the sample location considers the total drainage area to that sampling location. Land use descriptions describe the land use of the contributing area to each site.

Site	**Location**	**Total Contributing Area to Sampling Location (km^2)**	**Contributing land use statistics**	**Site Characteristics**
GORE 2	43°24'48.9" N, 80°06'23.7" W	4.01	42.4 % agriculture, 27% wetland, 15.1 % forest, 1.9 % urban, 0.2% open water, 13.3% undifferentiated	Headwater site
GORE 3	43°23'59.0" N, 80°11'29.9" W	2.14	64.4 % agriculture, 13.2 % wetland, 11.8% forest, 0.3% urban, 10.3% undifferentiated	Headwater site
VALENS	43°22'56.4" N, 80°07'51.9" W	12.42	43.7 % agriculture, 24.3% wetland, 19.4% forest, 2.3% urban, 10.3% undifferentiated	Downstream of Valens Reservoir
SAFARI	43°21'10.8" N, 80°04'20.4" W	49.54	38.3 % agriculture, 34.1% wetland, 14.4% forest, 2.8 % urban, 0.1% open water, 10.3% undifferentiated	Mid-catchment, greatest relative wetland contribution, Water Survey of Canada site
CON4WE	43°18'00.8" N, 80°03'57.5" W	83.93	42.7 % agriculture, 30.2 % wetland, 12.5 % forest, 3.6 % urban, 0.5 % open water, 0.5 % extraction, 9.7% undifferentiated	Mid-catchment, downstream of agricultural field
HWY5	43°16'59.3" N, 80°03'12.0" W	125.48	61.4 % agriculture, 13.7% wetland, 5.6% forest, 7.8% urban, 0.3% open water, 2.2% extraction, 10 % undifferentiated	Mid-catchment, Water Survey of Canada site
CROOKS	43°16'31.5" N, 80°00'04.4" W	139.42	49.2 % agriculture, 22.9 % wetland, 10.9 % forest, 5.8 % urban, 0.7% open water, 9.5% undifferentiated, 1% extraction	Downstream of Christie Reservoir
HARVEST	43°16'56.1" N, 79°58'38.5" W	13.06	58.7 % agriculture, 7.9% wetland, 2.8 % forest, 11.7 % urban, 1 % open water, 8.6 % extraction, 9.3 % undifferentiated	Downstream of Lafarge Quarry Reservoir
DUNDAS	43°15'55.1" N, 79°57'53.0" W	158.65	48.8 % agriculture, 20.8 % wetland, 10.8 % forest, 7.7 % urban, 0.7% open water, 9.5% undifferentiated, 1.5% extraction	Water Survey of Canada site, Outlet of catchment

Table 4.1: Summary statistics of average DOC concentration, Fluorescence Index (FI), Freshness Index (**β/α**), Humification Index (HIX), $SUVA_{254}$, and E2/E3 for all samples over the 2016-2018 study period. Number of samples used to calculate differential statistics are listed beside the average and standard deviation value.

Year	**Site**	**DOC (mg/L)**	**FI**	**β/α**	**HIX**	**$SUVA_{254}$**	**E2/E3**
2016							
	GORE2	2.07 ± 1.42 (15)	1.54 ± 0.03 (17)	0.64 ± 0.04 (17)	0.9 ± 0.02 (17)	3.72 ± 2.16 (13)	4.55 ± 0.31 (17)
	GORE3	2.25 ± 2.23 (15)	1.60 ± 0.04 (16)	0.66 ± 0.04 (16)	0.91 ± 0.02 (16)	3.25 ±1.07 (14)	5.11 ± 0.49 (16)
	VALENS	6.54 ± 0.62 (14)	1.56 ± 0.04 (16)	0.75 ± 0.02 (16)	0.84 ± 0.01(16)	2.65 ± 0.13 (13)	7.34 ± 0.53 (16)
	SAFARI	8.29 ± 0.81 (14)	1.46 ± 0.02 (15)	0.58 ± 0.01 (15)	0.92 ± 0.01 (15)	4.03 ± 0.45 (13)	5.27 ± 0.19 (15)
	CON4WE	9.52 ± 1.69 (13)	1.5 ± 0.03 (12)	0.60 ± 0.02 (12)	0.92 ± 0.02 (12)	3.99 ± 0.22 (12)	5.38 ± 0.26 (14)
	HWY5	11.65 ± 3.3 (15)	1.54 ± 0.03 (16)	0.64 ± 0.03 (16)	0.90 ± 0.02 (16)	3.46 ± 0.78 (14)	5.73 ± 0.37 (16)
	HARVEST	2.67 ± 0.62 (15)	1.66 ± 0.04 (14)	0.79 ± 0.06 (14)	0.81 ± 0.06 (14)	2.40 ± 1.05 (14)	5.96 ± 1.28 (15)
	CROOKS	8.91 ± 0.71 (15)	1.55 ± 0.03 (15)	0.67 ± 0.03 (15)	0.89 ± 0.01 (15)	3.26 ± 0.28 (14)	6.52 ± 0.66 (15)
	DUNDAS	4.97 ± 0.72 (15)	1.56 ± 0.03 (14)	0.69 ± 0.02 (14)	0.89 ± 0.01 (14)	3.04 ± 0.53 (14)	6.19 ± 0.52 (16)
2017							
	GORE2	8.37 ± 11.26 (12)	1.54 ± 0.02 (8)	0.61 ± 0.04 (8)	0.89 ± 0.06 (8)	3.33 ± 3.36 (8)	5.26 ± 0.2 (8)
	GORE3	3.02 ± 2.16 (10)	1.57 ± 0.02 (7)	0.61 ± 0.02 (7)	0.93 ± 0.01 (7)	2.80 ± 1.46 (8)	5.33 ± 0.6 (7)
	VALENS	14.88 ± 11.17 (11)	1.54 ± 0.04 (8)	0.69 ± 0.04 (8)	0.84 ± 0.05 (8)	1.71 ± 1.14 (8)	7.47 ± 0.55 (8)
	SAFARI	15.06 ± 8.01 (12)	1.50 ± 0.02 (9)	0.55 ± 0.02 (9)	0.94 ± 0.01 (9)	3.55 ± 0.97 (9)	5.39 ± 0.2 (9)
	CON4WE	18.06 ± 8.80 (11)	1.52 ± 0.02 (8)	0.56 ± 0.02 (8)	0.95 ± 0.01 (8)	3.16 ± 1.30 (7)	5.39 ± 0.22 (9)
	HWY5	13.14 ± 5.88 (11)	1.53 ± 0.03 (7)	0.58 ± 0.02 (7)	0.94 ± 0.01 (7)	3.63 ± 0.82 (7)	5.63± 0.37 (7)
	HARVEST	7.68 ± 8.44 (11)	1.64 ± 0.04 (9)	0.72 ± 0.05 (9)	0.87 ± 0.04 (9)	1.88 ± 0.90 (9)	7.57 ± 1.31 (8)
	CROOKS	15.97 ± 9.25 (11)	1.53 ± 0.02 (7)	0.62 ± 0.03 (7)	0.92 ± 0.02 (7)	2.84 ± 1.48 (7)	5.82 ± 0.32 (7)
	DUNDAS	13.79 ± 10.35(10)	1.54 ± 0.02 (7)	0.61 ± 0.02 (7)	0.92 ± 0.01 (7)	2.48 ± 1.42 (6)	5.85 ± 0.26 (7)
2018							
	GORE2	5.22 ± 5.00 (19)	1.54 ± 0.03 (19)	0.62 ± 0.06 (19)	0.88 ± 0.07 (19)	2.4 ± 0.90 (19)	5.53± 0.59 (19)
	GORE3	3.73 ± 1.48 (19)	1.57 ± 0.03 (19)	0.62 ± 0.04 (19)	0.91 ± 0.04 (19)	2.41 ± 0.99 (19)	6.31 ± 1.99 (19)
	VALENS	9.53 ± 5.92 (19)	1.55 ± 0.05 (20)	0.72 ± 0.03 (19)	0.84 ± 0.02 (19)	2.18 ± 0.81 (19)	7.22 ± 0.99 (19)
	SAFARI	11.8 ± 2.88 (18)	1.48 ± 0.02 (18)	0.55 ± 0.02 (18)	0.94 ± 0.01 (18)	3.65 ± 0.72 (18)	5.41 ± 0.12 (18)
	CON4WE	13.01 ± 7.03 (18)	1.51 ± 0.02 (17)	0.56 ± 0.02 (17)	0.94 ± 0.01 (17)	3.89 ± 0.86 (17)	5.39 ± 0.19 (17)
	HWY5	12.91 ± 6.07 (18)	1.52 ± 0.02 (18)	0.58 ± 0.01 (18)	0.93 ± 0.01 (18)	3.41 ± 0.85 (18)	5.55 ± 0.24 (18)
	HARVEST	5.77 ± 3.83 (18)	1.65 ± 0.05 (18)	0.72 ± 0.06 (18)	0.87 ± 0.04 (18)	2.07 ± 0.80 (18)	7.33 ± 1.67 (18)
	CROOKS	12.45 ± 5.93 (18)	1.53 ± 0.02 (16)	0.63 ± 0.03 (16)	0.91 ± 0.02 (16)	3.05 ± 0.97 (16)	6.07 ± 0.73 (16)
	DUNDAS	8.60 ± 4.01 (18)	1.54 ± 0.02 (18)	0.64 ± 0.03 (18)	0.92 ± 0.01 (18)	2.91 ± 0.68 (18)	6.37 ± 0.69 (18)

Table 4.2: Dunn's Test of Multiple Comparisons (p-values) for same site comparions over the 2016-2018 study period. Post-hoc test used to identify which years were significantly different from another. P-values are bolded where there is statistical significance ($p<0.05$). Empty boxes in the table indicate there is no significant different for that specific parameter and site, therefore a post-hoc was not completed.

SITE	**DOC**	**FI_2005**	**β/α**	**HIX_2002**	**SUVA$_{254}$**	**E2/E3**
GORE 2						
2016 - 2018	**0.001244496**				**0.003314789**	**1.09E-06**
2016 - 2017	**0.004662258**				0.073426194	**0.000401381**
2017 - 2018	0.354978616				0.160926095	0.19712077
GORE 3						
2016 - 2018	**0.002615044**		**0.006470834**			**0.003676905**
2016 - 2017	**0.089847255**		**0.007975334**			0.114497719
2017 - 2018	0.143736772		0.403043712			0.148272728
VALENS						
2016 - 2018	**0.000199305**		**6.01E-05**	**0.004903983**		
2016 - 2017	**0.001340433**		**0.008014564**	**0.027694187**		
2017 - 2018	0.252770019		0.060114571	0.172139356		
SAFARI						
2016 - 2018	**1.78E-05**	**5.93E-05**	**7.50E-05**	**2.48E-05**		
2016 - 2017	**2.78E-05**	**0.018614966**	**0.000312676**	**0.001885232**		
2017 - 2018	0.384413608	**0.046385134**	0.33007458	0.12515502		
CON4WE						
2016 - 2018	**2.24E-05**		**7.66E-05**	**2.81E-05**		
2016 - 2017	**0.000964244**		**0.000725898**	**0.011438682**		
2017 - 2018	0.133618185		0.361930885	**0.03420994**		
HWY5						
2016 - 2018			**6.85E-05**	**1.62E-05**		
2016 - 2017			**0.000498642**	**0.01080978**		
2017 - 2018			0.462971165	**0.03118598**		
HARVEST						
2016 - 2018	**6.38E-05**		**0.004644238**	**0.010147304**		**0.001087716**
2016 - 2017	**0.001284345**		**0.011582142**	**0.01857878**		**0.01149383**
2017 - 2018	0.197026582		0.408042382	0.389691153		0.294733802
CROOKS						
2016 - 2018	**5.92E-06**	**0.008479553**	**0.004379269**	**0.000694847**		**0.004980185**
2016 - 2017	**1.51E-05**	0.092389948	**0.017406112**	**0.01501684**		**0.042571827**
2017 - 2018	0.343501679	0.198564692	0.296987258	0.160592258		0.235813619
DUNDAS						
2016 - 2018	**0.000116221**		**6.95E-05**	**6.69E-05**		
2016 - 2017	**0.001326089**		**0.000301394**	**0.001573549**		
2017 - 2018	0.189457909		0.156507183	0.134240236		

Table 4.3: Three-year averages and standard deviations of DOC concentration (mg/L) and indices data across all monitoring sites from 2016-2018.

Site	**DOC (mg/L)**	**FI**	**β/α**	**HIX**	**$SUVA_{254}$**	**E2/E3**
GORE 2	5.01 ± 6.89	1.54 ± 0.03	0.62 ± 0.05	0.89 ± 0.05	3.02 ± 2.05	5.05 ± 0.65
GORE 3	3.06 ± 1.99	1.58 ± 0.04	0.63 ± 0.04	0.91 ± 0.03	2.77 ± 1.15	5.71 ± 1.64
VALENS	10.02 ± 7.49	1.55 ± 0.04	0.72 ± 0.04	0.84 ± 0.03	2.24 ± 0.81	7.34 ± 0.58
SAFARI	11.57 ± 5.18	1.48 ± 0.02	0.56 ± 0.02	0.93 ± 0.01	3.75 ± 0.72	5.31 ± 0.16
CON4WE	13.36 ± 7.21	1.51 ± 0.02	0.57 ± 0.03	0.93 ± 0.02	3.78 ± 0.86	5.36 ± 0.22
HWY5	12.55 ± 5.17	1.53 ± 0.03	0.60 ± 0.04	0.92 ± 0.02	3.47 ± 0.80	5.65 ± 0.34
HARVEST	5.25 ± 5.25	1.65 ± 0.04	0.74 ± 0.06	0.85 ± 0.06	2.14 ± 0.91	6.99 ± 1.68
CROOKS	12.21 ± 6.53	1.53 ± 0.02	0.64 ± 0.04	0.91 ± 0.02	3.09 ± 0.90	6.33 ± 0.66
DUNDAS	8.66 ± 6.55	1.55 ± 0.02	0.65 ± 0.04	0.91 ± 0.02	2.89 ± 0.79	6.20 ± 0.57

Table 4.4: Results from Spearman rho correlation test of DOC and DOM quality indices against percent land use cover. P values are bolded where there is statistical significance ($p<0.05$). Rho values (R) range from -1 to +1.

Agriculture						
	DOC	FI	β/α	HIX	SUVA	E2/E3
P-value	**2.18E-08**	**<2.20E-16**	**<2.20E-16**	**4.10E-05**	**5.40E-06**	**2.40E-09**
R	-0.29	0.61	0.45	-0.23	-0.25	0.33
Wetland						
	DOC	FI	β/α	HIX	SUVA	E2/E3
P-value	**<2.20E-16**	**<2.20E-16**	**<2.20E-16**	**1.00E-15**	**3.30E-16**	**<2.20E-16**
R	0.44	-0.74	-0.66	0.43	0.44	-0.47
Urban						
	DOC	FI	β/α	HIX	SUVA	E2/E3
P-value	**4.60E-06**	**5.20E-03**	**8.50E-04**	0.3600	0.4600	**4.00E-08**
R	0.24	0.19	0.19	-0.05	-0.04	0.30

Table 4.5: Results from linear regression of log DOC concentration -log discharge relationships by site. P values indicate if slopes are significantly different from zero. P values are bolded where there is statistical significance ($p<0.05$).

	Watershed Scale (All Sites)	**GORE2**	**GORE3**	**VALENS**	**SAFARI**	**CON4WE**	**HWY5**	**HARVEST**	**CROOKS**	**DUNDAS**
Slope	0.1614	0.5713	-0.07201	0.07772	0.08021	0.08452	-0.02943	0.108	-0.09147	0.1802
F	57.37	5.976	0.3466	1.237	6.402	4.499	1.153	3.531	1.325	6.643
P-value	**<0.0001**	**0.0195**	0.5609	0.2738	**0.0155**	**0.0411**	0.2901	0.0691	0.2667	**0.0148**

Table 4.6: Loadings from the Principal Component Analysis. Loadings range from -1 to +1, and are interpreted similar to correlations.

	PC1	PC2	PC3	PC4	PC5
DOC	0.11	-0.85	0.12	-0.49	0.14
FRESH (β/α)	-0.57	0.14	0.14	-0.10	0.79
HIX	0.52	-0.18	-0.42	0.48	0.54
SUVA	0.44	0.46	-0.23	-0.71	0.19
E2/E3	-0.45	-0.13	-0.86	-0.13	-0.17

Table 5.1: Results from correlation of PC1 along with land use, stream temperature, and discharge. Correlations for PC1 vs. land use were determined using the Spearman Rho correlation test, whereas PC1 vs. stream temperature and discharge used the Pearson correlation test. P values are bolded where the variables are statistically correlated.

	% Wetland	% Agriculture	Stream Temperature (°C)	logDischarge (m^3s)
R	0.64	-0.39	-0.19	0.33
P-value	**<2.2 E-16**	**1.1 E-10**	**0.003**	**6.0E-8**
Test	Spearman	Spearman	Pearson	Pearson

FIGURES

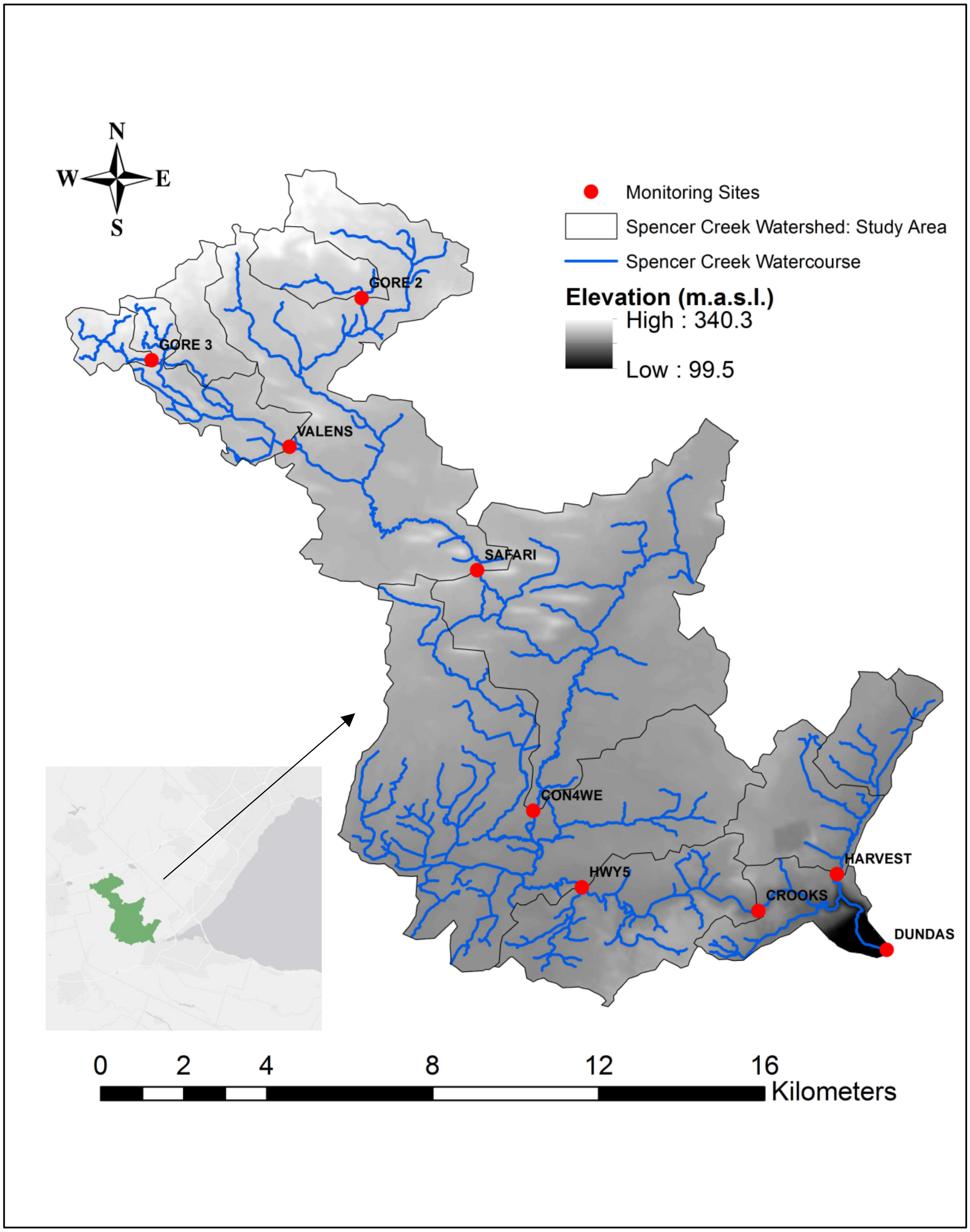

Figure 3.1: Map of the study area in the Spencer Creek watershed. All monitoring sites are symbolized by red circles, with the watercourse in blue.

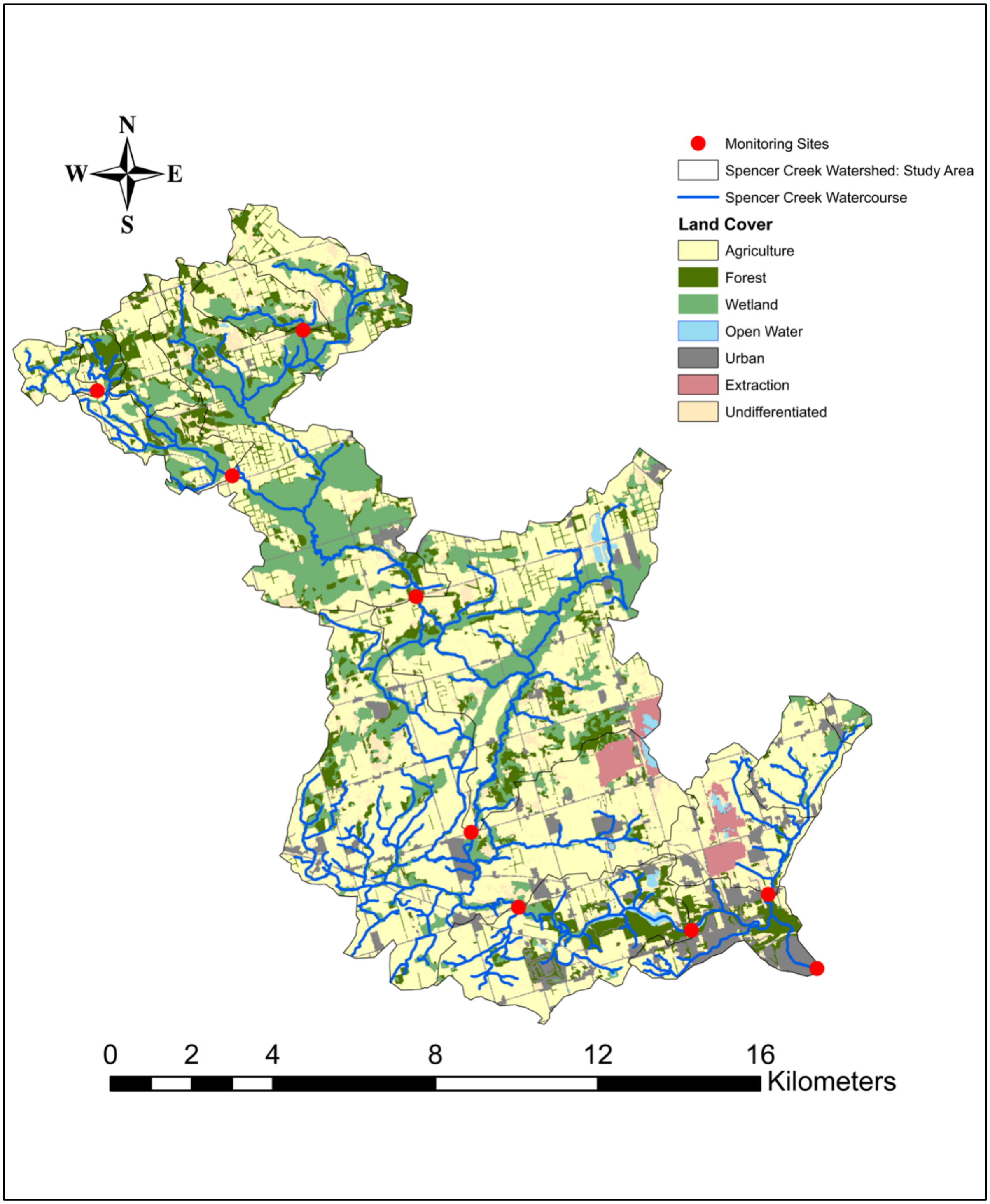

Figure 3.2: Land use map of the study area within the Spencer Creek watershed. A land use analysis on ArcGIS was performed merging the Southern Ontario Land Use Information System 2.0 (2016) layer and the Agriculture Canada Annual Crop Inventory (2016) layer. Spencer Creek is 49% agriculture, 21% wetland, 11% forest, 8% urban, 2% extraction, 1% open water, and 10% undefined.

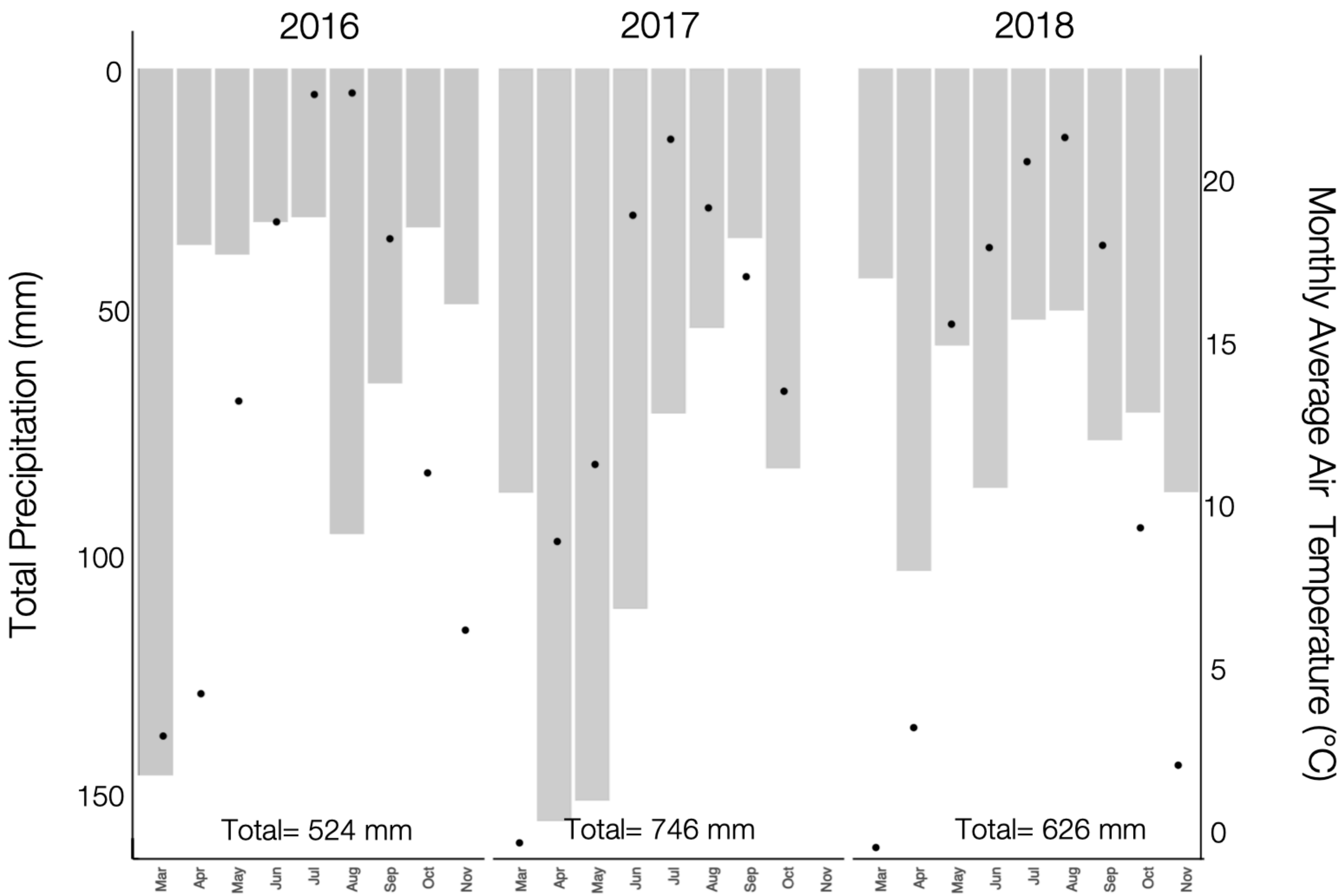

Figure 4.1: Total precipitation and monthly average air temperature during the 2016-2018 study period. Data obtained from the Hamilton RBG Weather Station (43.28 N, 79.88 W).

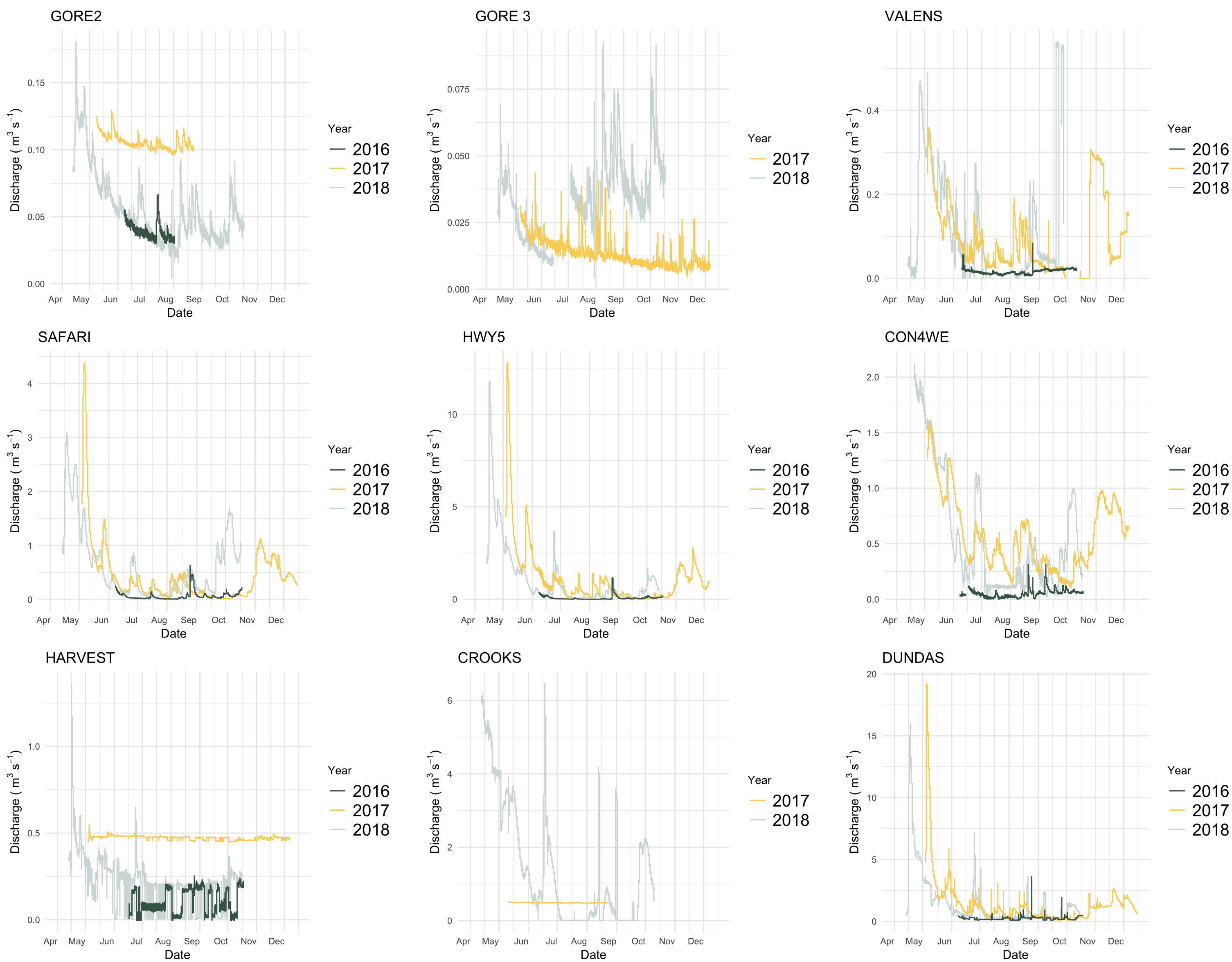

Figure 4.2: Discharge (m^3/s) over 2016-2018. Note, Y axes scales differ due to differences in discharge magnitudes.

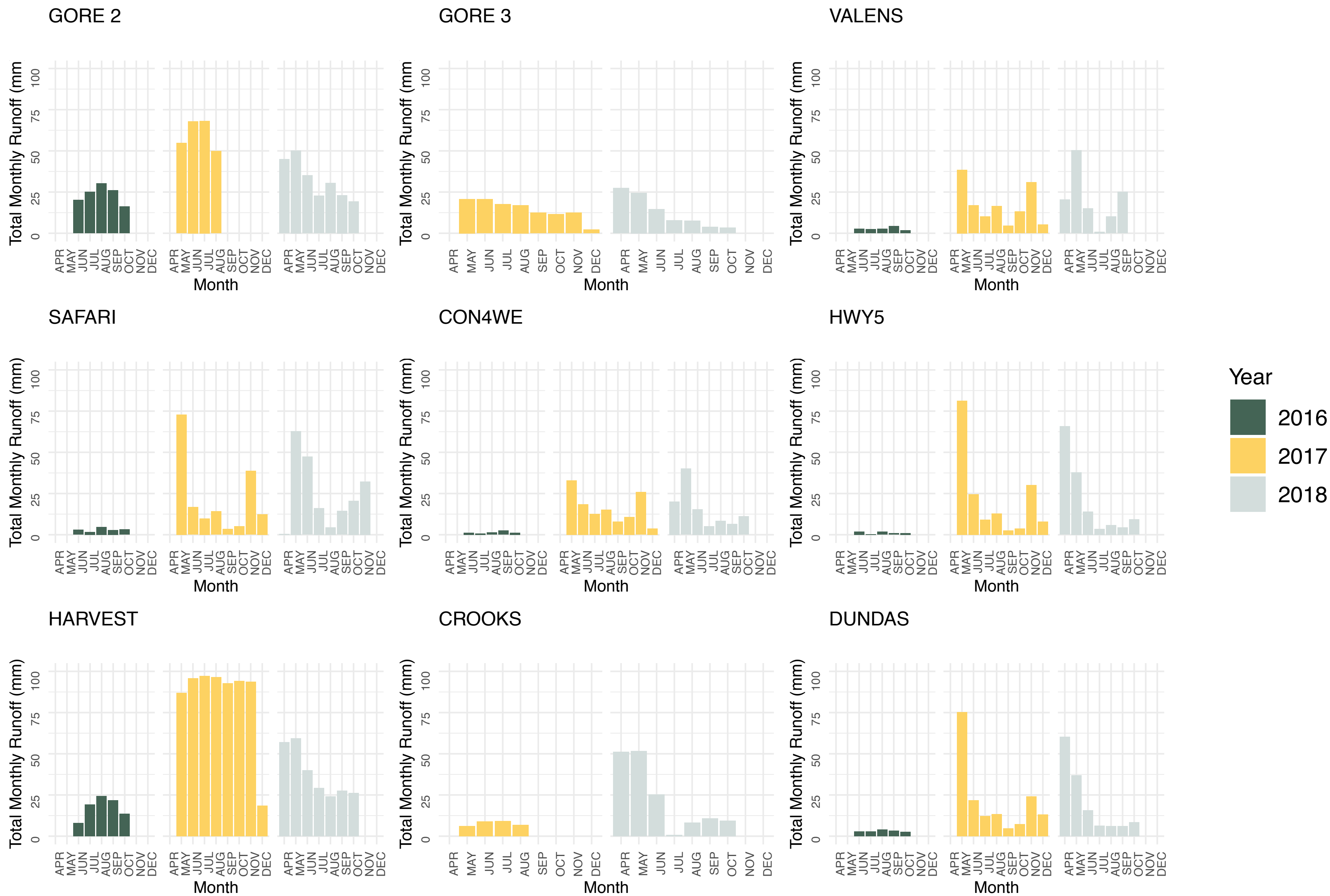

Figure 4.3: Total monthly runoff (mm) over 2016-2018. Runoff was normalized to the total contributing area to each site.

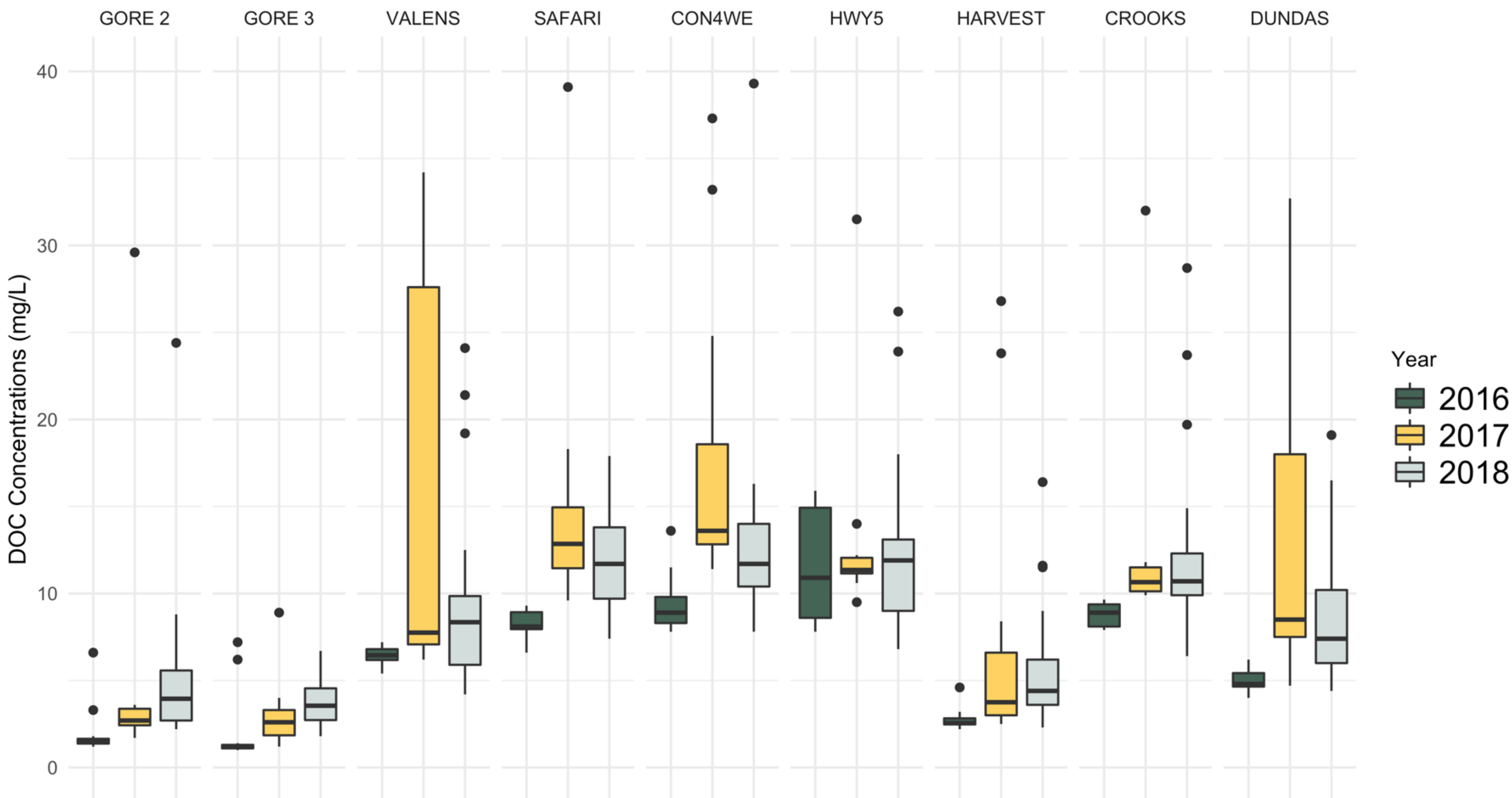

Figure 4.4: Boxplot of DOC concentration (mg/L) distribution at all sites over 2016-2018.

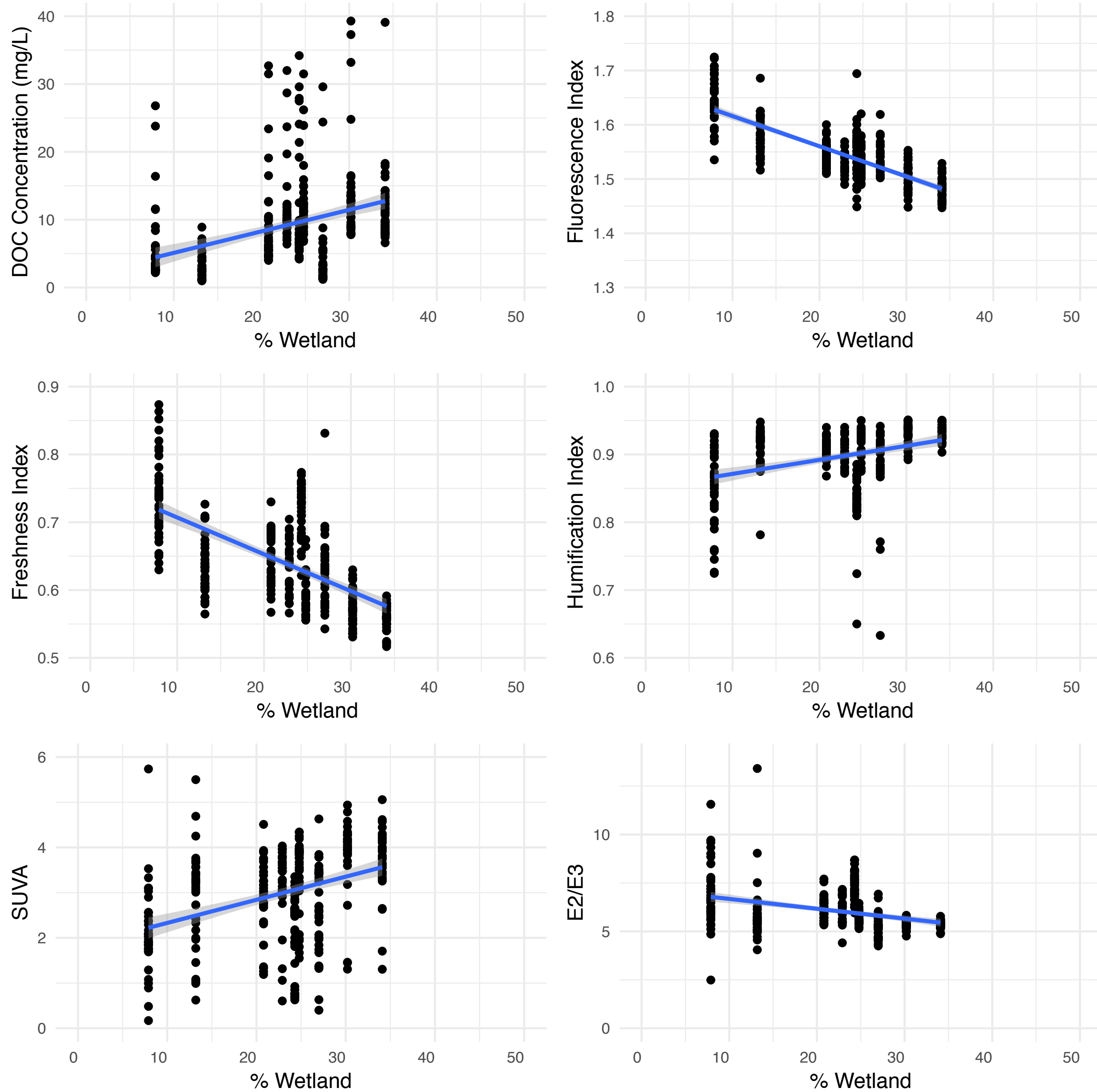

Figure 4.5: DOC concentrations and indices vs. percent contributing wetland cover. Trendlines indicate significant correlations between the variables (Table 4.4).

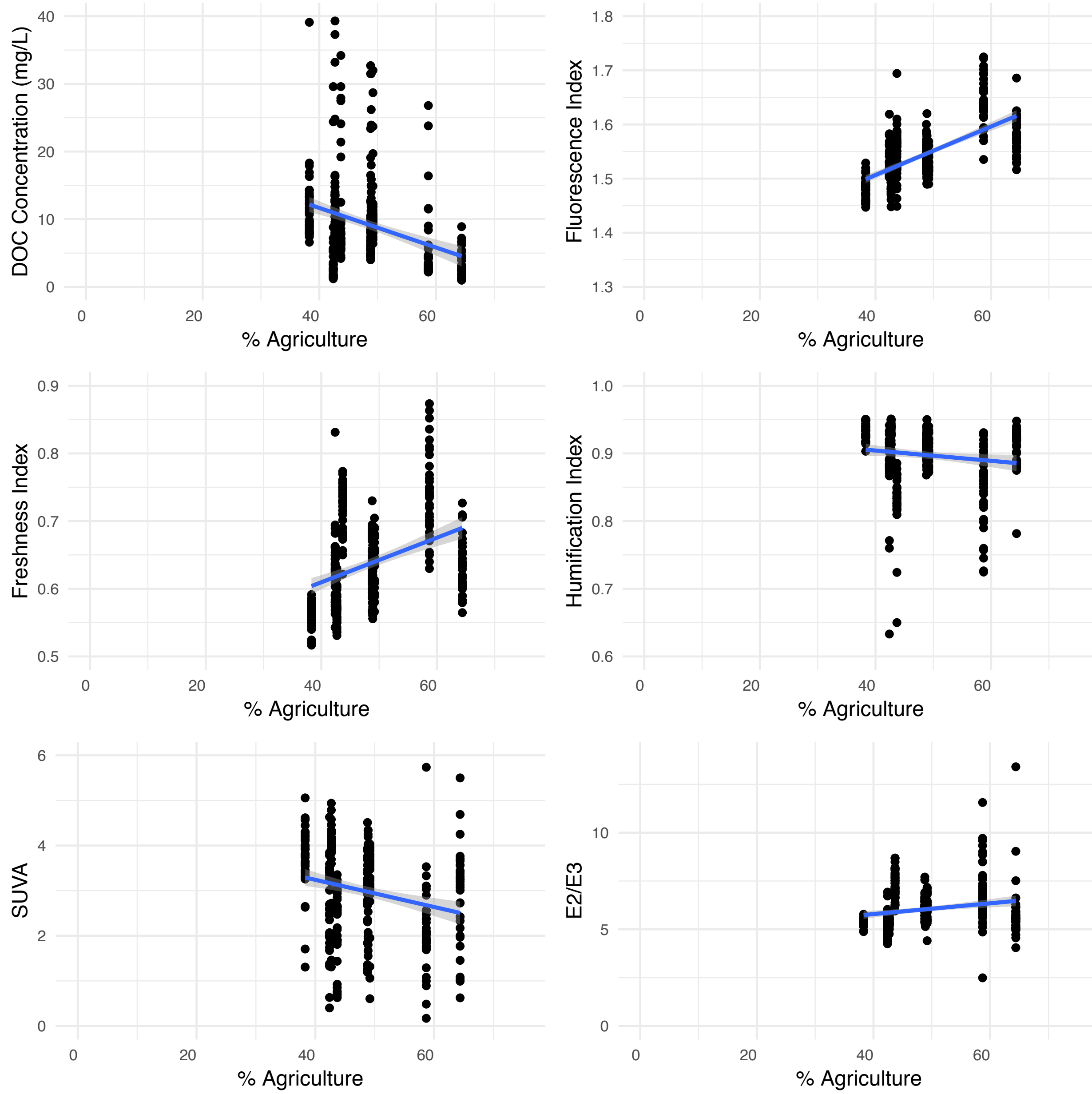

Figure 4.6: DOC concentrations and indices vs. percent contributing agricultural cover. Trendlines indicate significant correlations between the variables (Table 4.4).

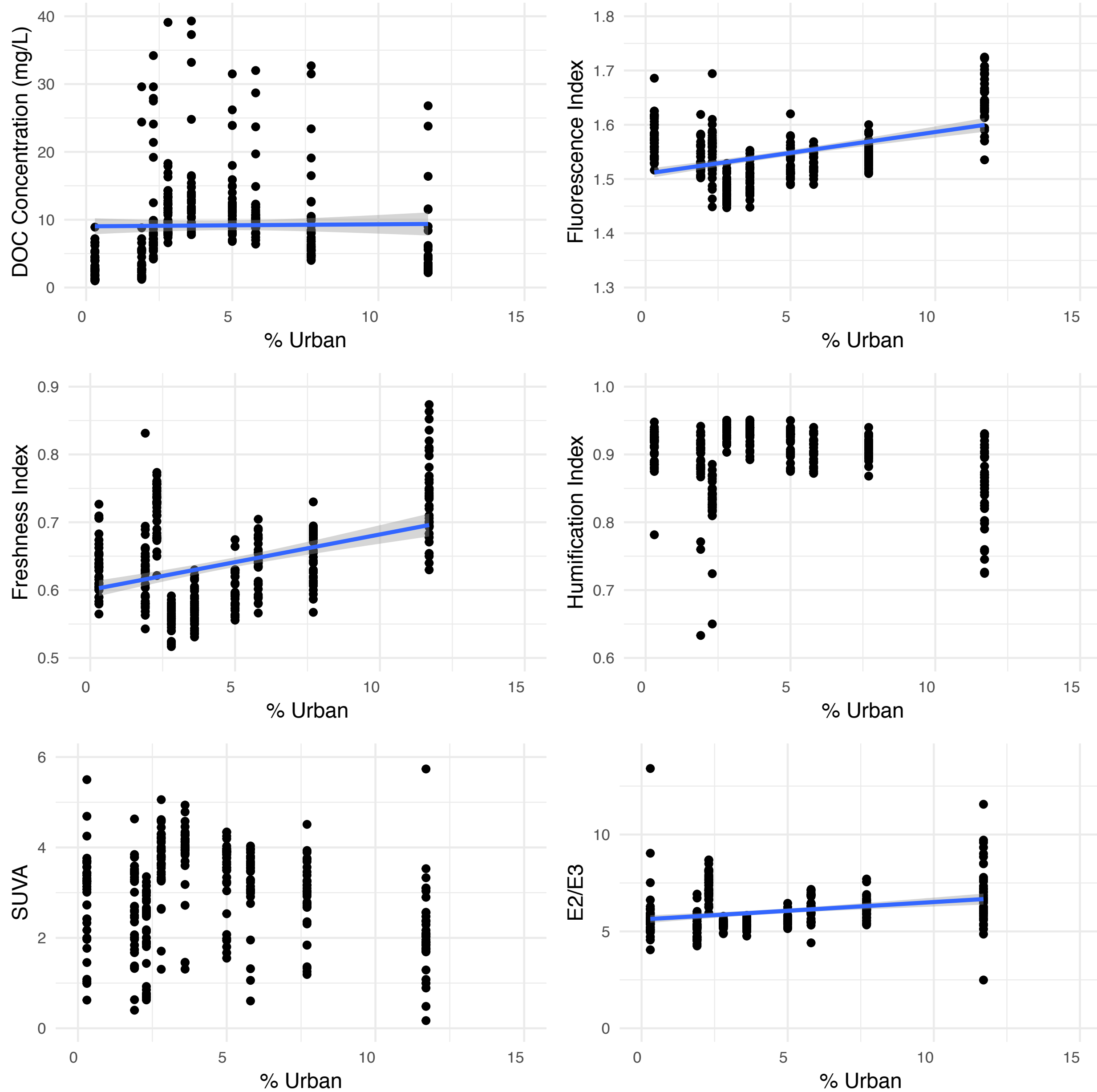

Figure 4.7: DOC concentrations and indices vs. percent contributing urban cover. Trendlines indicate significant correlations between the variables (Table 4.4).

Figure 4.8: DOC concentrations (mg/L) over time, for the 2016-2018 study period

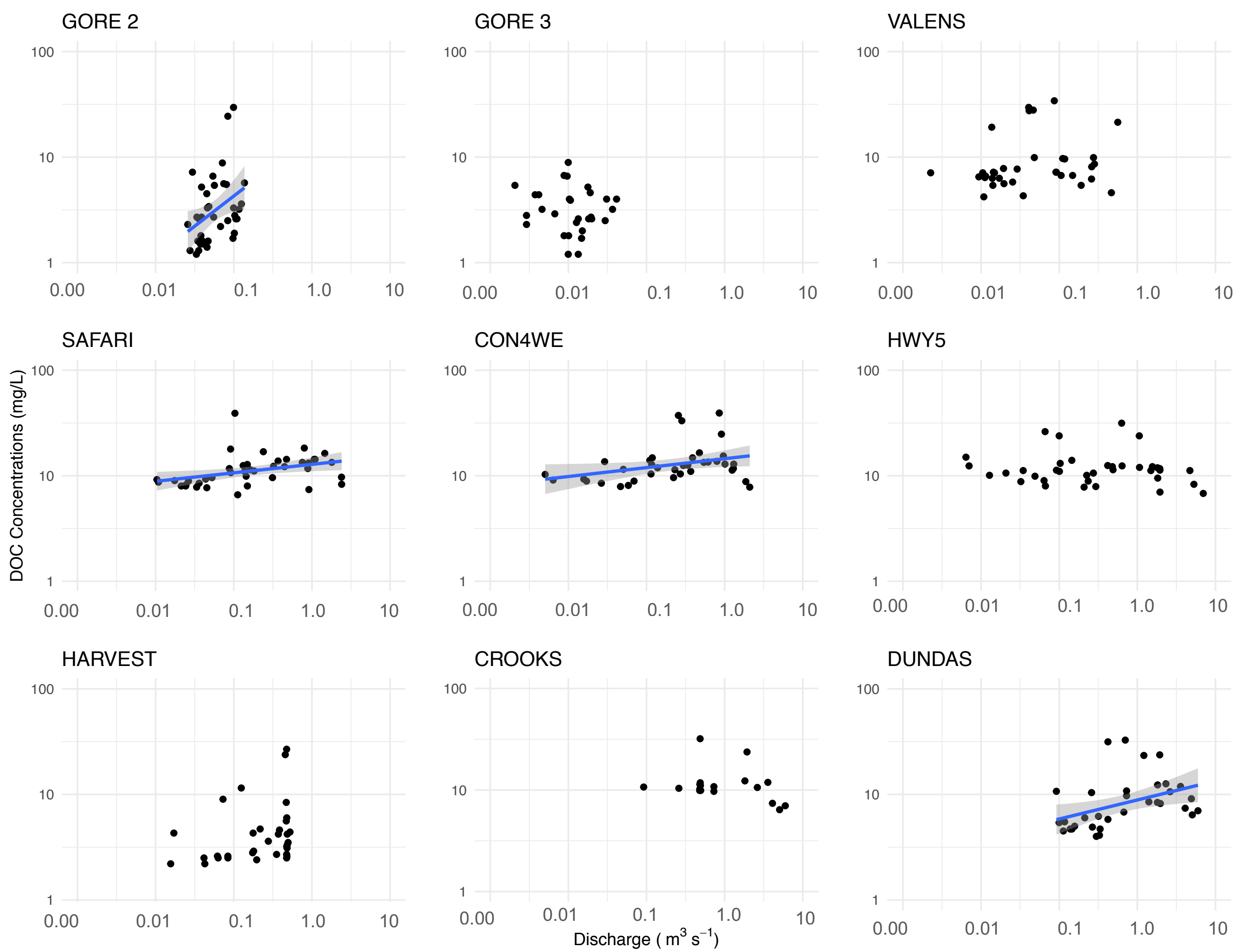

Figure 4.9: Log DOC concentration- log discharge relationships by site over 2016-2018. Trendlines indicate significant relationships between the variables ($p<0.05$) (Table 4.5).

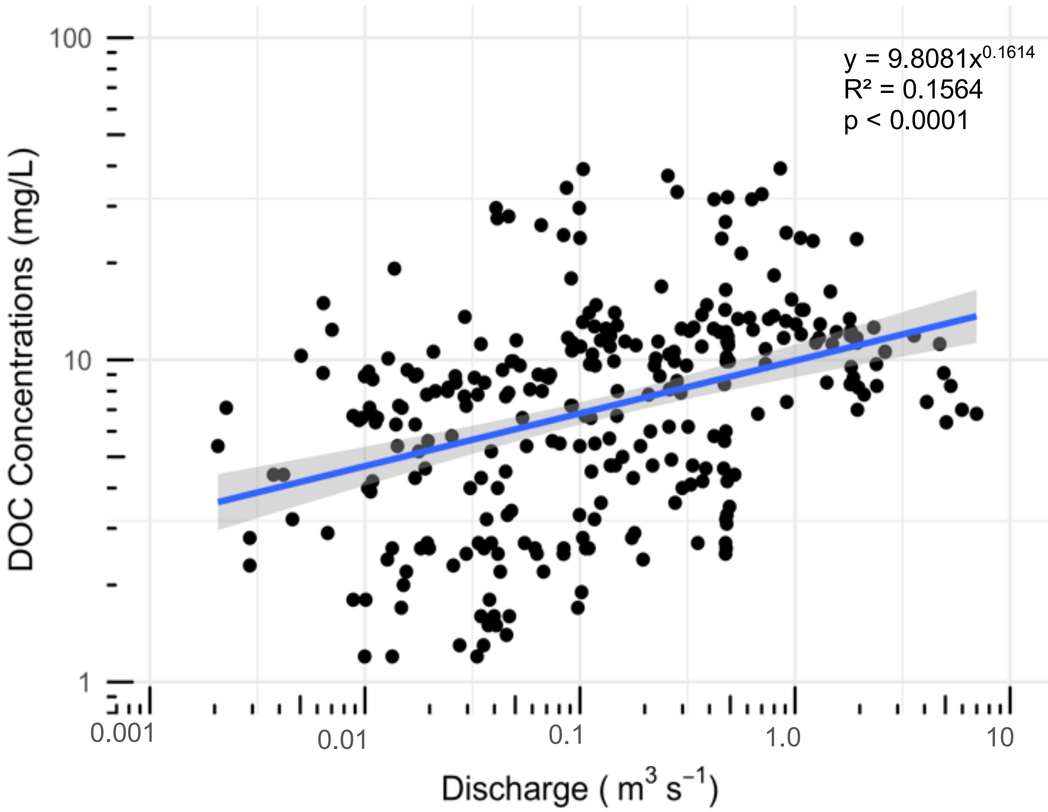

Figure 4.10: Watershed scale log DOC concentration- log discharge plots on logarithmic axes. All points of instantaneous concentration and discharge collected over 2016-2018 are plotted here with a trendline displaying a significant positive slope of 0.16 ($p < 0.05$).

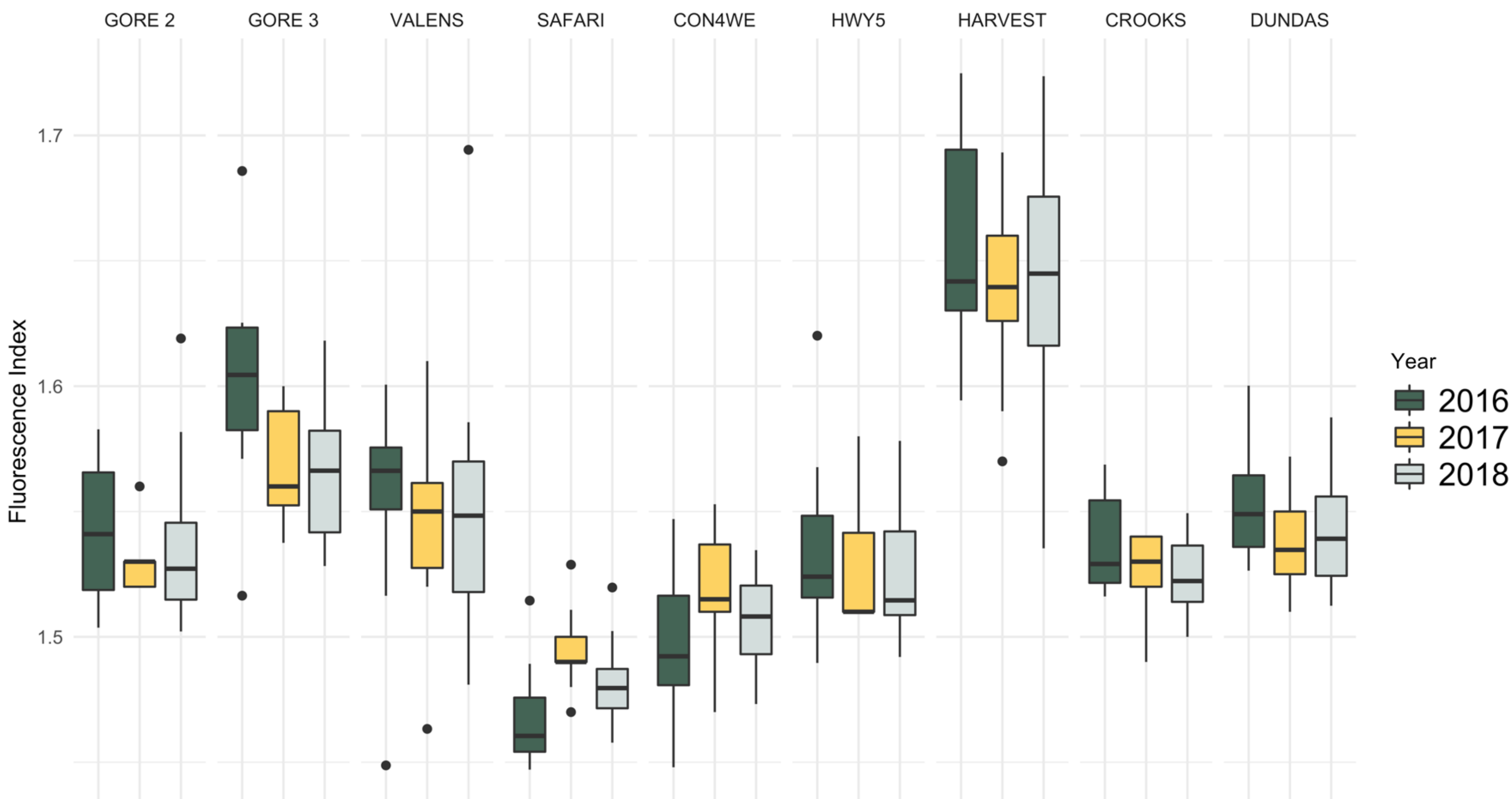

Figure 4.11: Boxplot of the Fluorescence Index (FI) distribution at all sites over 2016-2018.

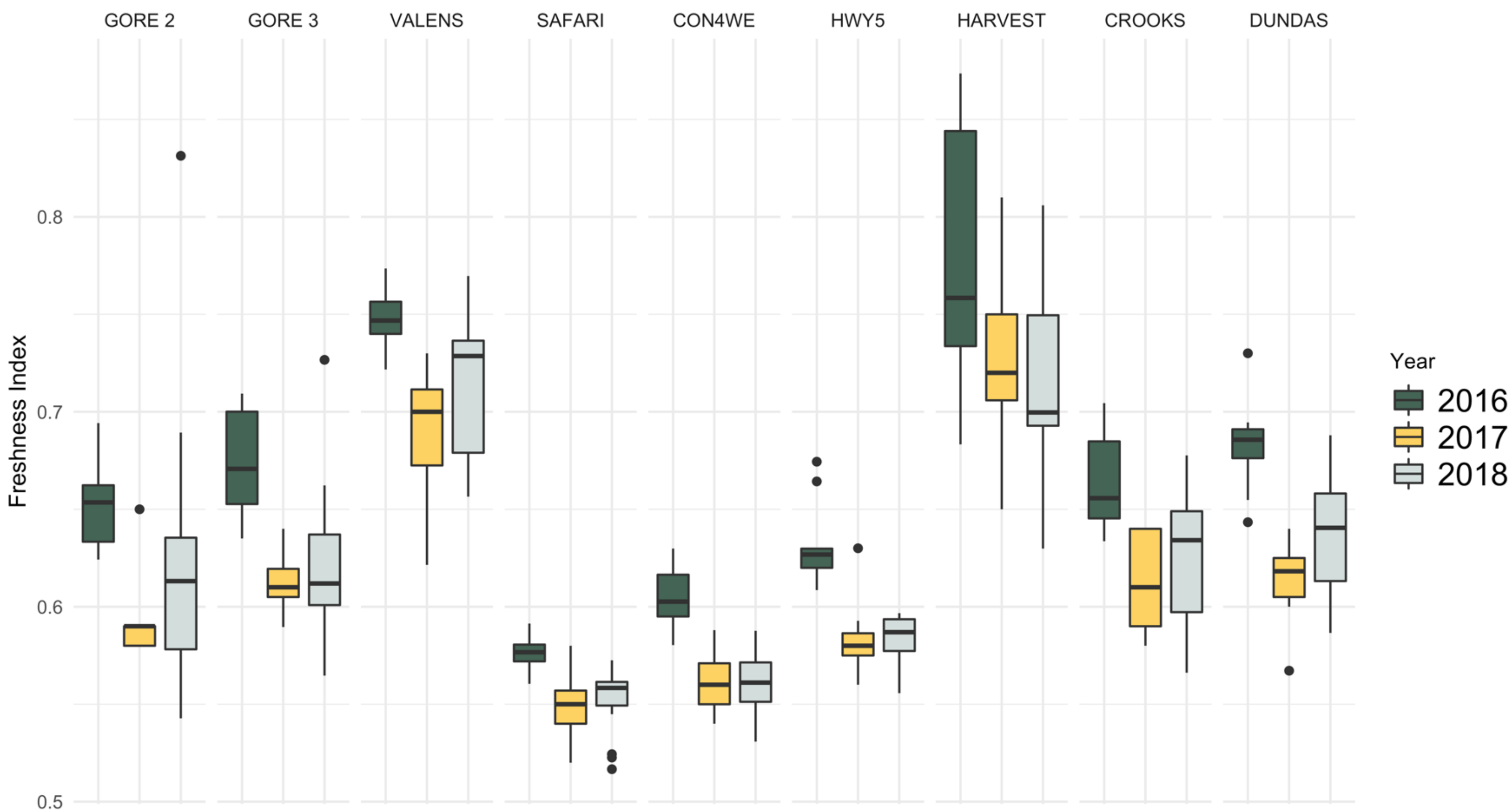

Figure 4.12: Boxplot of the Freshness Index (β/α) distribution at all sites over 2016-2018.

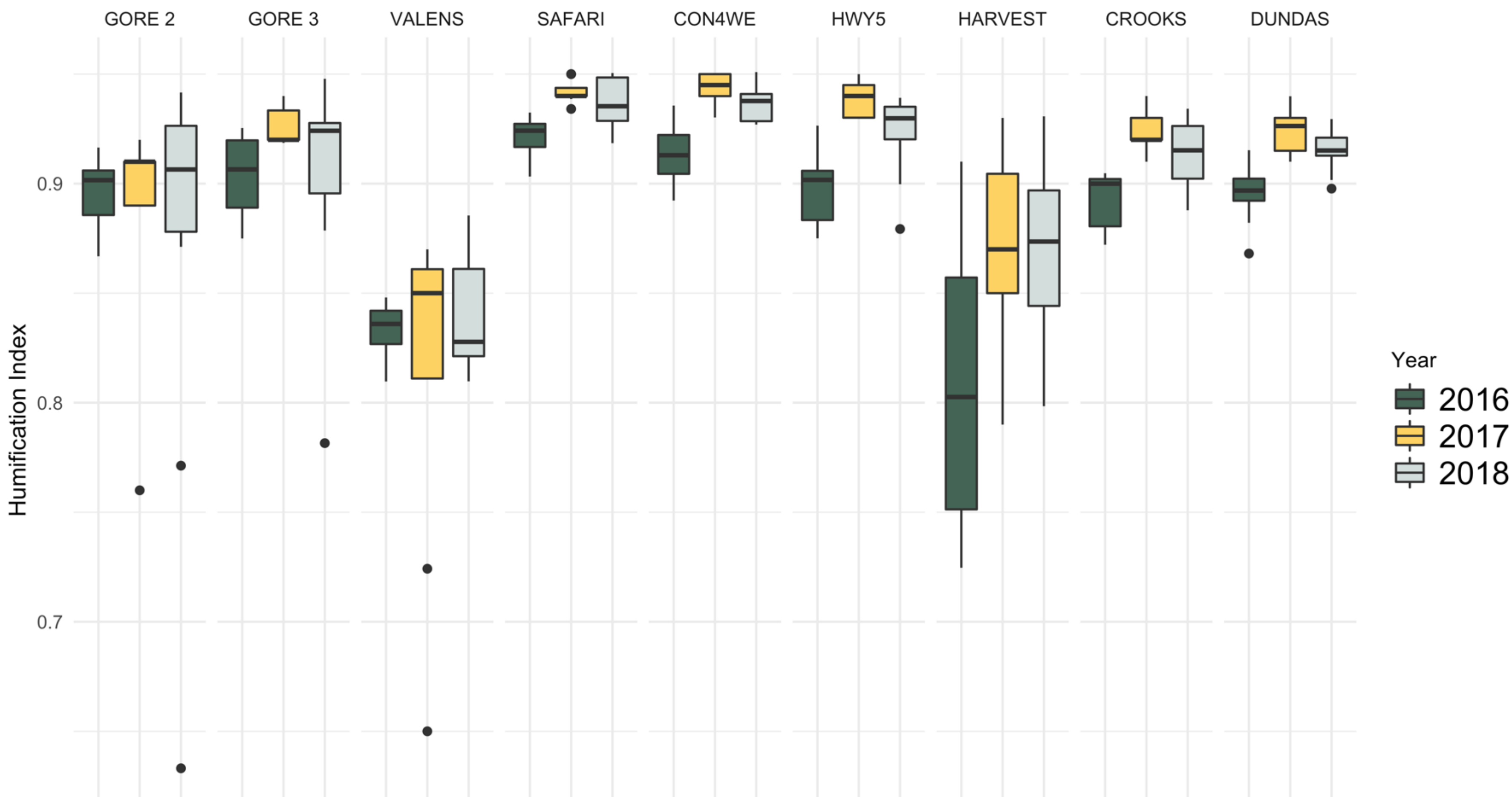

Figure 4.13: Boxplot of the Humification Index (HIX) distribution at all sites over 2016-2018.

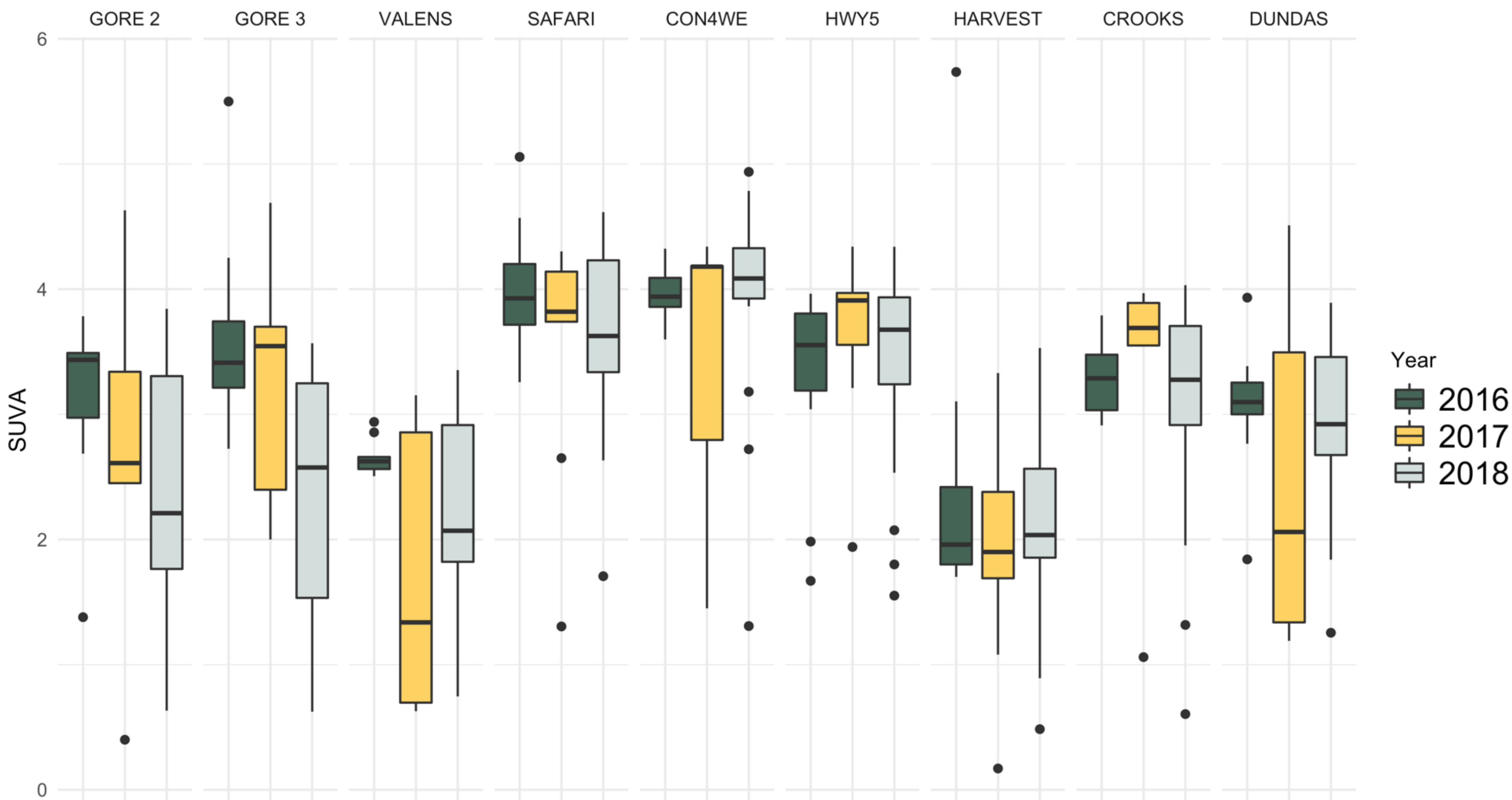

Figure 4.14: Boxplot of the $SUVA_{254}$ (L/mg-M) distribution at all sites over 2016-2018.

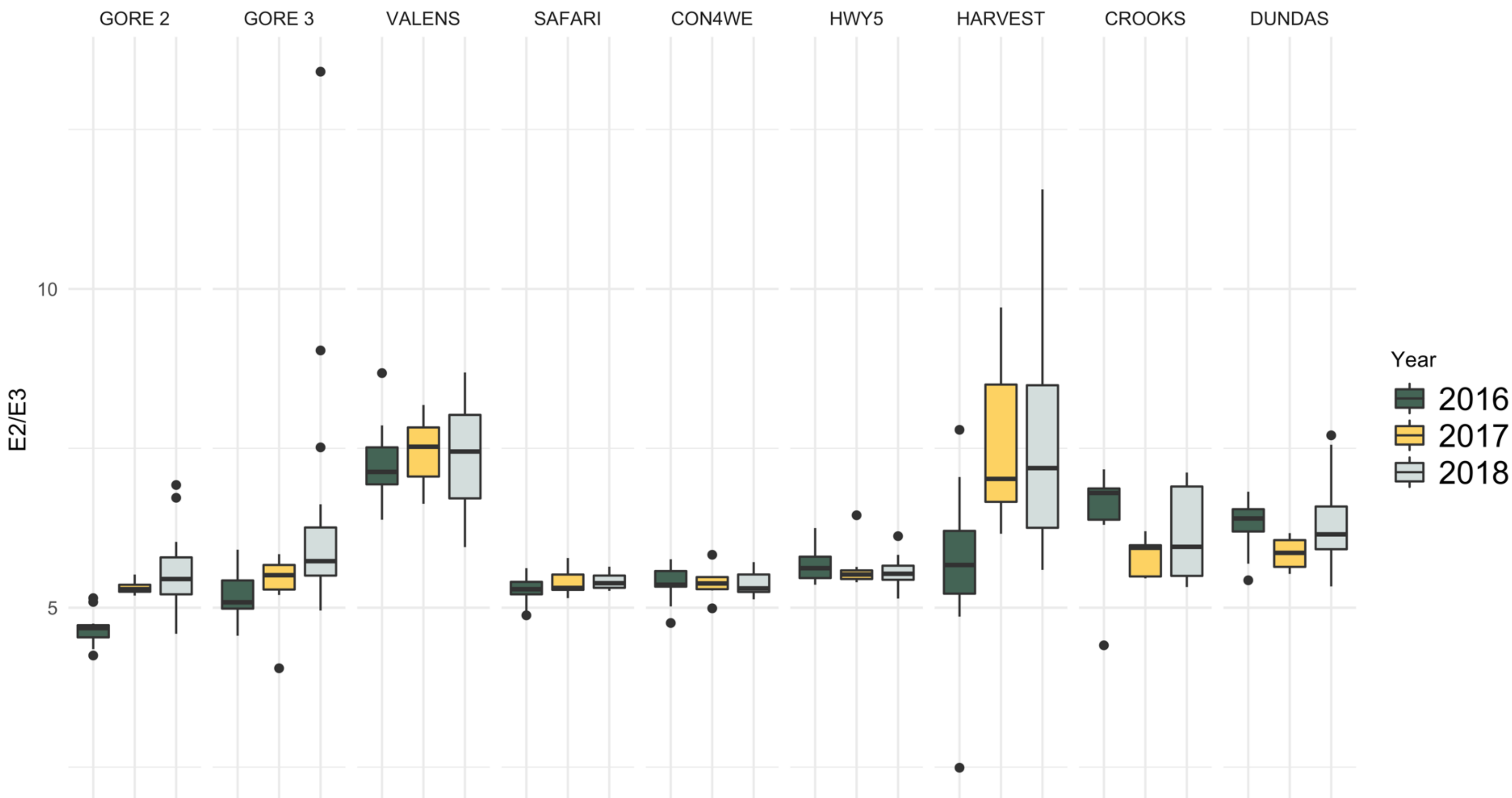

Figure 4.15: Boxplot of the E2/E3 distribution at all sites over 2016-2018.

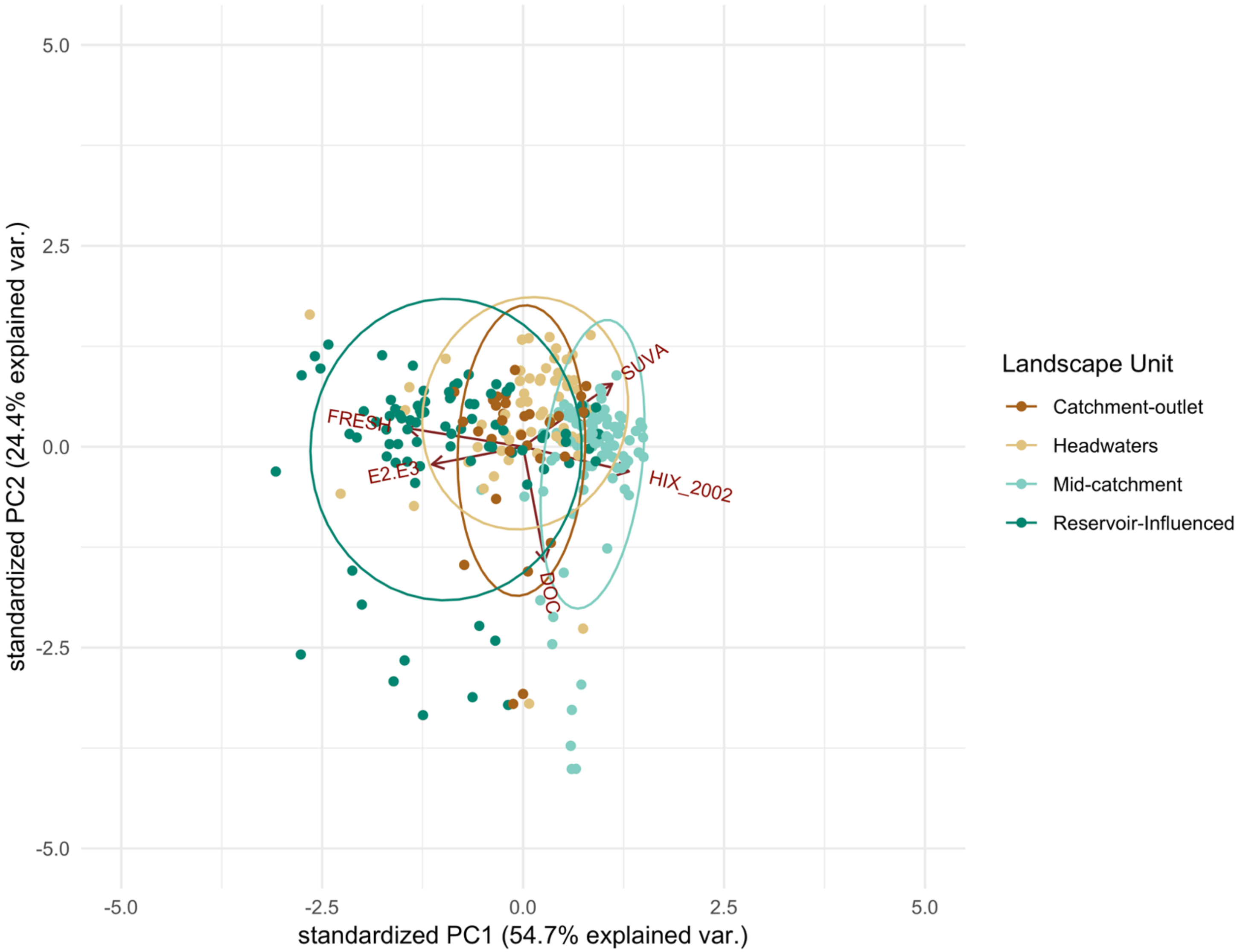

Figure 4.16: PCA analysis for DOC and indices data collected over the study period for all 9 sites. Biplots of the PCA are coloured according to these landscape groupings, with ellipses on the plot representing 80% probability of values being within the shape.

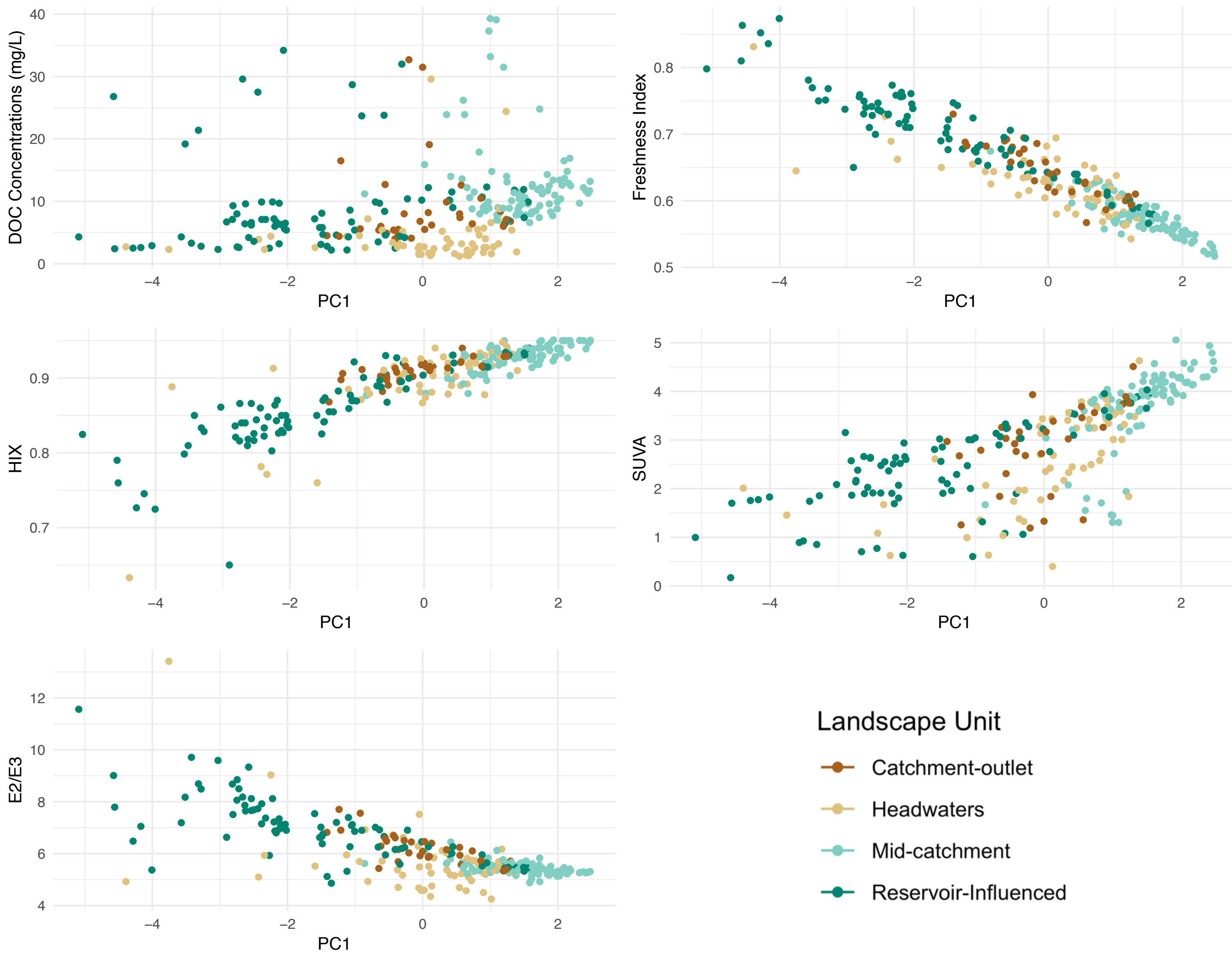

Figure 4.17: Regressions of PCI to DOC concentrations and DOM indices. Samples are grouped by landscape units within the watershed.

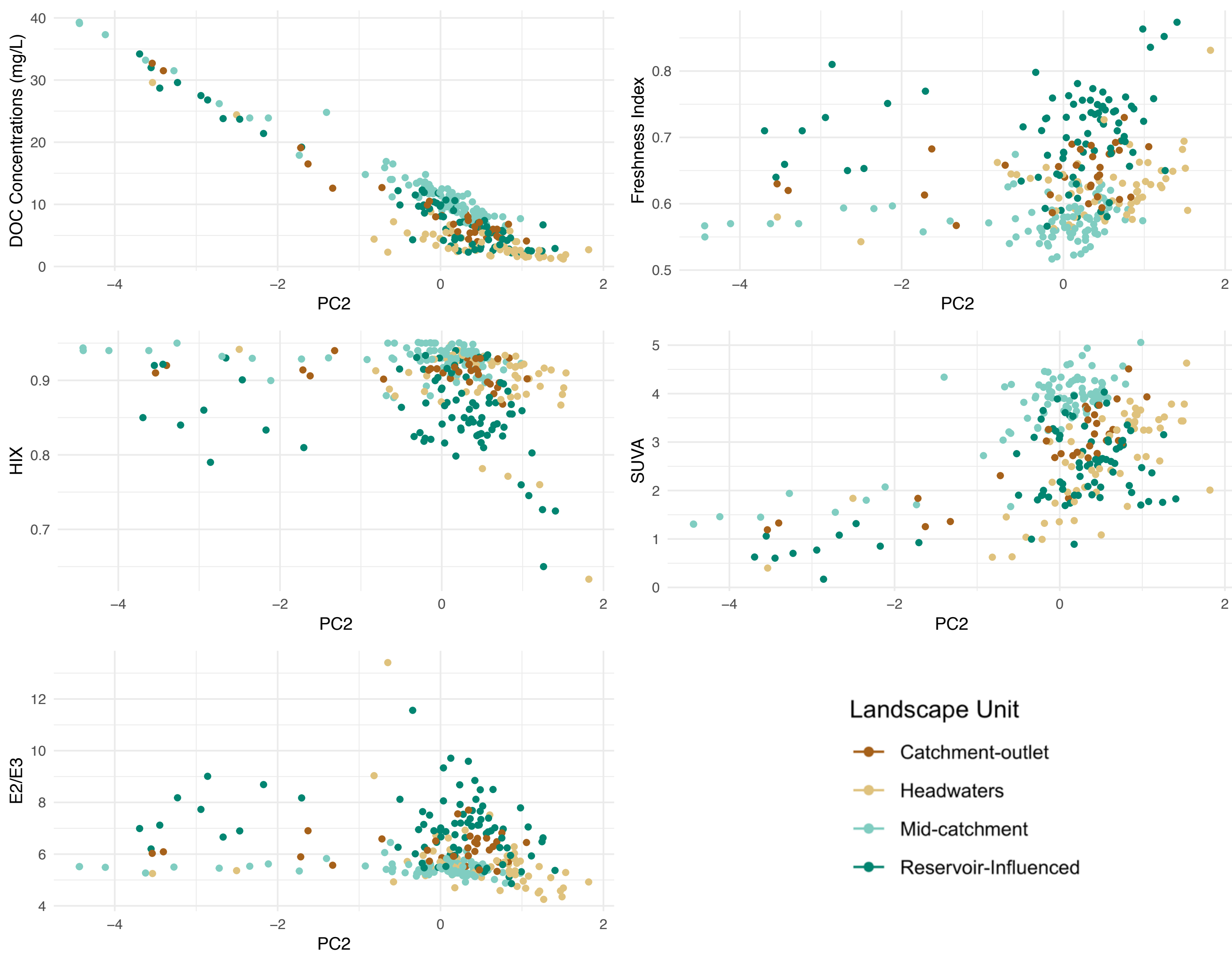

Figure 4.18: Regressions of PC2 to DOC concentrations and DOM indices. Samples are grouped by landscape units within the watershed.

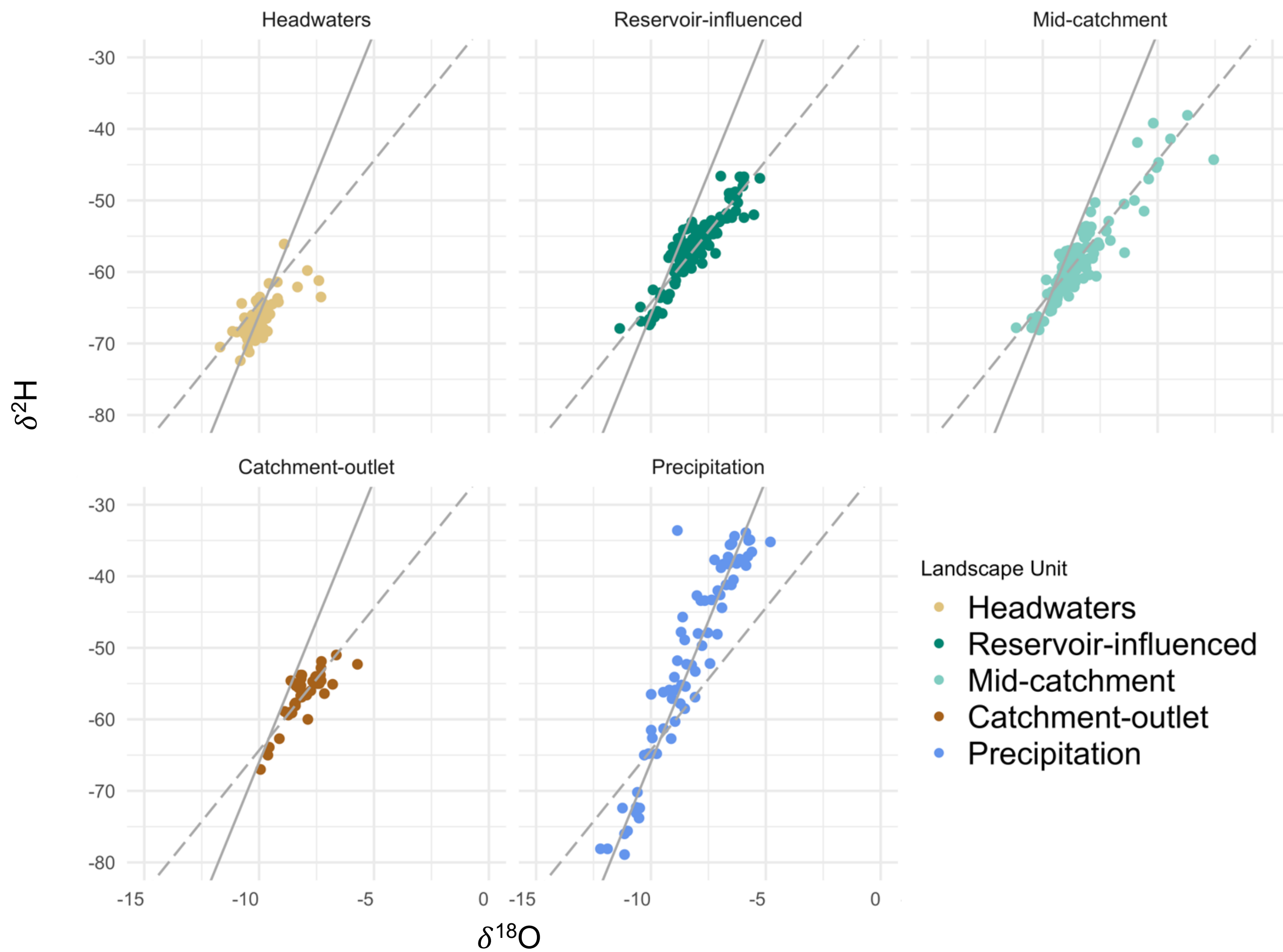

Figure 4.19: Plot of δ^2H ‰ vs. δ^{18}O ‰ over 2016-2018 across the different landscape units. The solid line is the LMWL whereas the dashed line is the LEL.

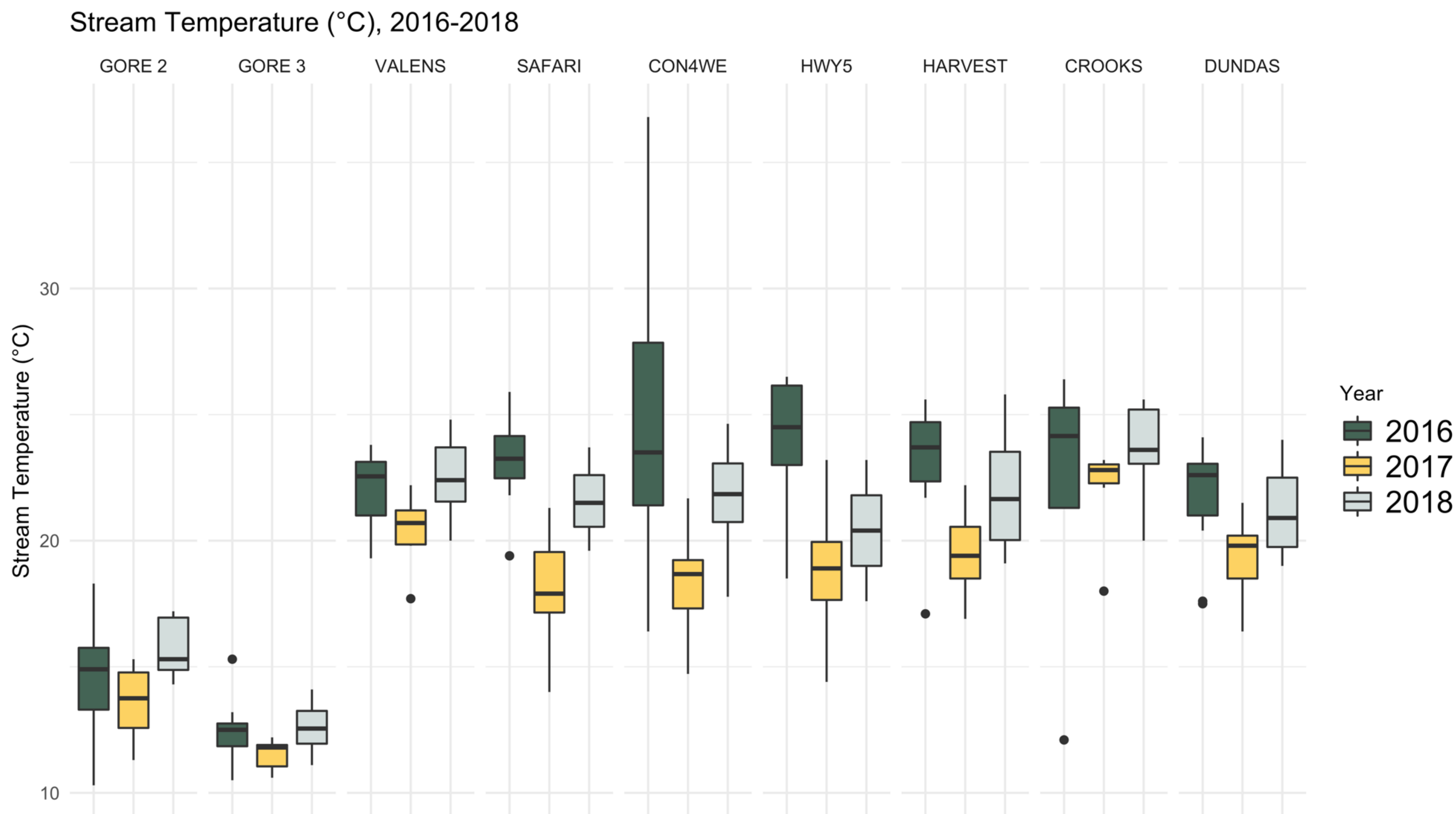

Figure 4.20: Boxplot of stream temperature (°C) distributions at all sites over 2016-2018.

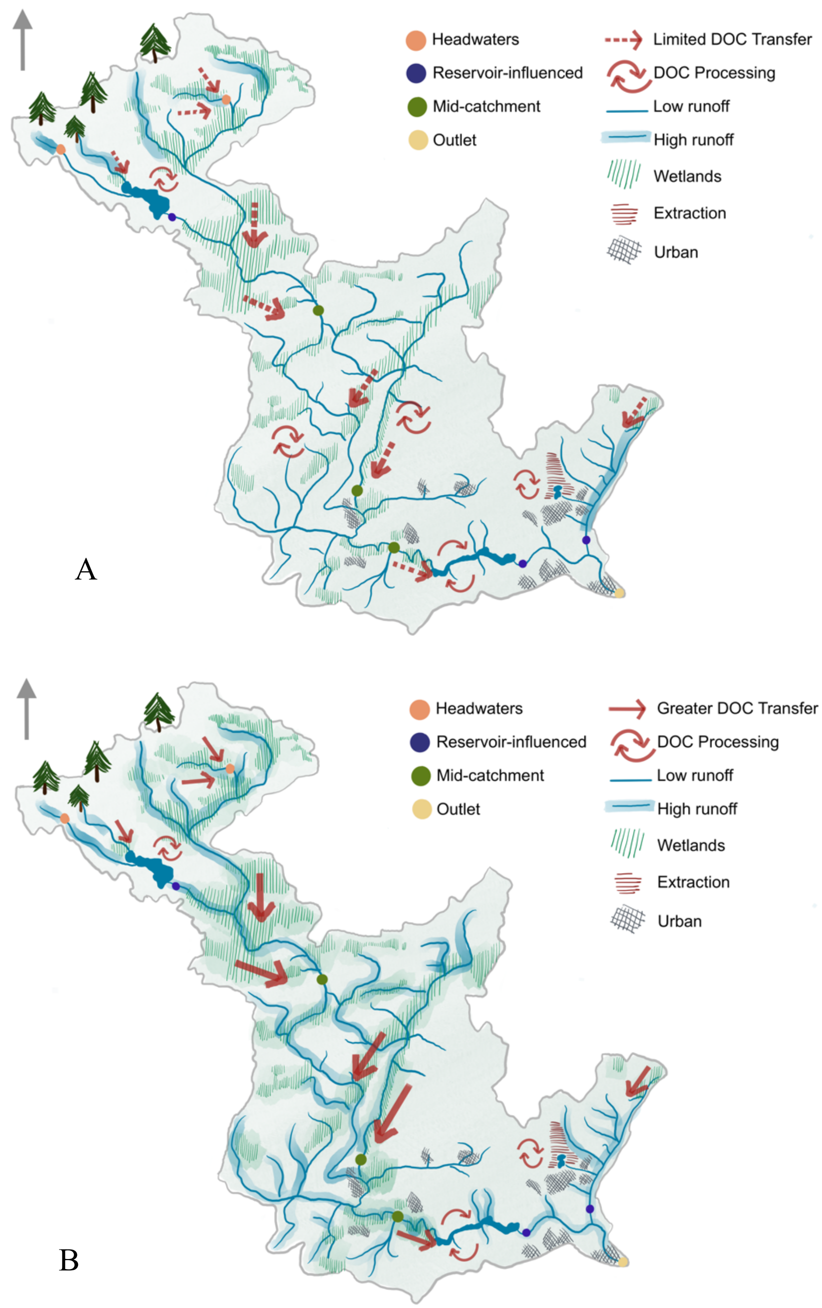

Figure 5.1: The proposed conceptual model of DOC transfer and water movement within the Spencer Creek watershed during (A) dry vs (B) wet conditions. Monitoring sites are grouped by landscape units. Dashed red arrows indicate limited DOC transfer whereas solid red arrows indicate greater transfer of DOC. The thickness of the red arrows indicates the magnitude of DOC concentrations relative to other regions in the watershed. Circular red arrows represent processing of DOM. Blue lines represent the watercourse through Spencer Creek during low runoff conditions, whereas the shaded blue lines represent higher runoff conditions. Shaded green wetland regions represent greater hydrologic connectivity between landscape and stream during wet conditions.

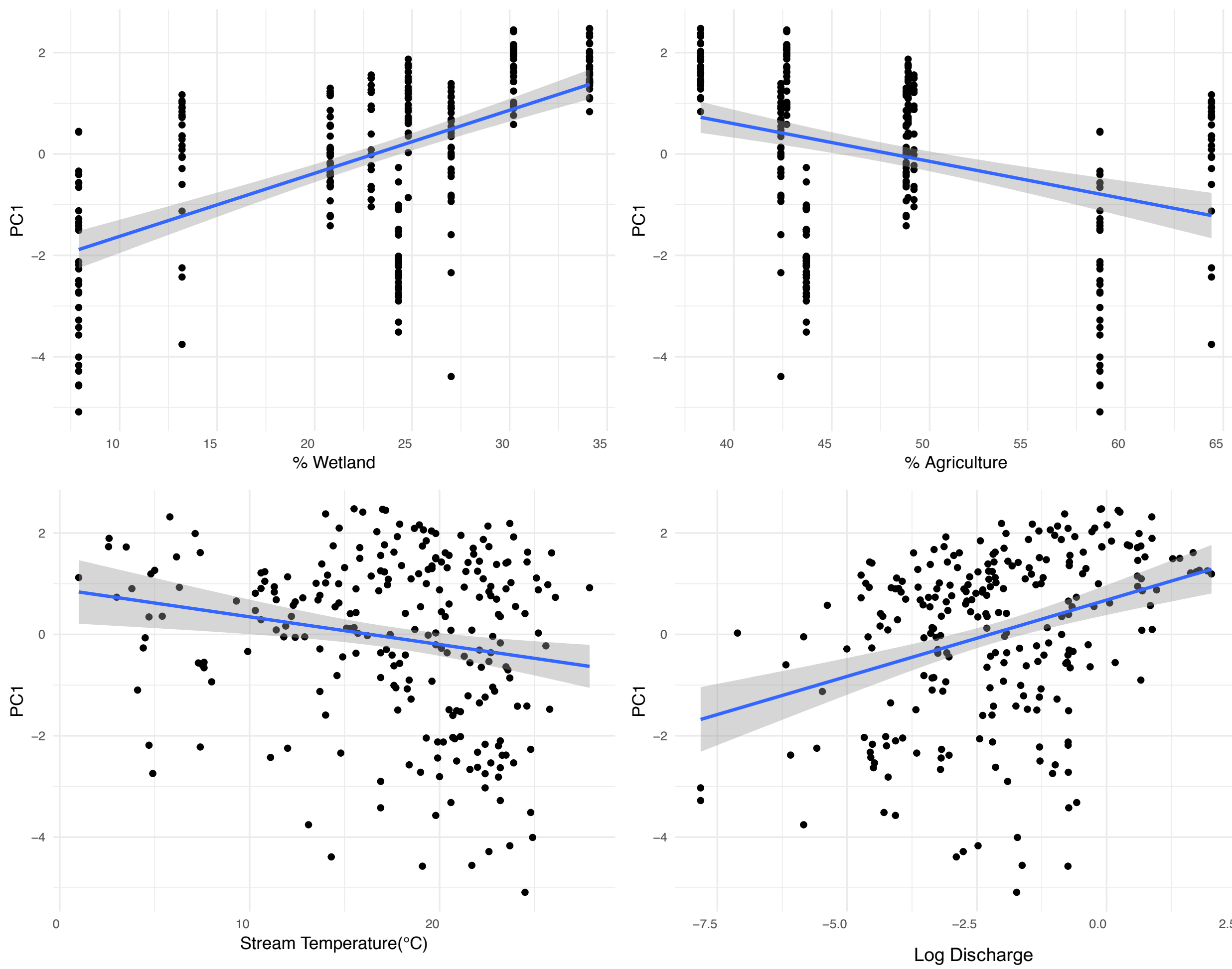

Figure 5.2: Correlation plots of PC1 versus land use, stream temperature, and log discharge. Trendlines indicate significant correlations between the variables (Table 5.1).

APPENDIX – Supplemental Data

Table A1: Kruskal Wallis Test results (p-values) for same site comparisons over the 2016-2018 study period. P values are bolded where there is statistical significance ($p<0.05$).

Site	DOC (mg/L)	FI	β/α	HIX	$SUVA_{254}$	E2/E3
GORE 2	**0.00264**	0.3156	0.1535	0.5265	**0.02361**	**2.71E-06**
GORE 3	**0.018**	0.06058	**0.01188**	0.1933	0.1184	**0.0265**
VALENS	**0.0005159**	0.4125	**0.0003481**	**0.03292**	0.1291	0.9731
SAFARI	**9.25E-06**	**0.0004938**	**8.05E-05**	**9.47E-05**	0.6401	0.32
CON4WE	**9.21E-05**	0.4213	**0.0001713**	**0.0002476**	0.1461	0.1577
HWY5	0.3406	0.4121	**7.44E-05**	**0.0001592**	0.4619	0.4802
HARVEST	**0.0002336**	0.5939	**0.01394**	**0.03084**	0.5062	**0.004341**
CROOKS	**2.54E-06**	**0.04932**	**0.01359**	**0.003035**	0.6352	**0.03595**
DUNDAS	**0.0002948**	0.1154	**8.55E-05**	**0.0001748**	0.491	0.09201

Table A2: Dunn's Test of Multiple Comparisons (p-values) for same site comparions over the 2016-2018 study period. Post-hoc test used to identify which years were significantly different from another. P-values are bolded where there is statistical significance ($p<0.05$). Empty boxes in the table indicate there is no significant different for that specific parameter and site, therefore a post-hoc was not completed.

SITE	DOC	FI_2005	β/α	HIX_2002	$SUVA_{254}$	E2/E3
GORE 2						
2016 - 2018	**0.001244496**				**0.003314789**	**1.09E-06**
2016 - 2017	**0.004662258**				0.073426194	**0.000401381**
2017 - 2018	0.354978616				0.160926095	0.19712077
GORE 3						
2016 - 2018	**0.002615044**		**0.006470834**			**0.003676905**
2016 - 2017	**0.089847255**		**0.007975334**			0.114497719
2017 - 2018	0.143736772		0.403043712			0.148272728
VALENS						
2016 - 2018	**0.000199305**		**6.01E-05**	**0.004903983**		
2016 - 2017	**0.001340433**		**0.008014564**	**0.027694187**		
2017 - 2018	0.252770019		0.060114571	0.172139356		
SAFARI						
2016 - 2018	**1.78E-05**	**5.93E-05**	**7.50E-05**	**2.48E-05**		
2016 - 2017	**2.78E-05**	**0.018614966**	**0.000312676**	**0.001885232**		
2017 - 2018	0.384413608	**0.046385134**	0.33007458	0.12515502		
CON4WE						
2016 - 2018	**2.24E-05**		**7.66E-05**	**2.81E-05**		
2016 - 2017	**0.000964244**		**0.000725898**	**0.011438682**		
2017 - 2018	0.133618185		0.361930885	**0.03420994**		
HWY5						
2016 - 2018			**6.85E-05**	**1.62E-05**		
2016 - 2017			**0.000498642**	**0.01080978**		
2017 - 2018			0.462971165	**0.03118598**		
HARVEST						
2016 - 2018	**6.38E-05**		**0.004644238**	**0.010147304**		**0.001087716**
2016 - 2017	**0.001284345**		**0.011582142**	**0.01857878**		**0.01149383**
2017 - 2018	0.197026582		0.408042382	0.389691153		0.294733802
CROOKS						
2016 - 2018	**5.92E-06**	**0.008479553**	**0.004379269**	**0.000694847**		**0.004980185**
2016 - 2017	**1.51E-05**	0.092389948	**0.017406112**	**0.01501684**		**0.042571827**
2017 - 2018	0.343501679	0.198564692	0.296987258	0.160592258		0.235813619
DUNDAS						
2016 - 2018	**0.000116221**		**6.95E-05**	**6.69E-05**		
2016 - 2017	**0.001326089**		**0.000301394**	**0.001573549**		
2017 - 2018	0.189457909		0.156507183	0.134240236		

Table A3: Kruskal Wallis Test results (p-values) for same year comparisons between the 9 sites. P-values are bolded where there is statistical significance ($p<0.05$).

Year	**DOC**	**FI_2005**	**β/α**	**HIX_2002**	**$SUVA_{254}$**	**E2/E3**
2016	**2.20E-16**	**8.65E-16**	**3.74E-09**	**1.02E-14**	**8.08E-11**	**2.20E-16**
2017	**7.78E-08**	**1.69E-06**	**3.74E-09**	**1.09E-08**	**0.04101**	**2.49E-08**
2018	**2.30E-15**	**2.20E-16**	**2.20E-16**	**2.20E-16**	**3.74E-11**	**1.60E-12**

Table A4: Dunn's Test of Multiple Comparisons (p-values) for same year comparisons between sites for DOC and FDOM indices. Post-hoc test was used to identify which sites were significantly different. P-values are bolded where there is statistical significance ($p<0.05$).

DOC

2016

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	0.44899945							
DUNDAS	**7.39E-05**	**7.09E-05**						
GORE2	**1.08E-08**	**6.88E-09**	**0.030652984**					
GORE3	**1.80E-09**	**1.04E-09**	**0.014394287**	0.37634766				
HARVEST	**3.08E-07**	**2.31E-07**	0.108174089	0.26271902	0.17103768			
HWY5	0.27207864	0.22289176	**2.47E-06**	**6.02E-11**	**7.19E-12**	**3.24E-09**		
SAFARI	0.19886064	0.22788633	**0.001380821**	**6.76E-07**	**1.36E-07**	**1.29E-05**	0.06745358	
VALENS	**0.00398176**	**0.00440068**	0.131517789	**0.00154831**	**0.00054234**	**0.00979682**	**0.00037738**	**0.03271171**

2017

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	0.13016792							
DUNDAS	**0.02104878**	0.17574627						
GORE2	**3.89E-05**	**0.00235949**	**0.033489994**					
GORE3	**4.27E-08**	**1.05E-05**	**0.000571019**	0.06796364				
HARVEST	**5.19E-05**	**0.00292665**	**0.038898524**	0.47220536	0.05945974			
HWY5	**0.08057915**	0.39143195	0.253932113	**0.00538573**	**3.37E-05**	**0.00656361**		
SAFARI	0.27725291	0.37621646	0.107451143	**0.00084172**	**2.52E-06**	**0.00106557**	**0.01992526**	
VALENS	0.20892276	0.17626394	0.49104995	**0.02898543**	**0.00041086**	**0.03391075**	0.25652099	0.10654195

2018

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	0.36358706							
DUNDAS	**0.01130453**	**0.02673598**						
GORE2	**1.87E-07**	**1.13E-06**	**0.002791307**					
GORE3	**2.26E-09**	**1.79E-08**	**0.000190089**	0.21391126				
HARVEST	**8.95E-06**	**4.06E-05**	**0.022237335**	0.2312383	0.06464475			
HWY5	0.4191381	0.44243908	**0.018952623**	**5.44E-07**	**7.69E-09**	**2.20E-05**		
SAFARI	0.4937369	0.36949652	**0.011778545**	**2.03E-07**	**2.49E-09**	**9.61E-06**	0.42528194	
VALENS	**0.01427915**	**0.03318176**	0.451825199	**0.00168237**	**9.76E-05**	**0.01547884**	**0.02370092**	**0.01486685**

FI

2016

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00808715**							
DUNDAS	**0.0015077**	0.26317717						
GORE2	**0.01804048**	0.3451364	0.14835593					
GORE3	**1.11E-06**	**0.00741209**	**0.04009586**	**0.00175329**				
HARVEST	**2.88E-10**	**2.52E-05**	**0.00038596**	**2.50E-06**	**0.0424101**			
HWY5	**0.04547655**	0.21315595	0.0771351	0.33886605	**0.00050884**	**4.85E-07**		
SAFARI	0.10133351	**4.77E-05**	**3.95E-06**	**0.0001452**	**7.71E-11**	**1.54E-15**	**0.00076474**	
VALENS	**0.00062773**	0.20154246	0.42945405	0.10239947	0.05187084	**0.00049178**	**0.04859679**	**7.91E-07**

2017

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	0.26377095							
DUNDAS	0.12688318	0.31089756						
GORE2	0.16245435	0.37475787	0.42457301					
GORE3	**0.0040326**	**0.02538025**	0.07211878	**0.0447268**				
HARVEST	**1.72E-05**	**0.0004117**	**0.00238941**	**0.00087724**	0.10154271			
HWY5	0.33681358	0.4192156	0.2428362	0.29810257	**0.01548728**	**0.00018467**		
SAFARI	0.08141229	**0.02304967**	**0.00590595**	**0.00800703**	**2.39E-05**	**5.72E-09**	**0.0376844**	
VALENS	0.06276064	0.19813702	0.36737709	0.29198879	0.12114731	**0.00515191**	0.14482677	**0.00147907**

2018

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.04756216**							
DUNDAS	**0.00174984**	0.11853891						
GORE2	**0.00977706**	0.27962445	0.26347742					
GORE3	**1.44E-06**	**0.0019199**	**0.04029218**	**0.00791535**				
HARVEST	**2.02E-11**	**7.67E-07**	**9.35E-05**	**4.96E-06**	**0.02073158**			
HWY5	0.09069715	0.35330695	0.05405987	0.15972029	**0.00036831**	**4.58E-08**		
SAFARI	**0.03737741**	**0.00028457**	**9.18E-07**	**1.32E-05**	**2.32E-11**	**8.95E-18**	**0.00077817**	
VALENS	**0.00038655**	0.0577808	0.35410895	0.15171557	0.07861789	**0.00027126**	**0.02155245**	**6.86E-08**

β/α

2016

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00131077**							
DUNDAS	**4.40E-05**	0.15491851						
GORE2	**0.044427**	0.06960323	**0.00625957**					
GORE3	**0.00367411**	0.34671574	0.07804111	0.13628006				
HARVEST	**4.11E-10**	**0.00038346**	**0.01046011**	**4.42E-07**	**7.13E-05**			
HWY5	0.05848064	0.05741959	**0.00494338**	0.45103419	0.11465149	**3.44E-07**		
SAFARI	0.17063934	**1.33E-05**	**1.35E-07**	**0.00217653**	**5.36E-05**	**3.39E-14**	**0.00355927**	
VALENS	**7.11E-10**	**0.00071337**	**0.01783202**	**8.15E-07**	**0.00013494**	0.38804317	**6.34E-07**	**4.42E-14**

2017

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00351856**							
DUNDAS	**0.00924513**	0.37120911						
GORE2	**0.02030646**	0.23667222	0.35285755					
GORE3	**0.00782991**	0.39377431	0.47641334	0.33043417				
HARVEST	**1.85E-07**	**0.01641573**	**0.00651905**	**0.00145493**	**0.00776066**			
HWY5	0.14172484	0.05809598	0.10706162	0.1826182	0.09654973	**7.22E-05**		
SAFARI	0.33659076	**0.00075052**	**0.00235745**	**0.00572585**	**0.00193456**	**6.93E-09**	0.06574814	
VALENS	**3.59E-06**	**0.05038324**	**0.02381919**	**0.00732402**	**0.02746165**	0.32083322	**0.00054997**	**2.32E-07**

2018

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**5.20E-05**							
DUNDAS	**1.46E-06**	0.25198385						
GORE2	**0.00041951**	0.24248744	0.0780282					
GORE3	**8.62E-05**	0.38655905	0.15975129	0.33402921				
HARVEST	**3.67E-13**	**0.0008864**	**0.00565056**	**3.36E-05**	**0.00018351**			
HWY5	**0.044932**	**0.0117558**	**0.00124913**	**0.0499149**	**0.01928904**	**1.37E-08**		
SAFARI	0.32997107	**6.28E-06**	**1.05E-07**	**6.10E-05**	**9.99E-06**	**5.63E-15**	**0.01510621**	
VALENS	**1.19E-13**	**0.00063347**	**0.00430534**	**2.05E-05**	**0.00012005**	0.47612392	**6.30E-09**	**1.54E-15**

HIX

2016

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00389202**							
DUNDAS	**0.00828787**	0.40625728						
GORE2	**0.03071934**	0.17906108	0.25534142					
GORE3	0.31025669	**0.00959549**	**0.01974966**	0.06920824				
HARVEST	**1.05E-07**	**0.00325368**	**0.00181573**	**0.00010621**	**2.07E-07**			
HWY5	**0.03588505**	0.16986937	0.24299176	0.47987758	0.07926276	**0.00010754**		
SAFARI	0.2049633	**0.00010919**	**0.00034282**	**0.00191666**	0.07866765	**1.05E-10**	**0.00254557**	
VALENS	**1.33E-08**	**0.00117437**	**0.00062232**	**2.31E-05**	**2.21E-08**	0.41116688	**2.42E-05**	**5.30E-12**

2017

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00328445**							
DUNDAS	**0.00574666**	0.4267868						
GORE2	**8.46E-05**	0.17993167	0.13431154					
GORE3	**0.01143952**	0.33416375	0.4036604	0.08721262				
HARVEST	**2.61E-06**	0.05468778	**0.03618668**	0.24660714	**0.01991825**			
HWY5	0.21435928	**0.03106397**	**0.04639886**	**0.00224029**	0.07536794	**0.0001721**		
SAFARI	0.33052096	**0.00893032**	**0.0149**	**0.00029994**	**0.0278062**	**1.10E-05**	0.34828351	
VALENS	**1.27E-07**	**0.01185385**	**0.00709442**	0.08174075	**0.00342213**	0.22703397	1.40E-05	**5.71E-07**

2018

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00065498**							
DUNDAS	**0.00022856**	0.42397624						
GORE2	**9.61E-06**	0.18251664	0.23142855					
GORE3	**0.00105641**	0.3917892	0.31432707	0.10849528				
HARVEST	**1.71E-09**	**0.00523776**	**0.00732595**	**0.04097472**	**0.00155194**			
HWY5	0.06218586	**0.04045733**	**0.022926**	**0.00291042**	0.06178817	**4.55E-06**		
SAFARI	0.47183644	**0.00043813**	**0.00014306**	**5.16E-06**	**0.00070493**	**6.46E-10**	0.05146625	
VALENS	**1.16E-13**	**4.59E-05**	**6.28E-05**	**0.00083474**	**5.99E-06**	0.08672063	**2.34E-09**	**2.93E-14**

SUVA254

2016

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00096755**							
DUNDAS	**9.13E-05**	0.25202544						
GORE2	**0.0024557**	0.40407452	0.18447161					
GORE3	**0.00172779**	0.4273218	0.19729404	0.4748664				
HARVEST	**6.61E-09**	**0.00358673**	**0.02166302**	**0.00198059**	**0.00204019**			
HWY5	**0.02404008**	0.12115614	**0.03307866**	0.18285045	0.16205921	**5.72E-05**		
SAFARI	0.42951979	**0.00143327**	**0.00013774**	**0.00357763**	**0.00253993**	**9.54E-09**	**0.03330266**	
VALENS	**4.15E-08**	**0.00808706**	**0.04011764**	**0.0046603**	**0.0048727**	0.40770214	**0.00019092**	**6.13E-08**

2017

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	0.2400357							
DUNDAS	0.12951816	0.32628724						
GORE2	0.18507218	0.43374189	0.38061535					
GORE3	0.23342085	0.49931376	0.32081766	0.43073928				
HARVEST	**0.01610211**	0.08183388	0.19583485	0.10260751	0.07403475			
HWY5	0.32526498	0.12318452	0.05891757	0.0862702	0.11594377	**0.00436599**		
SAFARI	0.37019769	0.13999206	0.06574722	0.0971122	0.13164857	**0.00409714**	0.44070701	
VALENS	**0.01200876**	0.06331818	0.1586402	0.07950597	0.05672273	0.42763396	**0.00321768**	**0.00300333**

2018

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.0072484**							
DUNDAS	**0.00059291**	0.23790151						
GORE2	**2.18E-06**	**0.02222489**	0.09201565					
GORE3	**3.81E-06**	**0.02910643**	0.11332085	0.45183115				
HARVEST	**3.22E-08**	**0.00223295**	**0.01405607**	0.18492686	0.15478211			
HWY5	0.08774202	0.12614844	**0.02774399**	**0.00053929**	**0.00081692**	**1.97E-05**		
SAFARI	0.2114199	**0.04557216**	**0.00663573**	**6.20E-05**	**0.00010013**	**1.49E-06**	0.28727445	
VALENS	**5.82E-08**	**0.00342323**	**0.02043822**	0.23385267	0.1984268	0.42841507	**3.37E-05**	**2.63E-06**

E2/E3

2016

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.0005852**							
DUNDAS	**0.00758269**	0.18847044						
GORE2	**0.00269626**	**2.19E-10**	**2.75E-08**					
GORE3	0.1619388	**6.48E-06**	**0.00020405**	**0.03239751**				
HARVEST	**0.032282**	0.07744474	0.28716519	**9.04E-07**	**0.00177492**			
HWY5	0.09395876	**0.02192651**	0.12493663	**9.92E-06**	**0.00855985**	0.28425043		
SAFARI	0.28542459	**5.22E-05**	**0.00111103**	**0.0125352**	0.33779918	**0.00698927**	**0.02699723**	
VALENS	**4.79E-07**	0.05120104	**0.00525671**	**4.81E-16**	**5.53E-10**	**0.00104005**	**0.00010399**	**1.23E-08**

2017

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.02085663**							
DUNDAS	**0.00871051**	0.37379872						
GORE2	0.2310488	**0.00375527**	**0.00132494**					
GORE3	0.28787775	0.08191333	**0.04325287**	0.10835229				
HARVEST	**1.44E-05**	**0.0259385**	0.0535038	**8.79E-07**	**0.00035963**			
HWY5	0.09714668	0.24316491	0.15434681	**0.02533126**	0.24316491	**0.00387074**		
SAFARI	0.49306831	**0.02005456**	**0.00833393**	0.23621219	0.28235859	**1.34E-05**	0.09438335	
VALENS	**8.43E-06**	**0.01984701**	**0.04230375**	**4.88E-07**	**0.00023712**	0.45353944	**0.00275239**	**7.81E-06**

2018

	CON4WE	CROOKS	DUNDAS	GORE2	GORE3	HARVEST	HWY5	SAFARI
CROOKS	**0.00223788**							
DUNDAS	**2.23E-05**	0.12776228						
GORE2	0.21900984	**0.01558468**	**0.00032392**					
GORE3	**0.00729354**	0.30334486	**0.04282275**	**0.04314906**				
HARVEST	**1.81E-07**	**0.01673991**	0.15393675	**4.41E-06**	**0.00295972**			
HWY5	0.11767217	**0.04330845**	**0.00165018**	0.3324988	0.10403406	**3.78E-05**		
SAFARI	0.42379748	**0.00354669**	**3.95E-05**	0.27774402	**0.01126016**	**3.40E-07**	0.15647883	
VALENS	**1.06E-08**	**0.00475094**	0.06842419	**3.42E-07**	**0.00057563**	0.32482502	**4.00E-06**	**2.03E-08**

Table A5: Kruskal Wallis Test results (p-values) for same year comparisons between the 4 landscape classifications. P-values are bolded where there is statistical significance ($p<0.05$).

Year	DOC	FI	β/α	HIX	$SUVA_{254}$	E2/E3
2016	**2.20E-16**	**3.44E-11**	**2.20E-16**	**2.42E-13**	**7.51E-11**	**2.20E-16**
2017	**5.93E-08**	**5.31E-05**	**2.20E-10**	**8.37E-10**	**0.004**	**3.68E-09**
2018	**3.62E-15**	**8.42 E-13**	**2.20E-16**	**2.20E-16**	**1.33E-11**	**4.91E-13**

Table A6: Dunn's Test of Multiple Comparisons (p-values) for same year comparisons between landscape classifications for DOC and FDOM indices. Post-hoc test was used to identify which sites were significantly different. P-values are bolded where there is statistical significance ($p<0.05$).

DOC

2016

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**1.09E-19**		
OUTLET	**0.009572734**	**1.35E-06**	
RESERVOIR	**2.35E-07**	**4.35E-06**	0.065249762

2017

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**8.16E-10**		
OUTLET	**0.001878555**	0.05600283	
RESERVOIR	**0.000187039**	**0.002549264**	0.371858914

2018

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**2.51E-17**		
OUTLET	**0.000138831**	**0.00343938**	
RESERVOIR	**3.60E-07**	**6.88E-05**	0.492374081

FI_2005

2016

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**7.56E-08**		
OUTLET	0.357544022	**0.000177853**	
RESERVOIR	0.164586195	**7.54E-12**	0.13323575

2017

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**0.000448272**		
OUTLET	0.247926178	**0.034453936**	
RESERVOIR	0.268660242	**3.56E-06**	0.1153886

2018

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**4.49E-09**		
OUTLET	0.260871572	**7.02E-05**	
RESERVOIR	0.229966182	**5.04E-13**	0.10593575

FRESH

2016

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**0.000773617**		
OUTLET	**0.012394827**	**1.25E-06**	
RESERVOIR	**3.66E-07**	**9.94E-19**	0.08541551

2017

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**0.000752211**		
OUTLET	**0.022377315**	**0.004143417**	
RESERVOIR	**0.001919298**	**2.34E-12**	0.42251102

2018

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**4.95E-07**		
OUTLET	0.082651733	**6.89E-08**	
RESERVOIR	**6.87E-06**	**2.43E-24**	**0.02663892**

HIX_2002

2016

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	0.089903695		
OUTLET	0.063153445	**0.004749785**	
RESERVOIR	**1.19E-08**	**4.54E-14**	**0.00485039**

2017

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**1.97E-05**		
OUTLET	0.29660749	**0.004927107**	
RESERVOIR	**0.048295981**	**2.32E-11**	**0.03270982**

2018

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**3.22E-07**		
OUTLET	0.44275204	**9.67E-05**	
RESERVOIR	**0.000845182**	**3.26E-19**	**0.00469493**

$SUVA_{254}$

2016

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**0.000421453**		
OUTLET	0.155646361	**8.74E-05**	
RESERVOIR	**0.001797502**	**1.67E-12**	0.10491461

2017

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**0.042909625**		
OUTLET	0.33216903	**0.047154614**	
RESERVOIR	0.066853126	**0.00017493**	0.27249046

2018

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**1.29E-09**		
OUTLET	0.072355368	**0.000930413**	
RESERVOIR	0.497000342	**3.76E-11**	0.06377307

E2/E3

2016

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**0.000267741**		
OUTLET	**1.05E-07**	**0.003407058**	
RESERVOIR	**1.17E-17**	**2.71E-08**	0.112375582

2017

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	0.231980272		
OUTLET	**0.00301079**	**0.008639201**	
RESERVOIR	**2.66E-08**	**2.96E-08**	0.102029256

2018

	HEADWATERS	MID-CATCHMENT	OUTLET
MID-CATCHMENT	**0.037376509**		
OUTLET	**0.001597573**	**3.72E-06**	
RESERVOIR	**8.67E-07**	**3.42E-13**	0.263099751