EFFECTS OF CLIMATE AND LAND USE

ON TERRESTRIAL

DISSOLVED ORGANIC

CARBON LOADING FROM

GLACIALLY FED AND LOWLAND

PUGET SOUND RIVER BASINS

by

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ABSTRACT

Effects of Climate and Land use on Terrestrial Dissolved Organic Carbon Loading from Glacially Fed and Lowland Puget Sound Rivers

Paula Cracknell

This study aims to compare how climate change and dominant land cover affect the quantity of dissolved organic carbon (DOC) loading into the South Puget Sound estuary in Washington State. DOC concentrations and flow measurement data spanning ten years (1999 to 2008) were obtained from publicly available data collected by Washington State Department of Ecology's ambient monitoring stations. Monitoring stations located at the mouth of seven rivers found within four watersheds were used in this study. Watersheds were delineated using ArcMap version 10.5 digital elevation model, and were identified as the Puyallup, Nisqually, Deschutes and South Hood Canal watersheds. All drain into the Puget Sound, which include areas that have chronically low dissolved oxygen. DOC loading data were compared to climate data (precipitation and temperature) and land use data (percentage of land cover) for correlation analysis. Results indicate that temperature and precipitation are weakly correlated with DOC loading once DOC loading data is normalized to account for watershed size. However, within individual watersheds, a rising trend of DOC loading correlated with increasing precipitation is apparent. Percentage of wetlands and developed land cover classification are positively correlated with increased DOC loading across all watersheds. Further study into how climate and land cover classification impact DOC loading into the Puget Sound region is recommended on a larger scale and over longer timescales throughout each watershed to assist with Puget Sound ecosystem recovery efforts.

Table of Contents

List of Figures

List of Tables

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1. INTRODUCTION

The long-term effects of climate change on coastal inland areas are expected to be substantial. Rising sea levels and salt water intrusion threaten the quality and quantity of inland freshwater systems, as well as the survival of estuarine biota (Marcogliese, 2016; Sutter et al., 2015). By the year 2100 surface air temperatures are predicted to increase globally between 1.4°C and 5.8°C, (IPCC, 2007), attendant to this increase in temperature, changes in hydrologic patterns due to increased precipitation will transport more terrestrial organic matter and pollutants into aquatic environments (Evans et al., 2005; Tian et al., 2013).

Under climate change scenarios (IPCC, 2007) for the Pacific Northwest, warmer ambient temperatures and increased winter precipitation is expected. Wetter, warmer climate could lead to longer growing seasons, creating a larger pool of terrestrially derived carbon transported to aquatic systems through runoff (Mote et al., 2003; IPCC, 2014; Littell et al., 2014). In addition, relationships between total carbon in aquatic systems, rising temperatures and increased gross primary productivity (GPP) have been observed in temperate wetlands (Ritson et al., 2014; Dinsmore et al., 2010) and temperate river systems in the United States (Butman et al., 2016).

Warmer and wetter climate may elevate terrestrially derived Dissolved Organic Carbon (DOC) loading from freshwater streams into estuarine environments (Bianchi, 2011; Dodds, 2006; Ritzon et al., 2014; Dinsmore et al., 2010). In the south Puget Sound in Washington State, increased DOC export from fresh to marine waters could also increase transport and settling of dissolved metals from terrestrial to aquatic environments (Guggenberger et al., 1994 et al., Fichot and Benner, 2014; Kellerman et al., 2014), cause brownification of drinking water systems (Fasching et al., 2014) and exacerbate ocean acidification and harmful algal blooms in the marine environment, all posing a significant environmental health risk for humans and aquatic life alike (Olson, 2017, Wallace et al., 2014).

Latitudes 40° North and above typically experience shorter growing seasons and nutrient limited soils in higher elevations where growth potential is significantly limited, resulting in lower nutrient and DOC concentrations in aquatic systems (Hood et al., 2006; Wise et al., 2011) However, recent research (Evans et al., 2012; Tian et al., 2013) has reported an increase of DOC concentrations from terrestrial origin into freshwater catchments across northern latitudes, (25° to 55° N) and increased organic carbon concentrations in northern streams and rivers, leading to greater CO_2 respiration into the atmosphere (Butman and Raymond, 2011). Carbon inputs from terrestrial sources to freshwater and estuarine environments can adversely impact aquatic ecosystem functioning. Increased DOC in freshwater systems is associated with transport of pathogens and metals, (Winterdahl et al., 2014; Hallegraeff, 1993) and promotes growth of bacteria and algae species that in excess can limit availability of dissolved oxygen in aquatic systems and become toxic (Wallace et al., 2014; Van de Waal et al., 2009).

Water quality regulation standards enforced by the EPA require states to create criteria for how each water body is used. Examples of designations for water bodies are swimming beaches, public drinking water supplies or shellfish protection areas. Numeric water quality criteria are used to describe the condition of water quality, and, to protect against disease and loss of biodiversity (Ecology, 2015). In Washington State, water quality criteria are categorized by numbers 1-5, the higher the number the more impaired the aquatic system is. Category 5 waters are listed as 303(d) impaired water bodies, and require that local and state governments and citizens to develop working plans towards improving water quality. Much of the Puget Sound and greater Salish Sea do not meet EPA water quality standards for many parameters ranging from temperature to high metal concentrations and presence of toxic substances (Ecology, 2015).

In addition, many areas throughout the Sound do not meet EPA requirements for dissolved oxygen levels and are listed as category 303(d) waterbodies (figure 1). Low dissolved oxygen (DO) is of concern throughout the Puget Sound. Low DO stresses marine life and leads to periodic fish kills in the Puget Sound (Deepe et al., 2013; Spietz et al., 2015). Dissolved oxygen levels can be further degraded when algae multiply and senesce during algal blooms.

Figure 1. Map of waterbodies listed on EPA and Ecology's 303(d) list of impaired waterbodies for dissolved oxygen. Red squares indicate category 5 waters for dissolved oxygen

Recent nutrient loading models (Pelletier et al., 2017; Roberts et al., 2014; Mohamedali et al., 2011) identify the South Puget Sound as a region with increased sensitivity to carbon flux (Pelletier et al., 2017) and dissolved oxygen levels (Mohamedali et al., 2011). DOC is transported to aquatic systems from decaying plant and animal matter, and soil erosion. As DOC is released throughout an aquatic system it provides substrate for phytoplankton, and nutritional energy to photosynthesizing cyanobacteria (Kirchman et al., 1991; Znachor and Nedoma, 2009; Larsson and Hagström,1979; Carney et al., 2016) which encourages both their rapid reproduction and death. Rapid growth and senescence of phytoplankton creates a physical barrier on the surface of water, preventing any mixing with air, effectively reducing subsurface dissolved oxygen and increasing water temperatures during periods of intense growth (Roberts et al., 2014).

DOC flux is intrinsically tied to climate. Temperature and hydrology changes associated with climate change alter terrestrial processes in soils, wetlands and vegetation growth and senescence (Evans et al., 2005). Climate change could be the driver of widespread DOC increase in northern aquatic systems (Tian et al., 2013). Live vegetation, leaf litter, root exudation and soil erosion contribute significantly to DOC in terrestrial streams through leachate (France et al., 1996; Roberts and Bilby, 2009). Land processes such as decomposition of soil and plant matter are well explored mechanisms for DOC flux in aquatic systems throughout the Puget Sound region (Awale et al., 2017; Gray et al., 2016; Roberts et al., 2009; Yano et al., 2004; Qualls et al., 1991).

Understanding how changes in climate, precipitation and dominant land type impact DOC flux in rivers draining into the Puget Sound remains poorly understood.

Investigating the effect of temperature and precipitation on DOC loading over time from rivers draining into areas of the South Puget Sound with chronically low dissolved oxygen will help to understand how, if at all, DOC flux changes in response to ambient climate conditions. The objective of this study is to investigate whether temperature and precipitation affects DOC loading from four South Puget Sound watersheds, South Hood Canal, Deschutes, Nisqually and Puyallup. The South Hood Canal and Deschutes watersheds are small lowland catchments (705.37 km^2 and 420 km^2 respectively), while the Puyallup and Nisqually are glacially fed rivers with larger basin sizes (2455 km^2 and 1399 km^2 respectively). Annual averages of DOC loading from each river over a period of ten years will be analyzed to identify patterns between DOC loading, climate and land cover, and to evaluate whether DOC loads are increasing over time.

While thirty-year climate cycles are typically analyzed for assessing climate related changes in the environment, (IPCC, 2014; Ault et al., 2014) the analysis of decadal temperature, precipitation and DOC loading values can illustrate a finer scale variance of climactically driven changes within single watersheds (Ault et al., 2014; Luo et al., 2013).

2.0 Literature Review

2.1 Introduction

By the year 2100 surface air temperatures are predicted to increase globally between 1.4°C and 5.8°C, (IPCC, 2007). Warmer ambient temperatures in the Pacific Northwest will result in longer growing seasons, increased soil and surface water temperatures, and increased GPP (Mote and Salathe, 2010; Leung and Wigmosta, 1999; Tian et al., 2013; Williams et al., 2014). Changes in annual precipitation, especially associated with prolonged dry periods and sudden severe storm events, put watersheds at increased risk of erosion and scouring, and increase the transport of pollutants (Khir-Eldien and Zahran, 2017; Yasarer et al., 2017). Longer growing seasons and transport of decaying plant matter and soils may elevate DOC availability and loading from freshwater streams into estuarine environments. Terrestrial DOC export from fresh to marine waters provide substrate for photosynthesizing bacteria and algae to bind to (Wear et al., 2015; Carney et al., 2016) and upon senescence these micro-organisms release more even more DOC (Lampert, 1978; Khangaonkar et al., 2012). In the South Puget Sound in Washington State, uncontrolled aquatic algae growth limit dissolved oxygen concentrations (Winter et al., 1975; Speitz et al., 2015; Schiebly et al., 2015) and in areas of the sound with chronically low dissolved oxygen (Fig.1), changes in DOC flux could adversely affect water quality and contribute to acidification in the Puget Sound (Pelltier et al., 2017).

In addition, rivers are a major source of CO_2. DOC is respired back to the atmosphere as inorganic Carbon, CO_2 (Butman and Raymond, 2011, Fasching et al., 2014). DOC export from rivers is understudied in the South Puget Sound region, and, as organic carbon is intrinsically tied with CO_2 respiration (Butman and Raymond, 2011) and ocean acidification, (Pelltier et al., 2017) understanding DOC export under changing climate can help inform restoration decisions in the South Puget Sound.

2.2 Dissolved Organic Carbon

Dissolved Organic Carbon is defined as aqueous organic material that passes through a 0.7 µm filter in fresh water, and a 0.2 µm in the marine environment (Kirchman et al., 1991). DOC solutes are part of the dissolved aqueous matrix and provide substrate (Arandia-Gorostidi et al., 2017) for free floating primary producing microorganisms such as cyanobacteria and diatoms (Bittar et al., 2015; Sarmento et al., 2016). DOC is comprised of decaying organic matter and organic rich material that provide the molecular substrate for other metals and compounds to bind to (Thingstad et al., 1997; Lange et al., 2016).

DOC has an integral role in healthy aquatic ecosystem functioning and carbon cycling. Through microbial respiration, much of the DOC in rivers is degassed into the atmosphere as $CO_{2,}$ (Butman & Raymond, 2011; Raymond & Bauer, 2011; Smith et al., 2017), or the carbon can be buried and stored in ocean sediment (Fasching et al., 2014). Although DOC is a naturally occurring and a necessary carbon species for supporting ecosystem wide food webs, excess DOC in aquatic systems can alter ecosystem functioning and environmental health (Harvey et al., 2002; Hansel and Carlson, 2014; Dhillon et al., 2013).

2.3 Carbon Cycling in Rivers

Carbon is stored on land in sediment and rock, vegetation, soils and living organisms. Eventually, terrestrial carbon is eroded by wind and precipitation, and much of the terrestrially derived carbon is transported to rivers and oceans as runoff (Fasching et al., 2014; Raymond et al., 2013). Rivers flush carbon from land to the ocean, and by doing so, rivers play a significant role in the global carbon cycle (Butman et al., 2016).

DOC comprises half of the total organic carbon in rivers, the other half is particulate organic carbon, larger particles of aqueous organic material that do not pass through a 0.7 µm filter (Kirchman et al., 1991). Total organic carbon export is often quantified together when accounting for riverine carbon flux, and DOC is of interest because it is directly available to microorganisms, facilitating CO_2 fluxes to the atmosphere (Butman et al., 2015).

Rivers in the United States transport 100 teragrams (TgC) of carbon per year to the ocean (Butman et al., 2015). However, much is unknown about terrestrial sources of carbon transport to rivers and how it is changing over time in response to intensified agricultural land use, and development. Butman et al., (2015) estimates that carbon flux from land to rivers increase by 0.1 to 0.2 pentagrams of carbon per year due to human disturbances such as deforestation and agricultural use, and most of the DOC in rivers is from young carbon leached from soils and vegetation. Younger DOC in rivers result from run off and recent land based disturbances, (Butman et al., 2015; Butman et al., 2016) and increased precipitation attendant to climate change, could increase the rate at which terrestrial DOC is transported to aquatic systems (Tian et al., 2013; Evans et al., 2012).

Additionally, higher DOC concentration in rivers is a concern under climate change models. Butman and Raymond (2011) estimated the amount of carbon degassed from streams in the United States is high, especially between latitudes of 25°N to 50°N. In their study, (2015) they estimate that 97 ± 32 Tg of CO_2 are degassed from rivers into the atmosphere each year. Further, their results show that CO_2 evasion from streams is positively correlated with precipitation, emitting more CO_2 from terrestrial origin into the atmosphere from regions in the United States with high snowpack and rainfall. In the Pacific Northwest, climate models predict dry, hot summers followed by warm and wet winters. Increased precipitation following long dry events could result in even more DOC runoff to rivers and potentially cause a positive feedback loop for CO_2 evasion to the atmosphere (Salathé et al., 2014; Butman and Raymond, 2011).

2.4 Environmental Health Risks of Excess DOC

Elevated DOC leads to freshwater brownification and acidification, harming aquatic organisms (Jones and Lennon, 2015). In systems that utilize surface waters for drinking water, elevated DOC reduces the effectiveness of chlorination in the treatment process, increasing risks of bacterial contamination and the formation of carcinogenic organochlorine compounds (McBean et al., 2010; Evans et al., 2005). The darkening of water associated with brownification limits light penetration causing early senescence of aquatic vegetation, leading to decomposition and transport of decaying matter and sediment erosion. This process can increase the likelihood of low dissolved oxygen and higher stream temperatures through limiting light penetration and microbial respiration in both freshwater and marine environments (Fasching et al., 2014; Pelltier et al., 2017). In addition, DOC particles bond with metals toxic to aquatic life, increasing their solubility in freshwater and molecular weight (McBean et al., 2010; Evans et al., 2005).

Research on DOC loading into coastal and estuarine systems is sparse (Evans et al., 2005; Tian et al., 2013; Mattson et al., 2015), and of these studies, none attempt to quantify riverine DOC loading into the Puget Sound Washington State. Increased occurrence of algal blooms and prolonged periods of low DO have been reported in the Puget Sound (Pelltier et al., 2017; Ahmed et al., 2017; Hallock, 2009), and increased nutrient loading including DOC has been reported in some areas (Pelltier et al., Mohamedali et al., 2011). However, how DOC loading from Puget Sound rivers is changing is unexplored, warranting further investigation into how much DOC is loading into the Puget Sound ecosystem, how this loading is correlated with climate and land use and if loading is increasing over time (see section 3).

2.5 The Puget Sound Ecosystem

The Puget Sound is a unique inland estuary nestled into the southernmost reach of the Salish Sea within Washington State. With 2,500 miles of shoreline, the Puget Sound is the second largest estuarine sea in the United States. The deep canals and finger like topography of these waters were created by the retreat of the Cordillerian ice sheet during the Last Glacial Maximum (Crandell et al., 1958). The glacial carving of the regions bathymetry gives the Salish Sea marine connectivity to the Pacific Ocean through the Strait of Juan de Fuca and the Strait of Georgia. The straits greatly influence marine circulation in the northern Salish Sea, and to a lesser extent, the Puget Sound (Mohamedali et al., 2011; Sutherland, 2011). Tidal circulation patterns in the Puget Sound have slow regeneration times, (replacing older, oxygen depleted water with fresh seawater) and can have periods of prolonged residence times. Mohamedali (2011) modeled regeneration of seawater in South Puget Sound, and found that in some areas (Hood Canal), regeneration can take 282 days to as long as 292 days in the Tacoma Basin. The slower tidal exchange with the Pacific Ocean make the Puget Sound especially sensitive to terrestrial pollutants (Feely et al., 2010; MacCready, 1999), land use changes in the near shore environment, and, to nutrient loading from the 10,000 rivers and streams draining into the Puget Sound (Mohamedali et al., 2011; Roberts & Bilby, 2009).

Slow water circulation in the Puget Sound combined with rapid urban sprawl in upstream watersheds have a significant impact on water quality (Moore et al., 2011). Washington State Department of Ecology has determined that much of the Sound fails to meet federal water quality standards under federal clean water act (Ecology, 2003; Mohamedali et al., 2011).

Many reaches of the Puget Sound and its adjacent watersheds fail to meet water quality criteria and frequently experience hypoxic events due to elevated temperatures and low dissolved oxygen (Mohamedali et al., 2011). In addition, toxic compounds are ubiquitous in this ecosystem and accumulate in organisms from all trophic levels in the marine food web (Norton et al., 2011). Impaired waters are a hazard to human health and the aquatic food web. Given the sensitivity of the Puget Sound, it is imperative that scientific research can drive solutions to improve water quality.

2.6 Dissolved Oxygen and Nutrient Loading

Identifying the mechanisms of pollution transport to the Puget Sound is key for developing strategies to mitigate impaired water quality. Many studies in the region have examined land use impacts, climate change and water temperature as contributing factors to impaired water quality. These studies have focused on the biological impacts of impaired waters, and its effects on salmonid populations, or shellfish biotoxins (Moore et al., 2011; Naiman et al, 1992; May, 1997). Other studies have focused on the interaction between terrestrially derived toxics and algal blooms associated with anthropogenic sources (Norton et al., 2011; Feely et al., 2010). While these issues are all intrinsically connected, research on loading of compounds from the surface waters to the Puget Sound are few.

Many areas in the Puget Sound fail to meet water quality standards for dissolved oxygen. Levels of DO in many reaches of the Sound are chronically low, with some areas regularly measuring at less than1 mg/L (Khangaonkar et al., 2012). Mohamedali et al., (2011) and Ahmed et al., (2014) identified nutrient loading from anthropogenic sources to be a major contributor to low DO in the South Puget Sound. Further, in areas with high anthropogenic nutrient loading, addition of nutrients reduced DO in already stressed regions of the sound by as much as 0.4 mg/L. Pelltier et al., (2017) also found that inputs of carbon increase DO sensitivity in the Puget Sound. Pelltier et al., (2017) found that increased ocean acidification also correlates with areas of the Puget Sound with chronically low DO.

Analyzing water quality data to determine loading into adjacent water bodies is typical when calculating total pollutant loads in a watershed. While loading of DOC has not been quantified in the South Puget Sound region, Mohamedali et al., (2011) developed a strategy for quantifying dissolved inorganic nitrogen (DIN) loading into the Puget Sound as part of the Department of Ecology’s efforts to identify mechanisms that contribute to low dissolved oxygen throughout the Salish Sea and Puget Sound. Daily nutrient concentrations were developed from historical ecological sampling efforts and long-term monitoring stations to assess changes throughout time. Loading was calculated using the following equation:

Daily Load= (predicted daily concentration) X (daily streamflow)

Equation 1. Calculation for estimating loading from rivers into the Puget Sound. Concentration is measured from mg/L and streamflow in cubic feet per second

Mohamedali et al. (2011) reports that DIN loading from rivers did not necessarily coincide with the size of the watershed or the size of the river. Some smaller rivers load more DIN into the Puget Sound than larger rivers. In addition, the seasonal loading of DIN into the Sound is not flow dependent. High levels of DIN were loading into the Puget Sound regardless of seasonal flow. DIN loading from rivers was correlated with watersheds with high development and agricultural intensity.

Mohamedali (2011) concluded that analyzing loading data on an annual scale in this study was more appropriate than a seasonal scale. Puget Sound watersheds are diverse, the headwaters of some rivers originate in mountainous regions and experience pulse flows during the spring snowmelt, while the headwaters of other rivers are at lower elevation and receive little or no flow associated with spring snow melt, rather, experience high flow events during storms in the fall and winter (Babson et al., 2006; Cuo et al., 2009). The diversity of South Puget Sound watersheds deems an annual loading analysis of DOC to be an appropriate temporal scale to analyze changes over time when looking at the Puget Sound as a whole.

Like nutrient loading, DOC can reduce DO in an aquatic system. Brownification associated with excess DOC limits light penetration and leads to local warming effects and hypoxia (Turner et al., 2008). Analyzing DOC loading from rivers in the southern Puget Sound on an annual time scale can help to understand how much DOC is entering the system from the mouths of rivers, and what environmental factors are correlated with DOC loading. Gaining a temporal and spatial understanding on DOC loading in the Puget Sound is imperative for improving water quality.

Dissolved Organic Carbon Export

2.7 Methods for Analyzing DOC Export from Rivers

Local research on riverine transport of DOC in the Puget Sound is currently not present in the literature, however, many studies analyzed DOC export globally and found varied results. Correlations of DOC export with land type and soil type have conflicting results. Curtis (1998) and Xenopoulos et al., (2003) sampled lakes in temperate regions, and found that watersheds with isolated wetlands not connected to flowing water had consistently higher concentrations of DOC export, while samples taken from clear montane lakes with poor soil composition and wetlands with connectivity to flowing water had lower concentration of DOC. The spatial correlation of elevated DOC and isolated wetland proximity indicate that areas with a variety of vegetation and humic soils have higher concentration of DOC runoff. The exception to this, Xenopoulous found, is coniferous lands with isolated wetlands have lower DOC concentration in nearby lakes than areas without coniferous forest. A possible mechanism for this is that forests use available carbon and store it in the vascular structure of vegetation (Xenopoulos et al., 2003; Michalzik et al., 2001).

The hydrography of lakes differs from rivers flowing to the sea (Wetzel, 2001). Huntington & Aiken (2013) argue that in a riverine system, particularly larger rivers, the diversity of the landscape can make it difficult to correlate variables such as land type, as discharge and flow direction may change several times and flow through a variety of land types before the river reaches the ocean.

Huntington & Aiken (2013) sampled monthly for DOC export along the entirety of the Penobscot River. DOC concentrations were analyzed using a correlation analysis for the variables of season, slope, area and distance to wetlands. Land values were obtained by calculating percentages in ArcGIS software. Statistical analysis identified that watershed slope, season (summer) and forest type (coniferous or hardwood) were negatively correlated with high DOC concentrations, while DOC concentration and percentage of watershed covered by isolated wetlands was positively correlated. Wetlands are naturally high in DOC and decaying vegetation that can load into rivers through the water table or in runoff.

Mattsson et al., (2015) identified that hydrology and precipitation are changing due to the warming climate. Total organic carbon (TOC) export was analyzed in thirty river basins flowing into the Baltic Sea. Land type and percentage were calculated using GIS software to obtain percentages of agricultural, peat, and forest catchments. Ten years of historical TOC and discharge data were obtained from the Finnish ambient monitoring network and were multiplied by flow to develop loading values of DOC. Mean temperature and precipitation during the study period were quantified and analyzed against the land type variables using the Spearmans rank correlation analysis. Results indicate that land type had no correlation with TOC, rather, increased flows associated with precipitation drove elevated TOC in the 30 basins sampled. The carbon species sampled was different, as TOC includes particulate and dissolved organic carbon, however the lack of correlation with peat and wetlands indicates that abiotic variation associated with climate change are affecting carbon in this boreal region.

Boreal regions are experiencing rapid environmental stresses due to climate change (Mattsson et al., 2015). Melting permafrost saturates groundwater and increases flooding events, while at the same time, larger and more frequent forest fires are occurring (Terrier et al., 2013; IPCC, 2014). Unstable soils and increased vegetation will increase DOC in this area that is already saturated with DOC. Understanding mechanisms and impacts of a changing climate in different ecosystems helps to understand how abiotic conditions can impact DOC loading globally.

2.8 Climate Change

Aquatic systems are sensitive to changes in temperature. Increased precipitation can overwhelm lowland areas and lead to flooding and significant erosion of stream channels. Likewise extended dry periods lower the water table leading to drought conditions that increase erosion in streams and rivers (Raymond & Oh, 2007). Increasing atmospheric CO_2 concentrations are amplifying climate variability, drought, and frequent storm events, especially in the northern latitudes (Tian et al., 2013; Butman & Raymond, 2011). Rivers are a major source of CO_2, and much of the DOC in aquatic systems is respired, and then degassed back into the atmosphere before reaching the oceans (Butman & Raymond, 2011).

Evans (2005) analyzed fifteen years of DOC measurements from a long-term data set of ambient monitoring collected by the UK Acid Waters Monitoring Network (AWMN). Historical data of DOC concentrations (mg/L) were analyzed using the Seasonal Kendall test to identify trends in DOC concentration. Results indicated that DOC concentration had increased at all sites. The magnitude of the trend was calculated using the Sen slope estimation method and revealed that DOC concentrations had increased 91% over the fifteen-year study period. The rate of increase was found to be proportional among all sites in the AWMN. A stepwise regression was performed to identify statistical relationships between variables and potential mechanisms for the increase. The variables analyzed were year and time of year, temperature, and chemical variables associated with acid rain. Increasing temperature was identified as the mechanism for increasing DOC on an annual scale, because warmer temperatures increase the length of the growing season for both terrestrial and aquatic plants and animals, and, the rate of senescence and regeneration of organic matter (Evans et al., 2005).

Warmer temperatures associated with climate change are impacting the ecological chemistry of systems worldwide. Temperature and precipitation have increased globally during the 21st century, (Hayhoe et al., 2007; Balch et al., 2012) and are expected to continue rising. Hydraulic alteration, intensified solar radiation and pulse flows from increased precipitation are some of the climate change effects that aquatic systems are experiencing (Butman & Raymond, 2011; Raymond & Oh, 2007).

DOC export in river systems is a result of the balance between primary production, decomposition of organic matter and terrestrial inputs. The quantity of DOC in aquatic systems is impacted by changing climate (Tian et al., 2013). Most studies analyzing changes in riverine DOC are localized to one area or a single river residing in one climate zone. Tian et al., (2013) analyzed fourteen years of DOC and flow data available from the USGS National Stream Quality Network (NSQN) from seven major watersheds in differing climactic zones throughout the United States. The variables of surface temperature, precipitation, and land cover types were used to predict DOC concentrations using a series of simple linear regressions. Precipitation had no linear correlation across sites and land type had some correlation as all sites shared similar percentages of wetlands. The strongest variable across all climate zones was temperature. Seasonal variation in temperature showed no correlation, however annual temperatures across sites was positively correlated and was concluded to be the mechanism for elevated DOC across seven climate zones revealing much about how increasing temperatures associated with climate change are impacting rivers regardless of the location of the river on a geodedic gradient.

Raymond and Oh (2007) found that temperature was not statistically correlated with DOC export across three watersheds in the agricultural hub of the United States. Using seven years of publicly available USGS DOC data, researchers used LOADEST modelling tools to assess how temperature, precipitation, discharge and land use correlated with DOC and export of other nutrients. Their results indicated that temperature had little correlation with DOC export, rather discharge associated with increased precipitation determined how much DOC was in the river systems at a given time. This study took place in watersheds with altered hydrology dominated by agriculture. This variable was not included in the model, however other studies have found that agricultural runoff during storm events is a major source of non-point source pollution, including DOC (Veum et al., 2009; Howarth et al., 2009).

The process of farming moves a lot of organic material. Farm machinery turn soils over and planting crops yields high qualities of decaying organic matter after harvest is complete. Physically altering land for farming practices results in nutrient rich soils that run off during storm events both into surface water, and ground water (Veum et al., 2009).

Bauer et al. reports that temperature, and flooding associated with storms is responsible for DOC loading from rivers into the coastal environment. Bauer et al., identifies land management as the primary driver of the increased DOC load in rivers and the coastal environment. Coastal areas generally have high populations, and agriculture is usually near rivers or streams for ease of irrigation. Researchers argue that human disturbance, by moving more soil and altering natural hydrology is the leading cause for annual increase of DOC in freshwater systems, rather than abiotic conditions.

2.9 DOC and Climate Change in the South Puget Sound

Rising temperature, reduced snowpack and increased precipitation attendant to climate change scenarios in Washington State, will negatively impact water quality (Mote and Salathè, 2010). Rising sea levels are expected to inundate low lying areas and near shore aquifers, (Mote and Salathè, 2010) and already have in islands throughout the Puget Sound (Banas et al., 2015). Increased nutrient and carbon loading are increasing the rate of ocean acidification, and can further reduce dissolved oxygen levels in the Puget Sound, (Pelltier et al., 2017; Mohamedali et al., 2011) while dryer summers reduce biodiversity and soil moisture in forest stands, increasing the risk of wildfire and erosion, leading to scouring of organic matter during the increased cold season precipitation under future climate scenarios (IPCC, 2014; Mote and Salathè, 2010; Pelltier et al., 2017; Khangaonkar, 2012; Terrier et al., 2013; Mote et al., 2013).

3.0 Conclusion

DOC flux in northern freshwater systems is increasing (Evans et al., 2008; Butman and Raymond, 2011; Tian et al., 2013). Freshwater systems have been altered considerably by humans, and coastal areas are increasingly experiencing hypoxic events due to human disturbance (Turner et al., 2008; Bauer et al., 2013). Climate change is a major challenge for limiting DOC export into the coastal environment, and how it will affect biota over time is not yet clear. However, there is a gap in the literature involving DOC loading into the Puget Sound estuary, and measuring variables of land use and temperature are important for identifying how elevated DOC enters aquatic systems.

The studies described in this literature review reveal that there are conflicting conclusions in what mechanisms explain changes in DOC loading to estuarine environments. However, the time scale in which to analyze DOC data suggests that annual time scales reveal the most about how loading is changing over time. In addition, the conclusions of these studies indicate that temperature, precipitation and land use are important variables that are positively correlated with elevated DOC levels in rivers. Whether climate or land use can illuminate how the South Puget Sound region is experiencing changes in DOC loading, and if changes in DOC loading are happening in the region is unknown and will be explored in this study.

3.0Methods

3.1 Study area and Sampling Sites

Four watersheds located in the South Puget Sound of Washington State were chosen due to their discharge into marine areas with chronically low dissolved oxygen levels. Two of the watersheds (Puyallup and Nisqually) are glacially fed from Mount Rainier with steep elevation changes, and two, (Deschutes and South Hood Canal) are in lowland forested and agricultural areas, rich in wetland and prairie soils. All DOC and discharge measurements were collected from Washington State Department of Ecology long term ambient monitoring water quality stations located near the mouth of each watershed river (figure 2). Coordinates for each station are in Table 1.

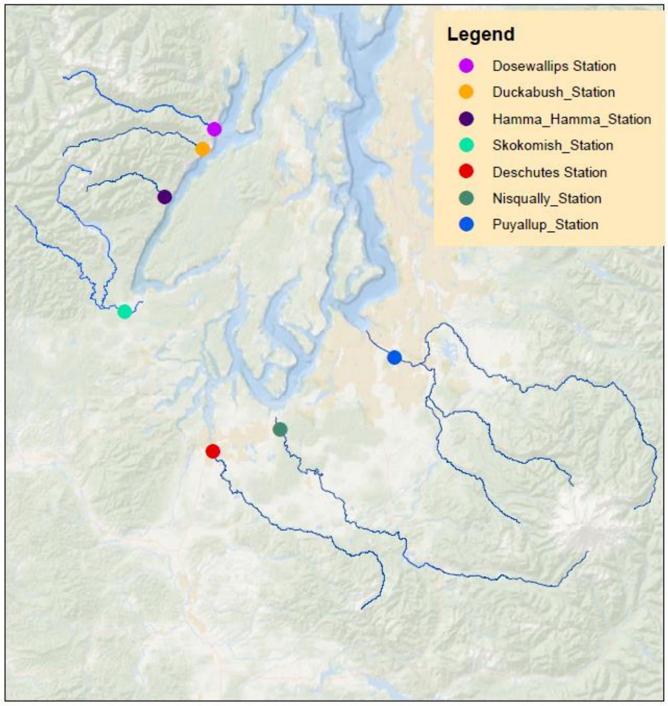

Figure 2. Locations of Ecology long term ambient monitoring stations where DOC concentrations and flow were used for this study.

River	Station Number	Latitude	Longitude
Nisqually	11A70	47.0620	-122.6964
Puyallup	10A050	47.2136	-122.3414
Deschutes	13A050	47.0151	-122.9026
Skokomish	16A070	47.3098	-123.1771
Dosewallips	16D070	47.6901	-122.8991
Duckabush	16C070	47.649	-122.9349
Hamma-Hamma	16B070	47.5501	-123.0529

Table 1. Station names and location for Ecology Long Term Ambient Freshwater Monitoring station where discharge and DOC samples were extracted for this study

3.1.2 Nisqually Watershed

The Nisqually Watershed includes the Nisqually River. The headwaters of the Nisqually River originate from the Nisqually Glacier on the southern side of Mount Rainer (Figures 3 and 4). The elevation of the river's headwaters is 1,466 meters, and the river quickly descends to sea level (0 meters) in the South Puget Sound. The total length of the Nisqually River is 130 km, and the watershed basin covers 1,970 km^2. Average discharge is 1,460 cubic feet per second (cfs) (Ahmed et al., 2014).

The terrain of Nisqually watershed varied. The headwaters are rocky with sparse vegetation, and quickly descend through forested regions, and grassland foothills with varied agricultural uses. Much of the Nisqually River passes through Joint Base Lewis-McChord and the Nisqually Indian Reservation to where it empties in Nisqually Reach in the South Puget Sound at the Billy Frank Jr. National Wildlife refuge north of Olympia Washington (Figure 3).

Figure 3. The Nisqually River Watershed and location of the Nisqually Ecology Ambient Monitoring Station

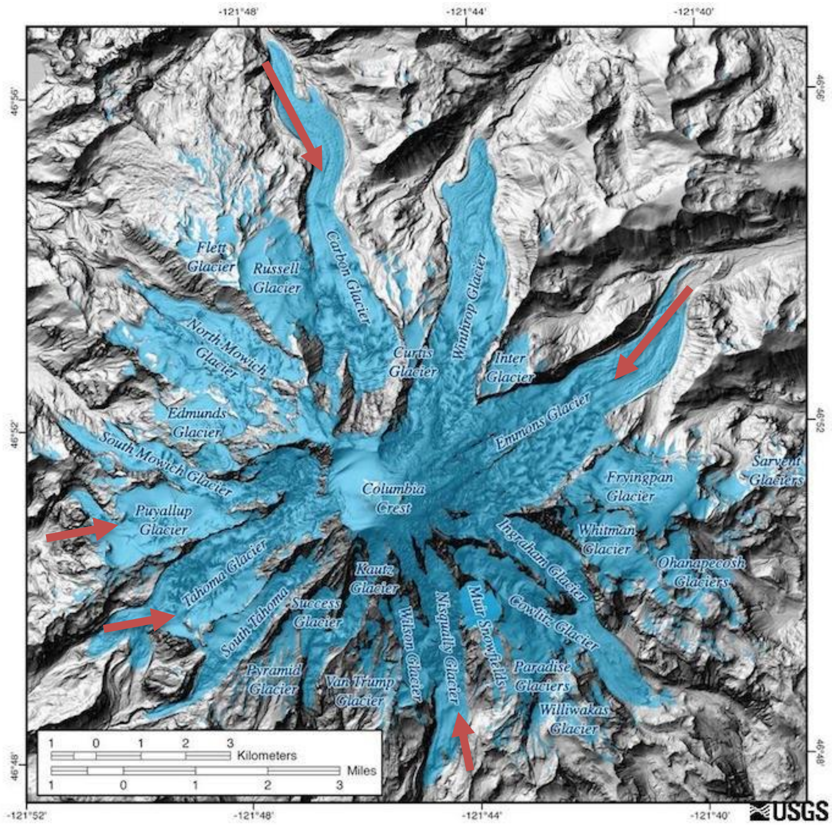

Figure 4. USGS Lidar image of Mount Rainier glaciers. Arrows depict glacial headwaters of the Nisqually Carbon, White and Puyallup Rivers. Image Source National Park Service

3.1.3 Puyallup Watershed

The Puyallup Watershed includes the Puyallup River, as well as the Carbon and White Rivers, which drain into the Puyallup before the rivers empty into the Puget Sound. The headwaters of the Puyallup River and its main tributaries are glacially fed from Mount Rainier. The Puyallup River begins in two forks, The North and South Puyallup Rivers. The north fork originates from the Puyallup Glacier, and the south fork from the Tahoma Glacier on Mount Rainier (figure 4). The two streams flow through Mount Rainier National Park until they join to form the mainstem Puyallup River.

Two major rivers with glacially fed headwaters (the Carbon and Emmons Glaciers) join the mainstem Puyallup River further downstream. The Carbon River and the White River, (figure 5) which originate from the Carbon and Emmons Glaciers on Mount Rainier (figure 4).

The Puyallup River and its tributaries originate at an elevation of 1,539 meters and descend to sea level (0 meters) to the where the river drains to Commencement Bay in Tacoma, South Puget Sound. The total length of the Puyallup, Carbon and White Rivers combined is 241km, and the Puyallup watershed basin covers 2455 km^2. Average discharge for the Puyallup River near the mouth is 3,313 cfs (Ahmed et al., 2014).

Much of the Puyallup basin is forested, with agricultural land dispersed throughout. The river passes through mountainous regions, national forest and privately owned forested areas, and the Puyallup Indian Reservation. The Puyallup drains to a heavily urbanized area in Commencement Bay in the city of Tacoma.

Figure 5. The Puyallup Watershed and location of the Puyallup Ecology Ambient Monitoring Station

3.1.4 Deschutes Watershed

The Deschutes watershed includes the Deschutes River. The headwaters of the Deschutes River are in lowland hills of the Gifford Pinchot National Forest, in Lewis County Washington. The total length of the Deschutes River is 80 km, and the watershed basin covers 420 km^2. Average annual discharge for the Deschutes River is 396 cfu. (Ahmed et al., 2014).

The terrain of the Deschutes watershed is varied. The headwaters are in national forest lands, and the river courses through agricultural valleys until it reaches the heavily urbanized South Puget Sound where the river drains to Budd Bay, in the city of Olympia (figure 6).

Figure 6. The Deschutes watershed and location of the Deschutes Ecology Ambient Monitoring Station

3.1.5 South Hood Canal Watershed

The South Hood Canal Watershed includes the Skokomish, Dosewallips, Duckabush and Hamma-Hamma Rivers (figure 7). The headwaters of all rivers in the watershed are in the Olympic Mountains, in the Olympic National Park. The Skokomish River is the largest River draining into Hood Canal, Puget Sound.

The Skokomish River including the North and South Fork is 69 km long, with average discharge of 1,210 cfu, the Dosewallips River is 45.8 km long, with average discharge of 446 cfs, the Duckabush River is 42.30 km long with average discharge of 416 cfs, and the Hamma Hamma is 27.73 km long with average discharge of 364 cfs (Ahmed et al., 2014; O' Connor, 1980). The basin size of the South Hood Canal Watershed, including the four rivers is 705.37 km^2.

The terrain of the South Hood Canal Watershed is varied. All four rivers in this watershed originate in rocky mountainous areas and descend through forested areas rich in wetlands and relatively little development.

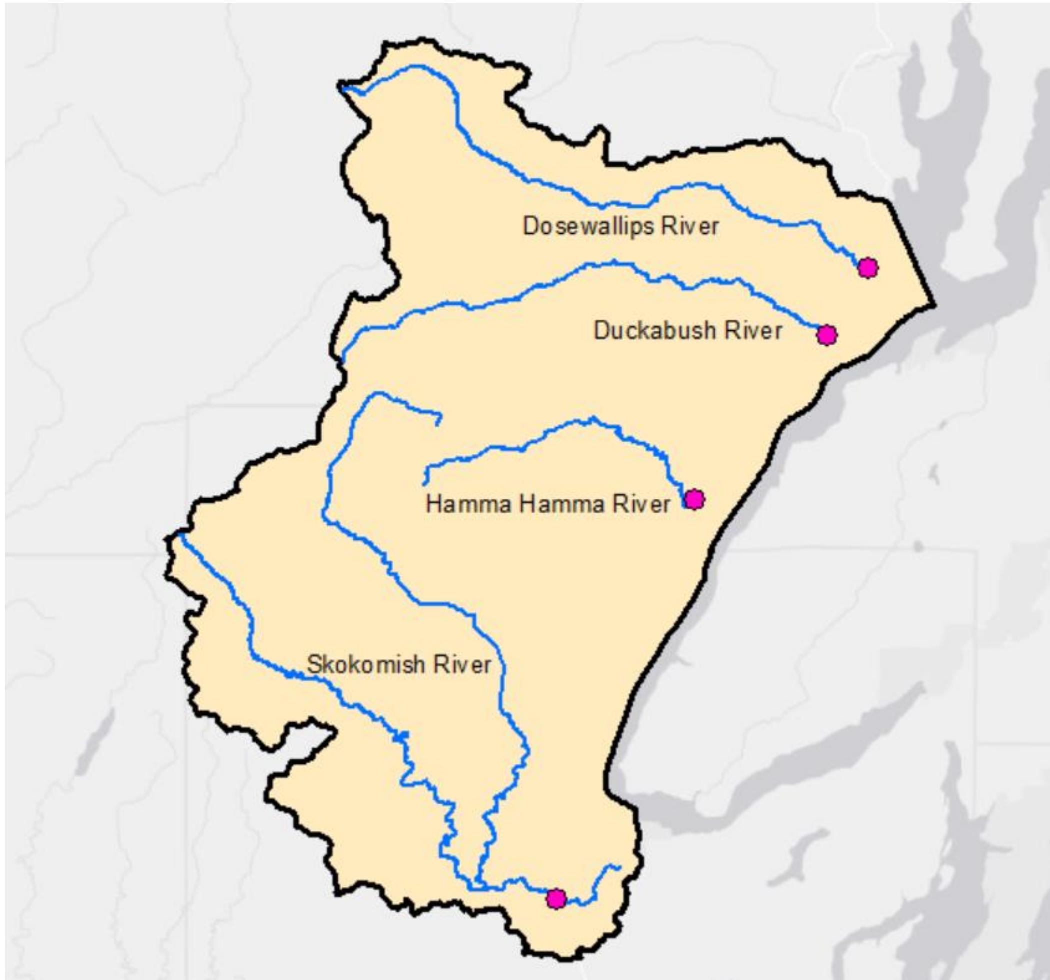

Figure 7. The South Hood Canal Watershed and locations of Ecology Ambient Monitoring Stations

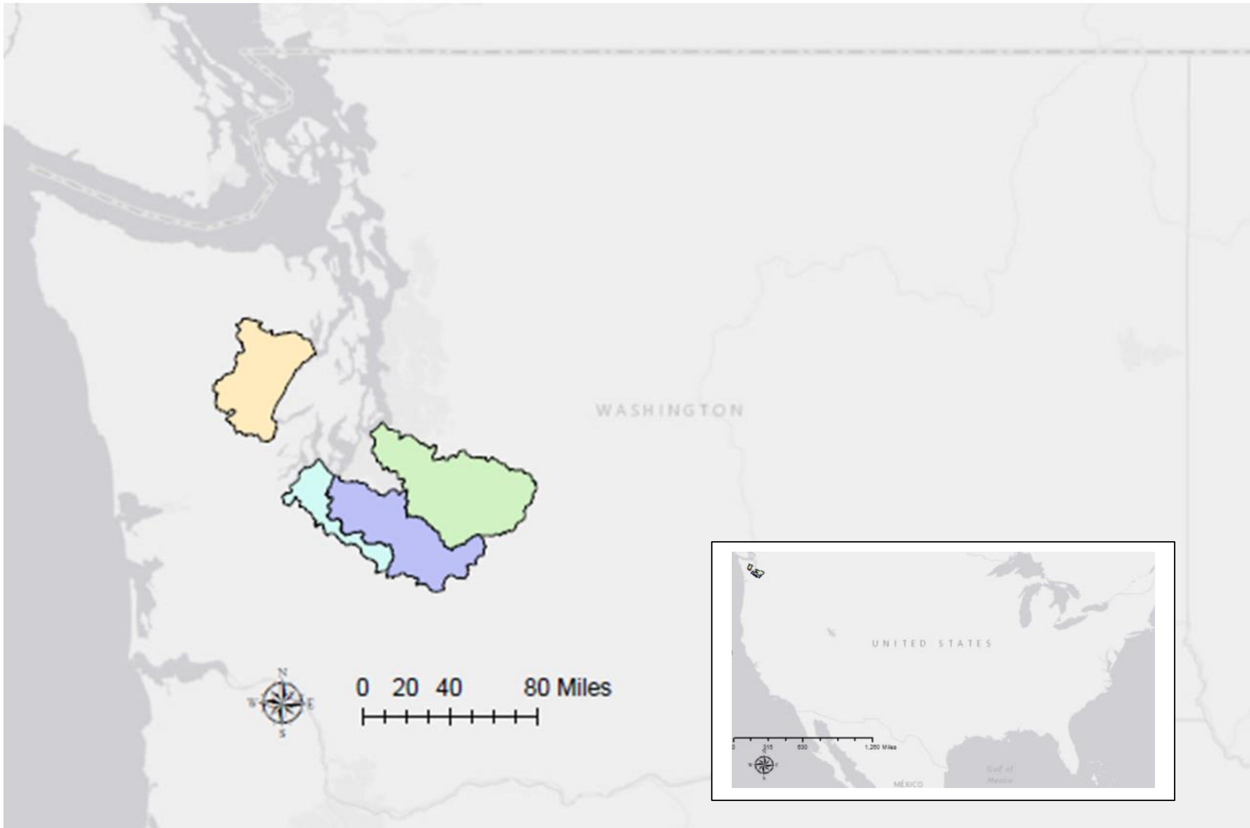

Figure 8. Study area locations in relation to Washington State and the United States

3.2 Watershed Delineations

Watershed delineations were made using the National Hydrography Dataset (2016) and Arc GIS version 10.5 digital elevation model (DEM). Arc DEM determines how water flows across the landscape to draw watershed boundaries. For the South Hood Canal Watershed, the Skokomish, Hamma Hamma, Dosewallips and Duckabush Rivers fall into the same DEM watershed, so loading values from all four of these rivers were summed to obtain the total loading value for the entire watershed (Figure 9). For the Puyallup River, the White and Carbon Rivers flow into the Puyallup, which eventually drains into the Puget Sound (Figure 11). These rivers were also included in the DEM, although DOC loads for these rivers were not individually quantified. Their contributions to the total DOC load is measured at a single location, the monitoring station at the mouth of the Puyallup River (figure 2). For the Deschutes, (Figure 12) the only river within the delineation boundary was the Deschutes River, likewise for the DEM of the Nisqually River (Figure 10).

3.3 Land Cover Values

Land cover types listed as percentage of each land cover class were obtained from the 2006 and 2001 National Land Cover Datasets (NLCD) available from the US EPA. Land cover was extracted for delineated watersheds using Arc GIS spatial analyst tools, and pixels were converted to percentages using the calculate geometry tool. Study areas contained thirteen different NLCD landcover types, which were merged into six major land types: Agricultural, Developed, Wetland, Forested, Rocky Slope and Glacial (Table 2). Apart from the glacial land cover class, land cover classes for agricultural, developed and forested land classes were merged to eliminate values with less than 0.01% of land cover, or to generalize land type.

Differences in land cover percentages between 2001 and 2006 NLCD layers were quantified and averaged to capture any changes in land cover during the study period.

NLCD land use/land cover type	Reclassification used in this study
Developed- Open Space	Developed
Developed- Low Intensity	Developed
Developed- Medium Intensity	Developed
Barren Land	Rocky Slope
Deciduous Forest	Forest
Evergreen Forest	Forest
Mixed Forest	Forest
Glacial	Glacial
Pasture/ Hay	Agriculture
Cultivated Crops	Agriculture
Palustrine Forested Wetland	Wetland
Palustrine Scrub/Shrub Wetland	Wetland

Table 2. NLCD Land Cover Reclassifications used in this study

3.4 Climate Data

Climate data, (temperature and precipitation) were obtained from the National Climatic Data Center (NCDC, 2011). Data were from 1999 to 2008 and were selected from different spatial scales throughout each watershed. Multiple weather stations were averaged within each watershed to capture the overall temperature and precipitation trends each year for the entire watershed. All weather stations that fell into the delineated watershed boundary were included and quantified.

Values were obtained by searching for the weather station coordinates on the NCDC mapping tool. Daily temperature and precipitation averages for the entire ten-year study period were obtained and averaged to assess monthly and annual averages for the entire watershed. All precipitation data was summed annually. Temperature data was obtained in units of Celsius (°C), and precipitation was measured in millimeters (mm).

3.5 Loading Values for DOC

All loading values used in this study were obtained from the South Puget Sound Dissolved Oxygen Study by Mohamedali et al., (2011) and Ahmed et al., (2014). In these studies, monthly DOC concentrations (mg/L) and daily flow measurements were obtained from long term ambient monitoring stations at the mouth of each river (figure 2). Loading values are the sum of concentration X flow and are used to obtain daily values (kg/day) of DOC loading into the South Puget Sound. Daily loading values were summed to obtain single annual values for each year (1999-2008) used in this study and are from publicly available on Ecology's Environmental Information Management (EIM) database that is accessible via Ecology's website.

3.6 Statistical Analyses of Climate Data and DOC

3.6.1 Climate Data

Data was assessed for normality and a linear regression analysis was performed using JMP SAS 13.0 statistical software to identify significant variables associated with annual DOC loading. For each watershed, DOC loading was the dependent y-axis variable, and temperature and precipitation were the independent x- axis variables. Variables were deemed significant when p value was less than 0.05. A full factorial ANOVA analysis was also used to assess changes within each individual watershed.

Watershed size was log transformed to assess normality. Once it was established that it was normally distributed, relationships between watershed size and other variables were assessed. Linear regression analysis was also performed on the normalized data to assess whether DOC loading is increasing over time, and if DOC loading is correlated with temperature and precipitation.

3.6.2 Land Cover Correlations

Land cover percentages and correlations with DOC loading were not normally distributed. Land cover data was analyzed using non-parametric methods. A Spearman's Rho rank correlation was used to illustrate relationships between land cover percentages and DOC loading. The Spearman's rank correlation compares the rank correlation coefficient (*r*) between two variables X and Y. The values of the variables are converted into ranks, then *r* is calculated as:

$$r = \frac{\sum_{i=1}^{n} [(R_i - R)(S_i - S)]}{\sum_{i=1}^{n} \sqrt{[(R_i - R)^2 (S_i - S)^2]}} ;$$

Equation 2. Spearman's Rho rank correlation equation (Yue et al., 2002)

Where R_i is the rank of the X value (land cover percentage) and S_i is the rank of the Y value (DOC loading) and R and S are the means of the R_i and S_i values (SAS Institute, 2015; Wang and Yin, 1996). This non-parametric correlation analysis works well with data that are not normally distributed and when comparing means across small sample sizes. Percent land cover was not distributed among all watersheds, especially compared to loading in Kg/day.

4.0 Results

4.1 Temperature Comparisons

Surface air temperatures were relatively uniform across all four watersheds studied. Averaged monthly temperature observations followed seasonal patterns (figure 9a), and varied between the high of 19.53°C and the low of 1.62°C. Average annual temperature in the Puyallup River watershed was lowest during all months compared to the Nisqually, Deschutes and South Hood Canal watersheds. Temperature was consistently higher in the Deschutes watershed during the study period.

Averaged mean annual temperatures 1999-2008 (figure 9b) show in greater detail the temperature differences between each watershed without seasonal interference. Glacially fed rivers, (Puyallup and Nisqually) had generally lower temperatures (Nisqually ~1°C lower; Puyallup ~3°C lower) than the Deschutes and South Hood Canal Watersheds.

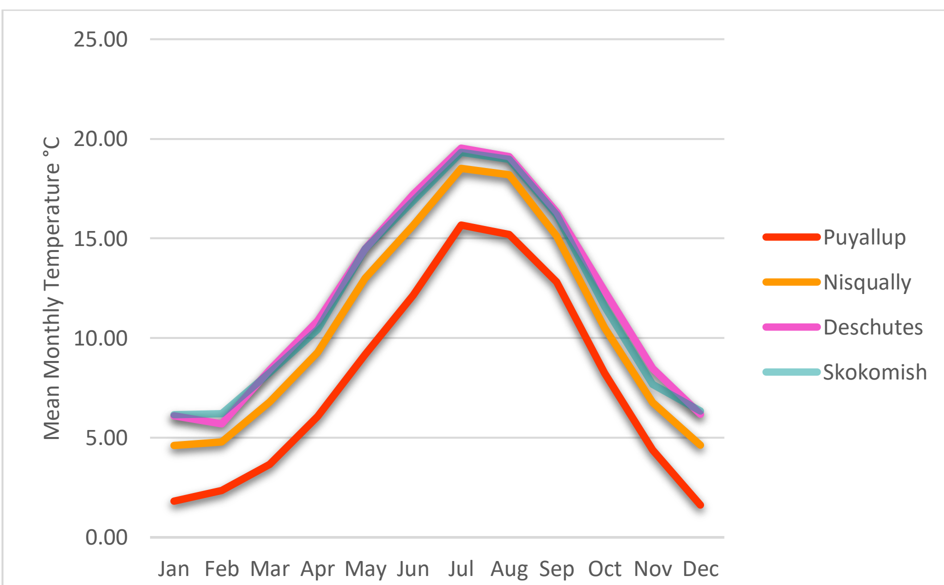

Figure 9a. Mean monthly surface temperatures averaged over the period 1999-2008

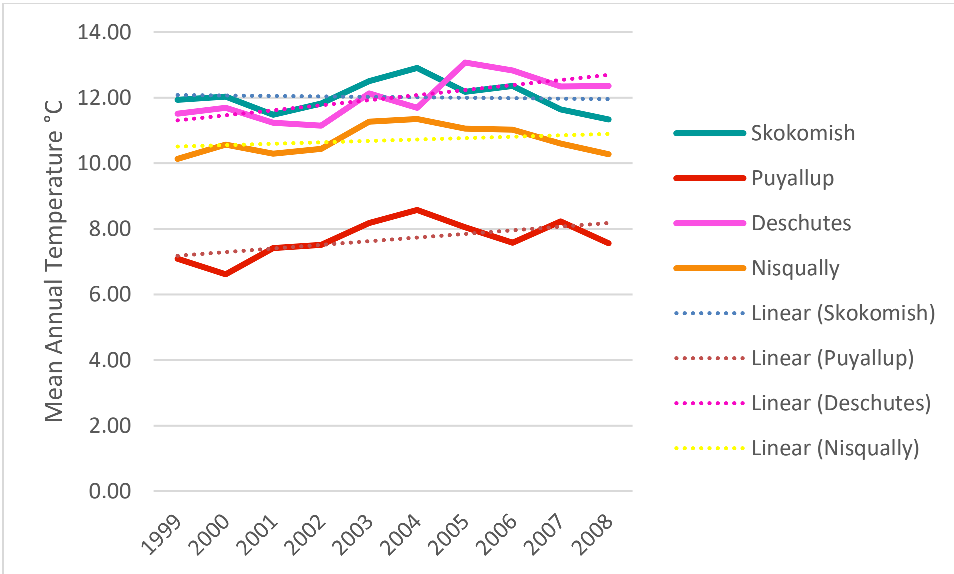

Figure 9b. Mean annual surface temperature averaged over the period 1999-2008

4.2 Precipitation Comparisons

Precipitation patterns were varied among the four watersheds. Precipitation data from the Deschutes watershed showed an insignificant, yet declining trend over the ten-year period, while the South Hood Canal, Puyallup and Nisqually Watersheds had variable (rising and falling) trends within each watershed (Figure 10). The Nisqually and Puyallup are glacially fed rivers, so much of the precipitation in the eastern reach of the watersheds is from snowpack, while the South Hood Canal Watershed received very little to no snow during the ten-year study period, and precipitation was almost solely in the form of rain.

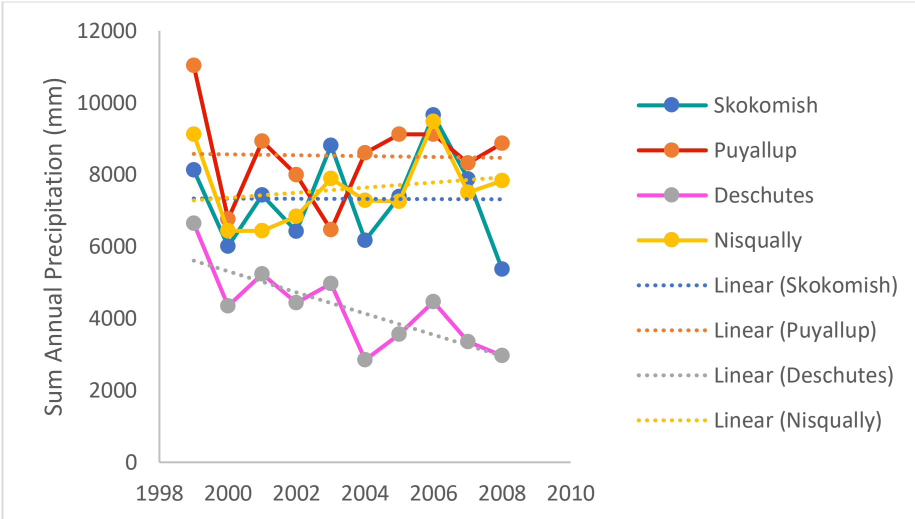

Figure 10. Sum precipitation over the period 1999-2008 and over all four watersheds

All four watersheds show a spike in DOC loading during the 2006-2007 El Niño year event. Flooding was reported along all four rivers during this particularly wet El Niño. DOC loading showed an increasing trend during the ten-year period, (Figure 11) with a slight dip in trend following the 2006-2007 El Niño.

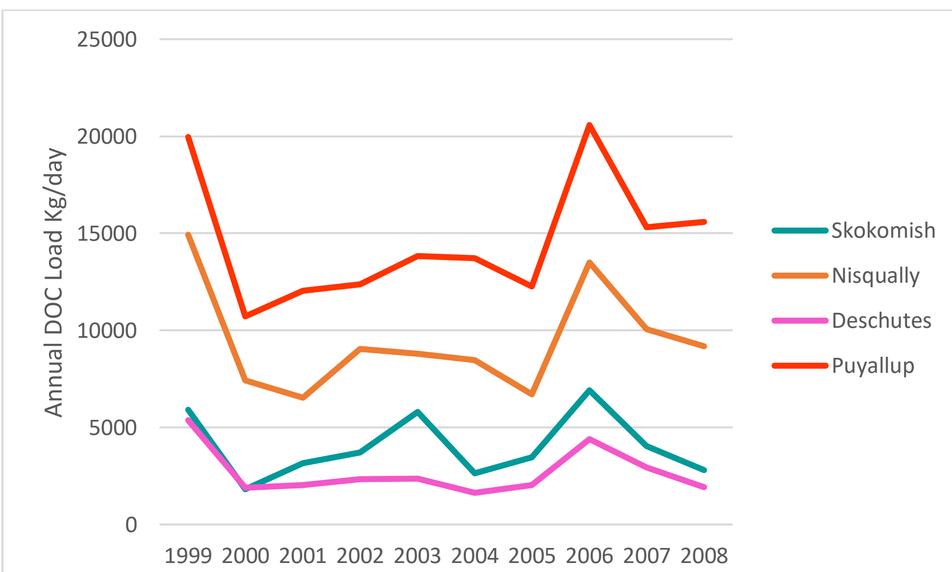

Figure 11. Average DOC loading per year in all four watersheds. Spikes in trendlines correspond to El Niño events Southern Oscillation events

4.3 Temperature and DOC

Figure 12 shows regression analysis of mean surface temperatures against mean annual DOC loading for all watersheds. In the combined analysis of all four watershed loading values, warmer mean surface temperatures are negatively correlated with DOC loading (R^2= 0.69, $p < 0.001$).

Mean annual surface temperatures among all four sites was highly variable, temperature ranged from 6°C to almost 12°C, and loading values were also much higher in rivers with larger drainage basins (Puyallup drainage basin 2455 Km^2, Nisqually 1339 Km^2, South Hood Canal 705.37 Km^2, Deschutes 420 Km^2).

The strong correlation between cooler temperatures and DOC loading could be due to regional differences, as well as differences in basin size. Statistical relationships between temperature and DOC loading among all four watersheds is insignificant.

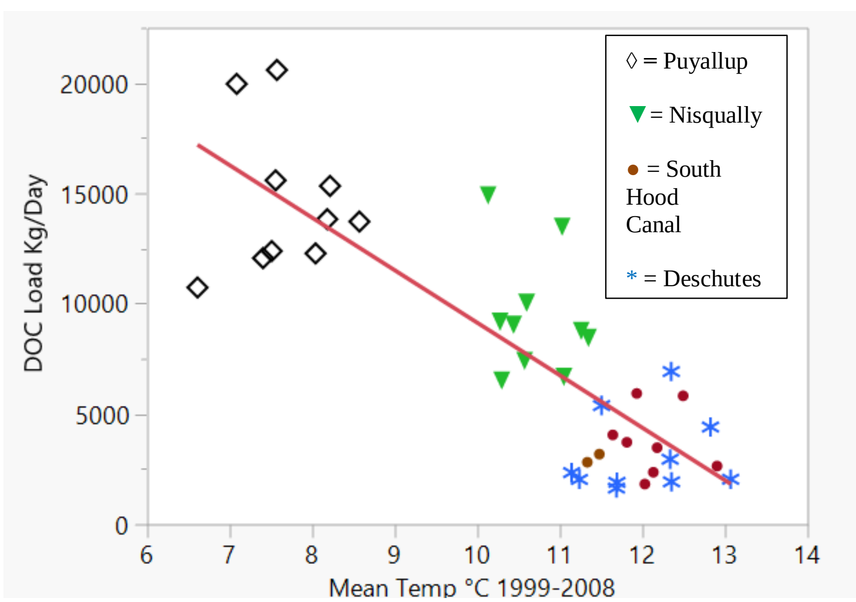

Figure 12. Mean annual temperature and annual DOC loading in all four watersheds

4.3.1 Temperature and DOC Normalized by Basin Size

Normalized data yielded different results. Normalizing loading by watershed size removes the possibility that basin size is skewing statistical results. Results of linear regression using normalized DOC data and temperature showed no statistical significance among the four watersheds (p=0.8829). Results from the full factorial ANOVA analysis (F= 4.7781, $p < 0.0584$) suggest that changes in DOC loading trends as a function of rising temperature are not present within each individual watershed.

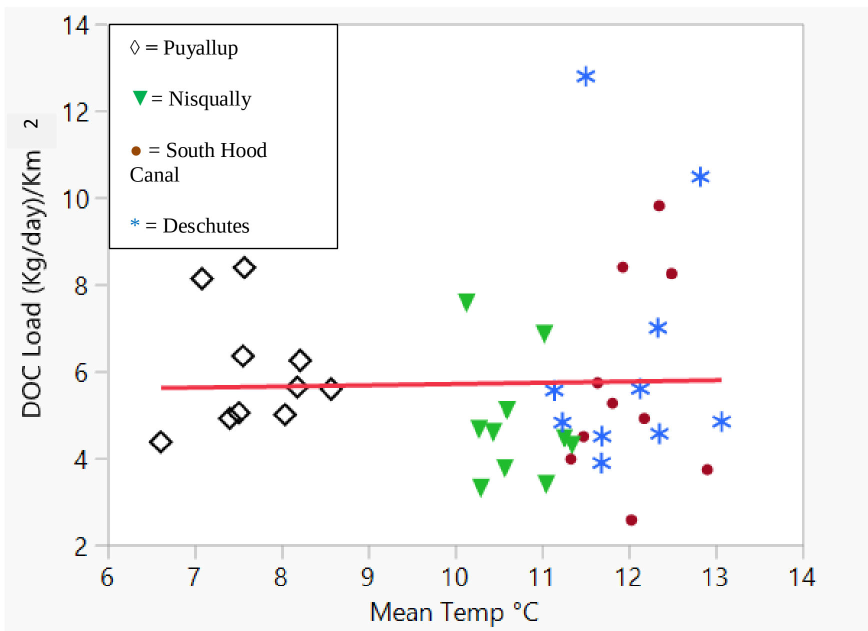

Figure 13. Normalized annual DOC loading and mean annual temperature in all four watersheds

4.4 Precipitation and DOC

Total precipitation ranged from 116 mm per year as the lowest precipitation data point in the Deschutes watershed, to 434 mm per year in the Puyallup watershed. Precipitation remained consistent during the ten-year study period except for the Deschutes watershed (figure 14). A significant drop in precipitation occurred in 2004 and precipitation levels remained lower than pre-2004 levels for the duration of the study. Linear regression results indicate that when all four watersheds are considered together, there is a strong positive correlation between total annual precipitation and mean annual DOC loading (R^2= 0.57, p < 0.001).

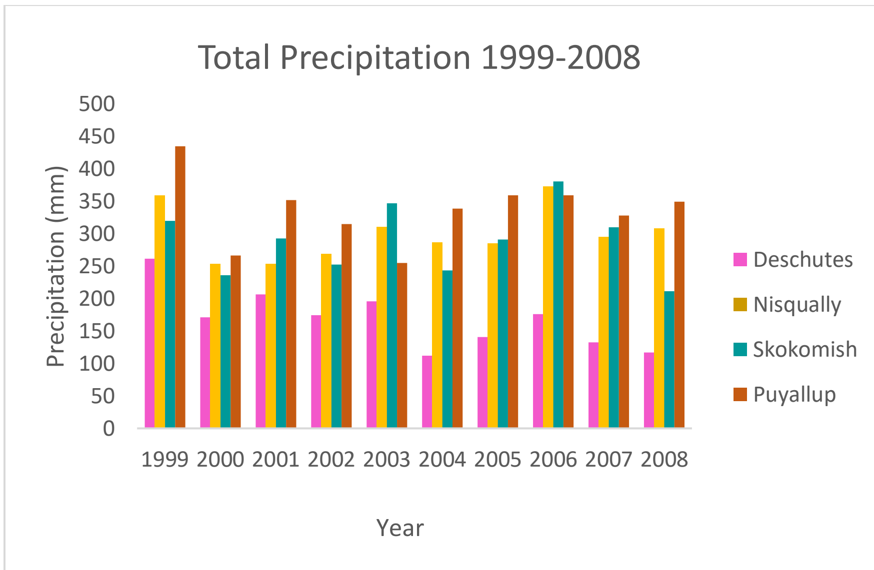

Figure 14. Total annual precipitation at all four watersheds 1999-2008

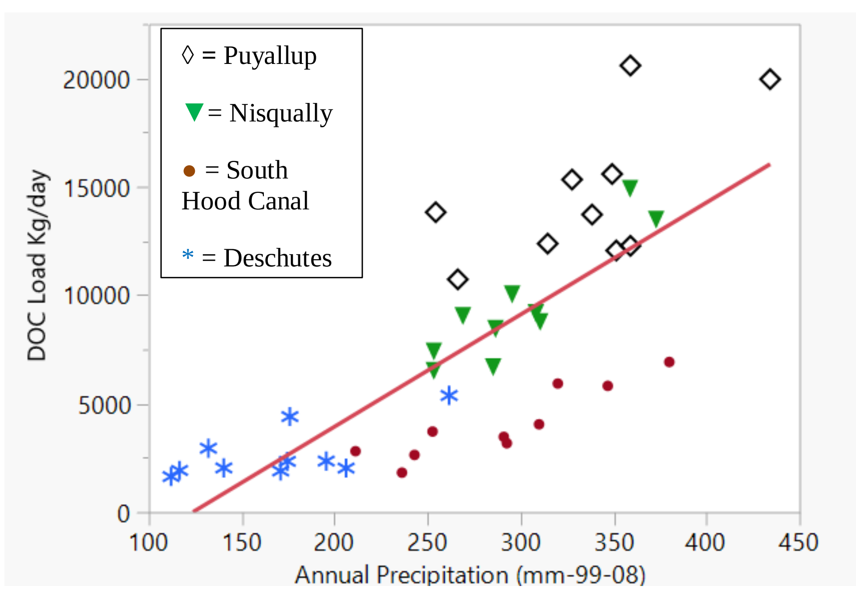

Figure 15. Total annual precipitation and DOC loading in all four watersheds

4.4.1 Precipitation and DOC Normalized by Basin Size

Normalizing watershed size and DOC loading by area (km^2) yielded different results with linear regression analysis and total precipitation between 1999-2008. Normalized loading data were statistically insignificant (*p*= 0.0740). Individual watersheds however, did show significant correlation between total precipitation and DOC loading. Results from full factorial ANOVA analysis (F= 6.84, p= 0.0293) indicate that within individual watersheds increasing DOC loads are positively correlated to precipitation. The Deschutes watershed particularly stands out, as unlike the non-normalized data, the Deschutes had a very strong correlation between increased precipitation and loading.

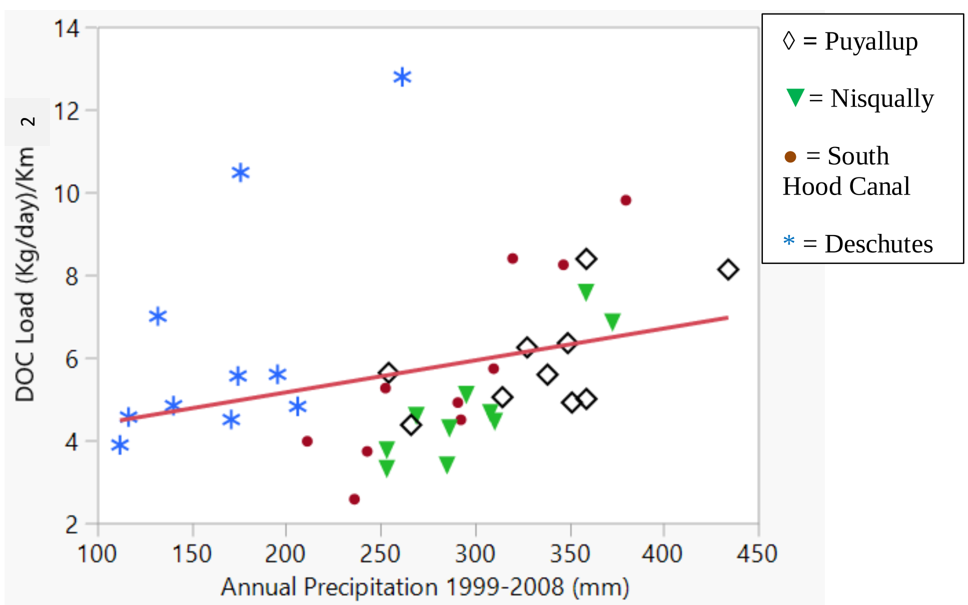

Figure 16. Total annual precipitation at all four watersheds 1999-2008

4.5 Land Cover and DOC Correlations

Percent land cover and DOC loading showed strong correlations for developed land cover (r_s= 1.0; *p*=0.001) and wetland land cover (r_s= 1.0; *p*=0.001). All other land cover types are weakly correlated with DOC loading. Table 3 presents the results of the Spearman's Rho (ρ) analysis, as well as the *p* values associated with each land cover type per watershed, and figures 17-20 depict the GIS results of the NLCD land cover types.

Land cover types were variable across all watersheds. Forest land cover was the most dominant land type, (> 50% in all watersheds) while percentages of all other land cover types varied (Table 4).

Variable	Spearman's ρ	*p* value
% Wetland	1.00	<0.0001
% Forest	-0.40	0.6000
% Agriculture	-0.20	0.8000
% Developed	1.00	<0.0001
% Glacial	-0.20	0.8000
% Rocky Slope	-0.80	0.2000

Table 3. Results from Spearman's ρ correlation analysis

NLCD Land Cover Type	Nisqually Percentage	Puyallup Percentage	Deschutes Percentage	Skokomish Percentage
Wetland	1.08	1.82	3.71	1.66
Forest	55.65	67.16	42.77	69.78
Agricultural	35.4	5.74	27.69	3.56
Developed	4.13	21.51	25.54	17.69
Glacial	0.09	3.09	0	1.77
Rocky Slope	3.65	0.69	0.29	5.54

Table 4. NLCD land cover types and percentage results

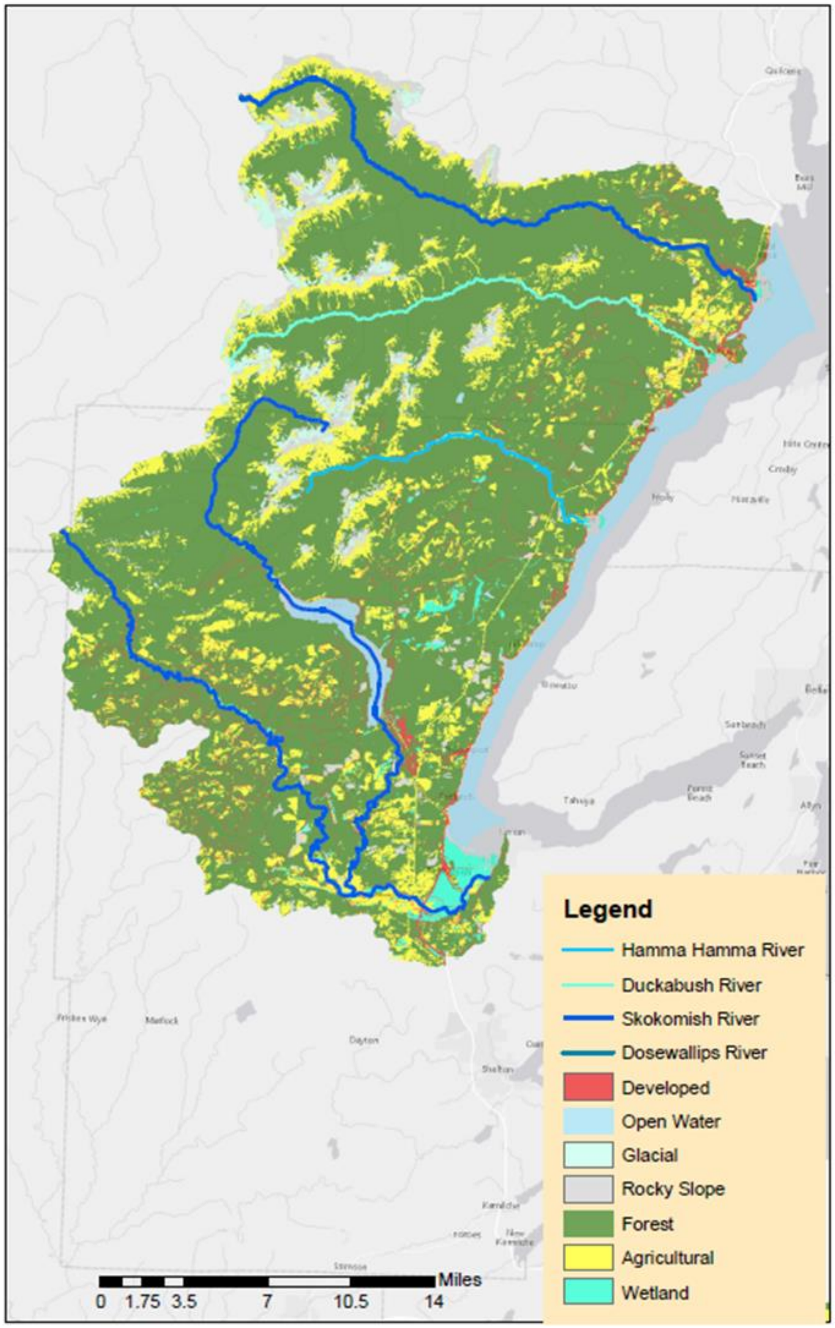

Figure 17. NLCD Land Cover results for the South Hood Canal Watershed

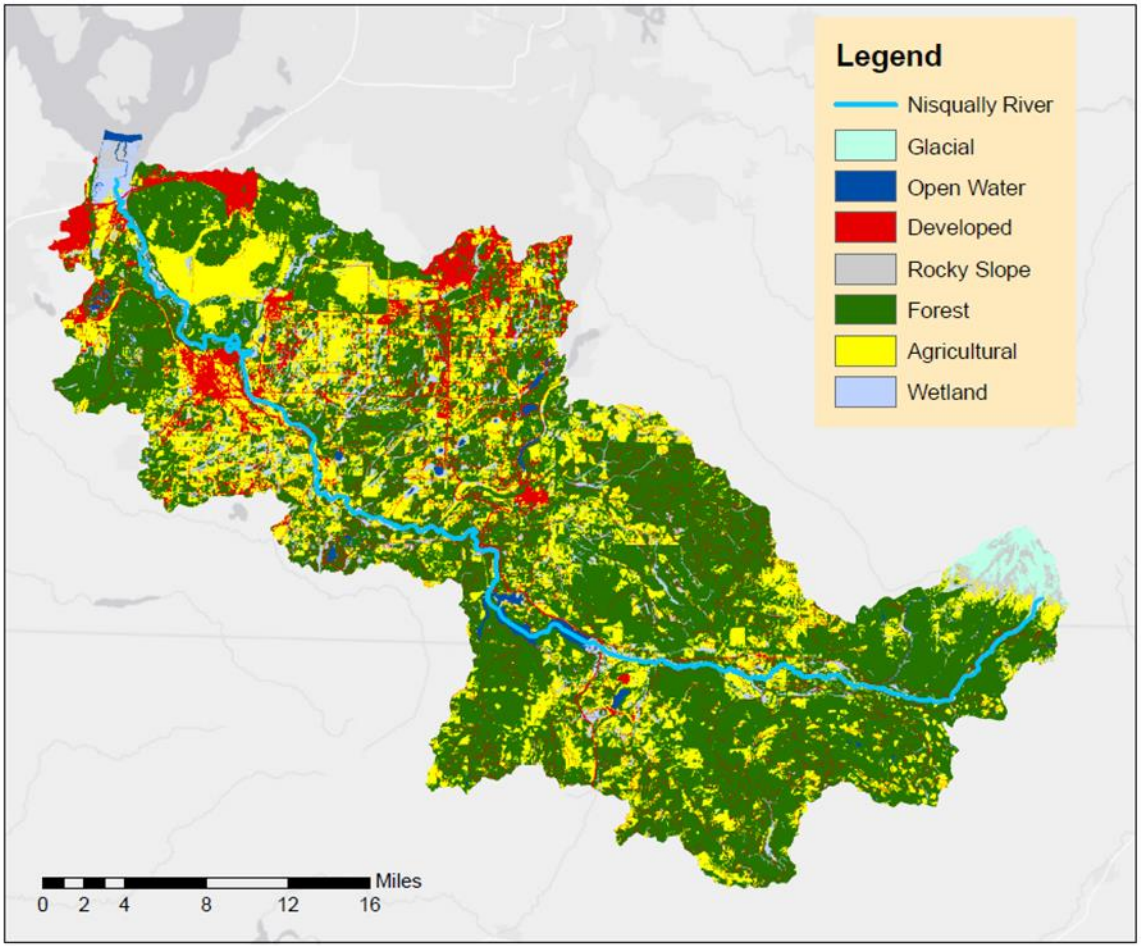

Figure 18. NLCD Land Cover results for the Nisqually River Watershed

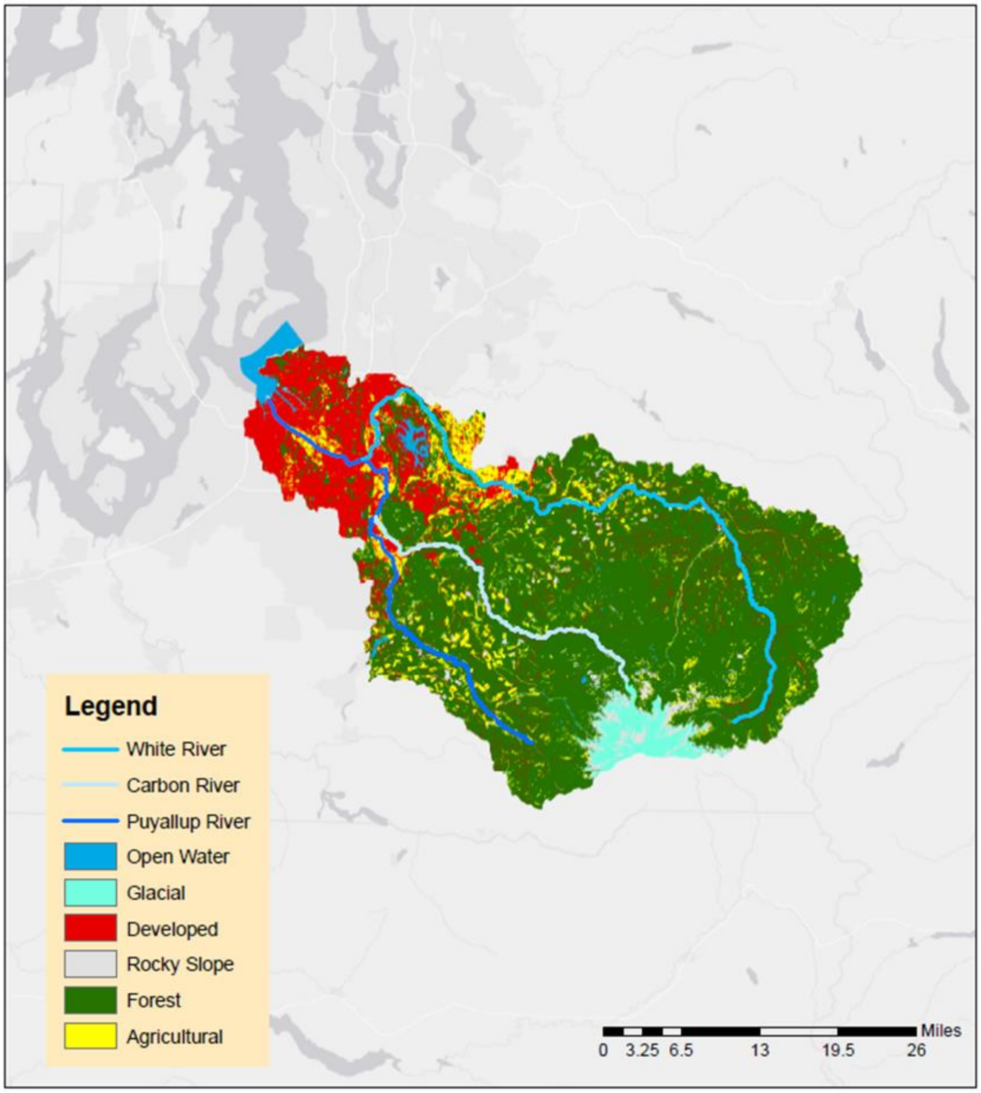

Figure 19. NLCD Land Cover results for the Puyallup River Watershed and tributaries

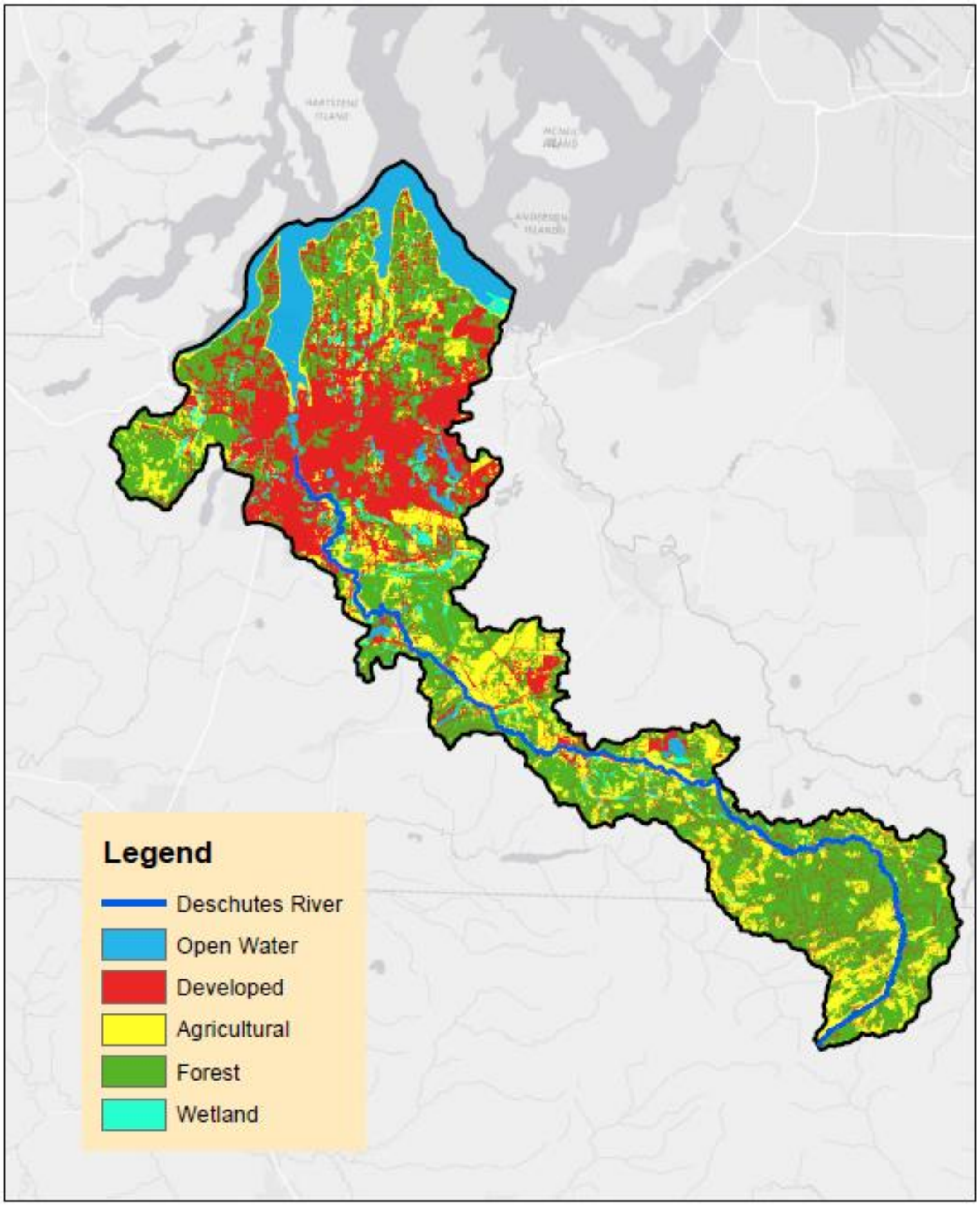

Figure 20: NLCD Land Cover results for the Deschutes River Watershed

5.0 Discussion

Differences in mean annual DOC loading across all four watersheds is primarily driven by the total amount of precipitation and size of watershed. Furthermore, wetland and developed land cover class percentages are positively correlated with DOC loading in all watersheds studied. Temperature was negatively correlated with DOC loading when the data from all four watersheds was combined in this South Puget Sound study and did not compare well with other studies in the literature (Tian et al., 2013; Evans et al., 2005) where positive correlations between increasing temperatures and DOC loading were found. The linear regression analysis of data not normalized by watershed size show that watersheds with cooler temperatures have higher DOC loading while watersheds with warmer annual temperatures have less. However, the negative correlation between temperature and DOC loading us a spurious correlation, due to the observation that the coolest watersheds are physically larger than the warmer watersheds. This will be described in more detail below.

Once DOC loading is normalized by the size of the watershed, the relationship between DOC and temperature is statistically insignificant across all watersheds. Major differences within each watershed however, do show an increase of DOC loading as a function of increasing temperature evident by an increasing trend line, however this increase was not statistically significant using either Linear Regression or Factorial ANOVA analyses. This was especially evident in the Deschutes watershed (Figure 13), which is the smallest watershed, yet data points on the linear regression graph showed increased loading correlated to warmer temperatures more so than the other watersheds.

The Deschutes watershed has the highest percentage of agricultural land class and developed land cover compared to the other watersheds. It is possible that intensified agricultural land use upstream of the heavily developed land near the mouth of the river are sources of DOC in the Deschutes watershed during warmer years. Another possible mechanism is that increased ambient temperatures could help facilitate riparian and aquatic vegetation growth, and lengthen the growing season for aquatic algae, which become DOC during decomposition.

5.1 Temperature and DOC

Unlike previous studies, (Tian et al., 2013; Evans et al., 2005) cooler temperatures were more closely correlated with DOC loading, and warmer temperatures were not. There are several mechanisms that could explain these results. The basin size of each watershed is drastically different, as well as average flow throughout the seasons. The Puyallup watershed had the coldest temperatures yet the largest DOC load and basin size of all watersheds studied. The origin of the Puyallup, Carbon and White Rivers are from glacial sources and the river experiences increased flow (cfs) during the spring snowmelt, as well as increased precipitation during the fall wet season towards the mouth of the river. Normalizing the data however shows that these results are due to the increase in flow rather than the actual increase of DOC related to temperature.

Normalized data reinforce the weak correlation between DOC loading and warmer temperature. Normalizing data show that DOC loading is staying constant regardless of watershed size across all four watersheds, however DOC loading is increasing as a function of temperature within each individual watershed, yet not enough to yield statistically significant results. Analyzing these data on a longer time scale would be prudent for detecting any significant relationships between DOC loading and temperature within individual watersheds.

These results also highlight the difficulty in analyzing water quality parameters for comparison across watersheds. Future studies should aim to examine watersheds that are similar in size, flow and source of headwaters to further improve insight into how temperature is affecting DOC loading in rivers draining into the Puget Sound. Temperatures and climatic patterns are changing in the region because of climate change (Wilhere et al., 2017; Gergel et al., 2017). Assessing the impact of climate change on DOC loading is unclear from this study.

5.2 The importance of precipitation on DOC

This study highlights the strong effect that precipitation has on DOC loading in the south Puget Sound. Basin size did not appear to be a confounding factor in the analysis of how increased precipitation affects DOC loading, as is evident by analyzing normalized data. The South Hood Canal basin is one of the smaller lowland watersheds analyzed in this study (705.37 km^2) and the Puyallup River basin the largest (2455 km^2), yet annual precipitation for the South Hood Canal watershed was comparable to annual precipitation in the Puyallup.

Additionally, the regression analysis of DOC loading and precipitation (figures 15 and 16) showed an increasing trend in DOC load as precipitation increased across all watersheds, regardless of basin size. Flooding is a normal occurrence in the South Hood Canal Watershed along all the rivers that were included in the DEM delineation. Flooding events likely result in larger quantities of DOC entering the rivers from upstream sources within landscape, rather than from the river channel itself. Nonetheless, precipitation and DOC loading are positively correlated among all sampling sites.

DOC loading also increased considerably during El Niño years (Figure 21). DOC loading spiked during and following El Niño events, indicating that discharge is driving DOC loading into the South Puget Sound. During intense precipitation events water levels rise rapidly as terrestrial runoff inputs reach rivers at high volumes and increase river discharge considerably (Budde, 2015). The input of terrestrial DOC into rivers during El Niño events yields higher loads of DOC delivered to the Puget Sound. These results indicate that storm events are particularly important for the transport of DOC to the marine waters of the South Puget Sound.

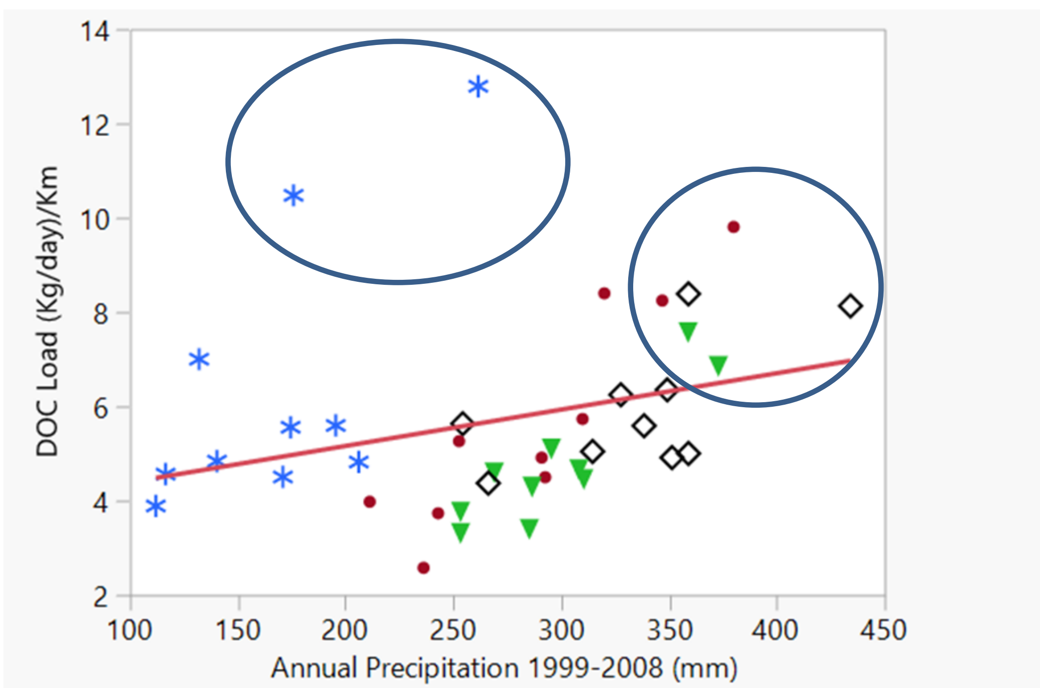

Figure 21. Annual Precipitation and normalized DOC data with El Niño years circled

5.3 Land Cover and DOC

Annual measurements of normalized DOC loading in all four watersheds demonstrated that wetland and developed land classes are correlated with increased DOC loading. Other studies, (Laudon et al. 2011; Andersson and Nyberg, 2008) discovered that wetland influence on DOC loading was substantial, that just 10% of wetland land cover can explain as much as 50% of DOC concentrations throughout the watershed. Likewise, Tian et al., (2013) quantified the effect of wetlands on DOC in large and small watersheds and found a strong correlation in smaller watersheds, but no difference in larger watersheds.

The results of this study are surprising, as all watersheds have such a small percentage of wetland land cover compared to basin size. Results indicate that DOC loading is positively correlated with wetland land cover, yet wetlands comprise less than 4% of land cover in all basins studied (Table 4). Wetlands are rich in organic carbon, and connectivity to major rivers throughout each watershed could result in higher delivery of DOC to rivers, especially during El Niño events.

The positive correlation between DOC loading and developed land cover is also surprising, as studies in the literature (Veeum et al., 2013; Oh et al., 2013; Stockmann et al., 2013) showed positive correlations between agricultural land use and DOC loads, however no studies were found that could explain mechanisms for how developed land cover and higher DOC loads are correlated. Data collection throughout the stream, including sampling locations throughout entire watersheds could help to investigate and understand the mechanisms behind land cover correlations and DOC loading.

Analyzing land cover as a percentage perhaps confounded the results of the Spearman's ρ calculation, and further studies should attempt to quantify the effect of wetlands by statistically analyzing the number of wetlands throughout the watershed rather than percentage. Additionally, a more representative sampling, by calculating DOC loading throughout the watershed, and not only at the mouth, could yield more definitive results in how land cover effects DOC loading throughout each watershed. The sampling locations, at the mouth of each river are in developed areas. Development and impervious surfaces could impact how much DOC is at the mouth of each river, and how much is distributed further upstream.

These results also highlight the difficulty in analyzing water quality parameters for comparison across watersheds. A larger sample size, analyzing more watersheds with comparable basin sizes, flow and headwaters could have provided more insight into how temperature is affecting DOC loading in rivers draining into the Puget Sound. Temperatures and climatic patterns are changing in the region because of climate change (Wilhere et al., 2017; Gergel et al., 2017). Assessing the impact of climate change on DOC loading is unclear from this study.

6.0 Conclusion

This study is the first to analyze climate effects and land cover on DOC loading in the South Puget Sound. Implementing methods used in other studies (Tian et al., 2013; Mohamedali et al., 2011) yielded different results relative to that found in this study.

Basin size was variable throughout each watershed as well as timing of pulse flows from snowmelt and seasonal precipitation was highly variable. Refining the methods for future studies is recommended.

Precipitation is positively correlated with DOC loading, as results from the South Hood Canal and the Puyallup Watersheds are comparable despite differences in each basin. Increased precipitation appears to be a major contributing factor to DOC loading in the four watersheds studied. Increased precipitation is expected to be attendant to climate change in the South Puget Sound region, therefore further studied into how terrestrial sourced DOC affects water quality in the tributary regions of these rivers is imperative for water resource planning.

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