Water Quality Dynamics in Pockwock Lake Tributaries

by

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Abstract

In forested watersheds, carbon, phosphorus, nitrogen, and suspended sediment, are affected by hydrologic regime, landscape characteristics, and forest management practices. These constituents can impact the quality and treatability of source water, which can increase treatment costs and the formation of harmful disinfectant by-products. A 12-month monitoring program was implemented in the Pockwock Lake Watershed prior to forest harvesting in five catchments to: (i) investigate the influence of different watershed attributes (e.g. size, topography, land cover) on hydrologic response and water quality, and (ii) characterize seasonal and event scale water quality variation. Clear seasonal water quality trends were identified for dissolved organic carbon and phosphorus. Catchment area and wetland coverage had the greatest correlation with hydrologic regime and water quality. Intensive sampling during rainfall events indicated that direct runoff typically only occurs during extreme events, and that Pockwock Lake catchments are transport-limited with respect to dissolved organic carbon loading.

List of Abbreviations and Symbols Used

BIX	Fluorescence Biological Index
BMP	Best Management Practice
$Ca_3(PO_4)_2$	Calcium Phosphate
cm	Centimetre
CO_2	Carbon Dioxide
DIC	Dissolved Inorganic Carbon
DNR	Department of Natural Resources
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DP	Dissolved Phosphorus
F-EEM	Fluorescence Excitation Emission Matrix
FI	Fluorescence Index
g	Gram
ha	Hectare
HIX	Humification Index
m^3	Metres cubed
mm	Millimetres
mS/cm	MilliSiemens per Centimetre
mg/L	Milligram per Litre
N	Nitrogen
N_2	Nitrogen Gas
NH_3N	Ammonia
NOM	Non-Organic Matter
NO_2^-	Nitrite
NO_3^-	Nitrate
NTU	Nephelometric Turbidity Units
OC	Organic Carbon
P	Phosphorus
PO_4^-	Orthophosphate
POC	Particulate Organic Carbon
SS	Suspended Solids
SUVA	Specific Ultraviolet Absorbance
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
UV	Ultraviolet
yr	Year

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CHAPTER 1: Introduction

1.1 Background

Forested watersheds supply drinking water for many communities across Nova Scotia. Although forested landscapes are commonly viewed as providing pristine source water, drainage from these landscapes may contain constituents that can impact both drinking water quality and treatability, such as carbon (C), suspended sediment (SS), and nutrients such as nitrogen (N) and phosphorus (P) (Pike et al., 2010). There are two forested watersheds used by Halifax Water to supply water to approximately 350,000 residents of the Halifax Regional Municipality, the Pockwock Lake watershed (5600 ha) and the Lake Major watershed (7000 ha) (Halifax Water, 2022). Previous studies (Hume et al., 2018; Cool et al., 2014; Creed et al., 2002) have shown that soil erosion and nutrient export from forested landscapes can be influenced by a variety of factors such as forestry management practices, soil type, bedrock, topography, land cover, and climatic variables (e.g., precipitation, air temperature). The motivation for this research was to understand how these factors influence the seasonal and temporal variability in the hydrology and water quality of tributaries draining to the Pockwock Lake water supply. This thesis is one component of a longer research program investigating the impacts of forest management practices on source water quality. It focused on baseline monitoring of several study catchments before forestry practices had taken place.

1.2 Problem Statement and Research Objectives

Forestry activities can contribute to increased soil erosion and impact several constituents that affect source water treatability. Dissolved organic carbon (DOC) is of particular concern, as elevated levels increase treatment costs (due to increased chemical usage) and can be a precursor to the formation of carcinogenic disinfection by-products (Hua et al., 2020). Other key constituents such as SS, N, and P can also impact treatability. Increased export of nutrients into water bodies can contribute to eutrophication and promote harmful algae blooms (HABs) that degrade water quality (Santos et al., 2015). These HABs can potentially produce toxic compounds that pose a risk to public health. Forest management has the potential to negatively or positively impact these water quality parameters, but there are knowledge gaps with respect to the short and long-term effects of alternative forestry practices on source water quality in the Atlantic region. A long-term field experiment has been established in the Pockwock Watershed to address these knowledge gaps. A series of forest management interventions has been implemented for several catchments in the watershed. Pre-and post-intervention monitoring has been initiated to document the water quality impacts. However, to characterize the effects of forestry interventions, we must first understand how other watershed attributes, such as topography, soils, wetland presence, and vegetation influence water quality. The temporal and spatial variation in water quality across forested watersheds must also be better understood to facilitate the design and assessment of monitoring programs. Therefore, the objectives of this research were to: 1) examine the relationship between water quality characteristics (concentrations and loadings of source water constituents) and catchment attributes, and 2) characterize temporal dynamics (seasonal and event time scales) of water quality characteristics of Pockwock Lake tributaries.

1.3 Approach

Water level loggers, *in-situ* sondes, and auto-samplers were installed in six study catchments during the summer of 2018. Streamflow records were generated using continuous stage measurements from water level loggers and stage-discharge relationships, which were developed from manual flow gauging measurements for each station. *In-situ* sondes were used to continuously measure a variety of water quality parameters, and regularly calibrated handheld sondes were used for quality control. Auto-samplers were installed to collect samples during intensive hydrologic events. These samples, along with bi-weekly to monthly grab samples, were analyzed for a suite of water quality parameters to provide insight on how these parameters change seasonally and during individual hydrologic events.

CHAPTER 2: Literature Review

2.1 Carbon, Nitrogen and Phosphorus Pools and Transport Processes in Forested Watersheds

The three main constituents that influence the functioning of aquatic environments, and source water treatability, are C, N, and P. The following sections discuss how these nutrients are cycled through forested watersheds.

2.1.1 Carbon

Inland water systems such as streams, lakes, and wetlands have a critical role in catchment and global scale C cycles (Aufdenkampe et al., 2011). The C entering these water bodies from the landscape can consist of organic carbon (OC) and dissolved inorganic carbon (DIC). The total organic carbon (TOC) pool can be further divided into dissolved organic carbon (DOC) and particulate organic carbon (POC). In most forested watersheds DOC comprises the majority of carbon exported through hydrologic pathways (Miettinen et al., 2020).

The amount of C stored within forested landscapes can be highly variable and is influenced by topography, soils, and the age and type of tree stand. The main C pools are in the canopy of the trees, freshly fallen leaf litter, forest floor, the organic rich A soil horizon, and wetlands (Webster et al., 2010). It has been shown in terrestrial ecosystems that approximatively 80% of the C is stored in the forest floor and soils (Ontl & Schulte, 2012). The C present is in either organic or inorganic forms. The forest floor and upper soil horizons are typically comprised of OC since it is sourced from decomposing organic matter such as leaf litter, fallen trees, and roots. The lower soil horizons have greater amounts of inorganic C sourced from weathering of rocks and minerals (Wang et. al., 2010).

There are several pathways for DOC transport in forested watersheds and they can vary significantly between catchments due to hydrologic and topographic characteristics. During baseflow conditions, these streams are primarily fed by groundwater flow (Van Gaelen et al., 2014). During hydrological events, instream DOC concentrations typically increase due to additional contributions of water moving through shallow organic-rich upper soil horizons. For example, Lambert et al. (2014) found that > 80% of the DOC flowing through a drainage basin was sourced through the upper soil horizons and forest floor of the riparian zone.

2.1.2 Nitrogen

Nitrogen is a limiting nutrient for both aquatic and terrestrial ecosystems; increased loading of N to aquatic ecosystems can lead to eutrophic conditions. Atmospheric deposition of N to terrestrial systems has increased 4-10 times in the past 150 years mainly due to N emissions from fossil fuel combustion, as well as the application of fertilizer for agricultural activities (Goodale et al., 2009). These contributions can result in increased transport of inorganic N from the landscape to streams, which contributes to aquatic acidification and may cause eutrophication in downstream water bodies.

The main forms of N are organic N, nitrate (NO_3^-), nitrite (NO_2^-), ammonia-N (NH_3-N), and nitrogen gas (N_2). Excessively high levels of nitrate can lead to adverse health effects, such as methemoglobinemia (Binkley et al., 1999). There are a few generalizations regarding N in forested watersheds, which have been outlined by Melillo (1981): (a) ~ 90% of the N in the ecosystem is organically bound N in the forest floor and soil horizons; (b) the remaining N is mostly organically bound in the vegetation; and (c) < 2% of the N is in inorganic form in the soil, mainly as ammonium. Decomposition of organic N found in plant and animal residues can produce inorganic forms, such as ammonium, which can be released back into the ecosystem and becomes available for uptake. Binkley et al. (2004) reported that in general, N measured in streams is made up of 45% nitrate, 10% ammonium, and 45% dissolved organic nitrogen (DON).

Nitrogen gas can be fixed from the atmosphere by certain plants (e.g. legumes), bacteria, and algae, which incorporate this N into organic matter (Tchobanoglous &

Schroeder, 1985). Nitrate is formed through oxidation of N, facilitated by microorganisms in plants, soils, and water (Pike et al., 2010). Nitrate levels in North American streams are typically low with an mean and median concentrations of 0.31 mg/L and 0.15 mg/L, respectively (Binkley 2004). Nitrate is the most prevalent form of N in aquatic systems due to its high mobility in soil, solubility, and stability (Health Canada, 2009). Nitrite is rarely detected in forested watersheds, as it rapidly oxidizes in this environment. Inputs of this form of N are typically associated with anthropogenic sources, such as sewage, fertilizers, and landfills (Pike et al., 2010). Ammonia concentrations are also typically low in aquatic systems since it is rapidly adsorbed to soil cation exchange sites or utilized by plants.

2.1.3 Phosphorus

Phosphorus is another limiting nutrient in most freshwater aquatic ecosystems (Santos et al., 2015). Increased loading can result in increased primary productivity (plant and algae growth). As this plant and algal biomass decomposes, microbial decomposition processes consume oxygen and lower the dissolved oxygen content in the water body. This can degrade water quality and threaten aquatic life. Phosphorus is naturally derived from the weathering of soil and bedrock minerals. Increased erosion caused by anthropogenic activities, such as forestry, can lead to P losses to aquatic systems (Rodgers et al., 2010). External inputs of P from anthropogenic sources such as fertilizer, sewage, and landfills are also important.

Phosphorus is naturally derived from the weathering of minerals in bedrock and soil, the most prominent mineral being calcium phosphate ($Ca_3(PO_4)_2$) in the apatite group (Nash, 1984). Cycling between plants, animals, soils, and water involves dissolved and particulate forms of P (Scatena, 2000). Phosphorus in freshwater has three forms; inorganic P, particulate organic P, and dissolved organic P (Environment Canada, 2005). Calcium phosphate and other phosphate minerals are converted into orthophosphate (PO_4^-) by microorganisms, which is an inorganic soluble form that is quickly assimilated by plants. This form of phosphate is then transferred to consumers and will decompose as organic P. Up to 95% of the P in freshwater is in the form of organic P, within cellular constituents of organisms, and adsorbed to inorganic and dead particulate organic matter (Wetzel, 2001).

The main fluxes of P within forested watersheds are uplift and weathering of bedrock that contain P minerals, and subsequent mobilization through multiple hydrologic pathways, i.e., overland flow, interflow, and groundwater flow (Shrestha et al., 2020). The main P pools are near the soil surface and on the forest floor; intense hydrologic events and associated overland flow are the main loss mechanisms of P in forested watersheds (Sohrt et al., 2017).

2.2 Watershed attributes that impact Carbon, Nitrogen and Phosphorus Processes

2.2.1 Soils

Natural soils normally exhibit a vertical stratification and possess descending soil horizons named O, A, B, C, and D, along with various sub-horizon modifying letters. The longer a soil remains undisturbed (un-eroded, un-plowed), the better developed the horizons will become, making them easier to recognize. Soil profiles and the horizons comprising them differ depending on a variety of factors, including bedrock composition, texture, overburden, climate, topography, and biological activity (Hall, 1998).

Due to prevailing wind currents, the Maritimes have been impacted by atmospheric deposition of sulphur (S) and N from the industrial revolution in northeastern United States and Eastern Canada. This has resulted in soil acidification over the past century; recent recovery from acidification due to industrial slowdown and implementation of best management practices has been observed in several regions (Anderson et al., 2017). The acidification of soils results in depletion of base cations (Fernandez et al., 2003).

Soils store a significant amount of C and it is estimated that 80% of C is stored in the forest floor (Ontl & Shulte, 2012). It is important to understand how C stored within the soil horizons will be affected by disturbances associated with forestry activities.

The O-horizon of a soil is the top horizon in a soil and represents upward accumulation of organic debris (litter) above the top of the mineral soil. The O-horizon is composed of three sub-horizons: O_L (leaf), O_F (fiber), and O_H (humus; Chesworth, 2008). During this accumulation, soil bacteria degrade and reduce the sizes of the organic molecules making up this organic debris, transforming it into amorphous organic matter called humus (which itself consists of black, insoluble humin; brown, partially soluble humic acid; and yellow soluble fulvic acid). The A-horizon is the top of the mineral soil and is commonly divided into A_H (humic) and A_E (elluviated) sub-horizons. The A_H sub-horizon is stained a dark color by soluble humate and fulvate molecules washed down from the surface by meteoric waters. The A_E-horizon is only present in chemically mature soils and is below the A_H-horizon. This sub-horizon is light in colour because leaching of soluble elements has removed color-imparting compounds from the soil, including iron, soluble bases, clays, and colloidal oxides. The intense leaching results in very low concentrations of trace elements (Hall, 1998).

Adsorption in the mineral soil horizons has a dominant control on the transport of DOC. The concentration of DOC will decrease deeper into mineral soil depths due to soil water percolation and increased residence time (Liu et al., 2014). DOC concentration is also inversely correlated with clay content and the amount of iron and aluminum oxides/hydroxides in watershed soils (Kalbitz et al., 2000). Decreasing soil pH increases the adsorption capacity as a result of increasing positive charge on the hydroxides (Liu et al., 2014). The maximum adsorption capacity occurs at a pH of 5. In contrast, adsorption capacity decreases in anaerobic soil conditions (Kalbitz et al., 2000).

San Clements et al. (2010), found that as soil acidity increases, the base buffering capacity decreases, and the buffering capacity of metals such as Al and Fe become increasingly important and results in them becoming mobilized. The authors hypothesized that Al has strong buffering capacity on P and that in acidic soils the increases in mobilization of Al will result in more leaching of P.

2.2.1 Tree Species

After forest harvesting or natural disturbances, rapidly growing forests sequester C, N, and P into biomass and are a large nutrient sink, reducing losses to aquatic systems (Lovett et al., 2004). Mature forests also retain nutrients through incorporation into the soil organic matter, but can become saturated (Magill et al., 2000).

Coniferous and non-coniferous tree species have an impact on the production of DOC. Zhang et al. (2013) found contradicting studies on the different tree species producing more DOC. Forest stands have varying species composition, age, and growth rates, which in turn impact litter fall and DOC production.

Non-coniferous forest have approximately two to three times the concentration of NO_3^- and NH_4^+ N in streams than conifer forests, but conifer forests have three to eight times the concentrations of organic N found in non-coniferous streams due to the difference in quality of soil the tree species produce (Binkley et al., 2004; Lovett et al., 2004). NO_3^- accounts for 60% of all dissolved N in non-coniferous forest streams and organic N accounts for about 80% of the dissolved N in streams draining coniferous forests (Binkley et al., 2004).

Unlogged old growth forests average about twice the N concentration in streams as compared to streams draining watersheds with > 75% of the forest regrowing post-harvest (Silsbee and Larson, 1982). The median concentration of P in forest floor soil solutions is typically three times larger in coniferous forest than in non-coniferous forests (Sohrt et al., 2017). This is the result of increased soil acidity from the needles of coniferous trees which increases leaching in the soil (San Clements et al., 2010). The concentration of P in stream water is typically twice as high in younger forests than in forests older than 100 years old (Binkley et al., 2004). Non-coniferous forests typically have two to three times the concentration of inorganic phosphate in streams than coniferous forest (Binkley et al., 2004)

2.2.2 Wetlands

Land cover has an important effect on the concentration and composition of DOC in streams. Topographic depressions that hold water in the form of wetlands, small lakes, or ephemeral ponds have important hydrological and ecological functions (Hayashi & van der Kamp, 2000). It has been shown that in wetland-dominated streams, the DOC and Specific Ultraviolet absorbance ($SUVA_{254}$) were higher than forest-dominated streams (Agren et al., 2007). Catchments with higher proportions of wetland area generate more aromatic, higher molecular weight DOC as a result of the DOC composition of soil water that becomes hydrologically connected to the streams (Agren et al., 2007).

Wetlands have been reported to act as sources, sinks, or as transformers of N and P, depending on the wetland type and hydrologic conditions (Devito et al., 1989). Dillion et al. (1991) observed high amounts of TP and TON exported from catchments downstream of peat wetlands, indicating that wetlands can be a major source of nutrients. Devito et al. (1989) found TP retention rates in several wetlands in Ontario to be less than 20% of input and TON export rates were also greater than inputs.

2.2.3 Topography

The topography of a watershed has an impact on nutrient pools D'Arcy & Carignan (1997) studied the influence of catchment topography on water quality in southeastern Quebec. They found that C and P losses are negatively correlated with slope while N losses are positively correlated. Soils have a strong vertical stratification of biogeochemical processes and the upper organic soil horizons are major zones of C and P production. The degree of contact between runoff water and organic rich soil horizons should increase with decreasing catchment slope, therefore catchments with lower slopes will export more C and P than catchments with higher slopes. In contrast, N is weakly retained by mineral soils and biogeochemical processes linking flow path to export are different than C and P.

Webster et al. (2011) outlined a topographic template for estimating soil C and found a strong negative correlation between DOC concentration and slope.

2.2.4 Anthropogenic

The direct and indirect effects of human activities, including land use practices, point source pollution, and diffuse pollution, control the supply and availability of C, N, and P in watersheds. Agriculture practices and the excessive application of fertilizers is the largest source of these nutrients in freshwater systems (Rodríguez-Blanco et al., 2015). Municipal landfill leachate can be highly concentrated in dissolved organic matter, inorganic compounds, and heavy metals, all of which can deteriorate water quality (Longe and Balogun, 2010). In forested watersheds, nutrient concentrations are typically < 15% of the levels of watersheds that have large agriculture and urban components (Omernik, 1976). The main impacts from human activity are associated with forestry activities and road construction. This can negatively affect nutrient fluxes and sedimentation.

2.3 Temporal and Spatial Variability in C, P, N concentrations and export

In recent years, the intensity and frequency of extreme weather events has been increasing across the eastern seaboard (Donat et al., 2013) and is predicted to continue (Jentsch et al., 2007). Increases in precipitation intensity can result in larger amounts of nutrients being leached from the forest floor and transported into streams and lakes (Warner et al., 2019). The intensity and duration of hydrologic events, as well as antecedent moisture conditions, determines how much direct runoff (overland flow) contributes to streamflow. Intense events can result in > 50% of streamflow originating as direct runoff, whereas less intense events will result in the streamflow response being dominated by groundwater. Groundwater contributions tend to have lower fluxes in nutrients due to sorption onto soil surfaces (Holman et al. 2008). The characteristics of these hydrologic events affect the fluxes and forms of nutrients transported to surface waters and in turn impact loading downstream (Shrestha et al., 2020). Seasonal variations in nutrient concentrations are also influenced by the seasonal changes in nutrient production (Koehler et al. 2009).

Seasonal variability in DOC concentrations in forested catchments typically follows an annual cycle with peak concentrations in the fall and minima in early spring (Van Gaelen et al., 2014). Annual DOC flushing in the fall is attributed to high biological activity and decomposition in the summer, followed by the input of fall leaf litter and further decomposition (Halliday et al., 2012). This increases the pools of organic matter in the forest floor and upper soil horizons which can then be flushed during fall hydrologic events.

The concentration of DOC in streams has been shown to increase during intense rainfall and snowmelt compared to baseflow conditions, independent of seasonal variation (Van Gaelen et al., 2014). The DOC that has accumulated in organic soils and forest floors from decaying organic matter is flushed by infiltrating rainfall, and a rising water table; this can result in diminished supplies of leachable DOC throughout the hydrologic event (Brooks et al., 1999). Multiple studies (Boyer et al., 2000; Hagedorn et al., 2000) have shown DOC to have multiple fold increases in concentration and loading during these hydrologic events.

The DOC concentration during storm events can have varying hysteresis, defined as the variation in stream solute concentration with discharge (Wagner et al., 2019). Pellerin et al., (2012) observed a counter clockwise hysteresis loop having elevated DOC concentrations on the falling limb of the discharge hydrograph, indicating that DOC sources are distal or transported by slow moving pathways. Hagedorn et al. (2000) found that peak concentrations of DOC on the falling limb of the hydrograph were caused by DOC rich topsoil contributions of water in later stages of the storm, with subsoil-based water pathways dominating during baseflow. In upland snow-dominated catchments, DOC concentration will typically peak prior to peak discharge, as the available carbon is leached from the forest floor, and then will decrease rapidly as the snowpack continues to melt (Lambert et al., 2014). The relationship between DOC concentration and stream discharge can indicate where DOC is produced in the watershed and whether the DOC flux is limited by carbon supply or hydrologic connectivity and mobilization (Zarnetske et al., 2018). If DOC is limited by carbon supply, then there are not sufficient sources of DOC and concentration will decrease as discharge decreases. Conversely, if DOC concentration remains elevated or increases as discharge decreases there is adequate supply of DOC and fluxes to the stream are limited by the mechanisms that transport the DOC.

The specific UV absorbance (SUVA, 254 nm) of DOC is also impacted during hydrologic events such as heavy rain and snow melt, independently of seasonal variation (Van Gaelen et al., 2014). This suggests that DOC has distinct source areas in a watershed that are mobilized during different parts of hydrologic events. Hood et al. (2006) found that SUVA-254 increased during storm events, indicating a change in the chemical character of DOC. The authors similarly inferred that DOC supplied during storm flow is likely from a different source pool than that during baseflow. It has been found that DOC present during the rising limb of the hydrograph are dominated by inputs from the riparian zone, while later in the event there is an increased contribution of water and DOC from the catchment hill slopes (McGlynn and McDonnell, 2003).

Nitrogen in undisturbed forested watersheds has been shown to be tightly retained in the ecosystem, with N export largely biologically controlled (Thompson et al., 2011). However, excess N inputs beyond what can be consumed by plants result in N saturation, which may then be exported and is controlled by hydrologic processes (Webster et al., 2016). There is significant seasonality in N export that coincides with biological activity. Peak nitrate concentrations have been observed during the winter in watersheds with a snowpack, this is the result of dormant vegetation and limited N uptake (Goodale et al., 2009). The N concentrations then decrease into spring and early summer due to increased growth of vegetation and uptake by periphyton (Bernhardt et al., 2003). Many watersheds, particularly those that are not impacted by snow related hydrology, are characterized by peak N in the summer (Webster et al., 2016). This summer peak has been attributed to increased soil microbial nitrification under ideal temperatures in the growing season; this accumulated mobile nitrate can be flushed into the streams during hydrologic events (Band et al., 2001). In the fall, there is a decline in N concentration after leaf abscission due to the instream uptake of N by fungi and bacteria as they decompose organic matter (Sebestyen et al., 2014). During hydrologic events, N peaks during the rising limb of the hydrograph or at peak discharge (Inamdar et al., 2006; Inamdar & Mitchell, 2007). These fluxes in N are primarily derived from throughfall and litter, in contrast to DOC, which is primarily sourced from flushing of mineral soils due to a rising water table.

Phosphorus concentrations have been observed to have both types of hysteresis depending on land use. Undeveloped watersheds have been observed to have an anticlockwise trajectory in upland moors, indicating slow release of P to the stream (Bowes et al., 2005). In contrast, Shrestha et al. (2020) observed P concentrations to be higher on the rising limb of the hydrograph in a forested New England stream. Especially in developed watersheds, P typically increases in concentration during the initial stage of hydrologic events, remains high during peak flow, and then subsides with decreased flow. Lloyd et al. (2016) analyzed the hysteretic behavior of 41 storms in a predominantly agricultural watershed in the Hampshire Avon catchment, UK, and found that all storms resulted in an increase in total phosphorus concentration on the rising limb of the hydrograph. In general, P sources during storm events are located near the soil surface and P is flushed through erosive overland flow (Sharpley, 1985).

2.4 DOC Characteristics

DOC has a critically important role in the cycling and distribution of energy and nutrients in terrestrial and aquatic ecosystems (Kaiser & Kalbitz, 2012). Ecologically, DOC is essential to the base of the aquatic food web, and impacts ecosystem productivity (Mistick & Johnson, 2020). In the past few decades, DOC concentration in Eastern North America have been reported to be increasing in surface waters (Monteith et al., 2007; Evans et al., 2005). There are various factors suggested to be causing the increasing concentrations of DOC, including recovery from acidification, CO_2 enrichment in the atmosphere, and rising temperatures (Van Gaelen et al., 2014). DOC is an important consideration in drinking water treatment. The rising concentration of C in terrestrial water bodies is of increasing concern because it is a precursor to harmful disinfection by-products (DBPs), such as trihalomethanes and haloacetic acids (Liang & Singer, 2003).

The concentration and character of DOC in water depends on both its source, and the fate and transport processes occurring in the catchment (adsorption, transformation, and degradation), which are strongly influenced by vegetation and soil type (Awad et al., 2015). The physical characteristics of DOC is also important in determining the potential treatability of the water. Stream water and surface flow generally have higher DOC concentrations and more aromatic and humic DOC compounds than groundwater (Inamdar et al., 2012).

UV-254 is a rapid measurement used to characterize organic matter in water, specifically organic compounds that contain aromatic rings or unsaturated carbon bonds. The absorbance of light at this wavelength is proportional to the concentration of organics in the water. SUVA is defined as the UV absorbance of a water sample at 254 nm, normalized for DOC concentration (Weishaar et al., 2003). Both metrics are important parameters for assessing drinking water treatability, as they characterize the aromaticity of DOC, which in turn affects the chemicals used to treat the water. Fluorescence excitation emission matrix (F-EEM) analysis is another tool that provides the relative abundances of humic-like (HA), fulvic-like (FA), and protein-like compounds that comprise DOC (Chen et al., 2003).

F-EEM analysis of stream water provides a fluorescence spectrum that can assess the origin and transformation degree of DOC through calculations of fluorescence indices (Huguet et al., 2009). The fluorescence index (FI) is used to distinguish between terrestrial and microbial sources of DOC. Terrestrial sources range from 1.2 to 1.5, while microbial sources range from 1.7 to 2 (Inamdar et al., 2012). The humification index (HIX) determines the degree of DOC maturation in soils. High values between 10 and 16 are a sign of strongly humified organic material originating from terrestrial systems and will have complex molecules with molecular weights characteristic of aromatics (Sensei et al., 1991). Low values (<4) are associated with autochthonous organic matter (Vacher, 2004). The fluorescence biological index (BIX) is a measure to characterize biological production of DOC. Values > 1 correspond to a predominately autochthonous origin of DOC and the presence of DOC recently released into stream water, whereas a low value (0.6-0.7) indicates lower DOC production in natural waters (Huguet et al., 2009).

2.5 Sediment Processes in Forested Watersheds.

Sediment transport in forested watersheds occurs naturally but is impacted by anthropogenic disturbances. Sediment entering streams is largely from surface erosion, streambank erosion, and mass movements such as landslides and rockfalls (Pike et al., 2010). These processes provide different size fractions of sediment supplied on different time scales. Mass movements have all size fractions, whereas surface erosion is predominantly fine size fractions. Soil formation is influenced by three-dimensional processes related to catena where the soils from each catena position are interconnected by the flow of water and the particulate and dissolved components in the water (Creed et al., 2002). There is an interplay in the catena between static factors (elevation, slope and aspect) which influence radiation, temperature, and moisture at the site and dynamic factors (relative position of the site within the catena) which impact the transport of particulate and dissolved components downslope (Young, 1972). Soils formed from the same provenance can differ because of variation in water erosional processes that result in differential conditions in drainage, transport, deposition of suspended and particulate components, leaching, translocation, and redeposition of soluble materials (Hall and Olson, 1991). Soil and sediments that are transported by hydrologic processes have a crucial impact on water quality by dictating the turbidity and total suspended solids (TSS) in the water body, which will impact drinking water quality, aquatic life, and habitat conditions (Pike et al, 2010).

Turbidity is a measurement of scattered and absorbed light from particles that otherwise would be transmitted with no change in direction or flux (U.S. Environmental Protection Agency, 1993). Turbidity in water is caused by organic and inorganic suspended materials and is typically expressed in Nephelometric Turbidity Units (NTU). High turbidity levels absorb light which reduces photosynthesis, visibility and heats the water causing dissolved oxygen to increase (Colley & Smith, 2001). Excessive turbidity negatively impacts aesthetic water quality for recreational use and consumption, and also interferes with disinfection processes during water treatment (Cavanagh et al., 1998a). TSS is another parameter related to the amount of sediments and organic particles suspended in water, but is a gravimetric measurement. Similar to turbidity, suspended solids restrict light penetration having adverse impacts on water quality. It also can impair water treatment processes (Cavanagh et al., 1998b).

Sediment transport processes in a forested watershed are related to hydrologic events and snowmelt (Pike et al, 2010). Forest harvest operations and haul road construction can result in increased erosion, which can have an adverse impact on water quality and treatability. These increases are influenced by road construction practices and the nature of the forest harvest methods. Roads that intercept runoff and subsurface flow can accelerate the transfer rate of water to streams, and change hydrograph characteristics (Wang, 2013.) These direct changes can essentially result in roads being hydrologically connected to streams, serving as channel extensions (Wang, 2013). The largest increase occurs during and immediately after road construction and harvest, as well as during road maintenance when armored layers are broken up and material added. During this phase, and up to one year after, there can be a relatively large increase in total suspended solids and turbidity (Luce and Black, 2001). These elevated levels often quickly decrease as the ground settles but may remain elevated for many years (Wang, 2013).

2.6 Impacts of Forest Management on Carbon, Nitrogen and Phosphorus

The demand of forestry products is steadily increasing as population and demand for wood products rises (Jannke, 2022). Forest harvesting has increased to meet this demand. There are several methods for tree harvesting, ranging from partial removal of the overstorey to removal of the entire overstory, with branches and foliage either left on site or completely removed. Harvesting can remove a large quantity of nutrients, such as C, N and P from the landscape (Hume et al., 2018). The changing landscape caused by forestry also has impacts on hydrologic processes; soil compaction and vegetation removal alters interception and infiltration rates and leads to increased overland flow (Feller et al., 2005). The removal of vegetation from forestry activities can increase bedrock weathering rates and soil erosion in the disturbed area, which releases nutrients and metals to drainage features. If the overstorey canopy is partially or fully removed, the microclimate will also be altered. This results in changes in the soil-plant interactions that can affect the capacity of the forest floor and soil to store nutrients and other elements (Jandl et al., 2007).

Forest harvesting reduces nutrient uptake by plants and interrupts the soil-plant microorganism cycle. However, this effect is short lived since pioneer vegetation rapidly regrows to reoccupy the cleared space (Vitousek, 1981). The newly established plant growth rapidly sequesters C, and to a lesser extent N through N fixating plants (Hume et al., 2018). In contrast to C and N, P availability and export is primarily geochemically controlled with new fluxes coming from weathering of soils and bedrock instead of biological processes. It therefore increases as C and N increase, but more slowly (Cleveland & Liptzin, 2007). However, the amount of labile P is significantly increased after forest harvesting. There is less uptake by plants and decomposition of logging residues (leaves, needles, branches) releases more labile P into the forest floor and upper soil horizons (Rodgers et al., 2010). This increases the rate of leaching from the forest floor and soil horizons, resulting in larger export during hydrologic events. Partial or whole tree removal also has a significant impact on P stocks. Yanai (1998) found that in a mature hardwood forest over 50% of the P is in branches, twigs, and foliage. Therefore, whole tree removal can remove over twice as much P from the ecosystem.

CHAPTER 3: Methods

3.1 Pockwock Study Area

Pockwock Lake, located between the communities of Hammonds Plains and Mount Uniacke, NS (Figure 2.1), supplies untreated drinking water to the J. Douglas Kline water treatment plan that then supplies treated drinking water to over 200,000 residents of the Halifax Regional Municipality. The contributing watershed (~5600 ha) has previously experienced timber harvesting, and additional timber harvesting activities are planned. Initial instrumentation of the watershed was conducted in the summer of 2018 by the forWater Atlantic Maritime research node at six locations on five tributaries to Pockwock Lake.

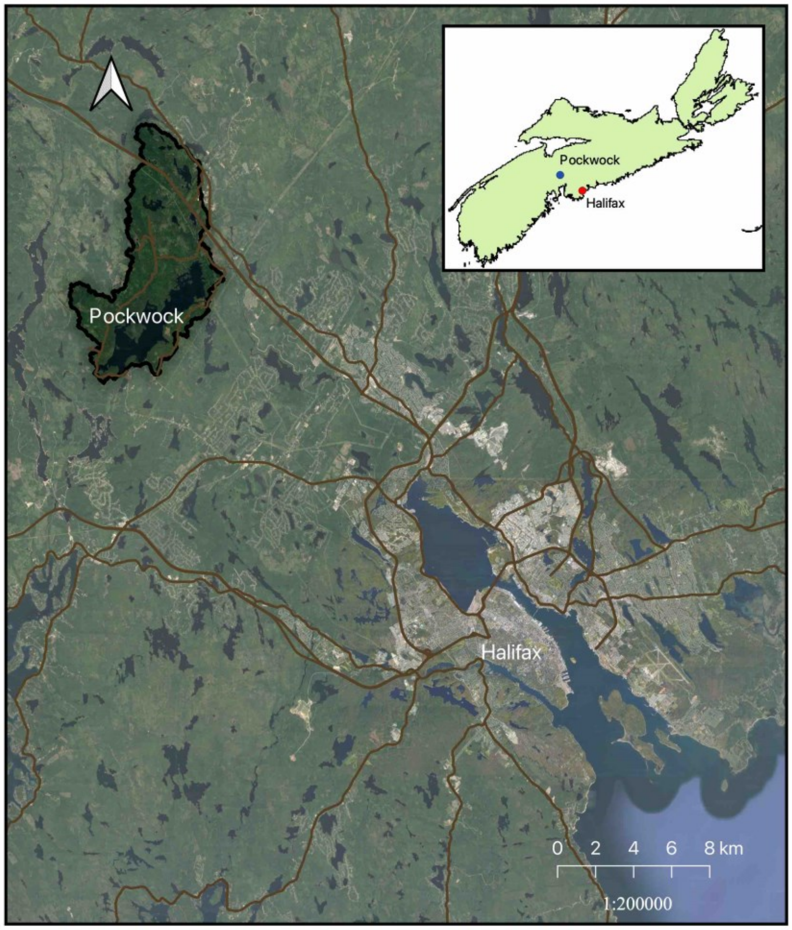

Figure 3.1 – **Location map of the Pockwock watershed relative to Halifax, NS.**

A twelve-month study period was chosen from the long-term monitoring program in Pockwock watershed to produce a full year of baseline water quality and hydrographic parameters at six monitoring sites prior to various timber harvesting operations commencing. The study period is between September 2018 and August 2019, spanning all four seasons. This allowed for interpretation of seasonal variance in the water quality and hydrographic parameters. Three of the monitoring catchments were also selected for intensive sampling during hydrologic events from the fall of 2018 to the fall of 2019.

3.1.1 Location and Access

The Pockwock lake tributary monitoring sites are located on the southern end of Hants County. The sites can be reached by taking Exit 3 on Highway 101 and then heading west onto the Pockwock Lake assess road. Alternatively, the sites can be accessed from the western side of the lake where the water treatment facility is located by heading north on Pockwock Road off Hammonds Plains Road.

3.1.2 Sample Sites

Six monitoring sites have been established on five tributaries on the north side of Pockwock Lake as shown in Figure 2.2. Each site has a piezometer, stilling well, in-situ sonde, and auto sampler installed for hydrographic and water quality data collection.

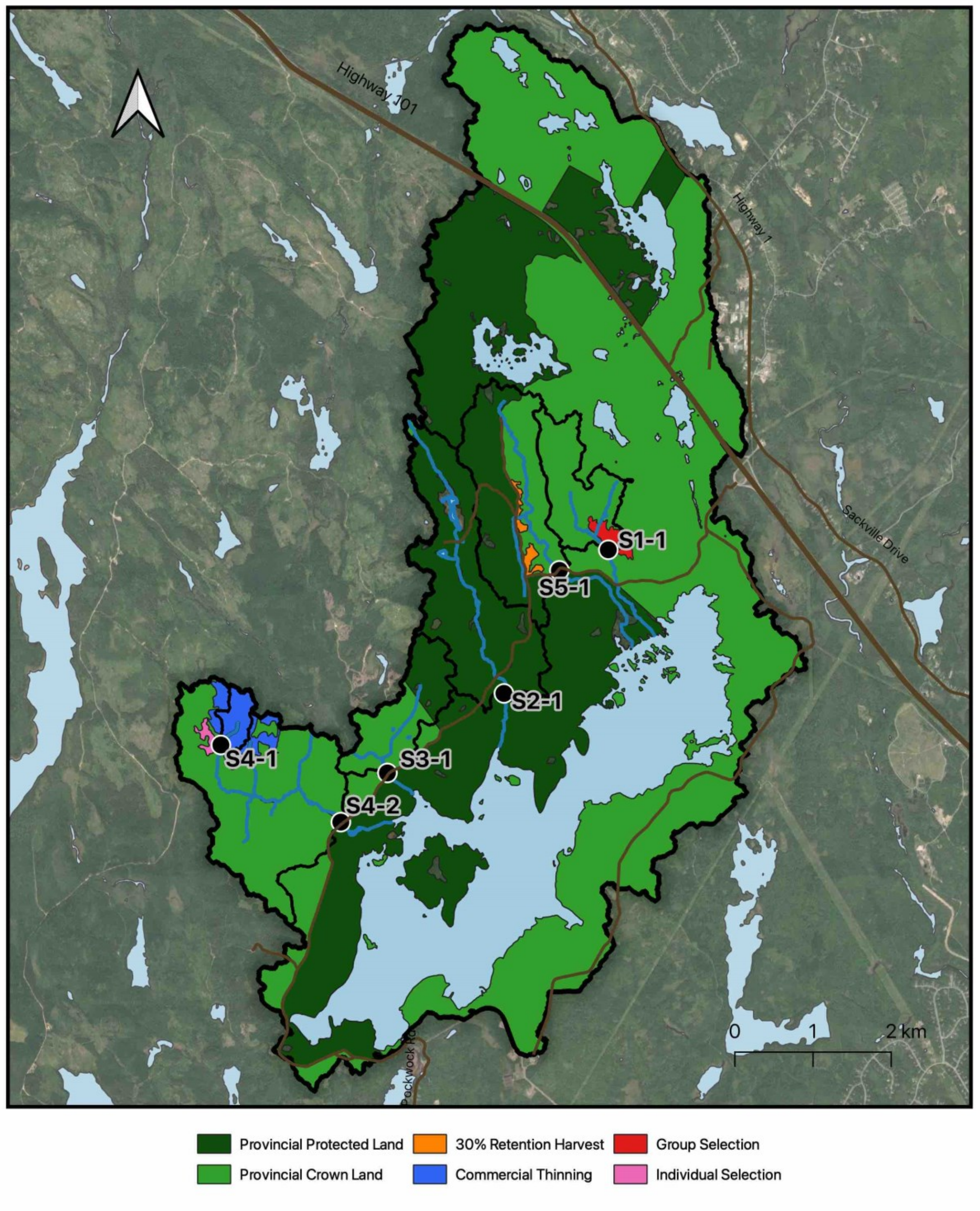

Figure 3.2 **– Pockwock watershed monitoring catchments with associated drainage area and planned 2020-2021 forest harvest indicated.**

Various forest management treatments have taken placed after the baseline monitoring was completed. They consisted of 30% retention harvest, commercial thinning, group selection, and individual selection (Table 2.1).

Variable retention harvest is the retention of a certain percentage of trees to maintain structural elements to promote habitat and ecologically biodiversity (Besse et al., 2019). The proposed harvest in Pockwock will retain at least 30% of the trees.

Commercial thinning is the removal of poor quality and clustered trees from an even aged mature stand, usually after a clear cut (DNR, 2021). This allows for the remaining trees to have increased exposure to sunlight and space to encourage growth. Roughly one third of the trees are removed; this will increase the risk of windthrow and windsnap of the remaining trees due to increased exposure (DNR, 2021). Areas with thin soils are at higher risk since they have poor root systems.

Individual selection is the systematic removal of trees at regular intervals to maintain an un-even aged stand. This allows for more space and sunlight to increase yield, establish new age classes, and increase the vitality of the overall stand. An un-even aged stand has at least three age classes (DNR, 2021) and trees are harvested from each class to remove the poorest quality trees and increase the quality of the stand over time. Less than one third of the stand is removed every 20 to 30 years, it is important to still leave snags and cavity trees to promote biodiversity (DNR, 2021).

Group selection is a variant of individual selection by which the un-even age stand of the area can be maintained with a series of patch cuts that will regenerate within a few years to form a new age stand. The size of the patch can widely vary depending on the area but typically ranges from 0.2-.8 hectares in size. Patch cuts are often logistically easier allowing the harvested wood to be extracted more efficiently.

Table 3.1 – The six Pockwock tributary monitoring catchments sites and their associated forest management treatment.

Monitoring Site ID	Stream	Treatment	Total Area (ha)	Planned Disturbance Area (ha)	Comment
S1-1	East of Long Gullies	Group Selection	123.8	10.2	Downstream of Wetland
S2-1	Peggy's Brook	Control	306.3		Provincial Protected Land
S3-1	Crane Nest Brook	Control	121.0		Future Forest Harvest
S4-1	Long Ponds	Commercial Thinning & Individual Selection	26.1	12.5	Headwater
S4-2	Long Ponds	Commercial Thinning & Individual Selection	401.0	82.6	Downstream of Wetland
S5-1	Long Gullies	Variable. Retention. Harvest (30%)	260.2	9.9	

3.1.3 Local Geology

Pockwock Lake and its tributaries are underlain by two dominant rock types: metasedimentary rocks of the Cambro-Ordovician Meguma Supergroup, and granitoid rocks of the of the Devono-Carboniferous South Mountain Batholith (Figure 2.3). All of the monitoring sites and associated tributaries are underlain by a medium- to coarse-grained megacrystic granodiorite of the South Mountain Batholith that lies north of Pockwock Lake and extends a few 100 metres to the central south side of the lake. The soil in subcatchments is partially derived from this bedrock and has a strong influence on water quality. The eastern and most of the southern side of the lake is underlain by the metasiltstone and slate of the

Goldenville Group. The west side of the lake is underlain by the Panuke Lake Leucomonzogranite.

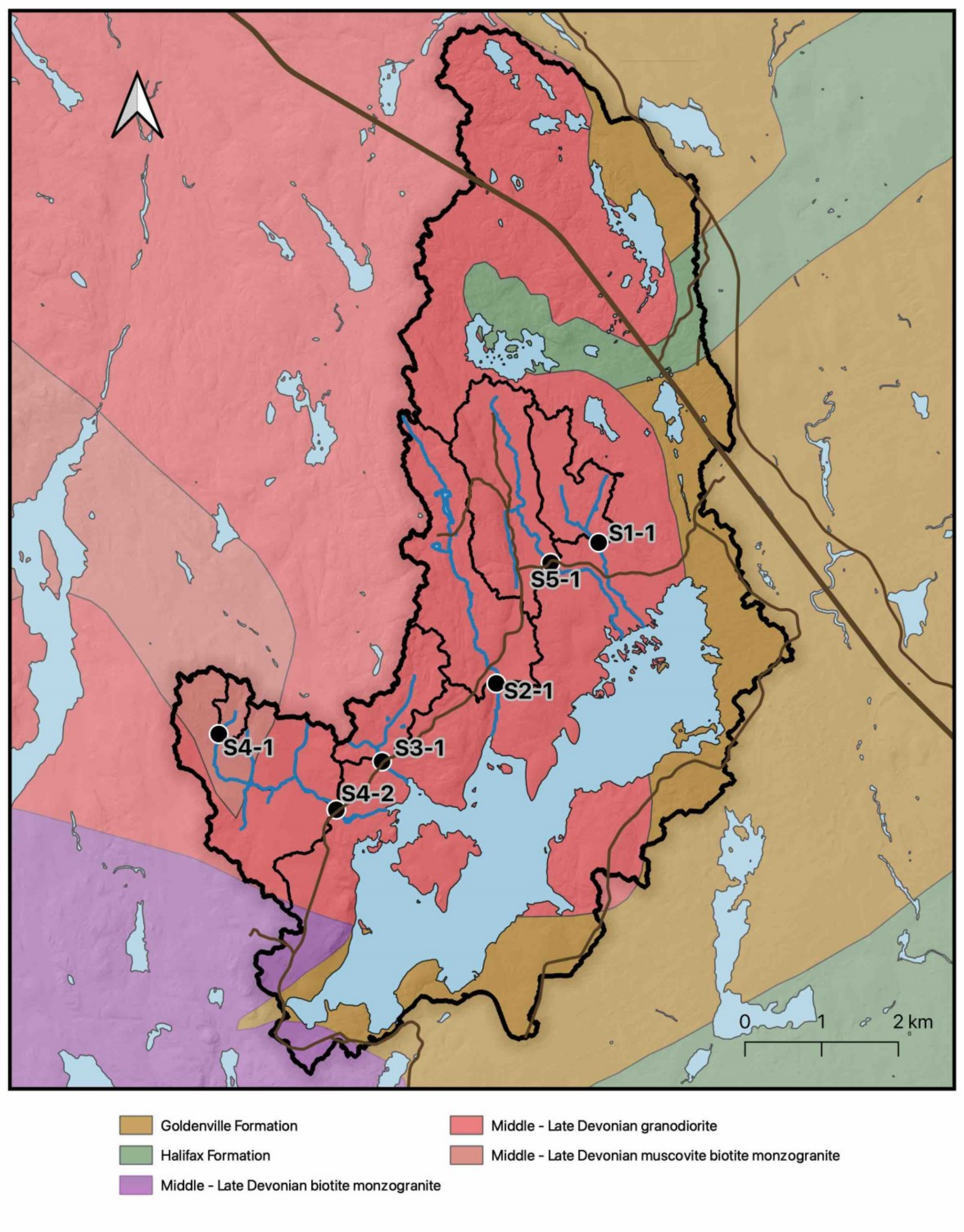

Figure 3.3 – **Pockwock watershed monitoring sites and bedrock geology map.**

The study area has experienced a complex glaciation history during the last ice age (Wisconsinan; 85 to 11 ka) with advance and retreats related to several ice centres in the Maritimes. Consequently, the surface has been completely glaciated and the last glacial episode of the Late Wisconsin ice sheet has largely removed evidence of earlier glacial episodes. Rocks at the surface have been smoothed, rounded and covered by a till of up to 5 m. Table 2.2 summarizes the surficial geology units.

The northern part of the watershed is mostly underlain by pre-last glaciation bedrock. The rest of the area has a several metres of thick stony till plain with a sandy matrix derived from local bedrock sources (Figure 2.4). Podsolization is the soil forming process in the Pockwock watershed area that has been taking place since the last glaciation.

Table 3.2 – Pockwock watershed surficial geology units.

UNIT	PERIOD	STAGE	GLACIATION	THICKNESS
Stony Till Plain	Quaternary	Wisconsinan	last glaciation	2 – 20 m
Bedrock	Pre-Quaternary	unknown	pre-last glaciation	unknown
Silty Drumlin	Quaternary	Wisconsinan	last glaciation	4 – 30 m
Stony Till Plain	Quaternary	Wisconsinan	last glaciation	2 – 20 m

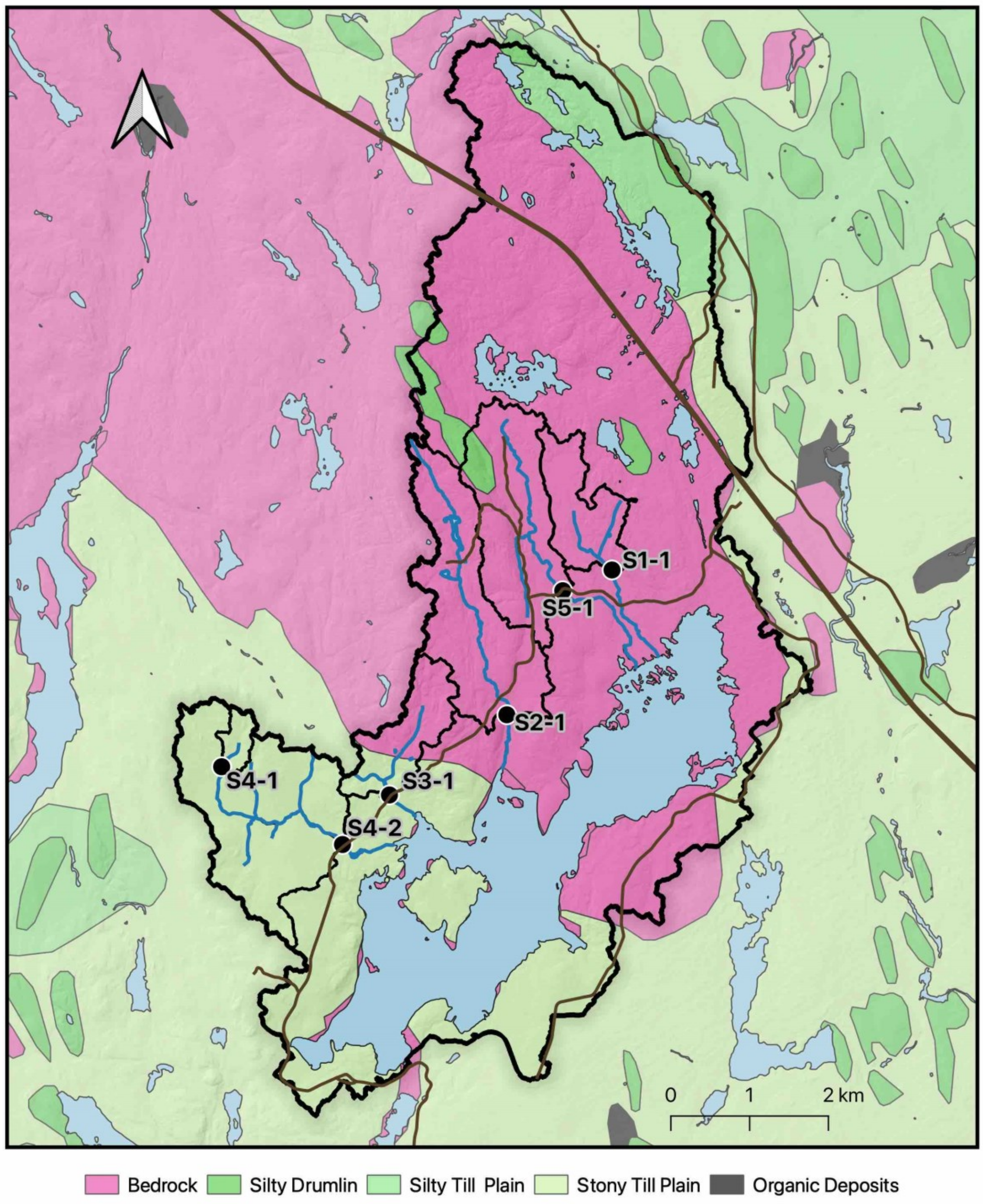

Figure 3.4 – Pockwock watershed monitoring sites surficial geology map.

3.1.4 Physiography, Vegetation and Hydrology

The Pockwock watershed has an elevation ranging from ~ 80 to 220 m (Figure 2.5) with the higher elevation areas underlain by the South Mountain Batholith granitic rocks. The area is well drained by streams north of the lake; the streams have reaches that expand into wetlands and still waters, while others are steep with rapids. The region receives over 1400 mm of precipitation annually and the mean temperature is 5.8 °C (Environment Canada).

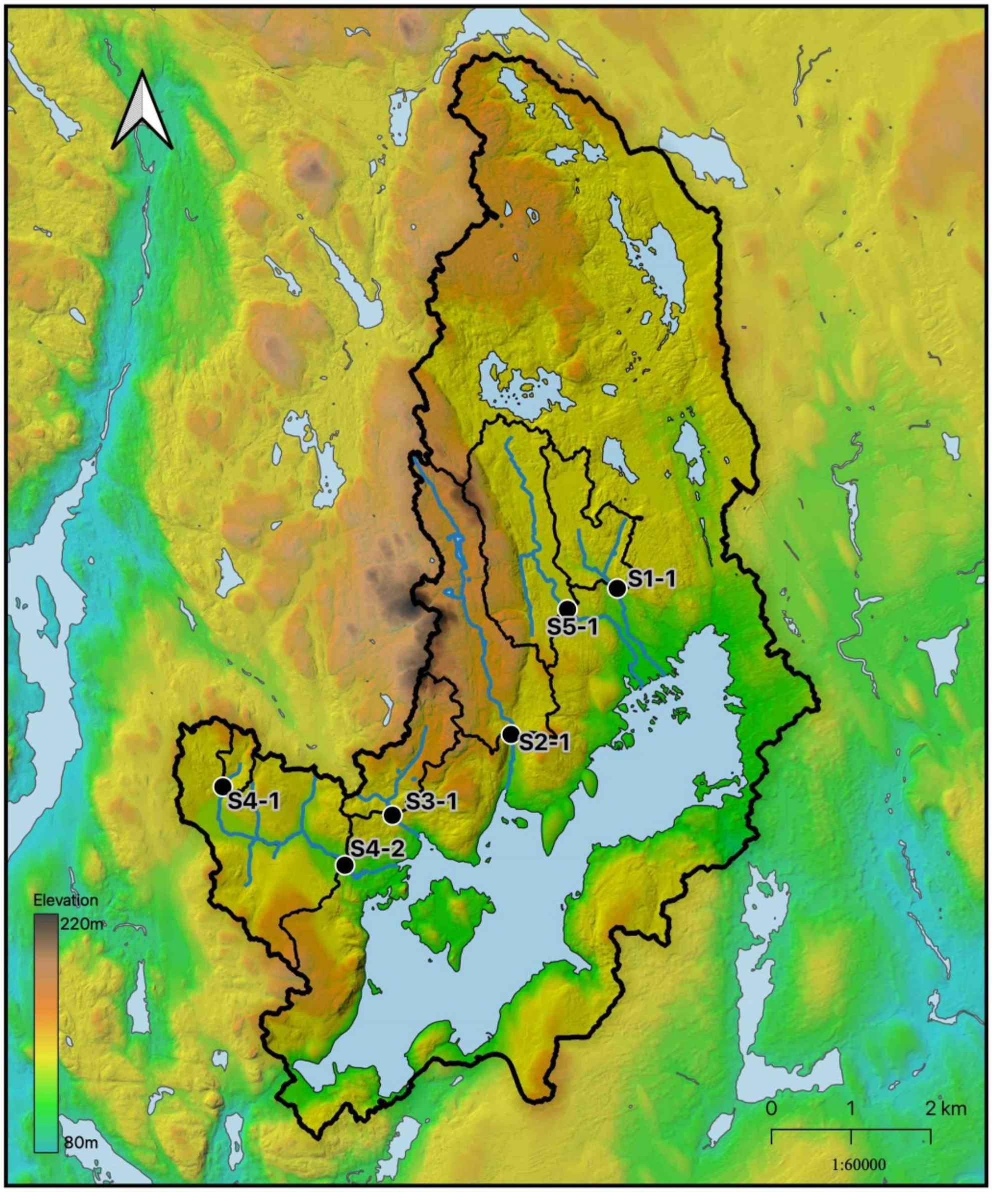

Figure 3.5 – Topographic map of Pockwock watershed.

The study area is in a typical Acadian Forest region with mixed wood composition of coniferous and non-coniferous trees with abundant ferns and moss throughout.

Typical tree species consist of red spruce (Picea rubens), balsam fir (Abies balsamea), white pine (Picea glauca), red maple (Acer rubrum), yellow birch (Betula alleghaniensis), and white birch (Betula papyrifera). However, due to the intensive history of forestry in the area, there is an uneven abundance of red spruce (Halifax Water, 2009). Figure 2.6 displays the forest inventory for the six Pockwock monitoring site catchments. Percentages of each forest class were calculated and summarized in Figure 2.7 to aid in understanding the impact on various water quality parameters. The mean slope and shape length were calculated from a 5 m DEM using the method presented by Jankowskj & Schindler (2019).

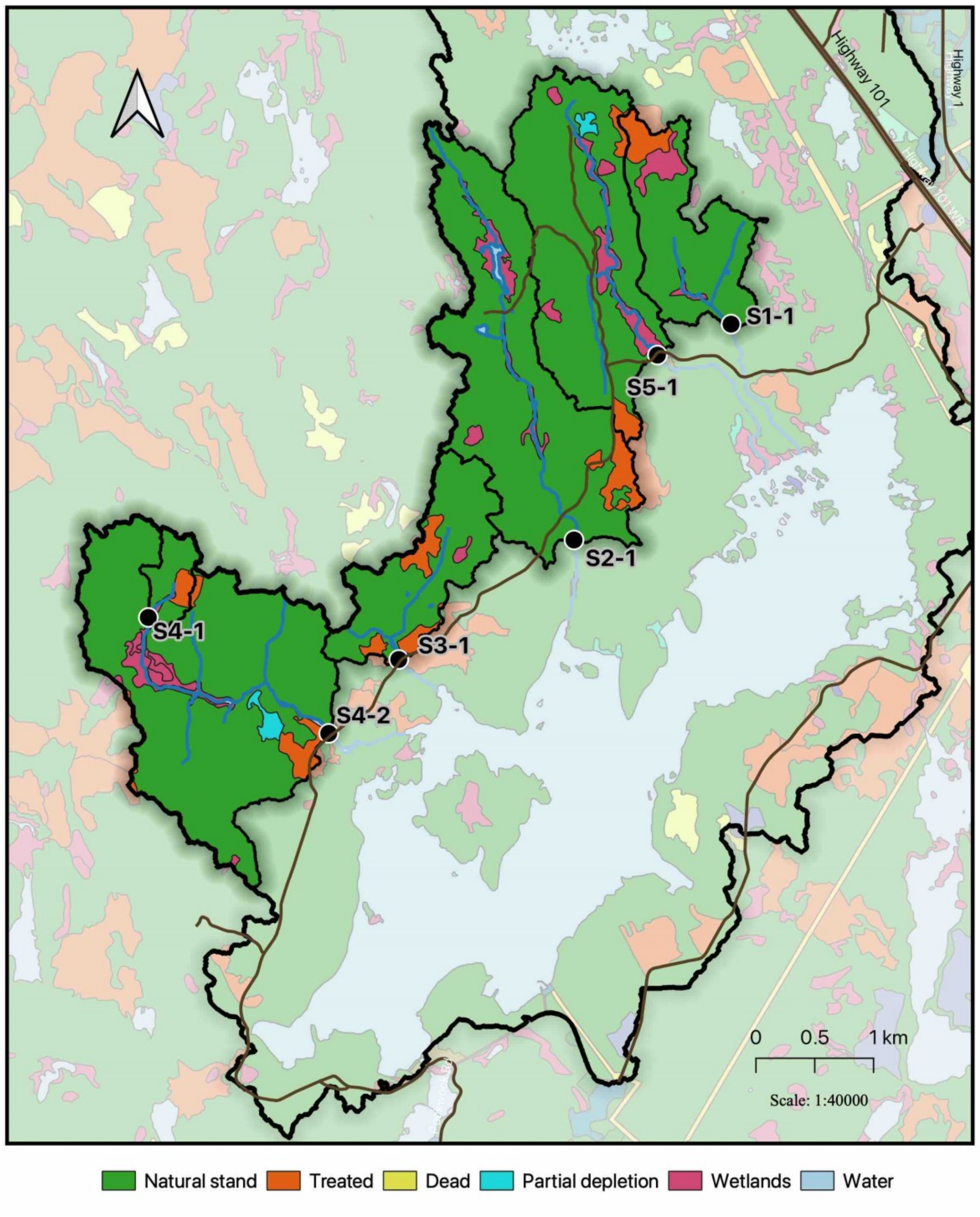

Figure 3.6 – **Forest inventory of the six Pockwock watershed monitoring site catchments.**

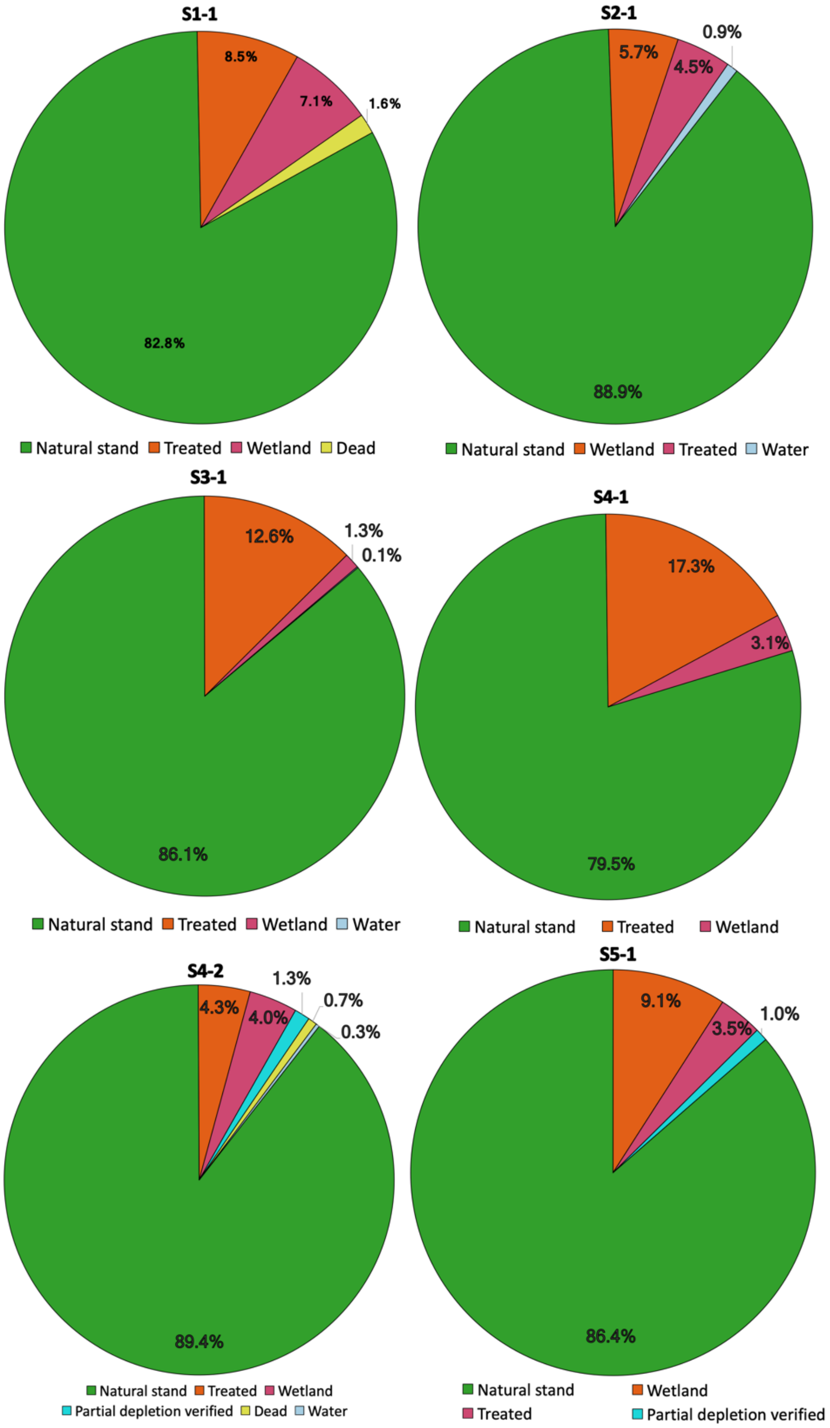

Figure 3.7 – **Forest inventory of the six Pockwock watershed monitoring catchments.**

3.1.5 Historical Activity

The Pockwock watershed and surrounding area has had an intensive forest management history since the early 1800s, with sawmills being constructed at the foot of Pockwock Lake and Pockwock Falls. In 2003, best management practices (BMPs) were developed by Halifax Water and the Pockwock Watershed Management Committee to aid in watershed management.

With the advancement of digitization, documentation of past forest harvest activities has recently become available. Datasets were obtained from James Steenberg, a senior research forester with the Nova Scotia Department of Natural Resource and Renewables. Forest harvesting has been well documented in Pockwock watershed on crown land since 1997 and is shown in Figure 2.8.

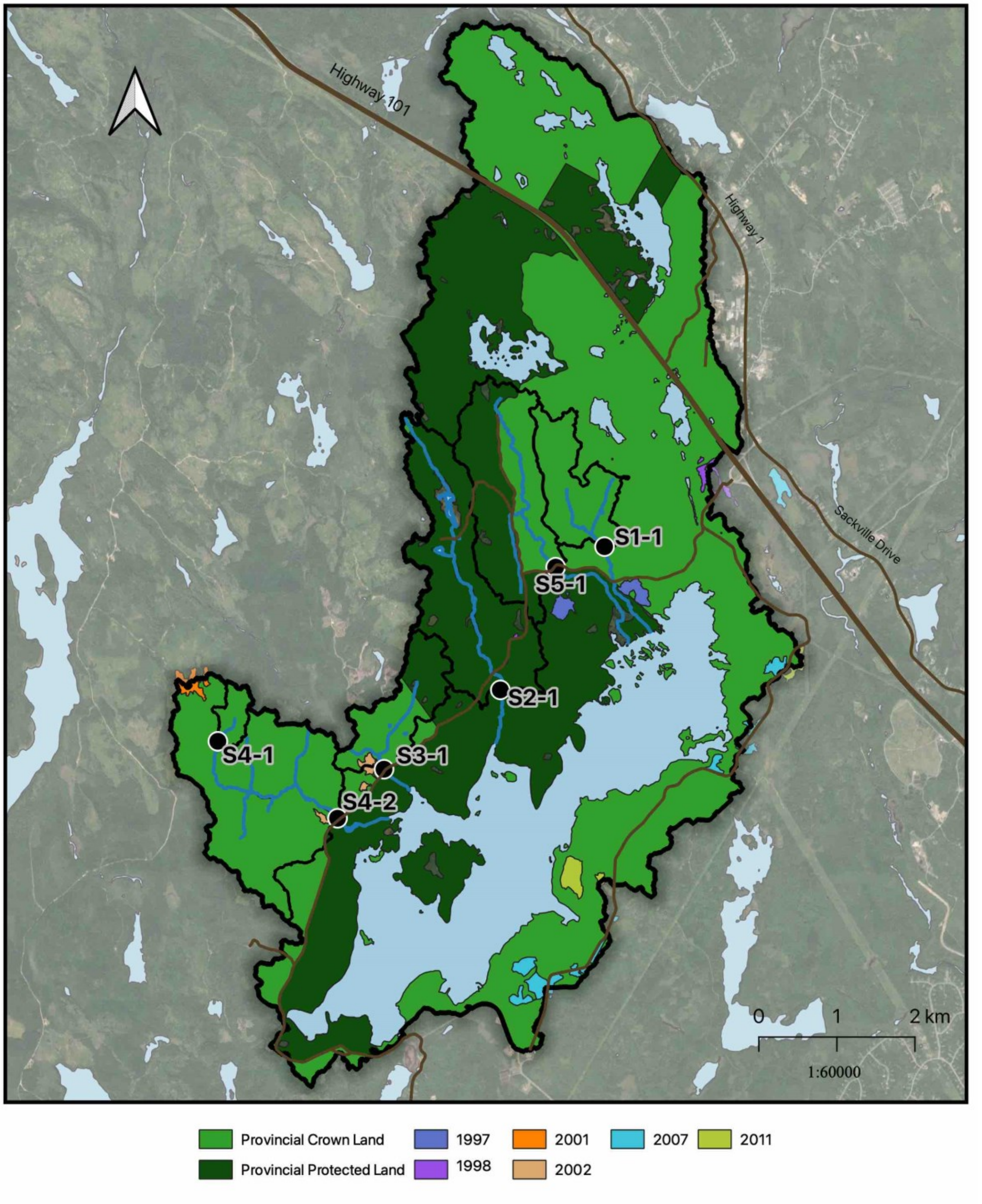

Figure 3.8 **– Forest harvests on crown land in Pockwock watershed since 1997.**

Forest harvesting on private land is not nearly as well documented and there is no official historical record. The Nova Scotia Department of Natural Resources and Renewables interpreted harvest dates of the Pockwock area using historic Landsat imagery as shown in Figure 2.9, however there is notable limitations, errors, and uncertainties with this method.

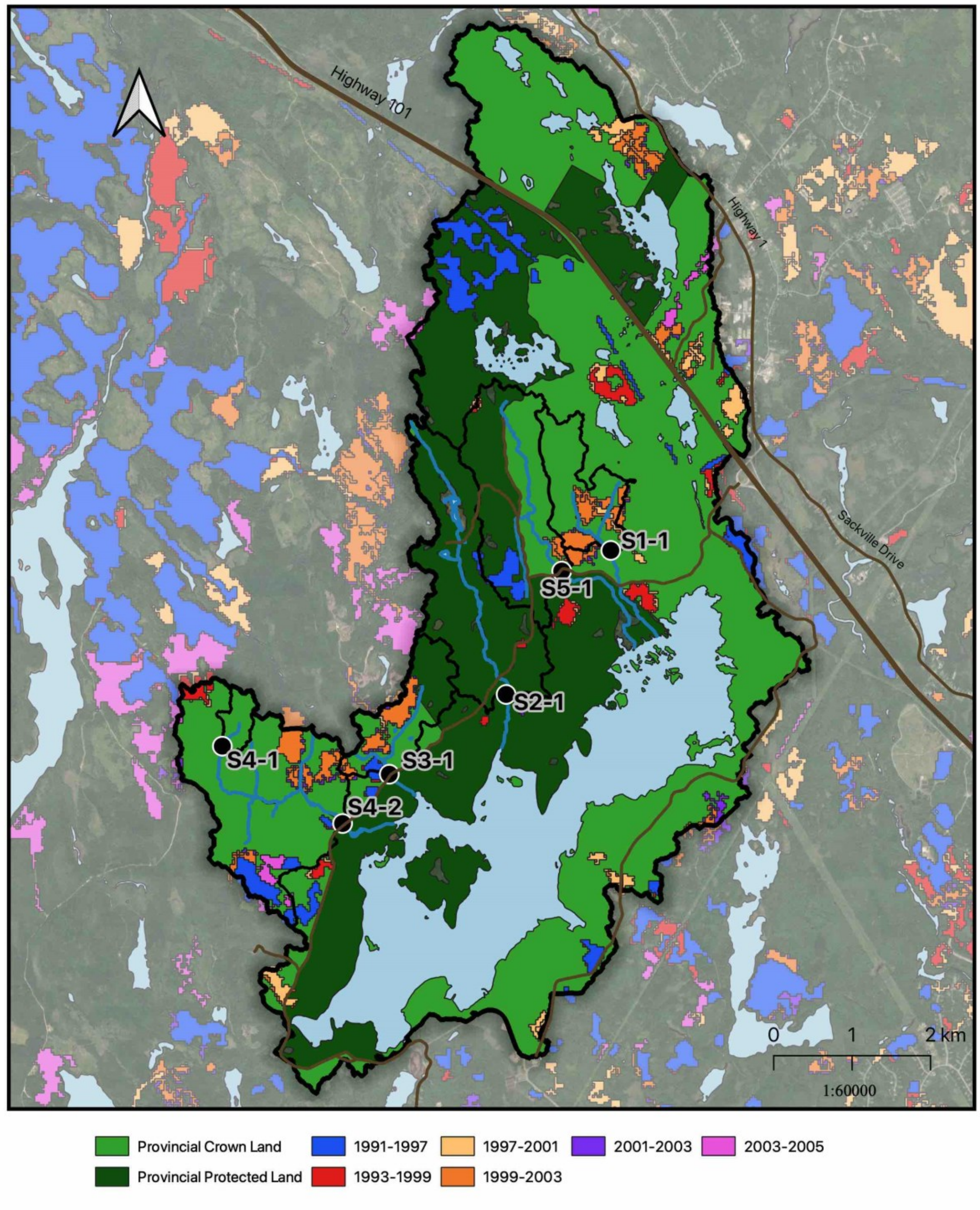

***Figure 3.9* – Forest harvest on crown and private land in Pockwock watershed since 1991 using Landsat imagery.**

3.2 Data Collection

A one year monitoring program was conducted from September 2018 to August 2019 at the six monitoring sites to collect water quality data and streamflow measurements. Intensive sampling during five selected hydrologic events from May to November 2019 was conducted to measure short term temporal variation in water quality parameters.

3.2.1 Stream Water and In-situ Measurements

Stream water collection has been ongoing since August 2018 by the forWater Atlantic Maritime research node at bi-weekly to monthly frequency depending on precipitation events and site access, notably during the winter and wet months. The samples were taken using a clean 1 L polyethylene bottle that had been rinsed three times with the sampling water before sample collection. Samples were then placed in a cooler with ice packs for transportation to the laboratory for analysis.

For the intensive sampling, auto samplers (ISCO, Lincoln, NE) were programmed to collect a 1 L sample every two hours for a 48-hour period. The auto samples were pre-programmed a day before the upcoming hydrologic event to allow for the capture of baseline conditions, rising limb, peak flow, and falling limb of the hydrograph. Three of the six monitoring catchments were chosen for intensive sampling. S2-1 is a control and will have no forestry activity occurring in its drainage catchment. S4-1 is located near the headwater of a stream that will have commercial thinning occurring upstream of it. S4-2 is 2.5 km downstream of S4-1 and was chosen to investigate the impact of a large area of wetland between the two catchments. Table 2.3 outlines the dates of the intensive sampling events. Samples were not captured at all sites during the dates due to technical difficulties.

Table 3.3 **–** Pockwock watershed selected monitoring catchments and intensive sampling dates.

Date	S2-1	S4-1	S4-2	48-hour rainfall (mm)
2019/05/14	Yes	Yes	Yes	19
2019/05/24	Yes	Yes	No	18
2019/07/23	Yes	Yes	Yes	21
2019/09/07	No	Yes	No	128
2019/11/12	Yes	Yes	Yes	47

Each monitoring site had a YSI EXOSonde2 (Hoskin Scientific LTD, Oakville, Ontario) installed to continuously pH, conductivity, temperature, total dissolved solids, and dissolved oxygen on a 30-minute interval. During each site visit, a YSI 650 MDS Sonde (Yellow Springs, OH, USA) was deployed to measure pH, conductivity, temperature, dissolved oxygen, and oxidation-reduction potential (ORP).

pH is a useful indicator of water quality because it has a strong effect on the solubility of many elements and the reaction rates of organic matter decay. Water with equal activities (concentrations) of H^+ and OH^- are neutral at pH 7 at 25 °C. When pH values are below 7, the solution is acidic, containing extra H^+ ions, whereas when pH values are above 7, the solution is considered basic, containing extra OH^- ions. At approximately 100 °C, the pH of neutral water (with equal concentrations of H^+ and OH^-) is 6.0 and at 0 °C the pH of neutral water is 7.5, as temperature influences the pH of neutrality. When exposed to air, carbon dioxide from the atmosphere dissolves into water to form carbonic acid and consequently lowers the pH of water (which otherwise would be neutral, with a pH of 7). Deionized water in equilibrium with CO_2 in the atmosphere ($f_{CO2} = 10^{-3.5}$) has a pH of 5.65.

Electrical conductivity is the ability of a material to transmit (conduct) an electric current and is commonly expressed in milliSiemens per centimetre (mS/cm). Electrical conductivity is a measurement that correlates with soil properties, including cation exchange capacity, water saturation, organic matter concentration, salinity, and other soil characteristics (Grisso et al., 2009). Temperature impacts the rate at which carbon is broken down on the forest floor, as well as DOC solubility within the soil horizon (Wallin et al., 2015).

Dissolved oxygen (DO) is a measure of the amount of oxygen dissolved in the stream, turbulence aeration, and photosynthesis occurring in the water body (Pike et al., 2010). DO is expressed in mg/L or as a percentage; the % saturation level is the maximum amount of DO that can be reached in the water body based on the temperature and atmospheric pressure. Water temperature is the most important factor in controlling DO concentrations. Decreases in DO are proportional to the increase in water temperature that can result from changing environment such as forest harvesting activities (Hanson et al., 2006). Increased deposition of organic matter and DOC in the stream may also increase the biological activity in the water body and further decrease DO (Brown, 1985). Increased levels of turbidity and total suspended solids also lower the DO concentrations by preventing movement of oxygen through the water column and into the streambed (Everest et al., 1987).

HOBO water level loggers (Onset Computer Corporation, Bourne, MA, USA) were installed at each monitoring site to collect continuous water level data on a 30-minute interval. They were installed in PVC pipe with holes throughout the bottom to allow free water flow. The pipe was secured to rebar hammered into the stream bed. An atmospheric logger was fastened to a tree at a height of 2 m at monitoring site S2-1 to measure barometric pressure.

3.2.2 Streamflow Measurements and Calculations

Discharge was measured at each monitoring catchment throughout the study period at various flow conditions using a SonTek FlowTracker Handheld-ADV (SonTek, San Diego, California). The location of each stream gauging cross section (Figure 2.2) were chosen based on relatively straight and uniform flow conditions. Woody debris and large rocks were moved at the start of the monitoring program to allow for more consistency in the measurements. Discharge was determined by measuring the cross-sectional width of the channel perpendicular to the flow direction. Each cross-section was then further broken down into subsections (n = 4 – 10) depending on the width of the stream, consistency of the subsections, and time of year. Each subsection varied in width from 10-60 cm and the water depth was measured at each location. The velocity area Six-Tenths-Depth method was used (Dingman, 2002). Total discharge (m^3/s) was then calculated using the following formula:

$$Q = \sum_{i=1}^{N} V_{avg} \cdot A_i \qquad [3.1]$$

where:

V_{avg} = average current velocity for each sub-section (m/s)

A_i = area of each sub-section (m^2)

Continuous hourly and daily flow was calculated for each of the monitoring sites using the data from HOBO water level loggers installed in each monitoring catchment and the stream gauging measurements. The pressures were corrected for barometric pressure using the HOBO water level logger installed in a tree near catchment S2-1, by subtracting the barometric pressure from the measured stream water pressure for each measurement. The water levels (m), at each catchment were calculated with the following formula:

$$h = \frac{P}{pg} \qquad [3.2]$$

where:

P = absolute pressure (Pa)

p = density of water at field temperature (kg/m^3)

g = acceleration due to gravity (m/s^2)

A regression analysis was done using the discharge and corresponding water levels by selecting the best fit R^2 value in Microsoft Excel™ to calculate a trend line.

3.2.3 Climate Measurements

The forWater Atlantic Maritime research node installed a weather station in the summer of 2018 at the old landfill site off of landfill road about 5 km southeast of Pockwock Lake. However, the datum set was not complete for the timeframe of the study period. The weather data was instead obtained by the nearest Environment and Climate Change Canada (ECCC) climate station at the Halifax Stanfield International Airport (44°52'48.060" N, 63°30'00.050" W) ~20 km east of Pockwock Lake.

3.3 Water Quality Parameters

The samples once collected were stored in a cooler with ice packs until the arrival to a laboratory and from which they were either processed, stored in a 4 °C fridge and processed within the 48-h hold time, or frozen and processed at a later date.

3.3.1 Total Organic Carbon and Dissolved Organic Carbon

Total and dissolved organic carbon (TOC; DOC) were measured in the Centre for Water Resources Studies laboratory using the High-Temperature Combustion Method (5310B; Standard Methods for Examination of Water and Wastewater, 1999). The analyzer used was a Shimadzu TOC-V_{cph} (Shimadzu, Boston, MA, USA.). DOC was filtered through a 0.45 µm Whatman membrane filter. The detection limit for DOC and TOC was 0.25 mg/L.

3.3.2 DOC Characteristics

UV-254 was measured with a 10 mm rectangular with an open top Far UV Quartz Cell (Hach, Loveland Colorado, USA) in a DR 5000 Spectrophotometer (Hach, Loveland Colorado, USA) with method 410 Organic UV-254, using sample water filtered through a 0.45 µm Whatman membrane filter. The specific ultraviolet absorbance (SUVA, L/mg-M) was calculated by dividing the UV-254(cm^{-1}) by the DOC (mg/L).

The F-EEM was measured with a 10 mm UV Quartz Cell in a Aqualog 0139S-3212-AL (Horiba Jobin Yvon Edison, NJ, USA) with the Determining Fluorescent Properties of NOM in Water (April 7, 2014) by Dalhousie University method, using filtered sample. A parallel factor analysis (PARAFAC) outlined by Stedmon and Bro (2008) was applied to the DOC F-EEMs results in MATLAB software. The FI, HIX, and BIX were then calculated from the PARAFAC results using the following formulas:

$$FI = \frac{X_{370,450}}{X_{270,500}} \qquad [3.3]$$

$$HIX = \frac{\sum_{em=435}^{480} X_{254,em}}{\sum_{em=300}^{345} X_{254,em}} \qquad [3.4]$$

$$BIX = \frac{X_{310,380}}{X_{310,430}} \qquad [3.5]$$

3.3.3 Turbidity and Total Suspended Solids

Turbidity was measured using Standard Method 2130 on a HACH Turbidimeter TL2350 (HACH, Loveland, CO, USA). The instrument was zeroed with Milli-Q water and non-filtered samples were analyzed. The detection limit using this method was 1 mg/L.

Total suspended solids (TSS) was measured by passing a known volume of sample through a Whatman 47 mm glass microfiber filter. The filters were pre-heated in a 100 °C oven for at least one hour in a tin foil tray, transferred and stored in a desiccator until used, transferred back into the over for at least six hours. TSS (mg/L) was calculated using the volume of the sample filtered (L), initial filter mass (mg), and final filter mass (mg).

3.3.4 Nutrients (Nitrogen and Phosphorus)

Total nitrogen (TN) was measured using the persulfate digestion method (Method 10071) from Hach Ltd. The detection range was between 0.5 and 25.0 mg/L N. Test 'N Tube vials were heated in a DRB200 reactor and analyzed in a DR 5000 spectrophotometer using the 350 N, Total LR TNT (25.0 mg/L limit) program.

Total and dissolved phosphorus were measured using the ascorbic acid method (Murphy and Riley, 1962). The detection limit was 1 μg/L using a 100-mm path length cell. The samples first had to be digested using the persulfate digestion method by Menzel and Corwin (1965). The samples for dissolved phosphorus were first filtered through a 0.45 μm cellulose membrane filter. The instrument used was a LKB Biochrom Ultrospec 4051 (SpectraLab, ON, Canada).

3.4 Data Analysis

3.4.1 Seasonal variation

To assess seasonal trends amongst the individual catchments, box and whisker plots were made in Microsoft Excel™.

3.4.2 Loading Estimates

Seasonal and annual loads of TOC, DOC, TP, DP, TN, and TSS were estimated for the study subcatchments. using the online LOADEST software tool (Runkel et al., 2004), which generates regression equations to predict constituent concentrations on unsampled dates.

3.4.3 Quality Assurance and Quality Control

Throughout laboratory analysis, duplicate and triplicate analysis was completed to characterize sample variability. Triplicates were done for one sample picked at random for each monitoring catchment sample batch for TOC, DOC, TN, and turbidity. TP and DP were analyzed in duplicate for all samples. TSS was analyzed in singular samples due to physical constraints on collecting and transporting multiple 1 L samples per monitoring catchment. Results are displayed in Appendix 3.

3.4.4 Statistical Analysis

To determine significant differences between monitoring catchments and the water quality parameters, various statistical analyses were conducted using Minitab statistical software. A one-way analysis of variance (ANOVA) was performed on individual water quality parameters to test the null hypothesis (H_O) that the five monitoring catchments are equal vs. the alternative hypotheses (H_a) that at least one mean is different using the following formula:

$$H_O = \mu_1 = \mu_2 = \mu_3 = \cdots = \mu_k \quad [3.6]$$

where:

μ = group mean

k = number of groups

A general linear model was used to compare seasonal variation in the water quality parameters for each of the monitoring catchments. Boxplots were created for each water quality parameter by monitoring catchment and categorized in the four seasons. This allowed for visualization of seasonal variation between monitoring catchments. Linear regressions were produced to define the relationship between TOC and DOC in each of the monitoring catchments. This allowed for TOC to be calculated from DOC when it is not analyzed. Linear regressions were also used to determine if there were correlations between discharge and concentration.

CHAPTER 4: Results and Discussion

4.1 Catchment Hydrology

Climate datum, stream gauging measurements, and continuous in-situ water level measurements were used to develop hydrographs for the five catchments from September 2018 to August 2019. Climate datum was obtained from the nearest ECCC weather station, Halifax Stanfield International Airport, and was compared to the 1981-2010 climate normals. Table 3-1 summarizes annual and seasonal variation in temperature and precipitation for 2018, 2019, the study period, and the climate normals. Average temperature during the study period was similar to climate normals with less than 1 °C variance on a seasonal and annual basis. The total annual rainfall during the study period was 9% higher than the climate normal with larger differences observed seasonally. The spring and fall rainfall amounts were 16% and 28% greater, respectively; the winter total precipitation was 18% lower and the summer total was 2% lower. Despite an increase in precipitation and similar temperatures to the climate normals, the average snowpack depth was lower during the study period. In summary, the study period possessed comparable climate to long-term normals observed in the region, with moderately higher precipitation.

Table 4.1 – Yearly and seasonal variation of temperature, precipitation, and snowpack measured at the Halifax Stanfield International Airport.

Time Frame	Max Temp (°C)	Min Temp (°C)	Mean Temp (°C)	Total Rain (mm)	Total Snow (cm)	Total Precip (mm)	Average Snow Depth (cm)
2018							
Full Year	12.0	2.6	7.4	1358	271	1601	2.1
Spring	9.6	0.4	4.9	468	103	566	3.1
Summer	23.9	13.2	18.6	302	0	302	0.0
Fall	13.0	4.2	8.6	468	47	507	0.6
Winter	1.3	-7.7	-3.2	298	121	404	3.5
2019							
Full Year	11.4	2.1	6.8	1283	222	1494	2.0
Spring	8.2	-0.8	3.7	507	68	572	2.3
Summer	23.4	12.9	18.2	292	0	292	0.0
Fall	13.5	4.4	9.1	401	31	431	0.6
Winter	0.3	-8.3	-4.0	249	123	365	4.5
Study Period							
Full Year	11.2	1.9	6.5	1305	235	1522	1.8
Spring	8.2	-0.8	3.7	341	68	406	3.0
Summer	23.4	12.9	18.2	292	0	292	0.0
Fall	13.0	4.2	8.6	468	47	507	0.6
Winter	-0.3	-9.0	-4.7	204	120	317	3.5
Climate Normals 1981-2010							
Full Year	11.3	1.9	6.6	1196	221	1396	3.0
Spring	9.2	-0.5	4.4	295	55	347	2.3
Summer	22.6	12.4	17.5	285	0	285	0.0
Fall	13.3	4.5	8.9	366	17	381	0.3
Winter	-0.1	-8.8	-4.5	250	149	383	9.3
Change Between Climate Normal and Study Period							
Full Year	-0.1 °C	0.0 °C	-0.1 °C	9.1%	6.2%	9.0%	-1.2 cm
Spring	-1.0 °C	-0.3 °C	-0.7 °C	15.6%	23.6%	17.2%	0.7 cm
Summer	0.8 °C	0.5 °C	0.7 °C	2.4%	0.0%	2.4%	0.0 cm
Fall	-0.3 °C	-0.3 °C	-0.3 °C	28.0%	176.5%	33.0%	0.3 cm
Winter	-0.2 °C	-0.2 °C	-0.2 °C	-18.5%	-19.6%	-17.3%	-5.8 cm

There were differences in annual water yield (m^3/yr/ha) between the study catchments (Table 3.2), and these differences were correlated with catchment characteristics. In general, higher slopes, smaller catchment areas, and smaller percentages of wetland produced greater water yield (per ha). Catchment S4-2 had the smallest water yield; this was the largest catchment and possessed a moderate percentage of wetland area (4%) and the lowest average slope (6.7°). Catchment S4-1 had the largest water yield; it was the smallest catchment and had a low wetland fraction (3.1%) and higher average slope (7.5°). Catchment area had the largest correlation (-0.73) with water yield, mean slope (degrees) is 0.57, and wetland percentage is -0.51. Lower slopes, and greater wetland percentages, would result in greater storage in the landscape, which would reduce runoff and facilitate evapotranspiration and groundwater recharge.

Table 4.2 – Study catchment characteristics.

Catchment	Area (Ha)	Wetland %	Mean Slope (degrees)	Yield (m^3/year/ha)
S1-1	124	8.7	6.7	6730
S2-1	306	4.5	8.2	13540
S3-1	121	1.3	8.6	14400
S4-1	26	3.1	7.5	27040
S4-2	401	4.7	6.1	2080

The annual hydrographs for all catchments are presented in Figures 3.1 and 3.2 (m^3/day; m^3/day/ha). Annual hydrographs for individual catchments are provided in Appendix A. In general, large rainfall events during the early summer, late fall, and early winter correlate with the largest flow values. During these times of the year soil moisture levels would be higher, and soils could potentially be frozen, resulting in less infiltration and more direct runoff. The late winter and early spring periods would also be influenced by the presence of a melting snowpack. All catchments respond quickly to rainfall events (< 1 day) indicating that runoff processes are driven by surface runoff or rapid interflow. Baseflow values are much lower than stormflow values, and the smaller catchments had non-measurable discharge during extended dry periods in the summer. Visual examination of the extended baseflow recession curves demonstrate that shallow groundwater flow are likely dominant sources of water to these streams during baseflow. Similar results were measured by Van Gaelen at al. (2014), who observed discharge rapidly rising up to several hundred times the base flow during large events and rapidly returning back to pre-event baseflow discharge. The Pockwock watershed has a shallow groundwater table flowing through fractured granite bedrock that is either exposed or overlain by thin till and soil. During rain events, contributions from interflow and surficial flow added large quantities of water to the stream causing the large spike in discharge.

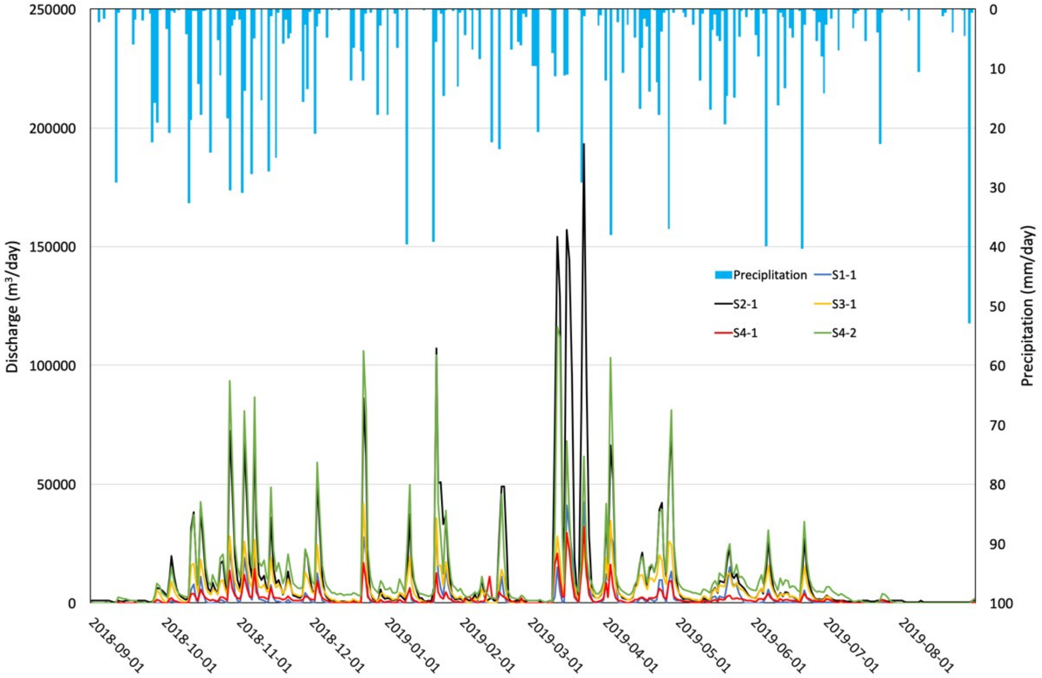

***Figure 4.1* – Hydrograph and hyetograph for the five monitoring catchments. The discharge has been averaged to daily values (m^3/day).**

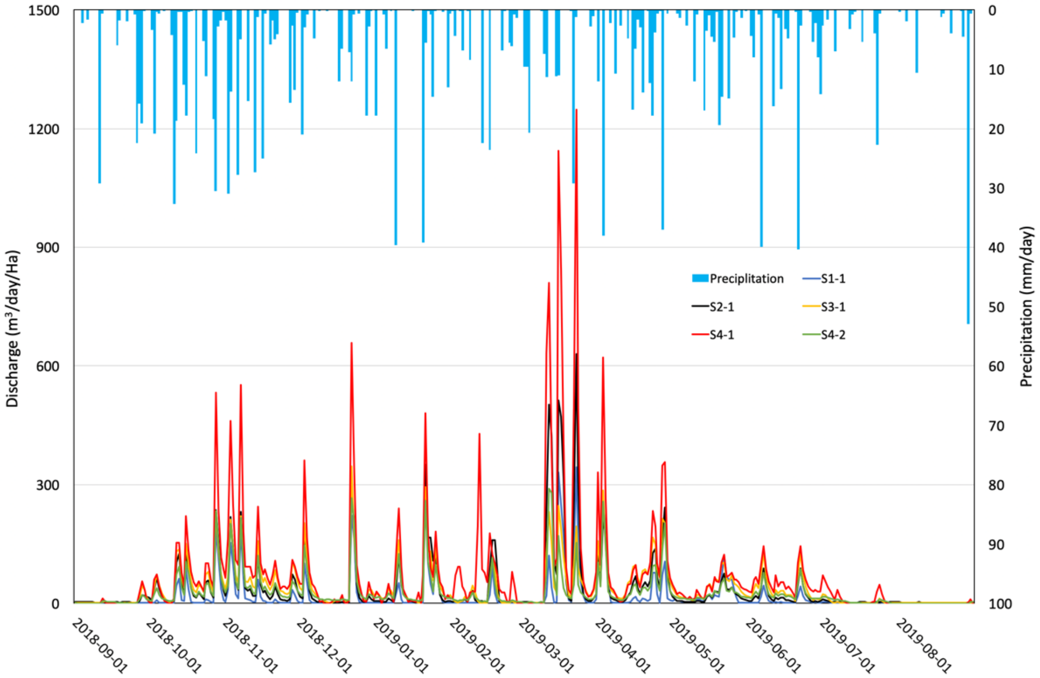

Figure 4.2 **– Hydrograph and hyetograph for the five monitoring catchments. The discharge has been averaged to daily values per unit area (m^3/day/ha).**

To better illustrate the effects of antecedent conditions on hydrograph response, air temperature and snowpack depth are plotted in Figure 3.7 for catchment S1-1. The addition of these variables helps explain the discharge peaks, especially in the early spring. The two largest discharge peaks in March are a result of temperatures rising above freezing point, and subsequent snowmelt runoff. A study on seasonal TOC export from boreal catchments in northern Sweden by Laudon et al. (2004) found that TOC export during spring melt was 50% to 68% of the annual TOC export from the seven catchments. The annual precipitation is this region is 600 mm of which 35% falls as snow. The study demonstrated the importance of snowpack on constituent loading and how varied it can be between years depending on the size of the total snowpack before spring melt.

There was a large precipitation event in late August that appeared to have little impact on streamflow. Even though soil moisture levels would have been relatively low at this time, and there would have been a full canopy, a streamflow response would have been expected for this magnitude of rainfall (50+mm). It is suspected that the magnitude of this precipitation event was less in the Pockwock watershed than what was recorded at the Halifax Stanfield International Airport. A climate station has since been installed adjacent to the watershed to provide more spatially representative precipitation data.

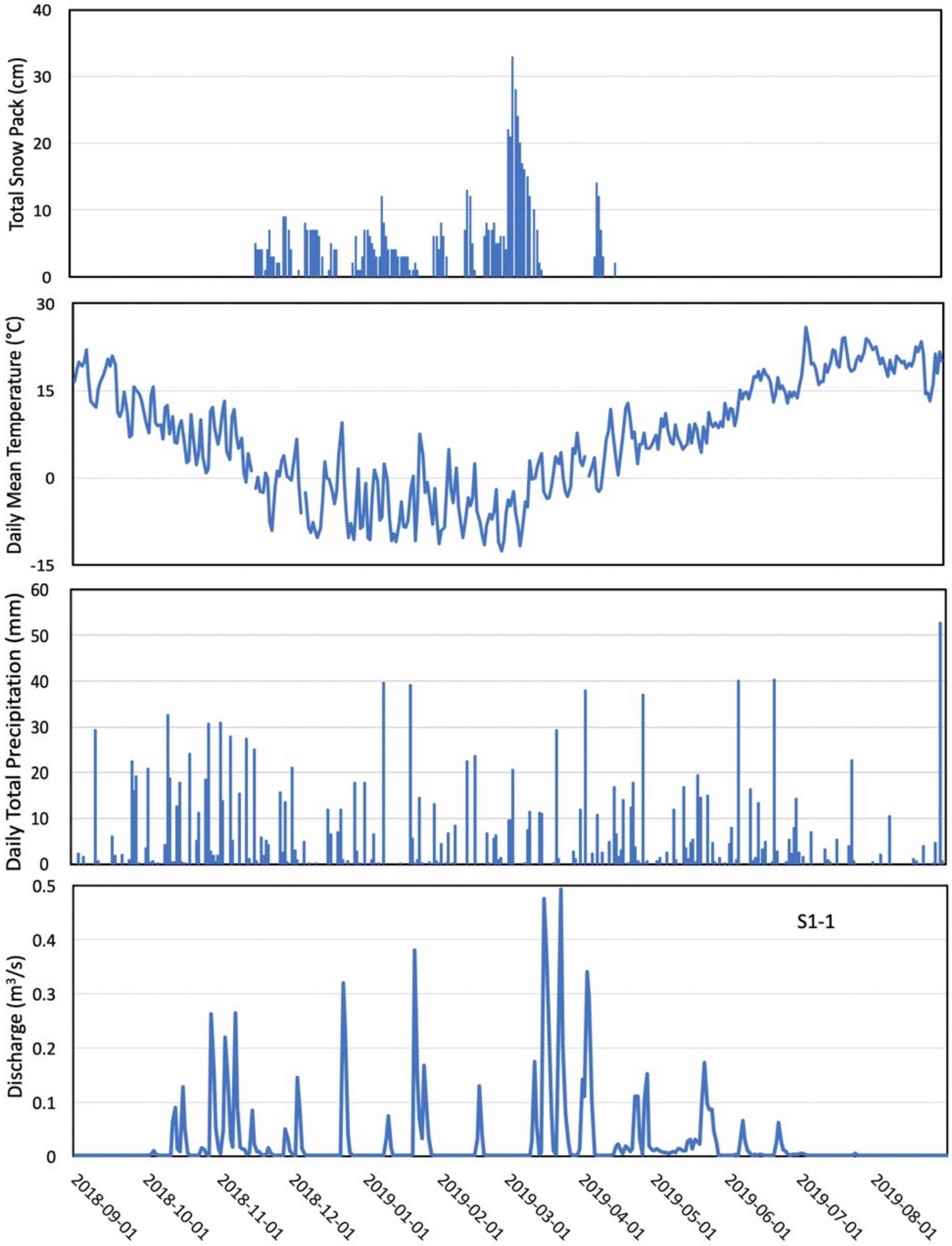

Figure 4.3 **– Stacked graphs of daily discharge, precipitation, temperature, and snowpack with a shared timescale on the x-axis for S1-1 monitoring catchment.**

4.2 Seasonal Water Quality Characteristics

Water samples were collected once or twice a month, depending on precipitation frequency and road access, from September 2018 to August 2019. The objective was to provide a baseline characterization of water quality before any forest harvesting had occurred. Each season has different temperature, precipitation, and vegetation growth characteristics, which produced seasonal trends in water quality. Presentation of various water quality parameters were therefore analyzed on a seasonal basis. Box and whisker plots were used to visualize the data, and one-way ANOVA and Tukey pairwise comparisons were used to determine if mean values of parameters amongst the streams and between the seasons were statistically different. The loads of water quality constituents were also estimated and expressed in kg/year/ha. Pearson correlation coefficients were computed to assess relationships between catchment characteristics, discharge, constituent concentrations, and loading.

4.2.1 Dissolved Organic Carbon and Total Organic Carbon

DOC and TOC concentrations varied across the five catchments, and between seasons (Figures 3.4 and 3.5). The one-way ANOVA showed significant differences in DOC and TOC concentrations between the catchments (Table 3.4). The majority of TOC was comprised of DOC, therefore the remainder of the discussion will focus on DOC trends. Catchment S1-1 has the highest average DOC concentration and was grouped separately from the other catchments; it also has the highest percentage of wetlands. Catchment S4-1 has the lowest average concentration of DOC and is grouped separate from the other catchments. It has the second lowest percentage of wetlands, but also is a small headwater catchment that dried up during the summer months. The concentrations measured in these catchments have large variation amongst each other. Except for sub catchment S4-1, the DOC concentrations are above a global average concentration of 10.4 mg/L from a meta-analysis done by Liu et al. (2021). Compared to this study, the Pockwock catchments also have above average DOC concentrations compared to other temperate forest catchments.

Computed Pearson correlation coefficients indicated that mean DOC concentration was highly correlated with the percentage of wetland (Table 3.5). Other catchment characteristics were only weakly correlated with DOC concentrations. These findings align with numerous previous studies which have found significant correlations between DOC concentrations and wetland coverage in forested watersheds (Cool et al., 2014).

The unit area loading of DOC produced the opposite trend (Table 3.5 and Figures 3.6 and 3.7). The highest areal loading rates were observed in catchments S4-1 and S3-1 and loading rates were negatively correlated with wetland percentages. This is due to the differences in hydrology between the catchments, where smaller catchments with less wetland area generally produced greater water yields per hectare (Table 3.2). Even though the catchments with a higher percentage of wetlands have a higher DOC concentration, the wetlands attenuate the flow of water through the catchment as they are placed in topographic depressions. Carbon dynamics have also been shown to correlate with wetland percentage as shown by Laudon et al. (2004). When comparing forested and wetland dominated catchments with similar daily discharge, the correlation between C loading and wetland percentage had a r^2 value of 0.72. Since the hydrology of the two catchments was comparable it was surmised that the wetlands contributed significantly to C loading. The same study also found a negative correlation ($r^2=0.83$) between C export and wetland percentage when just looking at the spring snowpack melting period. The suggested explanation for this is a result of different hydrologic flow paths during spring melt as a large fraction of snow melt is transported as surface flow over ice and frozen peat, whereas in the forested catchments the flows are through subsurface flow paths across riparian soils rich in C. The contrasting results highlight the importance in understanding the individual hydrology of each catchment.

Table 4.3 - Statistical analysis of annual DOC and TOC concentrations (mg/L).

Catchment	Mean	Standard Deviation	Grouping
DOC			
S1-1	17.40	7.54	A
S2-1	13.18	4.36	B
S3-1	12.57	4.52	B
S4-1	7.93	2.60	C
S4-2	11.19	4.95	B C
TOC			
S1-1	18.03	7.58	A
S2-1	12.77	4.18	B
S3-1	13.85	4.87	B
S4-1	8.17	2.81	C
S4-2	11.76	5.20	B C

Table 4.4 - Pearson correlation coefficients between catchment drainage area characteristics and DOC concentration and export.

	Area (Ha)	Mean Slope (degrees)	Shape Length	Wetland %
DOC concentration (mg/L)	0.05	-0.09	0.37	0.65
DOC export (kg/Ha/yr)	-0.50	0.67	-0.56	-0.84

There were also seasonal differences in DOC/TOC concentrations and export (Table 3.6 and Figures 3.6 and 3.7). In general, the four seasons can be grouped into two categories: fall-summer and spring-winter. The summer and fall are warmer, with vegetation growth in the summer and plant biomass decay in the fall. There is more organic matter accumulated on the forest floor, which is mineralized to produce DOC that would be available for transport during hydrologic events. Concentrations of DOC are also higher during the summer months due to lower streamflows (i.e., less dilution).

Table 4.5 - Statistical analysis of seasonal DOC concentrations for each individual catchment.

Catchment	**Grouping**			
	Fall	Summer	Spring	Winter
S1-1	A	A	B	B
S2-1	A	A B	B	B
S3-1	A	A	B	B
S4-1	A	A B	B	A B
S4-2	A	B	C	B C

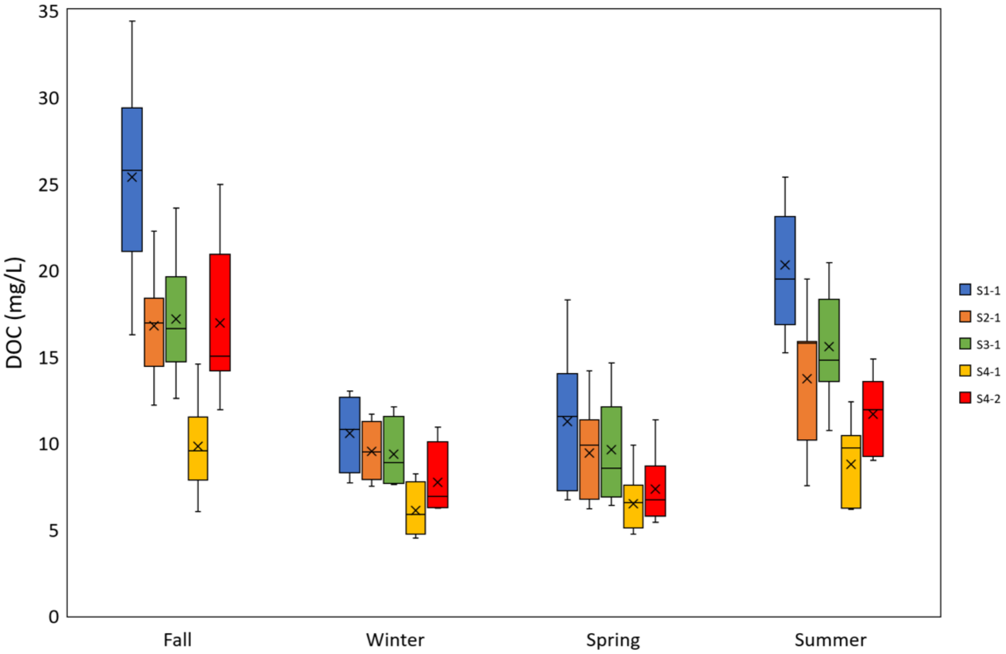

Figure 4.4 – Seasonal variability in DOC concentrations.

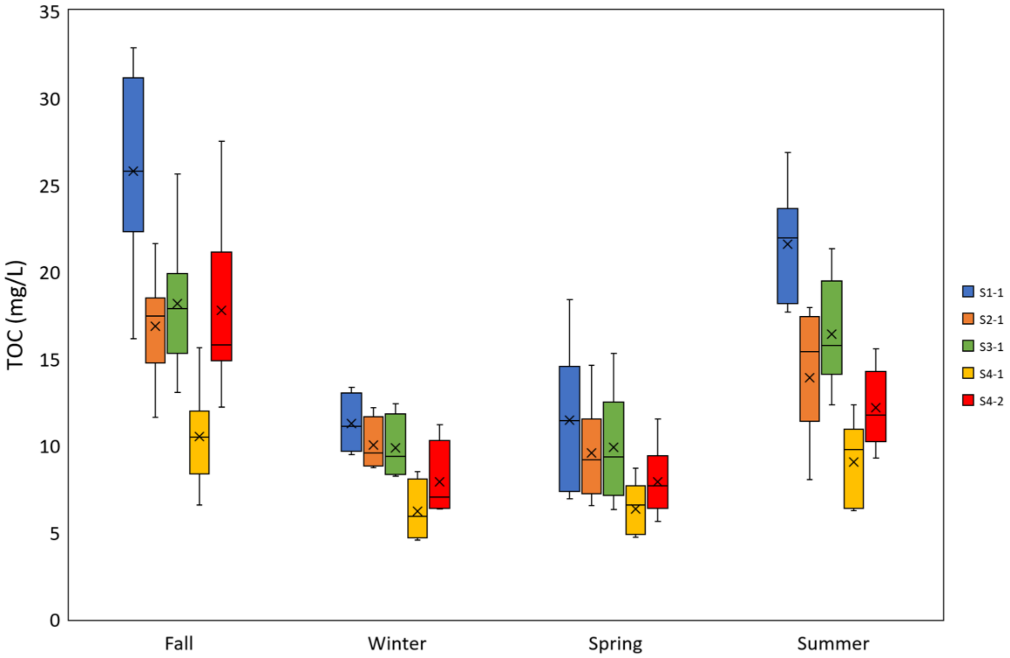

Figure 4.5 – Seasonal variability in TOC concentrations.

The DOC and TOC seasonal loading trends indicate that the majority of the export occurs during seasons with higher streamflow, and highest DOC concentrations. The fall season has the greatest precipitation and highest concentration of DOC and TOC, resulting in the largest seasonal loading rates. The spring has the second largest DOC loading rates, even though the DOC concentrations are lower. This is because the spring has the greatest overall discharge due to increased rainfall in the spring and melting of the winter snowpack, also noted by Laudon et al. (2004). The summer has the lowest DOC loading because of decreased streamflow, even though average concentrations are higher than the spring and winter. DOC and TOC loading is strongly correlated with the slope of the catchment (Table 3.5), as catchments with higher slopes generally have more discharge per hectare. Similar findings were observed by Lee et al. (2019), who noted that steeper slopes have faster runoff velocity and shallower soil depths, resulting in higher DOC export. The watershed total area (-0.5) and shape length (-0.56) were moderately negatively correlated to loading. This is also linked to water yield, as larger catchments have more storage and losses as compared to smaller flashier catchments.

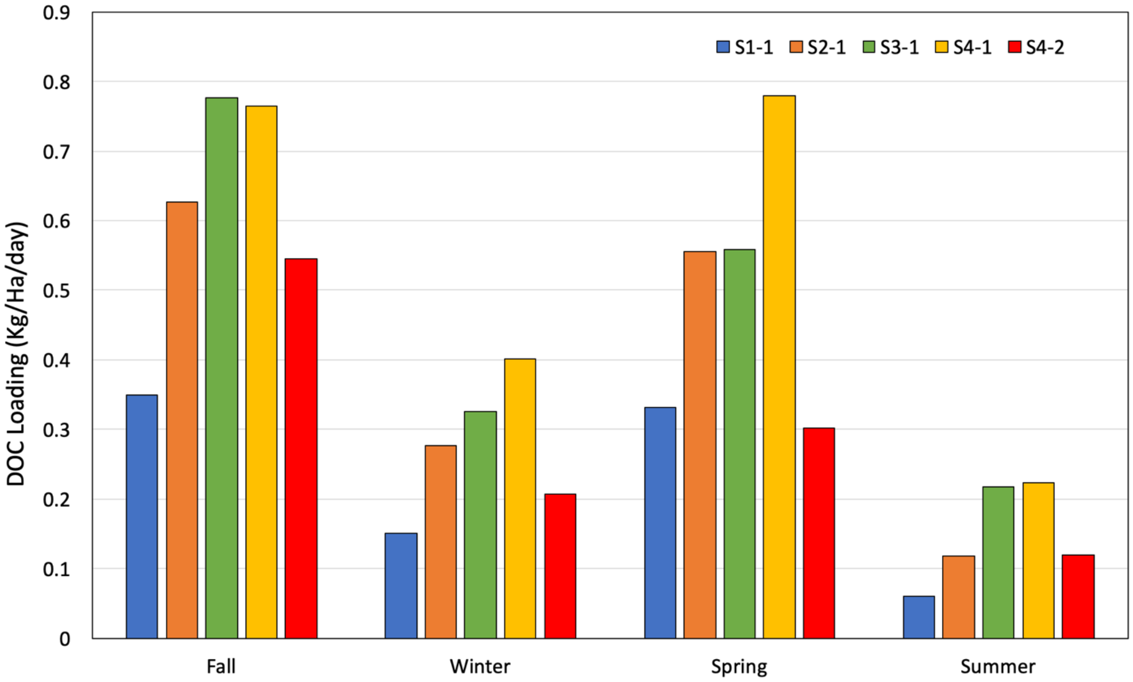

Figure 4.6 – DOC seasonal loading rates.

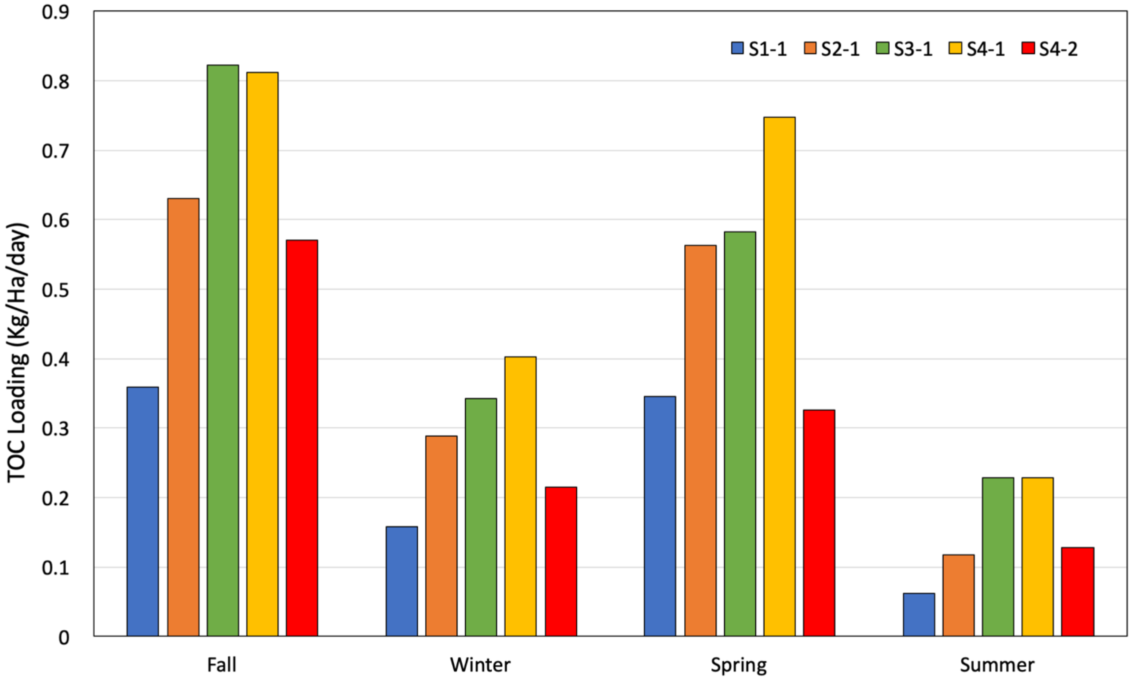

Figure 4.7 – TOC seasonal loading rates.

Linear regressions between DOC and TOC concentrations showed that these two parameters are strongly correlated, and that the majority of TOC is comprised of DOC (Figure 3.8). This finding was also noted by Miettinen et al. (2020).

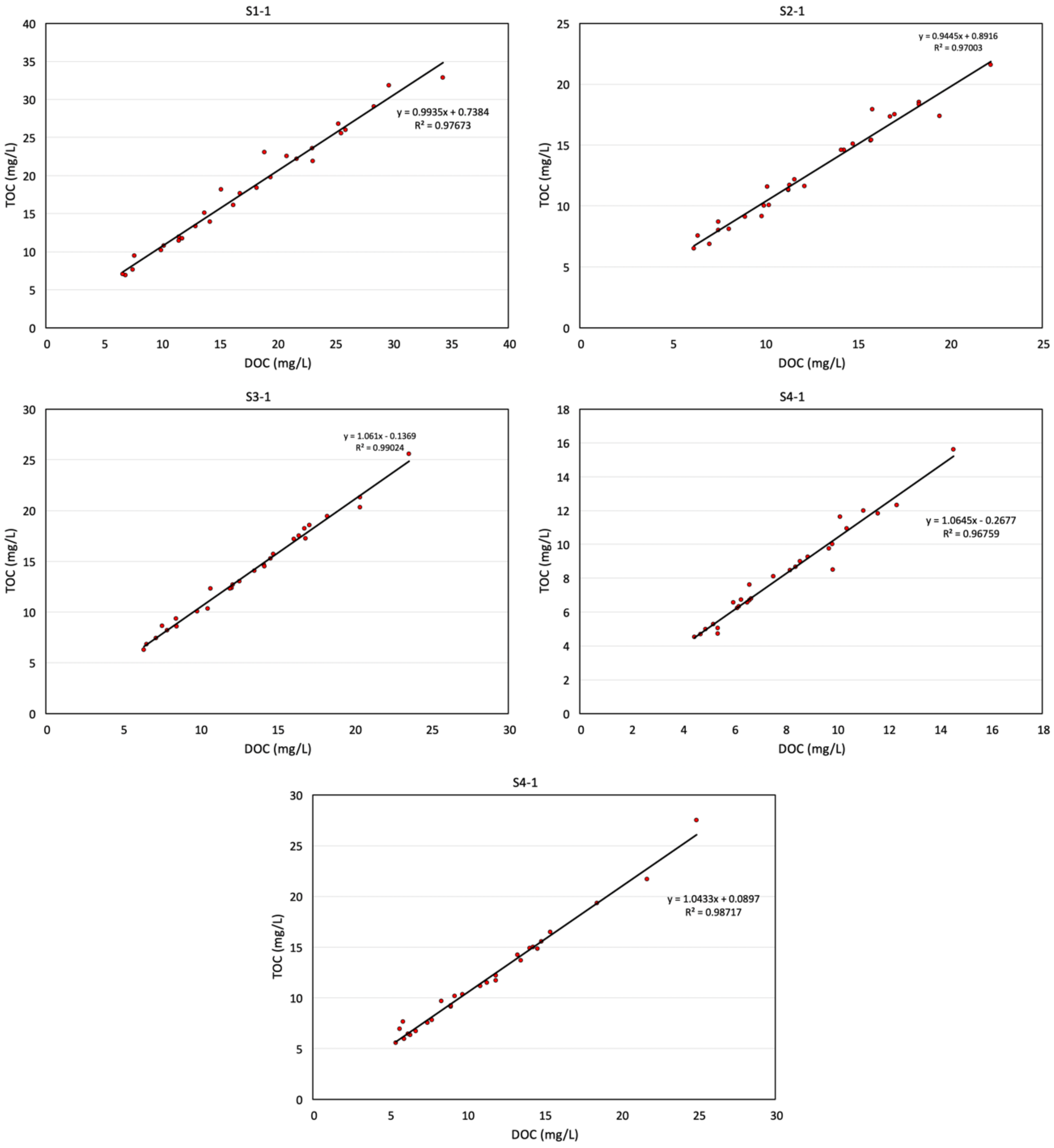

***Figure 4.8* – Linear regression between DOC and TOC concentrations for each study catchment.**

Seasonal patterns of DOC and TOC concentrations were similar to those observed in other Nova Scotia forested watersheds. Zhang et al. (2013) studied small, forested watersheds in Southwestern Nova Scotia. They found that DOC concentrations followed a seasonal cycle with (i) increasing levels after fall leaf off, (ii) decreasing levels to a minimum in April, and (iii) gradually increasing levels to a maximum in June.

4.2.2 DOC Characteristics

The average UV-254 values ranged from 0.365 (S4-1) to 0.897 (S1-1) across the study catchments. Statistically, the catchments presented as three distinct groupings (Table 3.7). There were also significant differences in UV-254 measurements between seasons (Table 3.8). Figure 3.9 illustrates UV-254 values across the seasons and catchments.

Table 4.6 - Statistical analysis of average annual UV-254 (cm^{-1}).

Catchment	Mean	Standard Deviation	Grouping
S1-1	0.897	0.348	A
S3-1	0.651	0.223	B
S2-1	0.608	0.189	B
S4-1	0.365	0.138	C
S4-2	0.558	0.239	B

Table 4.7 - Statistical analysis of seasonal values of UV-254 for each individual catchment.

Catchment	Grouping			
	Fall	Summer	Spring	Winter
S1-1	A	A	B	B
S2-1	A	A B	C	B C
S3-1	A	A	B	B
S4-1	A	A	B	A B
S4-2	A	B	C	B C

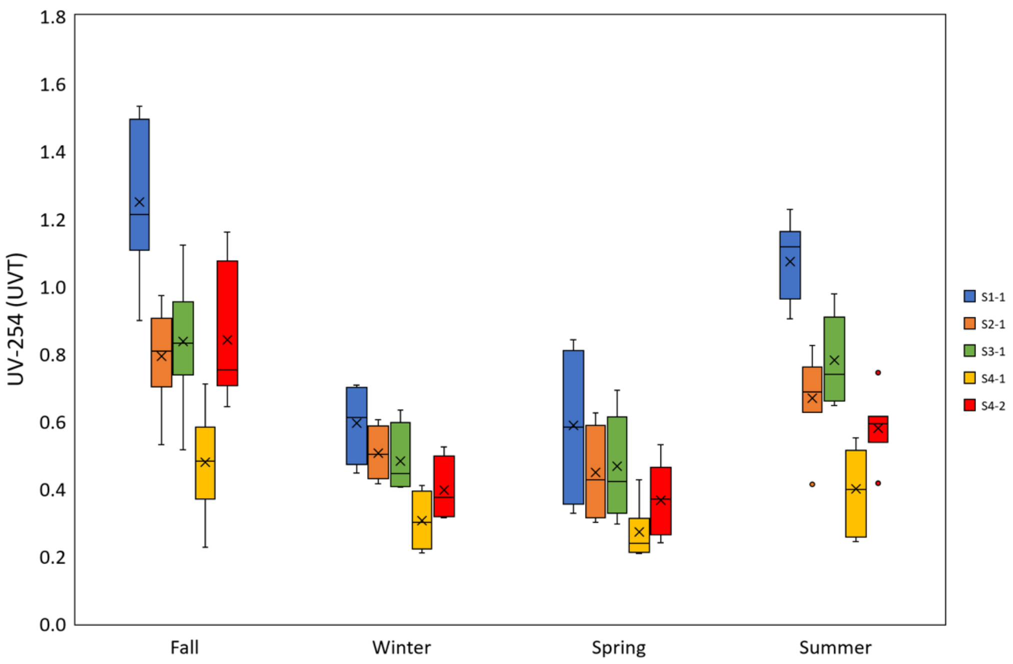

Figure 4.9 – Seasonal variation in UV-254.

The UV-254 measurements follow a very similar trend to DOC and TOC and are strongly correlated to the percentage of wetland in the catchments. UV-254 is used widely in the drinking water treatment sector to provide a rapid measurement of the concentration of organic matter, specifically the aromatic components, in source water. SUVA is computed by dividing UV-254 by DOC concentration, thus the UV-254 is normalized to the overall organic load in the water. This provides a characterization of the aromaticity of the organic matter, independent of the concentration of organics in the water. A high SUVA value indicates a large portion of aromatic organic compounds, which have more potential to react with disinfectants and create harmful DBPs.

There was variability in SUVA measurements between the catchments (Table 3.9 and Figure 3.15), but the range was less than those observed for UV-254 and DOC concentration. Catchments S1-1 and S4-2 were grouped together and possessed the highest SUVA values, these two catchments also have the greatest percentage of wetlands. S4-1 has the lowest SUVA value and is a small headwater catchment with a low percentage of wetlands.

Table 4.8. Statistical analysis of SUVA values (L/mg-M).

Catchment	**Mean**	**Standard Deviation**	**Grouping**	
S1-1	5.25	0.55	A	
S4-2	5.03	0.59	A	
S2-1	4.90	0.54	A	B
S3-1	4.96	0.46	A	B
S4-1	4.57	0.60		B

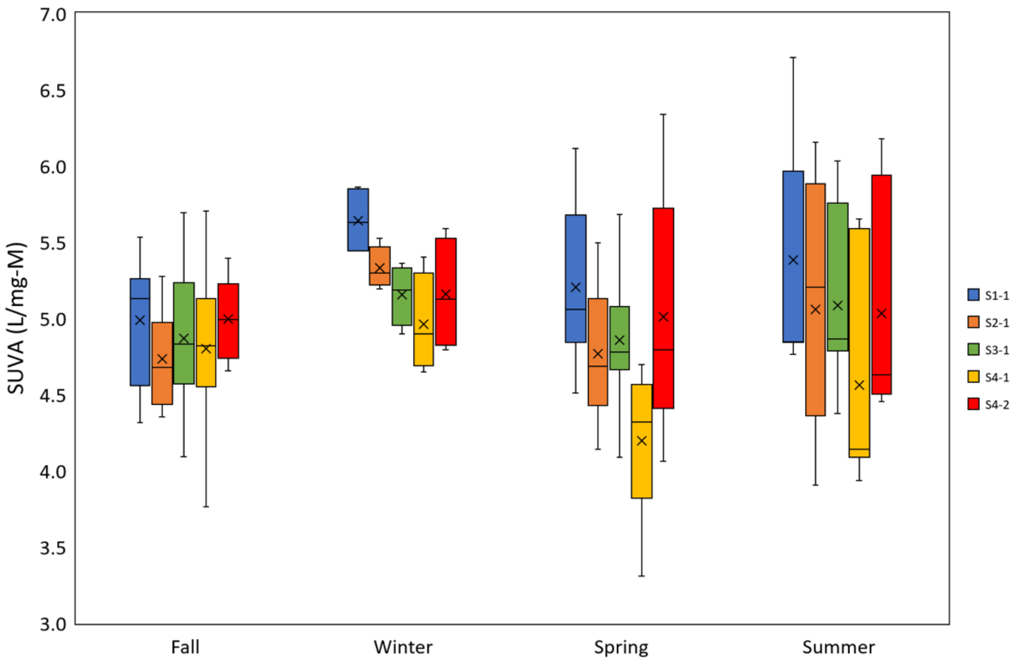

Figure 4.10 – SUVA seasonal variation in SUVA.

The percentage of wetland area were also significantly correlated to UV-254 and SUVA (Table 3.10).

Table 4.9- Pearson correlation coefficients relating catchment drainage area characteristics to UV-254 and SUVA.

	Area (Ha)	**Mean Slope (degrees)**	**Shape Length**	**Wetland %**
UV-254	0.06	-0.13	0.36	0.67
SUVA	0.36	-0.36	0.53	0.66

The SUVA values are comparable to other studies. Agren et al. (2008) reported a similar range of SUVA (3.8-5.6 L/ mg-m) in boreal streams and observed differences in streams draining wetland and forested dominated catchments, with SUVA values higher in wetland-dominated streams. Wallin et al., (2015) monitored two distinctly different catchments in Sweden (peat dominated vs coniferous tree dominated) and also found that SUVA values ranged from 3.4 to 5 L/mg-m s, however they observed little difference between the contrasting catchments. This indicated that upland forested mineral soils can export DOC with similar characteristics as peatland systems, and that caution is required when extrapolating findings. The SUVA values are all well above the low range of <2 L/mg-M and there are several values above the high range of >6 L/mg-M as outlined by Hua et al. (2020). Elevated SUVA has several impacts on drinking water treatment. The presence of these compounds allows for the use of coagulation-based treatment processes but elevated values increase coagulant chemical dosage requirements and lead to more DBP formation.

4.2.3 Turbidity and Suspended Solids

There was no statistically significant difference in turbidity levels among the five catchments (Figure 3.11), or between seasons for individual catchments. In general, turbidity values are low and often < 1 NTU. Hydrologic events, and associated runoff, generated the highest values of turbidity, but the highest measurements recorded during the monitoring period did not exceed 3.5 NTU.

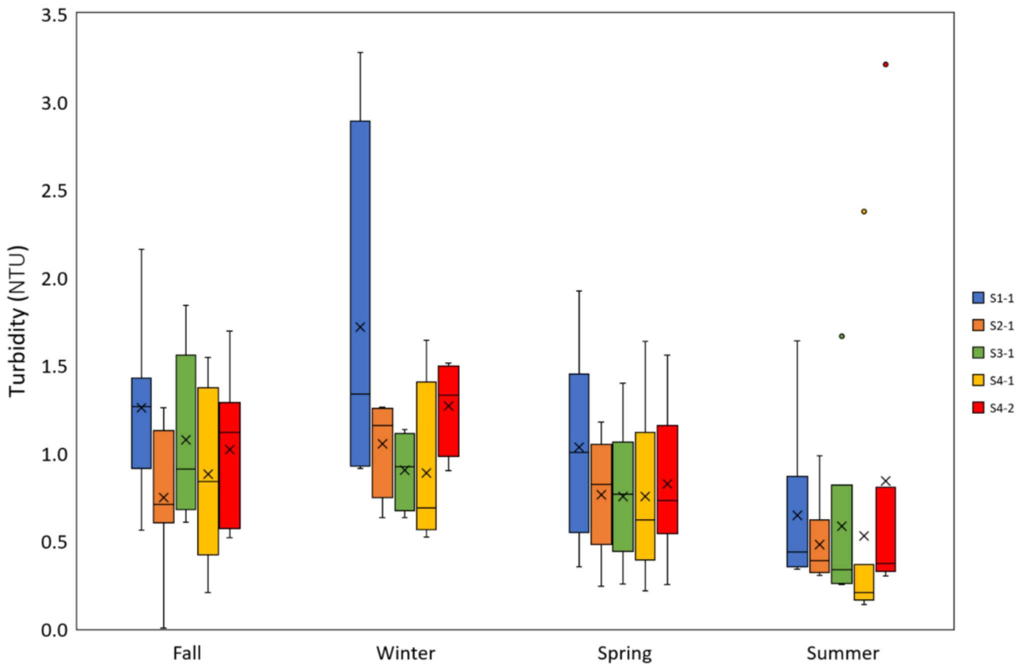

Figure 4.11 – Seasonal variability in turbidity values.

TSS concentrations were also not significantly different amongst the five catchments, or between seasons (Figure 3.12). The TSS concentrations were often below the detection limit (1 mg/L) but there were several elevated TSS measurements that coincided with hydrologic events.

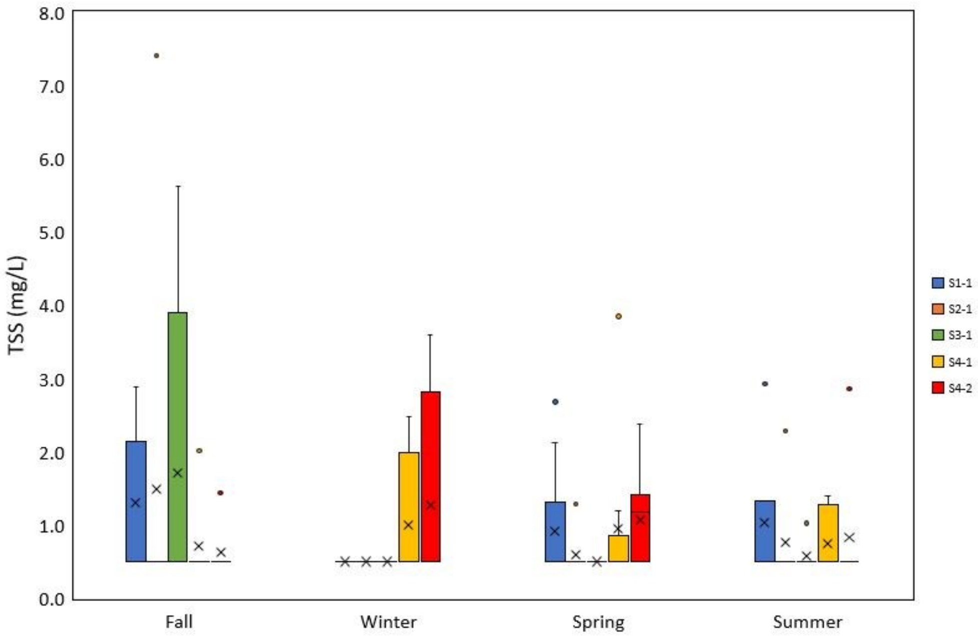

Figure 4.12 – Seasonal variation in total suspended solids.

The study catchments are underlain by granite bedrock and shallow glacial overburden, thus would be expected to have limited sediment supply. Road networks within the study catchments would be the primary source of mineral sediment materials to these streams. Wang et al. (2013) monitored sedimentation in streams from 1999-2005 after road and stream crossing construction. The sediment loads increased by 1.8-fold and was caused by erosive introduction of soil from construction. The sedimentation loading decreased once vegetation was re-established but remained elevated for the entire study period.

4.2.4 Nutrients (Phosphorus and Nitrogen)

Phosphorus (TP and DP) concentrations varied between catchments (Table 3.11, Figures 3.18 and 3.19). Catchment S1-1 has the highest concentration of TP and DP and was significantly different from the other catchments. S4-1 has the lowest concentration TP and DP and was grouped separately as well. The remaining three catchments were not significantly different from each other. TP concentrations were higher than DP, indicating a fraction of P is in particulate. There was no statistical difference in P concentration between seasons within each catchment (Figure 3.18 and 3.19).

Table 4.10- Statistical analysis of TP and DP concentrations.

Catchment	**Mean**	**Standard Deviation**	**Grouping**	
		TP		
S1-1	12.20	5.29	A	
S2-1	9.20	3.93	A	B
S3-1	9.89	5.13	A	B
S4-1	7.48	3.18		B
S4-2	10.63	4.06	A	B
		DP		
S1-1	8.06	3.82	A	
S2-1	6.08	2.74	A	B
S3-1	6.06	2.64	A	B
S4-1	5.02	2.27		B
S4-2	6.14	2.42	A	B

DP and TP average concentrations are strongly correlated to the percentage of wetland in the catchment (Table 3.12). As noted with DOC, wetlands correlate with increased P concentrations. Wetlands possesses organic soils that would have low P adsorption capacity, therefore P from decaying organic matter can be more efficiently transported to receiving waters by runoff (Cummins & Farrell, 2003). Rodgers et al. (2010) monitored the impact of P release from forest harvesting in a peat-dominated catchment and observed an increase from 6 $\mu g L^{-1}$ to a peak of 429 $\mu g L^{-1}$ one year after harvesting; elevated P concentrations were observed for three years post harvesting. DP and TP both have a moderate negative correlation to the catchment slope, consistent with the findings of D'Arcy & Carignan (1997).

Table 4.11 - Pearson correlation of catchment drainage area characteristics in relation to DP and TP concentration and export.

	Area (Ha)	**Mean Slope (degrees)**	**Shape Length**	**Wetland %**
DP average concentration (mg/L)	0.08	-0.34	0.31	0.82
DP export (kg/Ha/yr)	-0.49	0.28	-0.68	-0.58
TP average concentration (mg/L)	0.30	-0.46	0.42	0.69
TP export (kg/Ha/yr)	-0.39	0.28	-0.60	-0.64

The TP and DP areal loading rates are shown in Figures 3.15 and 3.16. The DP and TP loading rates are negatively correlated with the percentage of wetlands in the catchments, which again can be attributed to lower water yields from these catchments.

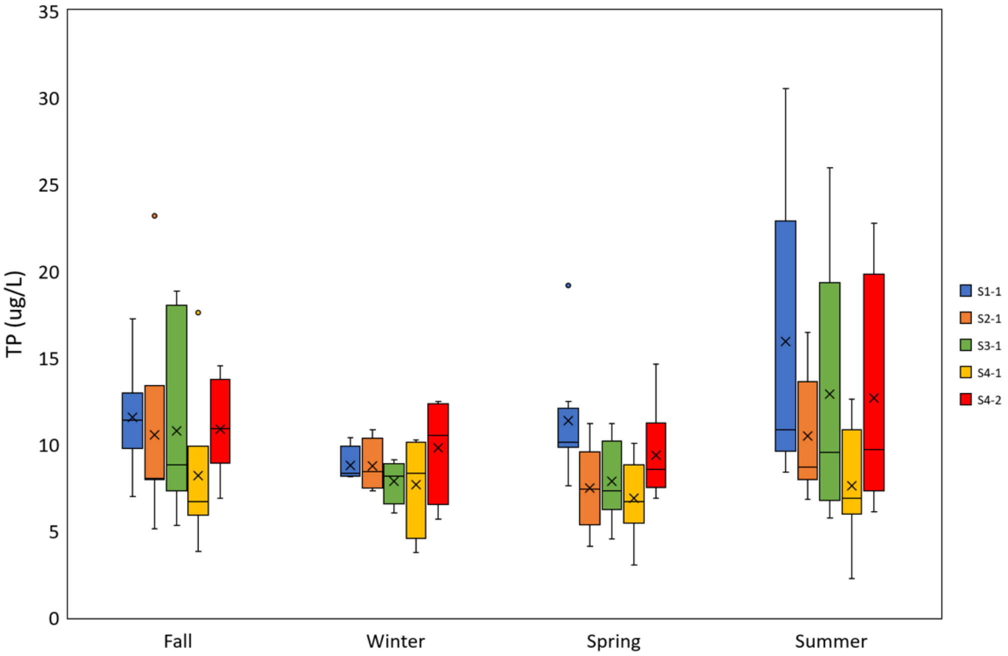

Figure 4.13 – Seasonal variation in TP concentrations.

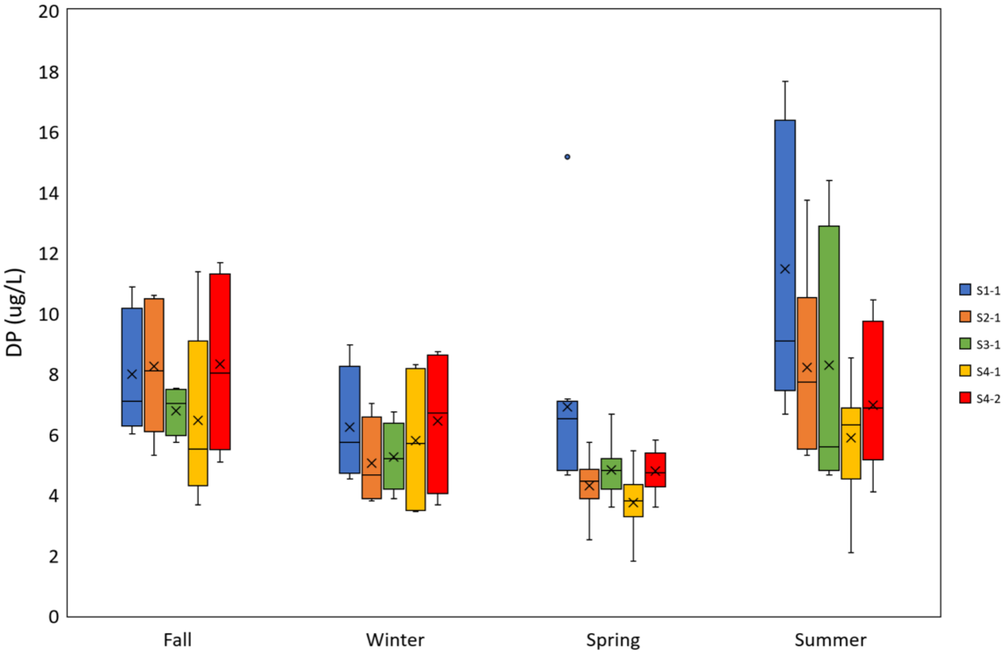

Figure 4.14 – Seasonal variation in DP concentrations.

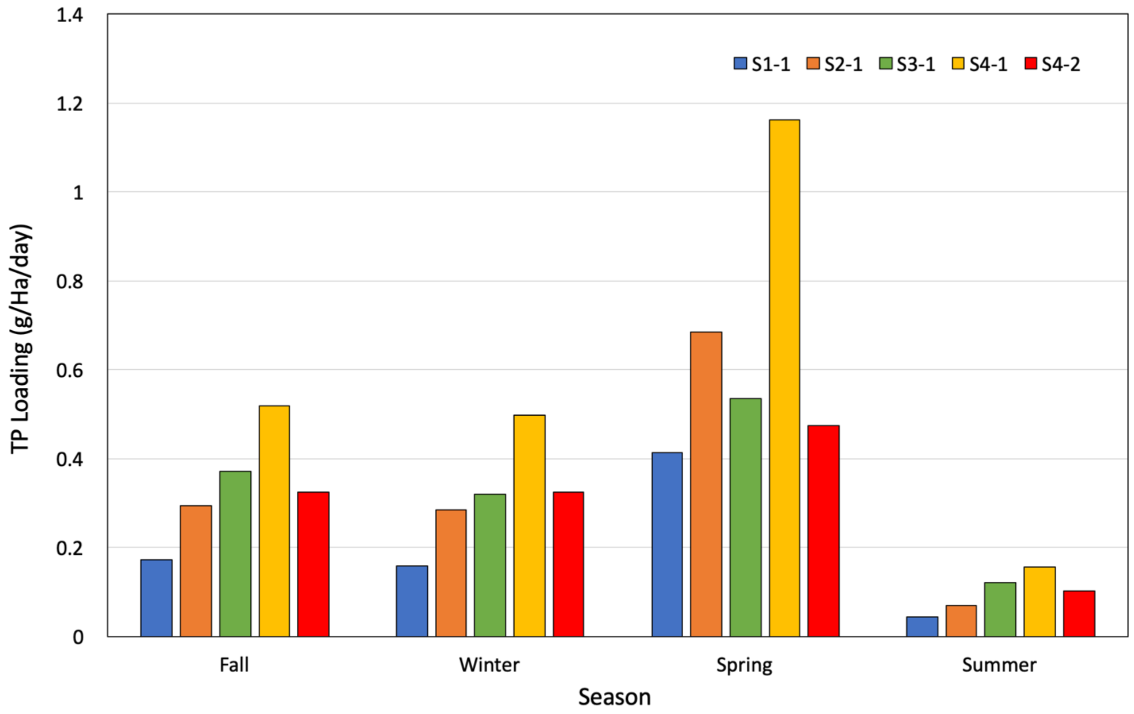

Figure 4.15 – TP seasonal loading rates.

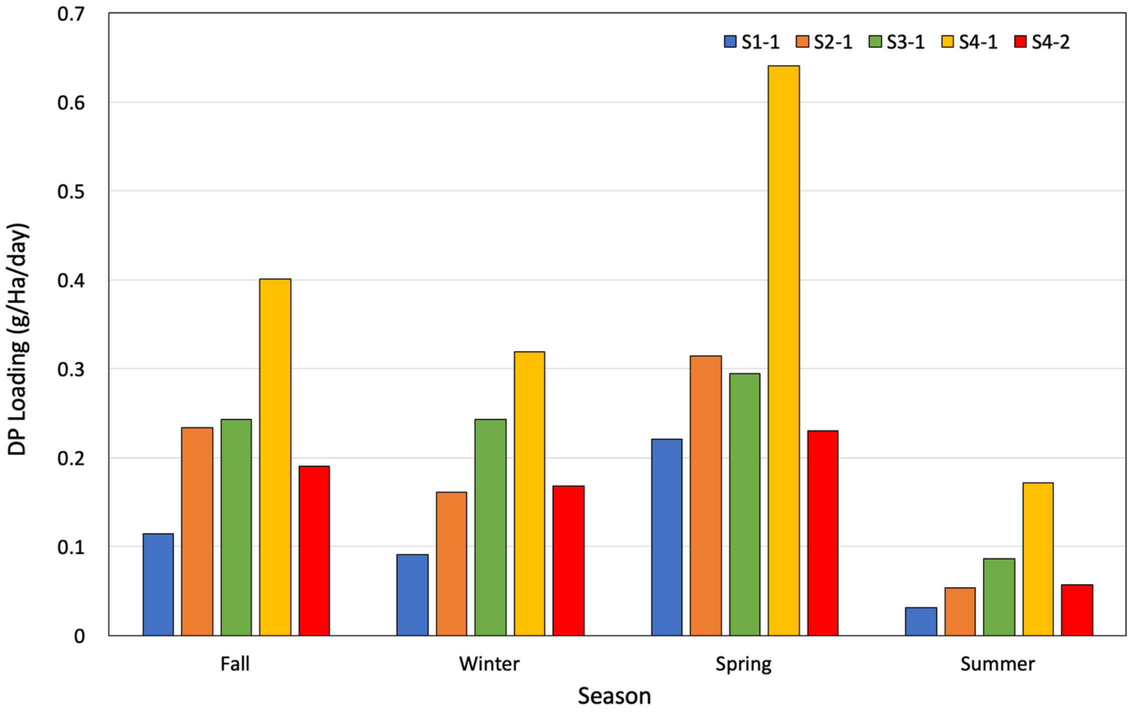

Figure 4.16 – DP seasonal loading rates.

There was no statistical difference in TN concentrations between the five catchments or between seasons within each catchment. TN concentrations were generally low and often below the detection limit (Figure 3.17). This was expected, as the study catchments are all forested and situated on granite bedrock. There is limited input from natural sources and the impacts of anthropogenic activities are minimal. TN areal loading rates are presented in Figure 3.18, with loading rates largely controlled by differences in water yield between the catchments. These N values are in line with the study from Binkley (2001) who found the average concentration of stream water nitrate to be 0.31 mg/L in North America. Nitrogen concentrations are lowest in Western Canada and have been found to be as low as 0.01 mg/L in BC coastal streams (Perrin et al. 1987).

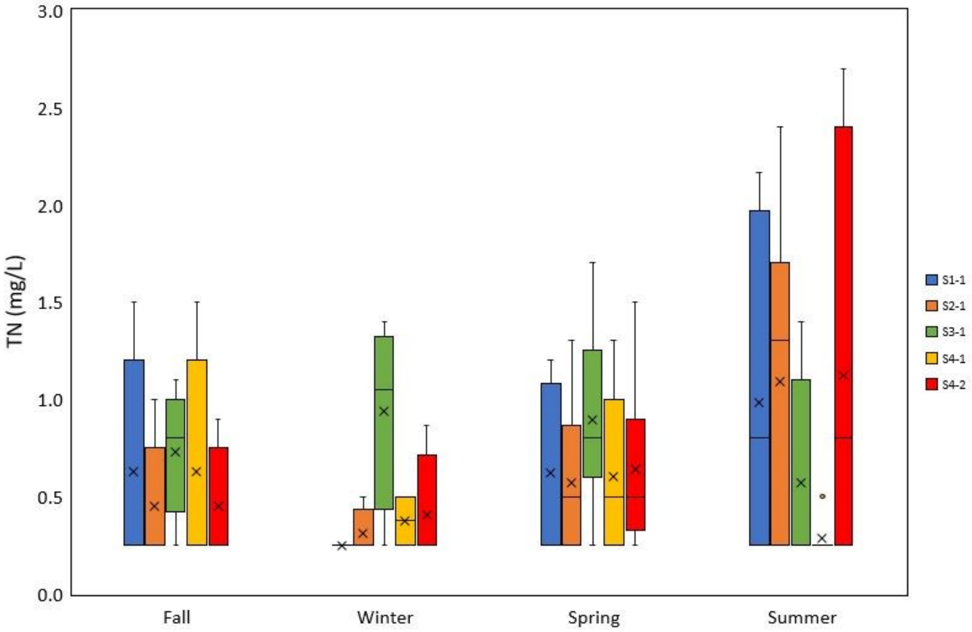

Figure 4.17 – Seasonal variation in TN concentrations.

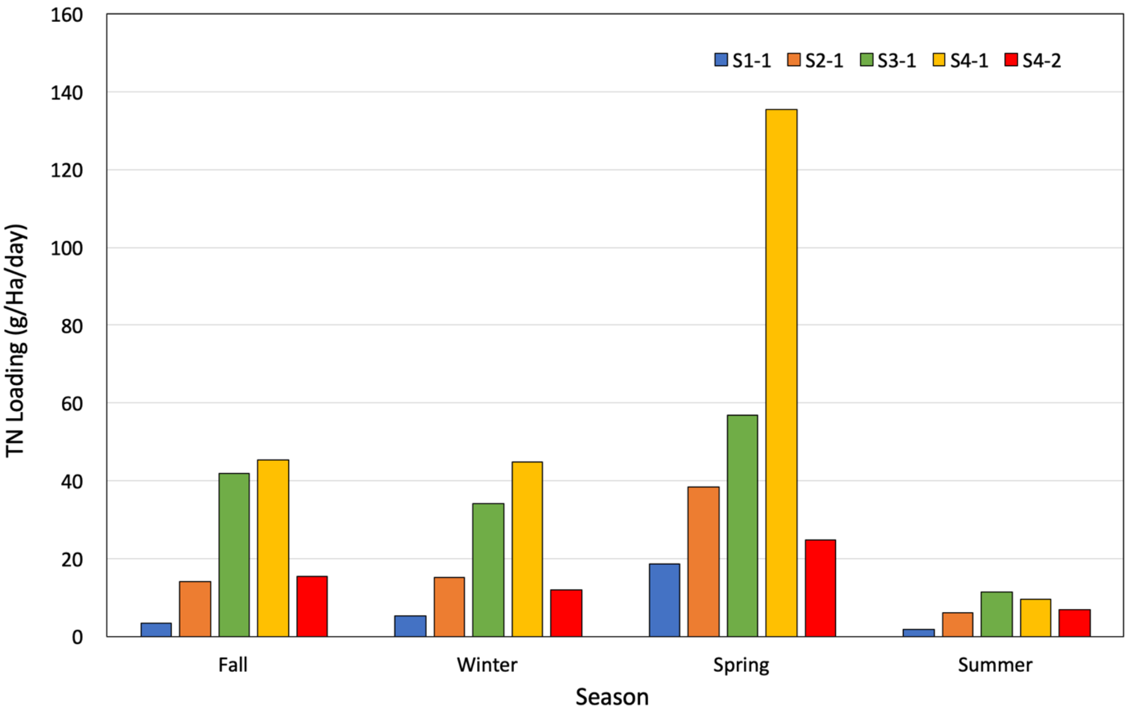

Figure 4.18 – Seasonal loading rates of TN.

4.3 Intensive Hydrologic Sampling

Intensive sampling was conducted during select hydrologic events, which were defined as ≥ 15 mm of rainfall within a 48-hour duration. Auto-samplers were pre-programmed to collect a 1 L sample every two hours for a 48-hour period. The intent was to sample during all stages of the hydrologic event: pre-event baseflow, rising limb, peak flow, and the falling limb. For practical reasons, only three of the six monitoring sites were sampled in this manner. They included (i) S2-1, which served as a control catchment; (ii) S4-1, which was to be subjected to commercial thinning and individual selection harvest; and (iii) S4-2, which is located further downstream of S4-1 and a large wetland complex.

Samples were analyzed for DOC, TOC, UV-254, SUVA, turbidity and TSS. Further characterization of DOC in terms of humic, fulvic, protein 1, protein 2, and soluble microbial protein like components, was also conducted using F-EEM. The fluorescence index (FI), fluorescence humification index (HIX), and the fluorescence biological index (BIX) were derived from the F-EEM spectra.

4.3.1 2019-05-14 Sampling Event

The first hydrologic event was captured on May 14-15th, 2019 and all three study catchments were sampled during this event. A total of 19 mm of rainfall occurred over a 31-hour period. The rain started 11 hours after the first sample was taken and peaked at hour 13 at a moderately low intensity of 2.5 mm/h. The sampling program only captured pre-event baseflow conditions and the rising limb of the hydrograph.

The S2-1 (Figure 3.19) catchment discharge started to increase at hour 15 and steadily rose throughout the rest of the sampling period from 0.014 to 0.078 m^3/s (474% increase). Concentration of DOC and TOC increased slightly (< 1 mg/L) during this period. Levels of UV-254 and SUVA, however, both began to decrease as soon as it began to rain, reaching a minimum 11 hours after the rainfall started. The two parameters then steadily increased throughout the remainder, indicating mobilization of more aromatic C compounds, presumably from organic-rich soil horizons. Both turbidity and TSS remained low throughout the event with no apparent trends. There were no apparent trends in the FI, HIX, and BIX throughout the sampling period.

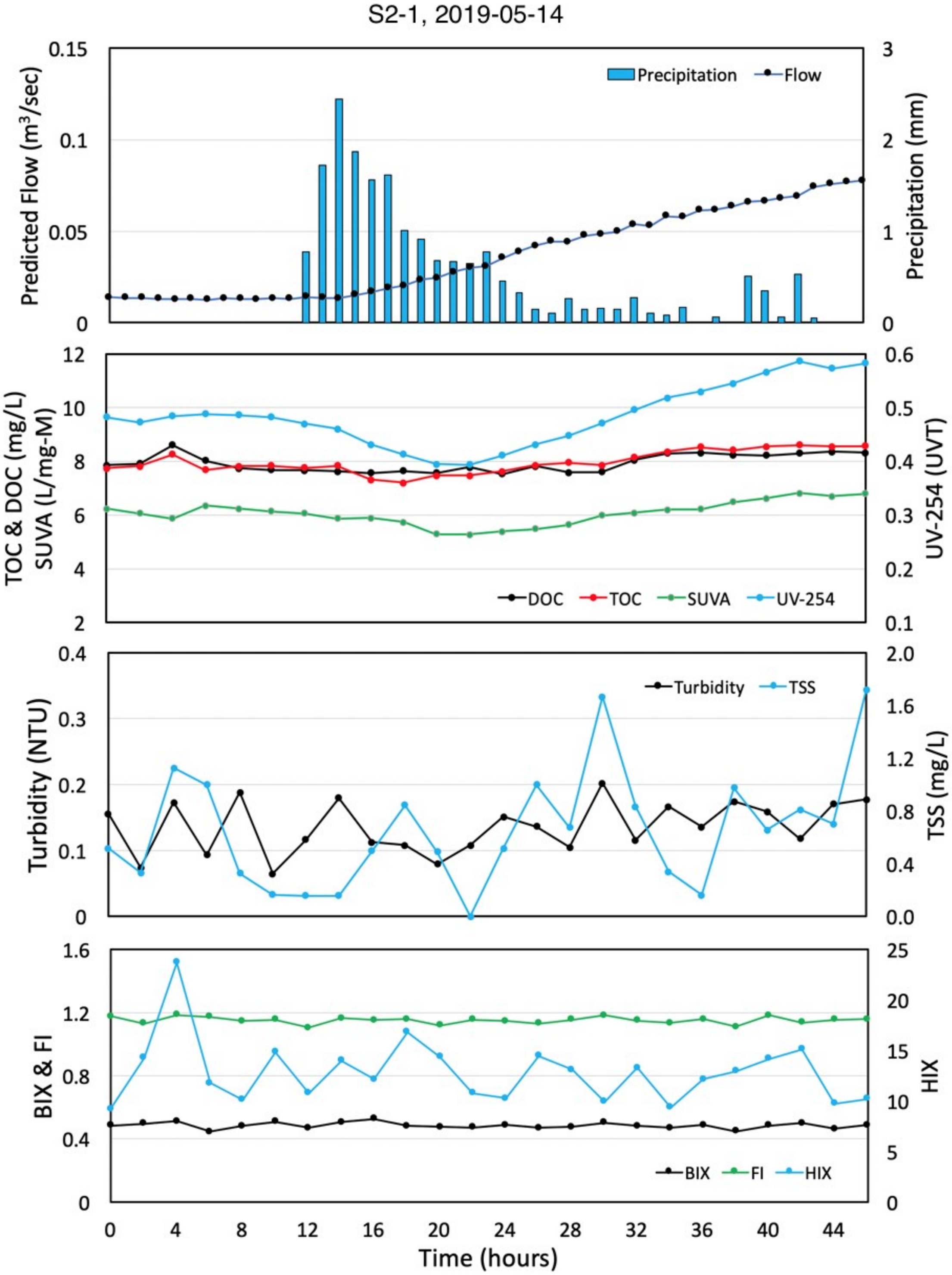

Figure 4.19 **– Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S2-1 throughout the hydrologic event captured on 2019-05-14 over a 48-hour period.**

S4-1 (Figure 3.20) discharge began to increase above pre-event baseflow levels at hour 15 and steadily increased until the end of the sampling period (0.004 to 0.015 m^3/s; 331% increase). Levels of DOC, TOC, and UV-254 all remained at pre-event baseflow values until hour 22 and then increased throughout the remainder of the sampling period. DOC concentrations increased from 4.6 to 6.2 mg/L and UV-254 increased from 0.209 to 0.305 cm^{-1}. SUVA began to slightly increase in value after hour 26 from 4.3 to 4.7 L/mg-M. There were no apparent trends in either TSS or turbidity.

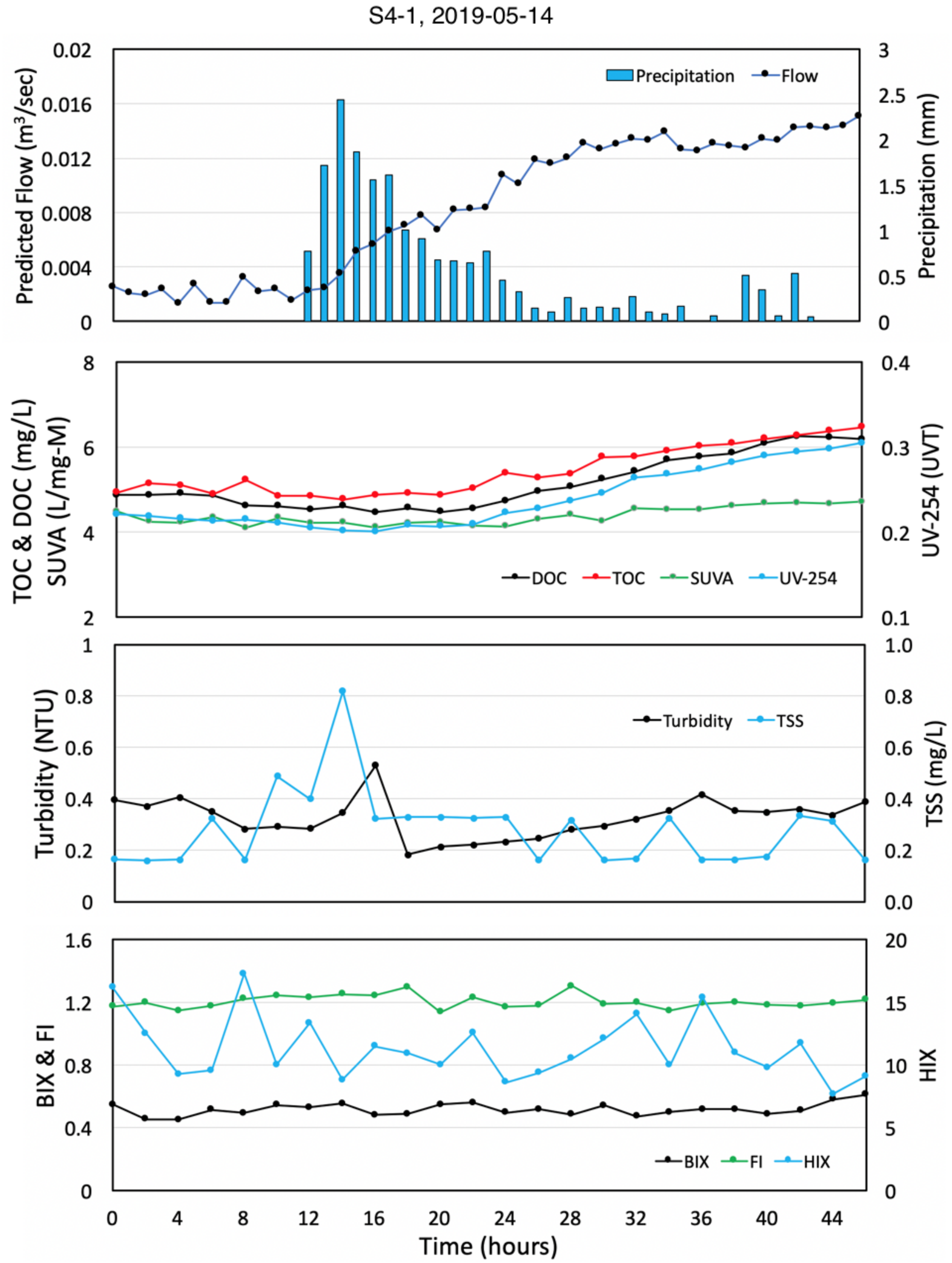

Figure 4.20 – **Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S4-1 throughout the hydrologic event captured on 2019-05-14 over a 48-hour period.**

Discharge at S4-2 (Figure 3.21) began to increase at hour 15, rising from 0.051 to 0.11 m^3/s (111% increase). S4-2 has the largest catchment area, lowest average slope, and greatest percentage of wetlands; all factors that are correlated with decreased discharge. The concentrations of DOC decreased once the rain started, reaching a minimum at hour 20, decreasing by 1 mg/L. The concentration then steadily increases until the end of the sampling period from 7.8 to 11 mg/L. Levels of UV-254 were unchanged until several hours after DOC concentrations started, and then increased from 0.395 to 0.431 cm^{-1}.

The time series trends indicated that this low intensity rainfall event generated negligible amounts of direct runoff, as indicated by the damped hydrograph response and lack of increase in turbidity or TSS. During the initial parts of the event, direct rainfall reaching the stream channel caused minor reductions in DOC/TOC concentrations due to dilution. As soil moisture levels increased, interflow mechanisms appear to have been initiated, as discharge increased, along with DOC concentrations and UV254. Water moving through organic rich soil horizons would have been contributing aromatic C compounds to the stream channel.

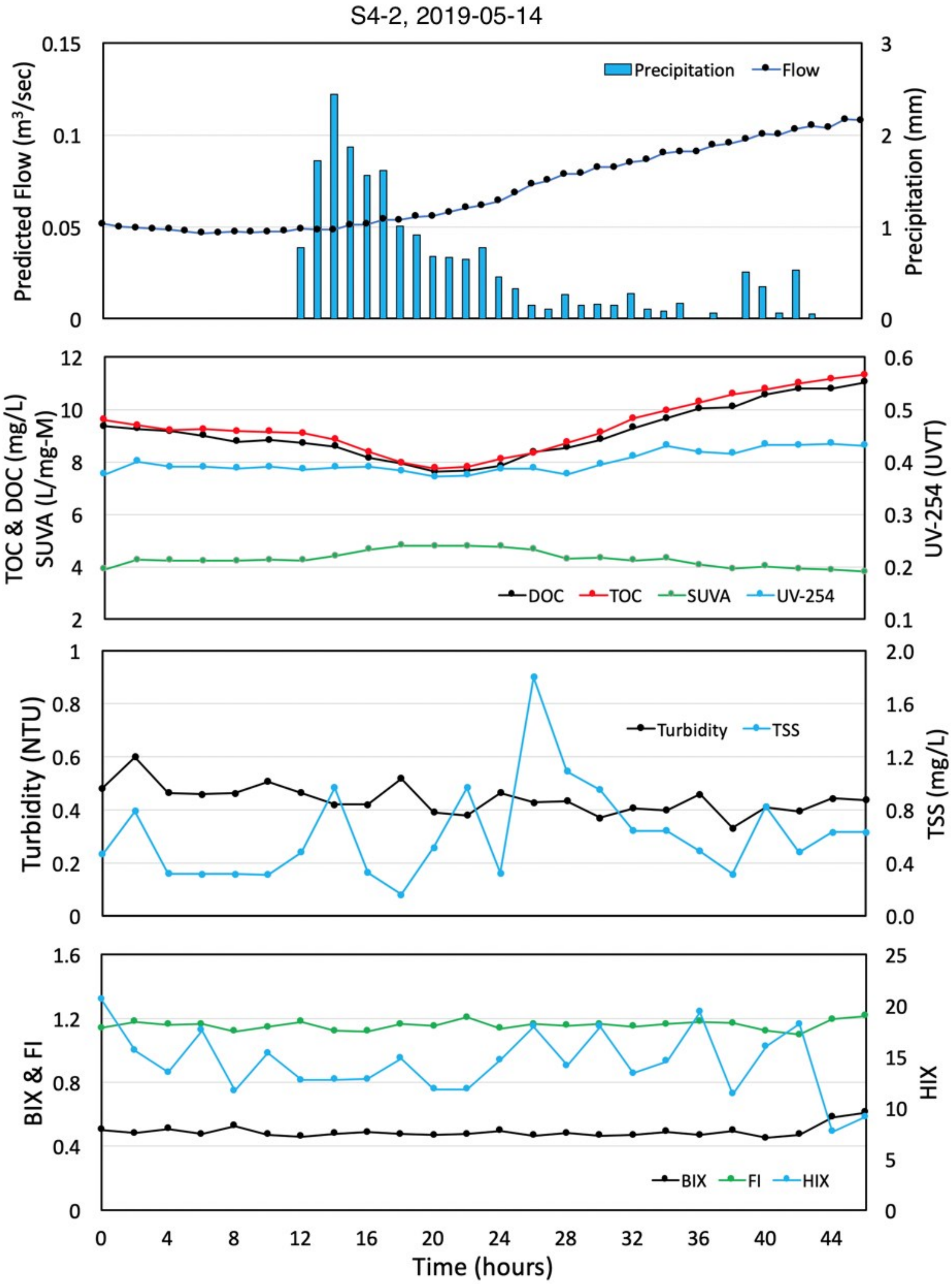

Figure 4.21 **– Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S4-2 throughout the hydrologic event captured on 2019-05-14 over a 48-hour period.**

4.3.2 2019-05-24 Sampling Event

The second hydrologic event was captured on May 24-25th, 2019 over a 48-hour period. Only two of the study catchments were monitored during this event due to technical errors with the auto sampler in S4-2. A total of 18 mm of rainfall occurred over a 31-hour period. The rainfall started three hours after the first sample was taken and peaked at hour six at a rate of 2 mm/h. This event was relatively low intensity and lasted a total of 13 hours. Samples were collected during pre-event baseflow conditions, rising limb, peak, and falling limb of the hydrograph.

S2-1 (Figure 3.22) discharge began to increase at hour 12 and peaked at hour 21, changing from 0.12 to 0.17 m^3/s (48% increase). The discharge remained elevated until hour 31 and then decreased to 0.12 m^3/s. The rising and falling limb of the hydrograph are weakly pronounced and the post-event discharge is higher than pre-event baseflow discharge. There were only small changes in all the parameters measured. Although this rainfall event was similar magnitude to the May 14th event (19 mm), ten days earlier, ~ 45 mm of rain fell between those dates. The pre-event discharge was already seven times that of the prior events. DOC concentrations were already elevated prior to the event.

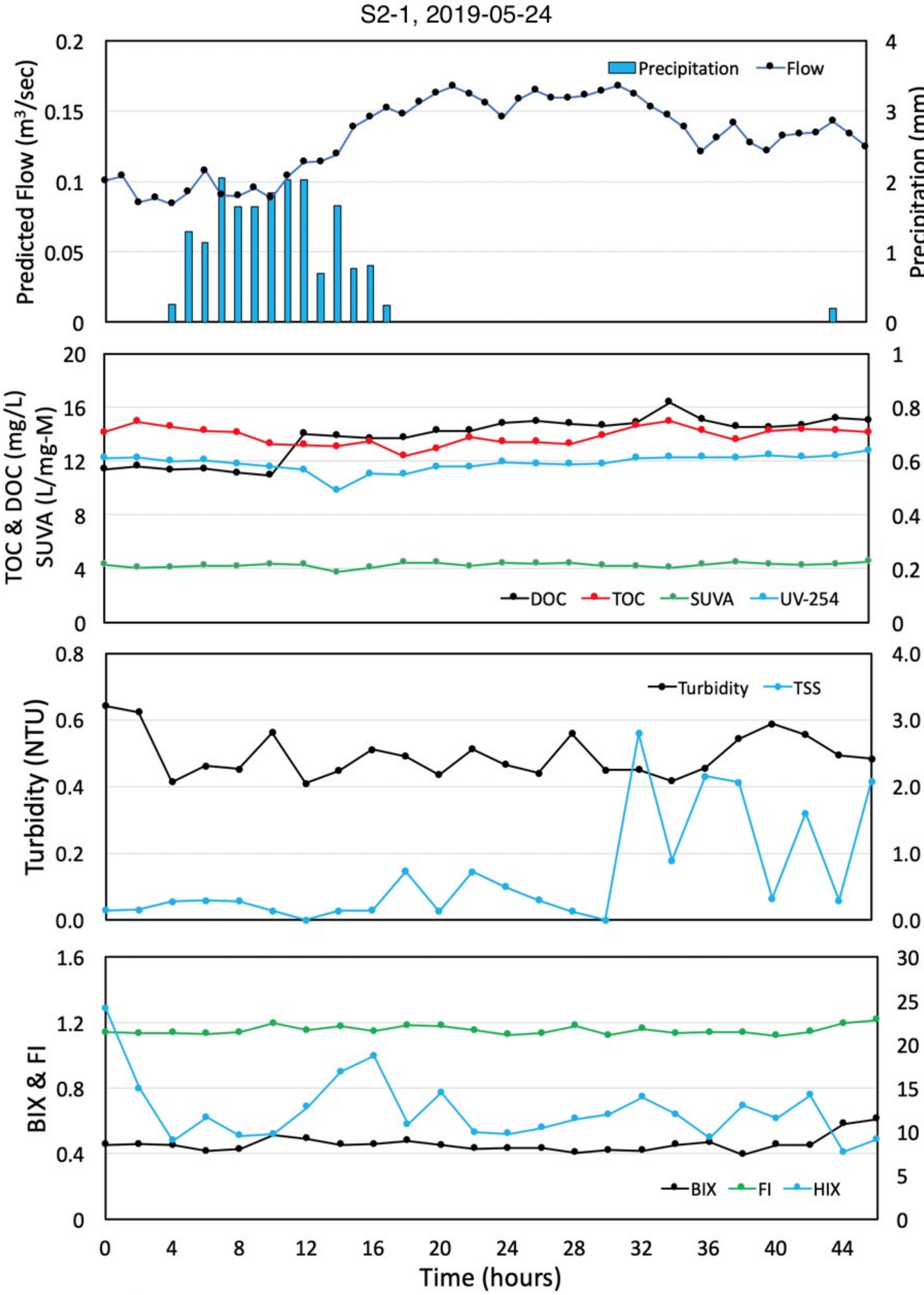

Figure 4.22 – **Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S2-1 throughout the hydrologic event captured on 2019-05-24 over a 48-hour period.**

Results for S4-1 (Figure 3.23) follows a similar trend to S2-1 with discharge increasing from 0.019 to a peak of 0.032 m^3/s (60% increase). Discharge remained elevated for several hours and then decreased to a discharge that was higher than that observed before the event.

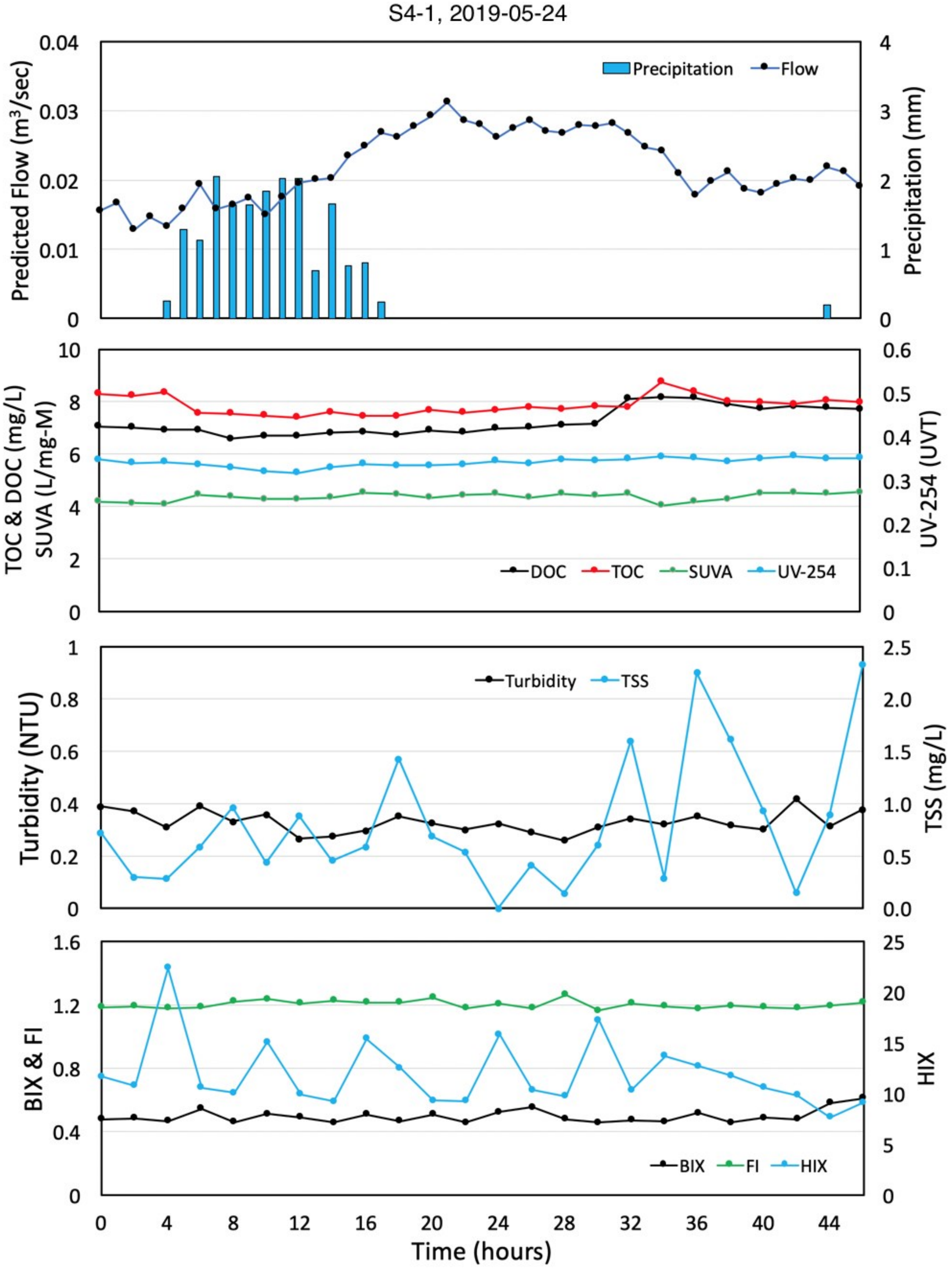

Figure 4.23 – **Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S4-1 throughout the hydrologic event captured on 2019-05-24 over a 48-hour period.**

4.3.3 2019-07-23 Sampling Event

The third hydrologic event was captured on July 23-24th, 2019 over a 48-hour period. All three of the study catchments were sampled during this event. A total of 21 mm of rainfall occurred sporadically over a 34-hour period, with two main periods of heavy rainfall ten hours apart. The rain started after the first sample was taken and peaked at hour six at a rate of 4.9 mm/h. Samples were collected during pre-event baseflow conditions, rising limb, peak, and falling limb of the hydrograph.

The S2-1 (Figure 3.24) discharge remained at pre-event baseflow levels until hour 22, when it increased from 0.009 to 0.017 m^3/s (87% increase). Discharge decreased slightly after the peak but remained elevated above pre-event baseflow conditions. This tributary was essentially dry prior to the event and the rainfall produced only small discharge increases relative to the two events captured in the spring. There was little rain in the weeks leading up to this event and the soil moisture levels would have been low. TOC, DOC, and UV-254 all steadily decreased once the precipitation started reaching minima around hour 14. The three parameters then steadily increased during the rest of the event to slightly above pre-event concentrations. The initial rainfall, and proximal transport pathways, appeared to dilute the stream water, then as the event progressed DOC was mobilized from the mineral and organic soil horizons. The event appeared to be transport-limited, as DOC continued to increase as the event progressed, even on the falling limb of the hydrograph. SUVA increased from 6.2 to 7.2 L/mg-M. during the first six hours of the event and then steadily decreased to 5.4 L/mg-M over the remainder of the event. UV-254 increased at a similar rate to that of DOC and TOC, indicating the overall aromaticity of the DOC decreased as the event progressed. Although HIX fluctuated greatly between samples, values generally decreased throughout the event, suggesting a decrease in the humic components of the DOC.

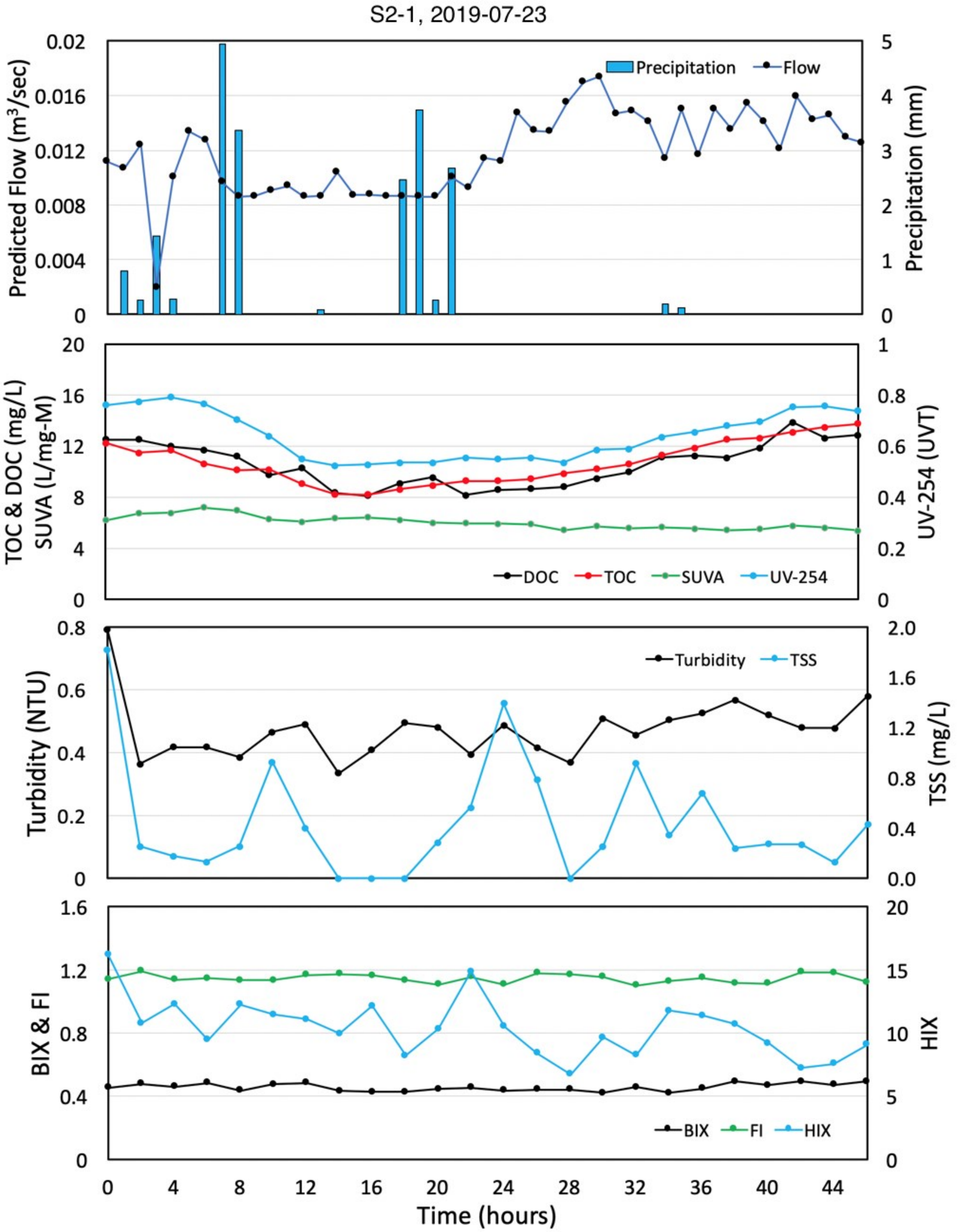

Figure 4.24 **– Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S2-1 throughout the hydrologic event captured on 2019-07-23 over a 48-hour period.**

The S4-1 (Figure 3.25) stream channel had no discharge at the start of the event and then sharply increased to a peak of 0.019 m^3/s at hour 25. The discharge peak lasted several hours and then decreased to a new level of 0.01 m^3/s. DOC, TOC, and UV-254 levels all initially dropped by ~15% as the start of the rainfall and then increased by ~70% after the first peak in rainfall and discharge. After this initial peak, DOC, TOC, and UV-254 then decreased again as the rainfall stopped and discharge decreased. The three parameters then steadily increased until the end of the event where the peak occurs, with levels decreasing several hours after the peak in discharge.

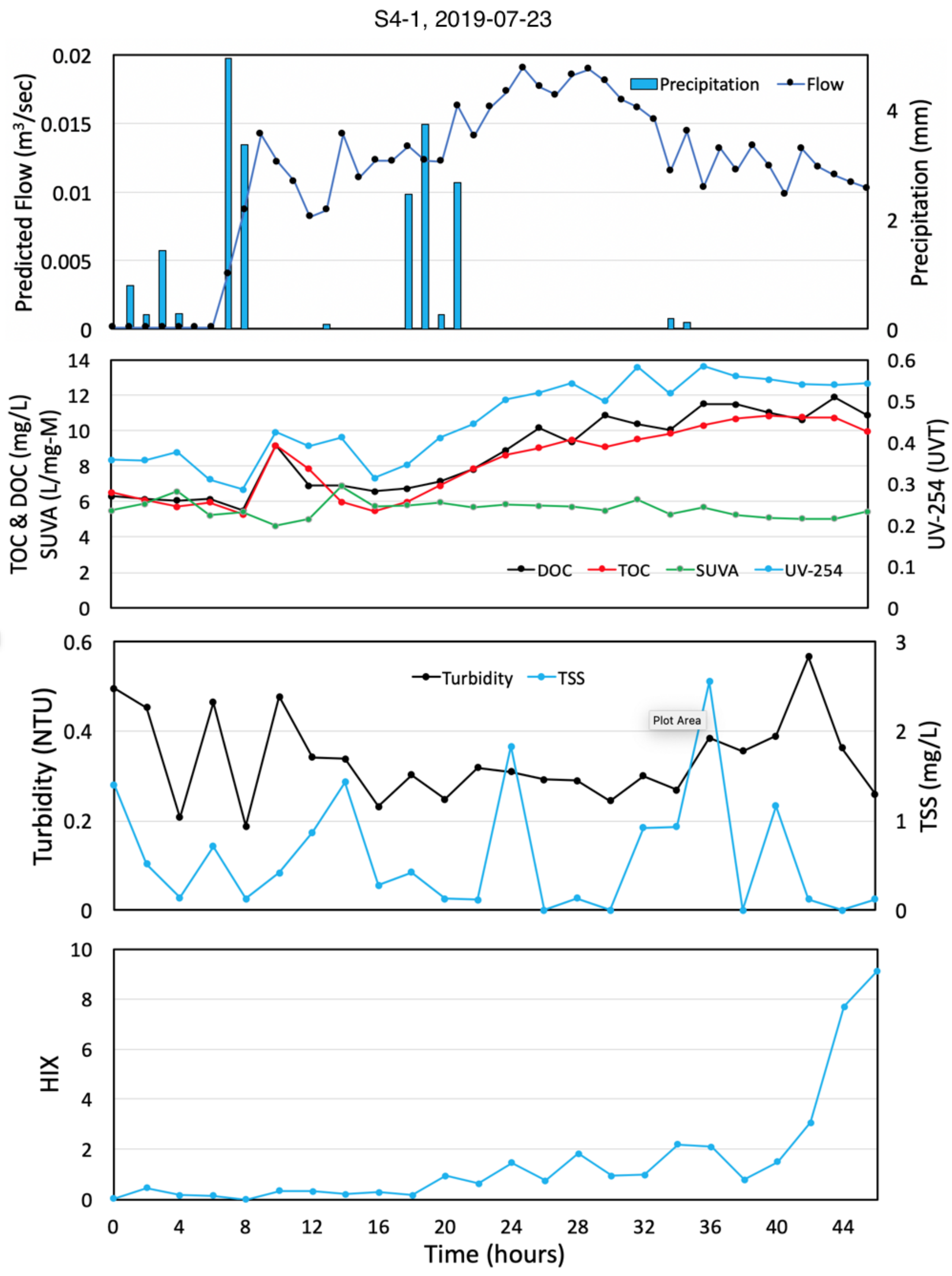

Figure 4.25 – **Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S4-1 throughout the hydrologic event captured on 2019-07-23 over a 48-hour period.**

S4-2 (Figure 3.26) had no discharge at the start of the event, then slow and steadily increased to 0.052 m^3/s at hour 42 after a long rising limb resulting from the bimodal rainfall. Discharge then decreased slightly but remained elevated for the rest of the event. TOC and DOC had little change throughout the entirety of the event. The concentration of TOC and DOC throughout the event are roughly the same concentration of S4-1 at the end of the event. S4-2 is a larger catchment S4-1 (a nested headwater catchment) and had little increase in discharge from the hydrologic event due to antecedent moisture conditions. Any influx of DOC from the transport pathways to the stream was not enough to change the concentration.

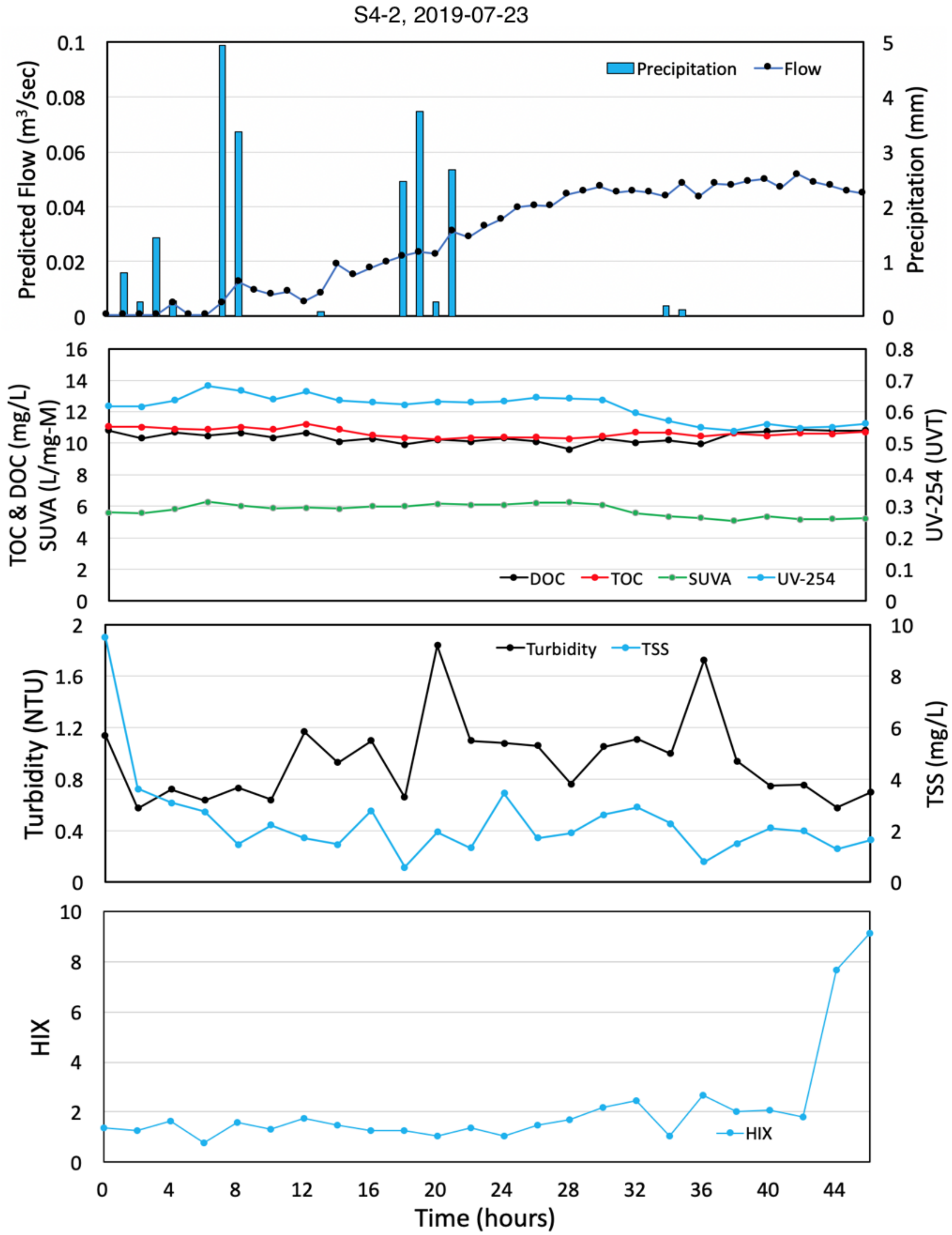

Figure 4.26 – **Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS and HIX in catchment S4-2 throughout the hydrologic event captured on 2019-07-23 over a 48-hour period.**

4.3.4 2019-09-07 Sampling Event

The fourth hydrologic event was captured on September 7th-8th, 2019. This event was Hurricane Dorian, which transitioned into a tropical storm as it arrived. A total of 128 mm of rain fell over a 17-hour period. The rainfall started after the second sample was taken but did not intensify until the 5th sample. The rainfall was intense for 8 hours, peaking at 30 mm/h at hour 16.

The event was only monitored at S4-1 (Figure 3.27) as the other two monitoring sites flooded, resulting in the autosamplers being tipped over. There was minimal rainfall in the weeks prior to the event, with no measurable pre-event discharge. The hydrograph has a sharp rising limb, peaking several hours after the peak rainfall intensity at 1.3 m^3/s, then quickly decreased. Samples were collected at all stages of the hydrograph. Both DOC and TOC quickly increased in concentration once the discharge began to increase; DOC increased from 5 mg/L to 17 mg/L, with peak concentrations occurring five hours after peak discharge. TOC and DOC then steadily decreased until the end of the event but were approximately three times higher in concentration than pre-event concentrations. A similar trend was observed with UV-254 levels.

Turbidity and TSS were closely correlated during the event. Concentrations were low until hour 14, sharply peaked at hour 18, and then rapidly decreased to background levels. Concentrations of TSS peaked at 48 mg/L and turbidity levels peaked at 46 NTU. This indicated that this event resulted in substantial sediment mobilization from the landscape and/or streambed. FI, HIX, and BIX fluctuated with no apparent relationship with discharge.

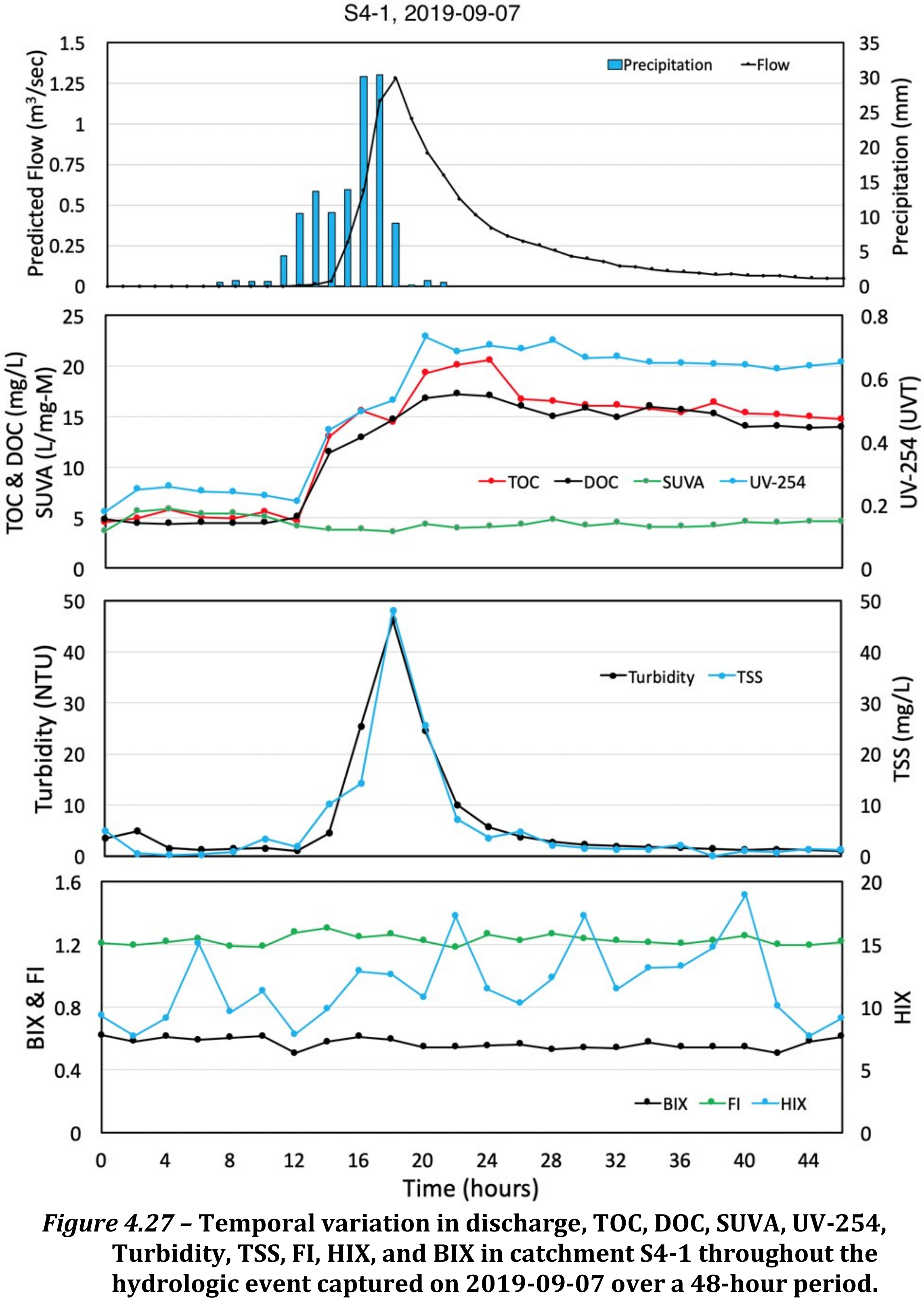

Figure 4.27 – **Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S4-1 throughout the hydrologic event captured on 2019-09-07 over a 48-hour period.**

4.3.5 2019-11-12 Sampling Event

The last hydrologic event was captured on November 12th-13th, 2019, with a total of 47 mm of rain falling over a 23-hour period. The rain started at hour five, with a peak intensity of 8 mm/h observed at hour ten. S2-1 (Figure 3.28) discharge began to increase when the rainfall started, and peaked once the rain ended, rising from 0.028 to 0.83 m^3/s (2800% increase). The pre-event discharge was higher than the peak flow of the first three events that were monitored, indicating wet antecedent conditions. The auto sampler malfunctioned before the last sample time, due to freezing issues. The DOC, TOC, and UV-254 trends were similar. All parameter levels initially decreased during the early part of the rainfall due to dilution from rainwater. Levels then steadily increase by about 55% and peaked a few hours after peak discharge and remained elevated.

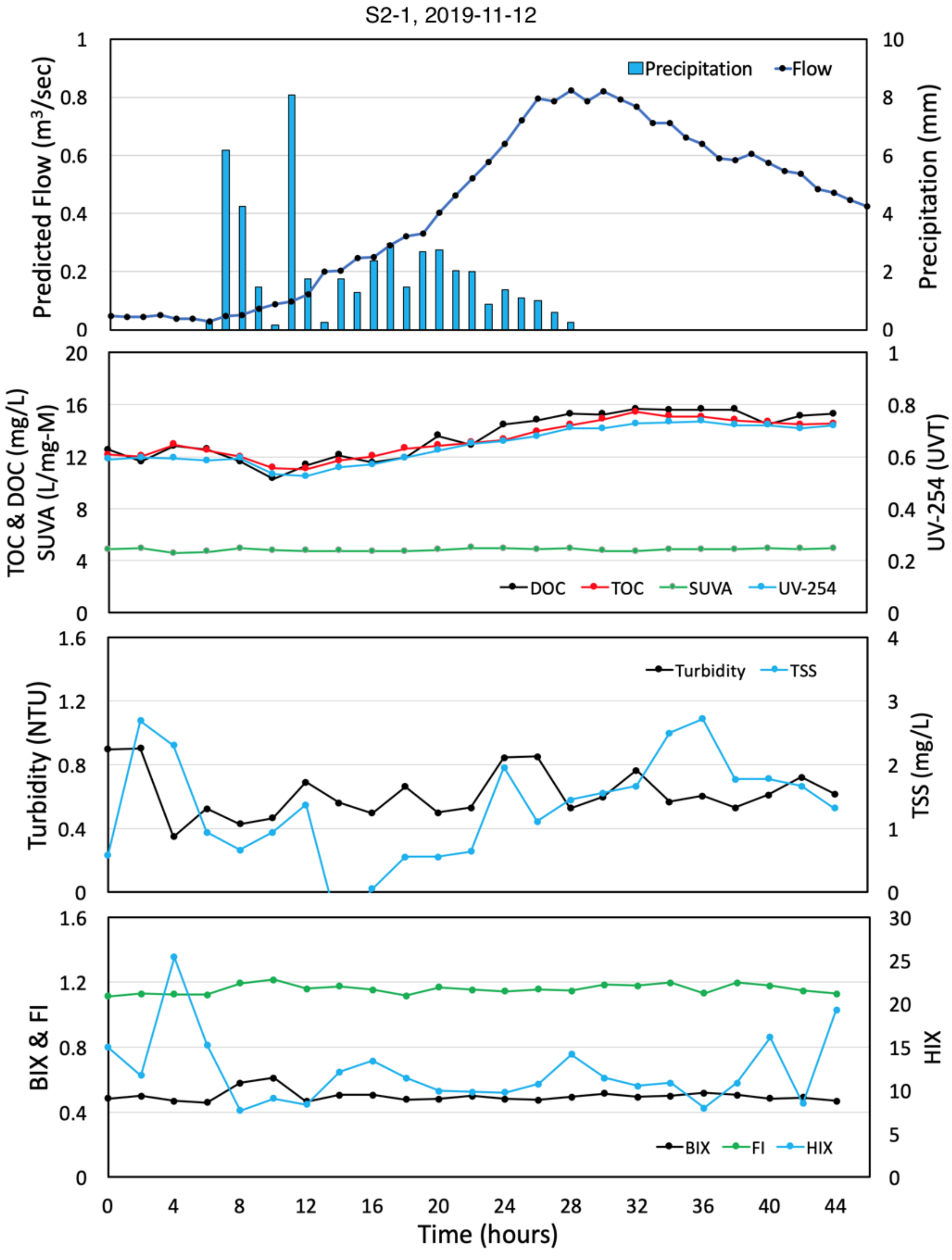

Figure 4.28 – **Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S2-1 throughout the hydrologic event captured on 2019-11-12 over a 48-hour period.**

S4-1 (Figure 3.29) discharge increased once the rain started and peaked a few hours before the rain ended, at 0.12 m^3/s. Six samples were missed due to technical difficulties associated with freezing conditions after the rainfall. DOC, TOC, and UV-254 followed similar trends, peaking at hour 26, the same time as the peak discharge.

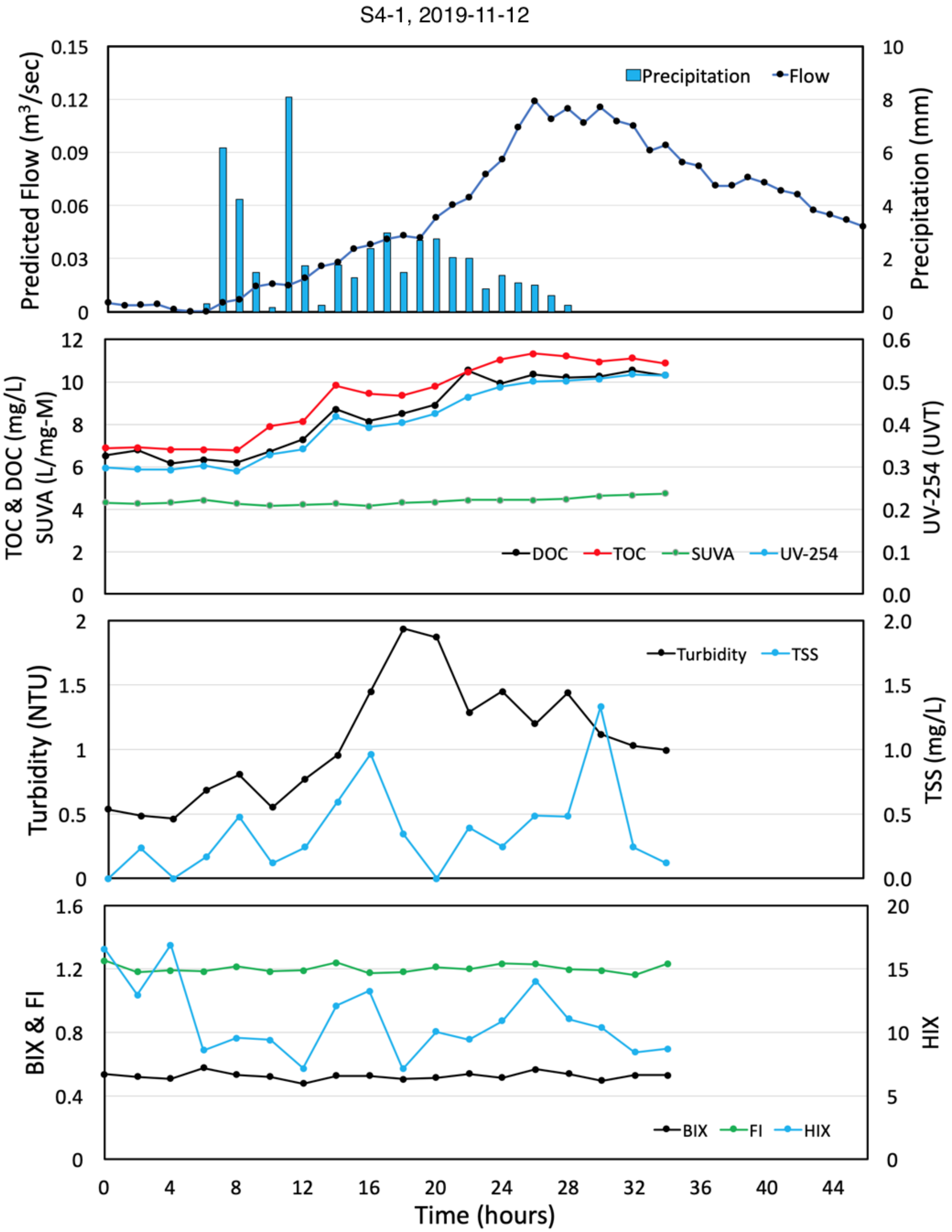

Figure 4.29 **– Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S4-1 throughout the hydrologic event captured on 2019-11-12 over a 48-hour period.**

S4-2 (Figure 3.30) discharge increased from 0.057 to 0.75 m^3/s (1200% increase) at hour 30. The discharge then steadily decreased during the rest of the sampling event. DOC, TOC, UV-254 trends are similar, with modest increases observed throughout the event. DOC concentrations increased from 10.8 mg/L to a peak concentration of 14.1 mg/L, and then decreased to 12.1 mg/L in the last sample collected.

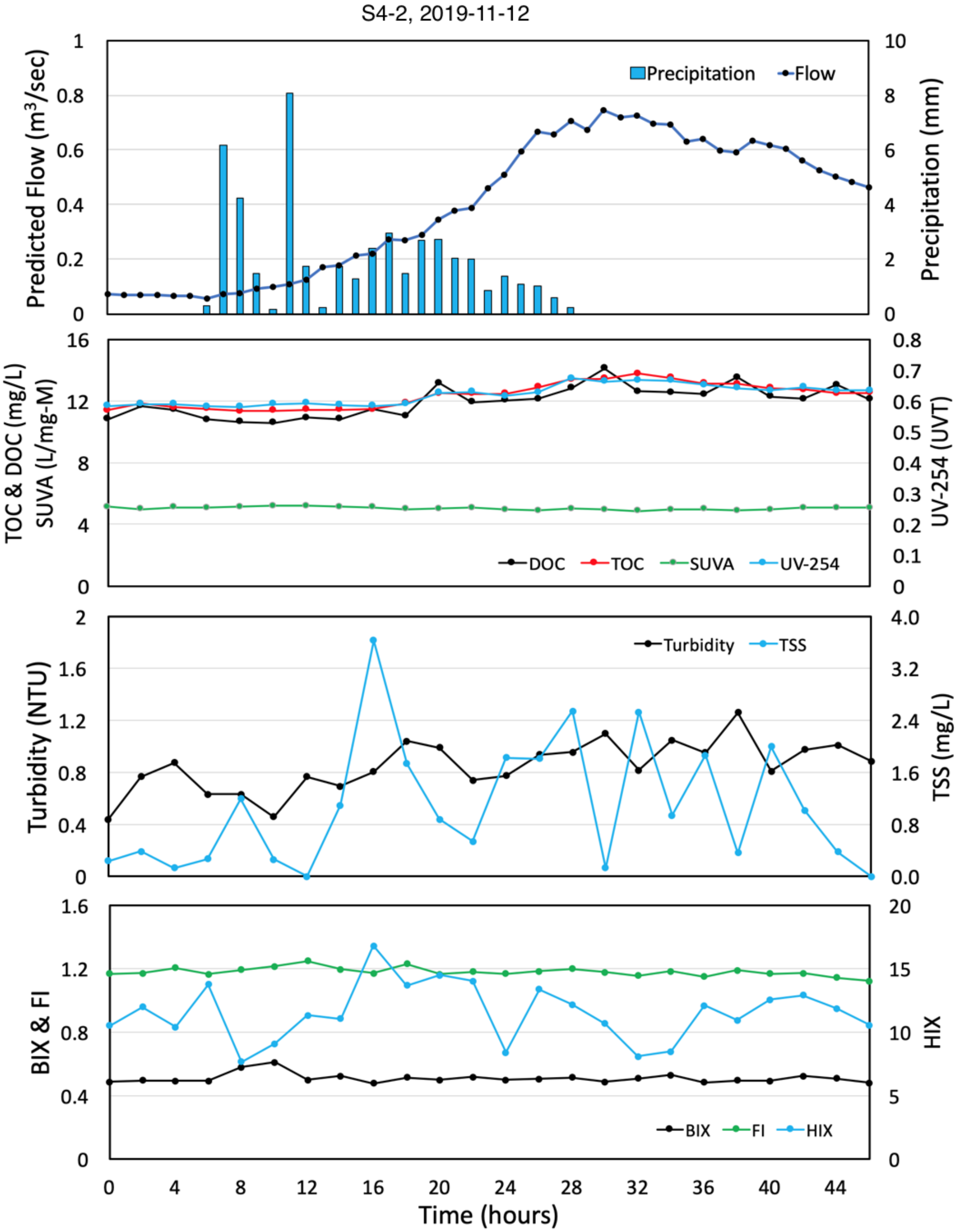

Figure 4.30 **– Temporal variation in discharge, TOC, DOC, SUVA, UV-254, Turbidity, TSS, FI, HIX, and BIX in catchment S4-2 throughout the hydrologic event captured on 2019-11-12 over a 48-hour period.**

In general, the event sampling indicated that DOC contributions to the stream were transport-limited, as concentrations of DOC remained elevated during the falling limb of the storm hydrographs. There was ample supply of DOC within the landscape that was mobilized once interflow was initiated. Van Gaelen et al. (2014) found similar outcomes in forested catchments in Belgium; however, the DOC concentration in a pasture-dominated catchment quickly decreased with discharge after peak flow. The DOC in the pasture was supply-limited and quickly flushed into the stream during hydrologic events. A meta-analysis of hydrologic transport limitations of C in watersheds across ecoregions of the United States by Zarnetske et al. (2018) reported that 80% of DOC flux in watersheds was transport-limited. The same study suggested that the potential reasoning for this is that hydrologic conditions that favour DOC mobilization also stimulate DOC production. DOC typically increases during hydrologic events and can increase by up to 240% during extreme events such as hurricane Dorian. Other researchers have reported similar findings of large DOC concentration increase of up to 350% (Hagedorn et al., 2000) and 450% (Boyer et al., 2000).

Turbidity and TSS concentrations remained relatively unchanged during four out of five events, indicating that direct surface runoff does not occur in these catchments, except during extreme precipitation events, such as Hurricane Dorian.

The FI, HIX, and BIX values also did not change markedly within the events, demonstrating that C sources are associated with landscape (allochthonous) sources. The FI values are all around 1.2 for the events, typical of terrestrial sourced DOC. HIX was highly varied between samples and events but was usually around 10, indicating a moderate humic character. The BIX values were consistently between 0.4 and 0.5, representative of low contributions from autochthonous C sources.

CHAPTER 5: Conclusion

The primary objective of this study was to characterize temporal and spatial variability in hydrologic regime and water quality within several Pockwock watershed subcatchments. With respect to hydrologic response, discharge was highest amongst all study catchments in the early spring due to snowmelt combined with precipitation and increased runoff from saturated/frozen ground. Elevated discharge was also observed during the late fall and winter months, and the lowest discharge was observed during summer months in all catchments. However, there were differences in hydrograph response, and annual water yield, amongst the catchments, and these differences were strongly correlated with watershed attributes. Catchment size and wetland coverage were negatively correlated with water yield while slope was positively correlated.

Concentrations of DOC and TOC were strongly correlated, with DOC accounting for ~95% of TOC in all the catchments. There were significant differences in average concentrations and total loading between the catchments, which again were correlated with watershed attributes. The concentration of DOC is strongly correlated to the percentage of wetland in the catchments, while the total loading was negatively correlated to wetland percentage, area and shape length of the watershed, and positively correlated to the mean slope. This was attributed to the differences in water yield between catchments. There were seasonal trends in DOC concentrations, with the lowest concentrations observed in winter and the highest concentrations in the fall. The DOC loading is highest in the shoulder seasons (spring, fall) due to elevated concentrations and discharge. Levels of UV-254 were strongly correlated to DOC concentration and followed similar trends. Both UV-254 and SUVA were also strongly correlated to wetland coverage, and these metrics indicated that DOC was primarily comprised of humic compounds.

Approximately 65% of TP is comprised of DP across all catchments. There is significant variation in P concentrations and loading amongst the catchments due to varying watershed attributes. DP and TP concentrations were strongly correlated to wetland percentage coverage. However, DP and TP loading were strongly negatively correlated to wetland percentage, as catchments with larger proportions of these land covers generated lower water yields. Nitrogen concentrations were low in all study catchments.

All of the monitoring catchments are underlain by granite bedrock and have either thin glacial till or barren bedrock with little soil development, which limits natural sediment supply. Turbidity and TSS concentrations were relatively low in all study catchments (< 1 NTU and 1 mg/L) during all seasons, but elevated values were observed during an intense rainfall event captured during the monitoring period. Intensive sampling during storm events indicated that there is ample supply of DOC in the Pockwock landscape, and contributions to the stream are typically transport-limited.

5.1 Recommendations for Future Research

This thesis has illustrated important aspects of the hydrology and water quality of Pockwock watershed tributaries, and several recommendations for future research to enhance this understanding has emerged from the research. Continued analysis of post-harvest water quality parameters to assess the impacts of the forest management regimes implemented is recommended. If any changes are detected, continued monitoring should be undertaken to assess how long these changes last for.

Representative climate data are critical for producing hydrographs and understanding annual water yields. The data used in this thesis were obtained from the Halifax Stanfield International Airport, 25 km away from Pockwock Lake. A climate station has since been installed adjacent to the Pockwock watershed and should be maintained to produce more spatially representative climate data for the watershed.

During this study, we were not able to capture hydrologic events during the winter season due to challenges with access and equipment failure due to freezing. Investments could be made into continuous year-round monitoring instrumentation for several parameters such as DOC and turbidity.

All five study catchments are underlain by granite bedrock. Lacey River watershed, the largest tributary to the lake, was not monitored and is underlain by rocks of the Goldenville and Halifax formation, as well as granites. This formation is composed of slates and other metasedimentary rocks. Weathering and erosion of these rocks would produce different geochemistry. Establishing a comparable monitoring program on this catchment would provide additional insight on how bedrock geology impacts water quality.

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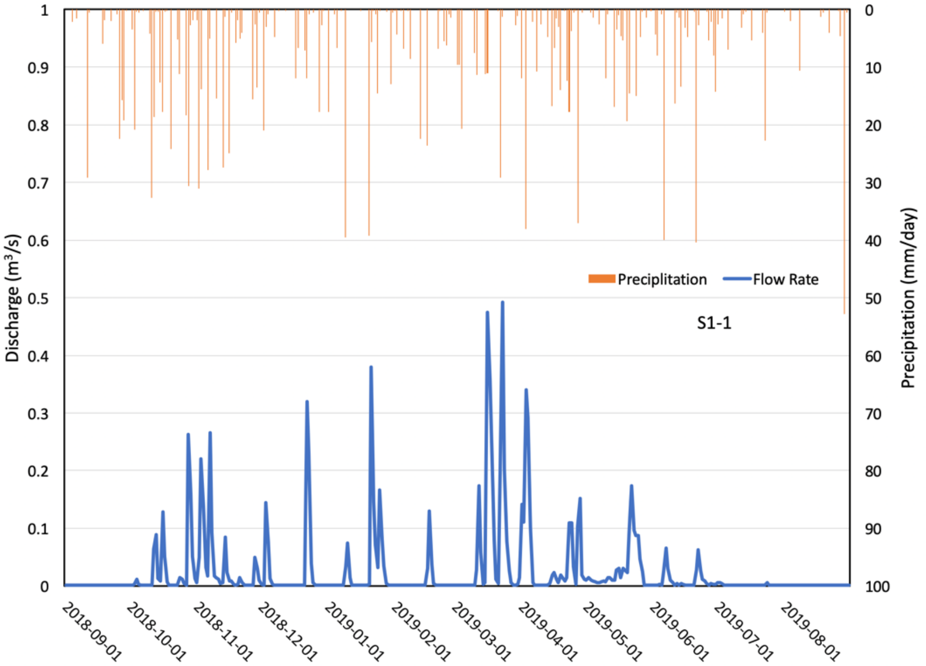
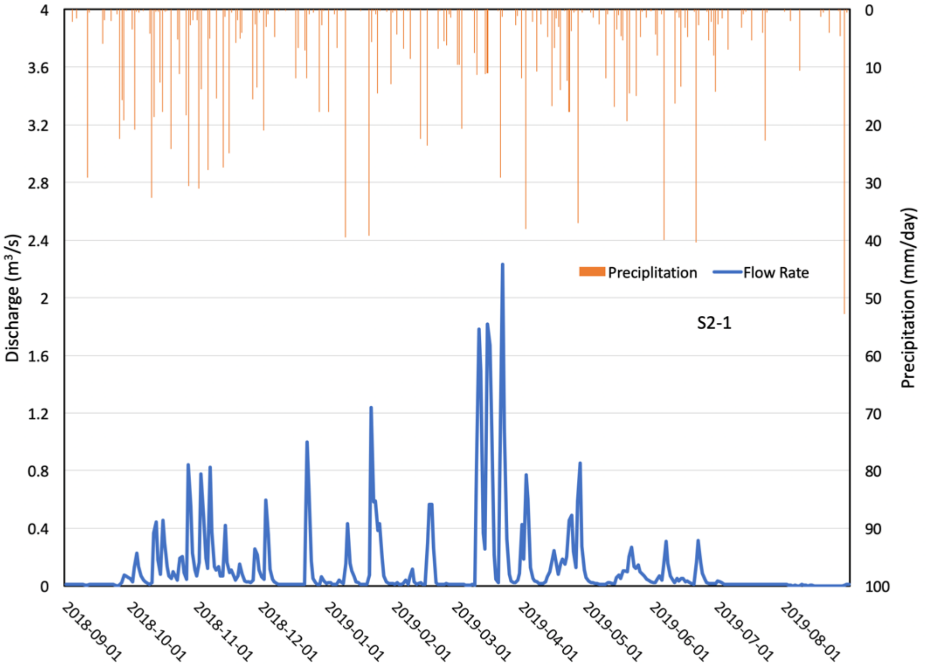
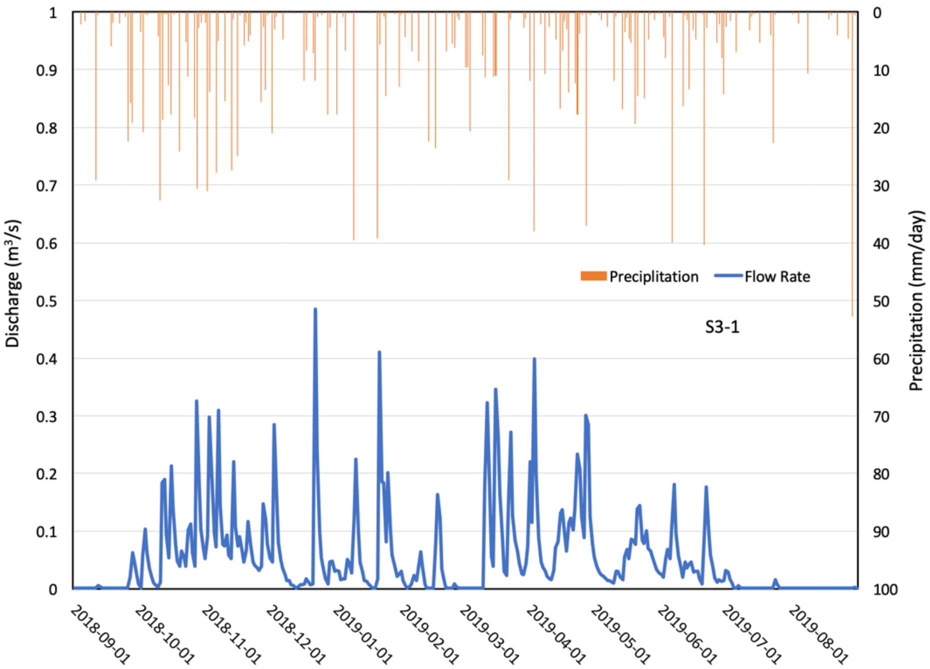
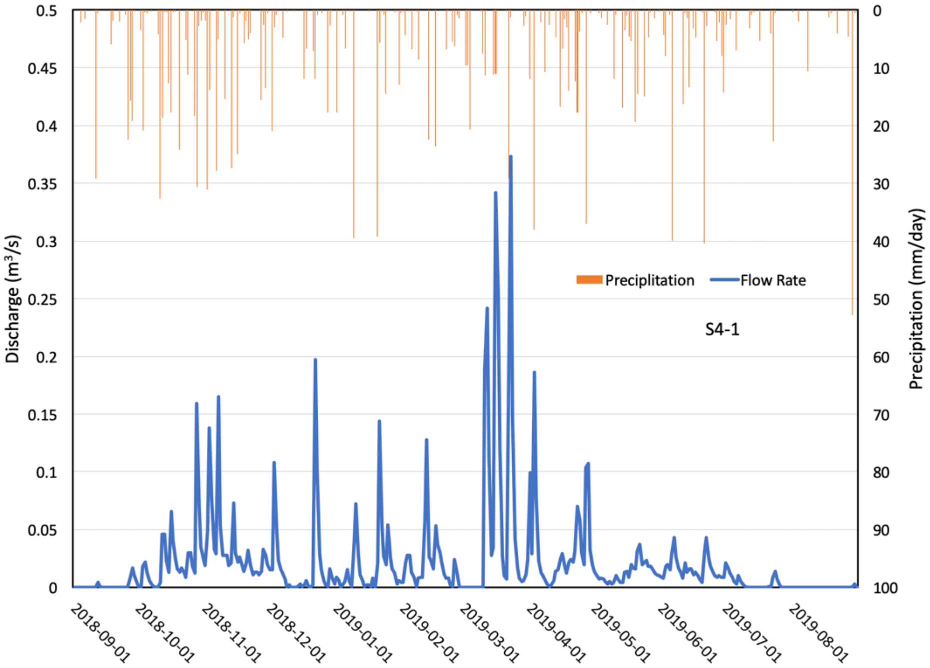
Appendix A: Monitoring Catchment Hydrographs






Discharge (m³/s)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Precipitation (mm/day)
0
10
20
30
40
50
60
70
80
90
100
Preciplitation
Flow Rate
S3-1
2018-09-01
2018-10-01
2018-11-01
2018-12-01
2019-01-01
2019-02-01
2019-03-01
2019-04-01
2019-05-01
2019-06-01
2019-07-01
2019-08-01


Discharge (m³/s)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Precipitation (mm/day)
0
10
20
30
40
50
60
70
80
90
100
Preciplitation
Flow Rate
S4-1
2018-09-01
2018-10-01
2018-11-01
2018-12-01
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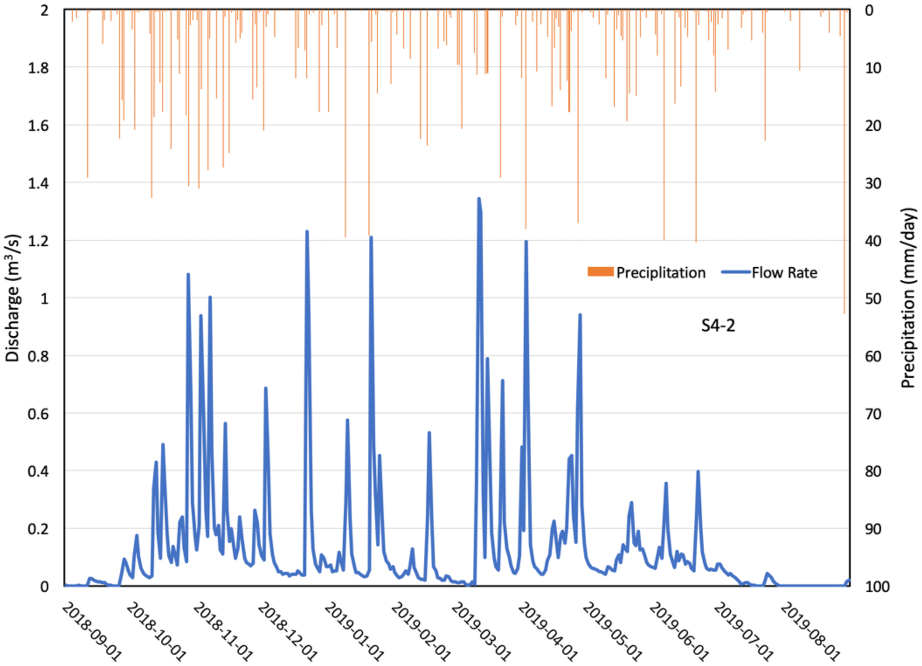
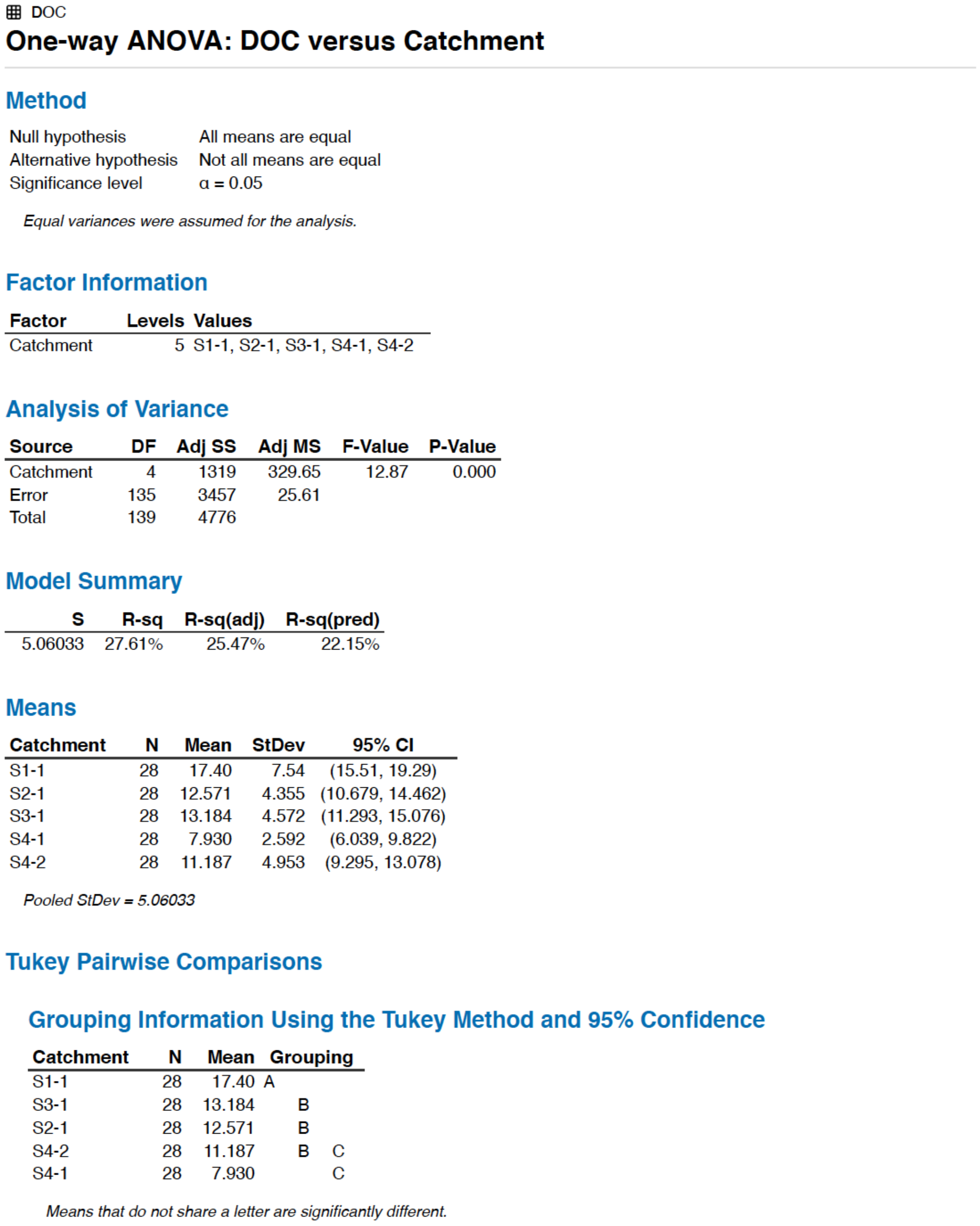
2019-03-01
2019-04-01
2019-05-01
2019-06-01
2019-07-01
2019-08-01


Discharge (m³/s)
Precipitation (mm/day)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
70
80
90
100
Precipitation
Flow Rate
S4-2
2018-09-01
2018-10-01
2018-11-01
2018-12-01
2019-01-01
2019-02-01
2019-03-01
2019-04-01
2019-05-01
2019-06-01
2019-07-01
2019-08-01

Appendix B: One-Way ANOVA



▦ DOC

One-way ANOVA: DOC versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	1319	329.65	12.87	0.000
Error	135	3457	25.61		
Total	139	4776			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
5.06033	27.61%	25.47%	22.15%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	28	17.40	7.54	(15.51, 19.29)
S2-1	28	12.571	4.355	(10.679, 14.462)
S3-1	28	13.184	4.572	(11.293, 15.076)
S4-1	28	7.930	2.592	(6.039, 9.822)
S4-2	28	11.187	4.953	(9.295, 13.078)

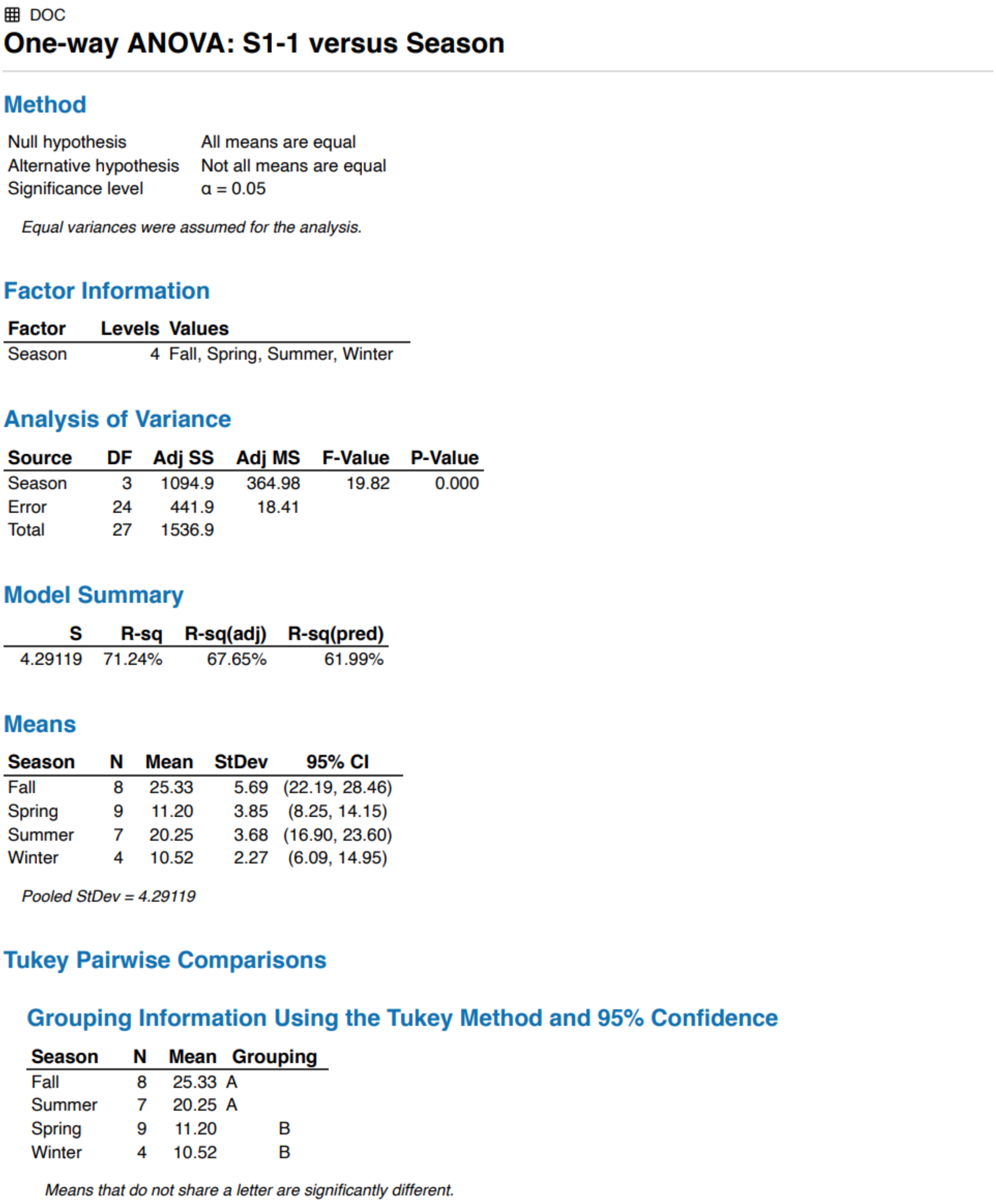
Pooled StDev = 5.06033

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Catchment	N	Mean	Grouping
S1-1	28	17.40	A
S3-1	28	13.184	B
S2-1	28	12.571	B
S4-2	28	11.187	B C
S4-1	28	7.930	C

Means that do not share a letter are significantly different.



▦ DOC

One-way ANOVA: S1-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	1094.9	364.98	19.82	0.000
Error	24	441.9	18.41		
Total	27	1536.9			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
4.29119	71.24%	67.65%	61.99%

Means

Season	N	Mean	StDev	95% CI
Fall	8	25.33	5.69	(22.19, 28.46)
Spring	9	11.20	3.85	(8.25, 14.15)
Summer	7	20.25	3.68	(16.90, 23.60)
Winter	4	10.52	2.27	(6.09, 14.95)

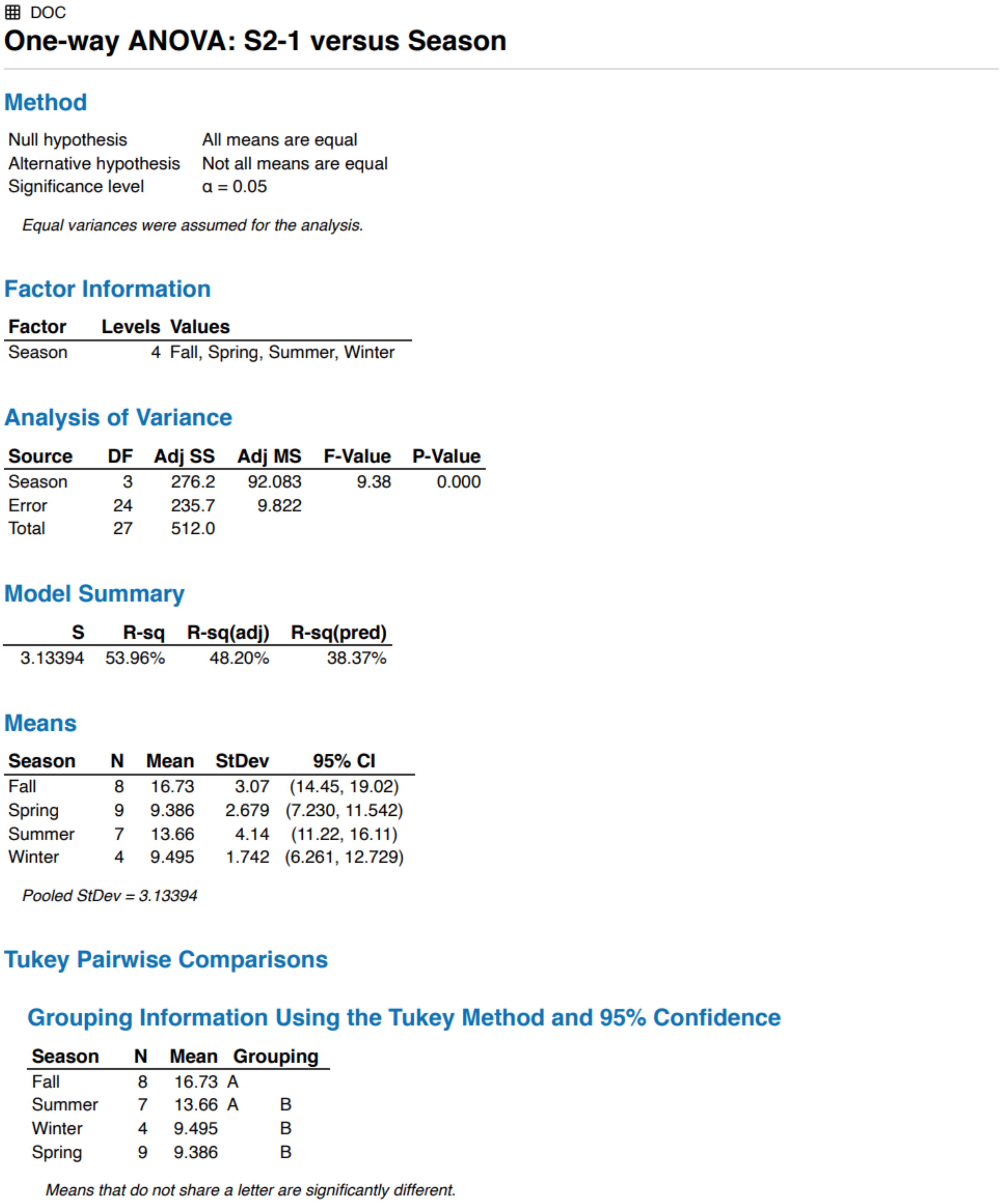
Pooled StDev = 4.29119

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping	
Fall	8	25.33	A	
Summer	7	20.25	A	
Spring	9	11.20		B
Winter	4	10.52		B

Means that do not share a letter are significantly different.



DOC

One-way ANOVA: S2-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	276.2	92.083	9.38	0.000
Error	24	235.7	9.822		
Total	27	512.0			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
3.13394	53.96%	48.20%	38.37%

Means

Season	N	Mean	StDev	95% CI
Fall	8	16.73	3.07	(14.45, 19.02)
Spring	9	9.386	2.679	(7.230, 11.542)
Summer	7	13.66	4.14	(11.22, 16.11)
Winter	4	9.495	1.742	(6.261, 12.729)

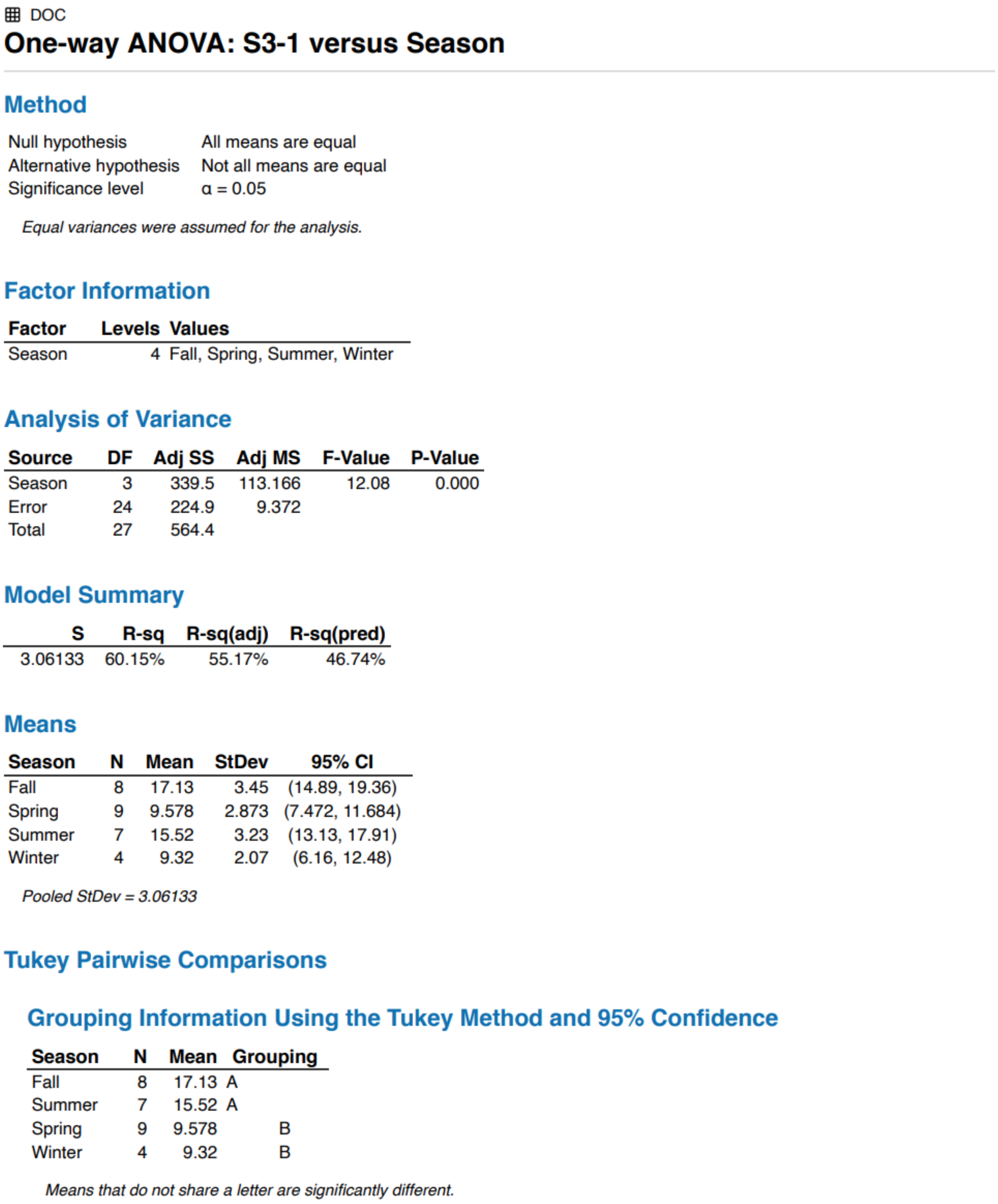
Pooled StDev = 3.13394

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping	
Fall	8	16.73	A	
Summer	7	13.66	A	B
Winter	4	9.495		B
Spring	9	9.386		B

Means that do not share a letter are significantly different.



▦ DOC

One-way ANOVA: S3-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	339.5	113.166	12.08	0.000
Error	24	224.9	9.372		
Total	27	564.4			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
3.06133	60.15%	55.17%	46.74%

Means

Season	N	Mean	StDev	95% CI
Fall	8	17.13	3.45	(14.89, 19.36)
Spring	9	9.578	2.873	(7.472, 11.684)
Summer	7	15.52	3.23	(13.13, 17.91)
Winter	4	9.32	2.07	(6.16, 12.48)

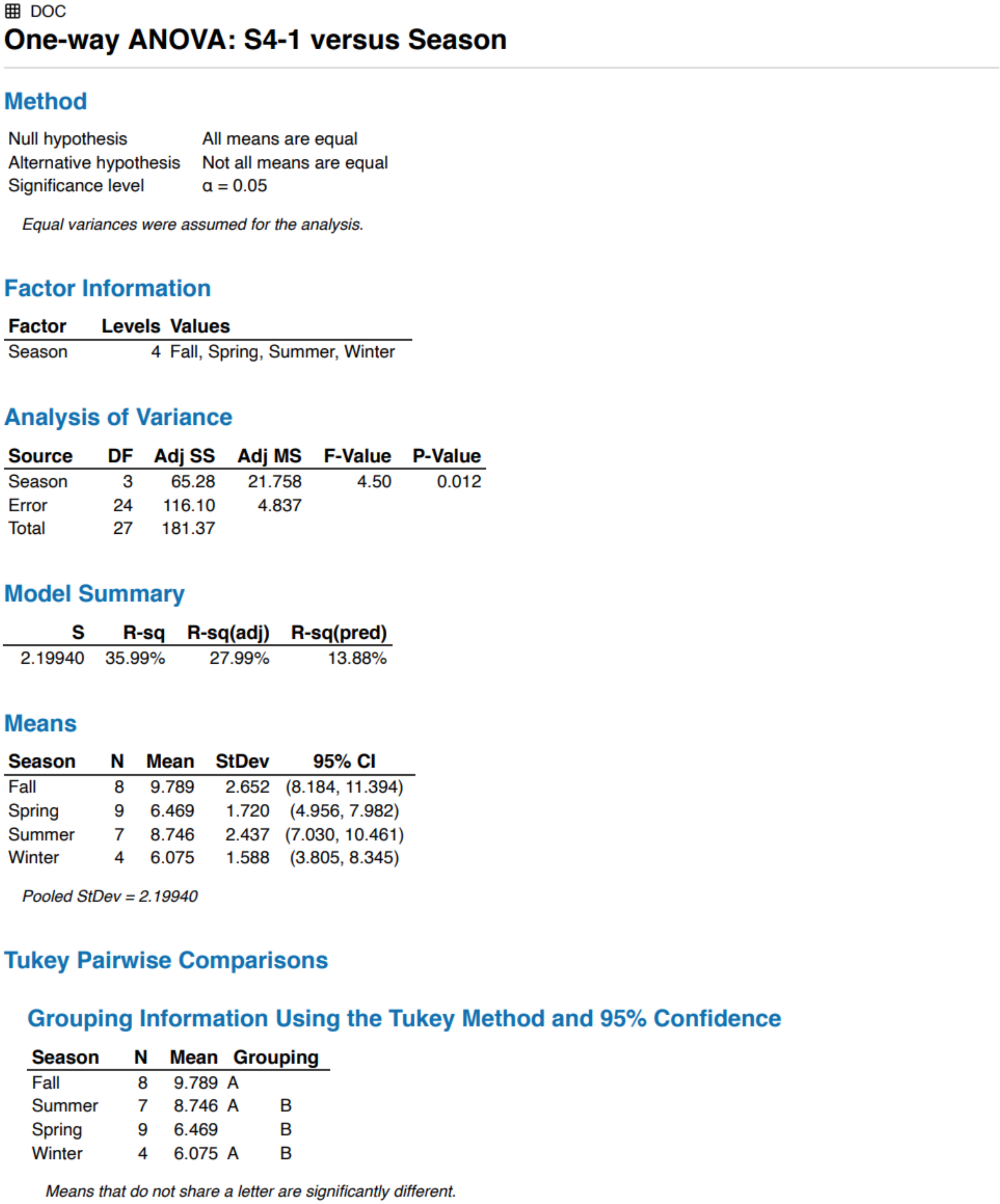
Pooled StDev = 3.06133

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping	
Fall	8	17.13	A	
Summer	7	15.52	A	
Spring	9	9.578		B
Winter	4	9.32		B

Means that do not share a letter are significantly different.



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One-way ANOVA: S4-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	65.28	21.758	4.50	0.012
Error	24	116.10	4.837		
Total	27	181.37			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.19940	35.99%	27.99%	13.88%

Means

Season	N	Mean	StDev	95% CI
Fall	8	9.789	2.652	(8.184, 11.394)
Spring	9	6.469	1.720	(4.956, 7.982)
Summer	7	8.746	2.437	(7.030, 10.461)
Winter	4	6.075	1.588	(3.805, 8.345)

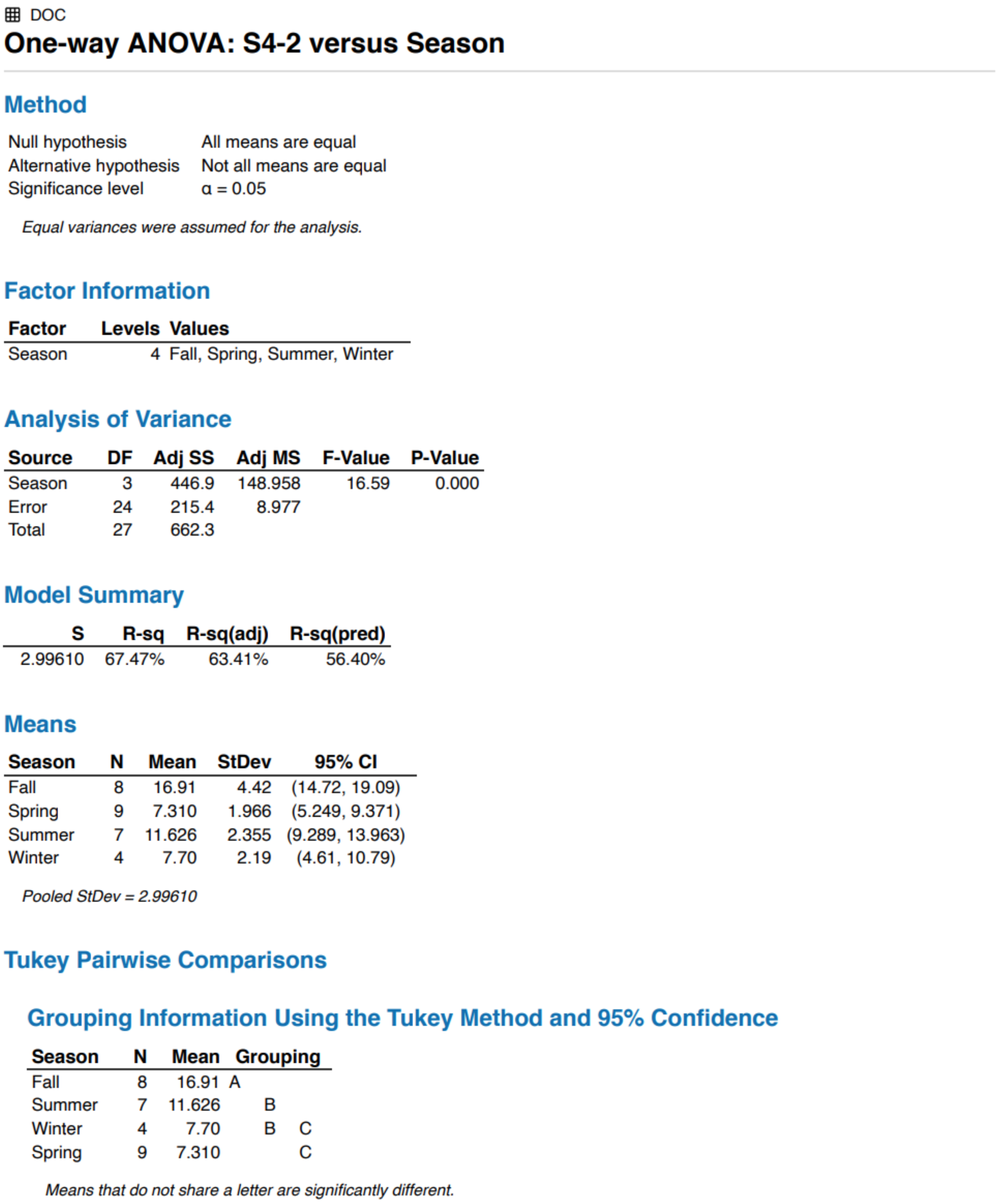
Pooled StDev = 2.19940

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping	
Fall	8	9.789	A	
Summer	7	8.746	A	B
Spring	9	6.469		B
Winter	4	6.075	A	B

Means that do not share a letter are significantly different.



DOC

One-way ANOVA: S4-2 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	446.9	148.958	16.59	0.000
Error	24	215.4	8.977		
Total	27	662.3			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.99610	67.47%	63.41%	56.40%

Means

Season	N	Mean	StDev	95% CI
Fall	8	16.91	4.42	(14.72, 19.09)
Spring	9	7.310	1.966	(5.249, 9.371)
Summer	7	11.626	2.355	(9.289, 13.963)
Winter	4	7.70	2.19	(4.61, 10.79)

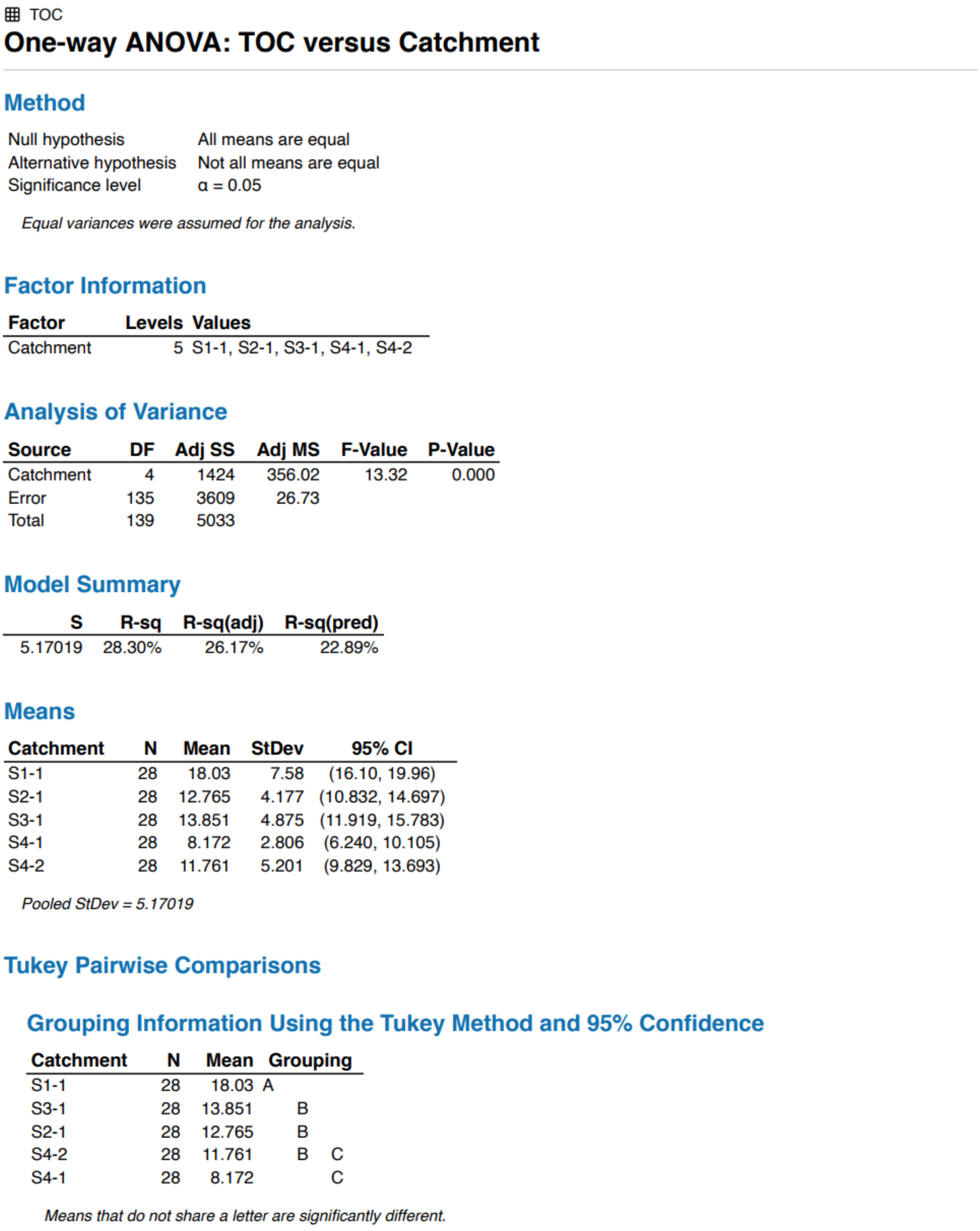
Pooled StDev = 2.99610

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping
Fall	8	16.91	A
Summer	7	11.626	B
Winter	4	7.70	B C
Spring	9	7.310	C

Means that do not share a letter are significantly different.



TOC

One-way ANOVA: TOC versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	1424	356.02	13.32	0.000
Error	135	3609	26.73		
Total	139	5033			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
5.17019	28.30%	26.17%	22.89%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	28	18.03	7.58	(16.10, 19.96)
S2-1	28	12.765	4.177	(10.832, 14.697)
S3-1	28	13.851	4.875	(11.919, 15.783)
S4-1	28	8.172	2.806	(6.240, 10.105)
S4-2	28	11.761	5.201	(9.829, 13.693)

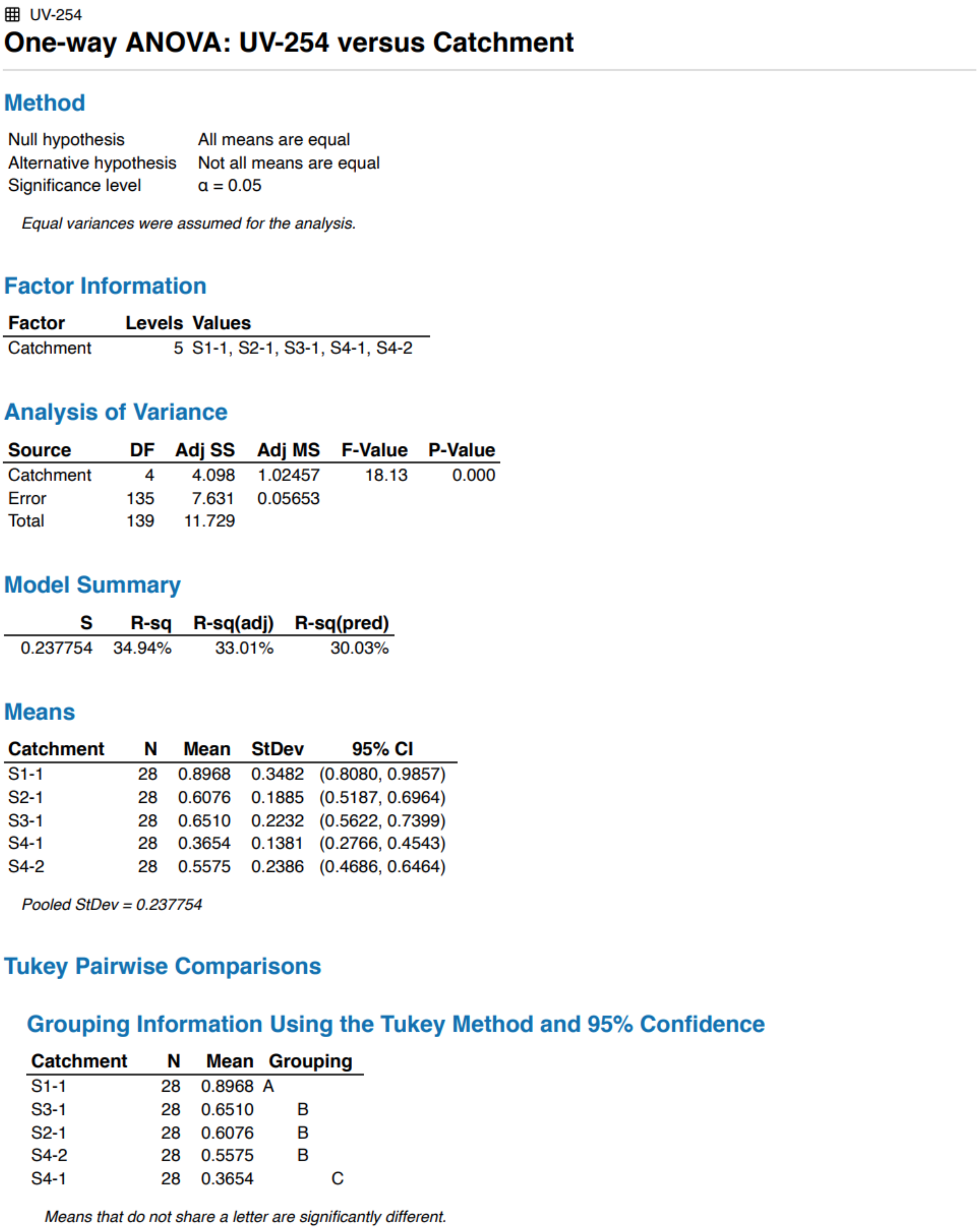
Pooled StDev = 5.17019

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Catchment	N	Mean	Grouping		
S1-1	28	18.03	A		
S3-1	28	13.851		B	
S2-1	28	12.765		B	
S4-2	28	11.761		B	C
S4-1	28	8.172			C

Means that do not share a letter are significantly different.



UV-254

One-way ANOVA: UV-254 versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	4.098	1.02457	18.13	0.000
Error	135	7.631	0.05653		
Total	139	11.729			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.237754	34.94%	33.01%	30.03%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	28	0.8968	0.3482	(0.8080, 0.9857)
S2-1	28	0.6076	0.1885	(0.5187, 0.6964)
S3-1	28	0.6510	0.2232	(0.5622, 0.7399)
S4-1	28	0.3654	0.1381	(0.2766, 0.4543)
S4-2	28	0.5575	0.2386	(0.4686, 0.6464)

Pooled StDev = 0.237754

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Catchment	N	Mean	Grouping		
S1-1	28	0.8968	A		
S3-1	28	0.6510		B	
S2-1	28	0.6076		B	
S4-2	28	0.5575		B	
S4-1	28	0.3654			C

Means that do not share a letter are significantly different.

▦ UV-254

One-way ANOVA: S1-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	2.4400	0.81333	23.41	0.000
Error	24	0.8338	0.03474		
Total	27	3.2738			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.186395	74.53%	71.35%	66.41%

Means

Season	N	Mean	StDev	95% CI
Fall	8	1.2474	0.2259	(1.1114, 1.3834)
Spring	9	0.5854	0.2101	(0.4572, 0.7137)
Summer	7	1.0709	0.1153	(0.9255, 1.2163)
Winter	4	0.5917	0.1208	(0.3994, 0.7841)

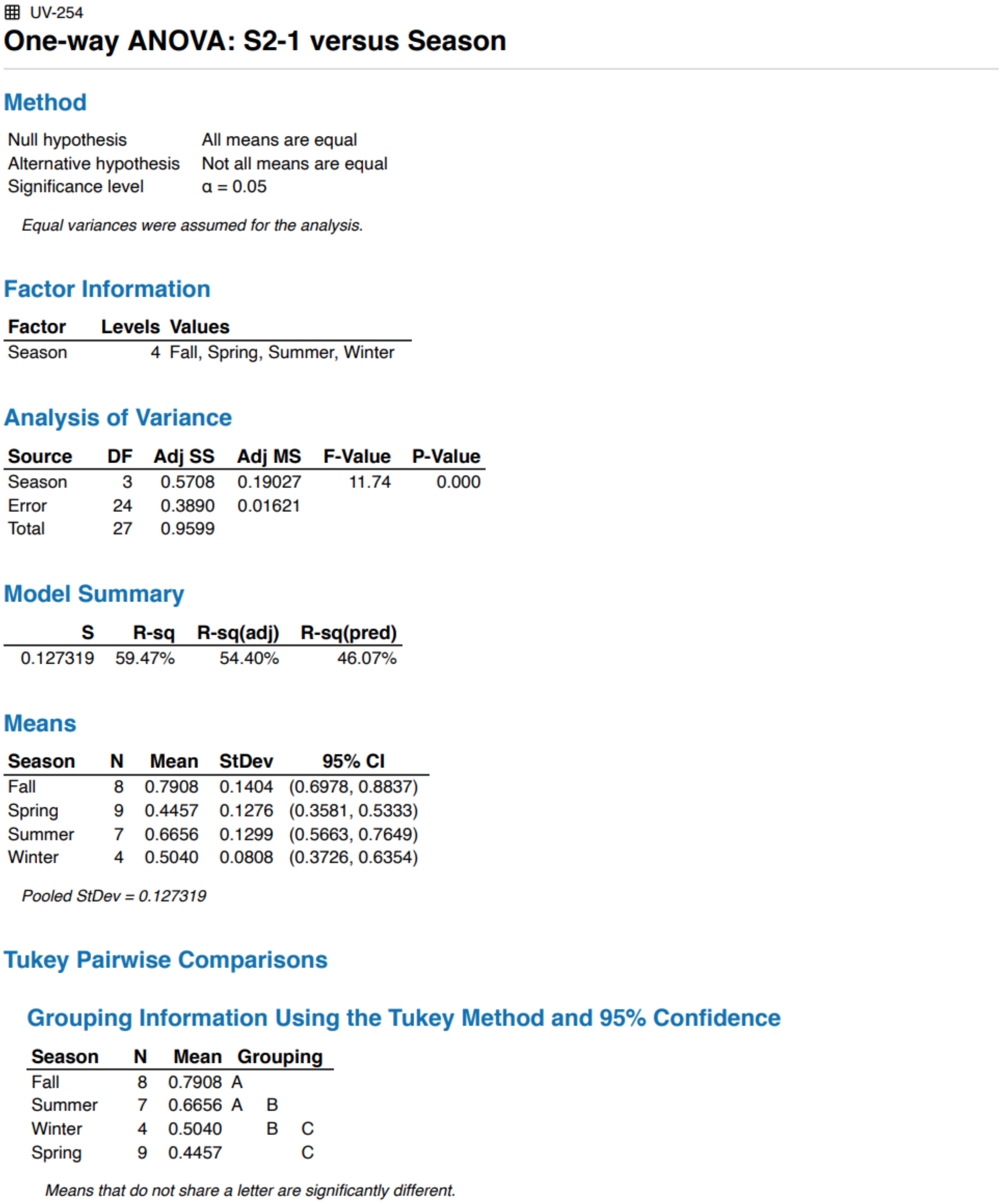
Pooled StDev = 0.186395

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping	
Fall	8	1.2474	A	
Summer	7	1.0709	A	
Winter	4	0.5917		B
Spring	9	0.5854		B

Means that do not share a letter are significantly different.



UV-254

One-way ANOVA: S2-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	0.5708	0.19027	11.74	0.000
Error	24	0.3890	0.01621		
Total	27	0.9599			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.127319	59.47%	54.40%	46.07%

Means

Season	N	Mean	StDev	95% CI
Fall	8	0.7908	0.1404	(0.6978, 0.8837)
Spring	9	0.4457	0.1276	(0.3581, 0.5333)
Summer	7	0.6656	0.1299	(0.5663, 0.7649)
Winter	4	0.5040	0.0808	(0.3726, 0.6354)

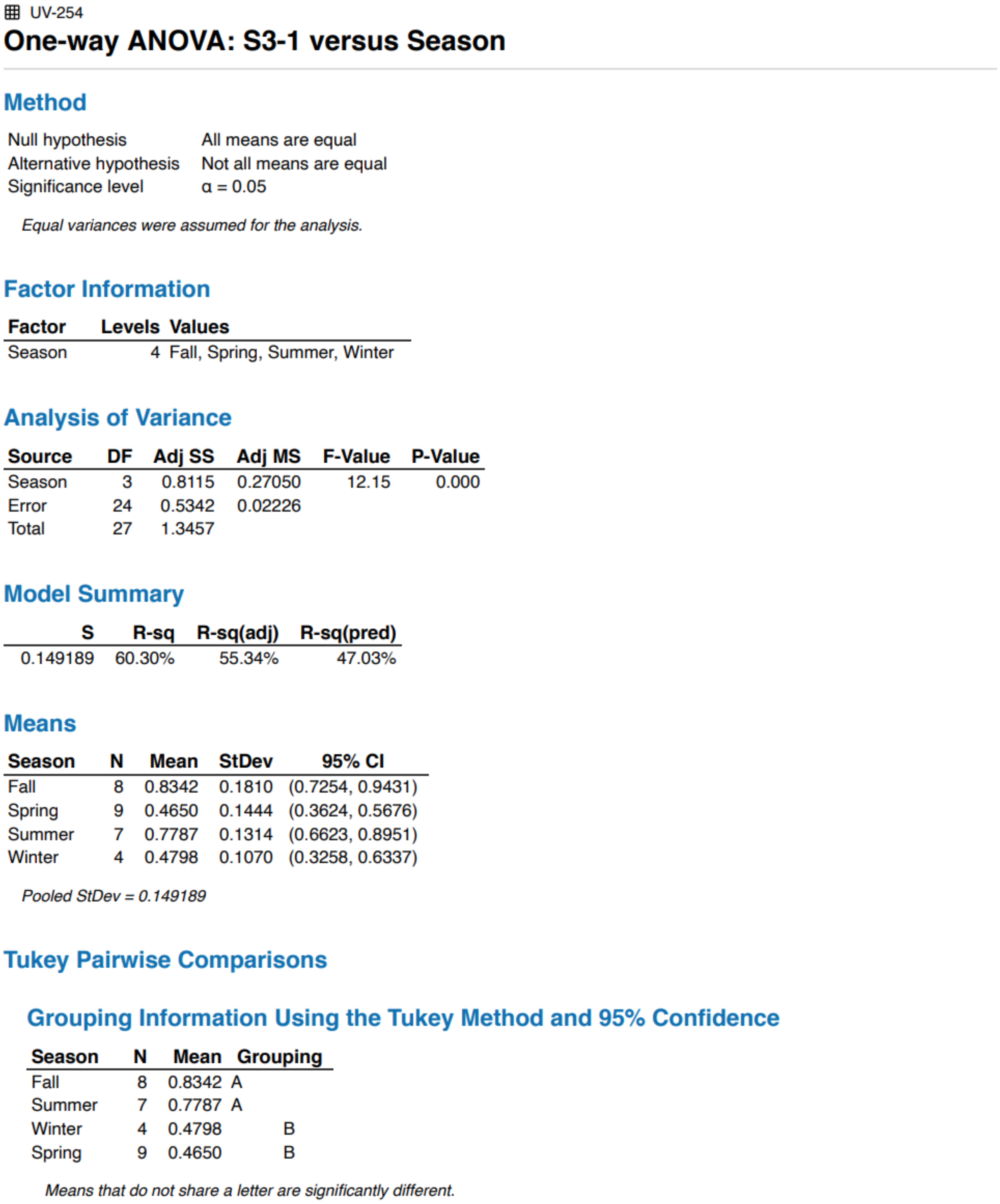
Pooled StDev = 0.127319

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping		
Fall	8	0.7908	A		
Summer	7	0.6656	A	B	
Winter	4	0.5040		B	C
Spring	9	0.4457			C

Means that do not share a letter are significantly different.



UV-254

One-way ANOVA: S3-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	0.8115	0.27050	12.15	0.000
Error	24	0.5342	0.02226		
Total	27	1.3457			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.149189	60.30%	55.34%	47.03%

Means

Season	N	Mean	StDev	95% CI
Fall	8	0.8342	0.1810	(0.7254, 0.9431)
Spring	9	0.4650	0.1444	(0.3624, 0.5676)
Summer	7	0.7787	0.1314	(0.6623, 0.8951)
Winter	4	0.4798	0.1070	(0.3258, 0.6337)

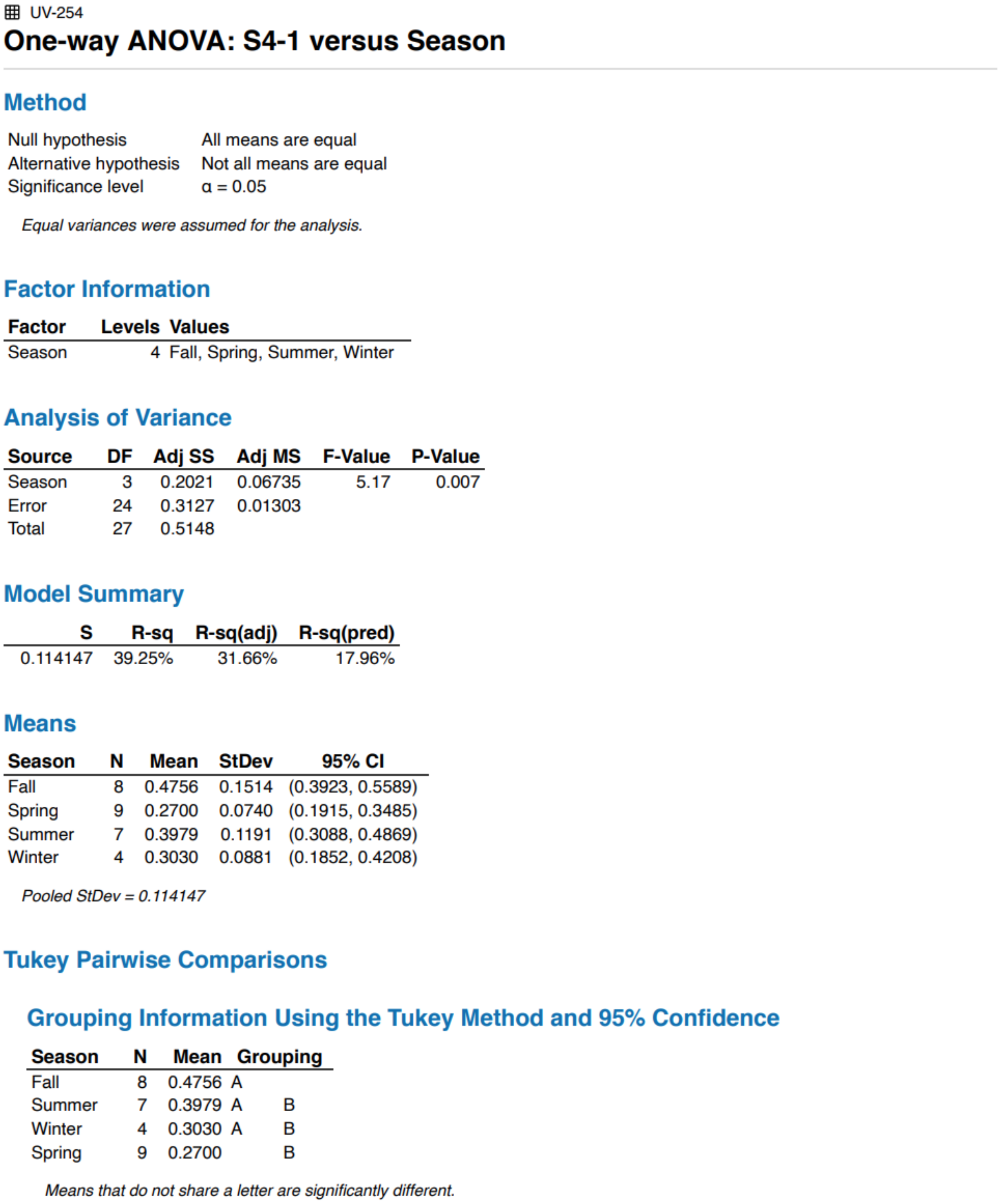
Pooled StDev = 0.149189

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping	
Fall	8	0.8342	A	
Summer	7	0.7787	A	
Winter	4	0.4798		B
Spring	9	0.4650		B

Means that do not share a letter are significantly different.



UV-254

One-way ANOVA: S4-1 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	0.2021	0.06735	5.17	0.007
Error	24	0.3127	0.01303		
Total	27	0.5148			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.114147	39.25%	31.66%	17.96%

Means

Season	N	Mean	StDev	95% CI
Fall	8	0.4756	0.1514	(0.3923, 0.5589)
Spring	9	0.2700	0.0740	(0.1915, 0.3485)
Summer	7	0.3979	0.1191	(0.3088, 0.4869)
Winter	4	0.3030	0.0881	(0.1852, 0.4208)

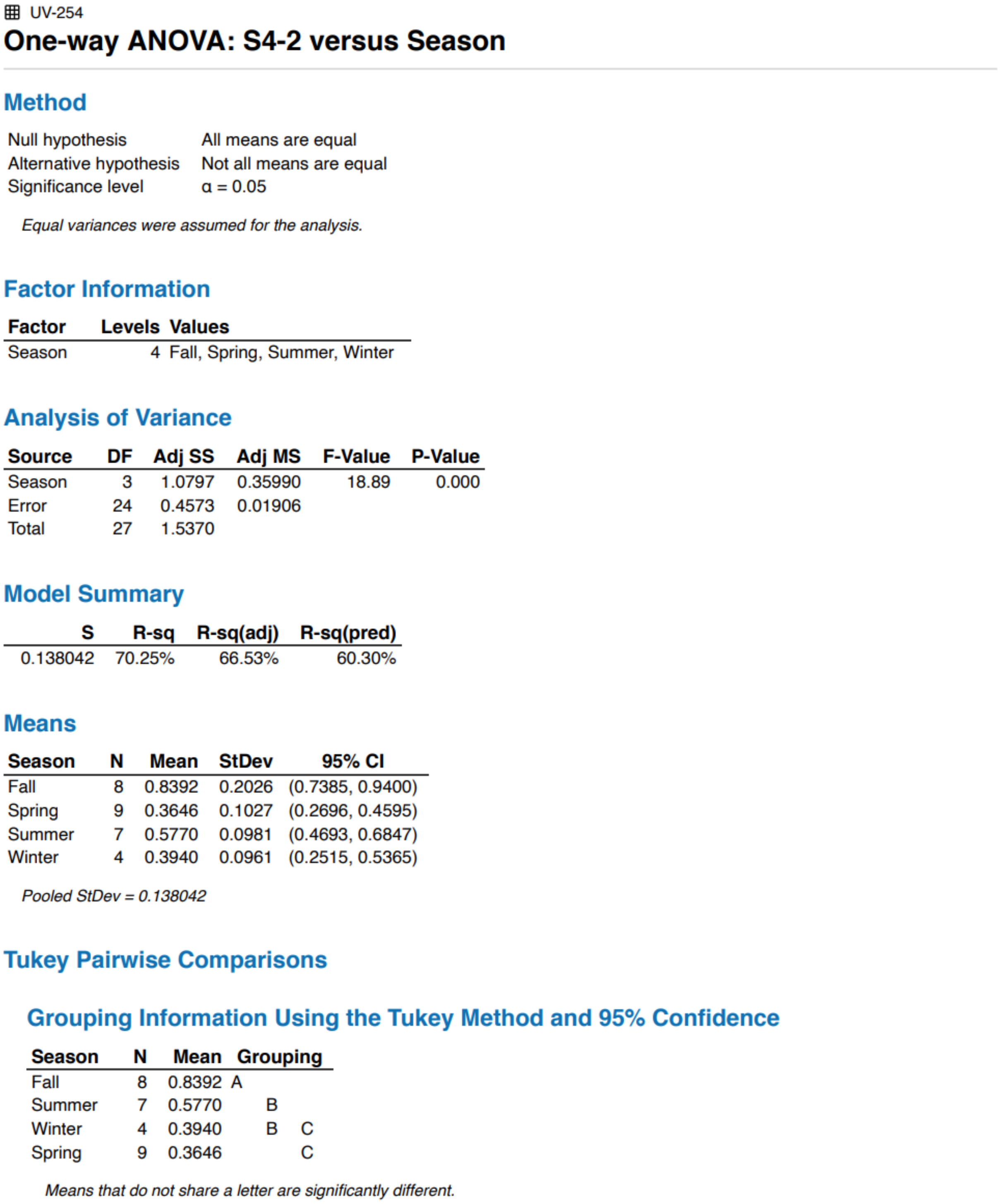
Pooled StDev = 0.114147

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping	
Fall	8	0.4756	A	
Summer	7	0.3979	A	B
Winter	4	0.3030	A	B
Spring	9	0.2700		B

Means that do not share a letter are significantly different.



UV-254

One-way ANOVA: S4-2 versus Season

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Season	4	Fall, Spring, Summer, Winter

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Season	3	1.0797	0.35990	18.89	0.000
Error	24	0.4573	0.01906		
Total	27	1.5370			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.138042	70.25%	66.53%	60.30%

Means

Season	N	Mean	StDev	95% CI
Fall	8	0.8392	0.2026	(0.7385, 0.9400)
Spring	9	0.3646	0.1027	(0.2696, 0.4595)
Summer	7	0.5770	0.0981	(0.4693, 0.6847)
Winter	4	0.3940	0.0961	(0.2515, 0.5365)

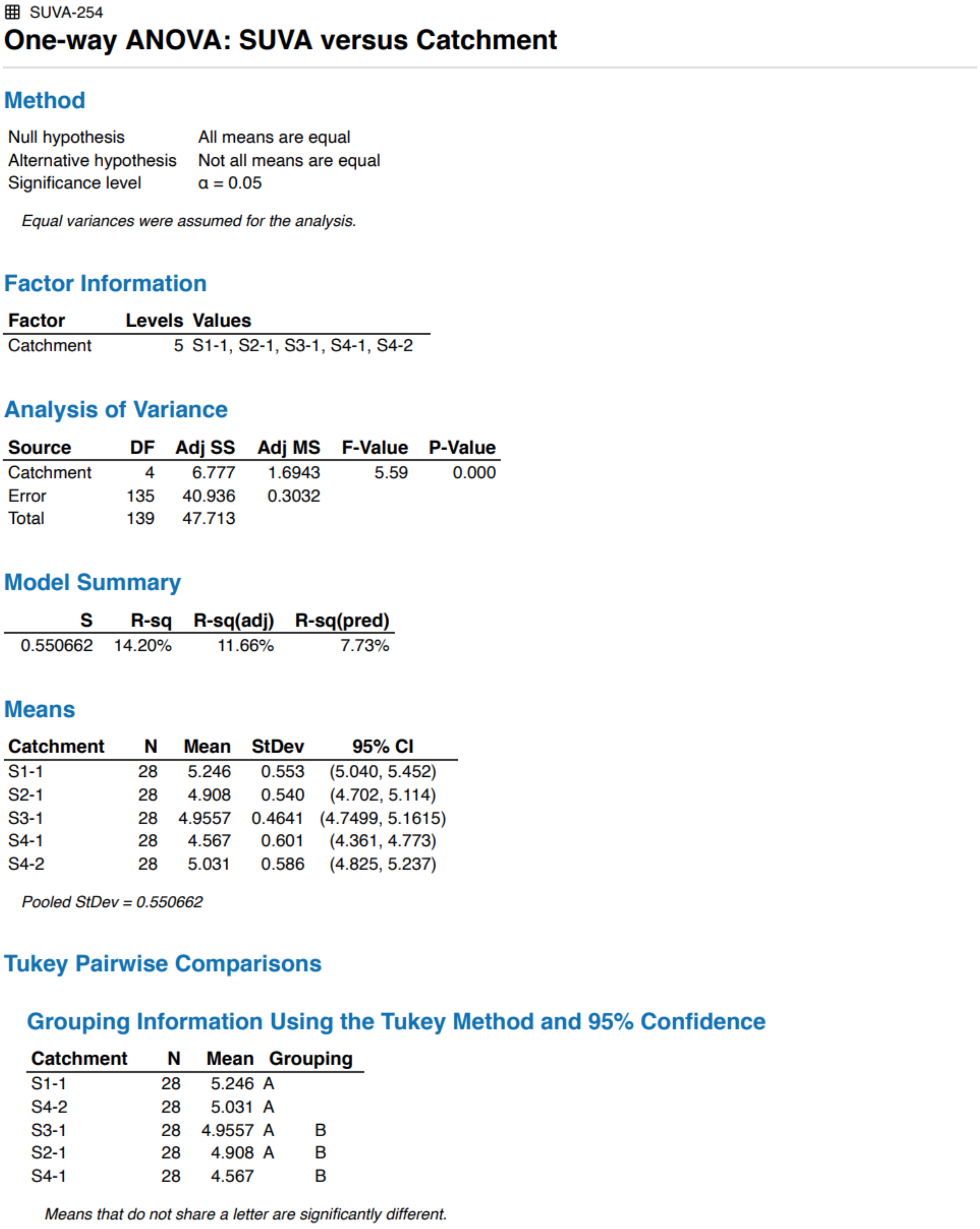
Pooled StDev = 0.138042

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Season	N	Mean	Grouping		
Fall	8	0.8392	A		
Summer	7	0.5770		B	
Winter	4	0.3940		B	C
Spring	9	0.3646			C

Means that do not share a letter are significantly different.



SUVA-254

One-way ANOVA: SUVA versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	6.777	1.6943	5.59	0.000
Error	135	40.936	0.3032		
Total	139	47.713			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.550662	14.20%	11.66%	7.73%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	28	5.246	0.553	(5.040, 5.452)
S2-1	28	4.908	0.540	(4.702, 5.114)
S3-1	28	4.9557	0.4641	(4.7499, 5.1615)
S4-1	28	4.567	0.601	(4.361, 4.773)
S4-2	28	5.031	0.586	(4.825, 5.237)

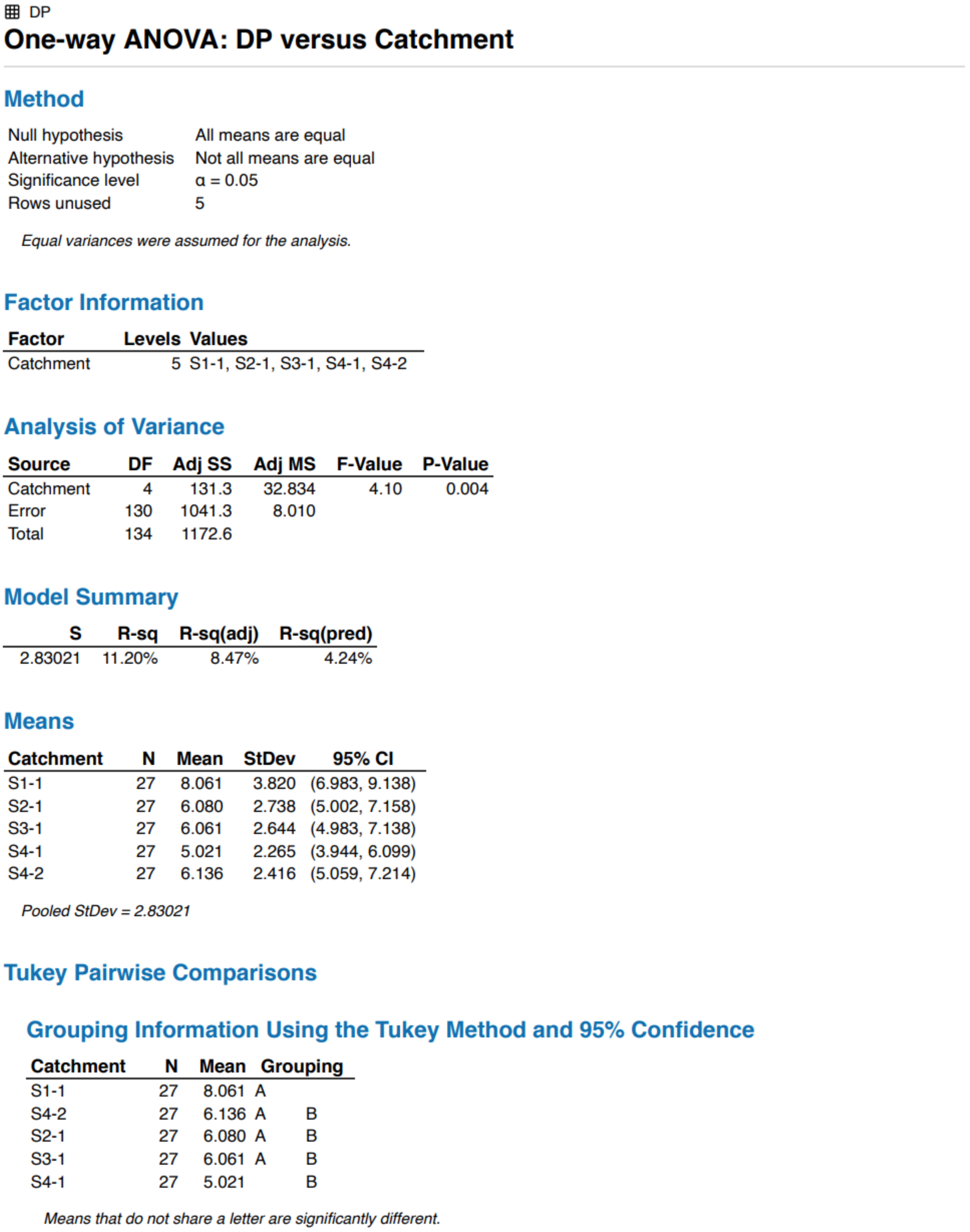
Pooled StDev = 0.550662

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Catchment	N	Mean	Grouping	
S1-1	28	5.246	A	
S4-2	28	5.031	A	
S3-1	28	4.9557	A	B
S2-1	28	4.908	A	B
S4-1	28	4.567		B

Means that do not share a letter are significantly different.



▦ DP

One-way ANOVA: DP versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05
Rows unused	5

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	131.3	32.834	4.10	0.004
Error	130	1041.3	8.010		
Total	134	1172.6			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.83021	11.20%	8.47%	4.24%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	27	8.061	3.820	(6.983, 9.138)
S2-1	27	6.080	2.738	(5.002, 7.158)
S3-1	27	6.061	2.644	(4.983, 7.138)
S4-1	27	5.021	2.265	(3.944, 6.099)
S4-2	27	6.136	2.416	(5.059, 7.214)

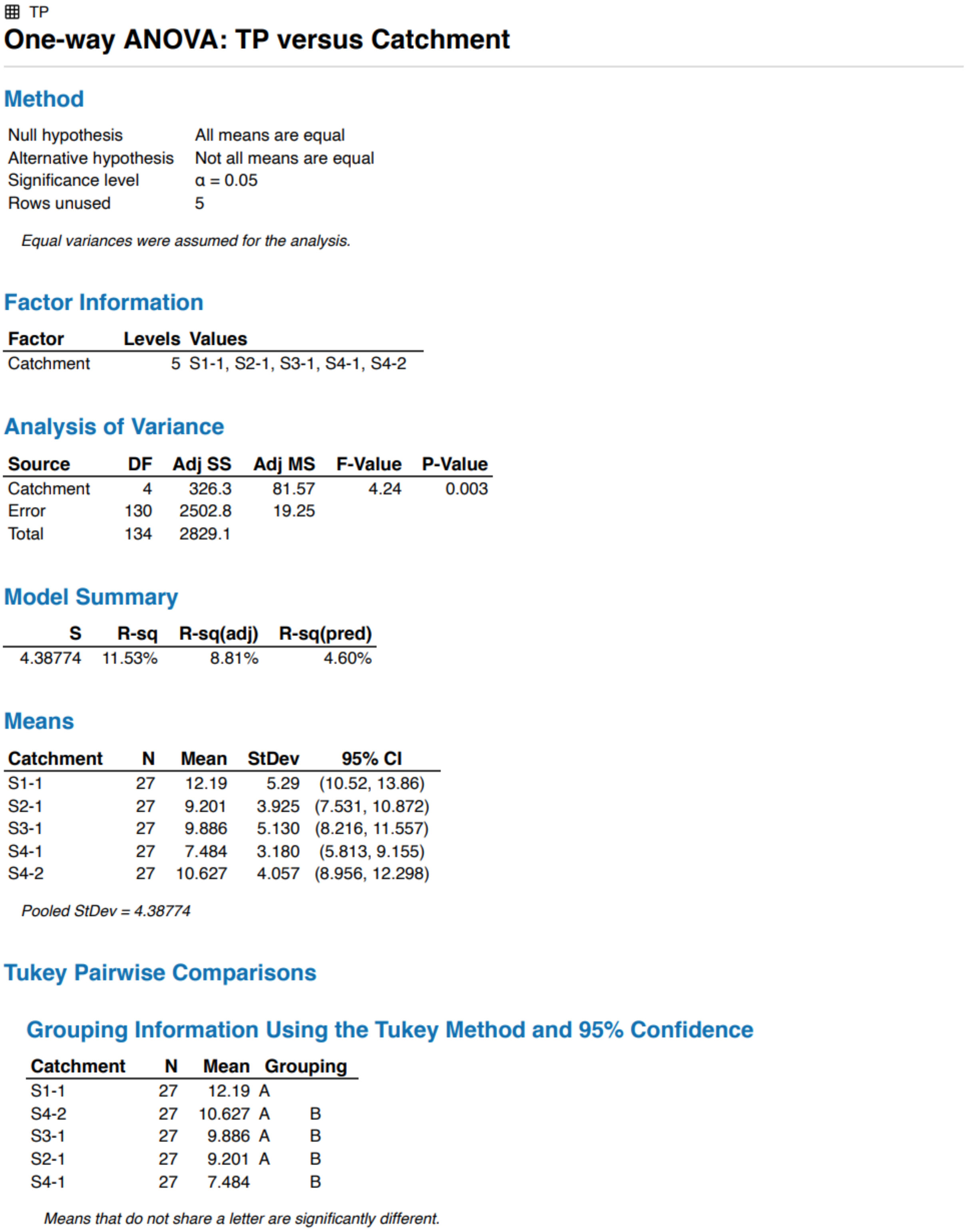
Pooled StDev = 2.83021

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Catchment	N	Mean	Grouping	
S1-1	27	8.061	A	
S4-2	27	6.136	A	B
S2-1	27	6.080	A	B
S3-1	27	6.061	A	B
S4-1	27	5.021		B

Means that do not share a letter are significantly different.



▦ TP

One-way ANOVA: TP versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05
Rows unused	5

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	326.3	81.57	4.24	0.003
Error	130	2502.8	19.25		
Total	134	2829.1			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
4.38774	11.53%	8.81%	4.60%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	27	12.19	5.29	(10.52, 13.86)
S2-1	27	9.201	3.925	(7.531, 10.872)
S3-1	27	9.886	5.130	(8.216, 11.557)
S4-1	27	7.484	3.180	(5.813, 9.155)
S4-2	27	10.627	4.057	(8.956, 12.298)

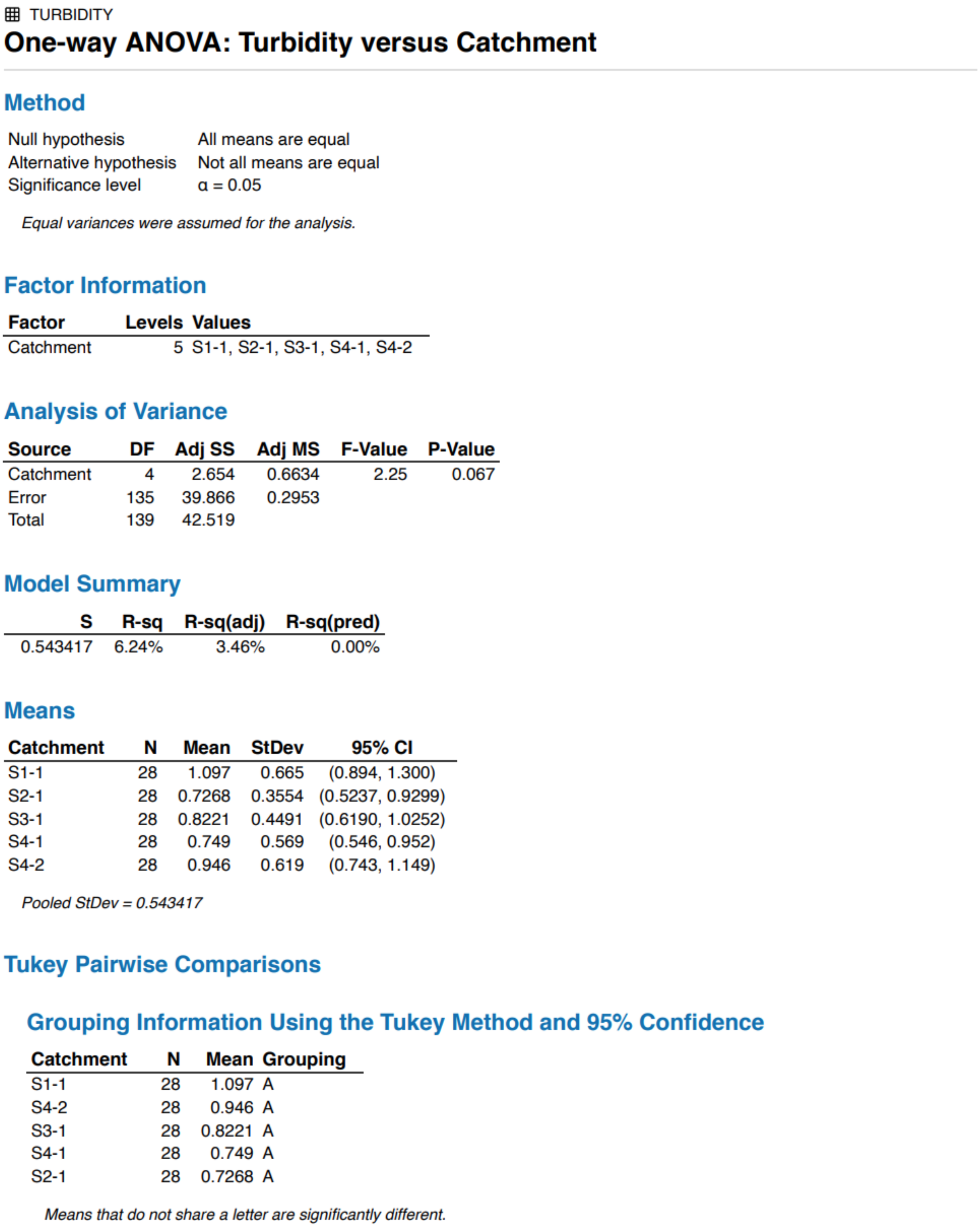
Pooled StDev = 4.38774

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Catchment	N	Mean	Grouping	
S1-1	27	12.19	A	
S4-2	27	10.627	A	B
S3-1	27	9.886	A	B
S2-1	27	9.201	A	B
S4-1	27	7.484		B

Means that do not share a letter are significantly different.



▦ TURBIDITY

One-way ANOVA: Turbidity versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	2.654	0.6634	2.25	0.067
Error	135	39.866	0.2953		
Total	139	42.519			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.543417	6.24%	3.46%	0.00%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	28	1.097	0.665	(0.894, 1.300)
S2-1	28	0.7268	0.3554	(0.5237, 0.9299)
S3-1	28	0.8221	0.4491	(0.6190, 1.0252)
S4-1	28	0.749	0.569	(0.546, 0.952)
S4-2	28	0.946	0.619	(0.743, 1.149)

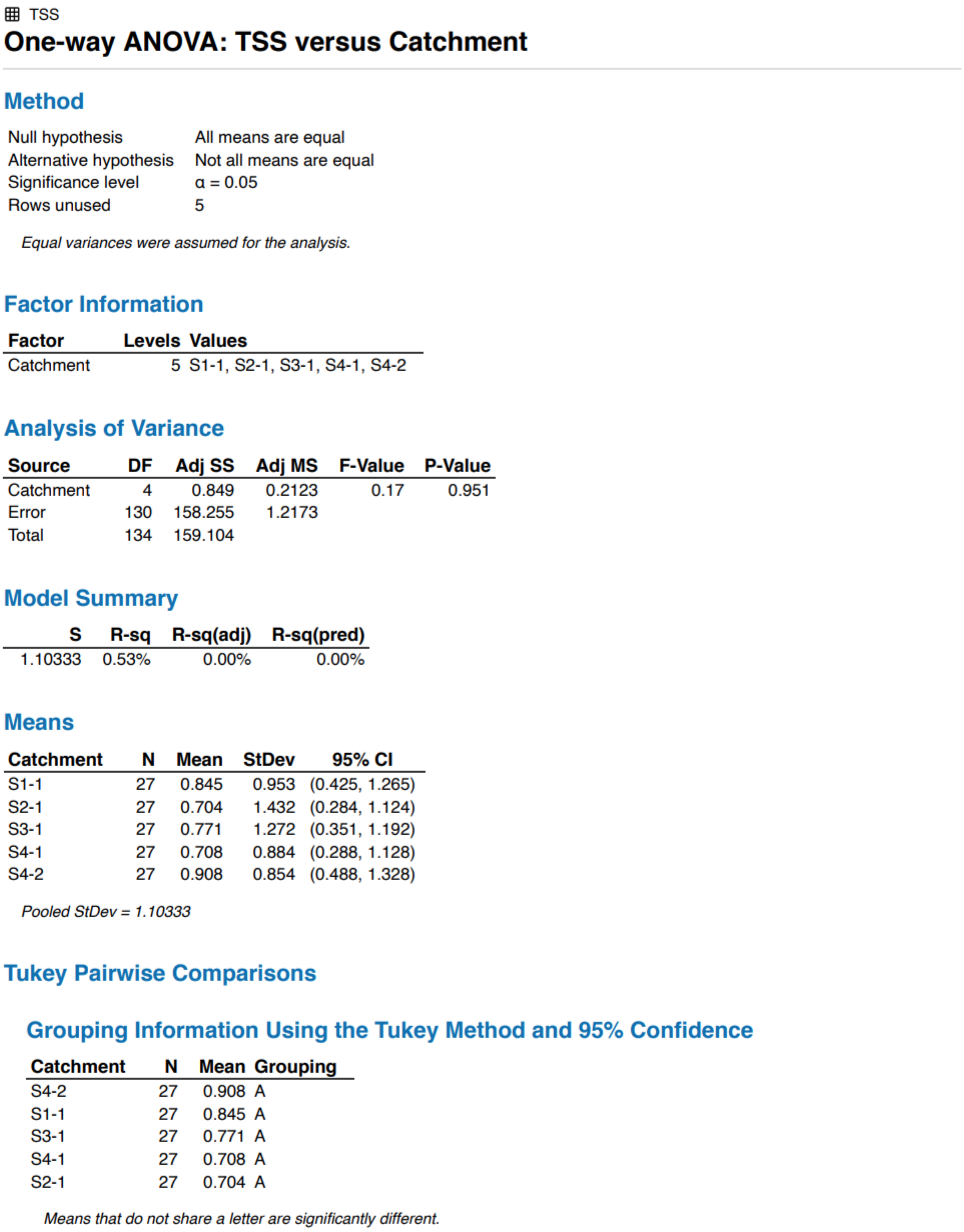
Pooled StDev = 0.543417

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Catchment	N	Mean	Grouping
S1-1	28	1.097	A
S4-2	28	0.946	A
S3-1	28	0.8221	A
S4-1	28	0.749	A
S2-1	28	0.7268	A

Means that do not share a letter are significantly different.



TSS

One-way ANOVA: TSS versus Catchment

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05
Rows unused	5

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Catchment	5	S1-1, S2-1, S3-1, S4-1, S4-2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catchment	4	0.849	0.2123	0.17	0.951
Error	130	158.255	1.2173		
Total	134	159.104			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
1.10333	0.53%	0.00%	0.00%

Means

Catchment	N	Mean	StDev	95% CI
S1-1	27	0.845	0.953	(0.425, 1.265)
S2-1	27	0.704	1.432	(0.284, 1.124)
S3-1	27	0.771	1.272	(0.351, 1.192)
S4-1	27	0.708	0.884	(0.288, 1.128)
S4-2	27	0.908	0.854	(0.488, 1.328)

Pooled StDev = 1.10333

Tukey Pairwise Comparisons

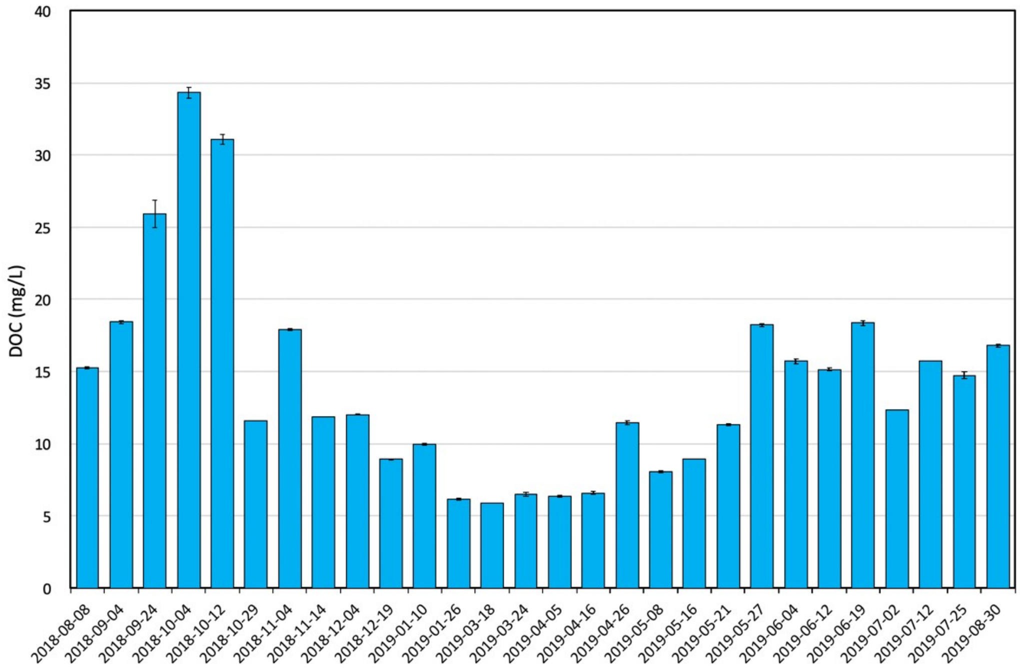
Grouping Information Using the Tukey Method and 95% Confidence

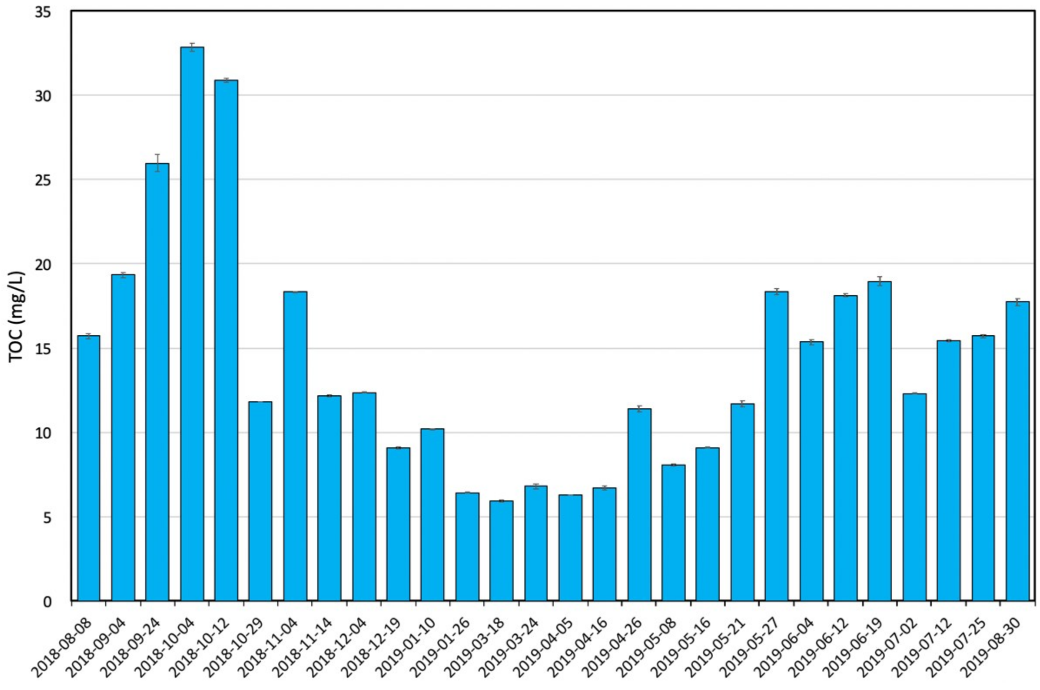
Catchment	N	Mean	Grouping
S4-2	27	0.908	A
S1-1	27	0.845	A
S3-1	27	0.771	A
S4-1	27	0.708	A
S2-1	27	0.704	A

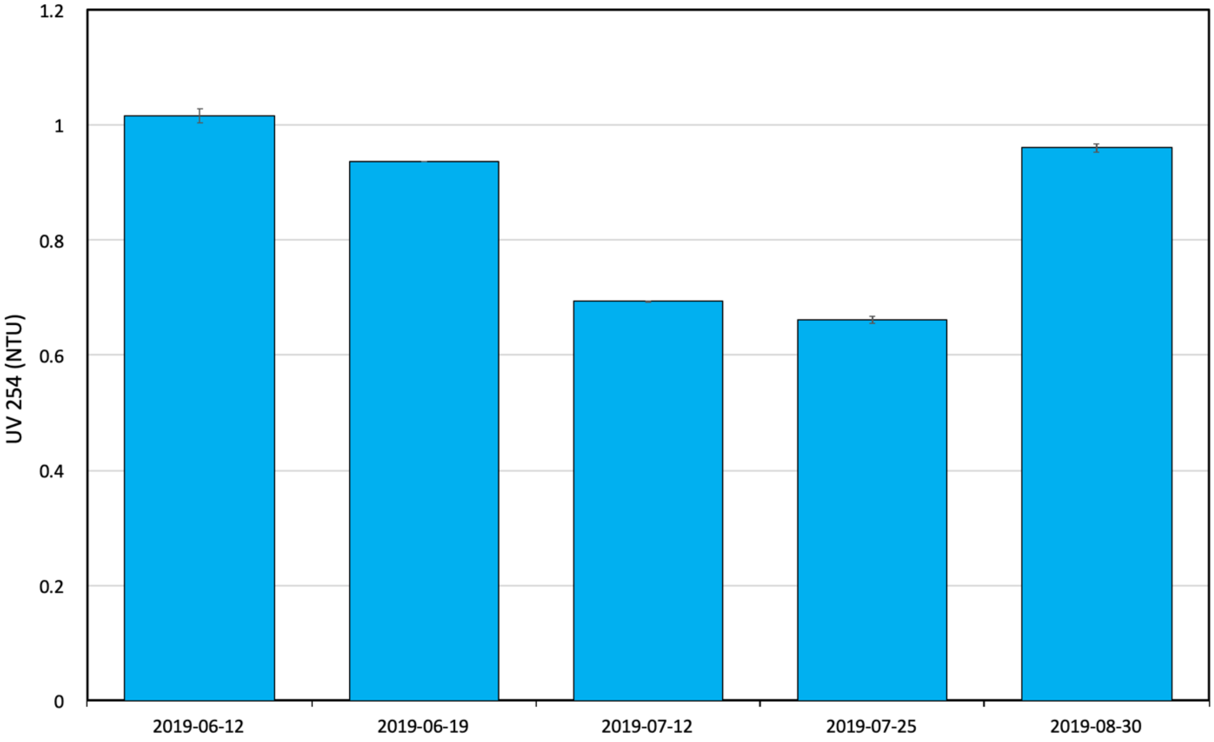
Means that do not share a letter are significantly different.

Appendix C: Data Quality Assessment

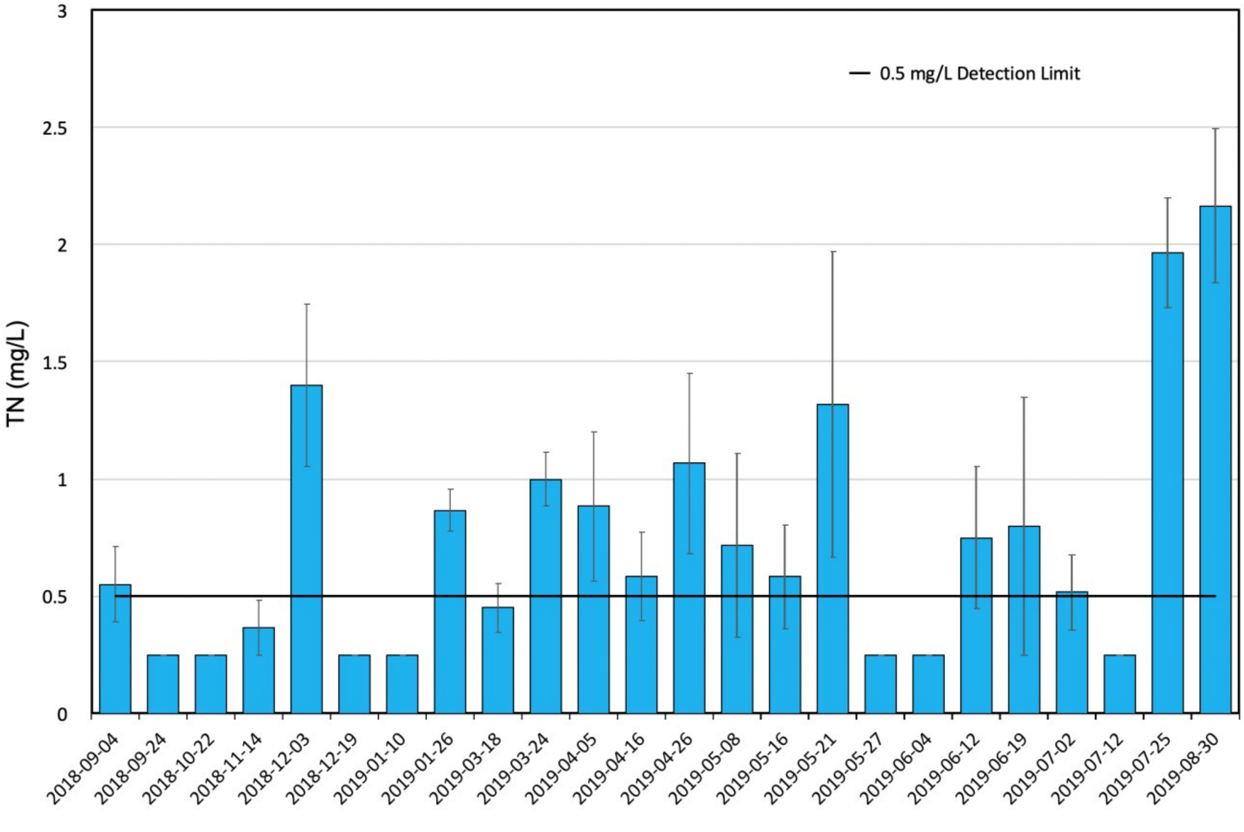
Triplicate samples were measured for DOC, TOC, UV-254, and TN on one sample chosen randomly for each sampling event.







1.2
1
0.8
0.6
0.4
0.2
0
UV 254 (NTU)
2019-06-12
2019-06-19
2019-07-12
2019-07-25
2019-08-30



3
2.5
2
1.5
1
0.5
0
TN (mg/L)
0.5 mg/L Detection Limit
2018-09-04
2018-09-24
2018-10-22
2018-11-14
2018-12-03
2018-12-19
2019-01-10
2019-01-26
2019-03-18
2019-03-24
2019-04-05
2019-04-16
2019-04-26
2019-05-08
2019-05-16
2019-05-21
2019-05-27
2019-06-04
2019-06-12
2019-06-19
2019-07-02
2019-07-12
2019-07-25
2019-08-30