Legacy Forest Harvesting Impacts on Phosphorus Transport Dynamics in Hardwood Dominated Canadian Shield Catchments: Evaluating Changing Source Availability and Source Channel Connectivity

by

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Author’s Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

This thesis consists in part of three manuscripts prepared as refereed papers that have not yet been submitted for publication (Chapters 2, 3, and 4). Chapters 1 and 5 were not written with the intent of publication. Exceptions to sole authorship of material are as follows:

Research presented in Chapter 2 is being prepared for publication as:

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This research was conducted at the University of Waterloo by Robert Fines under the supervision of Micheal Stone. Robert Fines was responsible for conceptualization, methodology, formal analysis, data curation, writing – original draft, writing – review and editing, and project administration. Micheal Stone was responsible for conceptualization, methodology, formal analysis, resources, writing – review and editing, supervision, project administration, funding acquisition. Kara Webster was responsible for conceptualization, resources, data curation, writing – review and editing, funding acquisition. Jason Leach was responsible for conceptualization, methodology, resources, data curation, writing – review and editing. James Buttle was responsible for conceptualization, methodology, writing – review and editing. Monica Emelko was responsible for conceptualization, writing – review and editing, funding acquisition.

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Abstract

Forests are critical to the safe provision of drinking water across the globe and provide over 4.1 trillion USD per year in savings to drinking water treatment costs. These supplies are threatened by climate change-exacerbated landscape disturbances such as wildfire, which can severely impact forest hydrologic and biogeochemical cycles. Potential increases in the transport of sediment and associated nutrients to streams networks are especially concerning because they can propagate downstream and lead to conditions that challenge drinking water treatment operations. Excess phosphorus loading is especially concerning in drinking water sources as it can cause the proliferation of cyanobacteria and other algae that can clog filtration processes or produce toxins that most plants are not equipped to treat, thereby leading to service disruptions or complete outages. Forest harvesting has been proposed as a potential mitigation strategy to lower fuel loads and reduces the risk of catastrophic wildfire, preventing negative impacts on water quality and treatability. However, this strategy needs to be adopted with caution as forest harvesting has the potential to increase phosphorus transport to stream networks, presenting a potential threat to downstream drinking water treatment operations and, thereby exacerbating the problems that they are supposed to mitigate. Accordingly, the objectives of this study were to evaluate the impacts of legacy forest harvesting on the physical processes (i.e., source channel connectivity and source availability) that control phosphorus transport from terrestrial to aquatic environments. This work was conducted on hardwood dominated, Canadian Shield catchments within the Turkey Lakes Watershed (TLW) of Ontario, Canada. A before-after-control-impact (BACI) study design was used to evaluate the immediate and legacy impacts (1-12 years after harvesting) of multiple forest harvesting strategies (i.e., clear-cut, shelterwood cut, and selection cut) on total phosphorus (TP) concentration and yield. Additionally, the hydrologic source areas contributing to stream flow were evaluated using end member mixing analysis (EMMA) in a legacy clear-cut (24 years after harvesting) and control catchment.

Phosphorus sources in those catchments were evaluated by measuring TP and soluble reactive phosphorus (SRP) in these source areas and analyzing soil samples for total particulate phosphorus (TPP) and phosphorus fractions throughout the soil profile. These results were used to explain the legacy impacts of harvesting on seasonal and event-based TP and SRP concentrations draining the clear-cut and control catchments. Results from the BACI study and seasonal and event sampling demonstrate that harvesting had a small but significant impact on TP stream concentrations. However, as many of these differences were below the detection limit (< 1 µg l^{-1}) the results are not practically significant. EMMA showed that stream water chemistry corresponds most with shallow groundwater and wetland groundwater chemistry in both catchments, suggesting that legacy forest harvesting has little impact on the primary water sources contributing to stream flow. Additionally, legacy forest harvesting appeared to have little impact on phosphorus source availability as there were few differences in phosphorus concentrations between the legacy clear-cut and control catchment within those source areas. Further evidence of this is demonstrated by the lack of differences in TPP and phosphorus fractions within the mineral soils between the two catchments. Finally, wetlands were identified as a major source of phosphorus delivered to streams as they are hydrologically connected with the stream channel and have measurable phosphorus concentrations. As legacy forest harvesting appears to have little long-term impacts on either hydrologic processes or phosphorus source availability its expected that little impact was observed on stream phosphorus concentration and yield. Results of the study suggest that forest harvesting may be a suitable land management strategy that promotes source water protection in hardwood-dominated Canadian Shield forested watersheds.

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Chapter 1. General Introduction

1.1. Forested Watersheds: A Critical Drinking Water Source

The natural storage and filtration capacity of forested watersheds (Ernst, 2004; MacDonald & Shemie, 2014) are critical to the provision of safe and reliable drinking water globally (Dudley & Stolton, 2003). These critical source water regions provide ~75% of the world's accessible freshwater (United Nations Department of Economic and Social Affairs, 2021) and ~4.1 trillion USD per year savings to global water treatment costs (Costanza et al., 1998). Over 80% of Canadians (Emelko et al., 2011) and 60% of Americans (Stein & Butler, 2004; Stein et al., 2005) rely on forested watersheds for their drinking water supply, highlighting that their importance cannot be understated. Climate change exacerbated natural disturbances pose a serious threat to drinking water treatment operations because they alter landscapes and change critical hydrological and biogeochemical processes that maintain high quality source water (Emelko et al., 2011; Sun & Vose, 2016). While disturbances such as insect infestation (Oulehle et al., 2019; Su et al., 2017) and ice storms (Houlton et al., 2003; Weitzman et al., 2020) may impact water quantity and quality, wildfire is the most concerning (Emelko & Sham, 2014; Robinne et al., 2019). This is because more precipitation reaches the land surface after wildfire (Williams et al., 2019), leading to increased erosion and solids runoff (Alessio et al., 2021; Silins et al., 2009). Solids-associated metals (Abraham et al., 2017), nutrients (Emelko et al., 2011; Gustine et al., 2022; Silins et al., 2014), and other contaminants (Crouch et al., 2006; Mansilha et al., 2019) also can be elevated. These include natural organic matter (NOM), which can not only be elevated, but transformed to more aromatic character (Blackburn et al., 2023; Emelko et al., 2011; Hohner et al., 2016). All of these effects on water quality can and have been observed after wildfires, even at large basin scales where dilution would be expected (Emmerton et al., 2020). They have also persisted for decades or longer in some regions (Emelko et al., 2016). While wildfires are not assured to have an effect on water quality and treatability, changing climate affects wildfire burned area, severity (Adams, 2013; White et al., 2017); therefore, associated threats to water quality and treatability are expected in the future.

Wildfires and other severe landscape disturbances can impact drinking water supplies when the transport of sediment and associated nutrients to streams increases (Hampton et al., 2022; Silins et al., 2014; Stone et al., 2014; Watt et al., 2021), leading to the propagation to reservoirs and lakes (Emelko et al., 2016; Stone et al., 2021) and challenges to drinking water treatment operations (Emelko et al., 2011; Emelko & Sham, 2014). While all water requires treatment (Emelko et al., 2019), elevated solids/turbidity can be readily treated by most conventional drinking water treatment approaches. In contrast, nutrients including more aromatic fractions of organic carbon are especially challenging and costly to treat (Blackburn et al., 2021, 2023; Kitis et al., 2002; Kundert et al., 2014; Price et al., 2017). The proliferation of cyanobacteria and other algae is especially concerning because they can clog filtration processes or produce toxins that most drinking water treatment plants are not typically equipped to treat, thereby leading to service disruptions or complete outages (Emelko et al., 2011; Emelko & Sham, 2014). To combat the increasing threat of severe landscape disturbance by wildfire, fuel load reduction strategies such as forest harvesting have been proposed as a potential mitigation strategy in drinking water supply watersheds to reduce the risk of wildfires (Deval et al., 2021; Emelko & Sham, 2014; Gannon et al., 2019; Webb, 2012). However, this strategy should be adopted with caution as forest harvesting can also impact water quantity (Buttle et al., 2018) and quality (Webster et al., 2022). Therefore, there is a critical need to better understand the impacts of forest harvesting on parameters related to drinking water treatment to avoid any unintended consequences by potential source water protection strategies.

Phosphorus is the limiting nutrient in freshwater aquatic ecosystems and it is a nutrient of concern particularly as it leads to dramatic increases of algae (Schindler, 1974; Schindler et al., 2016). A threshold relationship between the proliferation of algal blooms and total phosphorus (TP) concentrations has been reported to range from 20 to 50 µg TP L^{-1} (Fastner et al., 2016; Vuorio et al., 2020; Xu et al., 2015).

However, recent studies indicate that algal blooms are increasingly being observed in low nutrient (< 10 µg TP L^{-1}) oligotrophic lakes across the North American continent, including throughout Ontario, Canada; these have been attributed to warmer temperatures and climate change-exacerbated landscape disturbances such as extreme precipitation (Karmakar et al., 2015; Stoddard et al., 2016; Winter et al., 2011). Therefore, as the impacts of climate change persist and possibly intensify, oligotrophic aquatic environments may become more susceptible to small increases in phosphorus loading. Notably this, combined with the increasing anthropogenic pressures on forest environments (Webster et al., 2015), highlight the critical need to better understand and quantify (1) key processes that control phosphorus transport from terrestrial to aquatic environments and (2) the impacts of landscape disturbances on these processes.

Forest harvesting impacts on phosphorus transport dynamics occur through changes in either biogeochemical or hydrological processes (Hoffmann et al., 2009; Kreutzweiser et al., 2008) that influence the size of phosphorus pools and their degree of hydrologic connectivity to stream channels (McMillan et al., 2018). Forest harvesting can increase or decrease phosphorus pools through changes in the rates of decomposition and mineralization (Guo et al., 2004; Gutiérrez del Arroyo & Silver, 2018) or through uptake from regenerating vegetation and sorption to mineral soil (Bowd et al., 2019; Evans et al., 2000; Hume et al., 2016). Hydrologic connectivity is increased after harvesting as vegetation removal and soil compaction reduce rates of evapotranspiration (Johnson et al., 2007; Jones, 2000; Mackay & Band, 1997; Murray & Buttle, 2005) and infiltration (Chanasyk et al., 2003; Naghdi et al., 2016; Startsev & McNabb, 2000). This reduces the water storage capacity of forested soils (Buttle et al., 2019) causing more frequent quick flow events (Buttle et al., 2019), higher water yields (Bosch & Hewlett, 1982; Buttle et al., 2018) and increased peak flows (Jones, 2000). The combined effects of the changing biogeochemical and hydrological processes accumulate at a catchment outlet and are observed through significant increases in phosphorus concentrations and yield (Ahtiainen & Huttunen, 1999; Deval et al., 2021), increasing yield only (Löfgren et al., 2009; Nieminen, 2004; Palviainen et al., 2014), or having no effect (Boggs et al., 2016; Webster et al., 2022). These variable responses are driven by differences in the harvesting impacts on either the biogeochemical or hydrological processes which depend on numerous factors such as harvesting strategy, forest type, topography, soils and climate (Kreutzweiser et al., 2008). Accordingly, to better explain variable harvesting responses, more research is needed to rigorously evaluate processes controlling the response of phosphorus transport dynamics to forest harvesting. Additionally, the majority of research to date has focused on the immediate (1 – 5 years) post-harvesting effects of forest harvesting on phosphorus transport dynamics (Ahtiainen & Huttunen, 1999; Boggs et al., 2016; Swank et al., 2001). However, some studies suggest that significant harvesting effects can perpetuate over a longer time period (> 10 years) (Palviainen et al., 2014) while no studies have evaluated the long term (> 20 years) impacts. Therefore, a potential threat to downstream aquatic ecosystems could exist through legacy harvesting impacts on phosphorus transport dynamics. It is critical that these impacts are quantified to determine the suitability of forest harvesting as a source water protection strategy.

1.2. Research Approach and Objectives

The overall goal of this thesis was to evaluate (1) the physical processes that control the transport of phosphorus from terrestrial to aquatic ecosystems and (2) the impacts of legacy forest harvesting on these processes. The specific objectives of this thesis research were designed to address this goal. They were to:

1) Assess the long-term impacts of changing environmental conditions (i.e., climate change and acidification recovery) and forest harvesting on phosphorus concentrations and yields draining forested headwater catchments within TLW;

2) Identify the prominent flow paths contributing to runoff generation using end member mixing analysis (EMMA) in a legacy (24 year) clear-cut and forested headwater catchment within TLW, and;

3) Characterize phosphorus sources throughout a hillslope and compare them to stream phosphorus concentrations and yields in a legacy (24 year old) clear-cut and forested headwater catchment within TLW.

Each objective was evaluated in one of three data chapters (Chapters 2-4) that were prepared for publication. Chapter 2 is associated with Objective 1, Chapter 3 with Objective 2, and Chapter 4 with Objective 3.

A long-term (31-year) water quantity and quality data set collected from the Turkey Lakes Watershed (TLW) and maintained by the Great Lakes Forestry Center; Natural Resources Canada, was used. These data were supplemented with data collected from an intensive field sampling program conducted in the Spring, Summer and Fall of 2021.

1.3. Study Site

1.3.1. History of Turkey Lakes Watershed

Established in 1979, TLW is one of the longest running experimental watershed research platforms in Canada (Morrison et al., 1999; Webster et al., 2021a). Numerous federal government agencies such as Natural Resources Canada (NRCAN), Environment and Climate Change Canada (ECCC) and Fisheries and Oceans Canada (DFO) were involved with the creation of TLW to evaluate the impacts of acid rain on terrestrial and aquatic ecosystems of the Canadian Shield (Foster et al., 2005; Morrison et al., 1999; Webster et al., 2021a). However, research expanded to include a number of other environmental issues such as habitat alterations, organic contaminants, forest management and climate change (Webster et al., 2021a). The research findings from studies in TLW have formed the scientific basis for policy development that resulted in the creation of both Canadian and International policy advances that include the Canada-U.S. Air Quality Agreement in 1991 (Foster et al., 2005; Webster et al., 2021a).

1.3.2. Site Description

Turkey Lakes Watershed (TLW; 47° 03´ N; 84° 25´ W) is in the Great Lakes – St. Lawrence Forest region within the Boreal Shield Ecozone of central Ontario (Figure 1.1). The watershed has a relief of ~300 m and drains an area of 10.5 km^2 (Semkin et al., 2002; Webster et al., 2021a). The underlying bedrock consists of Precambrian metamorphic basalt (i.e., silicate greenstone) with occasional outcrops of felsic igneous rock overlain by a two component till consisting of a silt-loam ablation till on top of a compacted sandy basal till (Hazlett et al., 2001; Semkin et al., 2002). Soils are predominantly orthic humo-ferric podzols (spodosols) with well-defined L and F horizons ~ 0.05 m thick (Hazlett et al., 2001). Organic soils are found in topographical depressions, riparian areas and wetlands (Webster, et al., 2021a). Forest cover consists mostly of uneven-aged, shade tolerant mature to over mature hardwoods, predominantly sugar maple (*Acer saccharum Marsh*) (90%) (Jeffries et al., 1988). Other tree species include yellow birch *(Betula alleghaniensis Britton*) (9%) and conifers (1%) (Jeffries et al., 1988; Semkin et al., 2002). Mean annual precipitation and temperature from 1980 to 2017 was 1203 mm and 4.5°C, respectively (Webster et al., 2021a). Snowfall comprises ~35% of annual precipitation with accumulation beginning in late October and melt occurring between March and May (Semkin et al., 2002).

1.3.3. Harvesting Experimental Design in TLW

A before-after-control-impact (BACI) study was conducted to quantify the impacts of three contemporary silvicultural harvesting practices (clear-cut, shelterwood cut and selection cut) on soil productivity, stand recovery, biodiversity and catchment hydrology (Buttle et al., 2018; Morrison et al., 1999). Harvesting occurred in the Summer and Fall of 1997, using a feller-buncher and cable skidder (Morrison et al., 1999). The pre- and post-treatment periods spanned from 1981 to 1997 and 1998 to 2012, respectively.

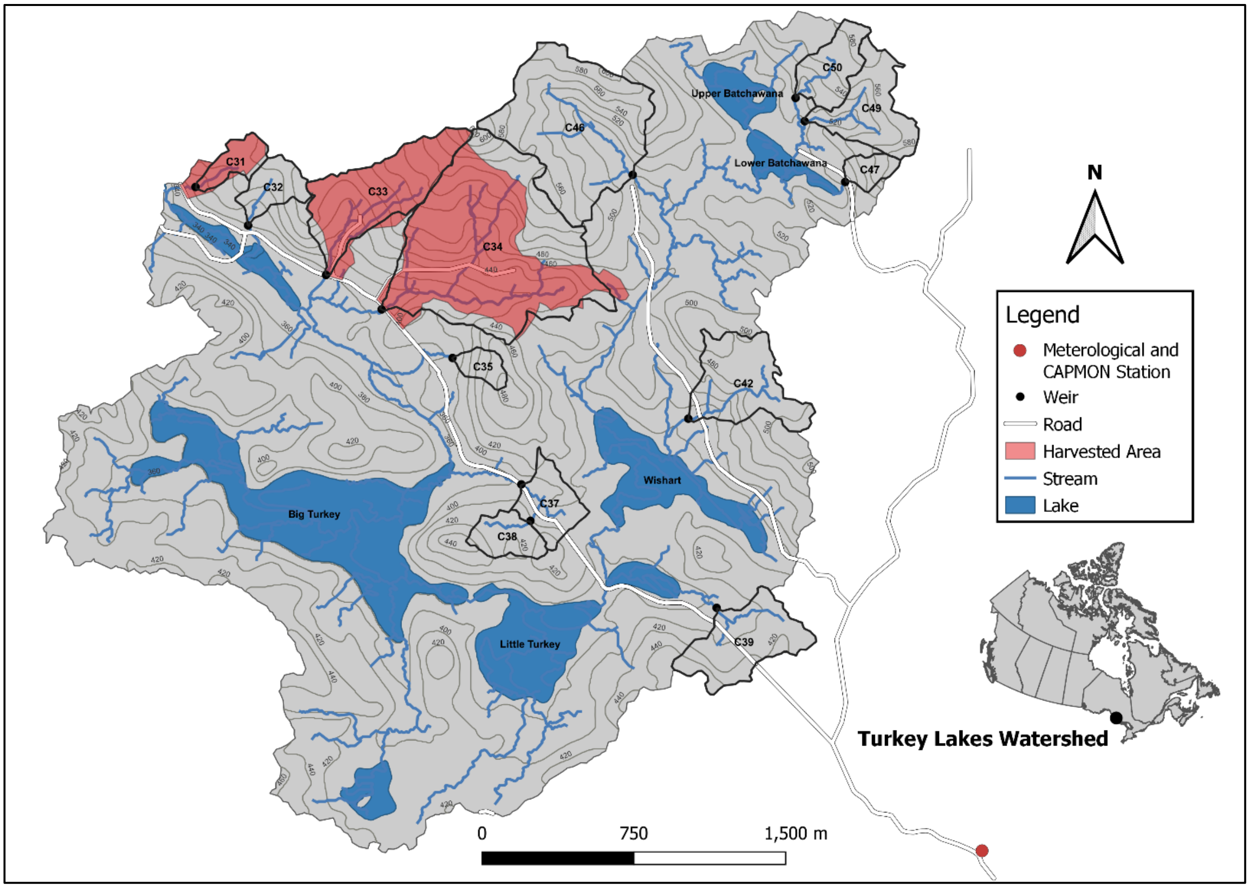

Figure 1.1 Map of Turkey Lakes Watershed study catchments, harvesting area, and meteorological station.

Catchment 31 (C31) was clear-cut and all trees with a diameter at breast height (DBH) ≥ 20 cm were removed (Buttle et al., 2018). Trees with a DBH between 10 and 20 cm were felled and left on site while trees with DBH ≤ 10 cm were left standing (Buttle et al., 2018; Leach et al., 2020). Catchment 33 (C33) was treated with a selection cut that removes individual mature and undesirable trees from the landscape (Leach et al., 2020). A forestry access road runs parallel to the stream channel in C33 for 750 m with culverts directing water towards the stream (Buttle et al., 2019). Catchment 34 (C34) was treated with a shelterwood cut that removed ~50% of mature trees (Leach et al., 2020). Harvesting resulted in a basal area reductions of 78%, 36%, 38% and stocking reductions of 76%, 43%, and 32% in C31, C33, and C34, respectively (Buttle et al., 2019). Selection and shelterwood silvicultural strategies are typical in Ontario's shade-tolerant hardwood forests (OMNRF, 2015). Clear-cut harvesting is not a recommended harvesting strategy for this forest type but was included to represent an intensive harvesting treatment (Morrison et al., 1999). Catchments C32, C35, and C46 were selected as controls because of similar biophysical characteristics and proximity to the harvested catchments. Characteristics of the catchments within TLW are presented in Table 1.1.

Table 1.1 Turkey Lakes Watershed catchment characteristics

Catchment	Silvicultural Treatment	Area (ha)	Weir Elevation (masl)	Total Relief (m)	Wetland Area (%)	Aspect	Harvested Area (%)
C31	Clear Cut	4.62	359	59	2.88	SW	100
C32	Control	6.74	352	107	1.00	SW	0
C33	Selection Cut	24.38	354	272	0.50	SW	100
C34	Shelterwood Cut	66.54	362	264	1.12	W	70
C35	Control	4.47	386	79	1.06	SW	0
C37	Control	15.30	385	103	12.40	W	0
C38	Control	8.50	415	34	25.00	W	0
C39	Control	17.42	379	80	1.90	W	0
C42	Control	15.69	408	110	6.60	W	0
C46	Control	44.21	485	141	1.40	SE	0
C47	Control	4.06	503	94	0.00	S	0
C49	Control	18.58	504	93	2.00	SW	0
C50	Control	11.61	507	83	7.60	SW	0

Chapter 2. Forest Harvesting in a Changing Climate: Seasonal Impacts on Phosphorus Concentration and Yields in Hardwood Dominated Headwater Catchments of the Canadian Shield

2.1. Abstract

Forests are critical sources of water in many regions globally, including Canada. Long-term studies of forest disturbance impact on water quality and quantity are needed for water security management—unfortunately, they are also scant. Here the results of a 31-year Before-After-Control-Impact (BACI) study of seasonal changes in total phosphorus (TP) concentrations and yields in hardwood-dominated, forested headwaters of the Turkey Lakes Watershed on the Canadian Shield are reported. Three harvest practices (clear-cut, shelterwood cut and selection cut) and multiple control catchments were evaluated during pre-harvest (1981-1997) and post-harvest (1998-2012) periods to describe: (1) long-term (31 years) changes in TP concentrations and yields within control and harvested catchments, and (2) immediate and legacy effects of the three contemporary harvesting approaches on TP concentration and yield. Stream TP concentration and yield declined from 1981 to 2012 in control catchments, likely in response to changing climate and/or acidification recovery. Significant increases in TP concentration were observed only in streams draining the clearcut and selection cut catchments, with the latter likely associated with hydrologic impacts of an access road established within the catchment during harvesting. TP yield increased significantly in all three harvested catchments with the largest harvesting effects occurring in the clear-cut and selection cut catchments. Significant seasonal harvesting effects were observed in the Spring TP concentrations in all three harvested catchments and in the Winter for the clear-cut. Seasonal impacts on TP yield were observed in all harvested catchments during all seasons. The observed increases in TP concentration and yield in the impacted catchments were (1) relatively small compared to previous

harvesting studies, and (2) lower than those frequently associated with dramatic increases in primary productivity. These results *may* suggest that aquatic ecosystem threats from contemporary harvesting-associated shifts in TP yields may be negligible in this region; however, the results are confounded because climate change-associated decreases in hydrologic connectivity and acidification recovery likely also muted the effects of forest harvesting on phosphorus concentrations and yields. Accordingly, this study also underscores the critical importance of concurrent description/study of ecohydrological processes that govern nutrient cycling across scales.

Keywords: Before-After-Control-Impact (BACI) Design, climate change, acidification recovery, Turkey Lakes Watershed, forest harvesting, source water protection

2.2. Introduction

The natural storage and filtration of water by forests is valued at ~4.1 trillion USD per year in savings to global drinking water treatment costs (Costanza et al., 1998; Neary et al., 2009). The majority of Canadians and 60% of the US population rely on forested watersheds for their drinking water supply (Emelko et al., 2011; Stein & Butler, 2004; Stein et al., 2005). Natural and anthropogenic disturbance on forested landscapes can threaten drinking water supplies through changes in water quantity and quality (Emelko et al., 2011; Emelko & Sham, 2014). Natural disturbances that impact water quantity and quality such as wildfire (Silins et al., 2014), insect infestation (Oulehle et al., 2019; Weitzman et al., 2020) and ice storms (Houlton et al., 2003; Su et al., 2017) are being amplified by changing climatic conditions (Seidl et al., 2017). This is especially apparent with wildfire as climate-exacerbated changes in precipitation and temperature are increasing the size, frequency and severity of wildfires throughout Canada and the US (White et al., 2017). These extreme landscape disturbances threaten drinking water supply through alterations to hydrological and biogeochemical cycles that intensify the transport of sediment and associated nutrients to receiving streams (Emelko et al., 2016; Shakesby & Doerr, 2006; Silins et al., 2009; Stone et al., 2014). These impacts are often long lasting and propagate large distances downstream, affecting aquatic environments through variable water quality that challenge water treatment operations and increases treatment costs (Emelko et al., 2016; Emelko & Sham, 2014; Silins et al., 2014; Stone et al., 2014, 2021; Watt et al., 2021).

Phosphorus is widely recognized as the limiting nutrient in freshwater aquatic ecosystems that can increase the risk of harmful algal blooms and challenge drinking water treatment operations (Emelko et al., 2016; Schindler, 1974; Schindler et al., 2016). Phosphorus is often tightly recycled in forested landscapes because of low inputs from mineral weathering and high demand from vegetation and microbial communities (Julich et al., 2017; Palviainen et al., 2010; Smeck, 1985). Phosphorus in forested soils is adsorbed to metal (Fe, Al, Mn)-oxy hydroxides or precipitated with Ca^{2+} (McConnell et al., 2020; Hoffmann et al., 2009; Penn & Camberato, 2019), resulting in exceedingly low soluble reactive phosphorus (SRP) concentrations in streams draining forested landscapes. Due to the affinity of phosphorus to mineral soil, sediment erosion is the primary vector for phosphorus transport from terrestrial to aquatic environments (Hatch et al., 2001; Ide et al., 2008; Kerr et al., 2011; Kreutzweiser et al., 2008; McDowell & Sharpley, 2002). Subsequently, once mineral bound phosphorus enters aquatic environments, it can desorb into the water column and promote algal proliferation (Orihel et al., 2017).

Numerous studies have reported a critical total phosphorus (TP) concentration threshold that promotes an increase in the growth of algal blooms and associated cyanobacterial biomass (Carvalho et al., 2013; Fastner et al., 2016; Schindler et al., 2016; Vuorio et al., 2020; Wagner & Adrian, 2009; Xu et al., 2015). This threshold varies depending on environmental conditions and the cyanobacterial taxa of interest, but typically ranges from 20 – 50 µg TP L^{-1} (Fastner et al., 2016; Vuorio et al., 2020; Xu et al., 2015). However, recent work has reported an increase in the occurrence of algal blooms in low nutrient

(< 10 μg TP L^{-1}), oligotrophic lakes, rivers, and streams across the North American continent and throughout Ontario, Canada; these have been attributed to warmer temperatures and climate change-exacerbated landscape disturbances such as extreme precipitation (Karmakar et al., 2015; Stoddard et al., 2016; Winter et al., 2011). Total phosphorus concentrations in oligotrophic lakes in forested regions across Ontario were below thresholds listed above and suggest that small increases in TP concentration may affect the quality and treatability of the water originating in these lakes. Accordingly, it is necessary to evaluate physical and biogeochemical water quality responses to forest management (i.e., harvesting) and climate exacerbated disturbances.

Forest harvesting has been recently proposed as a potential management strategy to protect drinking water supply because of the increasing effects of climate change exacerbated landscape disturbances (Deval et al., 2021; Emelko & Sham, 2014; Gannon et al., 2019; Webb, 2012). However, forest harvesting also can degrade water quality through changes to hydrological and biogeochemical processes on the landscape (Boggs et al., 2016; Deval et al., 2021; Kreutzweiser et al., 2008);. Harvesting reduces water storage capacity in forested soils through increased water inputs caused by a reduction in evapotranspiration, interception (Johnson et al., 2007; Jones, 2000; Mackay & Band, 1997; Murray & Buttle, 2003) and infiltration (Chanasyk et al., 2003; Naghdi et al., 2016; Startsev & McNabb, 2000). These changes often increase surface runoff volumes (Chanasyk et al., 2003) and shallow subsurface lateral flow (Monteith et al., 2006a, 2006b) which often leads to increased phosphorus transport to receiving streams via erosion, especially after disturbance (Emelko et al., 2016), and flushing of the phosphorus-rich upper soil profile (Backnäs et al., 2012; Evans et al., 2000; Macrae et al., 2005; Whitson et al., 2005). Harvesting can also alter phosphorus pools on the landscape through changes in rates of mineral weathering, leaching, microbial activity, organic material supply, soil temperature and soil moisture (Kreutzweiser et al., 2008). In some regions, harvesting has significantly increased both phosphorus concentration and yield (Ahtiainen & Huttunen, 1999; Deval et al., 2021), significantly increased yield only (Löfgren et al., 2009;

Nieminen, 2004; Palviainen et al., 2014), or had no or varied effects on either yield and concentration (Boggs et al., 2016; Webster et al., 2022). For these reasons its critical to better understand, quantify, and mitigate these effects to prevent unintended consequences on drinking water supply.

The varied responses of phosphorus concentration and yield to harvesting are governed by differences in climate, topography, soil conditions, harvest intensity, forest types, rates of regeneration, and time since disturbance (Kreutzweiser et al., 2008). Understanding the conditions in which forest harvesting impacts phosphorus concentration and yield is critical to identifying when harvesting is a suitable source water protection strategy. It is widely acknowledged that the largest effects of harvesting on water quality occur immediately after harvesting (1-5 years) (Ahtiainen & Huttunen, 1999; Boggs et al., 2016; Swank et al., 2001). However, there is a paucity of long-term studies on these effects (> 10 years) (Webster et al., 2015). While Palviainen et al. (2014) found that small harvesting effects can last for many years after disturbance very little is known about the seasonal effects of forest harvesting on phosphorus concentration and yield. Therefore, to better understand the long-term forest harvesting impacts on phosphorus transport dynamics careful review and analysis of long term data is necessary to better understand the long term seasonal impacts.

Water quantity and quality in forested landscapes can change rapidly in response to disturbance pressures such as harvesting or changing environmental conditions (Buttle et al., 2018; Webster et al., 2022). Previous studies have documented the effects of changing environmental conditions on hydrology and biogeochemistry at the Turkey Lakes Watershed (TLW), a forest ecosystem research site located in central Ontario, Canada, that has operated since 1979 and is the location of the study presented herein. These reported findings include changing climate (Buttle et al., 2018), recovery from acid rain (Webster et al., 2021b) and forest harvesting (Webster et al., 2022). Notably despite the changing climatic conditions observed in TLW, forest harvesting still changed the prominent flow paths contributing to stream flow (Monteith et al., 2006a), reduced water travel times (Leach et al., 2020) and increased annual and seasonal water yields (Buttle et al., 2018). Additionally, Buttle et al. (2018) reported limited harvesting impacts on numerous hydrological variables immediately after disturbance. This was attributed to the years immediately following harvesting being abnormally dry, suggesting that changing climatic conditions may have limited the hydrologic response to harvesting (Buttle et al., 2018). Similarly, Webster et al. (2022) found the combined influence of changing climatic conditions and recovery from acid rain influenced the response of water quality to forest harvesting. Consequently, depending on the solute in question, changing environmental conditions and harvesting either had an antagonistic (mitigative) or agonistic (synergistic) relationship (Webster et al., 2022). Accordingly, these studies show how changing environmental conditions can influence the magnitude and recovery of harvesting effects on water quantity and quality. More study is therefore needed to better understand how changing environmental conditions will influence the hydro-chemical consequences of forest harvesting and create any potential threats to drinking water supply.

Given the importance of forested watersheds as a primary source of drinking water for Canadians juxtaposed with climate exacerbated landscape change impacts on water quality, the primary goal of this study is to understand annual and seasonal changes in TP concentration and TP yield at the Turkey Lakes Watershed. The objectives of the study are to: 1) evaluate long-term changes across all seasons and each season individually within undisturbed forested catchments to discern potential effects of environmental change in the study area; and 2) determine the immediate and long term effects across all seasons and each season individually of three harvesting treatments (shelterwood, selective, clear-cut) on phosphorus concentrations and yields using multiple controls in a before-after-control-impact (BACI) design.

2.3. Methods

A description of the study site and experimental design are provided in sections 1.3.2 and 1.3.3 in Chapter 1.

2.3.1. Field and Laboratory Analyses

Meteorological (Environment and Climate Change [ECCC] Canadian Air and Precipitation Monitoring Network (CAPMoN) Algoma site) data were collected at a site located 600 m outside of TLW (Figure 1.1, Webster, et al., 2021a). Air temperature was measured every 10 minutes by sensors located on the top of a 10 m tower and averaged to produce a daily mean value (Webster, et al., 2021a). Precipitation depths were measured daily using a standard rain gauge and a Nipher-shielded snow gauge (Webster et al., 2021a). Bulk precipitation samples consisting of both wet-only precipitation and dry deposition were collected weekly and analyzed for sulphate (SO_4^{2-}), nitrate (NO_3^-) and total phosphorus (TP) using standard methods at the Great Lakes Forestry Center Water Chemistry Laboratory, Sault Ste. Marie, Ontario (Webster et al., 2021b). Each study catchment was instrumented with a 90^o v-notch weir, stilling basin and water level logger to estimate continuous stream flow (Beall et al., 2001). Stage discharge relationships were used to calculate instantaneous discharge converted to a mean daily discharge (Beall et al., 2001). The discharge record was continuous from in 1981 to 2012 for all catchments except for C46, which ended in 2007 (Leach et al., 2020). Water samples were collected at the weir notch daily during snowmelt and biweekly to monthly for the remainder of the year (Leach et al., 2020). TP concentrations were analyzed at the Great Lakes Forestry Centre Water Chemistry Laboratory on a Technicon Autoanalyzer II using the molybdophosphoric blue method with a detection limit of 1 µg L^{-1} (Environment Canada, 1979).

2.3.2. Statistical Analyses

Stream flow and water chemistry data from 1981 to 2012 were summarized by season for each water year (WY) defined from September 1st to August 31st and seasons were defined as Fall (September to November), Winter (December to February), Spring (March to May) and Summer (June to August). Mean daily flow was summed and converted to a seasonal water yield (mm). Total phosphorus concentrations were converted to seasonal flow-weighted TP concentrations (Palviainen et al., 2015). Total phosphorus yield was calculated as the product of seasonal water yield and seasonal flow-weighted TP concentration according to the method of Rekolanien et al. (1991). The data were log transformed for statistical analysis. A 10% significant level ($\alpha = 0.1$) was considered sufficient for indicating a significant impact as water quality parameters are highly variable in forested headwater systems (Emelko et al., 2016).

Temporal trends in TP concentration and yield across all seasons (i.e., all seasonal values in one time series) were evaluated using the Seasonal Mann-Kendall trend test; individual seasonal trends were evaluated using the Mann-Kendall trend test (Hirsch et al., 1982; Hirsch & Slack, 1984). These tests are commonly used to identify monotonic trends such as those associated with hydrologic recovery from harvesting (Buttle et al., 2018) and recovery from acid rain (Webster et al., 2021b). Trend tests were conducted on all the monitored TLW headwater catchments described in Table 1.

To quantify the effects of harvesting on TP concentration and TP yield, a BACI paired catchment approach with multiple controls—the predominant method for identifying landscape disturbance impacts on water quantity and quality (Brown et al., 2005; Neary, 2011)—was used. An ordinary least squares linear regression model was fit between a control and treatment catchment during the calibration period (before 1997). Simple linear regression was used to predict the expected value of TP concentration and TP yield in the treatment catchments after the calibration period (i.e., after 1997). Differences between observed and predicted values represents treatment effects (Moore & Scott, 2005). For these linear regressions, control catchments (C32, C35 and C46) and treatment catchments (C31, C33, and C34) were used. Regression equations can be seen in Table A1.

The Mann Whitney U Test and an extra sum of squares analysis of covariance (ANCOVA) were used to evaluate differences in TP concentration and yield between the treatment and control catchments. The Mann Whitney U test was used to evaluate differences between the predicted and observed values (Gravelle et al., 2009), both seasonally and over the entire post-harvesting period. Using a previously reported approach (Buttle et al., 2018; Moore & Scott, 2005), ANCOVA was used to compare two linear models. The first model ignores the treatment effect and combines the pre- and post-treatment data into one linear regression:

$$y = \beta_0 + \beta_1 x_1 + \varepsilon \tag{1.1}$$

where y = the parameter of interest in the treatment catchment, x_1 = the parameter of interest in the control catchment, β_0 and β_1 are regression coefficients and ε is an error term assumed to be independent, normally distributed, and homoscedastic. The second model includes a dummy variable x_2 that is equal to 0 or 1 in the pre and post harvesting period, respectively:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1 x_2 + \varepsilon \tag{1.2}$$

During the post harvesting period when $x_2 = 1$ the equation rearranges to:

$$y = (\beta_0 + \beta_2) + (\beta_1 + \beta_3)\, x_1 + \varepsilon \tag{1.3}$$

with a null hypothesis of no change between the control catchments or harvesting effect shown as:

$$H_0\text{: } \beta_2 = \beta_3 = 0$$

A partial F-test was then used to evaluate if the difference between the two models was significant.

Two additional methods were used to assess treatment effects on TP concentration and TP yield. The first compared the range of differences between observed and predicted values before and after 1997 (i.e., the year which harvest occurred). A treatment impact was indicated if the range of differences after harvesting was outside the range observed before harvesting (Buttle et al., 2018). The second method compared the ratio of positive to negative differences between observed and predicted values before and after 1997. A change in this ratio highlights systematic differences (consistently positive or negative) that may not be identified by other statistical tests (Buttle et al., 2018).

2.4. Results

2.4.1. Objective 1: Effects of Changing Environmental Conditions on TP Concentration and TP Yield in Forested Catchments

2.4.1.1. Temporal Change in Meteorological Conditions and Wet Deposition

From 1983 to 2012 WY, total annual precipitation generally declined and mean annual temperature increased. Notably, mean annual concentrations of sulphate, nitrate, and TP deposition also decreased over time (Figure 2.1).

2.4.1.2. Temporal trends in TP concentration and TP yield for undisturbed control catchments

Results from the Seasonal Mann - Kendall Trend test show a varied response of TP concentration and TP yield between 1981 and 2012 WY for all seasons (Figure 2.2a). TP concentrations declined significantly in most catchments (Kendall τ ranging from -0.138 to -0.257, $p \leq 0.1$) however, no significant change was observed in catchments C42 and C50. Conversely, TP concentration increased significantly (Kendall τ ranging from 0.12 to 0.236, $p \leq 0.1$) in the wetland dominated catchments C37 and C38. The TP yields in most catchments decreased significantly over the study period (Kendall τ ranging from -0.147 to -0.389, $p \leq 0.05$). In contrast there was not significant change in TP yield in C38.

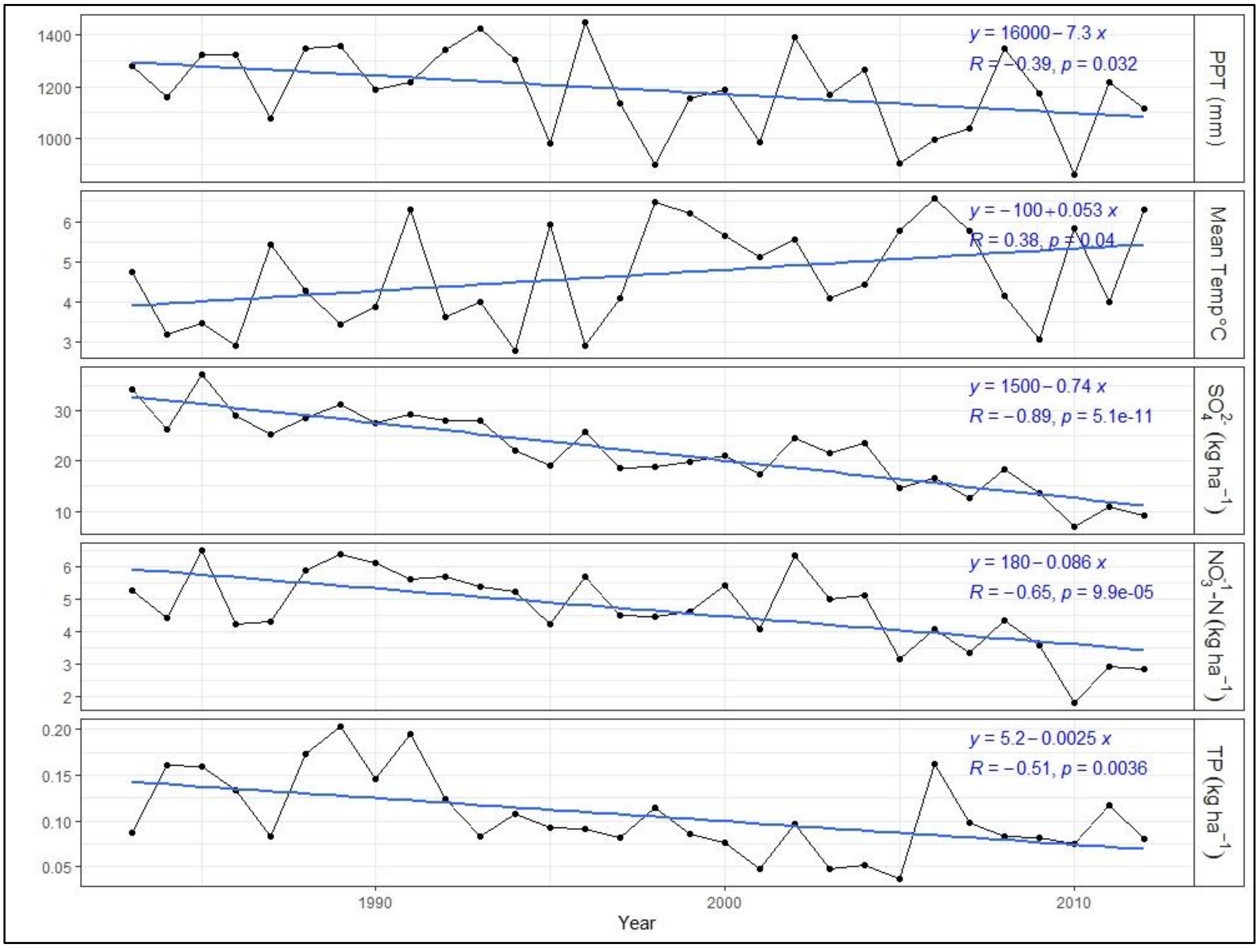

Figure 2.1 Long-term(1983 to 2012 WY) trends in precipitation, temperature and wet deposition chemistry at the TLW meteorological and CAPMON station. Blue lines and equations represent the line of best fit with the corresponding equation.

Individual seasonal trends using the Mann-Kendall trend test for TP concentration varied across the undisturbed catchments. TP concentrations in C35, C47 and C49 in the Fall decreased significantly (Kendall τ ranging from -0.227 to -0.389, $p \leq 0.1$) while TP concentration increased significantly in C38 (Kendall τ: 0.275, $p \leq 0.05$). TP concentration trends generally did not change in the Winter or Spring. Exceptions included significant declining TP concentration trends in C42 during the Winter (Kendall τ: -0.258, $p \leq 0.1$), significant declining TP concentration trends in C46 during the Spring (Kendall τ: -0.243, $p \leq 0.1$) and significant increasing TP concentration trends in C37 and C38 during the Spring (Kendall τ ranging from 0.252 to 0.282, $p \leq 0.05$). Finally, Summer TP concentrations were highly variable but declined significantly over time in C35, C39, C46 and C47 (Kendall τ ranging from -0.277 to -0.458, p ≤

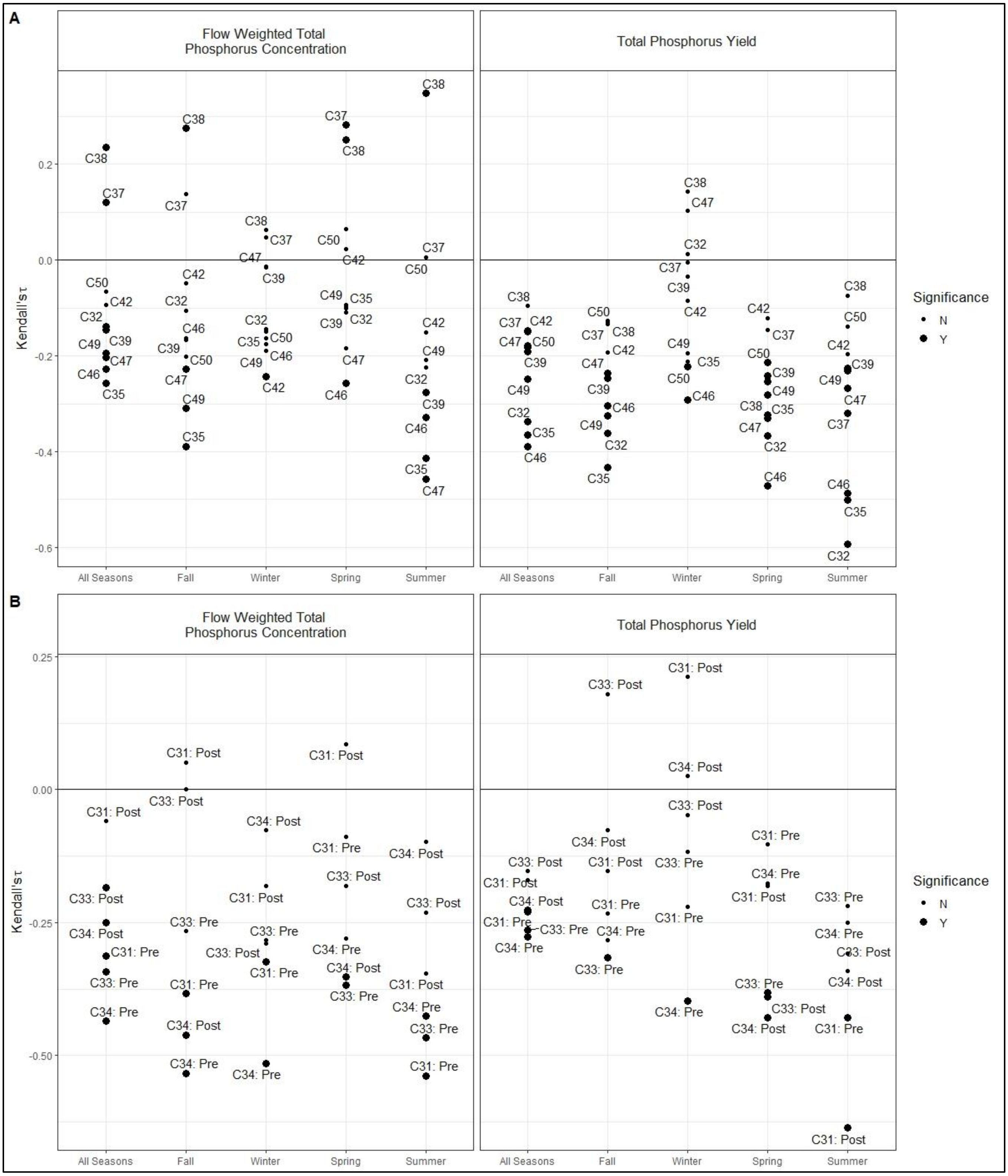

Figure 2.2 Kendall Tau statistics for TP concentration and yield in harvested and control (non harvested) catchments at TLW for all seasons and individual seasons. Larger points reflect a significant trend at a 10% (α = 0.1) significance level. Plot A shows the trends in non harvested catchments from 1981 to 2012. Plot B shows the pre (1981 – 1997 WY) and post (1998 – 2012 WY) trends in the harvested catchments. Increasing and decreasing trends are shown by positive and negative Kendall Tau statistics, respectively.

0.05), increased significant in C38 (Kendall τ: 0.349, $p \leq 0.05$), while significant changes were not observed in C32, C37, C42 and C49.

The individual seasonal TP yields were variable but generally decreased over time. There was a significant decline in Fall TP yields in catchments C32, C35, C39, C46, C47 and C49 (Kendall τ ranging from -0.236 to -0.433, $p \leq 0.1$). TP yields in the winter were stable in most catchments, however there was a significant declining trend in C46 and C50 (Kendall τ ranging from -0.223 to -0.292, $p \leq 0.1$). Spring seasonal TP yields declined significantly in all catchments (Kendall τ ranging from -0.214 to -0.472, $p \leq 0.1$), except for C37 and C42. TP yield decreased significantly in the Summer (Kendall τ ranging from -0.232 to -0.594, $p \leq 0.1$) for all catchments except for C38, C42 and C50, where no significant trend was observed.

2.4.2. Objective 2: Harvesting Effects on TP Concentration and TP Yield

2.4.2.1. Temporal Trends in TP Concentration and TP Yield for Harvested Catchments

Temporal trends for TP concentration in the harvested catchments for the pre harvesting periods (1981 to 1997 WY) varied seasonally and between catchments (Figure 2.2b). Across all seasons, TP concentration declined significantly in the clear-cut (Kendall τ: -0.313, $p \leq 0.05$), selection cut (Kendall τ: -0.343, $p \leq 0.05$), and shelterwood cut (Kendall τ: -0.436, $p \leq 0.05$) during the pre harvesting period. After harvesting (1998 to 2012 WY) TP concentration continued to decline significantly in the selection cut (Kendall τ: -0.184, $p \leq 0.1$) and shelterwood cut (Kendall τ: -0.250, $p \leq 0.05$). No significant change in TP concentration was observed in the clear-cut during the post harvesting period. Significant seasonal trends in the pre harvesting period were observed in the clear-cut and shelterwood cut during the Fall and Winter (Kendall τ ranging from -0.324 to -0.533, $p \leq 0.1$), in the selection cut during the Spring (Kendall τ: -0.368, $p \leq 0.05$), and in all three harvested catchments during the Summer (Kendall τ ranging from -0.426 to -0.538, $p \leq 0.05$). Significant seasonal trends in the post harvesting period were observed in the shelterwood cut during the Fall and Spring (Kendall τ ranging from -0.352 to -0.462, $p \leq 0.1$).

Similarly, TP yield trends in the harvested catchments was varied (Figure 2.2b). Pre harvesting trends for TP yield across all seasons showed a significant decline in all three harvested catchments (Kendall τ ranging from -0.230 to -0.277, $p \leq 0.05$). However, no significant trends were observed in any of the harvested catchments after harvesting. Significant individual seasonal trends were observed during the Fall and Spring prior to selection cut harvesting (Kendall τ ranging from -0.317 to -0.382, $p \leq 0.1$), during the winter prior to the shelterwood cut (Kendall τ: -0.397, $p \leq 0.05$), and during the Summer prior to the clear-cut (Kendall τ: -0.429, $p \leq 0.05$). Significant seasonal trends were observed during the Spring after the selection and shelterwood cuts (Kendall τ ranging from -0.390 to -0.429, $p \leq 0.05$), and during the Summer after the clear-cut (Kendall τ: -0.636, $p \leq 0.05$).

2.4.2.2. Harvesting effects on flow-weighted total phosphorus concentration

Small but significant increases in flow-weighted TP concentration (Mann Whitney U Test, ANCOVA $p \leq 0.1$) were observed in the clear-cut (compared to C32 and C46) and the selection cut (compared to C35) (Table 2.1). Harvesting effects were largest in the clear-cut, followed by the selection cut and smallest in the shelterwood cut catchments (Figure 2.3 and A1). Mean harvesting effects on TP concentration ranged from 1 ± 1 μg L^{-1}, 0 ± 1 to 1 ± 1 μg L^{-1}, and 0 ± 1 to 0 ± 2 μg L^{-1} for the clear-cut, selection cut and shelterwood cut, respectively (Table 2.1). Harvesting effects were mostly within the range observed before harvesting except for a few extreme values in the clear-cut and shelterwood cut catchments. The largest harvesting effects occurred 3 to 9 years after harvesting (Figure 2.3). The ratio of positive to negative harvesting effects increased in the clear-cut (largest increase: 1.26 to 2.00) and selection cut (largest increase: 0.85 to 1.60) and decreased in the shelterwood cut (largest decrease: 1.07 to 0.58).

The largest seasonal effect of harvesting on TP concentration occurred in the Spring with significantly higher TP concentrations (Mann Whitney U Test, ANCOVA $p \leq 0.1$) for all three harvested catchments (compared to C46) and in the clear-cut and selection cut catchments (compared to C35) (Table

Table 2.1 Summary table of harvesting impacts on flow weighted TP concentration (µg L^{-1}) for the clear-cut, selection cut, and shelterwood cut catchments compared to all controls for all seasons combined and each individual season. Values reported include, number of observations in the post harvesting time period (n), mean ± standard deviation (SD) of harvesting effects with the Mann Whitney U Test on observed and predicted values in the post harvesting time period, p-values from ANCOVA on the simple and complex linear regressions between control and harvested catchments (regressions that did not meet the assumptions were removed and replaced with a "-"), ratio of positive to negative differences in both the pre harvesting and post harvesting time period, and the number of post harvesting effects outside of the pre harvesting range.

		C32						C35						C46					
Season	Catchment	n	Mean ± SD (p-value)*	ANCOVA p-value	Ratio Pre	Ratio Post	# Effects Outside Pre Harvest Range	n	Mean ± SD (p-value)*	ANCOVA p-value	Ratio Pre	Ratio Post	# Effects Outside Pre Harvest Range	n	Mean ± SD (p-value)*	ANCOVA p-value	Ratio Pre	Ratio Post	# Effects Outside Pre Harvest Range
All Seasons	Clear Cut	47	1 ± 1 (0.257)	0.078	1.250	1.470	Above: 4, Below: 0	50	1 ± 1 (0.128)	-	1.250	1.780	Above: 1, Below: 0	36	1 ± 1 (0.071)	0.051	1.260	2.000	Above: 0, Below: 0
	Selection Cut	51	0 ± 1 (0.284)	0.269	1.250	1.320	Above: 1, Below: 0	52	1 ± 1 (0.195)	0.062	0.850	1.600	Above: 1, Below: 0	37	0 ± 1 (0.291)	0.173	1.000	1.640	Above: 0, Below: 0
	Shelterwood Cut	49	0 ± 1 (0.451)	-	1.070	0.580	Above: 1, Below: 0	51	0 ± 1 (0.678)	-	1.060	0.960	Above: 1, Below: 0	37	0 ± 2 (0.983)	0.22	1.140	0.850	Above: 1, Below: 0
Fall	Clear Cut	11	0 ± 1 (1.000)	0.956	1.143	0.833	Above: 1, Below: 0	13	0 ± 1 (1.000)	-	0.667	0.857	Above: 1, Below: 0	9	1 ± 1 (0.796)	-	1.000	1.250	Above: 1, Below: 0
	Selection Cut	11	0 ± 1 (0.478)	0.318	1.333	1.750	Above: 0, Below: 0	13	0 ± 1 (0.687)	-	0.875	1.600	Above: 0, Below: 0	9	0 ± 1 (0.863)	-	1.000	1.250	Above: 0, Below: 0
	Shelterwood Cut	11	0 ± 1 (0.519)	0.685	1.500	0.222	Above: 0, Below: 0	13	0 ± 1 (0.479)	0.492	0.600	0.444	Above: 0, Below: 0	9	0 ± 1 (0.863)	0.214	1.000	0.800	Above: 0, Below: 0
Winter	Clear Cut	11	1 ± 1 (0.478)	0.135	1.200	1.750	Above: 2, Below: 0	11	1 ± 1 (0.076)	-	0.700	2.667	Above: 1, Below: 0	10	1 ± 2 (0.165)	-	1.500	1.500	Above: 5, Below: 0
	Selection Cut	14	0 ± 1 (0.982)	0.941	1.500	1.000	Above: 1, Below: 0	12	0 ± 1 (0.478)	0.175	0.400	1.400	Above: 1, Below: 0	10	0 ± 1 (1.000)	-	0.857	1.500	Above: 1, Below: 0
	Shelterwood Cut	12	1 ± 2 (1.000)	0.798	0.833	1.000	Above: 0, Below: 0	11	1 ± 2 (1.000)	-	0.545	1.200	Above: 0, Below: 1	10	1 ± 3 (0.853)	-	0.875	0.429	Above: 0, Below: 0
Spring	Clear Cut	15	1 ± 1 (0.116)	-	1.833	2.750	Above: 1, Below: 0	15	1 ± 1 (0.033)	0.189	4.667	6.500	Above: 1, Below: 0	10	2 ± 1 (0.019)	0.023	3.250	4.000	Above: 0, Below: 0
	Selection Cut	15	1 ± 1 (0.202)	-	1.125	2.000	Above: 1, Below: 0	15	1 ± 1 (0.074)	0.402	1.125	2.750	Above: 1, Below: 0	10	1 ± 1 (0.015)	0.01	1.429	9.000	Above: 0, Below: 0
	Shelterwood Cut	15	0 ± 1 (0.902)	-	0.889	0.500	Above: 1, Below: 0	15	1 ± 1 (0.285)	0.59	4.667	2.000	Above: 1, Below: 0	10	1 ± 1 (0.036)	0.476	3.250	4.000	Above: 0, Below: 0
Summer	Clear Cut	10	1 ± 2 (1.000)	0.185	0.833	1.000	Above: 2, Below: 2	11	0 ± 2 (0.478)	-	1.333	0.833	Above: 3, Below: 0	7	0 ± 1 (0.805)	0.885	0.444	2.500	Above: 2, Below: 0
	Selection Cut	11	0 ± 1 (0.519)	0.808	1.167	0.833	Above: 0, Below: 1	12	0 ± 1 (0.887)	-	1.143	1.000	Above: 0, Below: 0	8	0 ± 1 (0.959)	0.892	0.750	0.600	Above: 0, Below: 4
	Shelterwood Cut	11	0 ± 1 (0.748)	0.98	1.167	0.833	Above: 1, Below: 1	12	0 ± 1 (0.178)	-	1.000	0.714	Above: 1, Below: 0	8	-1 ± 1 (0.382)	0.816	0.556	0.333	Above: 1, Below: 2

*Mann Whitney U Test p-value

-Assumptions not met for ANCOVA test

Figure 2.3 Harvesting effects or differences between the observed and predicted values from the calibration regressions on flow weighted TP concentration (μg L^{-1}) for the harvested catchments compared to all control catchments during all seasons combined and each individual seasons.

2.1). A significant increase (Mann Whitney U Test, $p \leq 0.1$) in Winter TP concentrations was observed in the clear-cut (compared to C35) (Table 2.1). There was no increase in TP concentration for the harvested catchments in the Fall and Summer. The ratio of positive to negative treatment effects generally increased (smallest increase: 0.83 to 1.00; largest increase: 1.43 to 9.00) between the pre and post harvesting periods. The range of treatment effects post harvest was mostly within the pre harvest range except for a few outliers (Table 2.1). Seasonal harvesting effects are presented in Figure 2.3 and A2.

2.4.2.3. Harvesting effects on total phosphorus yield

Total phosphorus yield increased in all harvested catchments with the largest response occurring in the clear-cut (Figure 2.4 and A3). Mean harvesting effects across all seasons ranged from 2 ± 3 to 3 ± 4 g ha^{-1} $season^{-1}$, 2 ± 3 to 3 ± 3 g ha^{-1} $season^{-1}$, and 1 ± 3 to 2 ± 4 g ha^{-1} $season^{-1}$ (Table 2.2) and annual harvesting effects ranged from -1 to 22 g ha^{-1} $year^{-1}$, 0 to 14 g ha^{-1} $year^{-1}$, and -4 to 21 g ha^{-1} $year^{-1}$ (Table 2.3) in the clear-cut, selection cut and shelterwood cut catchments, respectively. Significant harvesting effects were observed in the clear-cut (compared to C35 and C46; Mann Whitney U Test, $p \leq 0.05$) and the selection cut (compared to all controls) (Mann Whitney U Test, ANCOVA $p \leq 0.05$) (Table 2.2). The largest harvesting effects occurred 3 to 9 years after harvesting (Figure 2.4). The range of harvesting effects was within the range observed before harvesting occurred suggesting a limited impact of harvesting on the magnitude of TP yield (Figure 2.4). However, when looking at the change in the positive to negative harvesting effects ratio it is clear there was a small increase in TP yield. The ratio increased in all three harvested catchments with the largest changes ranging from 1.17 to 11.5, 1.18 to 16.33 and 1.38 to 8.25 for the clear-cut, selection cut and shelterwood cut catchments, respectively (Table 2.2).

Seasonal effects of harvesting on TP yield were observed in all seasons and were the largest in the Spring, consistent with the results observed for TP concentration. Significant increases (Mann Whitney U Test, ANCOVA, $p \leq 0.1$) in the Spring TP yield were observed in all harvested catchments (compared to all

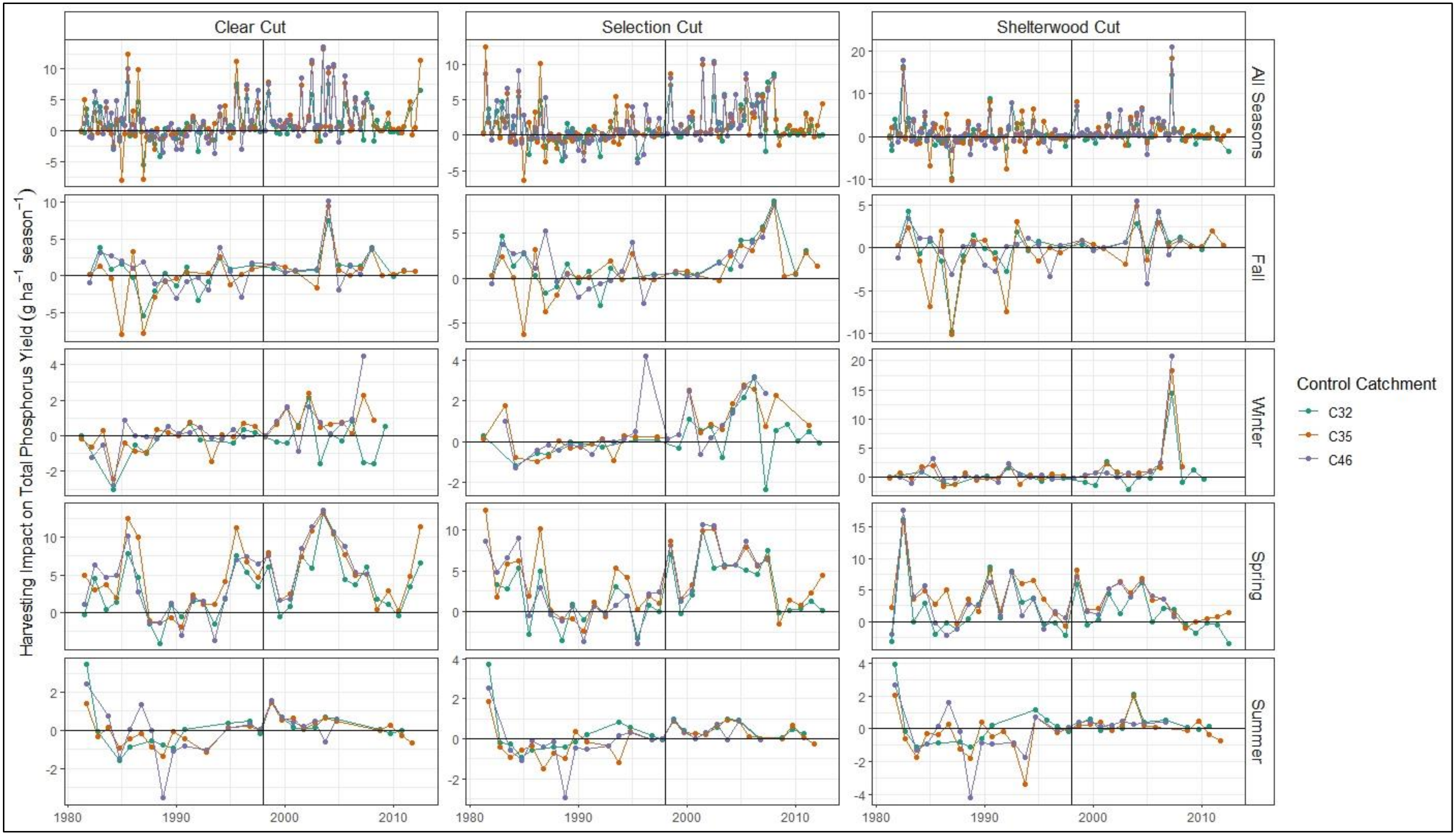

Figure 2.4 Harvesting effects or differences between the observed and predicted values from the calibration regressions on TP yield (g ha^{-1} season^{-1}) for the harvested catchments compared to all control catchments during all seasons combined and each individual seasons.

Table 2.2 Summary table of harvesting impacts on flow weighted TP concentration (g ha^{-1} $season^{-1}$) for the clear-cut, selection cut, and shelterwood cut catchments compared to all controls for all seasons combined and each individual season. Values reported include, number of observations in the post harvesting time period (n), mean ± standard deviation (SD) of harvesting effects with the Mann Whitney U Test on observed and predicted values in the post harvesting time period, p-values from ANCOVA on the simple and complex linear regressions between control and harvested catchments (regressions that did not meet the assumptions were removed and replaced with a "-"), ratio of positive to negative differences in both the pre harvesting and post harvesting time period, and the number of post harvesting effects outside of the pre harvesting range.

		C32						C35						C46					
Season	Catchment	n	Mean ± SD (p-value)*	ANCOVA p-value	Ratio Pre	Ratio Post	# Effects Outside Pre Harvest Range	n	Mean ± SD (p-value)*	ANCOVA p-value	Ratio Pre	Ratio Post	# Effects Outside Pre Harvest Range	n	Mean ± SD (p-value)*	ANCOVA p-value	Ratio Pre	Ratio Post	# Effects Outside Pre Harvest Range
All Seasons	Clear Cut	47	2 ± 3 (0.197)	-	1.250	3.27	Above: 2, Below: 0	50	2 ± 4 (0.050)	-	1.170	11.5	Above: 1, Below: 0	36	3 ± 4 (0.048)	-	1.440	8	Above: 4, Below: 0
	Selection Cut	51	2 ± 3 (0.014)	-	1.120	6.29	Above: 7, Below: 0	52	2 ± 3 (0.002)	< 0.001	1.180	16.33	Above: 0, Below: 0	37	3 ± 3 (0.008)	-	0.940	11.33	Above: 2, Below: 0
	Shelterwood Cut	49	1 ± 3 (0.440)	-	0.930	1.58	Above: 0, Below: 0	51	2 ± 3 (0.162)	-	1.060	4.1	Above: 1, Below: 0	37	2 ± 4 (0.164)	-	1.380	8.25	Above: 1, Below: 1
Fall	Clear Cut	11	2 ± 2 (0.047)	0.035	1.500	10	Above: 2, Below: 0	13	1 ± 3 (0.243)	0.103	1.143	12	Above: 2, Below: 0	9	2 ± 3 (0.113)	-	1.000	8	Above: 1, Below: 0
	Selection Cut	11	3 ± 3 (0.008)	0.036	1.800	Inf	Above: 2, Below: 0	13	2 ± 2 (0.019)	0.014	1.500	12	Above: 3, Below: 0	9	3 ± 3 (0.063)	0.096	1.286	Inf	Above: 1, Below: 0
	Shelterwood Cut	11	1 ± 1 (0.478)	0.017	0.875	1.75	Above: 0, Below: 0	13	1 ± 2 (0.545)	0.335	0.600	3.333	Above: 1, Below: 0	9	1 ± 3 (0.796)	0.536	1.667	2	Above: 2, Below: 1
Winter	Clear Cut	11	0 ± 1 (0.949)	0.204	0.833	0.833	Above: 2, Below: 0	11	1 ± 1 (0.116)	-	0.889	10	Above: 1, Below: 0	10	1 ± 1 (0.105)	0.152	0.875	4	Above: 3, Below: 0
	Selection Cut	14	1 ± 1 (0.104)	0.004	0.667	2.5	Above: 5, Below: 0	12	1 ± 1 (0.004)	0.001	1.000	Inf	Above: 0, Below: 0	10	1 ± 1 (0.009)	0.045	0.625	9	Above: 2, Below: 0
	Shelterwood Cut	12	1 ± 4 (0.799)	0.391	0.833	1	Above: 0, Below: 1	11	3 ± 5 (0.065)	0.02	0.889	10	Above: 0, Below: 1	10	3 ± 6 (0.075)	-	1.500	9	Above: 0, Below: 0
Spring	Clear Cut	15	5 ± 4 (0.024)	0.008	2.400	6.5	Above: 0, Below: 0	15	6 ± 4 (0.002)	0.038	3.250	Inf	Above: 1, Below: 0	10	7 ± 4 (0.003)	0.015	3.250	Inf	Above: 0, Below: 0
	Selection Cut	15	4 ± 3 (0.041)	0.014	1.667	6.5	Above: 0, Below: 0	15	5 ± 3 (0.009)	0.052	3.250	14	Above: 0, Below: 0	10	7 ± 3 (0.002)	0.003	1.833	Inf	Above: 0, Below: 0
	Shelterwood Cut	15	1 ± 3 (0.744)	0.334	1.429	1.143	Above: 0, Below: 0	15	3 ± 3 (0.098)	0.971	7.500	6.5	Above: 0, Below: 0	10	4 ± 2 (0.036)	0.318	2.400	Inf	Above: 0, Below: 0
Summer	Clear Cut	10	0 ± 1 (0.105)	0.361	0.571	4	Above: 2, Below: 0	11	0 ± 1 (0.171)	-	0.556	4.5	Above: 5, Below: 0	7	0 ± 1 (0.165)	-	1.600	6	Above: 4, Below: 0
	Selection Cut	11	0 ± 0 (0.010)	0.065	0.625	10	Above: 9, Below: 1	12	0 ± 0 (0.021)	0.066	0.364	11	Above: 5, Below: 0	8	0 ± 0 (0.105)	-	0.400	3	Above: 0, Below: 0
	Shelterwood Cut	11	0 ± 1 (0.065)	0.192	0.625	4.5	Above: 3, Below: 2	12	0 ± 1 (0.755)	0.565	0.455	2	Above: 2, Below: 0	8	0 ± 0 (0.130)	-	0.556	Inf	Above: 1, Below: 0

*Mann Whitney U Test p-value

-Assumptions not met for ANCOVA test

Table 2.3 Annual harvesting effects on TP yield from similar BACI studies.

Region	Number of Sites	Data Record Length	Disturbance Type	Area Disturbed (%)	Treatment Effect on Phosphorus Yield	Study
Eastern Finland	6	15 Years (Pre: 4 Years, Post: 16 Years)	Clear Cut, Site Preparation, Fertilization	13 - 58%	Annual Total Phosphorus Yield: 0 - 1100 g/ha area	Ahtiainen and Huttunen, 1999
Northern Sweden	5	8 Years (Pre: 2 Years, Post: 6 Years)	Clear Cut, Clear Cut with Buffer Strip	30 - 73%	Annual Total Phosphorus Yield: 10 - 40 g/ha	Löfgren et al. 2009
North Eastern Texas, USA	13	8 Years (Pre: 3 Year, Post: 5 Years)	Clear Cut, Site Preparation, Fertilization	-	Annual Total Phosphorus Yield: 0 - 1069.0 g/ha	McBroom et al. 2008
Southern Finland	5	8 Years (Pre: 2 Years, Post: 6 Years)	Clear Cut, Site Preparation, Peatland Drainage	40 - 70%	Annual Disolved Phosphorus Yield: 16.0 - 40.0 g/ha	Nieminen, 2004
Eastern Finland	4	Varied (Pre: 4 - 9 Years, Post: 9 - 15 Years)	Clear Cut with Buffer Strips	8 - 34%	Annual Orthophosphate Yield: 2 g/ha	Palviainen et al. 2014
North Carolina, USA	2	20 Years (Pre: 7 Years, Post: 13 Years)	Clear Cut, Road Construction, Site Preparation	100%	Annual Orthophosphate Yield: 10 - 40 g/ha	Swank et al. 2001
Northern Idaho, USA	7	24 Years (Pre: 5 Years, Post: 19 Years)	Clear Cut, Partial Cut, Road Construction	9 - 50.5%	Annual Total Phosphorus Yield: 27 - 88 g/ha	Deval et al. 2021
North Carolina, USA	6	6 Years (Pre: 3 Years, Post: 3 Years)	Clear Cut with Buffer Strips, Site Preparation, Tree Planting	30 - 100%	Mean Annual Total Phosphorus Yield: 100 - 250 g/ha	Boggs et al. 2016
Northeast Victoria, Australia	2	11 Years (Pre: 8 Years, Post: 3 Years)	Wildfire, Salvage Logging	-	Annual Particulate Phosphorus Yield: 880 - 6200 g/ha	Smith et al. 2012
C31, TLW	1	31 Years (Pre: 16 Years, Post: 14 Years)	Clear Cut	100%	Annual Total Phosphorus Yield: -1 - 22 g/ha	This Study
C33, TLW	1	31 Years (Pre: 16 Years, Post: 14 Years)	Selection Cut	100%	Annual Total Phosphorus Yield: 0 - 14 g/ha	This Study
C34, TLW	1	31 Years (Pre: 16 Years, Post: 14 Years)	Shelterwood Cut	70%	Annual Total Phosphorus Yield: -4 - 21 g/ha	This Study

controls) except for the shelterwood cut (compared to C32) (Table 2.2). TP yield in the selection cut (compared to all controls), clear-cut (compared to C32) and shelterwood cut (compared to C32) increased significantly (Mann Whitney U Test, ANCOVA, $p \leq 0.1$) in the Fall. Significant increases (Mann Whitney U Test, ANCOVA, $p \leq 0.1$) occurred in the Winter for the clear-cut (compared to C46), the selection cut (compared to all controls) and the shelterwood cut (compared to C35 and C46) (Table 2.2). Finally, significant increases (Mann Whitney U Test, ANCOVA, $p \leq 0.1$) in the Summer occurred in the clear-cut and shelterwood cut (compared to C32) and in the selection cut (compared to all controls) (Table 2.2). The ratio of positive to negative harvesting effects increased in all seasons and the number of values outside the pre harvesting range was largest in the Summer and Winter. Seasonal linear regressions between the control and harvested catchments pre and post harvesting can be seen in Figure A4.

2.5. Discussion

2.5.1. Temporal Trends in Phosphorus Concentration and Yield

The decline in TP concentration over the study period can be explained by changing environmental conditions in TLW that include climate warming, recovery from acid rain and declines of phosphorus atmospheric deposition. The warming and drying trends in TLW described by Buttle et al. (2018) and shown in Figure 2.1 may have reduced hydrological connectivity between the hillslope and stream channel. Total P concentrations in streams typically increase with increasing flow (Hoffmann et al., 2009; Kreutzweiser et al., 2008), suggesting that reduced hillslope channel connectivity would decrease TP concentrations. Reductions in soil sulfate and nitrate concentrations (Figure 2.1) due to recovery from acid rain deposition (Webster, et al., 2021b) and reductions in atmospheric phosphorus deposition (Figure 2.1) are contributing factors that help to explain the observed reduction in stream TP concentrations. The increase in soil pH due to a decrease in acid rain over the study period will limit the potential for phosphorus release from soils (Sherman et al., 2006). As soils recover from acidification and the mobilization of iron and aluminum oxides decreases, it is expected that phosphorus sorption within soils will increase reducing the amount of phosphorus available for transport to the stream network (Davidson et al., 2003; Mengistu et al., 2014). Finally, phosphorus deposition can be a critical nutrient source in geologically low phosphorus landscapes where rates of mineral weathering of phosphorus from bedrock are low (Eimers et al., 2018) and as phosphorus deposition decreases, the availability of phosphorus on the landscape will also be reduced. The combined and cumulative effects of these factors (climate change, recovery from acid rain, reduced phosphorus deposition) should reduce phosphorus availability and lead to a reduction of TP concentrations, as observed at TLW. Trends in TP yield are more easily explained as both TP concentration (this study) and flow (Buttle et al., 2018; Webster, et al., 2021b), the main components that make up TP yield, have both decreased through time.

Unlike most catchments which showed no change or declining TP concentration trends, the wetland dominated catchments (C37 and C38) showed increasing TP concentrations over time. As the presence of wetlands in a watershed plays a critical role in controlling stream water chemistry including the supply of phosphorus to stream channels (Fritz et al., 2018; Leach et al., 2020; O'Brien et al., 2013), it is likely catchments with substantial wetland cover would respond differently to changing environmental conditions then those without. The changing meteorological conditions due to climate change in TLW may have caused TP concentrations to increase in the wetland dominated catchments in one of two ways; (1) warmer temperatures may have increased the rates of decomposition and mineralization resulting in larger soluble phosphorus pools (Hoffmann et al., 2009) and (2) the hydrologic contributions from wetlands to total stream flow under drier conditions would have increased as hillslopes will become increasingly disconnected from the stream channel while wetlands act as sponges that release water through dry periods (Lane et al., 2020; Leach et al., 2020). Wetlands are sources of phosphorus to streams particularly under anoxic conditions where the reduction of Fe (III) to Fe (II) may release Fe associated phosphorus (Davidson et al., 2003; Liptzin & Silver, 2009; Mengistu et al., 2014; O'Brien et al., 2013) and as wetlands contribute more water to total stream flow, phosphorus concentrations within the streams may also increase.

Trends in TP concentration and yield within seasons were similar to the trends observed across all seasons. Notably TP concentration and yield in most catchments did not change or declined significantly (Figure 3a). Seasonal declines in TP concentration were most prominent during the Summer and Fall. Summer declines in TP concentration have likely been driven by increasing dryness within TLW during the Summer (Creed et al., 2015), which would limit stream flow and any subsequent phosphorus transport. Declines in TP concentration and yield during the Fall are less easily explained as Fall storms have intensified and which would likely mobilize nutrients from litterfall (Creed et al., 2015). Increases in stream TP concentrations would be expected. In contrast, here, Fall TP concentrations generally declined; the causal factors for these declines are not clear. Over the study period, TP concentrations and yields were the most stable during the Winter. This is surprising as numerous studies have reported major hydroclimatic changes occurring during Winter (Creed et al., 2015; Grogan et al., 2020; Hardy et al., 2001). Increasing temperatures during the Winter have caused higher fractions of precipitation falling as rainfall (Grogan et al., 2020; Hardy et al., 2001), increasing the occurrence of rain on snow events, which can rapidly increase stream flow (Berghuijs et al., 2016; Li et al., 2019; Silins et al., 2014). Additionally, warmer Winter temperatures reduce snowpack depths (Hardy et al., 2001) thereby altering soil freeze thaw dynamics and soil biogeochemical cycles (Blankinship & Hart, 2012). These changes can impact the hydrologic cycle and affect downstream transport of nutrients to aquatic environments (Grogan et al., 2020). Therefore, the stability of TP concentration and yield during the Winter within the catchments at TLW is surprising and unexplained. Future work should focus on identifying how changing Winter conditions may impact nutrient cycling and subsequent transport to stream networks.

2.5.2. Effects of Forest Harvesting on Phosphorus Concentration and Yield

The results indicate that clear-cut and selection cut forest harvesting operations significantly increased TP concentrations at TLW. However, as mean harvesting effects were small (< 2 µg L^{-1}), these increases are unlikely to impact aquatic ecosystems as statistical significance does not always equate to biological significance (Schindler, 1977). Similar studies have reported that harvesting had no effect on phosphorus concentrations in the boreal forest in southern Finland (Nieminen, 2004), northern Sweden (Löfgren et al., 2009), hardwood forests in North Carolina, USA (Boggs et al., 2016) and mixed conifer stands in northern Idaho, USA (Deval et al., 2021). The efficient recycling and retention of phosphorus in forested landscapes, high binding capacity of phosphorus to mineral soils, and/or low rates of mineral weathering of surficial geology (Backnäs et al., 2012; Eimers et al., 2018; Emmerton et al., 2019) may contribute to the limited effects of forest harvesting on phosphorus concentrations and yields in impacted streams. Furthermore, the relative absence of overland flow in TLW may also limit the mobility and transport of sediment-associated phosphorus to receiving streams (Hoffmann et al., 2009; Kreutzweiser et al., 2008).

Results from the ANCOVA, Mann-Whitney U Test and changes in the positive to negative harvesting effects ratio all show that TP yield responded significantly to forest harvesting at TLW. Significant changes in hydrology in response to forest harvesting (Buttle et al., 2018, 2019) concurrent with minimal change in TP concentrations show that changes in TP yield are being driven by shifting hydrological conditions and not changes in phosphorus pools on the landscape. Unlike TP concentration, TP yield typically increases after forest harvesting with annual increases ranging from 10 to 1000 g ha^{-1} $year^{-1}$ (Table 2.4). In the present study, maximum annual harvesting effects ranged from 14 to 22 g ha^{-1} $year^{-1}$ which is lower than the maximum harvesting effects observed in the literature (Table 2.4). Notably, the observed harvesting effects within this study are lower than studies which experienced additional disturbance effects such as road construction, site preparation and fertilization (Ahtiainen & Huttunen, 1999; Boggs et al., 2016; Deval et al., 2021 and McBroom et al., 2008). Studies that only included the effects of timber removal have reported a similar range of harvesting treatment effects on TP yield as those observed at TLW (Löfgren et al., 2009; Palviainen et al., 2014). Accordingly, harvesting-related activities other then direct tree removal may be the primary driver of deteriorated water quality in the other investigations. Thus, the effects of timber removal and associated activities such as road construction, stream crossings and site preparation should be evaluated separately and concurrently.

Surprisingly, harvesting effects on TP concentration and yield were larger in the selection cut than the shelterwood cut, despite the lower harvesting intensity. This is likely related to the road network within the selection cut catchment that runs parallel to the stream and reroutes overland flow into the stream channel. Buttle et al. (2018) found the road network to have a similar impact, with the selection cut catchment showing a larger harvesting impact on annual and seasonal water yield when compared to either the clear-cut or shelterwood cut catchments. This further supports the notion described above that harvesting related infrastructure (i.e., road networks, stream crossings and site preparation) may be the primary driver of impacts on water quantity and quality in forested landscapes.

Unsurprisingly, TP concentration harvesting effects observed in the Spring, the most hydrologically connected time of year at TLW (Buttle et al., 2018), were larger than the those observed in the other seasons. The large response observed in the Winter was unexpected and may be caused by Winter warming, rain on snow and/or more frequent freeze thaw events (Casson et al., 2012). Surprisingly, harvesting had little influence on TP concentration in the Fall as it would be assumed that leaf senescence would increase phosphorus pools that could be flushed out during Fall storms (Creed et al., 2015). The largest seasonal effects on TP yield were observed in the Spring and Fall while the smallest were measured in the Winter and Summer. This is unsurprising as the magnitude of harvesting effects on seasonal runoff was largest in the Spring and Fall and smallest in the Winter and Summer (Buttle et al., 2018).

2.5.3. Combined and Competing Effects on Phosphorus Concentration and Yield

The TLW catchments are responding to a range of changing environmental conditions, including climate change (Buttle et al., 2018) and recovery from acid rain (Webster et al., 2021b). These changing environmental conditions likely influence the response of these catchments to forest harvesting. Climate warming can alter TP concentrations and yields through changing hydrological connectivity that limits the ability for phosphorus to be transported from the landscape to stream networks (Dillon & Molot, 1997). Soil acidification can increase the mobilization of Al and Fe in soils which can increase the risk of phosphorus leaching to surface waters (Sherman et al., 2006). As soils recover from acidification it can be expected that the rate of phosphorus leaching will decrease through changes in phosphorus solubility within forested soils (Penn & Camberato, 2019). However while previous studies in the Canadian Shield report that soil acidification has had no effect on phosphorus sorption, more and work is needed to better understand these processes (Baker et al., 2015). The combined effect of changing climate, recovery from acid rain and reduction in phosphorus deposition may have reduced the specific effect of harvesting on phosphorus transport dynamics and a larger harvesting effect may have been masked. The limited responses of TP concentration and yield in the first three years after harvesting (Figure 2.3 and 2.4) were likely driven by the particularly dry conditions in TLW that reduced hydrologic connectivity between the landscape and stream channels (Buttle et al., 2018). As the impacts of forest harvesting on water quality are typically greatest in the first three years immediately after harvesting (Ahtiainen & Huttunen, 1999; Swank et al., 2001), the timing of this dry period likely limited associated responses in TP concentrations and yields.

2.5.4. Implications for Drinking Water Treatability

The limited effects of forest harvesting on TP concentrations and yields in TLW (mean increases < 2 µg L^{-1} and <10 g ha^{-1} $season^{-1}$) are unlikely to increase the probability of harmful algal bloom occurrence as TP concentration thresholds associated with increased algal production typically range from 20 – 50 µg TP L^{-}

^{1} (Fastner et al., 2016; Vuorio et al., 2020; Xu et al., 2015). While landscape disturbance by both harvesting and wildfire can increase phosphorus concentrations in lakes on the Canadian Shield, wildfire typically has a larger effect (Carignan et al., 2000; Pinel-Alloul et al., 2002). Wildfire can significantly increase SRP and TP concentrations (Emelko et al., 2016; Silins et al., 2014) and yields ranging from 880 to 6200 g ha^{-1} $year^{-1}$ (Smith et al., 2012) which can dramatically increase algal production in impacted streams to downstream aquatic environments such as drinking water reservoirs (Emelko et al., 2016; Silins et al., 2014). Therefore, under changing climatic conditions with the increased risk of wildfire, forest harvesting strategies, especially those designed to limit linear features such as roads, may represent a suitable source water protection strategy because it creates more diverse and resilient forests to drought and wildfire. However, it has recently been observed that the increasing occurrence of algal blooms in oligotrophic lakes throughout Ontario and North America may be strongly linked to climate change (Karmakar et al., 2015; Stoddard et al., 2016; Winter et al., 2011). Therefore, small increases in TP concentration and yield from disturbed forested landscapes such as those observed in this study may increase algal production in the future.

2.6. Conclusion

Changing climatic conditions, recovery from acid rain and reduced levels of phosphorus deposition explain the decreasing trends observed for TP concentration and yield at TLW. Small but significant harvesting effects were observed in the clear-cut and selection cut for TP concentration and in all harvested treatments for TP yield. Unsurprisingly the largest harvesting effects were observed in the clear-cut catchment for both TP concentration and yield; however, the selection cut with the lowest harvesting intensity showed the second largest impact on both TP concentration and TP yield. This is surprising but may serve as an example of how harvesting related activities such as road construction, stream crossings and site preparation may have a larger impact on water quality than timber removal. Buttle et al. (2018)

reported that harvesting effects on water quantity were not observed until three years after disturbance, providing a potential explanation to the lagged effect harvesting had on TP concentration and yield. Seasonal harvesting effects on both TP concentration and yield were largest in the Spring. Significant harvesting effects on both TP concentration and yield were observed in the Winter and may be a result of the changing climatic conditions occurring at TLW due to changes in the vernal window. While harvesting significantly increased TP concentration and yield, these increases were very small when compared to other harvesting experiments and lower than those typically associated with excess algal growth. Therefore, forest harvesting on hardwood dominated Canadian Shield catchments, is unlikely to pose any threat to downstream aquatic environments and may be a suitable source water protection strategy to make forests more resilient and reduce potential water quality impact from changing climate.

Chapter 3. Legacy Forest Harvesting Impacts on Source Contributions to Streamflow: Evidence using End Member Mixing Analysis at Turkey Lakes Watershed

3.1. Abstract

Forests are critical water supply regions that are increasingly threatened by natural and anthropogenic disturbance. Evaluation of runoff generating processes within harvested and forested headwater catchments provides insight into disturbance impacts on water quality and drinking water treatability. In this study, an extensive hydrologic dataset collected at the experimental Turkey Lakes Watershed (TLW) located on the Canadian Shield was used to quantify sources of stormflow in legacy clear-cut (24-years post harvesting) and forested (control) headwater catchments using an end member mixing analysis (EMMA) model. Stream water, groundwater, soil water and throughfall water quality were evaluated during Spring snowmelt, stormflow and Fall wet up. Groundwater chemistry was similar to stream water chemistry in both catchments, suggesting that groundwater is a major contributor to stream flow. Water chemistry in small wetlands within the study catchments was also comparable to stream water chemistry, suggesting that wetlands are also important contributors. Differences in wetland position between the legacy clear-cut and control catchments appeared to have a greater influence on source contributions than the harvesting impact. Results from this study provide insight into runoff generation processes that reflect event/seasonal flow dynamics and discuss the impacts on water quality.

Keywords: Forested headwater catchments; hillslope channel connectivity; runoff generation processes; principal component analysis; wetlands; solutes

3.2. Introduction

Forested landscapes are critical for the provision of safe and reliable drinking water to a majority of Canadians and 60% of the US population—60% of the world's largest cities also rely on forests for water (Emelko et al., 2011; MacDonald & Shemie, 2014; Stein & Butler, 2004; Stein et al., 2005). The ecosystem services of tropical and temperate forests have been valued at $23.32 trillion USD per year (de Groot et al., 2012; Sun & Vose, 2016) with savings to global drinking water treatment costs valued at ~4.1 trillion USD per year (Costanza et al., 1998). Landscape disturbance threatens water supply through alterations to hydrologic and biogeochemical cycles that ultimately change water quantity and quality—these threats are further exacerbated by compound disturbance (e.g., heavy precipitation following wildfire) (Caretta et al., 2022; Emelko et al., 2011; Smith et al., 2011). Forest disturbance typically intensifies the water cycle resulting in more water moving through the landscape (Buttle et al., 2018; Jones, 2000), which increases the transport of sediment and nutrients to stream channels (Neary et al., 2009; Silins et al., 2009; Smith et al., 2011; Webster et al., 2022). Sediment and nutrients are transported downstream (Emelko et al., 2016; Stone et al., 2014, 2021) and challenge drinking water treatment operations (Emelko et al., 2011). However, the varied hydrologic responses of forested catchments to landscape disturbance (Buttle, 2011; Creed et al., 2019; Jones et al., 2012; M. Zhang et al., 2017) make predicting disturbance effects difficult (McDonnell et al., 2018). Explaining this variability requires an understanding of the impacts of landscape disturbance on water movement and storage in a variety of forested landscapes (Creed et al., 2019; Leach et al., 2020; McDonnell et al., 2018) and is essential to evaluating potential risks to drinking water treatment operations (Emelko et al., 2011; McDonnell et al., 2018).

Harvesting of trees is a common anthropogenic disturbance in many forested ecosystems (Webster et al., 2015). In addition to industrial forestry and silviculture, harvesting is increasingly advocated as a techno-ecological nature-based solution (TE-NBS) (Blackburn et al., 2021) for mitigating climate change-exacerbated landscape disturbance (e.g., wildfire) threats to drinking water treatability

(Blackburn et al., 2021; Emelko & Sham, 2014). Critically, however, harvesting can impact water storage and flow paths. Vegetation removal associated with harvesting can reduce rates of precipitation interception, transpiration and increase water content of forest soils (Jones, 2000; Mackay & Band, 1997; Murray & Buttle, 2003). Additionally, heavy equipment can change the physical characteristics of forest soils by increasing soil bulk density and reducing soil porosity and infiltration rates (Chanasyk et al., 2003; Startsev & McNabb, 2000; Whitson et al., 2003; Williamson & Neilsen, 2000). These changes may increase soil saturation (Johnson et al., 2007; Murray & Buttle, 2005) and reduce the water storage capacity of soils after harvesting (Buttle et al., 2019; Nijzink et al., 2016). Reduced water storage capacity can increase the proportion of water transported via overland flow (Chanasyk et al., 2003) and shallow subsurface pathways (Monteith et al., 2006b, 2006a) that result in more frequent quick flow events (Buttle et al., 2019; Sørensen et al., 2009). Notably, these combined changes result in higher annual and seasonal water yields (Bosch & Hewlett, 1982; Buttle et al., 2018) and increased peak flows (Jones, 2000).

Long-term experimental watersheds, such as the Turkey Lakes Watershed (TLW) provide detailed historical hydro-chemical data that can be used to evaluate complex hydrological processes (Webster et al., 2021b). Previous work at TLW has shown that shallow soil water is a major contributor to stream flow during snowmelt (Hazlett et al., 2001) and that perched water tables over less permeable/impermeable soil layers direct flow through the upper soil profile (Semkin et al., 2002). Threshold relationships were observed between quick flow and precipitation (Buttle et al., 2019) and streamflow generation is controlled through transmissivity feedback (rapid streamflow increases as the water table approaches soil surfaces) (Monteith et al., 2006a). Harvesting increased the proportion of water moving through the upper soil profile (Buttle et al., 2018; Monteith et al., 2006a), reduced travel times (Leach et al., 2020; Monteith et al., 2006b) and decreased the root zone storage capacity resulting in a reduced precipitation threshold required for quick flow production (Buttle et al., 2019). Accordingly, increased annual and seasonal water yields draining harvested catchments were observed with some signs of recovery 15 years after harvesting (Buttle et al., 2018). Collectively, this work has described key impacts of forest harvesting on hydrologic response during the first 15 years post-harvest. However, few studies have been conducted to evaluate the longer term (> 20 years) legacy impacts of forest harvesting on hydrologic processes that control stream flow generation.

EMMA is a commonly used tool that attempts to explain observed stream water chemistry composition as a mixture of different source areas or "end members" assuming a linear mixing process (Ali et al., 2010; Christophersen et al., 1990; Christophersen & Hooper, 1992; James & Roulet, 2006). End members are pre-defined hydrologic source areas such as groundwater, soil water, precipitation, etc. that are hypothesized to contribute water to stream flow. The dimensionality of stream water chemistry data sets is removed using principal component analysis (PCA) and potential end members are projected into the mixing subspace defined by the stream water chemistry (Christophersen & Hooper, 1992; Hooper, 2001). End members are then evaluated for their ability to explain stream water chemistry in the mixing subspace and mass balance equations are used to calculate relative end member contributions to stream flow (Ali et al., 2010; Christophersen & Hooper, 1992). Diagnostic tools using eigenvector and residual analysis have been developed to estimate the number of end members required to explain the stream water chemistry without prior knowledge of the existing end members (Hooper, 2003).

EMMA has provided numerous insights regarding runoff generation processes and water quality. Most studies define end members differently making direct comparisons difficult (Inamdar, 2011). However, most studies have demonstrated that three end members are sufficient to explain stream water chemistry (Ali et al., 2010; Katsuyama et al., 2001) and that the prominent end member contributing to stream water can change depending on antecedent soil moisture conditions (Ali et al., 2010; Burns et al., 2001). For example, at the Panola Mountain Research Watershed in Georgia, USA, end member contributions to stream flow changed from outcrop runoff to riparian groundwater with increasing antecedent moisture conditions (Burns et al., 2001). Similarly, the number of end members contributing to stream flow increased from two to three under higher antecedent moisture conditions as the transient saturated groundwater end member was only contributing to stream flow under wet antecedent moisture conditions in the Kiryu experimental watershed, Japan (Katsuyama et al., 2001).

Additional insights into how changing end members contribute to water quality have also been assembled. For example, snowmelt was identified to drive episodic acidification within stream water by diluting base cations at the Hubbard Brook Experimental Forest in New Hampshire, USA (Wellington & Driscoll, 2004). This dilution effect shifted during Summer storms as the end member contributions from upper soil horizons became more prominent and supplied organic acids to the stream channel (Wellington & Driscoll, 2004). At the H.J. Andrews Experimental Forest in Oregon, USA, EMMA was used to identify lateral subsurface flow originating from the organic and upper soil horizons as the dominant end member contributing dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) to the stream network during the rising limb of the hydrograph (van Verseveld et al., 2008). These studies highlight the utility of EMMA for discerning end member contributions to stream water under different antecedent soil moisture conditions and the subsequent impacts on water quality. However, few studies have utilized EMMA to evaluate landscape disturbance impacts on runoff generation processes or inform the suitability of forest harvesting as a source water protection strategy.

This study presents the results from an intensive field sampling program that characterized water chemistry of multiple end members contributing to stream flow in a legacy clear-cut and forested control catchment on the Canadian Shield. Increased knowledge of these runoff generation processes is critical to explaining water quality responses to landscape disturbance. The specific objectives of this study were to: 1) assess the primary end member contributions to stream flow in a legacy clear-cut (> 20 years post-harvest) and unharvested (control) catchments using end member mixing analysis, and; 2) assess temporal variability in end member contributions to stream flow during snowmelt, Summer storm events and Fall.

3.3. Methods

3.3.1. Study Site and Experimental Design

The catchments used for the EMMA were C31 (clear-cut) and C32 (control). Full descriptions of these catchments and the harvesting experimental design can be seen in sections 1.3.2 and 1.3.3 in Chapter 1. One notable difference between the two catchments is the position of the wetland relative to the catchment outlet. In C31, the wetland is in the upper parts of the catchment near the stream initiation point, whereas in C32, the wetland is located immediately above the catchment outlet (Figure 3.1). Images of field sites can be seen in Figure B1.

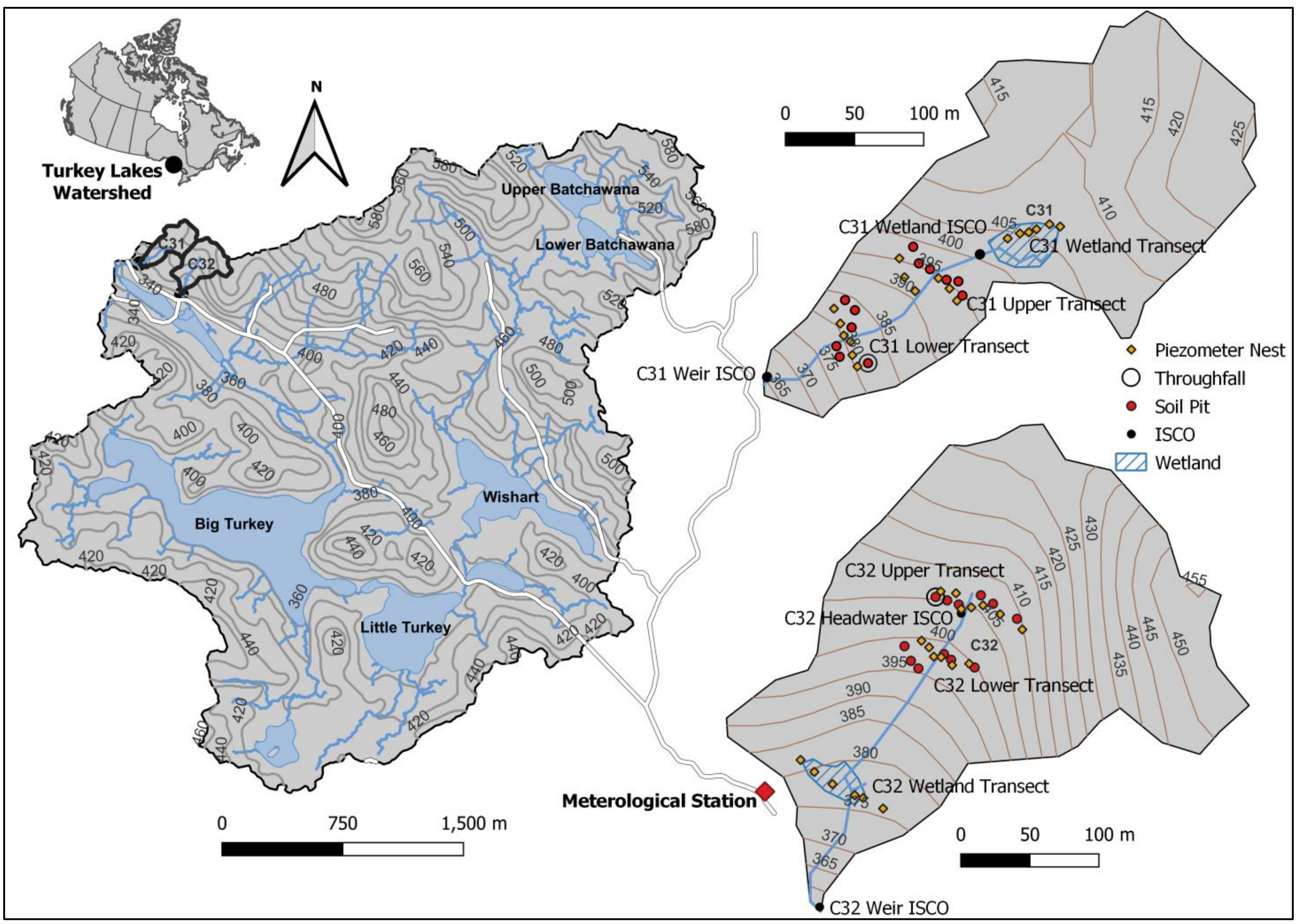

Figure 3.1 Maps of Turkey Lakes Watershed (left) and sub catchments C31 (clear-cut; top right) and C32 (control; bottom right). Locations of stream water sampling sights, groundwater piezometers, soil pits, throughfall collectors and wetlands are marked.

3.3.2. Field Methods

3.3.2.1. Flow and Stream Water Chemistry

C31 and C32 were instrumented with 90° v-notch weirs, stilling basins and Steven's Smart PT SDI-12™ pressure and temperature transducers to measure continuous stream flow at the basin outlet every 10 minutes. Stage discharge rating curves were used to calculate instantaneous discharge. In addition, level loggers were placed in the upper parts of the stream channel near the stream initiation point. In C31, the stream originated from a small wetland referred to as C31 wetland and, in C32, the stream starts at the bottom of a hillslope referred to as the C32 initiation point. At these sampling locations, only stream stage was recorded as creating a stage discharge rating curve was not possible due to the stream channel size and logistical constraints. Stream water samples were collected at all four locations using ISCO 6700 automated water samplers and stored in acid-washed triple rinsed 1L polypropylene sampling bottles. ISCO samplers were programmed to collect daily composite (4 times a day) water samples during the snowmelt and Fall sampling periods. Additionally, the rising and falling limbs of select Summer storms were sampled with ISCO samplers programmed to collect a sample every 0.5 to 2 hours depending on the predicted size and length of the storm. A total of five storms were sampled during the Summer. Finally, water samples were collected by hand with 500 mL HDPE sampling bottles at all sampling locations to characterize baseflow conditions. All sampling bottles were acid washed and triple rinsed before being used in the field.

3.3.2.2. Groundwater

The ablation and basal till groundwater end member chemistry was characterized by collecting water samples from piezometer nests (Monteith et al., 2006b, 2006a). Piezometer nests consisted of two drive-point piezometers (Solinst Canada Ltd, Ontario, Canada) with 10 or 25 cm screens and an inside diameter (i.d.) of 2 or 4 cm that were driven into the ablation or basal till (Monteith et al., 2006a). Each catchment was instrumented with a total of 12 piezometer nests in two transects located in the upper and lower parts of the catchments. Each transect ran perpendicular to the stream channel with three piezometer nests located on each side of the channel. Average depths of the piezometers were 0.45 ± 0.05 m and 0.40 ± 0.03 m in the ablation till and 1.09 ± 0.19 m and 0.93 ± 0.09 m in the basal till in C31 and C32, respectively (Monteith et al., 2006a). In addition, wetland groundwater was characterized by a single transect of 4 cm i.d. piezometers installed to an average depth of 0.39 ± 0.03 m and 0.37 ± 0.03 m into the wetlands of C31 and C32, respectively. Groundwater samples collected using a peristaltic pump were obtained weekly during the snowmelt and Fall sampling periods and during each storm event. Groundwater samples were also collected once per month during the Summer to characterize stream water chemistry during Summer baseflow. Piezometers were purged for five minutes or until dry and then sampled the next day to allow the basal till piezometers sufficient time to recharge (Monteith et al., 2006b).

3.3.2.3. Soil Water

Soil pits with two zero tension lysimeters were installed to collect unsaturated soil water flowing through the soil profile next to each piezometer nest (excluding wetlands). Soil pits were dug by hand to an average depth of 0.65 ± 0.10 m and 0.64 ± 0.10 m in C31 and C32, respectively. Lysimeters were installed directly below the LFH layer and 20 cm below the LFH mineral soil interface. Lysimeter construction consisted of PVC pipe (15.23 cm i.d.), PVC sheeting and a plastic screen mesh over the top to create a contact point between the lysimeter and soil/LFH layer. Additionally, the mineral soil lysimeters had glass wool and a mixture of soil and deionized water was placed on top of the plastic screen mesh to strengthen the contact between the lysimeter and the soil matrix. Water drained from the lysimeters into acid washed triple rinsed 1 L HDPE plastic sampling bottles. Sample bottles were placed in a plastic tote within each soil pit to protect them from the elements. All lysimeters were installed in the Fall of 2020 to allow six months to equilibrate with the soil profile before sample collection in the spring of 2021. Two of the soil pits were completely saturated preventing the installation of the lysimeters. As these soil pits were in small depressions, a drive point piezometer was installed to a depth of 20 cm approximately one meter in front of the soil pit to sample water flowing through the upper parts of the soil profile. Soil water samples were collected once a week during the snowmelt and Fall sampling period and after each storm event. Fresh sampling bottles were placed in the soil pits before each storm to ensure any sample collected was representative of each storm. Lysimeter samples were also collected once a month in the Summer corresponding with the groundwater sampling described above.

3.3.2.4. Throughfall

A throughfall collector was installed in each catchment to characterize precipitation chemistry. These collectors were constructed from plastic funnels with a mesh zip tied over the top to prevent clogging from leaf litter. The funnel was placed on a steel post next to a soil pit with a sample line running from the funnel to a 1L HDPE sampling bottle within the tote containing the lysimeter sample bottles. Throughfall water samples were collected under the same sampling schedule as the lysimeters described above.

3.3.3. Laboratory Methods

All water samples were analyzed at the accredited Water Chemistry Laboratory in the Great Lakes Forestry Centre of the Canadian Forest Service in Sault Ste. Marie, Ontario, Canada. Water samples were analyzed for SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, Na^-, Al^{3+}, Ba^{2+}, Sr^{2+} and DOC using standardized procedures and quality control methods (Webster, et al., 2021b). Water chemistry tracers were selected based on tracers used in previous EMMA studies (Ali et al., 2010; Burns et al., 2001; Hooper, 2001; Wellington & Driscoll, 2004). Due to the COVID-19 pandemic there were several closures of the water chemistry laboratory, sample freezing and storage for up to four months before processing and analysis could be completed. Images of laboratory equipment can be seen in Figure B3.

3.3.4. End Member Mixing Analysis Model

End members used in the EMMA were selected based on physical characteristics of the catchments, existing monitoring equipment and a prior understanding of the hydrological processes within TLW (Creed et al., 2003; Leach et al., 2020; Monteith et al., 2006a, 2006b; Semkin et al., 2002). Specific end members selected included basal till groundwater, ablation till groundwater, wetland groundwater, mineral soil percolate, LFH percolate and throughfall. Stream and end member sampling occurred during four different flow conditions defined as snowmelt, Summer, Summer storms and Fall.

3.3.4.1. Tracer Selection

Assumptions required for EMMA include: (i) tracer concentrations within end members need to be constant in time; and (ii) tracers must be sufficiently different between end members, and; (iii) tracers need to exhibit conservative behavior (Ali et al., 2010; Christophersen et al., 1990; Christophersen & Hooper, 1992; Hooper, 2001). For the first assumption, end member tracers were grouped by season to remove any seasonal effects. The second assumption was tested using the Kruskal-Wallis H-test and tracer variability ratio (TVR). The Kruskal-Wallis H-test confirms for each tracer that at least one end member is significantly different ($p \leq 0.05$) from another (Ali et al., 2010). The TVR ratio, typically used in sediment source fingerprinting studies, was used to determine if the difference in tracer concentrations between two end members was larger than the variation within either end member (Pulley & Collins, 2018). TVR was calculated using Eq. 1 for each tracer and each end member group pairing:

$$TVR = \frac{\frac{\tilde{X}_{max} - \tilde{X}_{min}}{\tilde{X}_{min}} * 100}{mean(CV_{End\ Member\ 1},\ CV_{End\ Member\ 2})} \tag{3.1}$$

where $\tilde{X}_{max}$ and $\tilde{X}_{min}$ are the maximum and minimum median tracer concentrations of the two potential end members, and CV is the coefficient of variation of either end member (Pulley et al., 2015; Pulley & Collins, 2018; Spencer et al., 2021). A TVR ratio ≥ 2 was required for the tracer to be included in the EMMA as recommended by (Pulley & Collins, 2018; Spencer et al., 2021). The third assumption was evaluated using bivariate plots that are commonly used to assess conservative mixing in EMMA studies (Ali et al., 2010; Hooper, 2003; James & Roulet, 2006; Spencer et al., 2021). Linear relationships between tracers suggest conservative behaviour as non linearity may be evidence of chemical reactions occuring between solutes (Christophersen & Hooper, 1992). A Pearson's r correlation coefficient ≥ 0.5 ($p < 0.01$) was used as the cutoff to represent a linear relationship between two tracers (Ali et al., 2010) and a tracer that had a linear relationship with at least one other tracer was deemed acceptable. All tracers that passed the critical assumptions unperdinning EMMA were considered appropriate.

3.3.4.2. End Member Mixing Analysis Model

Once tracer selection was complete, the mixing sub-space (or U space) was created for each sampling location under the different flow conditions to create a 2-dimensional (2D) mixing sub-space (Christophersen & Hooper, 1992). Two dimensions were selected for ease of visualization (Spencer et al., 2021). Stream water chemistry (*n* samples x *p* tracers) was standardized and centered (subtracted by the mean and divided by the standard deviation) to create equal weighting between tracers. PCA was conducted on the correlation matrix of the standardized and centered data using the prcomp function in R (R Core Team, 2021). PCA analysis was completed on all tracers and every combination of four up to *p* tracers was computed and the PCA model that explained the most variation in two dimensions was retained (Burns et al., 2001; Wellington & Driscoll, 2004). Median ± median absolute deviation (MAD) end member tracer concentrations were then standardized and centered around the stream water chemistry and projected into the mixing subspace defined by the stream water chemistry. If all end members are characterized correctly and conservative mixing does occur, then end members are bound within the stream water chemistry.

The diagnostic tool described by Hooper, (2003) was used to confirm that a two-dimensional mixing subspace was appropriate. Residual analysis between the original stream water chemistry and the orthogonal projections for each solute was completed with a random pattern between the residuals and the original stream water chemistry describing a good mixing subspace. If a random pattern was not observed then additional eigenvectors (dimensions) were retained until a random pattern was observed (Ali et al., 2010; Hooper, 2003; Liu et al., 2008). Additionally, the fit between the orthogonal projections and observed stream water chemistry was evaluated using the relative root-mean-square error (RRMSE) for each solute and dimension:

$$RRMSE = \frac{\sqrt{\sum_{i=1}^{n}\left(\hat{X}_{ip} - X_{ip}\right)^2}}{n\,\bar{X}_p} \tag{3.2}$$

where n represents the number of stream water samples, $\bar{X}_p$ represents the median concentration of solute p, $\hat{X}_{ip}$ is the orthogonal projection from the mixing space and X_{ip} is the observed concentration of solute p in sample i. Tracers with a RRMSE < 15% were deemed appropriate for EMMA (James & Roulet, 2006).

3.4. Results

3.4.1. Hydrometeorological Characterization

Stream flow sampling during snowmelt occurred from 2021-03-25 to 2021-05-09 and captured the latter half of snowmelt which typically starts at the beginning of March in these study catchments (Webster et al., 2021a). Total precipitation during this period was 117.5 mm and runoff in the clear-cut and control catchment was 140.1 mm and 151.6 mm, respectively. Maximum daily runoff for the clear-cut and control catchment was 16.6 mm day^{-1} and 16.6 mm day^{-1}, respectively (Table 3.1). Fall sampling occurred from 2021-10-09 to 2021-10-30 with a total precipitation of 97.9 mm, and total stream flow of 18.5 mm and 27.4 mm in the clear-cut and control catchment, respectively. Peak daily streamflow was 5.1 mm day^{-1} in the clear-cut and 2.7 mm day^{-1} in the control catchment (Table 3.1). The number of zero flow days observed during the field sampling period at the four sampling locations was highest in the C32 initiation point with 124 zero flow days (Table 3.2). The clear-cut and clear-cut wetland experienced 48 and 65 zero flow days, respectively, while the control catchment had no zero flow days (Table 3.2).

Table 3.1 Precipitation and streamflow statistics for the clear-cut and control catchment during the snowmelt and Fall sampling periods.

Parameter	Snowmelt	Fall
Precipitation Volume (mm)	117.5	97.9
2 Day Antecedent Precipitation (mm)	23	10.3
7 Day Antecedent Precipitation (mm)	24.3	25.6
14 Day Antecedent Precipitation (mm)	53.5	39.5
Peak Daily Precipitation (mm day^{-1})	17.8	27.5
Total Stream Flow (mm)	C31: 140.1, C32: 151.6	C31: 18.5, C32: 27.4
Peak Daily Runoff (mm day^{-1})	C31: 16.6, C32: 16.6	C31: 5.1, C32: 2.7
Stream Yield (%)	C31: 119.2, C32: 130.3	C31: 18.9, C32: 28

Table 3.2 Number of zero flow days observed at the four sampling locations during the sampling period from 2021-03-25 to 2021-10-30.

Location	Number of Zero Flow Days*
Clear Cut	48
Control	0
Clear Cut Wetland	65
Control Headwater	124

*Spans the field sampling period of this study from 2021-03-25 to 2021-10-30

Two Summer storms (storm 1 and storm 4) selected for end member mixing analysis occurred from 2021-05-24 to 2021-05-26 and 2021-06-24 to 2021-06-26 for storm 1 and storm 4, respectively. Total precipitation of storm 1 was 25.4 mm, and total stream flow for the clear-cut and control was 2.1 mm and 1.7 mm, respectively. Peak instantaneous stream flow was 0.3 L s^{-1} ha^{-1} and 0.3 L s^{-1} ha^{-1} in the clear-cut and control catchment, respectively (Table 3.3). Total precipitation for storm 4 was 14.1 mm, while total stream flow was 2.8 mm for the clear-cut and 1.9 mm for the control. Peak instantaneous stream flow was 0.7 L s^{-1} ha^{-1} and 0.2 L s^{-1} ha^{-1} for the clear-cut and control catchments, respectively (Table 3.3). Antecedent 2-, 7- and 14-day precipitation metrics shown were 25.7 mm, 26.0 mm, and 41.8 mm for storm 1 and 14.1 mm, 22.2 mm, and 43.9 mm for storm 4 (Table 3.3).

Table 3.3 Precipitation and streamflow metrics for the clear-cut and control catchment during the two Summer storms.

Parameter	Storm 1	Storm 4
Precipitation Volume (mm)	25.4	14.1
2 Day Antecedent Precipitation (mm)	25.7	14.1
7 Day Antecedent Precipitation (mm)	26	22.2
14 Day Antecedent Precipitation (mm)	41.8	43.9
Peak Instantaneous Precipitation Rate (mm 10 $minutes^{-1}$)	3.4	2.4
Total Stream Flow (mm)	C31: 2.1, C32: 1.7	C31: 2.8, C32: 1.9
Peak Instantaneous Runoff Rate (L $s^{-1}ha^{-1}$)	C31: 0.6, C32: 0.3	C31: 0.7, C32: 0.2
Stream Yield (%)	C31: 8.2, C32: 6.7	C31: 19.5, C32: 13.6

3.4.2. Tracer Selection

The number of samples needed for each end member during the four flow conditions was evaluated to ensure sufficient data were available for end member characterization. Few observations were available for the ablation and basal till end members during the Summer storm sampling periods (Table 3.4) because the groundwater table was often below the ablation and basal till piezometers. Accordingly, the Summer and Summer storm data were combined to create the end members for this period. It was hypothesized that there would be no difference in tracer concentration between these two sampling periods as they both occurred during the dry Summer months. It should be noted that even after combining the data, only 1 data point was available for either the ablation or basal till in the control catchment. One data point is not sufficient to characterize these end members, but they were still included in EMMA as the variation around the groundwater end members is small (Figure 3.2). To be consistent with the changes made for the ablation and basal till end members, all end member data for the Summer and Summer storms sampling periods were combined. Significant differences (Kruskal-Wallis H-test $p \leq 0.05$) were found between all end members for all tracers in both the clear-cut and control catchments (Figure 3.2). TVR ratios (data not shown) were > 2 for all end member comparisons for all tracers for both clear-cut and control catchments. A bivariate plot of stream water chemistry in the clear-cut during snowmelt is shown in Figure 3.3 and highlights that each tracer behaves conservatively as each has a Pearson's r correlation coefficient ≥ 0.5 (Ali et al., 2010). All bivariate plots can be seen in Figure B3 – B14. A summary of the tracer selection processes is shown in Table 3.5.

Table 3.4 Number of observations available for each end member under the different flow conditions in the clear-cut and control catchment.

		Number of Observations			
Catchment	End Member	Snowmelt	Summer Storms	Summer	Fall
C31	Throughfall	3	4	6	3
	LFH Percolate	10	17	35	15
	Wetland Groundwater	34	14	16	13
	Mineral Soil	17	10	11	9
	Ablation Till	15	3	2	3
	Basal Till	12	4	4	4
C32	Throughfall	3	3	6	2
	LFH Percolate	2	6	19	7
	Wetland Groundwater	0	3	8	5
	Mineral Soil	4	3	8	5
	Ablation Till	33	0	1	3
	Basal Till	24	0	1	4

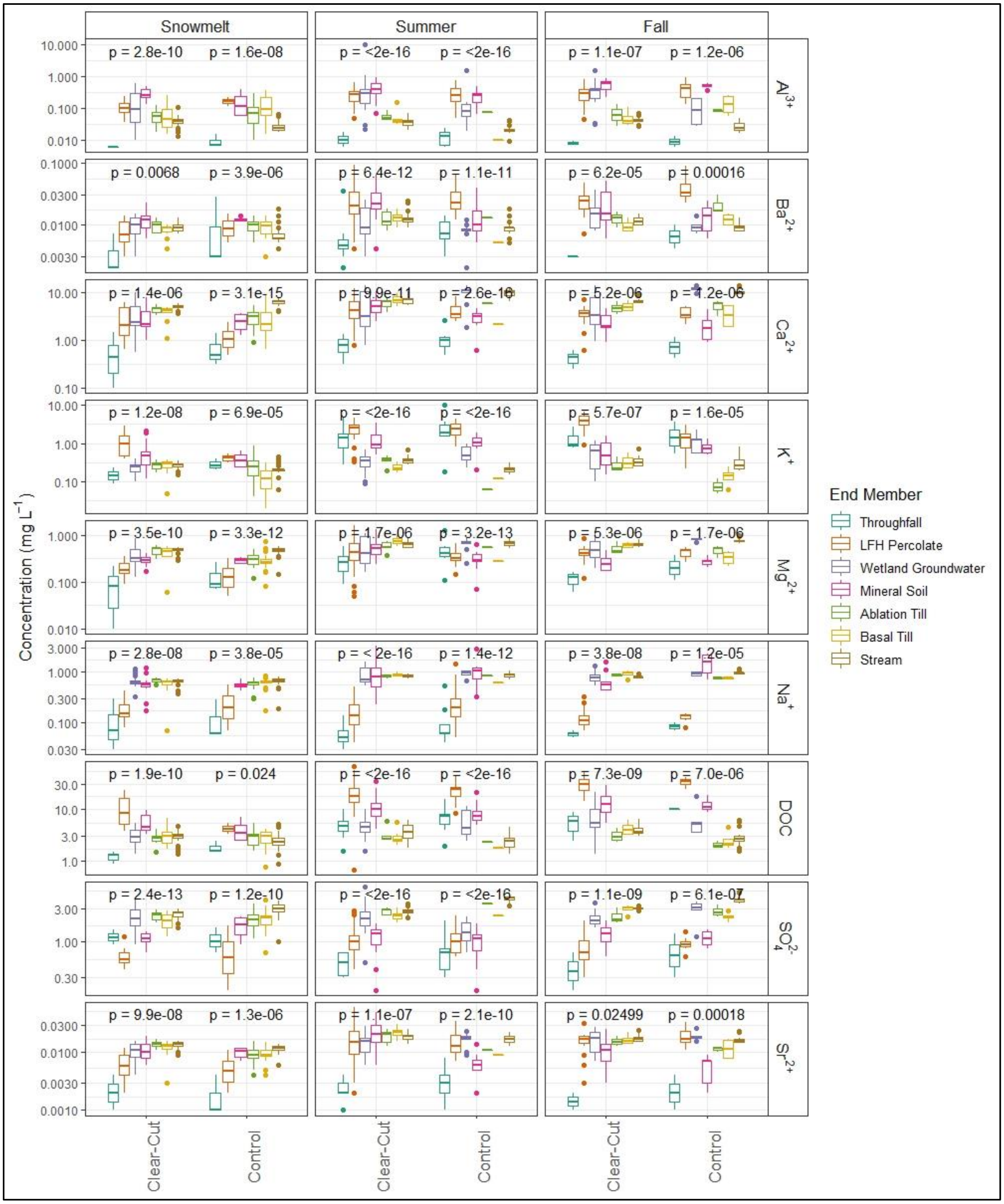

Figure 3.2 Boxplots of tracer concentrations for each end member and stream chemistry in the clear-cut (C31) and control (C32) catchments during the snowmelt, Summer and Fall sampling periods. Results from the Kruskal Wallis H-test are shown above.

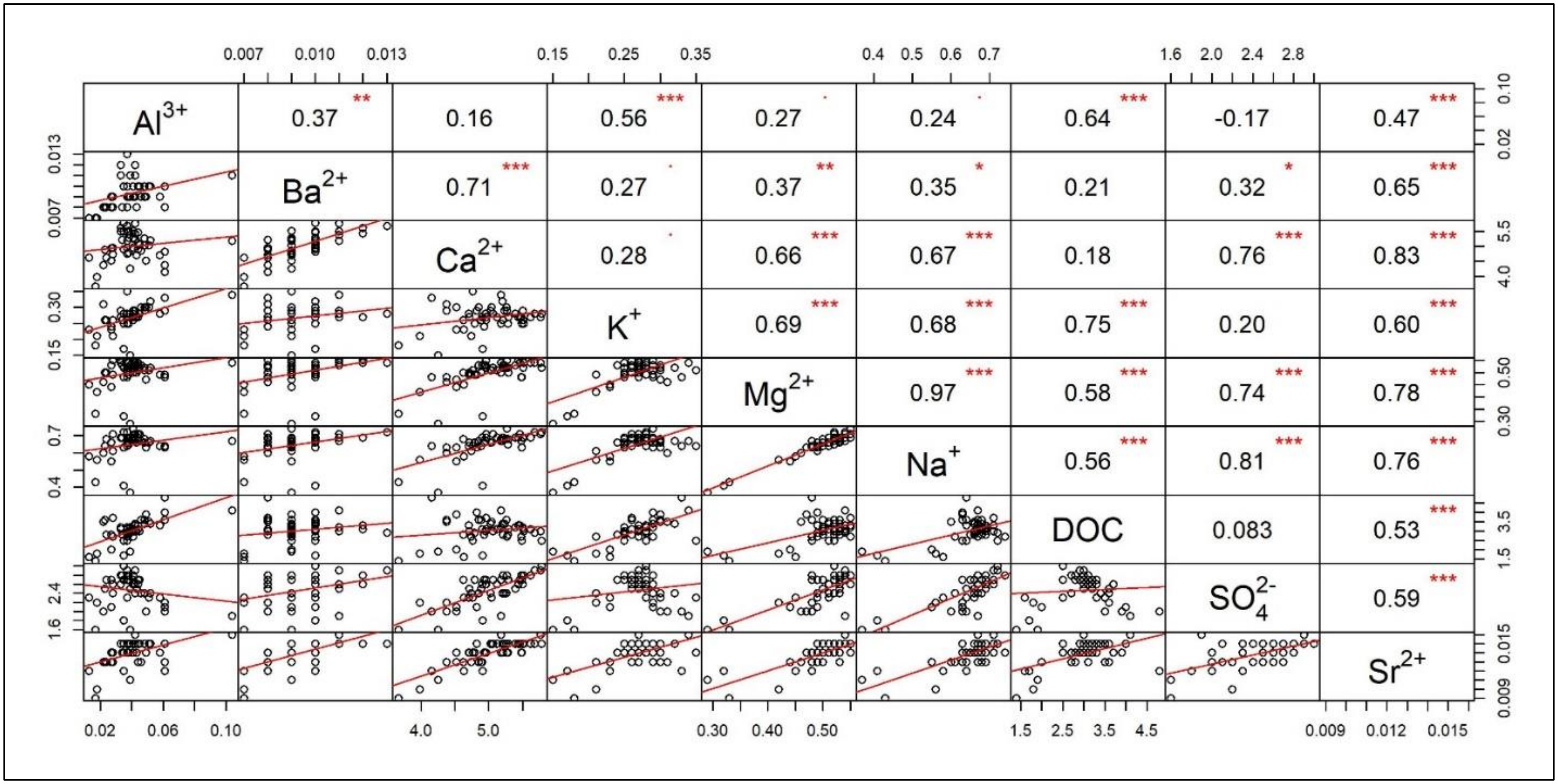

Figure 3.3 Example bivariate plot from the clear-cut catchment (C31) during snowmelt. Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

Table 3.5 Summary of tracers that passed the tracer selection criteria and those chosen for the final EMMA model in the clear-cut, control, and clear-cut wetland sampling locations for snowmelt, the two Summer storms, and the Fall sampling period.

Location	**Flow Condition**	**Tracer Selection**	**Al^{3+}**	**Ba^{2+}**	**Ca^{2+}**	**K^{+}**	**Mg^{2+}**	**Na^{+}**	**DOC**	**SO_4^{2-}**	**Sr^{2+}**
Clear-Cut	Snowmelt	Passed Tracer Selection	✓	✓	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✗	✗	✗	✓	✓	✓	✗	✓	✗
	Storm 1	Passed Tracer Selection	✓	✗	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✓	✗	✓	✗	✓	✗	✓	✓	✗
	Storm 4	Passed Tracer Selection	✓	✓	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✓	✗	✗	✗	✓	✗	✓	✓	✓
	Fall	Passed Tracer Selection	✓	✓	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✓	✗	✓	✗	✓	✗	✗	✓	✓
Control	Snowmelt	Passed Tracer Selection	✓	✗	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✓	✗	✗	✗	✓	✓	✗	✓	✗
	Storm 1	Passed Tracer Selection	✓	✓	✓	✓	✓	✓	✗	✓	✗
		Used in EMMA Model	✗	✗	✓	✓	✓	✓	✗	✗	✗
	Storm 4	Passed Tracer Selection	✓	✓	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✗	✗	✓	✗	✓	✓	✗	✓	✗
	Fall	Passed Tracer Selection	✓	✓	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✗	✗	✓	✓	✓	✓	✗	✗	✗
Clear-Cut Wetland	Snowmelt	Passed Tracer Selection	✓	✓	✓	✗	✓	✓	✓	✓	✓
		Used in EMMA Model	✗	✗	✓	✗	✓	✗	✓	✗	✓
	Storm 1	Passed Tracer Selection	✓	✓	✓	✗	✓	✓	✓	✓	✓
		Used in EMMA Model	✗	✗	✓	✗	✓	✓	✓	✓	✗
	Storm 4	Passed Tracer Selection	✓	✗	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✓	✗	✓	✗	✓	✓	✓	✗	✗
	Fall	Passed Tracer Selection	✓	✓	✓	✓	✓	✓	✓	✓	✓
		Used in EMMA Model	✗	✗	✓	✗	✓	✓	✗	✓	✗

3.4.3. End Member and Stream Characterization

Solute concentrations ordered by throughfall, LFH percolate, wetland groundwater, mineral soil percolate, ablation till, basal till and stream water (Figure 3.2) indicate that concentrations either increased or decreased sequentially from throughfall to the basal till groundwater end members. Generally, concentrations of Ca^{2+}, Mg^{2+}, Na^{-}, SO_4^{2-} and Sr^{2+} were highest in the ablation and basal till groundwater end members and lowest in the throughfall and LFH percolate end members (Figure 3.2). Conversely, Al^{3+}, K^{+} and DOC were elevated in the throughfall and LFH end members and lower in the ablation and basal till groundwater end members (Figure 3.2). One exception to the above patterns was Ba^{2+} which showed the largest concentrations in the wetland groundwater and mineral soil percolate end members and the lowest concentrations in the throughfall end member (Figure 3.2). There were few differences in these patterns between either the clear-cut and control catchments or the snowmelt, Summer and Fall flow conditions.

Tracer concentrations that were highest in the groundwater end members (Ca^{2+}, Mg^{2+}, Na^{-}, SO_4^{2-} and Sr^{2+}) increased in concentration throughout snowmelt in both the control and clear-cut catchments (Figure 3.4) while showing episodic decreases with increasing flow rates. During the Fall wet-up, stream concentrations of Ca^{2+}, Mg^{2+}, Na^{-}, SO_4^{2-} and Sr^{2+} decreased as flow increased and then showed no change as flow stabilized. During the Summer storms Ca^{2+}, Mg^{2+}, Na^{-}, SO_4^{2-} and Sr^{2+} were inversely related with increasing stream flow (Figure 3.5). The opposite pattern was observed for Al^{3+}, K^{+} and DOC which were highest in the throughfall and LFH end members and increased with increasing flow during snowmelt, Fall and Summer storms (Figures 3.4 and 3.5). No pattern was observed for Ba^{2+} in stream water for any sampling period (Figures 3.4 and 3.5).

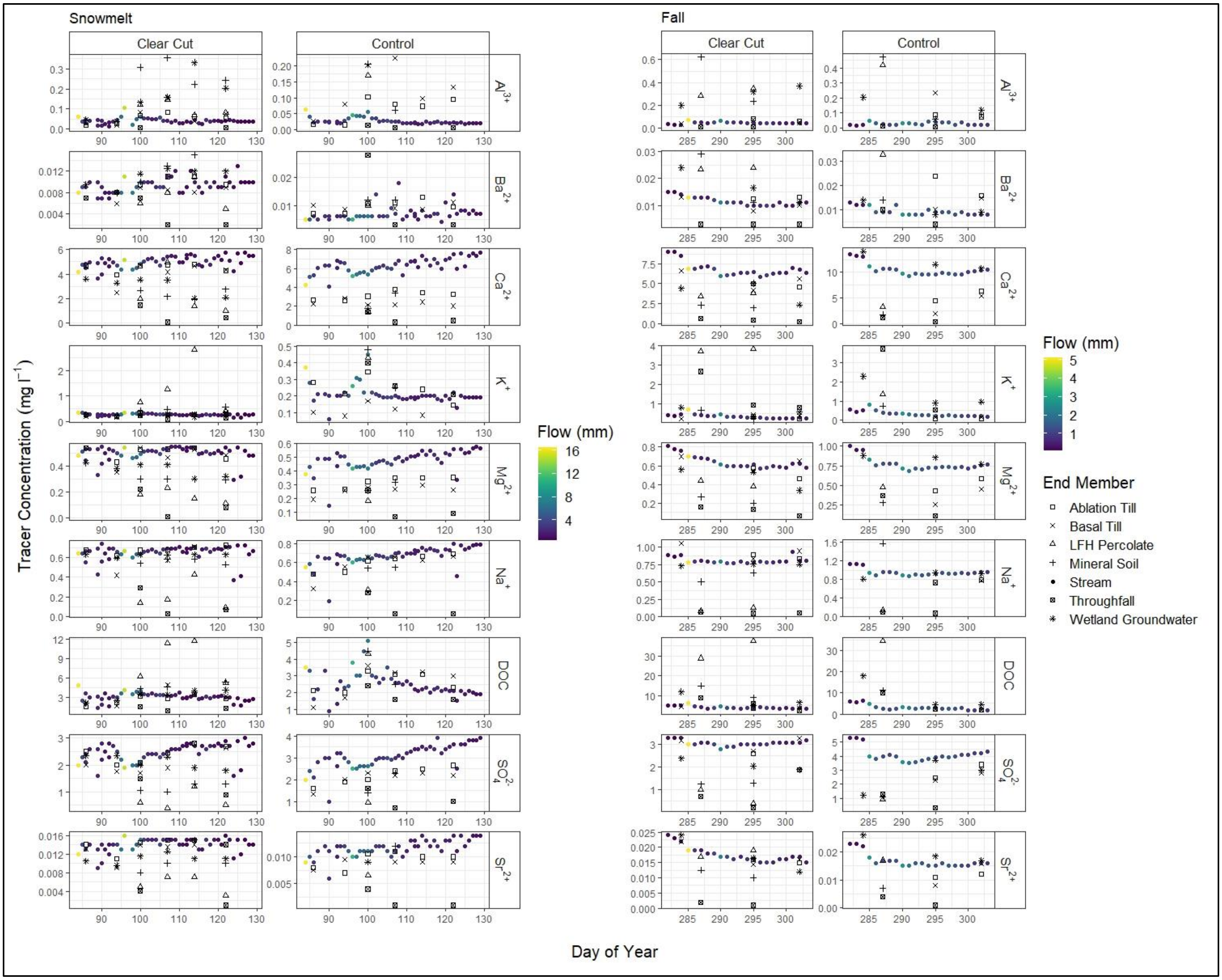

Figure 3.4 Time series of median end member and stream water tracer concentrations (mg L^{-1}) on the day of sampling for the Snowmelt and Fall sampling periods. Colour represents daily stream runoff (mm) and symbols represent the different end members.

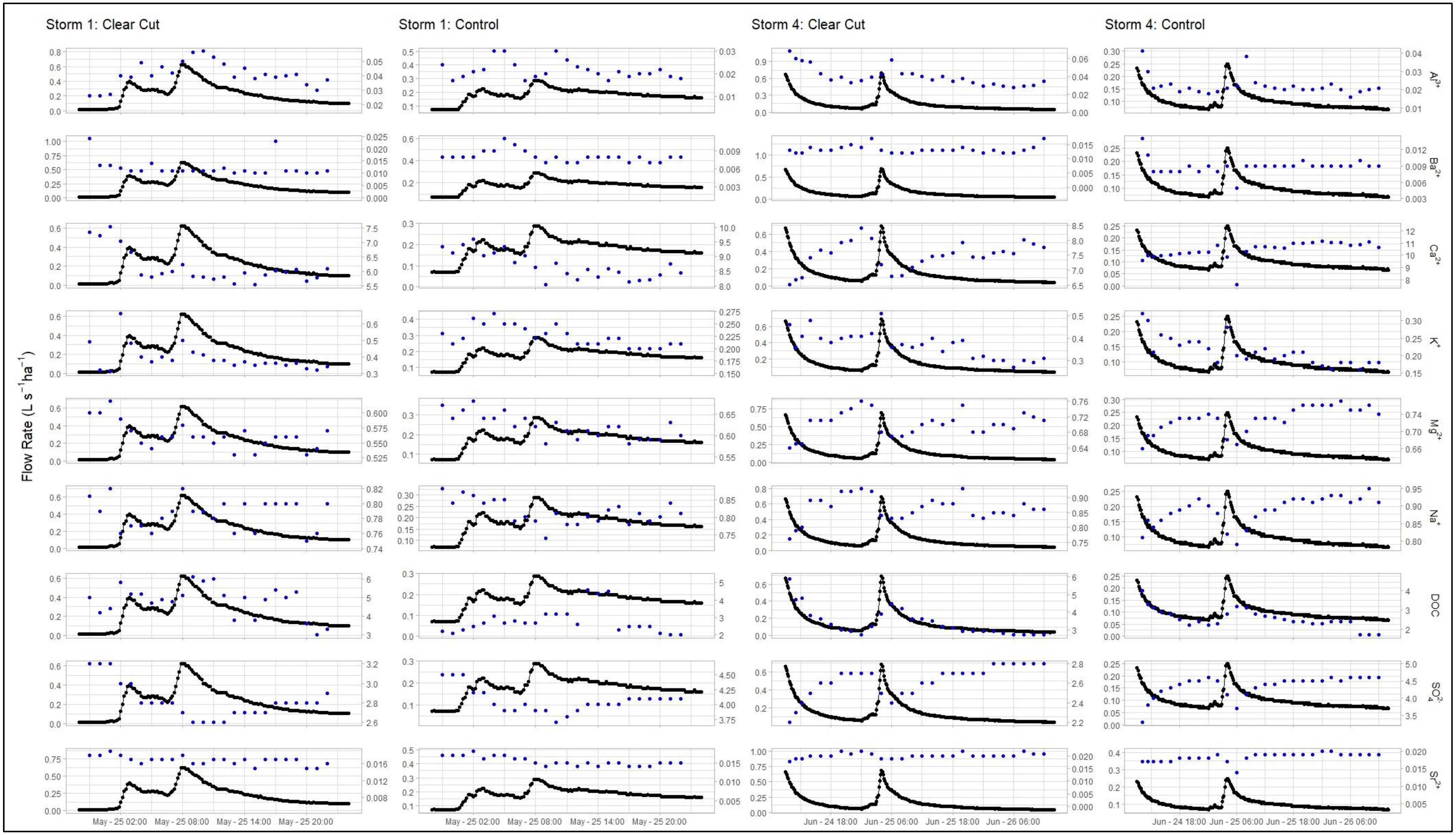

Figure 3.5 Hydrograph (black line) and tracer (blue dots) response of stream water during the two Summer storms. Stream runoff is in L s^{-1} ha^{-1} and tracer concentrations are in mg L^{-1}.

3.4.4. EMMA Results

Stream water chemistry was not bounded by end members in the data set (mixing subspace) and therefore hydrograph separation was not possible. However, prominent end members contributing to the stream water mixture were identified based on their proximity to stream water values as described by Spencer et al. (2021).

3.4.4.1. Snowmelt

During snowmelt, two principal components (PCs) explained 97.4%, 98.2% and 95.5% of the variance for the clear-cut, control, and clear-cut wetland, respectively (Figure 3.6). The ablation and basal till groundwater end members were most like stream water chemistry for all three sampling locations, with the wetland end member being the next closest for the clear-cut and clear-cut wetland. No wetland groundwater data were available in the control catchment during snowmelt. Throughfall and LFH percolate end members were most dissimilar from the stream water for all three end members. Higher flow rates in the clear-cut and control catchments trended towards the LFH percolate and mineral soil percolate end members. No obvious pattern was observed for increasing stream stage in the clear-cut wetland and loadings trended away from the end members. Exceptions include K^+ in the clear-cut and control trending towards the mineral soil and LFH percolate end members and DOC in the clear-cut wetland trending towards wetland groundwater, mineral soil and LFH percolate in PC2.

3.4.4.2. Summer Storms

In the clear-cut, control, and clear-cut wetland, two PCs explained 97.8%, 96.6% and 97.3% of the variance during storm 1 (Figure 3.7). Stream water values were closest to the ablation and basal till end members in the clear-cut, control, and clear-cut wetland. Additionally, the wetland groundwater and mineral soil water percolate were close to the stream water values in the control and mineral soil percolate in the clear-cut wetland. Increasing stream flow trended towards the wetland groundwater, throughfall, mineral soil, and LFH percolate in the clear-cut and clear-cut wetland. No pattern was discerned visually for increasing stream flow in the control catchment. In the clear-cut catchment, Al^{3+} trended towards the wetland groundwater, mineral soil and LFH percolate end member while Mg^{2+} and Ca^{2+} trended towards the ablation and basal till end members. In the control catchment, Mg^{2+} and Ca^{2+} trended towards the wetland groundwater end member, while K^{+} trended towards the throughfall, mineral soil, and LFH percolate end members. For the clear-cut wetland, SO_4^{2-} trended towards the ablation till end member while Mg^{2+} and Ca^{2+} trended towards the basal till end member.

For storm 4, two PCs explained 98.3%, 97.3% and 98.2% of the variance in the clear-cut, control, and clear-cut wetland, respectively (Figure 3.7). Stream water chemistry was closest to the ablation and basal till end members in the clear-cut and clear-cut wetland, while wetland groundwater and ablation till end members were closest in the control. Increasing stream flow trended towards the mineral soil and LFH percolate in the clear-cut and towards all end members in the control. No pattern was discerned visually with increasing stream flow in the clear-cut wetland. DOC trended towards the mineral soil and LFH percolate in the clear-cut, while all loadings trended away from end members in the control. DOC and Al^{3+} trended towards the wetland groundwater and LFH percolate in the clear-cut wetland.

3.4.4.3. Fall

Two PCs explained 99.1%, 99.4% and 99.2% of the variance in the clear-cut, control, and clear-cut wetland, respectively (Figure 3.6). The ablation and basal till groundwater end members were closest to the stream water values at the clear-cut weir and clear-cut wetland while the mineral soil percolate end member was closest to the stream water values in the control catchment. Higher flow rates trended towards the LFH percolate and wetland groundwater in the clear-cut and control catchments, respectively. Most loadings trended away from the end members. Exceptions include K^{+} moving towards wetland groundwater in the control, and SO_4^{2-} towards all end members in PC1 for the clear-cut wetland.

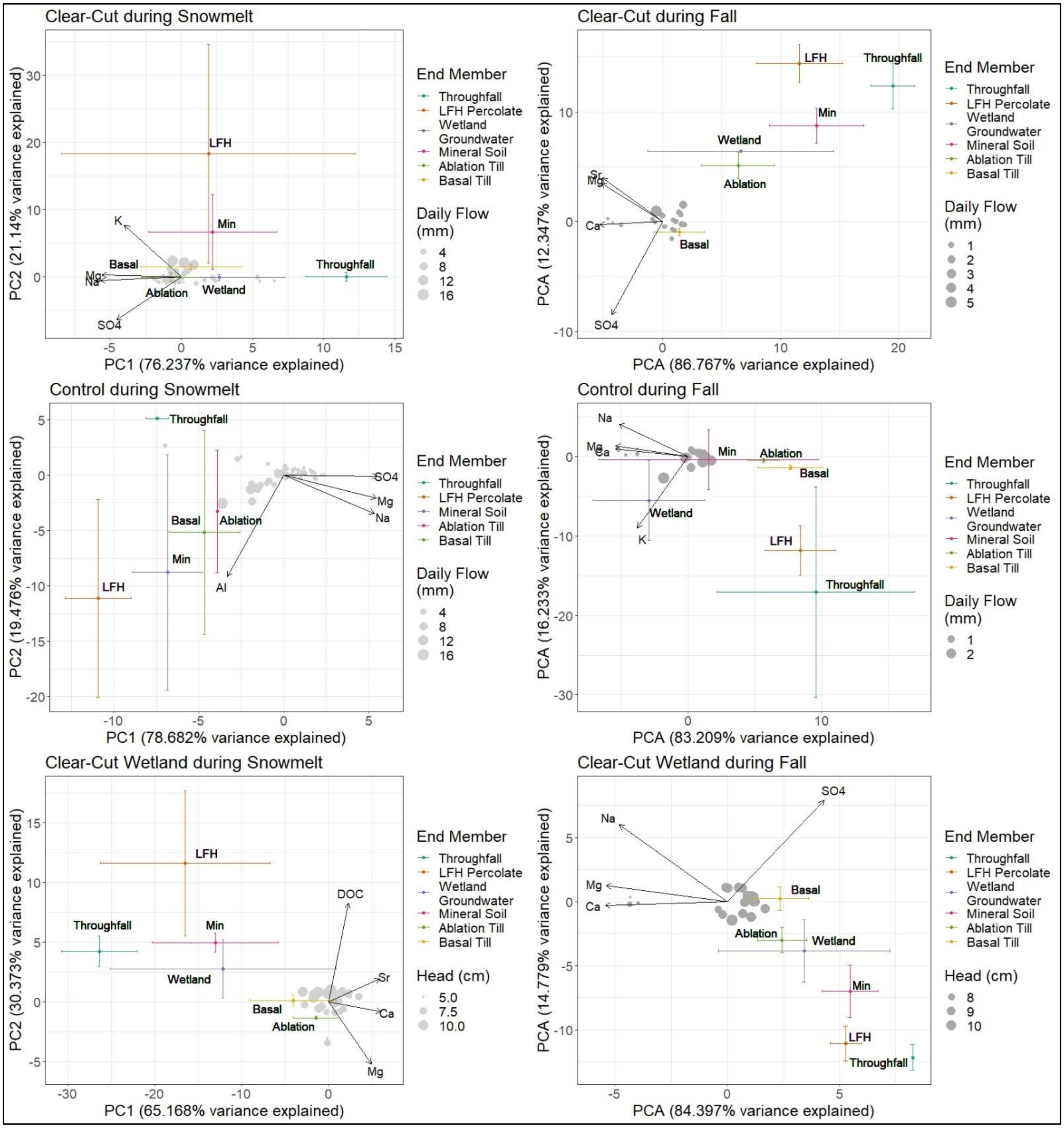

Figure 3.6 EMMA models for the clear-cut, control and clear-cut wetland sampling locations during the Snowmelt and Fall sampling periods using the first two principal components that explain stream water chemistry. Grey circles show stream water points with circle size denoting either stream flow (mm) for the clear-cut and control catchment or head (cm) for the clear-cut wetland. Coloured points and error bars denote the median ± MAD end member tracer concentrations that were projected into the mixing subspace defined by the stream water chemistry. Arrows denote the loadings from the principal component analysis (PCA) for each tracer used in the EMMA model.

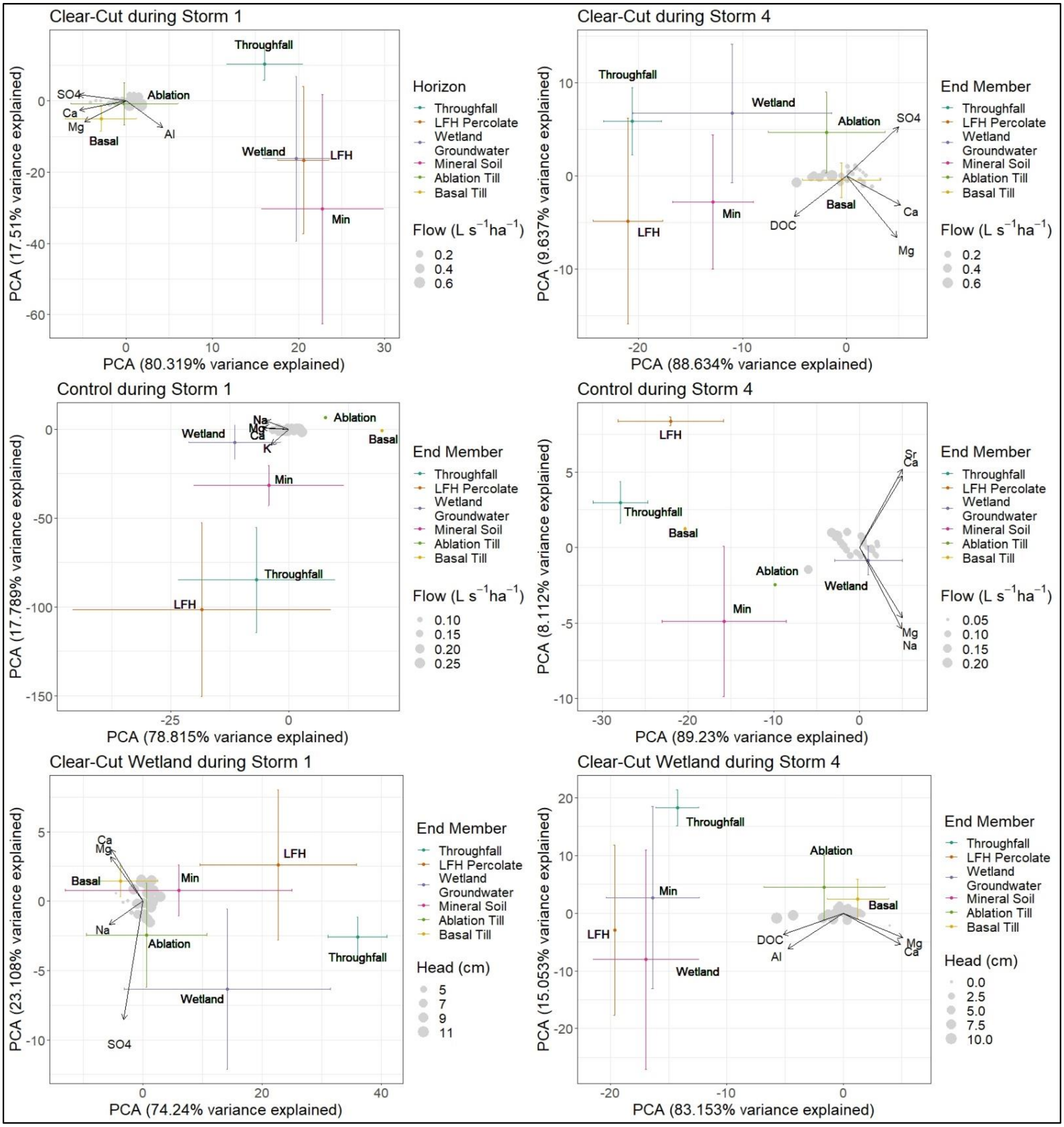

Figure 3.7 EMMA models for the clear-cut, control, and clear-cut wetland sampling locations during storm 1 and storm 4 using the first two principal components that explain the most variation in stream water chemistry. Grey circles show stream water points with circle size denoting either stream flow (L s^{-1} ha^{-1}) for the clear-cut and control catchment or head (cm) for the clear-cut wetland. Coloured points and error bars denote the median ± MAD end member tracer concentrations that were projected into the mixing subspace defined by the stream water chemistry. Arrows denote the loadings from the principal component analysis (PCA) for each tracer used in the EMMA model.

3.4.4.4. Residual Analysis

Residuals analysis (RRMSE <15%) confirmed that a two-dimensional mixing space was sufficient to explain the stream water chemistry for most sample locations for a range of flow conditions (Figure 3.8). Exceptions included the clear-cut wetland during storm 4 as DOC was above the 15% cut off in the EMMA model (Figure 3.8). If stream water chemistry was properly bound by the end members, then a 3-dimensional mixing space (4 end members) would be required to explain the stream water chemistry in clear-cut wetland during storm 4.

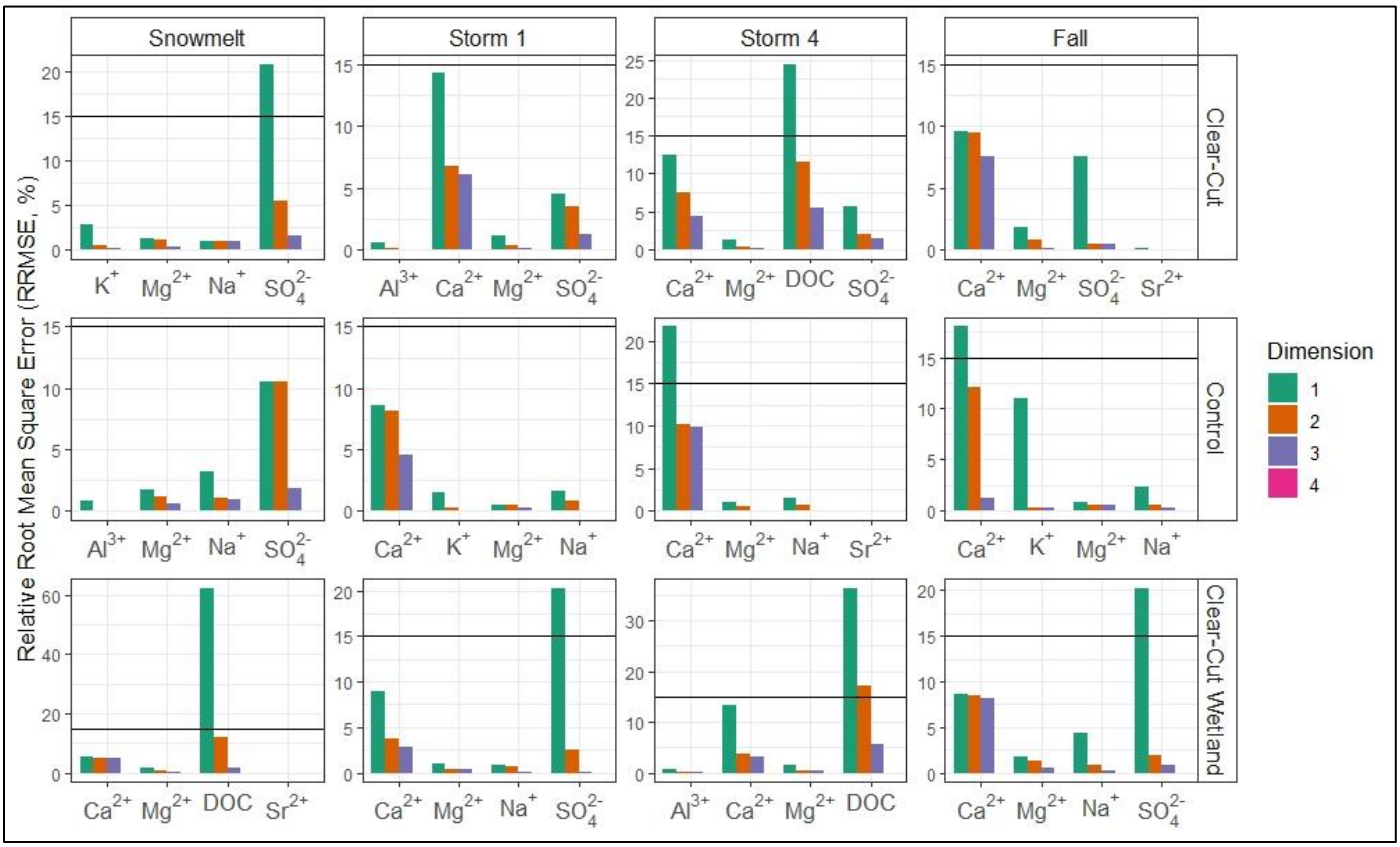

Figure 3.8 Relative root mean square error (RRMSE, %) for the tracers used in the EMMA models. Horizontal line represents the 15% cut off threshold recommended by James & Roulet, (2006). Colour represents the RRMSE explained by each principal component or dimension of the mixing subspace.

3.5. Discussion

3.5.1. Validity of EMMA at TLW

Three end members are required to explain stream water chemistry in the catchments (Figure 3.8) (Hooper, 2003) and the data provided herein are comparable to other studies (Ali et al., 2010; Katsuyama et al., 2001). However, hydrograph separation in the present study was not completed because the stream water was not bound by end members within the mixing subspace. The only scenario where hydrograph separation could have been calculated was for the clear-cut wetland and the control catchment during Storm 1 (Figure 3.7). However, this analysis still provides key insight into hydrologic processes that control runoff generation within these catchments and forms the conceptual framework to explain changes in stream chemistry. Studies have reported that while end members were not bound by stream water chemistry they were previously used to infer runoff generating processes in the Rocky Mountains of Alberta (Spencer et al., 2021) and Canadian Shield of Quebec (Ali et al., 2010). The lack of bounding of stream water by end member tracer concentrations could be caused by a missing end member that contributes to stream water (Ali et al., 2010; Spencer et al., 2021). Figure 3.2 and Figure 3.4 show that concentrations of Ca^{2+}, Mg^{2+}, Na^{-}, SO_4^{2-} and Sr^{2+} within stream water lay outside the range observed in all the end members, which suggests that another end member is missing from this analysis. Missing end members could include a deeper groundwater source or a specific hillslope position that contribute to preferential inflows that was not sampled in this study. Ali et al. (2010) discussed the important role that aspect and specific hillslope positions, such as gullies, played in contributing to stream flow in the hardwood forests of the Hermine catchment at the Station de Biologie des Laurentides, Quebec, Canada, a study area having many similarities to the TLW. Additionally, specific hillslope positions or preferential inflows have been shown to influence stream water quality parameters such as DOC (Ploum et al., 2021) and temperature (Leach et al., 2017). Notably, the sampling design employed in this study may have precluded measurement of the complete range of water quality parameters for soil water and preferential surface flow pathways that contribute end members to stream flow.

It has been suggested that EMMA is not appropriate for hydrograph separation because spatial and temporal variation in solute end member chemistry with changing antecedent moisture conditions violates the assumptions of this procedure (Inamdar et al., 2013). In the present study, end member chemistry was split by season to minimize these changes; however, the variability in solute chemistry (Figures 3.6 and 3.7) and shifting median end member solute concentrations (Figure 3.4) suggest these assumptions were invalidated (Ali et al., 2010; Inamdar et al., 2013). Accordingly, this provides further support that hydrograph separation using the mass balance equations should be avoided. Notably, this observation combined with the labor intensive sampling regime required for EMMA may lead to the perception that it is not a cost effective method for discerning hydrologic processes. However, using the proximity of end members to stream water chemistry within the mixing subspace (Figures 3.6 and 3.7) and the hydro-chemical response of stream water (Figures 3.4 and 3.5), inferences on hillslope channel connectivity and runoff generation processes were still observed. Additionally, this study highlights the importance of utilizing appropriate and thus different EMMA models to represent different hydrologic scenarios as shown by Ali et al. (2010).

3.5.2. Insights into Hydrologic Processes

Solute chemistry in ablation and basal till groundwater were the end members most similar to stream water in the mixing subspace, highlighting their role as primary sources contributing to stream water. This pattern was consistent across all three sampling locations with few seasonal differences (Figures 3.6 and 3.7). This observation agrees with the results of previous work at TLW which show that during snowmelt a perched water table over the basal till routed water through the ablation till before reaching the stream channel (Hazlett et al., 2001; Semkin et al., 2002). Stream water chemistry at high flows trended towards the wetland groundwater, mineral soil water and LFH percolate (Figures 3.6 and 3.7), suggesting that the upper portions of the soil profile are only hydrologically connected during higher flow conditions. Figure 3.4 supports this with Al^{3+}, K^+ and DOC concentrations which are highest in the LFH percolate, mineral soil water and wetland groundwater end members, peaking in stream water at higher flows. Similar studies have shown that groundwater is often the dominant contributing end member to stream water in forested headwater catchments (Burns et al., 2001; Fuss et al., 2016; Katsuyama et al., 2001) and only under higher flow conditions do the upper parts of the soil profile and hillslope become hydrologically connected (Ali et al., 2010; Detty & Mcguire, 2010).

Few seasonal differences in end member contributions to stream flow were observed and were rarely consistent among the three sampling locations. Exceptions were observed with the wetland groundwater and mineral soil percolate end members being closest to stream water values for the control catchment during the Fall and Summer storms (Figure 3.6; Figure 3.7). The lower contributions from the ablation and basal till may be due to the lack of data from these end members in the control catchment during Summer. Given that few groundwater samples were collected during storm events and a stream response to storms was still observed, it could be hypothesized that these end members were not major contributors to stream water as there was rarely enough ground water to collect a sample. Additionally, the proximity of the wetland to the catchment outlet explains the prominent contributions of wetland groundwater to streamflow in the control catchment.

3.5.3. Wetland Contributions to Stream Flow

While groundwater contributions were the primary source of water within the clear-cut and control catchments, wetland groundwater contributions were an important secondary source, especially during Summer storms (Figures 3.6 and 3.7). This is especially apparent in the control catchment, where the wetland is directly upstream of the catchment outlet. During the Summer storms, wetland groundwater solute chemistry was closest to stream water in the mixing subspace in the control catchment while the groundwater end members were closest in the clear-cut (Figure 3.7). The wetland signal within the clear-cut may be diluted by hillslope contributions as the wetland is near the stream initiation point, unlike its location directly above the catchment outlet in the control. Further support for this hypothesis is the number of zero flow days observed in these catchments. Flow was sustained in the control catchment during the Summer (no zero flow days) while the clear-cut had 48 zero flow days (Table 3.2). While these differences may be caused by the impacts of legacy harvesting, they are more likely the result of differences in wetland position between the two study catchments. Studies have shown that small wetlands can act as sponges that fill up during wet periods and slowly drain, sustaining flow during dry periods (Wagener et al., 2007; Webster et al., 2015). Work exploring the effect of wetland cover on mean water travel times supports this theory as the relationship between travel times and wetland cover is dependent on the antecedent moisture conditions (Lane et al., 2020; Leach et al., 2020). During wet time periods, wetlands rapidly transport water laterally through the upper parts of the soil profile due to low water storage capacity and high hydraulic conductivities (Leach et al., 2020). During dry periods, wetlands may act as a small reservoir collecting water from surrounding hillslopes and slowly draining into the stream channel (Lane et al., 2020; Leach et al., 2020). Notably, in the present study, stream flow within the control catchment was mostly sourced by wetland groundwater. The proximity of the wetland to the control catchment outlet maintained flow throughout the Summer.

3.5.4. Legacy Harvesting Effects on End Member Contributions to Stream Flow

Despite the differences in wetland groundwater contributions to stream flow between the control and clear-cut catchments, there are few differences between the clear-cut and control catchments suggesting legacy forest harvesting has limited impact on the prominent end member contributions to stream flow. Previous work at TLW found that forest harvesting increased the proportion of water moving through the upper parts of the soil profile based on $K:SiO_2$ molar ratios four years after harvesting (Monteith et al., 2006a). If harvesting was still impacting these flow paths, it would be expected that the clear-cut mineral soil and LFH percolate end member contributions to stream water would be larger than in the control. As no differences were observed in end member contributions to stream flow between the control and clear-cut catchments, it can be assumed that harvesting induced flow path changes have recovered. As signs of flow path recovery have been observed 15 years after harvesting (Buttle et al., 2018), it is reasonable to assume a complete recovery may have occurred by the time of this study. This suggests that forest harvesting may be a suitable source water protection strategy on this landscape as there are limited long-term harvesting impacts on runoff generation processes that most affect stream water quality. However, recent work conducted at TLW has shown how harvesting impacts on stream flow and hillslope runoff in a low intensity selection harvest have persisted until 2020 (Leach et al., 2022). This evidence in combination with the high variability observed in end member concentrations suggest the results from this study should be interpreted cautiously.

3.5.5. Implications for Water Quality

Previous work has provided insights to the behavior of numerous water quality parameters and their response to harvesting at TLW (Webster et al., 2022; Webster, et al., 2021b). Solutes such as K^+ and DOC were still elevated in the study catchments 21 years after harvesting—these responses were attributed to long-term changes in solute demand/availability and hillslope channel connectivity (Webster et al., 2022). As both solutes are generally associated with shallow flow paths it follows that mineral soil and LFH end members may contribute more to stream flow in harvested catchments. However, the results from EMMA did not support this hypothesis and may suggest that changes in solute availability on the landscape are driving the observed harvesting response. This shows the importance of quantifying not only hillslope channel connectivity, but also nutrient and solute availability when evaluating the suitability of landscape management decisions such as forest harvesting as source water protection strategies.

Previous studies have identified wetlands as a critical source of numerous water quality parameters at TLW (Creed et al., 2003; Leach et al., 2020; Mengistu et al., 2014). Solutes such as DOC, dissolved organic nitrogen (DON), total phosphorus (TP) and total dissolved phosphorus (TDP) were all elevated in catchments with large wetland fractions at TLW (Creed et al., 2003; Mengistu et al., 2014). The unique biogeochemical processes occurring in these wetlands heavily influence the solubility, lability and mobility of the above nutrients (Creed et al., 2003; Mengistu et al., 2014). The results from this study clearly show the important influence wetlands play in runoff generation within these headwater catchments, providing further evidence of their influence on both water quantity and quality. Wetlands appear to have a disproportionately larger influence on stream water quantity and quality than other landscape features such as hillslopes. Therefore special care should be taken by land managers to ensure wetland protection given their sensitivity to landscape disturbance (Webster et al., 2015).

3.6. Conclusion

End member mixing analysis was used to evaluate the dominant sources of hillslope runoff that contribute to the generation of stream flow in a legacy clear-cut and control catchment at TLW. Tracer concentrations either increased (Ca^{2+}, Mg^{2+}, Na^{-}, SO_4^{2-} and Sr^{2+}) or decreased (Al^{3+}, K^{+} and DOC) sequentially from throughfall to the basal till groundwater end members. Stream water was not bounded by end members in the mixing subspace and making hydrograph separation impossible using this data set. Despite this limitation, the results suggest that ablation and basal till groundwater end members were the major contributors to stream flow in both the legacy clear-cut and control catchments, during snowmelt and Fall. Groundwater originating from wetlands adjacent to the stream was also identified as a prominent source of stream flow in both catchments. During the Summer storms wetland groundwater was the dominant source of stream flow to the control catchment. However, wetland position in the landscape and the degree of hydrologic connectivity to the stream channel influenced the contributions of wetland groundwater to stream flow. There were few differences between end member contributions to stream flow in the legacy clear-cut and control catchments suggesting hydrologic recovery had largely occurred 24 years post-harvesting. Future studies should focus on identifying critical hillslope positions or preferential inflows that likely represent large contributions to stream flow within these catchments.

Identifying these critical positions may increase the chances of hydrograph separation using EMMA and provide more quantitative insight into the impacts of changing antecedent moisture conditions and landscape disturbances on runoff generation processes. This study also shows the utility of EMMA for explaining the hydrologic processes that control water quality and treatability responses to landscape disturbances. This kind of analysis is useful for developing and evaluating source water protection and climate change adaptation strategies and drinking water safety plans.

Chapter 4. Legacy Harvesting Impacts on the Source and Concentration of Phosphorus in a Hardwood Dominated Catchment on the Canadian Boreal Shield

4.1. Abstract

Harvesting can alter the source and transport dynamics of phosphorus in forested headwater catchments, but the nutrient export response can vary over time with treatment type, forest cover, landscape characteristics and regional hydro-climatology. While several studies have highlighted these impacts at relatively short time scales (< 10 years) less information is available regarding the longer time scales (> 20 years). Legacy forest harvesting impacts on phosphorus sources were evaluated in headwater catchments of the Turkey Lakes Experimental Watershed by measuring hillslope phosphorus concentrations in throughfall, forest floor (LFH) percolate, mineral soil percolate, wetland groundwater, ablation till groundwater and basal till groundwater in a legacy clear-cut (24 years after harvesting) and forested control catchment. Total particulate phosphorus (TPP) and particulate phosphorus fractions were also evaluated in soil profiles on different hillslope positions in these catchments. Harvesting impacts on these phosphorus sources were related to phosphorus concentration and yields in streams draining these catchments under seasonal and event flow conditions. Legacy forest harvesting impacts on phosphorus sources were limited as few significant differences in phosphorus concentrations or soil TPP and phosphorus fractions were observed between the two catchments. This explained stream phosphorus concentration as few significant differences between the legacy clear-cut and control catchment were observed. Wetlands were identified as a critical source of phosphorus to stream channels in both catchments and may be particularly susceptible to the impacts of forest harvesting. Total phosphorus concentrations were significantly higher in stream water draining the legacy clear-cut than the control

during snowmelt and two Summer storms ($p \leq 0.05$). However, as median differences were below the detection limit (< 1 µg l^{-1}), these differences have no practical significance. Furthermore, as stream phosphorus concentrations were low in both catchments (<1 – 10 µg l^{-1}), there is little risk of these catchments proliferating excess algal growth in downstream aquatic environments and provides evidence that forest harvesting is a suitable as a source water protection strategy on Canadian Shield catchments.

Keywords: hillslope; particulate phosphorus fractionation; wetland; forest soils; headwater streams

4.2. Introduction

Forested watersheds are critical source water regions (Costanza et al., 1998) that supply 33% of the world's largest cities with the majority of their drinking water (National Research Council, 2008). This critical water supply is being threatened by climate exacerbated disturbance such as drought and wildfire (Robinne et al., 2019, 2020) that alter hydrological pathways and biogeochemical cycles in forested landscapes which lead to an increase in the transport of sediment and associated nutrients to stream networks (Emelko et al., 2016; Silins et al., 2009; Smith et al., 2012). Notably, these land disturbance effects can propagate long distances downstream (Emelko et al., 2016; Stone et al., 2014, 2021) and challenge drinking water treatment operations (Emelko et al., 2011, 2016). Land management strategies that reduce fuel loads such as forest harvesting have been proposed as a potential mitigation strategy to protect critical forested source water regions (Deval et al., 2021; Emelko & Sham, 2014; Gannon et al., 2019). Previous studies have reported that in some cases forest harvesting can negatively impact water quantity and quality (Buttle et al., 2018; Kreutzweiser et al., 2008; Webster et al., 2022). To consider the efficacy of forest harvesting as a potential mitigation strategy to protect critical forested source water regions a better understanding of how forest harvesting impacts hydrologic and biogeochemical cycles and the transport of sediment associated nutrients to stream networks over a range of temporal scales is critical.

The before-after-control-impact (BACI) study design is used to quantify the effects of forest harvesting on water quality (Brown et al., 2005; Neary, 2016). Most BACI studies have evaluated the immediate (≤ 5 years) forest harvesting impacts on water quantity and quality and show that the largest harvesting impacts typically occur directly after disturbance (Ahtiainen & Huttunen, 1999; Boggs et al., 2016; Swank et al., 2001). Fewer studies indicate that significant forest harvesting impacts can persist over a longer time period (> 10 years) (Palviainen et al., 2014). Typical forest harvesting rotations occur on the scale of decades (Himes et al., 2022; Kula & Gunalay, 2012; Lutz et al., 2016; Roberge et al., 2016) and considerably less is known about the legacy impacts (> 20 years) of forest harvesting on water quality and its potential longer term impacts on drinking water resources.

Logistical and financial constraints influence the sample design of BACI studies (Brown et al., 2005). Water chemistry is sampled at a range of temporal frequencies (weekly, bi-weekly, monthly) but during higher flow periods such as snowmelt, high sampling frequency (i.e., daily) sampling is often used (Deval et al., 2021; Löfgren et al., 2009; Palviainen et al., 2010; Swank et al., 2001; Webster et al., 2022). Accordingly, the use of variable sampling frequencies can preclude the measurement of highly variable behaviour observed in many water quality parameters (Bieroza et al., 2018; Johnes, 2007; Piniewski et al., 2019; Turgeon & Courchesne, 2008). While some BACI studies involve high frequency water chemistry sampling (Boggs et al., 2016), more work is needed to fully capture the forest harvesting effects on water quality parameters.

Phosphorus is the limiting nutrient for primary productivity in freshwater aquatic environments and can promote algae (including potentially toxin forming cyanobacteria) proliferation (Schindler, 1974; Schindler et al., 2016), which can challenge drinking water treatment operations, leading to service disruptions and even outages (Emelko et al., 2011; Emelko & Sham, 2014). Forest harvesting effects on phosphorus concentrations and yields in stream networks are variable. Some studies report significant increases in both phosphorus concentration and yield (Ahtiainen & Huttunen, 1999; Deval et al., 2021), yield only (Löfgren et al., 2009; Nieminen, 2004; Palviainen et al., 2014) while in other cases no effect is observed (Boggs et al., 2016; Webster et al., 2022). Differences in the observed responses are related to harvesting effects on the hydrological or biogeochemical processes that control the transport of phosphorus from the landscape to stream networks (Kreutzweiser et al., 2008; McMillan et al., 2018). Several studies highlight the impacts of forest harvesting on hydrological processes (Bosch & Hewlett, 1982; Buttle et al., 2018; Neary et al., 2009). Consequently, as phosphorus is often described as being transport limited (Hoffmann et al., 2009) it is notable that a more consistent harvesting response is not observed. Accordingly, this suggests that impacts to phosphorus biogeochemical cycling may play an important role in controlling the response of phosphorus concentration and yield within stream networks as forested landscapes shift from transport- to source-limited after harvesting. Therefore, evaluating the response of phosphorus cycling and pools to forest harvesting in relation to their connectivity to stream channels may be critical to determining the suitability of forest harvesting as a land management tool that prioritizes source water protection.

Phosphorus pools within forested ecosystems are present in dissolved and particulate inorganic and organic forms (Smeck, 1985) and a range of biogeochemical processes influence the transfer of phosphorus from one pool to another (Smeck, 1985). Soluble inorganic phosphorus, often referred to as orthophosphate (PO_4^{3-}) is the most bioavailable dissolved form of phosphorus and is introduced into soils through mineral weathering, atmospheric deposition, decomposition and mineralization of organic material (Achat et al., 2013; Kreutzweiser et al., 2008; Likens, 2004; Smeck, 1985). Orthophosphate within the soluble inorganic pool is either utilized by plants and microbial communities, recycled back into the organic pool (Achat et al., 2013; Attiwill & Adams, 1993; Kreutzweiser et al., 2008), adsorbed to Al, Fe, Mn oxides or precipitated out with Ca to form secondary mineral complexes (Gérard, 2016; Penn & Camberato, 2019; Smeck, 1985) or leached from soil to surface waters (Smeck, 1985). Typically the rates of biological and geochemical uptake are so large that the rates of phosphorus leaching from forested soils to stream networks is quite small (Attiwill & Adams, 1993; Lang et al., 2016; Likens, 2004; Wood et al., 1984). Phosphorus transport from terrestrial to aquatic environments mostly occurs under higher flow conditions that activate preferential flow pathways and flush out the upper parts of the soil profile (Backnäs et al., 2012; Makowski et al., 2020). Due to the high sorption capacity of phosphorus to mineral soil and the limited transport of orthophosphate to stream channels, soil erosion is the primary vector of phosphorus transport from forested ecosystems to stream channels (Hoffmann et al., 2009; Kreutzweiser et al., 2008).

Forest harvesting impacts phosphorus cycling through alterations to numerous biogeochemical processes (Kreutzweiser et al., 2008). Increases in soil moisture, temperature, inputs of organic matter, reduced vegetation uptake and mixing of organic matter with mineral soils increase soluble phosphorus pools through higher rates of decomposition and mineralization (Guo et al., 2004; Gutiérrez del Arroyo & Silver, 2018; Kreutzweiser et al., 2008). These increases can be counteracted by uptake from regenerating vegetation, sorption to mineral soil and losses due to erosion and leaching (Bowd et al., 2019; Evans et al., 2000; Hume et al., 2016; Kreutzweiser et al., 2008). However, these counteracting processes often occur simultaneously and change in relative importance over time and can result in either a net Increase (Evans et al., 2000; Guo et al., 2004; Piirainen et al., 2004), net decrease (Bowd et al., 2019; Hume et al., 2016; Pennock & van Kessel, 1997), or no effect (Macrae et al., 2005; Vincent et al., 2013) on phosphorus pools within forested soils. Generally phosphorus availability has a tendency to increase immediately after harvesting (Guo et al., 2004), but quickly decreases as early successional species recolonize the landscape and increase their nutrient demands (Akselsson et al., 2008). However, the changing relative importance of these processes makes it challenging to predict the response of phosphorus pools to forest harvesting.

Few studies to date have rigorously quantified and tried to relate changes in phosphorus pool availability and/or pool size to stream water quality.

The objectives of this study are to evaluate the legacy (24 year) impacts of forest harvesting on phosphorus pools within forested landscapes to examine how changing phosphorus availability may control phosphorus responses in streams under different flow conditions at the Turkey Lakes Watershed (TLW). Specific objectives are to: 1) examine differences in phosphorus concentrations and forms in water sources throughout the soil profile in a legacy clear-cut and control catchment; 2) evaluate differences in total particulate phosphorus and phosphorus form in mineral soils throughout the soil profile at upper, middle and lower hillslope transect locations in legacy clear-cut and control catchment; and 3) quantify differences in phosphorus concentrations and yields draining a legacy clear-cut and control catchment using high frequency water chemistry sampling under different flow conditions.

4.3. Methods

4.3.1. Study Site and Experimental Design

For a full description of the study site and experimental design see sections 1.3.2 and 1.3.3 in Chapter 1.

4.3.2. Field Methods

Phosphorus source areas were defined as throughfall, LFH percolate, mineral soil percolate, wetland groundwater, ablation till groundwater and basal till groundwater as done in Chapter 3. For a full description of the sampling instrumentation and frequencies see section 3.3.2 in Chapter 3. In addition, during the installation of lysimeters (section 3.3.2.3) soil samples were collected from each pit for particulate phosphorus fractionation. In the Fall of 2020 samples were collected from the A, B and when possible, C horizon/basal till. B horizon samples in each pit were collected as a composite of all B horizon layers. Each soil sample was collected with a metal trowel and stored in Ziplock plastic bags until laboratory analysis could be conducted.

4.3.3. Laboratory Methods

Water samples were analyzed for total phosphorus (TP) and soluble reactive phosphorus (SRP) with a Technicon Autoanalyzer II using the automated molybdophosphoric blue method with a detection limit of 1 µg L^{-1} at the accredited Great Lakes Forestry Center Water Chemistry Laboratory (Environment Canada, 1979). Soluble reactive phosphorus samples were filtered through a 0.45 µm filter before analysis. Due to laboratory closures caused by the COVID-19 pandemic water samples were frozen for up to 4 months before processing and analysis could occur.

Soil samples were air dried and then analyzed for particle size distribution using sieves and hydrometers (A.S.T.M, 1964; Lamb, 1951). Particle size distributions can be seen in Figure C1. Additionally, all material that passed through a #200 sieve (< 74 µm) was retained and sent to a commercial laboratory (ACT Labs, Burlington, ON, Canada) for particulate phosphorus fractionation according to the method developed by Pettersson et al. (1988) and described by Emelko et al. (2016) and Stone & English, (1993). Sequential extractions proceed in the order of (1) 1.0M NH_4Cl at a pH of 7 for 2 hours, two times and is considered the loosely sorbed phosphorus fraction (NH_4Cl – RP); (2) 0.1M $NaHCO_3.Na_2S_2O4$ for 30 minutes, at 40°C with a pH of 7 considered the reductant soluble phosphorus that is primarily bound to Fe (BD-P); (3) 1.0 M NaOH for 16 hours considered metal oxide bound phosphorus (NaOH-RP); (4) 0.5 M HCl for 24 hours considered apatite phosphorus (AP) that is associated with Ca and Mg carbonates; (5) 1.0 M NaOH for 24 hours at 85 °C considered organic or refractory phosphorus (OP) that is typically unreactive (Emelko et al., 2016; Stone & English, 1993; Tullio, 2022). The sum of the first three fractions comprises the non-apatite inorganic phosphorus fraction (NAIP) which is considered the most bioavailable particulate phosphorus fraction as phosphate (PO_4^{3-}) can easily desorb from soils into surrounding waters (House, 2003; Jarvie et al., 2002; Tullio, 2022). After each extraction and centrifugation the ammonium molybdate/stannous chloride method using a Technicon Autoanalyzer II was used to measure phosphorus concentrations within the supernatants (Emelko et al., 2016). Total particulate phosphorus (TPP) was defined as the sum of the NAIP, AP and OP fractions.

4.3.4. Statistical Analysis

Data preparation included the removal of all stream water chemistry values reported on zero flow days. As ~50% of reported TP and SRP concentrations in stream water were below the detection limit of 1 $\mu g\ L^{-1}$ these values were set to half the detection limit (0.5 $\mu g\ L^{-1}$). This was done for data visualization and to ensure enough data were available for statistical analysis. The same approach to data treatment was conducted for sequential phosphorus fractionation data where all values below the detection limit were set to half the detection limit. Total phosphorus and SRP export were calculated as the product of daily water yield and the daily water composite chemistry sample for the snowmelt and Fall sampling periods. Total phosphorus and SRP export were calculated using the instantaneous flow rate and high frequency water chemistry sampled for two Summer storms. For the Summer storms, the water sampling frequency did not match the flow rate frequency, and water samples were interpolated using the last observation carried forward technique (Zhang & Thorburn, 2022). All export data were normalized to units of per hectare per day value. Data normality was checked with the Shapiro-Wilk test. All data were nonparametric, and the Mann-Whitney U and Kruskall-Wallis tests were used to evaluate significant differences. All statistical analyses were performed in R-Studio (R Core Team, 2021).

4.4. Results

4.4.1. Source Area Phosphorus Concentrations

Few significant differences in source area phosphorus concentrations were observed between the clear-cut and control catchment (Figure 4.1a). Exceptions include TP concentrations in the LFH percolate being significantly higher (Mann-Whitney U Test; $p \leq 0.05$) in the clear-cut than the control catchment during snowmelt and Summer. Soluble reactive phosphorus concentrations in the LFH percolate were significantly higher (Mann-Whitney U Test; $p \leq 0.05$) in the clear-cut than the control during Summer. In the basal till groundwater, TP and SRP concentrations were significantly higher (Mann-Whitney U Test; $p \leq 0.05$) in the clear-cut during snowmelt. Soluble reactive phosphorus concentrations in the mineral soil percolate were significantly higher (Mann-Whitney U Test; $p \leq 0.05$) in the control catchment during the Fall. Total phosphorus and SRP concentrations differed significantly (Kruskal-Wallis Test; $p \leq 0.05$) between source areas in both the clear-cut and control catchment (Figure 4.1b). Generally, TP and SRP concentrations decreased with depth through the soil profile (Table 4.1).

Table 4.1 Number of observations (n) and the median ± IQR for TP and SRP concentrations (µg L^{-1}) in the clear-cut and control catchment during the snowmelt, Summer and Fall sampling periods.

		Snowmelt		Summer		Fall	
End Member	Catchment	Total Phosphorus (µg L^{-1})	Soluble Reactive Phosphorus (µg L^{-1})	Total Phosphorus (µg L^{-1})	Soluble Reactive Phosphorus (µg L^{-1})	Total Phosphorus (µg L^{-1})	Soluble Reactive Phosphorus (µg L^{-1})
Throughfall	Clear Cut	n: 3, 7.6 ± 4.8	n: 3, 3 ± 7.5	n: 10, 55 ± 53.8	n: 10, 7.8 ± 102.1	n: 3, 8 ± 4	n: 3, 1.3 ± 0.6
	Control	n: 3, 7.7 ± 8.5	n: 3, 0.5 ± 0.6	n: 9, 50.9 ± 238.2	n: 9, 5.2 ± 35.1	n: 2, 13.2 ± 7.4	n: 2, 0.8 ± 0.3
LFH Percolate	Clear Cut	n: 10, 15.7 ± 29.6	n: 10, 5.7 ± 13.5	n: 52, 38.2 ± 21.8	n: 52, 10.8 ± 16.5	n: 15, 12.4 ± 6.4	n: 15, 6.6 ± 2.8
	Control	n: 2, 3 ± 0.7	n: 2, 0.5 ± 0	n: 25, 20.7 ± 10.8	n: 25, 3.5 ± 2.7	n: 7, 14 ± 5.7	n: 7, 6 ± 2
Wetland Groundwater	Clear Cut	n: 34, 4.9 ± 10.1	n: 34, 0.5 ± 0	n: 30, 10.4 ± 16.4	n: 30, 0.5 ± 0.5	n: 13, 18.4 ± 14.9	n: 13, 1.5 ± 1.4
	Control	-	-	n: 11, 13.7 ± 6.5	n: 11, 1.1 ± 0.8	n: 5, 9.7 ± 9.2	n: 5, 1 ± 0.6
Mineral Soil	Clear Cut	n: 17, 10.6 ± 14.9	n: 17, 0.5 ± 0	n: 21, 24.5 ± 14.6	n: 21, 2.6 ± 13.4	n: 9, 19.3 ± 16.9	n: 9, 1.5 ± 1.4
	Control	n: 4, 6.2 ± 4.9	n: 4, 0.5 ± 0	n: 11, 31.7 ± 13.6	n: 11, 4.8 ± 21.8	n: 5, 49.8 ± 33.5	n: 5, 9.6 ± 27.3
Ablation Till	Clear Cut	n: 15, 2.8 ± 4.8	n: 15, 0.5 ± 0	n: 5, 3.5 ± 56.9	n: 5, 0.5 ± 37.2	n: 3, 9.6 ± 6.3	n: 3, 0.5 ± 0
	Control	n: 33, 1.7 ± 2.4	n: 33, 0.5 ± 0	n: 1, 0.5 ± 0	n: 1, 0.5 ± 0	n: 3, 2.6 ± 0.5	n: 3, 0.5 ± 0
Basal Till	Clear Cut	n: 12, 3.2 ± 3.8	n: 12, 0.5 ± 0	n: 8, 3 ± 2	n: 8, 0.5 ± 0	n: 4, 2.8 ± 0.8	n: 4, 0.5 ± 0
	Control	n: 24, 0.5 ± 0.7	n: 24, 0.5 ± 0	n: 1, 2.1 ± 0	n: 1, 0.5 ± 0	n: 4, 3.6 ± 1.3	n: 4, 0.5 ± 0

Seasonal differences in TP and SRP concentrations within each source area were sometimes observed (Figure 4.1c). Significant seasonal differences in throughfall TP concentrations (Kruskal-Wallis Test; $p \leq 0.05$) were observed in both the control and clear-cut catchment. Significant seasonal effects on TP concentrations in LFH percolate were observed in both catchments as well as SRP concentrations in the control catchment (Kruskal-Wallis Test; $p \leq 0.05$). Significant seasonal effects on TP and SRP concentrations within wetland groundwater was also observed in the clear-cut (Kruskal-Wallis Test; p ≤

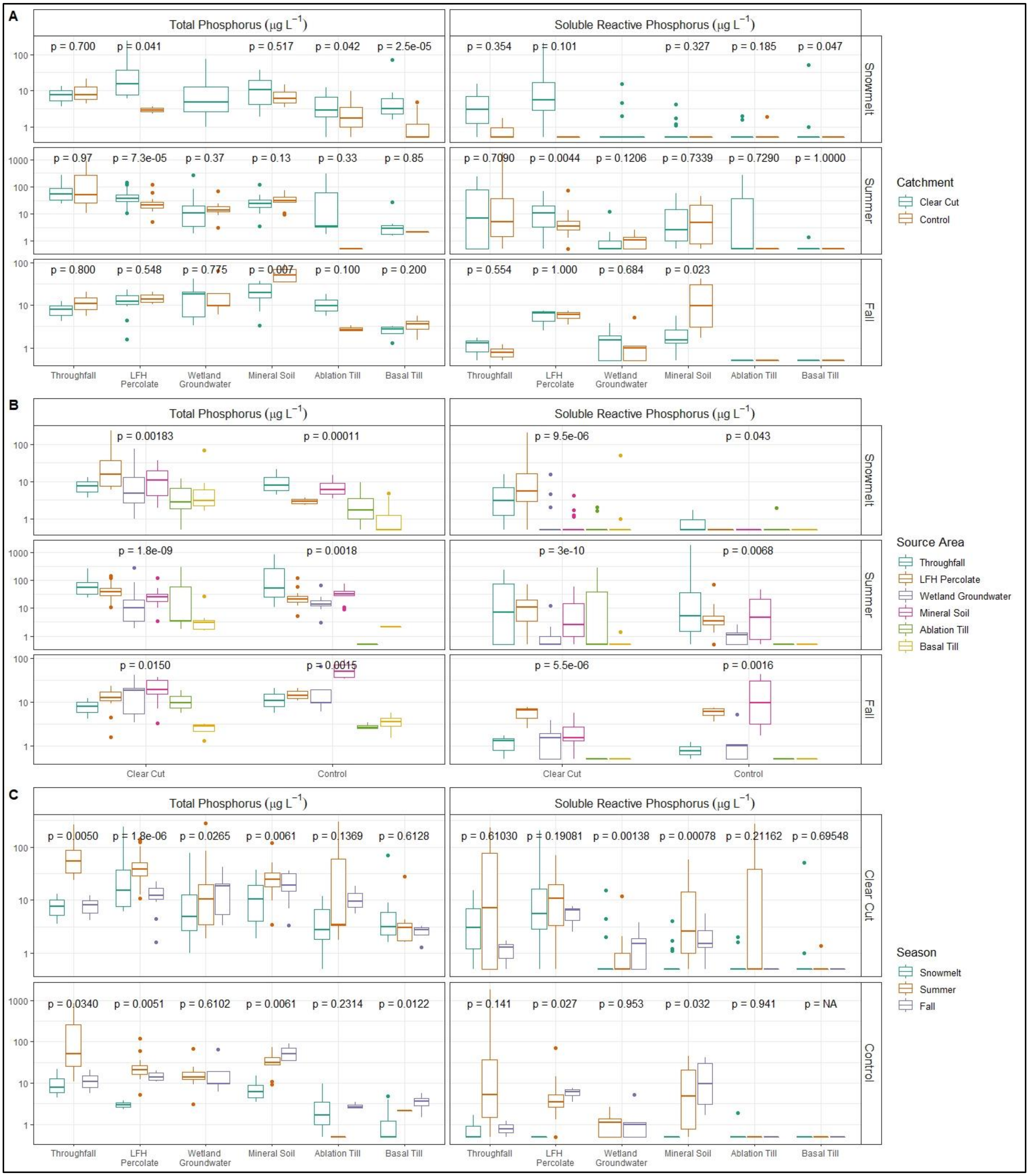

Figure 4.1 TP and SRP concentrations (μg L^{-1}) in hillslope source areas. A) Comparing the clear-cut and control. B) Comparing the source areas. C) Comparing Seasonal Differences. Results from the Mann-Whitney U Test (Panel A) or Kruskal Wallis test (Panel B and C) are shown above.

0.05). Significant seasonal effects were observed in mineral soil water for both TP and SRP concentrations (Kruskal-Wallis Test; $p \leq 0.05$) in both catchments. For the observed significant differences listed above, the largest seasonal concentrations occurred in either the Summer or Fall sampling periods. The lowest median TP and SRP concentrations mostly occurred during snowmelt (Table 4.1).

4.4.2. Soil Particulate Phosphorus Fractions

Total particulate phosphorus concentrations increased with increasing depth through the soil profile in both catchments (Table 4.2). The NAIP fraction was largest in the A (Clear-cut: 57.4 – 78.2 %; Control: 51.6 – 79.7 %) and B (Clear-cut: 54.3 – 79.1%; Control: 41.0 – 82.5%) horizons in both catchments. In the C horizon the NAIP (Clear-cut: 20.4 – 42.1%; Control: 30.3 – 53.3%) and AP (Clear-cut: 29.6 – 66.7%; Control: 10.7 – 51.3%) fractions were comparable. Within the NAIP fraction the metal oxide bound phosphorus was the largest fraction in all soil horizons while the loosely sorbed phosphorus fraction was smallest (Table 4.2). Few significant differences between the clear-cut and control catchment for TPP and particulate phosphorus fractions were observed (Figure 4.2a). One exception was that OP concentrations in the B horizon were significantly higher in the control catchment then the clear-cut (Mann-Whitney U Test; $p \leq 0.05$). Total particulate phosphorus and individual particulate phosphorus fractions increased with decreasing hillslope position in the A and B soil horizons (Figure 4.2b). No relationship was observed between hillslope position and particulate phosphorus content in the C soil horizon. Significant differences (Kruskal-Wallis Test; $p \leq 0.05$) between hillslope positions were observed for TPP, NAIP, AP, and OP in the B horizon and OP in the A horizon in the clear-cut catchment. Differences in particulate P form were not observed between hillslope positions in the control catchment.

4.4.3. Phosphorus Transport in Streams

Total phosphorus and SRP concentrations within the clear-cut, control, and clear-cut wetland at TLW were small with median concentrations ranging from <1 – 5 $\mu g\ L^{-1}$ (Table 4.3). This is especially apparent for SRP concentrations in which many median concentration values were below the detection limit. Significant

Table 4.2 Median ± IQR (% of TPP) and number of observations (n) for total particulate phosphorus and particulate phosphorus forms of the A, B and C horizons in the clear-cut and control catchment.

Catchment	Soil Horizon	n	Total Particulate Phosphorus (µg P g^{-1})	Loosely Sorbed Phosphorus (µg P g^{-1})	Reductant Soluble Phosphorus (µg P g^{-1})	Metal Oxide Bound Phosphorus (µg P g^{-1})	Nonapatite Inorganic Phosphorus (µg P g^{-1})	Apatite Phosphorus (µg P g^{-1})	Organic Phosphorus (µg P g^{-1})
Clear Cut	A	12	252.4 ± 170.6	5 ± 0 (0.6-2.9%)	23.8 ± 19.4 (1.2-17.7%)	125.5 ± 169.2 (42.4-73.6%)	171.7 ± 159.4 (57.4-78.2%)	5 ± 0 (1-5.5%)	75.1 ± 22 (19-39.7%)
	B	11	411.6 ± 194.2	5 ± 0 (0.5-1.3%)	10 ± 0 (1-2.7%)	257 ± 99.5 (51.8-77.2%)	272 ± 99.5 (54.3-79.1%)	16 ± 28.4 (1.2-7%)	134 ± 17.5 (17.6-38.9%)
	C	4	495 ± 110.5	5 ± 1.2 (0.8-2.2%)	10 ± 3.1 (1.9-3.4%)	170.5 ± 27.8 (16.2-37.9%)	188 ± 20.9 (20.4-42.1%)	167.5 ± 100.2 (29.6-66.7%)	120.5 ± 30.8 (12.9-29.2%)
Control	A	12	250.2 ± 225.5	5 ± 0 (0.6-3%)	21.2 ± 13.7 (1.3-14.3%)	142.5 ± 224.9 (42.6-76.2%)	170.8 ± 208.2 (51.6-79.7%)	5 ± 0 (0.7-3.3%)	75.6 ± 11.8 (19.2-45.4%)
	B	12	376.8 ± 168.8	5 ± 0 (0.6-2.1%)	10 ± 0 (1.2-6.7%)	248 ± 108.2 (38.5-79.6%)	263 ± 111 (41-82.5%)	5 ± 25.8 (1-36.9%)	88.5 ± 44.2 (16.5-39%)
	C	5	482.9 ± 153.4	10 ± 0 (1.3-3%)	10 ± 0 (1.3-3%)	163 ± 21 (26.6-47.4%)	183 ± 21 (30.6-53.3%)	216 ± 194.2 (10.7-51.3%)	113 ± 34 (16.4-36.1%)

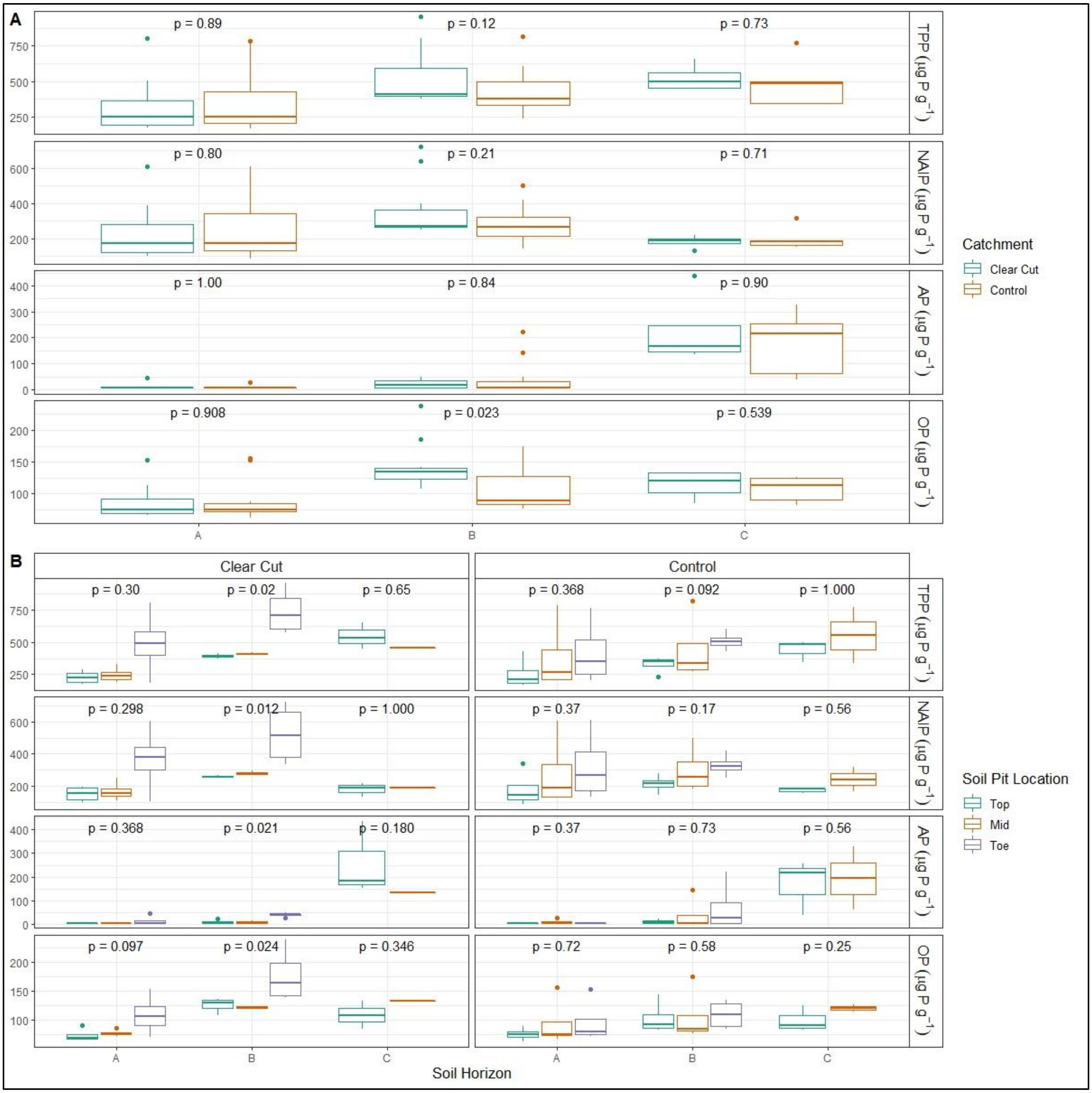

Figure 4.2 TPP and particulate phosphorus forms in mineral soils within the A, B and C horizons. A) Compares differences between the clear-cut and control catchment. B) Compares hillslope positions. Results from the Mann-Whitney U Test (A) or Kruskal Wallis test (B) are shown above.

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Table 4.3 TP and SRP concentrations (µg L^{-1}) in stream water under different flow conditions in the clear-cut, clear-cut wetland and control catchment. Number of observations (n) and median ± interquartile range (IQR) are shown.

Flow Conditions	Location	Total Phosphorus (µg L^{-1})	Soluble Reactive Phosphorus (µg L^{-1})
Snowmelt	Clear Cut	n: 49, 1.4 ± 0.5	n: 50, 0.5 ± 0.5
	Clear Cut Wetland	n: 30, 2.3 ± 1.5	n: 30, 0.8 ± 0.6
	Control	n: 47, 1 ± 0.9	n: 47, 0.5 ± 0.5
Storm 1	Clear Cut	n: 24, 1.3 ± 0.9	n: 24, 0.5 ± 0.6
	Clear Cut Wetland	n: 24, 4.1 ± 1.9	n: 24, 1.2 ± 0.4
	Control	n: 24, 0.5 ± 0.6	n: 24, 0.5 ± 0.5
Storm 4	Clear Cut	n: 27, 1 ± 1.1	n: 27, 0.5 ± 0
	Clear Cut Wetland	n: 26, 3 ± 1.9	n: 26, 0.5 ± 0
	Control	n: 27, 0.5 ± 0	n: 27, 0.5 ± 0
Summer	Clear Cut	n: 11, 1.1 ± 0.8	n: 11, 0.5 ± 0
	Clear Cut Wetland	n: 13, 5.2 ± 3.3	n: 13, 1 ± 0.8
	Control	n: 15, 0.5 ± 0.8	n: 15, 0.5 ± 0
Fall	Clear Cut	n: 22, 0.5 ± 0.7	n: 22, 0.5 ± 0
	Clear Cut Wetland	n: 22, 3.2 ± 1.1	n: 22, 0.5 ± 0
	Control	n: 22, 0.5 ± 0.7	n: 22, 0.5 ± 0

seasonal differences (Kruskal-Wallis Test; $p \leq 0.05$) were seen for both TP and SRP concentrations in all three stream water sampling locations (Figure 4.3). Seasonal TP and SRP concentrations were largest during snowmelt in the clear-cut and control catchment (Figure 4.3; Table 4.3). In the clear-cut wetland TP and SRP concentrations were largest during Summer baseflow and storm 1, respectively (Figure 4.3; Table 4.3).

The temporal change in TP concentration as a function of stream flow (Figure 4.4) show that the largest TP concentrations occurred during the largest flow events. However, a strong relationship between stream flow and TP concentration was not observed as lots of scatter occurred. Hydrographs with SRP concentrations were not shown as most data points lie below the detection limit. The highest concentrations were observed in the clear-cut wetland with median concentrations ranging from 2.3 – 5.2 µg TP L^{-1} and 0.5 – 1.2 µg SRP L^{-1} (Table 4.3). The clear-cut wetland had significantly higher (Mann-

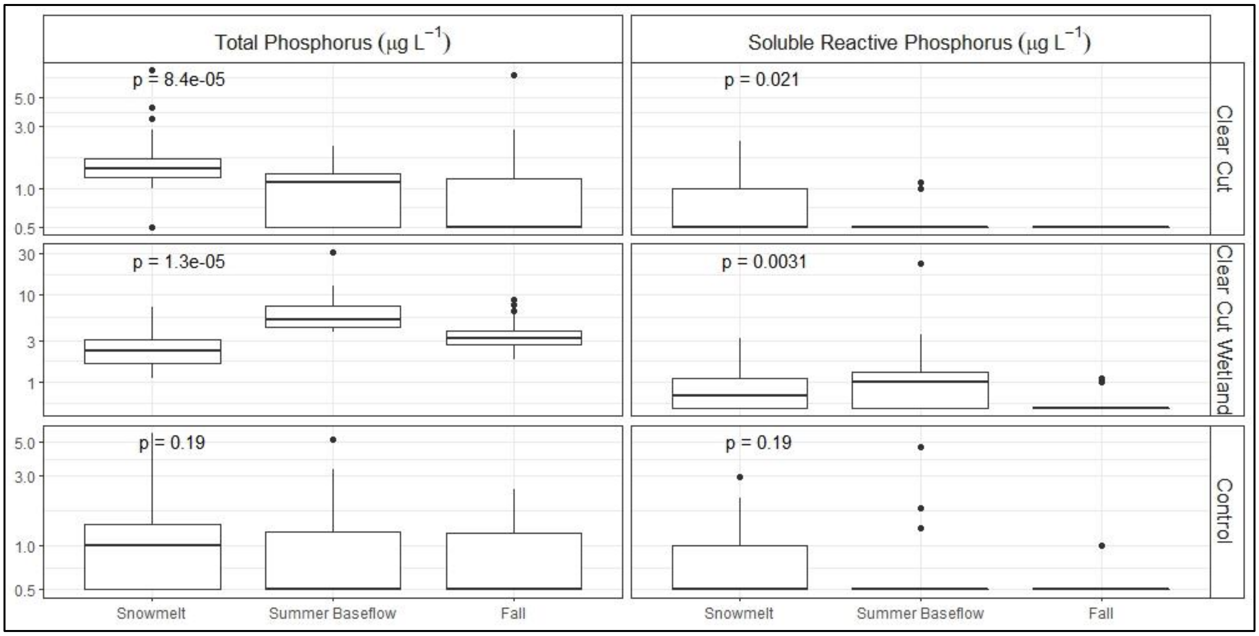

Figure 4.4 Seasonal and Summer storm event differences of TP and SRP concentrations (µg L^{-1}) in the clear-cut, clear-cut wetland and control catchment in stream water. Results from the Kruskal Wallis test are shown in the top right corner.

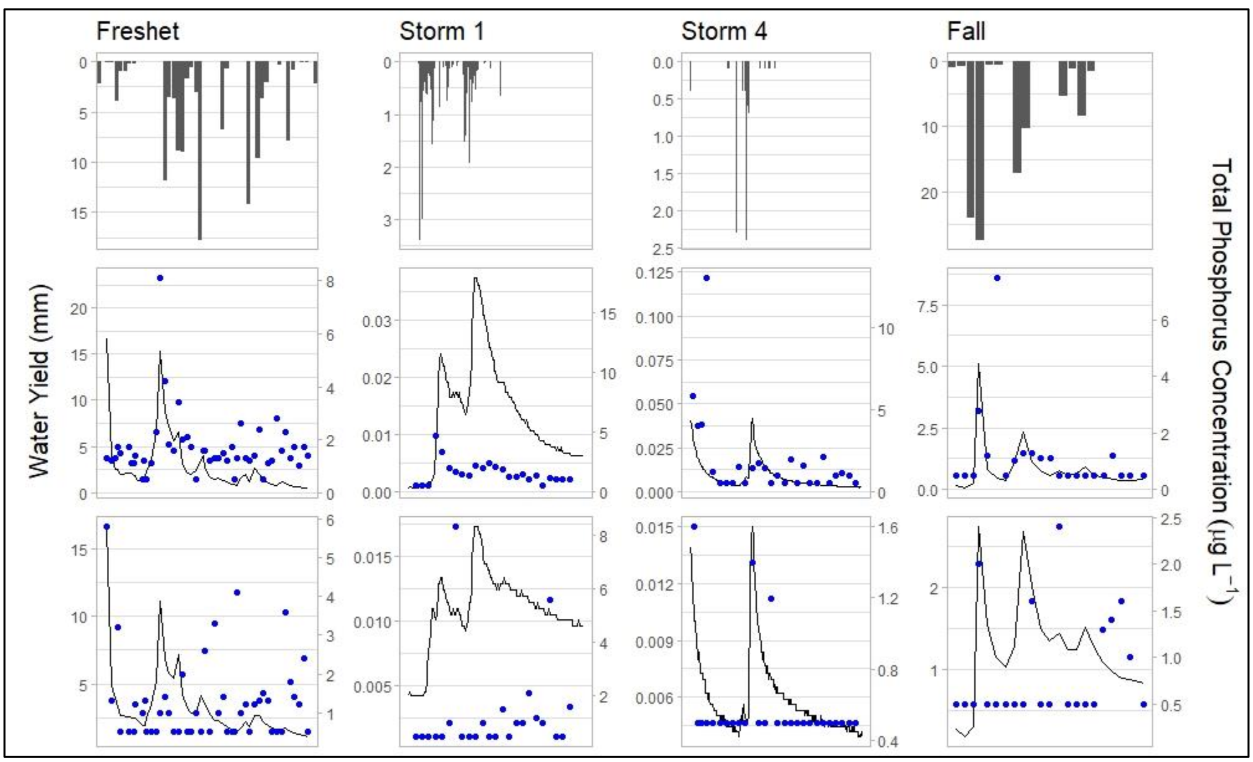

Figure 4.3 Precipitation (mm), stream flow (mm) and TP concentrations (µg L^{-1}) in the clear-cut and control catchment during the snowmelt, two Summer storms and Fall sampling period. Stream flow and precipitation in the snowmelt and Fall plots represent the daily water/precipitation yield while stream flow and precipitation for the Summer storms represents the 10-minuet water/precipitation yield. Precipitation, clear-cut and control catchment responses are shown in the top, middle and bottom row, respectively.

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Whitney U Test; p ≤ 0.05) TP concentrations than the clear-cut for all flow types and SRP concentrations during snowmelt, storm 1 and the Summer baseflow conditions (Figure 4.5). Harvesting effects on TP concentrations were observed during snowmelt and both Summer storms as the clear-cut had significantly higher TP concentrations (Mann-Whitney U Test; p ≤ 0.05) than the control (Figure 4.5). No significant differences for SRP concentrations were observed between the clear-cut and control catchment.

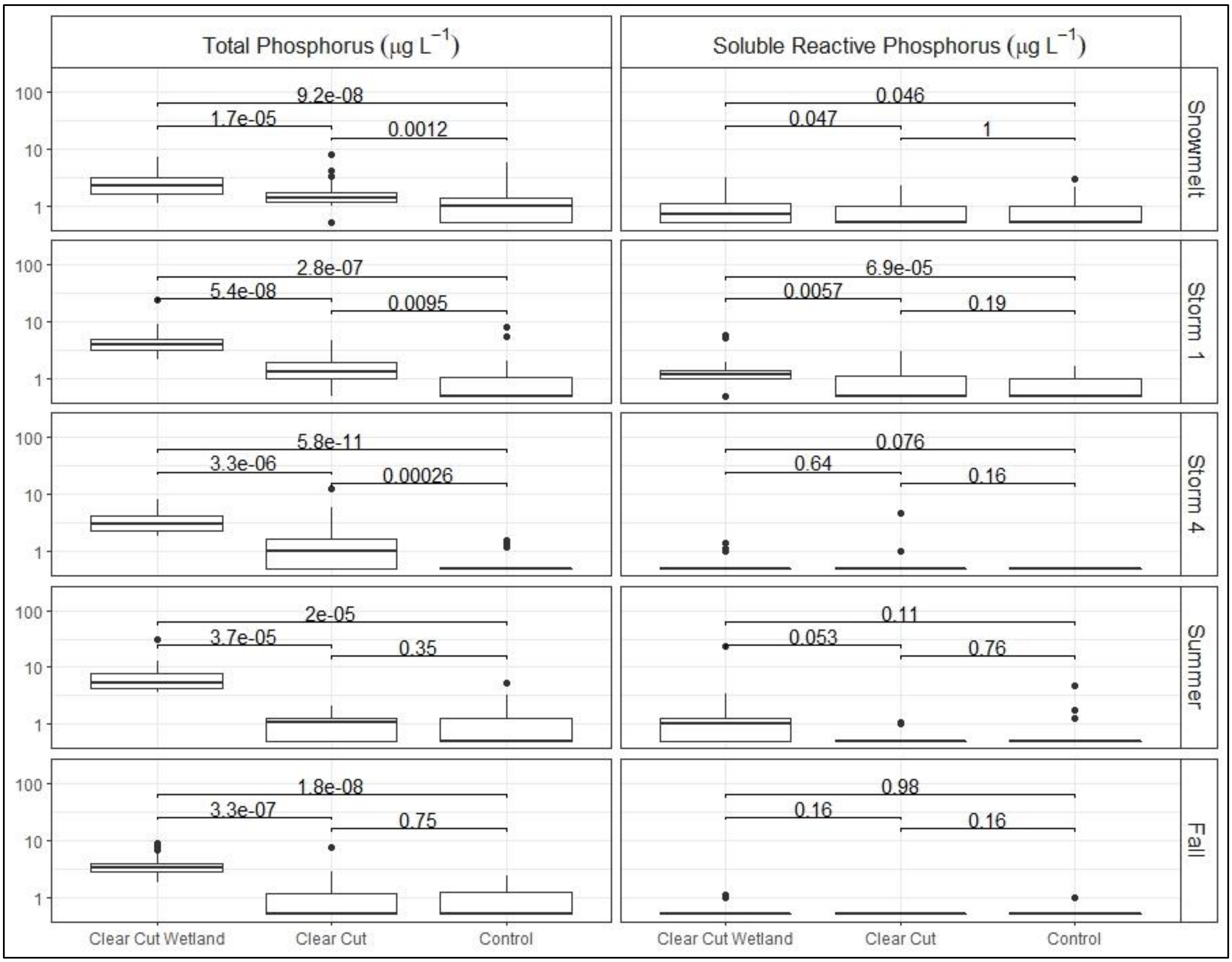

Figure 4.5 TP and SRP concentrations (µg L^{-1}) the clear-cut, clear-cut wetland and control catchment under the different flow conditions. Values shown above the boxplots are the p values from the Mann Whitney U Test.

Differences in TP and SRP export were driven by changes in both water yield and phosphorus concentration. Daily runoff was similar between both catchments during snowmelt (percent difference of 7.6%), greater in the clear-cut than the control during both Summer storms (percent differences ranging from 22 – 44%), and greater in the control during the Fall (percent difference of 32.5 %) (Figure 4.6). Daily TP and SRP yield was largest during snowmelt and smallest during the Fall for both catchments. Differences in TP yield between the two catchments were observed with the clear-cut with larger TP yields for snowmelt, Summer storms and Fall (percent difference ranging from 12.3 – 422.1 %). SRP yield was larger in the clear-cut during the Summer storms (percent difference ranging from 58.6 – 93.9 %) and in larger in the clear-cut during the Summer storms (percent difference ranging from 58.6 – 93.9 %) and in the control during snowmelt and Fall (percent difference ranging from 34.7 – 41.2 %).

4.5. Discussion

4.5.1. Legacy Harvesting Impacts on Phosphorus Sources

Total phosphorus and SRP concentrations in water from hillslope source areas generally decreased with increasing depth through the soil profile. Concentrations were highest in the throughfall and LFH percolate while lowest in the ablation and basal till groundwater (Figure 4.1b; Table 4.1). These patterns agree with past literature as loosely sorbed phosphorus is highest in organic material which acts as a phosphorus source (Achat et al., 2013) and lowest in mineral soils where Al, Fe, Mn and Ca oxides adsorb high levels of phosphorus thus acting as a sink (Evans et al., 2000; Penn & Camberato, 2019; Smeck, 1985). Significant seasonal differences seen in both the clear-cut and control catchment during the Summer were mostly limited to the throughfall, LFH, mineral soil and wetland groundwater sources (Figure 4.1c). These were likely driven by increased temperatures and biological activity that increase rates of decomposition and mineralization allowing for phosphorus pools to accumulate and be subsequently flushed out after rain events (Huang & Schoenau, 1997; Kreutzweiser et al., 2008; Segal et al., 1990; Shaw & Cleveland, 2020).

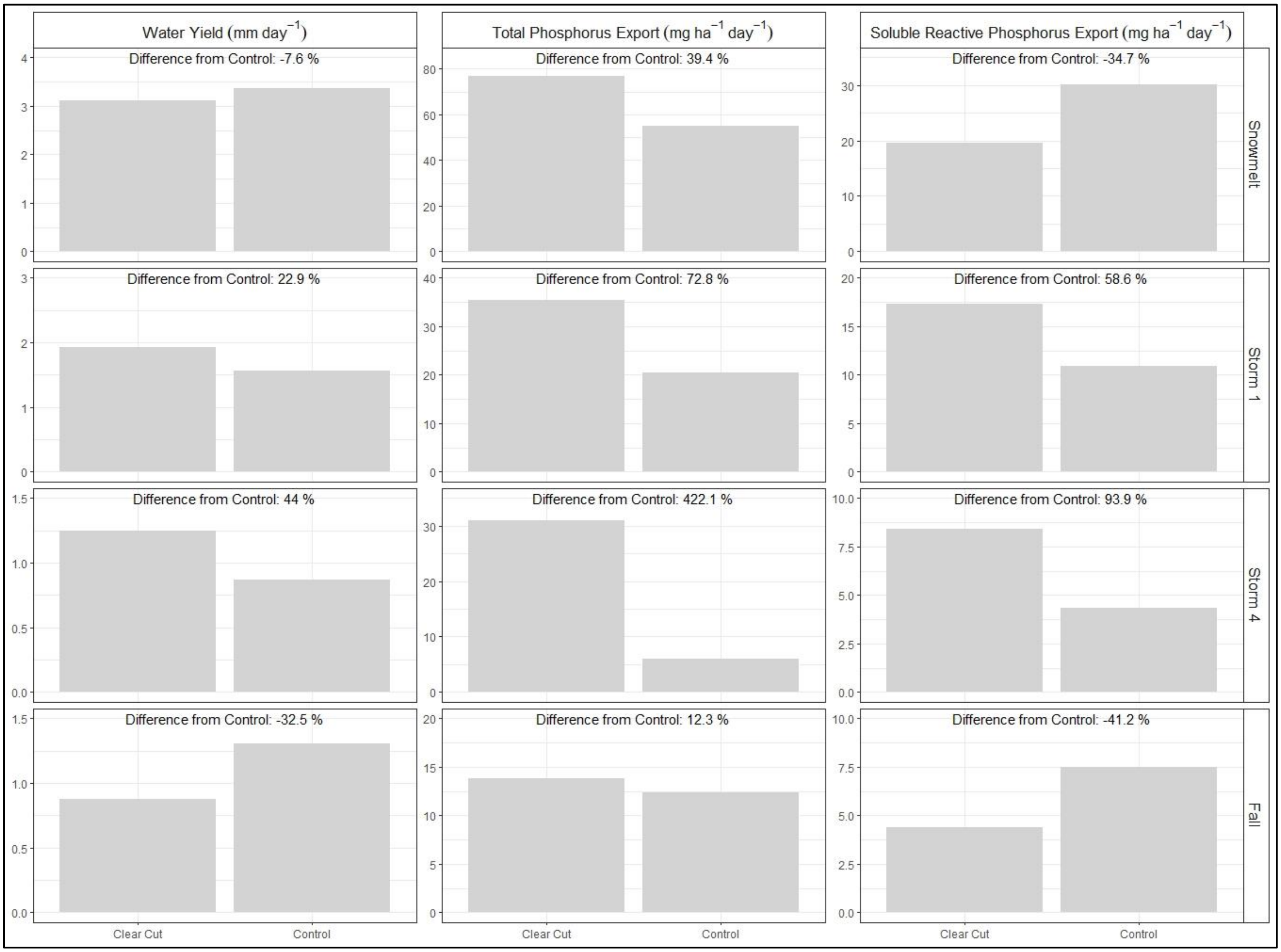

Figure 4.6 Daily water yield (mm day^{-1}), TP yield (mg ha^{-1} day^{-1}) and SRP yield (mg ha^{-1} day^{-1}) for the clear-cut and control catchment under the different flow conditions. Percent difference between the clear-cut and control catchment is shown above the bar plots.

Significant harvesting effects on TP and SRP concentrations draining the different hillslope source areas were rare and occurred mostly in the LFH percolate (Figure 4.1a). Monteith et al. (2006b) described how the LFH layer within the clear-cut at TLW was eliminated within the first 4 years after harvesting and has been recovering since. This change may explain the observed increases in TP and SRP concentrations draining the LFH layer as this source area may still be recovering from the impacts of forest harvesting.

Piirainen et al. (2004) found a similar result with a 3x increase in TP flux draining out of the O horizon in a mixed boreal forest in Eastern Finland, three years after forest harvesting. The results from TLW further support this and show that elevated phosphorus leaching from the forest floor may have persisted for more than 20 years. The observed increases could be caused by forest floor disturbance from heavy equipment, deposition of logging residuals and increased rainfall intensities driven by reduced canopy interception (Kreutzweiser et al., 2008; Piirainen et al., 2004).The increase in phosphorus leaching from the forest floor was buffered by mineral soil as few significant differences were observed between the mineral soil percolate or the ablation and basal till groundwater source areas (Figure 4.1a). This is unsurprising as forest harvesting rarely increases phosphorus concentrations in groundwater (Evans et al., 2000; Macrae et al., 2005) as mineral soils have high phosphorus binding capacity (Evans et al., 2000; Piirainen et al., 2004). Accordingly, this suggests that forest harvesting can increase phosphorus sources on the landscape; however, these increases are most likely isolated to forest floor percolate and pose little risk to stream water quality as this source is rarely hydrologically connected to the stream channel (Evans et al., 2000; Neary et al., 2009; Piirainen et al., 2004).

4.5.2. Particulate Phosphorus Fractions within Soils

Total particulate phosphorus and individual particulate phosphorus fractions within the mineral soils in the clear-cut and control catchment were comparable to other forested soils. The TPP values in this study ranged from 250 – 500 mg TP kg^{-1} (Table 4.2) which is comparable to previous studies (100 – 1000 mg TP kg^{-1}; Table 4.4). Total particulate phosphorus content increased with increasing soil depth (Table 4.2) which agrees with the results of other studies from boreal shield catchments in south-central Ontario (Baker et al., 2015). However, this pattern does not always occur as TPP content has shown a decreasing pattern with soil depth in Alberta, Canada (Whitson et al., 2005), Finland (Backnäs et al., 2012), and the Sierra Nevada Mountains, California, USA (Homyak et al., 2014). The loosely sorbed phosphorus which is associated with phosphorus concentrations in runoff (Macrae et al., 2005; Pote et al., 1996, 1999), which

Table 4.4 Total particulate phosphorus and particulate phosphorus forms from different studies in forested soils.

Location	Land Use	Soil Type	Soil Horizon	Phosphorus Fraction	Phosphorus Content mg P kg^{-1} soil (% of Total Phosphorus)	Reference
Alberta, Canada	Forest and Clear Cut Harvesting	Glay Luvisols, Eutric Brunisols, Gleysols and Organic	Surface Soils (0-10 cm)	Water Extractable Phosphorus	Forest Floor and Surface Soils: > 70 (7%); Mineral Soil: < 2 (0.7%)	Macrae et al., 2005
				Total Phosphorus: H_2SO_4 and Copper (II) Sulphate	Forest Floor and Surface Soils: > 1000; Mineral Soil: < 300	
Alberta, Canada	Clear Cut Harvesting	Luvisolic	LFH, Ae, Bt, BC, and Ck1	Total Phosphorus: Kjeldahl digestion	LFH: 1350; Ae: 610; Bt: 420; BC: 470; Ck1: 588	Whitson et al., 2005
Germany	Forest	Range of soils mostly cambisols	Surface soils (0-5 cm) and subsoils (73-106 cm)	Total Phosphorus: HF	Surface Soils: 196 - 2966; Subsoils: 175 - 1844	Stahr et al., 2018
Koskela, Finland	Forest	Podzol	E, B1, B2 and BC	Soluble Inorganic Phosphorus: 1 M NH_4Cl	E: 0.3 ± 0.3 (0.3 %); B1: < 0.4 (0.1%); B2: < 0.4 (0.1%); BC: <0.4 (0.2 %)	Backnas et al., 2012
				Total Phosphorus: 0.5 M H_2SO_4	E: 110.8 ± 40.8; B1: 308.8 ± 76.0; B2: 274.2 ± 30.6; BC: 204.0 ± 37.0	
New Zealand	Forest at different succesional stages defiend as seedling (10 years), sapling (25 years), pole (120 years), mature(>150 years)	Soils derived from greywacke, loess and colluvium	Surface soils (0-10 cm)	Total Phosphorus: $HNO_3/HClO_4$	Seedling: 399 ± 67; Sapling: 706 ± 120; Pole: 592 ± 171; Mature: 671 ± 80	Brandtberg et al., 2010
North Eastern United States and Europe	Forest	Varied	Upper parts of the B horizon	Soluble Inorganic Phosphorus: 1 M NH_4Cl	3.72 (0.9%)	SanClements et al., 2010
				Reducible Metal Hydroxide Phosphorus: 0.11 M $NaHCO_3$-$Na_2S_2O_2$	22.3 (5.3%)	
				Al Hydroxide and Organic Phosphorus: 0.1 M NaOH	315.93 (74.7%)	
				Apatite Phosphorus: 0.5 M HCl	28.5 (6.7 %)	
				Residual Phosphorus: 1 M NaOH	52.66 (12.4%)	
Ontario, Canada	Forest	Poorly developed podzols and brunsols	LFH, Ah, Ae, Bhf, Bf	Total Phosphorus: 0.5 M H_2SO_4	LFH: ~1239; Ah: 248 - 341; Ae: ~93; Bhf: 310 - 403; Bf: ~434	Baker et al., 2015
Sierra Nevada, California, USA	Alpine/Forest	Entisols, Inceptisols and Spodosols	A Horizon (0-10 cm) and B Horizon (10-60 cm)	Freely exchangeable inorganic phosphorus: Anion exchange membrane strip	A: 7 (0.8%); B: 3 (0.5%)	Homyak et al., 2013
				Plant Available Phosphorus: 0.5 M $NaHCO_3$	A: 115 (13.3%); B: 50 (8.4%)	
				Al/Fe Associated Phosphorus: 0.1 M NaOH	A: 534 (61.6%); B: 362 (60.6%)	
				Ca Associated Phosphorus: 1 M HCl	A: 124 (14.3%); B: 119 (19.9%)	
				Residual Phosphorus: Microwave Extract Concentrated HNO_3 and HCl	A: 20 (2.3%); B: 14 (2.3%)	
				Total Phosphorus: Sum of Fractions	A: 867; B: 597	

are largely comprised of the smallest fraction of TPP (0.6 – 3%; Table 4.2). This is comparable to other forested catchments (<1%; Table 4.4); however, comparisons should be made with caution as different extraction methods are often used (Backnäs et al., 2012; Homyak et al., 2014; Macrae et al., 2005; SanClements et al., 2010). The largest phosphorus fraction was bound to metal oxides (16 – 79%; Table 4.2) and is unsurprising as Fe and Al oxides play a significant role in phosphorus retention within mineral soils (Homyak et al., 2014; Penn & Camberato, 2019; SanClements et al., 2010). Overall, these results show that phosphorus content in the soils at TLW is like other forested catchments and that leaching of phosphorus from these soils would be small due to the small loosely soluble fraction.

Legacy forest harvesting appears to have no impact on TPP or phosphorus fractions as there were few significant differences between the clear-cut and control catchment (Figure 4.2a). While studies have shown the response of soils to forest harvesting is highly varied (Gu et al., 2017; Kreutzweiser et al., 2008), there is substantial evidence showing that phosphorus content may decrease in legacy harvested catchments as early successional species establish themselves on the landscape (Akselsson et al., 2008; Bowd et al., 2019; Hume et al., 2016; Pennock & van Kessel, 1997). As these differences were not observed at TLW, the question arises why was a decline in soil phosphorus content not observed and what processes or conditions drive these varied responses? One hypothesis is that nitrogen limitations within TLW forests (Kreutzweiser et al., 2008) may limit forest regeneration, preventing the depletion of phosphorus levels within soils (Vincent et al., 2013). More work is needed to explore this hypothesis in order too understand the complex interactions of nutrient limitations, forest growth and the subsequent impacts on water quality.

One factor that did influence TPP and phosphorus fractions within the soils at TLW was hillslope position. Total particulate phosphorus and its fractions within the A and B horizons was significantly larger at the toe hillslope positions (Figure 4.2b). The increases in phosphorus content at the toe hillslope positions may be problematic due to their proximity to the stream channel (Hoffmann et al., 2009). While few studies have explored the role of hillslope position on phosphorus content in forested catchments, this area has been widely explored in agricultural landscapes. Studies have found that TP and loosely soluble phosphorus increase with decreasing hillslope position (Honeycutt et al., 1990; Mage & Porder, 2013; Plach et al., 2022; Smeck, 1973) because of the continuous transport of phosphorus downslope through leaching and erosion (Gu et al., 2017). This may present a driver of to excess phosphorus transport to the stream channel if soils become phosphorus saturated or under high flow conditions (Hoffmann et al., 2009); however, as phosphorus levels are significantly lower in forested catchments than agricultural the chances of this are very low (Zhou et al., 2022).

4.5.3. Forested Wetlands a Phosphorus Source

The complex hydrologic and biogeochemical processes within wetlands make their influence on water quantity and quality in forested catchments quite significant (Webster et al., 2015). The results from this study are no exception as TP and SRP concentrations draining the clear-cut wetland were significantly higher than those draining both the clear-cut and control catchments (Figure 4.4). Previous studies have shown how small wetlands can act as phosphorus sources at TLW (Creed et al., 2003; Leach et al., 2020; Mengistu et al., 2014; Chapter 2) and elsewhere (Casson et al., 2019; O’Brien et al., 2013). The contributions of phosphorus from wetlands to stream channels are often disproportionately higher than their extent within the catchment as the processes within wetlands greatly affect the solubility, lability and mobility of phosphorus (Mengistu et al., 2014). Redox conditions common in wetland promote the reduction of Fe(III) and subsequent release of Fe(II) including any associated phosphorus which increases the soluble phosphorus pool within wetlands and subsequent transport to stream networks (Mengistu et al., 2014; O’Brien et al., 2013).

While wetlands act as significant sources of phosphorus to stream channels, their impacts do not always perpetuate downstream. Contributions of phosphorus from wetlands to catchment outlets can depend on the level of hydrologic connectivity between the wetland and stream channel. Devito et al.

(2000) found that the response of TP concentrations in Boreal Plain lakes to forest harvesting was dependent more on the degree of wetland connectivity to the lake than total wetland area. O'Brien et al. (2013) found that while TP concentrations draining wetlands were high, concentrations at the catchment outlet were significantly smaller which is comparable to patterns of TP and SRP in the present study (Figure 4.4). These differences were likely driven by biogeochemical processes occurring in the stream channel and dilution from hillslope contributions to stream flow between the wetland and the catchment outlet (O'Brien et al., 2013). Notably this further highlights the importance of wetlands and wetland position within a catchment for water quality and should be considered when making land management decisions.

4.5.4. Legacy Impacts of Harvesting on Phosphorus Transport Dynamics

While the results from this study do show significant differences in TP concentrations between the clear-cut and control catchment during snowmelt and the two Summer storms (Figure 4.4) these differences are below the detection limit (< 1 μg l^{-1}) (Table 4.3). Therefore, it cannot be stated with any certainty that legacy forest harvesting has a significant impact on TP concentrations at TLW. Even if a significant harvesting effect is occurring, it is irrelevant as TP and SRP concentrations draining these catchments are so much lower (<1 – 10 μg L^{-1}) than the TP thresholds required for significant proliferation of harmful algal blooms (20 – 50 μg L^{-1}) (Fastner et al., 2016; Vuorio et al., 2020; Xu et al., 2015). A lack of legacy harvesting response on TP or SRP concentrations is not surprising as many studies have shown forest harvesting impacts can be short lived (Ahtiainen & Huttunen, 1999), small (Deval et al., 2021), or have no effect at all (Boggs et al., 2016). Legacy harvesting effects on TP and SRP yields were slightly larger with percent and absolute differences between the clear-cut and control catchment ranging from -40 – 400% and 0 – 25 mg ha^{-1} day^{-1} (Figure 4.6). However, compared to other studies these impacts are still very small as values reported in other studies range from 0 – 1000 g ha^{-1} $year^{-1}$ (0 - 2740 mg ha^{-1} day^{-1}, Chapter 2).

In summary, forest harvesting can impact phosphorus transport dynamics through changes in either source availability or source channel connectivity (McMillan et al., 2018). Therefore, it is not surprising that no legacy harvesting impact was observed. The results of this study clearly show for most source areas there is no harvesting effect on phosphorus pools (Figure 4.1 and 4.2). Results from Chapter 3 further support this observation as there were few differences in the prominent flow paths contributing to stream flow between the clear-cut and control catchment 24 years after disturbance which suggests legacy forest harvesting had no impact on source channel connectivity. Therefore, it can be assumed that legacy harvesting has minimal if any impact on the phosphorus transport dynamics at TLW and provides evidence that intelligent forest harvesting may be used as a wildfire mitigation strategy on this landscape.

4.6. Conclusion

This study explored the legacy impacts of forest harvesting on phosphorus sources in water draining through the hillslope and phosphorus content in mineral soil to explain phosphorus transport dynamics observed in streams under different flow conditions. Significant differences were observed for TP and SRP concentrations draining from the LFH layer but were mitigated by mineral soil. Few differences were observed for the total phosphorus content and fractions in mineral soil and were like the values seen in other forested environments. Additionally, loosely soluble phosphorus fractions were the lowest fraction of TPP suggesting that mineral soil at TLW has a high capacity to retain phosphorus moving through the soil profile. A lack of harvesting effect on TPP and phosphorus fractions within the mineral soil was attributed to these catchments being nitrogen limited. Wetlands were identified as a critical source of phosphorus and the degree of wetland channel connectivity is critical to a wetland's contribution of phosphorus to the stream channel. Despite intensive high frequency water sampling that captures the rising and falling limb of the hydrograph no significant harvesting impacts were observed for SRP in the streams. Significant harvesting impacts for TP concentrations were observed during snowmelt and Summer storms; however, these differences were so small (below the detection limit) they are unlikely to have any negative impacts on downstream aquatic environments. From this analysis it can be discerned that legacy forest harvesting has little impact on phosphorus transport dynamics as the few differences identified in phosphorus sources are unlikely to impact stream water. Therefore, legacy forest harvesting on the hardwood dominated forests of the Canadian Shield poses little risk to the proliferation of harmful algal blooms that negatively impact drinking water treatment operations.

Chapter 5. Synthesis and Future Directions

5.1. Synthesis

Climate exacerbated landscape disturbances such as wildfire can pose serious threats to drinking water supplies originating on forested landscapes (Emelko et al., 2011; Robinne et al., 2019). Among their many impacts on water quality and treatability, wildfires can accelerate the transport of sediment and associated contaminants to stream networks; these impacts can propagate downstream to aquatic environments such as lakes and reservoirs (Emelko et al., 2016; Hampton et al., 2022; Silins et al., 2014; Smith et al., 2011). Phosphorus is the limiting nutrient for primary productivity in freshwater aquatic ecosystems (Schindler, 1974; Schindler et al., 2016); it can promote the proliferation of algae that challenge drinking water treatment operations and potentially produce toxins of human and ecosystem health concern (Emelko et al., 2011; Emelko & Sham, 2014). Forest harvesting has been proposed as a mitigation strategy for source water protection by reducing fuel loads and lowering the chances of catastrophic wildfires (Deval et al., 2021; Emelko & Sham, 2014; Gannon et al., 2019). However, as forest harvesting also may increase phosphorus concentrations and yields (Boggs et al., 2016; Deval et al., 2021) research is required to evaluate the suitability of such approaches. The work presented in this thesis evaluates the impacts of legacy forest harvesting on phosphorus transport dynamics (Chapter 2 and 4) and the primary processes that control phosphorus transport (source availability, Chapter 4; and source channel connectivity; Chapter 3) from terrestrial to aquatic environments in TLW on the Canadian Shield. Thus, this research informs the use of forest harvesting as a land management strategy that prioritizes source water protection in forested watersheds located on the hardwood dominated Canadian Shield.

Chapter 2 evaluates temporal changes in TP concentration and yields within forested catchments and quantifies the harvesting impacts of three different harvesting strategies using a 31-year water quantity and quality data set and BACI study design. Results demonstrate that TP concentrations and yields generally decreased over time which is comparable to the results from previous studies (Eimers et al., 2009; O'Brien et al., 2013; Pinder et al., 2014). The observed decreases in TP concentrations and yields were attributed to changes in climate and/or recovery from acid rain. Significant increases in TP concentration (mean increases < 2 μg L^{-1}) were observed in the clear-cut and selection cut catchments. Significant increases in TP yield (annual increases < 25 g ha^{-1} $year^{-1}$) were observed in all harvested catchments. While legacy forest harvesting impacts were statistically significant the data are much lower than in previous forest harvesting studies (Ahtiainen & Huttunen, 1999; Boggs et al., 2016; Deval et al., 2021; McBroom et al., 2008) and are unlikely to cause excess algal growth (Fastner et al., 2016; Vuorio et al., 2020; Xu et al., 2015). Changing environmental conditions (climate change and recovery from acid rain) may have attenuated any harvesting impacts on phosphorus concentration and yield through changes in phosphorus source availability and source channel connectivity—additional work is needed to evaluate these potential relationships. A conceptual diagram of the interaction of multiple potential disturbance impacts on TP concentrations and yields is presented in Figure 5.1.

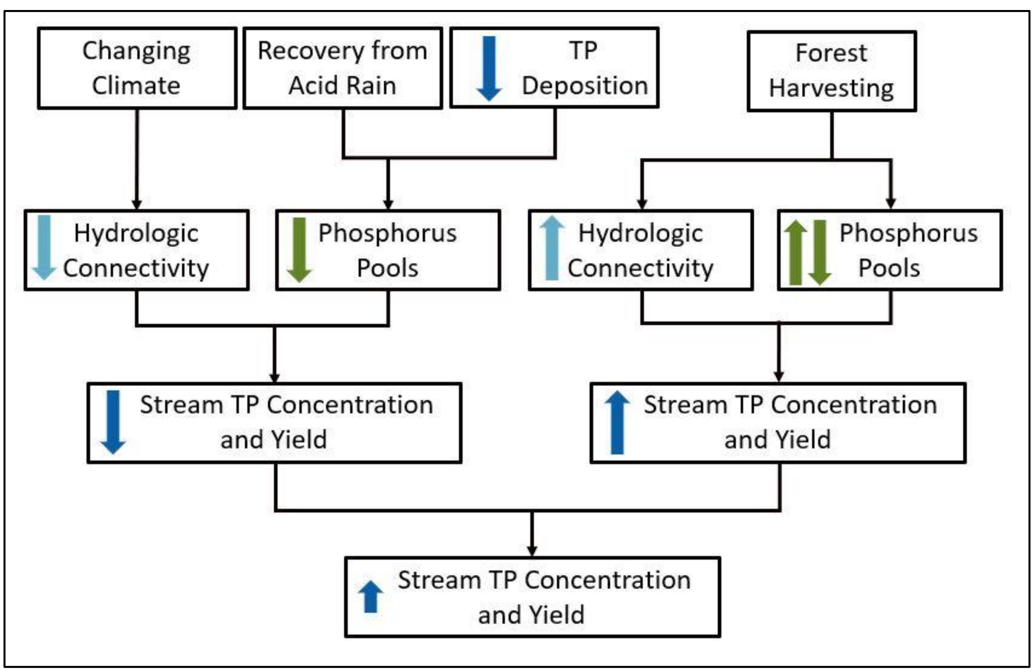

Figure 5.1 Conceptual diagram of how changing environmental conditions and forest harvesting may interact to limit the harvesting impacts on TP concentrations and yields in TLW. Arrow direction within each box denotes the expected response with downward facing arrows describing a decline and upward facing arrows describing an increase.

The prominent runoff generation processes in a legacy clear-cut and control catchment were evaluated using EMMA and described in Chapter 3. Results show that the chemistry of stream water and groundwater was comparable which suggests that groundwater was the dominant source of runoff within both catchments. This finding is consistent with previous studies conducted in TLW (Hazlett et al., 2001; Semkin et al., 2002) and elsewhere (Burns et al., 2001; Fuss et al., 2016; Katsuyama et al., 2001). Notably, wetlands were identified as important sources of stream water in all study catchments. All differences in runoff generating processes between the legacy clear-cut and control catchment could be attributed to wetland position, suggesting legacy harvesting had no impact on runoff 24 years after disturbance.

Expanding upon the results in Chapter 2, Chapter 4 specifically examined the impacts of legacy harvesting on phosphorus concentrations and yields 24 years after disturbance. Additionally, primary hillslope phosphorus sources were evaluated in Chapter 4. In combination with the results from EMMA in Chapter 3 (that identified dominant source areas to stream flow), these results explain observed stream water phosphorus concentrations. Small, but significant differences in TP concentration between the legacy clear-cut and control catchment were observed. However, as these differences were below the detection limit (< 1 µg L^{-1}), it cannot be concluded with certainty that legacy harvesting had a significant impact on phosphorus concentrations. Wetlands were identified as a primary source of phosphorus to stream channels as wetland concentrations were significantly higher than those draining the legacy clear-cut and control catchments. Legacy harvesting had little impact on phosphorus sources throughout the hillslope with the exception of the LFH percolate, which had significantly higher TP and SRP concentrations in the legacy clear-cut compared to the control catchment. However, as the LFH layer is rarely hydrologically connected to the stream channel (Chapter 3) it is unlikely to have any impact on stream phosphorus concentrations.

5.2. Future Research Directions

Phosphorus concentrations draining the study catchments were very low (1 – 10 µg L^{-1}) and are similar to data reported from other forested catchments (Deval et al., 2021; Palviainen et al., 2014, 2015). The results from Chapters 3 and 4 suggest the low phosphorus concentrations (< 1 µg L^{-1}) are attributed to the prominent source areas of stream water (i.e., groundwater) in these catchments. The largest phosphorus sources within the hillslope (throughfall and LFH percolate) were poorly connected hydrologically to the stream channel, limiting the amount of phosphorus that could be transported to the stream. It is hypothesized that wetlands are the primary source of phosphorus transported to stream channels because they are both strongly connected hydrologically to streams (Chapter 3) and have measurable phosphorus concentrations (Table 4.1; Figure 5.2). Additionally, as phosphorus has a high binding capacity to mineral soil (Gérard, 2016; Penn & Camberato, 2019; Smeck, 1985), soil erosion via surface runoff is a primary vector for the transport of phosphorus from terrestrial to aquatic ecosystems (Hoffmann et al., 2009; Kreutzweiser et al., 2008). In forested catchments, surface runoff is relatively uncommon (Neary et al., 2009) and was rarely observed in the study catchments (personal observation). Therefore, it is not surprising that phosphorus concentrations within the streams were so low as erosion induced by surface runoff would have rarely occurred. However, future work should further explore the complex relationships and impacts of forest harvesting on wetland contributions to stream water quality and erosional processes that transport fine sediment and associated nutrients to stream channels.

While this thesis evaluated harvesting impacts on phosphorus concentrations and yields draining small headwater catchments, it has not fully explored the impacts of harvesting related infrastructure such as road networks and stream crossings. Studies have shown that roads can greatly alter stream water quantity (Buttle et al., 2018; Wemple & Jones, 2003) and quality (Beschta, 1978; Brown et al., 2013; Forsyth et al., 2006). Road networks redirect surface and shallow subsurface runoff from hillslopes to

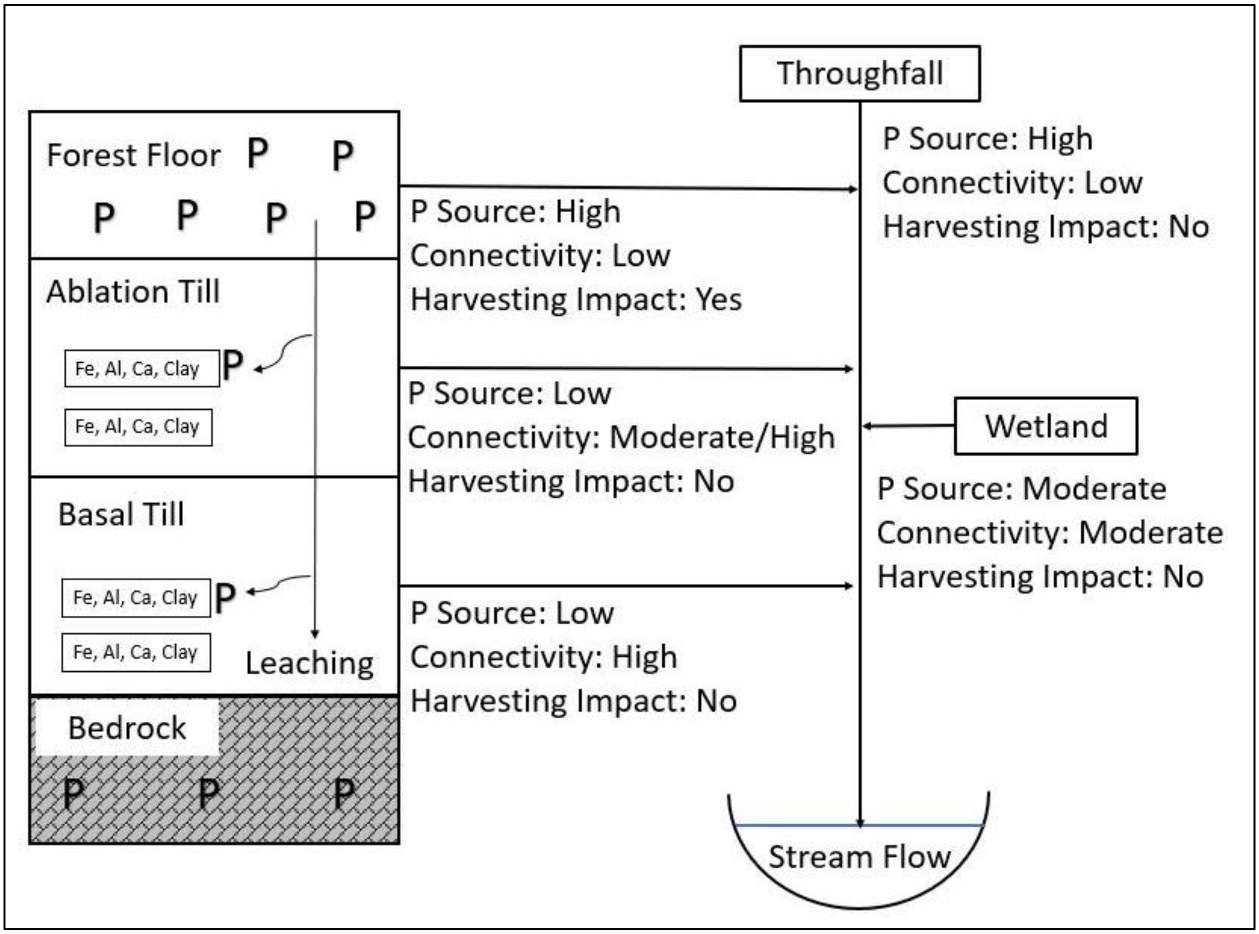

Figure 5.2 Conceptual diagram describing source area contributions to stream flow and their relative phosphorus concentrations. P Source refers to the amount of phosphorus measured within any end member or source area as described in Chapter 4. Connectivity refers to the level of hydrologic connectivity between the end member or source area as described in Chapter 3. Harvesting impact refers to if harvesting impacted either phosphorus levels or the degree of hydrologic connectivity based on the combined results of Chapters 3 and 4.

stream channels which reduces rainfall runoff response times and increases peak flows (Storck et al., 1998; Wemple & Jones, 2003). This corresponds with higher rates of erosion (Beschta, 1978; Brown et al., 2013; Forsyth et al., 2006) that transport nutrients, heavy metals and organic material into stream networks (Emelko et al., 2011; Rachels et al., 2020). The influence of roads can be seen in Chapter 2, with phosphorus concentration and yield in the selection cut (lowest harvesting intensity) responded more to forest harvesting than the shelterwood cut. This was also previously observed in other allied TLW studies (Buttle et al., 2018; Kreutzweiser & Capell, 2001; Webster et al., 2022) and shows that road construction may have a larger impact on water quality than timber removal. Therefore, the results from this study may not reflect the full range of harvesting effects on phosphorus transport dynamics. Future research efforts should focus on the impacts of forest harvesting on larger catchments, so as to include the influences of road networks, stream crossings and landings on water quality parameters such as phosphorus.

5.3. Threats to Drinking Water Treatability

The results from this thesis show that as the immediate harvesting impacts on phosphorus concentrations and yields were small in Chapter 2 (< 2 μg L^{-1}; < 25 g ha^{-1} $year^{-1}$) and Chapter 4 (< 1 μg L^{-1}; < 30 mg ha^{-1} day^{-1}), thus suggests little threat to downstream drinking water treatability. Additionally, as TP concentrations and yields appear to be declining temporally in response to changing climate and recovery from acidification (Chapter 2), it is unlikely that water draining from these catchments will deliver enough phosphorus to exacerbate proliferation of algae in downstream lakes. However, these conclusions should be interpreted with caution, as other parameters not studied in this thesis such as total suspended sediment, turbidity, and dissolved organic carbon (Emelko et al., 2011) also impact drinking water treatment operations. Future work should focus on better understanding the relationships between landscape disturbance in a changing climate, phosphorus loading and the subsequent influence on primary productivity.

Throughout this thesis, wetlands were consistently identified as critical landscape features that control water quantity and quality and is in agreement with similar studies conducted within TLW (Creed et al., 2003; Leach et al., 2020; Mengistu et al., 2014). Also, as wetlands can be particularly sensitive to landscape disturbance such as forest harvesting (Webster et al., 2015), there could be an elevated risk to downstream drinking water treatment operations if they are disturbed. Therefore, in the interest of source water protection, special care should be taken when conducting harvesting operations around wetlands. It should be noted that, this is already practiced as significant protections around wetlands are already designated within the Ontario Ministry of Natural Resources Forest Management Guidelines (OMNR, 2010). Future work should continue to evaluate the effectiveness of these protections under the changing climatic conditions to ensure that the protection of source waters is maintained.

It can be concluded, based on the results from this thesis, that intelligent forest harvesting strategies can be conducted on hardwood dominated Canadian Shield catchments without any significant impacts to phosphorus concentrations or yields. Therefore, forest harvesting may be an appropriate land management strategy that promotes source water protection on this landscape. Future research opportunities include evaluating the impacts of harvesting related infrastructure such as road networks and stream crossings on phosphorus transport dynamics, further exploring the influence of wetlands on water quantity and quality within these catchments, identify the impacts of forest harvesting on other parameters that threaten drinking water treatment operations, and assess the combined impacts of changing climatic conditions and nutrient loading on freshwater lakes. Answering these questions in combination with the results from this study will better identify the suitability of forest harvesting as a land management strategy that promotes source water protection in the hardwood dominated Canadian Shield forests.

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Appendix A Supplementary Material for Chapter 2

Table A1 Linear regression equations used for estimating predicted harvesting behaviour in the BACI study design.

		Control C32					Control C35					Control C46				
	Catchment	n	Intercept	Slope	SEE	Adjusted r^2	n	Intercept	Slope	SEE	Adjusted r^2	n	Intercept	Slope	SEE	Adjusted r^2
Flow Weighted Total Phosphorus Concentration																
4	Clear Cut	54	0.285 ± 0.094 **	0.763 ± 0.088 **	0.309	0.591	63	0.353 ± 0.102 **	0.677 ± 0.093 **	0.362	0.466	61	0.261 ± 0.121 **	0.698 ± 0.103 **	0.371	0.437
5	Selection Cut	54	0.024 ± 0.102 (ns)	0.88 ± 0.092 **	0.314	0.637	61	0.281 ± 0.115 **	0.614 ± 0.102 **	0.395	0.378	60	0.163 ± 0.127 (ns)	0.698 ± 0.109 **	0.390	0.416
6	Shelterwood Cut	56	0.319 ± 0.1 **	0.727 ± 0.089 **	0.353	0.553	66	0.424 ± 0.116 **	0.561 ± 0.103 **	0.421	0.318	62	0.181 ± 0.121 (ns)	0.744 ± 0.103 **	0.371	0.465
Total Phosphorus Yield																
7	Clear Cut	54	0.161 ± 0.087 *	0.913 ± 0.055 **	0.490	0.843	63	-0.125 ± 0.095 (ns)	0.945 ± 0.059 **	0.535	0.808	61	-0.557 ± 0.143 **	1.069 ± 0.081 **	0.605	0.747
8	Selection Cut	53	-0.429 ± 0.099 **	1.086 ± 0.063 **	0.544	0.853	61	-0.622 ± 0.12 **	1.069 ± 0.073 **	0.644	0.785	60	-0.982 ± 0.159 **	1.17 ± 0.09 **	0.667	0.746
9	Shelterwood Cut	56	0.476 ± 0.075 **	0.802 ± 0.048 **	0.431	0.838	66	0.292 ± 0.087 **	0.774 ± 0.053 **	0.505	0.769	62	-0.099 ± 0.111 (ns)	0.926 ± 0.063 **	0.471	0.782

Note:
* p-value ≤ 0.1
** p-value ≤ 0.05
(ns) p-value > 0.1

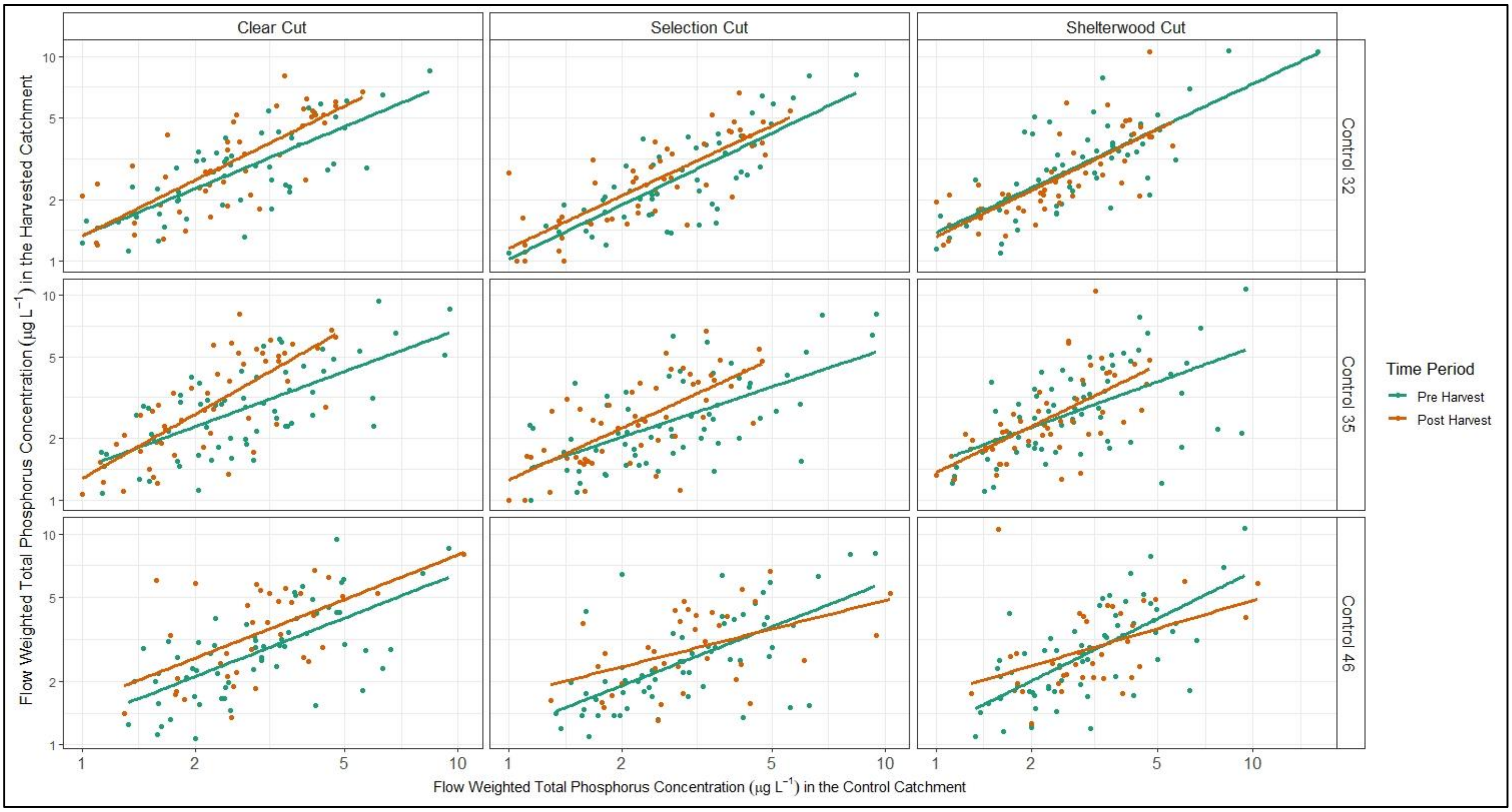

Figure A1 Linear regression relationships pre and post harvest between control and harvested catchments across all seasons for flow weighted total phosphorus concentration (μg L^{-1}).

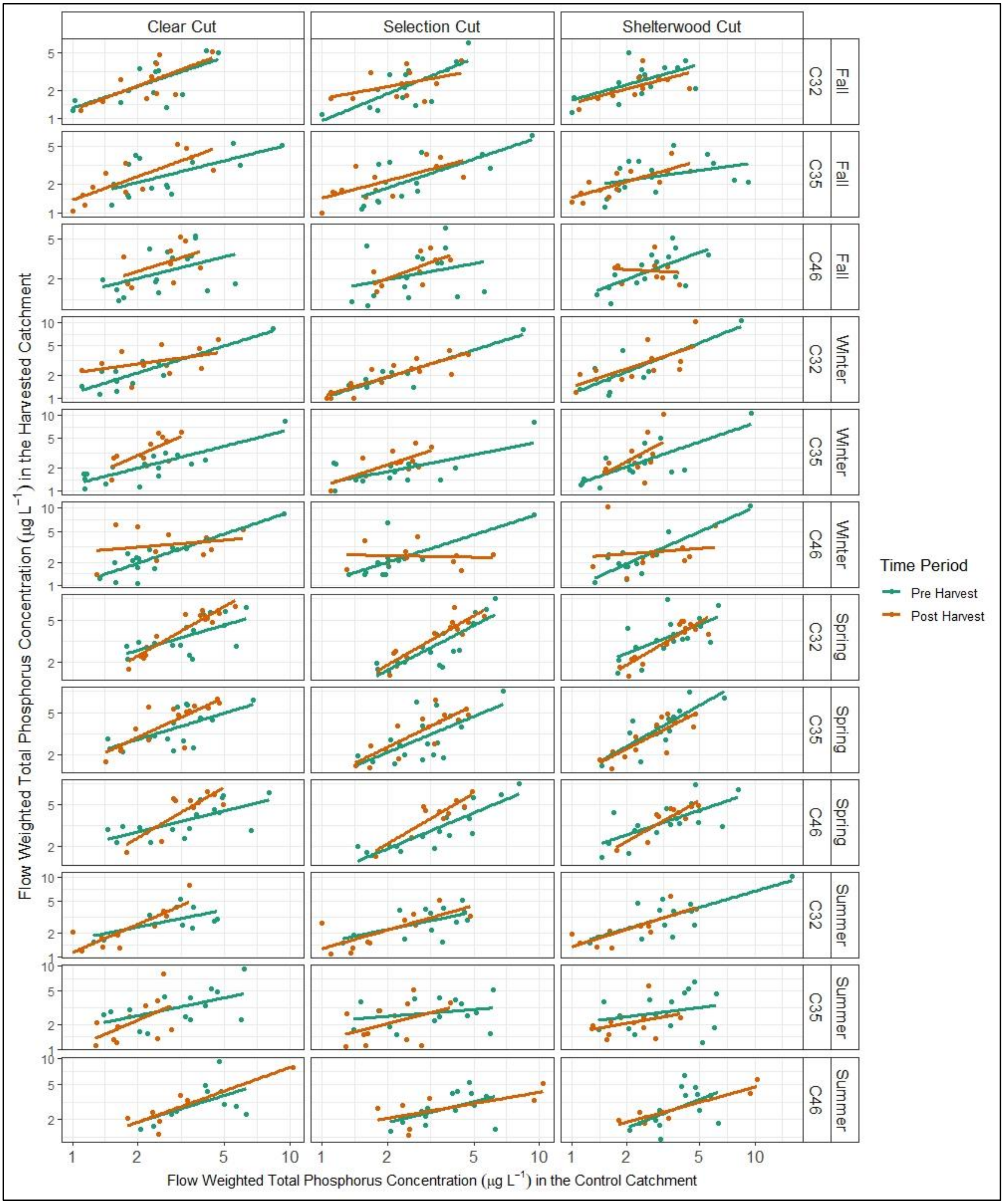

Figure A2 Linear regression relationships pre and post harvest between control and harvested catchments for individual seasons for flow weighted total phosphorus concentration (μg L^{-1}).

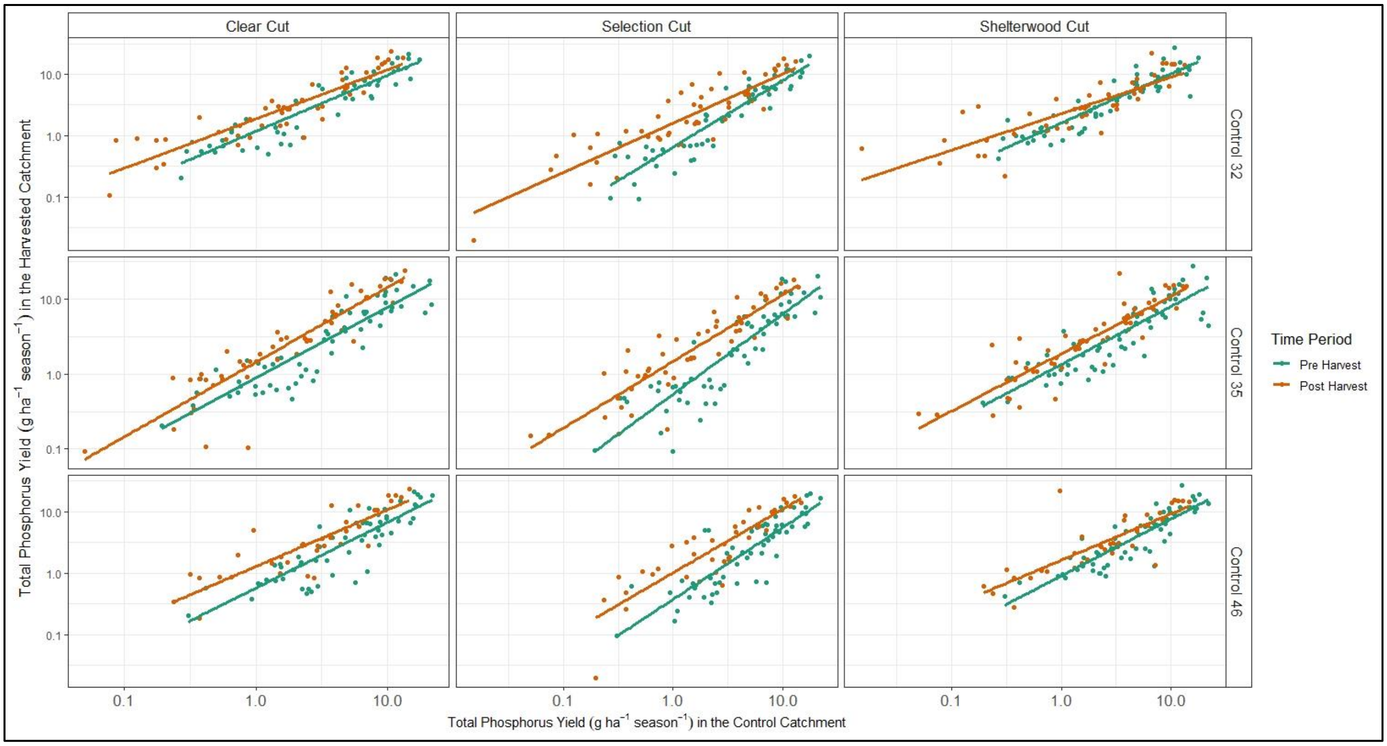

Figure A3 Linear regression relationships pre and post harvest between control and harvested catchments across all seasons for total phosphorus yield (g ha^{-1} season^{-1}).

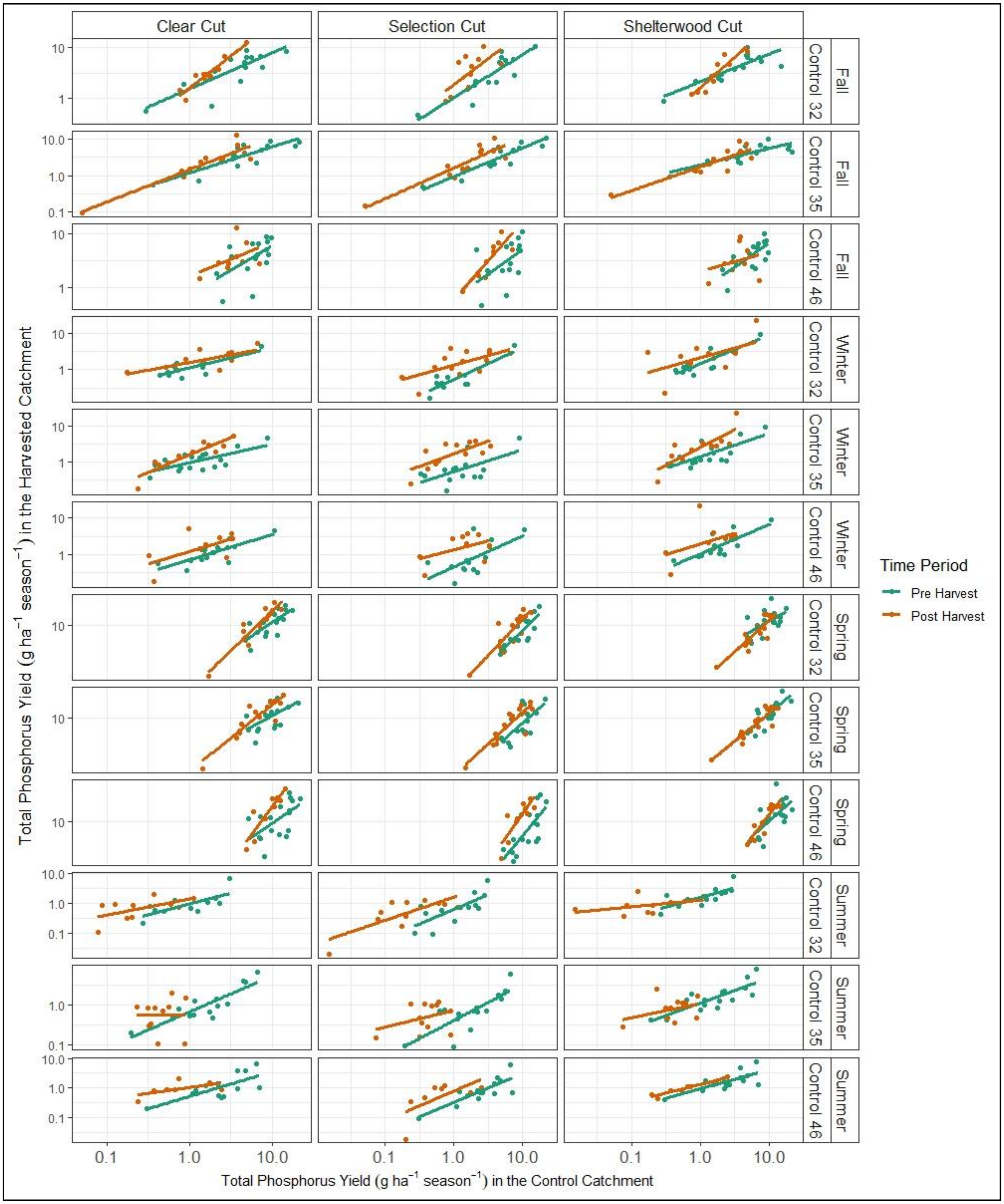

Figure A4 Linear regression relationships pre and post harvest between control and harvested catchments for individual seasons for total phosphorus yield (g ha^{-1} season^{-1}).

Appendix B Supplementary Material for Chapter 3

Figure B1 Images of field sites at TLW A) watershed divide in C32 B) hillslope in C32 before leaf out C) wetland in C32 during Fall D) wetland in C31 during Spring E) hillslope in C32 near weir F) stream channel in C32 before snowmelt.

A

B

C

D

E

F

Figure B2 Images of field equipment used in TLW: A) shows two lysimeter pits in C32 B) throughfall collector in C31, C) mineral soil zero tension lysimeter during instillation, D) ISCO automated sampler being programed E) mineral soil zero tension lysimeter before instillation, F) peristaltic pump collecting groundwater.

Figure B3 Images of laboratory set up in the Great Lakes Forestry Centre: A) water sample splitting apparatus that filters water samples from field bottles to laboratory bottles, B) water sample laboratory bottles.

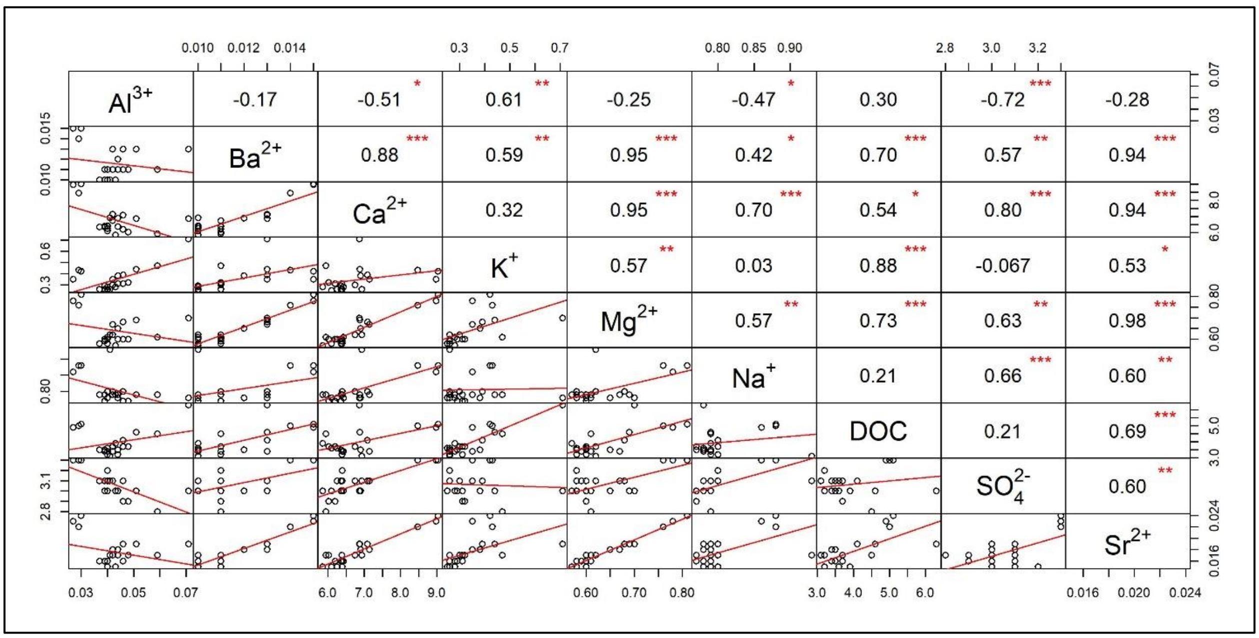

Figure B4: Bivariate plot for the clear-cut during the Fall. Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

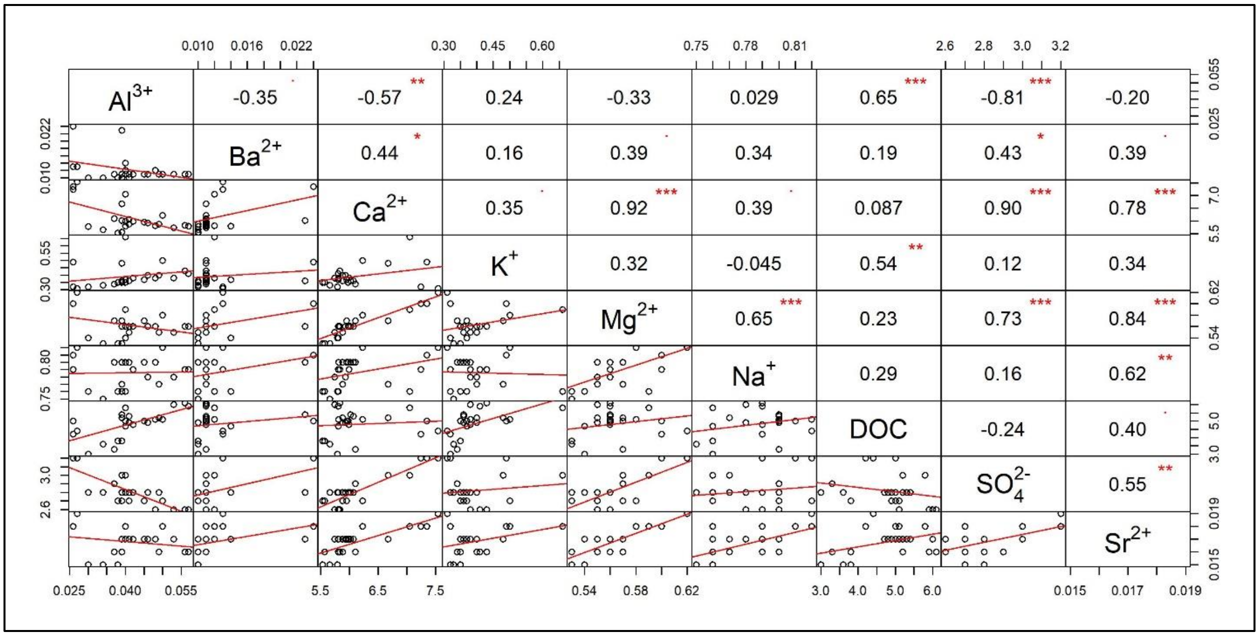

Figure B5: Bivariate plot for the clear-cut during storm 1 Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

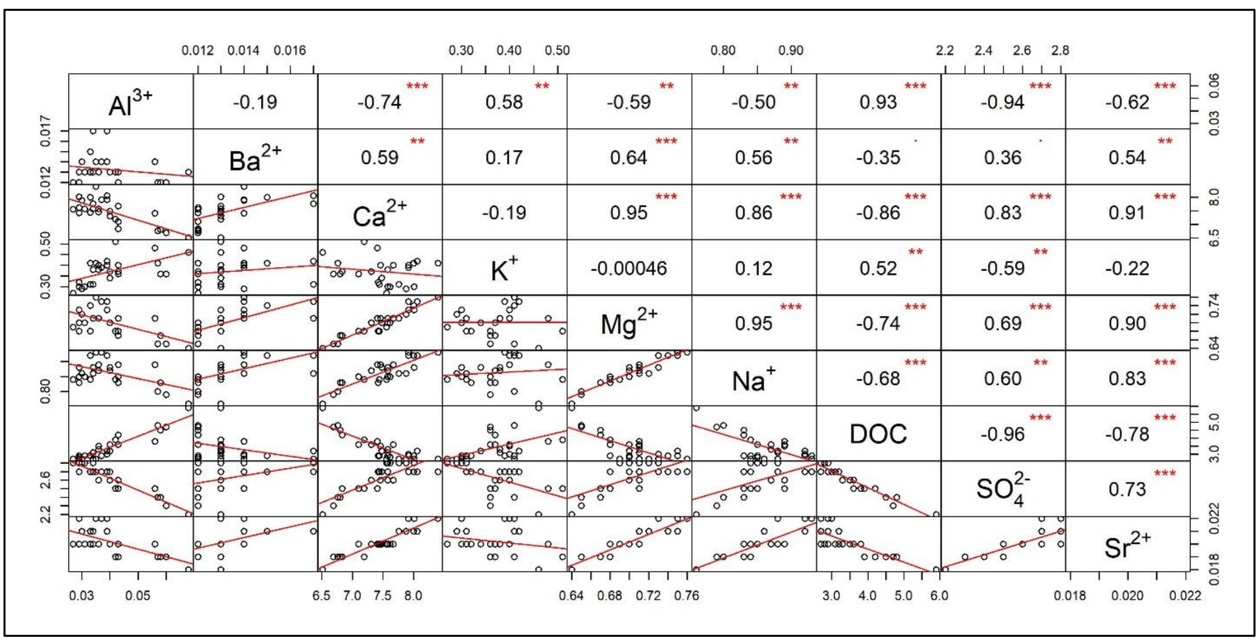

Figure B6: Bivariate plot for the clear-cut during storm 4 Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

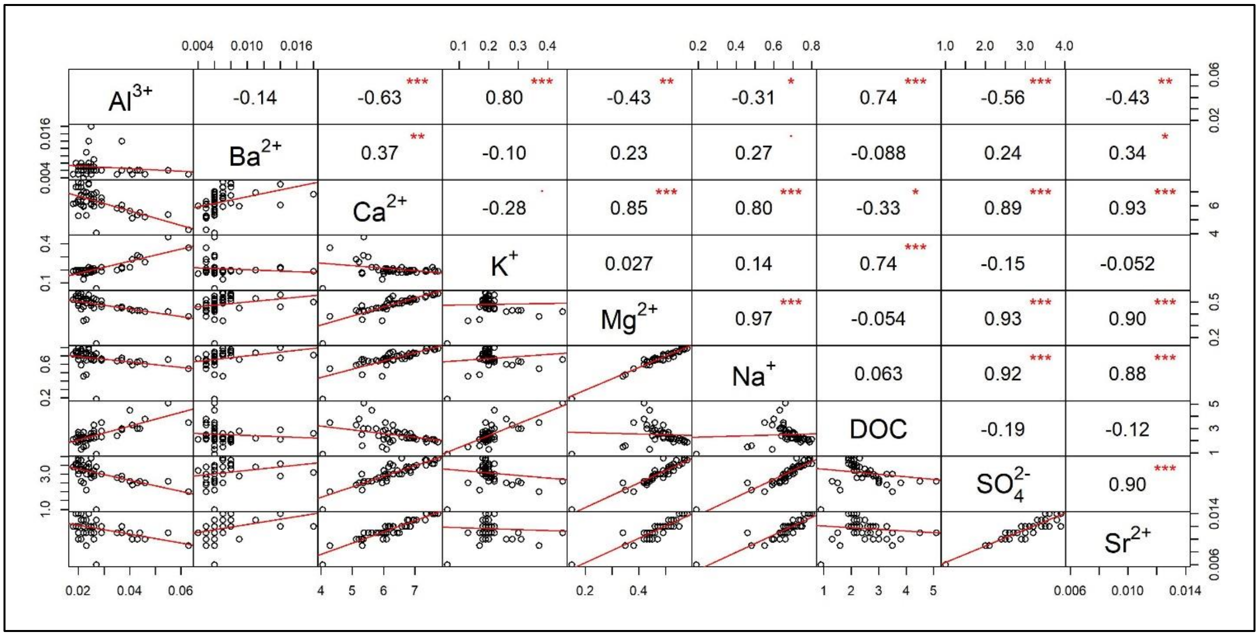

Figure B7: Bivariate plot for the control during snowmelt Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

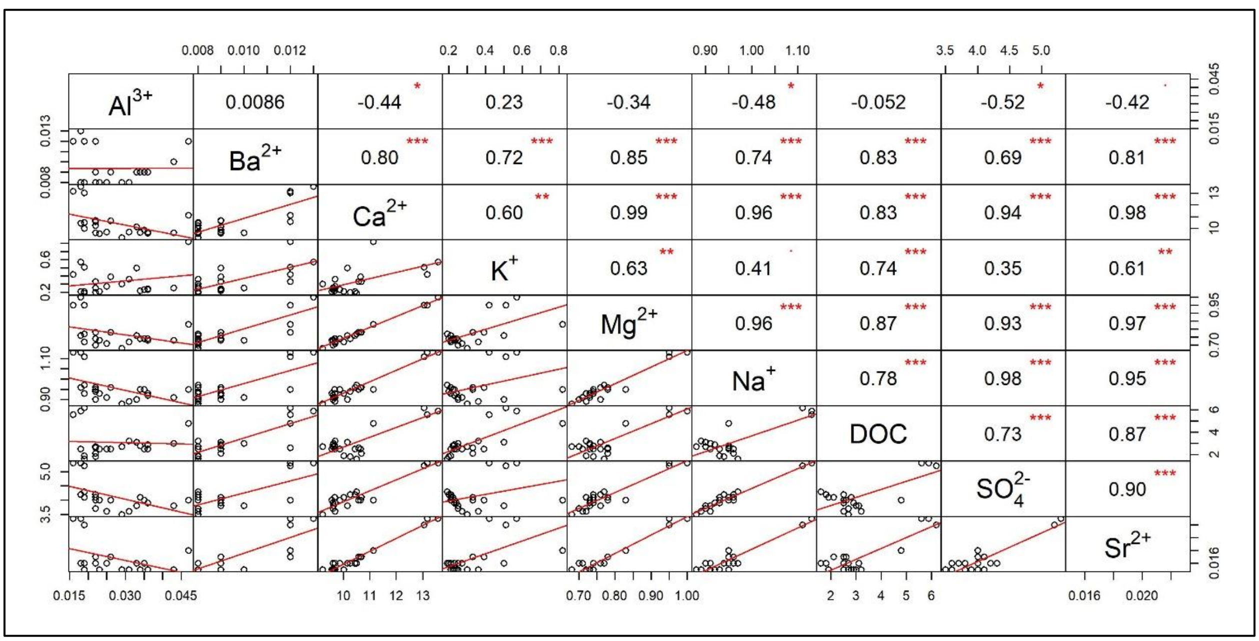

Figure B8: Bivariate plot for the control during the Fall Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

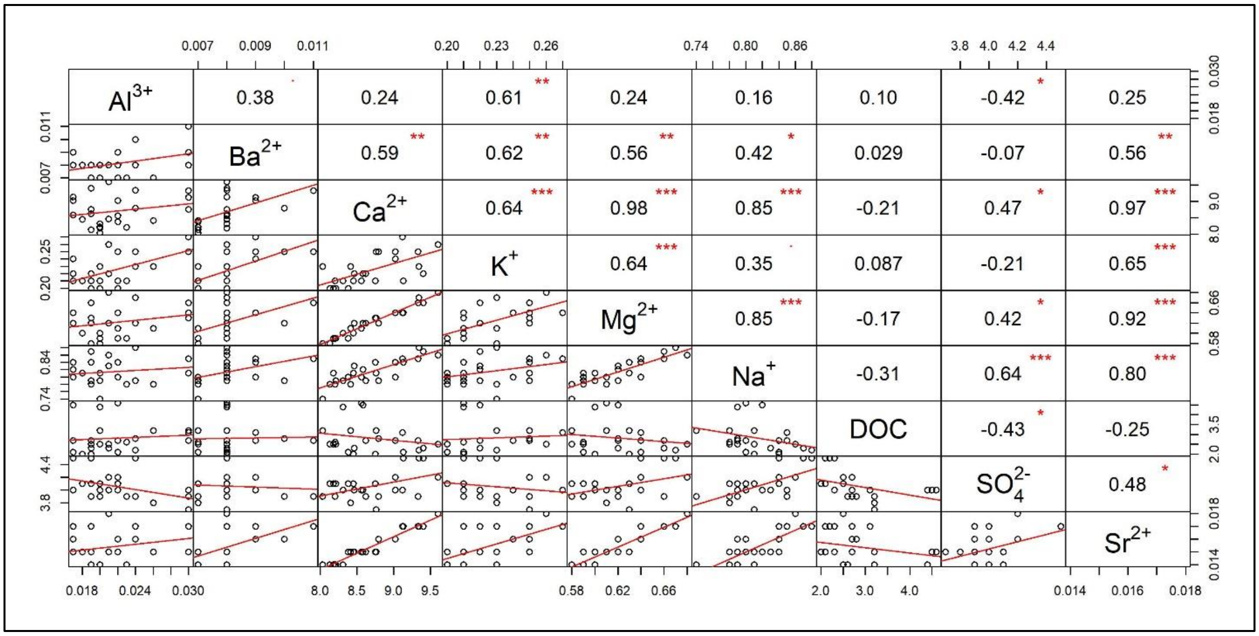

Figure B9: Bivariate plot for the control during storm 1 Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

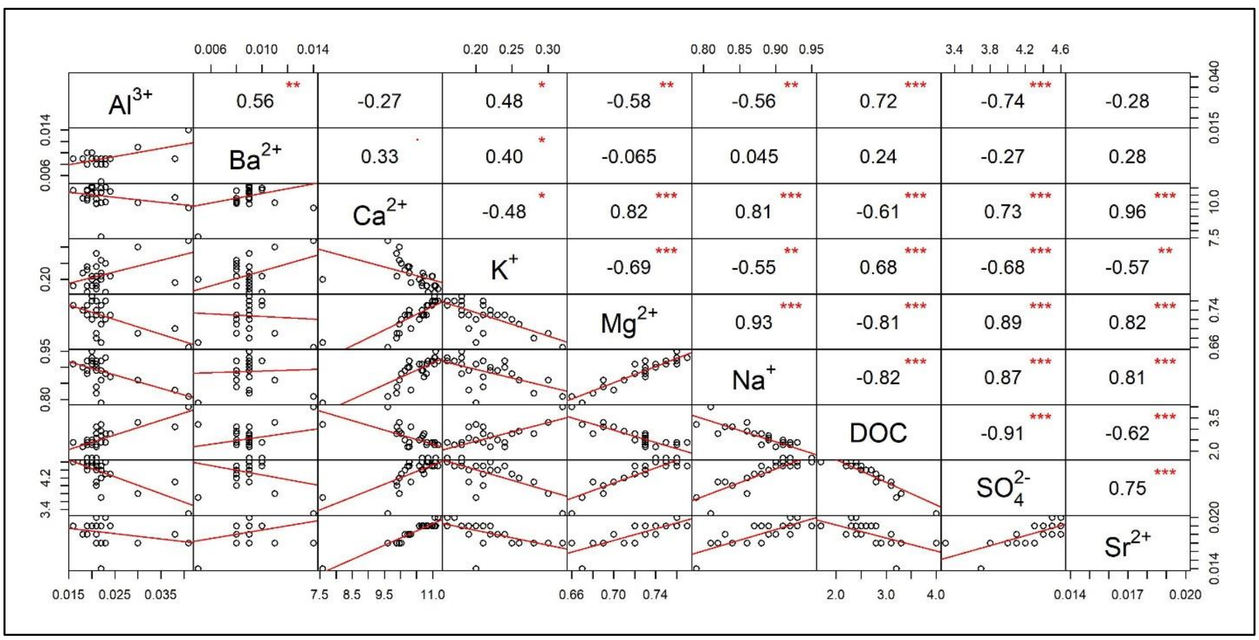

Figure B10: Bivariate plot for the control during storm 4 Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

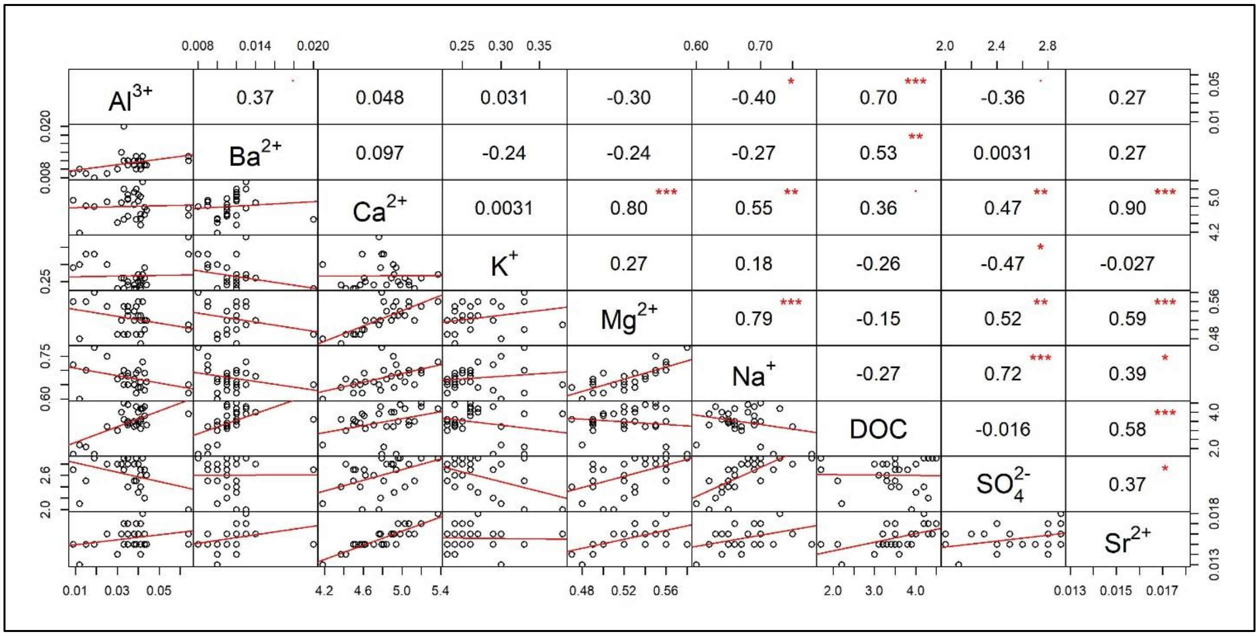

Figure B11: Bivariate plot for the clear-cut wetland during snowmelt Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

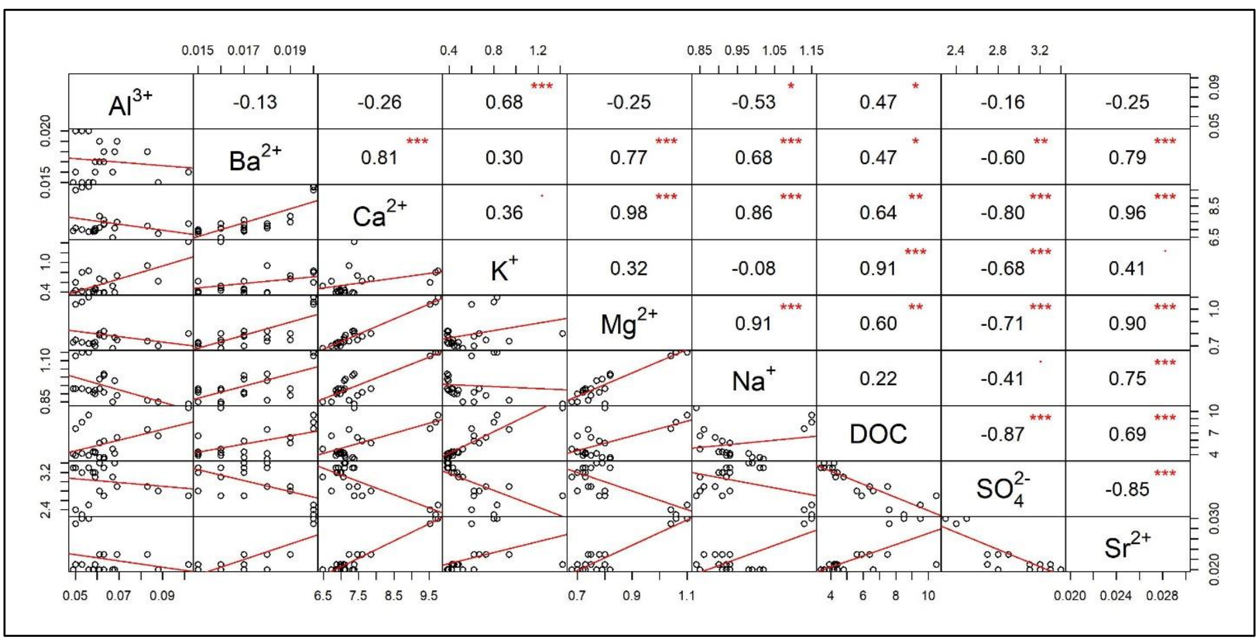

Figure B12: Bivariate plot for the clear-cut wetland during the Fall Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

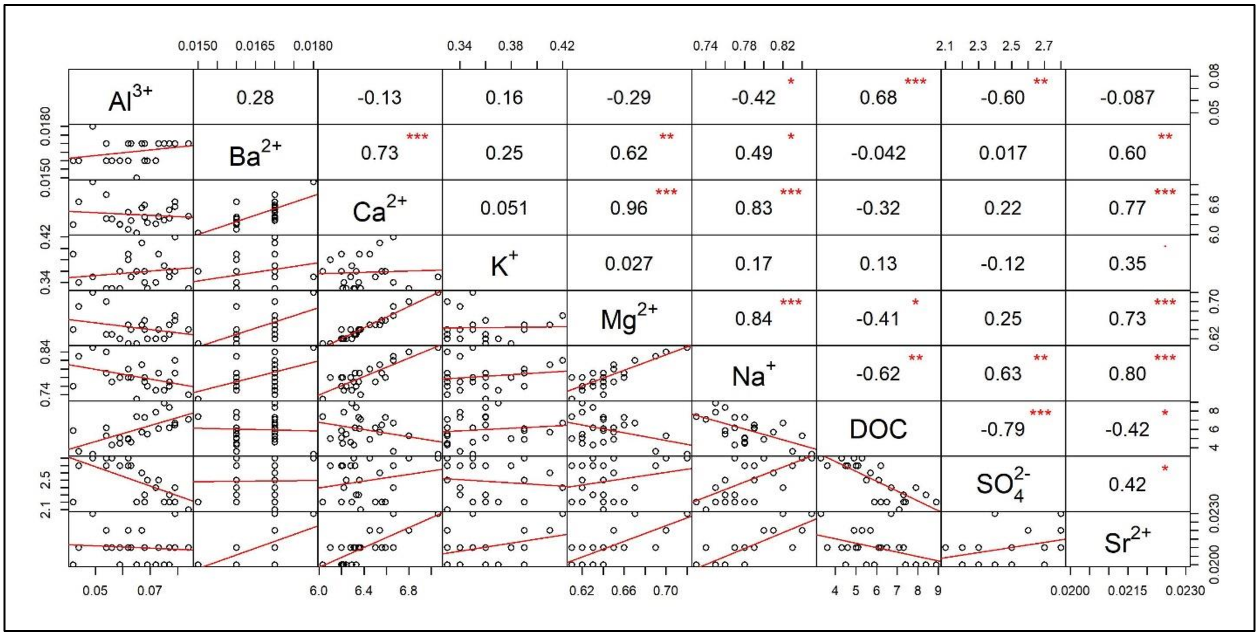

Figure B13: Bivariate plot for the clear-cut wetland during storm 1 Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

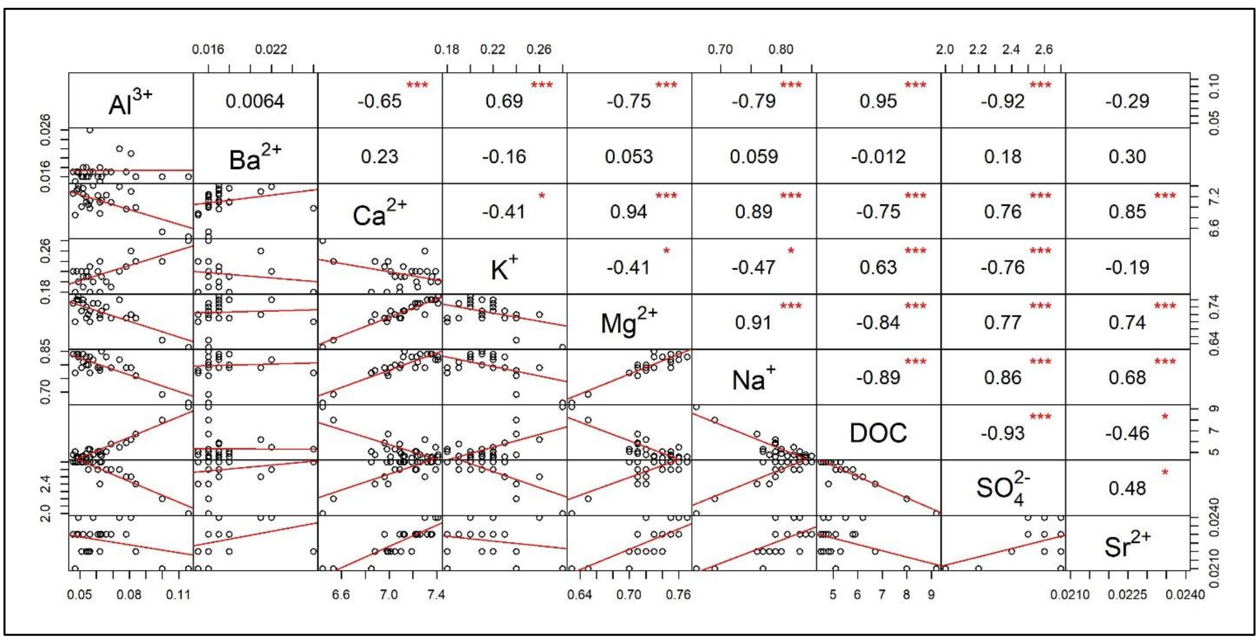

Figure B14: Bivariate plot for the clear-cut wetland during storm 4. Top right of the plot represents the Pearson's correlation coefficient and level of significance (p ≤ 0.05, ** p ≤ 0.01, *** p ≤ 0.001, **** p ≤ 0.0001) for the linear relationships between each tracer. Red line shows the line of best fit using linear regression.*

Appendix C Supplementary Material for Chapter 4

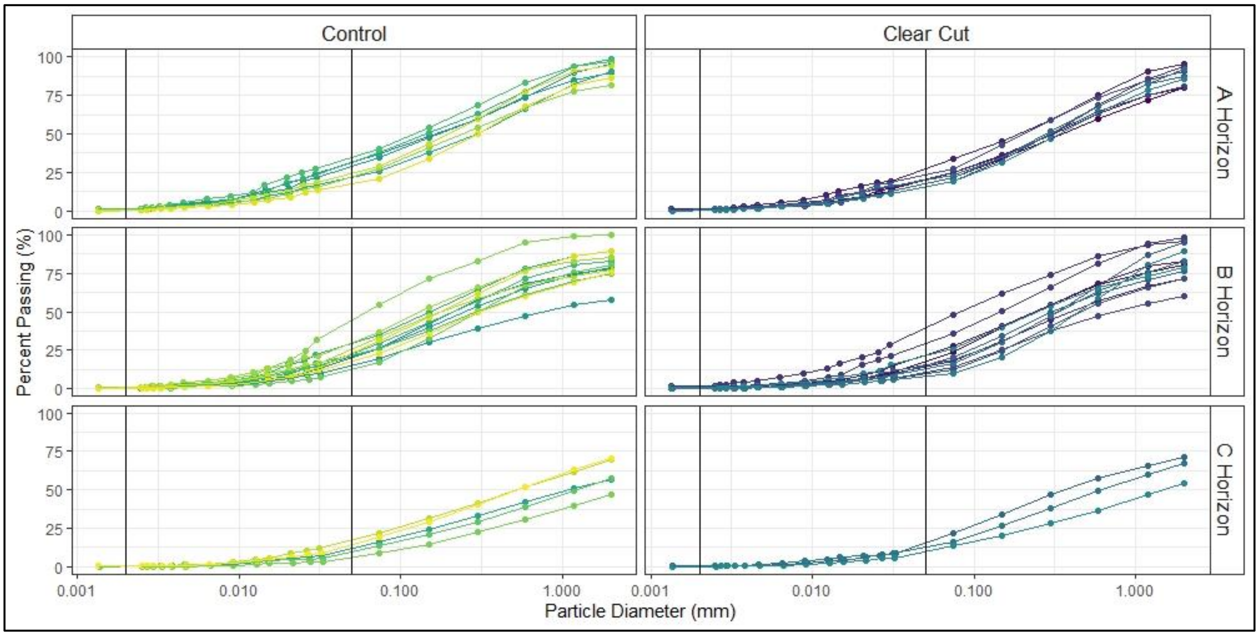

Figure C1 Particle size distribution of soils in the A, B and C horizon in the control and clear-cut catchments. Colours represent different soil pits samples from each catchment.