University of Alberta

Natural Variation and Short-term Impact of Aspen Harvesting on Surface Stream Chemistry in the Boreal Plains

by

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Abstract

This thesis describes the natural variation and influence of aspen harvesting on stream chemical concentration and flow-weighted export from catchments typical of the Western Boreal Plain, Alberta, Canada. The catchment stream discharge and stream chemical concentrations presented are taken from a subset of a five-year paired catchment (2005-2010) HEAD2 NSERC-CRD study. Nutrients, major anions, major cations and two minor ions were monitored from second-order streams draining a 18.3 km^2 reference catchment (R1) and compared to a 9.9 km^2 experimental catchment (H1) for two years of pre-harvesting (2005-2006) and two years of sequential harvesting (2007-2008). Preliminary analyses showed that non-harvest high flows had a total average instantaneous export greater than 10 times that of low flows. Summer storms and beaver dam breakages had stream export equivalent to or greater than spring melt. Intensive upland aspen harvesting showed no significant differences in major cation and anion export post-harvest with the exception of increased SO_4^{2-} .

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Introduction

1.1 Background

A decade ago the focus of hydrological research and modeling was on the Boreal Shield and mountainous terrain (Buttle et al., 2000). Few studies examined the Boreal Plains, even though they comprise more than a quarter of Canada's ecoregions and cross three provinces. The differences in climate, relief and geology between Boreal Shield and Boreal Plains can change the dominant hydrological processes responsible for water quantity and quality (Buttle et al., 2000). Unlike the Boreal Shield, the Boreal Plains are a heterogeneous mixture of both weather and geology; each is important for hydrology and biogeochemistry. The underlying assumptions driving the modeling of hydrological processes, such as an impermeable layer that mimics topography, or the connectivity between uplands and water bodies, must be carefully chosen based on study across ecoregions. Indeed, Creed and Band (1998) note that export patterns based upon topography work only in areas with homogeneous climate, forest and soil cover. They suggest that regionalization of hydrological processes is difficult, if not impossible, in an area of high natural variability such as the Boreal Plains. Upon examination of the ecoregions and the assumptions inherent in past studies, Buttle et al. (2000) suggested that future research should focus upon the Boreal Plains.

Since the beginning of the new millennium, more studies have been done on the Boreal Plains regarding climate, run-off, snow melt, stream contributions, soil moisture, chemistry and connectivity (Buttle et al., 2005; Price et al., 2005). These studies have begun to address the processes inherent in the hydrology and biogeochemistry of the Western Boreal Plains (WBP). McEachern et al. (2006) examined sloped and low-lying catchment stream chemistry in northern boreal Alberta to describe the hydrologic processes. They suggested that lowland catchments stored snowmelt in the spring that was then discharged about equally with older groundwater in the summer. They also suggested that groundwater routed through organic soils dominated the summer low-flow in streams of lowland catchments (McEachern et al., 2006). The Terrestrial and Riparian Organisms, Lakes and Streams (TROLS) program examined lake chemistry pre- and post-harvest in the Boreal Plains and suggested that although harvesting may increase total phosphorus and cyanobacteria in lakes (Prepas et al., 2001), the amount of total phosphorus was most strongly correlated to lake position, connections to wetlands (Devito et al., 2000) and weather (Prepas et al., 2001). All the aforementioned authors agree that the hydrogeology of the Boreal Plains is complex and that the controls of surface water chemistry are inadequately understood. Without knowledge of the natural variation in stream concentration and export, measures of human disturbance could be erroneously based upon previous studies performed in areas with completely different hydrology and biogeochemistry. This could seriously impact the management of the Boreal Plain ecosystem. To address this problem, this study will describe the natural variation in stream chemistry concentration and chemical export of two typical WBP streams.

Recent studies reflect the rapid development of the Boreal Plains for forestry, mining, oil and gas extraction and recreation (AEP, 1998; Ducks Unlimited Canada, 2008). This expanding land use has the potential to impact water quality in the numerous streams running through the land (Feller, 2005) in both the short and long term. Oil and gas companies are concerned with developing the land into a sustainable ecosystem. Flow variability creates concern for erosion during high-flow and biological sustainability during low-flow. Stream nutrients are also of concern for forestry, agriculture and recreational managers since eutrophication of water bodies often occurs from the transport of nitrates and phosphates into the stream, which results in algae blooms and increased cyanobacteria. Stream water export is an essential tool for studying these concerns. Stream export can be used to determine a catchment's loss or retention of nutrients, which can impact the health of that ecosystem. At the same time it also acts as a source of necessary nutrients or toxins to receiving water bodies.

Stream water composition in the Boreal Plains is the end result of complex hydrological processes that occur in a heterogeneous landscape (Gibson et al., 2002; Price et al., 2005). Climate, soil properties and vegetation all act to influence the dominant role that flowpath, biochemical transformations and source areas have on the chemistry of stream water (Devito et al., 2005a). This study will examine the impact of harvesting on the hydrology and biogeochemistry of catchments to determine the likely change in export—caused by such harvesting—that can be expected in WBP streams.

1.1.1 Harvesting in the Western Boreal Plain

Upland harvesting is not new. Forestry companies have harvested upland areas throughout the Boreal Shield and mountains on the west and east coasts of Canada for decades. Studies have shown that, outside the WBP, harvesting uplands increases stream chemical export because of increases in infiltration, decomposition, transformations and water export from the catchment (Feller, 2005). When considering the WBP, the literature suggests that several different hypotheses predicting changes in stream chemical export caused by upland harvesting are possible. The scenarios that follow present three hypotheses and predictions. Testing these hypotheses is the motivation for the question addressed by this thesis (see section 1.2).

Scenario 1: Harvesting trees can increase infiltration due to decreased interception and evapotranspiration. Snow interception is controlled by leaf area and snowfall (Buttle et al., 2000). Harvesting the trees decreases the leaf area. Winkler (2001) found that the snow water equivalent (SWE) and daily melt rates increased in clear-cut areas compared to forested areas. Murray and Buttle (2003) confirmed these observations: clear-cuts accumulated more snow and the snow melted faster than in forested areas. Snow cover in cuts was twice that of mature boreal forest and, because the insulating properties of snow allow easier soil thaw, snow-melt was about three times faster (Pomeroy et al., 1997). Soil moisture increased in a clear-cut in British Columbia (Elliot et al., 1998), possibly due to decreased interception and decreased evapotranspiration losses. Too much soil moisture may delay regeneration and limit reforestation (Elliot et al., 1998; Roy et al., 1997). In general, cut-blocks were able to store more soil water (Buttle et al., 2000), although Pomeroy et al. (1997) discovered that this soil water was usually stored below the root level of the immature regenerating forest. Because of this increase in soil moisture, upland saturation can occur more frequently. This causes increased export from the catchment due to an increase in the quantity of run-off, especially in high-intensity events such as spring melt.

Increased soil moisture and radiation can also impact transformation and decomposition rates in upland soils. Transformations caused by vegetative loss, uptake and decomposition, as well as microbial action, frequently occur as a result of harvesting. Micro-organisms increase dissolved nutrients by changing chemical species into more mobile forms that can be flushed into the stream (Creed et al., 1996; Hornberger et al., 1994). Increases in net nitrification and net mineralization have been reported as effects of harvesting (Carmosini et al., 2003; Likens et al., 2002; Martin and Hornbeck, 2000); however Westbrook et al. (2006) reported no difference in soil-dissolved organic N mobilization rates between harvested and forested areas on the Boreal Shield. At Hubbard Brook, increased nitrification led to acidification of the soil, which mobilized base cations (Martin and Hornbeck, 2000) and enhanced SO_4^{2-} adsorption to mineral soil (Likens et al., 2002). Kauffman et al. (2003) determined that Cl^- was leaching from soil/root/organic fractions; they attributed this to decaying roots and litter. Increases in the concentration of K^+ , Ca^{2+} and Cl^- in soil and stream water because of increased decomposition of litter and branches and decreased vegetative uptake have also been reported (Carignan et al., 2000; Martin and Hornbeck, 2000; Watmough and Dillon, 2003).

Flowpath was the dominant process in studies on the Canadian Shield because of the humid climate, minimal amounts of soil storage and a topography that mimics the bedrock. The increase in stream water, with harvesting, of DOC, N, K^+ ,

Ca^{2+} and P is often attributed to the flowpath shifting from subsurface to surface organic layers (Carignan et al., 2000; Duchesne and Houle, 2006; Semkin et al., 2002; Ukonmaanaho and Starr, 2002).

Hypothesis 1: It could be suggested that, with the removal of upland aspen from WBP catchments, decreased interception and evapotranspiration along with increased infiltration might increase soil moisture in the upland. Soil could become saturated; upland depressions might fill up and overflow, connecting down the slope along surface organic layers to the stream. With increased soil moisture, increased transformations and decomposition could occur as well, carrying more nutrients to the stream. In such a case, it would be expected that chemical export of DOC, Ca^{2+} , Cl^- , K^+ , total nitrogen and total phosphorus would increase with harvesting.

Scenario 2: In the Boreal Plains, the climate and deep heterogeneous geology may prevent this first scenario from occurring. The WBP are located in a sub-humid ecoregion where, on average, precipitation is approximately equal to potential evapotranspiration, with slight precipitation deficits most years (Devito et al., 2005b). Precipitation and evapotranspiration dominate water budgets (Ferone and Devito, 2004) and have a simultaneously annual peak during late summer storms (Devito et al., 2005b). Thus the time of the year with the most available water is also the time of the year with the most demand for it. In addition, the timing of WBP precipitation means that spring melt is often minor; recent studies (Redding and Devito, 2008) have indicated that soil freeze in the WBP is permeable enough for infiltration to occur more often than surface run-off. The ratio and timing of precipitation thus impacts soil moisture, soil storage and the transport of ions in both run-off and subsurface flow.

The WBP are composed of a heterogeneous mixture of sand, silt and clay deposited by receding glaciers. Deep glacial deposits occur throughout the landscape of the Boreal Plains. Uplands can be composed of silty sand >10 m in depth. Coarse grained materials are responsible for catchment recharge and base-flow. Fine-grained materials have little or no run-off because of a large amount of soil and depression storage. Indeed, Devito et al. (2005b) determined that the water balance in the WBP is dominated by soil storage, evapotranspiration and vertical recharge. They concluded that significantly large run-off would occur once every 20 years, approximately, when the uplands, draws and wetlands became connected. (Usually the uplands are disconnected from the stream.) Redding and Devito (2008) verified that lateral flow in forested uplands would occur only after soils were wetted to $>$0.75 m deep and rainfall $>$15-20 mm fell in a storm. The frequency of such an event is low. For the uplands to connect to the streams, the upland soil storage would need to be filled, and then any depression storage capacity exceeded as well. Hence upland depressions may reflect local changes in flow well before, if ever, streams do.

Hypothesis 2: It could be alternatively suggested that, with the removal of upland aspen from WBP catchments, decreased interception and evapotranspiration, along with increased infiltration, may increase the vertical recharge and sub-surface mineral flow of the uplands to the stream. There would be increased export from the stream, but it would occur through the mineral sub-surface rather than the surface organic flowpath. This could change the expected ion export, since mineral layers can increase or decrease concentrations of ions. For example, Na^+ and Cl^- concentrations can increase in water moving through clay or moraine soils whereas SO_4^{2-} and phosphorus can decrease with water passage through mineral soils. P solubility is decreased with Ca^{2+} - and Fe^{2+} - rich soils (Macrae et al., 2005). SO_4^{2-} adsorbs to Al and Fe^{2+} hydroxides in mineral soils (Ukonmaanaho and Starr, 2002), and sorption is enhanced with decreasing pH (Likens et al., 2002; Martin and Hornbeck, 2000). Phosphorus solubility and mobility in groundwater can be controlled by redox conditions (Price et al., 2005). Phosphorus concentrations can also be controlled by the pH of the surrounding environment. In addition, the longer the flowpath, the more likely it is that salts will dissolve into the water (Toth, 1999). This is especially true in geology with more recent deposits of heterogeneous material, such as the WBP. Although increased decomposition and transformations may occur in the upland as well, the WBP soil has a high physical and chemical buffering capacity that prevents DOC and phosphorus from moving very far from the source (Macrae et al., 2005). Therefore it would be likely that with upland aspen harvesting, the WBP stream would increase in Ca^{2+} , Cl^- , K^+ and total nitrogen export, but that DOC and phosphorus export would remain unchanged or decrease slightly because of adsorption to the mineral soil.

Scenario 3: Both of the previous hypotheses depend on the uplands connecting to the stream in order to increase stream export. Alternatively, the WBP climate and large upland soil storage, combined with clonal aspen regeneration, may serve to disconnect uplands from the stream, and so prevent any response to harvesting. Indeed, by using isotopes to evaluate evaporation, throughflow, residence time and run-off, Gibson (2001) and Gibson et al. (2002) found that forest disturbance didn't change the run-off/precipitation ratios. Kalef (2002) found that harvesting upland aspen had limited effects on run-off and N production in a groundwater-fed wetland basin. Devito et al. (2005b) emphasized the importance of small variations in soil storage restricting connectivity and masking the influence of harvesting on water and nutrient flow. However, Kalef (2002) did not compare the experimental catchment to a reference catchment and Devito et al. (2005b) did not have data for conditions before harvesting. Although these previous studies imply that soil storage or groundwater interactions might mask any effects of harvesting on stream chemistry, there is a need to compare pre-harvest and post-harvest conditions between reference and experimental catchments.

Even with upland connection to the stream occurring only during extreme wet periods (Devito et al., 2005b), there may not be a change in upland soil chemistry that is communicated to the stream. Aspen is a fast growing clonal tree used increasingly in the pulp and paper industry. Aspen and balsam poplar, common to the Boreal Plains, use their existing root systems to regenerate and are therefore able to access any excess soil water generated from decreased interception and increased infiltration (Buttle et al., 2000). If trees are harvested with minimal soil compaction, their root networks remain intact and continue to function. Suckers appear quickly and within two growing seasons regain >60% leaf area index (LAI) (Devito, unpublished data). The window in which increased infiltration, increased decomposition and decreased uptake occur on an aspen upland is very small. Macrae et al. (2005) found no difference in soil moisture between reference and harvested uplands in the Boreal Plains.

Biologically available ions such as NO_3^- continue to be in demand and may not be available for transport because harvested aspens have an intact root system and regenerate quickly. Jerabkova and Prescott (2007) examined the hypothesis that clear cutting changes the soil environment from NH_4^+ dominated to NO_3^- dominated. They determined that clear-cutting and aspen growth did not change the soil composition and that NH_4^+ was the predominant form of N in Boreal soil. Also, Macrae et al. (2006) determined that there was no difference between reference and harvested catchments in the WBP for NH_4^+ or NO_3^- concentrations in surface run-off. Indeed, they suggested that topography, although subtle, controlled the soil concentrations of NH_4^+ and NO_3^- in the WBP. They found that after harvesting, there was no impact on soil NO_3^- concentrations in the aspen uplands. Studies suggest that although there is more NH_4^+ available in the aspen uplands after harvesting, there is also more NH_4^+ used in immobilization and aspen regeneration, thus preventing any change to surface run-off (Carmosini et al., 2002; Macrae et al., 2006).

Not only could stream export remain unchanged by harvesting because of disconnect with the upland, but it could also be masked by natural variability. Stream export may be dominated by the connection and disconnection of specific sources to the stream. Devito et al. (2005b) discovered that run-off in the Boreal Plains came primarily from ephemeral draws and wetlands. McDonnell (2003) and Gibson et al. (2002) found that run-off could be generated from very specific sources such as wetlands and ephemeral draws. Wetlands and ephemeral draws contained the majority of the catchment's available NO_3^- (Macrae et al., 2006). Even with intensive upland harvesting, stream chemistry may be dominated by ephemeral and wetland sources that prevent a measurable response — especially in nutrient concentrations.

Nutrient export may also be masked by dominating in-stream transformations. Hill (1982) emphasized that in-stream transformations could cause SRP to decrease and K^+ and Na^+ to increase along a stream reach. In addition, the Boreal Plains are rife with beavers (*Castor canadensis*) and successive beaver dams along the streams are a common occurrence. Margolis et al. (2001) found that dissolved NO_2^-+NO_3^- , SO_4^{2-} and Fe^{2+} decreased but pH, DOC and dissolved NH_4^+ increased downstream of a beaver dam. The in-stream transformations may be the dominant factor controlling aspects of stream chemistry (such as nitrogen); these may mask any changes coming from the uplands that are caused by harvesting. In addition to the effects of wetland sources or in-stream transformations, sensitivity to climate changes could also mask any changes in stream export due to harvesting. Paterson et al. (1998) and Schindler (1998) suggested that climate change may outweigh the consequences of harvesting.

Hypothesis 3: WBP surface stream chemical export may not change with upland aspen harvesting because of either masking or disconnect with the upland. The effects of wetlands and ephemeral draws along with in-stream transformations may dominate the natural variability of stream export, obscuring any changes to upland sources. In addition, changes to upland sources caused by harvesting may not be noticeable simply because of disconnect with the stream. Either of these cases would prevent stream chemical export from increasing after upland harvesting.

Keeping these scenarios in mind, this thesis will strive to describe the natural variation in WBP stream chemical export and test whether upland aspen harvesting increases that export.

1.2 Study Question and Hypotheses

HEAD2 NSERC-CRD is a large, multi-investigator project examining meteorology, hydrology, biogeochemistry and modeling within the scope of upland aspen harvesting on the WBP. This thesis research is part of the HEAD2 NSERC-CRD project and examines the biogeochemistry of streams before and after harvesting in order to answer the following questions:

> *What is the natural variation in stream chemical export from WBP catchments and does upland aspen harvesting increase that chemical export?*

The natural variation in stream chemical export is expected to be large interannually because of the varying connectivity of wetlands and ephemeral draws to the streams caused by climate and antecedent moisture conditions. This varying connectivity may result in “pulses” of nutrients into the streams because of water table draw-down and subsequent flushing. It is expected that summer export of major cations and anions may be greater than that from spring melt annually because of intensive summer storms, but that nutrient export will continue to be greatest during spring melt due to the lack of vegetative activity during the preceding fall and winter.

To summarize the scenarios discussed in section 1.1: The primary hypothesis is that chemical export will increase with upland aspen harvesting. Stream chemical export is a function of the connectivity of uplands and wetlands to the stream. Harvesting can decrease interception and transpiration and with increased infiltration can cause increasing soil moisture and decreasing soil storage and can increase the connectivity of the uplands to the stream. Upland changes in moisture and radiation may cause transformational changes that are communicated to the stream through the increased connectivity. Wetter conditions along with increased radiation will increase decomposition, increasing the mobilization and potential export of DOC, N, K^+ , P, Cl^- and Ca^{2+} if the flowpath runs through the surface organic layer.

The second hypothesis—that the flowpath from the uplands runs through the sub-surface mineral layer—suggests that increases in N, K^+ , Cl^- and Ca^{2+} export will still be seen but DOC and P will continue to be adsorbed by the mineral soil and will remain unchanged (Figure 1.1).

The third hypothesis is that there may be no change at all in stream chemical export with upland harvesting. There may be no transformational changes in the uplands of the Boreal Plains caused by harvesting because of the sub-humid climate, large soil storage and rapid aspen regeneration. However, even if transformational changes occur, those changes may not be communicated to the stream because of upland disconnect. In addition, wetlands or in-stream transformations caused by beaver activity may dominate the stream's chemical export, masking any changes in upland sources (Figure 1.1). All these conditions would preclude any change in stream chemical export caused by upland aspen harvesting.

The objectives of this thesis are 1) to describe the natural variation in stream chemical concentrations and export and 2) to test if upland aspen harvesting impacts stream chemical concentrations and export.

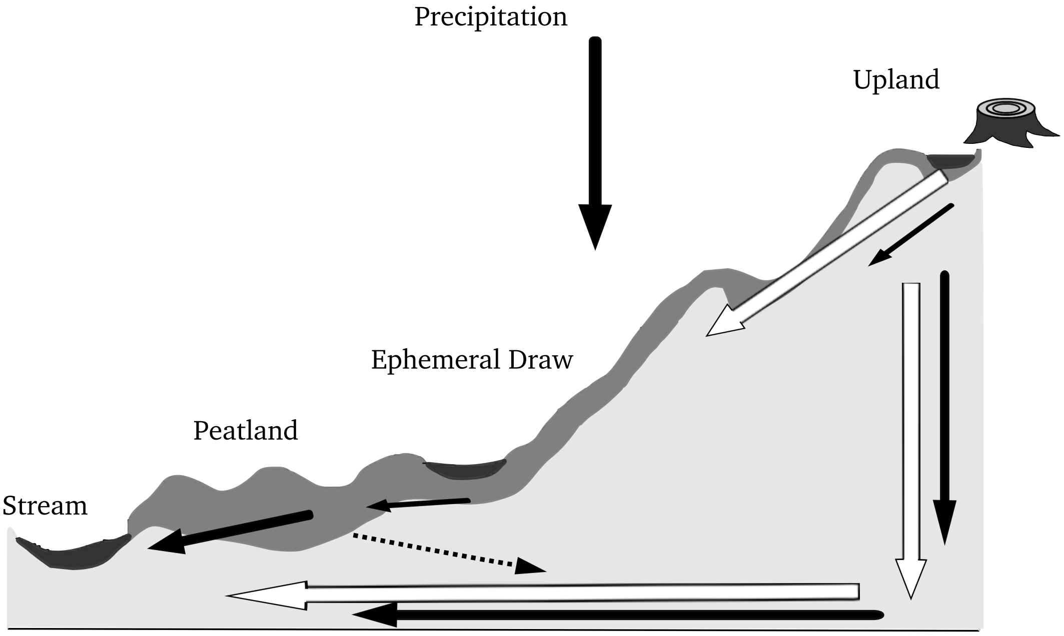

Figure 1.1: Hypotheses when upland aspen harvesting occurs on WBP catchments. The white arrows indicate the first and second hypotheses: that upland soil storage fills, causing greater surface and sub-surface connections to the stream, thereby increasing the export of certain ions (Ca^{2+} , K^{+} , Cl^{-} , N). The black arrows indicate the third hypothesis: that the stream export—water flow and chemical transport—remains unchanged. This is because the upland soil stores any excess moisture, which may not be great since the rapid regeneration of aspen occurs simultaneously with the majority of annual precipitation. This prevents large run-off from occurring at the surface or in the sub-surface organic layer.

1.3 Experimental Design

1.3.1 Paired Catchment Approach

A paired catchment approach, in conjunction with pre-harvest and post-harvest analysis, was designed as part of the five-year HEAD2 NSERC-CRD project. The AlPac Catchment Experiment (ACE) was selected because it was a regional high, had a heterogeneous landscape that included several different landforms, and was relatively undisturbed by human impact (the closest agriculture is $>$20 km away). Catchments were delineated by topography and wetland networks and include two large (R1: 18.3, H1: 9.9 km^2) with continuous outflows, and three smaller catchments (R2: 1.0, H2: 2.1, H3: 0.6 km^2) with discontinuous outflows (Figure **??**). This study examined the export from the two large catchments (R1 and H1). It utilized data collected from 2005 to 2008 across four field seasons of a five-year project. The harvesting occurred during non-snowfall accumulation periods; this maximized the impact harvesting might have on soil structure and thus infiltration, run-off and hydrological connectivity. Monitoring began on the outflow of H1 and R1 in the spring of 2005. Harvesting of H1 began in July, 2007 (Table 1.1, Figure 1.2). This thesis compared 2.5 years of pre-harvest outflow data to 1.5 years of post-harvest outflow data. A large percentage ($>$80%) of the catchment was harvested (Table 1.1) in order to maximize the effect harvesting might have on the upland hydrology and biogeochemistry. For details on the harvest, refer to section 1.4: Site Characteristics.

The paired catchment approach was used to compare the large reference catchment (R1) to the large harvested catchment (H1) (Table 1.1) to test whether upland harvesting impacts the chemical export in surface streams. The catchments were sufficiently large to contain similar proportions of complex landform characteristics thus containing a similar integration of landform and precipitation runoff response.

The pre-harvest conditions in H1 were used to establish correlations with R1 in order to determine any likely change in export caused by harvesting. R1 was compared to H1 in both its pre- and post-harvested conditions in order to eliminate spatial or temporal effects. If R1 stream export was different from that of H1 post-

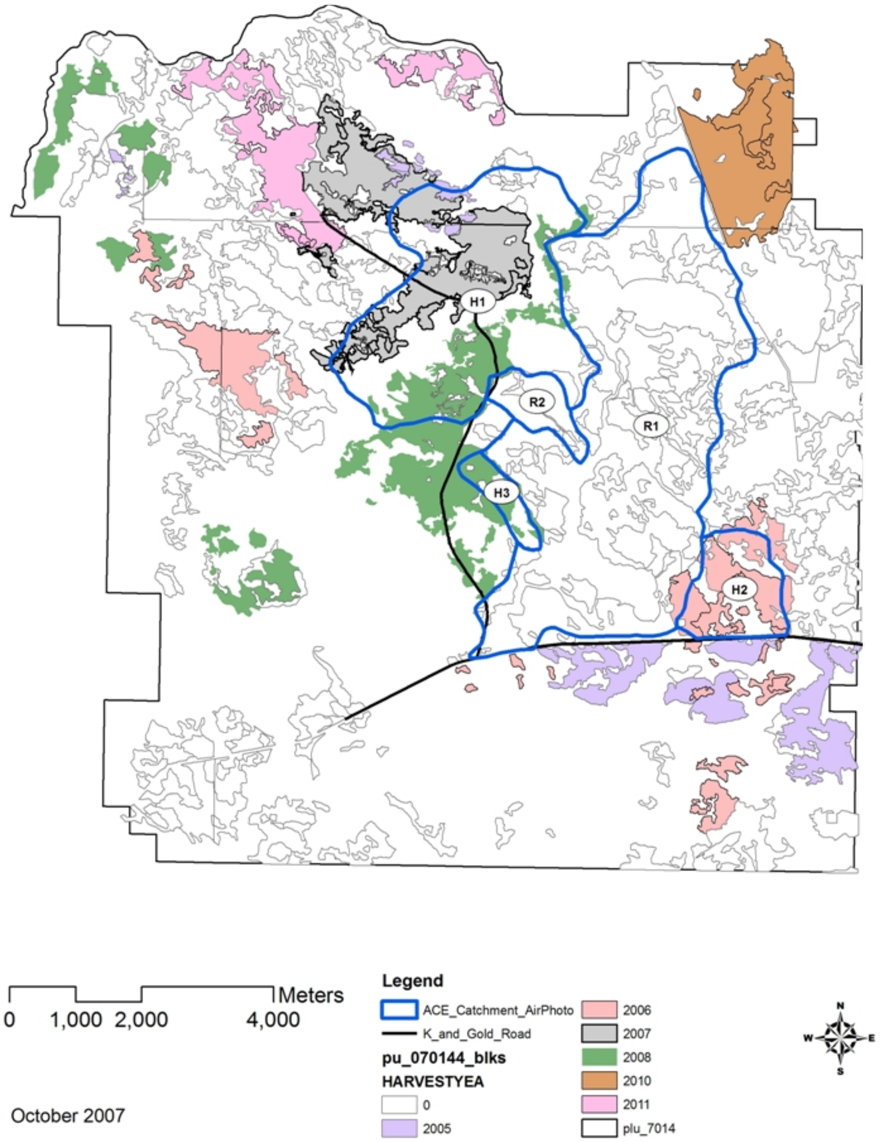

Figure 1.2: Harvesting Plan for ACE. Approximately 82% of upland aspen was harvested from H1 in 2007 and early 2008. Harvesting began on H1 on July 2, 2007. See Methods: Site Description, and Table 1.2 for harvesting details. The solid line above denotes the catchment boundaries.

Table 1.1: Spatial and Temporal Design. The large catchments used for this thesis are listed on the left. Temporal analysis runs from left to right, comparing pre-harvested to post-harvested conditions. Spatial analysis runs from top to bottom, comparing reference and harvested catchments. Light grey bars indicate the data for forested (reference) sites and dark grey bars indicate data for the harvested site. SFS indicates south-facing-slope and NFS indicates north-facing-slope.

Catchment	**%Upl Harvest**	**2005**	**2006**	**2007**	**2008**
Reference 1 (R1)	0				
Harvested 1 (H1)	82	SFS NFS			

harvest then the difference could be due either to harvesting or to spatial variations in the catchment hydrology. Spatial variations in hydrology would be evident if the same difference existed between the pre-harvest stream export of R1 and H1. Otherwise, the difference could be due to harvesting. Similarly, if pre-harvest export was different from post-harvest export in H1 then the difference could be due to harvesting or due to temporal variations in weather patterns affecting the hydrology. If post-harvest export was also different than that of R1 then temporal variation could be eliminated, leaving harvesting as the most probable cause. To ensure accuracy, both methods of comparison will be used in this thesis.

1.4 Site Characteristics

1.4.1 Climate

The study area was located in the Boreal Plain Ecozone (Ecoregions Working Group, 1989) about 200 km northeast of Edmonton, Alberta (longitude 112.1N, latitude 55.0W). The climate was sub-humid with average precipitation: potential evapotranspiration (PET) ratios are close to 1. However, this area was mainly characterized by longer dry cycles with periodic wetting every 10 to 20 years (Buttle et al., 2005; Ferone and Devito, 2004). Snow accumulation usually began in late October and melted in late March or April. Thirty-year normals (1971-2000) of annual precipitation were 504 mm, of which 122 mm occurred as snow and 259 mm as summer rainstorms from June to August (Environment Canada, 2009). Thus approximately 24% of annual precipitation was snow whereas 51% arrived as summer storms. Note that the majority of precipitation arrived during the time of most vegetative demand in the mid- to late summer. In addition, daily rainfall was usually less than 5 mm (74/110 days of rain) (Environment Canada, 2009), which has large implications on interception and infiltration in this region. Thirty-year normals of summer (July) and winter (January) temperatures were 16.2 °C and -14.9 °C respectively (Environment Canada, 2009). During the study period from 2005 to 2008 annual precipitation was 340, 455, 385 and 545 mm respectively (Environment Canada Atmore Weather Station, 2009).

1.4.2 Lithology and Surface Cover

The study area covered about 30 km^2 of low-relief, hummocky terrain. Hill slopes in this study area could change by 40 m of elevation over 2 km (Figure 1.3) and were composed of heterogeneous lithology. Geologic units include veneers, moraine, lacustrine and glacial fluvial till. Local conditions were a mixture of clay, silt and sand. Sand and clay lenses were dispersed throughout most silty areas. Soil depths were usually less than 1 m although the oxidized surface layer could range from 3 to 6 m. Surficial geology was 20 to 120 m deep. Aspen uplands had between 6 to 10 cm of organic material; ephemeral draws and depressions often had between 10 to 20 cm. Sandy pine areas were composed of a few centimeters of lichen, moss and needles. Peatlands had greater than 30 cm of sphagnum that could range up to 4 m.

1.4.3 Vegetation

Uplands were composed mainly of aspen (*Populus tremuloides*) with intermittent stands of balsam poplar (*Populus balsamifera*) and white spruce (*Picea glauca*). Hazelnut and prickly rose (*Rosa acicularis*) dominated the upland understory. Dry sandy areas in the upland supported pine, blueberries (*Vaccinium* spp.), lichen and brown moss (*Drepanocladus* spp.; *Warnstorfla* spp.). Black spruce (*Picea mariana*), alder (*Alnus* spp.), birch (*Betula* spp.), willow (*salix* spp.), and Labrador tea

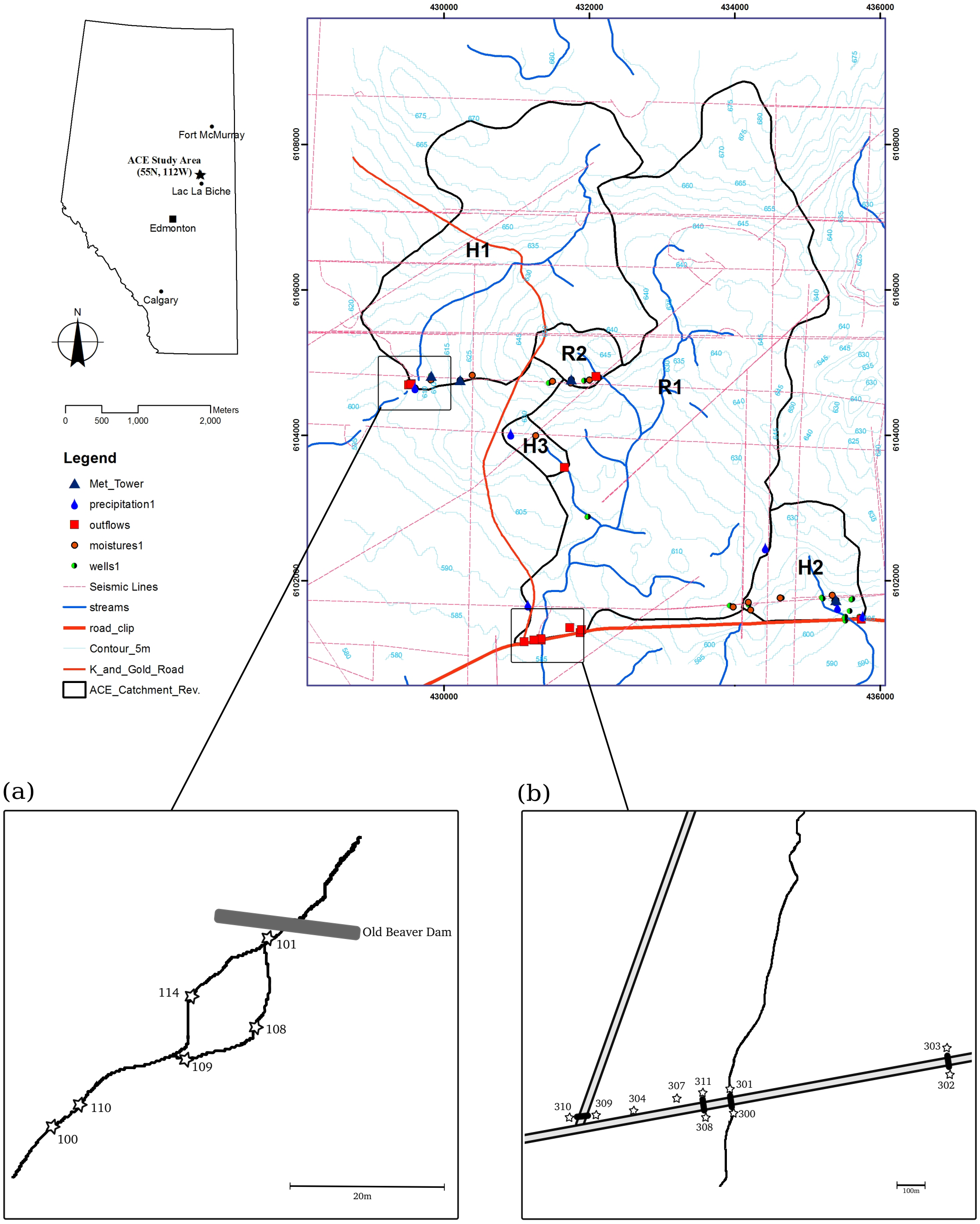

Figure 1.3: Instrumentation of ACE catchments. Catchment boundaries are solid black lines, streams solid blue lines and outflow sites are red squares. Contour lines are in light blue. The paired catchment approach compares the stream chemical concentration and instantaneous chemical export of the large reference catchment (R1) to that of the large harvested catchment (H1). (a) Close up of H1 outflow sites. Stars show the location of the sites where water samples were taken and instantaneous discharge measured. (b) Close up of R1 outflow sites. Stars show the location of the sites where water samples were taken and instantaneous discharge measured. Thick dark lines show the location of culverts running beneath the road.

(*Ledum groenlandicum*) were often interspersed between aspen uplands and peatlands or ephemeral draws. Peatlands were composed of mosses (*sphagnum* spp.) with stunted black spruce and some tamarack (*Larix laricina*) dispersed throughout. Lining the edges of sections of the streams were grasses.

1.4.4 Outflows and Beaver Dams

Beavers were trapped in 2005 and 2006 and the dams abandoned during the project. H1 had several beaver dams above and below the sample site. A channel was utilized for flow measurements and water sampling after the downstream dam broke in the winter of 2004-2005. The upstream dam at H1 had piping installed under it to ensure continued channel flow. R1 also had problems with beavers: they would block up the culverts with vegetation and mud. During the summer months several high flows resulted from dam breakage, a common occurrence in WBP. As these are natural and common occurrences, these events were included in the data set.

1.4.5 Harvesting

Alberta-Pacific (AlPac) Forest Industries, Incorporated, partnered with the research team to construct and maintain roads as well as organize the timing and location of harvesting. The large east-west road (K-road) was built in 1998 (Figure 1.2). H1 was accessed by trail along some seismic lines from 2005 until the main north-south road (Figure 1.2) was constructed in January, 2007. The north-south road was lengthened across the H1 stream in late 2007/early 2008. It was maintained by grading several times throughout the year and had to be reconstructed in places after heavy summer storms. Culverts were installed along the road in accordance with forestry guidelines and regularly maintained. Logging roads and skidder trails were created within each harvested catchment on the start date specified in Table 1.2 and were reclaimed before the final clearance date by dragging overburden composed of branches and mixed organic-mineral soil over the top of the road surface.

Harvesting was done with log fellers. Trees were then debranched, bunched, skidded and piled on site. H1 was harvested over successive years to mitigate climate influence. Harvesting on H1 began in the north-west section on the south-

Table 1.2: Harvesting locations and quantities in the H1 catchment. Aspen trees were harvested from the uplands. Start dates are when the roads were first put in and trees were first harvested. Skid clearance is the date when the all the trees were placed into piles along the road. Haul clearance is the date when all the piles of logs were hauled off site. Brush piles were burned between the haul and final clearance dates. Final clearance is the date when the roads were reclaimed. TBD are dates occurring after the scope of this thesis research.

Location	**Start Harvest**	**Skid Clearance**	**Haul Clearance**	**Final Clearance**	**Hectares**
North	07/02/07	09/18/07	04/08/08	12/31/08	168
North	09/05/07	11/15/07	07/21/08	12/31/08	186
North	10/19/07	04/08/08	07/21/08	12/31/08	4
South	07/01/08	08/21/08	TBD	TBD	99
South	08/05/08	08/21/08	12/07/08	TBD	50

facing-slope in July, 2007; wood was piled by April, 2008, and was hauled, with branch piles burnt and the roads reclaimed, by the end of December, 2008 (Table 1.2). Harvesting on the north-facing-slope began in July, 2008 and wood was piled by the end of August. While AlPac harvested the aspen uplands, smaller quota holders were also allowed to harvest conifers (white spruce were logged from December, 2006 through February, 2007) which may have had an impact on the catchment hydrology. However, the area of upland cut by AlPac was much greater than the area of conifers removed. With 82% of the upland aspen removed, the potential impacts on the hydrology were certainly maximized.

1.5 Data Collection and Quality Control

1.5.1 Outflow Hydrology

To determine export, the stream discharge (Q) must be ascertained. Point measurements were taken at low-flow, timing the volume captured in a bucket placed in a well-defined channel of the stream. A combination of surface velocity with a float or stream current metering for average velocity across the stream depth profile was used at higher flows.

Inconsistencies among the three types of point measurements used were investigated. Surface velocities were often overestimates of flow. During low flow (< 10 L/s), bucket measurements are quite reliable; during high flow, current meter values are considered more reliable. So when all three measurements were used to determine one flow, current meter values were used for the flow value during high-flow and bucket measurements were used during low. The point measurements used in this study are preliminary measurements. There are missing data for total cumulative discharge from both R1 and H1 and several extreme high flows were not caught with spot measurements.

Point measurements were taken at least once a week during the field season (April-September) and about once a month during winter low-flow periods. Measurement frequency was based on flow, occurring at most twice a day during spring melt and summer storms.

The R1 outflow had a series of beaver dams that caused the stream to widen to more than 0.5 km and resulted in a number of tributaries, which exited at three culverts (sites 300, 302 and 308) and one ditch (site 304). Discharge was measured at all four locations. At R1, during low-flow with only the continuous culvert (site 300/301) active, measurements taken at this site were considered to be the total flow from the catchment (Figure 1.3b). As the other culverts and the ditch became active, the total flow was considered to be the sum of all the flows (Figure 1.3b). Chemistry was primarily sampled at the main outlet (site 300) with less frequent sampling at the other sites for comparison.

The H1 outflow was measured using the original stream channel (site 100) from 2005 to 2007 (Figure 1.3a). A flume was built at the end of the 2007 field season about 5 meters upstream (site 110) to improve the accuracy of the discharge measurement. Ice was chipped out of the H1 outflow before spring melt, approximately 2 m up- and downstream from the sample site (100 or 110), in order to maintain a channel. Bucket measurements and chemistry sampling primarily occurred upstream at a narrow, deep, well-defined channel (site 108 and 109) on one of two tributaries to the outflow. Discharge measurements were considered total stream flow when taken at site 100 or 110 or when both channels (site 108 and site 114) were measured and added together (Figure 1.3a).

Stream flow was measured to determine the changes in water yield and chemical export following upland aspen harvesting. This project used point measurements of Q to determine the natural variation in chemical export and the effect upland harvesting had on chemical export.

1.5.2 Outflow Chemistry

An analysis of water samples measuring the concentration of anions, cations and nutrients is necessary to determine the surface chemical export from a catchment. Water samples were taken from the R1 and H1 outflows manually and with an automatic sampler.

Manual water chemistry samples were taken from outflows throughout the year at a frequency based on stream flow. R1 was sampled at site 301 (continuous culvert) and at site 302 when it was flowing (Figure 1.3b). H1 was sampled at site 100, and then site 110 when the flume was built, as well as upstream at sites 108 and 109 (Figure 1.3a). Samples were taken approximately every 10 to 14 days during the summer field season (April-September) and once a month during the rest of the year (when there was flow). During periods of high-flow, such as during spring melt and after summer storms, additional samples were taken at the outflows to catch the pre-peak, peak and post-peak flows. Occasionally, manual sampling was not able to catch all the storm flows because of scheduling, which is why automatic samplers were also used.

Automatic samplers (ISCO) were installed at R1 and H1 outflows during the spring and removed in the fall. Automatic sampling was performed once a day at 16:00 (MST) during spring melt and summer storms as well as every other day during the summer and fall. A coarse filter was used on the intake pipe. The intake hose was rinsed twice before sampling. The auto-sampler did not seal the samples nor store them at 4 °C, so the samples could sit in the auto-sampler over varying lengths of time and fluctuations in temperature. Therefore automatic samples were submitted for cation or anion analysis only if manual samples were unable to catch the peak flows. Analyses on perishable nutrients (P and N) were not conducted.

The remaining samples were removed from the apparatus and were stored at 4 °C at the University of Alberta.

All water chemistry samples were coarse-filtered at the time of sampling and placed in 1 L dark polyethylene bottles. (The bottles were acid-rinsed and sterilized and then rinsed three times with sample before filling.) Samples were kept at 4 °C and submitted for analysis within 48 hours of sampling or removal from autosamplers. Water chemistry sample analysis was provided by the Limnology Lab at the University of Alberta.

Dates and sites for water samples were double-checked against submission records and field notes. Water samples were assumed to be in equilibrium with the surrounding environment and so were ionically balanced to identify errors and outliers: 93% of the data is balanced (+/-12%).

1.6 Data Analysis

1.6.1 Data sets

The data set used to describe flow and concentration over time (Figure 2.1) as well as the comparison of flow to ion concentration (Figure 2.3) used the complete data set of spot flow measurements and chemistry samples. However, there were holes in the data where either chemistry samples were not taken for every point-flow measurement or point-flow measurements were not taken for every chemistry sample. In addition, sampling at one catchment did not always occur at the same time as at the other. A subset of data was therefore selected for calculating the mean concentrations, mean instantaneous chemical export and total mean instantaneous chemical export. This subset of data was based on the criterion that point-flow measurement and chemistry sampling for both R1 and H1 had to be taken within 24 hours of each other to be included. This subset represented 75% of the complete data set (Figure 2.1). Unfortunately, the extreme high flows of R1 did not meet the criterion of the subset except for one point post-harvest (Figure 2.1). This one extreme high-flow point doubled the total mean export for R1, skewing the data and results. Since the subset did not contain any extreme high flows pre-harvest, and the H1 summer high-flow post-harvest was missing, this point was excluded from the analysis. The necessary use of subsets and the missing data are what makes this analysis preliminary. Conclusions based on this study should be re-examined employing newer and more complete data sets.

1.6.2 Discharge

For purposes of this thesis, discharge is the amount of surface stream water leaving the catchment. This thesis utilizes preliminary instantaneous discharge data. Instantaneous discharge is reported in units of L/s. Discharge is important for determining the total chemical export of a catchment. Stream discharge will vary with changes to a catchment's hydrological input (such as precipitation) and antecedent conditions (such as the amount of soil storage available from the previous hydrologic year).

1.6.3 Chemical Concentration

Chemical concentration is the amount of a chemical in a certain volume of water. This thesis reports chemical concentration in units of mg/L and μg/L. Chemical concentrations in stream water are important for ecological reasons. Streams with small discharge will have small export even if the chemical concentrations are quite high. High concentrations of salt provide a strenuous environment for spawning fish and other aquatic organisms. High nitrate and phosphate concentrations have the potential for encouraging localized algae blooms. From a managerial position, high concentrations of nitrates ($>$3 mg/L) are often cited as anthropogenic in origin, implying causal relationships when there may be none. With these considerations in mind, this thesis reports and utilizes chemical concentration to fully describe the natural variability of chemicals in Boreal Plain stream water.

The concentration of certain ions in stream water is essential for calculating chemical export. It is also important for determining possible processes occurring within the catchment. For example, if concentrations of nitrate decrease while export remains unchanged, this implies that biological uptake of nitrate has occurred as well as an increase in discharge. This thesis utilizes chemical concentration to infer the changes that occur in the catchment with intensive upland aspen harvesting.

For chemical concentration all pertinent years of data were used to calculate the average instantaneous concentration for each categorical box (see section 1.6.4). Occasionally an outflow was sampled at multiple points along the discharge area on the same day. In such cases a non-weighted average concentration of all the sites sampled on that day was used for the total average calculation.

1.6.4 Chemical Export

The export for each catchment was calculated by multiplying the instantaneous flow by the chemical concentration in each water sample taken on that day. The export was normalized by catchment area (R1: 18.3, H1: 9.9 km^2). Total average export was the sum of the average export of TN, TP, DOC, Cl^- , SO_4^{2-} , HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} and Si^{4+} for each category.

Chemical export is important to both the catchment losing the chemicals and to the water body receiving them. The ecological health of a catchment is based upon the necessary chemicals being available for uptake and growth. Chemical export can indicate that essential nutrients (such as potassium) are being lost from the catchment—which may result in stunted forest growth or a change in species dominance. Export is also important for determining the total loading a receiving water body receives from its sources. A stream with high nitrate export may indicate that eutrophication will occur in a lake downstream. This thesis compared total instantaneous export on reference and harvested catchments to determine if there was a change in stream chemical export caused by intensive upland aspen harvesting.

1.6.5 Categorical Boxes

The hydrologic year was separated into four boxes based on two criteria: flow and vegetation. A sample was considered high-flow if the instantaneous flow was greater than 10 L/s and low-flow if it was less than 10 L/s. In this thesis vegetation activity referred to the period during which upland trees and shrubs take up copious amounts of water and nutrients to start and maintain new growth (leaf-out until senescence). Vegetation was considered to be active after spring melt until September 30th. High flow with little active vegetation (HFNV) was spring melt and was defined temporally by the hydrograph rise and fall. High-flow with active vegetation (HFAV) was the summer season when instantaneous flows were greater than 10 L/s. Low-flow with active vegetation (LFAV) was the summer season when instantaneous flows were less than 10 L/s. Low-flow with little active vegetation (LFNV) was fall, winter and early spring before spring melt. For 2005 to 2008 there were no high-flow events before spring melt. The reference catchment (R1) and harvested catchment (H1) were split between pre- and post-harvest data. Samples taken before July 2^{nd}, 2007 were considered pre-harvest and those taken later were post-harvest. For clarity, Table 1.3 gives a list of dates representing the categorical boxes.

1.6.6 Statistics

The mean and median of each category was calculated for R1 and H1 pre- and post-harvest for stream chemical concentration and chemical export. Categories with more than 3 data points often had the mean and median differ by a large amount, implying that the data was not normally distributed. This precluded the use of t-tests and ANOVA to compare significant differences between categories. The non-parametric Kruskal-Wallis test was therefore used to determine if there were any significant differences between categories. Post-hoc analysis of the results was carried out using the Mann-Witney U-test without the Bonferroni correction. The statistical software R was used to calculate these statistical analyses. A difference was considered significant in this thesis when the p-value was less than $\alpha = 0.05$.

Table 1.3: Categorical boxes listed by date over the study time (2005 to 2008). Boxes are defined by flow (high or low) and by vegetation (active or not-active): high-flow non-active vegetation (HFNV), high-flow active vegetation (HFAV), low-flow active vegetation (LFAV), low-flow non-active vegetation (LFNV).

Category	**R1**		**H1**	
	Pre-harvest	**Post-harvest**	**Pre-harvest**	**Post-harvest**
HFNV	12/04/05–22/05/05 20/04/06–22/05/06 13/04/07–21/05/07	07/04/08–21/05/08	12/04/05–22/05/05 10/04/06–22/05/06 13/04/07–21/05/07	13/04/08–26/05/08
HFAV	23/05/05–30/09/05 23/05/06–30/09/06 22/05/07–01/07/07	02/07/07–30/09/07 22/05/08–30/09/08	23/05/05–30/09/05 23/05/06–30/09/06 22/05/07–01/07/07	02/07/07–30/09/07 27/05/08–30/09/08
LFAV	23/05/05–30/09/05 23/05/06–30/09/06 22/05/07–01/07/07	02/07/07–30/09/07 22/05/08–30/09/08	23/05/05–30/09/05 23/05/06–30/09/06 22/05/07–01/07/07	02/07/07–30/09/07 27/05/08–30/09/08
LFNV	01/01/05–11/04/05 01/10/05–19/04/06 01/10/06–12/04/07	01/10/07–06/04/08 01/10/08–30/11/08	01/01/05–11/04/05 01/10/05–19/04/06 01/10/06–12/04/07	01/10/07–12/04/08 01/10/08–30/11/08

Chapter 2

Results

The natural variation of WBP stream chemistry was described and harvesting impacts were tested using surface stream chemistry samples and point measurements of stream discharge. This provided a preliminary analysis of mean stream chemical concentration and instantaneous chemical export.

Natural variability was discussed by examining the stream chemical concentration and instantaneous chemical export of R1 and H1 in the pre-harvest years. The impact of upland harvesting was investigated by comparing R1 and H1 pre-harvest to R1 and H1 post-harvest. Because of an incomplete hydrologic record, several extreme high-flow events were missing from this data set for both R1 and H1 pre- and post-harvest. Therefore, the resulting export was an underestimate and the importance of spring melt in comparison to summer storms was inconclusive because of the missing extremes.

The mean and median were both calculated to determine the appropriate statistical method to use to test for significant differences between categories. Although the median values were generally lower than the mean values, the trends across categories were similar. Mean values were discussed in the text to emphasize the range of change possible between categories. Median values, since they are more conservative, were used in the statistics to test if there was a significant difference (p-value $< \alpha = 0.05$) between categories. If the p-value given by the test was $< \alpha = 0.05$) then the difference in medians between two categories was considered significant and the null hypothesis that they are the same could be rejected. However, if the p-value was $> \alpha = 0.05$ then the null hypothesis could not be rejected and no statistical conclusions about the difference between two categories could be made.

2.1 Natural Variability of Catchment Export in the Boreal Plains

The instantaneous flow and chemical concentrations for R1 and H1 taken from 2005 to 2008 were detailed in Figure 2.1, with the subset of data used for the following analyses highlighted black. The inter-annual variation of flow was evident by the existence of extreme high-flow points in some years and not in others (Figure 2.1 and Figure 2.2). The annual discharge of the catchment may be significantly different from year to year based on the frequency of these high-flow events. The total mean instantaneous export of R1 (Table 2.1) demonstrated that annual variation in export was large. This was especially true during HFAV when the magnitude and timing of summer storms and beaver dam breakages differed from year to year.

Table 2.1: Total mean instantaneous export ($mg/s/km^2$) grouped by flow and vegetative activity. The mean ion export of TN, TP, DOC, Cl^- , SO_4^{2-} , HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} and Si^{4+} was totaled. The subset of data where flow and concentrations of both R1 and H1 taken <24 hours apart was used here. Export has been normalized by catchment area. Categorical boxes were defined by flow (high or low) and by vegetation (active or not-active): high-flow non-active vegetation (HFNV), high-flow active vegetation (HFAV), low-flow active vegetation (LFAV), low-flow non-active vegetation (LFNV).

	R1		**H1**	
	Pre	**Post**	**Pre**	**Post**
HFNV	392	425	955	498
HFAV	564	271	978	475
LFAV	51	42	90	93
LFNV	34	31	96	19

The subset of chemical and hydrological data was used to determine the mean and median chemical concentration, instantaneous export and total mean instantaneous export described in the tables in this chapter (Table 2.2, Table 2.3 and Table 2.1). These tables were categorized into flow- and vegetation-based regimes:

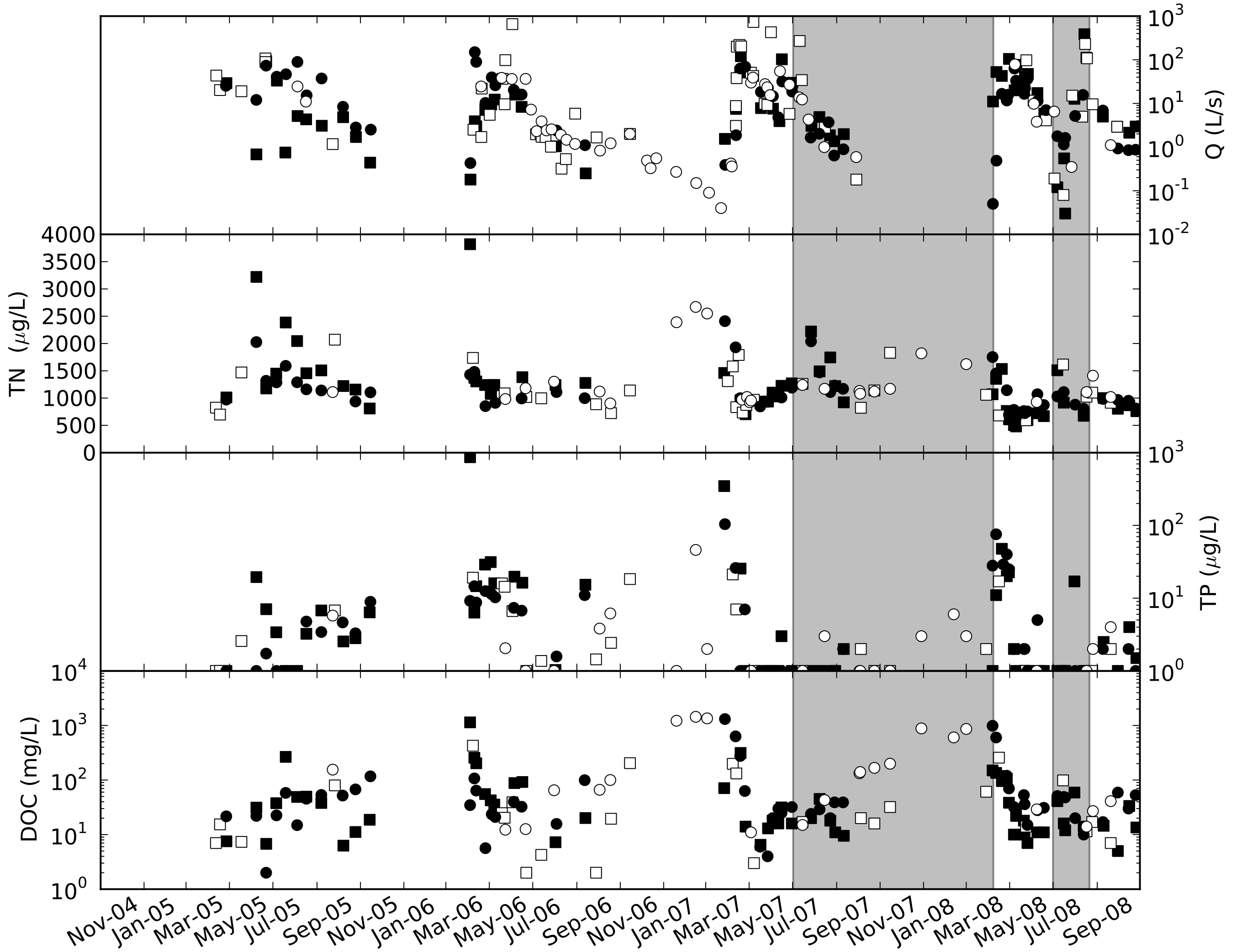

Figure 2.1: Point flow and ion concentrations of R1 (squares) and H1 (circles) during the study period. Flow values have not been normalized by catchment area. Representative ion species of major cations and anions were selected based on similar trends. Other than TN and Ca^{2+} , the scales for flow and concentration are logarithmic because they change over several orders of magnitude. The subset of data used for calculating mean ion concentrations and export is coloured black. The grey coloured area indicates when upland aspen harvesting occurred on H1.

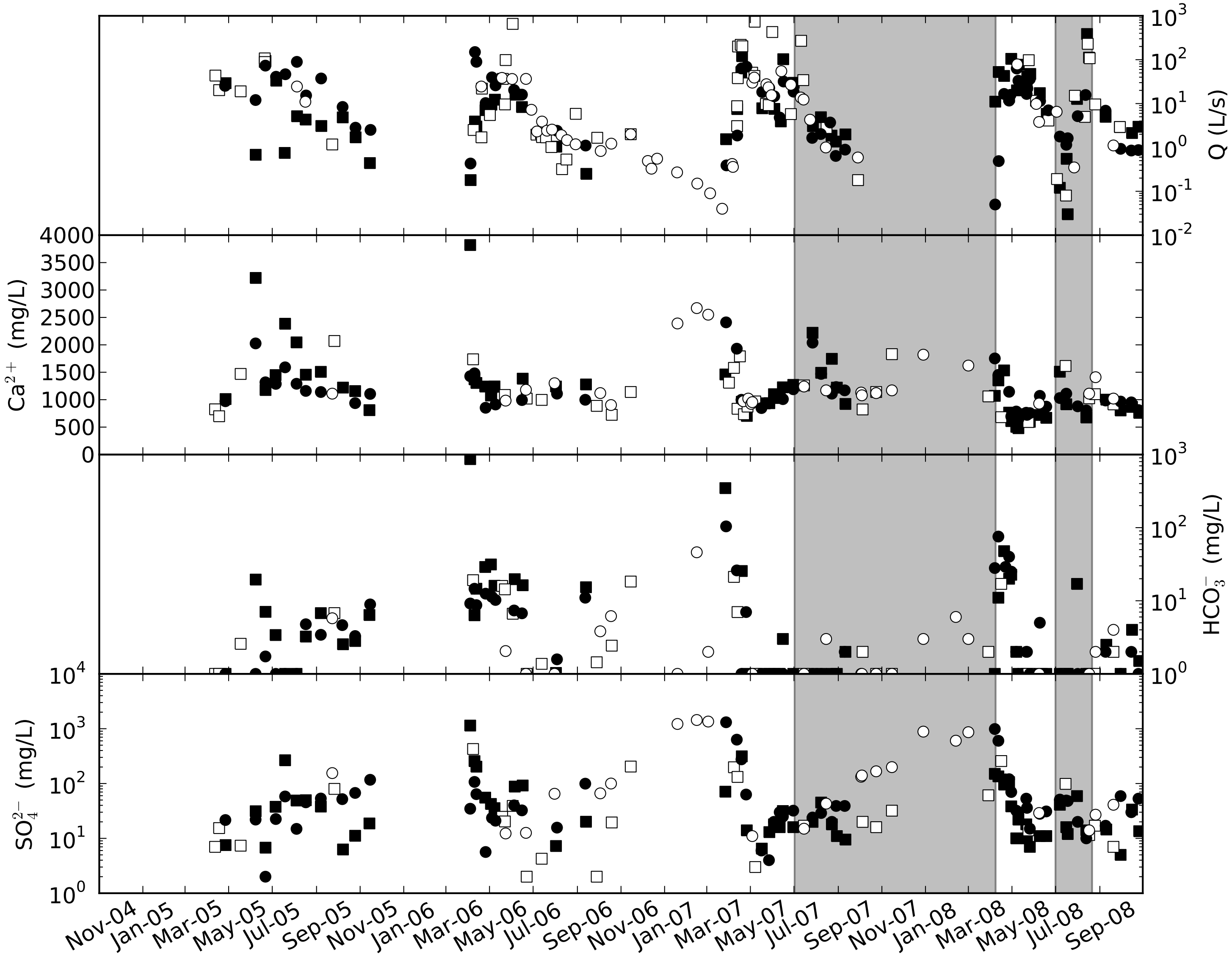

Figure 2.1: (continued) Point flow and ion concentrations of R1 (squares) and H1 (circles) during the study period.

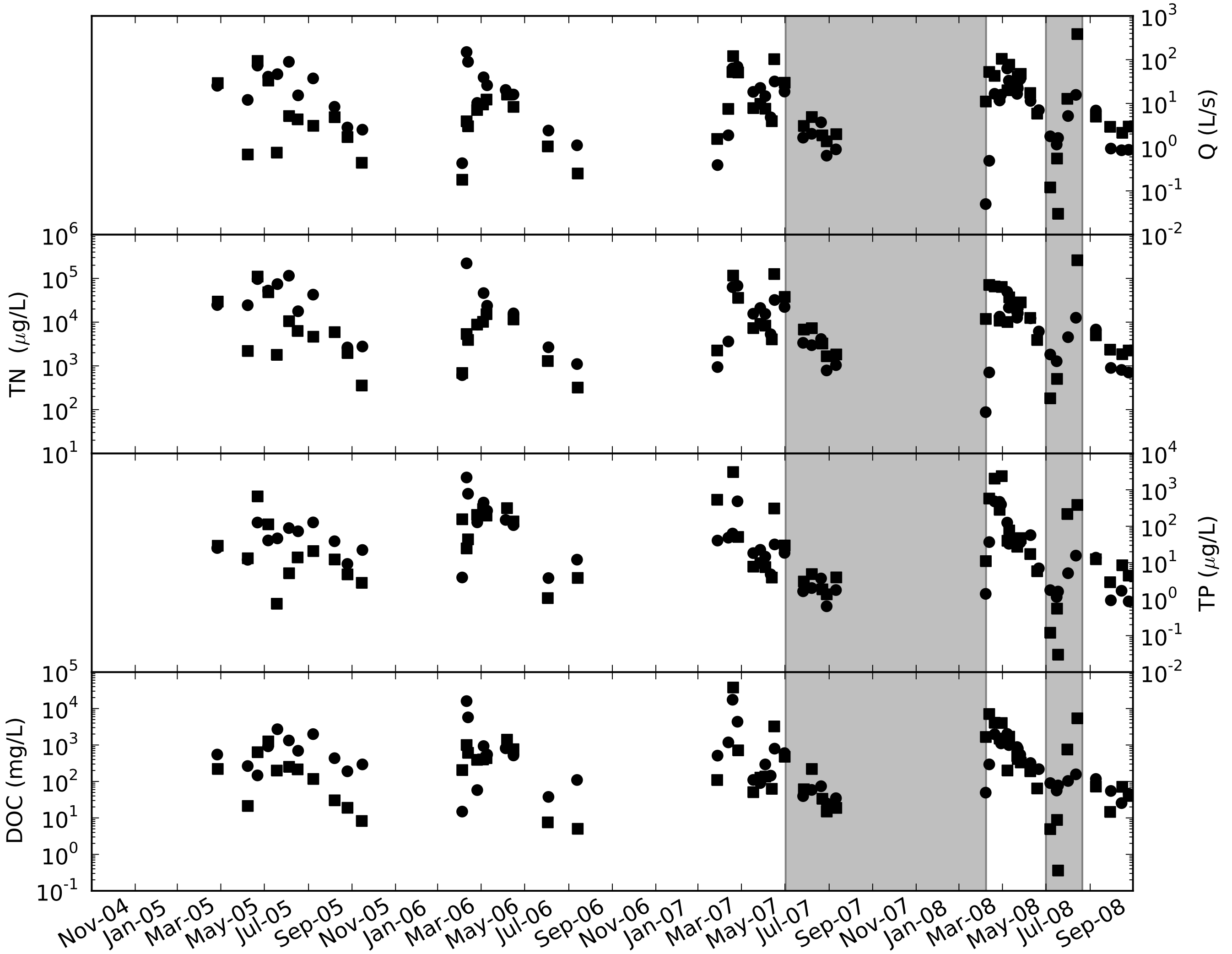

Figure 2.2: Point flow and ion export of R1 (squares) and H1 (circles) during the study period. Flow values and export have not been normalized by catchment area. Representative ion species of major cations and anions were selected based on similar trends. The scales for flow and export are logarithmic because they change over several orders of magnitude. Only the subset of data used for calculating export is included. The grey coloured area indicates when upland aspen harvesting occurred on H1.

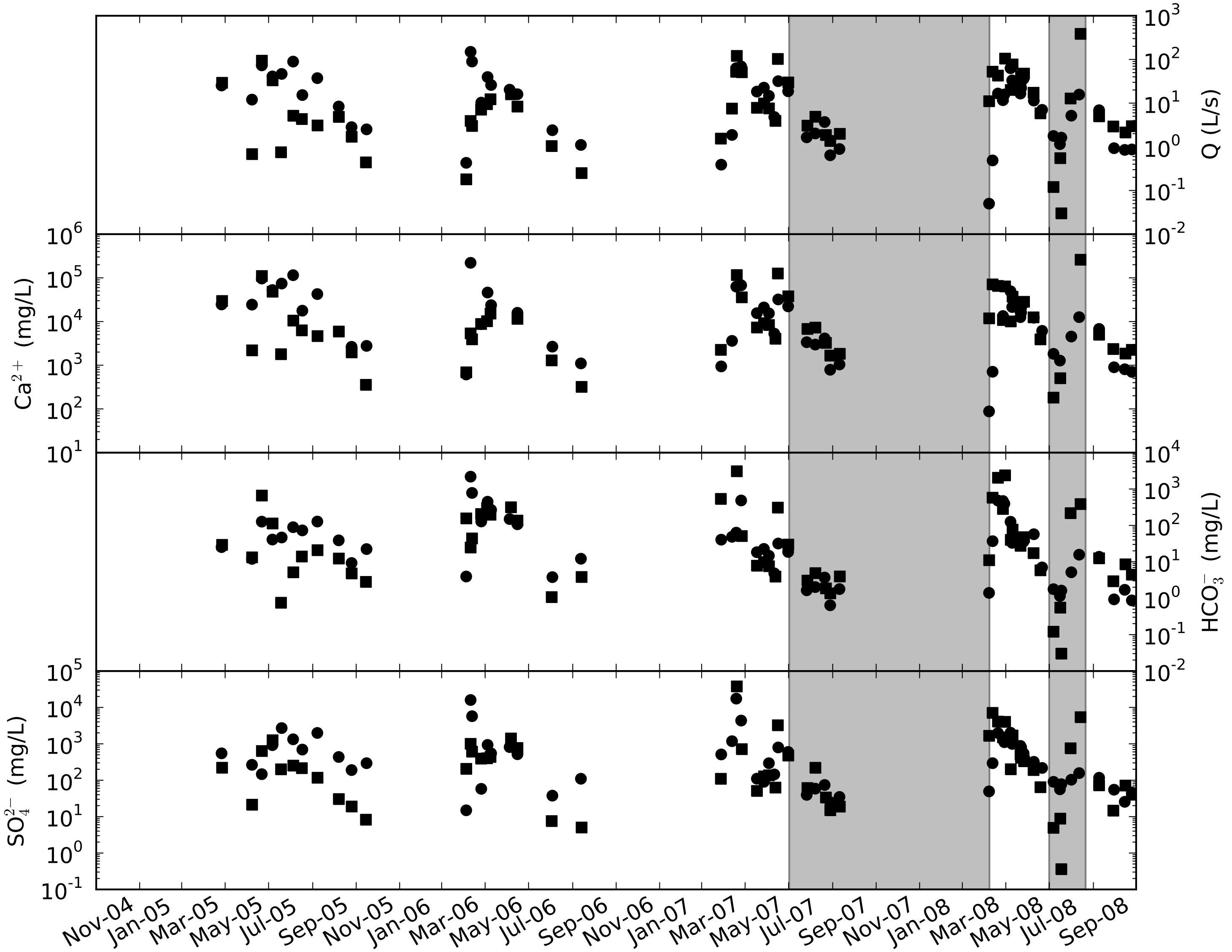

Figure 2.2: (continued) Point flow and ion export of R1 (squares) and H1 (circles) during the study period.

HFNV, HFAV, LFAV, and LFNV. For clarity, a preliminary box-plot (Figure 2.4) was also used to describe the mean instantaneous export of R1 and H1. Figure 2.4 showed that there was a large decrease in export for all ions in the post-harvest period of R1 with the exception of SO_4^{2-} and NO_2^-+NO_3^- ; SO_4^{2-} export increased fourfold while NO_2^-+NO_3^- export remained the same during HFNV (Table 2.3). The decrease in ion export over time, although noticeable in mean trends (Table 2.3), was not statistically significant for R1.

Table 2.2: Mean and median ion concentrations grouped by flow and vegetative activity. Median concentrations are in bold. The subset of data with flow and concentrations of both R1 and H1 taken <24 hours apart was used here. Minimum and maximum values are in parenthesis. Unit concentration is mg/L except for N and P where it is μg/L. The number of data points for each category is indicated by n = . Categorical boxes were defined by flow (high or low) and by vegetation (active or not-active): high-flow non-active vegetation (HFNV), high-flow active vegetation (HFAV), low-flow active vegetation (LFAV), low-flow non-active vegetation (LFNV).

(a)

		R1		**H1**	
		Pre	**Post**	**Pre**	**Post**
Ca^{2+}	**HFNV**	20.8, **19.7** (18-25) n=5	25.7, **21.8** (16-48) n=8	19.0, **19.1** (16-22) n=9	22.8, **21.7** (21-28) n=6
	HFAV	29.6, **27.7** (24-41) n=6	24.5, **22.5** (20-33) n=4	31.9, **30.1** (24-44) n=13	23.9, **22.6** (20-29) n=3
	LFAV	39.3, **37.7** (25-60) n=10	46.0, **45.9** (26-60) n=10	45.0, **48.4** (34-53) n=3	45.1, **43.8** (31-56) n=11
	LFNV	26.6, **25.7** (19-38) n=10	35.1, **35.3** (31-39) n=3	41.9, **44.3** (23-61) n=6	46.6, **36.3** (35-75) n=5
Mg^{2+}	**HFNV**	5.0, **5.0** (4-6) n=5	6.7, **5.6** (4-13) n=8	5.9, **5.8** (5-7) n=9	6.9, **6.7** (6-9) n=6
	HFAV	7.1, **6.5** (6-10) n=6	5.8, **5.7** (5-7) n=4	9.0, **8.8** (1-15) n=12	6.9, **6.6** (6-8) n=3
	LFAV	9.0, **9.0** (5-13) n=9	10.4, **10.6** (6-13) n=10	12.9, **14.0** (10-15) n=3	12.5, **11.0** (9-17) n=11
	LFNV	9.7, **8.1** (5-19) n=10	8.0, **7.6** (7-9) n=3	13.9, **15.5** (5-20) n=5	13.5, **10.3** (9-23) n=5
Na^{+}	**HFNV**	6.2, **6.5** (5-7) n=5	9.8, **8.4** (6-16) n=8	9.2, **8.3** (7-14) n=9	12.7, **12.6** (10-15) n=5
	HFAV	10.7, **9.6** (8-16) n=6	8.9, **9.0** (8-10) n=4	15.6, **14.8** (13-27) n=13	15.0, **15.5** (13-17) n=3
	LFAV	9.8, **9.7** (9-12) n=10	9.7, **10.8** (1-12) n=10	17.7, **17.4** (16-19) n=3	15.8, **17.0** (1-19) n=11
	LFNV	8.9, **9.1** (5-16) n=10	9.9, **10.1** (9-10) n=3	17.1, **18.7** (5-24) n=6	19.1, **17.9** (17-23) n=5
K^{+}	**HFNV**	2.6, **2.6** (2-3) n=5	2.5, **2.4** (2-4) n=8	2.8, **2.0** (1-5) n=9	2.6, **1.9** (1-5) n=5
	HFAV	1.2, **1.2** (0-2) n=6	1.1, **1.1** (1-2) n=4	0.9, **0.9** (0-2) n=12	0.8, **0.9** (1-1) n=3
	LFAV	1.5, **1.3** (0-4) n=9	0.9, **0.9** (0-1) n=10	1.0, **0.9** (1-1) n=3	0.7, **0.5** (0-2) n=11
	LFNV	3.1, **2.2** (0-9) n=9	1.5, **1.6** (1-2) n=3	4.3, **1.7** (0-16) n=6	1.1, **0.8** (1-2) n=5

Table 2.2: Mean and median (bold) ion concentrations grouped by flow and vegetative activity (continued).

(b)

		R1		H1	
		Pre	**Post**	**Pre**	**Post**
HCO_3^-	**HFNV**	97.8, **98.9** (85-114) n=5	122.8, **92.5** (78-237) n=8	102, **105** (79-116) n=8	116, **118** (95-143) n=6
	HFAV	134, **127** (114-183) n=6	107, **106** (95-122) n=4	176, **165** (124-258) n=13	125, **111** (111-152) n=3
	LFAV	188, **183** (138-280) n=10	201, **205** (126-253) n=11	230, **248** (179-262) n=3	226, **216** (164-283) n=12
	LFNV	144, **151** (85-208) n=8	164, **159** (149-183) n=3	244, **257** (105-344) n=6	257, **201** (192-408) n=5
Cl^-	**HFNV**	1.9, **2.1** (1-3) n=5	1.7, **1.9** (1-3) n=8	1.4, **0.9** (1-5) n=9	1.0, **0.6** (0-2) n=5
	HFAV	0.7, **0.7** (0-1) n=6	0.6, **0.4** (0-1) n=4	0.4, **0.4** (0-1) n=12	0.2, **0.2** (0-0) n=3
	LFAV	1.1, **0.8** (0-3) n=9	1.1, **1.0** (0-3) n=11	0.5, **0.5** (0-1) n=3	0.2, **0.2** (0-1) n=12
	LFNV	2.2, **1.7** (1-7) n=9	1.2, **1.3** (1-1) n=3	3.9, **1.4** (1-17) n=6	1.1, **0.9** (1-2) n=5
SO_4^{2-}	**HFNV**	1.1, **1.2** (1-1) n=5	4.2, **1.9** (1-12) n=8	2.8, **1.6** (1-12) n=9	8.0, **9.3** (1-13) n=5
	HFAV	0.4, **0.3** (0-1) n=6	1.2, **0.7** (0-3) n=4	1.1, **0.2** (0-7) n=13	8.6, **9.4** (5-11) n=3
	LFAV	1.7, **0.3** (0-15) n=10	0.3, **0.3** (0-1) n=11	0.2, **0.0** (0-1) n=3	0.5, **0.4** (0-1) n=12
	LFNV	1.5, **1.6** (0-4) n=9	0.3, **0.2** (0-0) n=3	1.7, **0.3** (0-9) n=6	1.5, **0.9** (0-3) n=5
DOC	**HFNV**	20.7, **21.9** (16-25) n=5	20.6, **19.3** (14-34) n=8	21.0, **22.1** (15-24) n=9	20.9, **21.4** (18-24) n=6
	HFAV	29.8, **30.1** (24-36) n=6	23.9, **21.8** (17-35) n=4	32.9, **29.6** (20-81) n=13	26.1, **25.3** (23-31) n=3
	LFAV	38.0, **34.3** (21-81) n=10	31.2, **27.3** (22-54) n=11	30.6, **30.6** (29-32) n=3	36.7, **30.3** (27-103) n=12
	LFNV	25.3, **27.2** (18-31) n=9	25.3, **27.6** (21-28) n=3	24.1, **24.9** (18-28) n=6	25.4, **26.6** (21-29) n=5
Fe^{2+}	**HFNV**	2.5, **2.4** (1-4) n=4	1.2, **1.1** (0-3) n=8	1.6, **1.2** (0-3) n=7	0.9, **0.6** (0-2) n=5
	HFAV	0.9, **0.8** (0-1) n=4	0.3, **0.2** (0-0) n=3	0.8, **0.8** (0-2) n=7	0.5, **0.4** (0-1) n=3
	LFAV	1.3, **1.1** (0-2) n=6	1.0, **1.0** (0-3) n=10	2.0, **2.1** (2-2) n=3	1.1, **0.9** (0-2) n=10
	LFNV	1.4, **1.2** (0-4) n=8	1.0, **0.8** (1-2) n=3	0.9, **1.0** (0-1) n=6	3.6, **1.5** (1-10) n=5
Si^{4+}	**HFNV**	3.1, **3.0** (3-4) n=4	4.6, **3.8** (3-8) n=8	3.2, **3.3** (3-3) n=8	4.0, **3.9** (3-5) n=6
	HFAV	5.2, **5.1** (4-6) n=6	4.6, **4.2** (3-7) n=4	4.3, **4.3** (3-7) n=9	2.9, **2.8** (3-3) n=3
	LFAV	6.0, **5.0** (5-9) n=4	7.0, **7.1** (4-9) n=11	3.4, **3.4** (3-3) n=1	5.6, **5.3** (3-8) n=12
	LFNV	5.0, **4.7** (3-7) n=9	6.6, **6.6** (6-7) n=3	6.3, **6.5** (3-8) n=6	6.0, **5.8** (5-8) n=5

Table 2.2: Mean and median (bold) ion concentrations grouped by flow and vegetative activity (continued).

(c)

		R1		H1	
		Pre	**Post**	**Pre**	**Post**
TN	**HFNV**	999, **1011** (704-1241) n=5	881, **750** (480-1533) n=8	1026, **976** (847-1480) n=8	806, **762** (648-1144) n=5
	HFAV	1211, **1225** (936-1449) n=5	645, **617** (597-721) n=3	1249, **1175** (931-2026) n=12	849, **755** (723-1070) n=3
	LFAV	1664, **1419** (1030-3220) n=10	1250, **1110** (669-2220) n=10	1069, **1100** (998-1110) n=3	1169, **1110** (873-2040) n=11
	LFNV	1479, **1240** (809-3820) n=9	755, **760** (636-869) n=3	1562, **1428** (937-2410) n=5	1140, **951** (736-1752) n=5
TDN	**HFNV**	930, **922** (583-1248) n=5	737, **661** (508-1084) n=8	914, **888** (727-1258) n=9	686, **692** (446-905) n=6
	HFAV	1238, **1175** (993-1494) n=6	824, **685** (477-1450) n=4	1105, **1110** (792-1516) n=13	777, **718** (692-921) n=3
	LFAV	1737, **1345** (963-3775) n=10	1013, **953** (616-1440) n=11	773, **943** (378-997) n=3	1015, **972** (880-1370) n=12
	LFNV	1363, **1167** (612-3460) n=9	768, **820** (619-865) n=3	1404, **1060** (969-2470) n=5	1062, **792** (779-1744) n=5
NH_4^+	**HFNV**	82.6, **35.6** (8-314) n=5	71.9, **67.0** (10-150) n=8	65.3, **23.6** (6-276) n=9	70.7, **61.5** (30-120) n=6
	HFAV	32.1, **23.8** (7-88) n=6	21.8, **10.5** (7-59) n=4	28.6, **25.0** (2-58) n=13	26.3, **28.0** (15-36) n=3
	LFAV	58.7, **34.6** (7-266) n=10	18.5, **14.5** (5-45) n=11	48.4, **30.0** (16-99) n=3	35.5, **35.0** (17-59) n=12
	LFNV	196.4, **55.3** (6-1140) n=9	23.7, **24.0** (14-34) n=3	368.7, **92.2** (35-1310) n=6	350.6, **81.0** (30-987) n=5
NO_2^-+NO_3^-	**HFNV**	15.0, **16.0** (1-31) n=5	13.3, **6.5** (1-48) n=8	7.5, **8.7** (1-15) n=9	16.5, **13.5** (1-40) n=6
	HFAV	5.9, **3.2** (1-20) n=6	5.0, **1.0** (1-17) n=4	2.5, **1.0** (1-7) n=13	2.7, **2.0** (1-5) n=3
	LFAV	6.6, **2.1** (1-19) n=10	1.2, **1.0** (1-3) n=11	4.5, **1.6** (1-11) n=3	1.2, **1.0** (1-2) n=12
	LFNV	141.6, **6.4** (1-865) n=9	2.2, **1.5** (1-4) n=3	26.0, **9.0** (3-104) n=6	21.9, **3.0** (1-76) n=5
TP	**HFNV**	221, **228** (145-284) n=5	108.2, **98.5** (51-213) n=8	112.5, **84.2** (32-268) n=8	70.3, **72.0** (24-113) n=6
	HFAV	124, **115** (94-194) n=6	43.0, **46.0** (35-48) n=3	93.8, **80.9** (38-147) n=13	48.7, **48.0** (34-64) n=3
	LFAV	375, **192** (71-1222) n=10	307, **190** (42-1584) n=10	162, **178** (94-215) n=3	130, **147** (60-174) n=11
	LFNV	189, **171** (87-340) n=9	111, **104** (97-132) n=3	260, **238** (97-467) n=6	464, **274** (81-1110) n=5
TDP	**HFNV**	116, **120** (85-158) n=5	54.1, **56.5** (32-69) n=8	64.5, **53.0** (21-123) n=9	40.8, **39.5** (18-68) n=6
	HFAV	80.7, **78.3** (45-126) n=6	72.5, **29.0** (18-214) n=4	50.0, **44.0** (23-89) n=13	26.0, **25.0** (22-31) n=3
	LFAV	205, **121** (38-706) n=10	51.6, **40.0** (18-167) n=11	65.4, **69.4** (56-71) n=3	44.5, **41.0** (24-70) n=12
	LFNV	97.0, **80.0** (13-215) n=9	37.8, **38.0** (30-46) n=3	42.9, **30.1** (12-125) n=6	46.2, **44.0** (6-88) n=5
SRP	**HFNV**	95.1, **86.4** (65-145) n=5	28.4, **26.2** (20-39) n=8	41.0, **29.2** (8-98) n=9	15.2, **15.5** (4-29) n=6
	HFAV	54.8, **55.0** (16-101) n=6	50.0, **14.5** (5-166) n=4	33.8, **31.7** (6-79) n=13	8.3, **9.0** (6-10) n=3
	LFAV	178.6, **88.6** (23-622) n=10	26.5, **12.5** (2-124) n=11	45.9, **51.1** (30-57) n=3	13.5, **15.5** (1-20) n=12
	LFNV	68.5, **42.0** (10-173) n=9	18.3, **18.0** (11-26) n=3	29.0, **20.4** (8-80) n=6	29.7, **10.0** (1-113) n=5

Table 2.3: Mean and median ion instantaneous export grouped by flow and vegetative activity. Median concentrations are in bold. The subset of data with flow and concentrations of both R1 and H1 taken <24 hours apart was used here. Export has been normalized by catchment area. Minimum and maximum values are in parenthesis. Unit export is mg/s/km^2 except for N and P where it is μg/s/km^2. The number of data points for each category is indicated by n = . Categorical boxes were defined by flow (high or low) and by vegetation (active or not-active): high-flow non-active vegetation (HFNV), high-flow active vegetation (HFAV), low-flow active vegetation (LFAV), low-flow non-active vegetation (LFNV).

(a)

		R1		H1	
		Pre	**Post**	**Pre**	**Post**
Ca^{2+}	**HFNV**	49.1, **39.9** (10-130) n=5	53.7, **42.5** (20-110) n=8	100.3, **76.4** (19-256) n=9	57.8, **37.2** (33-133) n=6
	HFAV	74.0, **61.7** (14-161) n=6	35.7, **34.2** (23-52) n=4	111.8, **67.8** (37-373) n=13	53.8, **45.6** (33-83) n=3
	LFAV	6.6, **5.6** (1-14) n=10	6.6, **6.4** (0-13) n=10	11.4, **11.7** (6-17) n=3	11.9, **8.8** (3-24) n=11
	LFNV	4.9, **4.0** (0-11) n=10	4.3, **4.6** (3-6) n=3	9.4, **10.3** (1-19) n=6	2.3, **2.7** (0-3) n=5
Mg^{2+}	**HFNV**	12.1, **9.4** (2-33) n=5	13.8, **11.2** (4-27) n=8	31.2, **23.4** (6-83) n=9	17.2, **11.5** (11-38) n=6
	HFAV	18.0, **14.7** (3-38) n=6	8.9, **8.8** (5-13) n=4	32.7, **17.8** (2-111) n=12	15.6, **13.2** (9-24) n=3
	LFAV	1.7, **1.7** (0-3) n=9	1.5, **1.4** (0-3) n=10	3.3, **3.4** (2-5) n=3	3.3, **2.5** (1-6) n=11
	LFNV	1.5, **1.4** (0-3) n=10	1.0, **1.0** (1-1) n=3	4.0, **3.0** (0-12) n=5	0.7, **0.8** (0-1) n=5
Na^{+}	**HFNV**	14.9, **9.1** (3-42) n=5	20.3, **14.4** (9-38) n=8	44.5, **45.6** (7-99) n=9	35.3, **24.6** (15-77) n=5
	HFAV	30.4, **18.4** (5-80) n=6	14.6, **14.7** (5-23) n=4	56.1, **31.7** (19-203) n=13	34.9, **28.8** (19-57) n=3
	LFAV	1.8, **1.9** (0-4) n=10	1.5, **1.4** (0-3) n=10	4.8, **4.2** (2-8) n=3	4.8, **3.0** (0-11) n=11
	LFNV	1.5, **1.1** (0-4) n=10	1.2, **1.2** (1-2) n=3	4.7, **4.4** (0-13) n=6	1.1, **1.5** (0-2) n=5
K^{+}	**HFNV**	7.0, **4.8** (1-20) n=5	5.8, **4.7** (2-14) n=8	21.0, **7.3** (2-82) n=9	6.1, **5.6** (2-12) n=5
	HFAV	2.9, **1.5** (1-10) n=6	2.2, **2.2** (1-4) n=4	2.8, **1.7** (0-15) n=12	2.0, **2.2** (1-3) n=3
	LFAV	0.3, **0.2** (0-1) n=9	0.1, **0.1** (0-0) n=10	0.3, **0.2** (0-1) n=3	0.2, **0.2** (0-0) n=11
	LFNV	0.5, **0.6** (0-1) n=9	0.2, **0.2** (0-0) n=3	0.4, **0.3** (0-1) n=6	0.1, **0.1** (0-0) n=5

Table 2.3: Mean and median (bold) ion instantaneous export grouped by flow and vegetative activity (continued).

(b)

		R1		H1	
		Pre	**Post**	**Pre**	**Post**
HCO_3^-	**HFNV**	237, **182** (46-651) n=5	252, **181** (94-515) n=8	582, **500** (105-1416) n=8	284, **202** (169-625) n=6
	HFAV	337, **266** (66-735) n=6	165, **162** (85-252) n=4	613, **350** (210-1826) n=13	276, **247** (175-407) n=3
	LFAV	32.5, **34.4** (2-63) n=10	26.6, **22.7** (0-58) n=11	58.7, **60.0** (29-87) n=3	57.8, **39.9** (18-119) n=12
	LFNV	19.0, **14.5** (2-46) n=8	20.1, **21.3** (13-26) n=3	67.6, **57.3** (5-202) n=6	13.0, **14.7** (2-17) n=5
Cl^-	**HFNV**	4.3, **2.7** (1-12) n=5	3.8, **2.2** (1-11) n=8	7.2, **5.4** (1-21) n=9	2.0, **2.5** (0-4) n=5
	HFAV	1.5, **1.0** (1-4) n=6	1.2, **0.8** (0-3) n=4	1.3, **0.8** (1-4) n=12	0.5, **0.7** (0-1) n=3
	LFAV	0.2, **0.1** (0-0) n=9	0.2, **0.1** (0-1) n=11	0.1, **0.1** (0-0) n=3	0.0, **0.0** (0-0) n=12
	LFNV	0.4, **0.4** (0-1) n=9	0.1, **0.2** (0-0) n=3	0.4, **0.3** (0-1) n=6	0.1, **0.1** (0-0) n=5
SO_4^{2-}	**HFNV**	3.1, **2.0** (0-9) n=5	13.6, **4.5** (0-61) n=8	11.9, **6.7** (1-25) n=9	25.2, **11.0** (4-84) n=5
	HFAV	1.2, **0.5** (0-3) n=6	1.5, **1.7** (0-2) n=4	3.0, **0.6** (0-15) n=13	22.5, **21.1** (6-40) n=3
	LFAV	0.1, **0.1** (0-0) n=10	0.0, **0.0** (0-0) n=11	0.1, **0.0** (0-0) n=3	0.2, **0.1** (0-1) n=12
	LFNV	0.2, **0.2** (0-0) n=9	0.0, **0.0** (0-0) n=3	0.1, **0.0** (0-0) n=6	0.1, **0.1** (0-0) n=5
DOC	**HFNV**	43.0, **35.0** (13-107) n=5	46.5, **47.8** (13-90) n=8	118.4, **89.3** (18-354) n=9	55.8, **36.6** (25-137) n=6
	HFAV	79.1, **57.9** (13-165) n=6	33.6, **31.3** (24-48) n=4	135.7, **59.8** (38-730) n=13	59.4, **50.2** (35-93) n=3
	LFAV	6.2, **4.6** (0-15) n=10	4.5, **3.8** (0-15) n=11	8.4, **7.4** (4-14) n=3	12.8, **5.6** (2-72) n=12
	LFNV	4.6, **3.5** (0-11) n=9	3.2, **3.2** (2-4) n=3	7.0, **5.3** (1-23) n=6	1.6, **2.0** (0-2) n=5
Fe^{2+}	**HFNV**	9.5, **5.0** (1-27) n=4	3.1, **2.9** (1-6) n=8	11.8, **4.2** (1-45) n=7	1.8, **2.0** (1-2) n=5
	HFAV	1.5, **1.3** (0-3) n=4	0.5, **0.6** (0-1) n=3	2.1, **1.5** (1-6) n=7	1.0, **0.9** (1-1) n=3
	LFAV	0.2, **0.2** (0-0) n=6	0.1, **0.1** (0-0) n=10	0.5, **0.5** (0-1) n=3	0.3, **0.2** (0-1) n=10
	LFNV	0.3, **0.2** (0-1) n=8	0.1, **0.1** (0-0) n=3	0.2, **0.2** (0-1) n=6	0.1, **0.1** (0-0) n=5
Si^{4+}	**HFNV**	8.8, **5.2** (2-23) n=4	10.0, **6.7** (4-21) n=8	19.3, **16.4** (3-52) n=8	10.2, **6.9** (5-24) n=6
	HFAV	13.7, **10.5** (3-29) n=6	6.7, **6.8** (4-9) n=4	14.9, **8.9** (5-35) n=9	6.7, **6.7** (3-10) n=3
	LFAV	1.4, **1.6** (0-2) n=4	0.9, **0.9** (0-2) n=11	1.6, **1.6** (2-2) n=1	1.4, **1.0** (0-4) n=12
	LFNV	0.9, **0.7** (0-2) n=9	0.8, **0.8** (1-1) n=3	1.8, **1.5** (0-6) n=6	0.3, **0.4** (0-0) n=5

Table 2.3: Mean and median (bold) ion instantaneous export grouped by flow and vegetative activity (continued).

(c)

		R1		H1	
		Pre	**Post**	**Pre**	**Post**
TN	**HFNV**	2258, **1613** (556-6331) n=5	1979, **1559** (551-3871) n=8	5944, **3575** (884-22338) n=8	2178, **1350** (1109-4988) n=5
	HFAV	3618, **2634** (501-6872) n=5	1206, **1392** (681-1546) n=3	4460, **2853** (1556-11637) n=12	1871, **1615** (1235-2762) n=3
	LFAV	278, **237** (17-630) n=10	179, **153** (10-397) n=10	305, **269** (111-534) n=3	309, **300** (80-685) n=11
	LFNV	222, **214** (19-480) n=9	93.4, **101.1** (56-123) n=3	214, **267** (62-365) n=5	57.5, **71.2** (9-82) n=5
TDN	**HFNV**	2094, **1422** (520-6068) n=5	1615, **1569** (504-3136) n=8	5600, **3775** (754-18988) n=9	1573, **1300** (1023-2838) n=6
	HFAV	3392, **2295** (532-7643) n=6	1089, **1123** (704-1408) n=4	3868, **2133** (1436-11035) n=13	1733, **1604** (1063-2532) n=3
	LFAV	312, **228** (16-1060) n=10	139.2, **98.3** (2-344) n=11	227, **105** (92-484) n=3	272, **205** (66-634) n=12
	LFNV	206, **204** (15-436) n=9	96.0, **100.7** (55-133) n=3	195, **246** (43-302) n=5	52.6, **59.6** (9-69) n=5
NH_4^+	**HFNV**	432.0, **23.8** (12-2063) n=5	141.4, **91.5** (11-387) n=8	513.1, **94.3** (6-1762) n=9	141, **127** (89-204) n=6
	HFAV	64.9, **51.5** (7-177) n=6	23.1, **20.3** (10-41) n=4	86.7, **70.1** (9-273) n=13	55.9, **54.9** (32-80) n=3
	LFAV	9.7, **6.9** (0-42) n=10	2.5, **1.0** (0-12) n=11	9.8, **11.1** (4-15) n=3	8.0, **6.7** (3-22) n=12
	LFNV	14.7, **6.0** (0-55) n=9	2.7, **2.2** (2-4) n=3	44.2, **36.8** (2-119) n=6	9.6, **5.0** (3-30) n=5
NO_2^-+NO_3^-	**HFNV**	39.8, **10.7** (2-168) n=5	37.0, **9.8** (1-130) n=8	49.3, **26.9** (2-220) n=9	25.9, **26.3** (3-49) n=6
	HFAV	13.1, **11.5** (1-36) n=6	4.4, **2.4** (1-12) n=4	6.7, **4.7** (1-15) n=13	4.6, **4.5** (4-6) n=3
	LFAV	1.1, **0.3** (0-7) n=10	0.2, **0.2** (0-1) n=11	0.7, **0.5** (0-1) n=3	0.3, **0.2** (0-1) n=12
	LFNV	6.0, **1.3** (0-29) n=9	0.3, **0.2** (0-0) n=3	2.8, **3.1** (0-5) n=6	0.9, **0.2** (0-4) n=5
TP	**HFNV**	637, **363** (75-1843) n=5	277, **236** (56-674) n=8	746, **244** (59-2780) n=8	138, **146** (82-166) n=6
	HFAV	314, **252** (60-611) n=6	79.9, **90.6** (45-104) n=3	325, **205** (87-1090) n=13	102, **107** (74-124) n=3
	LFAV	39.7, **46.3** (2-75) n=10	35.8, **21.0** (2-161) n=10	37.6, **43.1** (24-46) n=3	30.3, **26.3** (11-58) n=11
	LFNV	36.6, **31.1** (2-88) n=9	13.1, **12.1** (12-16) n=3	42.3, **35.8** (15-82) n=6	16.3, **8.9** (6-36) n=5
TDP	**HFNV**	336, **191** (44-1036) n=5	144, **111** (25-392) n=8	466, **179** (39-1755) n=9	82.5, **85.4** (42-115) n=6
	HFAV	219, **152** (34-476) n=6	76.4, **69.8** (17-149) n=4	182.2, **85.0** (55-613) n=13	57.4, **55.8** (36-80) n=3
	LFAV	23.3, **24.1** (2-46) n=10	6.3, **4.7** (0-17) n=11	17.4, **17.2** (8-27) n=3	11.7, **8.7** (3-33) n=12
	LFNV	19.6, **17.2** (0-46) n=9	4.7, **5.3** (3-6) n=3	8.4, **6.0** (0-21) n=6	3.1, **3.9** (0-4) n=5
SRP	**HFNV**	297, **138** (34-951) n=5	75.2, **57.1** (16-217) n=8	304, **117** (15-1138) n=9	27.2, **29.8** (15-37) n=6
	HFAV	154, **117** (17-358) n=6	47.5, **34.7** (5-116) n=4	130.7, **59.9** (19-483) n=13	18.2, **22.0** (10-22) n=3
	LFAV	18.5, **22.0** (1-41) n=10	2.7, **1.1** (0-13) n=11	11.3, **13.7** (6-15) n=3	3.1, **2.1** (1-11) n=12
	LFNV	13.6, **10.0** (0-37) n=9	2.3, **2.9** (1-3) n=3	5.1, **4.3** (0-10) n=6	1.7, **0.9** (0-6) n=5

The Kruskal-Wallis test determined that there were significant differences between categories (Table 2.4). The Mann-Witney U-test identified which categories were significantly different from each other. The Mann-Witney U-test table for SO_4^{2-} was included in the results as a representation of the statistical data (Table 2.5). Appendix A includes the statistical tables of all the ions studied in this thesis. Statistical analysis of the subset of data — excluding extreme high flows — revealed that although spring melt (HFNV) showed some significant differences between years for Na^+ , SO_4^{2-} , Si^{4+} and P concentrations (Table A.1), there were no significant differences in export for R1 (Table A.2). Summer low flows (LFAV) also showed some significant differences in nutrient (N and P) concentrations (Table A.1) although export was significantly different only for P (Table A.2). In general, chemical export was not significantly different from year to year for the same catchment if extreme high-flow events are disregarded.

Table 2.4: Kruskal-Wallis test for significant change in ion concentration and export between any of the categories (R1/H1, pre/post, high-flow/low-flow, active vegetation/non-active vegetation): p-values $< \alpha = 0.05$ are considered significant in this thesis. Degrees of freedom (df) = 15.

(a) Concentration

Ion	KW χ^2	p-value
Ca^{2+}	72.7	1.47e-09
Mg^{2+}	56.2	1.10e-06
Na^+	68.2	9.25e-09
K^+	50.1	1.17e-05
HCO_3^-	71.4	2.51e-09
Cl^-	68.7	7.56e-09
SO_4^{2-}	58.8	4.06e-07
DOC	54.9	1.83e-06
Fe^{2+}	29.6	1.35e-02
Si^{4+}	51.8	6.00e-06
TN	43.1	1.53e-04
TDN	49.8	1.30e-05
NH_4^+	30.5	1.04e-02
NO_2^-+NO_3^-	37.1	1.23e-03
TP	44.2	1.03e-04
TDP	41.8	2.39e-04
SRP	51.1	8.06e-06

(b) Export

Ion	KW χ^2	p-value
Ca^{2+}	87.2	3.29e-12
Mg^{2+}	80.8	4.92e-11
Na^+	86.9	3.72e-12
K^+	84.1	1.23e-11
HCO_3^-	86.7	4.10e-12
Cl^-	86.2	4.96e-12
SO_4^{2-}	84.4	1.07e-11
DOC	85.2	7.62e-12
Fe^{2+}	64.2	4.69e-08
Si^{4+}	75.0	5.55e-10
TN	83.4	1.65e-11
TDN	88.6	1.84e-12
NH_4^+	73.3	1.12e-09
NO_2^-+NO_3^-	75.3	4.96e-10
TP	77.9	1.66e-10
TDP	87.2	3.32e-12
SRP	83.7	1.46e-11

Table 2.5: Mann-Witney U-test of SO_4^{2-} export: p-values $< \alpha = 0.05$ are in bold. The major diagonal is greyed out since this category is always perfectly correlated with itself. This table is also symmetric around the major diagonal since the test is symmetric. The subset of data with flow and concentrations of both R1 and H1 taken <24 hours apart is used here. Pre-harvest data was collected before July 2, 2007. Post-harvest data was collected after July 2, 2007, when harvesting began on H1. Categorical boxes are defined by flow (high or low) and by vegetation (active or not-active): high-flow non-active vegetation (HFNV), high-flow active vegetation (HFAV), low-flow active vegetation (LFAV), low-flow non-active vegetation (LFNV).

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.247	**0.001**	**0.001**	0.435	1.000	**0.000**	**0.036**	0.060	0.503	**0.036**	**0.004**	**0.016**	0.190	**0.002**	**0.008**
		HFAV	0.247	1.000	**0.000**	0.145	**0.029**	0.662	**0.000**	**0.024**	**0.002**	0.898	0.095	**0.015**	**0.004**	**0.038**	**0.007**	**0.009**
		LFAV	**0.001**	**0.000**	1.000	**0.035**	**0.000**	**0.003**	0.251	0.811	**0.000**	**0.000**	0.692	0.713	**0.001**	**0.002**	0.283	0.859
		LFNV	**0.001**	0.145	**0.035**	1.000	**0.000**	**0.042**	**0.007**	0.100	**0.000**	**0.030**	0.282	0.224	**0.001**	**0.003**	0.247	0.190
R1	**Post**	HFNV	0.435	**0.029**	**0.000**	**0.000**	1.000	0.284	**0.000**	**0.012**	0.606	**0.045**	**0.012**	**0.001**	0.171	0.683	**0.000**	**0.002**
		HFAV	1.000	0.662	**0.003**	**0.042**	0.284	1.000	**0.001**	**0.036**	**0.042**	0.566	0.071	**0.009**	**0.016**	0.286	**0.004**	**0.016**
		LFAV	**0.000**	**0.000**	0.251	**0.007**	**0.000**	**0.001**	1.000	0.659	**0.000**	**0.000**	0.885	0.098	**0.000**	**0.001**	**0.004**	0.145
		LFNV	**0.036**	**0.024**	0.811	0.100	**0.012**	**0.036**	0.659	1.000	**0.009**	**0.007**	0.700	0.548	**0.036**	0.057	0.136	0.393
H1	**Pre**	HFNV	0.060	**0.002**	**0.000**	**0.000**	0.606	**0.042**	**0.000**	**0.009**	1.000	**0.003**	**0.009**	**0.000**	0.606	0.940	**0.000**	**0.001**
		HFAV	0.503	0.898	**0.000**	**0.030**	**0.045**	0.566	**0.000**	**0.007**	**0.003**	1.000	**0.039**	**0.003**	**0.010**	**0.032**	**0.002**	**0.007**
		LFAV	**0.036**	0.095	0.692	0.282	**0.012**	0.071	0.885	0.700	**0.009**	**0.039**	1.000	0.381	**0.036**	0.057	0.295	1.000
		LFNV	**0.004**	**0.015**	0.713	0.224	**0.001**	**0.009**	0.098	0.548	**0.000**	**0.003**	0.381	1.000	**0.004**	**0.010**	0.385	0.931
H1	**Post**	HFNV	**0.016**	**0.004**	**0.001**	**0.001**	0.171	**0.016**	**0.000**	**0.036**	0.606	**0.010**	**0.036**	**0.004**	1.000	0.905	**0.000**	**0.008**
		HFAV	0.190	**0.038**	**0.002**	**0.003**	0.683	0.286	**0.001**	0.057	0.940	**0.032**	0.057	**0.010**	0.905	1.000	**0.001**	**0.016**
		LFAV	**0.002**	**0.007**	0.283	0.247	**0.000**	**0.004**	**0.004**	0.136	**0.000**	**0.002**	0.295	0.385	**0.000**	**0.001**	1.000	0.879
		LFNV	**0.008**	**0.009**	0.859	0.190	**0.002**	**0.016**	0.145	0.393	**0.001**	**0.007**	1.000	0.931	**0.008**	**0.016**	0.879	1.000

Figure 2.1 also describes intra-annual variation in flow. Although the point stream discharges have not been finalized with a continuous record, it is evident that low-flow exists for the majority of the flow season. High-flow responses occurred quickly with little "ramp-up" or "ramp-down" time. The extreme high flows in Boreal Plain streams occurred during spring melt and summer storms as well as after beaver dam breakages (Figure 2.1). Summer storm events caused just as great a flow response from the catchment as spring melt (Figure 2.1). However, the chemical composition of high-flow events do differ: major cations, major anions and TP concentrations were significantly different between summer storms and spring melt (Table A.1). Comparison of the R1 and H1 pre-harvest HFNV (spring melt) ion concentrations with those from HFAV (summer storms) showed that K^+ , Cl^- , SO_4^{2-} , TN and TP concentrations were greater during spring melt than during summer storms (Table 2.2). Ca^{2+} , Mg^{2+} , Na^+ , HCO_3^- and DOC concentrations were greater during summer storms than in spring melt (Table 2.2). However, whether spring melt or summer storms had the greatest export depends on the ion in question: HFNV had the highest export for K^+ , SO_4^{2-} , Cl^- , TN and TP whereas HFAV had the highest export for Ca^{2+} , HCO_3^- and DOC (Table 2.3). Ca^{2+} and HCO_3^- were the main cation and anion exported from the catchment. They were at least 2 and 20 times higher respectively than other major cation and anion export (Table 2.3). Although chemical concentrations did significantly differ between summer storms and spring melt there were no statistically significant differences in chemical export (Table A.2).

Although high flows in the WBP have similar chemical export, they differ significantly from low flows in ion export. Statistical analysis of all high-flow:low-flow pairings in R1 shows that ion export is dominated by flow (Table A.2). This is also evident in Figure 2.2. All the ions examined in this study had much greater export during high flows than during low flows: Ca^{2+} , HCO_3^- , Cl^- , K^+ , Si^{4+} and DOC had a ten-fold difference in export between high and low flows, SO_4^{2-} had a ten- to hundred-fold difference, TN and TP had a ten- to twenty-fold difference (Table 2.3). The difference in ion concentrations between high and low flows was not as significant. Although major cations and anions differed significantly in concentration between HFNV and LFAV for R1, the concentration was not consistently different between both high-flow and both low-flow categories (Table A.1). Nutrients did not show a significant difference in concentration between high and low flows at all (Table A.1).

In general, the trends in chemical concentration for most ions described in Figure 2.1 showed a sharp drop in concentration during spring melt with a longer climb in concentration over the summer. Table 2.2 shows that HCO_3^- and major cations had their highest concentrations during low-flow. Although highest concentrations did occur during low flows, the reverse—that lowest concentrations occurred during high flows—was not evident. In fact, high flows (>10 L/s) typically clustered around the median concentration of major cations and anions (Figure 2.3). K^+, Fe^{2+}, NH_4^+ and TP had high flows that were above the median concentration (Figure 2.3). Although flow dominated the chemical export of a catchment, it did not necessarily dominate the chemical composition.

Table 2.2 shows that the highest concentrations of Cl^-, NH_4^+ and NO_2^-+NO_3^- occurred during periods with non-active vegetation. However, ion concentrations were not significantly different between active vegetation and non-active vegetation periods for any of the nutrients (Table A.1). SO_4^{2-} was the only ion that showed significant differences in concentration depending on vegetative activity, although Ca^{2+}, K^+, Cl^-, and DOC did show some significant differences in ion concentration when vegetative activity and flow was combined (Table A.1). Vegetative activity did seem to impact K^+, Cl^-, SO_4^{2-}, NH_4^+ and NO_2^-+NO_3^- ions by decreasing the export slightly in each flow group, but could not significantly dominate the mean trend of flow (Table 2.3). In general, SO_4^{2-} was the only ion in surface stream water to be significantly impacted by vegetative activity.

Trends were difficult to distinguish for ion concentrations with large ranges of variation and few data points. This is especially true for the nutrient data where variation in concentration ranged up to twenty- or thirty-fold (see LFNV for NH_4^+ in Table 2.2). Despite this, it can be seen qualitatively that pulses of high nutrient concentration occurred throughout the hydrological year of WBP catchments (Figure 2.1). As discussed above, these pulses of nutrients in the stream were not significantly linked to either flow or vegetative activity alone (Table A.1).

The variation in nutrient concentration and export was significantly different from catchment to catchment. Spring melt showed significant differences in P concentrations between R1 and H1 pre-harvest, while low-flow showed significant differences in N (Table A.1). NH_4^+ and NO_2^-+NO_3^- export showed very large variability, especially in the R1 catchment (Table 2.3). Nutrients were not the only ions to be impacted by catchment. Concentrations of Mg^{2+} , Na^+ , HCO_3^- and Fe^{2+} were significantly different between R1 and H1 pre-harvest (Table A.1) during summer storms. However, Mg^{2+} and Na^+ were the only major cations and anions with significant differences in export (Table A.2). Table 2.3 and Figure 2.5 show that export from H1 was greater than from R1 for all ions except K^+ , Cl^- , NO_2^-+NO_3^- and SRP during high-flow periods. In general, R1 had chemical concentrations (except during summer storms) and export similar to those of H1 for all major cations and anions with the exception of Na^+ .

It is important to note that although the concentrations and export of the major cations and anions were similar between catchments, the magnitudes of R1 export and H1 export did not always correspond in time. Extreme high export in one catchment was not necessarily reflected in the other (Figure 2.1 and Figure 2.5). Beaver dam breakages did account for some of this variability but not for all. Extreme high flow events that vary from catchment to catchment may have had a large and significant impact on the total chemical export of these WBP catchments.

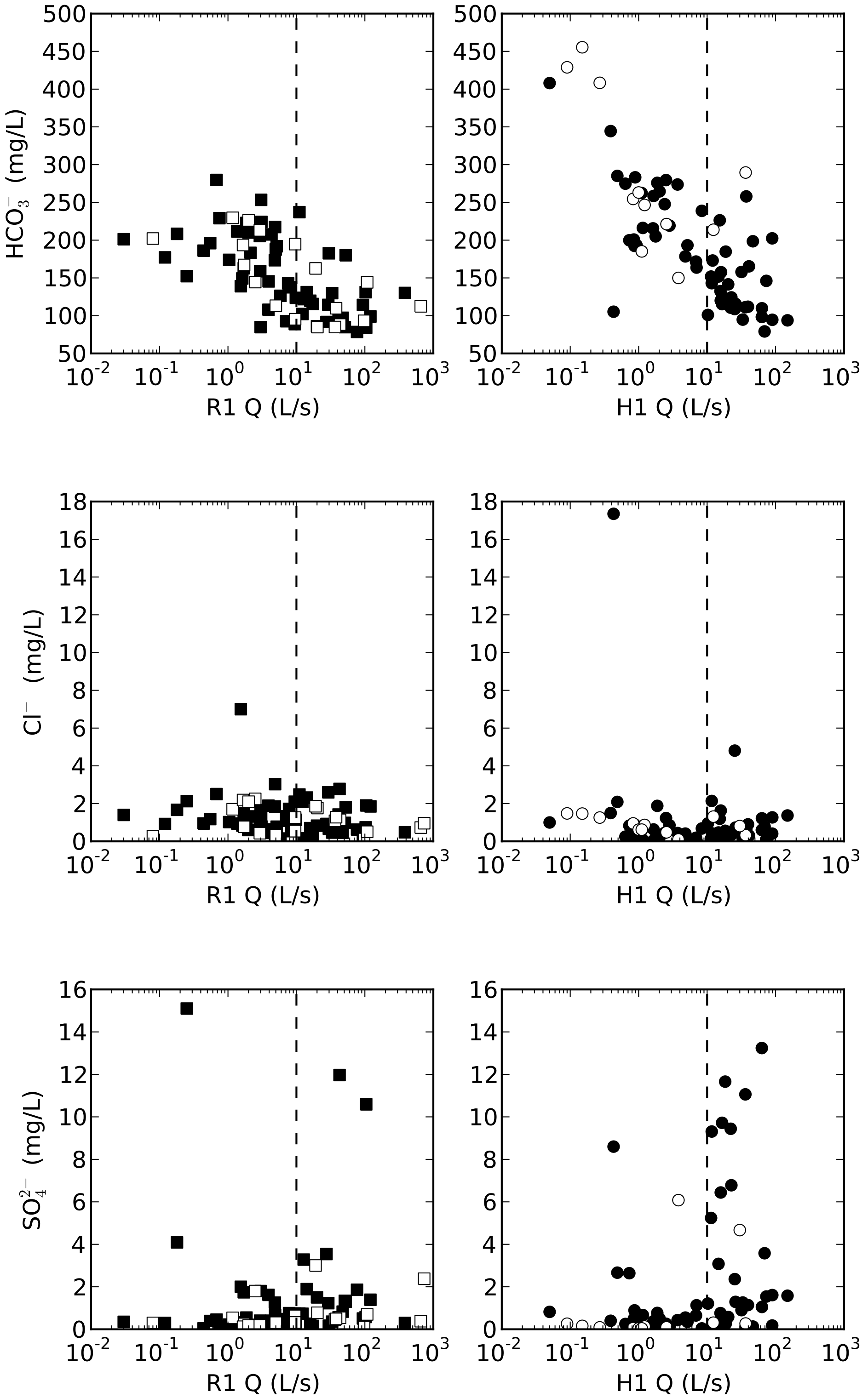

Figure 2.3: The variation of ion concentration with flow. Point flow measures are on a log scale and are not normalized by catchment area. R1 is the sub-figure on the left (squares), H1 is on the right (circles). White shapes indicate the pre-harvest period (before July 2, 2007) and black shapes are post-harvest. The dotted vertical line at 10 L/s indicates the distinction used in this thesis between low-flow and high-flow.

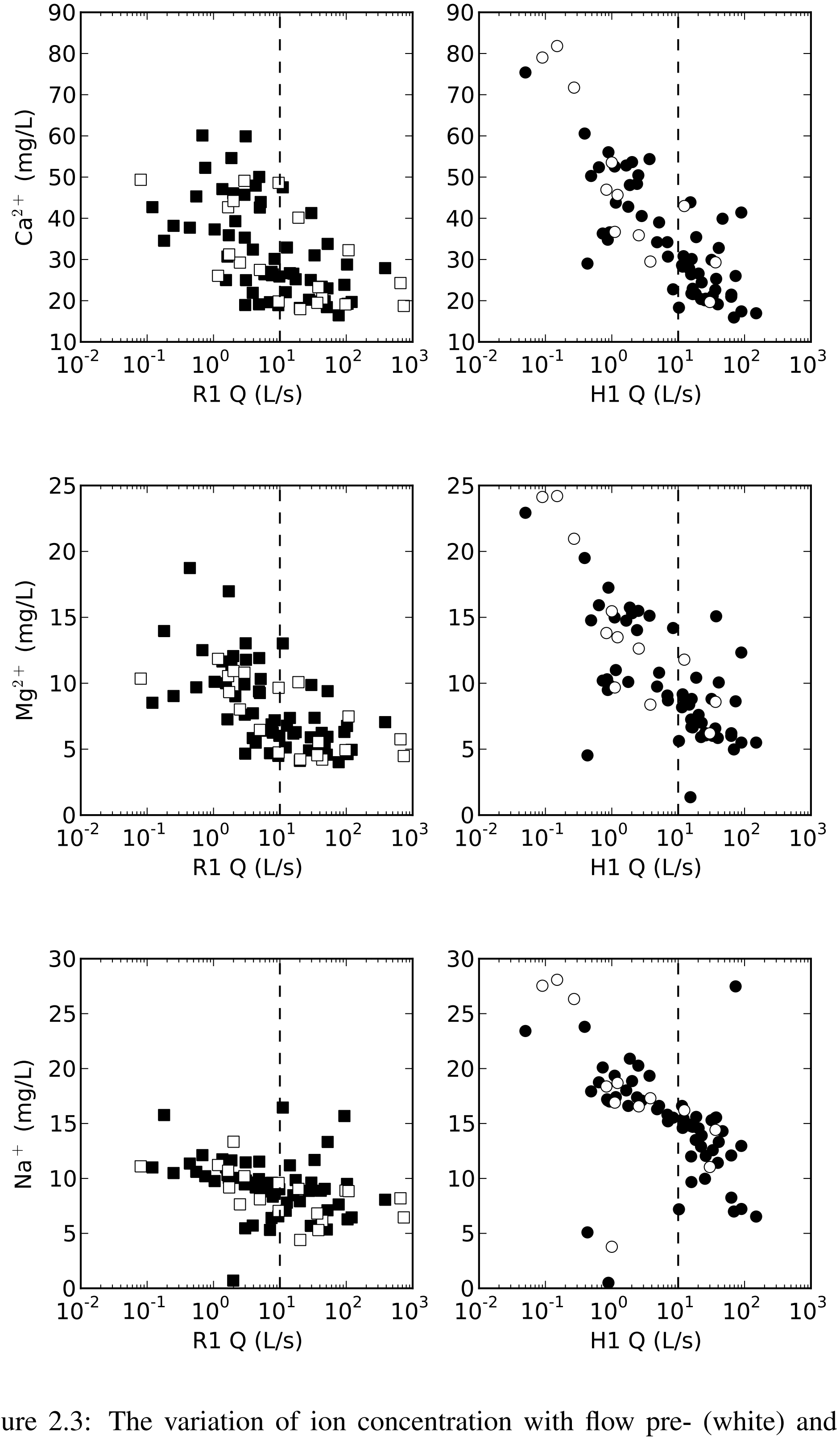

Figure 2.3: The variation of ion concentration with flow pre- (white) and post- (black) harvest (continued).

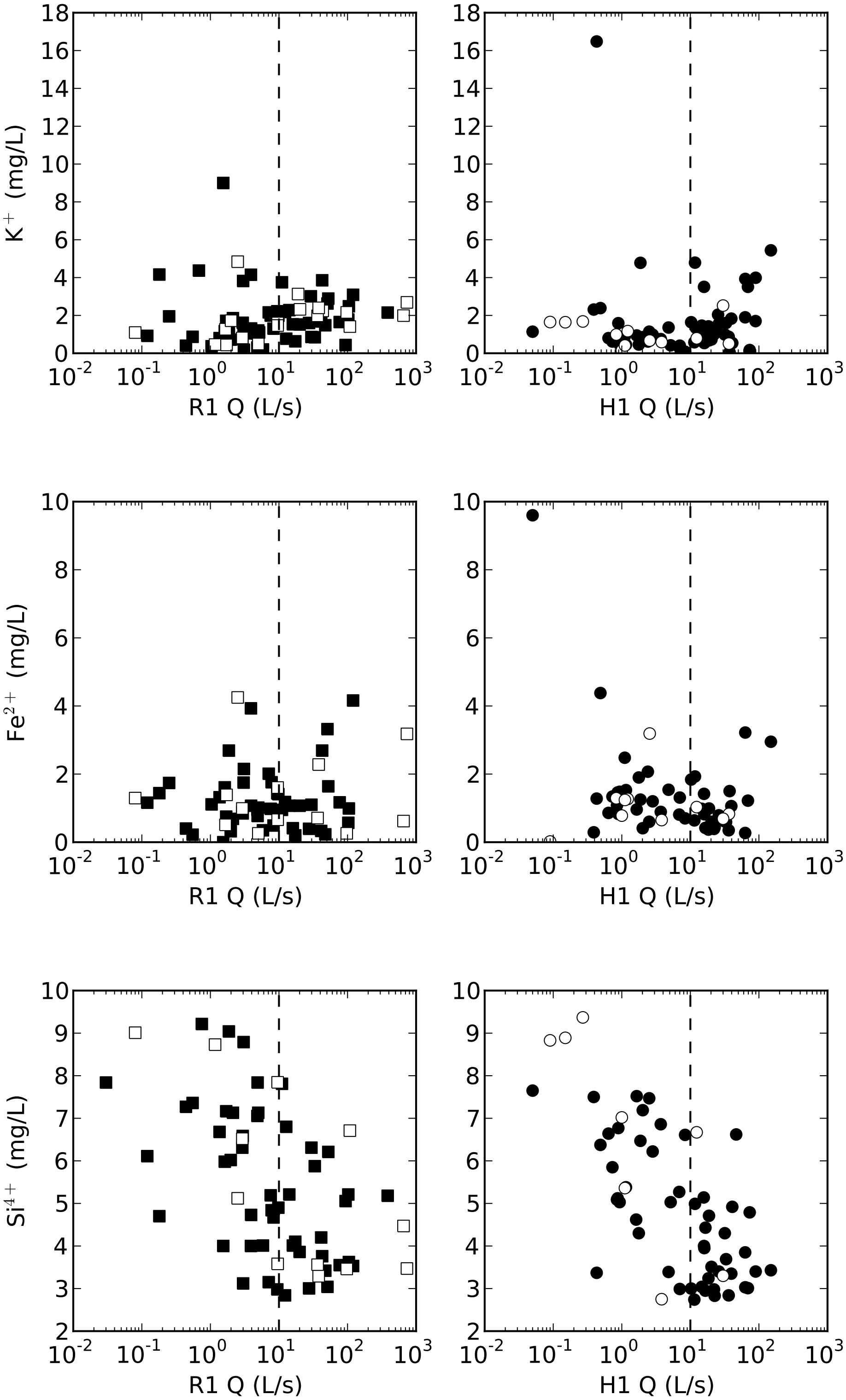

Figure 2.3: The variation of ion concentration with flow pre- (white) and post- (black) harvest (continued).

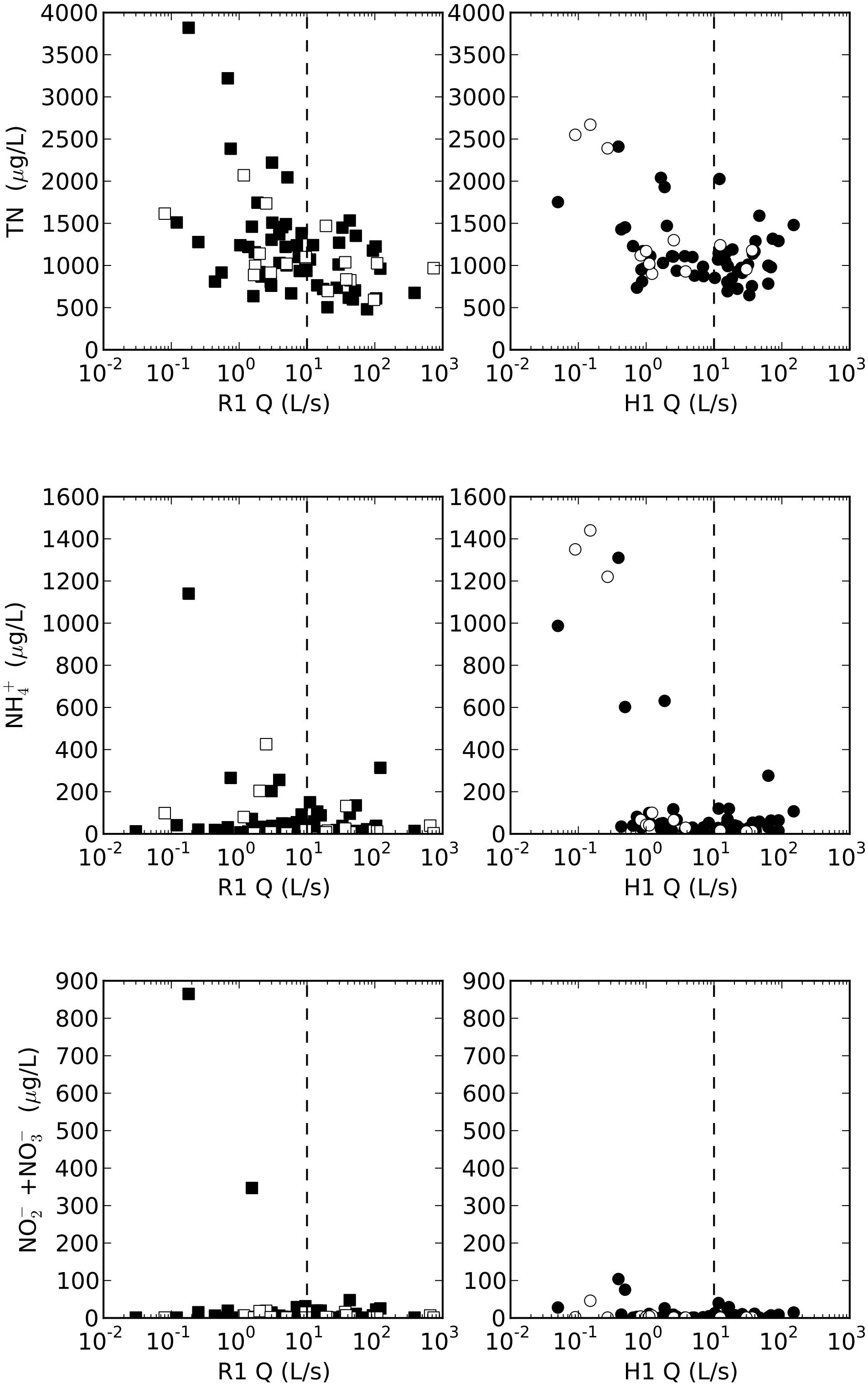

Figure 2.3: The variation of ion concentration with flow pre- (white) and post- (black) harvest (continued).

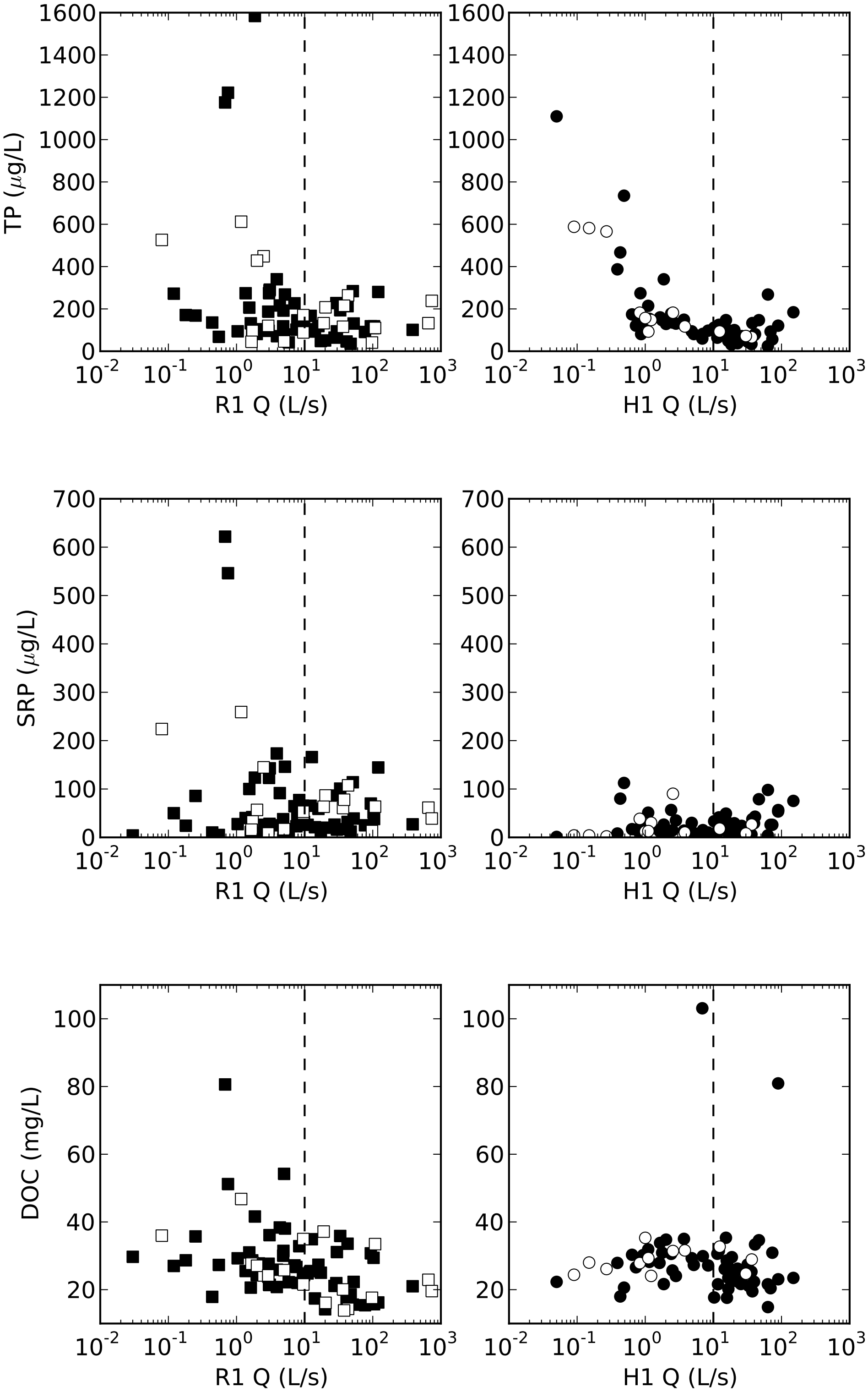

Figure 2.3: The variation of ion concentration with flow pre- (white) and post- (black) harvest (continued).

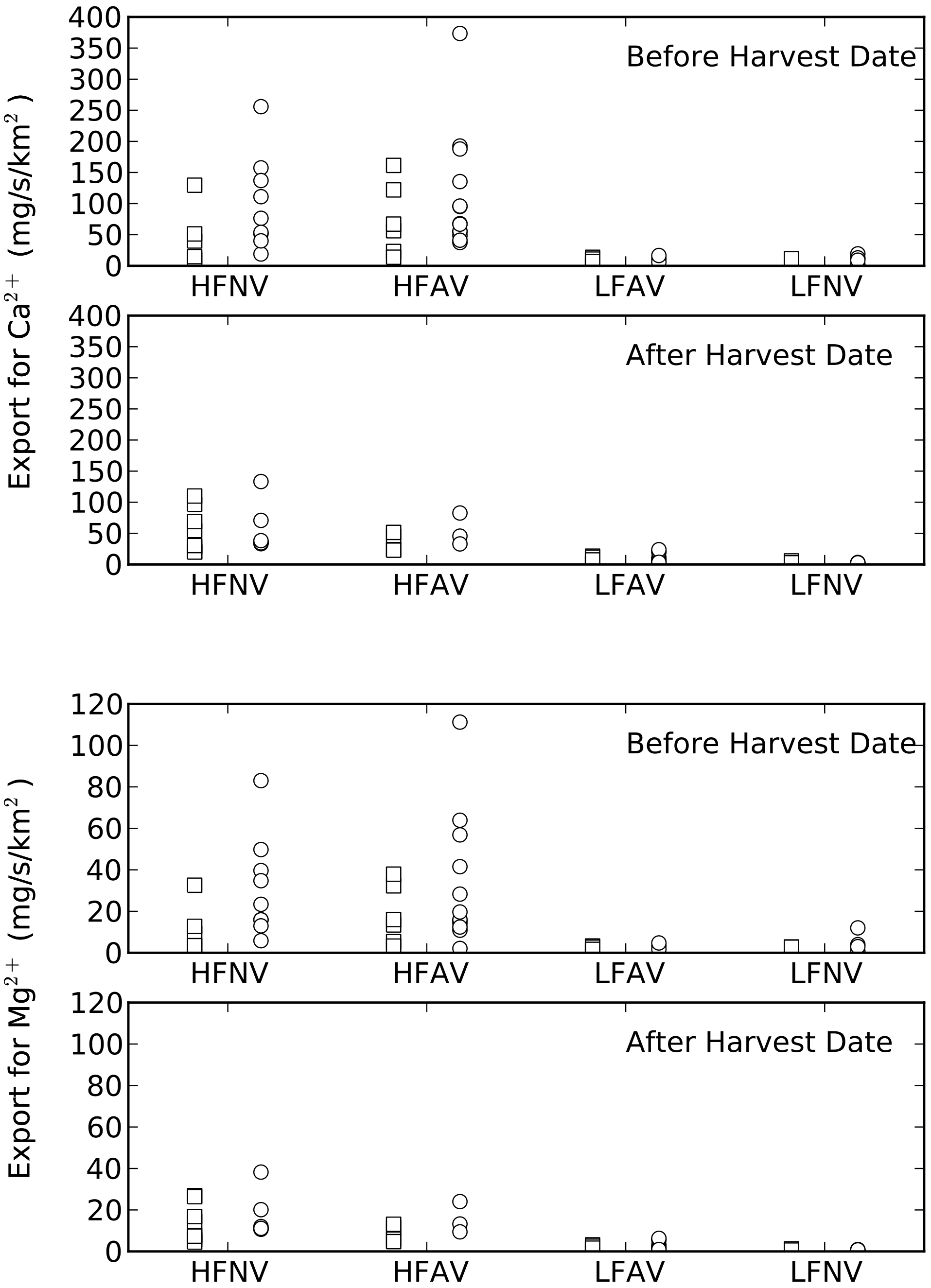

Figure 2.4: R1 and H1 ion export before and after the harvest date (July 2, 2007), grouped by flow and vegetative activity. The subset of data in which flow and concentrations of both R1 and H1 were taken <24 hours apart is used here. Export has been normalized by catchment area. Pre-harvest values are located on the top sub-figure with post-harvest values on the bottom. R1 is indicated by squares, H1 by circles.

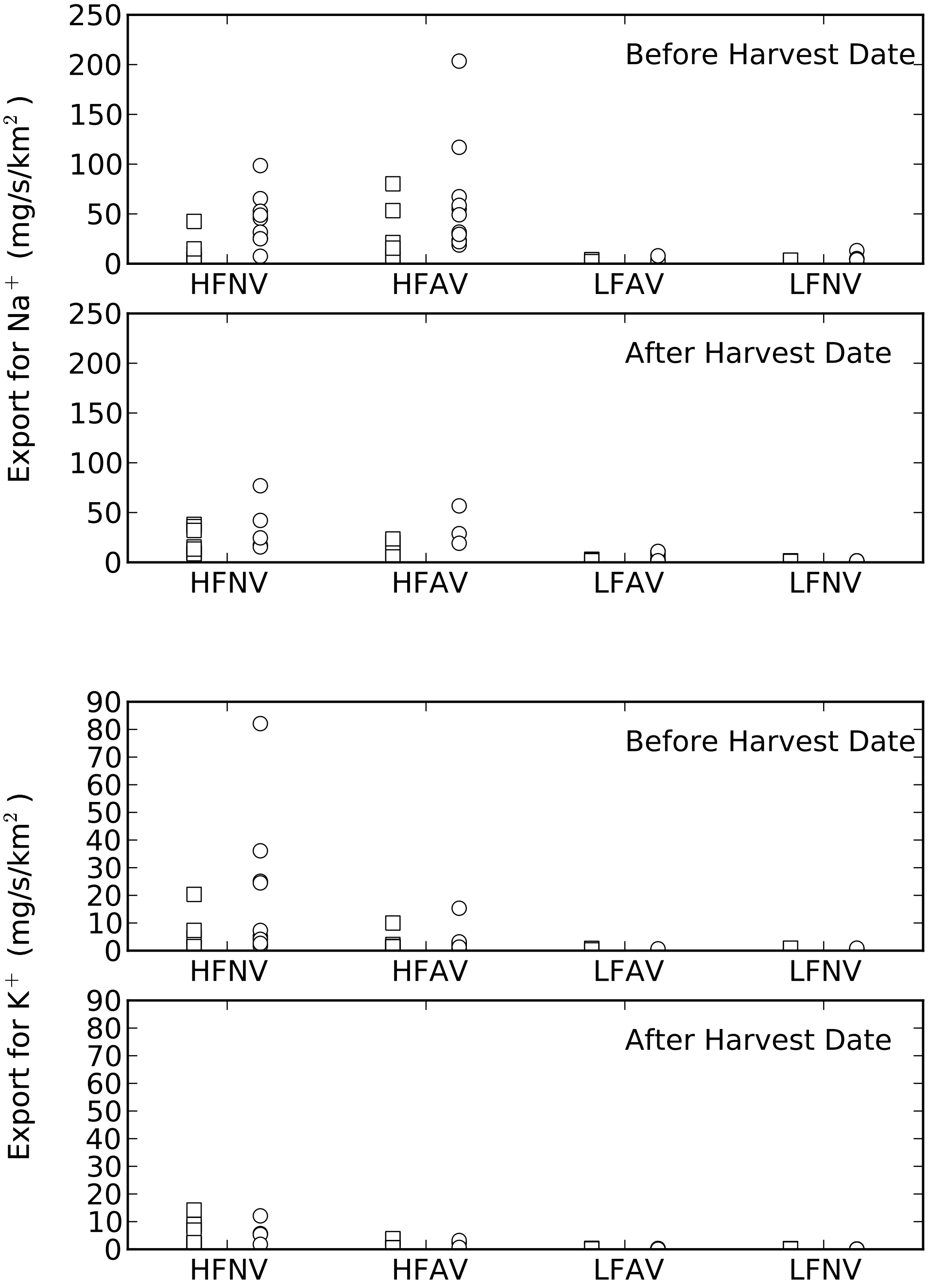

Figure 2.4: R1 (square) and H1 (circle) ion export pre- and post-harvest (continued).

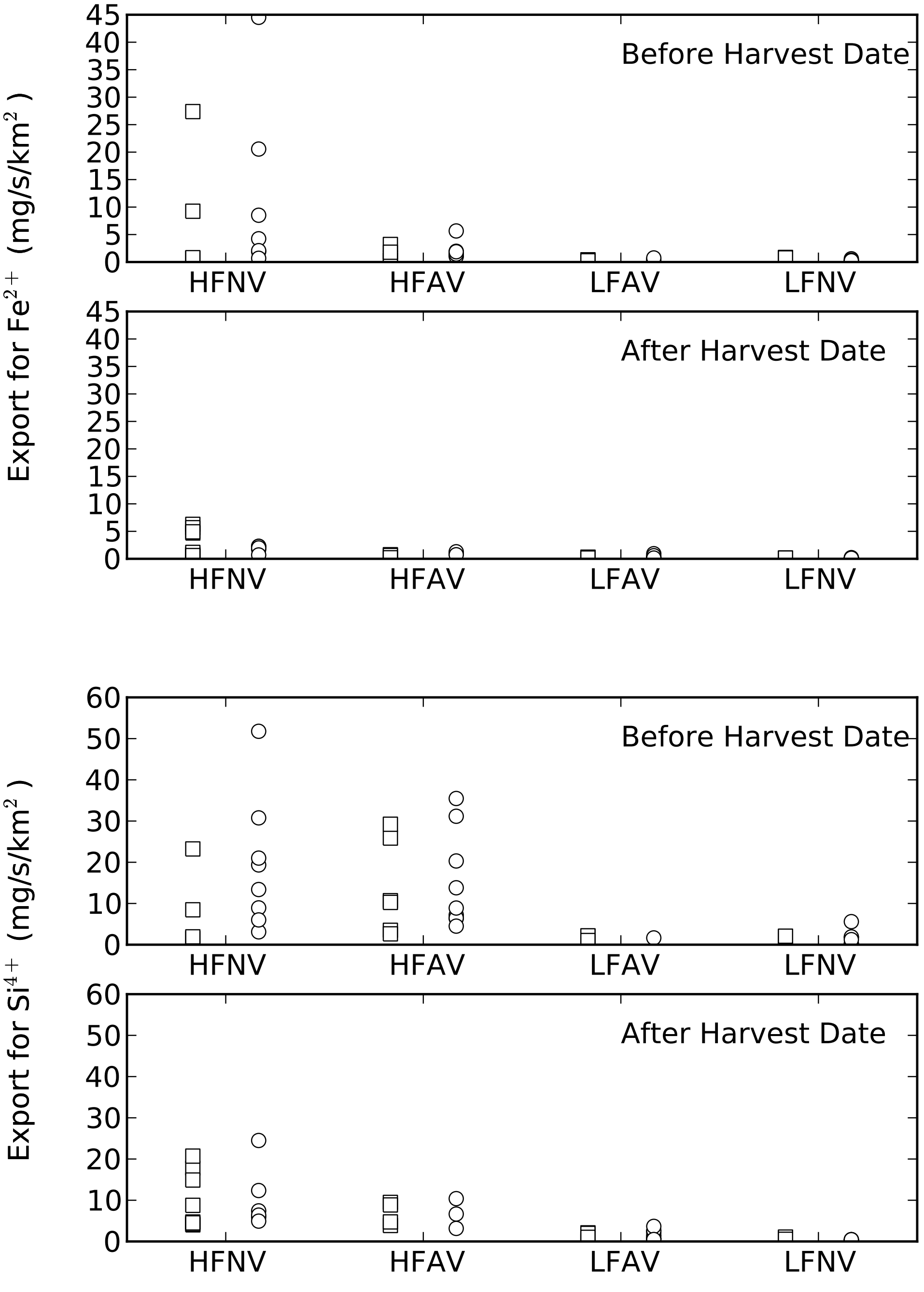

Figure 2.4: R1 (square) and H1 (circle) ion export pre- and post-harvest (continued).

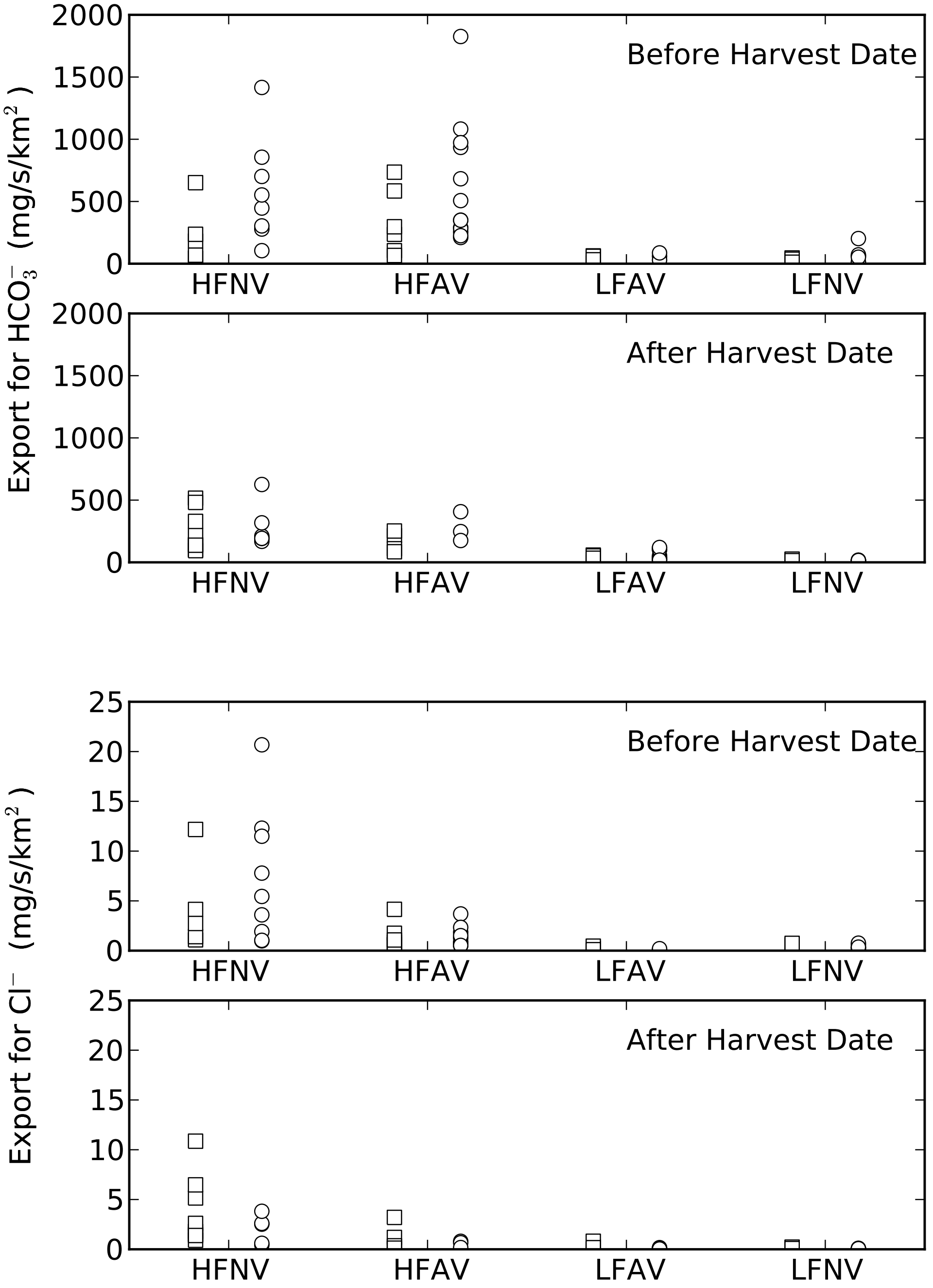

Figure 2.4: R1 (square) and H1 (circle) ion export pre- and post-harvest (continued).

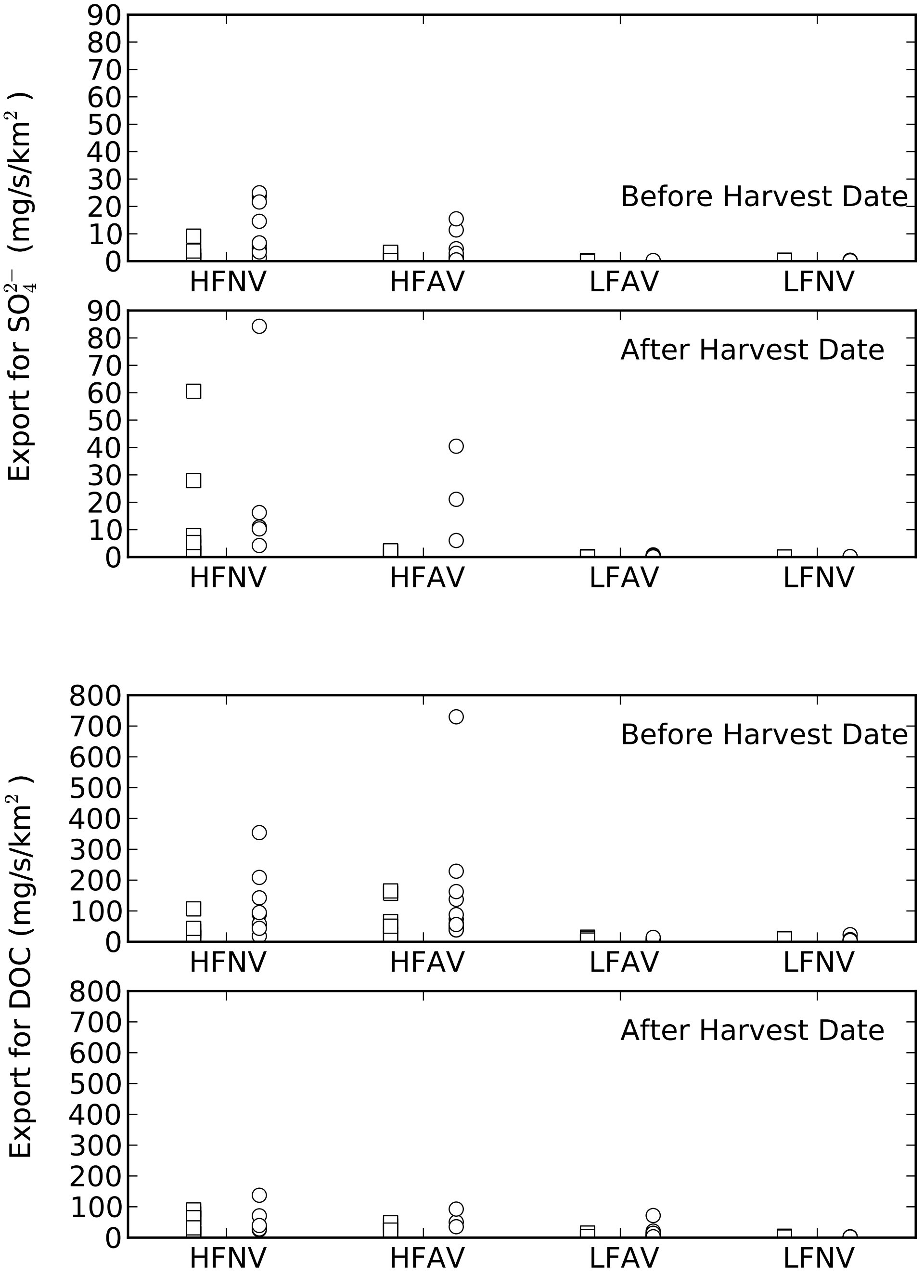

Figure 2.4: R1 (square) and H1 (circle) ion export pre- and post-harvest (continued).

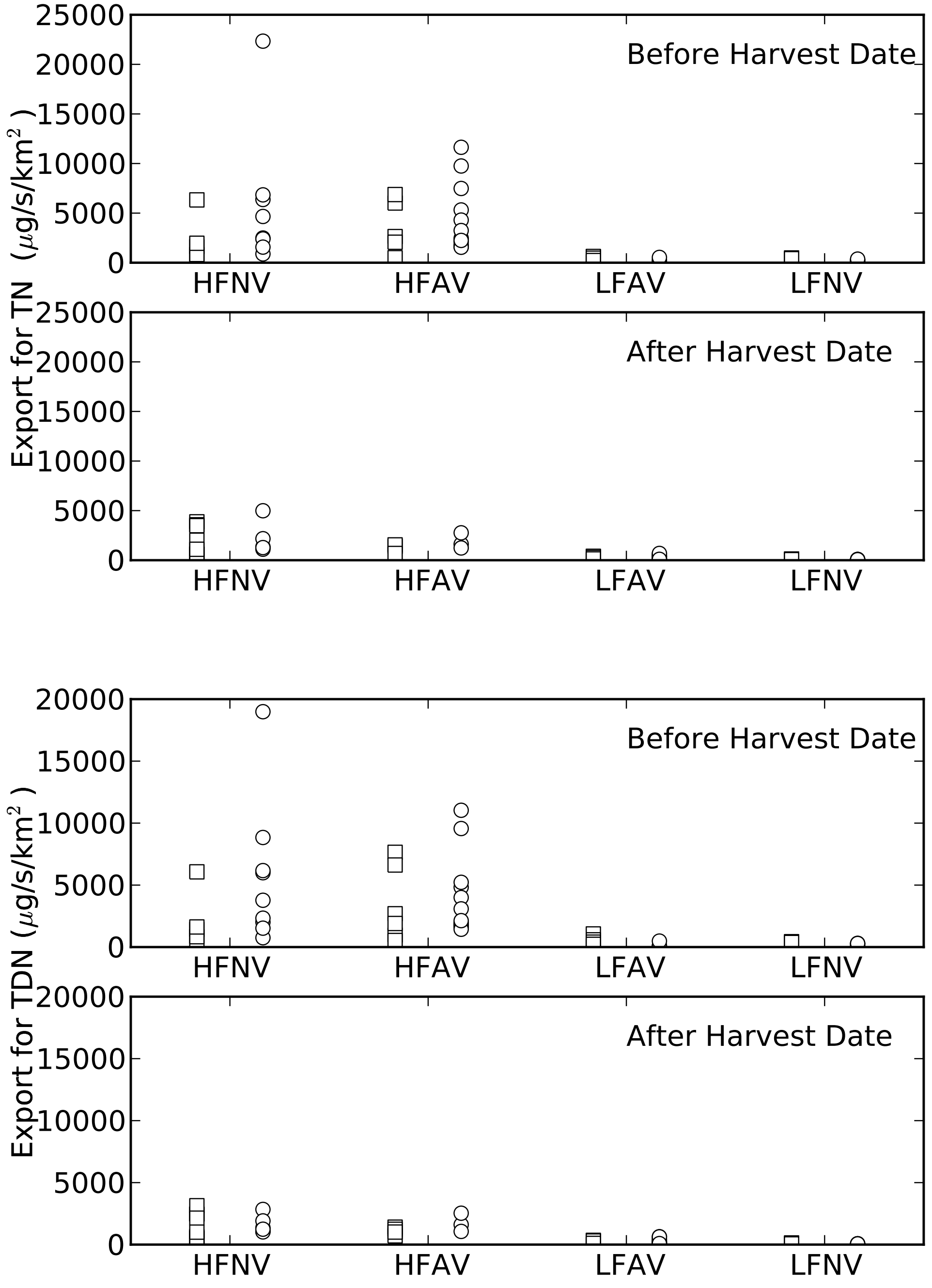

Figure 2.4: R1 (square) and H1 (circle) ion export pre- and post-harvest (continued).

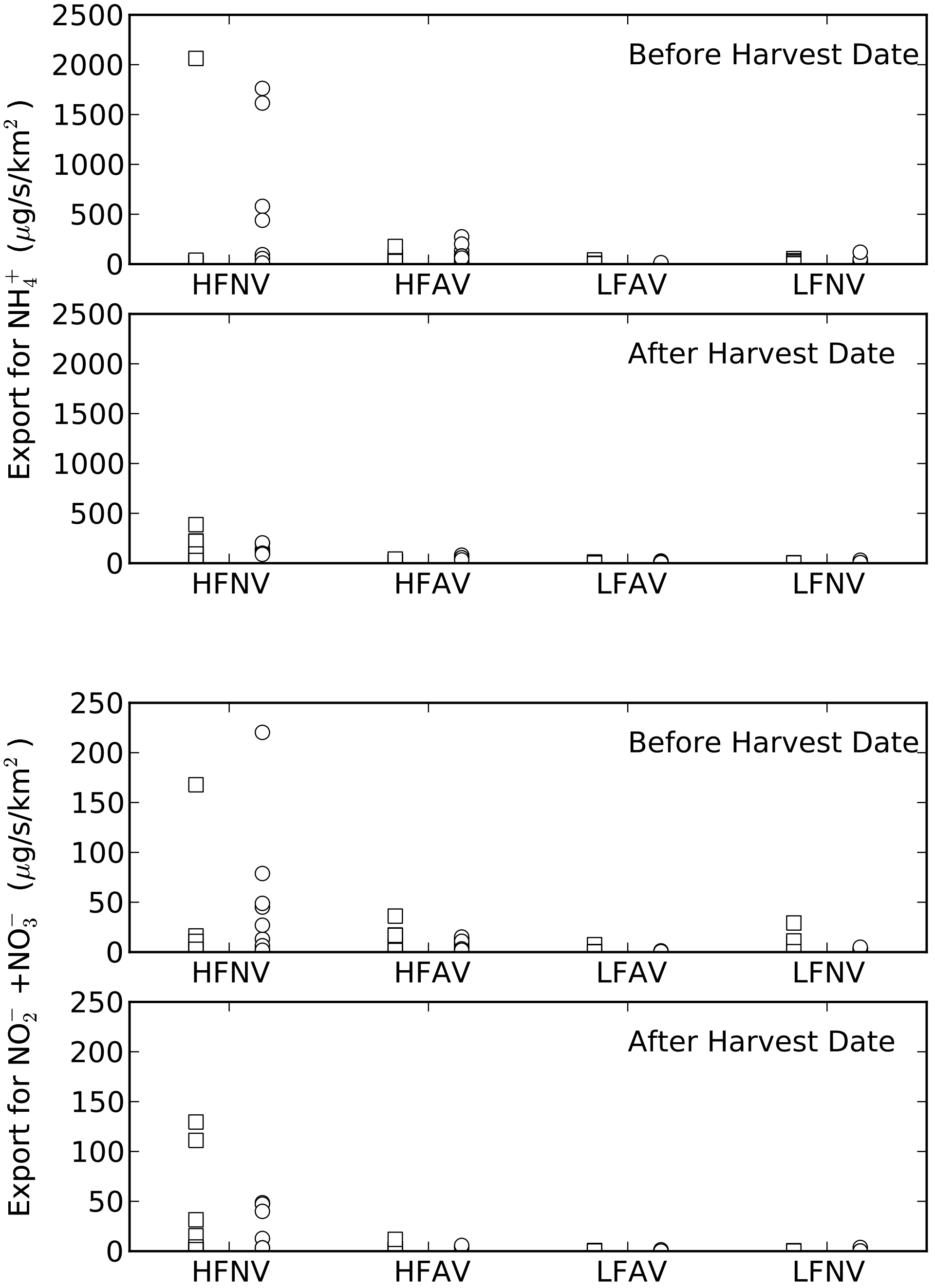

Figure 2.4: R1 (square) and H1 (circle) ion export pre- and post-harvest (continued).

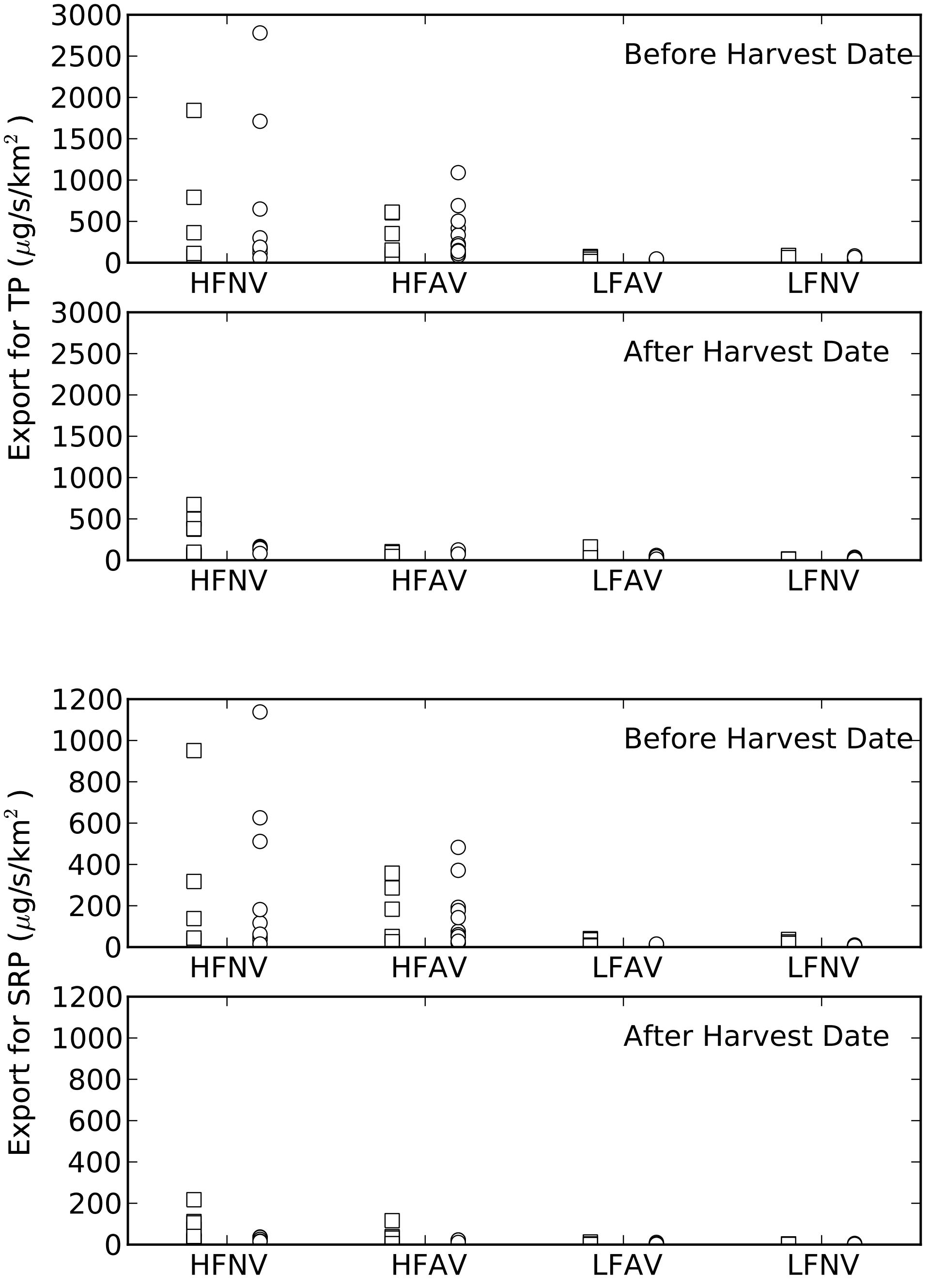

Figure 2.4: R1 (square) and H1 (circle) ion export pre- and post-harvest (continued).

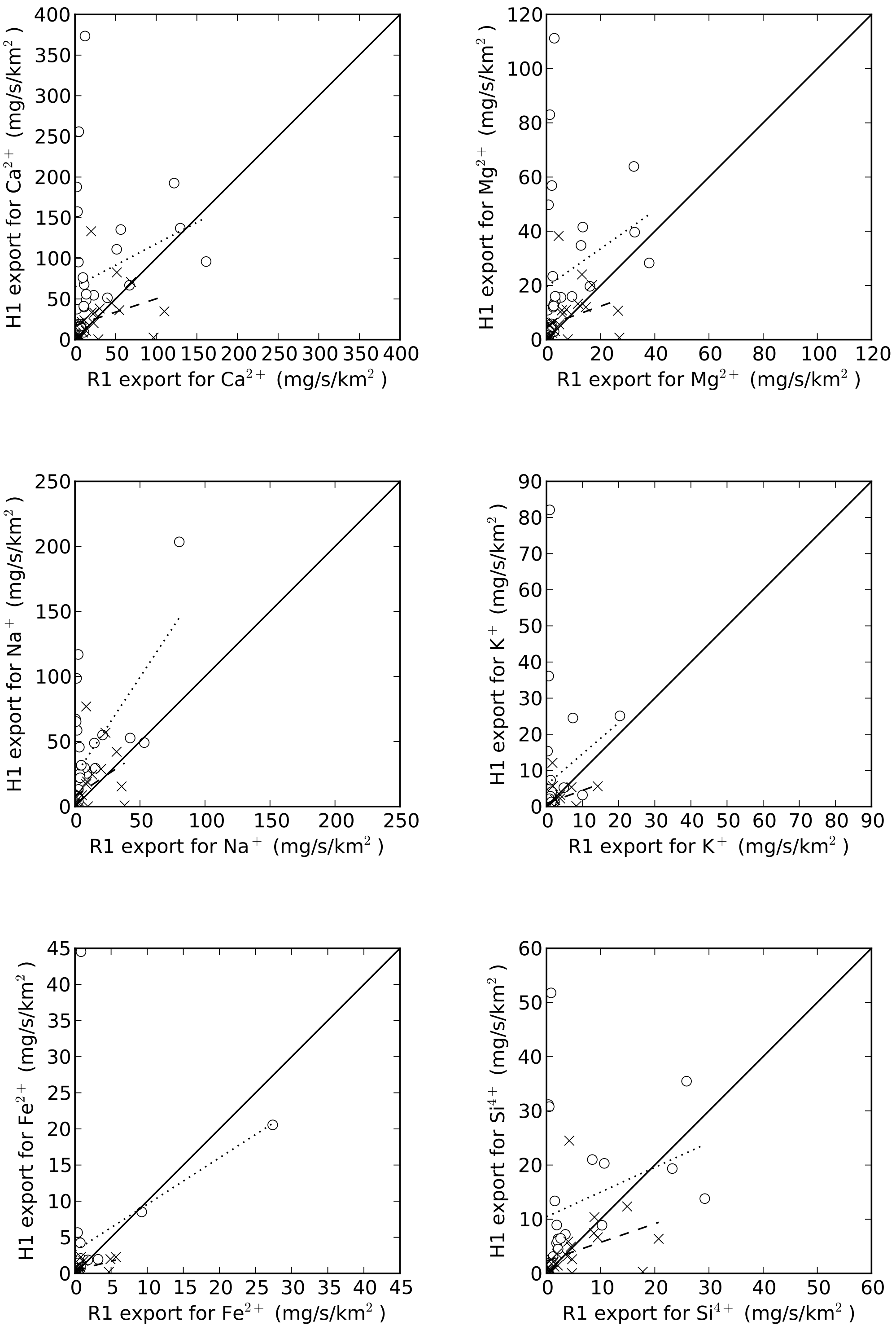

Figure 2.5: Mean ion export: H1 compared to R1. The subset of data in which flow and concentrations of both R1 and H1 were taken <24 hours apart is used here. Export has been normalized by catchment area. Pre-harvest values are indicated by circles with a small dotted regression line. Post-harvest values are indicated by X with a long dotted regression line. A solid line indicates the 1:1 relationship between catchments.

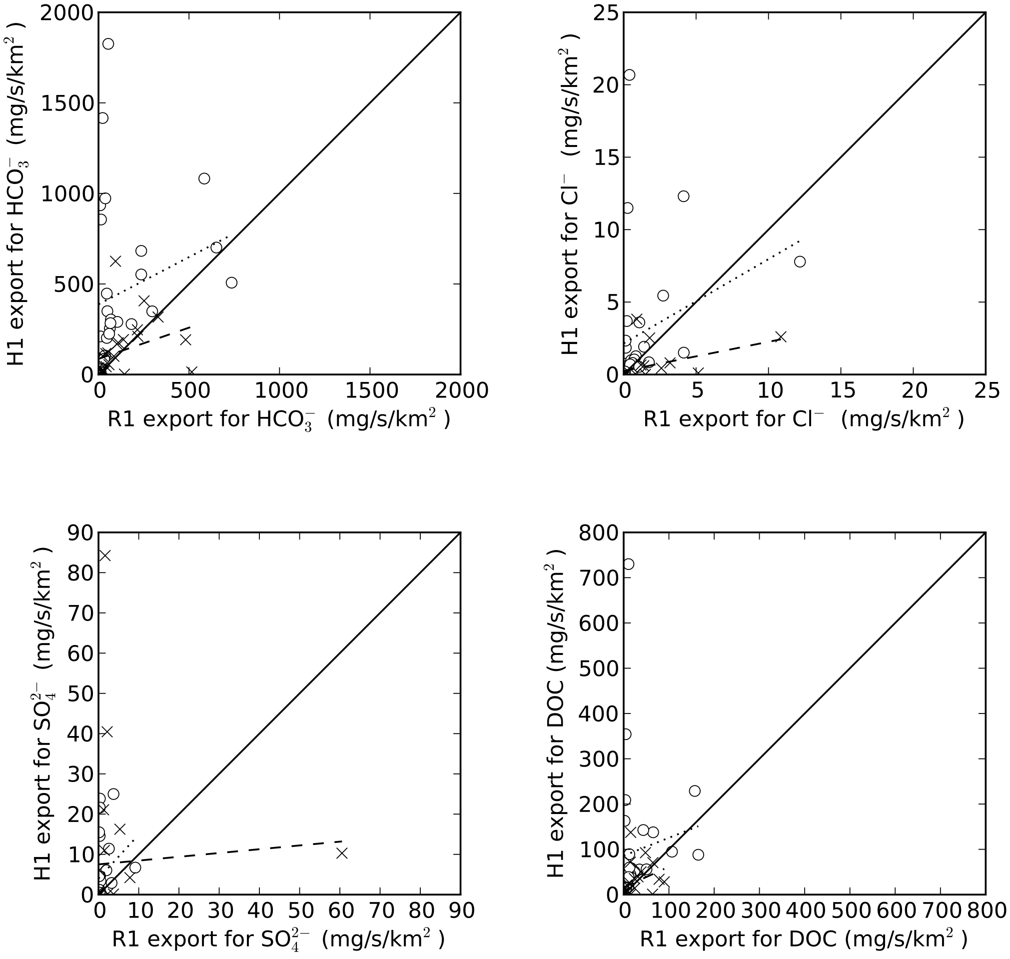

Figure 2.5: H1 mean ion export in comparison to R1 pre (circles) and post (X) harvest (continued).

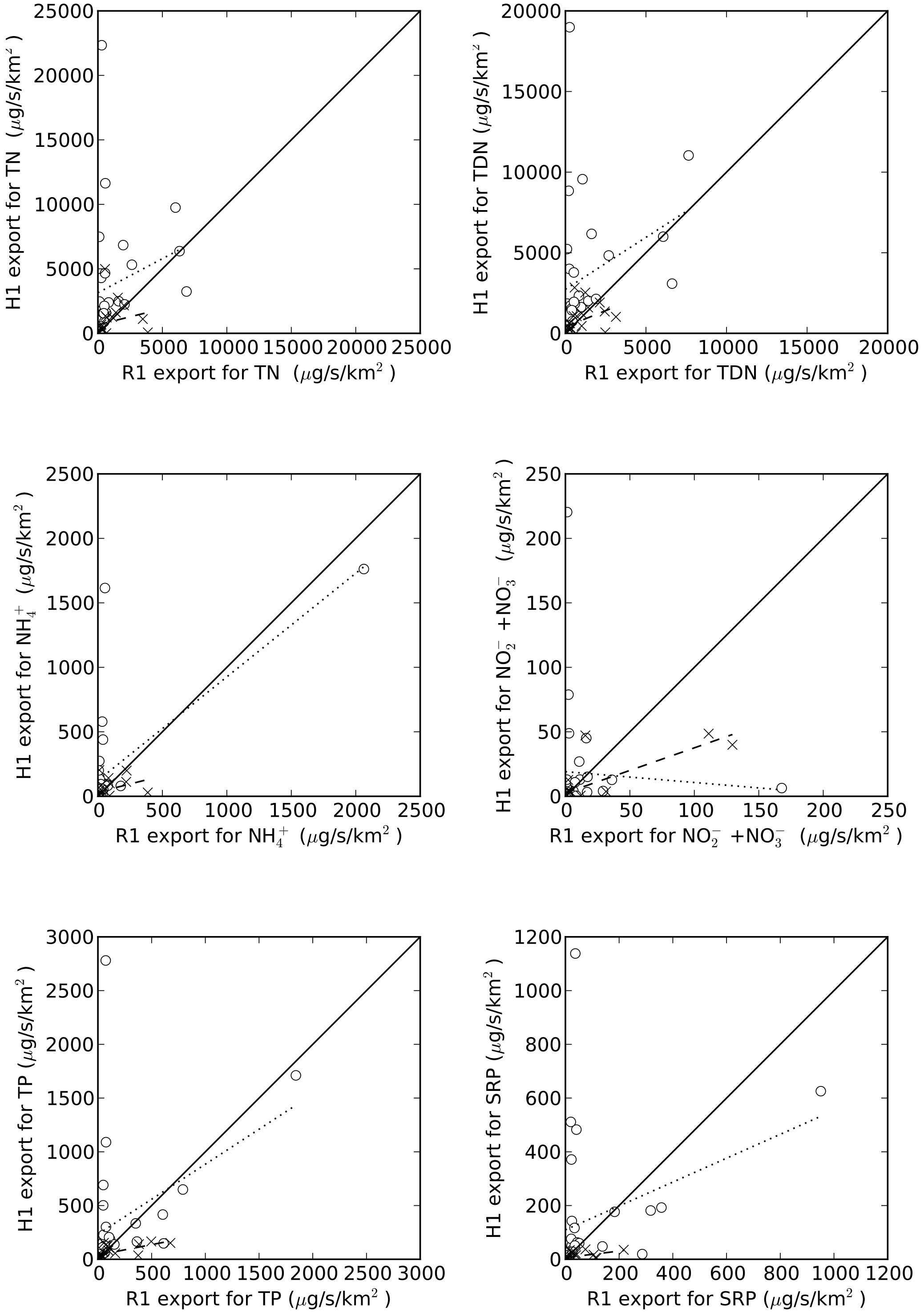

Figure 2.5: H1 mean ion export in comparison to R1 pre (circles) and post (X) harvest (continued).

2.2 Impact of Aspen Harvesting on Catchment Chemical Concentration and Export

The impact of intensive upland aspen harvesting on chemical concentration and export in the H1 catchment stream can be described by comparing R1 and H1 pre-harvest to R1 and H1 post-harvest. Figure 2.1 shows the instantaneous flow and ion concentrations of point samples in the R1 and H1 surface streams. While there was a large range in flow between extreme high flows and low flows, there was not an obvious increasing trend in flow for H1 post-harvest (Figure 2.1). Similarly, it is difficult to find an obvious trend in chemical concentrations post-harvest, especially for the highly variable nutrient concentrations. However, in general it can be stated that R1 and H1 concentrations did have similar seasonal patterns and magnitudes (Figure 2.1), allowing R1 to be a fairly good reference state. The only exception to this was significant differences in Na^+ concentrations and export between the two catchments under pre-harvest conditions (Table A.1 and Table A.2).

In order to examine the stream concentrations in greater detail, the mean concentration of each ion was computed in Table 2.2 for the pre-harvest and post-harvest period, based on seasonal flow and vegetative activity. R1 and H1 catchments did react similarly post-harvest for the majority of the ions (Table 2.2). Both R1 and H1 had increases in concentration post-harvest of Ca^{2+} , HCO_3^- , SO_4^{2-} and Si^{4+} during HFNV (Table 2.2). Both had decreases in concentration post-harvest of Ca^{2+} , HCO_3^- , TN, TP and Si^{4+} during HFAV (Table 2.2). During low flows, both catchments saw decreases in concentrations of K^+ , NH_4^+ and NO_2^-+NO_3^- (Table 2.2). There were no significant differences between R1 and H1 post-harvest for concentrations of Ca^{2+} , K^+ , DOC, and Fe^{2+} (Table A.1). In addition, there were no significant differences in export for Ca^{2+} , Mg^{2+} , K^+ , HCO_3^- , DOC, Fe^{2+} , TN, TDN, NO_2^-+NO_3^- , TP and TDP (Table A.2). Although a great many of the ion concentrations and exports studied in this thesis remained unchanged when harvesting occurred, it is the few that did change that are the most interesting.

In a comparison of R1 to H1, Cl^- and SO_4^{2-} concentrations were significantly different post-harvest for both high and low flows (Table A.1). Cl^- decreased in concentration and SO_4^{2-} increased (Table 2.3). However, Cl^- showed significant differences in export only during LFAV whereas SO_4^{2-} export was significantly different for both LFAV and both high flows (Table A.2). Although SO_4^{2-} concentration in both catchments increased post-harvest during high flows, only H1 showed an increase in SO_4^{2-} concentration during LFAV (Table 2.2). R1 was significantly different from H1 post-harvest during LFAV for Mg^{2+} , N and P concentrations (Table A.1). NH_4^+ and NO_2^-+NO_3^- concentrations increased for H1 during HFNV whereas for R1 they decreased (Table 2.2). Similarly, Table 2.2 shows that concentrations of TN increased during LFAV, and for TP, SRP and Fe^{2+} during LFNV, for H1 alone. However, only NH_4^+ and SRP significantly decreased in export post-harvest during LFAV (Table A.2 and Table 2.3). SRP also significantly decreased during spring melt post-harvest(Table A.2 and Table 2.3).

Figure 2.3 describes how ion concentration changed with flow both before harvesting occurred on H1 and after. There are many ions where a difference between pre- and post-harvest concentration was clearly noticeable. HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ and Si^{4+} concentrations in H1 shifted towards greater flow and less concentration post-harvest whereas R1 concentrations remained evenly distributed (Figure 2.3). There was a slight shift towards greater flow for Cl^- and DOC in H1 post-harvest that was not evident in R1 (Figure 2.3). K^+ , SRP and SO_4^{2-} shifted towards greater flow and greater concentration post-harvest in H1 (Figure 2.3). This is also true for R1 SO_4^{2-} post-harvest (Figure 2.3). For TN, TP, NH_4^+ and NO_2^-+NO_3^- it is more difficult to discern any clear shift. It is also true that the range in variation in R1 is larger, with a shallower slope, than in H1 in some cases (e.g. HCO_3^- in Figure 2.3), which makes any change in ion concentration and flow more difficult to clearly discern for R1 and thereby more difficult to compare with H1.

Comparison of H1 pre-harvest with H1 post-harvest reveals that ion concentrations did decrease significantly; Ca^{2+} , TN, TDN and SRP differed during high flows, Mg^{2+} , HCO_3^- and TDP differed during HFAV, and Fe^{2+} differed during low flows (Table A.2 and Table 2.3). SO_4^{2-} was the only ion to increase significantly in concentration during HFAV (Table A.2 and Table 2.3). However, most of the major cations and anions did not see a significant change in export post-harvest (Table A.2). Only SO_4^{2-} , TDN and P saw significant differences in export during high flows while Cl^- and NO_2^-+NO_3^- were significantly different during LFNV (Table A.2). Na^+ was not significantly different in export for H1 post-harvest (Table A.2).

Table 2.1 describes the total mean instantaneous export pre- and post-harvest for H1. It is evident that other than during LFAV where export remained about the same, all other seasons saw a large (>48%) decrease in export post-harvest for H1 (Table 2.1). There was also a decrease in export post-harvest for R1 during HFAV (52%) but R1 had an increase in total export post-harvest during HFNV of 8% (Table 2.1). That increase for R1 could be due to the slight increase in the major cation and HCO_3^- export shown in Table 2.3. The mean instantaneous export displayed in Table 2.3 and Figure 2.4 shows a general trend of decreasing export for almost all ions in all categories for both R1 and H1. The exceptions to the general trend include the major cations of R1 during HFNV mentioned above, as well as increasing SO_4^{2-} export during high flows for both R1 and H1 post-harvest (Table 2.3 and Figure 2.4). DOC export in H1 increased slightly during LFAV post-harvest as well (Table 2.3). Low flows had a less clearly discernible change in export (Figure 2.4), but that may be due to the low concentrations of several of the ions (Table 2.2 and Table 2.3). Table 2.1 shows the total mean export of LFNV for H1 decreasing by 80%.

Figure 2.4 demonstrates that the mean export of both R1 and H1 ions decreased post-harvest mainly because of a decreased range. With the exception of SO_4^{2-} , the range of high export was reduced rather than there being a shift downwards (Figure 2.4). For low flows, it may not be possible to shift downwards any lower as the concentrations hit the lower limits of detection. This would compress the range. But there are examples—such as HCO_3^- and Ca^{2+} —where the range could have been shifted lower during high flow and was simply compressed instead (Figure 2.4). Both Table 2.3 and Figure 2.4 clearly show the decreasing export from both R1 and H1 catchments post-harvest.

Despite the decreasing trend in export for R1 and H1 demonstrated by Table 2.3, Table 2.1 and Figure 2.4, there were no significant differences in major cation and anion export post-harvest with the exception of SO_4^{2-} during high flows and Cl^- during low flows (Table A.2). Examination of Table 2.2 and Table 2.3 shows that SO_4^{2-} increased significantly whereas Cl^- decreased. P concentration and export decreased significantly post-harvest during high flows, whereas NO_2^-+NO_3^- export decreased significantly only during LFNV (Table A.2, Table 2.2 and Table 2.3).

Chapter 3

Conclusions and Discussion

3.1 Natural Variability of Catchment Export in the Boreal Plains

The first objective of this thesis — to describe the natural variation in stream export — was accomplished by describing both the large reference catchment R1 over four field seasons from 2005 to 2008 and the large harvested catchment H1 during the pre-harvest period (2005 to July 2, 2007). The variability discovered between catchments, between years and between seasons based on flow and vegetative activity are important components of Boreal Plain stream chemistry.

Export was not significantly different between R1 and H1 (Table A.2) even though Table 2.1 shows large pre-harvest differences in the total magnitude of normalized export. Table 2.3 and Figure 2.5 also show that H1 export was greater than R1, especially during high flows. Figure 2.1 and Figure 2.2 show occasional extreme high flows occurred in one catchment and not the other. In Figure 2.5 the greatest export in R1 did not always correspond with the greatest export in H1, although the data was collected on the same day. It could be suggested that extreme episodic high flows that are not consistent between catchments could be the cause of these qualitative differences. Beaver dam breakages and intense convective summer storms focused in a small area may have caused this discrepancy between catchments. It could also be argued that catchment response may have been different between catchments because of the hydrological connections to the stream—even though these two catchments were selected because they had similar lithology and surface cover, as well as a similar percentage of upland and wetland areas. However, because of the exclusion of extreme high flow events in the statistical data set, it is inconclusive whether or not the characteristics of intense convective storms typical of the Boreal Plains during the summer, and successive beaver dams along stream reaches, are likely to cause total export differences between catchments.

In general, the chemical ion concentrations (Table 2.2) had similar magnitudes and the seasonal responses of export between R1 and H1 (Table 2.3) had similar trends (with the exception of Na^+). The significant difference in H1 Na^+ concentration and export could be the result of localized catchment water flowing through saline deposits to the stream. Source area characteristics may be the cause of this difference rather than R1 and H1 having different hydrological connections.

There was very little significant inter-annual variation of stream chemical concentration and export for R1 (Table A.1 and Table A.2). Export of the all the major cations and anions, while decreasing qualitatively, were not significant for this study. However, the few significant differences in concentration, along with qualitative analysis, does provide inferences about the processes occurring on the catchment. The concentrations of Na^+ , SO_4^{2-} and Si^{4+} significantly increased while those of N and P significantly decreased during spring melt post-harvest (Table A.1). SO_4^{2-} export increased substantially between the R1 pre-harvest and post-harvest period (Table 2.3, Figure 2.4) for high and low flows. This could indicate that previously unconnected wetlands or ephemeral draws were flushing into the stream (Devito et al., 1999). In addition, nutrients such as NH_4^+ and NO_2^-+NO_3^- had a wide range in concentration throughout the study period. This large range may be due to different contribution areas of the catchment connecting up to the stream. Macrae et al. (2006) found a large variation of NH_4^+ and NO_2^-+NO_3^- concentrations in soil and surface water across their WBP catchment. They suggested that spatial differences in NO_2^-+NO_3^- concentrations were caused by the production of NO_2^-+NO_3^- caused by the repeated exposure of deeper organic layers in ephemeral draws and wetlands during dry periods that were followed by wet years of flushing (Kalef, 2002; Macrae et al., 2006). Ephemeral draws or isolated wetlands may become hydrologically connected to the stream once a threshold saturation point is reached, thus allowing flushing of nutrients into the stream. Varying hydrological connectivity as well as extreme flow events could therefore create large variations in nutrient export between years for the same catchment, without any human influence.

The variability of export between years was insignificant for R1: only P export was significantly decreased post-harvest for R1 (Table A.2). Both periods showed that the greatest export occurred during high flows — export from the catchment was at least 10 times greater during high flows than during low flows (Table 2.3 and Table 2.1). High flows in this case refer to both spring melt and summer storms. In many other catchments the dominant hydrologic event is spring melt. However, in the Boreal Plains summer storms and beaver dam breakages are of equal hydrologic importance to surface stream export. Analysis of the pre-harvest period of R1 shows that K^+ , SO_4^{2-} , Cl^- , N and P had the highest average instantaneous export during spring melt (HFNV) whereas Ca^{2+} , HCO_3^- , Na^+ , Mg^{2+} , DOC and Si^{4+} had the highest average instantaneous export during summer storms and beaver dam breakages (Table 2.3). Both spring melt and summer storms are of great importance to the stream chemical export of Boreal Plain catchments.

The importance of high flows to the catchment export may due to ion concentrations as well as flow (Q). It is common for high flows to have lower concentrations of ions because of dilution and shorter contact time with soil (Freeze and Cherry, 1979). This was true for ions such as HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ and Si^{4+} in Boreal Plain streams (Figure 2.3). However, K^+ , Cl^- , SO_4^{2-} , DOC, NH_4^+ , NO_2^-+NO_3^- , and SRP showed no such trend and in fact their concentrations remained independent of flow (Figure 2.3). With increased flow and little decrease in concentration, the chemical export from a catchment during high flow would be quite large, as it was in this study (Table 2.1). It is noticeable that the ions not impacted by dilution are those often associated with surface flow or subsurface flow through organics (Buttle et al., 2000). They are also the ions most associated with vegetative demand.

Although flow regimes dominated chemical export, vegetative activity did moderately decrease the export of K^+ , Cl^- , SO_4^{2-} , NH_4^+ and NO_2^-+NO_3^- (Table 2.3). SO_4^{2-} export was the only ion significantly decreased by vegetative activity (Table A.2). A change in vegetative demand may therefore have had a moderate impact on the chemical concentrations of these few ions, which in turn may have slightly changed the export of the catchment. However, the lower concentrations of these ions in comparison to major cations and anions (Table 2.2), as well as the inter-annual variability, made it improbable that total chemical export would be impacted. Thus vegetative activity was of less importance to overall chemical export than flow.

Although total chemical export may not have been impacted by the aforementioned ions, the importance of their concentration and catchment export stems from the fact that they are nutrients. The Boreal Plains are similar to other regions where nutrients are mostly lost from the catchment during high-flow. TN export was 10–15 times larger during high-flow than during low-flow (Table 2.3). The majority of that was dissolved nitrogen with NH_4^+ a greater contributor than NO_2^-+NO_3^- (Table 2.3). Although nutrient export is important for maintaining catchment health and preventing eutrophication of receiving water bodies, it is difficult to predict in the streams of the Boreal Plains. The range of variability was so great, during both low flows and high flows, that inferences of catchment processes based solely on this study could suggest misleading and possibly invalid relationships.

Low flows are also of great importance to the biota living in and around the streams because ion concentration. Although most of the export occurred during high flow, the concentrations of several ions peaked during low-flow (Table 2.2). Cl^- , K^+ , NH_4^+ and NO_2^-+NO_3^- had their highest average concentrations during fall and winter (LFNV) and HCO_3^- , Ca^{2+} , Mg^{2+} , DOC, Si^{4+} , TN and TP had their highest average concentrations during summer low flow (LFAV). Table 2.2 shows that the maximum concentrations of NH_4^+ , NO_2^-+NO_3^- and TN were 1.1 mg/L, 0.9 mg/L and 3.8 mg/L respectively. Phosphorus concentrations were slightly less, with maximum values of SRP and TP at 0.6 mg/L and 1.5 mg/L respectively. Not only were nutrient concentrations high, but the surface water was quite salty as well, with maximum concentrations of 280 mg/L, 60 mg/L, 19 mg/L, 16 mg/L and 15 mg/L for HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ and SO_4^{2-} respectively (Table 2.2).

In summary, this study reveals that although similar catchments in the Boreal

Plains have similar trends and processes, the magnitude of export and the timing of extreme high flow events can be different. There was little inter-annual variability evident in total export although stream ion concentration did differ significantly for ions such as SO_4^{2-} and for nutrients. Within a catchment, the total export was dominated by high-flow rather than vegetative impacts. Summer storms and beaver dam breakages were equal to spring melt in importance for stream chemical export. Vegetative activity did not dominate export but it did dominate the chemical concentration of several nutrients. Nutrient variability was quite large and concentrations did not change based on flow as did concentrations of the major cations and anions.

3.2 Impact of Aspen Harvesting on Catchment Export in the Boreal Plains

The second objective of this thesis was to determine whether stream surface export increased with intensive upland aspen harvesting. Previous studies have suggested that stream export may increase due to upland water saturation travelling through surface organic layers or sub-surface mineral layers to reach the stream. Alternatively, it has been suggested that export may not increase at all if uplands are disconnected from streams. Preliminary analysis shows that total mean export did not increase with harvesting. The only significant increase in export was SO_4^{2-} (Table A.2). SO_4^{2-} doubled its pre-harvest values during spring melt (HFNV) and increased by seven-fold during summer storms (HFAV) — the only ion to increase greatly post-harvest (Table 2.3). DOC export also showed a slight increase during summer low flows after harvesting (Table 2.3). The few other ions that had significant differences in export all decreased (Table A.2 and Table 2.3). Qualitatively, there was a general decrease in export post-harvest for H1: Ca^{2+} by $>40\%$, HCO_3^- and DOC by $>50\%$ and TN and TP decreased by $>60\%$ of pre-harvest values (Table 2.3) (although summer low flows (LFAV) were an exception). Despite this qualitative decrease, major cations and anions (with the exception of SO_4^{2-}) showed no significant difference in export post-harvest for H1.

The results of this study indicate that intensive upland harvesting did not increase chemical export in stream water from a WBP catchment. This implies that uplands were hydrologically disconnected from the stream, or that upland chemistry was not a dominant force controlling stream chemical export, or that upland chemistry and hydrology were not significantly changed with intensive aspen harvesting. Qualitative examination of the results may provide inferences about the processes inherent in Boreal Plain catchments.

There is a decreasing trend in chemical export—except for SO_4^{2-} —with harvesting; the shift of Ca^{2+} , Mg^{2+} , Na^+ , HCO_3^- , Cl^- , Fe, TN, TP and SRP post-harvest indicates less export from H1 than from R1 (Figure 2.5). A decrease in total export might result from a simple decrease in water from the same sources along the same flowpath. In such a case, the flow would decrease and the concentrations of ions would remain the same. However, Figure 2.3 describes a trend of increased flow in H1 post-harvest with several changes in ion concentration. There were shifts toward greater flow with less concentration and greater flow with greater concentration (Figure 2.3) depending on the ion. This implies that a decrease in export could be due to changes in sources, flowpath and/or transformations.

According to Figure 2.3, the major cations, HCO_3^- and Si^{4+} , shifted post-harvest towards greater flow with less concentration, indicating that groundwater sources were being diluted rather than remaining the same. Mean concentrations in Table 2.2 support a decrease in concentration for H1 post-harvest during high flows.

Although dilution may explain some of the decreased export during high flows in H1 post-harvest, the significant increase in SO_4^{2-} concentration and export implies a change in stream source. The increase in SO_4^{2-} in concentration and export (Table 2.2 and Table 2.3) indicates either that a previous stream source began producing more SO_4^{2-} or that a new source heavy in SO_4^{2-} connected to the stream. Because of the decreased total export qualitatively shown by this study and the lack of increased soil moisture or increased surface run-off found in other studies of the WBP (Macrae et al. 2005, Devito et al, 2005) it is unlikely that harvesting increased surface connections to additional wetlands or ephemeral draws and in this way added new sources to the stream. It is more likely that the three years of precipitation deficit (see Section 1.4 Site Characteristics) and then aspen sucker demand dried out deep organic deposits of previously wet sources of the stream. A decreasing water table allows oxidation of reduced S compounds to SO_4^{2-} which is then flushed into the stream once the source is reconnected via high-flow (Devito et al., 1999; Eimers et al., 2006). High-flow from spring melt, summer storms and beaver dam breakages exhibited increases in SO_4^{2-} concentration and export after harvesting (Table 2.2 and Figure 2.4). It could be expected that increases in NO_2^-+NO_3^- would occur also. Indeed, the mean concentration of NO_2^-+NO_3^- increased two-fold during spring melt with harvesting (Table 2.2). However, the vegetative demand for NO_2^-+NO_3^- could have been great enough that no increased concentration or export was seen during periods of vegetative activity (Table 2.2 and Table 2.3). Thus transformations occurring at source areas to the stream are likely to have impacted the surface stream chemical export after harvesting. However, in contrast to what previous studies suggest, this is not because the uplands increased in soil moisture and connected via surface run-off to the stream. Instead, harvesting exacerbated the water table draw-down in connected ephemeral draws and wetlands, and caused SO_4^{2-} and NO_2^-+NO_3^- production and release during high flows.

The transformations and the biological demand of nutrients in source areas during low-flow periods is of critical importance to catchment stream composition and export. Although this thesis does not utilize the data collected at potential sources sites to determine harvesting impacts directly, stream composition during low flows did give some indication of source activity. With the exception of SO_4^{2-}, major cation and anion concentrations remained the same during low-flow post-harvest (Table 2.2). H1 showed significant decreases in Fe^{2+} and P concentrations during low-flow as well as decreased K^+, Cl^- and SRP export (Table A.1 and Table A.2). During summer low-flow the mean concentrations of SO_4^{2-} and DOC increased slightly, balancing out the decrease in K^+, NH_4^+, NO_2^-+NO_3^- and SRP (Table 2.2). Although increases in SO_4^{2-} and DOC concentration indicate that there may have been some flushing of connected ephemeral draws and wetlands, nutrient concentrations decreased, indicating possible increased biological demand. Harvesting mature clonal aspen stresses the parent root, inspiring dense rapid growth of offshoots. Carmosini (2000) showed that harvesting did not change the total organic N of a WBP catchment's soil. Carmosini et al. (2002) showed that increased gross mineralization was matched by high immobilization rates, thus preventing accrual of NH_4^+. Macrae et al. (2006) added that rapid sucker regeneration would increase N demand, which would, along with immobilization, prevent the increase in total organic N in the soil of harvested uplands. Upland aspen harvesting should therefore not result in an influx of nutrients but rather in a concerted uptake. Indeed, the results of this study indicate a decrease in nutrient concentration and export during periods of vegetative activity (Table 2.2 and Table 2.3).

It can thus be hypothesized that groundwater sources flow through source areas such as ephemeral draws before connecting up to the stream. Accumulation of SO_4^{2-} and NO_2^-+NO_3^- in such source areas occurs during the low-flow in the summer and throughout the dry fall and winter. Spring melt rushes through those source areas, mixing old groundwater with ephemeral nutrients and flushing to the stream. Source areas with large accumulations of SO_4^{2-} will continue to release high concentrations of SO_4^{2-} while NO_2^-+NO_3^- is consumed by biological demand during high-flow summer events but flushed with more dilute groundwater. The groundwater could be more dilute in the summer because of infiltration of spring melt and summer precipitation; Redding and Devito (2005) found that the soil was quite porous during spring melt. This would explain the similar ion concentrations and chemical export trends for H1 and R1 when the pre-harvest and post-harvest periods are compared.

In conclusion, preliminary data suggest that chemical export did not significantly increase with upland aspen harvesting. Qualitatively, chemical export decreased with harvesting—with the exception of SO_4^{2-}. Decreased major cation and anions may indicate less concentrated groundwater reaching the stream. Decreased nutrients may indicate increased biotic uptake. Increased SO_4^{2-} may indicate more frequent drying out and flushing of connected ephemeral draws and wetlands. Resource managers should therefore be concerned about increased flushing from intensive upland harvesting of source areas such as ephemeral draws where high concentrations of nutrients may be stored. An increase in nutrient export from upland sources is unlikely with harvesting. This study suggests that upland harvesting may be less important to stream chemistry and export than the frequency and magnitude of ephemeral draw and wetland water-table fluctuations that occur with great natural variation over the years in the Boreal Plains.

3.3 Future Work

This study is part of the larger HEAD2 NSERC-CRD project. Complete analyses of the two large paired catchments examined in this study as well as three small catchments are currently taking place. Integration of this study with the other data sets collected on this site could test how intensive upland aspen harvesting impacts catchment processes and give a more comprehensive picture of the variability of nutrients and stream flow in natural catchments.

This thesis utilized preliminary discharge data to calculate export. The key future research needed to firmly establish the results presented in this thesis is a continuous hydrograph of the catchment outflow, to test whether water export increased with harvesting and to allow a detailed seasonal and inter-annual description of variation. The continuous data could fill in the missing extreme flows that were not included in this study.

Soil samples and pools taken across different landscape units should identify whether any transformational processes occurred in the uplands with aspen harvesting. This will help determine if there is an increase in nutrient concentrations due to increased decomposition and transformations or whether there is a decrease in nutrients due to biotic uptake. Soil samples and pools were taken from ephemeral draws and wetlands and monitored over precipitation deficits and excesses These samples will help to determine if there are the chemical changes to these stream sources with upland harvesting.

Soil moisture, tensiometers and water levels taken on transects from uplands to streams could determine the connectivity of the uplands to the stream via surface or subsurface pathways. They could also determine if the catchment uplands become saturated with water because of harvesting (which would imply connection between hydrological units) or whether it becomes drier because of increased sapling growth. In addition, the water levels in ephemeral draws and wetlands have been closely monitored in conjunction with surface chemistry. This could be used to determine if transformations are occurring on a regular basis with drought and flushing. Water levels could also be used to infer connection of these important sources to the stream.

Analysis of electrical conductivity and catchment-wide water samples from different landscape units and possible stream sources may complete connections between the sources to the stream along specific flowpaths. These projects could be used to investigate the processes behind both the hydrology and biogeochemistry of Boreal Plains catchments and the response of catchments to intensive upland aspen harvesting.

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Appendix A

Statistical analysis of significance

A.1 Mann-Witney U-test

Table A.1: Mann-Witney U-test of ion concentrations. p-values $< \alpha = 0.05$ are in bold. The major diagonal is greyed out as by definition the Wilcoxon coefficient is 1. This table also symmetric by definition around the major diagonal. The subset of data where flow and concentrations of both R1 and H1 were taken <24 hours apart is used here. Pre-harvest data was collected before July 2, 2007. Post-harvest data was collected after July 2, 2007 when harvesting began on H1. Categorical boxes are defined by flow (high or low) and by vegetation (active or not-active): high flow non-active vegetation (HFNV), high flow active vegetation (HFAV), low flow active vegetation (LFAV), low flow non-active vegetation (LFNV).

(a) Ca^{2+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.009**	**0.001**	0.129	0.622	0.095	**0.001**	**0.036**	0.298	**0.000**	**0.036**	**0.009**	0.329	0.111	**0.000**	**0.008**
		HFAV	**0.009**	1.000	0.093	0.368	0.228	0.329	**0.003**	0.262	**0.000**	0.416	**0.048**	0.180	**0.015**	0.171	**0.003**	**0.030**
		LFAV	**0.001**	0.093	1.000	**0.015**	**0.016**	**0.028**	0.190	0.811	**0.000**	0.115	0.371	0.713	**0.001**	**0.024**	0.197	0.594
		LFNV	0.129	0.368	**0.015**	1.000	0.515	1.000	**0.000**	0.112	**0.010**	0.088	**0.049**	**0.022**	0.492	1.000	**0.000**	**0.008**
R1	**Post**	HFNV	0.622	0.228	**0.016**	0.515	1.000	0.724	**0.004**	0.133	0.167	0.064	**0.024**	**0.029**	0.852	0.683	**0.001**	**0.011**
		HFAV	0.095	0.329	**0.028**	1.000	0.724	1.000	**0.003**	0.071	0.060	0.095	**0.036**	0.052	0.931	0.905	**0.001**	**0.008**
		LFAV	**0.001**	**0.003**	0.190	**0.000**	**0.004**	**0.003**	1.000	**0.049**	**0.000**	**0.000**	0.937	0.792	**0.000**	**0.011**	0.809	0.679
		LFNV	**0.036**	0.262	0.811	0.112	0.133	0.071	**0.049**	1.000	**0.009**	0.439	0.400	0.548	**0.024**	0.057	0.139	0.393
H1	**Pre**	HFNV	0.298	**0.000**	**0.000**	**0.010**	0.167	0.060	**0.000**	**0.009**	1.000	**0.000**	**0.009**	**0.000**	**0.008**	**0.020**	**0.000**	**0.001**
		HFAV	**0.000**	0.416	0.115	0.088	0.064	0.095	**0.000**	0.439	**0.000**	1.000	**0.039**	0.179	**0.001**	**0.045**	**0.001**	**0.026**
		LFAV	**0.036**	**0.048**	0.371	**0.049**	**0.024**	**0.036**	0.937	0.400	**0.009**	**0.039**	1.000	0.714	**0.024**	0.057	0.769	1.000
		LFNV	**0.009**	0.180	0.713	**0.022**	**0.029**	0.052	0.792	0.548	**0.000**	0.179	0.714	1.000	**0.009**	**0.038**	0.591	0.931
H1	**Post**	HFNV	0.329	**0.015**	**0.001**	0.492	0.852	0.931	**0.000**	**0.024**	**0.008**	**0.001**	**0.024**	**0.009**	1.000	0.610	**0.000**	**0.004**
		HFAV	0.111	0.171	**0.024**	1.000	0.683	0.905	**0.011**	0.057	**0.020**	**0.045**	0.057	**0.038**	0.610	1.000	**0.001**	**0.016**
		LFAV	**0.000**	**0.003**	0.197	**0.000**	**0.001**	**0.001**	0.809	0.139	**0.000**	**0.001**	0.769	0.591	**0.000**	**0.001**	1.000	0.661
		LFNV	**0.008**	**0.030**	0.594	**0.008**	**0.011**	**0.008**	0.679	0.393	**0.001**	**0.026**	1.000	0.931	**0.004**	**0.016**	0.661	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(b) Mg^{2+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.004**	**0.002**	**0.028**	0.622	0.056	**0.001**	**0.036**	**0.033**	**0.010**	**0.036**	0.095	**0.008**	**0.016**	**0.000**	**0.008**
		HFAV	**0.004**	1.000	0.113	0.635	0.414	0.429	**0.007**	0.262	**0.039**	**0.044**	**0.048**	0.126	0.809	1.000	**0.001**	**0.009**
		LFAV	**0.002**	0.113	1.000	0.780	0.093	**0.019**	0.278	0.600	**0.006**	1.000	0.100	0.083	0.111	0.260	**0.031**	0.112
		LFNV	**0.028**	0.635	0.780	1.000	0.146	0.371	0.436	1.000	0.111	0.817	0.287	0.310	0.551	0.733	0.114	0.129
R1	**Post**	HFNV	0.622	0.414	0.093	0.146	1.000	0.724	**0.016**	0.376	0.962	0.097	**0.024**	**0.045**	0.561	0.570	**0.002**	**0.011**
		HFAV	0.056	0.429	**0.019**	0.371	0.724	1.000	**0.003**	**0.036**	0.593	**0.013**	**0.036**	0.151	0.410	0.286	**0.000**	**0.008**
		LFAV	**0.001**	**0.007**	0.278	0.436	**0.016**	**0.003**	1.000	0.077	**0.000**	0.198	0.161	0.075	**0.008**	**0.014**	0.223	0.371
		LFNV	**0.036**	0.262	0.600	1.000	0.376	**0.036**	0.077	1.000	**0.016**	0.516	0.100	0.250	0.154	0.229	**0.011**	**0.036**
H1	**Pre**	HFNV	**0.033**	**0.039**	**0.006**	0.111	0.962	0.593	**0.000**	**0.016**	1.000	**0.002**	**0.016**	0.083	0.051	0.053	**0.000**	**0.003**
		HFAV	**0.010**	**0.044**	1.000	0.817	0.097	**0.013**	0.198	0.516	**0.002**	1.000	0.097	0.065	**0.044**	**0.045**	**0.009**	0.051
		LFAV	**0.036**	**0.048**	0.100	0.287	**0.024**	**0.036**	0.161	0.100	**0.016**	0.097	1.000	0.393	**0.028**	0.057	0.885	1.000
		LFNV	0.095	0.126	0.083	0.310	**0.045**	0.151	0.075	0.250	0.083	0.065	0.393	1.000	0.120	0.190	0.441	0.690
H1	**Post**	HFNV	**0.008**	0.809	0.111	0.551	0.561	0.410	**0.008**	0.154	0.051	**0.044**	**0.028**	0.120	1.000	1.000	**0.002**	**0.008**
		HFAV	**0.016**	1.000	0.260	0.733	0.570	0.286	**0.014**	0.229	0.053	**0.045**	0.057	0.190	1.000	1.000	**0.001**	**0.016**
		LFAV	**0.000**	**0.001**	**0.031**	0.114	**0.002**	**0.000**	0.223	**0.011**	**0.000**	**0.009**	0.885	0.441	**0.002**	**0.001**	1.000	1.000
		LFNV	**0.008**	**0.009**	0.112	0.129	**0.011**	**0.008**	0.371	**0.036**	**0.003**	0.051	1.000	0.690	**0.008**	**0.016**	1.000	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(c) Na^+

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.004**	**0.001**	0.254	**0.019**	**0.008**	**0.013**	**0.036**	**0.007**	**0.000**	**0.036**	0.082	**0.008**	**0.016**	**0.013**	**0.008**
		HFAV	**0.004**	1.000	0.875	0.428	0.345	0.177	0.792	0.905	0.328	**0.017**	**0.024**	0.093	0.126	0.067	**0.010**	**0.004**
		LFAV	**0.001**	0.875	1.000	0.579	0.460	0.099	0.247	0.692	0.447	**0.000**	**0.007**	**0.031**	**0.019**	**0.004**	**0.002**	**0.001**
		LFNV	0.254	0.428	0.579	1.000	0.573	0.859	0.199	0.573	0.549	**0.000**	**0.007**	**0.042**	0.055	**0.014**	**0.002**	**0.001**
R1	**Post**	HFNV	**0.019**	0.345	0.460	0.573	1.000	0.833	0.460	0.630	0.963	**0.006**	**0.024**	0.059	0.127	0.073	**0.006**	**0.002**
		HFAV	**0.008**	0.177	0.099	0.859	0.833	1.000	**0.040**	0.071	1.000	**0.000**	**0.036**	0.082	**0.016**	**0.016**	**0.013**	**0.008**
		LFAV	**0.013**	0.792	0.247	0.199	0.460	**0.040**	1.000	0.371	0.400	**0.000**	**0.007**	**0.022**	**0.028**	**0.002**	**0.002**	**0.001**
		LFNV	**0.036**	0.905	0.692	0.573	0.630	0.071	0.371	1.000	0.600	**0.004**	0.100	0.167	0.143	0.057	**0.043**	**0.036**
H1	**Pre**	HFNV	**0.007**	0.328	0.447	0.549	0.963	1.000	0.400	0.600	1.000	**0.000**	**0.009**	**0.036**	**0.029**	**0.020**	**0.002**	**0.001**
		HFAV	**0.000**	**0.017**	**0.000**	**0.000**	**0.006**	**0.000**	**0.000**	**0.004**	**0.000**	1.000	**0.025**	0.106	**0.026**	0.703	**0.011**	**0.004**
		LFAV	**0.036**	**0.024**	**0.007**	**0.007**	**0.024**	**0.036**	**0.007**	0.100	**0.009**	**0.025**	1.000	0.905	**0.036**	0.114	0.640	0.571
		LFNV	0.082	0.093	**0.031**	**0.042**	0.059	0.082	**0.022**	0.167	**0.036**	0.106	0.905	1.000	0.082	0.171	0.393	0.792
H1	**Post**	HFNV	**0.008**	0.126	**0.019**	0.055	0.127	**0.016**	**0.028**	0.143	**0.029**	**0.026**	**0.036**	0.082	1.000	0.413	**0.013**	**0.008**
		HFAV	**0.016**	0.067	**0.004**	**0.014**	0.073	**0.016**	**0.002**	0.057	**0.020**	0.703	0.114	0.171	0.413	1.000	0.077	**0.016**
		LFAV	**0.013**	**0.010**	**0.002**	**0.002**	**0.006**	**0.013**	**0.002**	**0.043**	**0.002**	**0.011**	0.640	0.393	**0.013**	0.077	1.000	0.141
		LFNV	**0.008**	**0.004**	**0.001**	**0.001**	**0.002**	**0.008**	**0.001**	**0.036**	**0.001**	**0.004**	0.571	0.792	**0.008**	**0.016**	0.141	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(d) K^+

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.004**	**0.019**	0.797	0.724	**0.008**	**0.001**	**0.036**	0.797	**0.002**	**0.036**	0.662	0.690	**0.016**	**0.000**	**0.032**
		HFAV	**0.004**	1.000	0.906	0.145	**0.029**	1.000	0.368	0.548	**0.026**	0.241	0.714	0.394	0.126	0.476	0.062	0.662
		LFAV	**0.019**	0.906	1.000	0.136	**0.036**	0.898	0.113	0.727	**0.031**	0.201	0.600	0.607	0.240	0.148	0.067	0.606
		LFNV	0.797	0.145	0.136	1.000	0.743	0.190	**0.028**	0.282	0.796	**0.017**	0.209	0.955	0.797	0.148	**0.030**	0.240
R1	**Post**	HFNV	0.724	**0.029**	**0.036**	0.743	1.000	**0.045**	**0.000**	0.194	0.815	**0.001**	**0.012**	0.662	0.883	**0.004**	**0.000**	**0.019**
		HFAV	**0.008**	1.000	0.898	0.190	**0.045**	1.000	0.310	0.786	0.083	0.154	0.393	0.537	0.222	0.325	0.052	0.421
		LFAV	**0.001**	0.368	0.113	**0.028**	**0.000**	0.310	1.000	**0.028**	**0.000**	0.921	0.937	0.181	**0.005**	0.479	0.121	0.768
		LFNV	**0.036**	0.548	0.727	0.282	0.194	0.786	**0.028**	1.000	0.209	0.071	0.200	1.000	0.571	0.057	**0.011**	0.250
H1	**Pre**	HFNV	0.797	**0.026**	**0.031**	0.796	0.815	0.083	**0.000**	0.209	1.000	**0.000**	**0.009**	0.607	0.739	**0.003**	**0.000**	**0.019**
		HFAV	**0.002**	0.241	0.201	**0.017**	**0.001**	0.154	0.921	0.071	**0.000**	1.000	0.828	0.174	**0.013**	0.952	0.255	0.712
		LFAV	**0.036**	0.714	0.600	0.209	**0.012**	0.393	0.937	0.200	**0.009**	0.828	1.000	0.381	0.071	0.629	0.225	0.881
		LFNV	0.662	0.394	0.607	0.955	0.662	0.537	0.181	1.000	0.607	0.174	0.381	1.000	0.792	0.171	**0.048**	0.360
H1	**Post**	HFNV	0.690	0.126	0.240	0.797	0.883	0.222	**0.005**	0.571	0.739	**0.013**	0.071	0.792	1.000	**0.016**	**0.001**	0.095
		HFAV	**0.016**	0.476	0.148	0.148	**0.004**	0.325	0.479	0.057	**0.003**	0.952	0.629	0.171	**0.016**	1.000	0.226	0.905
		LFAV	**0.000**	0.062	0.067	**0.030**	**0.000**	0.052	0.121	**0.011**	**0.000**	0.255	0.225	**0.048**	**0.001**	0.226	1.000	0.192
		LFNV	**0.032**	0.662	0.606	0.240	**0.019**	0.421	0.768	0.250	**0.019**	0.712	0.881	0.360	0.095	0.905	0.192	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(e) HCO_3^-

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.009**	**0.001**	0.093	1.000	0.222	**0.000**	**0.036**	0.622	**0.000**	**0.036**	**0.009**	0.126	0.063	**0.000**	**0.008**
		HFAV	**0.009**	1.000	**0.005**	0.755	0.345	0.177	**0.002**	0.095	**0.001**	**0.009**	**0.048**	0.065	0.310	0.762	**0.000**	**0.004**
		LFAV	**0.001**	**0.005**	1.000	0.101	**0.021**	**0.001**	0.512	0.692	**0.000**	0.648	0.217	0.147	**0.001**	**0.014**	0.093	0.129
		LFNV	0.093	0.755	0.101	1.000	0.279	0.354	**0.005**	0.776	0.161	0.238	**0.048**	**0.020**	0.414	0.683	**0.002**	**0.011**
R1	**Post**	HFNV	1.000	0.345	**0.021**	0.279	1.000	0.524	**0.009**	0.194	0.721	**0.025**	**0.048**	**0.008**	0.414	0.368	**0.002**	**0.011**
		HFAV	0.222	0.177	**0.001**	0.354	0.524	1.000	**0.001**	**0.036**	0.222	**0.000**	**0.036**	**0.030**	0.931	0.413	**0.000**	**0.008**
		LFAV	**0.000**	**0.002**	0.512	**0.005**	**0.009**	**0.001**	1.000	0.060	**0.000**	0.063	0.368	0.062	**0.000**	**0.006**	0.288	0.583
		LFNV	**0.036**	0.095	0.692	0.776	0.194	**0.036**	0.060	1.000	**0.012**	0.800	0.200	0.167	**0.024**	0.114	**0.018**	**0.036**
H1	**Pre**	HFNV	0.622	**0.001**	**0.000**	0.161	0.721	0.222	**0.000**	**0.012**	1.000	**0.000**	**0.012**	**0.008**	0.108	**0.048**	**0.000**	**0.002**
		HFAV	**0.000**	**0.009**	0.648	0.238	**0.025**	**0.000**	0.063	0.800	**0.000**	1.000	0.082	**0.046**	**0.001**	**0.010**	**0.005**	**0.026**
		LFAV	**0.036**	**0.048**	0.217	**0.048**	**0.048**	**0.036**	0.368	0.200	**0.012**	0.082	1.000	0.714	**0.024**	0.057	0.945	0.786
		LFNV	**0.009**	0.065	0.147	**0.020**	**0.008**	**0.030**	0.062	0.167	**0.008**	**0.046**	0.714	1.000	**0.026**	0.114	0.291	0.931
H1	**Post**	HFNV	0.126	0.310	**0.001**	0.414	0.414	0.931	**0.000**	**0.024**	0.108	**0.001**	**0.024**	**0.026**	1.000	0.610	**0.000**	**0.004**
		HFAV	0.063	0.762	**0.014**	0.683	0.368	0.413	**0.006**	0.114	**0.048**	**0.010**	0.057	0.114	0.610	1.000	**0.001**	**0.016**
		LFAV	**0.000**	**0.000**	0.093	**0.002**	**0.002**	**0.000**	0.288	**0.018**	**0.000**	**0.005**	0.945	0.291	**0.000**	**0.001**	1.000	0.721
		LFNV	**0.008**	**0.004**	0.129	**0.011**	**0.011**	**0.008**	0.583	**0.036**	**0.002**	**0.026**	0.786	0.931	**0.004**	**0.016**	0.721	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(f) Cl^{-}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.013**	0.109	0.256	0.608	**0.021**	0.054	0.134	0.062	**0.003**	**0.036**	0.314	0.142	**0.019**	**0.002**	0.059
		HFAV	**0.013**	1.000	0.262	**0.001**	**0.020**	0.464	0.122	**0.048**	**0.036**	0.067	0.262	**0.026**	1.000	**0.019**	**0.002**	0.177
		LFAV	0.109	0.262	1.000	0.052	0.163	0.083	0.704	0.354	0.479	**0.002**	0.051	0.216	0.505	**0.007**	**0.000**	0.789
		LFNV	0.256	**0.001**	0.052	1.000	0.888	**0.004**	**0.011**	0.064	**0.014**	**0.000**	**0.009**	0.456	0.147	**0.003**	**0.000**	0.083
R1	**Post**	HFNV	0.608	**0.020**	0.163	0.888	1.000	**0.011**	0.215	0.413	0.277	**0.001**	**0.012**	0.755	0.093	**0.004**	**0.000**	0.305
		HFAV	**0.021**	0.464	0.083	**0.004**	**0.011**	1.000	0.145	0.250	0.060	0.526	1.000	**0.030**	0.690	0.111	0.051	0.095
		LFAV	0.054	0.122	0.704	**0.011**	0.215	0.145	1.000	0.769	0.882	**0.005**	0.060	0.256	0.692	**0.019**	**0.000**	0.777
		LFNV	0.134	**0.048**	0.354	0.064	0.413	0.250	0.769	1.000	0.600	**0.017**	0.100	0.714	0.786	0.057	**0.011**	0.653
H1	**Pre**	HFNV	0.062	**0.036**	0.479	**0.014**	0.277	0.060	0.882	0.600	1.000	**0.001**	**0.018**	0.388	0.518	**0.003**	**0.000**	0.841
		HFAV	**0.003**	0.067	**0.002**	**0.000**	**0.001**	0.526	**0.005**	**0.017**	**0.001**	1.000	0.346	**0.002**	0.316	0.060	**0.010**	**0.007**
		LFAV	**0.036**	0.262	0.051	**0.009**	**0.012**	1.000	0.060	0.100	**0.018**	0.346	1.000	**0.024**	0.786	0.057	0.051	**0.036**
		LFNV	0.314	**0.026**	0.216	0.456	0.755	**0.030**	0.256	0.714	0.388	**0.002**	**0.024**	1.000	0.329	**0.010**	**0.001**	0.429
H1	**Post**	HFNV	0.142	1.000	0.505	0.147	0.093	0.690	0.692	0.786	0.518	0.316	0.786	0.329	1.000	0.219	**0.039**	0.548
		HFAV	**0.019**	**0.019**	**0.007**	**0.003**	**0.004**	0.111	**0.019**	0.057	**0.003**	0.060	0.057	**0.010**	0.219	1.000	0.952	**0.016**
		LFAV	**0.002**	**0.002**	**0.000**	**0.000**	**0.000**	0.051	**0.000**	**0.011**	**0.000**	**0.010**	0.051	**0.001**	**0.039**	0.952	1.000	**0.002**
		LFNV	0.059	0.177	0.789	0.083	0.305	0.095	0.777	0.653	0.841	**0.007**	**0.036**	0.429	0.548	**0.016**	**0.002**	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(g) SO_4^{2-}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.004**	**0.017**	0.364	**0.040**	0.310	**0.000**	**0.036**	0.147	0.138	**0.036**	0.177	**0.032**	0.111	**0.006**	0.841
		HFAV	**0.004**	1.000	0.480	**0.026**	**0.001**	0.537	0.525	0.381	**0.000**	0.629	0.364	1.000	**0.004**	**0.010**	0.291	**0.017**
		LFAV	**0.017**	0.480	1.000	**0.027**	**0.005**	0.244	0.888	0.865	**0.004**	0.686	0.444	0.870	**0.017**	**0.028**	0.129	**0.017**
		LFNV	0.364	**0.026**	**0.027**	1.000	0.200	0.364	**0.006**	0.064	0.666	0.088	0.063	0.194	**0.019**	0.089	**0.009**	0.898
R1	**Post**	HFNV	**0.040**	**0.001**	**0.005**	0.200	1.000	**0.045**	**0.000**	**0.012**	0.481	**0.008**	**0.019**	**0.029**	0.354	0.570	**0.000**	0.284
		HFAV	0.310	0.537	0.244	0.364	**0.045**	1.000	0.156	0.250	**0.042**	0.374	0.134	0.537	**0.016**	0.063	0.799	0.421
		LFAV	**0.000**	0.525	0.888	**0.006**	**0.000**	0.156	1.000	1.000	**0.000**	1.000	0.389	0.687	**0.000**	**0.001**	0.056	**0.002**
		LFNV	**0.036**	0.381	0.865	0.064	**0.012**	0.250	1.000	1.000	**0.009**	1.000	0.658	0.905	**0.036**	0.057	0.136	**0.036**
H1	**Pre**	HFNV	0.147	**0.000**	**0.004**	0.666	0.481	**0.042**	**0.000**	**0.009**	1.000	**0.009**	**0.016**	**0.026**	0.083	0.414	**0.000**	0.298
		HFAV	0.138	0.629	0.686	0.088	**0.008**	0.374	1.000	1.000	**0.009**	1.000	0.275	0.826	**0.006**	**0.020**	0.288	0.138
		LFAV	**0.036**	0.364	0.444	0.063	**0.019**	0.134	0.389	0.658	**0.016**	0.275	1.000	0.358	**0.036**	**0.050**	0.170	0.072
		LFNV	0.177	1.000	0.870	0.194	**0.029**	0.537	0.687	0.905	**0.026**	0.826	0.358	1.000	**0.017**	0.067	0.682	0.126
H1	**Post**	HFNV	**0.032**	**0.004**	**0.017**	**0.019**	0.354	**0.016**	**0.000**	**0.036**	0.083	**0.006**	**0.036**	**0.017**	1.000	0.730	**0.000**	**0.032**
		HFAV	0.111	**0.010**	**0.028**	0.089	0.570	0.063	**0.001**	0.057	0.414	**0.020**	**0.050**	0.067	0.730	1.000	**0.002**	0.190
		LFAV	**0.006**	0.291	0.129	**0.009**	**0.000**	0.799	0.056	0.136	**0.000**	0.288	0.170	0.682	**0.000**	**0.002**	1.000	**0.014**
		LFNV	0.841	**0.017**	**0.017**	0.898	0.284	0.421	**0.002**	**0.036**	0.298	0.138	0.072	0.126	**0.032**	0.190	**0.014**	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(h) DOC

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.017**	**0.005**	0.147	0.724	0.690	**0.013**	0.250	0.898	**0.003**	**0.036**	0.247	0.784	0.111	**0.000**	0.151
		HFAV	**0.017**	1.000	0.428	0.088	**0.020**	0.126	0.733	0.262	**0.000**	0.966	0.905	**0.026**	**0.005**	0.257	0.682	0.082
		LFAV	**0.005**	0.428	1.000	**0.028**	**0.002**	**0.019**	0.349	0.161	**0.001**	0.313	0.692	**0.022**	**0.004**	0.142	0.674	0.055
		LFNV	0.147	0.088	**0.028**	1.000	0.114	0.438	0.175	0.727	0.161	0.110	0.064	0.529	0.111	0.710	**0.012**	0.898
R1	**Post**	HFNV	0.724	**0.020**	**0.002**	0.114	1.000	0.435	**0.007**	0.279	0.541	**0.003**	0.085	0.142	0.605	0.073	**0.001**	0.143
		HFAV	0.690	0.126	**0.019**	0.438	0.435	1.000	0.069	0.571	0.898	0.075	0.250	0.537	1.000	0.286	**0.037**	0.421
		LFAV	**0.013**	0.733	0.349	0.175	**0.007**	0.069	1.000	0.555	**0.000**	0.706	0.555	0.122	**0.002**	0.571	0.218	0.267
		LFNV	0.250	0.262	0.161	0.727	0.279	0.571	0.555	1.000	0.209	0.439	0.100	0.714	0.243	0.629	**0.018**	0.881
H1	**Pre**	HFNV	0.898	**0.000**	**0.001**	0.161	0.541	0.898	**0.000**	0.209	1.000	**0.000**	**0.009**	0.113	0.479	**0.020**	**0.000**	0.112
		HFAV	**0.003**	0.966	0.313	0.110	**0.003**	0.075	0.706	0.439	**0.000**	1.000	0.800	**0.029**	**0.003**	0.296	0.376	0.173
		LFAV	**0.036**	0.905	0.692	0.064	0.085	0.250	0.555	0.100	**0.009**	0.800	1.000	**0.024**	**0.028**	0.229	0.945	**0.036**
		LFNV	0.247	**0.026**	**0.022**	0.529	0.142	0.537	0.122	0.714	0.113	**0.029**	**0.024**	1.000	0.065	0.352	**0.001**	0.537
H1	**Post**	HFNV	0.784	**0.005**	**0.004**	0.111	0.605	1.000	**0.002**	0.243	0.479	**0.003**	**0.028**	0.065	1.000	**0.025**	**0.001**	0.082
		HFAV	0.111	0.257	0.142	0.710	0.073	0.286	0.571	0.629	**0.020**	0.296	0.229	0.352	**0.025**	1.000	0.103	0.556
		LFAV	**0.000**	0.682	0.674	**0.012**	**0.001**	**0.037**	0.218	**0.018**	**0.000**	0.376	0.945	**0.001**	**0.001**	0.103	1.000	**0.014**
		LFNV	0.151	0.082	0.055	0.898	0.143	0.421	0.267	0.881	0.112	0.173	**0.036**	0.537	0.082	0.556	**0.014**	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(i) Fe^{2+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.057	0.114	0.283	0.050	0.057	**0.036**	0.229	0.230	**0.024**	1.000	0.067	0.111	0.057	0.076	0.905
		HFAV	0.057	1.000	0.476	0.570	0.671	0.057	1.000	0.629	0.412	0.927	0.057	0.914	0.905	0.229	0.479	0.111
		LFAV	0.114	0.476	1.000	0.852	0.846	**0.024**	0.492	0.548	0.731	0.153	0.167	0.589	0.429	**0.048**	0.428	0.177
		LFNV	0.283	0.570	0.852	1.000	1.000	0.085	0.573	0.776	0.694	0.536	0.194	0.414	0.524	0.133	0.897	0.222
R1	**Post**	HFNV	0.050	0.671	0.846	1.000	1.000	**0.019**	0.423	0.474	0.602	0.132	0.125	0.651	0.509	**0.040**	0.505	0.067
		HFAV	0.057	0.057	**0.024**	0.085	**0.019**	1.000	**0.049**	0.100	**0.017**	**0.017**	0.100	**0.048**	0.071	0.100	**0.007**	**0.036**
		LFAV	**0.036**	1.000	0.492	0.573	0.423	**0.049**	1.000	1.000	0.193	0.740	0.077	0.875	0.953	0.310	0.650	**0.040**
		LFNV	0.229	0.629	0.548	0.776	0.474	0.100	1.000	1.000	0.517	0.517	0.200	0.714	0.571	0.100	0.811	0.250
H1	**Pre**	HFNV	0.230	0.412	0.731	0.694	0.602	**0.017**	0.193	0.517	1.000	0.165	0.517	0.295	0.343	0.067	0.536	0.268
		HFAV	**0.024**	0.927	0.153	0.536	0.132	**0.017**	0.740	0.517	0.165	1.000	**0.017**	0.886	0.639	0.117	0.364	**0.018**
		LFAV	1.000	0.057	0.167	0.194	0.125	0.100	0.077	0.200	0.517	**0.017**	1.000	**0.024**	0.071	0.100	**0.014**	0.786
		LFNV	0.067	0.914	0.589	0.414	0.651	**0.048**	0.875	0.714	0.295	0.886	**0.024**	1.000	0.931	0.262	0.313	**0.030**
H1	**Post**	HFNV	0.111	0.905	0.429	0.524	0.509	0.071	0.953	0.571	0.343	0.639	0.071	0.931	1.000	0.571	0.513	0.151
		HFAV	0.057	0.229	**0.048**	0.133	**0.040**	0.100	0.310	0.100	0.067	0.117	0.100	0.262	0.571	1.000	**0.014**	**0.036**
		LFAV	0.076	0.479	0.428	0.897	0.505	**0.007**	0.650	0.811	0.536	0.364	**0.014**	0.313	0.513	**0.014**	1.000	0.075
		LFNV	0.905	0.111	0.177	0.222	0.067	**0.036**	**0.040**	0.250	0.268	**0.018**	0.786	**0.030**	0.151	**0.036**	0.075	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(j) Si^{4+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.010**	**0.029**	**0.017**	**0.016**	**0.032**	**0.005**	0.057	0.444	0.089	0.800	**0.019**	0.067	0.661	**0.009**	**0.016**
		HFAV	**0.010**	1.000	0.914	0.443	0.245	0.537	**0.014**	**0.048**	**0.002**	0.066	0.286	0.093	**0.015**	0.067	0.482	0.247
		LFAV	**0.029**	0.914	1.000	0.395	0.283	0.286	0.327	0.400	**0.008**	0.148	0.400	0.610	**0.038**	0.114	0.952	0.556
		LFNV	**0.017**	0.443	0.395	1.000	0.531	1.000	**0.023**	0.354	**0.014**	0.377	0.485	0.216	0.261	0.076	0.374	0.182
R1	**Post**	HFNV	**0.016**	0.245	0.283	0.531	1.000	0.724	**0.007**	0.133	**0.012**	0.888	0.444	0.142	0.852	0.073	0.153	0.171
		HFAV	**0.032**	0.537	0.286	1.000	0.724	1.000	**0.031**	0.143	**0.007**	0.606	0.333	0.247	0.329	0.111	0.187	0.222
		LFAV	**0.005**	**0.014**	0.327	**0.023**	**0.007**	**0.031**	1.000	0.391	**0.000**	**0.002**	0.147	0.451	**0.002**	**0.007**	**0.045**	0.141
		LFNV	0.057	**0.048**	0.400	0.354	0.133	0.143	0.391	1.000	**0.019**	**0.036**	0.500	0.905	**0.024**	0.057	0.427	0.393
H1	**Pre**	HFNV	0.444	**0.002**	**0.008**	**0.014**	**0.012**	**0.007**	**0.000**	**0.019**	1.000	**0.030**	0.846	**0.008**	**0.045**	0.202	**0.002**	**0.004**
		HFAV	0.089	0.066	0.148	0.377	0.888	0.606	**0.002**	**0.036**	**0.030**	1.000	0.600	**0.050**	0.776	0.260	**0.019**	**0.012**
		LFAV	0.800	0.286	0.400	0.485	0.444	0.333	0.147	0.500	0.846	0.600		0.571	0.571	0.800	0.228	0.333
		LFNV	**0.019**	0.093	0.610	0.216	0.142	0.247	0.451	0.905	**0.008**	**0.050**	0.571	1.000	**0.041**	**0.019**	0.482	0.537
H1	**Post**	HFNV	0.067	**0.015**	**0.038**	0.261	0.852	0.329	**0.002**	**0.024**	**0.045**	0.776	0.571	**0.041**	1.000	0.352	**0.010**	**0.004**
		HFAV	0.661	0.067	0.114	0.076	0.073	0.111	**0.007**	0.057	0.202	0.260	0.800	**0.019**	0.352	1.000	**0.025**	0.063
		LFAV	**0.009**	0.482	0.952	0.374	0.153	0.187	**0.045**	0.427	**0.002**	**0.019**	0.228	0.482	**0.010**	**0.025**	1.000	0.562
		LFNV	**0.016**	0.247	0.556	0.182	0.171	0.222	0.141	0.393	**0.004**	**0.012**	0.333	0.537	**0.004**	0.063	0.562	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(k) TN

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.222	**0.008**	0.147	0.524	**0.032**	0.679	0.143	0.833	0.130	0.571	0.151	0.222	0.413	0.427	1.000
		HFAV	0.222	1.000	0.129	0.898	0.171	**0.016**	0.859	**0.036**	0.127	0.959	0.250	0.548	**0.016**	**0.032**	0.364	0.841
		LFAV	**0.008**	0.129	1.000	0.243	**0.012**	**0.002**	0.143	**0.007**	**0.003**	0.080	0.063	0.859	**0.003**	**0.004**	**0.020**	0.129
		LFNV	0.147	0.898	0.243	1.000	0.059	**0.003**	0.661	**0.018**	0.139	0.651	0.209	0.606	**0.004**	**0.011**	0.287	0.606
R1	**Post**	HFNV	0.524	0.171	**0.012**	0.059	1.000	0.461	0.101	1.000	0.279	0.069	0.376	**0.045**	0.943	0.865	0.107	0.222
		HFAV	**0.032**	**0.016**	**0.002**	**0.003**	0.461	1.000	**0.008**	0.229	**0.004**	**0.001**	0.057	**0.016**	0.111	**0.029**	**0.005**	**0.016**
		LFAV	0.679	0.859	0.143	0.661	0.101	**0.008**	1.000	**0.049**	0.360	0.628	0.937	0.310	**0.040**	0.119	0.916	0.768
		LFNV	0.143	**0.036**	**0.007**	**0.018**	1.000	0.229	**0.049**	1.000	**0.048**	**0.004**	0.100	**0.036**	0.786	0.857	**0.013**	0.250
H1	**Pre**	HFNV	0.833	0.127	**0.003**	0.139	0.279	**0.004**	0.360	**0.048**	1.000	**0.031**	0.306	0.093	**0.045**	0.109	0.231	0.833
		HFAV	0.130	0.959	0.080	0.651	0.069	**0.001**	0.628	**0.004**	**0.031**	1.000	0.295	0.442	**0.006**	**0.013**	0.281	0.442
		LFAV	0.571	0.250	0.063	0.209	0.376	0.057	0.937	0.100	0.306	0.295	1.000	0.393	0.250	0.114	0.876	0.786
		LFNV	0.151	0.548	0.859	0.606	**0.045**	**0.016**	0.310	**0.036**	0.093	0.442	0.393	1.000	**0.032**	**0.032**	0.308	0.310
H1	**Post**	HFNV	0.222	**0.016**	**0.003**	**0.004**	0.943	0.111	**0.040**	0.786	**0.045**	**0.006**	0.250	**0.032**	1.000	0.730	**0.023**	0.151
		HFAV	0.413	**0.032**	**0.004**	**0.011**	0.865	**0.029**	0.119	0.857	0.109	**0.013**	0.114	**0.032**	0.730	1.000	**0.031**	0.286
		LFAV	0.427	0.364	**0.020**	0.287	0.107	**0.005**	0.916	**0.013**	0.231	0.281	0.876	0.308	**0.023**	**0.031**	1.000	0.496
		LFNV	1.000	0.841	0.129	0.606	0.222	**0.016**	0.768	0.250	0.833	0.442	0.786	0.310	0.151	0.286	0.496	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(l) TDN

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.082	**0.013**	0.240	0.222	0.421	0.510	0.250	0.699	0.200	0.786	0.151	0.082	0.286	0.493	1.000
		HFAV	0.082	1.000	0.635	0.776	**0.003**	0.052	0.062	**0.024**	**0.005**	0.148	**0.048**	0.792	**0.002**	**0.010**	**0.022**	0.429
		LFAV	**0.013**	0.635	1.000	0.400	**0.001**	**0.028**	**0.017**	**0.007**	**0.000**	0.054	**0.014**	0.513	**0.000**	**0.002**	**0.003**	0.099
		LFNV	0.240	0.776	0.400	1.000	**0.006**	0.147	0.295	0.100	0.077	0.316	0.100	1.000	**0.008**	0.050	0.166	0.438
R1	**Post**	HFNV	0.222	**0.003**	**0.001**	**0.006**	1.000	0.943	**0.041**	0.776	0.114	**0.004**	1.000	**0.030**	0.852	0.461	**0.034**	0.127
		HFAV	0.421	0.052	**0.028**	0.147	0.943	1.000	0.180	0.786	0.112	**0.038**	1.000	0.056	0.931	0.413	0.065	0.095
		LFAV	0.510	0.062	**0.017**	0.295	**0.041**	0.180	1.000	0.088	0.261	0.223	0.456	0.126	**0.015**	0.138	0.853	0.827
		LFNV	0.250	**0.024**	**0.007**	0.100	0.776	0.786	0.088	1.000	0.145	**0.031**	0.700	**0.036**	0.548	1.000	**0.011**	0.786
H1	**Pre**	HFNV	0.699	**0.005**	**0.000**	0.077	0.114	0.112	0.261	0.145	1.000	**0.023**	1.000	**0.012**	**0.026**	0.106	0.070	0.898
		HFAV	0.200	0.148	0.054	0.316	**0.004**	**0.038**	0.223	**0.031**	**0.023**	1.000	0.080	0.587	**0.002**	**0.011**	0.135	0.459
		LFAV	0.786	**0.048**	**0.014**	0.100	1.000	1.000	0.456	0.700	1.000	0.080	1.000	0.143	0.548	0.629	0.348	0.786
		LFNV	0.151	0.792	0.513	1.000	**0.030**	0.056	0.126	**0.036**	**0.012**	0.587	0.143	1.000	**0.004**	**0.016**	0.082	0.310
H1	**Post**	HFNV	0.082	**0.002**	**0.000**	**0.008**	0.852	0.931	**0.015**	0.548	**0.026**	**0.002**	0.548	**0.004**	1.000	0.476	**0.003**	0.126
		HFAV	0.286	**0.010**	**0.002**	0.050	0.461	0.413	0.138	1.000	0.106	**0.011**	0.629	**0.016**	0.476	1.000	**0.018**	0.413
		LFAV	0.493	**0.022**	**0.003**	0.166	**0.034**	0.065	0.853	**0.011**	0.070	0.135	0.348	0.082	**0.003**	**0.018**	1.000	0.429
		LFNV	1.000	0.429	0.099	0.438	0.127	0.095	0.827	0.786	0.898	0.459	0.786	0.310	0.126	0.413	0.429	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(m) NH_4^+

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.662	0.859	0.898	0.622	0.346	0.364	0.571	1.000	0.775	1.000	0.126	0.429	0.730	0.712	0.151
		HFAV	0.662	1.000	0.329	0.607	0.142	0.429	0.421	1.000	0.689	0.831	0.714	**0.026**	0.093	0.762	0.281	0.082
		LFAV	0.859	0.329	1.000	0.842	0.424	0.099	**0.032**	0.469	0.905	0.522	0.937	**0.031**	0.181	0.240	0.974	0.075
		LFNV	0.898	0.607	0.842	1.000	0.963	0.298	0.149	0.727	0.730	0.357	1.000	0.328	0.864	0.503	0.696	0.364
R1	**Post**	HFNV	0.622	0.142	0.424	0.963	1.000	0.057	**0.026**	0.376	0.541	0.192	0.630	0.282	0.852	0.173	0.463	0.354
		HFAV	0.346	0.429	0.099	0.298	0.057	1.000	0.570	0.393	0.240	0.289	0.143	**0.017**	**0.030**	0.461	0.057	**0.032**
		LFAV	0.364	0.421	**0.032**	0.149	**0.026**	0.570	1.000	0.350	0.080	0.087	0.161	**0.002**	**0.004**	0.647	**0.004**	**0.005**
		LFNV	0.571	1.000	0.469	0.727	0.376	0.393	0.350	1.000	0.864	0.800	0.700	**0.024**	0.095	1.000	0.247	0.071
H1	**Pre**	HFNV	1.000	0.689	0.905	0.730	0.541	0.240	0.080	0.864	1.000	0.471	1.000	0.066	0.224	0.604	0.859	0.112
		HFAV	0.775	0.831	0.522	0.357	0.192	0.289	0.087	0.800	0.471	1.000	0.704	**0.002**	**0.028**	0.624	0.399	**0.014**
		LFAV	1.000	0.714	0.937	1.000	0.630	0.143	0.161	0.700	1.000	0.704	1.000	0.167	0.300	0.400	0.942	0.294
		LFNV	0.126	**0.026**	**0.031**	0.328	0.282	**0.017**	**0.002**	**0.024**	0.066	**0.002**	0.167	1.000	0.485	**0.019**	**0.008**	0.931
H1	**Post**	HFNV	0.429	0.093	0.181	0.864	0.852	**0.030**	**0.004**	0.095	0.224	**0.028**	0.300	0.485	1.000	**0.038**	**0.044**	0.521
		HFAV	0.730	0.762	0.240	0.503	0.173	0.461	0.647	1.000	0.604	0.624	0.400	**0.019**	**0.038**	1.000	0.101	**0.032**
		LFAV	0.712	0.281	0.974	0.696	0.463	0.057	**0.004**	0.247	0.859	0.399	0.942	**0.008**	**0.044**	0.101	1.000	**0.023**
		LFNV	0.151	0.082	0.075	0.364	0.354	**0.032**	**0.005**	0.071	0.112	**0.014**	0.294	0.931	0.521	**0.032**	**0.023**	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(n) NO_2^-+NO_3^-

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.513	0.411	0.789	0.821	0.239	0.054	0.541	0.340	0.130	0.541	0.784	0.782	0.371	**0.042**	0.833
		HFAV	0.513	1.000	0.867	0.315	0.644	0.274	**0.022**	0.694	0.589	0.275	0.896	0.092	0.467	0.441	**0.016**	0.712
		LFAV	0.411	0.867	1.000	0.202	0.492	0.319	**0.033**	0.794	0.834	0.216	0.931	0.090	0.205	0.508	**0.024**	0.418
		LFNV	0.789	0.315	0.202	1.000	0.384	0.056	**0.001**	0.115	0.477	**0.010**	0.229	0.864	0.637	0.052	**0.000**	0.548
R1	**Post**	HFNV	0.821	0.644	0.492	0.384	1.000	0.176	**0.032**	0.531	0.694	0.109	0.601	0.399	0.512	0.378	**0.021**	0.603
		HFAV	0.239	0.274	0.319	0.056	0.176	1.000	0.868	0.495	0.319	0.725	0.495	**0.050**	0.068	0.662	0.812	0.119
		LFAV	0.054	**0.022**	**0.033**	**0.001**	**0.032**	0.868	1.000	0.144	**0.011**	0.220	0.144	**0.000**	**0.009**	0.240	0.889	**0.013**
		LFNV	0.541	0.694	0.794	0.115	0.531	0.495	0.144	1.000	0.301	0.767	0.825	**0.048**	0.298	1.000	0.115	0.453
H1	**Pre**	HFNV	0.340	0.589	0.834	0.477	0.694	0.319	**0.011**	0.301	1.000	**0.032**	0.638	0.442	0.405	0.177	**0.008**	0.736
		HFAV	0.130	0.275	0.216	**0.010**	0.109	0.725	0.220	0.767	**0.032**	1.000	0.459	**0.004**	**0.046**	0.849	0.180	0.114
		LFAV	0.541	0.896	0.931	0.229	0.601	0.495	0.144	0.825	0.638	0.459	1.000	0.262	0.298	0.854	0.115	0.453
		LFNV	0.784	0.092	0.090	0.864	0.399	**0.050**	**0.000**	**0.048**	0.442	**0.004**	0.262	1.000	0.575	**0.042**	**0.000**	0.429
H1	**Post**	HFNV	0.782	0.467	0.205	0.637	0.512	0.068	**0.009**	0.298	0.405	**0.046**	0.298	0.575	1.000	0.229	**0.004**	1.000
		HFAV	0.371	0.441	0.508	0.052	0.378	0.662	0.240	1.000	0.177	0.849	0.854	**0.042**	0.229	1.000	0.173	0.317
		LFAV	**0.042**	**0.016**	**0.024**	**0.000**	**0.021**	0.812	0.889	0.115	**0.008**	0.180	0.115	**0.000**	**0.004**	0.173	1.000	**0.008**
		LFNV	0.833	0.712	0.418	0.548	0.603	0.119	**0.013**	0.453	0.736	0.114	0.453	0.429	1.000	0.317	**0.008**	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(o) TP

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	**0.017**	0.768	0.364	**0.006**	**0.016**	0.594	**0.036**	**0.030**	**0.001**	0.393	1.000	**0.004**	**0.016**	**0.019**	1.000
		HFAV	**0.017**	1.000	0.220	0.088	0.301	**0.019**	0.713	0.714	0.181	0.282	0.604	0.093	**0.041**	**0.010**	0.525	0.177
		LFAV	0.768	0.220	1.000	0.842	**0.034**	**0.008**	0.631	0.287	0.055	**0.008**	0.573	0.875	**0.011**	**0.004**	0.152	0.859
		LFNV	0.364	0.088	0.842	1.000	**0.027**	**0.006**	0.780	0.100	**0.036**	**0.003**	0.864	0.637	**0.003**	**0.003**	0.152	0.606
R1	**Post**	HFNV	**0.006**	0.301	**0.034**	**0.027**	1.000	**0.048**	0.315	0.539	0.834	0.697	0.194	**0.029**	0.181	**0.028**	0.206	0.093
		HFAV	**0.016**	**0.019**	**0.008**	**0.006**	**0.048**	1.000	0.054	0.114	0.214	0.113	0.114	**0.019**	0.762	1.000	**0.010**	**0.032**
		LFAV	0.594	0.713	0.631	0.780	0.315	0.054	1.000	0.692	0.146	0.067	0.937	0.368	0.082	0.054	0.314	0.391
		LFNV	**0.036**	0.714	0.287	0.100	0.539	0.114	0.692	1.000	0.497	0.521	0.700	0.167	0.167	0.057	0.368	0.393
H1	**Pre**	HFNV	**0.030**	0.181	0.055	**0.036**	0.834	0.214	0.146	0.497	1.000	1.000	0.279	**0.029**	0.491	0.154	0.310	**0.045**
		HFAV	**0.001**	0.282	**0.008**	**0.003**	0.697	0.113	0.067	0.521	1.000	1.000	0.082	**0.012**	0.244	0.130	**0.011**	**0.026**
		LFAV	0.393	0.604	0.573	0.864	0.194	0.114	0.937	0.700	0.279	0.082	1.000	0.548	0.167	0.057	0.225	0.571
		LFNV	1.000	0.093	0.875	0.637	**0.029**	**0.019**	0.368	0.167	**0.029**	**0.012**	0.548	1.000	**0.009**	**0.010**	0.301	0.931
H1	**Post**	HFNV	**0.004**	**0.041**	**0.011**	**0.003**	0.181	0.762	0.082	0.167	0.491	0.244	0.167	**0.009**	1.000	0.610	**0.015**	**0.030**
		HFAV	**0.016**	**0.010**	**0.004**	**0.003**	**0.028**	1.000	0.054	0.057	0.154	0.130	0.057	**0.010**	0.610	1.000	**0.018**	**0.032**
		LFAV	**0.019**	0.525	0.152	0.152	0.206	**0.010**	0.314	0.368	0.310	**0.011**	0.225	0.301	**0.015**	**0.018**	1.000	0.281
		LFNV	1.000	0.177	0.859	0.606	0.093	**0.032**	0.391	0.393	**0.045**	**0.026**	0.571	0.931	**0.030**	**0.032**	0.281	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(p) TDP

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.082	0.768	0.298	**0.004**	0.151	**0.009**	**0.036**	**0.029**	**0.000**	**0.036**	0.052	**0.004**	**0.016**	**0.000**	**0.016**
		HFAV	0.082	1.000	0.263	0.689	0.061	0.177	**0.027**	**0.048**	0.224	**0.012**	0.381	**0.041**	**0.026**	**0.010**	**0.005**	0.082
		LFAV	0.768	0.263	1.000	0.447	**0.045**	0.099	**0.013**	**0.014**	0.060	**0.004**	0.371	**0.007**	**0.022**	**0.004**	**0.002**	**0.019**
		LFNV	0.298	0.689	0.447	1.000	0.112	0.240	**0.031**	0.064	0.161	**0.021**	0.600	**0.050**	0.066	**0.034**	**0.015**	0.060
R1	**Post**	HFNV	**0.004**	0.061	**0.045**	0.112	1.000	0.378	0.173	0.125	0.962	0.491	0.125	0.081	0.220	**0.014**	0.142	0.509
		HFAV	0.151	0.177	0.099	0.240	0.378	1.000	1.000	1.000	0.518	0.633	0.393	0.662	0.714	0.556	0.646	1.000
		LFAV	**0.009**	**0.027**	**0.013**	**0.031**	0.173	1.000	1.000	0.769	0.503	0.434	0.126	0.350	0.725	0.191	0.735	0.913
		LFNV	**0.036**	**0.048**	**0.014**	0.064	0.125	1.000	0.769	1.000	0.209	0.296	0.100	0.548	1.000	0.400	0.515	0.571
H1	**Pre**	HFNV	**0.029**	0.224	0.060	0.161	0.962	0.518	0.503	0.209	1.000	0.570	0.600	0.145	0.388	0.076	0.277	0.438
		HFAV	**0.000**	**0.012**	**0.004**	**0.021**	0.491	0.633	0.434	0.296	0.570	1.000	0.146	0.106	0.510	**0.023**	0.289	0.844
		LFAV	**0.036**	0.381	0.371	0.600	0.125	0.393	0.126	0.100	0.600	0.146	1.000	0.167	0.095	0.057	**0.048**	0.250
		LFNV	0.052	**0.041**	**0.007**	**0.050**	0.081	0.662	0.350	0.548	0.145	0.106	0.167	1.000	0.818	0.914	0.213	0.429
H1	**Post**	HFNV	**0.004**	**0.026**	**0.022**	0.066	0.220	0.714	0.725	1.000	0.388	0.510	0.095	0.818	1.000	0.669	0.616	1.000
		HFAV	**0.016**	**0.010**	**0.004**	**0.034**	**0.014**	0.556	0.191	0.400	0.076	**0.023**	0.057	0.914	0.669	1.000	0.060	0.190
		LFAV	**0.000**	**0.005**	**0.002**	**0.015**	0.142	0.646	0.735	0.515	0.277	0.289	**0.048**	0.213	0.616	0.060	1.000	0.527
		LFNV	**0.016**	0.082	**0.019**	0.060	0.509	1.000	0.913	0.571	0.438	0.844	0.250	0.429	1.000	0.190	0.527	1.000

Table A.1: Mann-Witney U-test of ion concentration (continued).

(q) SRP

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.082	0.953	0.190	**0.002**	0.151	**0.005**	**0.036**	**0.019**	**0.001**	**0.036**	**0.017**	**0.008**	**0.016**	**0.002**	0.056
		HFAV	0.082	1.000	0.220	0.955	0.108	0.247	**0.027**	0.095	0.388	0.106	0.714	0.132	**0.020**	**0.010**	**0.004**	0.143
		LFAV	0.953	0.220	1.000	0.356	**0.026**	0.075	**0.004**	**0.028**	0.053	**0.018**	0.371	**0.022**	**0.004**	**0.002**	**0.000**	**0.019**
		LFNV	0.190	0.955	0.356	1.000	0.059	0.190	**0.025**	0.100	0.190	0.126	0.864	0.066	**0.008**	**0.006**	**0.002**	0.060
R1	**Post**	HFNV	**0.002**	0.108	**0.026**	0.059	1.000	0.354	0.238	0.102	0.700	0.612	0.085	0.573	0.061	**0.004**	**0.000**	0.093
		HFAV	0.151	0.247	0.075	0.190	0.354	1.000	0.533	1.000	0.364	0.387	0.250	1.000	0.582	0.286	0.458	0.421
		LFAV	**0.005**	**0.027**	**0.004**	**0.025**	0.238	0.533	1.000	0.769	0.112	0.106	0.088	0.481	0.960	0.744	0.853	0.865
		LFNV	**0.036**	0.095	**0.028**	0.100	0.102	1.000	0.769	1.000	0.165	0.225	0.100	0.905	0.697	0.114	0.277	0.393
H1	**Pre**	HFNV	**0.019**	0.388	0.053	0.190	0.700	0.364	0.112	0.165	1.000	0.764	0.482	0.479	**0.039**	**0.020**	**0.002**	0.190
		HFAV	**0.001**	0.106	**0.018**	0.126	0.612	0.387	0.106	0.225	0.764	1.000	0.239	0.467	**0.032**	**0.023**	**0.006**	0.208
		LFAV	**0.036**	0.714	0.371	0.864	0.085	0.250	0.088	0.100	0.482	0.239	1.000	0.262	**0.028**	0.057	**0.011**	0.250
		LFNV	**0.017**	0.132	**0.022**	0.066	0.573	1.000	0.481	0.905	0.479	0.467	0.262	1.000	0.297	0.134	0.372	0.583
H1	**Post**	HFNV	**0.008**	**0.020**	**0.004**	**0.008**	0.061	0.582	0.960	0.697	**0.039**	**0.032**	**0.028**	0.297	1.000	0.830	0.707	1.000
		HFAV	**0.016**	**0.010**	**0.002**	**0.006**	**0.004**	0.286	0.744	0.114	**0.020**	**0.023**	0.057	0.134	0.830	1.000	0.128	0.711
		LFAV	**0.002**	**0.004**	**0.000**	**0.002**	**0.000**	0.458	0.853	0.277	**0.002**	**0.006**	**0.011**	0.372	0.707	0.128	1.000	0.633
		LFNV	0.056	0.143	**0.019**	0.060	0.093	0.421	0.865	0.393	0.190	0.208	0.250	0.583	1.000	0.711	0.633	1.000

Table A.2: Mann-Witney U-test of ion export. p-values $< \alpha = 0.05$ are in bold. The major diagonal is greyed out as by definition the Wilcoxon coefficient is 1. This table is also symmetric by definition around the major diagonal. The subset of data where flow and concentrations of both R1 and H1 were taken <24 hours apart is used here. Pre-harvest data was collected before July 2, 2007. Post-harvest data was collected after July 2, 2007 when harvesting began on H1. Categorical boxes are defined by flow (high or low) and by vegetation (active or not-active): high flow non-active vegetation (HFNV), high flow active vegetation (HFAV), low flow active vegetation (LFAV), low flow non-active vegetation (LFNV).

(a) Ca^{2+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.429	**0.008**	**0.003**	0.622	0.548	**0.005**	**0.036**	0.083	0.059	0.250	0.052	0.792	0.730	**0.038**	**0.008**
		HFAV	0.429	1.000	**0.000**	**0.000**	0.662	0.792	**0.000**	**0.024**	0.689	0.467	**0.048**	**0.004**	0.937	0.762	**0.003**	**0.004**
		LFAV	**0.008**	**0.000**	1.000	0.481	**0.000**	**0.001**	1.000	0.937	**0.000**	**0.000**	0.217	0.428	**0.000**	**0.002**	0.132	0.310
		LFNV	**0.003**	**0.000**	0.481	1.000	**0.000**	**0.001**	0.353	1.000	**0.000**	**0.000**	**0.049**	0.181	**0.000**	**0.002**	**0.024**	0.165
R1	**Post**	HFNV	0.622	0.662	**0.000**	**0.000**	1.000	1.000	**0.000**	**0.012**	0.200	0.089	**0.012**	**0.001**	0.491	0.808	**0.001**	**0.002**
		HFAV	0.548	0.792	**0.001**	**0.001**	1.000	1.000	**0.001**	**0.036**	0.438	0.173	**0.036**	**0.004**	0.931	0.905	**0.001**	**0.008**
		LFAV	**0.005**	**0.000**	1.000	0.353	**0.000**	**0.001**	1.000	0.469	**0.000**	**0.000**	0.161	0.492	**0.000**	**0.002**	0.223	0.055
		LFNV	**0.036**	**0.024**	0.937	1.000	**0.012**	**0.036**	0.469	1.000	**0.009**	**0.004**	0.100	0.548	**0.024**	0.057	0.126	0.143
H1	**Pre**	HFNV	0.083	0.689	**0.000**	**0.000**	0.200	0.438	**0.000**	**0.009**	1.000	0.845	**0.009**	**0.001**	0.145	0.260	**0.000**	**0.001**
		HFAV	0.059	0.467	**0.000**	**0.000**	0.089	0.173	**0.000**	**0.004**	0.845	1.000	**0.004**	**0.000**	0.058	0.102	**0.000**	**0.000**
		LFAV	0.250	**0.048**	0.217	**0.049**	**0.012**	**0.036**	0.161	0.100	**0.009**	**0.004**	1.000	0.714	**0.024**	0.057	0.885	**0.036**
		LFNV	0.052	**0.004**	0.428	0.181	**0.001**	**0.004**	0.492	0.548	**0.001**	**0.000**	0.714	1.000	**0.002**	**0.010**	0.591	0.247
H1	**Post**	HFNV	0.792	0.937	**0.000**	**0.000**	0.491	0.931	**0.000**	**0.024**	0.145	0.058	**0.024**	**0.002**	1.000	0.914	**0.000**	**0.004**
		HFAV	0.730	0.762	**0.002**	**0.002**	0.808	0.905	**0.002**	0.057	0.260	0.102	0.057	**0.010**	0.914	1.000	**0.001**	**0.016**
		LFAV	**0.038**	**0.003**	0.132	**0.024**	**0.001**	**0.001**	0.223	0.126	**0.000**	**0.000**	0.885	0.591	**0.000**	**0.001**	1.000	**0.000**
		LFNV	**0.008**	**0.004**	0.310	0.165	**0.002**	**0.008**	0.055	0.143	**0.001**	**0.000**	**0.036**	0.247	**0.004**	**0.016**	**0.000**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(b) Mg^{2+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.429	**0.007**	**0.005**	0.622	0.548	**0.003**	**0.036**	**0.042**	0.104	0.250	0.222	0.329	0.413	0.052	**0.008**
		HFAV	0.429	1.000	**0.001**	**0.000**	0.852	0.792	**0.000**	**0.024**	0.272	0.437	0.095	**0.030**	1.000	0.762	**0.010**	**0.004**
		LFAV	**0.007**	**0.001**	1.000	0.661	**0.000**	**0.001**	0.780	0.482	**0.000**	**0.000**	0.100	0.364	**0.000**	**0.003**	0.175	0.190
		LFNV	**0.005**	**0.000**	0.661	1.000	**0.000**	**0.001**	0.912	0.469	**0.000**	**0.000**	0.077	0.310	**0.000**	**0.002**	0.072	0.099
R1	**Post**	HFNV	0.622	0.852	**0.000**	**0.000**	1.000	0.943	**0.000**	**0.012**	0.093	0.135	**0.024**	**0.019**	0.491	0.808	**0.001**	**0.002**
		HFAV	0.548	0.792	**0.001**	**0.001**	0.943	1.000	**0.001**	**0.036**	0.240	0.279	0.071	0.056	0.792	0.730	**0.013**	**0.008**
		LFAV	**0.003**	**0.000**	0.780	0.912	**0.000**	**0.001**	1.000	0.371	**0.000**	**0.000**	0.077	0.440	**0.000**	**0.002**	0.114	0.075
		LFNV	**0.036**	**0.024**	0.482	0.469	**0.012**	**0.036**	0.371	1.000	**0.009**	**0.004**	0.100	0.571	**0.024**	0.057	0.060	0.393
H1	**Pre**	HFNV	**0.042**	0.272	**0.000**	**0.000**	0.093	0.240	**0.000**	**0.009**	1.000	0.862	**0.009**	**0.002**	0.145	0.199	**0.000**	**0.001**
		HFAV	0.104	0.437	**0.000**	**0.000**	0.135	0.279	**0.000**	**0.004**	0.862	1.000	**0.018**	**0.004**	0.180	0.212	**0.000**	**0.000**
		LFAV	0.250	0.095	0.100	0.077	**0.024**	0.071	0.077	0.100	**0.009**	**0.018**	1.000	0.786	**0.024**	0.057	0.885	**0.036**
		LFNV	0.222	**0.030**	0.364	0.310	**0.019**	0.056	0.440	0.571	**0.002**	**0.004**	0.786	1.000	0.052	0.063	0.743	0.222
H1	**Post**	HFNV	0.329	1.000	**0.000**	**0.000**	0.491	0.792	**0.000**	**0.024**	0.145	0.180	**0.024**	0.052	1.000	1.000	**0.000**	**0.004**
		HFAV	0.413	0.762	**0.003**	**0.002**	0.808	0.730	**0.002**	0.057	0.199	0.212	0.057	0.063	1.000	1.000	**0.001**	**0.016**
		LFAV	0.052	**0.010**	0.175	0.072	**0.001**	**0.013**	0.114	0.060	**0.000**	**0.000**	0.885	0.743	**0.000**	**0.001**	1.000	**0.000**
		LFNV	**0.008**	**0.004**	0.190	0.099	**0.002**	**0.008**	0.075	0.393	**0.001**	**0.000**	**0.036**	0.222	**0.004**	**0.016**	**0.000**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(c) Na$^+$

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.247	**0.003**	**0.001**	0.435	0.310	**0.001**	**0.036**	**0.029**	**0.010**	0.250	0.247	0.095	0.111	0.069	**0.008**
		HFAV	0.247	1.000	**0.000**	**0.000**	0.852	0.931	**0.000**	**0.024**	0.272	0.106	0.095	**0.026**	0.662	0.610	**0.007**	**0.004**
		LFAV	**0.003**	**0.000**	1.000	0.853	**0.000**	**0.001**	0.579	0.692	**0.000**	**0.000**	0.077	0.147	**0.001**	**0.002**	0.132	0.310
		LFNV	**0.001**	**0.000**	0.853	1.000	**0.000**	**0.001**	0.796	0.937	**0.000**	**0.000**	**0.049**	0.093	**0.001**	**0.002**	**0.036**	0.594
R1	**Post**	HFNV	0.435	0.852	**0.000**	**0.000**	1.000	1.000	**0.000**	**0.012**	0.074	**0.025**	**0.012**	**0.005**	0.127	0.283	**0.001**	**0.002**
		HFAV	0.310	0.931	**0.001**	**0.001**	1.000	1.000	**0.001**	**0.036**	0.190	0.117	0.071	**0.017**	0.548	0.730	**0.013**	**0.008**
		LFAV	**0.001**	**0.000**	0.579	0.796	**0.000**	**0.001**	1.000	0.811	**0.000**	**0.000**	**0.049**	0.093	**0.001**	**0.002**	**0.036**	0.679
		LFNV	**0.036**	**0.024**	0.692	0.937	**0.012**	**0.036**	0.811	1.000	**0.009**	**0.004**	0.100	0.381	**0.036**	0.057	0.060	0.786
H1	**Pre**	HFNV	**0.029**	0.272	**0.000**	**0.000**	0.074	0.190	**0.000**	**0.009**	1.000	0.948	**0.018**	**0.001**	0.364	0.414	**0.000**	**0.001**
		HFAV	**0.010**	0.106	**0.000**	**0.000**	**0.025**	0.117	**0.000**	**0.004**	0.948	1.000	**0.004**	**0.000**	0.336	0.245	**0.000**	**0.000**
		LFAV	0.250	0.095	0.077	**0.049**	**0.012**	0.071	**0.049**	0.100	**0.018**	**0.004**	1.000	0.905	**0.036**	0.057	0.769	**0.036**
		LFNV	0.247	**0.026**	0.147	0.093	**0.005**	**0.017**	0.093	0.381	**0.001**	**0.000**	0.905	1.000	**0.004**	**0.010**	0.961	0.177
H1	**Post**	HFNV	0.095	0.662	**0.001**	**0.001**	0.127	0.548	**0.001**	**0.036**	0.364	0.336	**0.036**	**0.004**	1.000	0.905	**0.000**	**0.008**
		HFAV	0.111	0.610	**0.002**	**0.002**	0.283	0.730	**0.002**	0.057	0.414	0.245	0.057	**0.010**	0.905	1.000	**0.001**	**0.016**
		LFAV	0.069	**0.007**	0.132	**0.036**	**0.001**	**0.013**	**0.036**	0.060	**0.000**	**0.000**	0.769	0.961	**0.000**	**0.001**	1.000	**0.027**
		LFNV	**0.008**	**0.004**	0.310	0.594	**0.002**	**0.008**	0.679	0.786	**0.001**	**0.000**	**0.036**	0.177	**0.008**	**0.016**	**0.027**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(d) K^+

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.429	**0.001**	**0.001**	0.724	0.548	**0.001**	**0.036**	0.240	0.328	**0.036**	**0.004**	0.690	0.286	**0.000**	**0.008**
		HFAV	0.429	1.000	**0.000**	**0.000**	0.059	0.931	**0.000**	**0.024**	**0.012**	0.892	**0.024**	**0.002**	0.082	0.914	**0.000**	**0.004**
		LFAV	**0.001**	**0.000**	1.000	0.340	**0.000**	**0.007**	0.315	0.864	**0.000**	**0.000**	1.000	0.456	**0.001**	**0.006**	0.552	0.190
		LFNV	**0.001**	**0.000**	0.340	1.000	**0.000**	0.112	0.113	0.727	**0.000**	**0.000**	0.727	1.000	**0.001**	**0.034**	0.295	0.083
R1	**Post**	HFNV	0.724	0.059	**0.000**	**0.000**	1.000	0.622	**0.000**	**0.012**	0.200	**0.039**	**0.012**	**0.001**	0.943	0.109	**0.000**	**0.002**
		HFAV	0.548	0.931	**0.007**	0.112	0.622	1.000	**0.001**	**0.036**	0.190	0.574	0.143	0.052	0.310	0.730	**0.000**	**0.008**
		LFAV	**0.001**	**0.000**	0.315	0.113	**0.000**	**0.001**	1.000	0.371	**0.000**	**0.000**	0.287	0.073	**0.001**	**0.002**	0.468	0.206
		LFNV	**0.036**	**0.024**	0.864	0.727	**0.012**	**0.036**	0.371	1.000	**0.009**	**0.018**	1.000	0.548	**0.036**	0.057	0.659	0.071
H1	**Pre**	HFNV	0.240	**0.012**	**0.000**	**0.000**	0.200	0.190	**0.000**	**0.009**	1.000	**0.001**	**0.009**	**0.000**	0.606	**0.020**	**0.000**	**0.001**
		HFAV	0.328	0.892	**0.000**	**0.000**	**0.039**	0.574	**0.000**	**0.018**	**0.001**	1.000	**0.009**	**0.002**	**0.027**	0.953	**0.000**	**0.000**
		LFAV	**0.036**	**0.024**	1.000	0.727	**0.012**	0.143	0.287	1.000	**0.009**	**0.009**	1.000	0.905	**0.036**	0.057	0.659	0.071
		LFNV	**0.004**	**0.002**	0.456	1.000	**0.001**	0.052	0.073	0.548	**0.000**	**0.002**	0.905	1.000	**0.004**	**0.038**	0.122	**0.017**
H1	**Post**	HFNV	0.690	0.082	**0.001**	**0.001**	0.943	0.310	**0.001**	**0.036**	0.606	**0.027**	**0.036**	**0.004**	1.000	0.063	**0.000**	**0.008**
		HFAV	0.286	0.914	**0.006**	**0.034**	0.109	0.730	**0.002**	0.057	**0.020**	0.953	0.057	**0.038**	0.063	1.000	**0.001**	**0.016**
		LFAV	**0.000**	**0.000**	0.552	0.295	**0.000**	**0.000**	0.468	0.659	**0.000**	**0.000**	0.659	0.122	**0.000**	**0.001**	1.000	0.069
		LFNV	**0.008**	**0.004**	0.190	0.083	**0.002**	**0.008**	0.206	0.071	**0.001**	**0.000**	0.071	**0.017**	**0.008**	**0.016**	0.069	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(e) HCO_3^-

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.537	**0.008**	**0.002**	0.724	0.548	**0.002**	**0.036**	0.065	**0.026**	0.250	0.177	0.537	0.556	**0.027**	**0.008**
		HFAV	0.537	1.000	**0.000**	**0.001**	0.662	0.931	**0.000**	**0.024**	0.228	0.210	**0.048**	**0.015**	0.937	0.914	**0.003**	**0.004**
		LFAV	**0.008**	**0.000**	1.000	0.315	**0.000**	**0.001**	0.512	0.692	**0.000**	**0.000**	0.217	0.263	**0.000**	**0.002**	0.203	0.310
		LFNV	**0.002**	**0.001**	0.315	1.000	**0.000**	**0.002**	0.492	0.776	**0.000**	**0.000**	**0.048**	0.108	**0.001**	**0.004**	**0.007**	0.943
R1	**Post**	HFNV	0.724	0.662	**0.000**	**0.000**	1.000	0.943	**0.000**	**0.012**	0.065	**0.025**	**0.012**	**0.008**	0.573	0.683	**0.001**	**0.002**
		HFAV	0.548	0.931	**0.001**	**0.002**	0.943	1.000	**0.000**	**0.036**	0.222	0.117	0.071	**0.017**	0.931	0.905	**0.009**	**0.008**
		LFAV	**0.002**	**0.000**	0.512	0.492	**0.000**	**0.000**	1.000	0.659	**0.000**	**0.000**	0.088	0.149	**0.000**	**0.001**	0.059	0.221
		LFNV	**0.036**	**0.024**	0.692	0.776	**0.012**	**0.036**	0.659	1.000	**0.012**	**0.004**	0.100	0.381	**0.024**	0.057	0.101	0.393
H1	**Pre**	HFNV	0.065	0.228	**0.000**	**0.000**	0.065	0.222	**0.000**	**0.012**	1.000	0.972	**0.012**	**0.001**	0.142	0.109	**0.000**	**0.002**
		HFAV	**0.026**	0.210	**0.000**	**0.000**	**0.025**	0.117	**0.000**	**0.004**	0.972	1.000	**0.004**	**0.000**	**0.029**	0.060	**0.000**	**0.000**
		LFAV	0.250	**0.048**	0.217	**0.048**	**0.012**	0.071	0.088	0.100	**0.012**	**0.004**	1.000	0.905	**0.024**	0.057	0.840	**0.036**
		LFNV	0.177	**0.015**	0.263	0.108	**0.008**	**0.017**	0.149	0.381	**0.001**	**0.000**	0.905	1.000	**0.015**	**0.019**	0.964	0.247
H1	**Post**	HFNV	0.537	0.937	**0.000**	**0.001**	0.573	0.931	**0.000**	**0.024**	0.142	**0.029**	**0.024**	**0.015**	1.000	0.914	**0.000**	**0.004**
		HFAV	0.556	0.914	**0.002**	**0.004**	0.683	0.905	**0.001**	0.057	0.109	0.060	0.057	**0.019**	0.914	1.000	**0.001**	**0.016**
		LFAV	**0.027**	**0.003**	0.203	**0.007**	**0.001**	**0.009**	0.059	0.101	**0.000**	**0.000**	0.840	0.964	**0.000**	**0.001**	1.000	**0.000**
		LFNV	**0.008**	**0.004**	0.310	0.943	**0.002**	**0.008**	0.221	0.393	**0.002**	**0.000**	**0.036**	0.247	**0.004**	**0.016**	**0.000**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(f) Cl^-

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.126	**0.001**	**0.001**	0.943	0.421	**0.000**	**0.036**	0.606	**0.037**	**0.036**	**0.004**	0.310	**0.016**	**0.000**	**0.008**
		HFAV	0.126	1.000	**0.000**	**0.002**	0.059	1.000	**0.001**	**0.024**	**0.026**	0.553	**0.024**	**0.009**	1.000	0.114	**0.000**	**0.004**
		LFAV	**0.001**	**0.000**	1.000	0.161	**0.000**	**0.029**	0.370	1.000	**0.000**	**0.000**	0.864	0.066	**0.002**	**0.034**	**0.009**	0.083
		LFNV	**0.001**	**0.002**	0.161	1.000	**0.000**	0.190	0.095	0.373	**0.000**	**0.001**	0.282	0.864	**0.019**	0.503	**0.004**	0.060
R1	**Post**	HFNV	0.943	0.059	**0.000**	**0.000**	1.000	0.354	**0.000**	**0.012**	0.277	**0.016**	**0.012**	**0.001**	0.435	**0.004**	**0.000**	**0.002**
		HFAV	0.421	1.000	**0.029**	0.190	0.354	1.000	**0.013**	0.143	0.147	1.000	0.071	0.247	0.841	0.413	**0.001**	**0.008**
		LFAV	**0.000**	**0.001**	0.370	0.095	**0.000**	**0.013**	1.000	0.368	**0.000**	**0.000**	0.769	**0.037**	**0.002**	**0.026**	0.104	0.510
		LFNV	**0.036**	**0.024**	1.000	0.373	**0.012**	0.143	0.368	1.000	**0.009**	**0.004**	0.700	0.167	**0.036**	0.114	**0.048**	0.143
H1	**Pre**	HFNV	0.606	**0.026**	**0.000**	**0.000**	0.277	0.147	**0.000**	**0.009**	1.000	**0.002**	**0.009**	**0.000**	0.112	**0.003**	**0.000**	**0.001**
		HFAV	**0.037**	0.553	**0.000**	**0.001**	**0.016**	1.000	**0.000**	**0.004**	**0.002**	1.000	**0.004**	**0.007**	0.442	0.103	**0.000**	**0.000**
		LFAV	**0.036**	**0.024**	0.864	0.282	**0.012**	0.071	0.769	0.700	**0.009**	**0.004**	1.000	0.167	**0.036**	0.114	0.070	0.143
		LFNV	**0.004**	**0.009**	0.066	0.864	**0.001**	0.247	**0.037**	0.167	**0.000**	**0.007**	0.167	1.000	**0.030**	0.762	**0.001**	**0.030**
H1	**Post**	HFNV	0.310	1.000	**0.002**	**0.019**	0.435	0.841	**0.002**	**0.036**	0.112	0.442	**0.036**	**0.030**	1.000	0.190	**0.000**	**0.008**
		HFAV	**0.016**	0.114	**0.034**	0.503	**0.004**	0.413	**0.026**	0.114	**0.003**	0.103	0.114	0.762	0.190	1.000	**0.001**	**0.016**
		LFAV	**0.000**	**0.000**	**0.009**	**0.004**	**0.000**	**0.001**	0.104	**0.048**	**0.000**	**0.000**	0.070	**0.001**	**0.000**	**0.001**	1.000	0.506
		LFNV	**0.008**	**0.004**	0.083	0.060	**0.002**	**0.008**	0.510	0.143	**0.001**	**0.000**	0.143	**0.030**	**0.008**	**0.016**	0.506	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(g) SO_4^{2-}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.247	**0.001**	**0.001**	0.435	1.000	**0.000**	**0.036**	0.060	0.503	**0.036**	**0.004**	**0.016**	0.190	**0.002**	**0.008**
		HFAV	0.247	1.000	**0.000**	0.145	**0.029**	0.662	**0.000**	**0.024**	**0.002**	0.898	0.095	**0.015**	**0.004**	**0.038**	**0.007**	**0.009**
		LFAV	**0.001**	**0.000**	1.000	**0.035**	**0.000**	**0.003**	0.251	0.811	**0.000**	**0.000**	0.692	0.713	**0.001**	**0.002**	0.283	0.859
		LFNV	**0.001**	0.145	**0.035**	1.000	**0.000**	**0.042**	**0.007**	0.100	**0.000**	**0.030**	0.282	0.224	**0.001**	**0.003**	0.247	0.190
R1	**Post**	HFNV	0.435	**0.029**	**0.000**	**0.000**	1.000	0.284	**0.000**	**0.012**	0.606	**0.045**	**0.012**	**0.001**	0.171	0.683	**0.000**	**0.002**
		HFAV	1.000	0.662	**0.003**	**0.042**	0.284	1.000	**0.001**	**0.036**	**0.042**	0.566	0.071	**0.009**	**0.016**	0.286	**0.004**	**0.016**
		LFAV	**0.000**	**0.000**	0.251	**0.007**	**0.000**	**0.001**	1.000	0.659	**0.000**	**0.000**	0.885	0.098	**0.000**	**0.001**	**0.004**	0.145
		LFNV	**0.036**	**0.024**	0.811	0.100	**0.012**	**0.036**	0.659	1.000	**0.009**	**0.007**	0.700	0.548	**0.036**	0.057	0.136	0.393
H1	**Pre**	HFNV	0.060	**0.002**	**0.000**	**0.000**	0.606	**0.042**	**0.000**	**0.009**	1.000	**0.003**	**0.009**	**0.000**	0.606	0.940	**0.000**	**0.001**
		HFAV	0.503	0.898	**0.000**	**0.030**	**0.045**	0.566	**0.000**	**0.007**	**0.003**	1.000	**0.039**	**0.003**	**0.010**	**0.032**	**0.002**	**0.007**
		LFAV	**0.036**	0.095	0.692	0.282	**0.012**	0.071	0.885	0.700	**0.009**	**0.039**	1.000	0.381	**0.036**	0.057	0.295	1.000
		LFNV	**0.004**	**0.015**	0.713	0.224	**0.001**	**0.009**	0.098	0.548	**0.000**	**0.003**	0.381	1.000	**0.004**	**0.010**	0.385	0.931
H1	**Post**	HFNV	**0.016**	**0.004**	**0.001**	**0.001**	0.171	**0.016**	**0.000**	**0.036**	0.606	**0.010**	**0.036**	**0.004**	1.000	0.905	**0.000**	**0.008**
		HFAV	0.190	**0.038**	**0.002**	**0.003**	0.683	0.286	**0.001**	0.057	0.940	**0.032**	0.057	**0.010**	0.905	1.000	**0.001**	**0.016**
		LFAV	**0.002**	**0.007**	0.283	0.247	**0.000**	**0.004**	**0.004**	0.136	**0.000**	**0.002**	0.295	0.385	**0.000**	**0.001**	1.000	0.879
		LFNV	**0.008**	**0.009**	0.859	0.190	**0.002**	**0.016**	0.145	0.393	**0.001**	**0.007**	1.000	0.931	**0.008**	**0.016**	0.879	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(h) DOC

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.329	**0.001**	**0.001**	0.943	0.548	**0.001**	**0.036**	0.060	**0.035**	0.071	**0.017**	0.662	0.286	**0.019**	**0.008**
		HFAV	0.329	1.000	**0.000**	**0.000**	0.573	0.792	**0.000**	**0.024**	0.529	0.521	**0.048**	**0.004**	0.818	0.762	**0.005**	**0.004**
		LFAV	**0.001**	**0.000**	1.000	0.447	**0.000**	**0.001**	0.426	0.573	**0.000**	**0.000**	0.573	0.958	**0.000**	**0.002**	0.456	0.055
		LFNV	**0.001**	**0.000**	0.447	1.000	**0.000**	**0.001**	0.766	0.864	**0.000**	**0.000**	0.282	0.776	**0.000**	**0.003**	0.219	0.060
R1	**Post**	HFNV	0.943	0.573	**0.000**	**0.000**	1.000	0.833	**0.000**	**0.012**	0.093	0.140	**0.024**	**0.005**	0.662	0.570	**0.002**	**0.002**
		HFAV	0.548	0.792	**0.001**	**0.001**	0.833	1.000	**0.000**	**0.036**	0.298	0.117	**0.036**	**0.004**	0.792	0.556	**0.004**	**0.008**
		LFAV	**0.001**	**0.000**	0.426	0.766	**0.000**	**0.000**	1.000	0.885	**0.000**	**0.000**	0.291	0.660	**0.000**	**0.001**	0.151	0.221
		LFNV	**0.036**	**0.024**	0.573	0.864	**0.012**	**0.036**	0.885	1.000	**0.009**	**0.004**	0.200	0.714	**0.024**	0.057	0.136	0.250
H1	**Pre**	HFNV	0.060	0.529	**0.000**	**0.000**	0.093	0.298	**0.000**	**0.009**	1.000	0.744	**0.009**	**0.001**	0.145	0.260	**0.000**	**0.001**
		HFAV	**0.035**	0.521	**0.000**	**0.000**	0.140	0.117	**0.000**	**0.004**	0.744	1.000	**0.004**	**0.000**	0.072	0.245	**0.000**	**0.000**
		LFAV	0.071	**0.048**	0.573	0.282	**0.024**	**0.036**	0.291	0.200	**0.009**	**0.004**	1.000	0.548	**0.024**	0.057	0.633	**0.036**
		LFNV	**0.017**	**0.004**	0.958	0.776	**0.005**	**0.004**	0.660	0.714	**0.001**	**0.000**	0.548	1.000	**0.002**	**0.010**	0.553	0.177
H1	**Post**	HFNV	0.662	0.818	**0.000**	**0.000**	0.662	0.792	**0.000**	**0.024**	0.145	0.072	**0.024**	**0.002**	1.000	0.476	**0.002**	**0.004**
		HFAV	0.286	0.762	**0.002**	**0.003**	0.570	0.556	**0.001**	0.057	0.260	0.245	0.057	**0.010**	0.476	1.000	**0.008**	**0.016**
		LFAV	**0.019**	**0.005**	0.456	0.219	**0.002**	**0.004**	0.151	0.136	**0.000**	**0.000**	0.633	0.553	**0.002**	**0.008**	1.000	**0.002**
		LFNV	**0.008**	**0.004**	0.055	0.060	**0.002**	**0.008**	0.221	0.250	**0.001**	**0.000**	**0.036**	0.177	**0.004**	**0.016**	**0.002**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(i) Fe^{2+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.486	**0.010**	**0.048**	0.570	0.114	**0.002**	0.057	0.927	1.000	0.114	**0.010**	0.730	0.629	**0.008**	**0.016**
		HFAV	0.486	1.000	**0.038**	0.073	0.368	0.229	**0.002**	0.057	0.109	0.527	0.229	**0.019**	0.730	0.857	**0.014**	**0.016**
		LFAV	**0.010**	**0.038**	1.000	1.000	**0.001**	0.262	0.368	0.548	**0.001**	**0.001**	0.095	0.937	**0.004**	**0.024**	0.958	0.329
		LFNV	**0.048**	0.073	1.000	1.000	**0.007**	0.776	0.762	1.000	**0.002**	**0.000**	0.630	0.950	**0.011**	0.085	0.633	0.943
R1	**Post**	HFNV	0.570	0.368	**0.001**	**0.007**	1.000	0.133	**0.000**	**0.012**	0.281	0.955	**0.048**	**0.003**	0.833	0.630	**0.000**	**0.002**
		HFAV	0.114	0.229	0.262	0.776	0.133	1.000	0.077	0.100	**0.033**	**0.017**	1.000	0.167	0.071	0.200	0.161	0.071
		LFAV	**0.002**	**0.002**	0.368	0.762	**0.000**	0.077	1.000	0.937	**0.000**	**0.000**	**0.028**	0.428	**0.001**	**0.007**	0.247	0.768
		LFNV	0.057	0.057	0.548	1.000	**0.012**	0.100	0.937	1.000	**0.017**	**0.017**	0.100	0.548	**0.036**	0.100	0.371	0.786
H1	**Pre**	HFNV	0.927	0.109	**0.001**	**0.002**	0.281	**0.033**	**0.000**	**0.017**	1.000	0.097	**0.033**	**0.001**	0.268	0.117	**0.000**	**0.003**
		HFAV	1.000	0.527	**0.001**	**0.000**	0.955	**0.017**	**0.000**	**0.017**	0.097	1.000	**0.017**	**0.001**	0.530	0.067	**0.000**	**0.003**
		LFAV	0.114	0.229	0.095	0.630	**0.048**	1.000	**0.028**	0.100	**0.033**	**0.017**	1.000	0.167	0.071	0.200	0.217	**0.036**
		LFNV	**0.010**	**0.019**	0.937	0.950	**0.003**	0.167	0.428	0.548	**0.001**	**0.001**	0.167	1.000	**0.004**	**0.024**	0.828	0.429
H1	**Post**	HFNV	0.730	0.730	**0.004**	**0.011**	0.833	0.071	**0.001**	**0.036**	0.268	0.530	0.071	**0.004**	1.000	0.250	**0.001**	**0.008**
		HFAV	0.629	0.857	**0.024**	0.085	0.630	0.200	**0.007**	0.100	0.117	0.067	0.200	**0.024**	0.250	1.000	**0.028**	**0.036**
		LFAV	**0.008**	**0.014**	0.958	0.633	**0.000**	0.161	0.247	0.371	**0.000**	**0.000**	0.217	0.828	**0.001**	**0.028**	1.000	0.254
		LFNV	**0.016**	**0.016**	0.329	0.943	**0.002**	0.071	0.768	0.786	**0.003**	**0.003**	**0.036**	0.429	**0.008**	**0.036**	0.254	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(j) Si^{4+}

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.257	0.343	**0.020**	0.570	0.413	**0.018**	0.057	0.214	0.330	0.800	0.114	0.610	0.886	0.058	**0.016**
		HFAV	0.257	1.000	**0.010**	**0.000**	0.852	0.931	**0.000**	**0.024**	0.573	0.776	0.286	**0.009**	0.818	0.476	**0.000**	**0.004**
		LFAV	0.343	**0.010**	1.000	0.199	**0.004**	**0.016**	0.226	0.629	**0.004**	**0.003**	1.000	0.762	**0.010**	**0.029**	1.000	0.111
		LFNV	**0.020**	**0.000**	0.199	1.000	**0.000**	**0.001**	0.882	0.864	**0.000**	**0.000**	0.600	0.456	**0.000**	**0.003**	0.169	0.147
R1	**Post**	HFNV	0.570	0.852	**0.004**	**0.000**	1.000	0.833	**0.000**	**0.012**	0.195	0.277	0.222	**0.008**	0.573	0.683	**0.000**	**0.002**
		HFAV	0.413	0.931	**0.016**	**0.001**	0.833	1.000	**0.000**	**0.036**	0.524	0.699	0.333	**0.017**	0.931	0.730	**0.000**	**0.008**
		LFAV	**0.018**	**0.000**	0.226	0.882	**0.000**	**0.000**	1.000	1.000	**0.000**	**0.000**	0.500	0.462	**0.000**	**0.001**	0.288	0.115
		LFNV	0.057	**0.024**	0.629	0.864	**0.012**	**0.036**	1.000	1.000	**0.012**	**0.009**	0.500	0.548	**0.024**	0.057	0.633	**0.036**
H1	**Pre**	HFNV	0.214	0.573	**0.004**	**0.000**	0.195	0.524	**0.000**	**0.012**	1.000	0.743	0.222	**0.001**	0.282	0.214	**0.000**	**0.002**
		HFAV	0.330	0.776	**0.003**	**0.000**	0.277	0.699	**0.000**	**0.009**	0.743	1.000	0.200	**0.001**	0.456	0.414	**0.000**	**0.001**
		LFAV	0.800	0.286	1.000	0.600	0.222	0.333	0.500	0.500	0.222	0.200		1.000	0.286	0.400	0.769	0.333
		LFNV	0.114	**0.009**	0.762	0.456	**0.008**	**0.017**	0.462	0.548	**0.001**	**0.001**	1.000	1.000	**0.004**	**0.019**	0.892	0.247
H1	**Post**	HFNV	0.610	0.818	**0.010**	**0.000**	0.573	0.931	**0.000**	**0.024**	0.282	0.456	0.286	**0.004**	1.000	0.914	**0.000**	**0.004**
		HFAV	0.886	0.476	**0.029**	**0.003**	0.683	0.730	**0.001**	0.057	0.214	0.414	0.400	**0.019**	0.914	1.000	**0.002**	**0.016**
		LFAV	0.058	**0.000**	1.000	0.169	**0.000**	**0.000**	0.288	0.633	**0.000**	**0.000**	0.769	0.892	**0.000**	**0.002**	1.000	**0.002**
		LFNV	**0.016**	**0.004**	0.111	0.147	**0.002**	**0.008**	0.115	**0.036**	**0.002**	**0.001**	0.333	0.247	**0.004**	**0.016**	**0.002**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(k) TN

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.421	**0.003**	**0.001**	1.000	1.000	**0.001**	**0.036**	0.127	0.104	**0.036**	**0.008**	0.841	0.905	**0.002**	**0.008**
		HFAV	0.421	1.000	**0.003**	**0.001**	0.435	0.730	**0.001**	**0.036**	0.833	0.799	0.071	**0.008**	0.421	0.413	**0.002**	**0.008**
		LFAV	**0.003**	**0.003**	1.000	0.720	**0.000**	**0.002**	0.393	0.287	**0.000**	**0.000**	0.811	0.768	**0.001**	**0.002**	0.705	**0.028**
		LFNV	**0.001**	**0.001**	0.720	1.000	**0.000**	**0.003**	0.497	0.282	**0.000**	**0.000**	0.600	0.898	**0.001**	**0.003**	0.412	0.060
R1	**Post**	HFNV	1.000	0.435	**0.000**	**0.000**	1.000	0.683	**0.000**	**0.012**	0.083	0.069	**0.012**	**0.002**	0.524	0.933	**0.001**	**0.002**
		HFAV	1.000	0.730	**0.002**	**0.003**	0.683	1.000	**0.002**	0.057	0.283	0.170	0.057	**0.016**	0.905	1.000	**0.003**	**0.016**
		LFAV	**0.001**	**0.001**	0.393	0.497	**0.000**	**0.002**	1.000	0.469	**0.000**	**0.000**	0.371	0.768	**0.001**	**0.002**	0.152	**0.040**
		LFNV	**0.036**	**0.036**	0.287	0.282	**0.012**	0.057	0.469	1.000	**0.012**	**0.004**	0.200	0.393	**0.036**	0.057	0.088	0.250
H1	**Pre**	HFNV	0.127	0.833	**0.000**	**0.000**	0.083	0.283	**0.000**	**0.012**	1.000	0.910	**0.012**	**0.002**	0.171	0.214	**0.000**	**0.002**
		HFAV	0.104	0.799	**0.000**	**0.000**	0.069	0.170	**0.000**	**0.004**	0.910	1.000	**0.004**	**0.000**	0.064	0.058	**0.000**	**0.000**
		LFAV	**0.036**	0.071	0.811	0.600	**0.012**	0.057	0.371	0.200	**0.012**	**0.004**	1.000	0.571	**0.036**	0.057	1.000	**0.036**
		LFNV	**0.008**	**0.008**	0.768	0.898	**0.002**	**0.016**	0.768	0.393	**0.002**	**0.000**	0.571	1.000	**0.008**	**0.016**	0.377	0.056
H1	**Post**	HFNV	0.841	0.421	**0.001**	**0.001**	0.524	0.905	**0.001**	**0.036**	0.171	0.064	**0.036**	**0.008**	1.000	0.905	**0.000**	**0.008**
		HFAV	0.905	0.413	**0.002**	**0.003**	0.933	1.000	**0.002**	0.057	0.214	0.058	0.057	**0.016**	0.905	1.000	**0.001**	**0.016**
		LFAV	**0.002**	**0.002**	0.705	0.412	**0.001**	**0.003**	0.152	0.088	**0.000**	**0.000**	1.000	0.377	**0.000**	**0.001**	1.000	**0.001**
		LFNV	**0.008**	**0.008**	**0.028**	0.060	**0.002**	**0.016**	**0.040**	0.250	**0.002**	**0.000**	**0.036**	0.056	**0.008**	**0.016**	**0.001**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(l) TDN

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.329	**0.005**	**0.001**	1.000	1.000	**0.000**	**0.036**	0.112	**0.046**	**0.036**	**0.008**	0.931	0.905	**0.001**	**0.008**
		HFAV	0.329	1.000	**0.002**	**0.000**	0.414	0.792	**0.000**	**0.024**	0.529	0.701	**0.024**	**0.004**	0.699	0.610	**0.000**	**0.004**
		LFAV	**0.005**	**0.002**	1.000	0.661	**0.001**	**0.003**	0.223	0.287	**0.000**	**0.000**	0.811	0.768	**0.000**	**0.002**	0.923	**0.019**
		LFNV	**0.001**	**0.000**	0.661	1.000	**0.000**	**0.001**	0.261	0.373	**0.000**	**0.000**	1.000	0.898	**0.000**	**0.003**	0.602	0.060
R1	**Post**	HFNV	1.000	0.414	**0.001**	**0.000**	1.000	0.724	**0.000**	**0.012**	0.059	0.089	**0.012**	**0.002**	0.755	0.683	**0.000**	**0.002**
		HFAV	1.000	0.792	**0.003**	**0.001**	0.724	1.000	**0.000**	**0.036**	0.147	0.059	**0.036**	**0.008**	0.662	0.556	**0.000**	**0.008**
		LFAV	**0.000**	**0.000**	0.223	0.261	**0.000**	**0.000**	1.000	0.885	**0.000**	**0.000**	0.555	0.441	**0.000**	**0.001**	0.118	0.180
		LFNV	**0.036**	**0.024**	0.287	0.373	**0.012**	**0.036**	0.885	1.000	**0.009**	**0.004**	0.700	0.571	**0.024**	0.057	0.136	0.393
H1	**Pre**	HFNV	0.112	0.529	**0.000**	**0.000**	0.059	0.147	**0.000**	**0.009**	1.000	0.556	**0.009**	**0.001**	**0.050**	0.148	**0.000**	**0.001**
		HFAV	**0.046**	0.701	**0.000**	**0.000**	0.089	0.059	**0.000**	**0.004**	0.556	1.000	**0.004**	**0.000**	**0.017**	**0.045**	**0.000**	**0.000**
		LFAV	**0.036**	**0.024**	0.811	1.000	**0.012**	**0.036**	0.555	0.700	**0.009**	**0.004**	1.000	1.000	**0.024**	0.057	0.840	**0.036**
		LFNV	**0.008**	**0.004**	0.768	0.898	**0.002**	**0.008**	0.441	0.571	**0.001**	**0.000**	1.000	1.000	**0.004**	**0.016**	0.721	0.095
H1	**Post**	HFNV	0.931	0.699	**0.000**	**0.000**	0.755	0.662	**0.000**	**0.024**	**0.050**	**0.017**	**0.024**	**0.004**	1.000	0.914	**0.000**	**0.004**
		HFAV	0.905	0.610	**0.002**	**0.003**	0.683	0.556	**0.001**	0.057	0.148	**0.045**	0.057	**0.016**	0.914	1.000	**0.001**	**0.016**
		LFAV	**0.001**	**0.000**	0.923	0.602	**0.000**	**0.000**	0.118	0.136	**0.000**	**0.000**	0.840	0.721	**0.000**	**0.001**	1.000	**0.001**
		LFNV	**0.008**	**0.004**	**0.019**	0.060	**0.002**	**0.008**	0.180	0.393	**0.001**	**0.000**	**0.036**	0.095	**0.004**	**0.016**	**0.001**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(m) NH_4^+

			R1								H1							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.662	**0.013**	0.060	0.354	0.841	**0.000**	**0.036**	0.518	0.336	0.071	0.931	0.126	0.730	**0.001**	0.056
		HFAV	0.662	1.000	**0.011**	**0.018**	0.142	0.662	**0.000**	**0.024**	0.328	0.467	0.095	0.589	**0.026**	0.914	**0.003**	**0.017**
		LFAV	**0.013**	**0.011**	1.000	0.780	**0.001**	**0.028**	0.085	0.469	**0.002**	**0.000**	0.469	**0.022**	**0.000**	**0.008**	0.821	0.953
		LFNV	0.060	**0.018**	0.780	1.000	**0.002**	0.112	0.067	0.600	**0.004**	**0.001**	0.864	0.145	**0.000**	0.050	0.917	1.000
R1	**Post**	HFNV	0.354	0.142	**0.001**	**0.002**	1.000	0.222	**0.000**	**0.012**	0.606	0.301	**0.048**	0.142	0.662	0.154	**0.000**	**0.006**
		HFAV	0.841	0.662	**0.028**	0.112	0.222	1.000	**0.001**	**0.036**	0.190	0.336	0.143	0.792	0.126	0.730	**0.004**	0.056
		LFAV	**0.000**	**0.000**	0.085	0.067	**0.000**	**0.001**	1.000	0.368	**0.000**	**0.000**	**0.038**	**0.003**	**0.000**	**0.001**	**0.001**	**0.019**
		LFNV	**0.036**	**0.024**	0.469	0.600	**0.012**	**0.036**	0.368	1.000	**0.009**	**0.004**	0.200	0.167	**0.024**	0.057	**0.018**	0.071
H1	**Pre**	HFNV	0.518	0.328	**0.002**	**0.004**	0.606	0.190	**0.000**	**0.009**	1.000	0.357	0.064	0.113	0.864	0.260	**0.001**	**0.007**
		HFAV	0.336	0.467	**0.000**	**0.001**	0.301	0.336	**0.000**	**0.004**	0.357	1.000	**0.014**	0.210	**0.036**	0.477	**0.000**	**0.003**
		LFAV	0.071	0.095	0.469	0.864	**0.048**	0.143	**0.038**	0.200	0.064	**0.014**	1.000	0.167	**0.024**	0.057	0.536	0.786
		LFNV	0.931	0.589	**0.022**	0.145	0.142	0.792	**0.003**	0.167	0.113	0.210	0.167	1.000	**0.015**	0.762	**0.032**	0.177
H1	**Post**	HFNV	0.126	**0.026**	**0.000**	**0.000**	0.662	0.126	**0.000**	**0.024**	0.864	**0.036**	**0.024**	**0.015**	1.000	**0.010**	**0.000**	**0.004**
		HFAV	0.730	0.914	**0.008**	0.050	0.154	0.730	**0.001**	0.057	0.260	0.477	0.057	0.762	**0.010**	1.000	**0.002**	**0.032**
		LFAV	**0.001**	**0.003**	0.821	0.917	**0.000**	**0.004**	**0.001**	**0.018**	**0.001**	**0.000**	0.536	**0.032**	**0.000**	**0.002**	1.000	0.646
		LFNV	0.056	**0.017**	0.953	1.000	**0.006**	0.056	**0.019**	0.071	**0.007**	**0.003**	0.786	0.177	**0.004**	**0.032**	0.646	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(n) NO_2^-+NO_3^-

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	1.000	**0.003**	0.112	0.833	0.548	**0.000**	**0.036**	0.518	0.443	**0.036**	0.177	0.537	0.413	**0.000**	**0.032**
		HFAV	1.000	1.000	**0.007**	0.181	0.852	0.792	**0.000**	**0.024**	0.181	0.467	**0.048**	0.180	0.310	0.352	**0.000**	**0.017**
		LFAV	**0.003**	**0.007**	1.000	0.095	**0.002**	**0.008**	0.051	0.692	**0.000**	**0.000**	0.469	**0.042**	**0.001**	**0.024**	0.254	0.513
		LFNV	0.112	0.181	0.095	1.000	0.093	0.298	**0.002**	0.100	**0.011**	0.144	0.482	0.864	**0.018**	0.503	**0.012**	0.060
R1	**Post**	HFNV	0.833	0.852	**0.002**	0.093	1.000	0.622	**0.000**	**0.012**	0.481	0.456	**0.024**	0.228	0.662	0.683	**0.000**	**0.011**
		HFAV	0.548	0.792	**0.008**	0.298	0.622	1.000	**0.000**	**0.036**	0.112	0.849	0.071	0.537	0.082	1.000	**0.001**	0.056
		LFAV	**0.000**	**0.000**	0.051	**0.002**	**0.000**	**0.000**	1.000	0.456	**0.000**	**0.000**	**0.022**	**0.000**	**0.000**	**0.001**	0.196	0.441
		LFNV	**0.036**	**0.024**	0.692	0.100	**0.012**	**0.036**	0.456	1.000	**0.009**	**0.004**	0.200	**0.048**	**0.024**	0.057	1.000	0.786
H1	**Pre**	HFNV	0.518	0.181	**0.000**	**0.011**	0.481	0.112	**0.000**	**0.009**	1.000	**0.036**	**0.009**	**0.018**	0.776	0.076	**0.000**	**0.004**
		HFAV	0.443	0.467	**0.000**	0.144	0.456	0.849	**0.000**	**0.004**	**0.036**	1.000	**0.007**	0.106	0.087	0.549	**0.000**	**0.004**
		LFAV	**0.036**	**0.048**	0.469	0.482	**0.024**	0.071	**0.022**	0.200	**0.009**	**0.007**	1.000	0.167	**0.024**	0.057	0.136	0.250
		LFNV	0.177	0.180	**0.042**	0.864	0.228	0.537	**0.000**	**0.048**	**0.018**	0.106	0.167	1.000	0.065	0.476	**0.001**	**0.030**
H1	**Post**	HFNV	0.537	0.310	**0.001**	**0.018**	0.662	0.082	**0.000**	**0.024**	0.776	0.087	**0.024**	0.065	1.000	0.257	**0.000**	**0.017**
		HFAV	0.413	0.352	**0.024**	0.503	0.683	1.000	**0.001**	0.057	0.076	0.549	0.057	0.476	0.257	1.000	**0.001**	0.063
		LFAV	**0.000**	**0.000**	0.254	**0.012**	**0.000**	**0.001**	0.196	1.000	**0.000**	**0.000**	0.136	**0.001**	**0.000**	**0.001**	1.000	0.959
		LFNV	**0.032**	**0.017**	0.513	0.060	**0.011**	0.056	0.441	0.786	**0.004**	**0.004**	0.250	**0.030**	**0.017**	0.063	0.959	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(o) TP

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.537	**0.001**	**0.002**	0.354	0.556	**0.003**	**0.036**	1.000	0.775	**0.036**	**0.009**	0.537	0.286	**0.000**	**0.008**
		HFAV	0.537	1.000	**0.001**	**0.003**	0.755	0.610	**0.002**	**0.024**	0.573	0.966	**0.024**	**0.009**	0.394	0.352	**0.000**	**0.004**
		LFAV	**0.001**	**0.001**	1.000	0.780	**0.001**	**0.036**	0.315	0.217	**0.000**	**0.000**	0.692	0.958	**0.000**	**0.004**	0.349	0.129
		LFNV	**0.002**	**0.003**	0.780	1.000	**0.004**	**0.020**	0.780	0.482	**0.001**	**0.000**	0.864	0.607	**0.001**	**0.006**	0.882	0.438
R1	**Post**	HFNV	0.354	0.755	**0.001**	**0.004**	1.000	0.933	**0.001**	**0.012**	0.442	0.414	**0.012**	**0.013**	0.950	0.933	**0.000**	**0.002**
		HFAV	0.556	0.610	**0.036**	**0.020**	0.933	1.000	**0.036**	0.057	0.283	0.245	0.114	**0.038**	0.476	0.686	**0.006**	**0.016**
		LFAV	**0.003**	**0.002**	0.315	0.780	**0.001**	**0.036**	1.000	0.469	**0.000**	**0.000**	0.469	0.313	**0.005**	**0.024**	0.557	0.594
		LFNV	**0.036**	**0.024**	0.217	0.482	**0.012**	0.057	0.469	1.000	**0.012**	**0.004**	0.100	**0.048**	**0.024**	0.057	0.088	0.786
H1	**Pre**	HFNV	1.000	0.573	**0.000**	**0.001**	0.442	0.283	**0.000**	**0.012**	1.000	0.645	**0.012**	**0.003**	0.142	0.109	**0.000**	**0.002**
		HFAV	0.775	0.966	**0.000**	**0.000**	0.414	0.245	**0.000**	**0.004**	0.645	1.000	**0.004**	**0.000**	0.210	**0.023**	**0.000**	**0.000**
		LFAV	**0.036**	**0.024**	0.692	0.864	**0.012**	0.114	0.469	0.100	**0.012**	**0.004**	1.000	0.905	**0.024**	0.057	0.456	0.071
		LFNV	**0.009**	**0.009**	0.958	0.607	**0.013**	**0.038**	0.313	**0.048**	**0.003**	**0.000**	0.905	1.000	**0.004**	**0.019**	0.350	0.082
H1	**Post**	HFNV	0.537	0.394	**0.000**	**0.001**	0.950	0.476	**0.005**	**0.024**	0.142	0.210	**0.024**	**0.004**	1.000	0.114	**0.000**	**0.004**
		HFAV	0.286	0.352	**0.004**	**0.006**	0.933	0.686	**0.024**	0.057	0.109	**0.023**	0.057	**0.019**	0.114	1.000	**0.001**	**0.016**
		LFAV	**0.000**	**0.000**	0.349	0.882	**0.000**	**0.006**	0.557	0.088	**0.000**	**0.000**	0.456	0.350	**0.000**	**0.001**	1.000	0.069
		LFNV	**0.008**	**0.004**	0.129	0.438	**0.002**	**0.016**	0.594	0.786	**0.002**	**0.000**	0.071	0.082	**0.004**	**0.016**	0.069	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(p) TDP

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	1.000	**0.003**	**0.002**	0.354	0.841	**0.000**	**0.036**	0.898	1.000	**0.036**	**0.004**	0.429	0.190	**0.000**	**0.008**
		HFAV	1.000	1.000	**0.001**	**0.003**	0.414	0.662	**0.000**	**0.024**	0.529	0.966	**0.024**	**0.002**	0.818	0.257	**0.000**	**0.004**
		LFAV	**0.003**	**0.001**	1.000	0.549	**0.004**	**0.028**	**0.006**	0.161	**0.000**	**0.000**	0.692	0.056	**0.001**	**0.008**	0.159	**0.040**
		LFNV	**0.002**	**0.003**	0.549	1.000	**0.004**	**0.019**	0.080	0.373	**0.000**	**0.000**	1.000	0.388	**0.001**	**0.011**	0.464	0.060
R1	**Post**	HFNV	0.354	0.414	**0.004**	**0.004**	1.000	0.943	**0.000**	**0.012**	0.236	0.336	**0.024**	**0.001**	0.852	0.570	**0.000**	**0.002**
		HFAV	0.841	0.662	**0.028**	**0.019**	0.943	1.000	**0.000**	**0.036**	0.438	0.566	0.143	**0.009**	0.931	0.413	**0.001**	**0.008**
		LFAV	**0.000**	**0.000**	**0.006**	0.080	**0.000**	**0.000**	1.000	1.000	**0.000**	**0.000**	0.060	0.525	**0.000**	**0.001**	0.134	0.267
		LFNV	**0.036**	**0.024**	0.161	0.373	**0.012**	**0.036**	1.000	1.000	**0.009**	**0.004**	0.100	0.548	**0.024**	0.057	0.136	0.393
H1	**Pre**	HFNV	0.898	0.529	**0.000**	**0.000**	0.236	0.438	**0.000**	**0.009**	1.000	0.292	**0.009**	**0.000**	0.113	0.050	**0.000**	**0.001**
		HFAV	1.000	0.966	**0.000**	**0.000**	0.336	0.566	**0.000**	**0.004**	0.292	1.000	**0.004**	**0.000**	0.639	**0.032**	**0.000**	**0.000**
		LFAV	**0.036**	**0.024**	0.692	1.000	**0.024**	0.143	0.060	0.100	**0.009**	**0.004**	1.000	0.167	**0.024**	0.057	0.233	**0.036**
		LFNV	**0.004**	**0.002**	0.056	0.388	**0.001**	**0.009**	0.525	0.548	**0.000**	**0.000**	0.167	1.000	**0.002**	**0.010**	0.437	0.052
H1	**Post**	HFNV	0.429	0.818	**0.001**	**0.001**	0.852	0.931	**0.000**	**0.024**	0.113	0.639	**0.024**	**0.002**	1.000	0.171	**0.000**	**0.004**
		HFAV	0.190	0.257	**0.008**	**0.011**	0.570	0.413	**0.001**	0.057	0.050	**0.032**	0.057	**0.010**	0.171	1.000	**0.001**	**0.016**
		LFAV	**0.000**	**0.000**	0.159	0.464	**0.000**	**0.001**	0.134	0.136	**0.000**	**0.000**	0.233	0.437	**0.000**	**0.001**	1.000	**0.019**
		LFNV	**0.008**	**0.004**	**0.040**	0.060	**0.002**	**0.008**	0.267	0.393	**0.001**	**0.000**	**0.036**	0.052	**0.004**	**0.016**	**0.019**	1.000

Table A.2: Mann-Witney U-test of ion export (continued).

(q) SRP

			R1								**H1**							
			Pre-harvest				**Post-harvest**				**Pre-harvest**				**Post-harvest**			
			HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV	HFNV	HFAV	LFAV	LFNV
R1	**Pre**	HFNV	1.000	0.662	**0.003**	**0.002**	0.171	0.310	**0.000**	**0.036**	1.000	0.503	**0.036**	**0.004**	**0.030**	**0.016**	**0.000**	**0.008**
		HFAV	0.662	1.000	**0.016**	**0.008**	0.345	0.792	**0.000**	**0.024**	0.689	0.966	**0.024**	**0.002**	0.093	0.067	**0.000**	**0.004**
		LFAV	**0.003**	**0.016**	1.000	0.400	0.055	0.099	**0.002**	0.077	**0.001**	**0.002**	0.573	0.073	0.220	0.945	**0.007**	**0.008**
		LFNV	**0.002**	**0.008**	0.400	1.000	**0.011**	**0.042**	**0.038**	0.209	**0.001**	**0.000**	1.000	0.328	0.088	0.260	0.082	0.083
R1	**Post**	HFNV	0.171	0.345	0.055	**0.011**	1.000	0.943	**0.000**	**0.012**	0.236	0.414	**0.012**	**0.001**	0.228	0.283	**0.000**	**0.002**
		HFAV	0.310	0.792	0.099	**0.042**	0.943	1.000	**0.001**	**0.036**	0.298	0.775	0.250	**0.030**	0.329	0.190	**0.001**	**0.016**
		LFAV	**0.000**	**0.000**	**0.002**	**0.038**	**0.000**	**0.001**	1.000	0.885	**0.000**	**0.000**	**0.011**	0.149	**0.000**	**0.003**	0.316	0.743
		LFNV	**0.036**	**0.024**	0.077	0.209	**0.012**	**0.036**	0.885	1.000	**0.009**	**0.004**	0.100	0.167	**0.024**	0.057	0.945	0.393
H1	**Pre**	HFNV	1.000	0.689	**0.001**	**0.001**	0.236	0.298	**0.000**	**0.009**	1.000	0.393	**0.009**	**0.000**	**0.026**	**0.020**	**0.000**	**0.001**
		HFAV	0.503	0.966	**0.002**	**0.000**	0.414	0.775	**0.000**	**0.004**	0.393	1.000	**0.004**	**0.000**	**0.029**	**0.023**	**0.000**	**0.000**
		LFAV	**0.036**	**0.024**	0.573	1.000	**0.012**	0.250	**0.011**	0.100	**0.009**	**0.004**	1.000	0.095	**0.024**	0.229	**0.009**	**0.036**
		LFNV	**0.004**	**0.002**	0.073	0.328	**0.001**	**0.030**	0.149	0.167	**0.000**	**0.000**	0.095	1.000	**0.002**	**0.010**	0.213	0.177
H1	**Post**	HFNV	**0.030**	0.093	0.220	0.088	0.228	0.329	**0.000**	**0.024**	**0.026**	**0.029**	**0.024**	**0.002**	1.000	0.257	**0.000**	**0.004**
		HFAV	**0.016**	0.067	0.945	0.260	0.283	0.190	**0.003**	0.057	**0.020**	**0.023**	0.229	**0.010**	0.257	1.000	**0.002**	**0.016**
		LFAV	**0.000**	**0.000**	**0.007**	0.082	**0.000**	**0.001**	0.316	0.945	**0.000**	**0.000**	**0.009**	0.213	**0.000**	**0.002**	1.000	0.130
		LFNV	**0.008**	**0.004**	**0.008**	0.083	**0.002**	**0.016**	0.743	0.393	**0.001**	**0.000**	**0.036**	0.177	**0.004**	**0.016**	0.130	1.000