

FOREST DISTURBANCE IMPACT ON FLOW PATTERNS AND ANION  
EXPORTS BY STREAMWATER FOR A BC COASTAL DOUGLAS-FIR  
HEADWATER CATCHMENT

by

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## **Abstract**

The effect of disturbances in a forest, including logging and road construction, alters many hydrological processes in a forested watershed, changing overall hydrologic flowpaths and nutrient cycling. Changes in hydrologic pathways and anion export within a forested watershed near Campbell River, British Columbia were studied, with streamwater samples collected since 2007 and analysed via ion chromatography. Using segmented regression analysis (SRA), this study examines the concentration-discharge relationship between stream nutrient export and streamflow at the base of the catchment over a 4-year period that includes road construction and a harvest event that took place in early 2011. Observations include much greater discharge post-disturbance, previous patterns in chloride ( $\text{Cl}^-$ ) and sulphate ( $\text{SO}_4^{2-}$ ) could not be discerned after disturbance, and nitrate ( $\text{NO}_3^-$ ) export were influenced by fertilization prior to disturbance but showed extremely low concentrations in the short period after logging. Changes in climate and precipitation patterns could explain several of the findings, while the short study period led to many uncertainties and difficulties in interpreting long-term trends and effects.

The analyses conducted in this study, examining the anion flux in the stream water as compared to discharge, is a means of understanding the post-disturbance hydrology, assessing and corresponding changes in water quality.

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## INTRODUCTION

The forest ecosystem plays a crucial role in many biogeochemistry processes, including the carbon cycle and hydrological cycle. Over 62 million hectares of diverse forests in British Columbia, Canada, provide a multitude of social, cultural, economic and biological values and services (Black et al., 2008). In British Columbia, 80% of the municipal water is drawn from surface water sources such as forested watersheds (Pike et al., 2010). Due to the importance of forests being source areas of drinking water, there is great concern in management activities that can potentially affect water quality. While water quality in British Columbia is generally high, factors such as bedrock geology, overlying vegetation, hydrology, internal cycling processes, natural and anthropogenic disturbances can lead to spatial and temporal variation in chemical composition of water and changes in water quality (Pike et al., 2005). Feller and Kimmins (1979) summarized that in early studies, once roads are built and the protective influence of the forest is removed, levels of streamflow, stream sediment load, and dissolved chemicals may increase.

The climate on the Pacific Northwest is characterized by mild winters with high precipitations and moderately warm summers which provide favourable environments for forest growth (Morgenstern et al., 2004). Streams in forested areas of southwestern British Columbia are characterized by high discharges from October or November until April due to winter storms and high frequency precipitation events (Feller and Kimmins, 1979). Undisturbed forest soils in the Pacific Northwest generally have sufficiently high infiltration capabilities to absorb most precipitation events and thus the runoff in these forest catchments tends to be dominated by subsurface flow (Winkler et al., 2009). However, these hydrological processes will be impacted by forest harvesting and the construction of roads, through decreased interception and evaporation, alteration of soil properties that controls the flow of water (Winkler et al., 2009).

The presence of a forest also modifies the chemistry of incoming precipitation due to vegetation and soil interactions (Pike et al., 2009). In forest ecosystems, uptake and retention of available forms of nutrients and carbon by biota can retard the chemical or

nutrient movements to surface waters while natural disturbances and management activities that disrupt or remove vegetations in a forest or alter stream flow path could change dissolved chemical particulate concentration and fluxes in water bodies (Pike et al., 2009). Small streams draining forested area in the Northwest Pacific usually have low concentrations of dissolved nutrients (Feller and Kimmins, 1979), but seasonal variations and internal nutrient cycling of the ecosystem may bring about spikes. At present there is insufficient literature available on watershed responses following a disturbance, such as road construction and harvesting, which leads to concerns and debates on environmental costs and land management practices.

Past studies all across North America had investigated the export of chemical nutrients by streamwater, and yield widely different results based on location and vegetation type. Chloride is biologically inactive and has low reactivity in soils (Binkley et al., 1982), leading scientists to propose the most likely source for chloride is from precipitation, and therefore having pronounced seasonal variation in regions where a wet season is found (Vitousek et al., 1982). Sulphate on the other hand, when deposited can be adsorbed and retained in the forest system, then later leached during storms to cause episodic increases (Huntington et al. 1994). Feller and Kimmins (1979) found that chloride and sulphate concentrations were not significantly related to discharge and hypothesized the concentration would likely increase on occasions when prevailing winds come directly from the sea or from industrial air pollution sources. Forested areas on Vancouver Island are likely to be influenced by the ocean; with seawater containing large amounts of chloride ( $\text{Cl}^-$ ) and sulphate ( $\text{SO}_4^{2-}$ ), processes such as sea spray or rainout are able to transport these ions into the nearby forests. In a previous study, concentrations of chloride and sulphate were observed to decrease with increasing distance from the coast (Wigington et al., 1998).

It is expected that along with disturbances, the internal nutrient cycling processes will be disrupted. Many studies on nutrient cycling and loss have given emphasis on nitrogen due to it being most often the limiting nutrient for forest growth, and excessive loss would impede forest re-growth after disturbance (Vitousek et al., 1982). Losses of nitrogen, especially in the form of nitrate, often increase more than the losses of many other nutrient elements following disturbance (Likens et al., 1970; Vitousek et al., 1979).

Furthermore, increased nitrification can influence directly or indirectly rates of nitrous oxide production and volatilization (Vitousek et al., 1982). A large amount of nitrogen is circulated annually throughout the undisturbed forests, with uptake of nitrogen equalling or slightly exceeding net nitrogen mineralization and much greater than losses (Vitousek et al., 1982). As a destructive event unfolds, the ability of the forest canopy to take up nitrate from precipitation is decreased (Binkley et al., 1982), also the forest's capacity and vegetation's ability to retain or absorb mineralized nitrogen is reduced, and much of the excess mineralized nitrogen may be lost (Vitousek et al., 1982). Within the streams, these anions may be absorbed to surfaces on the streambed, utilized and released by aquatic vegetation, or undergo chemical transformation from one form to another (Feller and Kimmins, 1979). For areas with snow accumulation, nitrate can be stored in the winter snowpack and gets concentrated by evaporation, which leads to high nitrate concentrations in the spring along with snowmelt and runoff (Feller and Kimmins, 1979, Likens et al., 1970). Although the basic processes of the nitrogen cycle is well understood, there is still uncertainty in the magnitudes and rates of nitrogen cycling at the watershed and river basin scale (Schlesinger et al., 2006).

In many forest practices, fertilizers are used to promote biomass growth, increase harvest volume, and reduce rotation length. In British Columbia, the Douglas fir stands on the west coast have been found to be N-limited due to having little N deposition from the remote location away from pollution sources (Jassal et al., 2008), and the soils become N deficient, therefore majority of fertilizers applied in this region uses N to improve growth (Pike and Perrin, 2005). Application of fertilizer not only encourages C sequestering but the boost in volume growth can provide some attractive financial returns (Jassal et al., 2008). However, through internal nutrient cycling processes, a fraction of these nutrients will end up in waterways and affect water quality. Nutrient pollution can exert a noticeable effect on the environment, particularly with N concentrations and exports as they relate to source water quality issues (Johnson et al., 2007). When vegetation is removed, soil temperature and moisture contents are generally higher, and nitrification may be rapid that the uptake by regrowing vegetation and immobilization by soil microbes are insufficient to prevent large losses of nitrate ( $\text{NO}_3^-$ ) in streamwater following disturbance (Vitousek et al., 1982). As nutrients are leached out and carried



downstream ecological problems such as eutrophication and hypoxia may arise (Vitousek et al., 2009). These chemicals in water will influence water and eventually air quality. A study in Coyote Creek in Southwestern Oregon found peak in nitrate-N concentrations three days after fertilization and another peak that developed several months later with the onset of autumn wet season (Binkley and Brown, 1993). Nitrate leaching as a result of forest disturbance rarely reaches levels limited by drinking water standards (Pike et al., 2009), however knock-on effects to the downstream ecosystem are possible at levels below drinking water standards. The fertilization process also presents an added incentive to monitor and explore the temporal changes of nitrate after fertilization from seasonal to annual scale.

As mentioned by Feller et al. (2005), in order to determine the effect of a perturbation on stream water chemistry, sampling should be done prior as well as after the perturbation in order to allow a more conclusive assessment of the effects of a disturbance on stream water chemistry. The objective for this study was to investigate the effects of forest disturbance on anion flux concentrations in association with stream discharge through comparing watershed response in its pre-harvest state with data from the period of disturbance and onwards. The results will shed light on the alteration of flow paths and changes in chemical export due to a disturbance, as well as assessing any changes in water quality via the trends in anions. The study hopes to contribute to further understanding of forest harvesting effects and is of use for forest life-cycle analysis. It is expected the flow patterns and trends in anion concentration would be impacted by the disturbance and show discerning patterns.

## METHODS

### Study Site Description

The study site is located on the Eastern side of Vancouver Island, British Columbia (49°51'N and 125°20'W), in the southwest region of Campbell River. The site

is about 100ha and is a forested watershed basin. Instruments such as an eddy covariance tower and remote sensors were set up back in 1997 by Andy Black from UBC for research purposes. This area is in a very dry maritime subzone of the coastal western hemlock biogeoclimatic zone. Disturbances such as fires, harvesting and replanting over the years left a patchwork of stands with different stand age and only small patches of old-growth (Chen et al., 2009).

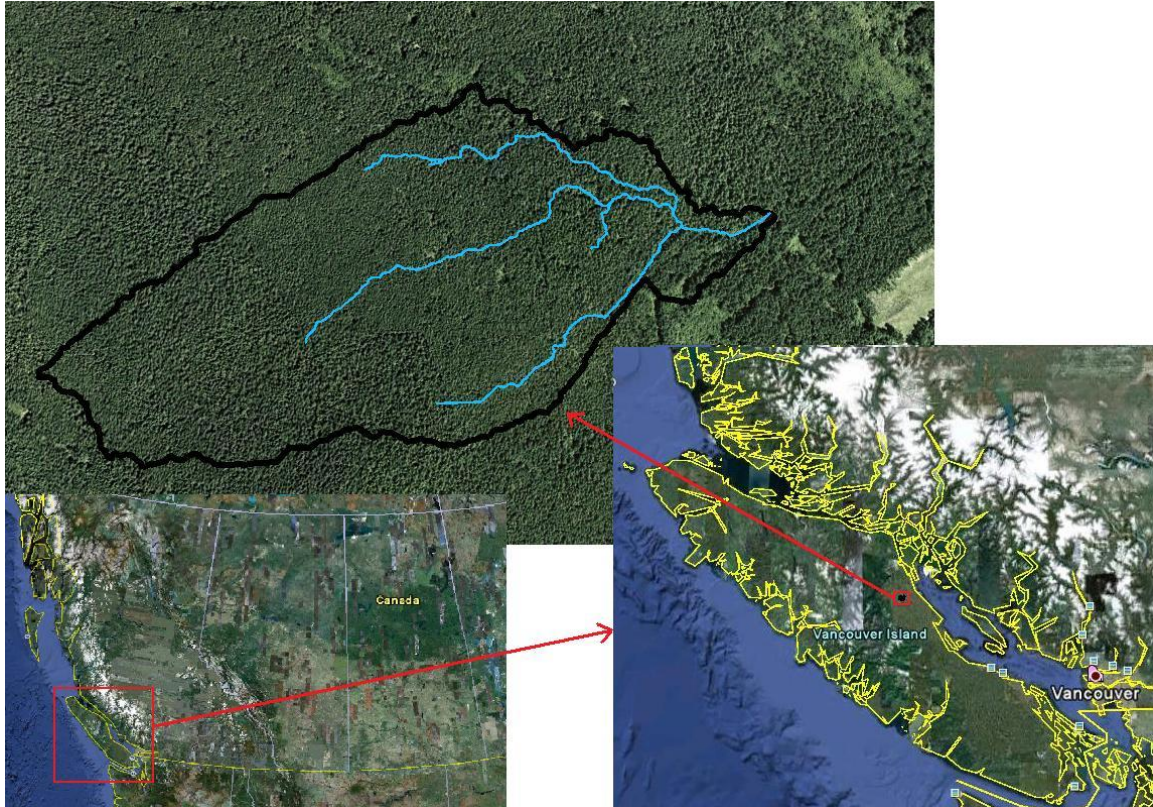


Figure 1: Map showing study site location near Campbell River on Vancouver Island, BC (Images from Google Earth).

The location was planted with Douglas-fir seedlings in 1949, code named DF49, and scheduled to be harvested in early 2011 (Chen et al., 2009). The site suffered a forest fire in 1949 and was re-established almost as a homogeneous stand. The stand ranges from 300 to 400m above sea level with 675-1900 trees per hectare (Humphreys et al., 2006). By the end of 2010, these 60-year old Douglas fir stand had reached the age typical of second-growth forests within a managed harvest cycle (Jassal et al., 2005). The forest was fertilized in early 2007 with urea that provided 200kg/ha of N to enhance biomass growth and production. The stand was scheduled to be harvested in early 2011.

Before the harvest took place, some construction was done in October and November of 2010 to a gravel road alongside the stream by widening it. This led to some disturbance on the side of the road as soils and vegetations were overturned, and may have influenced streamwater which was within 10-15m from the road. The harvesting was done in January and February of 2011, and Figure 2 shows how the disturbed forest looks in the late stages of harvesting.



Figure 2: Overview of the study site, with the stream and the logged forest in the background, photo taken on Feb 9, 2011 by UBC Ecohydro Group

### Field Sampling and Collection

An autosampler was placed in the stream and programmed to collect water samples at regular intervals beginning in November 2007. Every 36 hours, the sampler allows a roughly 1L container to fill up with stream water. Afterwards the container is placed in a large round cartridge and sorted chronologically. Once every month the samples are retrieved from the stream, transported back to the lab, and stored in the fridge to keep the temperature low. Grab samples were collected to compare with samples collected by autosampler to evaluate any changes to chemistry occurring post-sampling and prior to retrieval. During the winter periods considered in this study, temperatures were generally quite low, suppressing chemical changes in the sampled water.

At the head of the river, a sharp-crested V-notch weir was installed to measure the river outflow. By measuring the elevation of the water surface above the point of V-notch, the discharge through the weir can be determined. The data is recorded every 30 minutes via a datalogger that keeps track of the height of the outflowing water at each interval. The UBC Ecohydro Research Group has been collecting and compiling data since 2007. This data is then converted to discharge data standard 90° V-notch equation using standard methods.





Figure 3: Image showing the streamwater flowing through a weir at the study site after disturbance had occurred

### Lab Preparation & Ion Chromatography Analysis

A filtering process was conducted first in order to remove the suspended particulate matter in the water samples. These filtered samples were then poured into a small clear plastic bottle and treated with 10 $\mu$ L of thymol acting as a disinfectant to prevent further microbial activity and degradation. Afterwards these filtered and treated

samples were stored in the fridge until time of analysis to maintain the low temperature of the samples.

A set of standard solutions, containing fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulphate anions were prepared. Crude chemical reagents containing each of seven anions such as Potassium Fluoride (KF), Potassium Chloride (KCl), etc. were used to make the standards. They were dried overnight in the oven at 350°C and immediately placed into desiccators to prevent any accumulation of water vapour. These procedures were done to ensure high accuracy in the measurements of anions, with anions in the water sample being usually in the  $\mu\text{g L}^{-1}$  range. Calculating the desired concentrations required for each anion, the reagents were weighed out using an analytical scale and added into a 250mL volumetric flask. Deionized water was added to the volumetric flask and mixed to create the stock solution. This stock solution was then further diluted down to the desired concentrations using deionized water into 500mL volumetric flasks. A set of standards containing 5 different levels of the anions to be measured was created. Table 1 illustrates the approximate concentrations prepared in the standards, where the standard levels encompass the typical range of concentrations encountered for each streamwater anion in the study region.

Table 1: List of anions and their concentrations in the standard solutions

Anions	Concentrations in Standard Solution ( $\text{mg L}^{-1}$ )				
	Level 1	Level 2	Level 3	Level 4	Level 5
Fluoride ( $\text{F}^-$ )	0.025	0.125	0.5	2.5	5
Chloride ( $\text{Cl}^-$ )	0.05	0.25	1	5	10
Nitrite ( $\text{NO}_2^-$ )	0.005	0.025	0.1	0.5	1
Bromide ( $\text{Br}^-$ )	0.005	0.025	0.1	0.5	1
Nitrate ( $\text{NO}_3^-$ )	0.0125	0.0625	0.25	1.25	2.5
Phosphate ( $\text{PO}_4^{3-}$ )	0.005	0.025	0.1	0.5	1
Sulphate ( $\text{SO}_4^{2-}$ )	0.05	0.25	1	5	10

These anions were analyzed at University of British Columbia's Soil Air and Water Laboratory via Ion Chromatography (IC) System (Metrohm Ltd., 861 Advance Compact IC, Switzerland). The ion chromatograph is an instrument that allows for the separation of ions and polar molecules based on their charge. Ion species separate differently depending on their size and the species type, and thus allowing for detection of various cations and anions in a solution.

About 15mL of each water sample was poured into a small vial and placed on the autosampler portion of the IC, which consists of a round spinning disk that holds the vials. The machine was able to automatically rotate and inject the volume in each individual sample vial and analyze them. For each run, the 5 level-set of standards were analyzed through the IC along with the water samples, with standards inserted throughout the run serving as controls to ensure consistency.

A chromatograph is generated after the IC analyzes each water sample. The IC is not able to directly measure the concentration of anions in the samples, but instead produces a chromatograph that shows ion conductivities over time. Each ion species has a different retention time upon passing through the column on the IC, depicted by peaks at specific locations on each chromatograph. The higher conductivity measured indicates a larger amount of anion passing through the IC column, resulting in a peak with larger area on the chromatograph (Refer to Figure 4 for an example chromatograph generated by the IC). Each graph was then examined and adjusted to minimize errors and eliminate inconsistencies. The computer program would automatically integrate the area under each peak for the anions and compute all the data into a table. By generating a linear regression with the 5 level of standards knowing both concentrations and peak area for each anion, the concentrations in each water samples were then interpolated based on the standards for that run.

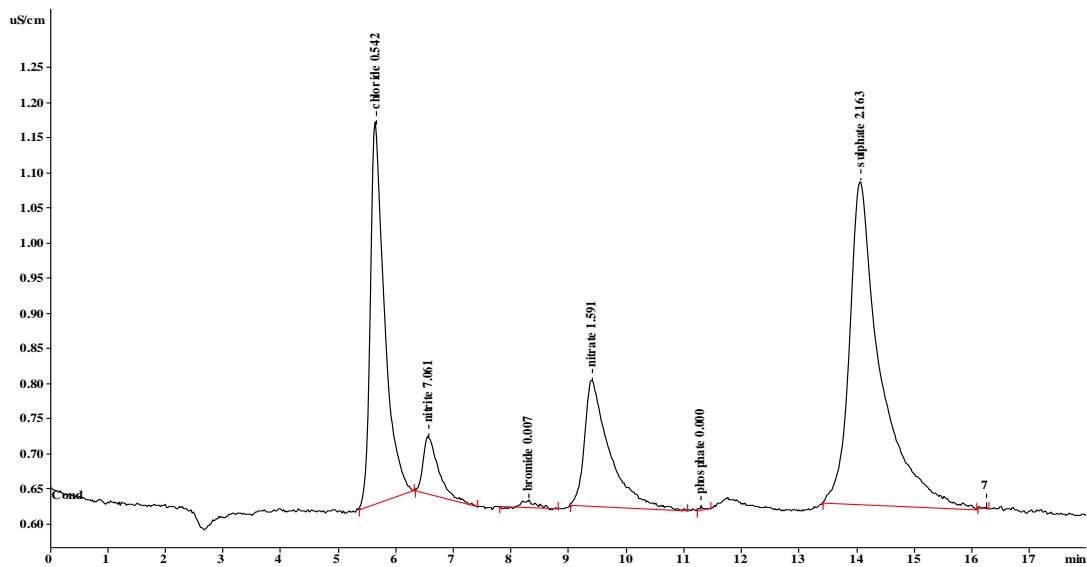


Figure 4: Example chromatograph that relates the conductivity (y-axis) and retention time (x-axis), peaks indicate the amount of each anion passing through the column at a specific time

## ANALYSIS & RESULTS

### Changes in flow pattern: Flow Duration Curves

Since water samples were collected starting from 2007, with road construction been done in October and November of 2010 followed by forest harvest in early 2011, the study focuses on the winter periods (November to April) to compare pre-disturbance vs. post-disturbance periods. Pre-disturbance winter period included November-April of 2007-2008, 2008-2009, and 2009-2010, and is compared to the short-term post-disturbance period of November 2010 - April 2011. These months in the Northwest Pacific are characterized by high amounts of precipitation and large flows (Feller and Kimmins, 1979). Johnson et al. (2007) noted the markedly differences in hydrologic processes and nutrient dynamics between winter and summer periods in their study. Thus, the careful selection of the period of interest also seeks to minimize seasonal trends in nutrients fluctuations.

Compiling all the available discharge data recorded in the winter periods from 2007 to 2011, flow duration curves (see Figure 5) were generated for both pre- and post-disturbance periods. Flow duration curves relate the discharge to the percentage of times that level of discharge is exceeded (Cole et al., 2003) and provide a nice first glance into the changes in flow patterns. It can be noted that there are more than 18,000 measurements of discharge taken over the pre-disturbance period used to generate the curve, and post-disturbance period consists of well over 6000 measurements.

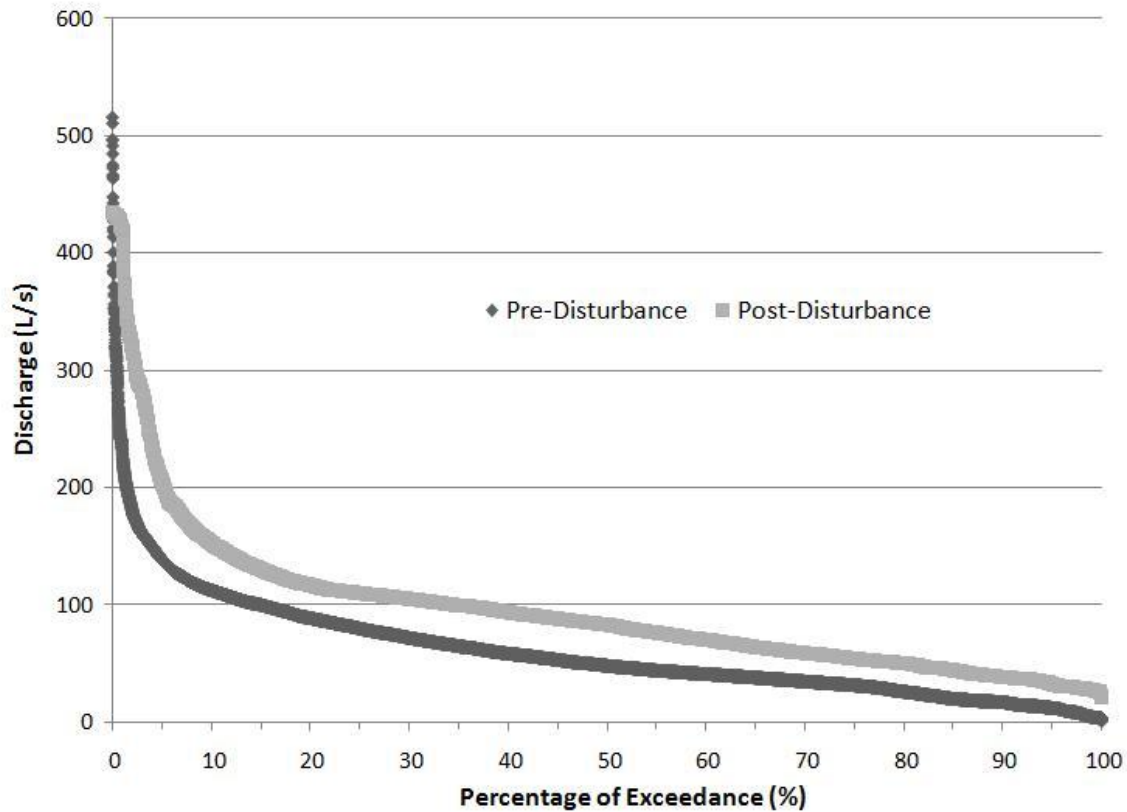


Figure 5: Flow duration curves for both pre and post-disturbance periods, each point shows the percentage of times (probability) that a flow will exceed the discharge level

Generally higher flows were observed much more frequently in the post-disturbance period. Only on rare occasions in the pre-disturbance period did the discharge reach extremely high levels of over 500 L/s and thus had very low chances of exceedance at those levels. For a better comparison of the differences, we can look at the different stages of flow duration level, at 95% exceedance (low flow), 50% exceedance (median flow), and 5% exceedance (high flow) levels. For example, a low flow level is the discharge that is equalled or exceeded 95% of the time during the computation period (Murdoch and Shanley, 2006a). These values are summarized in Table 2.

Table 2: Stream Discharge before and after disturbance at different flow levels

Flow Duration Levels	Before Disturbance (L/s)	After Disturbance (L/s)
Minimum flow observed	0.33	21.10
Low flow (95% Exceedance)	11.53	32.27
Median flow (50% Exceedance)	47.48	83.06
High flow (5% Exceedance)	138.47	203.85



At all flow levels, the post-disturbance segment resulted in higher discharge. In the winter period prior to disruption, it was found that the lowest flow observed during this period was 0.33 L/s, compared to after the disturbance all flows were measured to show a discharge greater than 21.1 L/s. At the 95% exceedance level, discharges after disturbance were seen to be more than twice greater than the prior to disturbance level. This difference was even greater at higher flow rates, with the high flows post-disturbance observed to be over 60 L/s larger than pre-disturbance flows.

### Stream Anion Export

In this experiment, anions found in the water samples were of interest, particularly chloride, nitrate, and sulphate. Phosphate ( $\text{PO}_4^{3-}$ ) and bromide ( $\text{Br}^-$ ) were below the detection limit in almost all samples, while nitrite ( $\text{NO}_2^-$ ) only showed intermittent detectability. The peaks for fluoride ( $\text{F}^-$ ) anions on the chromatographs were not consistent over time, and thus accurate values for the concentrations would be difficult to obtain. Therefore, the remaining anions chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulphate ( $\text{SO}_4^{2-}$ ) were chosen to be further analyzed. These anions were found to have the highest concentrations of the anions evaluated and hence were most detectable. Furthermore, these were anticipated to generate the most useful information related to changes in hydrological flowpath following forest harvest.

With data for anion concentrations and discharge of the stream, concentration-discharge (C-Q) relationships can be used to calculate sediment and chemical loads in streams and rivers (Murdoch and Shanley, 2006a). The relationship between flow and concentration is assumed to be consistent over the period of interest. Long-term data sets can be split into temporal segments, given that within each segment there is sufficient data to establish a significant C-Q relationship, the concentrations then can be compared amongst the segments to determine trends (Johnson et al., 2007). This relatively recently developed method is known as the Segmented Regression Analysis (SRA) (Murdoch and Shanley, 2006a).

For this study, SRA was performed by splitting the available data into two segments, one prior to the disturbance and the other post-disturbance. Data from winter periods (November to April) with the same months chosen as the flow duration curves

were analyzed. The rationale for analyzing the periods this way was that disturbance had occur in the wet and cool winter months which grants a comparison with the other winter periods. The more active growth season in the summer months (May to October) would be expected to demonstrate different flowpaths and anion export patterns and was excluded from the segments. Independent regression analyses were performed on each anion ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) corresponding to the discharge found at both segments. Any extreme outliers were taken out from the analysis after checking with the IC results and corresponding date of measurement. The significance of the C-Q relationship was verified using analysis of variance (ANOVA), and any concentration trends would be deemed significant if the p-value is less than 0.005. It is inherently assumed that the concentration-discharge relationship between those periods chosen in each segment is consistent (Murdoch and Shanley, 2006a).

#### Chloride ( $\text{Cl}^-$ )

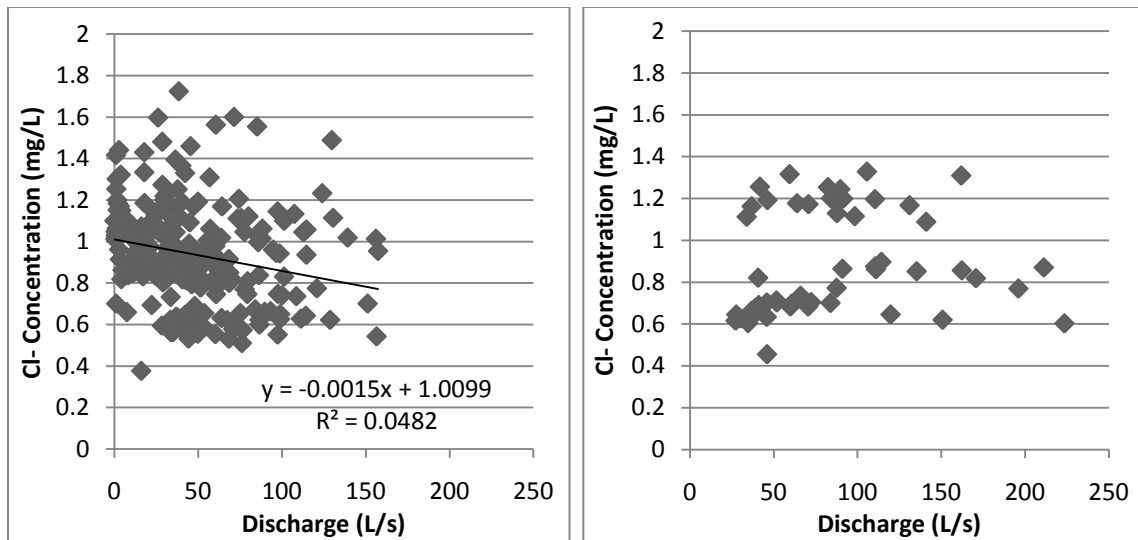


Figure 6: Chloride concentration-discharge relationships for pre-disturbance (left) and post-disturbance (right), a significant relationship for pre-disturbance period is present ( $p < 0.005$ ) while no significant relationship was found for post disturbance ( $p = 0.48$ , linear trendline not shown)

Prior to the disturbance event, chloride in the stream showed a slight negative correlation with discharge. Even though the values had high fluctuations and the  $r^2$  value was very low indicating only a small portion of the points can be explained by the linear regression, the regression relationship established had a high significance nonetheless.  $\text{Cl}^-$  concentrations were found to be ranging from 0.4mg/L to less than 1.8mg/L in the pre-

disturbance years while a narrower range of 0.4mg/L to 1.4mg/L was observed post-disturbance. At the high discharges end in the post-disturbance graph, there tend to be fewer records of high  $\text{Cl}^-$  concentrations. However, given the amount of fluctuations and scatter in that period, no definite patterns could be observed and regression analysis showed no significance in the regression relationship generated. Thus, the data implies any relationship that may have existed before the disturbance between flow and chemical export of chloride was disrupted.

#### Sulphate ( $\text{SO}_4^{2-}$ )

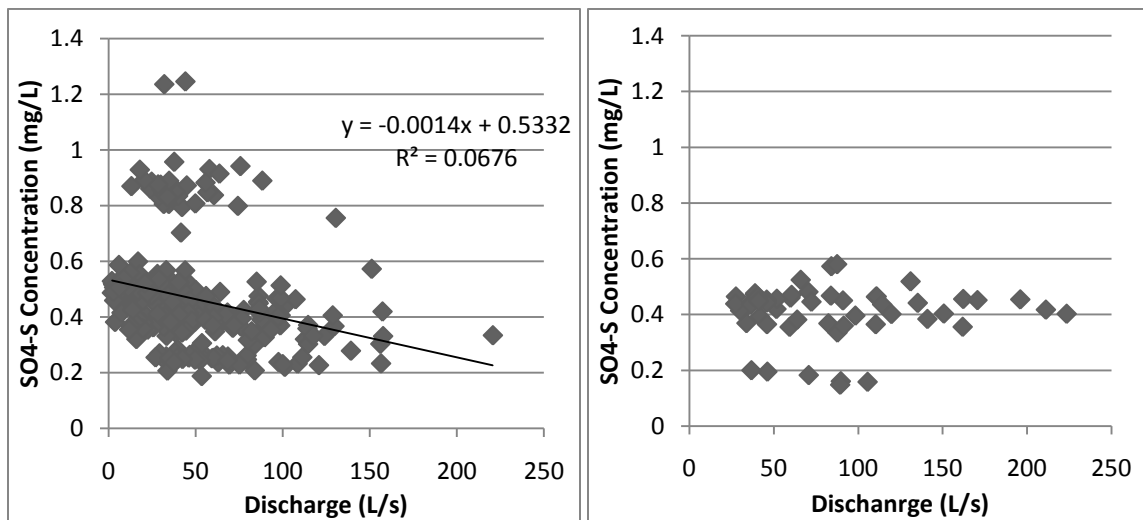


Figure 7: Sulphate concentration-discharge relationships for pre-disturbance (left) and post-disturbance (right), a highly significant relationship observed for pre-disturbance period ( $p\text{-value} < 0.005$ ) but no relationship found for post-disturbance ( $p = 0.389$ , linear trendline not shown)

The analysis of sulphate anions generated similar results to chloride. A more statistically significant negative correlation for sulphate C-Q than chloride was found in the pre-disturbance period. Although the regression line created for the plot does not visually seem to fit well with the clusters of points presented, the higher concentrations at the lower flows probably led to this overall negative correlation. After road construction and harvesting, this correlation again seemed to have disappeared, and the range of the exported sulphate was much lower than in pre-disturbance time, all samples were found to contain less than 0.6mg/L of sulphate compared to a much wider range in pre-disturbance times with concentrations up to 1.2mg/L.

In both graphs, there appears to be two cluster groups at different concentrations. In the pre-disturbance most of the sulphate exported falls in the range of 0.2-0.6 mg/L, however a cluster of higher concentration sulphate found above 0.8 mg/L was observed. Upon checking the dates, these higher concentrations were found in consecutive days from mid-November of 2008 to mid-January of 2009 and were also processed through the IC in one-run. In the post-disturbance plot, most concentrations were found around 0.4mg/L with several measurements showing lower concentrations at about 0.2mg/L. However, these were not found on consecutive days and were observed during November of 2010 around the time of the disturbance event.

#### Nitrate ( $\text{NO}_3^-$ )

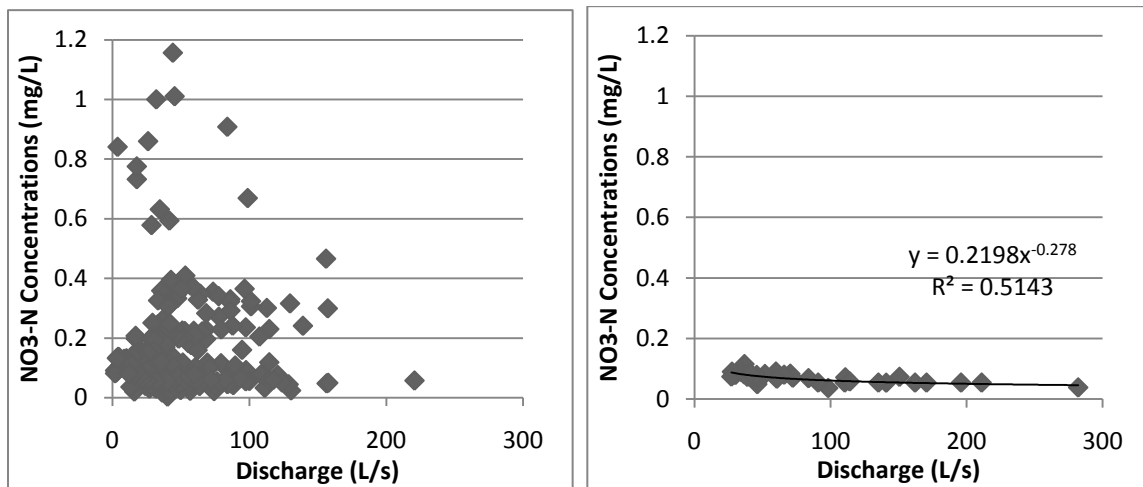


Figure 8: Nitrate concentration vs. discharge relationship for pre-disturbance period (left) and post-disturbance period (right), no significant relationship found for pre-disturbance period ( $p = 0.718$ , trendline not shown), post-disturbance data can be best described by a first-order decay power relationship ( $p < 0.005$ )

Nitrate in this forested watershed tells a different story from chloride and sulphate, the opposite is observed as no significant patterns could be identified for the period prior to the disturbance. The nitrate relationship post-logging was better characterized by a first-order decay power relationship which had a higher  $r^2$  value compared to a simple linear relationship which was also statistically significant. The relationship implied that there is rapid decrease in amount of nitrate with the increase of discharge at low flows but the decreasing trend gradually smoothed out at higher flows. These two segments displayed a very noticeable difference in the range of concentration

values. In the post-disturbance months the concentration were shown to be all around 0.1mg/L, but values as high as up to 1.2mg/L was observed with the majority of the measurements between 0 to 0.4mg/L.

The elevated nitrate concentrations in the earlier years may be from the addition of fertilizer in 2007. Studies have found post-fertilization nitrate peaks up around to 4mg/L (Binkley and Brown, 1993), while nitrate concentrations at DF49 do not peak to that level, the application of fertilizers would still bring about significant amounts of nitrate into waterways. To assess the carry-over effect of the fertilizer, temporal variations of nitrate in the winter periods were plotted in Figure 9.

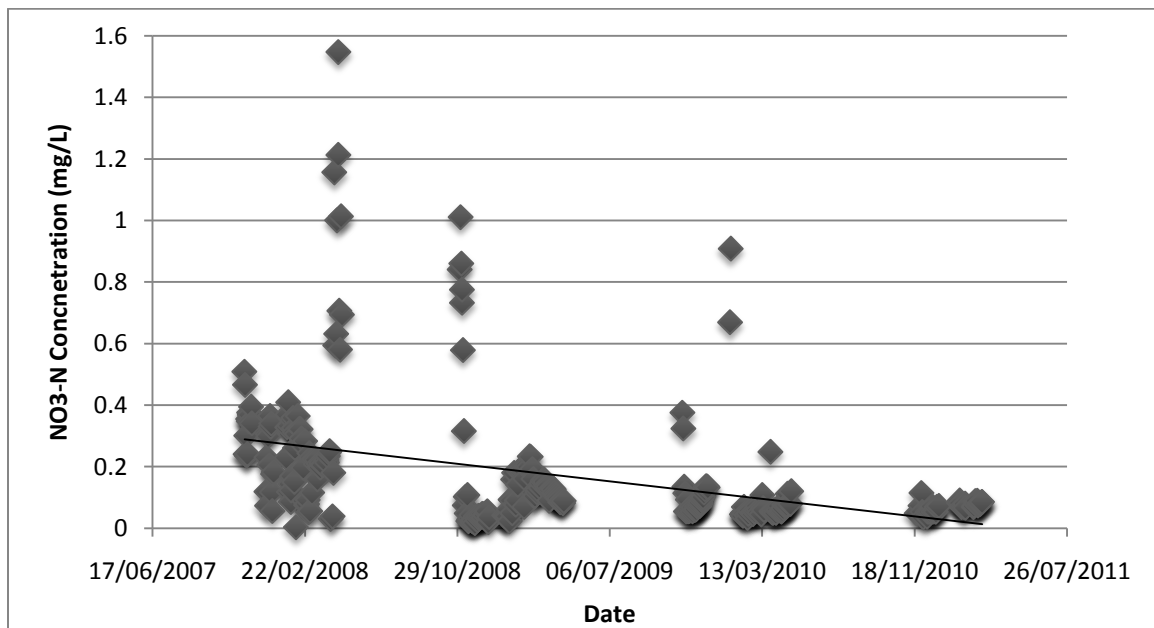


Figure 9: concentration of nitrate-N in winter periods from late 2007 to early 2011, includes both pre and post-disturbance data

A general decreasing trend over time is observed, with in winter period of 2007-2008 having the greatest concentration of exported nitrate-N showing up. There were some pronounced peaks in the winter periods for the years before disturbance. Late April 2008 and early November 2008 both recorded some consecutive high concentration nitrate readings, in winter of 2009-2010 any abrupt peaks were much milder compared to previous years. Finally in the most recent winter after the disturbance, no extreme values were found. The high amount of export nitrate at the end of 2007 is a strong indication of the influence from fertilizers. As time progressed, the nitrate in the system was seen to have quickly reverted back to having much lower N and perhaps being N-limited similar

to before any fertilization. This graph does show some important interannual variations that could not be otherwise distinguished from the pre-disturbance segment which combined three years worth of data.

## DISCUSSION

### Flow Duration Curves

At first glance, flow patterns from the flow duration curves provided solid evidence supporting a higher flow in the post-disturbance period. The removal of vegetation cover led to reduction of interception and evaporation of water (Wrinkler et al., 2009), resulting in high discharge volume after harvesting. Despite a significantly greater discharge, other effects may confound this finding. The winter of 2010 into early 2011 was a La Niña year, and thus the Pacific Northwest is predicted to receive more incoming precipitation and experience wet winters (Morgenstern et al., 2004). This extra precipitation could contribute the higher discharge observed in the post-disturbance period. The precipitation data recorded at DF49 (refer to Appendix I) displayed a much higher incoming precipitation for December in 2010, although December of 2009 also recorded high values. The difference is that for the pre-disturbed segment three years worth of data were used while the other segment only had one year of data. Any high values found in 2009 may be offset by average or low values from other years. With only one year of data in the post-disturbance period, a year with abnormally high precipitation inputs would skew towards higher discharges at all flows shown through the flow duration curve. It is uncertain how much of the increase in discharge was actually due to the disturbance as oppose to any climatological effects. However, this finding offers a starting point for looking at the differences in hydrological flowpaths before and after the disturbance.

### C-Q of Chloride and Sulphate

Chloride and sulphate anions were recognized to have slight negative correlations with increasing discharge in the years prior to the harvest whereas following the disturbance these correlations could no longer be seen. As mentioned before, it has been suggested that regions close to the ocean receives precipitation with high concentrations of sea salts (Feller and Kimmins, 1979; Vitousek et al., 1982), and likely determines the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations in streamwater, thus the concentrations of these anions detected would be coupled with the incoming precipitation. The decreasing trend in chemical concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  can be explained by the dilution effect of the less-concentrated rainwater in stronger precipitation events (Huntington et al., 1994; Feller, 2005). The insignificant C-Q for the post-disturbance may well be that there are not enough data points to construct a significant relationship. In the research of Murdoch and Shanley (2006b), they found the compilation of multiple-year segments was required to develop significant C-Q relations. Sulphate and chloride data from post-disturbance clearly supports the idea that single-year segments would not be sufficient for establishment of significant C-Q relation. The post-disturbance period only marks the early stages, which probably explains why no significant relationship could be observed due to alterations in the forest nutrient cycling pathways as the system tries to adapt to the changes.

Feller and Kimmins (1984) saw declining levels of sulphate in stream water after harvesting consistent with the findings here. Sulphate is involved in many reactions that dictate its net retention or release. Mineral adsorption process, incorporation into soil organic matter, uptake by plants are able to retain S in the system (Huntington et al., 1994). The disturbance might have led to decline in activity of S-oxidizing bacteria and increased sulphate reduction due to increased anaerobic conditions, or enhanced adsorption in the mineral soils that cause the general decrease in  $\text{SO}_4^{2-}$  after harvesting (Feller, 2005). The peculiar clusters observed in the concentration-discharge graphs were probably due to the short-term effects caused by the disturbance or weather impacts. A re-evaluation of those particular samples could perhaps facilitate a more confident explanation.

### Watershed Nitrate Dynamics

Nitrate was seen to have much higher concentrations in the pre-logging years, most likely due to the influence of the fertilization that took place, but no significant C-Q relations could be generated with the large amount of fluctuations and variability despite having multi-year observation. Any enhancement in nitrate loss post-disturbance observed by Vitousek et al. (1982) or Feller and Kimmins (1984) was not observed in this case, this may be due to the already low amount of nitrate in the system as the site is N-limited, or perhaps not enough time had lapsed after the disturbance to allow significant amount of nitrate to be transported away from the forest ecosystem.  $\text{NO}_3$  movement to stream water can be retarded if enhanced denitrification due to forest harvesting offsets the enhanced nitrification from additional soil moisture (Feller, 2005). Binkley and Brown (1993) had summarized the effect on clearcutting on forests with various vegetation types and found either no change or a slight increase. Even in very low concentrations, the measurements generated a significant C-Q relation that is negatively related to discharge. Dilution due to higher flows could again explain the lower concentrations observed at high flows, particularly in late 2010. Biologically active chemicals, such as nitrate, will respond depending on the intensity of biological demands for the chemicals and the accumulation prior to the increase in water flow (Feller, 2005). In this N-limited watershed, biological demand for nitrate is high and the frequent precipitation events in the winter months could dampen any accumulation. However, usually in the month of October when the first big rainfall hits the Pacific Northwest, the export of nitrate spikes as the water is able to flush out the previously accumulated nitrate in the system. This is known as the “Birch effect” characterized by high nitrate low flow and is observed during the transitions between drying and wetting phase (Jarvis et al., 2007). The October nitrate concentration data for most years indeed had some very high amount of export nitrate (graph not shown), and the nitrate peak found at the beginning of November 2008 (Figure 9) may be attributed to this effect perhaps due to a delay in the initial winter storm that year, resulting in some high concentrations when used for the analysis of the pre-disturbance segment.

Pre-disturbance nitrate data can be seen to be greatly influenced by the fertilizer application at the beginning of 2007 from Figure 9. Once these fertilizers have drained



through the system after a few years, the post-disturbance data showed a much less variable range of nitrate export. Most studies supported that N fertilization does not lead to excessive concentrations of nitrate-N in streams (Binkley and Brown, 1993), but when Hetherington (1985) examined nitrogen concentrations in streamwater after fertilization of urea on Vancouver Island, he found peak in concentration occurred about two months after fertilizer application, during the period when heavy rains drained the soils. Concentrations of nitrate-N reached a maximum of 9.5mg/L during the peak but then quickly returned to pretreatment levels during the first winter and showed only a minor peak the following year (Hetherington, 1985). By selecting those years right after fertilization, the direct impact on nitrate movement to the stream might have considerably clouded the background nitrate concentrations a forest site is expected to show in its pre-harvested state. On the other hand, it does signify the carry-over effect of the fertilizer was only on a scale of a year or two.

#### Sampling and Analysis Variability

Interannual climate variation remains as a plausible mechanism that could account for the differences observed in flow patterns and the rate of anion export, some recent studies with watershed response of N suggested deviation from long-term stream water chemistry may be influenced by these variations (Park et al. 2003). It was assumed that in the winter periods, the forest site would be subjected to similar meteorological conditions, and there would be minimal interannual variability, thus data from 3 winter periods could be analyzed in one group. However, events such as El Niño or La Niña, or a rain-on-snow event that occurred in December of 2008, results in unwanted deviations from the normal conditions representative of the study period. These differences in turn, influence the patterns on stream water chemistry. For nitrate, variations in temperature and moisture conditions affect plants uptake and N mineralization, so the rate and timing of biotic responses may lead to N leaching or N retention (Goodale et al., 2003). This again points to the advantages of having longer segments, despite having 3-years worth of data the ‘noise’ from interannual variation still interferes with the determination of trends.

Another thing to consider was whether the sampling interval for streamwater was too coarse. With discharge records every 30 minutes it was clear to see the increasing or decreasing patterns over short amount of time, but with water samples collected every 36 hours, perhaps small precipitation events might not be accounted for. However, in comparison with other studies, Murdoch and Shanley (2006a), and Gökblak et al. (2008) only collected weekly water quality samples but over a much longer period, the assumption was that sparser data sets over longer segments of time could overrule the effects of short-term climatic, seasonal, or storm-to-storm variability and reveal trends at specified discharges. With only three-years and one-year worth of data to work with but shorter intervals of collection time, it may be that these short-term effects were not well masked thus leads to difficulties in determining trends. If this forested site had another control site to compare with, certain patterns could be better explained, such as distinguishing the extra flow due to La Niña and the change in flow due to disturbance.

There had been several adjustments done to the IC machine throughout the experimental period, but the re-running of samples did not hint at any huge differences between runs. However, a more rigid analytical procedure was in place for the more recent samples as the anion concentrations were determined within a week after retrieval from the field, giving more confidence in the data from post-disturbance. Sometimes extremely low concentrations may interfere with the detection limit of the IC machine, this was not a problem with chloride as all water samples collected showed a consistent peak for chloride, nitrate and sulphate were more variable, especially post-disturbance nitrate, several samples were found to have undetectable nitrate concentrations leading to uncertainty in concluding whether these anions were entirely absent or they were simply before the detection limit. Any missing data points missing from either technical difficulties or below machine detection limit were not included in the SRA for C-Q relationship, which accounts for roughly 25% in each analyzed segment, a portion that could be of enough importance to alter some of the outcome. Much fewer data points were available for analysis in the post-disturbance segment, this may lead to uncertainties and imbalance in generating trends as certain point could be weighed more heavily to skew the relationship in a certain direction.

### Summary and Future Research Considerations

The available data used for this study only reached March of 2011, any long-term effects of harvesting on water chemistry and flow patterns were not explored. In such a short observational time period after a disturbance, the system might not have had adequate time to stabilize and requires the continuation of monitoring. Patterns from this study would not be sufficient to explain the trends of a longer term effect post-disturbance. Analysis segments should include data from multi-years to overlook the interannual variations. Analyzing data from similar watersheds in the area to act as a control for comparison could lead to further understanding in the phenomena observed. Climate factors were also important factors which drove the watershed response but were not analyzed in depth in this study.

In the short-term post-disturbance data analyzed, there were indeed differences observed in all aspects of the flow patterns and anion exports. The findings were: much higher flows in the post-disturbance segment; chloride and sulphate anions showed negative C-Q relations prior to disturbance but this could not be established after the disturbance; nitrate fluctuated greatly in the years leading up to the disturbance most likely with significant contributions from fertilization in 2007, the disturbance resulted in low concentrations of nitrate exported but generated a significant C-Q relation. It is uncertain how much of these differences can be accounted for the effect of the disturbance as opposed to other factors such as fertilization, meteorological differences over the years, or sampling and analysis methods adopted. Nonetheless, the discharges and the patterns founded and unfounded for the anions between the two periods of study provided some basic insights on forest disturbance and the complexity in these types of studies.

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Appendix I. Monthly Precipitation and Temperature Data for site DF49 from 2007-2010

