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Understanding Hydrological and Biogeochemical Processes in the HJ Andrews Forest

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ABSTRACT

It has been well-established that mountains are seeing exacerbated rates of warming compared to their lower-elevation counterparts, posing a threat to the billions of people that rely on them as a source of water. However, while shifting hydrology and biodiversity in these regions in response to increasing temperatures have been widely understood, little is known about the implications of Earth's changing climate on water chemistry, specifically freshwater carbon levels. Here we examine data from a fully harvested catchment (WS01) in the HJ Andrews Experimental Forest, a long-term ecological research (LTER) site located in the Oregon Cascades, in order to determine how fluxes in dissolved organic carbon (DOC) and inorganic carbon (DIC) respond to climactic, hydrologic, and land-use modulations. The watershed-scale reactive transport model HBV-BioRT was used to simulate hydrology as well as the biogeochemical reactions that produce DOC and DIC over a seventeen-year period from 2004 to 2017. Results show that lateral flow was the most dominant flowpath in the catchment in the wet springs and winters, accounting for an inter-annual average of 50.3% of total annual discharge. Groundwater flow was also a large contributor to the streamflow, responsible for 40.3% of annual flow and becoming most prominent during the arid summers as a sole source to the river. The watershed also exhibited concentration-discharge flushing behavior of DOC, or increasing concentrations with higher discharge, and dilution of DIC, or decreasing concentrations with higher discharge. The model revealed that DOC was most reflective of seasonal upper zone hydrological highs and lows, while DIC peaked during the dry summer when baseflows prevailed. These results suggest that due to increased reliance on older water from deeper groundwater supplies as the climate warms and higher surface-level transpiration from younger plants, clear-cut mountainous catchments can expect to see lowered export of DOC from these regions to marine environments, an important carbon sinking process and source to aquatic life. Consequently, higher fluxes of DIC can be expected in the stream which can subsequently be evaded to the atmosphere as CO_2. We suggest similar future study on controlled old-growth watersheds in the mountainous Western United States to further characterize the possibly differentiating role of land-use on watershed hydrology and biogeochemistry in response to warming.

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Chapter 1: INTRODUCTION

Mountains act as vital players in the global water cycle, with runoff from snow and glacial melt being an important hydrological source for riverine systems around the world (Beniston et al., 1997; Zhi et al., 2020). Over a fifth of Earth's land mass can be described as mountainous, and these "water towers" are directly responsible for supporting around 10% of the human populace and even more so indirectly (Messerli et al., 2004).

These mountain watersheds have also disproportionately seen increases in temperature and aridity compared to their low-elevation counterparts over the past century (Wang et al., 2013). Research has been extensively conducted on what these climate modulations mean for hydrology and biodiversity in such regions, and the consensus points to a shift from precipitation as snowfall to rainfall, leading to decreased discharge (Jenicek et al., 2018). This poses a threat to water security and ecological diversity in these sites, as arid areas already rely on mountain discharge for up to 90% of their freshwater. However, apart from this predicted decrease in water availability, little is known about the implications of warming and its resulting effect on hydrological partitioning for stream chemistry in sites of higher altitude.

Mountains are also known to be a sizeable deliverer of terrestrial carbon into the ocean due to their geomorphology contributing to rapid downstream export (Wohl et al., 2012). Carbon typically enters bodies of water through either the erosion and respiration of surrounding soil and vegetation or the weathering of underlying silicate and carbonate rocks (Bluth & Kump, 1994). As illustrated in Figure 1, it has been hypothesized that biotic processes such as plant uptake, respiration, and microbial activity which produce carbon dioxide and organic carbon are closely

associated with the nutrient-rich subsurface soil zone, while increasing depth shifts to abiotic interactions such as weathering of rocks and ion exchange that produce inorganic carbon (Zhi et al., 2022).

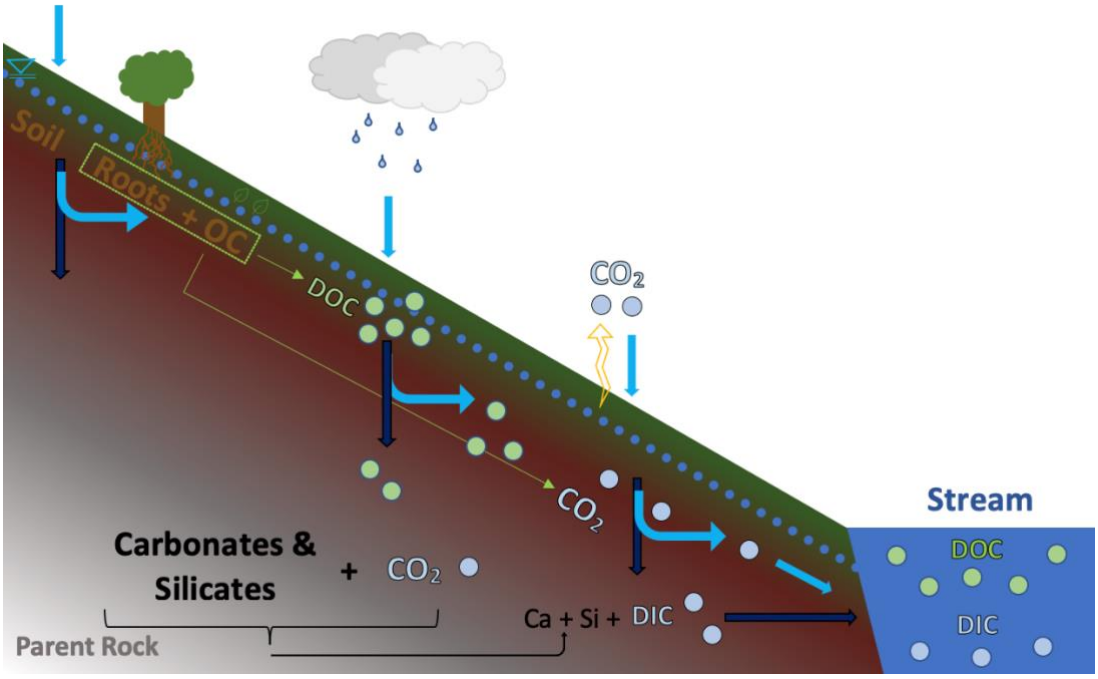

Figure 1. Hillslope Organic and Inorganic Carbon Reactions in the lower and upper zones

The former processes which contribute to dissolved organic carbon (DOC) play a vital role in aquatic ecosystems as a microbial food source and driver of acidity and nutrient mobilization (Ågren et al., 2007; Hagedorn et al., 2000). More broadly, fluxes in river and soil carbon are tied to changes in atmospheric CO_2 levels and can also be reflective of anthropogenic influence on the surrounding riverine area. It is commonly known that CO_2 is a major greenhouse gas and driver of rising temperatures and radiative forcing, with international efforts being made to lower human-induced climate change and fully define carbon cycling (Solomon et al., 2009). The removal of organic carbon from terrestrial vegetative land sources into marine sedimentary sinks

is connected by riverine systems, and larger fluxes from inland waters mobilizing the oceanic sequestration of DOC can offset elevated CO_2 concentrations (Repasch et al., 2022). Conversely, the mineralization of carbon in soil due to this transport is known to release inorganic carbon, with subsequent vertical gaseous carbon dioxide evasion augmenting the magnitude of atmospheric CO_2 (Battin et al., 2009; Wallin et al., 2012). There is still a gap, however, in understanding the overarching mechanisms and drivers of DOC and dissolved inorganic carbon (DIC) transport from montane sources (Williams et al., 1998). If better quantified, accounting for the role of mountains can help balance the global carbon budget more effectively.

This study uses data from the HJ Andrews Experimental Forest, a long-term ecological research (LTER) site located in the Oregon Cascades to model changing hydrology and freshwater quality in mountainous watersheds. This LTER site not only resides at an elevation of 1,350 to 5,340 feet above sea level, but also has undergone extensive harvesting, which makes its streamwater dynamics an especially interesting case study in how mountainous areas are affected by human activity. The specific type of harvesting that has occurred in this catchment is clear-cutting, or a practice in which a forested area is uniformly logged. Studies have shown that in the years following the full harvesting of a catchment area, DOC concentrations increase notably due to heightened mobilization of soil organic carbon (Fujii et al., 2021; Schelker et al., 2012). Soil organic matter is home to a sizable carbon pool, and clear-cutting is known to destabilize terrestrial organic carbon, making it more loosely bound to the catchment area and susceptible to leaching and dissolution into stream water as DOC in the short-term (Piirainen et al., 2002). Given this, land-use is an additional variable that must be considered when addressing the current knowledge gap in how climate and hydrology work to control the concentrations and fluxes of DOC and DIC in high elevation sites such as this one.

Chapter 2: BACKGROUND

Watershed Hydrology and Biogeochemistry

Prior to delving into the specifics of high-elevation watersheds however, it is important to understand the mechanics of a watershed and the hydrological and biogeochemical processes that define them. Throughout this study, the terms watershed and catchment will be used interchangeably, both words referring to the overlying land delineated by the drainage of a stream system (Brooks et al., 2012). Looking at the movement of water through such areas and the complex reactions that occur due to such transport as two separate entities has historically been the approach by hydrologists and geochemists alike, however a recent push for a more synergistic approach has paved the way for watershed-scale reactive transport models that can couple the two (Li, 2019).

Conceptually, this project utilized the two-box model to define the vertical structure of watershed subsurface. This divides our catchment subsurface into an upper soil zone, and a lower, deeper groundwater zone. The lower zone is dominated by groundwater baseflow and serves as a source to the riverine system during dryer or low precipitation periods. The upper zone is dominated by shallow soil interflow, and when the vadose zone is saturated or unable to keep pace with precipitation overland flow runs off on the surface (Li, 2019). The behavior of water in these vertically separated compartments intertwines with the transport of chemical species and solutes throughout the catchment. Understanding flow paths is essential to qualify the nature of and quantify the extent of reaction chemistry at the surface and subsurface of the watershed respectively.

Study Site

To investigate the stream chemistry dynamics of mountainous watersheds in response to a changing climate, we collated data from the HJ Andrews Experimental Forest, a long-term ecological research (LTER) site established in 1948, funded by the NSF, and located in the Oregon Cascades. Spanning around 6400 hectares and receiving much of its flow from the westward drainage of the Cascade Mountain range, the climate, hydrology, vegetation, geology, and water chemistry of this site has been extensively studied over the past seventy or so years (Anderson et al., 2005). Figure 2 further illustrates the topography and hydrology of the forest.

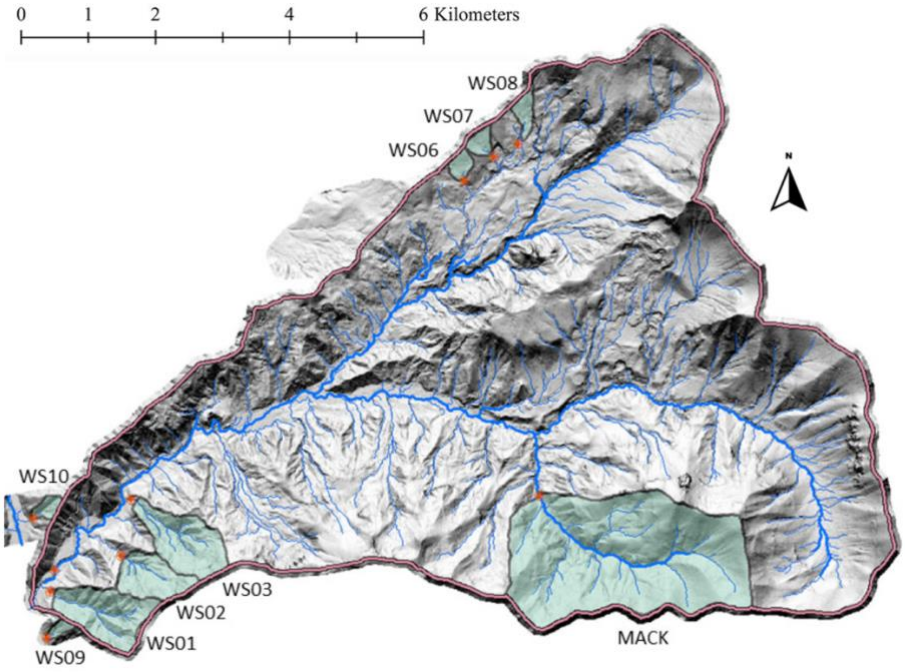

Figure 2. Map of the HJ Andrews Experimental Forest, with delineated watersheds (OSU, 2022)

The experimental forest is primarily dominated by hydrologically altered volcaniclastic rocks in low elevations, with intermediate and higher elevation areas composed of lava flows of basaltic

and andesitic origin (Swanson & Jones, 2002). Soil profiles are quite shallow and loamy, with high porosity and water retention rates leading to minimal overland flow. This storage serves as a source for the bountiful vegetation throughout the forest in dryer months, which is mainly comprised of shrubs, deciduous trees, and Douglas firs which were planted in response to harvesting over the years.

The forest has 9 experimental watersheds and corresponding gauges which collect stream chemistry and flow discharge measurements (OSU, 2022). Additionally, four main weather stations surrounding the gauging stations take important meteorological measurements such as temperature, humidity, radiation, wind speed, snow, and soil moisture; precipitation chemistry was also measured at these locations with less regularity. Watersheds 1 and 2 were of particular interest to us, as WS01 was 100% clear-cut 40-50 years ago while the adjacent WS02 was retained as an unharvested control for the catchment. Relevant attributes of these two catchments are further summarized in Table 1.

Table 1. HJ Andrews Watershed Characteristics and Land-use History

Watershed	Gaged Area (ha)	Gage Elev (m)	Max Elev (m)	Year of Origin	Management History
1	96	439	1027	~1500 AD	100% clearcut 1962-66
2	60	545	1079	~1500 AD	Reference, no harvest

However, though extensive stream chemistry sampling has been taken throughout the watersheds dividing the site since the mid-20th century, only watershed 1 (WS01) had an accompanying primary meteorological station close enough in proximity (PRIMET) that continuously measured precipitation, temperature, and other catchment attributes necessary for hydrological and

biogeochemical modeling. The measurement periods and regularity of the data employed in this study are outlined in Table 2.

Table 2: Summary of data used in analysis from the WS01 catchment at the HJ Andrews Experimental Forest, OR.

WS01	Sampling Location	Period of Record	Frequency
Precipitation	PRIMET Meteorological Station	3/1979 – 9/2018	Daily
Precipitation chemistry	PRIMET Meteorological Station	9/1994 – 3/2019	Every Three Weeks
Stream flow	Andrews Watershed 1 Gaging Station	10/1952 – 9/2019	Daily
Stream chemistry	Andrews Watershed 1 Gaging Station	5/2003 – 9/2018	Every Three Weeks
Radiation	PRIMET Meteorological Station	5/1972 – 9/2018	Daily
Temperature	PRIMET Meteorological Station	9/1994 – 3/2019	Daily

Watershed 2 (WS02) did have a corresponding weather station CS2MET, as seen in Figure 3, however data availability is comparatively sparse and insufficient for the models used. Nevertheless, WS01 is of interest as the focal point of this study due to its location's potential to shed light on high elevation hydrological processes, but also for its implications on the dynamics of carbon in montane watersheds that have undergone harvesting.

Figure 3. Map of watersheds with nearby weather stations

Chapter 3: METHODOLOGY

HBV-light

This study employed the dual-pronged reactive transport model, HBV-BioRT. The foundation of this approach began with calibration of HBV-light, a runoff simulator based upon the HBV model developed by the Swedish Meteorological and Hydrological Institute in the 1970's. This software uses daily precipitation (P), temperature (T), discharge (Q), and evapotranspiration (ET) data to simulate catchment runoff and flow partitioning by depth (Seibert, 1996). Additional tuning parameters of the model account for elevation, gaged area, snow routine, soil characteristics, and zone-dependent hydrology.

Corresponding to the principles of the two-box configuration discussed earlier which is recreated visually in Figure 4, the model uses measured P, T, Q, and ET to calculate the balance of water in the different catchment zones. In this configuration, we consider precipitation in the forms of rain or snow as our major system inputs, while total discharge (Q) as the sum of overland flow (Q_0), lateral riparian flow (Q_1) and groundwater flow (Q_2) are the major outputs. The model begins with a snow routine, using precipitation and temperature to estimate the partitioning between snowpack, snowmelt, and rain. Soil parameters also define the water storage and soil moisture, as well as calculate the actual evapotranspiration leaving the watershed compared to the given evapotranspiration. An additional percolation parameter (PERC) can be adjusted to determine how much water remains in the surface and upper zones (Q_0, Q_1), and how much infiltrates into the lower zone (Q_2). A threshold parameter (UZL) further defines when flow breaks through into overland runoff, and the speed of discharge from each zone (K_0, K_1, and K_2)

can be tuned as well until the simulated sum (Q_{sim}) of Q_0, Q_1, and Q_2 reflects measured discharge data sufficiently.

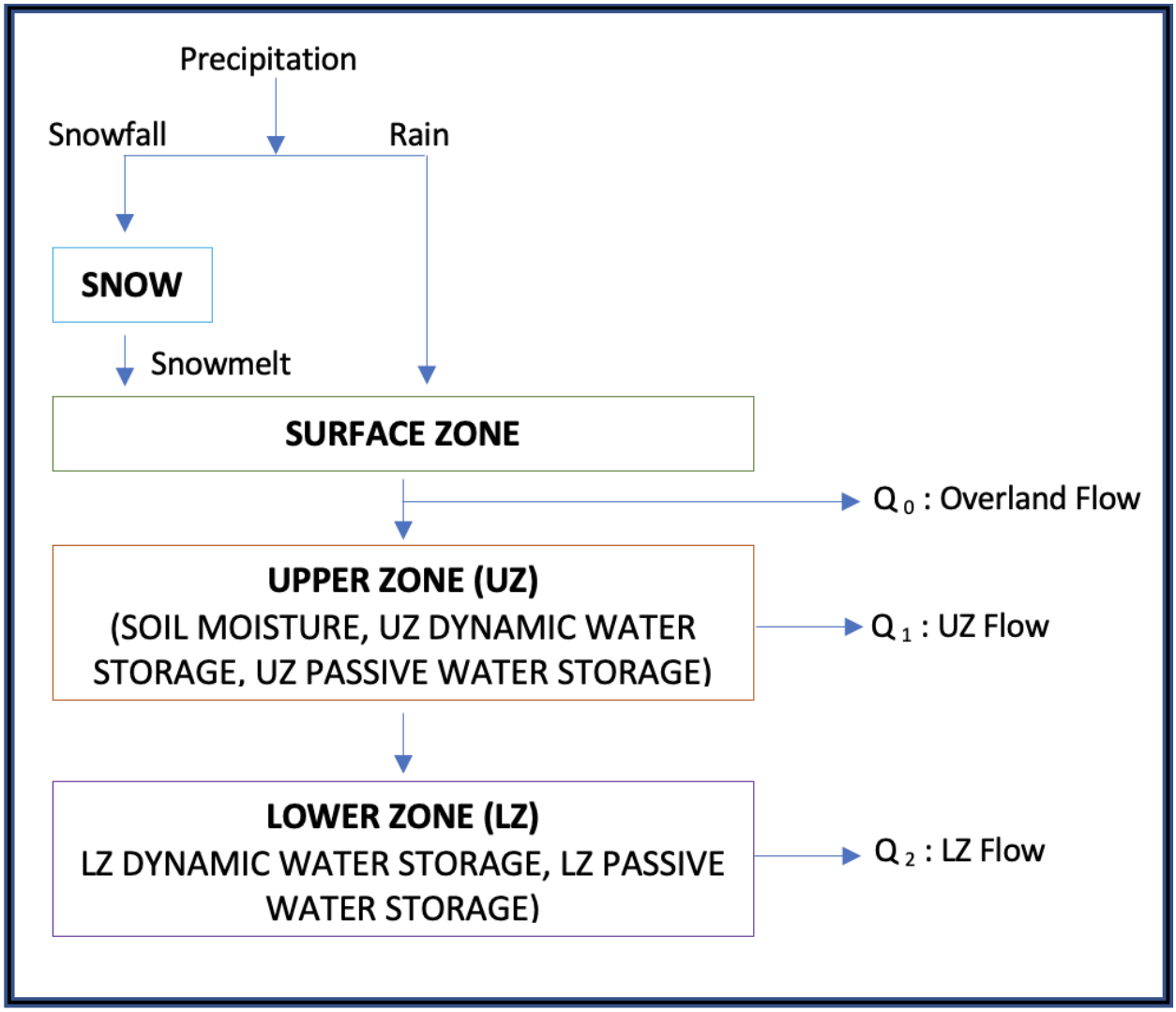

Figure 4. Two-Box Model showing flow paths between zones, primarily the UZ and LZ

While weighted daily average precipitation, temperature, and discharge data was available, no evapotranspiration measurements had been taken in the forest that were available publicly. Thus, the Hargreaves-Samani model, which uses mean daily extraterrestrial radiation R_s ($MJ/m^2/day$)

and daily temperature data (°C) to estimate potential evapotranspiration (PET) rates was utilized to fill this gap (Almorox & Grieser, 2015).

$$PET = 0.0023 * R_s * (T_{max} - T_{min})^{0.5} * (T_{mean} + 17.8)$$

The simulation period for this particular study was chosen to run from January 1st, 2004, to December 31st, 2017. HBV-light was also given a warm-up period of three years from January 1st, 2001, to December 31st, 2003, in order for the variables in the model to acclimatize from standard values to values that more reflect the meteorology of the specific catchment (Seibert, 1996).

BioRT

Prior to modelling the biogeochemical behavior of watershed 1, we decided to perform temporal and concentration-discharge (CQ) analyses on WS01 and WS02 and focus on their similarities and differences for additional insight on the nuances between old-growth watersheds (WS02) and their harvested analogs (WS01). Afterwards, the output and parameters from HBV-light in addition to precipitation chemistry was used as the input for BioRT, a reactive transport model which can be used to simulate both biotic and abiotic reactions at the watershed scale to generate simulated stream and subsurface water chemistry values of various solutes in different zones (Zhi et al., 2022). Additional input files include initial catchment conditions and solute concentrations in each zone, the primary and secondary chemical species to be modelled, and a database of chemical species and their corresponding reactions, Debye-Huckel parameters, charges, and molecular weights. With all this information and adjustment of the undefined parameters, total stream concentrations, concentrations in the upper and lower zones, and reaction rates of each species can be generated as a function of time throughout the designated period.

Calibration of the model was performed initially by only including chloride as a solute, as it is a non-reactive tracer and relatively stable in natural systems which makes it useful in adjusting catchment characteristics such as porosity and passive water storage. Once the soil parameters were adjusted through tracer modelling, an upper zone soil organic carbon (SOC) decomposition reaction was added to the model as follows in order to understand primarily organic carbon behavior (DOC), in addition to inorganic carbon fluctuation patterns in the stream (CO_2).

$$SOC \leftrightarrow 0.8\ DOC + 0.2\ DIC$$

However, the above reaction is primarily suitable in capturing the behavior of the more immediate subsurface, as shallower soils provide more suitable conditions for respiration in the form of abundant oxygen, microbial activity, and organic matter. To account for the anoxic conditions of the lower zone, a deep zone decomposition reaction which uses DOC as an electron acceptor to further transform organic carbon in this region (SOZ-lz(s)) into carbon dioxide was added.

$$SOC - lz(s) + DOC \leftrightarrow DIC$$

Finally, the chemical sorption of DOC onto the soil underlying the catchment was defined in the model through the addition of the following reaction. In this, X represents the functional groups on the soil surface prior to sorption, while XDOC is the soil with DOC attached to its surface.

$$XDOC \leftrightarrow X + DOC$$

To execute these reactions, it is important to note that BioRT required an input of daily precipitation chemistry for the simulation period of primary species (in this case, pH, Cl-, DOC, DIC, SOC, and X-) to model simulated stream chemistry values of designated solutes. However, the HJ Andrews database only had measurements taken every three weeks and thus interpolation between the 20-day periods between collections was required. Furthermore, DIC itself was not measured in the meteorological gauge, thus alkalinity values were used in lieu of this under the assumption that at the lower pH values of precipitation (4-5.5), alkalinity concentrations are fully representative of DIC concentrations in the form of aqueous carbon dioxide (CO_2) as displayed by the Bjerrum plot in Figure 5.

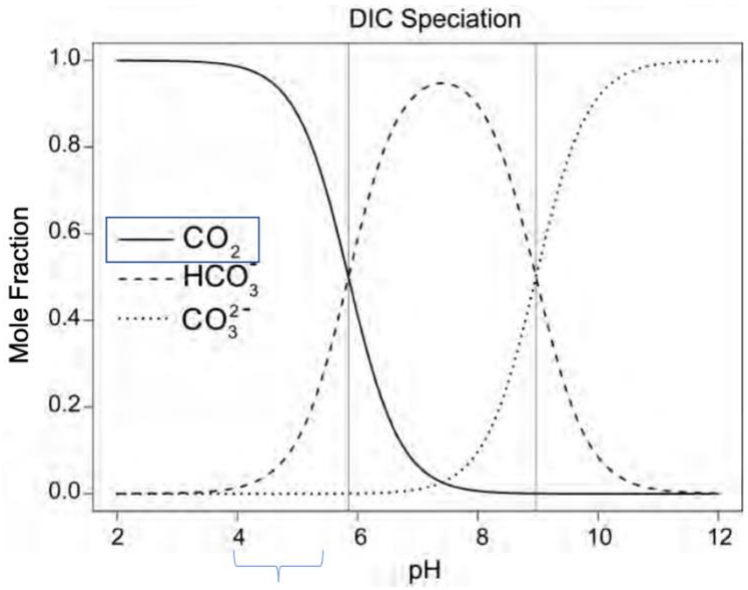

Figure 5. Bjerrum curves with pH dependence of carbonate speciation (Pimenta & Grear, 2018)

Chapter 4: RESULTS AND DISCUSSION

Modelled Hydrology

With a Nash-Sutcliffe model efficiency of 0.75 indicating a good fit, the average simulated total annual discharge over the 14-year period was found to be 1547.693 mm/year compared to the measured value of 1038.334 mm/year. Precipitation was found to be 2197 mm/yr overall, while evapotranspiration centered around 542 mm/yr. Table 3 shows a tabulated summary of the most influential parameters on the model results, the discussed annual averages for major inputs to the system's hydrology (precipitation via rainfall and/or snowmelt) in addition to the outputs of discharge and evapotranspiration.

Table 3. Selected model parameters and annual totals of hydrological inputs/outputs

PERC	3.75 mm/d
β	3
FC	200 mm
Precipitation	2197 mm/yr
Simulated Discharge	1548 mm/yr
Simulated Evapotranspiration	542 mm/yr

The percolation parameter (PERC) describes the quantity of water that can move from the upper box of our model to the lower zone, and the best result was obtained at a relatively high value of 3.75 mm/d. The field capacity (FC), which describes maximum soil moisture, was set quite high as well at 200 mm. This reflects that the catchment's affinity for infiltration is much higher than influent precipitation, meaning that the soils of the watershed are quite porous and able to retain large quantities of water below the surface to act as a source for the lush vegetation of the forest in the more arid time periods of the year (Waring & Franklin, 1979). The shape factor (β), which describes the non-linear relationship between discharge and precipitation as seen below, was set

as a reasonably large exponent of 3 to lower simulated discharge (as soil moisture is always below field capacity) and increase evapotranspiration for a better fit.

$$\frac{Discharge}{Precipitation} = \left(\frac{Soil\ Moisture}{Field\ Capacity}\right)^{\beta}$$

Modelled hydrology found that discharge mirrored the behavior of precipitation, with storm events being drivers of peak flow periods as shown in Figure 6. Of the total streamflow, the shallow zone discharge which is driven by rainfall and snowmelt Q_1 was the most dominant flow path contributing to 50.34% of total discharge. Q_2, or deeper zone discharge, was a steady and solid source of water for the stream, contributing to 40.31% of flow and seeing a very slight increase over the period of 17 years this model was run. Q_0, or surface runoff, was a much lower contributor at 9.35%.

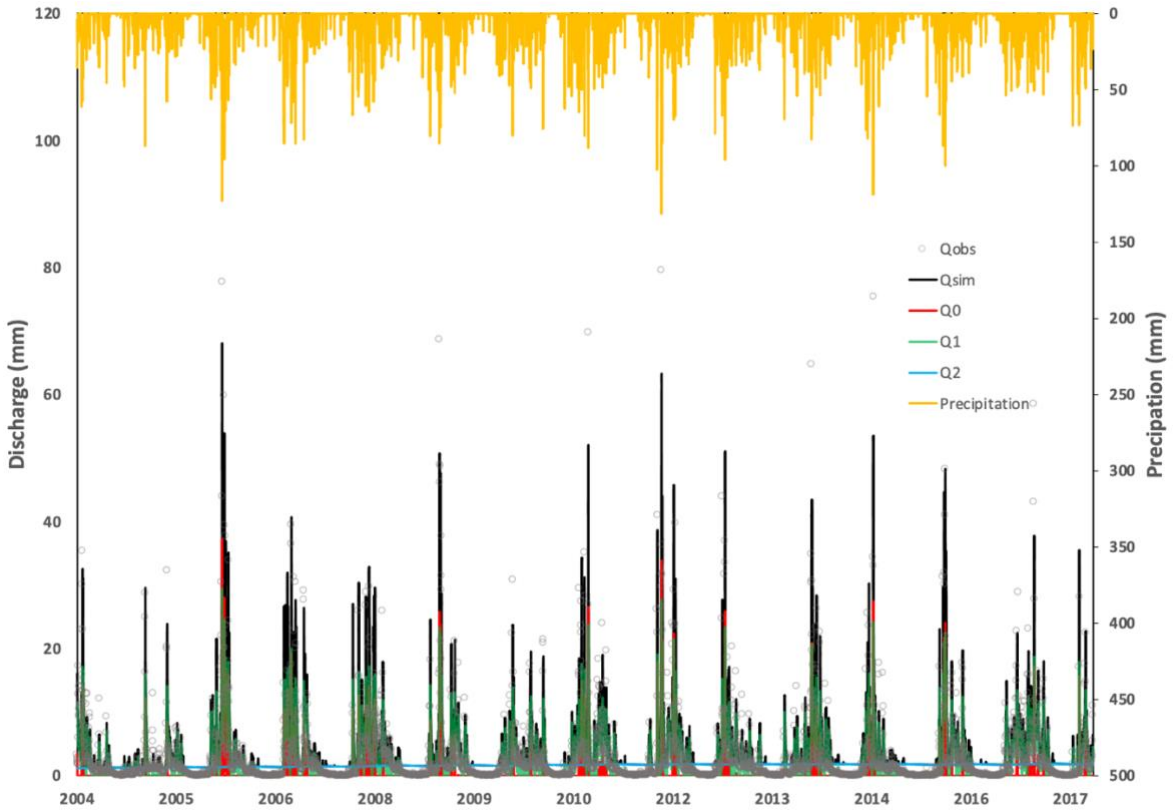

Figure 6. Daily Simulated/Observed discharge from 2004-2017, including flow partitioning

However, annual graphical analysis in Figure 7 showed that in years with higher precipitation, overland flow peaked as the watershed became saturated, while the stream's dependence on groundwater as a hydrological source decreased. For example, 2012 had a record high of 2895.3 mm of cumulative precipitation, with surface flow contributing to almost 15% of runoff and Q_2 diminishing to a role of under 30% of flow. Consequently, in the dryer years, overland flow was almost nonexistent as deeper flow paths became more active to provide water to the catchment. 2013 was a notably low-precipitation year at 1514.5 mm of total rainfall, and Q_0 contributed 0.18% while lower-zone flows increased in dominance to make up 64.36% of total flow.

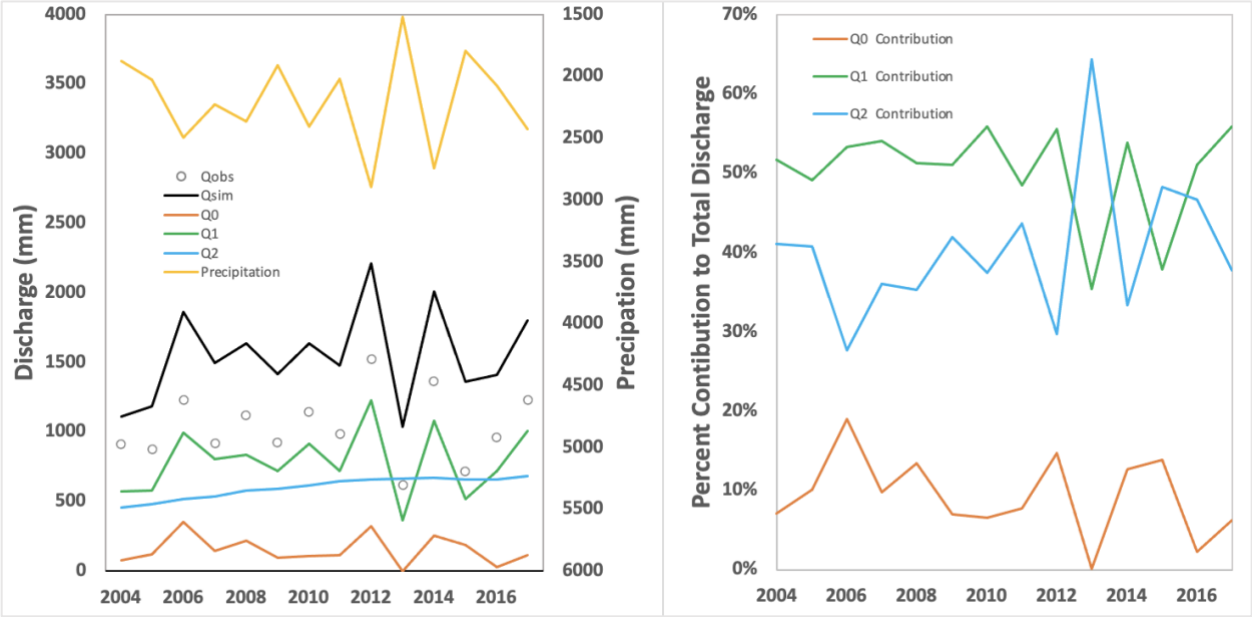

Figure 7. Annual Total Discharge from 2004-2017, including flow partitioning and streamflow contributions

Inspection of simulated flow distributions against measured discharge data throughout the most recently modeled year of 2017 in Figure 8 shows the seasonal variation of hydrological paths. Surface runoff is overall quite low, only peaking from a value of zero to mirror highs of the lateral flow (Q_1). The latter dominates during months of high rainfall or snowmelt, notably in the months of March and October. Lower zone flow doesn't experience the same dramatic

fluctuations in value but is a persistent source of water for the stream that takes over during the dryer and warmer months between June and September.

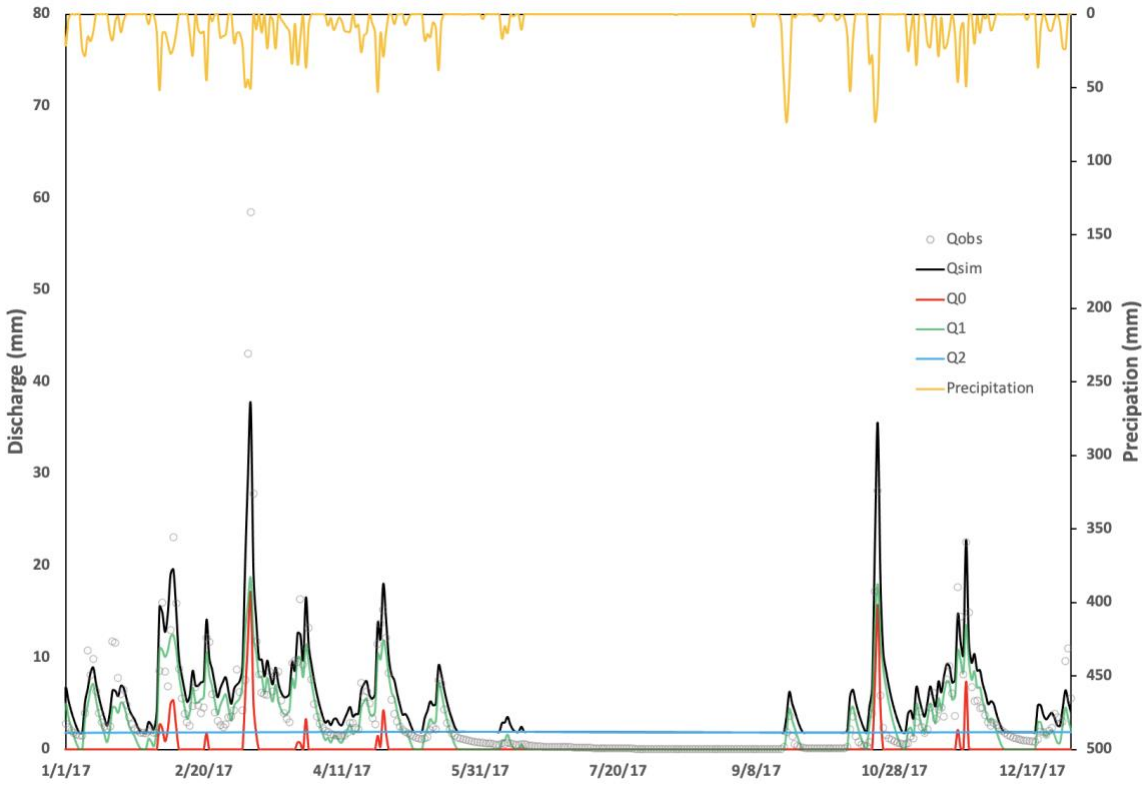

Figure 8. Daily Simulated/Observed discharge in 2017, including flow partitioning

Taking a closer look at seasonality, it is clear that summer streams are almost unusually deficient. The climate of the central Cascades is already a study in extremes, with the "Mediterranean" weather conditions leading to hot, dry summers and cold, wet winters ((Johnson et al., 2021). However, clearcutting may have further exacerbated the stream deficiency in the middle of the year, and the younger Douglas-firs dominating this harvested catchment are known to undergo more evapotranspiration within arid mid-year periods due to their higher leaf areas compared to old-growth conifers (Perry & Jones, 2016). Time-series analysis in Figure 9 shows that peaks in daily AET and PET generally correspond with higher temperatures, lower discharge, and lower precipitation from the June to September periods of each year.

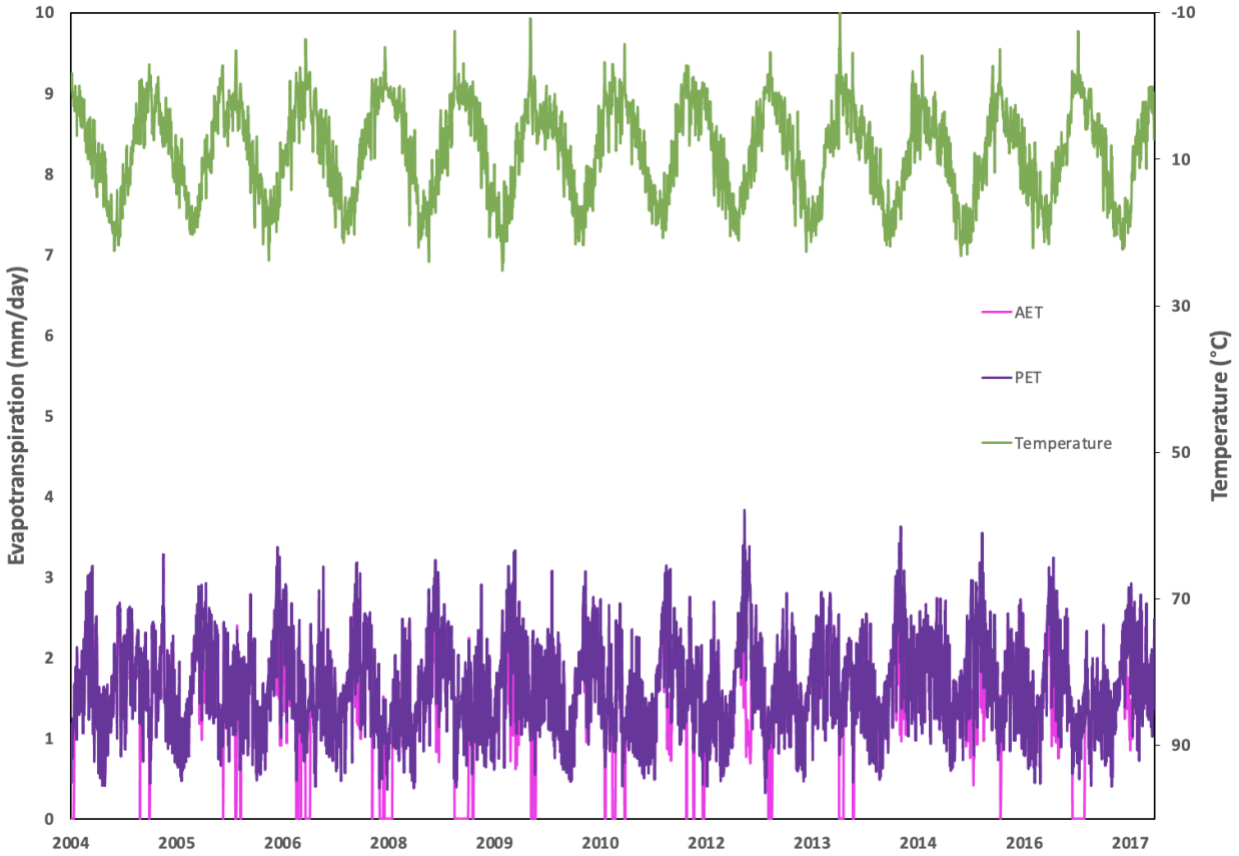

Figure 9. Time-series of Simulated Evapotranspiration and Temperature

Aside from seasonal evapotranspiration trends, modelled results showed that actual evapotranspiration (AET) averaged 542 mm/year while potential evapotranspiration (PET), or the amount that could be transpired by vegetation in optimal conditions with limitless soil moisture, was only slightly higher at 601 mm/year. Cumulative annual averages of actual evapotranspiration (AET) and potential evapotranspiration (PET) were then divided by corresponding precipitation values to obtain evaporative and aridity indices respectively. When plotted against each other as in Figure 10, model results also suggest that the HJ Andrews WS01 catchment is extremely energy limited with generally low ratios of actual and potential evapotranspiration to precipitation. This indicates overall humid conditions despite the arid summers, resulting in the high precipitation during the rest of the year overshadowing

evapotranspiration, meaning that the watershed is limited by atmospheric demand (Carey et al., 2010).

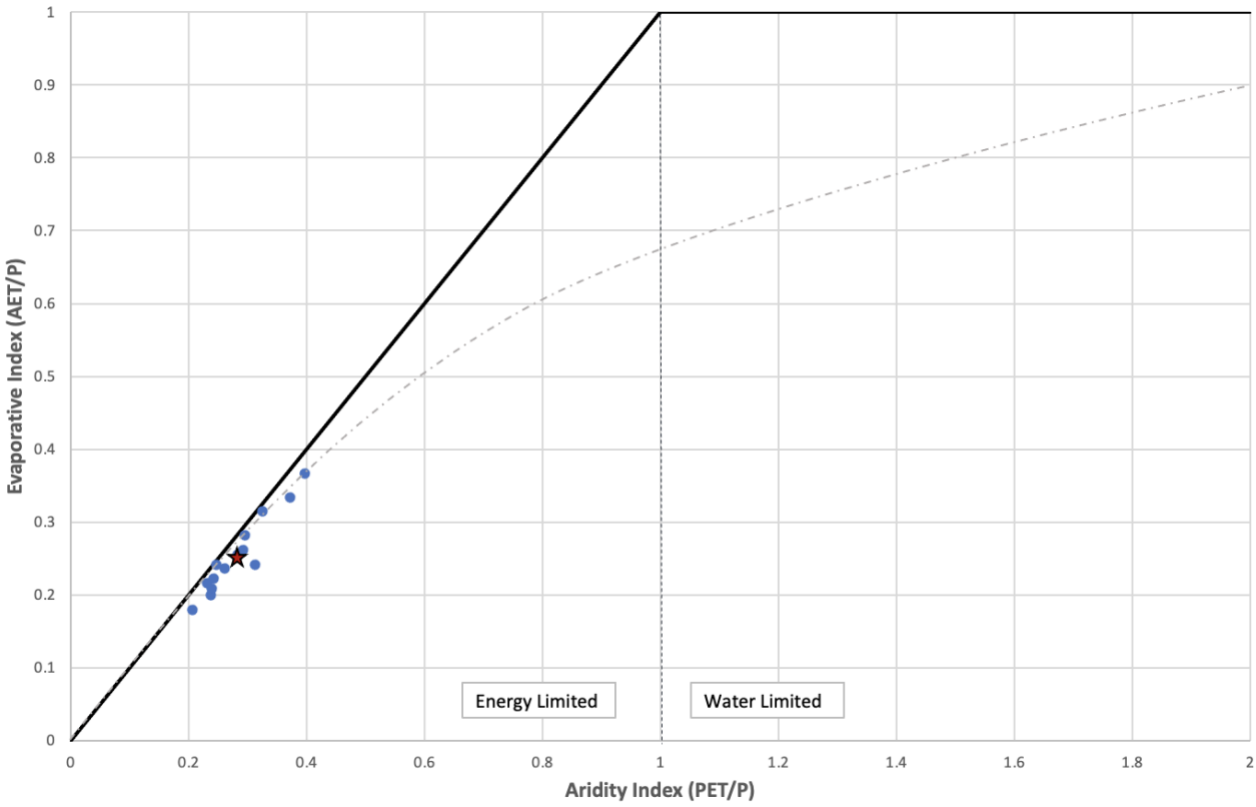

Figure 10. Annual (blue) and Overall (red) Evaporative vs Aridity indices against Budyko curve

Nevertheless, the northwest pacific region of the United States has seen temperature increases of 0.6°-0.8° over the past century, with weather projections in this area suggesting further exacerbated warming of 2-5° C and conversely low discharge due to lowered precipitation and snowpack by the turn of the next century (Abatzoglou et al., 2014; Mote et al., 2005). While this meteorological shift also implies an earlier snowmelt period and higher rainfall events during the spring, lower flows during the summer can have negative implications for residential and industrial water supply as well as on aquatic animals that depend on reliable flow patterns and stream temperatures for survival (Tohver et al., 2014; Farley et al., 2011).

Stream Chemistry

Monthly and annual time-series analysis of DOC concentrations (Figure 11) in both watersheds revealed similar annual behavioral patterns. WS02 concentrations centered at a mean of 1.36E-04 mol/L, while WS01 sat slightly lower at 1.07E-04 mol/L on average. Monthly trends were more reflective of seasonal variation and export of DOC, and the temporality of highs and lows are similar throughout both catchments, although the unharvested watershed 2 tends to have maximum DOC concentrations higher than watershed 1 during yearly peaks. The harvested forests floors are also home to less course woody debris and live biomass which are important DOC sources, WS02 having 894 mg/ha of biomass while WS01 only has 167 mg/ha of biomass (Lajtha & Jones, 2018). Land carbon stocks are believed to take time on the magnitude of centuries to fully replenish, and our temporal analysis shows that even decades after clearcutting, DOC and its potential sources remain depleted in harvested watersheds compared to their unharvested analogs (Gray et al., 2016).

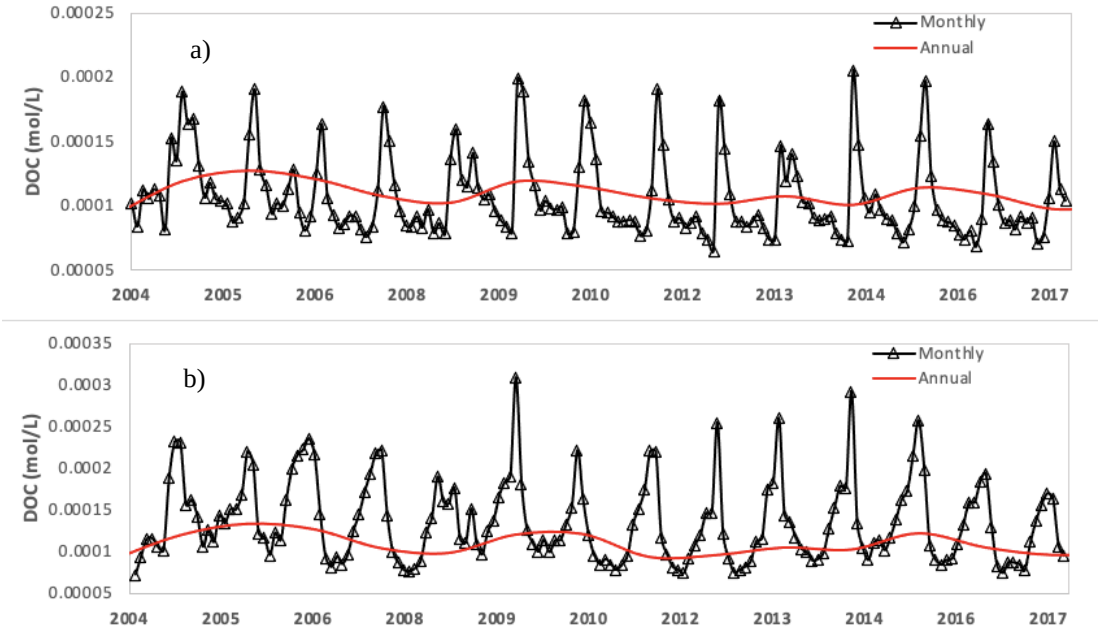

Figure 11. Annual and Monthly DOC time series graphs for a) WS01 and b) WS02

This seems to indicate that although clearcutting initially lowers soil organic carbon and causes it to be mobilized by streamwater instead, this effect is temporary. Eventually, as the system continues to export the excess nutrients to regain equilibrium, the aquatic environment once again depends on transport of terrestrial carbon. However, since the soil has seen such a rapid loss of carbon that is difficult to recover even after 4 to 5 decades, the riverine concentrations of DOC eventually lower along with their terrestrial input, reflecting the organic matter depletion as a result of harvesting in the long run.

Concentration-discharge (CQ) analysis in Figure 12 revealed that the two watersheds had near-identical behaviors for most solutes, aside from DOC. Tracers such as chloride behaved chemostatically due to their non-reactive nature, while alkalinity (which was used as an inorganic carbon indicator), calcium, and magnesium displayed dilution behavior.

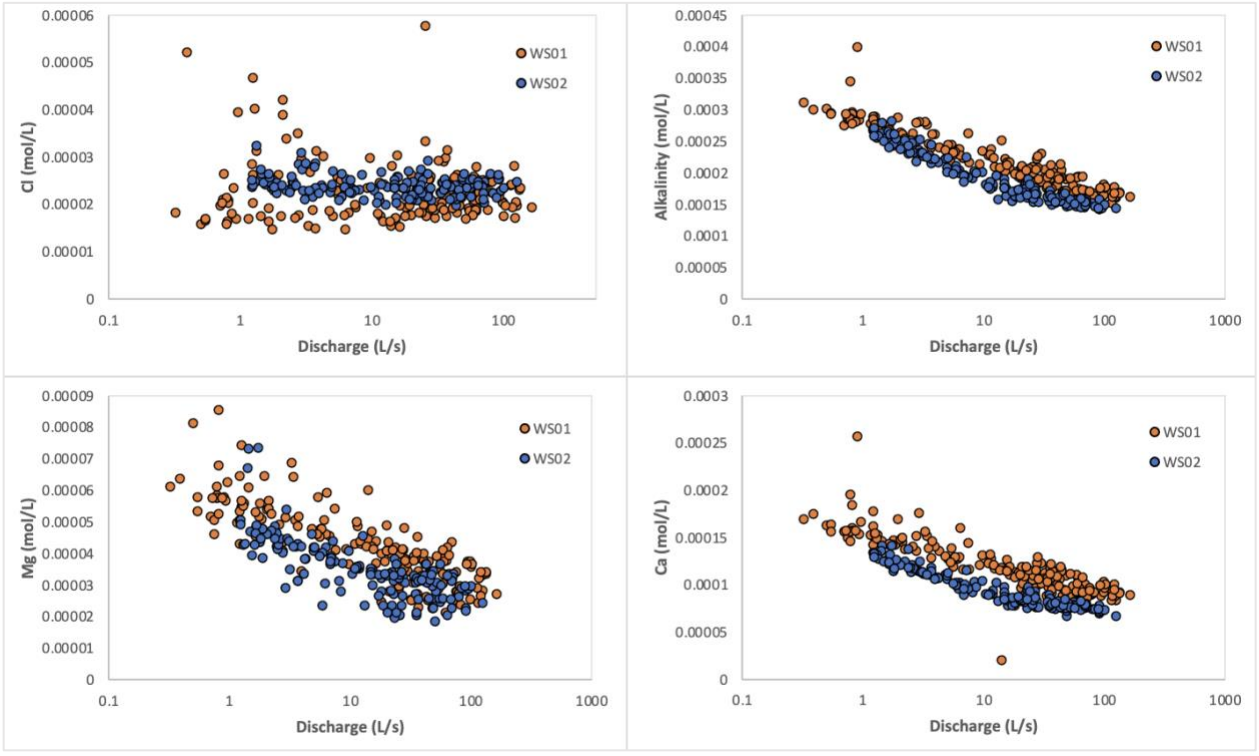

Figure 12. C-Q graphs of Chloride, Alkalinity, Magnesium and Calcium

This aligns with the shallow-deep hypothesis, which theorizes that major cations and inorganics have higher groundwater concentrations due to underlying geology which are then subject to dilution by precipitation and high-flow events (Zhi & Li, 2020). In accordance with the hypothesis, we would usually expect to see DOC flushing behavior. This is because organic solutes such as carbon and nitrogen are often more abundant in the shallow zone due to soil respiration and photosynthesis and tend to have low groundwater concentrations as a result. We observed this in WS01, which displayed slight flushing behavior bordering on hysteresis. However, WS02 exhibited a pronounced dilution effect, which is considered highly unusual. These contrasting patterns are illustrated in Figure 13. This indicates that the control watershed could have an important groundwater organic carbon source, which was perhaps damaged in some way by clearcutting, explaining the lowered DOC concentrations at low flow in WS01.

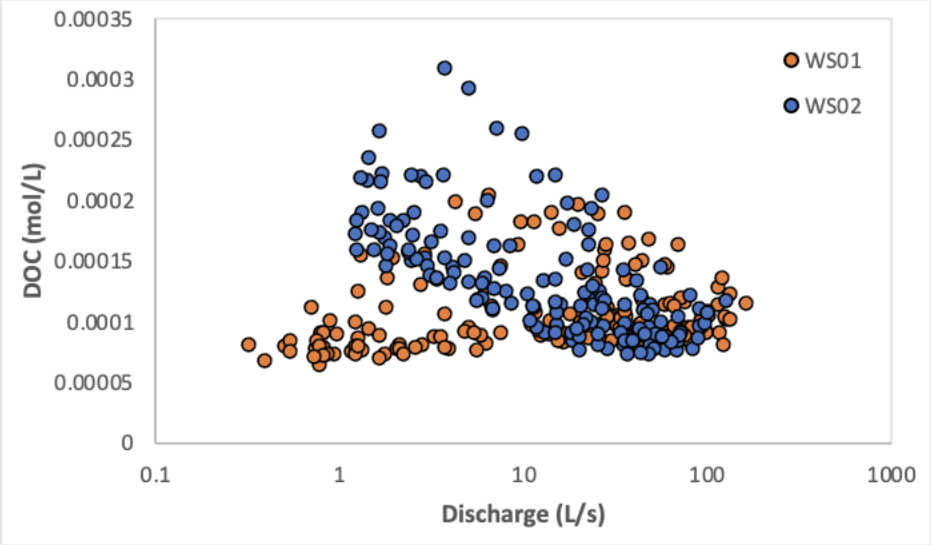

Figure 13. C-Q graph of Dissolved Organic Carbon in WS01 and WS02

We also generated hysteresis figures (Figure 14) of DOC C-Q behaviors throughout the water years of 2005 to 2018. Although large sporadic precipitation events led to often indecipherable

zigzagging of riverine organic carbon concentrations, the year 2013 had smaller and more consistent storm patterns which clearly revealed the seasonal export of DOC in both watersheds.

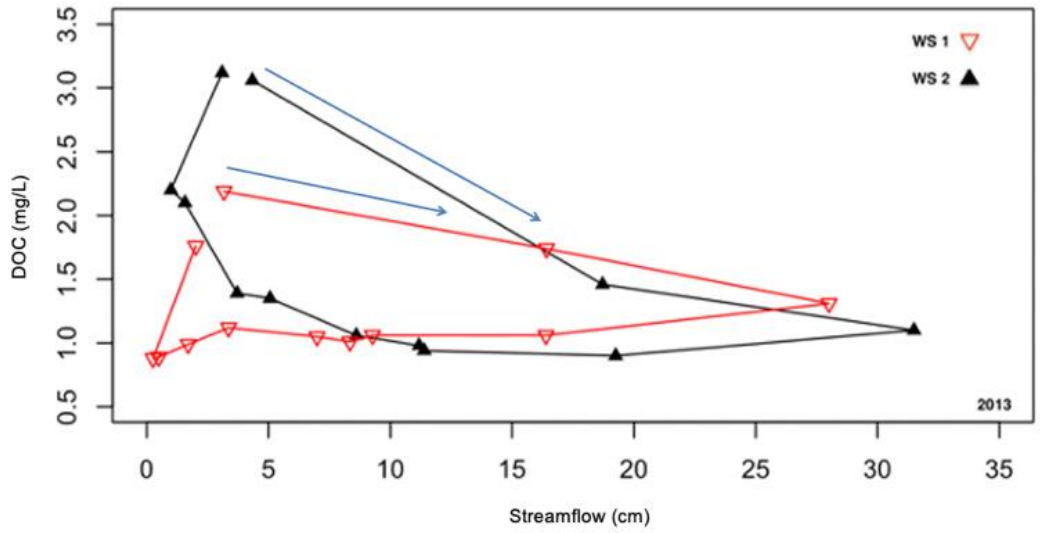

Figure 14. Hysteresis of monthly DOC behavior in WS01 and WS02 against streamflow

The clockwise loop for watershed 2 shows that DOC concentrations peak at the beginning of the water year, before being exported out during late fall and early winter (Lajtha & Jones, 2018). After this, throughout late spring and early summer DOC is produced to replenish the original streamwater organic carbon levels. It is clear to see that WS02 in general has much higher baseflow concentrations of DOC than WS01. Although watershed 1 does exhibit looping behavior, the export and influx of DOC is much less pronounced, and the low-flow concentrations are usually quite similar to the high-flow conditions.

Modelled Stream Chemistry

BioRT results were generally able to characterize the temporality of peaks and dips in the behavior of dissolved organic carbon (DOC) in the stream. However, as shown in Figure 15, the model tended to overestimate DOC concentration during periods of high flow, while underestimating concentrations during lower discharge periods. During high discharge periods in response to precipitation events or snowmelt, the total discharge is composed of "younger" water (Q_0, Q_1) from the upper zone where the decomposition of soil organic carbon into DOC and minimal CO_2 dominates. Under low flow regimes, we see a larger contribution of groundwater (Q_2) to the river, and the decreased concentrations reflect DOC consumption due to the secondary lower zone decomposition reaction discussed earlier. It is important to note that measured carbon data was only plotted on a monthly basis compared to the diurnal simulated values, so the extent of the highs and lows of the model's output may not have been captured in the gauged stream chemistry.

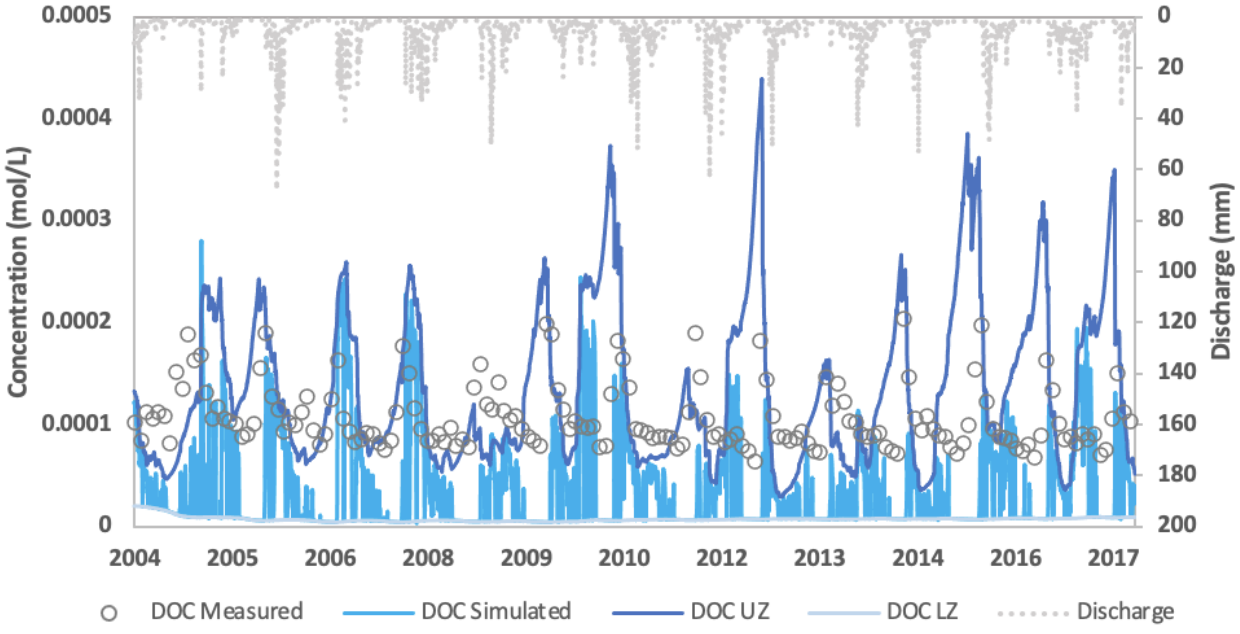

Figure 15. DOC modelled stream chemistry from 2004-2017

However, upper zone dissolved organic carbon concentrations were found to be much higher than those found in the lower zone, averaging 1.35E-04 mol/L and 6.28E-06 mol/L respectively. A closer look at seasonal variations in DOC export (see Figure 16) further confirmed that upper zone reaction rates and hydrology are the primary drivers of temporal fluctuations of organic carbon. Increased DOC production in the riparian zone during the warmer period from early June to late September shows the positive relationship between organic carbon production and temperature. Nevertheless, the overall river chemistry does not end up reflecting this temperature dependence due to low discharge during this time, and organic carbon ultimately decreases in the stream during the summer.

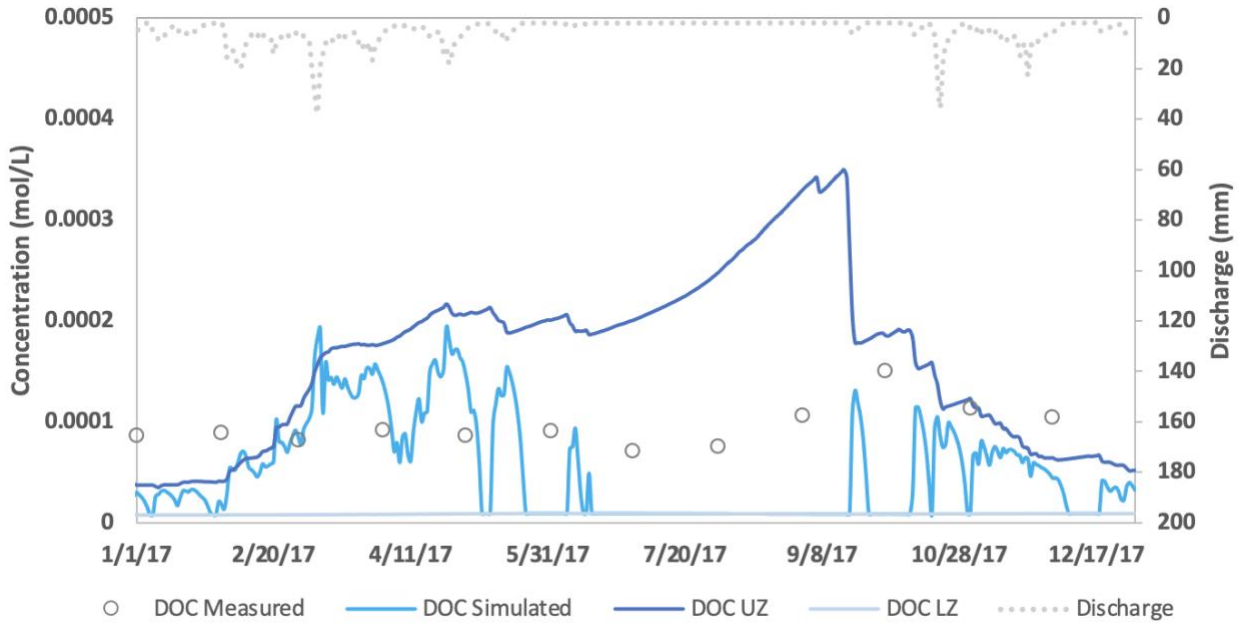

Figure 16. 2017 DOC modelled stream chemistry

Model outputs for dissolved inorganic carbon, while also largely capturing the overall stream fluxes of the species, seemed to underestimate DIC concentrations during discharge peaks as seen in Figure 17. Because the lower zone decomposition reaction uses DOC from the upper

zone as an electron acceptor to source stream inorganic carbon, it conceptually aligns that upper zone DIC is much lower than that found in groundwater. Indeed, average upper zone inorganic concentrations centered around 1.12E-05 mol/L, while the lower zone average level was larger at 1.38E-04 mol/L. This confirms that upper zone organic carbon percolation into deeper catchment areas and subsequent decomposition is a major contributor to the dominance of inorganics with depth in the HJ Andrews experimental forest, especially given that the minimal carbonate rock content underlying the catchment does not contribute to DIC in deeper zones due to weathering (Corson-Rikert et al., 2016). Additionally, modeling revealed that sorption is not a major organic carbon sink compared to microbial DOC consumption into DIC, with sorbed DOC (XDOC) average concentrations relatively minimal in both the upper and lower zones at 2.84E-06 mol/L and 2.51E-12 mol/L respectively.

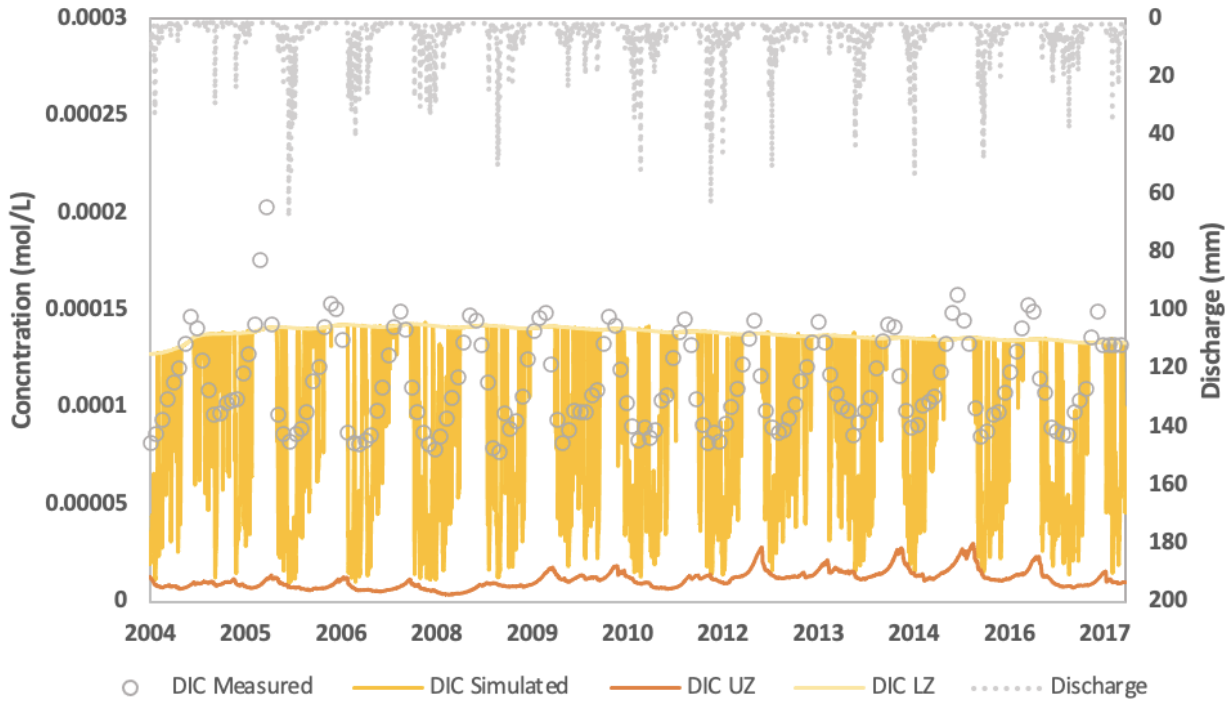

Figure 17. DIC modelled stream chemistry from 2004-2017

Inorganic carbon sees an opposite seasonal pattern to that of DOC, in that streamwater concentrations increase during dryer intermediate periods of the year while lowering during the wetter and colder months (Figure 18). DIC remains largely stagnant in the upper and lower zones alike year-round, and its presence in the stream is largely dependent on the extent of precipitation events diluting inorganic carbon concentrations in the first and final thirds of the year, and low-discharge summers flushing out more recalcitrant carbon from groundwater flow. Given this, further calibration by increasing the reaction coefficient defining DIC production in the upper zone from its current value of 0.2 within the BioRT reaction database is suggested, to increase the level of riparian inorganic carbon and avoid the periodic underestimation during high flow observed in the simulated stream chemistry in the months following October through May.

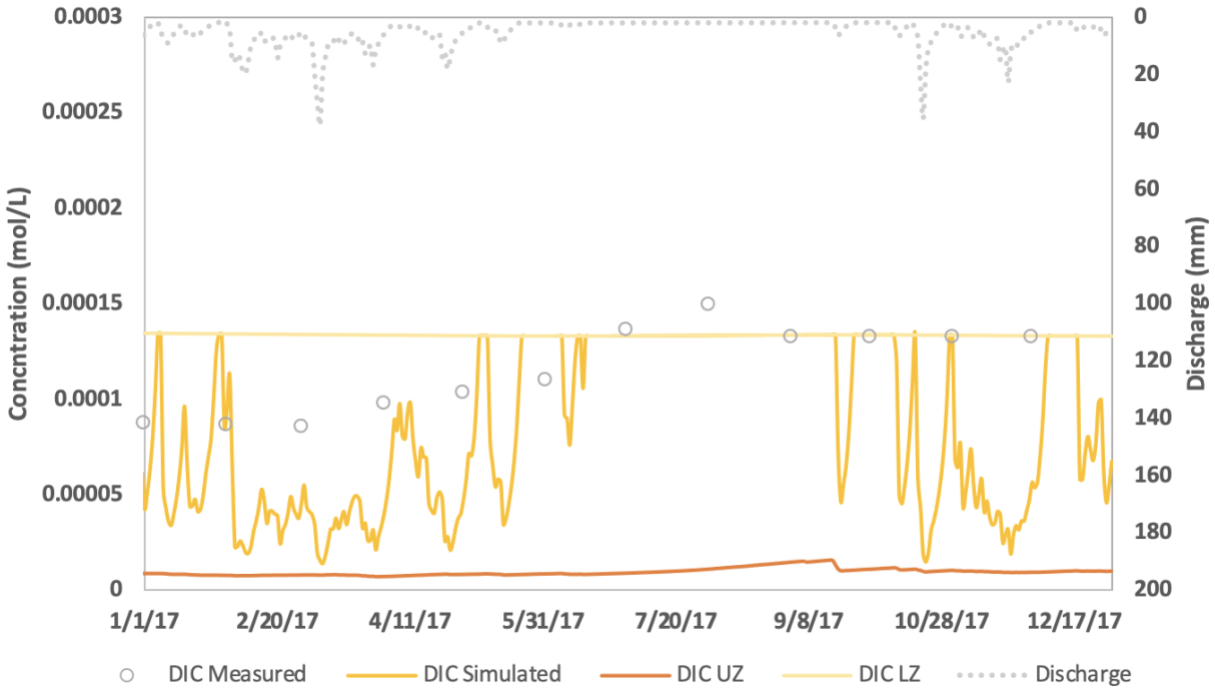

Figure 18. 2017 DIC modelled stream chemistry

Generated stream chemistry values from BioRT were plotted against HBV-light's discharge output in Figure 19 to further quantify concentration-discharge relationships for the fourteen-year period. As expected, DOC exhibited flushing behavior, although variations in storm events led to diverging DOC values under intermediate flow patterns. The modelled stream chemistry was also able to successfully capture the hysteretic behavior of DOC, showing increasing organic carbon production with discharge until watershed saturation leads to large amounts of overland and lateral flow contributing to the stream and ensuing DOC export. Conversely, DIC showed a strong dilution pattern with more, although minimal, divergence under low-flow conditions. These CQ relationships follow the tenants of the shallow-deep hypothesis as periods of low discharge are characteristic of groundwater chemistry dominated by inorganic carbon sourced from lower zone uptake of DOC, while increasingly with discharge organic carbon governs stream carbon composition due to the contribution of decomposition in the upper zone to the more active lateral flows at this time.

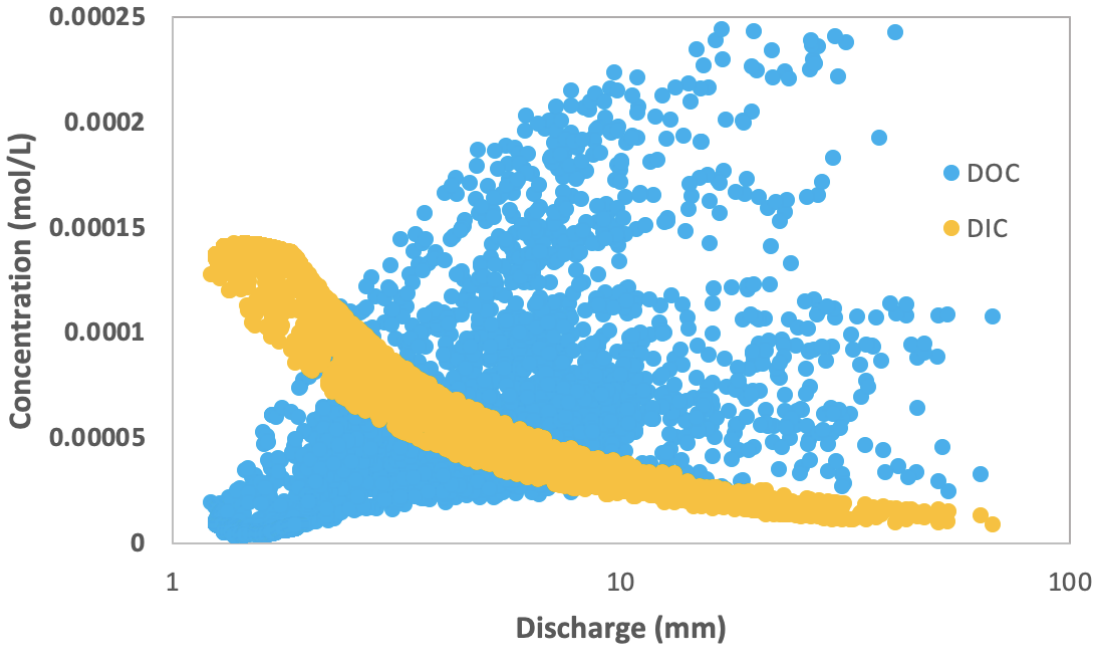

Figure 19. C-Q graph of Dissolved Organic Carbon and Inorganic Carbon model outputs

Chapter 5: CONCLUSION AND FUTURE WORK

This study paired hydrological, meteorological, precipitation and stream chemistry data from the mountainous and harvested Watershed 1 (WS01) located in the HJ Andrews Forest of the Oregon Cascades. Hydrological modelling of WS01 suggests that the dramatic variation of the catchment's flow partitioning is a result of both climactic and ecological variables, as displayed by significant summer deficiencies. The catchment was found to be severely energy limited, with the predominance of lateral flow during the early spring and winter reflective of precipitation and snowmelt contribution. Lateral flow fractions ranged from 35.5% to 56% during low precipitation and high precipitation periods respectively, while baseflow ranged from 27.7% to 64.4% of total discharge as conditions shifted from wet to dry. Notably, the extent of summer streamflow depletion and reliance on groundwater flow during this season indicates the vulnerability of the site's streamwater supply to aridity changes brought forth by exacerbated elevation-dependent warming, as well as the younger forest biota due to clear-cutting undergoing higher vegetative transpiration rates.

Time-series and C-Q analysis of measured data also revealed that harvested forests suffer from soil carbon loss compared to their old-growth counterparts, which over time reflects on dissolved organic carbon concentrations. Modelling of WS01 depicted the importance of upper zone soil respiration and lower zone decomposition in stream organic and inorganic carbon appearance. Hydrology and biogeochemistry are closely intertwined, with model results showing DOC flushing with increased upper zone flow, and DIC dilution with discharge due to dominance in the lower zone. Simulated upper zone average DOC concentrations were two orders of magnitude higher than lower zone levels, while overall riparian DIC concentrations were an order of magnitude smaller than groundwater levels. Lowered surface and upslope flow in the

future could lead to a further decline of organic carbon concentrations and potentially pose a problem to the river ecosystems relying on organic matter, which is already low as the catchment continues to recover from harvesting, as an oxygen source. Increased inorganic carbon due to stream dependence on groundwater as climate warms can also lead to larger amounts of carbon dioxide evasion contributing to the atmospheric CO_2 budget.

Overarchingly, this study also reveals the potential usefulness of reactive transport models in estimating more frequent hydrology and biogeochemistry data than is currently measured due to the limitations of collection. Suggested future work includes application of the HBV-BioRT model on the control watershed WS02 to investigate the source of its unique organic carbon dilution pattern, potentially revealing an underlying geological or lithological contribution distinct to the Cascades that was altered by land-use changes in our studied watershed.

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APPENDIX A. HBV-Light Annual Summaries

Year	Total Q (mm)	Annual Q0 (mm)	Annual Q1 (mm)	Annual Q2 (mm)	Q0 Contribution	Q1 Contribution	Q2 Contribution	Observed Q (mm)
2004	1113.19	79.12	576.31	457.76	7.11%	51.77%	41.12%	911.61
2005	1186.36	120.32	582.69	483.35	10.14%	49.12%	40.74%	878.38
2006	1865.67	353.96	994.55	517.16	18.97%	53.31%	27.72%	1229.49
2007	1494.11	146.76	808.06	539.29	9.82%	54.08%	36.09%	921.94
2008	1635.58	218.91	839.14	577.53	13.38%	51.31%	35.31%	1121.59
2009	1414.88	99.55	722.18	593.14	7.04%	51.04%	41.92%	927.25
2010	1640.05	107.99	916.76	615.30	6.58%	55.90%	37.52%	1142.97
2011	1481.33	115.31	718.19	647.83	7.78%	48.48%	43.73%	988.03
2012	2211.87	325.31	1228.51	658.06	14.71%	55.54%	29.75%	1521.61
2013	1037.94	1.86	368.06	668.01	0.18%	35.46%	64.36%	621.18
2014	2009.09	255.89	1083.08	670.11	12.74%	53.91%	33.35%	1363.78
2015	1363.89	188.49	516.46	658.94	13.82%	37.87%	48.31%	719.30
2016	1408.68	32.22	719.04	657.42	2.29%	51.04%	46.67%	961.11
2017	1805.06	113.68	1010.10	681.27	6.30%	55.96%	37.74%	1228.42
Average	**1547.69**	**154.24**	**791.65**	**601.80**	**9.35%**	**50.34%**	**40.31%**	**1038.33**

Year	Annual AET (mm)	Annual PET (mm)	Aridity Index	Evaporative Index
2004	589.83	608.91	0.32	0.31
2005	571.94	599.29	0.30	0.28
2006	555.47	605.60	0.24	0.22
2007	525.62	581.71	0.26	0.24
2008	472.11	563.38	0.24	0.20
2009	460.28	596.97	0.31	0.24
2010	579.49	595.22	0.25	0.24
2011	517.55	571.60	0.28	0.26
2012	521.72	597.80	0.21	0.18
2013	555.66	601.88	0.40	0.37
2014	592.02	633.75	0.23	0.22
2015	599.14	666.82	0.37	0.33
2016	542.38	605.35	0.29	0.26
2017	506.73	582.14	0.24	0.21
Average	542.14	600.74	0.28	0.25

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- Developed experience in the analysis of biogeochemical cycles using software such as XGBOOST, HBV, and BioRT with Dr. Li Li
- Used machine learning techniques to model bicarbonate concentrations across the US and pinpoint most influential environmental attributes

Jun. – Aug. 2021 **NSF Climate Science REU, Pennsylvania State University**
Project: Comparing the Dynamics of Dissolved Organic Carbon in Harvested and Unharvested Watersheds within the Oregon Cascades (Accepted AGU Abstract)

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Taught physics, differential equations, and engineering mechanics to college underclassmen

Aug. 2021 **Summer Program Instructor, Fairfax Collegiate**
Introduced basic Aerospace Engineering and Forensic Science concepts to students ranging from 5^{th}-8^{th} grade

LEADERSHIP

Aug. 2020 – present **Treasurer, Minorities in EMS**
Worked on initiatives to support diversity in the earth and mineral sciences, foster a sense of community, and promote professional development

Jan. 2020 – May 2021 **Learning Assistant**, **Physics 212**
Provided answers to student questions in electricity and magnetism course within and outside of class, in addition to facilitating problem solving sessions and providing written explanations

SKILLS

Programming: R, MATLAB, Mathematica

AWARDS

May 2021 Best Poster at Celebration of Undergraduate Engagement (CUE)
Nov 2020 ePoster Presentation Award at ABRCMS