# BIOPHYSICAL CONTROLS ON NITROGEN AND PHOSPHORUS CONCENTRATIONS IN ALASKAN COASTAL TEMPERATE RAINFOREST STREAMS

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Master of Science

by
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# ABSTRACT

Thousands of watersheds drain from the perhumid coastal temperate rainforest (PCTR) of southeast Alaska into the nearshore estuary. This region is characterized by high rates of precipitation which interacts with terrestrial ecosystems and transports nutrients downstream. Modeling N and P fluxes from land to sea in the PCTR is needed to 1) incorporate nutrient losses into regional terrestrial productivity models and 2) determine the magnitude of this subsidy to downstream aquatic ecosystems. In order to develop estimates of these fluxes, models of stream water N and P concentrations are needed which can be scaled across the landscape. In this study, we develop statistical models for both organic and inorganic forms of N and P using biophysical watershed characteristics and stream chemistry data from a large-scale synoptic survey including 57 independent watersheds with varying degrees of wetland extent, topography, and natural and anthropogenic disturbance legacies. We also take into account the influence of salmon spawning events and seasonal controls on stream chemistry. Overall, dissolved organic nitrogen (DON) comprised 81% of total dissolved N in fall and 69% in spring, while dissolved organic phosphorus (DOP) comprised 59% of total dissolved phosphorus in fall and 69% in spring. The overall dominance of DON and DOP over inorganic forms emphasizes the importance of soil development and leaching of organic matter on stream chemistry in the PCTR, and the significance of variables that indicate organic rich soils in the landscape in our final models supports this finding. Our final statistical models show that the presence of salmon spawning in the fall increased inorganic forms on N and P, as well as DOP. Interestingly, neither salmon spawning nor disturbance variables related to successional nitrogen fixing vegetation were retained in our final DON model. The proportion of the watershed with slopes $<5°$ was the best predictor of stream DON concentrations. Overall, these models were able to explain 65% of the variance in DON, 32% DOP, 56% DIN and 38% SRP. Our results suggest that season, salmon spawning activity, topographic slope variables indicative of organic rich soils, disturbance legacy and successional vegetation are useful predictors of stream N and P.

# BIOGRAPHICAL SKETCH

Elizabeth (Liz) Kreitinger holds a B.S. from the Department of Natural Resources at Cornell University. She is grateful to have had the opportunity to return to Ithaca, NY after several years of work and adventure to peruse a graduate degree from her alma mater while collaborating with scientists at the US Forest Service in Juneau, Alaska.

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Finally, I'd like to thank my parents, Mary and Joe, for always encouraging me to continue exploring and learning, and Wade, whose enthusiasm and curiosity for the natural world inspire me every day.

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# CHAPTER 1

# BIOPHYSICAL CONTROLS ON NITROGEN AND PHOSPHORUS CONCENTRATIONS IN ALASKAN COASTAL TEMPERATE RAINFOREST STREAMS

## *1.1 Introduction*

Thousands of watersheds drain directly from the coastal mountains of Southeast Alaska to the nearshore estuary. This region is part of the perhumid coastal temperate rainforest (PCTR), which stretches from coastal British Columbia through Southeast Alaska, and is defined by high annual precipitation (Figure 1). Approximately 370 $km^3$ $y^{-1}$ of freshwater is exported from land to sea along the coastal margin of Southeast Alaska; equivalent to 60% the annual discharge of the Mississippi River, from a drainage area 13% of its size (Neal et al. 2010; NPS 2018). However, no estimates of hydrologic nitrogen (N) and phosphorus (P) export currently exist at the ecosystem scale for this region. Runoff from non-glacial streams accounts for 68-78% of the discharge from Southeast Alaska. Estimates of hydrologic N and P export from these streams are needed to 1) incorporate nutrient losses into regional terrestrial productivity models and 2) determine the magnitude of this subsidy to downstream aquatic ecosystems.

PCTR soils are characterized by high rates of organic matter accumulation and leaching (D’Amore et al. 2015a). Wetlands occupy 22% of the PCTR landscape, in contrast to 5.5% in the lower 48 states (Dahl, 2006; USFWS 2009). Compared to other temperate forests, the PCTR has some of the highest organic matter stocks in the world (Gorham et al. 2007). Hydrologic transport of dissolved organic matter (DOM) from these wetlands and organic soils is an important source of dissolved organic carbon (DOC) to coastal streams (Fellman et al. 2009a; D'Amore et al. 2016). Wetlands have also been documented as sources of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) to streams. In previous site specific studies of PCTR stream nutrient concentrations, dissolved organic nitrogen (DON) was 80% of total dissolved nitrogen (TDN) and dissolved organic phosphorus (DOP) was the dominant fraction of total dissolved phosphorus (TDP) (Fellman et al. 2009a).

Research from other temperate forests substantiate the potential importance of DOM exports from soils to streams. In analogous temperate rainforests of southern Chile receiving low levels of atmospheric N deposition, DON was the dominant component of TDN relative to inorganic nitrogen (DIN) (Kortelainen et al. 1997; Perakis and Hedin 2002). The dominance of DON relative to DIN in stream water has also been documented in other northern temperate forests (Sollins and McCorison 1981; Campbell et al. 2000; Goodale et al. 2000). High rates of N and P loss as organic forms compared to relatively low input rates could contribute to the long term limitation of terrestrial productivity in ecosystems like the PCTR (Vitousek et al. 1998), while promoting hotspots of metabolism downstream.

The chemical quality and composition of DOM in streams is reflective of both terrestrial and aquatic processes, with the relative influence of the terrestrial ecosystems decreasing as stream order increases (Vannote et al. 1980). Many studies have found landscape soil, vegetation, and topographic attributes to be useful predictors of stream chemistry at the watershed scale (Aitkenhead-Peterson et al. 2005, 2007; Kortelainen et al. 2006). Research within the PCTR has shown that biophysical characteristics of watersheds can be useful predictors of stream chemistry, which may be magnified by the relatively short, steep nature of streams in the region  (Brookshire, E.N.J., Valett, H.M., Gerber 2009; Fellman et al. 2009a). However, in stream processes cannot be discounted. In particular, spawning salmon have been documented to influence stream chemistry through sediment disturbance and fertilization, and can significantly increase stream N and P concentrations or have a negative effect on stream nutrients, complicating the story of terrestrial and aquatic drivers of stream chemistry (Chaloner et al. 2002; Hood et al. 2007; Janetski et al. 2009; Tiegs et al. 2009). The largest salmon spawning events in southeast Alaskan streams occur between late summer and fall, which also coincides with high seasonal precipitation. Our study considers the complex influence of landscape factors, season and salmon spawning on concentrations of organic and inorganic N and P. We developed statistical models that can be useful predictors of watershed N and P loading in this region spanning >4° latitude, with varying climate, parent material, topography, vegetation, and legacies of natural and anthropogenic disturbance.

D'Amore et al. (2016) established a framework for testing the relationship between stream DOC concentration and wetland cover, season and salmon spawning activity in non-glacial PCTR streams. Glacial streams were excluded from this analysis due to their differing hydrologic regimes and chemical signatures. In the present study, we test if similar relationships exist between stream water DON, DOP and slope attributes; slope attributes have been shown to be stronger predictors of DOC than wetland extent, likely due to mapping inaccuracy of wetlands in the PCTR (Creed et al. 2003; D'Amore et al. 2015a, 2016). We also test other biophysical variables that may influence stream chemistry including disturbance history, successional vegetation, and topography to improve prediction of DON and DOP as well as inorganic N and P. In order to make the models useful for predicting stream nutrient concentrations in non-glacial streams throughout the region, we selected additional variables that are mapped throughout the PCTR. These concentration models provide the first steps toward regional N and P flux estimates from terrestrial to aquatic systems in the PCTR which will improve our understanding of current and future limitations on net primary productivity across the coastal margin.

Figure 1. The extent of the Northeast Pacific coastal temperate rainforest, including the Alaska perhumid coastal temperate rainforest region (D’Amore et al. 2016).

Source: Inforain, Ecotrust, Pacific GIS, & Conservation International

## ***1.2 Methods***

### *1.2.1 Study Area*

This investigation was conducted in the Alaska drainage basin of the PCTR which extends 800 km from Dixon Entrance in the south to Yakutat at the northern extent (Figure 2). The basin encompasses approximately 8.5 million ha of the Pacific Mountain system, where the landscape transitions abruptly from sea level to rocky alpine ecosystems. Parent material throughout the region includes coarse-textured Holocene deposits or a combination of colluvium, glacial drift deposits and weathered bedrock (Krosse 1993).

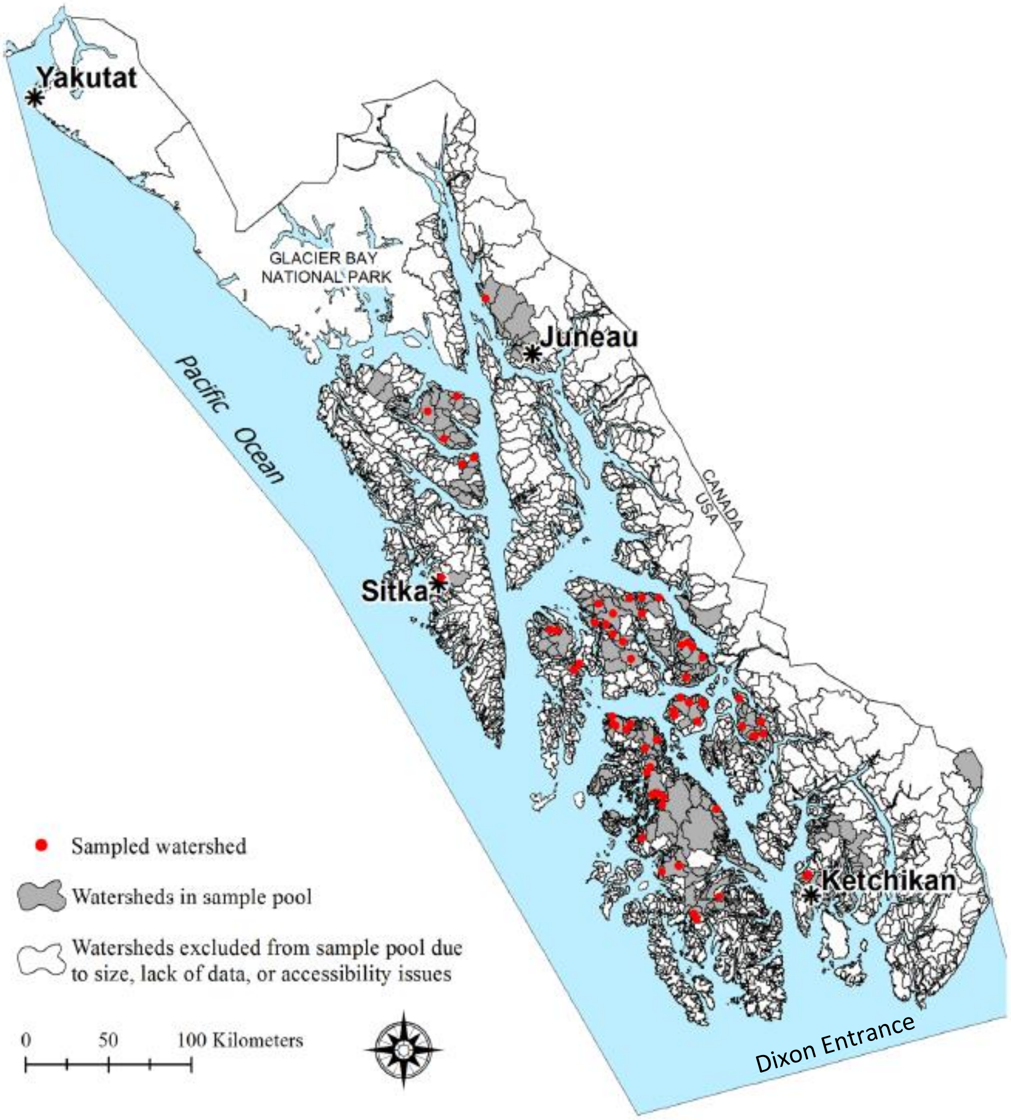
Temperature and precipitation in the PCTR vary based on topography, elevation and latitude (Farr and Hard 1987). The average summer temperature is approximately 18° C while winter temperatures near the coast hover around freezing (WRCC 2019) . Oceanic pressure systems and orographic effects drive precipitation throughout the PCTR, and evapotranspiration rates are relatively low (Neal et al. 2010). Annual rainfall ranges from 150 to 500 cm, with maximum precipitation occurring in September and October (Alaback 1996). This abundant precipitation interacts with PCTR soils, playing an important role in soil development and transport of materials from soils to streams. Soils are generally 50-150 cm deep, but some have been documented up to 500 cm in deep peatlands. Many soil taxonomic groups are represented resulting from heterogeneity in topography, including Spodosols which exist on well drained upland slopes and Histosols dominate wetland areas throughout the landscape (D’Amore et al. 2012).

PCTR vegetation communities vary with topography and the resulting hydrologic gradients (D’Amore et al. 2015b; Bisbing et al. 2016). Spagnum-dominated peatlands with *Pinus contorta* (shore pine) are common on gentle slopes and mixed conifer forests with low overstory diversity are found across the uplands. *Picea sitchensis* (Sitka spruce) is the dominant tree species in steeper wetlands and uplands, and mixes with *Tsuga heterophylla* (western hemlock) and *Tsuga mertensiana* (mountain hemlock) which dominate on drier soils. Deciduous tree species include *Populus balsamifera* (black cottonwood), *Alnus rubra* Bong, *Alnus viridis* (red and Sitka alder) and *Salix spp*. (willows). *Callitropsis nootkatensis* (Alaskan yellow cedar) also occur in smaller patches.

### *1.2.2 Site Selection*

In the initial phase of site selection, watersheds ≥ 121.4 ha (300 acres) draining to saltwater were identified from the USFS level 6 Hydrologic Unit Code (HUC) data layer in ArcGIS (ESRI 2005). In total, 2,689 discrete watersheds were identified in the sample pool before being further filtered on the basis of accessibility. After filtering for accessibility, removing watersheds with poorly defined boundaries, and using random stratified sampling to select from the remaining watersheds to achieve a broad distribution of proportional wetland area, 65 watersheds were identified for sampling (Figure 2). For more details on watershed selection see D’Amore et al. 2016. A list of watersheds used for this investigation and their attributes are included in Appendix A.

Figure 2. Alaska perhumid coastal temperate rainforest zone with all watersheds in the initial sample pool, the candidate pool after screening, and sampled watersheds (D’Amore et al. 2016).



### *1.2.3 Sample Collection*

Sampling was conducted during spring (mid-June) and fall (late September to early October) of 2005 to capture seasonal descending and ascending hydrograph trends. Water was collected from streams near the outflow into coastal waters but above tidal influence. Acid rinsed polyethylene bottles were pre-rinsed with site water and used to collect water samples from each stream. Samples were filtered through pre-combusted, glass fiber filters (nominal pore size 0.7 µm) immediately after sampling, then stored in cool conditions and analyzed within 72 hours.

Sample locations were recorded using a handheld GPS. Those coordinates were used to build updated watershed boundaries in ArcGIS for use in subsequent analysis. A total of 61 watersheds were sampled in spring. Four streams were not resampled in the fall due to accessibility issues. The 57 streams that were resampled in the fall were used for analysis in this study.

### *1.2.4 Laboratory Analysis*

Stream water samples were analyzed at the USFS Juneau Forestry Sciences Lab in Juneau, AK for N and P concentrations. Total dissolved nitrogen (TDN) was quantified by high-temperature combustion on a Shimadzu TOC-V Organic Carbon and Total Nitrogen Analyzer. Lower detection limit (LDL) for TDN was 100 µg N $L^{-1}$.

Nitrate ($NO_3^-$) and ammonium ($NH_4^+$) were measured with ion chromatography (Dionex anion DX-600, cation ICS-1500), and TDN was analyzed using a separate module on a Shimadzu TOC/TN-V. DON was calculated as the difference between TDN and DIN ($NO_3^- + NH_4^+$). TDP was quantified using the persulfate digestion technique (Valderrama

1981) and the ascorbic acid method (Murphy and Riley 1962). Soluble reactive phosphorus (SRP) was quantified using the ascorbic acid method, and DOP was calculated based on the difference between TDP and SRP. Low P detection of 1.0 μg P $L^{-1}$ was achieved with a 10 cm quartz flow through cell.

### *1.2.5 Biophysical Parameters*

Percent wetland area was used in the site selection process and was also in the pool of independent variables examined during model selection. The USFWS National Wetlands Inventory (NWI) data layer (USFWS 2009) was used to calculate the percent area within each watershed covered by mapped wetlands. All wetland types identified in the NWI layer were summed into a single NWI-Wet value. Both NWI-Wet and its separate components were tested during model selection. Wetland types in the PCTR include palustrine forested wetlands (NWI-PF), palustrine emergent wetlands (NWI-PE), palustrine scrub-shrub (NWI-PS) wetlands and palustrine unconsolidated bottom ponds (NWI-PUB) which on average account for 25%, 12%, 2% and .2% of the land area in our study watersheds, respectively (Cowardin et al. 1979; USFWS 2009). Lakes (NWI-Lac1, NWI-Lac2) were also included in the calculation of NWI-Wet, but not evaluated independently since they occurred in too few watersheds to meet statistical assumptions. NWI-Wet cover by watershed is summarized in Appendix A.

In addition to the NWI wetland variables, topographic characteristics were calculated from the USGS National Elevation Dataset 2 arc second Alaska digital elevation model (DEM) using ArcGIS and evaluated during model selection. These variables included average watershed slope in degrees (SlopeAvg), percent of the watershed with 0-

5° slopes (Slopes0-5), percent of the watershed with 0-10° slopes (Slopes0-10), percent of the watershed with greater than 20° (Slopes>20), and percent of the watershed with greater than 30° (Slopes>30). Average watershed elevation in meters (ElevAvg) and max watershed elevation in meters (ElevMax) were also used. Variables that affect hydrologic transport processes that were included are watershed area in hectares (WsArea), main stem stream slope in degrees (StrmSlope), stream length in km (StrmLen) and proportion of the watershed mapped as karst (Karst).

Several variables to assess forest vegetation, logging and disturbance histories were calculated based on the USFS-TND managed stands and roads GIS layers in addition to Alaskan state and Native Cooperation GIS layers. Proportions of the watershed logged at 5, 10 and 20 years prior to sampling (Harv5, Har10, Harv20, respectively) were tested in addition to a layer representing logging at all times prior to sampling (HarvAll). To quantify disturbance related to roads, proportion of the watersheds mapped as roads was calculated (Roads). Finally, a layer indicating the proportion of the watershed mapped as tall shrubs (TallShrub) was included. The TallShrub layer includes areas mapped with willow and Sitka alder, which is a host to N fixing bacterium. Other biophysical characteristics that may be useful predictors of stream chemistry, but were not tested due to lack of spatial coverage across the region, include soil C:N and extent of hydric soils. A list of variables calculated for this analysis, summary statistics and their sources are included in Appendix B.

### *1.2.6 Observation of Salmon Runs*

To evaluate the influence of spawning salmon on N and P concentrations, the presence or evidence of large salmon spawning events was recorded at each stream.

Evidence of spawning prior to sampling included an abundance of salmon carcasses within the stream or riparian areas. Based on these observations, 38 streams were assigned as fish bearing (Fish-Y) and 19 streams were assigned as non-fish bearing (Fish-N). The large runs that leave evidence are most likely to alter stream nutrient concentrations, but the magnitude and timing of the runs relative to sampling may contribute to variability in our results. This observational assessment is biased towards large salmon runs; however, no regional dataset currently exists on the magnitude of salmon runs for individual streams. These salmon observations allow us to evaluate their possible influence on concentrations of N and P in coastal watersheds across the PCTR.

### *1.2.7 Statistical Analysis*

#### *Reducing Independent Variable Pool*

For each response variable (DON, DOP, DIN, and SRP) the pool of potentially controlling watershed characteristics was evaluated and reduced. Each independent variables was first screened using regression plots and significance of each bivariate relationship. In order to reduce spurious model results, variables uncorrelated with stream chemistry values ($p<.05$) were removed from the sample pool. Next, variables were screened for multicollinearity. We identified correlated groups of variables with a Pearson’s R statistic of $> 0.8$ or $< -0.8$. To avoid multicollinearity in our models, we selected the highest performing variable from each correlated group to retain in the model selection process. Prior to all subset-model selections, variance inflation factors (VIFs) were checked for each model containing the remaining independent variables to ensure all VIFs were $<4$ (Burnham and Anderson 2004). Based on unsuitability of model fits, DIN and SRP were log transformed and variable screening was repeated with the transformed data.

### *All Combinations Model Selection*

For each response variable, two fixed effect models were developed with data subset by season (fall and spring) and one mixed effect model was developed with the addition of a random effect of watershed-ID to the parameters to account for repeated measures. The separate fall and spring models were developed to help identify independent variables that may have important seasonal effects but for which the significance is lost when the data were combined. Based on our ecological understanding that biological controls of stream chemistry vary seasonally, during the final step of mixed-model selection, season was allowed to interact with each of the remaining main effects. No interaction terms were evaluated for the separate fall and spring models.

All subset-model selections were used to find an optimal set of main effects based on AIC with the "glmulti" function in R (Calcagno 2010). The final models were selected by first finding the model with the lowest AIC. If all terms in the lowest-AIC model were significant ($p<.05$), that model was chosen as the final model. If any terms in the lowest-AIC model were not significant (excluding main effects of significant interaction terms), the model with lowest AIC and all significant terms was selected as the final model. All final models fell within a threshold of < 3 delta-AIC of the best-AIC model for each response. Choosing models with highly significant terms gives us more confidence that we are not overfitting our dataset and the <3 delta-AIC threshold provides strong evidence in support of our final models (Burnham and Anderson 2004). Adjusted $R^2$ values are presented for final fixed-effect models; marginal and conditional coefficients ($R^2_{GLMM(F)}$, $R^2_{GLMM(M)}$) are presented for final mixed effect models (Nakagawa and Schielzeth 2013).

Diagnostics of the final models were assessed to check for normality of residuals and potential leverage points. Slight heteroscedasticity was observed in the DOP plots of residual versus fitted values, but not enough to warrant transformation. Log transformation of DIN and SRP concentrations significantly improved normality of residuals. The fall DOP measurement for watershed 26W was an influential point (Cooks distance > 0.5). The fall 26W DON point was also high compared to values from other watersheds, but was not identified as a leverage point in the DON models. Since we have no reason to suspect the fall data from 26W is non-representative, interpretations in the results and discussion section are based on the model with it included.

## *1.3 Results and Discussion*

### *1.3.1 Dominance of organic forms in overall chemistry*

DON was the dominant form of N in 82% of stream samples, and median $NO_3^-$-N concentrations were approximately three times greater than $NH_4^+$-N. The median ratio of DON:TDN across all watersheds was greater in the fall (0.91, range 0.27-0.96) than in the spring (0.70, range 0.21 - 0.98). The median TDN concentration was also higher during the fall (240 µg-N $L^{-1}$, range 108-1117) than in the spring (177 µg-N $L^{-1}$, range 79-320) (Table 1; Appendix C).

Similar to the trend observed in DON, DOP was also the dominant component of TDP in 82% of the samples, but the median ratio of DOP:TDP across all watersheds showed a trend opposite of DON and was lower in the fall (0.62, range 0.23-0.83) than spring (0.75, range 0.21-0.96). Median TDP concentration was higher in the fall (9.1 µg-P $L^{-1}$, range 4.8-73.3) than in the spring (8.2 µg-P $L^{-1}$, range 1.6-35.4).

The dominance of DON as a fraction of TDN is consistent with results from analogous regions (Meybeck 1982; Campbell et al. 2000; Perakis and Hedin 2002; Scott et al. 2007). In conifer forests of the US, on average, TDN is comprised of 80% DON, 17% $NO_3^-$ and 3% $NH_4^+$. (Binkley et al. 2004). Hedin et al. (1995) characterized TDN concentrations from forested watersheds in southern Chile receiving low levels of atmospheric N deposition, and found that DON made up 95% of the TDN pool, and that $NO_3^-$ and $NH_4^+$ comprised relatively small fractions of TDN (0.2% and 4.8%, respectively). PCTR forest also receive low mean annual N deposition, and in Juneau, AK deposition is 0.43 kg N $ha^{-1}$ $yr^{-1}$, which is an order of magnitude lower then temperate rainforests of the Northeastern US (NADP 2005). Low rates of atmospheric inputs, occluded P in soils, and relatively large losses of N and P from “leaky” soil organic pools could contribute to long term nutrient limitation in forested ecosystems (Hedin et al. 1995; Vitousek et al. 1998).

Table 1. Summary statistics of stream nitrogen and phosphorus concentrations by season. N=57. *ND*=below detection limit. All units are in µg-N $L^{-1}$ or µg-P $L^{-1}$ except ratios of organic to total N and P.

| | Fall | | | | | Spring | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Med | Mn | Max | SD | Min | Med | Mn | Max | SD |
| TDN | 108 | 241 | 277 | 1117 | 173 | *ND* | 178 | 189 | 321 | 60 |
| DON | 56 | 199 | 207 | 537 | 88 | 34 | 123 | 130 | 287 | 60 |
| DIN | *ND* | 17 | 70 | 580 | 119 | 4 | 47 | 59 | 232 | 52 |
| $NO_3^-$ | *ND* | 9 | 47 | 286 | 77 | *ND* | 37 | 49 | 229 | 49 |
| $NH_4^+$ | *ND* | *ND* | 23 | 301 | 52 | *ND* | 9 | 10 | 38 | 8 |
| DON:TDN | 0.27 | 0.91 | 0.81 | 0.99 | 0.20 | 0.21 | 0.70 | 0.69 | 0.98 | 0.21 |
| TDP | 4.8 | 9.1 | 12.7 | 73.3 | 12.0 | 1.6 | 8.2 | 9.3 | 35.4 | 4.8 |
| DOP | 2.1 | 5.2 | 6.8 | 27.4 | 4.5 | 0.3 | 5.9 | 6.3 | 15.2 | 2.4 |
| SRP | 1.5 | 3.1 | 5.9 | 45.9 | 8.1 | 0.4 | 2.2 | 3.1 | 26.9 | 3.8 |
| DOP:TDP | 0.23 | 0.62 | 0.59 | 0.83 | 0.14 | 0.21 | 0.75 | 0.69 | 0.96 | 0.17 |

### *1.3.2 Season and fish presence as predictors of DON, DOP, DIN and SRP*

The transfer of marine derived nutrients from the Gulf of Alaska to streams with annual salmon spawning has been well documented and previous studies in the PCTR have shown that the occurrence of salmon runs can significantly influence the composition of DOM and increase stream nutrient concentrations (Gende et al. 2006; Hood et al. 2007; Rex et al. 2014). To examine the role of salmon on stream chemistry in our study, we first compared summary statistics of stream chemistry based on Season and Fish status (Figure 3 & 4; Appendix D). These data suggest an influence of salmon spawning on DOP, SRP, and DIN, since the Fish-Y streams had significantly higher ($P<0.001$) mean concentrations compared to Fish-N streams in fall. DON concentrations were not significantly higher in Fish-Y streams compared to Fish-N streams in the fall ($P>0.1$) Differences in means for organic and inorganic N and P were not significantly different between Fish-Y and Fish-N streams in the spring ($P>0.8$), suggesting no strong residual or priming effect that lasted throughout the year.

We found that Fish was a significant predictor ($P<0.5$) of DON, DIN, SRP and DOP in all the fall subset models, but not the spring models (Tables 2, 3, 4 and 5). The Fall:Fish interaction was retained in the final mixed models for DIN, SRP and DOP but not for DON. This adds support to the trend in overall stream chemistry that there is an increase in nutrient concentrations during large spawning events in the fall, but the effect on stream chemistry does not carry over into the spring, although the potential of hyporheic storage and release of nutrients has been suggested by other studies (O’Keefe, T.C. and Edwards 2002). Also, this suggests that the influence of terrestrial controls are more important than salmon derived nutrients for stream DON concentrations on an annual basis.

The effect of season was significant in the final mixed model for DON. In the fall, DON concentrations are estimated to be 53.97 µg -N $L^{-1}$ higher than spring. For DOP, the effect of fall alone was less significant ($P>0.1$); however, the Fall:Fish interaction was highly significant ($P<0.001$) for DOP, estimating an additional 4.99 µg -P $L^{-1}$ compared to Fish-N streams in the fall. The fact that the Fall:Fish interaction was retained in the DOP model but not DON suggests that the salmon spawning effect is relatively more important for DOP than DON compared to terrestrial controls. This may be a consequence of higher N:P ratios in terrestrial wetland DOM (~35:1) compared to salmon carcasses (15:1) (Ashley and Slaney 1997; Fellman et al. 2009a).

Both fall and the Fall:Fish interaction were retained in our best model for stream DIN. The final model estimates for streams without large salmon runs indicated that fall DIN concentrations were 14% ($p<0.05$) lower than spring concentrations (holding all other variables constant). This suggests: (1) that DIN may be diluted during higher fall flows, (2) that there is increased DIN supply to streams during the spring, or (3) both. We might expect elevated flushing of $NO_3^-$ during the spring when mineralized-N is mobilized and biological uptake is low; however, our spring measurements were taken in June, which is well into the growing season. The apparent increase of DIN in the spring could be due to higher nitrification rates resulting in more available $NO_3^-$ available for leaching. The many outlying data points for DIN (Figure 3) in fall Fish-N streams suggest that while overall dilution maybe occurring, there are important sources of DIN besides fish that could be watershed specific.

Unlike DIN, fall had a positive effect on SRP even without the fish interaction. SRP is estimated to increase by 48% in the fall (holding other variables constant) ($p=0.07$). Elevated SRP levels in the fall could be a result of decreased biological uptake during the end of the growing season, or an effect of increased activation of flow paths through mineral soil connecting SRP sources to the stream. With these models, causation cannot be inferred from the coefficients and we recommend against over interpretation, particularly of main effects such as season that are also significant within interaction terms. The season interaction terms tell a clearer story: that fall salmon runs increase DIN and SRP by approximately 30% ($P<0.05$) compared to spring concentrations.

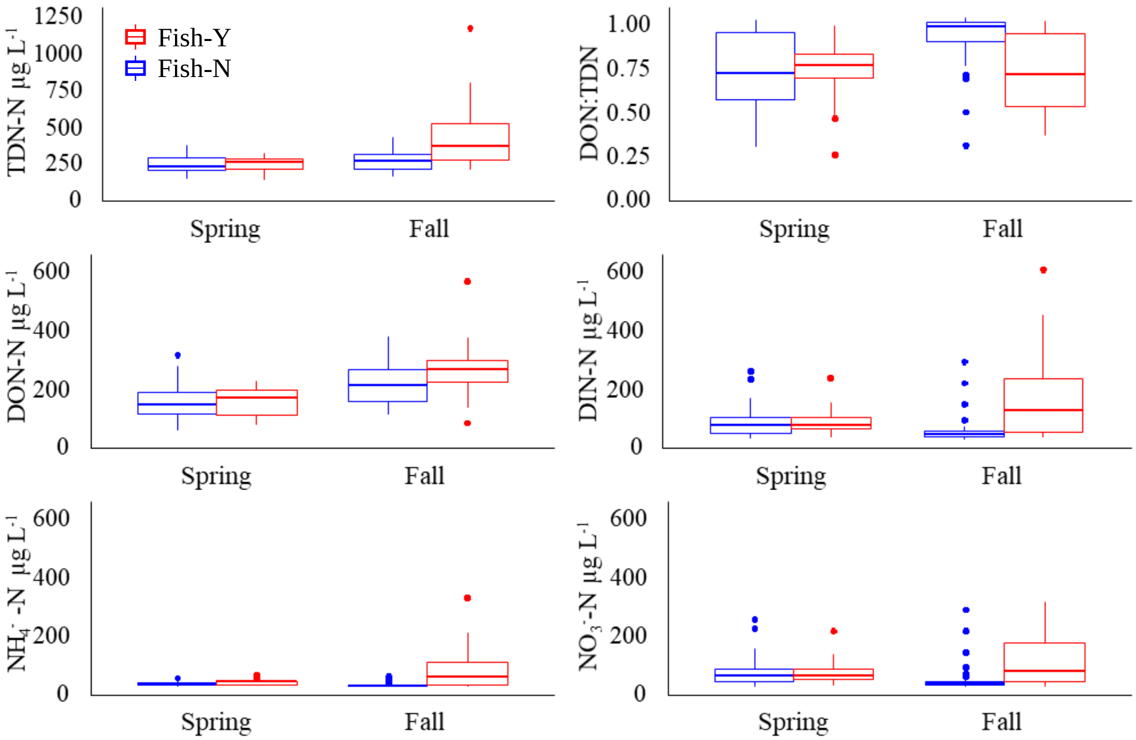


Figure 3. Summary boxplots of nitrogen forms in spring and fall samples, separated by fish bearing (Fish-Y) and non-fish bearing (Fish-N) streams.

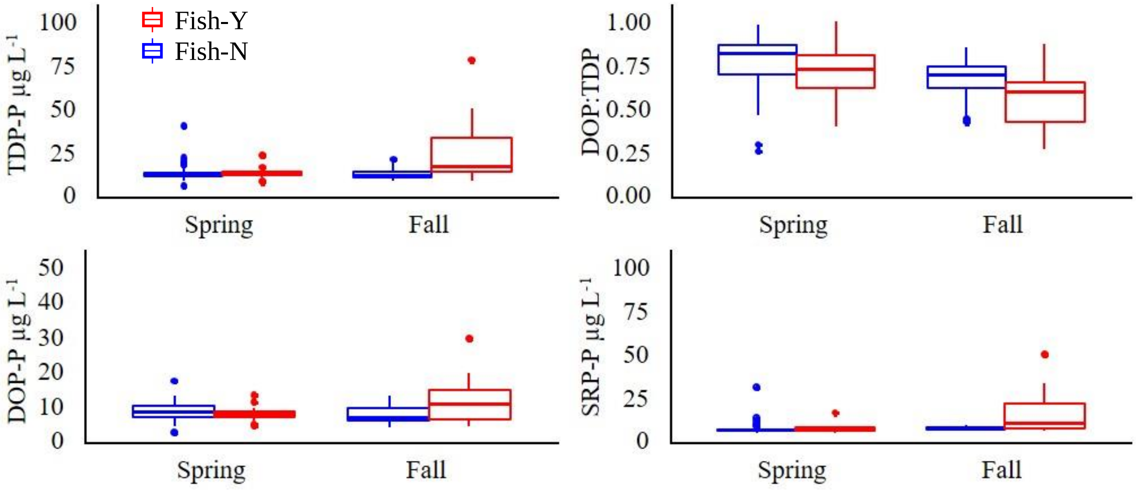


Figure 4. Summary boxplots of phosphorus forms in spring and fall samples, separated by fish bearing (Fish-Y) and non-fish bearing (Fish-N) streams.

Table 2. Final models for DON (µg N $L^{-1}$) for fall, spring and combined data.

| | Fall | | | Spring | | | Combined | | |
|---|---|---|---|---|---|---|---|---|---|
| | *B* | *CI* | *p* | *B* | *CI* | *p* | *B* | *CI* | *p* |
| (Intercept) | 114.50 | 87.84 – 141.16 | <.001 | 79.23 | 61.27 – 97.20 | <.001 | 79.23 | 57.27 – 101.19 | <.001 |
| Fish-Y | 33.98 | 0.92 – 67.04 | .044 | -- | -- | -- | -- | -- | -- |
| Slp0-5 | 3.03 | 2.20 – 3.85 | <.001 | 2.23 | 1.63 – 2.83 | <.001 | 2.23 | 1.49 – 2.97 | <.001 |
| NWI-PUB | 60.07 | 9.79 – 110.35 | .020 | -- | -- | -- | -- | -- | -- |
| Fall | | | | | | | 53.97 | 25.17 – 82.77 | <.001 |
| Fall:Slp0-5 | | | | | | | 0.99 | 0.03 – 1.96 | .049 |
| Observations | 57 | | | 57 | | | 114 | | |
| adj. $R^2$ | .563 | | | .490 | | | | | |
| $R^2_{GLMM(F)}/R^2_{GLMM(M)}$ | | | | | | | .596 / .652 | | |

"- -" indicates that the variable was tested during all subsets model selection but not retained in the final model. Predictors that were tested but not retained in any final models for DON: NWI-PF, TallShrub, MaxElv_km. Interaction terms for the combined season model that were tested but not retained in the final model: Fall:NWI-PUB. Seasonal interaction terms were only evaluated in the combined models.

Table 3. Final models for DOP (μg P $L^{-1}$) for fall, spring and combined data.

| | Fall | | | Spring | | | Combined | | |
|---|---|---|---|---|---|---|---|---|---|
| | *B* | *CI* | *p* | *B* | *CI* | *p* | *B* | *CI* | *p* |
| (Intercept) | 3.50 | 1.80 – 5.21 | <.001 | 5.96 | 4.98 – 6.94 | <.001 | 4.56 | 3.29 – 5.83 | <.001 |
| Fish-Y | 4.03 | 1.89 – 6.17 | <.001 | -- | -- | -- | -1.19 | -2.91 – 0.52 | .176 |
| Slp0-5 | 0.08 | 0.03 – 0.14 | .003 | -- | -- | -- | 0.06 | 0.03 – 0.09 | <.001 |
| HarvAll | -- | -- | -- | 0.04 | 0.00 – 0.08 | .042 | 0.05 | 0.01 – 0.09 | .020 |
| TallShrub | -- | -- | -- | -0.13 | -0.24 – -0.02 | .025 | -- | -- | -- |
| Fall | | | | | | | -1.15 | -2.52 – 0.22 | .105 |
| Fall:Fish-Y | | | | | | | 4.99 | 2.62 – 7.36 | <.001 |
| Observations | 57 | | | 57 | | | 114 | | |
| adj. $R^2$ | .300 | | | .150 | | | | | |
| $R^2_{GLMM(F)}/R^2_{GLMM(M)}$ | | | | | | | .302 / .322 | | |

“- -” indicates that the variable was tested during all subsets model selection but not retained in the final model. Predictors that were tested but not retained in any final models for DOP: NWI-PF, MnElv_km, NWI-pub. Interaction terms for the combined season model that were tested but not retained in the final model: Fall:HarvAll, Fall:Slp0-5. Seasonal interaction terms were only evaluated in the combined models.

Table 4. Final models for log(DIN) (µg N $L^{-1}$) for fall, spring and combined data.

| | Fall | | | Spring | | | Combined | | |
|---|---|---|---|---|---|---|---|---|---|
| | *B* | *CI* | *p* | *B* | *CI* | *p* | *B* | *CI* | *p* |
| (Intercept) | 1.93 | 1.40 – 2.46 | <.001 | 3.16 | 2.72 – 3.60 | <.001 | 3.00 | 2.57 – 3.43 | <.001 |
| Fish-Y | 1.51 | 0.88 – 2.13 | <.001 | -- | -- | -- | 0.17 | -0.39 – 0.73 | .558 |
| Roads | 0.49 | 0.09 – 0.89 | .018 | 0.36 | 0.03 – 0.69 | .031 | 0.41 | 0.12 – 0.70 | .008 |
| TallShrub | 0.10 | 0.05 – 0.16 | <.001 | 0.06 | 0.01 – 0.10 | .011 | 0.08 | 0.04 – 0.12 | <.001 |
| Fall | | | | | | | -0.94 | -1.32– -0.57 | <.001 |
| Fall:Fish-Y | | | | | | | 1.36 | 0.71 – 2.01 | <.001 |
| Observations | 57 | | | 57 | | | 114 | | |
| adj. $R^2$ | .445 | | | .120 | | | | | |
| $R^2_{GLMM(F)}/R^2_{GLMM(M)}$ | | | | | | | .412 / .557 | | |

"- -" indicates that the variable was tested during all subsets model selection but not retained in the final model. Predictors that were tested but not retained in any final models for DIN: NWI-PE, NWI-Wet. Interaction terms for the combined season model that were tested but not retained in the final model: Fall:Roads, Fall:TallShrub. Seasonal interaction terms were only evaluated in the combined models.

Table 5. Final models for log(SRP) (µg P $L^{-1}$) for fall, spring and combined data.

| | Fall | | | Spring | | | Combined | | |
|---|---|---|---|---|---|---|---|---|---|
| | *B* | *CI* | *p* | *B* | *CI* | *p* | *B* | *CI* | *p* |
| (Intercept) | 1.58 | 1.12 – 2.03 | <.001 | 0.50 | 0.21 – 0.79 | <.001 | 0.49 | 0.24 – 0.74 | <.001 |
| Fish-Y | 0.83 | 0.48 – 1.18 | <.001 | -- | -- | -- | 0.13 | -0.23 – 0.48 | .487 |
| Slp0-5 | -- | -- | -- | 0.01 | 0.00 – 0.02 | .007 | 0.01 | 0.01 – 0.02 | <.001 |
| MnElv_km | -1.88 | -3.30 – -0.47 | .010 | -- | -- | -- | -- | -- | -- |
| Fall | | | | | | | 0.27 | -0.01 – 0.56 | .065 |
| Fall:Fish-Y | | | | | | | 0.80 | 0.30 – 1.29 | .003 |
| Observations | 57 | | | 57 | | | 114 | | |
| adj. $R^2$ | .398 | | | .109 | | | | | |
| $R^2_{GLMM(F)}/R^2_{GLMM(M)}$ | | | | | | | .356 / .381 | | |

"- -" indicates that the variable was tested during all subsets model selection but not retained in the final model. Predictors that were tested but not retained in any final models for SRP: NWI-pf. Interaction terms for the combined season model that were tested but not retained in the final model: Fall:Slp0-5. Seasonal interaction terms were only evaluated in the combined models.

### *1.3.3 Slope, wetlands and organic rich soils as predictors of DON, DOP and SRP*

Average NWI-Wetland area across the sampled watersheds was 43% and ranged widely from 2–95%. Simple correlation plots explored during the variable screening phase showed that wetland extent was correlated with DON ($p<0.05$), but not with DOP ($p>1.0$). Other variables that are indicators of organic rich soils were stronger predictors of both DON and DOP. Slp0-5 was chosen as an alternative because it was most strongly correlated with DON and DOP during correlation screening. This is consistent with the findings of D'Amore et al. (2016), which concluded areas with the lowest topographic relief (Slp0-5 and Slp0-10) may better predict terrestrial sources of DOC to streams than the NWI wetland maps. At or near-surface soil saturation in PCTR soils is common where slopes are <10˚, and organic matter accumulates in these poorly drained areas at the bottom of hillslopes (D'Amore et al. 2015b). The Slp0-5 variable was retained in all final models for DON and DOP (with the exception of DOP in spring) with a highly significant ($p<0.001$) positive effect. For both DON and DOP, the coefficients for Slp0-5 are larger in the fall only models than the spring models, suggesting that these flatter areas are sources of more DOM during the fall than spring. The interaction between Fall:Slp0-5 was retained for DON but not DOP, adding to evidence that organic matter leaching has a strong influence on stream DON throughout the year, but particularly in the fall, which is supported by othr work showing increased mobilization of DOM from wetlands during times of higher discharge (Fellman et al. 2009b). The strong influence of Slp0-5 on DON may be masking the Fish signal, causing it to be dropped from the final DON mixed model.

Similar to the final fall DOC models of D'Amore et al. (2016), palustrine unconsolidated-bottom ponds (NWI-Pub) were retained in our final fall model for DON.

The exact role of these ponds in regulating stream chemistry cannot be inferred from the correlation. However, explanations may include that these ponds facilitate higher rates of transfer of N rich DOM from surrounding peat to streams, particularly during the fall when there is more precipitation and potentially increased hydrologic connectivity between these ponds and streams. NWI-Pub could also be an indicator of older, deeper wetlands that store more organic matter per unit surface area.

Slp0-5 was a significant positive predictor of SRP concentrations in the final combined season model. In the fall model, mean elevation was retained, as SRP decreased with increasing mean elevation. Although the relationship was not strong enough to remove one of these variables during screening, Mean elevation was negatively correlated with Slp0-5, so they are likely indicators of similar landscape functions; however, the relationship was not strong enough to remove one of these variables during screening.

While no slope or wetland variable was retained in the final DIN models, we did notice significant negative correlation between several NWI variables (i.e. extent of wetlands) and DIN during the variable screening phase. Anecdotally, it is not immediately clear why the extent of wetland soils was negatively correlated with DIN, but wetlands can have high biotic demand for N, and represent sites where DIN is quickly assimilated (Fellman and D’Amore 2007; Bisbing and D’Amore 2018). Alternatively, denitrification may be occurring in saturated soils and removing $NO_3^-$ from local or upslope sources. Results from other regions suggest the upper portions of watersheds may represent a relatively larger source of DIN, which decreases longitudinally down the stream (Hood et al. 2003).

### *1.3.4 Logging legacy and successional forest vegetation as predictors of DOP and DIN*

Variables related to the disturbance history of the watersheds were significant predictors of stream N and P concentrations. The Roads variable was retained in the final models for DOP and DIN, as concentrations increased with the extent of roads within the watersheds even though that extent was relatively small (average=1%, range 0-3%). In many areas of the PCTR, logging and associated roads have left a mosaic landscape of primary and secondary growth forests. In total, 53 of the 57 watersheds used in this study had some area previously harvested for timber. The average percent watershed area harvested (HarvAll) in our study was 16% (range 0-66%). Since HarvAll and Roads are closely correlated (Pearson's R=0.92, p<0.001), we suggest that they maybe interchangeable as predictors and interpret their effect as general indicators of the legacy of timber harvest within watersheds. The variable TallShrub was also retained in the best DIN model. The TallShrub layer is representative of the proportion of the landscape covered by Sitka alder and willow. Similarly to red alder, Sitka alder and willow may contribute to inorganic N in streams through N fixation. In our study, TallShrub had an average watershed cover of 3% (range 0-22%). In Southeast Alaska, and much of the PCTR, red alder invades clearings left by logging, often forming thick, uniform regrowth (Deal et al. 2004). These transitional stands develop over 50-100 years until the alder is succeeded by spruce and hemlock (Worthington and Ruth 1962). Clearcutting has been the primary method of silviculture in Southeast Alaska since the 1950s and mature alder stands or mixed alder-conifer stands currently occupy much of the previously logged area. Alder are one of few deciduous tree species in the region and are also hosts to symbiotic nitrogen fixing microbes. Many studies have documented increases of organic and inorganic N in alder stand soils and associated streams (Compton et al. 2003). Previous research into the role of red alder stands on soil P is mixed, but suggests that alder also plays a role in redistributing soil P from inorganic to organic pools as a result of increase demand, uptake, and leaf litter production (Compton and Cole 1998). These processes may explain the positive effect of harvest on stream DOP concentrations.

It is interesting that Roads and TallShrub were retained in the best DIN model but not for DON. These areas maybe contributing to elevated stream DON concentrations, but the effect of disturbance or successional vegetation maybe obscured in the outlet stream chemistry because of the overriding influence of DON leaching from organic soils. For DIN, the relative effect of natural and anthropogenic disturbance on stream nutrient concentrations maybe magnified because, in this ecosystem, except in areas subsidized by alder or salmon, inorganic N is quickly assimilated by plants and microbes before being transported to streams.

### *1.3.5 Effect of watershed and model overall fit*

Our ability to predict stream nutrient concentrations varied between nutrients and season. Overall, our final mixed-effect model for DON had the highest significance and best overall fit, followed by DIN, SRP and DOP (Figure 6). In all our final mixed effect models, the fit of the combined random and fixed-effects ($R^2_{GLMM(F)}$) was greater than the fit associated with the fixed-effects alone ($R^2_{GLMM(M)}$). This indicates that there is variance in the final models that is directly related to some watershed attributes not included in our models.

Other studies have shown that variables including watershed soil C:N, vegetation composition, and wetland cover can explain 73% of the DON export in Nova Scotia, 70% of DON export in Colorado and 79% of the variance in DON concentrations in streams and rivers of the northeastern US (excluding those with waste-water inputs) (Hood et al. 2003; Pellerin et al. 2004; Aitkenhead-Peterson et al. 2005). The fixed effects of our final DON model explained 60% of the variance in DON concentrations, which is high but notably lower than these other studies. In Finland, Kortelainen et al. (2006) found that mean slope was the best predictor of stream TDP and explained 56% of the variation in undisturbed boreal catchments. Our final model for DOP, which includes slope, explains 30% of the variation in DOP concentration and shows that legacies of disturbance including logging and road construction may play a role in DOP export.

For all nutrients, the adj$R^2$ for our final fall models were higher than final spring models (Tables 2, 3, 4 and 5). This maybe the result of increased hydrologic connectivity between soils and streams during the fall which would strengthen the relationship between landscape variables and stream chemistry. The inclusion of Fish as a predictor also improves our ability to predict nutrient concentrations in the fall.  Lower model fits in spring could also be an effect of increased in-stream uptake and processing of nutrients during the spring growing season, which could obscure the relationship between terrestrial ecosystems and nutrient concentrations in the stream.

### *1.4 Conclusions*

This study included watersheds that represent a wide range of wetland cover (2-95%) and slope derived attributes, and provides a new look at the controls of stream N and

P across a range of landscape types spanning 87,700 km2and >4° of latitude. The overall dominance of DON and DOP over inorganic forms emphasizes the importance of long term controls on soil development and leaching of organic matter on stream chemistry in the PCTR. The significance of factors that represent organic rich soils in the landscape in our final models supports this finding.

There is still considerable variability in stream nutrient concentrations that is not accounted for in our models, however, given the inability to control for antecedent precipitation, size and timing of salmon runs for a study of this scale, we were still able to identify highly significant predictors of stream chemistry. Proportion of the watershed with slope 0-5$^o$ appears to be a particularly important predictor of stream chemistry. This is promising since variables generated from digital elevation models (DEMs) in this region are likely to become more refined in the future as technology and resolution improves, which may improve our ability to predict DON and DOP.

Future research into hydrologic controls of DOM export to streams should include investigation of wetland ponds, particularly those that occur in peat, and the connectivity versus export of DOM during the wettest times of year. Temperatures in Southeast Alaska are predicted to increase in the future and the timing of precipitation will likely also become more variable (SNAP 2009). Thus, the timing and magnitude of hydrologic DOM transport and associated processes are likely to change as a result. Seasonal drought and the hydrologic disconnection of wetlands could constrain delivery of N and P to aquatic ecosystems, while exposing a reactive stockpile of terrestrial organic matter to increased rates of decomposition.

Our data also clearly demonstrate that large salmon spawning events increase stream N and P concentrations during the fall where and when they occur. However, the relative influence of terrestrial ecosystems should be considered as a potentially important sources of N and P to aquatic systems downstream, particularly since organic matter from terrestrial systems including wetlands has been shown to be labile and a potentially important source of energy and nutrients to microbes (Fellman et al. 2008).

These models are intended to be applied at a regional scale to estimate stream nutrient concentrations across the PCTR. For any given watershed, it is likely that the models will over or underestimate the observed water chemistry, whoever these models provide necessary information for developing hydrologic flux estimates of stream N and P for this region. The rate of N and P transfer from terrestrial to aquatic systems across the PCTR from small precipitation fed watersheds could have important implications for primary productivity across the coastal margin.

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# APPENDIX A

**Table A.1 Sample site locations and attributes.** WSID is a label identifier for each sampled watershed. NWI-Wet is the proportion of a watershed covered by wetlands (see Appendix B for details). Fish describes whether a stream had evidence of large spawning salmon events (Y=Yes, N=No). Latitude and longitude are referenced to the North American Datum of 1983 (NAD83).

| **WSID** | **NWI-Wet** | **Fish** | **WshedArea (hectares)** | **Longitude (west)** | **Latitude (north)** |
|---|---|---|---|---|---|
| 1N | 16.74 | N | 260 | 133.899150 | 56.617370 |
| 1BN | 37.09 | N | 521 | 132.648140 | 56.672530 |
| 2N | 44.06 | N | 611 | 133.216020 | 55.927180 |
| 3N | 8.83 | N | 186 | 133.293670 | 56.981630 |
| 4N | 31.93 | N | 919 | 132.664980 | 56.436560 |
| 4W | 59.06 | Y | 3130 | 133.137620 | 55.891980 |
| 5N | 31.88 | N | 2619 | 133.440750 | 56.316940 |
| 6N | 33.59 | N | 3207 | 132.780400 | 56.546330 |
| 7W | 85.63 | Y | 356 | 133.250370 | 56.051620 |
| 8N | 14.78 | N | 519 | 133.930710 | 56.599420 |
| 8W | 67.65 | N | 1142 | 132.743240 | 56.717990 |
| 9N | 27.90 | Y | 13304 | 135.481320 | 58.073550 |
| 9W | 53.86 | Y | 1905 | 133.048610 | 56.326750 |
| 10N | 35.81 | N | 322 | 132.524810 | 55.363430 |
| 10W | 54.30 | N | 1067 | 131.751860 | 55.491760 |
| 11N | 39.88 | Y | 2610 | 132.815550 | 55.210140 |
| 12N | 32.63 | Y | 1504 | 133.146870 | 55.900150 |
| 12W | 59.95 | Y | 3649 | 132.062900 | 56.233720 |
| 13N | 24.79 | N | 672 | 132.634990 | 56.417940 |
| 14N | 22.75 | N | 2597 | 135.113750 | 57.723420 |
| 14W | 80.70 | N | 17317 | 133.675890 | 56.872690 |
| 15N | 7.40 | Y | 2952 | 134.160860 | 56.832790 |
| 16W | 57.13 | N | 675 | 132.343150 | 56.417500 |
| 17N | 17.12 | Y | 2970 | 135.306080 | 57.059370 |
| 17W | 59.87 | N | 1036 | 131.763580 | 55.484540 |
| 18N | 27.53 | N | 778 | 132.929620 | 56.720280 |
| 18W | 86.63 | Y | 1883 | 133.309970 | 55.722950 |
| 19N | 12.21 | N | 717 | 134.945080 | 57.746470 |
| 20N | 19.47 | N | 5688 | 135.186970 | 57.782090 |
| 21W | 55.83 | N | 720 | 133.674640 | 56.844440 |
| 23N | 36.38 | Y | 1101 | 133.398532 | 57.000707 |
| 23W | 95.26 | N | 269 | 133.281590 | 56.916250 |
| 24N | 6.74 | N | 392 | 134.902280 | 58.592490 |
| 24W | 59.14 | Y | 1821 | 133.043430 | 56.368640 |
| 25W | 73.88 | N | 6388 | 133.714200 | 56.905400 |
| 26N | 21.71 | N | 268 | 132.909710 | 56.455280 |
| 26W | 66.74 | Y | 1084 | 133.123290 | 55.879800 |
| 28W | 57.64 | N | 4210 | 132.157380 | 56.195430 |
| 30N | 16.57 | N | 2061 | 132.985460 | 55.531390 |
| 30W | 66.31 | N | 5834 | 133.354450 | 56.764700 |
| 31N | 20.48 | N | 161 | 133.573990 | 56.351070 |
| 31W | 60.44 | N | 399 | 133.397450 | 56.311160 |
| 32W | 50.27 | N | 1075 | 132.779630 | 56.758030 |
| 33N | 28.77 | Y | 1404 | 133.125200 | 55.484890 |
| 33BN | 47.87 | N | 4008 | 132.133500 | 56.338490 |
| 34W | 67.95 | N | 5118 | 133.676160 | 56.814860 |
| 35N | 16.29 | Y | 2009 | 133.542400 | 56.333230 |
| 36W | 50.30 | N | 1356 | 133.199650 | 56.090240 |
| 37W | 52.17 | N | 271 | 132.828510 | 55.268940 |
| 38W | 57.55 | N | 995 | 132.323490 | 56.267960 |
| 40N | 38.69 | N | 1281 | 132.806690 | 56.439350 |
| 41W | 52.10 | Y | 667 | 133.263180 | 56.153870 |
| 42N | 35.91 | N | 617 | 132.539310 | 55.838180 |
| 42W | 66.05 | Y | 1420 | 133.134840 | 56.238740 |

**Table A.1** ***continued***

| WSID | NWI-Wet | Fish | WshedArea (hectares) | Longitude (west) | Latitude (north) |
|---|---|---|---|---|---|
| 44N | 14.11 | Y | 1901 | 134.113450 | 56.837410 |
| 45W | 85.17 | N | 617 | 135.136380 | 58.064790 |
| 47N | 1.71 | Y | 299 | 133.577800 | 56.299530 |
|  | 57 | ***N*** | 57 |  |  |
|  | 1.7 | **Min** | 160.8 |  |  |
|  | 95.3 | **Max** | 17317.2 |  |  |
|  | 43.04 | **Mean** | 2155.45 |  |  |
|  | 39.88 | **Median** | 1100.66 |  |  |
|  | 23.37 | **Std** | 2979.77 |  |  |

# APPENDIX B

**Table B.1 Explanatory variables used in the exploratory regression analysis.**

| **Variable Name** | **Description** | **Mn** | **SD** | **Range** | **Data Source*** |
|---|---|---|---|---|---|
| NWI-Wet | Proportion of watershed in wetlands. Wetlands were defined as all land area within a watershed not classified as "Upland" in the NWI GIS layer. | 43.04 | 23.27 | 1.71-95.26 | USFWS National Wetlands Inventory GIS dataset (NWI), provided by the U.S. Forest Service, Tongass National Forest (USFS-TNF). Dataset used for analysis was extracted from TNF GIS library on 7/28/2004. Dataset publication date is 2002. Metadata available from http://seakgis.alaska.edu. |
| NWI-PE | Proportion of watershed in NWI class Palustrine-Emergent. | 12.22 | 10.16 | 0.04-40.94 | |
| NWI-PF | Proportion of watershed in NWI class Palustrine-Forested. | 27.73 | 18.51 | 0-65.35 | |
| NWI-PS | Proportion of watershed in NWI class Palustrine-Scrub-Shrub. | 2.36 | 4.95 | 0-34.04 | |
| NWI-PUB | Proportion of watershed in NWI class Palustrine-Unconsolidated Bottom (ponds and small lakes < 8 hectares). | 0.20 | 0.31 | 0-1.39 | |
| NWI-Lac1 | Proportion of watershed in NWI class Lacustrine-Limnetic. | 0.38 | 1.00 | 0-5.2 | |
| NWI-Lac2 | Proportion of watershed in NWI class Lacustrine-Littoral. | 0.05 | 0.20 | 0-1.22 | |
| LakesFS | Proportion of watershed with lakes, from US Forest Service dataset. | 0.68 | 1.10 | 0-4.64 | USFS-TNF *Lakes* GIS layer. Dataset used for analysis was copied from TNF GIS library on 9/14/2007. Dataset publication date is 2003. Metadata available in the SEAK Hydro dataset from http://seakgis.alaska.edu. |
| Hydric | Proportion of watershed classified as hydric soils. | 47.99 | 25.13 | 0-98.94 | USFS-TNF *Soils* GIS layer. Dataset did not have complete coverage for study area, variable was dropped from all-subsets regression. |
| StrmLen | Length of watershed stream main stem, in kilometers, from sample point to head waters. | 8.64 | 6.49 | 2.09-33.19 | USFS-TNF *Streams* GIS layer. Dataset used for analysis was copied from TNF GIS library on 11/26/2006. Mainstem stream arcs were then edited to extend the upstream end to the watershed boundary, or apparent headwaters, using ancillary datasets including contours, DEMs, and orthophotos or other remotely-sensed imagery. Metadata for the most recent version of this dataset can be downloaded from: Metadata available in the SEAK Hydro dataset from http://seakgis.alaska.edu. |
| StrmSlope | Main channel slope, in degrees. Computed as the difference in elevation between two points located at 10% and 85% of the distance along the main channel from the outlet to the watershed divide. | 3.26 | 3.07 | 0.07-17.07 | USFS-TNF *Streams* GIS layer (above) and U.S. Geological Survey digital elevation model (see USGS DEM link below). |

**Table B.1** ***continued***

| **Variable Name** | **Description** | **Mn** | **SD** | **Range** | **Data Source*** |
|---|---|---|---|---|---|
| WsArea | Watershed area, hectares. | 2155.45 | 2966.56 | 160.84-17317.19 | USFS-TNF *HUC* (hydrologic unit code) GIS layer. Hydrologic units were mapped at the subwatershed level (USGS HUC level 6). Dataset copied from the TNF GIS library on 7/24/2004. |
| HarvAll | Proportion of watershed logged, any age. | 15.75 | 14.65 | 0-66.36 | For Forest Service lands, USFS-TNF *Mgdstds* (managed stands) 8/23/2005 and *Roads* GIS layers were copied from the TNF GIS library on 8/23/2005 and 7/28/2005, respectively. State of Alaska Department of Natural Resources, Division of Forestry, provided a GIS layer of timber harvest on state lands called *SSE_HarvesUnits*. *SSE_HarvesUnits* was received via email on 1/30/2006. In March, 2006, Sealaska Native Corporation provided GIS layers for timber harvest and roads on lands managed by Sealaska. Harvest areas and roads for all layers were verified, and updated if needed, for each sample watershed using imagery from Google Earth, USFS digital orthophotos, and U.S. Census Bureau digital orthophotos. |
| Harv5 | Proportion of watershed logged in the 5 years prior to sampling. | 0.53 | 1.91 | 0-10.48 | |
| Harv10 | Proportion of watershed logged in the 10 years prior to sampling. | 1.46 | 2.75 | 0-10.48 | |
| Harv20 | Proportion of watershed logged in the 20 years prior to sampling. | 3.92 | 4.60 | 0-20.31 | |
| Roads | Proportion of watershed roaded. To quantify road disturbance, all road widths were assumed to be 35 feet (10.7 meters). Roads running through clearcuts were counted as part of the logged area (HarvAll, Harv5, etc.) and not included in the Roads calculation. | 0.96 | 0.76 | 0-3.06 | |
| TallShrub | Proportion of watershed mapped as "TallShrub" cover | 2.90 | 5.50 | 0-22.45 | USFS-TNF *Landcover* GIS layer. Level 2 Dataset copied from the SEAK GIS library. http://seakgis.alaska.edu/ |
| Karst | Proportion of watershed mapped as karst. | 13.19 | 25.23 | 0-99.99 | USFS-TNF *karstmap* draft GIS layer. Copied from TNF GIS library 4/23/2004. |
| SlopeAvg | Mean watershed slope, in degrees. | 13.87 | 5.45 | 4.71-25.19 | USGS National Elevation Dataset. 2 arc second Alaska DEMs (approx 60 meter). Downloaded from http://seamless.usgs.gov on 12/4/2008. |
| Slopes0-5 | Proportion of watershed in 0 to 5 degree slopes ($0 \leq \text{slope} \leq 5$). | 22.95 | 19.03 | 0.77-75.06 | |
| Slopes0-10 | Proportion of watershed in 0 to 10 degree slopes ($0 \leq \text{slope} \leq 10$). | 43.11 | 23.29 | 3.87-88.79 | |
| Slopes>20 | Proportion of watershed in greater than 20 degree slopes ($\text{slope} > 20$). | 26.81 | 20.37 | 0-73.11 | |
| Slopes>30 | Proportion of watershed in greater than 30 degree slopes ($\text{slope} > 30$). | 7.81 | 9.09 | 0-40.11 | |
| ElevAvg | Average watershed elevation, in meters. | 267.77 | 117.84 | 60.43-573.26 | |
| ElevMax | Maximum watershed elevation, in meters. | 660.40 | 217.85 | 152.21-1139.7 | |

*Some of the USFS-TNF GIS datasets listed above can be downloaded from the Southeast Alaska GIS Library, http://seakgis.alaska.edu.
Table adapted from D’Amore at al. 2016

# APPENDIX C

**Table C.1 Watersheds and their DON, DOP, DIN and SRP concentrations by season.** WSID is a label identifier for each sample watershed. Values under detection limit are marked as ND.

| | **DON** | | **$NO_3^-$** | | **$NH_4^+$** | | **DOP** | | **SRP** | |
|---|---|---|---|---|---|---|---|---|---|---|
| **WSID** | **Fall** | **Spring** | **Fall** | **Spring** | **Fall** | **Spring** | **Fall** | **Spring** | **Fall** | **Spring** |
| 1N | 100 | 95 | 6.6 | 196.8 | 32 | 7 | 6.6 | 59.4 | 3.8 | 3.7 |
| 1BN | 286 | 287 | 3.4 | 12.5 | 14 | 12 | 8.1 | 4.0 | 1.9 | 2.3 |
| 2N | 138 | 158 | 10.2 | 55.6 | ND | 28 | 4.8 | 20.7 | 2.5 | ND |
| 3N | 160 | 117 | 4.9 | 8.5 | ND | ND | 10.4 | 1.2 | 4.6 | 8.9 |
| 4N | 85 | 34 | 9.2 | 41.2 | 14 | 19 | 4.4 | 16.8 | 2.6 | 1.7 |
| 4W | 321 | 200 | 52.2 | 5.4 | 109 | 5 | 16.8 | 2.9 | 8.6 | 4.0 |
| 5N | 104 | 62 | 36.5 | 36.3 | ND | 9 | 4.0 | 21.5 | 2.8 | 1.1 |
| 6N | 118 | 160 | 8.0 | 19.7 | ND | 8 | 7.4 | 8.3 | 1.9 | 1.1 |
| 7W | 255 | 176 | 23.1 | 55.5 | 39 | 13 | 10.3 | 20.6 | 13.9 | 2.3 |
| 8N | 111 | 98 | 9.3 | 46.8 | ND | ND | 3.9 | 13.4 | 3.0 | 2.9 |
| 8W | 209 | 233 | 6.8 | 16.3 | 6 | ND | 7.7 | 3.0 | 3.2 | 2.3 |
| 9N | 187 | 142 | 225.3 | 108.4 | ND | 13 | 6.0 | 29.2 | 4.6 | 2.9 |
| 9W | 195 | 55 | 5.1 | 187.0 | 11 | 21 | 6.3 | 63.2 | 4.4 | 1.8 |
| 10N | 102 | 53 | 15.1 | 36.5 | ND | 14 | 4.2 | 22.0 | 1.5 | 1.0 |
| 10W | 190 | 149 | 8.6 | 16.2 | ND | ND | 7.2 | 4.4 | 3.9 | 1.7 |
| 11N | 266 | 177 | 148.0 | 40.2 | 132 | 12 | 12.4 | 12.4 | 21.9 | 2.2 |
| 12N | 321 | 120 | 245.6 | 33.6 | 180 | 8 | 17.5 | 15.1 | 28.1 | 1.2 |
| 12W | 199 | 123 | 6.9 | 16.0 | 6 | 14 | 3.6 | 6.7 | 1.9 | 3.5 |
| 13N | 118 | 44 | 7.1 | 64.9 | ND | 10 | 3.4 | 24.1 | 1.6 | 2.1 |
| 14N | 159 | 129 | 185.4 | 127.8 | ND | 11 | 5.2 | 83.8 | 2.7 | 2.7 |
| 14W | 341 | 217 | 3.4 | 5.6 | 20 | ND | 9.0 | 1.7 | 4.4 | 4.6 |
| 15N | 275 | 52 | 144.1 | 21.4 | 36 | 5 | 12.7 | 6.2 | 7.6 | 3.6 |
| 16W | 161 | 82 | 5.5 | 52.4 | ND | 11 | 6.6 | 15.8 | 2.7 | 1.4 |
| 17N | 203 | 53 | 57.2 | 66.5 | 55 | 8 | 11.6 | 20.2 | 3.1 | 4.5 |
| 17W | 238 | 188 | 2.6 | 17.0 | ND | ND | 9.4 | 2.3 | 3.9 | 5.7 |
| 18N | 154 | 125 | 11.9 | 40.1 | ND | 20 | 5.3 | 15.5 | 3.7 | 1.9 |
| 18W | 56 | 88 | 78.6 | 73.0 | 40 | 38 | 10.3 | 41.1 | 21.2 | 3.9 |
| 19N | 216 | 105 | 114.3 | 128.2 | 6 | 14 | 2.4 | 450.8 | 2.4 | 2.2 |
| 20N | 96 | 72 | 259.4 | 127.6 | ND | 14 | 3.4 | 56.6 | 2.5 | 2.3 |
| 21W | 339 | 200 | 4.5 | 4.2 | 9 | ND | 11.1 | ND | 5.6 | 26.9 |
| 23N | 243 | 160 | 4.8 | 12.1 | 4 | ND | 2.6 | 1.7 | 9.3 | 12.2 |
| 23W | 352 | 250 | 3.0 | 4.1 | 6 | ND | 8.4 | ND | 2.9 | 7.3 |
| 24N | 202 | 107 | 5.6 | 12.6 | 5 | 7 | 5.6 | 6.3 | 1.7 | 1.7 |
| 24W | 344 | 166 | 6.7 | 21.9 | ND | 24 | 8.6 | 12.1 | 1.8 | 4.0 |
| 25W | 295 | 166 | ND | 3.9 | ND | ND | 6.6 | 1.1 | 5.4 | 5.2 |
| 26N | 224 | 48 | 31.5 | 101.8 | ND | 25 | 3.1 | 42.5 | 3.7 | 1.4 |
| 26W | 537 | 168 | 279.4 | 26.8 | 301 | 17 | 27.4 | 12.8 | 45.9 | 2.5 |
| 28W | 249 | 144 | 3.7 | 7.2 | 6 | 5 | 3.5 | 3.9 | 5.6 | 2.4 |
| 30N | 87 | 70 | 29.7 | 50.9 | ND | 8 | 4.1 | 18.4 | 2.3 | 1.1 |
| 30W | 202 | 96 | 4.5 | 46.5 | ND | ND | 4.9 | 15.4 | 2.2 | 1.5 |

**Table C.1 *continued***

| | DON | | $NO_3^-$ | | $NH_4^+$ | | DOP | | SRP | |
|---|---|---|---|---|---|---|---|---|---|---|
| **WSID** | **Fall** | **Spring** | **Fall** | **Spring** | **Fall** | **Spring** | **Fall** | **Spring** | **Fall** | **Spring** |
| 31N | 244 | 287 | 3.9 | 10.9 | ND | 23 | 7.3 | 4.1 | 2.4 | 2.6 |
| 31W | 135 | 145 | 5.4 | 70.6 | ND | 10 | 2.1 | 24.7 | 3.2 | ND |
| 32W | 171 | 119 | 2.8 | 16.4 | ND | 10 | 4.7 | 7.8 | 2.1 | 1.6 |
| 33N | 258 | 182 | 285.9 | 38.7 | 136 | 13 | 13.9 | 9.3 | 29.0 | 1.6 |
| 33BN | 251 | 143 | 3.0 | ND | ND | 5 | 3.7 | 1.6 | 1.8 | 2.1 |
| 34W | 238 | 131 | 4.0 | 34.2 | ND | ND | 3.8 | 9.5 | 2.3 | 2.1 |
| 35N | 109 | 69 | 41.0 | 36.9 | 4 | ND | 2.4 | 23.6 | 2.5 | 1.3 |
| 36W | 156 | 109 | 9.9 | 43.1 | ND | 9 | 3.6 | 18.4 | 3.1 | 1.1 |
| 37W | 127 | 81 | 62.4 | 229.5 | ND | ND | 2.1 | 58.5 | 3.0 | ND |
| 38W | 198 | 102 | 8.7 | 7.1 | ND | 7 | 2.9 | 3.6 | 2.1 | 2.0 |
| 40N | 238 | 65 | 3.3 | 88.7 | ND | 8 | 3.7 | 40.6 | 1.7 | 1.6 |
| 41W | 156 | 123 | 26.6 | 43.0 | 16 | 11 | 4.4 | 12.8 | 5.6 | ND |
| 42N | 146 | 106 | 42.9 | 60.2 | ND | 9 | 4.3 | 23.0 | 3.1 | 1.2 |
| 42W | 195 | 140 | 23.6 | 42.9 | ND | ND | 4.3 | 13.1 | 3.1 | 2.3 |
| 44N | 236 | 72 | ND | 22.0 | 23 | 9 | 4.3 | 7.7 | 3.4 | 4.1 |
| 45W | 321 | 233 | 36.1 | 27.6 | 0 | 6 | 4.8 | 9.3 | 4.0 | 3.9 |
| 47N | 194 | 159 | 61.7 | 72.2 | 34 | 12 | 7.3 | 27.6 | 5.9 | 1.4 |
| ***N*** | 57 | 57 | 57.0 | 57.0 | 57 | 57 | 57.0 | 57.0 | 57.0 | 57.0 |
| **Min** | 56 | 34 | ND | ND | ND | ND | 2.1 | ND | 1.5 | ND |
| **Max** | 537 | 287 | 285.9 | 229.5 | 301 | 38 | 27.4 | 450.8 | 45.9 | 26.9 |
| **Mean** | 207 | 130 | 47.2 | 49.0 | 23 | 10 | 6.8 | 25.5 | 5.9 | 3.1 |
| **Median** | 199 | 123 | 9.2 | 36.9 | 4 | 9 | 5.2 | 13.1 | 3.1 | 2.2 |
| **Std** | 88 | 60 | 77.1 | 49.3 | 52 | 8 | 4.5 | 60.1 | 8.1 | 3.8 |
| **Coeff of Var** | 42 | 46 | 163.4 | 100.5 | 232 | 79 | 66.9 | 235.7 | 136.9 | 122.5 |

# APPENDIX D

**Table D.1 Summary statistics of stream nitrogen and phosphorus concentrations by season.** N=57. *ND*=under detection limit. All units are in µg-N L$^{-1}$ or µg-P L$^{-1}$ except ratios of organic to total N and P.

| | Fall | | | | | Spring | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Minimum | Median | Mean | Maximum | Stdev | Minimum | Median | Mean | Maximum | Stdev |
| TDN | 108 | 241 | 277 | 1117 | 173 | 80 | 178 | 189 | 321 | 60 |
| DON | 56 | 199 | 207 | 537 | 88 | 34 | 123 | 130 | 287 | 60 |
| DIN | 2 | 17 | 70 | 580 | 119 | 4 | 47 | 59 | 232 | 52 |
| NO3 | *ND* | 9 | 47 | 286 | 77 | 1 | 37 | 49 | 229 | 49 |
| NH4 | *ND* | 4 | 23 | 301 | 52 | *ND* | 9 | 10 | 38 | 8 |
| DON:TDN | 0.27 | 0.91 | 0.81 | 0.99 | 0.20 | 0.21 | 0.70 | 0.69 | 0.98 | 0.21 |
| TP | 4.2 | 13.9 | 19.1 | 73.2 | 14.3 | 3.3 | 8.9 | 9.8 | 23.4 | 4.5 |
| PP | *ND* | 2.8 | 6.8 | 42.4 | 9.5 | *ND* | 1.3 | 1.9 | 12.3 | 2.1 |
| TDP | 4.8 | 9.1 | 12.7 | 73.3 | 12.0 | 1.6 | 8.2 | 9.3 | 35.4 | 4.8 |
| DOP | 2.1 | 5.2 | 6.8 | 27.4 | 4.5 | 0.3 | 5.9 | 6.3 | 15.2 | 2.4 |
| SRP | 1.5 | 3.1 | 5.9 | 45.9 | 8.1 | 0.4 | 2.2 | 3.1 | 26.9 | 3.8 |
| DOP:TDP | 0.23 | 0.62 | 0.59 | 0.83 | 0.14 | 0.21 | 0.75 | 0.69 | 0.96 | 0.17 |

**Table D.2 Summary statistics of stream nitrogen and phosphorus concentrations by season for non-fish bearing (Fish-N) streams.** N=38. *ND*=under detection limit. All units are in µg-N L$^{-1}$ or µg-P L$^{-1}$ except ratios of organic to total N and P.

| | Fall | | | | | Spring | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Minimum | Median | Mean | Maximum | Stdev | Minimum | Median | Mean | Maximum | Stdev |
| TDN | 108 | 207 | 221 | 370 | 82 | 94 | 174 | 189 | 321 | 63 |
| DON | 85 | 181 | 191 | 352 | 76 | 34 | 118 | 132 | 287 | 66 |
| DIN | 2 | 12 | 30 | 264 | 52 | 4 | 48 | 58 | 232 | 55 |
| NO3 | *ND* | 7 | 26 | 259 | 52 | 1 | 36 | 49 | 229 | 53 |
| NH4 | *ND* | 2 | 4 | 32 | 6 | *ND* | 8 | 9 | 28 | 7 |
| DON:TDN | 0.27 | 0.94 | 0.87 | 0.99 | 0.16 | 0.26 | 0.68 | 0.69 | 0.98 | 0.23 |
| TP | 4.2 | 11.3 | 15.3 | 41.5 | 10.6 | 3.3 | 8.5 | 9.4 | 21.3 | 4.6 |
| PP | *ND* | 2.7 | 7.0 | 32.5 | 9.1 | *ND* | 1.1 | 1.7 | 12.3 | 2.3 |
| TDP | 4.8 | 7.3 | 8.4 | 16.7 | 3.0 | 1.6 | 8.1 | 9.6 | 35.4 | 5.5 |
| DOP | 2.1 | 4.8 | 5.4 | 11.1 | 2.3 | 0.3 | 6.3 | 6.5 | 15.2 | 2.6 |
| SRP | 1.5 | 2.7 | 3.0 | 5.6 | 1.1 | 0.5 | 2.1 | 3.1 | 26.9 | 4.4 |
| DOP:TDP | 0.38 | 0.65 | 0.63 | 0.81 | 0.11 | 0.21 | 0.77 | 0.71 | 0.94 | 0.17 |

**Table D.3 Summary statistics of stream nitrogen and phosphorus concentrations by season for fish bearing (Fish-Y) streams.** N=19. *ND*=under detection limit. All units are in µg-N L$^{-1}$ or µg-P L$^{-1}$ except ratios of organic to total N and P.

| | Fall | | | | | Spring | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Minimum | Median | Mean | Maximum | Stdev | Minimum | Median | Mean | Maximum | Stdev |
| TDN | 154 | 314 | 389 | 1117 | 244 | 80 | 199 | 188 | 263 | 55 |
| DON | 56 | 236 | 239 | 537 | 101 | 52 | 140 | 128 | 200 | 49 |
| DIN | 8 | 95 | 150 | 580 | 167 | 10 | 47 | 61 | 208 | 46 |
| NO3 | *ND* | 52 | 90 | 286 | 99 | 5 | 39 | 49 | 187 | 42 |
| NH4 | *ND* | 34 | 59 | 301 | 79 | 3 | 12 | 12 | 38 | 9 |
| DON:TDN | 0.32 | 0.67 | 0.69 | 0.98 | 0.22 | 0.21 | 0.72 | 0.68 | 0.95 | 0.18 |
| TP | 7.0 | 18.3 | 26.7 | 73.2 | 17.7 | 4.4 | 10.1 | 10.6 | 23.4 | 4.1 |
| PP | *ND* | 3.4 | 6.3 | 42.4 | 10.5 | *ND* | 2.0 | 2.2 | 5.8 | 1.8 |
| TDP | 4.9 | 13.1 | 21.3 | 73.3 | 17.7 | 3.8 | 8.2 | 8.9 | 19.0 | 3.0 |
| DOP | 2.4 | 8.6 | 9.6 | 27.4 | 6.3 | 2.4 | 5.8 | 5.8 | 10.8 | 2.0 |
| SRP | 1.8 | 5.9 | 11.7 | 45.9 | 12.1 | 0.4 | 2.5 | 3.1 | 12.2 | 2.5 |
| DOP:TDP | 0.23 | 0.55 | 0.51 | 0.83 | 0.16 | 0.36 | 0.68 | 0.66 | 0.96 | 0.16 |