Biogeochemistry (2021) 152:253–270
https://doi.org/10.1007/s10533-020-00752-w

Streamflow variability controls N and P export and speciation from Alaskan coastal temperate rainforest watersheds

Jason B. Fellman · Eran Hood · David V. D'Amore · Richard T. Edwards

Received: 5 May 2020 / Revised: 21 December 2020 / Accepted: 31 December 2020 / Published online: 16 January 2021

Abstract The perhumid coastal temperate rainforest (PCTR) of northwestern North America is projected to become warmer and wetter in coming decades, with largely unquantified implications for the magnitude and speciation of riverine nitrogen (N) and phosphorus (P) export from PCTR ecosystems. We collected streamwater at weekly to monthly intervals for a year and intensively during two multi-day storms (one each in summer and the autumn rainy season) from streams draining three of the most common landcover types in southeast Alaska (poor fen, forested wetland and upland forest). Our goal was to investigate how seasonal and episodic (stormflows) changes in runoff influence the magnitude and species of dissolved N and P exported from PCTR watersheds. Riverine yields of total dissolved N and P ranged from 238 to 406 kg km^2 $year^{-1}$ for N and 11 to 17 kg km^2 $year^{-1}$ for P and were dominated by organic nutrient forms. Yields of N and P showed a varied response to runoff, with both hydrologic transport and source limitation of nutrient yields observed across the landcover types. During stormflows, log transformed ratios of dissolved inorganic N to soluble reactive P decreased from prestorm levels of $\sim$ 1.0 to 1.5 to less than 0.3 during peak flow at all sites, illustrating that storms induce ephemeral changes in inorganic nutrient export and stoichiometry. Our findings highlight the pulsed nature of dissolved N and P export from PCTR watersheds suggesting that future changes in the seasonality and intensity of precipitation may influence the flow of terrestrial nutrients to marine ecosystems.

Keywords Nutrients · Biogeochemistry · Stoichiometric ratio · Runoff · Stream · Storm

Responsible Editor: Jacques C. Finlay.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10533-020-00752-w.

J. B. Fellman (✉) · E. Hood
Department of Natural Sciences and Alaska Coastal Rainforest Center, University of Alaska Southeast, Juneau, AK, USA
e-mail: jbfellman@alaska.edu

D. V. D'Amore · R. T. Edwards
Forest Service, U.S. Department of Agriculture, Pacific Northwest Research Station, Juneau, AK, USA

Introduction

Catchment export of nitrogen (N) and phosphorus (P) depends on a tradeoff between the capacity of terrestrial and aquatic ecosystems to retain these nutrients, and removal via downstream transport and atmospheric losses (for N). For instance, large rainfall events typically comprise a small portion of the annual hydrograph, however the associated stormflows can have a disproportionately large influence on seasonal and annual N and P yields because of the high concentrations and runoff that occurs during storms (Correll et al. 1999; Vidon et al. 2012, 2018; Mooney and McClelland 2012). At the catchment scale, our understanding of how streamflow variability differentially alters the source and transport processes that control the speciation of N and P exported is still limited (Collins et al. 2017; Maranger et al. 2018). Elucidating these catchment-scale controls on nutrient yields is critical considering the importance of N and P to the structure and function of downstream ecosystems including: periphyton growth (Dodds et al. 2002), community composition (Poxleitner et al. 2016), uptake of terrestrially-derived organic carbon (Rosemond et al. 2015), and occurrence of harmful algal blooms (Michalak et al. 2013).

Individual species of dissolved N and P may be differentially transported through catchments at varying time scales and efficiencies depending on season, hydrologic conditions, and characteristics of the stream network (e.g. slope, bed sediment characteristics). For instance, nitrate (NO_3^-) is extremely mobile in groundwater because of its negative ionic charge (Hill et al. 1999; Inamdar et al. 2004), while soluble reactive P (SRP) is readily sorbed to soils (Olander and Vitousek 2004). This results in higher ratios of inorganic N to SRP in groundwater than surface water, as observed in tropical forests (Saunders et al. 2006) and in northern watersheds dominated by mixed forest/grassland (Green et al. 2007). Unlike for NO_3^-, dissolved organic N (DON) loss is especially pronounced during high flow events that flush abundant DON to streams from organic matter rich soil surface horizons (Petrone et al. 2007; Martin and Harrison 2011). Therefore, understanding how seasonal and episodic changes in catchment runoff impacts the speciation of lateral N and P export from catchments is necessary; especially, in light of the substantial anthropogenic loading of N and P to surface waters that has occurred during the last few decades in many regions (Galloway et al. 2004; Beusen et al. 2016; Powers et al. 2016).

Although constituent yields are very much influenced by flow, evaluating the relationship between catchment runoff and N and P yields over a range of hydrological conditions can elucidate whether lateral export and speciation is controlled by production in the terrestrial ecosystem or by hydrologic connectivity between terrestrial source pools and surface waters (Zarnetske et al. 2018; Boix Canadell et al. 2019). For instance, an increase in N concentration with high flow events indicates a pool of exportable N exists within catchment soils but its delivery to surface water is transport limited. Conversely, N source limitation exists within the catchment if N concentrations decrease with increasing flow associated with a storm. To date, most studies that characterize the relationship between runoff during storm events and constituent yields from forested catchments have focused on dissolved organic carbon (Fellman et al. 2009; Raymond and Saiers 2010; Vidon et al. 2008). However, the impacts of high flow events on organic and inorganic N and P species are less well understood.

We collected streamwater (weekly to monthly) for a year and intensively during two multi-day storms (one each in summer and during the autumn rainy season) from three small (< 0.5 km^2) sub-catchments that drain the most common landcover types in southeast Alaska (poor fen, forested wetland and upland forest). Our goal was to evaluate how seasonal and episodic changes in streamflow influence the magnitude and form of dissolved N and P export from coastal temperate rainforest watersheds. We did not quantify particulate N and P because total elemental loads are typically dominated by dissolved forms in forested and wetland streams in the region (Hood et al. 2020). We also use an empirical model (power law relationship between runoff and nutrient yield) to assess the relative importance of dissolved N and P availability in soil source pools and hydrologic transport for controlling yields of organic and inorganic N and P species from the three landcover types. Our findings provide insight into how hydrologic and biogeochemical drivers interact to control lateral export of dissolved N and P and speciation from undisturbed temperate forest ecosystems that are not subjected to anthropogenic N and P loading.

Methods

Site description

This study was conducted in the 24 km^2 Peterson Creek watershed, located near Juneau, AK in the northern portion of the perhumid coastal temperate rainforest (PCTR; Fig. 1). Peterson Creek watershed,

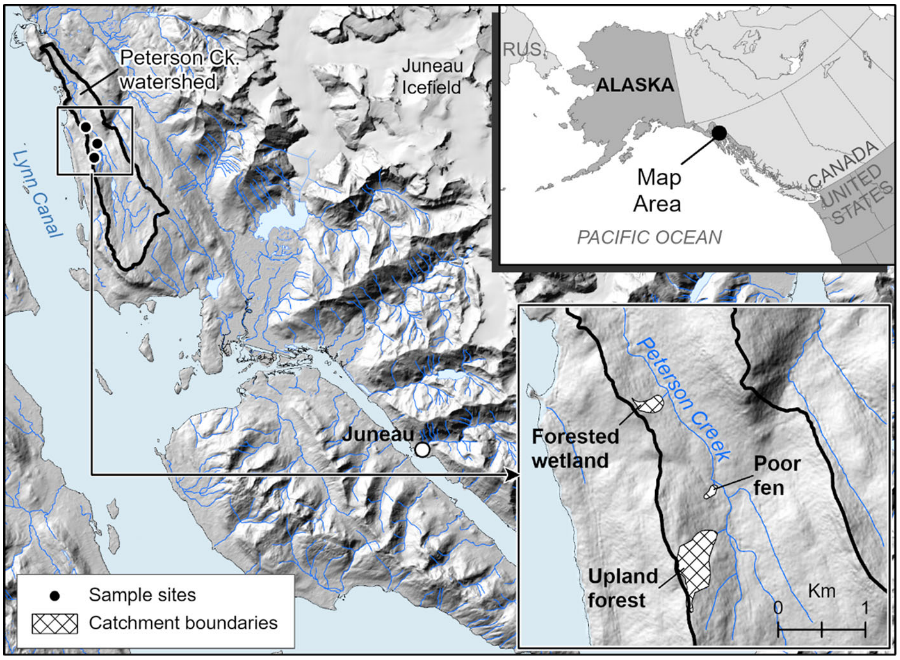

Fig. 1 Map of the study sub-catchments within the Peterson Creek watershed, near Juneau, AK

which drains into the coastal marine waters of southeast Alaska, contains a mix of physiographic features that include alpine areas, productive rainforest, and wetlands. The watershed is broadly representative of the larger PCTR in terms of watershed size and landcover. The study area has a temperate climate (mild winters and cool, wet summers) with mean monthly temperature ranging from 2 to 14 °C at sea level. Mean annual precipitation in the Juneau area exceeds 1800 mm annually at sea level, with much of it falling as rain during the late summer and autumn (D'Amore et al. 2015). Peterson Creek watershed has gradual relief (mean watershed elevation of 309 m) consisting of a landscape mosaic of organic carbon rich wetlands, which occupy 34% of the watershed area, mixed with coniferous forest dominated by *Picea sitchensis* and *Tsuga heterophylla*. Annual wet inorganic N deposition near the study watershed has been collected for 15 years as part of the National Atmospheric Deposition Program (NADP, AK02) and averages 0.43 kg N ha^{-1} $year^{-1}$.

Surface water was collected from three headwater streams draining a poor fen (area of 0.01 km^2), forested wetland (area of 0.06 km^2) and upland forest (area of 0.24 km^2) in the Peterson Creek watershed. The study streams represent the dominant landcover types within the watershed and throughout the PCTR, which consists of approximately 78% upland forests, 12% forested wetlands, and 9% poor fens (D'Amore et al. 2015). These sub-catchments were identified using wetland classification categories for the region (Cowardin et al. 1979) and by characterizing soil hydrological regimes (i.e. water table fluctuations) that dominate these landscape types (D'Amore et al. 2010, 2015). The poor fen is a histosol with soils composed of deep (> 2 m), moderately decomposed organic material (dysic, Typic Cryohemist). The forested wetland consists of > 0.5 m of well-decomposed peat overlaying glacial till (Terric Cryosaprist, Maybeso series). The forested wetland formed over the same deposits as the poor fen, but the steeper slope (average of 10%) at the site leads to greater soil hydraulic conductivity and a much deeper layer of permanent soil saturation (D'Amore et al. 2010). The upland forest is dominated by spodosols (Lithic Haplocryod), with moderately deep and well-drained soils, owing to the steeper gradient (average of 19%) relative to the two wetland sites. More detailed site and soil descriptions are available in D'Amore et al. (2015).

Field and laboratory methods

Surface water samples were collected throughout 2006 from streams draining each landcover type weekly from May through October and monthly during the remainder of the year. The May through October sampling period was the approximate length of the snow free season, and accounts for ~ 60% of total annual flow that occurs from Peterson Creek (Fellman, unpub. 7-year period of record). Streamwater samples were field-filtered through pre-combusted (> 4 h at 400 °C), glass fiber filters (pore size 0.7 μm) and stored in the refrigerator in pre-cleaned high density poly-ethylene bottles until analysis within 72 h of collection. Automated water samplers (ISCO model 3700) installed at the three sub-catchment sites were used to collect one liter of streamwater every 4–8 h over the course of two storms: July 19–22 and September 6–9. These two events were selected under different temperature (summer vs. fall) and hydrologic regimes (saturated vs. unsaturated antecedent soil moisture conditions) to assess how seasonality influences lateral N and P export. Water samples were removed from the ISCO daily, filtered through pre-combusted (> 4 h at 400 °C) GF/F filters and stored in the fridge in pre-cleaned high density poly-ethylene bottles until analysis within 72 h of collection.

Stream discharge at the three study sites was measured continuously throughout the study period (15 min intervals) using V notch weirs (Plasti-Fab) equipped with pressure transducers (Solinist LeveLogger). Barometric pressure transducers (Solinist Levelogger) located at each site were used to correct pressure transducers for atmospheric pressure changes. Manufacturer supplied rating curves were used to convert the weir stage to volumetric discharge.

Streamwater total dissolved N (TDN) concentrations were analyzed via high temperature combustion on a Shimadzu TOC/TN-V analyzer, with a lower detection limit of 0.1 mg N L^{-1}. Concentrations of NO_3-N and NH_4-N were measured via ion chromatography (Dionex ICS-1500 and 2500), with lower detections limits of ~ 2.5 and 5 μg L^{-1}, respectively. Dissolved organic N (DON) was calculated as the difference between TDN and dissolved inorganic N (DIN = NH_4-N + NO_3-N) because nitrite concentrations were frequently below the lower detection limit of ~ 5 μg L^{-1}. Soluble reactive P (SRP) was measured via the ascorbic acid method (Murphy and Riley 1962) using a 10 cm quartz flow through cell to enable the detection of low concentrations (~ 1 μg L^{-1}). We assume reactive phosphorus to be orthophosphate, although recognize that our SRP concentrations may be an overestimate of the true orthophosphate concentration in our study streams because SRP may include organic forms of P that react with the reagents involved in SRP analysis (Maruo et al. 2016). Total dissolved P (TDP) was measured by persulfate digestion together with the ascorbic acid method (Valderrama 1981). Dissolved organic P (DOP) was calculated by differencing TDP and SRP.

Annual flux and yields of N and P

Annual dissolved streamwater N and P export were calculated using daily discharge and our routine N and P measurements using the U.S. Geologic Survey LoadEstimator program (LoadEst; Runkel et al. 2004). LoadEst. calculates daily N and P loads (kg day^{-1}) by applying the best fit among nine models available in LoadEst. The Akaike Information Criteria (AIC) was used to select the model that best fit the data for each nutrient species at each site. Daily export was summed to produce seasonal and annual fluxes from each landcover type, and area-weighted yields were derived by normalizing the annual N and P flux by the watershed area of the landcover type. Standard errors (± 1) for annual N and P yields were generated in LoadEst.

Statistical analyses

Linear regression was used to assess the relationship between runoff and either concentrations or molar ratios of N to P across the sampling period. If necessary, data were log transformed to satisfy the basic assumptions of regression analyses. All molar ratios of N to P were log transformed to reduce bias as described in Isles (2020). To compare N and P concentrations to variations in discharge, we used the mean daily discharge (Q_w) when surface water was collected normalized to mean annual daily discharge (Q_w/Q_{mean}), as described in Hilton et al. (2012).

We used the relationship between runoff and nutrient yields (rather than concentrations) to evaluate the relative importance of sub-catchment source pools and hydrologic transport for controlling stream N and P export (Moatar et al. 2017; Zarnetske et al. 2018;

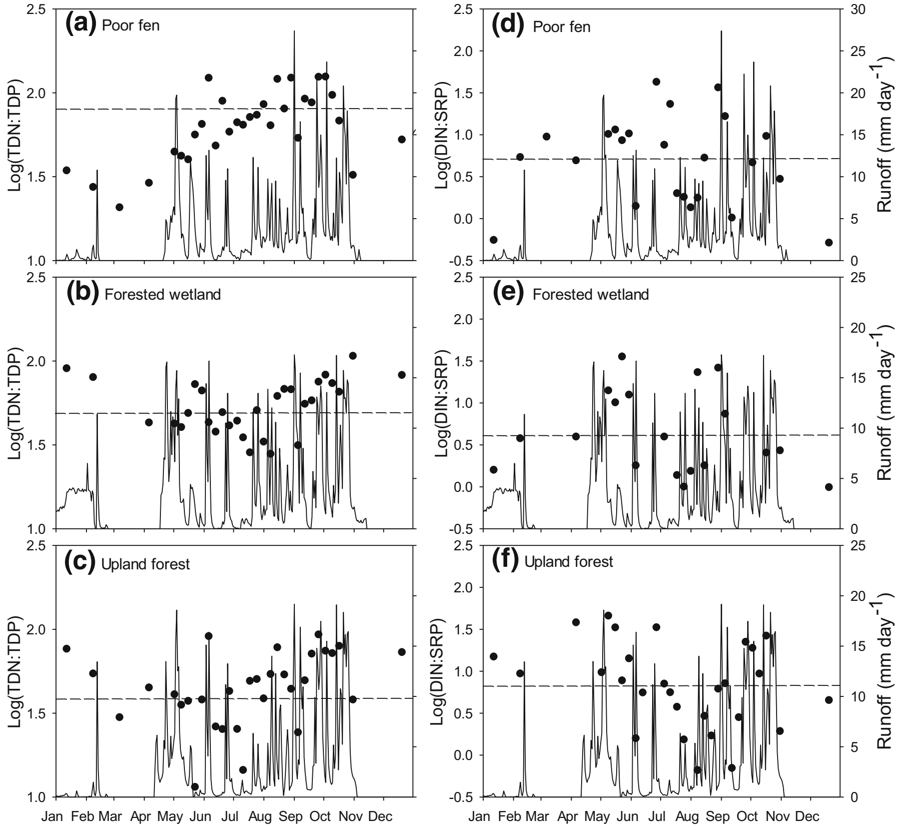

Fig. 2 Streamwater molar ratios of log transformed. **a–c** TDN to TDP and **d–f** DIN to SRP versus runoff (solid black line) for the poor fen, forested wetland and upland forest across the year-long sampling period. Horizontal dashed line in each plot indicates annual mean at each site

Boix Canadell et al. 2019). We quantified this relationship because yields incorporate variability in flow making it better suited than concentration-discharge relationships for evaluating N and P balances at the catchment-scale. We used a power function ($F = aQ^b$) between runoff (Q) and nutrient yields (F) where a is the concentration normalization coefficient and b is the slope coefficient that indicates whether watershed N and P yields are transport ($b > 1$) or source ($b < 1$) limited (Zarnetske et al. 2018; Boix Canadell et al. 2019). Discrete models were developed for all species of N and P in the three sub-catchment streams and we report the coefficient of determination and b values for the linear fit in log space. The models do not account for temporal autocorrelation as previously noted (Vaughan et al. 2017; Boix Canadell et al. 2019). All statistical analyses were performed in SPSS software.

Results

Sub-catchment runoff

Daily runoff was generally highest in the forested wetland (mean of 3.4 ± 4.3 mm day^{-1}) followed by the poor fen (mean of 2.9 ± 4.5 mm day^{-1}) and upland forest (mean of 2.8 ± 4.5 mm day^{-1}; Fig. 2a-f). However, daily runoff in the upland forest had a slightly greater coefficient of variation (CV = 1.5) than in the poor fen (CV = 1.4) and forested wetland (CV = 1.3). Runoff dynamics in all three streams showed strong seasonality, with extended periods of low flow (< 1 mm day^{-1}) in the winter months (December through April) followed by a snowmelt pulse that generally lasted from late April through mid-May. Sub-catchment runoff during the summer months of June and July occurred mainly through pronounced rainfall peaks that often exceeded 15 mm day^{-1} followed by periods of low flow. At all sites, peak daily runoff generally occurred during the autumn wet season (August through October).

Seasonal concentration and export of N and P

Streamwater TDN concentrations ranged from 95 to 502 µg N L^{-1} across all sites, with mean concentrations nearly 50% greater in the wetland streams than the upland forest (Fig. 3a–c; Fig. S1–S3). In contrast, mean TDP concentrations were similar across the three sub-catchment types. Concentrations of DON on average accounted for more than 90% of TDN at all sites, with DIN concentrations generally less than 10 µg N L^{-1}. Similar to DON, DOP was the dominant fraction of TDP for all sites (> 70%), with SRP concentrations generally less than 4 µg P L^{-1} (Fig. 3a–c; Fig. S1–S3).

Dissolved N and P concentrations were analyzed over a large range of flows, with Q_w/Q_{mean} ranging from 0.03 to 3.7 on the day of sampling (Fig. 4a–d). However, ~ 75% of the stream sample dates had a Q_w/Q_{mean} of < 1.0 indicating the majority of our measurements occurred during below average flow. Over this range, the highest DIN concentrations at all sites were observed during below average flows with Q_w/Q_{mean} <1.0 (Fig. 4a). In contrast, higher DON and P concentrations during above average flows with Q_w/Q_{mean} >1.0 resulted in a modest positive correlation between Q_w/Q_{mean} and SRP ($r^2 = 0.22$, $P < 0.001$, $F = 23.2$), DON ($r^2 = 0.29$, $P < 0.001$, $F = 33.9$) and DOP ($r^2 = 0.14$, $P < 0.001$, $F = 14.0$) for all sites together. Streamwater log(DIN:SRP) showed no clear pattern with Q_w/Q_{mean}, although ratios were highest when Q_w/Q_{mean} <1.5 and decreased with increasing flow such that log(DIN:SRP) were all below 1.2 during higher flows (Q_w/Q_{mean} >2.0; Fig. 4e). Similarly, log(TDN:TDP) varied widely across all sites and sample dates (Fig. 4f).

Mean log(TDN:TDP) during the year-long study period were highest in the poor fen (1.8) followed by the forested wetland (1.7) and upland forest (1.6, Fig. 2a–c). Streamwater log(TDN:TDP) in the poor fen was related to daily runoff ($r^2 = 0.18$, $p = 0.02$, $F = 6.2$), and varied seasonally, with ratios increasing from a low of 1.3 in March to their fall maximum of 2.1 before decreasing following the fall wet season (Fig. 4a). In the forested wetland, log(TDN:TDP) was not related to runoff ($r^2 = 0.02$, $p = 0.50$, $F = 0.5$), but varied seasonally, with ratios generally above 1.7 during the late fall and winter months and below 1.6 during the spring and summer months (Fig. 2b). In contrast, streamwater log(TDN:TDP) in the upland forest did not follow a distinct seasonal pattern but rather was moderately related to daily runoff ($r^2 = 0.18$, $p = 0.02$, $F = 6.4$) across the study period (Fig. 2c).

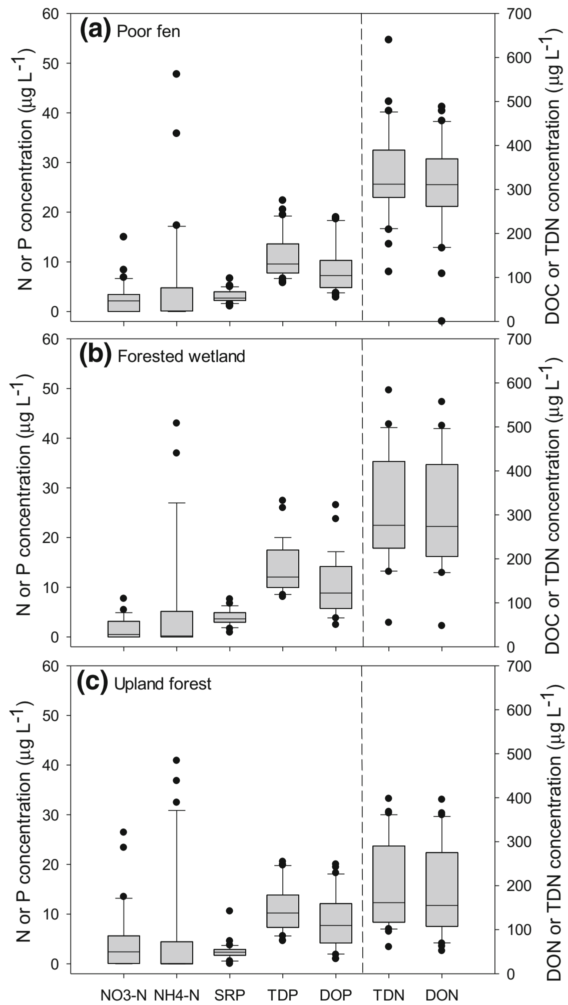

Fig. 3 Box plots of streamwater N and P concentrations for the **a** poor fen, **b** forested wetland and **c** upland forest across the year-long sampling period. N = 31 for each parameter. The line within the box is the median, dots are the 10th and 90th percentile points and the vertical bars are the 25th and 75th percentiles

Annual log molar ratios of DIN to SRP at all sites were substantially less than those of TDN:TDP reflecting that TDN had a larger organic fraction than TDP (Fig. 2d–f). Streamwater log(DIN:SRP) were highly variable, ranging from < − 0.2 to 1.7 at all sites, and values were not related to daily runoff (all $r^2 < 0.02$, $p > 0.53$). Log ratios of DIN to SRP were typically less than 0.7 in the wetland sites (annual mean of 0.7 in the poor fen and 0.6 in the forested

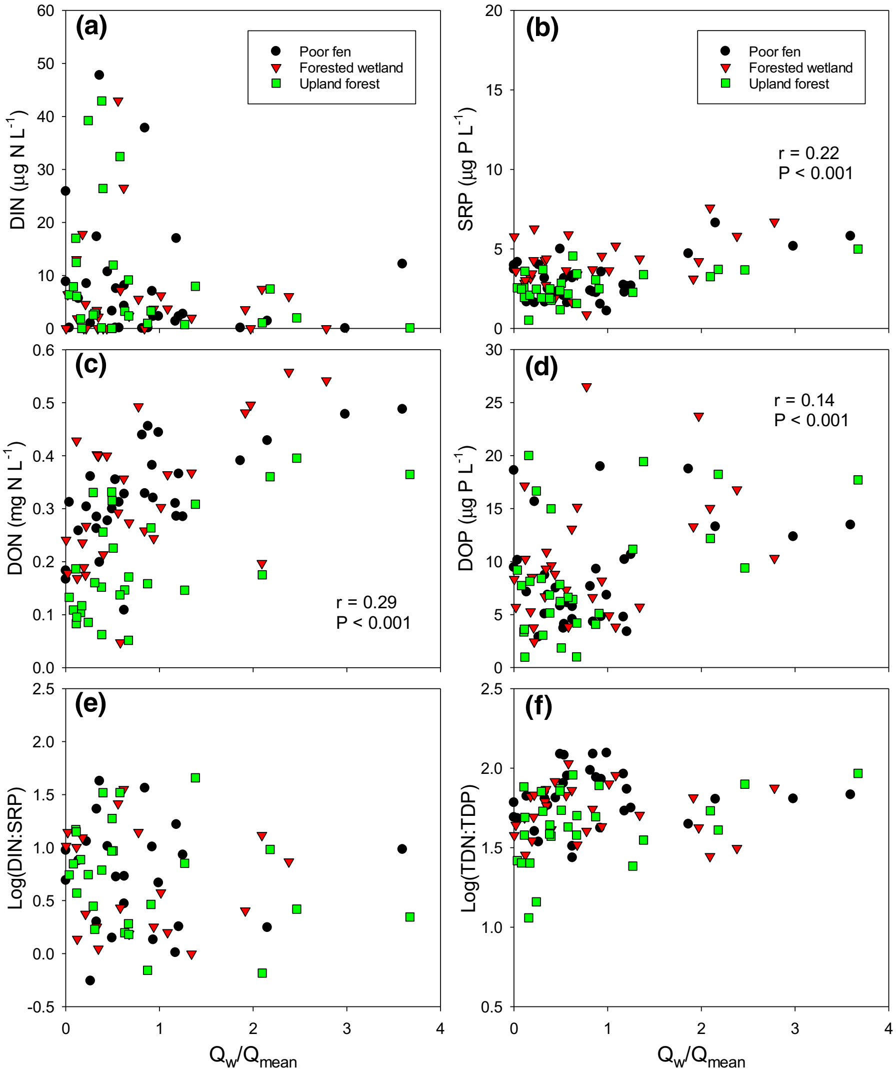

Fig. 4 Relationship between mean daily discharge (Q_w) normalized to mean annual daily discharge (Q_{mean}) and **a** DIN, **b** SRP, **c** DON, **d** DOP, **e** log(DIN:SRP) and **f** log(TDN:TDP) for the poor fen, forested wetland and upland forest across the year-long sampling period

wetland) and less than 0.8 in the upland forest (annual mean of 0.8).

Annual yields of TDN and TDP in the two wetland streams were almost double that of the upland forest (Table 1). The speciation of total dissolved N and P yield was similar in all sites, with organic N accounting for > 90% of the annual TDN yield and organic P accounting for > 70% of the annual yield of TDP (Table 1). Similar to total dissolved N and P, yields of DOP and especially DON were larger in the two wetland streams compared to the upland forest. Inorganic dissolved N and P yields were low (< 5.0 kg km^2 year^{-1} for both N and P) compared to dissolved organic N and P for all sites, except for NH_4-N in the forested wetland, which exceeded 17 kg km^2 year^{-1}.

The speciation of N and P yields varied seasonally across sites, with yields of most species peaking during the wet season months of August through October (Fig. 5a–d). Nearly 76% of the annual DIN yield from the forested wetland occurred during August through October, whereas DON, SRP and DOP yields from the site were more evenly distributed throughout the year (Fig. 5b–d). In the upland forest, inorganic N and P yields from August through October (2.6 and 1.4 kg km^2, respectively) accounted for only a third of annual DIN yield but 68% of total annual SRP yield from the site. Yields of dissolved N and P were low in the winter months of November through April at all three sites (range of 6 to 24% of the total annual yields), except in the forested wetland where

Table 1 Annual yields (± 1 SE) of dissolved N and P in the poor fen, forested wetland and upland forest

	Poor fen kg km^2 year^{-1}	Forest wetland kg km^2 year^{-1}	Upland forest kg km^2 year^{-1}
TDN	405.8 (39.2)	372.9 (58.6)	235.8 (28.4)
TDP	12.6 (1.3)	17.1 (2.3)	10.7 (1.2)
NH_4-N	2.9 (2.5)	17.6 (12.1)	3.7 (3.4)
NO_3-N	2.4 (1.3)	2.2 (0.7)	3.4 (0.9)
SRP	2.4 (0.5)	3.5 (0.5)	2.1 (0.4)
DON	400.5 (41.0)	353.1 (67.6)	228.7 (32.1)
DOP	10.2 (2.2)	13.6 (3.4)	8.6 (2.8)

more than 25% of the total annual yields of SRP and DON occurred during winter.

Hydrologic vs. source limitation of N and P yields

A power model was a strong fit to the relationship between daily runoff and dissolved yields of N and P for the three sub-catchments (all $r^2 > 0.8$ except for NH_4-N). The slope coefficients for all N and P species ranged from 0.51 to 1.44 across the three sub-catchments indicating both transport and source limitation of dissolved N and P yields over the year-long study period (Fig. 6a). In particular, b values for DIN averaged 0.88 driven by the strong source limitation exhibited for NH_4 (mean b value = 0.68) and NO_3 (mean b value = 0.67) across sites (Fig. 6b). However, b values averaged 1.12 for DON across sites indicating a contrast in the main driver, from source to hydrologic transport, of DON yields from the study streams (Fig. 6b). For P yields, the average slope coefficient for DOP was 1.31 while SRP was 0.97 suggesting SRP production and mobilization are nearly equal to changes in runoff (Fig. 6c).

Stormflow concentrations and speciation of N and P

Peak runoff during the July and September storms ranged from 2x–4x mean daily runoff across the three sites. Streamwater DON concentrations in the poor fen more than doubled from pre-storm levels during the July storm and increased 35% during the September storm, but subsequently decreased to near pre-storm levels on the falling limb of both storm hydrographs (Fig. 7a, b). Similarly, DON concentrations increased during both storms in the forested wetland and upland forest, with the magnitude of increase greater in July than in the September storm (Fig. 7c–f). Pre-storm DON concentrations at all sites were higher before the fall storm (average of 211 µg N L^{-1}) than before the summer storm (average of 182 µg N L^{-1}), contributing to a greater percent increase in concentration during the summer relative to the fall storm.

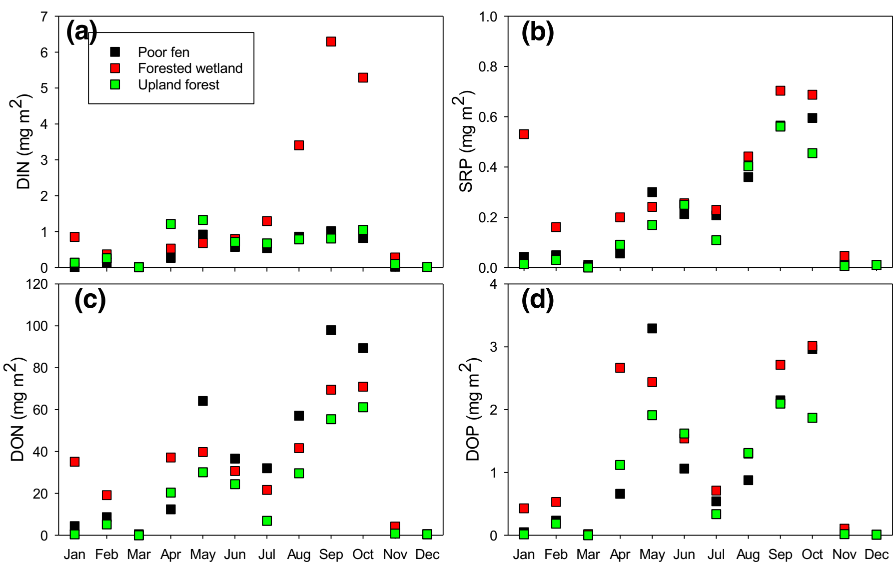

Fig. 5 Monthly yields of **a** DIN, **b** SRP, **c** DON and **d** DOP for the poor fen, forested wetland and upland forest across the year-long sampling period

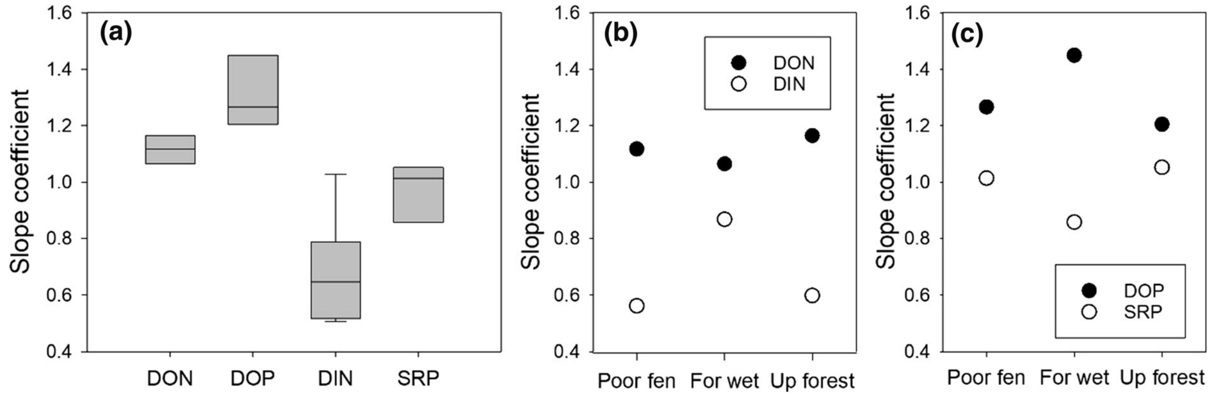

Fig. 6 Box plots of the slope coefficients (*b* values) grouped by **a** dissolved organic and inorganic N and P for all three sub-catchment types together. The line within the box is the median, dots are the 10th and 90th percentile points and the vertical bars are the 25th and 75th percentiles. Scatter plots of slope coefficients (*b* values) for **b** DON and DIN (includes NO_3^- and NH_4^+) and **c** SRP and DOP vs. the poor fen, forested wetland (for wet) and upland forest (up forest)

In contrast to DON, DIN concentrations at all sites decreased with flow, particularly during the summer storm (Fig. 7a–f). The greatest overall percent decrease in DIN occurred during the summer storm in the upland forest, when concentrations decreased from a pre-storm maximum of 17.1 to 2.4 μg N L^{-1} a few hours before peak flow. These event-driven shifts in N speciation resulted in a severalfold increase in the ratio of DON to DIN during peak flow at all sites and changes were especially pronounced in the upland forest and forested wetland during the September storm.

Streamwater DOP and SRP concentrations generally tracked runoff during both storms at all sites, with the percent increase in concentrations from prestorm levels greater during the July than the September storm (Fig. 8a–f). The increase in DOP was most pronounced at the forested wetland, where concentrations increased from prestorm levels an average of 8 μg P L^{-1} or ~ 70% over both storms. Prestorm SRP concentrations at all sites were generally lower than DOP, but increased by a larger percent (average of ~ 400% across both storms and all sites) during storms compared to DOP (average of 47% across both storms and all sites). These changes in P concentration were exemplified by log(DIN:SRP), which decreased from prestorm levels at all sites to ratios < 0.2 as a result of the pronounced increase in SRP concomitant with the decrease in DIN during storm flows (Fig. 9a–d). Alternatively, log(TDN:TDP) in the wetland sites either decreased slightly or changed little during peakflow of both storms, but in the upland forest, ratios increased from prestorm levels of ~ 1.3 to more than 1.5 during peak flow (Fig. 9e, f).

Discussion

Seasonal export and stoichiometric ratios of N and P

Our findings support the notion that catchment runoff is a strong control on the magnitude and ratio of dissolved N to P exported from forested watersheds (Green et al. 2007; Green and Finlay 2010; Blackburn et al. 2017; Koskelo et al. 2018). Previous studies in forested and wetland watersheds receiving low amounts of N deposition have shown that DON dominates the dissolved N load in streamwater (Hedin et al. 1995; Campbell et al. 2000; Pellerin et al. 2004; Oyarzún et al. 2005). The fact that DON accounted for $> 90\%$ of the TDN load in our study streams is further evidence that lateral DON export is the primary pathway of N loss from temperate forested watersheds where plant productivity is limited by N (Perakis 2002; Neff et al. 2003; Sponseller et al. 2018). Streamwater DOP was also the dominant species ($> 70\%$) of TDP in our study confirming that organic P is the dominant species of lateral P loss from forested watersheds in the PCTR and similar to other regions that do not receive elevated anthropogenic (e.g. fertilizer runoff) inputs (Devito and Dillon 1993; Seitzinger et al. 2005; Hood et al. 2019).

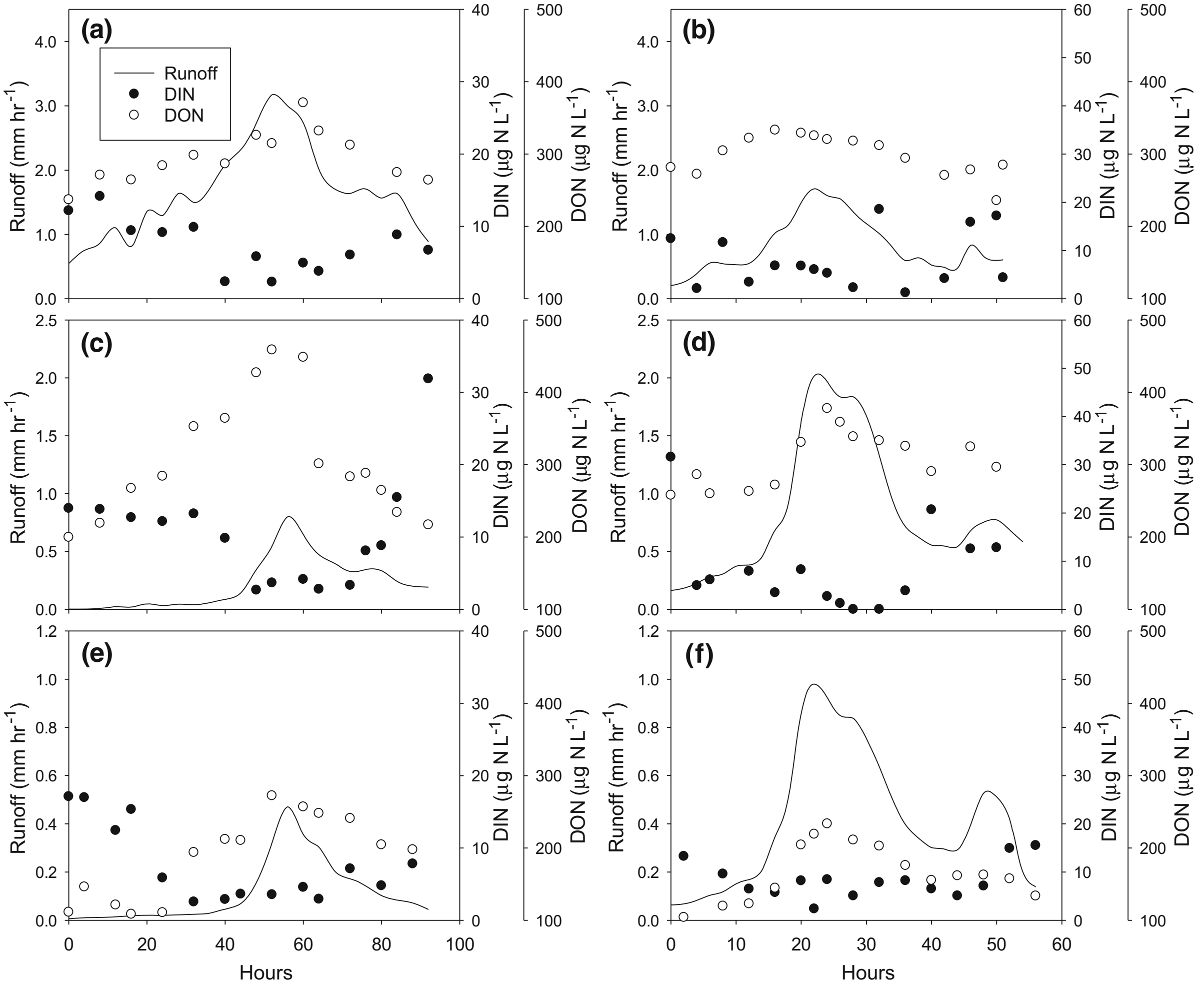

Fig. 7 Runoff and streamwater concentrations of DIN and DON for the poor fen (**a**, **b**), forested wetland (**c**, **d**) and upland forest (**e**, **f**) during the July 19–22 and September 6–9 storms

Dissolved organic N yields from our small, headwater sub-catchments (Table 1) were greater than those found in northern wetlands (Sponseller et al. 2018) and boreal forested watersheds (Aitkenhead-Peterson et al. 2005; Blackburn et al. 2017), montane forests of the Rocky Mountains (Hood et al. 2003; Kaushal and Lewis 2005), and temperate forested watersheds of the eastern U.S.A (Brookshire et al. 2007; Campbell et al. 2000), but similar to coastal temperate South America (Perakis and Hedin 2002). Yields of dissolved organic carbon (DOC) in the relatively small watersheds of southeast Alaska and coastal British Columbia are among the highest reported on Earth (D'Amore et al. 2015; Oliver et al. 2017). Thus, the DON yields observed in this study suggest that the high runoff, fluctuating water tables and large soil organic matter pools (D'Amore et al. 2015) that promote high DOC export from small PCTR watersheds also promote DON export to coastal ecosystems. This contrasts with DIN yields from the study streams, which were less than forested watersheds in other regions, especially those subject to anthropogenic inputs (e.g. fertilizer application; Scott et al. 2007; Stanley and Maxted 2008), elevated N deposition (Seitzinger et al. 2010) or an abundance of N-fixing alders (Compton et al. 2003; Shaftel et al. 2012). These results suggest that tight biotic demand of DIN previously observed in PCTR soils limits that potential pool of exportable N to stream networks (Bisbing and D'Amore 2018).

Streamwater N and P yields from the three sub-catchments varied seasonally, which is consistent with

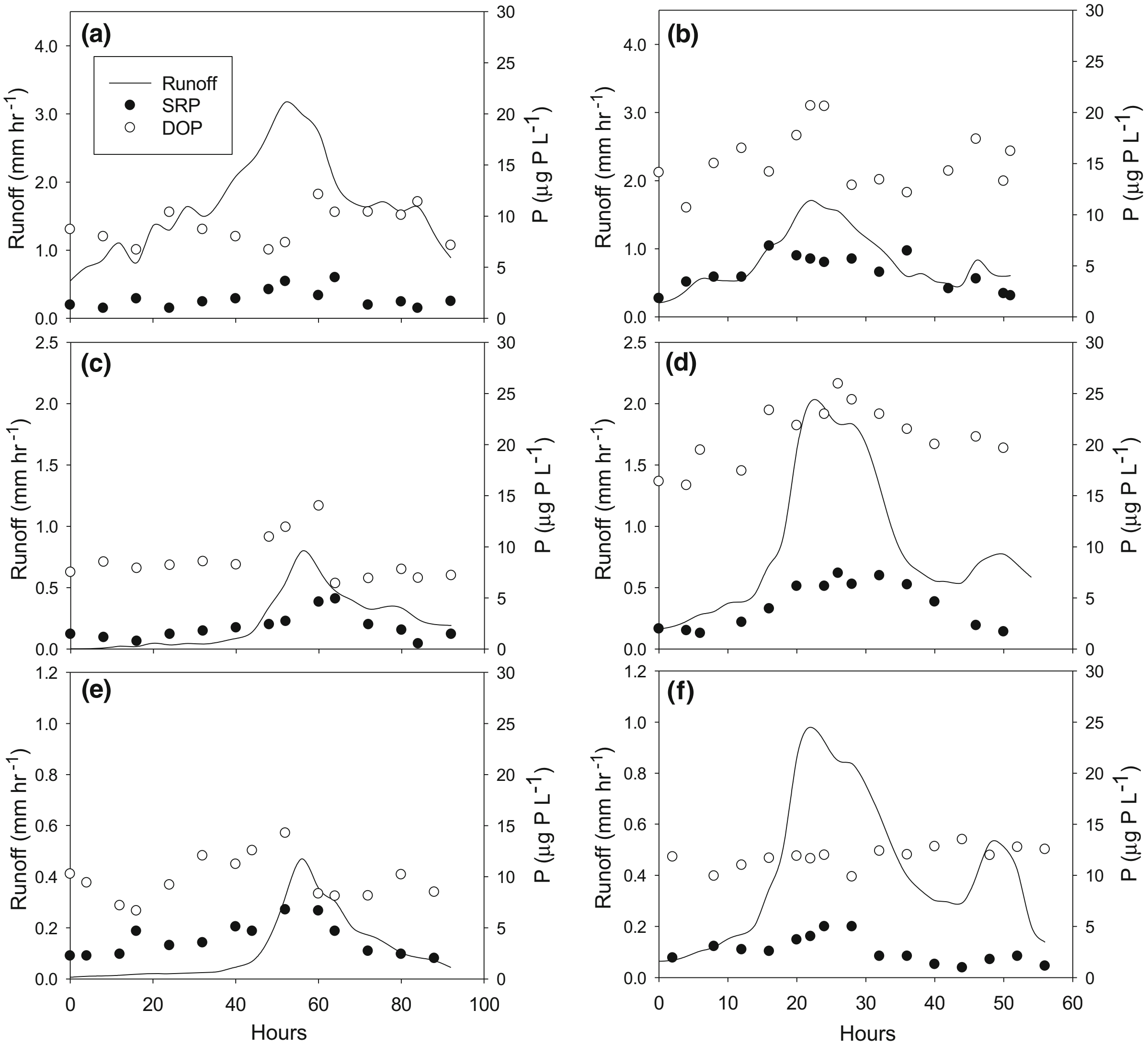

Fig. 8 Runoff and streamwater concentrations of SRP and DOP for the poor fen (**a**, **b**), forested wetland (**c**, **d**) and upland forest (**e**, **f**) during the July 19–22 and September 6–9 storms

studies of temperate forests showing distinct seasonal patterns in nutrient export (Sponseller et al. 2014; Lin et al. 2019). Our finding that the greatest fraction of stream DON and DOP yield from all sites occurred during August through October (autumn rainy season) supports previous research in the region showing that most of the DOC flux occurs during this period when frequent frontal storms moving off the Gulf of Alaska (GOA) deliver heavy precipitation to coastal southeast Alaska (D'Amore et al. 2015; Oliver et al. 2017; Hood et al. 2019). Watershed yields of dissolved N and P were also substantial during May through July, with an average of 30% of annual N and P export occurring during this 3-month period despite presumably high demand in terrestrial ecosystems during the summer. The May through July loss of N and P was especially pronounced in the poor fen, where an average of 36% of TDN and TDP occurred during this period. Similarly, previous studies show that peatlands of northern Minnesota have low retention efficiencies of N (∼ 50%) and P (∼ 25%; Verry and Timmons 1982) during the growing season despite strong nutrient limitation of plant productivity (Hill et al. 2014).

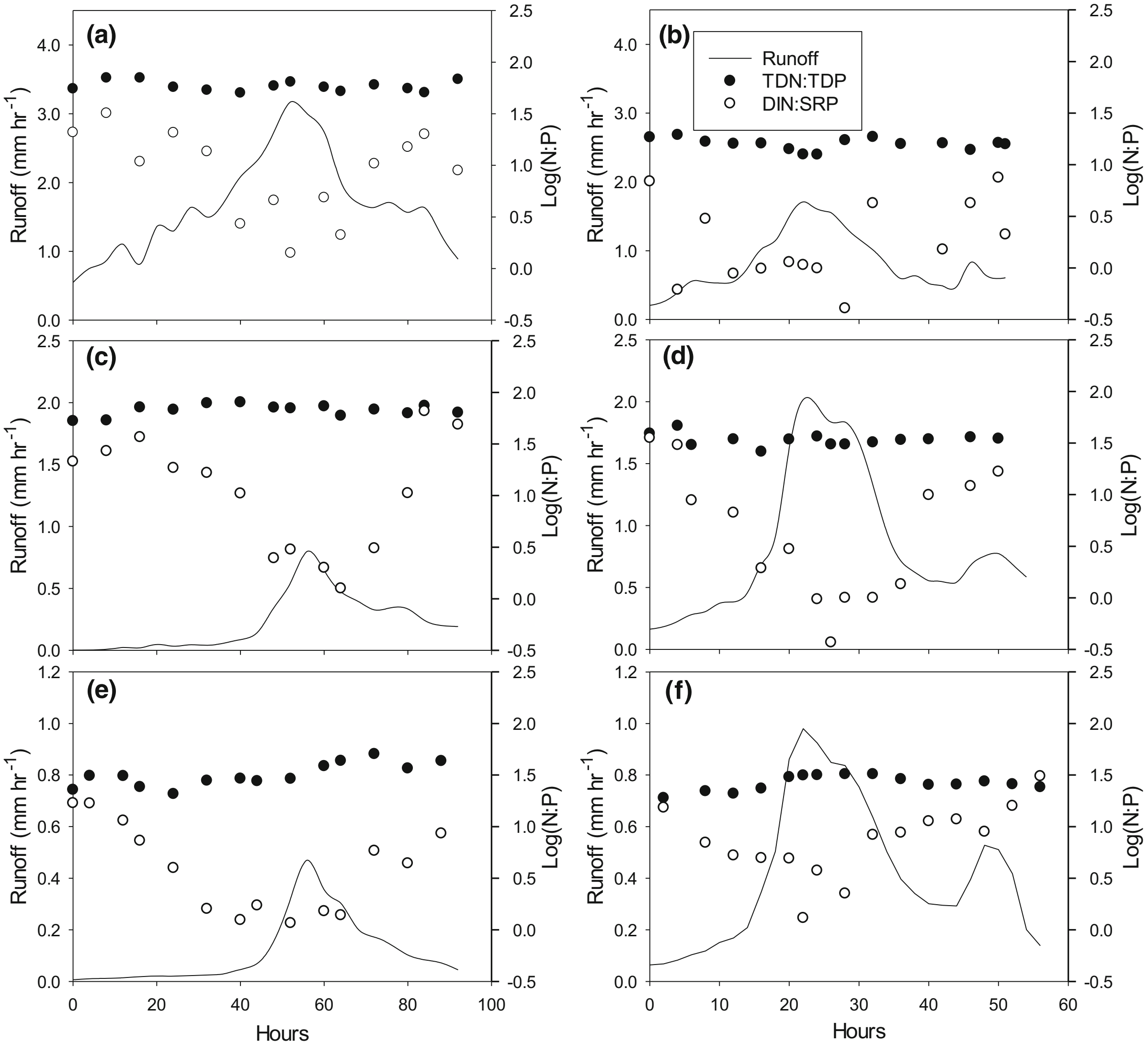

Fig. 9 Runoff and log transformed molar ratios of **a–c** TDN to TDP and **d–f** DIN to SRP for the poor fen (**a**, **b**), forested wetland (**c**, **d**) and upland forest (**e–f**) during the July 19–22 and September 6–9 storms

Streamwater P concentrations generally showed less seasonal variation than N at all sites. Streamwater log(TDN:TDP) in the forested wetland and upland forest were generally 25–50% lower during May through October than the rest of the year even though there was minimal seasonal variation in TDP concentrations (Fig. S1–S3). Since DON (dominant fraction of TDN) production in PCTR soils is typically high during the mid to late summer (Fellman et al. 2008; D'Amore et al. 2010), either tight biotic retention of N by both forested ecosystems and/or limited hydrologic transport of DON during summer low flow conditions likely resulted in the seasonal depression in log(TDN:TDP) in the two sites. Furthermore, log (DIN:SRP) showed no clear seasonal pattern across all sites and was not related to runoff suggesting terrestrial nutrient retention and hydrology interact to control patterns of nutrient export and speciation across the three sub-catchments (Sponseller et al. 2014). An improved understanding of the soil processes that create soluble pools of nutrients available for lateral transfer and how climate shifts might impact these soil source pools would help to elucidate the controls on terrestrial N and P transfer to streams.

It is well accepted that N, P or some form of co-limitation can constrain stream ecosystem production in a wide range of streams (Francoeur 2001; Dodds et al. 2002; Diemer et al. 2015; Docherty et al. 2018). In our study, mean log(DIN:SRP) was 0.7 for all sites together indicating nutrient delivery to streams occurs in ratios that favor inorganic N limitation over P. However, mean log(TDN:TDP) was 1.7 for all sites together suggesting that if streams are able to readily mineralize organic forms of N (Brookshire et al. 2005; Lutz et al. 2011), P may limit overall production by stream communities. Estimates of the delivery of bioavailable DON to headwater streams do not reveal the organic N contribution to stream production or the extent to which it alleviates stream N limitation. The ability of stream ecosystems to capitalize on these terrestrial inefficiencies and use organic N likely depends on inorganic N supply and the chemical quality of DOM, with organic N contained in amino acids and other monomers readily metabolized by stream communities (Volk et al. 1997; Fiebig 1997; Benner and Kaiser 2011). Although this study does not evaluate the extent to which N and P control stream ecosystem production relative to other factors (e.g., light, temperature), our findings suggest that seasonal and event-driven shifts in N and/or P could constrain production in PCTR streams.

Hydrologic control of N and P yields

Organic N and P yields are seldom investigated together in catchment-scale studies and we found evidence of a strong hydrologic control on their export from the study sites. The power law relationship between nutrient yields and runoff (*b* values > 1.0) and the correlations between Q_w/Q_{mean} and organic N and P concentrations provide several lines of evidence that soils in all three major landcover types we studied contain large pools of soluble organic N and P that are seldom depleted by high flows. These results suggest that the hydrologic transport limitation commonly observed for DOC in many forested and wetland watersheds across the U.S.A. (Creed et al. 2015; Zarnetske et al. 2018) may also control organic N and P export.

Unlike for organic N and P, *b* values for the power law relationship between DIN yields and runoff were well below 1.0 indicating source- rather than transport-limitation of DIN yields from the study sub-catchments. This is likely the result of strong biotic retention in the terrestrial ecosystem (Perakis and Hedin 2001; Bisbing and D'Amore 2018). On the other hand, *b* values for SRP were close to 1.0 suggesting changes in runoff were similar to SRP production and transport to surface water. This finding highlights the complex interplay between hydrological and biological processes that control N and P speciation and yields where sub-catchment soils likely swing between strongly retentive and passive flow through networks depending on hydrologic conditions and seasonality. Overall, our findings suggest that a broader understanding of watershed nutrient dynamics cannot be achieved without a mechanistic understanding of the impacts of seasonal and event-driven changes in runoff on the concentration and speciation of N to P exported from forested watersheds.

Stormflows alter N and P export and stoichiometric ratios

Our storm sampling reveals how episodic changes in runoff can impact the export and speciation of N and P. During storms in the PCTR, streamflow is generated almost entirely from flow through organic matter rich surface soil horizons because soil water table levels are elevated into the hydrologically active surface horizons (Emili and Price 2006; D'Amore et al. 2015). This results in the rapid flushing of DOC to surface water (Sanderman et al. 2009; Fellman et al. 2009; Wilson et al. 2013), as observed in this study for DON and, to a lesser extent, DOP across all landscape types. There was also a greater response for TDP (driven mainly by SRP) concentrations during stormflows than for TDN, similar to previous studies showing shallow subsurface flow is generally enriched in SRP relative to N due to the transport of P-rich particles (Correll et al. 1999) and less potential for P soil sorption (Olander and Vitousek 2004).

The positive correlation between Q_w/Q_{mean} and seasonal N and P concentrations highlights the episodic nature of high flow events in terms of N and P export, particularly in organic forms (Inamdar and Mitchell 2007), from PCTR watersheds. Strong retention across the terrestrial–aquatic interface presumably limits inorganic N and P delivery to streams during baseflow (Gerber and Brookshire 2014). However, storm flowpaths may bypass baseflow nutrient and organic matter controls in terrestrial ecosystems

(Wilson et al. 2016; Coble et al. 2016; Lin et al. 2019), thereby exporting a pulse of both inorganic and organic forms of N and P to the stream. Other studies of temperate forested watersheds have similarly shown that more than 70% of N, P and DOC export occur during high flow events (Royer et al. 2006; Bhat et al. 2007; Raymond and Saiers 2010). In an extreme case, P export during Hurricane Irene accounted for an estimated 50% of the annual dissolved P flux from temperate forested streams on the eastern coast of the U.S.A (Vidon et al. 2018). Future research that involves sampling storms at different times of the year and across a wider range of discharge is necessary to enhance our understanding of the impacts of high flow events on seasonal and annual N and P (and speciation) export.

Event-driven shifts in streamwater N and P concentrations were evident in stoichiometric ratios during both storms, as exemplified by the decrease in log(DIN:SRP) to < 0.3 during peakflow in all sites. However, this convergence of log(DIN:SRP) was ephemeral because once baseflow resumed following the storm, log(DIN:SRP) diverged and became more similar to the annual averages at each site. Therefore, event-driven changes in soil hydrology, likely towards a predominance of shallow subsurface flow, increased the similarity between stream types with regards to log(DIN:SRP). These results concur with previous research showing that event-driven shifts in watershed hydrology can result in ephemeral changes in the degree of similarity in N to P ratios (Green et al. 2007). Our findings provide evidence that stormflows send pulses of nutrients to downstream ecosystems that alter stoichiometric ratios and induce transient shifts in the export of terrestrial nutrients. In the PCTR, the substantial DON and DOP yields observed here and the close proximity to the ocean of many small and steeply sloping watersheds that are common to the region likely results in the bulk of these terrestrial nutrients being transported to coastal marine ecosystems. Therefore, our findings support the notion that a distributed network of small, ungauged near-coastal watersheds export terrestrial nutrients to the sea of similar (or greater) magnitude than larger monitored rivers (Destouni et al. 2008).

Conclusions

Temperature in the PCTR is projected to increase 1.7–5.5 °C by 2100 and precipitation is predicted to increase 80–560 mm by 2100, with an increasing amount of precipitation falling as rain rather than snow at sea level (Shanley et al. 2015). These changes will increase the frequency and intensity of storms in the region (Sharma and Déry 2020) as well as alter N and P cycling (e.g., nitrogen mineralization; Bisbing and D'Amore 2018) in the tightly linked terrestrial and aquatic ecosystems in the region. Our findings indicate that stormflows could become an even larger driver of N and P export and stoichiometry under future climate regimes. However, we still have a limited understanding of how generalizable our findings are to stormflows over the course of the year or how N and P export and speciation might be impacted when multiple storms occur during a short period of time, such as during the autumn wet season. Therefore, future research on the impact of stormflows on nutrient pulsing in headwater catchments will be a valuable next step in determining the effects of changing climate on the nutrient status of temperate forested ecosystems, with potential implications for changes in nutrient stoichiometry of their receiving waters. Overall, our findings contribute new data on seasonal and event-driven nutrient export and thus broaden the perspective of the hydrologic control on N and P stoichiometry in temperate forested watersheds.

Acknowledgements The authors wish to acknowledge Karen Michael and Jacob Berkowitz for laboratory and field assistance and Frances Biles for map preparation. The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Funding This study was funded by the U.S. Department of Agriculture National Research Initiative (2005-35102-16289), Alaska EPSCoR (OIA-1753748) and the USDA Forest Service Pacific Northwest Research Station in Juneau, Alaska.

Data availability Available upon request to corresponding author.

Code availability Not applicable.

Compliance with ethical standards

Conflict of interest Not applicable.

References

Aitkenhead-Peterson JA, Alexander JE, Clair TA (2005) Dissolved organic carbon and dissolved organic nitrogen export from forested watersheds in Nova Scotia: identifying controlling factors: DOC and DON export. Global Biogeochem Cycles. https://doi.org/10.1029/2004GB002438

Barnett TP, Adam JC, Lettenmaier DP (2005) Potential impacts of a warming climate on water availability in snow-dominated regions. Nature 438:303–309. https://doi.org/10.1038/nature04141

Benner R, Kaiser K (2011) Biological and photochemical transformations of amino acids and lignin phenols in riverine dissolved organic matter. Biogeochemistry 102:209–222. https://doi.org/10.1007/s10533-010-9435-4

Beusen AHW, Bouwman AF, Van Beek LPH et al (2016) Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum. Biogeosciences 13:2441–2451. https://doi.org/10.5194/bg-13-2441-2016

Bhat S, Hatfield K, Jacobs JM et al (2007) Surface runoff contribution of nitrogen during storm events in a forested watershed. Biogeochemistry 85:253–262. https://doi.org/10.1007/s10533-007-9131-1

Bisbing S, D'Amore DV (2018) Nitrogen dynamics vary across hydrologic gradients and by forest community composition in the perhumid coastal temperate rainforest of southeast Alaska. Can J For Res 48:180–191. https://doi.org/10.1139/cjfr-2017-0178

Blackburn M, Ledesma JLJ, Näsholm T et al (2017) Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal forest catchment. J Geophys Res 122:324–339. https://doi.org/10.1002/2016JG003535

Boix Canadell M, Escoffier N, Ulseth AJ et al (2019) Alpine glacier shrinkage drives shift in dissolved organic carbon export from quasi-chemostasis to transport limitation. Geophys Res Lett 46:8872–8881. https://doi.org/10.1029/2019GL083424

Brookshire ENJ, Valett HM, Thomas SA, Webster JR (2005) Coupled cycling of dissolved organic nitrogen and carbon in a forest stream. Ecology 86:2487–2496. https://doi.org/10.1890/04-1184

Brookshire ENJ, Valett HM, Thomas SA, Webster JR (2007) Atmospheric N deposition increases organic N loss from temperate forests. Ecosystems 10:252–262. https://doi.org/10.1007/s10021-007-9019-x

Campbell JL, Hornbeck JW, McDowell WH et al (2000) Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry 49:123–142

Coble AA, Marcarelli AM, Kane ES et al (2016) Temporal patterns of dissolved organic matter biodegradability are similar across three rivers of varying size. J Geophys Res 121:1617–1631. https://doi.org/10.1002/2015JG003218

Collins SM, Oliver SK, Lapierre J-F et al (2017) Lake nutrient stoichiometry is less predictable than nutrient concentrations at regional and sub-continental scales. Ecol Appl 27:1529–1540. https://doi.org/10.1002/eap.1545

Compton JE, Church MR, Larned ST, Hogsett WE (2003) Nitrogen export from forested watersheds in the Oregon Coast Range: The role of N-fixing red alder. Ecosystems 6:773–785. https://doi.org/10.1007/s10021-002-0207-4

Correll DL, Jordan TE, Weller DE (1999) Transport of nitrogen and phosphorus from Rhode River watersheds during storm events. Water Resour Res 35:2513–2521. https://doi.org/10.1029/1999WR900058

Cowardin LM, Carter V, Golet FC, La Roe ET (1979) Classification of wetlands and deepwater habitats of the United States. Office of the Biological Services (FWS/OBS-79/31)

Creed IF, McKnight DM, Pellerin BA et al (2015) The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum. Can J Fish Aquat Sci 72:1272–1285. https://doi.org/10.1139/cjfas-2014-0400

D'Amore DV, Fellman JB, Edwards RT, Hood E (2010) Controls on dissolved organic matter concentrations in soils and streams from a forested wetland and sloping bog in southeast Alaska. Ecohydrology 3:249–261. https://doi.org/10.1002/eco.101

D'Amore DV, Edwards RT, Herendeen PA et al (2015) Dissolved organic carbon fluxes from hydropedologic units in Alaskan coastal temperate rainforest watersheds. Soil Sci Soc Am J 79:378. https://doi.org/10.2136/sssaj2014.09.0380

Destouni G, Hannerz F, Prieto C et al (2008) Small unmonitored near-coastal catchment areas yielding large mass loading to the sea. Global Biogeochem Cycles 22:GB4003. https://doi.org/10.1029/2008GB003287

Devito KJ, Dillon PJ (1993) The influence of hydrologic conditions and peat oxia on the phosphorus and nitrogen dynamics of a conifer swamp. Water Resour Res 29:2675–2685. https://doi.org/10.1029/93WR00622

Diemer LA, McDowell WH, Wymore AS, Prokushkin AS (2015) Nutrient uptake along a fire gradient in boreal streams of Central Siberia. Freshw Sci 34:1443–1456. https://doi.org/10.1086/683481

Docherty CL, Riis T, Hannah DM et al (2018) Nutrient uptake controls and limitation dynamics in north-east Greenland streams. Polar Res 37:1440107. https://doi.org/10.1080/17518369.2018.1440107

Dodds WK, Smith VH, Lohman K (2002) Nitrogen and phosphorus relationships to benthic algal biomass in temperate streams. Can J Fish Aquat Sci 59:865–874. https://doi.org/10.1139/f02-063

Emili LA, Price JS (2006) Hydrological processes controlling ground and surface water flow from a hypermaritime forest–peatland complex, Diana Lake Provincial Park, British Columbia, Canada. Hydrol Process 20:2819–2837. https://doi.org/10.1002/hyp.6077

Fellman JB, D'Amore DV, Hood E, Boone RD (2008) Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. Biogeochemistry 88:169–184. https://doi.org/10.1007/s10533-008-9203-x

Fellman JB, Hood E, Edwards RT, D'Amore DV (2009) Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. J Geophys Res. https://doi.org/10.1029/2008JG000790

Fiebig DM (1997) Microbiological turnover of amino acids immobilized from groundwater discharged through hyporheic sediments. Limnol Oceanogr 42:763–768. https://doi.org/10.4319/lo.1997.42.4.0763

Francoeur SN (2001) Meta-analysis of lotic nutrient amendment experiments: detecting and quantifying subtle responses. J N Am Benthol Soc 20:358–368. https://doi.org/10.2307/1468034

Galloway JN, Dentener FJ, Capone DG et al (2004) Nitrogen cycles: Past, present, and future. Biogeochemistry 70:153–226. https://doi.org/10.1007/s10533-004-0370-0

Gerber S, Brookshire ENJ (2014) Scaling of physical constraints at the root-soil Interface to macroscopic patterns of nutrient retention in ecosystems. Am Nat 183:418–430. https://doi.org/10.1086/674907

Green MB, Finlay JC (2010) Patterns of hydrologic control over stream water total nitrogen to total phosphorus ratios. Biogeochemistry 99:15–30. https://doi.org/10.1007/s10533-009-9394-9

Green MB, Nieber JL, Johnson G et al (2007) Flow path influence on an N:P ratio in two headwater streams: a paired watershed study. J Geophys Res. https://doi.org/10.1029/2007JG000403

Hedin LO, Armesto JJ, Johnson AH (1995) Patterns of nutrient loss from unpolluted, old-growth temperate forests: evaluation of biogeochemical theory. Ecology 76:493–509. https://doi.org/10.2307/1941208

Hill AR, Kemp WA, Buttle JM, Goodyear D (1999) Nitrogen chemistry of subsurface storm runoff on forested Canadian Shield hillslopes. Water Resour Res 35:811–821. https://doi.org/10.1029/1998WR900083

Hill BH, Elonen CM, Jicha TM et al (2014) Ecoenzymatic stoichiometry and microbial processing of organic matter in northern bogs and fens reveals a common P-limitation between peatland types. Biogeochemistry 120:203–224. https://doi.org/10.1007/s10533-014-9991-0

Hilton RG, Galy A, Hovius N et al (2012) Climatic and geomorphic controls on the erosion of terrestrial biomass from subtropical mountain forest. Global Biogeochem Cycles. https://doi.org/10.1029/2012GB004314

Hood E, Fellman JB, Edwards RT et al (2019) Salmon-derived nutrient and organic matter fluxes from a coastal catchment in southeast Alaska. Freshw Biol 64:1157–1168. https://doi.org/10.1111/fwb.13292

Hood EW, Williams MW, Caine N (2003) Landscape controls on organic and onorganic nitrogen leaching across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range. Ecosystems 6:0031–0045. https://doi.org/10.1007/s10021-002-0175-8

Hood E, Fellman JB, Spencer RGM (2020) Glacier loss impacts riverine organic carbon transport to the ocean. Geophys Res Lett. https://doi.org/10.1029/2020GL089804

Inamdar SP, Mitchell MJ (2007) Storm event exports of dissolved organic nitrogen (DON) across multiple catchments in a glaciated forested watershed. J Geophys Res 112:G02014. https://doi.org/10.1029/2006JG000309

Inamdar SP, Christopher SF, Mitchell MJ (2004) Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. Hydrol Process 18:2651–2661. https://doi.org/10.1002/hyp.5572

Isles PDF (2020) The misuse of ratios in ecological stoichiometry. Ecology 101:e01353. https://doi.org/10.1002/ecy.3153

Kaushal SS, Lewis WM (2005) Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA. Biogeochemistry 74:303–321. https://doi.org/10.1007/s10533-004-4723-5

Koskelo AI, Fisher TR, Sutton AJ, Gustafson AB (2018) Biogeochemical storm response in agricultural watersheds of the Choptank River Basin, Delmarva Peninsula, USA. Biogeochemistry 139:215–239. https://doi.org/10.1007/s10533-018-0464-8

Lin J, Compton JE, Leibowitz SG et al (2019) Seasonality of nitrogen balances in a Mediterranean climate watershed, Oregon US . Biogeochemistry 142:247–264. https://doi.org/10.1007/s10533-018-0532-0

Lutz BD, Bernhardt ES, Roberts BJ, Mulholland PJ (2011) Examining the coupling of carbon and nitrogen cycles in Appalachian streams: the role of dissolved organic nitrogen. Ecology 92:720–732. https://doi.org/10.1890/10-0899.1

Maranger R, Jones SE, Cotner JB (2018) Stoichiometry of carbon, nitrogen, and phosphorus through the freshwater pipe: stoichiometry of carbon, nitrogen, and phosphorus. Limnol Oceanogr Lett 3:89–101. https://doi.org/10.1002/lol2.10080

Martin RA, Harrison JA (2011) Effect of high flow events on in-stream dissolved organic nitrogen concentration. Ecosystems 14:1328–1338. https://doi.org/10.1007/s10021-011-9483-1

Maruo M, Ishimaru M, Azumi Y et al (2016) Comparison of soluble reactive phosphorus and orthophosphate concentrations in river waters. Limnology 17:7–12. https://doi.org/10.1007/s10201-015-0463-6

Michalak AM, Anderson EJ, Beletsky D et al (2013) Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. Proc Natl Acad Sci 110:6448–6452. https://doi.org/10.1073/pnas.1216006110

Moatar F, Abbott BW, Minaudo C et al (2017) Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resour Res 53:1270–1287. https://doi.org/10.1002/2016WR019635

Mooney RF, McClelland JW (2012) Watershed export events and ecosystem responses in the Mission–Aransas National Estuarine Research Reserve, South Texas. Estuaries Coasts 35:1468–1485. https://doi.org/10.1007/s12237-012-9537-4

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36. https://doi.org/10.1016/S0003-2670(00)88444-5

Neff JC, Chapin FS, Vitousek PM (2003) Breaks in the cycle: dissolved organic nitrogen in terrestrial ecosystems. Front Ecol Environ 1:205–211. https://doi.org/10.1890/1540-9295(2003)001[0205:BITCDO]2.0.CO;2

Olander LP, Vitousek PM (2004) Biological and geochemical sinks for phosphorus in soil from a wet tropical forest. Ecosystems. https://doi.org/10.1007/s10021-004-0264-y

Oliver AA, Tank SE, Giesbrecht I et al (2017) A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia. Biogeosciences 14:3743–3762. https://doi.org/10.5194/bg-14-3743-2017

Oyarzún CE, Godoy R, De Schrijver A et al (2005) Water chemistry and nutrient budgets in an undisturbed evergreen rainforest of Southern Chile. Biogeochemistry 71:107–123. https://doi.org/10.1007/s10533-005-4107-5

Pellerin BA, Wollheim WM, Hopkinson CS et al (2004) Role of wetlands and developed land use on dissolved organic nitrogen concentrations and DON/TDN in northeastern U.S. rivers and streams. Limnol Oceanogr 49:910–918. https://doi.org/10.4319/lo.2004.49.4.0910

Perakis SS (2002) Nutrient limitation, hydrology and watershed nitrogen loss. Hydrol Process 16:3507–3511. https://doi.org/10.1002/hyp.5078

Perakis SS, Hedin LO (2001) Fluxes and fates of nitrogen in soil of an unpolluted old-growth temperate forest, southern Chile. Ecology 82:2245–2260. https://doi.org/10.1890/0012-9658(2001)082[2245:FAFONI]2.0.CO;2

Perakis SS, Hedin LO (2002) Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. Nature 415:416

Petrone K, Buffam I, Laudon H (2007) Hydrologic and biotic control of nitrogen export during snowmelt: A combined conservative and reactive tracer approach. Water Resour Res. https://doi.org/10.1029/2006WR005286

Powers SM, Bruulsema TW, Burt TP et al (2016) Long-term accumulation and transport of anthropogenic phosphorus in three river basins. Nat Geosci 9:353–356. https://doi.org/10.1038/ngeo2693

Poxleitner M, Trommer G, Lorenz P, Stibor H (2016) The effect of increased nitrogen load on phytoplankton in a phosphorus-limited lake. Freshw Biol 61:1966–1980. https://doi.org/10.1111/fwb.12829

Raymond PA, Saiers JE (2010) Event controlled DOC export from forested watersheds. Biogeochemistry 100:197–209. https://doi.org/10.1007/s10533-010-9416-7

Rosemond AD, Benstead JP, Bumpers PM et al (2015) Experimental nutrient additions accelerate terrestrial carbon loss from stream ecosystems. Science 347:1142–1145. https://doi.org/10.1126/science.aaa1958

Royer TV, David MB, Gentry LE (2006) Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: implications for reducing nutrient loading to the Mississippi River. Environ Sci Technol 40:4126–4131. https://doi.org/10.1021/es052573n

Runkel RL, Crawford CG, Cohn TA (2004) Load Estimator (LOADEST): a Fortran program for estimating constituent loads in streams and rivers. U.S. Geological Survey Techniques and Methods, Reston

Sanderman J, Lohse KA, Baldock JA, Amundson R (2009) Linking soils and streams: sources and chemistry of dissolved organic matter in a small coastal watershed: chemistry of dissolved organic matter. Water Resour Res. https://doi.org/10.1029/2008WR006977

Saunders TJ, McClain ME, Llerena CA (2006) The biogeochemistry of dissolved nitrogen, phosphorus, and organic carbon along terrestrial-aquatic flowpaths of a montane headwater catchment in the Peruvian Amazon. Hydrol Process 20:2549–2562. https://doi.org/10.1002/hyp.6215

Scott D, Harvey J, Alexander R, Schwarz G (2007) Dominance of organic nitrogen from headwater streams to large rivers across the conterminous United States: organic nitrogen in U.S. rivers. Global Biogeochem Cycles. https://doi.org/10.1029/2006GB002730

Seitzinger SP, Harrison JA, Dumont E et al (2005) Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: an overview of global nutrient export from watersheds (NEWS) models and their application. Global Biogeochem Cycles. https://doi.org/10.1029/2005GB002606

Seitzinger SP, Mayorga E, Bouwman AF et al (2010) Global river nutrient export: a scenario analysis of past and future trends. Global Biogeochem Cycles. https://doi.org/10.1029/2009GB003587

Shaftel RS, King RS, Back JA (2012) Alder cover drives nitrogen availability in Kenai lowland headwater streams, Alaska. Biogeochemistry 107:135–148. https://doi.org/10.1007/s10533-010-9541-3

Shanley CS, Pyare S, Goldstein MI et al (2015) Climate change implications in the northern coastal temperate rainforest of North America. Clim Change 130:155–170. https://doi.org/10.1007/s10584-015-1355-9

Sharma AR, Déry SJ (2020) Linking atmospheric rivers to annual and extreme river runoff in British Columbia and Southeastern Alaska. J Hydrometeorol 21(11):2457–2472. https://doi.org/10.1175/JHM-D-19-0281.1

Sponseller RA, Temnerud J, Bishop K, Laudon H (2014) Patterns and drivers of riverine nitrogen (N) across alpine, subarctic, and boreal Sweden. Biogeochemistry 120:105–120. https://doi.org/10.1007/s10533-014-9984-z

Sponseller RA, Blackburn M, Nilsson MB, Laudon H (2018) Headwater mires constitute a major source of nitrogen (N) to surface waters in the boreal landscape. Ecosystems 21:31–44. https://doi.org/10.1007/s10021-017-0133-0

Stanley EH, Maxted JT (2008) Changes in the dissolved nitrogen pool across land cover gradients in Wisconsin streams. Ecol Appl 18:1579–1590. https://doi.org/10.1890/07-1379.1

Valderrama JC (1981) The simultaneous analysis of total nitrogen and total phosphorus in natural waters. Mar Chem 10:109–122. https://doi.org/10.1016/0304-4203(81)90027-X

Vaughan MCH, Bowden WB, Shanley JB et al (2017) High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. Water Resour Res 53:5345–5363. https://doi.org/10.1002/2017WR020491

Verry ES, Timmons DR (1982) Waterborne nutrient flow through an upland-peatland watershed in Minnesota. Ecology 63:1456–1467. https://doi.org/10.2307/1938872

Vidon P, Wagner LE, Soyeux E (2008) Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. Biogeochemistry 88:257–270. https://doi.org/10.1007/s10533-008-9207-6

Vidon P, Hubbard H, Cuadra P, Hennessy M (2012) Storm phosphorus concentrations and fluxes in artificially drained landscapes of the US Midwest. Agric Sci 03:474–485. https://doi.org/10.4236/as.2012.34056

Vidon P, Karwan DL, Andres AS et al (2018) In the path of the Hurricane: impact of Hurricane Irene and Tropical Storm Lee on watershed hydrology and biogeochemistry from

North Carolina to Maine, USA. Biogeochemistry 141:351–364. https://doi.org/10.1007/s10533-018-0423-4
Volk CJ, Volk CB, Kaplan LA (1997) Chemical composition of biodegradable dissolved organic matter in streamwater. Limnol Oceanogr 42:39–44. https://doi.org/10.4319/lo.1997.42.1.0039
Wilson HF, Saiers JE, Raymond PA, Sobczak WV (2013) Hydrologic drivers and seasonality of dissolved organic carbon concentration, nitrogen content, bioavailability, and export in a forested New England stream. Ecosystems 16:604–616. https://doi.org/10.1007/s10021-013-9635-6
Wilson HF, Raymond PA, Saiers JE et al (2016) Increases in humic and bioavailable dissolved organic matter in a forested New England headwater stream with increasing discharge. Marine Freshw Res 67:1279. https://doi.org/10.1071/MF15286
Zarnetske JP, Bouda M, Abbott BW et al (2018) Generality of hydrologic transport limitation of watershed organic carbon flux across ecoregions of the United States. Geophys Res Lett 45:11702–11711. https://doi.org/10.1029/2018GL080005