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**Key Points:**

- Theory suggests light availability determines maximum stream productivity with nutrient limitation driving decline from the maximum
- In high-light low-nutrient Greenland streams, light controlled maximum productivity while *N* supply controlled the decline from maximum
- Decline from maximum can evaluate nutrient limitation better than productivity stimulation by considering both light and nutrient effects

**Supporting Information:**

Supporting Information may be found in the online version of this article.

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# Nutrient Limitation Induces a Productivity Decline From Light-Controlled Maximum

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**Abstract** Nutrient impacts on productivity in stream ecosystems can be obscured by light limitation imposed by canopy cover and water turbidity, thereby creating uncertainties in linking nutrient and productivity regimes. Evaluations of nutrient limitations are often based on a response ratio (RR) quantifying productivity stimulation above ambient levels given augmented nutrient supply. This metric neglects the primacy of light effects on productivity. We propose an alternative approach to quantify nutrient limitations using a "decline ratio" (DR), which quantifies the productivity decline from the maximum established by light availability. The DR treats light as the first-order control and nutrient depletion as a disturbance causing productivity decline, allowing separation of nutrient and light influences. We used DR to assess nutrient diffusing substrate (NDS) experiments with three nutrients (nitrogen [N], phosphorus [P], iron [Fe]) from five Greenland streams during summer, where light is not limited due to the lack of canopy and low turbidity. We tested two hypotheses: (a) productivity maximum (i.e., highest chlorophyll-*a* among NDS treatments) is controlled by light and (b) DR depends on both light and nutrients. The productivity maximum was strongly predicted by light ($R^2 = 0.60$). The productivity decline induced by N limitation (i.e., $\mathrm{DR}_N$) was best explained by light availability when parameterized with either dissolved inorganic nitrogen concentration ($R^2 = 0.79$) or N:Fe ratio ($R^2 = 0.87$). These predictions outperformed predictions of RR for which light was not a significant factor. Reversing the perspective on nutrient limitation from "stimulation above ambient" to "decline below maximum" provides insights into both light and nutrient impacts on stream productivity.

**Plain Language Summary** Increased nutrient loading is a major concern in flowing water systems by causing increased photosynthesis and algal blooms. In many streams, however, canopy cover and water turbidity lower the light available for plants and algal growth, which in turn can reduce nutrient impacts. To account for the idea that light is the primary control on stream photosynthesis, and that nutrients play a secondary role on stream productivity, we sought to determine the upper bound of productivity based on light alone, and then explore how variation in nutrient supply affects the decline from this light-determined maximum. We applied this "decline from maximum" approach in Greenland streams with minimal canopy cover, high water clarity, and low nutrient loads, and confirmed our expectation that light and nutrients are primary and secondary influences on stream productivity. Productivity declines in response to nutrient depletion were well predicted by light availability together with either nitrogen concentration or molar ratio of concentrations between nitrogen and iron. Our results support the "decline from maximum" approach as a useful framework for studying both light and nutrient effects on stream productivity and thus an appropriate assessment tool to better understand the effects of nutrients on stream productivity.

## 1. Introduction

Nutrients are key controls on ecosystem productivity (Field et al., 1998). Increased nutrient loading from anthropogenic sources (Carpenter et al., 1998), especially of nitrogen (N) and phosphorus (P), is a major concern for aquatic ecosystem management because of changes in ecological function that arise from increased autotrophic production (Smith, 2003; Wurtsbaugh et al., 2019). Nutrient stimulation of productivity implies ambient "nutrient limitation," indicating that primary producers are constrained by the supply rate of nutrients. This idea was first introduced in agriculture where yield increases were observed following the addition of single nutrient, known as Liebig's Law of the Minimum (De Baar, 1994), though co-limitation wherein two or more nutrients

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simultaneously constrain productivity is widely recognized (Harpole et al., 2011). A conceptual model of alleviating limitation focuses on productivity functions (e.g., biomass accrual) following nutrient enrichments from ambient levels quantified by a response ratio (RR) relating enriched-to-ambient conditions. This model is the basis of most field experiments, with comprehensive syntheses of nutrient limitation conducted in marine (Downing et al., 1999), lentic (Elser et al., 1990), and lotic systems (Francoeur, 2001). Synthesis across hundreds of experiments suggests nutrient limitation is common in terrestrial, marine and freshwater ecosystems, and across ecoregions (Elser et al., 2007), exemplifying why nutrient enrichment is among the grand environmental challenges of the 21st century (Sutton et al., 2013).

Despite the established importance of nutrients in many aquatic ecosystems and strong correlation between nutrient concentration and nutrient limitation of respiration (Burrows et al., 2015), in-stream productivity has often been weakly linked with nutrient supply (i.e., concentration, stoichiometry), constraining our understanding of in-stream nutrient limitation thresholds (Dodds et al., 2002; Keck & Lepori, 2012). In marine and lentic ecosystems, nutrient concentrations or stoichiometry effectively predict autotrophic biomass (i.e., chlorophyll-*a*) (Brown et al., 2000; Moon et al., 2021), limiting nutrient type (Bergström, 2010; Guildford & Hecky, 2000), and spatial patterns of nutrient limitation (Browning & Moore, 2023; Moore et al., 2013). In contrast, in flowing waters, inferences about limitation of primary production are confounded by advective flow, light, and disturbance effects. Because dissolved nutrients are continuously transported downstream, nutrient supply rates in flowing waters are highly affected by advection (Webster & Patten, 1979), suggesting that nutrient concentrations or ratios alone cannot directly inform nutrient limitation because they do not accurately quantify the supply rate, which is controlled by flow (King et al., 2014). In addition, light inputs and flow disturbance regimes are dominant controls on in-stream productivity, overriding straightforward inferences of nutrient limitation (Bernhardt et al., 2022). Nutrient supply was correlated with autotrophic nutrient limitation across multiple rivers in western US (Reisinger et al., 2016), although this may be because light limitation is less likely in large rivers than small streams. Under dense canopy conditions, nutrient additions did not increase productivity (Kominoski et al., 2018; Mosisch et al., 2001). Consequently, productivity in streams is considered less limited by nutrients than in lakes and oceans (Francoeur, 2001), or at least that nutrient limitation is harder to detect (Bernhardt et al., 2018).

The emerging paradigm of stream metabolic function suggests light is the dominant control of stream productivity, implying that light regimes are a prerequisite for understanding nutrient impacts. The metabolic regimes concept for streams (Bernhardt et al., 2018) posits that irradiance attenuated by canopy and water clarity sets the expected upper bounds for primary productivity. The primary role of light regulating lotic productivity is also empirically supported by shade cloth and canopy cover experiments (Boston & Hill, 1991; Gjerløv & Richardson, 2010; Heaston et al., 2018; Quinn et al., 1997), field observations comparing light availability and whole-reach primary production (Kirk et al., 2021; Reisinger et al., 2019), and data syntheses (Bernhardt et al., 2022; Savoy et al., 2019). This light-determined productivity is secondarily affected by disturbances (e.g., high flow events) that reduce productivity from the upper bound. This framework helps explain why stream nutrient enrichment experiments showed benthic biomass responses to N additions were related to both light intensity and N:P ratio (Tank & Dodds, 2003). Similarly, in Arctic streams, the magnitude of N limitation is regulated by temperature and light inputs rather than nutrient concentration (Myrstener et al., 2018). Even at the reach scale, the magnitude of nutrient limitation appears to be controlled by light availability when nutrient supply rate was longitudinally homogeneous (Warren et al., 2017). Following these strong links between light and nutrient limitation, we hypothesized that light availability determines the maximum potential productivity, while nutrient limitation emerges principally as a decline from that energy-imposed maximum, indicating constraints on biological activity due to nutrient scarcity.

Building on the metabolic regimes concept, we propose to characterize nutrient limitation based on the decline from the light-determined potential maximum productivity caused by limited nutrient supply. This method has subtle but important differences from diagnosing nutrient limitations based on stimulation above ambient levels (i.e., using RR) by explicitly considering the primacy of lotic ecosystem energetics when detecting nutrient supply constraints. In lakes, this divergence from maximum productivity approach has been used to study relative limitations of $N$ and $P$ by assuming that the maximum chlorophyll-*a* ($\mathrm{Chl}_{\mathrm{max}}$) is observed under nutrient saturation, thereby diagnosing nutrient limitation as the difference between $\mathrm{Chl}_{\mathrm{max}}$ and observed chlorophyll-*a* under varying nutrient levels (Jones et al., 2011). A recent synthesis using this method showed that, in lakes, $N$ and $P$ concentrations and their ratio predict decline of chlorophyll-*a* from the maxima (Moon et al., 2021). In terrestrial ecosystems, this decline-from-maximum approach has been used to quantify nutrient limitation as the difference

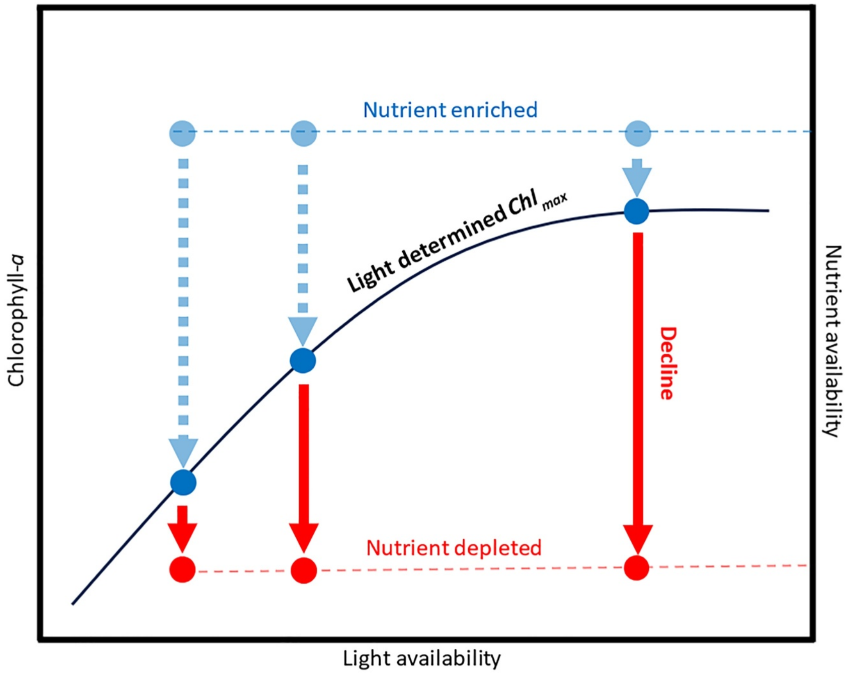

**Figure 1.** A conceptual framework of nutrient limitation as productivity decline from light-determined maximum productivity ($Chl_{max}$). Under nutrient enriched condition (dashed blue line), light determines productivity (i.e., chlorophyll-*a*) by following light-productivity saturating relationship (black solid curve), which becomes the upper bound of productivity (solid blue dots). When a nutrient is depleted (not amended; red dashed line), low nutrient level causes decline of productivity (red arrows) from the maximum to the constrained level (red dots). Therefore, nutrient limitation as decline ratio (i.e., difference between $Chl_{max}$ and nutrient-depleted chlorophyll-*a*; lengths of red arrows) is determined by both light and nutrient regimes.

between the potential maximum productivity, predicted from climatic factors (e.g., light) and disturbances (e.g., land use), and observed productivity from remote sensing data (Fisher et al., 2012). This idea of productivity decline from the maxima has not been applied in lotic ecosystems nor to discriminate the effects of light and nutrients. We anticipated that comparing light-controlled maximum productivity under nutrient saturation and observed productivity under nutrient limitation will yield novel insights about light effects on in-stream nutrient limitation.

To explore the decline-from-maximum approach to assess in-stream nutrient limitation, by using autotrophic biomass (chlorophyll-*a*) as the proxy of productivity, we tested two hypotheses (Figure 1): (a) light availability predicts the upper bound of productivity (i.e., $Chl_{max}$) when nutrients are adequately supplied and (b) decline from $Chl_{max}$ is controlled by nutrient availability (e.g., concentration, stoichiometry). To test these hypotheses, we conducted nutrient diffusing substrate (NDS) experiments over two summers in Greenland, where nutrient limitation is most likely due to high light conditions (24 hr daylight, lack of tree canopy) and low nutrient supply rates (Martin et al., 2020). The decline-from-maximum approach was implemented using NDS experiments considering nutrient limitation of *N*, *P*, and Fe. We included Fe because trace element limitation in flowing waters is increasingly evident (Fitzgibbon & Costello, 2023), and coastal and inland Greenland watersheds exhibit contrasting Fe weathering patterns (Deuerling et al., 2019). We continuously dosed one study stream that exhibited strong N limitation with both *N* and *P*, and compared NDS responses between ambient and dosed reaches to explore how altered nutrient loading relieves nutrient limitation.

## 2. Methods

### 2.1. Nutrient Diffusing Substrate and the Inference of Nutrient Limitation

Nutrient diffusing substrate enrichment experiments are the most widely used technique to examine in-stream nutrient limitation (Ardón et al., 2021). Artificial substrates with nutrient amendments are deployed on the stream bottom where in situ colonization of substrates can occur. Using inorganic substrates (e.g., fritted glass) preferentially selects for colonization by autotrophic biomass, our primary focus here. Because different mixtures of nutrients can be amended, NDS is an effective way to compare the autotrophic growth with and without nutrient additions (Tank et al., 2017). We thus applied the decline-from-maximum approach using NDS experiments, which enable simple comparisons of autotrophic biomass, a proxy of productivity, between nutrient saturated and depleted conditions; we acknowledge that autotrophic biomass is not the same as productivity. We examined limitation status of three nutrients ($N$, $P$, Fe) by comparing eight treatments: control (C), +N, +P, +Fe, +NP, +NFe, +PFe, and +NPFe.

Nutrient limitation is commonly assessed in NDS studies as productivity stimulation by nutrient addition—that is, the difference of autotrophic growth between the unamended control and treatments with varying nutrient amendments. The magnitude of nutrient limitation is quantified using a RR (Johnson et al., 2009; Reisinger et al., 2016):

$$\mathrm{RR_X} = X_i/\mathrm{Chl}l_\mathrm{C} \tag{1}$$

where $X_i$ is the chlorophyll-$a$ ($\mu$g cm$^{-2}$) on the $i$th replicate of each treatment $X$ and $\mathrm{Chl_C}$ is the mean chlorophyll-$a$ on the controls. Response ratio values higher than 1 ($\mathrm{RR} > 1$) indicate limitation by amended nutrient(s), while RR values equal to or lower than 1 ($\mathrm{RR_X} \leq 1$) imply no response or even inhibition. Using the quantitative RR approach, the limitation status of a site (e.g., sole- and co-limitation of nutrients) can be established by two-way analysis of variance (ANOVA) (Tank & Dodds, 2003).

To implement a metric that quantifies decreases from light-determined maximum chlorophyll-$a$ levels, we modified the RR equation by the fractional productivity (Frac) of each treatment compared with the maximum productivity (Moon et al., 2021):

$$\mathrm{Frac_X} = X_i/\mathrm{Chl_{max}} \tag{2}$$

where $\mathrm{Frac_X}$ is the fractional productivity value defined as the ratio of treatment $X$ and $\mathrm{Chl_{max}}$, which is the highest observed mean chlorophyll-$a$ among treatments (i.e., the potential maximum productivity in the absence of nutrient limitation). Although $\mathrm{Chl_{max}}$ might be expected in the treatment enhancing all three nutrients (here, +NPFe), chlorophyll-$a$ of the +NPFe treatment ($\mathrm{Chl_{NPFe}}$) sometimes had lower chlorophyll-$a$ than some treatments missing one nutrient (i.e., $\mathrm{Chl_{NP}}$, $\mathrm{Chl_{NFe}}$) possibly because of inhibition effects. Thus, when $\mathrm{Chl_{NP}}$ or $\mathrm{Chl_{NFe}} > \mathrm{Chl_{NPFe}}$, we selected $\mathrm{Chl_{NP}}$ or $\mathrm{Chl_{NFe}}$ as $\mathrm{Chl_{max}}$ because addition of the third nutrient caused a decline in chlorophyll-$a$. The highest possible Frac value is thus 1 for the treatment for which we observed $\mathrm{Chl_{max}}$. This chlorophyll-$a$ upper bound value was compared with all other treatments with lower chlorophyll-$a$ values, which thus resulted in $\mathrm{Frac} < 1$. Lower Frac values indicate greater productivity declines, suggesting greater limitation due to nutrient depletion given the potential productivity upper bound.

We defined the decline ratio (DR) as the highest Frac value among treatments that lack a particular nutrient, either $N$, $P$, or Fe:

$$DR_{Nut} = \text{Maximum Frac among } \mathrm{Frac}_{w/o\ Nut} \tag{3}$$

where Nut is the missing nutrient from the amendment ($N$, $P$, Fe). For example, $\mathrm{DR_N}$ is the highest Frac value among the four treatments lacking N amendment: $\mathrm{Frac_C}$, $\mathrm{Frac_P}$, $\mathrm{Frac_{Fe}}$, and $\mathrm{Frac_{PFe}}$. While multiple factors may constrain productivity (e.g., depletion of other nutrients, sedimentation, inhibition), DR values reflect the potential lower bound of productivity constraint caused by nutrient depletion (i.e., minimum magnitude of nutrient limitation). The highest possible DR is one, indicating no nutrient limitation, and lower DR means stronger nutrient limitation (i.e., more productivity constraint by nutrient depletion). We considered $\mathrm{Frac_C}$, the productivity decline from $\mathrm{Chl_{max}}$ to $\mathrm{Chl_C}$ (chlorophyll-$a$ of the control treatment), as $\mathrm{DR_{All}}$ which is the productivity constraint when all tested nutrients are unenriched. The DR therefore effectively and concisely compares the limitation of each nutrient by summarizing nutrient impacts in single value.

### 2.2. Field Experiment—Greenland

### 2.2.1. Study Sites

Nutrient limitation experiments were conducted June–August 2022 and June–July 2023 in southwestern Greenland, where distance from the edge of the Greenland ice sheet, and thus time since glacial retreat, impacts stream solute chemistry (Deuerling et al., 2019; Martin et al., 2020; Pain et al., 2020; Scribner et al., 2015). Five sites were included in this study (Table S1 in Supporting Information S1), all of which were covered by ice in the past, but none of which drain glacial meltwater and thus are considered deglaciated and have soils that are approaching chemical equilibrium with the non-ice environmental conditions (Martin et al., 2024). Two sites are in the Lake Helen watershed near Kangerlussuaq ~175 km inland from the coast and proximal to the edge of the Greenland Ice Sheet. One of the two sites is a lake outlet (LH5) and the other (LH6) is ~1 km downstream of LH5. Three sites are in two watersheds (herein referred to as S1 and S3) near the coastal town of Sisimiut. Two of them are in the S1 watershed and one in the S3 watershed with the latter smaller and steeper. The two sites in the S1 watershed are separate sub-watersheds with streams from different headwater sources (S1T5, S1LakeA). The S3 site is near its outlet to the fjord. Coastal watersheds, S1 and S3, have older exposure ages (i.e., time after glacial retreat) and wetter and warmer climates than inland Lake Helen watershed and thus more mature ecosystems and less reactive soil minerals (Table S2 in Supporting Information S1; Pain et al., 2020).

### 2.2.2. Nutrient Diffusing Substrate

Nutrient diffusing substrates (NDS) were made by filling polycon cups with agar solution with different nutrient treatments (by weight, 2% for no or single nutrient amendments and 3% for multiple nutrient amendments): no amendment (control; C), 0.5 M $NH_4Cl$ (+N), 0.5 M $KH_2PO_4$ (+P), and 0.2 M $C_{10}H_{12}FeN_2O_8$ (+Fe), and co-amendments of these chemicals (Tank et al., 2017). Each NDS array had 40 cups divided into five replicates for each of eight treatments (C, +N, +P, +Fe, +NP, +NFe, +PFe, and +NPFe).

Fritted glass disks (catalog no. 528–042; LECO Corporation, St Joseph, Michigan, USA) were placed on top of each polycon cup, which were randomly positioned on L-shaped plastic bars and tightly fixed with silicone glue and cable ties. Prior to deployment, prepared cups were wrapped and stored at 4°C to minimize drying and exposure to light. Prepared NDS sets were anchored at the stream bottom with stakes at both ends of the bars.

We deployed NDS arrays twice in 2022 at our five study sites. The arrays were deployed in the S1 and S3 watersheds between 18 June–3 July and 21–30 July, and in the Lake Helen watershed between 5–18 July and 2–12 August. We refer to the two deployment periods as "early" and "late", respectively. Light availability was substantially lower later in the summer season due to the lower sun on horizon and persistently cloudy weather. In the S1 and S3 watersheds, discharge was also higher in early than late deployments due to high meltwater contribution. In contrast, discharge consistently increased throughout the summer in Lake Helen watershed. These variations in light and flow suggest environmental conditions were independent between the two deployments even at the same sites. The late deployment was shorter but long enough to observe differences in biomass accumulation among treatments. At LH5, Fe was not amended for the early deployment.

Post-experiment NDS disks were immediately put in plastic bags with stream water and kept frozen until measurement of chlorophyll-*a* concentrations. We extracted chlorophyll-*a* by submerging disks in 10 mL of 90% acetone for 24 hr. Chlorophyll-*a* was measured as a mass per unit area ($\mu g\ cm^{-2}$) with a UV-VIS spectrometer (Horiba Scientific, Kyoto, Japan) using trichromatic equations based on the absorbances at three wavelengths (630, 647, 664 nm), which were corrected by the absorbance at 750 nm indicating turbidity (Aminot & Rey, 2000). Chlorophyll-*a* below detection (i.e., no autotrophic growth) is indicated by the absorbance of 750 nm equivalent to or higher than absorbances at the other three wavelengths. Chlorophyll-*a* values were used to calculate DR for each nutrient (*N*, *P*, Fe) and RR for each of eight treatments. To examine sole- or co-limitations of the three nutrients, we applied three two-way ANOVAs (Tank & Dodds, 2003) coupling different sets of nutrients (N and P, N and Fe, P and Fe). Chlorophyll-*a* measurements from S1T5 early deployment were not used for further analysis because of high sedimentation that led to no detectable chlorophyll-*a* on 18 among 40 NDS samples and substantial water-column light attenuation, preventing examination of light effects using stream surface light.

### 2.2.3. Continuous Whole-Reach Nutrient Enrichment

In 2023, we conducted a continuous whole-reach nutrient enrichment experiment at LH6. We continuously dosed the stream with N and P for three weeks (25 June–15 July) to sustain elevated nutrient loading. We installed two continuous drips using peristaltic pumps (Geotech Inc., Denver, Colorado, USA) at the 2022 NDS deployment location and ~250 m downstream from that site (Figure S1 in Supporting Information S1). The upper drip delivered nitrate solution (12 kg $KNO_3$ in 114 L barrel) to the stream at a dosing rate of 0.7 ml $s^{-1}$ while the downstream drip dosed phosphate solution (3 kg $KH_2PO_4$ in 114 L barrel) with a dosing rate of 0.4 ml $s^{-1}$. These two drips created three experimental stream segments, including a control section (upstream of the N drip), a nitrate increased segment (+N), and a nitrate and phosphate increased segment (+NP). To examine changes of nutrient limitation status under these elevated nutrient levels, we deployed NDS amended with *N* and *P* (C, +N, +P, +NP) in each of these three segments, from which chlorophyll-*a*, DR, and RR were obtained.

### 2.2.4. Light, Temperature, and Flow Regimes

Light intensity was measured continuously with lux loggers (Onset HOBO Pendant, Bourne, Massachusetts) deployed near stream surface at all sites except LH5, whose light regime was assumed identical to LH6. We converted light intensity (lumens $m^{-2}$ $s^{-1}$) to photosynthetic photon flux density (PPFD; μmol $m^{-2}$ $s^{-1}$) using a calibration factor of 0.0185 for sunlight provided by Apogee Instruments (Logan, UT). This conversion allowed us to use light measured from the loggers as a proxy of photosynthetically active radiation (PAR). We calculated mean daily PAR during each deployment and multiplied the deployment length (86,400 s $d^{-1}$ × deployment days) to quantify cumulative light availability (ΣPAR; μmol $m^{-2}$) of each deployment due to varying deployment length. Water temperature was measured continuously from in situ HOBO U26 dissolved oxygen data loggers (Onset, Bourne, Massachusetts), installed at all sites.

Flow hydrographs were created for each site based on rating curves. Water depth was measured continuously using HOBO U20 water level data loggers (Onset, Bourne, Massachusetts) adjusted for barometric pressure from nearby loggers (Van Essen Instrument, Delft, Netherlands) in Kangerlussuaq and Sisimiut. Discharge at each site was estimated multiple times using the cross-sectional method with stream velocities measured with a digital flow meter (Xylem, Rye Brook, New York) in 2022. In 2023, discharge was estimated only at LH6, where we conducted continuous nutrient enrichment. As flows were ~10 times higher in 2023 than 2022, we used dilution gauging with salt (NaCl) to estimate discharge (Day, 1976) instead of the flow meter. High-resolution discharge time series were obtained by converting continuous water depth to discharge by applying rating curves constructed from our point estimates of both (mean rating curve $R^2 = 0.88$). For LH5, where discharge was not measured in the field, we used the discharge measurements of LH6 assuming the same flow from upstream to downstream.

### 2.2.5. Stream Chemistry

We measured concentrations of dissolved inorganic nitrogen (DIN), total P (TP), and total Fe (TFe) to evaluate natural background fluctuations. Water samples were collected with a peristaltic pump connected to tubing installed in the middle of the stream. Stream water was collected after pumping sample water through an in-line filter (0.45 μm glass fiber filters). Nutrient samples were frozen and stored in the dark until analyzed. For DIN, concentrations of $NO_3^-$ and $NH_4^+$ were measured by ion chromatography (Dionex ICS-1600 [cation] and ICS-2100 [anion], Dionex, Sunnyvale, California). Because streams were generally neutral (pH ~ 7) across experimental periods, we did not correct ammonium concentrations for pH, although we do note that LH5 had a more alkaline pH during the late deployment period (pH = 8.6). The sum of the two ion concentrations is reported as DIN. Phosphorus and iron concentrations were measured with a Thermo Element2 Inductively Coupled-Plasma Mass Spectrometer (Thermo Fisher Scientific GmbH, Dreieich, Germany). Measurement dates and results are summarized in Table S3 in Supporting Information S1.

We calculated mean DIN, TP, and TFe concentrations during each deployment for further statistical analysis. However, for the deployments where TP was not detected from all measurements (early deployment of S1T5, early and late deployments of S1LakeA), we used half of the detection limit (0.15 μg $L^{-1}$) as a mean TP concentration.

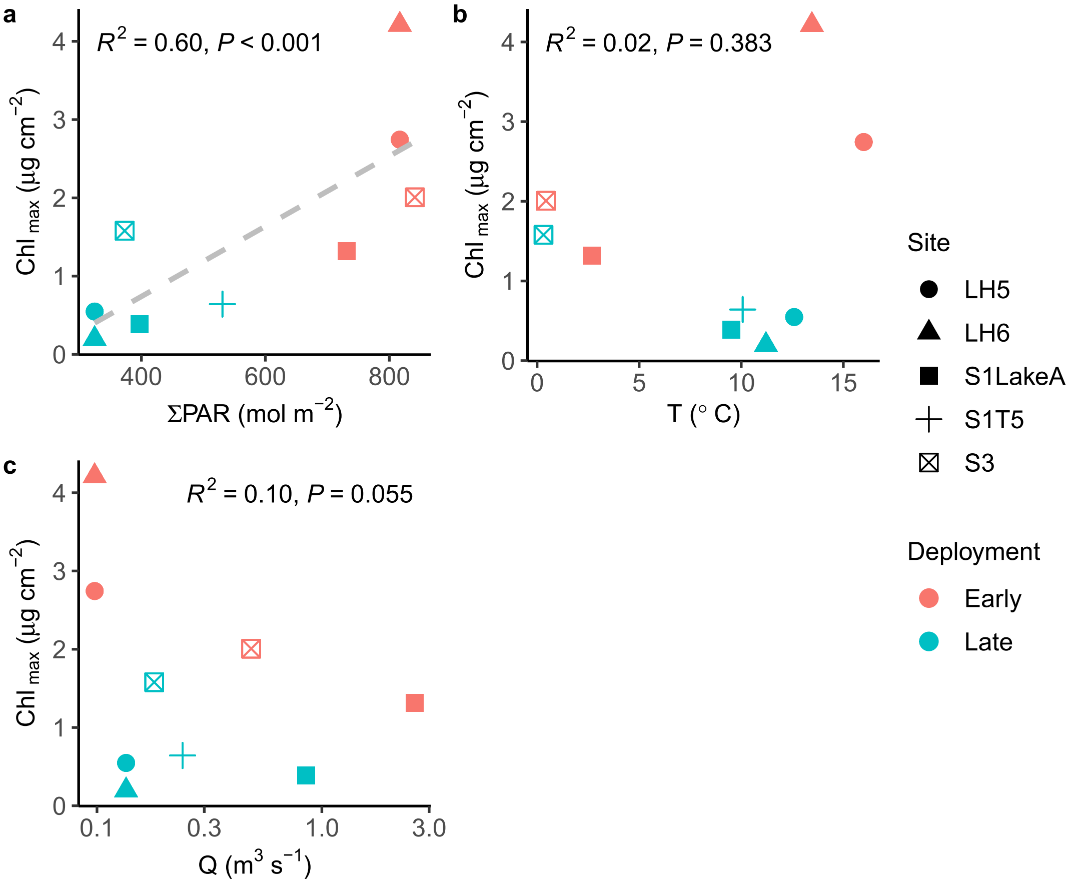

**Figure 2.** Relationship of the maximum chlorophyll-*a* among nutrient diffusing substrate treatments ($\mathrm{Chl_{max}}$; µg cm$^{-2}$) with (a) light availability (ΣPAR; mol m$^{-2}$), (b) water temperature (T; °C), and (c) discharge (Q; m$^3$ s$^{-1}$).

### 2.2.6. Statistics

One sample *t*-test was used to check whether DR is significantly lower than 1, and paired *t*-test was used to compare DR between NDS treatments (95% confidence interval). We used linear regression to explore the drivers of maximum productivity ($\mathrm{Chl_{max}}$; light, water temperature, discharge) and nutrient limitations (DR and RR; light, nutrient concentrations or ratios). Discharge and nutrient values (concentrations, ratios) were log-transformed as they vary across multiple orders of magnitude. We also implemented multi-variate regression models of $\mathrm{Chl_{max}}$, DR, and RR based on their corresponding predictors but with no interactions using lm function in *R* (Core Team 2013) to test the abiotic effects on the maximum productivity and the co-effect of light and nutrients on nutrient limitations.

## 3. Results

### 3.1. Light and Chlorophyll-*a*

The upper bound of productivity ($\mathrm{Chl_{max}}$) was significantly positively correlated with light availability (ΣPAR) ($R^2$ = 0.60; Figure 2a). In contrast, neither water temperature nor discharge were correlated with $\mathrm{Chl_{max}}$ (Figures 2b and 2c). Inclusion of either temperature or discharge improved prediction of $\mathrm{Chl_{max}}$ ($R^2 \approx 0.7$), though they were not statistically significant predictors (Table S4 in Supporting Information S1). In nearly every deployment, $\mathrm{Chl_{max}}$ was from the +NPFe treatment; only the late deployment at LH6 had $\mathrm{Chl_{max}}$ from +NFe treatment, whose mean chlorophyll-*a* was higher than that of +NPFe treatment (Figure S2 in Supporting Information S1).

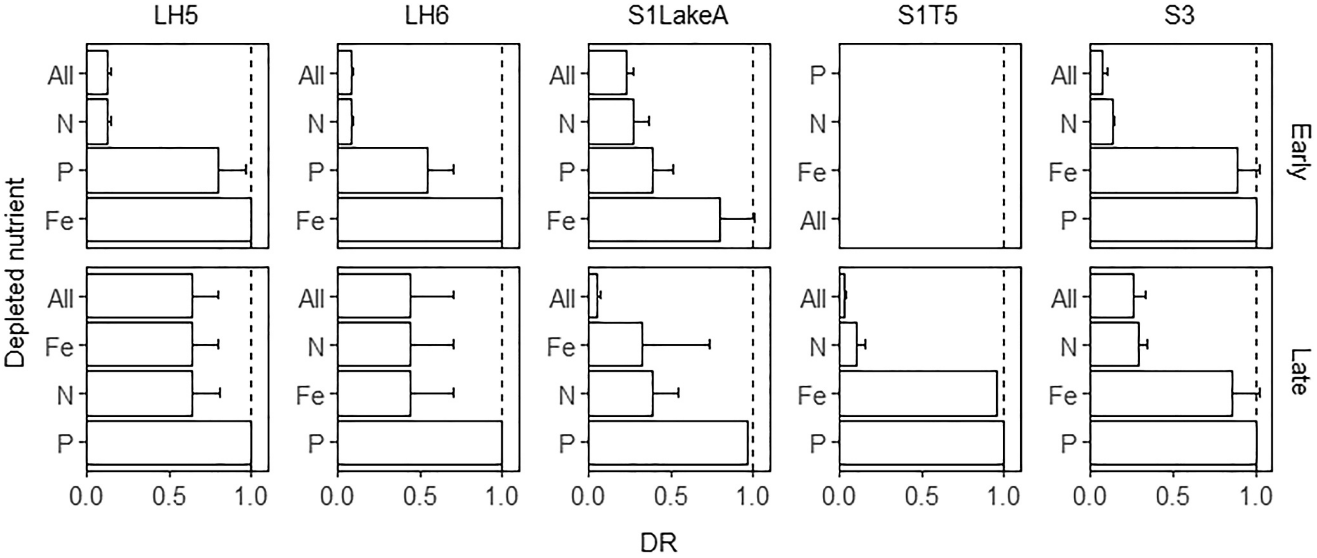

**Figure 3.** Decline ratio (DR; chlorophyll-*a* decline from $\mathrm{Chl}_{\max}$ by the absence of a nutrient) in Greenland streams. Lower decline ratio indicates stronger nutrient limitation (more decline from the upper bound). The *y*-axis of each deployment is arranged from small to high decline ratio (DR) (i.e., strong to weak limitation). The vertical dashed line indicates DR = 1 where absence of a nutrient does not lead to productivity decline (i.e., chlorophyll-*a* of no nutrient enrichment = $\mathrm{Chl}_{\max}$) suggesting no nutrient limitation. Chlorophyll-*a* of the early deployment at S1T5 was not detected due to high sedimentation on nutrient diffusing substrate.

### 3.2. Decline Ratios

Among the three nutrients ($N$, $P$, Fe), the $\mathrm{DR_N}$ was lowest in all deployments (Figure 3), ranging between 0.09 and 0.35 except late deployment of LH5 ($\mathrm{DR_N} = 0.71$), indicating persistent and dominant N limitation across sites and deployment periods. Decline ratio values of nutrients sourced from mineral weathering ($P$, Fe) varied more. At the inland LH sites, P limitation was observed in the early deployment, though it was far weaker than $N$ ($\mathrm{DR_N} < \mathrm{DR_P}$, $p < 0.01$), whereas Fe co-constrained productivity with N in the late deployments ($\mathrm{DR_N} = \mathrm{DR_{Fe}}$), suggesting shifting seasonal patterns of secondary limitation. In both the early and late deployments at the coastal sites, S1T5 and S3 had $\mathrm{DR_P}$ and $\mathrm{DR_{Fe}} \approx 1$, suggesting no limitation. S1LakeA was the only site where DR values for all three nutrients were <1 (though $p = 0.1$ for $\mathrm{DR_{Fe}}$), with $\mathrm{DR_P} < \mathrm{DR_{Fe}}$ ($p < 0.01$) in the early deployment, and $\mathrm{DR_{Fe}} \approx \mathrm{DR_N}$ in the late deployment when $\mathrm{DR_P} \approx 1$. Chlorophyll-*a* declines from $\mathrm{Chl}_{\max}$ when all three nutrients were not amended ($\mathrm{DR_{All}}$) were similar to $\mathrm{DR_N}$ in all deployments except the two S1 watershed sites in the late deployment, when $\mathrm{DR_{All}} < \mathrm{DR_N}$ ($p < 0.01$), suggesting potential additional factor constraining autotrophic growth when all nutrients are low.

The $\mathrm{DR_N}$ values were significantly negatively correlated with $\mathrm{Chl}_{\max}$ ($R^2 = 0.45$) and light availability (measured as ΣPAR; $R^2 = 0.63$) and significantly positively correlated with N:Fe ratio ($R^2 = 0.56$) (Figure 4), indicating both light and nutrient effects on primary N limitation. In contrast, $\mathrm{DR_N}$ values were not significantly correlated with DIN concentration ($R^2 = 0.32$, $p = 0.12$), DIN flux, and N:P ratio (Figure S3 in Supporting Information S1). Prediction of $\mathrm{DR_N}$ was best when using both light availability and either DIN concentration ($R^2 = 0.79$) or N:Fe ratio ($R^2 = 0.87$), while including $\mathrm{Chl}_{\max}$ with the nutrient values also yielded strong predictions ($R^2 = 0.68$ with DIN and 0.70 with N:Fe) (Table 1). $\mathrm{DR_P}$ values were not significantly correlated with any examined factors, while $\mathrm{DR_{Fe}}$ values were significantly positively correlated with $\mathrm{Chl}_{\max}$ and ΣPAR (Figure S3, S4 in Supporting Information S1).

Using RR, inferences of nutrient limitation magnitudes and patterns were different from results using DR across space and time (Figure S5 in Supporting Information S1, Table S5 in Supporting Information S1). Nutrient limitation based on RR was complex in the S1 watershed with two co-limitations ($N$ + Fe and $P$ + Fe during the early season deployment, $N + P$ and $N$ + Fe during the late season) with inconsistent indications of primary and secondary limitation. When comparing RR and DR, $\mathrm{DR_N}$ and $\mathrm{RR_{NP}}$ showed a significant negative correlation ($R^2 = 0.79$) (Figure S6 in Supporting Information S1). However, $\mathrm{RR_{NP}}$ was significantly correlated with N:Fe ratio but not significantly with other associated factors, including $\mathrm{Chl}_{\max}$, ΣPAR, N:P, DIN concentrations, and DIN fluxes (Figure S7 in Supporting Information S1). Prediction of $\mathrm{RR_{NP}}$ also did not substantially improve with

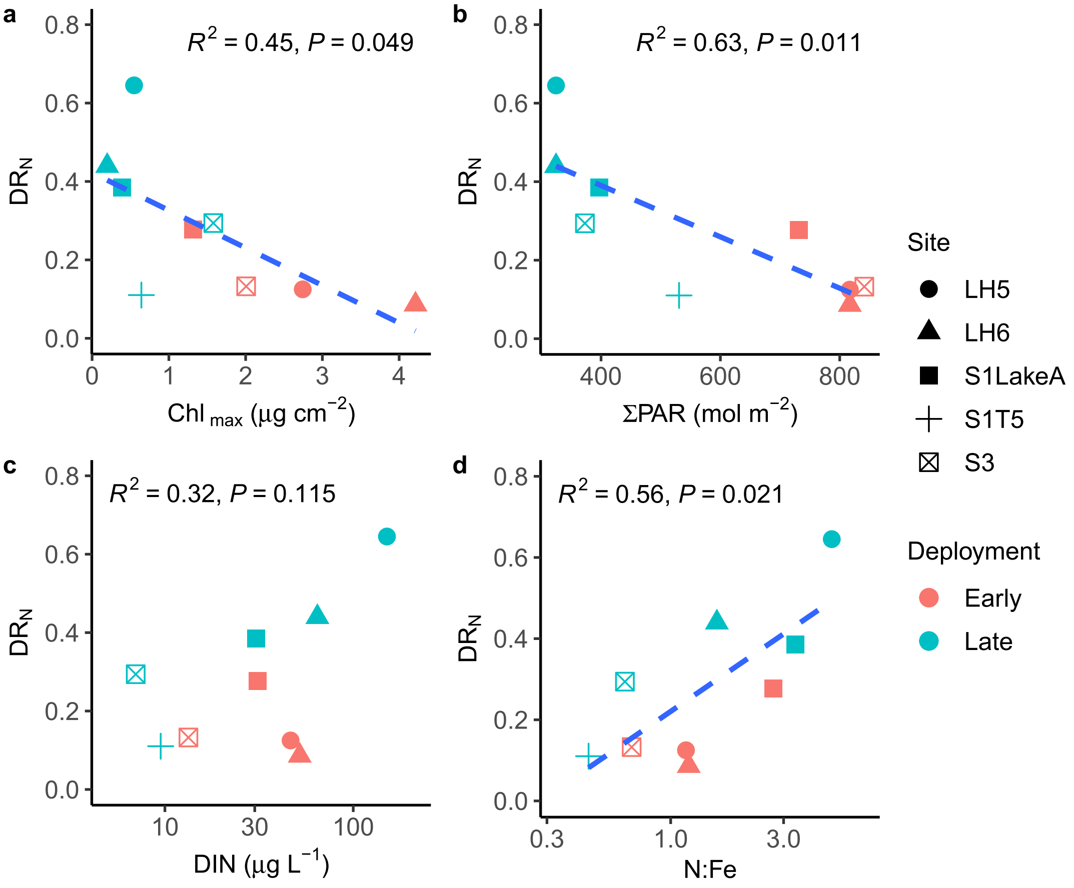

**Figure 4.** Relationship between decline ratio of nitrogen ($DR_N$; chlorophyll-*a* decline from $Chl_{max}$ by the absence of N) and associated factors, (a) maximum productivity ($Chl_{max}$; µg cm$^{-2}$), (b) light availability (ΣPAR; mol m$^{-2}$), (c) dissolved inorganic nitrogen concentration (µg L$^{-1}$), and (d) N:Fe ratio.

the inclusion of ΣPAR or $Chl_{max}$ with DIN concentration or nutrient ratios (Table S6 in Supporting Information S1). These results suggest that, despite using the same observations, inferences from DR and RR are different, and thus they can be used as complementary methods.

**Table 1**
*Multi-Variate Prediction Models of $DR_N$ With Different Configurations of Dissolved Inorganic Nitrogen Concentration, N:Fe Ratio, Maximum Productivity ($Chl_{max}$), and Light Availability (ΣPAR)*

| Model | Predictor | Slope | SE | P | Adjusted $R^2$ |
|---|---|---|---|---|---|
| 1 | log (DIN) | 0.24 | 0.09 | 0.03* | 0.68 |
| | $Chl_{max}$ | −0.10 | 0.03 | 0.02* | |
| 2 | log (DIN) | 0.21 | 0.07 | 0.03* | 0.79 |
| | ΣPAR | −0.0006 | 0.0001 | 0.00** | |
| 3 | log (N:Fe) | 0.33 | 0.11 | 0.03* | 0.70 |
| | $Chl_{max}$ | −0.07 | 0.03 | 0.06 | |
| 4 | log (N:Fe) | 0.30 | 0.07 | 0.01** | 0.87 |
| | ΣPAR | −0.0005 | 0.0001 | 0.00** | |

### 3.3. Effect of Continuous Dosing on Nutrient Limitation

Nutrient diffusing substrate responses during our continuous nutrient dosing experiment showed the highest chlorophyll-*a* occurred in the +NP treatment for all three reaches (Figure 5a), but only slightly lower chlorophyll-*a* for the +*N* treatment. These maximum chlorophyll-*a* values did not substantially vary across the three reaches, indicating similar controls of upper-bound biomass accumulation (e.g., light) other than *N* availability. The coupling between $Chl_{max}$ and ΣPAR in this 2023 experiment followed their significant positive relationship from the 2022 NDS experiments (Figure S8 in Supporting Information S1). In contrast, the chlorophyll-*a* of the control and +*P* NDS treatments substantially increased from the control to +*N* and +NP experimental reaches (Figure 5a). These contrasting responses of chlorophyll-*a* to continuous nutrient dosing between ambient (control, +P) and *N* enriched conditions (+N, +NP) resulted in an increase of $DR_N$ from the control to the +NP reach (Figure 5b) and a decline of $RR_N$ and $RR_{NP}$ (Figure S9 in Supporting Information S1).

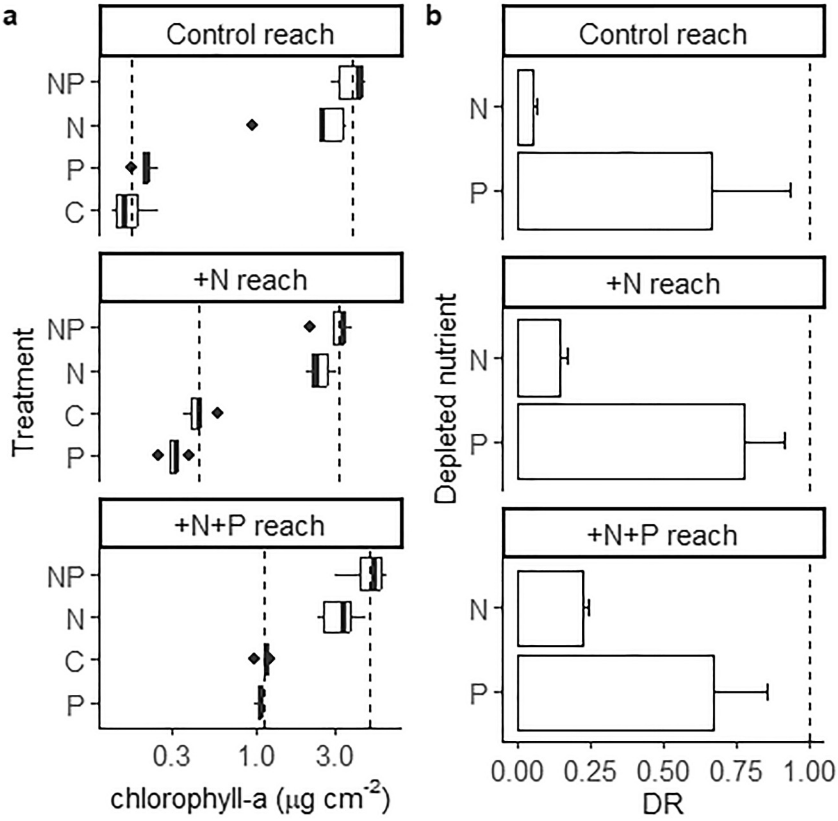

**Figure 5.** Results of 2023 nutrient diffusing substrate (NDS) experiment with continuous nutrient dosing. (a) Chlorophyll-*a* accumulation increased in ambient conditions with nutrient dosing but the upper bound ($\mathrm{Chl}_{\max}$) was consistent, suggesting that the maximum productivity is determined by light not by nutrient supply. Vertical dashed lines indicate ambient (control) chlorophyll-*a* (left) and $\mathrm{Chl}_{\max}$ (highest chlorophyll-*a* among NDS treatments; right), and (b) while N was primarily limiting across reaches ($\mathrm{DR}_\mathrm{N} < \mathrm{DR}_\mathrm{P}$), $\mathrm{DR}_\mathrm{N}$ increased with nutrient dosing but $\mathrm{DR}_\mathrm{P}$ did not, indicating that both *N* and *P* addition alleviated only primary N limitation. Vertical dashed lines indicate decline ratio = 1, which indicates no nutrient limitation.

While *P* limitation was minimal from the perspective of stimulation above ambient conditions ($\mathrm{RR}_\mathrm{P} \approx 1$), $\mathrm{DR}_\mathrm{P}$ was consistently lower than one ($p < 0.01$) despite continuous *P* dosing (Figure 5b), suggesting consistent secondary *P* limitation regardless of whole-reach nutrient enrichment. Consistently low $\mathrm{DR}_\mathrm{P}$ values across the experimental reaches indicate that both *N* and *P* additions alleviated only *N* limitation but not *P* limitation. This distinction exemplifies the utility of the DR approach to discriminating individual nutrient effects.

## 4. Discussion

### 4.1. Light and Nutrients Both Influence Stream Productivity

The significant correlation between $\mathrm{Chl}_{\max}$ and ΣPAR indicates light availability is the dominant regulatory control on the upper bound of stream productivity in these Arctic streams (Figure 2), as posited for stream metabolic regimes more broadly (Bernhardt et al., 2018). A strong correlation between light availability and $\mathrm{Chl}_{\max}$ under nutrient enriched conditions has been observed in NDS experiments under spatially varying canopy cover (Warren et al., 2017). However, observations of light-nutrient co-limitation have been based on contrasts between light and dark conditions, implicitly neglecting the more nuanced effect of light variation on productivity under nutrient limitation in well-lit systems (Mosisch et al., 2001). Our results suggest that light constrains maximum potential productivity even in clear water streams lacking a canopy and thus constrains the upper-bound of stimulatory effects of nutrient additions. This is most clearly evident from the observation that $\mathrm{Chl}_{\max}$ values did not significantly vary across the experimental reaches during the continuous nutrient dosing experiment (Figure 5a), supporting our contention that further nutrient enrichment has no additional effect on maximum productivity determined by solar energy inputs. Considering light as the control of maximum productivity explains why NDS treatments with all three nutrients enriched (*N*, *P*, Fe) did not always generate higher chlorophyll-*a* than treatments missing either *P* or Fe (Figure S2 in Supporting Information S1).

While temperature and discharge were uncorrelated with $Chl_{max}$ (Figures 2b and 2c), their inclusion did improve the predictive ability for $Chl_{max}$ ($R^2 \approx 0.7$), indicating their potential regulating effects on maximum productivity. Experimentally, increased temperature elevated productivity in both ambient and nutrient-enriched conditions (Cross et al., 2022), suggesting that, particularly in cold water streams, thermal regimes are relevant to predicting primary production. Productivity can also be inhibited where scouring floods impact biomass accrual (Blaszczak et al., 2023; Uehlinger, 2006). By regulating water depth and clarity, flow can also impose constraints on productivity by changing benthic light intensity (Kirk et al., 2021). The shallow, persistently clear-water streams in our study site, therefore, do not necessarily reflect the multivariate controls on productivity maxima that might persist in streams more generally, though we note that the primacy of light controls here aligns with the emerging contention that light is the dominant regulator at continental scales (Bernhardt et al., 2022).

Treating light as the first-order determinant of stream productivity enabled us to explain clear light effects on the magnitude of nutrient limitation (Figure 4, Table 1). While the role of light has been widely acknowledged as a co-limiting factor, along with nutrients, for stream productivity (Myrstener et al., 2022; Tank & Dodds, 2003; Warren et al., 2017), no tools have been available to explicitly and simultaneously consider light and nutrient supply rates as predictors. Light effects have been considered as overriding factors of nutrient limitation only when light availability is below a certain threshold level (Mosisch et al., 2001; Warren et al., 2017), above which variation in light has been assumed not to affect productivity responses to nutrient addition. However, our results strongly suggest an upper threshold of light limitation should not be assumed because light controls temporal variation in primary production even in clear, well-lit rivers (Kirk et al., 2021). Moreover, a core tenet of the metabolic regimes concept is that light availability defines the envelope of productivity (Bernhardt et al., 2018), with disturbance and nutrient supply driving a decline from this maximum level. The significant negative relationship between ΣPAR and $DR_N$ (Figure 4b), derived by treating light as the first-order determinant of stream productivity, shows a strong effect of light on nutrient limitation, reducing the propensity for limitation at low light, and amplifying it under high light conditions. Predictions of $DR_N$ were better when including either DIN concentration or nutrient ratio (N:Fe) and light availability (ΣPAR), especially compared with predictions based solely on the concentration or ratio (Table 1). We further observed during our continuous dosing experiment that the magnitude of primary N limitation declined with increasing $DR_N$ as nutrient supply was increased while $Chl_{max}$ was unchanged (Figure 5). Together, these results suggest that nutrient effects on productivity need to be determined in the context of overarching controls of light, and indeed, that light effects on productivity need to consider nutrient supply, particularly in low concentration settings.

At the inland (LH) sites and one of the coastal sites (S1LakeA), the secondary limiting nutrient shifted from *P* to Fe between early and late deployments (Figure 3). This change potentially suggests secondary limitations can be controlled by temporal changes in source water provenance during the melt season that are distinct from variation in light. Water sources change from snowmelt in the early summer to active layer sources later in the summer. Meltwater has higher N:P ratios than vegetation and soil in Greenland (Anderson et al., 2017), suggesting greater likelihood of *P* limitation in the early summer, aligned with what we observed. Fe was consistent throughout summer in other Arctic streams in Svalbard (Gödde et al., 2024), but increased in Alaska (Barker et al., 2014), which may explain spatially uneven evidence of Fe limitation. To further explore shifting *P* and Fe impacts over the melt season in the Arctic, observations of DR from NDS experiments at sites with more obvious *P* or Fe limitations coupled with temporal hydrology variation and nutrient sources are necessary.

Differences between $DR_{All}$ and DR values for individual nutrients indicate that a primary limiting nutrient usually but not always determines overall nutrient effects constraining productivity (chlorophyll-*a*). Similar $DR_N$ and $DR_{All}$ values at most of our NDS experiments (Figure 3) suggest that overall nutrient effects were different from N limitation. However, $DR_{All}$ was lower than other values at the S1 sites, where TP concentrations were below detection for both deployments (Table S3 in Supporting Information S1). One possibility is an inhibition effect as increased heterotrophy (high respiration, low productivity) is expected under oligotrophic conditions (Dodds, 2006). Nutrient addition in oligotrophic conditions may increase primary production not only by autotrophic stimulation but also by removing inhibitory effects. This relationship between nutrient level and inhibition could explain why productivity is often stimulated by both N and P when enriched separately, which is not explained by the conventional concept of nutrient limitation (Harpole et al., 2011). Further studies to monitor both autotrophic and heterotrophic activities under different nutrient levels are needed to test this hypothesis of oligotrophic inhibition effects as a plausible cause of nutrient co-limitation.

### 4.2. Utility of Decline Ratio

The change in denominator between calculating DR and RR (Equations 1–3) has led to divergent interpretations of nutrient limitation. While RR may be a better indicator for quantifying the increase of productivity from ambient levels, DR misses this stimulatory effect because it uses $\mathrm{Chl}_{\mathrm{max}}$ as the denominator, which may not change with environmental conditions other than light. In contrast, DR better exhibits which nutrient most constrains productivity. A single DR value emerges for each nutrient, enabling direct comparison among nutrients to easily discriminate primary and secondary limitations. While RR provides direct information about limitation when only two nutrients are evaluated (Tank & Dodds, 2003), examining more than two nutrients yields seven or more RR values (Figure S5, Fitzgibbon & Costello, 2023), for which conventional two-way ANOVA may not be applicable, complicating nutrient limitation inferences. For example, our late NDS deployment at S1T5 suggested Fe stimulation ($\mathrm{RR}_{\mathrm{Fe}} > 1$; Figure S5 in Supporting Information S1). However, the chlorophyll-*a* increase with the addition of *N* when co-added with *P* and Fe was an order of magnitude higher than with Fe addition alone ($\mathrm{RR}_{\mathrm{NP}}$ and $\mathrm{RR}_{\mathrm{NFe}} > \mathrm{RR}_{\mathrm{Fe}}$), indicating *N*, not Fe, most stimulated productivity. This result highlights complications arising from RR when the primary limiting nutrient is different from the nutrient that most constrains productivity. In contrast, DR results from that site simply capture the ubiquitous importance of *N* across deployment periods and sites ($\mathrm{DR}_{\mathrm{N}} \leq \mathrm{DR}_{\mathrm{P}}$ and $\mathrm{DR}_{\mathrm{Fe}}$) (Figure 3). We argue that while there is utility in both approaches, DR is more appropriate for understanding how productivity is constrained by nutrient supply.

Our approach provides a theoretical framework to quantify how nutrient limitation intersects with productivity regimes in flowing waters. Notably, predictions of $\mathrm{RR}_{\mathrm{NP}}$ using DIN concentration or nutrient ratios did not substantially improve with inclusion of light availability (Table S6 in Supporting Information S1). Despite the strong correlation between $\mathrm{RR}_{\mathrm{NP}}$ and $\mathrm{DR}_{\mathrm{N}}$ (Figure S6 in Supporting Information S1) and their identical source data, using $\mathrm{DR}_{\mathrm{N}}$ produced a substantially better prediction model of the controls on productivity variation (Table 1, Table S3 in Supporting Information S1). This difference is likely due to the distinction between ambient productivity, which couples all existing limitations and disturbances (Sanderson et al., 2009), and maximum productivity, which is well predicted by light availability alone (Figure 2a). Therefore, the decline ratio framework may be more appropriate to evaluate the relative importance of light and nutrients on productivity.

Streams in the Arctic have strong expectations of nutrient limitation (i.e., high light, low nutrient supply; Myrstener et al., 2021). As such, a broader application of our approach is needed to confirm DR effectiveness for predicting nutrient limitation in settings with less obvious nutrient limitation. By considering nutrient limitation as a constraint that decreases primary production from potential maximum determined by energy availability (Bernhardt et al., 2018), the decline-from-maximum idea can be applied to whole-reach scale assessments where nutrient impacts have not yet been clearly defined due to a lack of coupled nutrient and metabolic data (Bernhardt et al., 2022) or where data are collected but nutrient experiments are physically impossible due to high discharge or low accessibility. Consequently, this framework can contribute to enhancing prediction models of in-stream nutrient limitation and productivity using datasets of light and nutrient availability, with important implications for understanding the variety of stream responses to elevated nutrients, and setting management targets for nutrient remediation efforts.

## Data Availability Statement

Nutrient diffusing substrate results and time series of abiotic factors (water temperature, light, discharge, water chemistry) collected from Greenland streams are available in a CUAHSI Hydroshare repository (https://doi.org/10.4211/hs.fbef1844a00e4926a6020d3607ef5dbd) (Shin, 2025).

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