Metabolism overrides photo-oxidation in CO₂ dynamics of Arctic permafrost streams

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Abstract

Global warming is enhancing the mobilization of organic carbon (C) from Arctic soils into streams, where it can be mineralized to CO₂ and released to the atmosphere. Abiotic photo-oxidation might drive C mineralization, but this process has not been quantitatively integrated with biological processes that also influence CO₂ dynamics in aquatic ecosystems. We measured CO₂ concentrations and the isotopic composition of dissolved inorganic C (δ¹³CDIC) at diel resolution in two Arctic streams, and coupled this with whole-system metabolism estimates to assess the effect of biotic and abiotic processes on stream C dynamics. CO₂ concentrations consistently decreased from night to day, a pattern counter to the hypothesis that photo-oxidation is the dominant source of CO₂. Instead, the observed decrease in CO₂ during daytime was explained by photosynthetic rates, which were strongly correlated with diurnal changes in δ¹³CDIC values. However, on days when modeled photosynthetic rates were near zero, there was still a significant diel change in δ¹³CDIC values, suggesting that metabolic estimates are partly masked by O₂ consumption from photo-oxidation. Our results suggest that 6–12 mmol CO₂-C m⁻² d⁻¹ may be generated from photo-oxidation, a range that corresponds well to previous laboratory measurements. Moreover, ecosystem respiration rates were 10 times greater than published photo-oxidation rates for these Arctic streams, and accounted for 33–80% of total CO₂ evasion. Our results suggest that metabolic activity is the dominant process for CO₂ production in Arctic streams. Thus, future aquatic CO₂ emissions may depend on how biotic processes respond to the ongoing environmental change.

Arctic streams and rivers are conduits for CO₂ evasion to the atmosphere (Kling et al. 1991; Stackpoole et al. 2017) that may further increase due to climate warming and the associated mobilization of carbon (C) stored in permafrost (Spencer et al. 2015; Wild et al. 2019; Zolkos et al. 2019). Organic C entering aquatic ecosystems can be converted to CO₂ through two distinct pathways: abiotically via photochemical oxidation (hereafter photo-oxidation; Granéli et al. 1996) and biotically via microbial mineralization (Tranvik 1988; Cole and Caraco 2001). In Arctic streams, photo-oxidation may contribute a large fraction of the CO₂ evaded to the atmosphere (Cory et al. 2014). Since this process is driven by sunlight, photo-oxidation should also increase stream CO₂ concentration from night to day (Bertilsson and Tranvik 2000). However, recent in situ observations of CO₂ dynamics in tundra, boreal, and alpine streams indicate net daytime uptake of CO₂ by photosynthesis (Peter et al. 2014; Crawford et al. 2016; Rocher-Ros et al. 2020). Thus, these two light-dependent processes have opposing effects on CO₂ concentrations and the balance between them will determine the change in CO₂ concentrations from day to night (Fig. 1a). Assessing diel changes in CO₂ concentrations can therefore aid in comparing the roles of biological and photochemical processing of C in Arctic freshwaters.

Photo-oxidation and microbial respiration of organic matter are typically studied in isolation, using approaches that incorporate different compartments of the stream ecosystem. These distinct approaches have likely impeded the resolution of the
rates in streams are most often assessed using open-system measures in the water column. By comparison, biological metabolic processes (Miller and Zepp 1995; Granéli et al. 1996; Bertilsson and Rocher-Ros et al. 2000; Osburn et al. 2001) and only accounts for processes. For example, photo-oxidation is often studied in bottles by the latter due to a high preferential biological uptake of $^{12}$CO$_2$ enriching oxidation equals photosynthesis (middle), the isotopic effect will be determined greater (left), equal (middle) or less (right) than photosynthesis. When photo-oxidation consumes CO$_2$. Panels in (b) describe diurnal changes in CO$_2$ concentration and $^{12}$C-DIC values resulting from three scenarios: photo-oxidation rate greater (left), equal (middle) or less (right) than photosynthesis. When photo-oxidation equals photosynthesis (middle), the isotopic effect will be determined by the latter due to a high preferential biological uptake of $^{12}$CO$_2$ enriching the DIC reservoir. In contrast, photo-oxidation releases $^{13}$CO$_2$ and $^{12}$CO$_2$ in the same proportion as the substrate composition. Note that this is a simplification since this effect also will depend on the reservoir size, pH and in situ isotope values.

**Fig. 1.** Conceptual representation of the effect of light-dependent processes on dissolved CO$_2$ concentration in streams. (a) The diel change in CO$_2$ concentrations (red line) is the balance of two opposing processes: photo-oxidation (orange line), which produces CO$_2$ and photosynthesis (green line), which consumes CO$_2$. Panels in (b) describe diurnal changes in CO$_2$ concentration and $^{12}$C-DIC values resulting from three scenarios: photo-oxidation rate greater (left), equal (middle) or less (right) than photosynthesis. When photo-oxidation equals photosynthesis (middle), the isotopic effect will be determined by the latter due to a high preferential biological uptake of $^{12}$CO$_2$ enriching the DIC reservoir. In contrast, photo-oxidation releases $^{13}$CO$_2$ and $^{12}$CO$_2$ in the same proportion as the substrate composition. Note that this is a simplification since this effect also will depend on the reservoir size, pH and in situ isotope values.

relative influences of abiotic and biotic processes on CO$_2$ emissions. For example, photo-oxidation is often studied in bottles (Miller and Zepp 1995; Grané et al. 1996; Bertilsson and Tranvik 2000; Osburn et al. 2001) and only accounts for processes in the water column. By comparison, biological metabolic rates in streams are most often assessed using open-system measures of oxygen (O$_2$) mass balance capturing hyporheic, benthic, and water column processes (Odum 1956; Grace et al. 2015; Hall et al. 2015; Schindler et al. 2017). Thus, to reconcile both approaches we need to evaluate the influences of photosynthesis and photo-oxidation at the ecosystem level. This can be achieved using in situ measures of the key signals and drivers of C processing (e.g., CO$_2$/O$_2$ concentrations, temperature, and light) at a temporal resolution that captures diel variation. For example, it is possible to estimate metabolic rates that affect the stream C balance—gross primary production (GPP) and ecosystem respiration (ER)—and independently compare them with dissolved CO$_2$ dynamics. Accordingly, photo-oxidation should generate CO$_2$ during the day, while GPP has an opposing effect (Fig. 1a).

Diel dynamics of dissolved inorganic C isotopes ($^{13}$C-DIC values) can provide complementary information to observations of O$_2$ and CO$_2$ concentrations, as photo-oxidation and photosynthesis impart contrasting effects on the $^{13}$C-DIC values (Fig. 1b) (Waldron et al. 2007; Giesler et al. 2013; Campeau et al. 2017). For example, past studies have shown clear diel patterns in stream $^{13}$C-DIC with more enriched values during daytime (Parker et al. 2005; Waldron et al. 2007), which has been explained by the high isotope fractionation of photosynthesis (Guy et al. 1993). By contrast, the isotope fractionation effect of photooxidation is generally small compared to photosynthesis and will thus only have a minor effect (Opsahl and Zepp 2001). Instead, photo-oxidation dilutes the $^{13}$C-DIC reservoir toward a value of the substrate, for example, dissolved organic carbon (DOC) that is around $-27‰$ (Peterson et al. 1986; Campeau et al. 2017). Like photooxidation, respiration will dilute the $^{13}$C-DIC reservoir toward a value similar to the organic C source respired (Giesler et al. 2013; Campeau et al. 2017). Furthermore, other processes such as degassing and carbonate weathering will increase the $^{13}$C-DIC values; the former due to isotopic fractionation where $^{12}$CO$_2$ is preferentially lost and the latter due to reservoir dilution since most carbonates are around 0‰ (Giesler et al. 2013, and references therein). Together, respiration, degassing, and weathering shape the average stream $^{13}$C-DIC values, yet their influence on diel patterns are most likely weak.

Given these opposing effects of photosynthesis and photo-oxidation on $^{13}$C-DIC, we can make predictions for diel patterns depending on the relative strength of these two processes (Fig. 1b). For instance, if photo-oxidation is the dominant process, depletion of $^{13}$C-DIC (leading to lighter $^{13}$C-DIC values) during daytime should be accompanied by higher daytime CO$_2$ concentrations (left panel, Fig. 1b). However, if the two processes are equal in magnitude (i.e., the same amount of C is processed by each), we would expect no diel change in CO$_2$ concentration but an enrichment in daytime $^{13}$C-DIC (leading to heavier $^{13}$C-DIC values) due to a stronger effect of isotope fractionation of photosynthesis as compared the isotope dilution by photo-oxidation (middle panel, Fig. 1b). Finally, if photosynthesis dominates, we expect a distinct diel pattern with lower daytime CO$_2$ concentration and a clear increase in daytime $^{13}$C-DIC values (right panel, Fig. 1b). Using diel $^{13}$C-DIC values in streams may thus be helpful in disentangling the relative importance of the two light-dependent processes.

By comparing photosynthetic rates modeled using the O$_2$ mass balance method with independently measured diurnal variation in $^{13}$C-DIC, it is possible to quantify the effect of photo-oxidation on whole-ecosystem estimates of C processing. Photo-oxidation consumes O$_2$ while producing
CO₂ (Laane et al. 1985), and therefore could mask O₂ production by photosynthesis during the day. In contrast, the diel pattern in δ¹³C in DIC will be mostly driven by photosynthesis (Fig. 1b). Therefore, the relationship between photosynthetic rates and diel changes in δ¹³C in DIC provides information about photo-oxidation rates. For instance, if there is a detectable diel change in δ¹³C in DIC values when photosynthetic rates are zero, the amplitude of this diel change in isotopic values can be interpreted as the effect of photooxidation. However, there are several uncertainties that can influence this interpretation, such as higher daytime respiration of labile OC recently produced by photosynthesis (Hotchkiss and Hall 2014; Schindler et al. 2017) and the assumed quotient between O₂ consumed and CO₂ produced, both for respiration (Berggren et al. 2012) and photo-oxidation (Miles and Brezonik 1981). Regardless, this approach can be applied to evaluate the dominant process influencing CO₂ emissions from streams while integrating processes occurring in the water column with those that occur in benthic and hyporheic sediments (Battin et al. 2008).

The aim of this study was to assess the relative importance of light-dependent processes for CO₂ dynamics in Arctic streams that drain continuous permafrost. The Kuparuk and Toolik Rivers (Alaska) were selected due to difference in size (first and fifth order) and the existence of published estimates of photo-oxidation in this area, including an adjacent first-order stream to Toolik River (Cory et al. 2014) and the Kuparuk River. We compare published photo-oxidation rates with estimates of stream metabolism and CO₂ evasion from measured stream CO₂ and O₂ concentrations, light, and temperature. We further constrained estimates of CO₂ production by photo-oxidation using sub-daily (6-h increments) samples analyzed for alkalinity, DOC, and δ¹³C in DIC values. We tested two contrasting hypotheses: (1) stream CO₂ dynamics are primarily driven by photochemical processes and (2) stream CO₂ dynamics are primarily driven by aquatic metabolism (Fig. 1). If photo-oxidation is the major driver, we predicted that CO₂ concentrations in streams would increase from night to day, when photo-oxidation rates would be greatest (Cory et al. 2014). By contrast, if GPP is the major driver, then CO₂ concentrations would decrease from night to day, when photosynthetic CO₂ fixation is greatest (Rocher-Ros et al. 2020).

Methods
Site description

We studied C cycling processes in two streams within the Kuparuk River watershed, on the North Slope of the Brooks Range in Arctic Alaska, near Toolik Field Station (Fig. S1). The climate in the upper Kuparuk watershed is characterized by a long cold season, with snow cover that spans ~8 months of the year. Mean annual air temperature recorded at the Toolik Field Station for the period 1989–2010 was −8.5°C (Cherry et al. 2014). The study was performed between the 18 July and 01 August 2018. Mean air temperature during the study was 13.4°C, while the historical average for this time period between 1989 and 2010 was 9.9°C. The precipitation during the study period was 63.2 mm (Fig. S2). Historically, July accounts for 44% of the annual precipitation (65 and 149 mm for July and annual precipitation respectively, for the period 1989–2010; Cherry et al. 2014). Weather data were obtained from the Environmental Data Center (Toolik Field Station, Institute of Arctic Biology 2019).

We sampled the first-order Toolik River (catchment area 5.6 km²) and the fifth-order stream Kuparuk River (131.9 km²; Fig. S1; Table 1). Both rivers drain tundra underlain by permafrost. Permafrost extent is continuous and soils thaw in summer to depths of 0.3 to up to 2 m, depending on topography (Shaver et al. 2014) that together indicate that water flow is mostly superficial (Rushlow and Godsey 2017) and groundwater inputs are restricted to springs (Bowden et al. 2014). Tussock tundra dominates the landscape, with patches of wet sedge and heath vegetation (Shaver et al. 2014). The riparian vegetation near streams consists of dwarf birch (Betula nana) and willow (Salix spp.), but with heights of <1 m, streams are unshaded.

Stream measurements and sample analysis

We deployed sensors to measure physical (depth, light, temperature) and chemical (CO₂, O₂) properties at a 10-min frequency, from 18 July to 01 August 2018. Water temperature and water level were recorded by HOBO water level loggers (model U20-001-04, Onset Computer Corporation). Water temperature) and chemical (CO₂, O₂) properties at a 10-min frequency, from 18 July to 01 August 2018. Water temperature and water level were recorded by HOBO water level loggers (model U20-001-04, Onset Computer Corporation). Light intensity was monitored by HOBO MX Temperature/Light loggers (model MX2202, Onset Computer Corporation), by recording every minute and averaging to a 10-min frequency. Light intensity (in lux) was converted to photosynthetic active radiation (PAR; in μmol m⁻² d⁻¹) using a conversion factor of 0.0185 according to Thimijan and Heins (1983). Dissolved CO₂ concentration was measured using eosGP CO₂ concentration sensors (Eosense) connected to CR1000 data loggers (Campbell Scientific). The CO₂ sensors were calibrated with standard gases in the laboratory before deployment in the field, using gas concentrations of 400, 2000, and 5000 ppm of CO₂. O₂ concentration was measured every 10 min using miniDOT oxygen sensors (Precision Measurement Engineering), fitted with a

| Site               | Coordinates (WGS 1984) | Area (km²) | Mean slope (degrees) | Elevation outlet (m) | Max. elevation (m) |
|--------------------|------------------------|------------|----------------------|----------------------|---------------------|
| Kuparuk River      | 68.6474, −149.4119     | 131.9      | 1.50                 | 741                  | 1522                |
| Toolik River       | 68.6468, −149.3192     | 5.6        | 0.61                 | 844                  | 983                 |
copper mesh to reduce biofouling. To verify the manufacturer-supplied calibration, we submerged sensors in oxygenated water achieved by intense bubbling for 1 h, and then logged O₂ continuously for 5 h after removing air stones, in order to reach equilibrium with the atmosphere after an initial supersaturation. We then added dry yeast and sugar to consume the dissolved oxygen. The sensors measured 100% O₂ saturation in oxygenated water and 0% after yeast and sugar was added, and therefore no further correction of observations was performed. Sensors were placed in the thalweg of each stream, with the O₂ logger facing downstream and the CO₂ sensor within in a perforated plastic pipe as a protective casing.

For the Kuparuk River, we obtained river discharge and depth from the Arctic Long-Term Ecological Research Program (http://arc-lter.ecosystems.mbl.edu). For Toolik River, discharge estimates were based on pressure measurements from HOBO water level loggers and an empirical rating curve (Fig. S3) based on five salt slug injections (Moore 2005). We used two conductivity sensors (model U24-001, Onset Computer Corporation) at separate locations during the salt releases to estimate travel time and therefore the water velocity and discharge. To assess lateral inputs of water that could affect metabolism estimates in Toolik River, we also performed multiple discharge measurements upstream (Fig. S4), but no significant inputs were detected for more than 1 km upstream. The average depth of the reach was estimated from the relationship between stream velocity (V), discharge (Q), and stream width (W): D = Q/(W × V) (Hall and Hotchkiss 2017). This reach depth was then related to the site depth measured by the pressure logger to obtain continuous estimates of the reach depth.

We collected water samples at 6-h intervals (6, 12, 18, and 24 h) for 6 d (27 July to 01 August 2018) at the same locations as the automated loggers for analysis of additional chemical constituents. We measured pH, alkalinity, and DOC from samples collected into pre-rinsed 1 liter bottles that were kept cool and subsampled in the lab within 6 h of collection. The samples for δ¹³CDIC analysis were collected with a syringe and 4 mL were injected into a 12 mL septum-sealed glass vial (Labco Limited) that had been preshuffled with He gas for 3 min.

pH was measured on a 150-mL aliquot of stream water (Accumet AB pH meter, Fisher Scientific). Samples for analysis of DOC of DOC were filtered through 0.45 μm filters prerinsed with stream water (Filtropur Sarstedt), and acidified with 8 M HCl (250 μL HCl to 50 mL of stream water). DOC concentration was measured as nonpurgeable organic C by nondispersive infrared gas analysis on a total organic C analyzer (TOC-L CPH, Shimadzu Scientific Instruments; limit of quantification = 8 μM). Alkalinity was measured on 30 mL of unfiltered water collected without headspace using a Metrohm automated titration system and a Metrohm Aquatrol Plus pH electrode (Metrohm AG). The samples were titrated to pH 4.5, which is the equivalence point between H⁺ and HCO₃⁻, with 0.1 M HCl and alkalinity was calculated from the difference in the amount of HCl used and the sample volume. DIC was calculated from alkalinity and ρCO₂ values using PHREEQCI (Parkhurst and Appelo 2013). Samples for δ¹³CDIC values determination were acidified with 100 μL of 99% H₃PO₄ as a preservative (Taipale and Sonninen 2009) and to transform all HCO₃⁻ and CO₂²⁻ ions to CO₂(g). δ¹³CDIC values were determined using a Gasbench II extraction line coupled to a Finnigan MAT 253 mass spectrometer. Results are given as per mil deviations from the standard (PDB) and denoted δ¹³Cᵣ and where R is the ratio of ¹³C/¹²C: δ¹³Cᵣ = (R_sample/ R_standard − 1) × 10³. From repeated measurements of standards, the reproducibility was calculated to be better than 0.1% for δ¹³C. All samples were stored at +4°C until analyses.

**Data analysis, metabolism, and CO₂ evasion**

All data were analyzed using R (R Core Team 2017; version 3.5.1). The dataset with daily values and an R script to reproduce the figures and tests can be found in the Supplementary Materials. Linear regressions were performed using the `lm` function, to assess the effect of GPP on diel changes in CO₂ evasion and δ¹³CDIC values. Amplitude of diel variation in δ¹³CDIC values were calculated from the lowest and highest value within each day, whereas diel variation in CO₂ evasion was calculated as the cumulative CO₂ evasion during the light hours minus the average CO₂ evasion rate during the night. We used the O₂, temperature, light, and depth time series to model stream metabolic rates and the gas transfer velocity using the `streamMetabolizer` package (version 0.10.9). This approach models O₂ concentrations using the following equation:

\[
O_2 = O_{2,0} + \left( \frac{GPP}{D} \times \frac{PAR_{t_2} - PAR_{t_1}}{\sum_{t=0}^{144} PAR} \right) + \frac{ER \times \Delta t}{D} + K_{O_2} \times (O_2_{sat} - O_2_{(t-\Delta t)}) \times \Delta t
\]

(1)

where \(O_{2,0}\) is the oxygen concentration at time \(t\) (g O₂ m⁻³), \(D\) is the channel depth (m), \(PAR\) is photosynthetically active radiation (μmol m⁻² s⁻¹), \(K_{O_2}\) is the gas reaeration coefficient of O₂ (d⁻¹), \(\Delta t\) is the time step (10 min), and \(O_2_{sat}\) is the concentration of O₂ in the water at 100% saturation. We used a Bayesian inverse model to solve for three parameters: GPP (g O₂ m⁻² d⁻¹), ER (g O₂ m⁻² d⁻¹), and the gas reaeration coefficient (\(K_{600}\) d⁻¹). Prior distributions for GPP and ER were based on existing rates measured in the nearby Ivishak spring (Hurny et al. 2014), with a mean of 1 and −5 g O₂ m⁻² d⁻¹ for GPP and ER, respectively. The model was run for 10,000 iterations, and the last 500 were used as the model results. To avoid problems regarding equifinality, where multiple solutions can produce the same model fit (Appling et al. 2018), we pooled \(K_{600}\) estimates within binned categories based on stream discharge, a physical variable that should capture
variations in the turbulence regime of a river. To model $K_{600}$, we provided prior distributions of $K_{600}$ for different discharge conditions. To do so, we first derived estimates of $K_{600}$ with the night-time regression method (Hornberger and Kelly 1975) using the function $\text{metab}_{\text{night}}()$ in streamMetabolizer. Figure S5 shows the initial estimates of $K_{600}$ and the final binned $Q-K_{600}$ relationship obtained from the metabolism model. We compared modeled $K_{600}$ estimates with those obtained from hydraulic measurements at Toolik River using the relationship $K_{600} = 951.5 \times (V \times S)^{0.75}$ (Raymond et al. 2012), where $K_{600}$ is the gas transfer velocity (or $D \times K_{600}$, m d$^{-1}$) and $S$ is the channel slope. The $K_{600}$ obtained from this hydraulic relationship was similar to the values of $K_{600}$ estimated by the metabolism model (Fig. S6).

The metabolism model in streamMetabolizer assumes constant ER throughout the day and estimates GPP as a linear function of light (Appling et al. 2018). This is a simplification of ecosystem processes where ER might be greater during the day (Hotchkiss and Hall 2014) due to higher temperature and/or the availability of more labile C released during photosynthesis (Schindler et al. 2017), and GPP can increase nonlinearly with light (Hanson et al. 2008). We additionally evaluated parameter estimates from BASE (Grace et al. 2015), a metabolism model that includes temperature-dependence of ER and a nonlinear relationship of GPP with light. We found that the metabolism estimates using BASE were similar to the estimates by streamMetabolizer (Supplementary Text S1) and we therefore report metabolic rates estimated by the more parsimonious streamMetabolizer model.

$CO_2$ exchange with the atmosphere ($E_{CO_2}$) was calculated as:

$$E_{CO_2} = K_{CO_2} \times D \times (\text{[CO}_2]_{aw} - \text{[CO}_2]_{aw})$$  \hspace{1cm} (2)

where $K_{CO_2}$ is (d$^{-1}$) is the gas reaeration coefficient obtained by the streamMetabolizer model, $D$ is the channel depth (m), $\text{[CO}_2]$ is the concentration of $CO_2$ measured in the water (w) or in equilibrium with the atmosphere (a) (mol m$^{-3}$) (Raymond et al. 2012). We used an atmospheric $CO_2$ concentration of 390 ppm, obtained from several air $CO_2$ measurements performed in the field with a hand-held $CO_2$ sensor (Vaisala DM70). The average atmospheric $pCO_2$ measured for the same period in the NOAA observatory of Point Barrow (~400 km from study site), was 397 ppm (https://www.esrl.noaa.gov/gmd/obop/bw/). To compare $CO_2$ consumed by GPP with observed $CO_2$ emissions, we assumed that 1 mol of $O_2$ is exchanged by 1 mol of $CO_2$ (Demars et al. 2016).

Results

Chemical and physical attributes of the streams

The study streams were supersaturated in $CO_2$ relative to the atmosphere. The partial pressure of dissolved $CO_2$ ($pCO_2$) was $925 \pm 3$ ppm in the Kuparuk River and $1878 \pm 16$ ppm in the Toolik River (mean $\pm$ 95% confidence interval). In contrast, both streams were undersaturated in $O_2$ (Figs. 2, 3). The $DO$ concentration was lower in the Kuparuk River compared to the Toolik River, with a mean of $0.33 \pm 0.02$ and $0.86 \pm 0.01$ mmol C L$^{-1}$, respectively. Bicarbonate ($HCO_3^-$) concentration in the Kuparuk River was $0.33 \pm 0.02$ mmol C L$^{-1}$ while in the Toolik River was $0.11 \pm 0.01$ mmol C L$^{-1}$ over the measurement period. Isotope values, $\delta^{13}C_{DIC}$, in the Kuparuk River were $-9.9 \pm 0.3\%$ while in the Toolik River were $-14.5 \pm 0.7\%$o. The physical properties of both streams are summarized in Table 2.

Temporal patterns in stream chemistry

Both the Kuparuk and Toolik Rivers generated diel variation in $CO_2$, $O_2$, and $\delta^{13}C_{DIC}$ values. $CO_2$ concentration consistently decreased from night to day, while $O_2$ saturation increased and $\delta^{13}C_{DIC}$ values increased during daytime. The diel changes in dissolved $CO_2$ concentration in the Toolik River (Fig. 3) averaged 17.4 mmol C m$^{-3}$ (436 ppm $CO_2$), and ranged between 14.5 and 21.3 mmol C m$^{-3}$. In the Kuparuk River (Fig. 2), the mean diel change in $pCO_2$ was 5.4 mmol C m$^{-3}$ (85 ppm $CO_2$) ranging between 2.7 and 8.2 mmol C m$^{-3}$. Mean diel amplitude of $\delta^{13}C_{DIC}$ values in the Toolik River was 2.9%o (range = 2.4–4.3%), while in the Kuparuk River was 1.4%o (range = 1.2–2.1%). $O_2$ saturation in the Toolik River had a mean diel change of 7.3% (range = 4.5–12.4%), and in Kuparuk the mean diel change was 2.4% (range = 1.6–4.1%).

Discharge was highest at the beginning of the study period and thereafter decreased until 27 July. A flood occurred 27–31 July, increasing discharge from 1.36 to 8.32 m$^3$ s$^{-1}$ in the Kuparuk River and from 0.05 to 0.48 m$^3$ s$^{-1}$ in the Toolik River (Figs. 2, 3). The increased flow rates coincided with dilution of $HCO_3^-$ in both streams (Figs. 2, 3) whereas a decrease in $CO_2$ concentration was apparent only in the Toolik River (Fig. 3). Water temperature followed a similar pattern to air temperature (Fig. S2), with lower temperatures at the beginning of the sampling period.

Metabolic rates and $CO_2$ evasion

The average rate of GPP was nearly fourfold greater in the Toolik River ($14.2 \pm 7.9$ mmol C m$^{-2}$ d$^{-1}$; mean $\pm$ SD; $n = 13$ d) compared to the Kuparuk River ($3.1 \pm 2.9$ mmol C m$^{-2}$ d$^{-1}$; $n = 11$ d). GPP was positively correlated with the diel change in $CO_2$ evasion with a slope less than 1 (slope = 0.38; Fig. 4a). GPP was also positively correlated with the diel change in $\delta^{13}C_{DIC}$ values ($r^2 = 0.98$; Fig. 4b). In the Toolik River, the mean diel change in $CO_2$ evasion was 60.3% lower when compared to mean GPP (Fig. 5). In the Kuparuk River, both GPP and the diel $CO_2$ change were smaller than in the Toolik River, and diel variation in $CO_2$ evasion was 75.3% of mean GPP (Fig. 5).

In contrast to the patterns of GPP, ER was greater in the Kuparuk River ($-263 \pm 51$ mmol C m$^{-2}$ d$^{-1}$) than in the Toolik River ($-75 \pm 55$ mmol C m$^{-2}$ d$^{-1}$) over the observation
period. ER rates were higher than GPP, and therefore net ecosystem production (NEP; NEP = GPP − ER) was negative. NEP was $-260 \pm 52 \text{ mmol C m}^{-2} \text{ d}^{-1}$ in Kuparuk River compared to $-61 \pm 51 \text{ mmol C m}^{-2} \text{ d}^{-1}$ in Toolik River (Fig. 6). CO$_2$ evasion ($E_{CO_2}$) to the atmosphere was approximately twofold higher in the Kuparuk (323 ± 56 mmol C m$^{-2}$ d$^{-1}$) compared to the Toolik River (186 ± 121 mmol C m$^{-2}$ d$^{-1}$) and the mean contribution of stream NEP to CO$_2$ evasion (NEP/ $E_{CO_2}$ × 100) was 80% in Kuparuk River and 33% in Toolik River.

**Discussion**

The aim of this study was to assess the relative importance of biotic and abiotic processes in generating CO$_2$ emissions from tundra streams that drain continuous permafrost. We observed that CO$_2$ concentration decreased from night to day due to photosynthetic activity, which is inconsistent with the hypothesis that photo-oxidation is the primary mechanism generating CO$_2$ in these streams (Cory et al. 2014). Instead, the observed patterns suggest significant contributions of photosynthesis to stream diel CO$_2$ dynamics. This result concurs with observations from other Arctic streams (Rocher-Ros et al. 2020), as well as streams in other biomes (Peter et al. 2014; Crawford et al. 2016; Reiman and Jun Xu 2018). Furthermore, stream NEP was a major contributor to stream CO$_2$ evasion, with ER rates measured in situ that were 10 times greater than previously reported photo-oxidation rates from streams in the study region (Cory et al. 2014). Overall, in situ observations of dissolved C dynamics indicate that metabolic processes play a dominant role in CO$_2$ evasion from Arctic streams draining permafrost.

**Light-dependent processes in Arctic streams**

Our results showed a marked decrease of $p$CO$_2$ from night to day in Arctic streams (Figs. 2, 3) that can be explained by
stream photosynthetic activity (GPP) (Fig. 4a). In addition to a correlation between diurnal amplitude of dissolved CO2 concentration and GPP, the role of photosynthesis is further supported by the strong positive relationship between the diel change in $\delta^{13}$CDIC and GPP (Fig. 4b). In both streams, average $\delta^{13}$CDIC values ($-10.0$ to $-14.5 \permil$) were more enriched than expected for DOC in these and other high-latitude streams, ($\sim -27 \permil$; Peterson et al. 1993; Giesler et al. 2013). If photo-oxidation strongly influenced diel variation in $\delta^{13}$CDIC, we would expect that the isotope values would be depleted and closer to $\delta^{13}$CDOC values during daytime (Fig. 1b, left panel). Instead, as CO2 decreased during daytime, $\delta^{13}$CDIC values increased, consistent with photosynthetic C-fixation as the primary driver of these dynamics (Fig. 1b, right panel). Thus, together, the metabolic rates derived from in situ O2 mass-balance and changes in the isotopic composition of DIC strongly suggest that photosynthesis is an important light-dependent process in these streams that drives diel changes in CO2 concentration and therefore evasion rates at sub-daily temporal scales.

![Fig. 3. Time series of stream solutes and physical properties in Toolik River. CO2 (a), O2 (b), discharge and temperature (e) were measured at 10-min intervals with sensors. $\delta^{13}$CDIC (c), DOC and HCO3 (d) were sampled every 6 h. In (a-c) light is shown as a secondary variable.](image)

| Site          | Discharge (m$^3$ s$^{-1}$) | Depth (m)   | Temp. (°C)     | Conductivity (µS cm$^{-2}$) | pH          | $k_{600}$ (m d$^{-1}$) |
|---------------|-----------------------------|-------------|----------------|-----------------------------|-------------|------------------------|
| Kuparuk River | 4.1 (2.3–6.2)               | 0.54 (0.49–0.63) | 9.4 (8.4–10.9) | 46.6 (42.6–51.3)            | 7.24 (6.99–7.42) | 7.6 (7.1–8.4)          |
| Toolik River  | 0.17 (0.07–0.23)             | 0.29 (0.18–0.39) | 11.4 (9.6–13.5) | 20.4 (16–26)                | 6.61 (6.50–6.71) | 2.2 (1.1–2.7)          |
Relationships between GPP and diel patterns in CO2 evasion and δ13CDIC values indicate a secondary role of photo-oxidation in generating CO2 evasion from tundra streams. GPP does not solely explain the diel change in CO2 evasion, which would require a 1 : 1 relationship between the two rates as observed in other Arctic streams (Rocher-Ros et al. 2020), but not in these Alaskan streams (Fig. 4a). Instead, the relationship deviated from 1 : 1, which could be caused by photo-oxidation of DOM. Photo-oxidation produces CO2 during the day and therefore reduces the effect of the photosynthetic uptake of CO2 (Fig. 1). Indeed, in both streams, we found a smaller diel amplitude in CO2 evasion than expected from the effect of photosynthetic activity alone (Fig. 5). A significant diel change in δ13CDIC values occurred even when the modeled rate of GPP was zero (Fig. 4b), suggesting that photosynthesis may be occurring but not detectable based on diel changes in O2. This may occur because photo-oxidation not only produces CO2 but also consumes O2 (Laane et al. 1985), and can therefore cause an underestimation of GPP derived from O2 mass balance due to O2 consumption by photooxidative reactions. The amount of C-fixation by photosynthesis but masked by photo-oxidation can be estimated from the x-intercept of the relationship between GPP and the diel change in δ13CDIC values, and thus represents an in situ estimate of photo-oxidation. This value was −9 mmol C m⁻² d⁻¹ (±3), well within the range of laboratory-measured photo-oxidation rates for streams of the study region (Cory et al. 2014; Fig. 5), and similar to lakes elsewhere (Granéli et al. 1996; Koehler et al. 2014; Vachon et al. 2016). These findings suggest that combining whole-system estimates of metabolism with diel observations of CO2 and δ13CDIC provides a promising approach for separating the relative role of light-dependent processes in streams.

A more pronounced difference between GPP and the diel change in CO2 evasion was observed in Toolik River than in the Kuparuk River (Figs. 4a, 5), which could also reflect the differences photo-oxidation. This pattern is consistent with laboratory results showing that photo-oxidation in the Kuparuk River was three times lower than in Imnavait Creek, an adjacent stream of similar size and DOC concentration to Toolik River.

\[
\begin{align*}
\text{Abisko} & : y = 2.2 \pm 0.91 x, \quad R^2 = 0.62, p < 0.001 \\
\text{Alaska} & : y = 0.52 \pm 0.38 x, \quad R^2 = 0.83, p < 0.001
\end{align*}
\]

**Fig. 4.** Diel patterns of CO2 evasion and δ13CDIC as a function of GPP. (a) Relationship between GPP and the absolute diel change in CO2 evasion. The dashed line denotes the 1 : 1 line, and shown in gray is data from tundra streams in Abisko, Sweden, with similar K600 (Rocher-Ros et al. 2020). (b) Relationship between GPP and the day-night difference in δ13CDIC. Note that the intercept with the y-axis is 1.1 and with the x-axis is −9 mmol C m⁻² d⁻¹ (95% confidence interval −12 to −6).

**Fig. 5.** CO2 production and consumption by light-dependent processes in tundra streams. Green bars show GPP measured in this study in the Kuparuk and Toolik Rivers. Yellow bars represent the published photo-oxidation rates (Cory et al. 2014) in the Kuparuk River and in Imnavait Creek, an adjacent stream of similar size and DOC concentration to Toolik River. Red bars show the observed diel change in CO2 evasion. Vertical black lines denote 1 standard error.
River (Fig. 5; Cory et al. 2014; Fig. S1 for location). Such contrasts indicate that DOC concentration regulates the relative importance of photo-oxidation, as higher DOC can sustain higher photo-oxidation rates (Bertilsson and Tranvik 2000). This mechanism is further supported by contrasts between streams in Alaska and DOC-poor streams in Arctic Sweden. Across these sites, DOC is highest at Toolik River (10 mg C L$^{-1}$), lower in the Kuparuk River (4 mg C L$^{-1}$), and lowest in streams studied in arctic Sweden (below 2 mg C L$^{-1}$; Giesler et al. 2014). For the Swedish streams, photosynthesis clearly explains diel amplitude in CO$_2$ emissions with the data falling close to the 1 : 1 relationship, whereas the slope of this relationship is shallower for the streams in Alaska (Fig. 4a). We interpret these differences as an effect of photo-oxidation that produces CO$_2$ simultaneously with consumption by GPP (Fig. 1). Overall, these differences highlight the importance of DOC loading as a mediator of light-dependent processes in Arctic streams.

Sources of CO$_2$ evaded from Arctic streams

In situ estimates of CO$_2$ evasion and whole-stream metabolic rates suggested that photo-oxidation was not the major contributor to CO$_2$ evasion from the studied Arctic streams. Stream NEP was strongly negative (ER > GPP), comprising 80% of CO$_2$ evasion from the Kuparuk river and 33% from the Toolik River, whereas published rates of photo-oxidation cannot sustain CO$_2$ evasion observed from either river (Fig. 6b,d). This is in contrast to previous work that compared measured rates of photo-oxidation to modeled estimates of CO$_2$ evasion, concluding that 79–89% of CO$_2$ evasion from rivers and streams of the study region is generated by photo-oxidation (Cory et al. 2014). Estimates of metabolic rates made in the present study are consistent with previous estimates in Kuparuk River, with GPP rates ranging from 3 to 46 mmol C m$^{-2}$ d$^{-1}$ using benthic chambers (Peterson et al. 1986) and ER rates averaging 286 mmol C m$^{-2}$ d$^{-1}$ estimated using a two-station metabolism model (Bowden et al. 2014), and thus uncertainty in our estimates of NEP is unlikely to contribute to this discrepancy. Instead, the discrepancy between our study and Cory et al. (2014) likely occurred because the CO$_2$ evasion estimates from streams in this area in this study are an order of magnitude higher than rates assumed in the previous study. Evasion rates applied in the previous study (from Kling et al. 1991) were based on observed pCO$_2$ and an assumed gas transfer velocity that is consistent with lakes (0.5 m d$^{-1}$, Wanninkhof et al. 1985). Thus, although the dissolved pCO$_2$ in Kuparuk River was similar between our observations and those of Kling et al. (1991) (925 and 812 ppm, respectively) our estimates of CO$_2$ evasion for Kuparuk River are 27-fold greater because the rates of reaeration modeled from diurnal variation in dissolved O$_2$ were 14–17 times greater than those observed in lakes. Recent decades have seen important developments in research on gas transfer velocities in streams (Raymond et al. 2012; Ulseth et al. 2019; Hall and Ulseth 2020), which show the contribution of turbulent conditions to greater physical evasion rates from streams and rivers than lakes (Raymond et al. 2013).

NEP and photo-oxidation did not entirely account for CO$_2$ evasion from either river, although the unexplained flux was greater in Toolik River (55%) than in the Kuparuk River (17%). This unaccounted-for CO$_2$ suggests that additional processes are contributing to emissions (Fig. 6). Soil water inputs of CO$_2$ are a likely contributor, and are relatively greater in small, headwater streams than in larger rivers (Hotchkiss et al. 2015), consistent with the observed contrast in CO$_2$ emissions between the first- and fifth-order rivers. Additionally, we
observed more depleted $\delta^{13}$C$_{\text{DIC}}$ values during stormflows, consistent with a shift toward respiration of DOC produced in soils (Giesler et al. 2013; Figs. 3, 6). Thus, increased inputs of soil-derived CO$_2$ following storms could explain the observed temporal pattern, as shallow flowpaths are activated during storms (Rushlow and Godsey 2017) and contain elevated concentration of dissolved CO$_2$ (10,000–30,000 ppm in summer; (Pokrovsky et al. 2015; Harms et al. in review).

Responses of carbon processing to climate change in Arctic streams

Stream metabolism contributed significantly to CO$_2$ evasion in two Arctic streams draining continuous permafrost. CO$_2$ evasion to the atmosphere from fluvial ecosystems as a result of terrestrial inputs is a critical component of the C cycle (Raymond et al. 2013; Butman et al. 2015). In the Arctic, mobilization of previously stored organic C is ongoing due to climate change (Feng et al. 2013; Wauthy et al. 2018). There-fore, understanding and partitioning the relative importance of biotic and abiotic processes responsible for this large efflux is key to predicting how it might change under continued climate warming. Both photo-oxidation and photosynthesis are dependent on light, but biological processes are additionally sensitive to other factors, which could alter their overall balance. For instance, primary producers and therefore GPP in Arctic streams are sensitive to nutrients (Benstead et al. 2004; Slavik et al. 2004; Myrstener et al. 2018), temperature (Demars et al. 2016; Song et al. 2018), and disturbances (Parker & Huryn, 2013). Therefore, nutrient limitation (Slavik et al. 2004; Myrstener et al. 2018) or scouring floods (Roberts et al. 2007; Kendrick et al. 2019) likely constrain rates of GPP and may thereby sustain the relative importance of photo-oxidation as a driver of diel CO$_2$ patterns. In contrast, increased nutrient inputs from warming soils and thawing permafrost (Keuper et al. 2012; Kendrick et al. 2018; Harms et al. 2019) or declining summer flows (Brabets and Walvoord 2009; Bennett et al. 2015) might cause increased metabolic rates, whereas declining discharge-normalized DOC concentration (Kendrick et al. 2018) might reduce the relative contribution of photo-oxidation. We suggest that the future role of Arctic fluvial networks in the processing of C and CO$_2$ evasion will be largely dependent on how stream metabolic processes react to ongoing climate change.

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Conflict of Interest
None declared.

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