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Global carbon dioxide efflux from rivers enhanced by high nocturnal emissions

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57 Abstract

58 Carbon dioxide (CO₂) emissions to the atmosphere from running waters are estimated to be 59 four times greater than the total carbon (C) flux to the oceans. However, these fluxes remain 60 poorly constrained because of substantial spatial and temporal variability in dissolved CO₂ concentrations. Using a global compilation of high frequency CO₂ measurements, we 61 demonstrate that nocturnal CO₂ emissions are on average of 27% (0.9 g C m⁻² d⁻¹) greater 62 63 than those estimated from diurnal concentrations alone. Constraints on light availability due 64 to canopy shading or water colour are the principal controls on observed diel (24 hr) variation, 65 suggesting this nocturnal increase arises from daytime fixation of CO₂ by photosynthesis. Because current global estimates of CO₂ emissions to the atmosphere from running waters 66 $(0.65 - 1.8 \text{ Pg C yr}^{-1})$ rely primarily on discrete measurements of dissolved CO₂ obtained 67 68 during the day, they substantially underestimate the magnitude of this flux. Accounting for 69 night-time CO₂ emissions may elevate global estimates from running waters to the atmosphere by 0.20-0.55 Pg C yr⁻¹. 70

71 Carbon dioxide (CO_2) emission from inland waters to the atmosphere is a major flux in the global carbon (C) cycle, and four-fold larger than the lateral C export to oceans¹. Streams and 72 rivers are hotspots for this flux, accounting for ~85% of inland water CO₂ emissions despite 73 covering <20% of the freshwater surface area². However, the magnitude of global CO₂ 74 75 emissions from streams and rivers remains highly uncertain with estimates updated over the past decade from 0.6 to 3.48 Pg C yr^{-1 (2,3)}. This revision follows improvements in the spatial 76 resolution for upscaling emissions^{2,4}, as well as new studies from previously underrepresented 77 areas such as the Congo⁵, Amazon^{6,7}, and global mountains⁸. Despite recent studies using 78 79 continuous measurements to show large day-night changes in stream and river water CO₂ concentrations^{9–13}, the global significance of sub-daily variation on overall CO₂ emissions 80 81 remains unexplored.

82 Diurnal cycles in solar radiation impose a well-known periodicity on stream biogeochemical 83 processes, creating diel (i.e., 24-hr period lengths) patterns for many solutes and gases, including nutrients, dissolved organic matter, and dissolved oxygen $(O_2)^{14}$. Indeed, diel 84 85 variation in O_2 arising from photosynthetic activity is the signal from which whole-system metabolic fluxes are estimated¹⁵. Photosynthetic production of O₂ is stoichiometrically linked 86 87 to the day-time assimilation of dissolved inorganic carbon (principally dissolved CO₂), 88 lowering CO₂ concentrations during the day. The resulting diel variation, with higher nighttime CO₂ concentrations when respiration reactions dominate, implies increased emissions at 89 90 night. Despite the obvious connection between photosynthesis and CO_2 consumption, the 91 implications for total aquatic CO_2 emissions has been neglected, most likely due to the lack of sub-daily measurements of CO₂ in water¹⁶. Other processes can also vary at sub-daily time 92 93 scales and could thus similarly drive diel changes in CO₂ emissions from streams, including interactions with the carbonate system¹⁷, photo-chemical oxidation of organic matter¹⁸, as 94 95 well as diel changes in discharge and subsequently lateral CO₂ inputs from terrestrial

96	environments ¹⁹ . Regardless of the driving forces, the overall magnitude, direction, and
97	significance of diel changes in CO ₂ emissions remain largely unknown at a global scale.
98	Current global estimates of CO ₂ emissions from running waters ^{2,4} rely almost exclusively on
99	manually collected samples that fail to incorporate sub-daily variability. Here, we assess
100	whether widespread reliance on discrete day-time sampling creates a strong temporal bias that
101	underestimates CO ₂ emissions from running waters. We use the most widely used global river
102	chemistry database (GLORICH ²⁰) and leverage recent technological advances in continuous,
103	sensor-based dissolved CO ₂ monitoring ¹⁶ to ask if this sampling bias is concurrent with
104	consistent day-night differences in CO ₂ emissions. We compiled high-resolution CO ₂ time
105	series representing a total of 52 years of continuous data from 66 streams worldwide
106	(Extended Data Fig. 1a; Table S1), spanning a wide range of drainage sizes (Extended Data
107	Fig. 1b), climate conditions, land cover, and stream physicochemical properties (Table S2).
108	We evaluated the generality of diurnal stream CO ₂ variation, quantified the significance of
109	these signals for CO ₂ emissions, and identified the main landscape factors that control diurnal
110	variation. Finally, we evaluated the potential bias in global estimates that arises from
111	neglecting nocturnal CO ₂ emissions.

113 **Results and Discussion**

114 Magnitude and bias of diel changes in CO₂ emissions

115 Water samples compiled in the GLORICH database²⁰ were primarily taken during the day,

116 with 90% of observations between 08:10 and 15:55 and a median sampling time of 11:25

117 (Figure 1a). Comparing this time window of manual sampling with sensor data synthesized in

this study, we found that only 10% of days had maximum CO₂ emissions within these hours,

and there was a consistent pattern of higher emission rates during night than day (Figure 1b).

120 Nocturnal emission rates were on average 27% greater than daytime rates across all sites, with 121 differences ranging from -12 to 193 % (Table S3). This overall pattern was globally 122 consistent, with 56 of 66 (85%) of sites showing higher average nocturnal CO₂ emission rates 123 (Figure 2a and Table S3). However, the observed ranges in diel change varied among biomes 124 (Figure 2b). Specifically, streams with the largest diel change in emissions drained temperate 125 forests, followed by montane grasslands; yet these biomes also had the largest internal 126 variation. We observed generally smaller diel changes, and less internal variability, for boreal 127 and tropical/sub-tropical systems. Despite such differences, the large variation observed 128 within most biomes suggests that controls on diel CO₂ emissions operate at finer spatial scales¹⁰. Further, because the GLORICH database – the foundation of current global estimates 129 of CO_2 emissions from inland waters² – relies primarily on discrete samples with a strong 130 daytime sampling bias, the geographically widespread diel variation in CO₂ emissions 131 132 introduces a systematic and potentially large error in estimates of aggregate flux rates.

133

134 Drivers of diel changes in CO₂ emissions

135 Diel patterns in stream CO₂ emissions result from a dynamic interplay between 136 biogeochemical and hydrological processes. These diel drivers include aquatic primary production^{10,12}, biological²¹ and photolytic oxidation of organic C¹⁸, and terrestrial import of 137 CO_2 from soil respiration and mineral weathering¹⁹. Additionally, diel changes in water 138 temperature can affect CO₂ emissions through its effect on the physical exchange rate 139 between air and water $(kCO_2)^{22}$. An initial exploration of our continuous data suggest that 140 141 aquatic processes generate considerable temporal variation in the magnitude of diel variation 142 in emissions (Figure 3). Specifically, for sites with annual records, the largest diel amplitudes 143 were consistently observed during summer, and in open canopy reaches (median = 0.76 g C

144 $m^{-2} d^{-1}$). Markedly reduced amplitudes were observed in streams with closed canopies 145 (median = 0.09 g C m⁻² d⁻¹), while intermediate amplitudes were evident at partially covered 146 sites (median=0.37 g C m⁻² d⁻¹). Overall, these observations are consistent with greater levels 147 of daytime CO₂ uptake in open canopy streams during summer, when warm temperatures and 148 greater incident light^{23,24} support elevated rates of photosynthesis¹⁰. By contrast, wintertime 149 diel changes in stream CO₂ emissions were more similar across canopy cover categories, 150 suggesting reduced aquatic photosynthesis.

151 We used structural equation modeling (SEM) to further resolve factors and causal 152 combinations that underpin variation in summertime diel emissions, the time-period for which 153 we have the most complete data set (Figure S1; Table S1). Our structural model consisted of 154 two levels of factor interaction, or metamodels (see method section for a more detailed 155 description of the SEM). First, we considered whether diel CO_2 emission patterns arise from parallel variation in kCO_2 and stream water pCO_2 , the two main factors determining aquatic 156 CO_2 emissions²⁵. The results from the SEM at this first level ($r^2=0.43$; Extended Data Fig. 2 157 158 and Table S4) suggest that diel variation in CO_2 emissions was mostly driven by variation in pCO_2 (β =0.65), whereas kCO_2 exerted a minor influence (β =0.02). Second, we used SEM to 159 160 identify significant relationships between environmental variables and diel changes in pCO_2 . This second SEM model ($r^2=0.46$; Extended Data Fig. 2 and Table S4) indicated that stream 161 162 canopy cover (β =-0.58) was the primary driver of diel variation of pCO₂. Together with the 163 observed seasonal patterns (Figure 3), our model supports the hypothesis that riparian canopy 164 cover drives diel pCO_2 variation by regulating the amount of light reaching the stream surface and, in turn, daytime rates of stream autotrophic CO₂ uptake^{15,26,27}. 165

Diel patterns in stream CO₂ emissions not only varied seasonally but also spatially, increasing
with channel size (Figure 4a). In larger river systems, terrestrial shading is reduced, increasing

168	the light available for primary producers ²³ , which ultimately explains the general increase in
169	gross primary production (GPP) with channel size ^{28,29} . However, larger rivers with open
170	canopies in our dataset did not necessarily exhibit significant diel change in CO ₂ emissions
171	(Figure 4b). The variability in diel CO ₂ amplitudes among these larger rivers likely arises
172	from differences in light-attenuation in the water column, linked to high concentrations of
173	dissolved organic matter (DOM) or suspended sediments that inhibit GPP ³⁰ (Figure 4c;
174	Extended Data Fig. 3). As such, light attenuation, either by canopy cover along small streams,
175	or by water colour, turbidity, and depth for larger river systems ³¹ , dictates the magnitude of
176	diel variation in CO ₂ emissions along river continua. We further explored the influences of
177	water colour at five sub-tropical Florida sites spanning a large range in DOC $(1.0 - 43.4 \text{ mg})$
178	L^{-1}) and ecosystem size (9 – 66 median discharge; m ³ s ⁻¹), and for which we have high
179	frequency CO_2 and fluorescent DOM (fDOM) measurements. These data confirm that diel
180	changes in CO_2 emissions are supressed above ca.70 ppb of fDOM (corresponding to ca. 20
181	mg L ⁻¹ DOC), even when incident light is relatively high (Figure 4d). Despite this potential
182	influence of water colour, more than 95% of the sites in the GLORICH database are below 20
183	mg L^{-1} DOC (Extended Data Fig. 4), and thus water colour as a constraint on diel CO ₂
184	patterns is likely not operating for most of the monitoring sites from which global estimates of
185	river CO ₂ emissions are currently derived.

The controls on diel variation in CO_2 emissions exerted by either canopy cover or water colour do not follow obvious geographical patterns (Figure 2b). However, the probability that one or both constraints operate is likely biome-specific, which may aid predictions of which regions of Earth are more prone to strong bias in upscaling. For example, boreal and tropical regions are typically characterized by forests with dense canopies and can support aquatic systems with dark, DOC-rich waters^{32,33} (Extended Data Fig. 5). Indeed, for these biomes we

193 observed, on average, a lower diel change in CO₂ emissions (Figure 2b). In this context, 194 observations from the sub-tropical Florida sites (Figure 4d) likely provide insight into the 195 expected dynamics for dark water systems elsewhere, including tropical rivers that are 196 otherwise poorly represented in our analysis. For some biomes (e.g., montane grasslands and 197 tundra), limited canopy cover and low catchment DOC production make light constraints on 198 aquatic GPP and diel CO₂ emissions less likely, while in other settings (e.g., human 199 dominated landscapes) land cover change and nutrient enrichment can amplify diel CO_2 variation by stimulating rates of algal photosythesis³⁰. Overall, we suggest that future efforts 200 201 to resolve the fine-scale spatial patterns of canopy cover and DOM in running waters are 202 needed to further refine our understanding of aquatic GPP and its implications for CO₂ 203 emissions.

204

205 Implications for global CO₂ emissions from running waters

206 Our analysis reveals important consequences for global estimates of CO₂ emissions from running waters: (1) current estimates based on discrete samples are heavily biased towards 207 208 day-time, (2) CO_2 emission rates are consistently higher at night-time due to variations in 209 aquatic pCO_2 and (3) this pattern is primarily driven by light availability and is widespread 210 across biomes and along river continua. To quantify this underestimation of CO₂ emissions 211 we compare the measured total emissions for each site with the emissions estimated 212 considering only the CO₂ concentrations observed between 10:00 and 14:00 (the interquartile sampling time in the GLORICH database (Figure 1a). Across all 66 sites, CO₂ emissions 213 214 integrated over a full day were 35% higher than those based on samples taken at midday (range: -7 - 369 %; 95% confidence interval: 14 - 47 %). Based on the two current global 215 estimates of stream CO₂ emissions of 0.6-1.8 Pg C yr^{-1 (2,4)}, and our estimate of this 216

218 from streams globally (95% confidence interval: 0.09 - 0.30; 0.25 - 0.84, respectively). However, given that the current global estimates of C emissions from running waters are still 219 highly uncertain and remain unbalanced by global C budgets³⁴, this additional flux of CO₂ 220 221 should be taken with caution as global estimates continue to be refined. We also emphasize other important sources of uncertainty in the global estimates of emissions 222 from running waters, upon which our calculations are based. For example, current estimates^{2,4} 223 224 are derived from indirect determinations of surface water CO₂ from alkalinity and pH, which can be highly biased^{35,36}. Further, the notoriously variable nature of hydrodynamic factors that 225 influence CO_2 emissions cannot easily be aggregated at large spatial scales^{37,38}. It is also 226 problematic that current estimates are biased towards observations from mid-to-high latitudes, 227 228 even though underrepresented tropical systems may be key contributors to global CO_2 emissions^{5,39}. Our study, while covering most biomes and spanning large gradients in canopy 229 230 cover and water colour, also suffers from this bias. Despite this, our assessment represents the first compilation of direct, high-frequency measurements of CO₂ in flowing waters from 231 232 across the globe, which helps refine global estimates of CO₂ emissions from inland waters. 233 While the magnitude of this global estimate will be improved with further measurements, the 234 broad consistency and strength of the patterns observed here suggest that nocturnal emissions of CO₂ from streams and rivers are a major unaccounted flux in the global C cycle. 235

proportional bias, we suggest that an additional $0.20 - 0.55 \text{ Pg C yr}^{-1}$ of CO₂ may be evaded

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342	Author contributions:
343	L.G-G, G.R-R, and R.A.S designed the study and wrote the paper with inputs from M.J.C.
344	L.G-G and G.R-R compiled, processed, and analyzed the data. Å.H. provided remote sensing
345	estimates. All authors contributed with data and commented on the earlier versions of this
346	manuscript.
347	
348	<u>Competing interests:</u>
349	The authors declare no competing interests.
350	
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355 Data availability

- 356 Data are freely available at Zenodo (https://doi.org/10.5281/zenodo.4321623). Data can be
- 357 explored interactively at: <u>https://gmrocher.shinyapps.io/night_co2_emissions_streams/</u>.

360 FIGURE LEGENDS

Figure 1. Magnitude and bias of diel variation in CO₂ emission fluxes from global streams.

a) Distribution of manual sampling times in the GLORICH database²⁰ together with the time of maximum CO₂ emission fluxes from sensor data (this study). b) Relationship between the median day and night CO₂ emission flux (g C m⁻² d⁻¹) for all study sites and days. The black 1:1 line indicates that 75.2 % of daily observations exhibit enhanced nocturnal emissions. The inset illustrates the distribution of observations in the densest region of the graph.

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Figure 2. Geographical distribution of diel variation in stream CO₂ emission fluxes. a) Global patterns of night versus day differences in CO₂ emission fluxes averaged by stream (in g C m⁻² d⁻¹; see Table S3 for a detailed summary). b) Night-day differences in CO₂ emission fluxes averaged by stream and grouped by biome (in %; see Table S3 for a more detailed summary). The black point and bar represent the mean and 95% bootstrapped confidence interval for each biome.

375

Figure 3. Seasonal pattern of diel changes in CO₂ emission fluxes from streams. Seasonal 376 variation in the night versus day difference of CO_2 emission fluxes (g C m⁻² d⁻¹) grouped by 377 riparian canopy cover category (open = yellow, intermediate = light green and closed = dark 378 379 green; 33, 16 and 17 sites and 5780, 3814 and 5130 daily observations, respectively; see 380 Methods and Table S2). The coloured solid lines are locally weighted regression (LOESS) 381 model fits for a visual interpretation. Panels at top and bottom show extreme positive and negative values, respectively (note y-axis breaks and change in scaling). Density plots show 382 distributions of night vs. day differences of CO₂ emission fluxes (g C $m^{-2} d^{-1}$) grouped by 383 canopy cover during summer. Differences between canopy levels were evaluated using the 384 385 non-parametric Kruskal-Wallis test.

386

Figure 4. Night vs. day differences in CO₂ emission fluxes along the river size and colour

continuum. Relationship between the night-day difference of CO₂ emission fluxes (%) and the median annual discharge (m³ s⁻¹) for **a**) streams (median discharge below 1.5 m³ s⁻¹,

390 Extended Data Fig. 1) coloured by canopy cover category, and b) larger rivers (median

discharge above 1.5 m³ s⁻¹, Extended Data Fig. 1). Each point represents a monthly average 391 392 for each site, except data from the six additional rivers (circles with grey error bars) obtained 393 from the literature (Table S5). c) Relationship between the night-day difference in CO_2 emission fluxes (%) and the mean dissolved organic carbon concentration (DOC, mg L^{-1}) for 394 streams (circles) and rivers (triangles), coloured by canopy cover category (Extended Data 395 Fig. 1). d) Relationship between the daily night-day difference of CO_2 emission fluxes (%) 396 397 and the daily fluorescent organic matter concentration (fDOM, ppb QSE, quinine sulfate 398 equivalent) for the five rivers in Florida with high-frequency water colour data (Extended 399 Data Fig. 1 and Table S5), coloured by incident light (as photosynthetic photon flux density, 400 PPFD).

401

402 Methods

403 Study sites and data acquisition

404 We compiled high-frequency dissolved CO_2 time-series (median temporal resolution = 39) 405 min; range 5 to 180 min) over at least eight days (median time series duration = 317 days; 406 range 8 to 1553 days) from 66 headwater streams worldwide (Figure 2a; Table S1). We used median annual discharge (which covaried with catchment surface area; Extended Data Fig. 5) 407 as a criterion to select streams (i.e., median annual discharge $< 1.5 \text{ m}^3 \text{ s}^{-1}$, catchment area <408 246 km²; orders 1 to 3⁴⁰). Selected streams come from multiple biomes, including tropical 409 410 forests and savanna, temperate forests, boreal forest and taiga, arctic tundra, high-mountain 411 forests and grasslands and, accordingly, a wide range of climatic and biogeographic 412 conditions (Table S2). Sites also encompass a variety of catchment features (e.g., land cover, 413 altitude, and surface area) and reach-scale hydrological, morphometric, and physicochemical 414 properties (Table S2). 415 High-frequency CO₂ measurements were obtained from a variety of sources, including

416 unpublished time-series, monitoring network platforms (e.g., StreamPulse,

417	https://data.streampulse.org/), and literature datasets $^{8-12,16,41-43}$ (Table S1). In all cases, CO ₂
418	was measured using <i>in-situ</i> automated sensors connected to data loggers (Table S1). The
419	measurement accuracy of the CO ₂ sensors ranged from $\pm 1\%$ to $\pm 3\%$. In addition, water
420	temperature (in all streams) and discharge (in 57 of 66 streams; continuous discharge derived
421	from water depth sensor data) were also measured at the same frequency as CO ₂ using <i>in-situ</i>
422	automated sensors. Additional datasets ^{13,44–47} were included in this study but not directly used
423	in the main analysis (only used to construct Figure 4b-d) because they were either from
424	considerably larger rivers (median discharge above 1.5 m ³ s ⁻¹ , Extended Data Fig. 1), based
425	on high-frequency but short-term deployments (< 8 days), and/or based in discrete (not high-
426	frequency) measurements of CO ₂ emissions (Details for these observations are found in Table
427	S5).

429 *Time-series processing*

We standardized each time-series to an hourly time step by resampling higher frequency measurements and interpolating lower frequency measurements. We also normalized CO₂ concentrations to CO₂ partial pressures (pCO₂, ppm), corrected for temperature and pressure variation, and removed obvious measurement errors (pCO₂ < 0 ppm. In total, the highfrequency dataset used for analysis included 457,637 hourly CO₂, temperature and discharge

435 observations. 32 time series covered at least one complete year, 7 covered more than 200 days

436 while the remaining 27 covered between 8 and 198 days, mostly during the summer (Fig. S1).

437

438 Compilation of ancillary variables

439 Stream reach canopy cover was determined by visually inspecting orthophotos of the study

sites. High-resolution orthophotos from Google Earth imagery were downloaded at the

highest resolution possible using the "ggmap" package in R (version 3.0.0), and classified in 441 442 three categories of "no cover" (0), "partly covered" (1), or "fully covered" (2). The "no 443 cover" category was selected when it was possible to see the full extent of the stream channel, 444 "partly covered" when some parts of the stream were visible, and "fully covered" when it was 445 not possible to detect the presence of a stream based on an orthophoto (Fig. S2). 446 Stream channel slope was determined by measuring the difference in elevation between the sampling location and 300 meters upstream following the channel. To do this, we downloaded 447 448 digital elevation models (DEM) at resolutions ranging between 1.9 - 14 m (depending on the 449 location) using the "elevatr" package in R (version 0.2.0). Then, for each site a raster of the 450 flow-accumulation was produced using the "whitebox" package in R (version 0.5.0), after initially breaching depressions for hydrological correctness. By combining the flow-451 452 accumulation raster with the DEM, we extracted the stream path and the elevation at the site 453 and 300 m upstream (in QGIS 3.2.1).

Land cover was determined using the Global Land Cover Maps (100m resolution; Copernicus Global Land Service) and the catchment boundaries delineated using a high resolution DEMs (2x2m) in QGIS 3.2.1. Biome classifications were performed according to Olson et al. (2001)⁴⁸.

Mean annual concentrations (not flow-weighted) of dissolved organic carbon (DOC), nitrate
(NO₃⁻), ammonium (NH²⁺), pH and conductivity for the study streams were obtained from
unpublished sources or extracted from the literature. Mean annual stream discharge, as well as
water temperature, were computed from continuous time series.

*Determination of CO*₂ *emissions*

464	We estimated CO ₂ emissions as the product of the gas transfer velocity (k_{CO2}) and the
465	concentration of dissolved CO ₂ relative to atmospheric equilibrium ²⁵ . A standardized gas
466	transfer velocity (k_{600}) was obtained based on the stream energy dissipation (eD) ⁴⁹ , defined as
467	the product of channel slope (S; m m ⁻¹), water velocity (V; m s ⁻¹) and acceleration due to
468	gravity (g; 9.8 m s ⁻²). We then calculated k_{600} as $k_{600} = e^{(3.1 + 0.35 \times \log(eD))}$ for eD < 0.02 m ⁻² s ⁻³ ;
469	and as $k_{600} = e^{(6.43 + 1.18 \times \log(eD))}$ for eD > 0.02 m ⁻² s ⁻³ . Water velocity was modelled using a
470	power-law relationship with discharge ²⁵ ; in 4 streams discharge data were not available and
471	we used a constant velocity of 0.2 m s ⁻¹ , the average velocity of the other sites. The k_{600} was
472	converted to a gas- and temperature-specific gas transfer velocity k_{CO2} , using the temperature-
473	dependent Schmidt numbers for CO_2^{25} . Potential day-night differences in gas exchange
474	required separate night and day k_{CO2} calculations with time-of-day specific velocity and
475	temperature values. The CO ₂ disequilibrium relative to the atmosphere was calculated as the
476	difference in water and air pCO_2 , converted to molar CO_2 concentrations using the
477	temperature-specific Henry's constant. Atmospheric pCO_2 was assigned monthly to each site
478	from the global average measured by the Global Monitoring Laboratory of NOAA
479	(https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html), which contains measurements
480	between 2007 to 2020 that spatially align with our study. We assessed the importance of sub-
481	daily changes in atmospheric concentrations by examining atmospheric measurements of
482	pCO_2 from 14 streams and 77 ecosystem flux towers of globally. We concluded that day-
483	night changes in atmospheric pCO_2 are small and inconsistent, and therefore poorly
484	constrained for extrapolation to other stream sites (See Supplementary Text 1).
485	Finally, to assess whether a day-time sampling bias exists, we determined the distribution of
486	sampling time in the GLORICH database ²⁰ . From the database, we filtered all sampling
487	occasions where both CO ₂ (calculated from alkalinity and pH) and the time of sampling were

488 available (n = 733,977, from 8,520 locations), we then extracted summary statistics such as 489 the median, 90% range, and the interquartile range to compare with sensor measurements.

490

491 Statistical analyses

492 We examined a variety of metrics to characterize sub-daily and between-day variation. To 493 quantify the underestimation in CO_2 emissions due to a day-time bias, we compared total CO_2 494 emissions estimated using hourly measurements with total emissions estimated from the 495 average measurements between 10:00 and 14:00, the interquartile range of the observations in 496 the GLORICH database. Given the non-normality of results among sites, we present 497 uncertainty as normal bootstrapped intervals using the "boot" package in R (version 1.3-24), with 10,000 replications. We quantified median CO_2 emissions (g C m⁻² d⁻¹) during the day 498 499 (between 12:00 and 17:00), median CO₂ emissions during the night (between 00:00 and 500 05:00), the absolute difference between day and night CO₂ emissions, and the relative 501 difference in CO_2 concentrations between day and night (in %; (($CO_2 \text{ NIGHT} - CO_2 \text{ DAY}$)/ CO_2 _{DAY})×100). Also, to evaluate differences between canopy levels we used the non-parametric 502 503 Kruskal–Wallis test.

504 We explored temporal patterns of day-night CO_2 emission differences to test the influence of 505 seasonality, local canopy cover, and their interaction. We used piecewise structural equation 506 modelling (SEM) to evaluate causal and directional links between physical and biological 507 parameters operating at the reach-scale (Table S2) and variance in daily day-night differences 508 in CO₂ emissions. SEM is a theory-oriented multivariate statistical approach capable of 509 testing a network of causal hypotheses by allowing evaluation of simultaneous influences rather than individual (bivariate) causes⁵⁰. We first devised a metamodel (or metamodels) 510 511 based on *a priori* theoretical knowledge and known mechanisms (see above and Figure 3).

512 The metamodel was fitted and tested using the function psem() in the *piecewiseSEM* R

513 Package (version 2.1). To evaluate the effect sizes of each relationship (or path) within

514 metamodels, the psem() model output provides estimates of individual (standardized) path

515 coefficients (β). The evaluation of goodness of fit and associated uncertainty is performed

516 through the coefficient of determination (r^2) and the residual standard error (RSE),

517 respectively. Compared with traditional variance-covariance based SEM, piecewise SEM

allows for fitting of models to different distributions through a generalized linear model

519 (GLM). SEM modelling was conducted using summer data only, which is when most of the

520 sites are represented (see Fig. S1).

521 **References methods**

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Day of the year

Night vs. day CO_2 flux difference (g C m⁻² d⁻¹)









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