Unaccounted CO₂ leaks downstream of a large tropical hydroelectric reservoir

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Recent studies show that tropical hydroelectric reservoirs may be responsible for substantial greenhouse gas emissions to the atmosphere, yet emissions from the surface of released water downstream of the dam are poorly characterized if not neglected entirely from most assessments. We found that carbon dioxide (CO₂) emission downstream of Kariba Dam (southern Africa) varied widely over different timescales and that accounting for downstream emissions and their fluctuations is critically important to the reservoir carbon budget. Seasonal variation was driven by reservoir stratification and the accumulation of CO₂ in hypolimnetic waters, while subdaily variation was driven by hydropower events caused by dam operation in response to daily electricity demand. This “carbopeaking” resulted in hourly variations of CO₂ emission up to 200% during stratification. Failing to account for seasonal or subdaily variations in downstream carbon emissions could lead to errors of up to 90% when estimating the reservoir’s annual emissions. These results demonstrate the critical need to include both limnological seasonality and dam operation at subdaily time steps in the assessment of carbon budgeting of reservoirs and carbon cycling along the aquatic continuum.

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Inland waters play an important role in the sequestration, transport, and mineralization of carbon (1). Despite recent advances in our understanding of carbon cycling along the aquatic continuum (2–6), major uncertainties remain regarding the impact of human modifications to river hydrology, especially those stemming from large dams (7). Model carbon budgets have been constructed for many artificial reservoirs throughout the world (8); however, a lack of standardized methodologies and criteria for delineating and attributing dam-driven carbon fluxes has generated biased and unclear metrics for carbon accounting (9). Given an ongoing dam construction continuum.

Significance

Hydroelectric reservoirs emit substantial amounts of CO₂, especially in the tropics. Since many such systems exist and many more will be built within decades, it is important to assess their role in the carbon cycle. A major source of emission that is rarely monitored and never at different timescales is the carbon released downstream of dams. We measured the seasonal and subdaily variability of CO₂ emission downstream of one of the world’s largest artificial reservoirs and find that its contribution is relevant for unbiased quantification of reservoir carbon budgets. These findings highlight the importance of subdaily variability in hydropower operation for downstream emission rates and call for appropriate analysis schemes to reassess the greenhouse gas footprint of this energy source.

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and subsequently the rate of CO₂ emission to the atmosphere (see Materials and Methods and SI Appendix). The combination of high-frequency measurements and long-term monitoring allowed us to assess the relative importance of reservoir stratification and dam operations on downstream CO₂ emissions and the magnitude of these emissions compared to other components of a conventional reservoir carbon budget.

Results and Discussion

CO₂ Hotspots Downstream of Large Dams. Dams interrupt the river continuum, and our analysis shows that they can create major discontinuities in CO₂ degassing as well. To evaluate this, we compared the specific emission rate just 3 km downstream of Kariba Dam with the whole Zambezi River, based on earlier field measurements (22). We found that this flux accounts for approximately one-fourth of the specific emission rate of the entire Zambezi River [1,040 mg C·m⁻²·d⁻¹ downstream of the dam compared to 4,290 mg C·m⁻²·d⁻¹ for the whole river (22)]. The quantification of this flux allows for calculating the CO₂ leaks.

There are multiple approaches for estimating the total magnitude of carbon emissions downstream of dams. We assess two options for the case of Kariba. The first approach considers degassing rates which, multiplied by the surface area of a predefined downstream river reach, yields the total annual emitted mass (15). A second approach subtracts the total carbon leakage measured at the outflow from the carbon flux into the reservoir. This assumes that essentially all of the dissolved inorganic carbon in excess of that which arrives from river inflows can be attributed to the reservoir and will be emitted to the atmosphere on a short timescale (23, 24). Both approaches lead us to conclude that the carbon leakage from Kariba Dam is important to the overall carbon budget of the Kariba Reservoir (Fig. 1).

The annual CO₂ emission from the Zambezi River downstream of Kariba Dam, calculated by integrating the hourly time series of the CO₂ atmospheric emission (the first approach), equals 377 g C·m⁻²·y⁻¹ (ranging between 331 and 382 g C·m⁻²·y⁻¹ depending on estimation methods; see Materials and Methods). This emission rate, applied to the Zambezi River between Kariba Dam and the confluence with the Kafue River (the first important discontinuity, located ∼75 km downstream; see SI Appendix, Fig. S1) would correspond to about 18 Gg C·y⁻¹ or 7 to 32% of the total net CO₂ uptake (−56 to −278 Gg C·y⁻¹; FC₀₂ surface of Fig. L4) of Lake Kariba (22–25). Using the second approach, which considers the difference between partial pressure of CO₂ (pCO₂) in the inflows (estimated using CO₂ saturation concentration and water temperature at Victoria Falls; 10 Gg C·y⁻¹) and the outflows, the estimated carbon leak doubles to 35 Gg C·y⁻¹ or 13 to 63% of the total net CO₂ uptake of Lake Kariba (Fig. 1). The variability in the importance of carbon leaks reflects the sensitivity to underlying assumptions and the large uncertainty surrounding the other components of the reservoir carbon budget. The magnitude of even the minimal values makes clear, though, that CO₂ outgassing downstream of Kariba Dam is significant and represents an important component of the carbon budget of the reservoir. Moreover, accounting for the CO₂ outgassing at the turbines, here not quantified (due to the lack of the sufficiently highly resolved vertical profiles of CO₂ within the reservoir’s water column and the hourly amount of water withdrawn from each withdrawal point), would make the total amount of CO₂ emissions occurring downstream of the dam even higher. This finding indicates that if we continue to omit downstream carbon emissions from assessments of reservoir carbon cycling, we may be systematically underestimating the role of reservoirs in the carbon balance of inland waters.

Seasonality of CO₂ Evasion. Any reservoir that has a prolonged season of stratification and that has sufficiently deep outlet points may discharge downstream hypolimnetic water enriched in CO₂. The mixing regime of reservoirs and their interaction with dam outlet points is therefore a key determinant of the magnitude and seasonal dynamics of downstream carbon emissions. We found that river water downstream of Kariba Dam was always oversaturated with CO₂. However, concentrations varied seasonally in response to stratification dynamics [seasonal stratification occurring between October and June and experiencing its maximum in February (26); Fig. 2A] from a minimum of 470 ppm, at the end of the reservoir mixing phase, to a maximum of 6,810 ppm at the beginning of the year, after CO₂ has accumulated over several months in the hypolimnion. High CO₂ concentration was also observed during the beginning of the mixing phase (July; Fig. 3B), when CO₂-rich hypolimnetic water is mixed into the epilimnion, resulting in elevated concentrations at the level of the water intakes to all turbines. This results in a range of CO₂ emissions rates downstream spanning two orders of magnitude, from 24 to 3,730 mg C·m⁻²·d⁻¹ (mean value of about 1,040 mg C·m⁻²·d⁻¹; Fig. 2B). Moreover, the observed fluctuations in CO₂ concentrations and emissions which we observed show a completely different seasonality compared to those upstream of Lake Kariba and at the Victoria Falls (Fig. 3B), where the seasonality of dissolved CO₂ relates to the floodplain dynamics, with maximum loads during peak flow condition (27).

Carbopeaking Linked to Dam Management. In addition to the seasonal variation observed in CO₂ concentration and outgassing, subdaily fluctuations driven by hydropower operation is also a significant source of variability. Previous work demonstrates that hydropower events can generate subdaily alterations in river water temperature, a process called “thermopeaking” (28, 29). Our analysis indicates that a similar link exists between hydropoaking fluctuations and variations in carbon emissions downstream of a dam. We propose the term “carbopeaking” to refer to subdaily fluctuations in CO₂ atmospheric emissions associated with dam hydropoaking (Fig. 4A and B).

Conceptually, carbopeaking is driven by variations in transport and concentration: An abrupt rise in water discharge potentially combined with a sudden increase in CO₂ concentration in the downstream river results in an ephemeral peak of CO₂ emissions to the atmosphere (Fig. 1 B and C). To date, the effect of hydropoaking on the water–air CO₂ exchange and more generally on the carbon budgets at the annual scale has never been considered, mainly because the CO₂ atmospheric emission of regulated rivers is often not measured at the subdaily timescale but rather calculated based on a few samples per year. However, we demonstrate that dam operation affects the temporal dynamics of CO₂ emission below dams and can generate large fluctuations of such emission.

Our subdaily measurements from below Kariba Dam provide direct evidence for the occurrence of carbopeaking. Rapid operational shifts at Kariba, related to energy demand, form two peaks in hydropower production each day: in the morning between 6 and 10 AM and in the early evening between 6 and 8 PM. The rate of change in discharge downstream of Kariba Dam reaches values up to ~550 m³·s⁻¹·h⁻¹—a magnitude that amounts to 30% of the yearly average discharge (1,500 m³·s⁻¹). Because this change in discharge in the case of Kariba Dam is associated with multiple turbine intakes located at different depths, the concentration of CO₂ also varies with discharge, reaching a maximum change rate of 2,140 ppm CO₂·h⁻¹ (see Materials and Methods). The combined effect of varying discharge and CO₂ concentration downstream of Kariba Dam generates subdaily fluctuations in CO₂ emissions four times
greater than those of upstream reference conditions. We found rates of change in hourly CO₂ efflux up to ∼870 mg C m⁻² d⁻¹, corresponding to a fluctuation of up to ∼200% in 1 h.

Although hydropeaking at Kariba occurred throughout the study year, and consistently contributed to peaks in carbon emissions, carbopeaking was most pronounced during months with reservoir stratification (Fig. 4A and B), reaching its apex during the maximum CO₂ accumulation in the reservoir hypolimnion. This indicates that CO₂ concentration rather than turbulence caused by the rate of discharge is the dominant control on carbopeaking (Fig. 4C). We also performed a sensitivity analysis considering a constant discharge value and the measured hourly variability in CO₂ concentrations, and we reached the same conclusion that carbopeaking is mainly driven by changes in concentration rather than by changes in discharge. However, we estimate that hydropeaking contributes about 20% to the carbopeaking we observe at Kariba (Fig. 4C), and its role is even more important if we consider that when the water discharge increases so does the water level (up to 2 m h⁻¹ at the location of our sensor) and therefore the area of the river and the air–water
interface (up to 15% at the location of our sensor), resulting in a proportionately higher total flux escaping the river surface per unit of time (Fig. 1). Thus, carbopeaking potentially occurs downstream of many stratified dams operating with a hydropowering regime worldwide. Moreover, such a link between power production peaks and CO₂ emissions shows that explicitly considering dam operations may be necessary for accurately calculating the CO₂ storage in reservoirs and a more complete understanding of the role of the aquatic continuum in global carbon cycling.

**Timescales Matter for Carbon Budgeting.** Scientists have called for increased monitoring of greenhouse gas emissions associated with hydropower reservoirs in the tropics to reassess the greenhouse gas footprint of this energy source (30, 31). We argue that it is critically important to include measurements of downstream carbon emissions at relevant timescales in order to accurately estimate carbon budgets for reservoirs. These timescales should include seasonal changes in CO₂ concentration in the reservoir but also subdaily peaks associated with dam operation. With an automated sensor at Kariba Dam we were able to integrate hourly data and estimate an annual downstream emission of 377 g C·m⁻²·y⁻¹. These findings highlight the potential errors associated with estimating annual emissions based on a single survey which could potentially overestimate emissions by up to 30% or underestimate emissions by up to 90% (see SI Appendix). Thus, monitoring carbon flux from dam tailwaters must be informed by the seasonality of mixing and CO₂ concentrations in the reservoir. In a review of large tropical hydropower reservoirs, 34 out of a total of 36 assessed reservoirs stratify, which shows the potential for this to be a significant error on estimates of CO₂ emissions and carbon budgets for hydropower reservoirs (19). Hence, one or two measurements in a year will likely lead to major errors.

In addition to seasonal variability, our analysis of carbopeaking below Kariba Dam indicates the importance of accounting for subdaily fluctuations in discharge to avoid systematic errors in upscaling. Measurements taken during one of the two daily hydro-/carbopeaks (midmorning, early evening) will be biased toward overestimation, whereas measurements taken during low discharge (predawn) will be biased toward underestimation (Fig. 5). A diligent surveyor could theoretically measure CO₂ flux monthly, weekly, or even daily, for maximum coverage of seasonality, and still yield a difference of up to 30% depending on how the timing of sampling was to align with carbopeaking patterns (Fig. 5). We find that accounting for carbopeaking dynamics is key to avoid biased estimates of carbon emission hotspots below dams.

Hydroelectric reservoirs are often used to flexibly produce electricity when demand is high and supply from other sources is

![Fig. 2. Reservoir CO₂ concentration in response to stratification dynamics generates seasonal variability of CO₂ atmospheric emission from the Zambezi River downstream of the dam wall. (A) Measured epilimnetic and hypolimnetic (or metalimnetic for March 2018) concentration of CO₂ in the water column of Lake Kariba just behind the dam on 18 March 2018, 9 July 2018 (lake mixing), 30 October 2018, and 16 February 2019 (maximum stratification of Lake Kariba) together with the water level in the reservoir and the relative depth of the intake of the three turbines. (B) Calculated degassing flux from the Zambezi River 3 km downstream of Kariba Dam (see Materials and Methods and SI Appendix) as a function of water discharge (Q) during the same four months. Gray lines indicate the monthly mean CO₂ flux.](https://doi.org/10.1073/pnas.2026004118)
insufficient; thus, their power production can be highly variable within a day, which causes significant subdaily flow fluctuations and increases the likelihood of carbopeaking worldwide. Among tropical rivers, our case study, the Zambezi River, is not the only documented example where hydropeaking occurs; hydropeaking has been documented in the Amazon Basin (32) and substantial subdaily flow variability has been reported downstream of the Malaysian Batang Ai Dam (33). Thus, it is necessary to have well-resolved temporal monitoring, not only of the surface fluxes (34) but also for the downstream emissions, in order to provide reliable reservoir carbon budgets. Even for the cases where the downstream emissions have been included, fluxes have been

![Fig. 3. Altered seasonality and enhanced subdaily fluctuations of water discharge (Q) and CO₂ concentration in the Zambezi River 3 km downstream of Kariba Dam. Yearly signal (A and B) (smoothed with time window of 24 h) and hourly fluctuations (C and D) of reconstructed water discharge (A and C) and calculated CO₂ concentration (B and D) in the Zambezi River 3 km downstream of Kariba Dam (thick lines) and upstream of the Victoria Falls (thin lines). See Materials and Methods and SI Appendix for calculation details.](image)

![Fig. 4. Carbopeaking is caused by hydropeaking and fluctuations of CO₂ dissolved concentration. (A and B) Hourly water discharge (Q) and calculated CO₂ concentration and flux during two specific days of the year: during Kariba's reservoir stratified season (12 February 2019) and during its mixed phase (25 July 2019). (C) Mean monthly carbopeaking absolute values (hourly variations of CO₂ atmospheric emission) together with the contribution of hydropeaking and concentration to the respective monthly carbopeaking value. (D) Monthly relative contributions of hydropeaking and concentration to carbopeaking.](image)
Moreover, the dam is equipped with six spilling gates for controlling the shared between Zambia and Zimbabwe. The Zambian hydropower station is framework realizable. The present study focused on CO\(_2\) availability of automated sensors capable of high-frequency fluctuations (15, 33). Having a well-resolved temporal CO\(_2\) estimate of the downstream emissions would also refine the global estimates of carbon emissions from hydroelectric reservoirs which currently often neglect the downstream emissions because their measurements are too limited and/or too poorly constrained to be meaningfully included in global upscaling efforts (8).

Both seasonal and subdaily measurements would be part of an ideal framework for estimating carbon emissions from the river surface below stratifying artificial reservoirs subject to high CO\(_2\) concentration in the hypolimnion. The availability of automated sensors capable of high-frequency measurements and long-term deployments make such an ideal framework realizable. The present study focused on CO\(_2\), but methane (CH\(_4\)) is an even more potent greenhouse gas (35) which also accumulates in the hypolimnia of lakes and then can be emitted to the atmosphere (8, 36, 37), and its emission from the reservoir surface can vary daily (38). Future research into the carbon cycling of dams and the emission hotspots downstream should therefore also assess methane fluxes in the downstream river system and their seasonal and subdaily variation.

Materials and Methods

Study Site. This study focuses on a 75-km reach of the Middle Zambezi River, from Kariba Dam to the confluence with the Kafue River. This is a low-gradient sand-bed river reach which has single-thread and braided channel patterns. The river’s slope (s) ranges from 1 x 10\(^{-4}\) to 3 x 10\(^{-4}\), and the river’s width from 150 to 1,800 m. The flow velocity (v) depends on the discharge emitted by the dam and ranges between 0.3 and 2.5 m \(\cdot\) s\(^{-1}\). Kariba Dam and its hydropower plant are transboundary structures, with management shared between Zambia and Zimbabwe. The Zambian hydropower station is equipped with six turbines and the Zimbabwean station has eight turbines. Moreover, the dam is equipped with six spilling gates for controlling the water level, but they are not in use because of structural problems of the dam. The turbine water intakes and the spilling gates are located at different depths: The sill elevations of the turbine intakes on the Zimbabwean side are at 447 m above sea level (a.s.l.) for the low-level intakes and 460 m a.s.l. for the high-level intakes; on the Zambian side the intakes are at 460 m a.s.l. and the six spilling gates at 457 to 466 m a.s.l. (39).

Sensor Deployment and Sampling. We monitored water quality by deploying three EXO2 probes (Yellow Springs Instruments) along the Middle Zambezi River at three distinct locations: the first one at Siavonga, 3 km downstream of Kariba Dam wall (latitude = 16.50441 S; longitude = 28.79071 E), the second one upstream of the Victoria Falls to have a reference condition of the Zambezi River (latitude = 17.82075 S; longitude = 25.65795 E), and the third one at Chirundu, about 75 km downstream of Kariba Dam (latitude = 15.98481 S; longitude = 28.88075 E). The EXO2 probes measured and recorded water temperature (T), conductivity (EC), pH, and dissolved oxygen (DO) from mid-March 2018 until the end of February 2019 with an hourly time resolution. The first probe was moored from a rock positioned roughly 2 m above the riverbed, so this probe also recorded the water-level fluctuations, while the other two were installed on floating mooring (pontoon and buoy) and so kept a constant depth of ∼1 m relative to the surface. Approximately every 3 mo all probes were recalibrated for pH and DO using standard buffer solutions of pH 4 and pH 7 and water-saturated air, respectively. We used all calibration values to correct the data in postprocessing for possible drift in measured parameters. In situ measurements and water samples were taken at various locations along the Zambezi River Basin to address the longitudinal variability and the influence of tributaries and to cross-validate the EXO2 probe measurements. We sampled 17 locations (including the EXO2 locations) along the Zambezi River and its tributaries and the surface and hypolimnion of Lake Kariba close to the dam wall in March, July, and November 2018 and February 2019. At each location we measured water temperature, DO, conductivity, and pH using YSI ProPlus and YSI ProODO multimeter probes (Yellow Springs Instruments). The pH and DO probes were calibrated before each measurement using standard buffer solutions of pH 4 and pH 7 and water-saturated air, respectively.

Moreover, we collected samples for alkalinity in 50-mL centrifuge tubes and kept them refrigerated until analysis at the Eawag laboratory in Switzerland. We used an 862 Compact Titrosampler (Metrohm) to measure alkalinity. This full dataset is deposited on the ETH Research Collection data portal under DOI 10.3929/ethz-b-000473097 (40). CO\(_2\) Concentration Measurements. In all sampling locations, we measured in situ the pCO\(_2\) in the water using an EGM-4 nondispersive, infrared gas analyzer (PP Systems), using the headspace technique. The EGM-4 was calibrated before each trip with certified gas standards of 1,017 ppM CO\(_2\) while 0 ppm CO\(_2\) is automatically performed by the instrument running the air through a soda lime absorbed column (“autozero” technology). For the headspace equilibrium technique, 30 mL of water was collected from 30 to 50 cm below water surface into five 60-mL polypropylene syringes and mixed with 30 mL ambient air of measured CO\(_2\) concentration (pCO\(_2\)\(_{a}\)) then gently shaken for 5 min to allow for equilibration of the two phases. The equilibrated headspace volume (30 mL) was then transferred into a dry syringe and directly injected into the EGM-4 analyzer to measure the partial pressure CO\(_2\) of the headspace in the syringe after equilibration (pCO\(_2\)\(_h\)). Water pCO\(_2\) was calculated from the ratio between the air and water volumes using the gas solubility at sampling temperature. The gas solubility (K\(_S\)) was calculated as in ref. 41 (assuming zero salinity) for the sampling temperature and for the temperature of the sample after equilibration (K\(_{0a}\), K\(_{0s}\), respectively):

\[
\ln K_S = A_1 + A_2 (100/T) + A_3 \ln (T/100),
\]

where the solubility K\(_S\) is expressed in moles per kilogram per atmosphere; A\(_1\), A\(_2\), and A\(_3\) are constants equal to 60.2409, 93.4517, and 23.3585, respectively, and T is the absolute water temperature in Kelvin. We then calculated the molar volume V\(_m\) (liters per mole) from the ideal gas law using the temperature and pressure of the sample. The water sample partial pressure pCO\(_2\) (parts per million) was then calculated as follows:

\[
pCO_2 = \left( V_{m} - V_{CO_2} \right) \frac{V_{CO_2}}{V_{m}} \frac{pCO_2}{K_{0s}} \left( K_{0a} \right)^{1/2}.
\]
where $V_h$ and $V_w$ are the volume of the headspace and the volume of water in the syringe, respectively, and $P_h$ is the atmospheric pressure in atmospheres.

**Rating Curve and Hydropeaking Characterization.** We reconstructed the relative rating curve for the probe located 3 km downstream of the Kariba Dam. For this purpose we used the probe measurements of relative water level fluctuations and the hourly time series of turbinated water provided by the Zambian power station (Zambia Electricity Supply Corporation, ZESCO) and the Zimbabwean power station (Zimbabwean Power Company, ZPC). We performed a fitting using a power model; the data and the resulting relative rating curve are reported in SI Appendix, Fig. S2.

Hydropeaking occurred throughout the study year at Kariba, leading to subdaily fluctuations of the Zambezi’s CO$_2$ exchange velocity. Two indicators, $P_h$ and $H_{P_h}$ (169 m$^3$ s$^{-1}$ h$^{-1}$) (20) characterize hydropeaking at Kariba and confirm its importance. The first is a dimensionless measure of the magnitude of hydropeaking and the second measures the temporal rate of discharge changes.

**CO$_2$ Concentration Calculation.** We used the conductivity record to calculate the alkalinity at the hourly time resolution. Conductivity and alkalinity are indeed highly correlated in our case study (see SI Appendix, Fig. S3A). The correlations between conductivity and alkalinity result from natural geological and climatic controls and are often used to assess anthropogenic impacts on streams or rivers (42, 43). Moreover, such clear correlation between EC and alkalinity may be highly correlated in our case study (see Fig. S2). We chose three models that require as input only the velocity and the slope of the river (models 3, 4, and 6; we discarded model 5 because the resulting velocity of exchange was much higher than the other models and thus a less conservative choice). The resulting $k_{CO2}$ ranges between 0.7 and 1.4 m d$^{-1}$, and $k_{CO2}$ is reported in SI Appendix, Fig. S4. We calculated the water flow velocity by running the one-dimensional steady version of Hec-Ras model for the Zambezi River downstream of Kariba Dam at different water discharges for the Zambezi River stretch from Kariba Dam to Chirundu (75 km downstream of Kariba Dam). We used critical concentrations from Matos et al. (49) estimated taking into account satellite images combined with the information of the simultaneous discharge in the river. The resulting longitudinal river slope is about $1.8 \times 10^{-4}$. Using this model, we derived the discharge velocity, the discharge-water depth, and the discharge-water surface width relationships at Siavonga (3 km downstream of Kariba Dam) needed for the calculation of CO$_2$ fluxes.

**Data Availability.** Time series and samples data have been deposited in the ETH Research Collection (DOI: 10.3929/ethz-b-000473097) (40).

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