

Geophysical Research Letters

RESEARCH LETTER

10.1029/2020GL090068

Key Points:

- We model potential evasion of terrestrially sourced headwater CO₂ from over 98,000 river and lake units in the Connecticut River watershed
- Lakes are responsible for approximately 25%-30% of potential CO₂ evasion, as influenced by streamflow and stream order
- Lake CO₂ evasion efficiency is a function of residence time and size, where larger lakes evade functionally 100% of CO₂ from upstream

Supporting Information:

· Supporting Information S1

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Citation:

Brinkerhoff, C. B., Raymond, P. A., Maavara, T., Ishitsuka, Y., Aho, K. S., & Gleason, C. J. (2021). Lake morphometry and river network controls on evasion of terrestrially sourced headwater CO₂. *Geophysical Research Letters*, 48, e2020GL090068. https://doi.org/10.1029/2020GL090068

Received 29 JUL 2020 Accepted 19 NOV 2020

Lake Morphometry and River Network Controls on Evasion of Terrestrially Sourced Headwater CO₂

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Abstract Lakes are central components of the inland water system distinct from, yet inextricably connected to, river networks. Currently, existing network-scale biogeochemistry research, although robust, typically treats each of these components separately or reductively. Here, we incorporate lake morphometry into a fully connected stream/lake network for the Connecticut River watershed and model potential evasion of terrestrially sourced headwater CO_2 as transported through the network, ignoring in-stream production. We found that approximately 25%–30% of total potential soil CO_2 evasion occurs in lakes, and percent evasion is inversely related to streamflow. A lake's ability to evade CO_2 is controlled by residence time and size: most lakes with residence time over 7 days or surface area greater than 0.004 km² evade functionally all terrestrial CO_2 entering from upstream, precluding further downstream transport. We conclude that lakes are important for soil CO_2 degassing and that this coupled river/lake approach is promising for CO_2 studies henceforth.

Plain Language Summary River networks are both delivery systems and active transformers of constituents (sediment, nutrients, biota, heat) as they carry them to the sea. An important and overlooked component of these networks are lakes: lakes dominate total water storage of surface water in river networks and have vastly different hydraulics than rivers. Despite this knowledge, most greenhouse gas (GHG) research addresses lakes and rivers separately or reductively. To address this, we built a fully connected model for over 98,000 rivers and lakes in the Connecticut River watershed and found that lakes emit substantially more carbon dioxide than rivers per unit (potentially 25%–30% of the total emission from the system), and that almost all lakes emit almost all the carbon dioxide that enters their waters. These findings demonstrate the importance of connected lakes to drainage network GHG exchange and corroborate the need to better integrate lakes into our understandings of GHG emissions from freshwater systems in a formalized framework.

1. Introduction

Inland waters play an important role in the global carbon cycle, contributing significant greenhouse gas (GHG) emissions to the atmosphere (Bastviken et al., 2011; Cole et al., 2007; Raymond et al., 2013). River networks are generally conceptualized as active biogeochemical reactors that mix, store, and evade GHGs and constituents transported from upstream together with those generated from in-stream production (Cole et al., 2007; see also; Raymond et al., 2016; Zarnetske et al., 2018). Ultimately, inland waters store, evade, and transport over half of the carbon that they receive from the terrestrial ecosystem before reaching the oceans (Hotchkiss et al., 2015), thereby playing a fundamental role in global carbon processes.

Running inland waters (hereafter termed 'rivers') are generally supersaturated with GHGs and exhibit a net evasive flux of these gases from water to air (Cole & Caraco, 2001; Jones et al., 2003). This flux $[M/L^2T]$ is relatively easy to calculate with in situ knowledge of the gas concentration gradient between the water $[gas]_{water}$ and the air $[gas]_{air}$ $[M/L^3]$ and the gas transfer velocity k [L/T] (Equation 1).

$$Flux = k \left(\left[gas \right]_{water} - \left[gas \right]_{air} \right)$$
 (1)

Because k is largely a function of surface water turbulence, and thus river channel hydraulics, landscape geomorphology (which drives channel hydraulics) fundamentally regulates how k manifests across streams

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and rivers (Raymond et al., 2012; Ulseth et al., 2019). More broadly, geomorphology and hydraulics affect GHG evasion from inland waters in two ways: first, while gas evasion from rivers is driven by surface turbulence (Zappa et al., 2007), evasion from lakes and reservoirs (hereafter referred to as 'lakes') is additionally influenced by turbulence from convection (particularly in small ponds - Holgerson et al., 2016; Read et al., 2012). The much longer residence times of lakes also allows for more gas evasion to occur (Catalán et al., 2016; Cheng & Basu, 2017). Second, in-stream GHGs are sourced from multiple landscape components. As a representative GHG, carbon dioxide (CO₂) is terrestrially sourced from soil respiration or decomposition in groundwater (Duvert et al., 2018; Hotchkiss et al., 2015). Terrestrial CO₂'s influence on stream evasion decreases downstream as the terrestrial edge to water volume ratio decreases and in-stream metabolic and abiotic processes become relatively more important due to longer residence times in larger rivers (Battin et al., 2008; Hotchkiss et al., 2015; Marx et al., 2017; Öquist et al., 2009; Raymond et al., 2016). Further, the majority of terrestrial CO₂ in the headwaters is thought to come from soil respiration (e.g. Hope et al., 2004; Johnson et al., 2008). Taken in aggregate, in-stream CO₂ is a complex manifestation of terrestrial inputs, in-stream processes, evasion to the atmosphere, and transport mechanics that are all in some way functions of the local landscape and discharge (Liu & Raymond, 2018). Thus, the heterogenous nature of a watershed's geomorphology makes it difficult to scale GHG evasion measurements to entire river networks.

In spite of these difficulties, researchers have attempted to upscale in situ GHG evasion measurements to either river networks (Borges et al., 2015; Butman & Raymond, 2011; Horgby et al., 2019; Hu et al., 2016; Lauerwald et al., 2015; Raymond et al., 2013) or large waterbodies data sets composed of thousands of lakes, reservoirs, and/or wetlands (Deemer et al., 2016; DelSontro et al., 2018; Holgerson & Raymond, 2016; Lauerwald et al., 2019; Soued et al., 2016). We have already established that different physical processes control gas evasion in rivers and lakes. However, most work on gas evasion at network scales neglects to acknowledge the two systems' intrinsic connectivity via transport mechanics and network topology (Crawford et al., 2014; Fergus et al., 2017; Gardner et al., 2019; Wetzel, 2001). This disconnect is beginning to be addressed in related subfields like sediment transport (Czuba & Foufoula-Georgiou, 2015; Czuba et al., 2017) and nutrient transport (Bertuzzo et al., 2017; Schmadel et al., 2018, 2019; Wollheim et al., 2008). A preliminary treatment of nitrous oxide emissions from rivers versus reservoirs has also been performed (Maavara et al., 2019). However, without a spatially explicit treatment of river/lake connectivity in the context of potential GHG evasion, our ability to accurately constrain network-scale evasion is limited.

We sought to answer the following questions, using terrestrially derived CO_2 sourced from headwaters as a representative GHG and a model of a fully coupled river/lake network: (1) How do lakes affect the evasion of terrestrially derived CO_2 , and how does this compare to evasion of this same CO_2 from rivers? and (2) how do lake residence times and sizes influence their ability to evade CO_2 transported from upstream (termed ' CO_2 evasion efficiency')? Using the Connecticut River's watershed, we explicitly incorporate lake morphometry into a network-scale potential evasion model with full conservation of mass and momentum and across a full hydrological flow regime to answer these questions (after validating the model – Section 3.1).

2. Methods

To construct the model outlined above, we merged hydrography with lake morphometry, streamflow routing, and a gas advection/evasion model. First, we outline our data set (Section 2.1), then we describe our CO_2 potential evasion model (Section 2.2), and finally we describe the experiment (Section 2.3).

2.1. Hydrography

We used the United States Geological Survey (USGS)'s NHDPlus High Resolution hydrography (NHD HR) to represent river network topology in the Connecticut River watershed. The Connecticut River is the largest river in the northeastern United States, draining nearly 30,000 km² from the Quebec border to its outlet in Long Island Sound. This data set includes waterbodies, a river network, and artificial 'throughflow' lines that topologically connect the waterbodies to the river network. We spatially mapped the attributes assigned to each waterbody classified by the USGS as a 'lake/reservoir' (treated as synonymous in the NHD HR and this study) to the artificial throughflow lines, such that the unique characteristics of each lake were embedded in the river network. It is worth stressing that reservoirs can have distinct morphometry from natural

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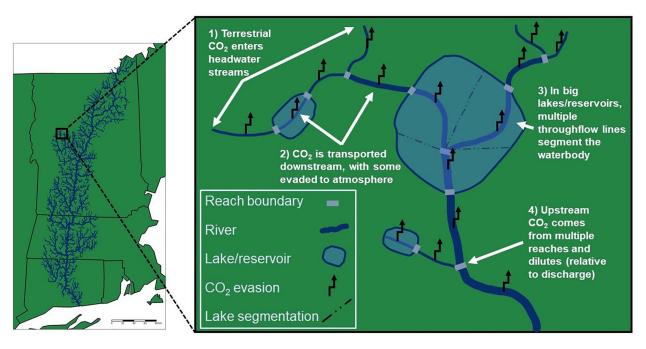


Figure 1. Conceptual representation of the model simulating potential evasion of terrestrial CO₂ (right) from our hydrography for the Connecticut River (left – U.S. Geological Survey, 2019b). River thickness corresponds to stream order, of which only third-eighth orders are mapped for visualization. Note that lateral CO₂ inputs to all rivers/lakes larger than first order are ignored.

lakes, but we use the term 'lake' interchangeably for easier readability. We make no claims in this study about differential impacts from natural versus anthropogenic waterbodies. Ultimately, our river network contained 98,254 reaches including throughflow lines that represent 14,884 total lakes. However, we still lack information on two crucial variables necessary for the $\rm CO_2$ advection/evasion model (Section 2.2): lake volume and river/lake discharge.

The USGS provides estimates for lake volume in their lower resolution hydrography (NHD), which they modeled using surrounding topography (Hollister & Milstead, 2010). We ran their same lake volume generation algorithm on our higher resolution data set's lakes that were $> 0.1~\rm km^2$ in surface area. For those smaller than $0.1~\rm km^2$, we used a statistical scaling function to predict volume from surface area (Cael et al., 2017, Text S1). Many larger lakes have multiple intersecting throughflow lines in the NHD HR, effectively segmenting the lake. When assigning lake volumes in these scenarios, we mapped relative portions of the lake to each throughflow line (Figure 1, Text S1).

For river/lake discharge, mean annual flow is not sufficient for our experiment: we are interested in a full flow regime reflecting not only average streamflow but also extreme floods, drought events, and the flashiness of the streamflow regime. Therefore, we built flow duration curves (which constitute the probability of exceedance of a range of streamflows) for every reach in the network. To do so, we downscaled runoff forcing data and routed it through our river network via the Hillslope River Routing model (HRR- Beighley et al., 2009) to generate daily discharge estimates at every reach in the network. We used daily runoff estimates from the 'Global Reach-Level A Priori Discharge Estimates for SWOT' data set (GRADES – Lin et al., 2019) for coarse-scale forcing data and used 1979–1989 as a case study. This process is outlined in Text S2. We validated our modeled flow duration curves at 87 stream gauges in the watershed for this time period (Figure S1, data accessed via the USGS's dataRetrieval R package), finding near perfect recovery of discharges > 1 m³/s and strong recovery of flow in the smallest streams (<1 m³/s, Figure S1).

2.2. CO₂ Advection/Evasion Model

Because our focus is on the role of lake/river connectivity, we are specifically interested in tracking the fate and transport of headwater CO₂ and we ignore downstream terrestrial inputs and in-stream processes,

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acknowledging that a full picture of carbon cycling should include these processes. We made this choice because we could not defend either where or how much terrestrial CO_2 to add further downstream. We can defend adding terrestrial CO_2 to the headwaters (Hotchkiss et al., 2015; Liu & Raymond, 2018; Marx et al., 2017; Winterdahl et al., 2016). Thus, we leave differential downstream CO_2 inputs and in-stream CO_2 generation for future work.

To model potential evasion of terrestrial CO_2 from the river network, we created a model that tracks distinct 'parcels' of CO_2 (i.e. the Lagrangian specification of the flow field) as they simultaneously evade gas to the atmosphere, move downstream, and interact with other CO_2 parcels from intersecting streams (Figure 1). This approach is in line with advection/evasion modeling previously performed for the Amazon River (Abril et al., 2014).

Conceptually, we introduce some amount of CO_2 into the headwaters of the network (the term 'headwater' is used interchangeably with first order here and throughout). Next, CO_2 is evaded within each reach via Equation 2 (Text S3 for derivation), where i refers to a specific reach, $[CO_2]_{i-1}$ is the inflowing CO_2 concentration from upstream $[M/L^3]$, and HRT is the hydraulic residence time [T]. Note $[CO_2]_{i-1}$ is sourced laterally in the first order. These terms are all defined explicitly for every reach in the network but k and HRT were calculated differently for lakes and rivers to reflect the distinct hydrological processes occurring in the two environments (Text S4). In short, stream and river k is modeled as a function of water column turbulence (Raymond et al., 2012) while lake k, which is largely wind and convection driven, is modeled using surface area as a reasonable proxy for wind shear and convection in the surface mixed layer (Raymond et al., 2013; Read et al., 2012):

$$\left[\operatorname{CO}_{2}\right]_{\operatorname{evaded},i} = \left[\operatorname{CO}_{2}\right]_{i-1} - \left\{\left[\operatorname{CO}_{2}\right]_{i-1} e^{-k_{i}*\operatorname{HRT}_{i}}\right\}$$
(2)

Any remaining in-stream CO_2 is then transported to the next reach immediately downstream. This process is continued for all downstream reaches until the most downstream river in the network is reached. When there are multiple inflows to a reach, the CO_2 inflow is 'diluted' and calculated as the mean CO_2 concentration across the inflows, weighted by discharge to favor larger rivers (Figure 1).

While we used an arbitrary CO_2 concentration to report ultimate results of the role of lakes, we validated our model by forcing it with field measurements of in-stream CO_2 concentrations made at three sub-catchments that met our validation requirements (Text S5, Figure S2): (1) the Salmon River (Aho & Raymond, 2019), (2) the West Branch Swift River, and (3) the Harvard Forest (both using USGS measurements again accessed via the dataRetrieval R package). To validate, we set the model input CO_2 concentration as measured in the field at the corresponding (and spatially explicit) stream reach and ran our model at the flow corresponding to the flow at the time of the field measurement. We then compared downstream model outputs to separate field validation measurements that were made at downstream locations later in time, thus allowing a validation of CO_2 passing downstream along a river network.

2.3. Experimental Design

With a validated model in hand, we introduced an arbitrary parcel of CO_2 (4,987 μ atm or 10 mg/L at a uniform stream temperature of 15 °C) into every first-order stream to represent CO_2 terrestrially sourced from soil respiration in the headwaters. We ignore terrestrial CO_2 inputs from groundwater for the sake of model parsimony, acknowledging that the headwaters are highly sensitive to groundwater inputs (Duvert et al., 2018). We also ignore the effects of the carbonate buffering system, which is well-known to influence riverine CO_2 emissions (Stets et al., 2017).

We then ran the model for a suite of 'characteristic discharges' extracted from the flow duration curves at all 98,254 reaches in the network. 'Characteristic discharges' were defined using exceedance probabilities from each reach's unique flow duration curve (i.e. Q_{10} is the discharge exceeded 10% of the time in a reach), and include Q_2 , Q_5 , Q_{10} , Q_{15} , Q_{25} , Q_{35} , Q_{50} , Q_{65} , Q_{75} , Q_{85} , Q_{90} , Q_{95} , Q_{98} , and Q_{mean} . Total network evasion was quantified as the sum of all CO_2 evaded into the atmosphere across all reaches. The percentage of evasion occurring in lakes was calculated as the ratio of total evasion from lakes to total network evasion. Finally, we

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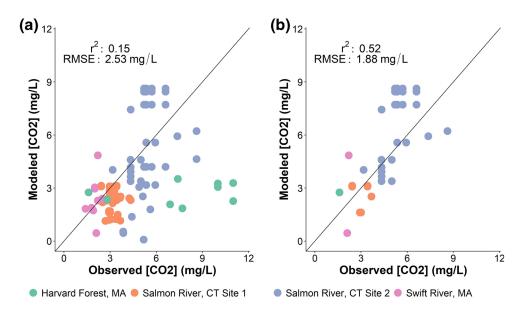


Figure 2. Modeled versus observed CO_2 concentrations for (a) all validation measurements and (b) after filtering for high flows, here defined as < 30% exceedance probability.

defined ' CO_2 evasion efficiency' as the sum of CO_2 evaded from all throughflow lines within a lake divided by the sum of CO_2 evaded and transported downstream.

3. Results and Discussion

3.1. Advection/Evasion Model Predicts Downstream Patterns in Terrestrial CO₂

Field measurements of downstream CO_2 concentrations are systematically underestimated by our model at the four sites tested when considering all flows (Figure 2a). However, when we filter for only high flow events (defined here as flow that is less than an exceedance probability of 30%), the model successfully reproduces observed in-stream CO_2 concentrations (Figure 2b). Below, we explore why this is the case and why we assert that Figure 2b successfully validates our model.

Raymond et al. (2016) and Zarnetske et al. (2018) suggested that river systems likely swing back and forth between transport and reactor states depending upon current flow conditions and water temperature. During low flow events, high residence times allow in-stream processes to occur and solute concentration is fundamentally influenced by biological removal/production. However, during flood events, residence times are short enough that there is not enough time for stream ecosystems to process solutes before advection, merely 'shunting' them downstream (Raymond et al., 2016). Similar relationships between water residence time and evasion have been studied in the specific context of CO_2 evasion (Duvert et al., 2018; Maavara et al., 2020; Marx et al, 2017). Therefore, because we modeled only advection/evasion of terrestrial CO_2 sourced from the headwaters and ignored in-stream processes, a fair validation must compare the model outputs to field measurements with as little influence from in-stream process as possible (i.e. high flows as previously established). Under this scenario, Figure 2b successfully validates our model. Note that this does not inhibit our ability to run the model on the entire flow regime, as it will simply produce evasion of terrestrially sourced CO_2 and not total in-stream evasion at lower flows, but our model cannot explicitly disentangle these sources.

3.2. Lakes Play an Outsized Role in Potential Evasion of Terrestrial CO2

At mean annual flow, about 28% of potential evasion of terrestrial CO_2 that enters the network at first-order terrestrial-aquatic interfaces occurs in lakes (green line in Figure 3a, Table S1). This occurs despite rivers outnumbering lakes by a factor of nearly 5.8 (at mean annual flow): the far longer residence times of lakes allow for significantly more CO_2 to be evaded to the atmosphere than in rivers. There is a non-linear

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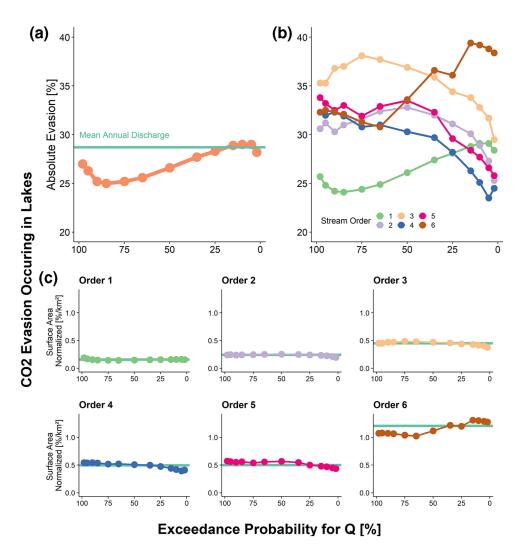


Figure 3. Percent of the total potential evasion of terrestrial CO₂ occurring in lakes in (a) the entire Connecticut River network at mean annual flow (green line) and across a full flow regime (orange points) and (b) stratified by order. (c) The relative importance of lakes within each stream order, normalized by the wetted surface area of that order, for the full flow regime and mean annual flow (green lines). Note that 50th percentile flows correspond to median, not mean, flow. (b) Suggests that the first-order trend dominates the network-wide trend, while orders 2–5 all exhibit similar trends. We suggest that order 6's trend is an artifact of its small number of lakes (16 in total, Figure S3).

relationship between discharge and the relative importance of lakes to potential evasion in the system (Figure 3a, orange points): lake influence increases marginally to 29% at flood flows but decreases slightly to approximately 25% at low flows. While rivers still dominate the total evasion budget at over 70% of total evasion, the unit evasion of lakes is much greater than streams.

The position of lakes in the network is also important. We find that lake importance fundamentally varies by stream order and streamflow, with more relative lake efflux in the first order at high flows, and more relative efflux in other orders at low-to-mid flows (Figure 3b). Across the entire flow regime, 'unit lake influence' (normalized by surface area) monotonically increases with stream order (Figure 3c), suggesting that the bigger lakes downstream (Figure S3) are more efficient evaders of terrestrial CO_2 (Figure 3b and Table S2). This increasing lake importance downstream occurs despite most absolute evasion occurring in the first order (Figure 4c). There are no lakes in the system's seventh or eighth orders.

Our results show that high flows expand the wetted extent of the network and substantially increase the surface area of the first order (e.g. Q_{10} has 181 km² of first-order rivers and lakes, while Q_{90} has only 156 km²).

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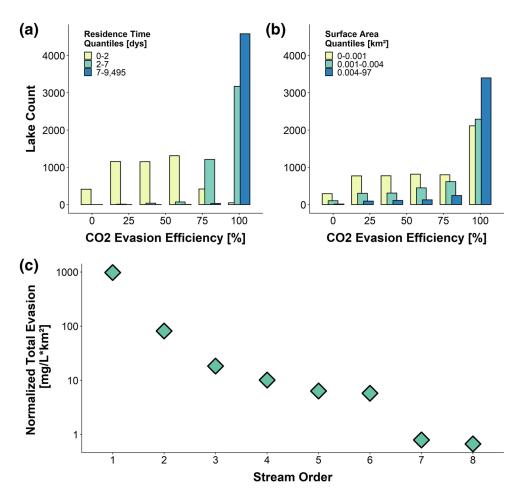


Figure 4. CO_2 evasion efficiency versus lake HRT (a) and size (b) for each lake at mean annual flow, binned by quantiles for visualization's sake. (c) Total evasion by order (at mean annual flow) and normalized by order surface area. There are no lakes in the seventh or eighth orders, though there is still almost 1 mg/L × km² of evasion occurring.

This likely causes the observed increases in the relative importance of first-order lakes at high flows (Figure 3b). Because of the sheer number of elements in the first order (both rivers and lakes), we suspect that the first order is largely responsible for the network-wide trend whereby lake importance increases with flow (i.e. Figure 3a orange points mimic the first-order green points in Figure 3b, but do not mimic any of the other stream orders). We conclude this because in all other stream orders (except the sixth), relative lake importance decreases with flow. The sixth-order trend is likely an artifact of its small number of lakes (16 in total, Figure S3). Thus we conclude that at high flows CO_2 parcels move downstream through the system quickly and diminish the effect of the long residence times in lakes. Finally, unit lake influence is largely constant within each order, regardless of flow across orders (Figure 3c).

3.3. Lake Morphometry and CO₂ Evasion Efficiency

Our results show that lake morphometry controls total evasion of terrestrial CO_2 from individual lakes based on their residence time and size. We calculated CO_2 evasion efficiency for every lake at mean annual flow and then compared this metric against lake surface area (Figure 4a) and mean annual HRT (Figure 4b), binning the results by quantiles to visualize similarly sized evasion efficiency distributions. CO_2 evasion efficiency generally scales with HRT (Figure 4a), which is intuitive and follows the structure of the advection/evasion model (Equation 2). There are effectively no lakes that are simultaneously low HRT and high efficiency, and likewise there are no high HRT, low efficiency lakes. Effectively all lakes with a mean annual

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residence time greater than 7 days evade all inflowing CO_2 (Figure 4a). However, evasion efficiency does not track with lake size in the same way: extremely small lakes (in Figure 4b, these are less than 0.004 km²) feature a full range of CO_2 evasion efficiencies, but, larger lakes are almost exclusively efficient evaders (Figure 4b). This suggests that there are very small lakes that still have high HRTs (due to low flow rather than a large size) and thus yield near 100% evasion efficiency.

Because most lakes are highly efficient evaders (and functionally all larger lakes evade 100% of CO_2), there are broad implications for carbon (C) cycling through river networks. We speculate that these larger lakes effectively reset the C cycling through the system, and so any field observations of large amounts of CO_2 downstream of a lake are likely due to internal decomposition of organic matter or a flood event flushing the floodplain rather than from upstream CO_2 . This directly influences our current understandings of differential C inputs along the stream-river continuum, adding additional complexity beyond the simple relationships previously identified between evasion and discharge (Hotchkiss et al., 2015) and residence time (Catalán et al., 2016).

These results agree with previous work highlighting the outsized role of small lentic waterbodies (lakes). Holgerson and Raymond (2016) found extremely small ponds ($<0.001~\text{km}^2$) are responsible for 15% of CO₂ emissions, while Cheng and Basu (2017) found half of total nitrogen removal from lentic waterbodies occurred in wetlands $<0.001~\text{km}^2$. Finally, small connected ponds ($<0.01~\text{km}^2$) are responsible for 34%, 69%, and 12% of nitrogen, phosphorous, and sediment retention in the northeastern US, respectively, and this is most pronounced in the headwaters (Schmadel et al., 2019). Here, however, we show that at mean annual flow lake influence for potential evasion of terrestrial CO₂ in the Connecticut River system is most pronounced downstream of the headwaters. Finally, we acknowledge that hydrologic connectivity is much broader than the connectivity between rivers and lakes. Upland ponds, the hyporheic zone, groundwater, wetlands, and floodplain zones are all hydrologically connected to the network (Godsey & Kirchner, 2014; Harvey & Gooseff, 2015; Harvey et al., 2019; Schmadel et al., 2019), and future work should focus on coupling these other components with our transport model.

This methodology is repeatable and scalable with a topologically connected network and CO_2 advection/ evasion model in hand. Future workers need only lake surface area extents and mean flow estimates to repeat this analysis in other watersheds or at larger scales. Further, while we only had access to static lake surface areas as defined within the NHD HR, dynamic lake surface area is easily calculated for large lakes, even at global scales, using remote sensing (e.g. Wang et al. 2014). Some novel combination of dynamic lake extent and CO_2 evasion efficiency is likely possible and would add needed nuance to this preliminary work relating lake size and evasion efficiency.

4. Conclusions

Lakes are fundamentally connected to river networks and act as stores within the river system for the constituents that move downstream and interact with in-stream processes and the landscape. This study represents a first attempt at testing, on CO_2 , the assertion that river/lake topology influences the form and function of fluvial geochemical processes at network scales (Gardner et al., 2019). Our promising results open the door for related work on lake influences on CO_2 originating from other sources, other GHGs, or even other landscape components. As GHG researchers move toward a more complete understanding of the complex interplay between terrestrial inputs, in-stream processes, evasion to the atmosphere, and landscape geomorphology within river networks, a better understanding of lakes' roles in these processes is necessary.

Data Availability Statement

The model, results, and code to reproduce our figures are available at https://doi.org/10.5281/zenodo.4135645. NHD HR hydrography is available at https://www.usgs.gov/core-science-systems/ngp/national-hydrography/access-national-hydrography-products. GRADES is available at http://hydrology.princeton.edu/data/mpan/GRADES/. USGS streamgauge information was obtained using the dataRetrieval R package available at https://github.com/USGS-R/dataRetrieval.

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Acknowledgments

C. B. Brinkerhoff was supported by a grant to C. J. Gleason through the NSF RoL FELS RAISE program (PI P.A. Raymond, Grant 1840243). We thank the two anonymous reviewers for their thoughtful and helpful comments that greatly improved this manuscript, including suggestions and language for extending our results. We also thank Ed Beighley for developing HRR and Peirong Lin for developing GRADES.

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