Global Biogeochemical Cycles

Supporting Information for

Improving predictions of stream CO2 fluxes through stream network models: a case study in the East River watershed, CO

Brian Saccardi[1]* and Matthew Winnick[1]

[1] Department of Geoscience, University of Massachusetts, Amherst

* Corresponding Author; Email: bsaccardi@umass.edu

Contents of this file

Text S1 to S3
Figures S1 to S4
Tables S1

Additional Supporting Information (Files uploaded separately)

Datasets S1
Zip folder S1
Code S1

Introduction

Included in this supplementary information are three text-file, three figures, one table, and one dataset. Text-file and figures 1 and 2 are in support of modeled parameters, including runoff calculations and benthic CO_2 concentrations above stream pCO_2. Text-file and figure 3, and table 1 are in support of conclusions depicting the skew often seen in pCO_2 data and the benthic contributions observed in the model. The dataset included are the sampled data from the east river with locations not represented by modeled points denoted:

Text S1.

Snowmelt in higher elevation sections of the East River was expected to contribute to discharge (Q) within the bases. To correct Q for elevation related snowmelt, data from Carroll & Williams (2019) was used to produce a regression between area normalized runoff and elevation. Using nine basins ranging in mean elevation from 3305 – 3549, areas of 0.9 – 84.0 km^2, and Q of 0.008 – 2.734 m^3/s; we calculated area normalized runoff and found that the equation,

$$r = 2.431 * 10^{-11} * e - 5.567 * 10^{-8} \quad (1)$$

fit the data with an R^2 of 0.46 (p = 0.04), where *r* is runoff in m/s and *e* is elevation in m. This was implemented in the model as the elevation corrected Q was added to stream sections discharge by multiplying the additional area by runoff.

Text S2.

To estimate realistic ranges of hyporheic zone pCO_2, we used published 20 cm benthic zone pore water geochemistry from the main stem of the East River from Nelson et al. (2019). In their study, Nelson et al. (2019) provide % surface water contributions based on conductivity measurements to estimate GW influences within the hyporheic zone. We calculate relative pCO_2 from their data using CrunchFlow reactive transport software (Steefel et al., 2015) to speciate the inorganic carbon system. Variable inputs include published pH and temperature along with estimated alkalinity based on the charge imbalance of published conservative cation (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anion concentrations (Cl^-, SO_4^{2-}). While absolute pCO_2 estimates are relatively uncertain, this exercise provides an estimate of relative pCO_2 offsets between the hyporheic zone and stream surface waters (SFig. 3). As shown, pore waters originally interpreted to reflect ~100% surface water (i.e. no GW influence) display elevated pCO_2 relative to stream waters from 0-1000 ppm, with the majority of values >300 ppm. These estimates strongly support our stream network model optimization, which found the best fit with observations assuming hyporheic zone pCO_2 is 600 ppm higher than stream waters.

Text S3.

For the purposes of understanding and comparing, means are a useful method of looking at data. However due to the right skew often seen in pCO_2 data distributions, the use of means in statistical upscaling may lead to elevated flux estimations. This has been recognized in Butman & Raymond (2011), where it was stated that in three of the regions stream order combinations, the mean of sample pCO_2 was an overestimation of the 'true' mean by up to 3-5%. Additionally, Raymond et al, (2013) used medians as it was noted that the mean pCO_2 of rivers was ~800 ppm higher then the median. While these represent recognition of the problems associated with statistical representations of pCO_2 data we can see in SFig. 4 that both the mean and the median are over representations of the mode or the pCO_2 values most likely to be seen across the landscape. This highlights an inherent problem with statistical upscaling of CO_2 fluxes as large quantities of data are needed in order to accurately determine the pCO_2 values that should be used lending additional support to methods such as proses based modeling where predictive power is strongest within the rang of pCO_2 most commonly measured.

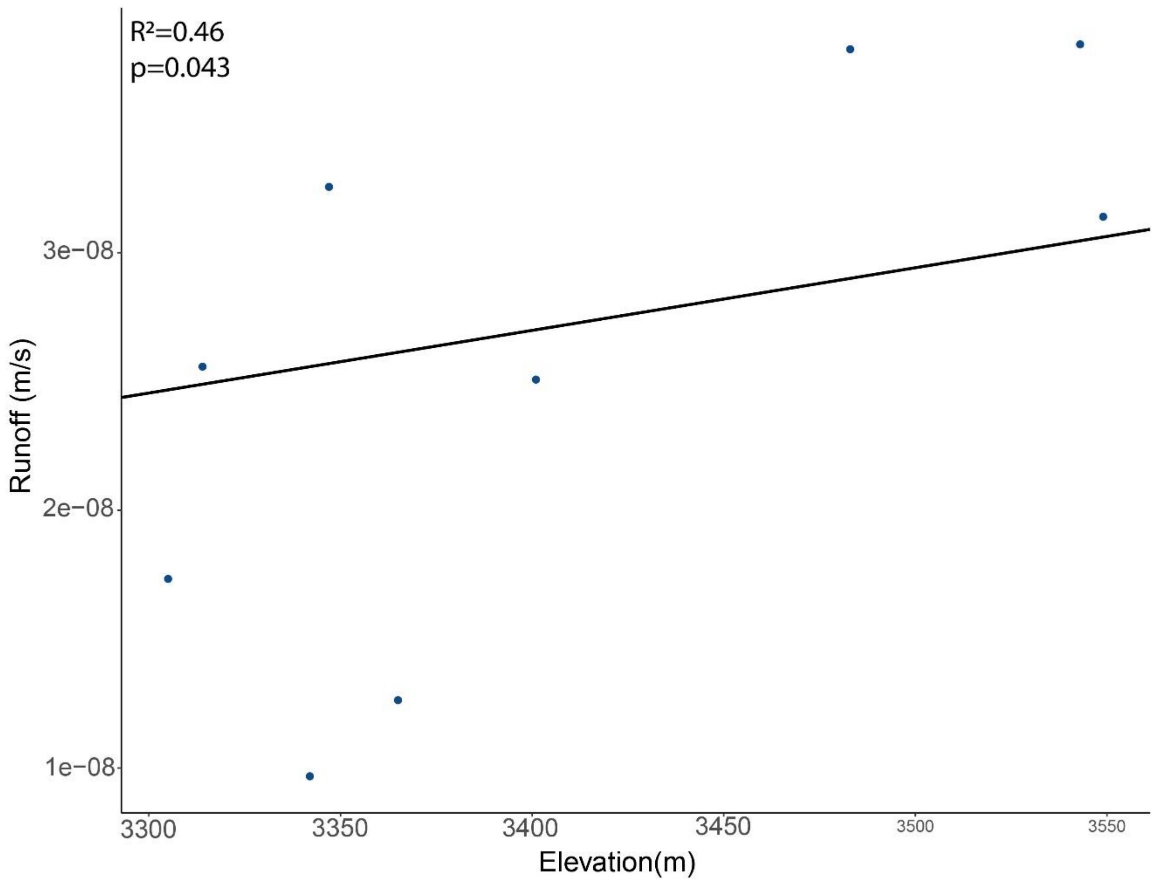

Figure S1. Model used to correct runoff due to additional runoff from snowmelt at higher elevations.

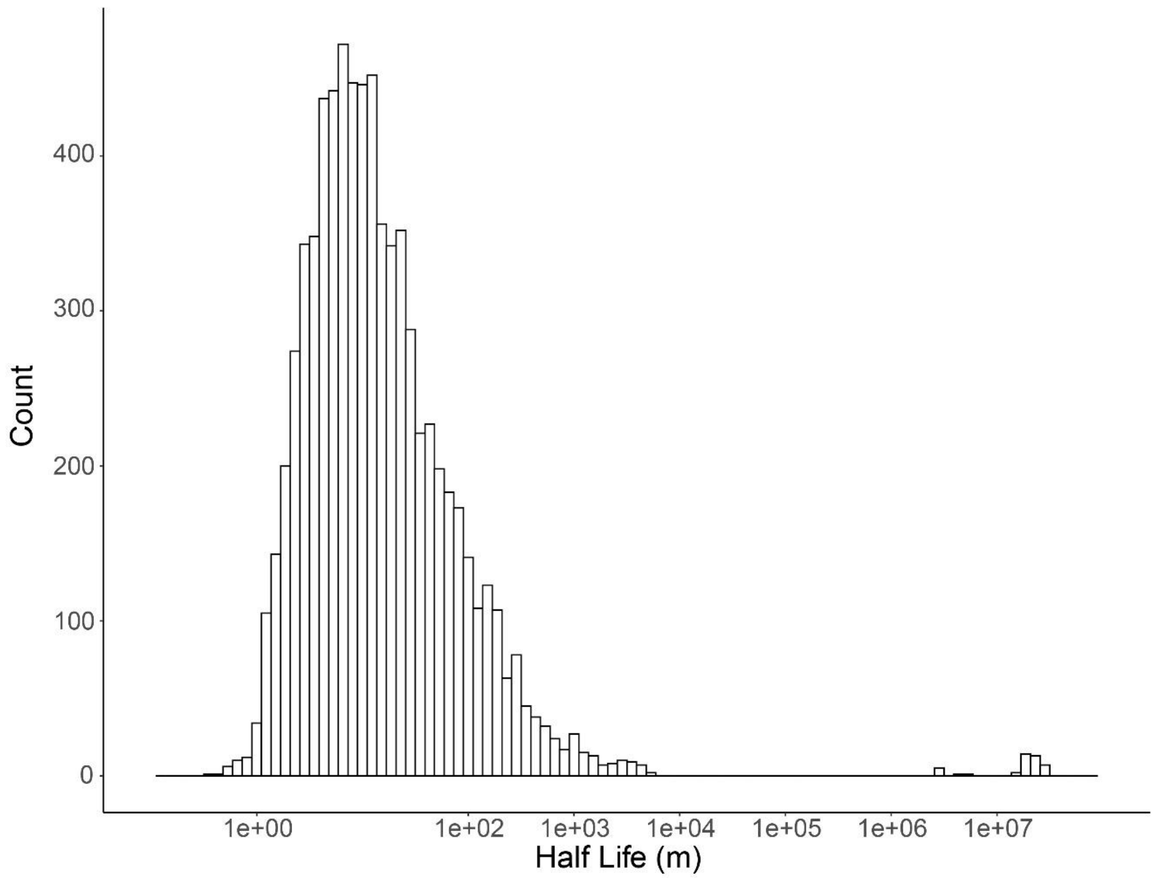

Figure S2. Half life of CO_2 within the model with a median of 11.06 m a max of 27,744,964 m and a min of 0.35 m.

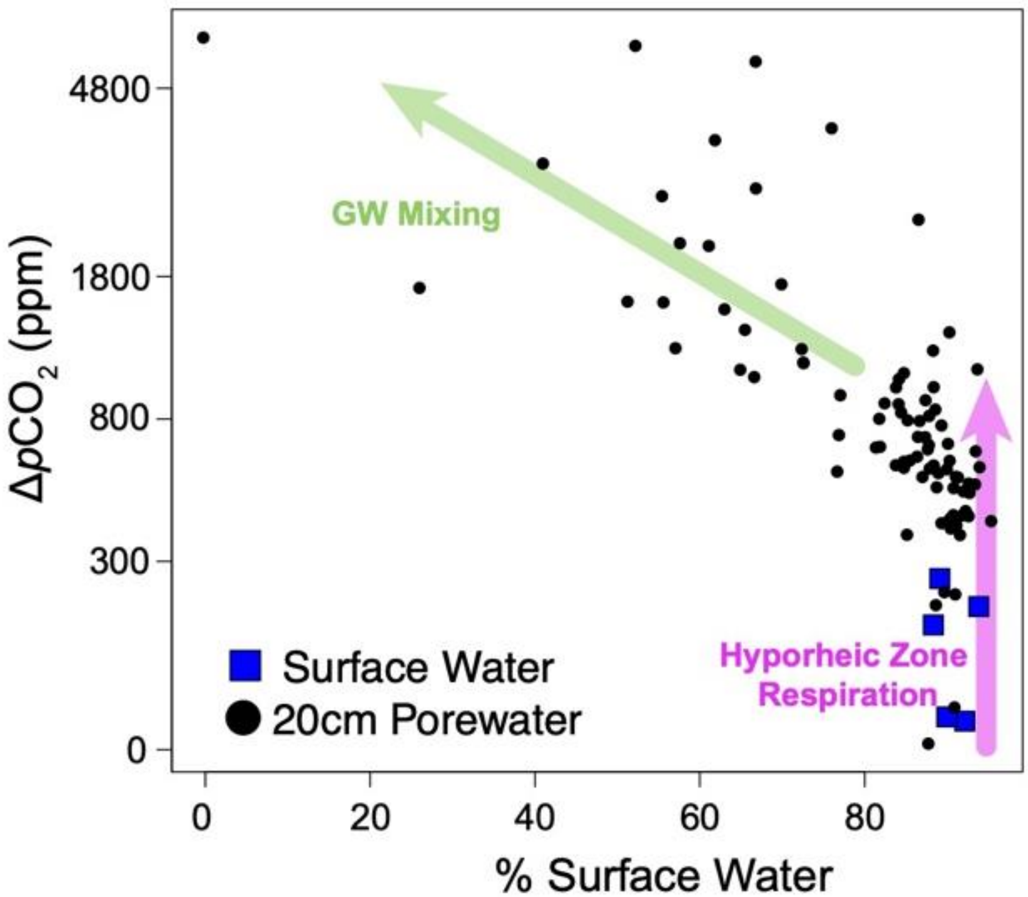

Figure S3. Calculated pCO_2 relative to minimum stream sample values from the Pumphouse reach hyporheic zone based on geochemical measurements of Nelson et al. (2019).

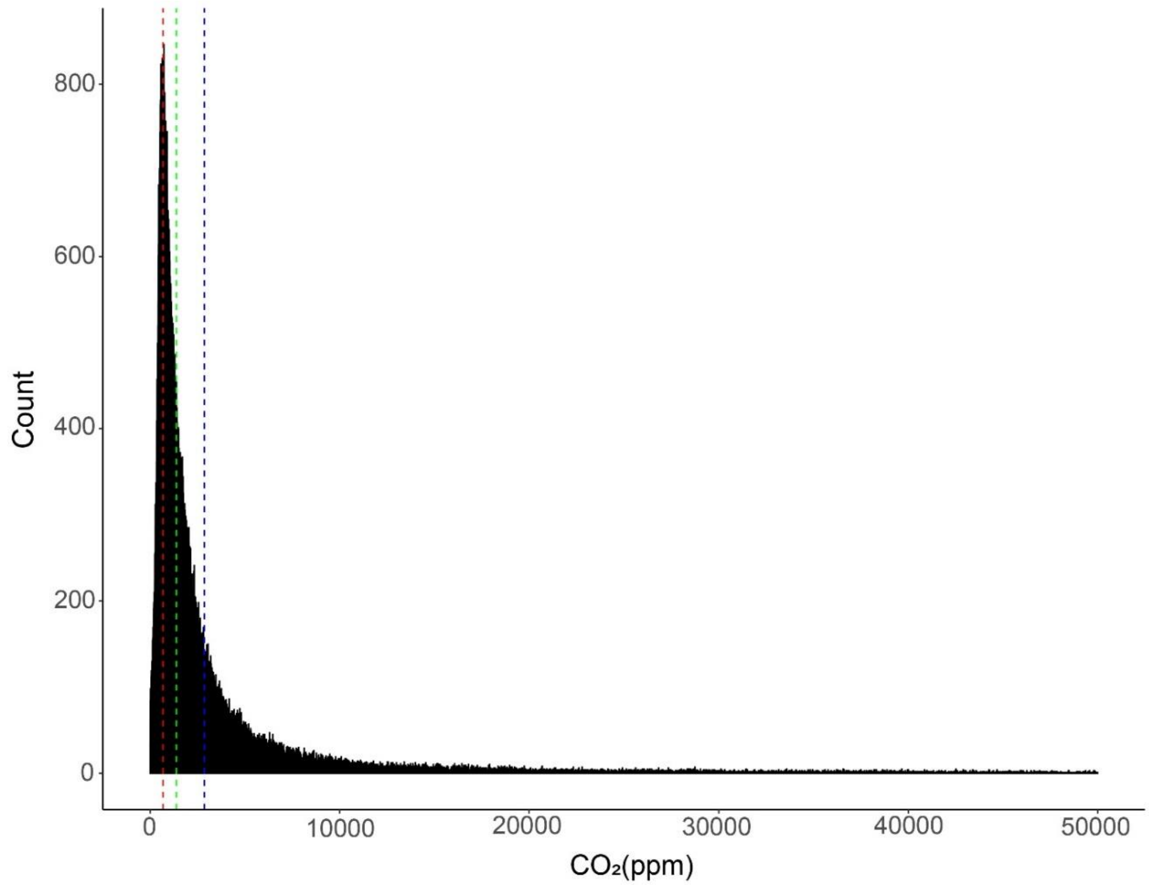

Figure S4. GLORICH dataset (Hartmann et al., 2014) containing 277,449 data points out of and available 283,856 as the data was cut to 50,000 to better show right skew. The dotted lines represent data mean (blue), median (green), and mode (red).

	all	1	2	3	4	5
%BZ CO2	42	24	34	47	74	93
%BZ CO2 in hotspots	21	7	20	16	70	91
% GW dominated	75	94	85	60	6	0
% GW dominated in hotspots	92	100	100	99	0	0

Table S1. The mean % of pCO_2 from benthic respiration across the East River and within hotspots for the entire basin and by stream order. The percent of the East River and hotspots by length that more than 50% of their CO_2 is from groundwater.

Dataset S1. Saccardi and Winnick Data contains the East River sample data including chemistry and corrected pCO_2 data (n=162) with the included column denoting whether data points were represented by NHDplus data point (n=121) and therefore used in the model.

Zip folder S1. Spatial Files Used in Model includes all data required to run the model including csv files such as 'catchment areas', 'names', 'NHId_remBM' and 'stream_reach' which contain NHDplus data. The shape files included are used for model calculations and graphs and include 'East_River_Lines', 'eastriverpump', and 'points'. The tiff filed included are a digital elevation model 'LargeDomain_DEM1' and the soil organic carbon map used in the Horgby MLRM 'SOC'. The remaining csv's contain the data for the discharge regression, snow plug locations, slope of each modeled point, watershed areas, and data used to make Sup Fig 4. Finally the 'Pointdata' csv are the data collected from the East River and used to validate the model.

Code S1. Stream Network Model is the R code in an R markdown format including directions on the setup and use of the code. This document requires R and RStudio to open.