HOW DO METABOLIC STOICHIOMETRIC RATIOS AND ALKALINITY INFLUENCE WHOLE-STREAM METABOLISM ESTIMATES FROM CARBON DIOXIDE SIGNALS?

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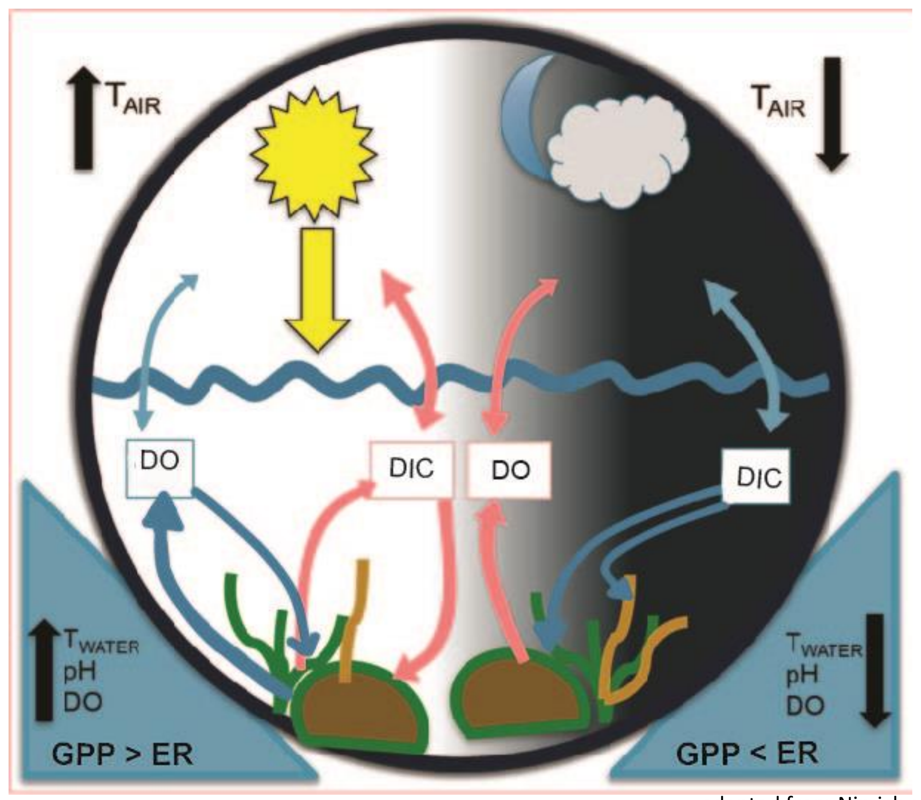
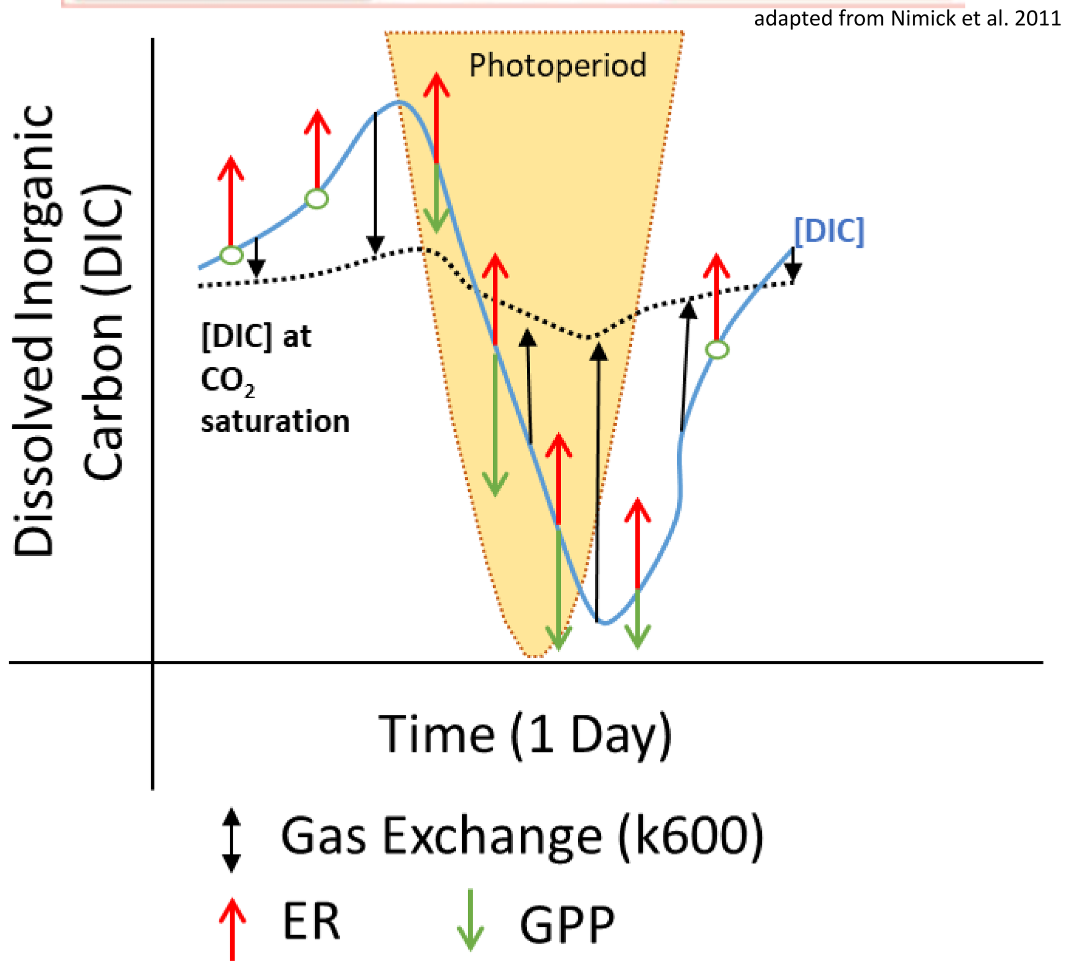
Motivation & Objectives

- Understanding stream metabolic regimes allows us to infer the nature of whole-watershed ecosystem function and energy movement through aquatic ecosystems.
- Metabolism measurements are conventionally based on DO signals, but recent advancements in sensor technology provide more information about metabolism in DIC signals. However, estimates of metabolism from DIC and DO are not matching.



adapted from Nimick et al. 2011



- Sensitivity analyses of the influence of O:C metabolic stoichiometric ratios on the inference of metabolism will advance understanding about the use of DO and DIC together.
- Sensitivity analyses of the influence of alkalinity on metabolism illustrates how carbonate equilibrium influences DIC modeling and the potential for the choice of static alkalinity to influence metabolism estimates.

References

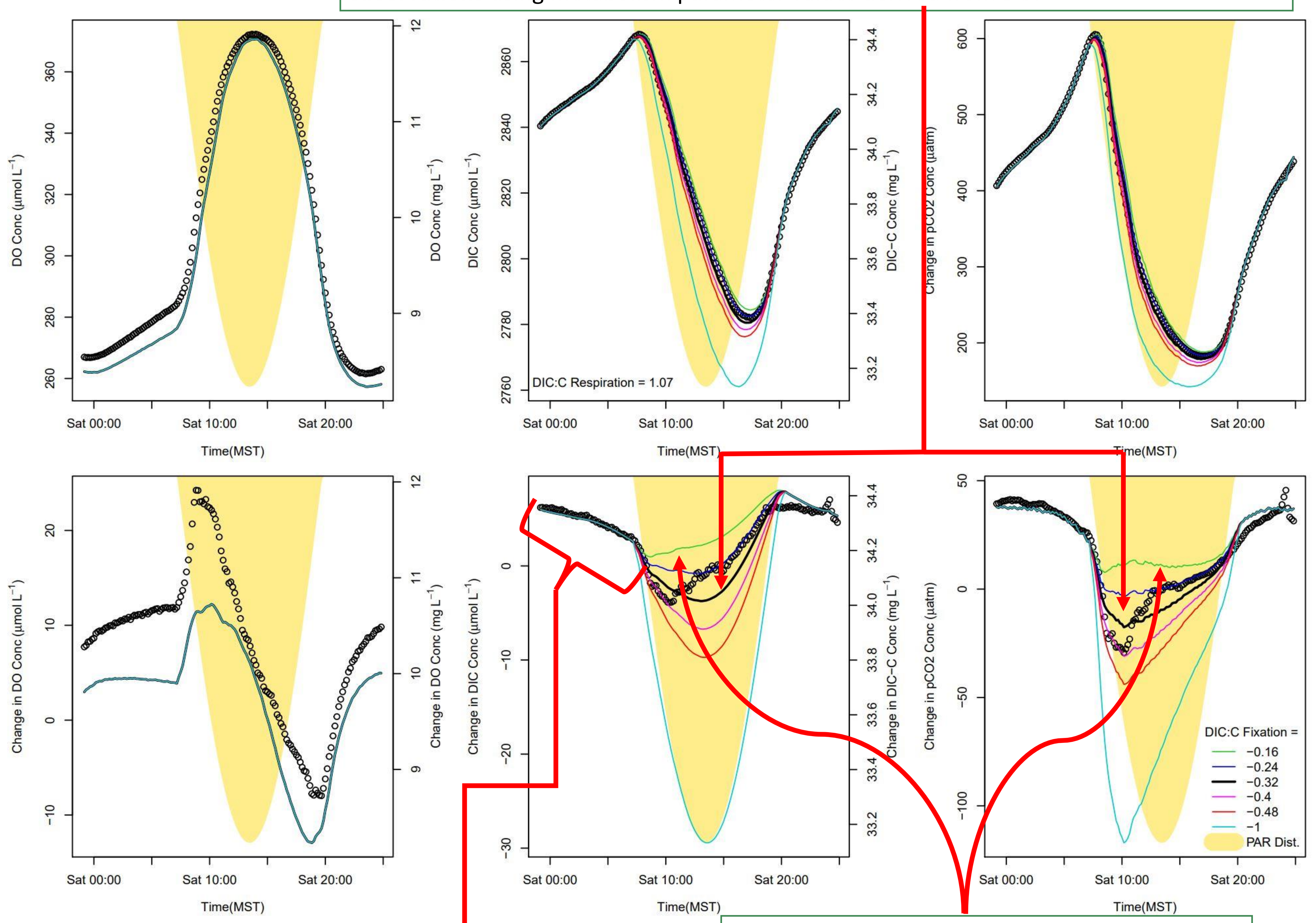
Nimick, D., Gammons, C., & Parker, S. (2011). Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review. *Chemical Geology*, *283*(1), 3-17. https://doi.org/10.1016/j.chemgeo.2010.08.017

Reynolds, J. C. (2001). Distributed in situ gas measurements for the analysis and modeling of biogeochemical changes in the Clark Fork River. Theses, Dissertations, Professional Papers. Paper 6584.

Sensitivity Analyses

The photosynthetic DIC:C fixation ratio was adjusted to determine what oxygen to carbon stoichiometry allows DIC metabolism estimates to match those from DO. Models simulated using data collected on September 12, 2014 in the Goldcreek reach of the Upper Clarkfork River.

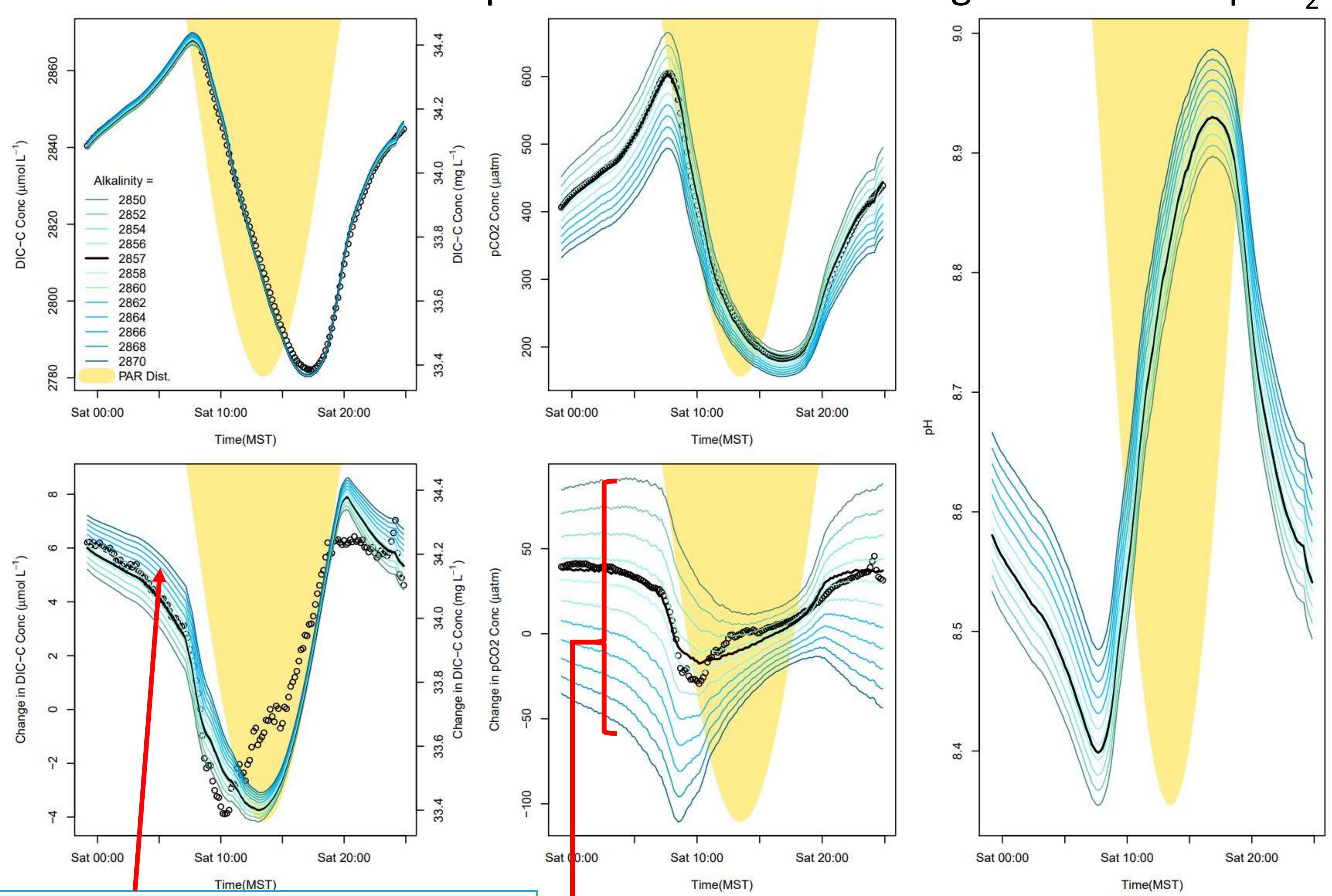
A stoichiometric ratio of -0.32 applied to the DIC model was necessary to match the pCO_2 observations using metabolism parameter values derived from DO.



Fixation ratio changes have no effect during the nighttime hours because fixation coincides with photosynthesis.

A lower magnitude DIC:C fixation ratio results in metabolism having a smaller influence on DIC and pCO_2 concentrations.

For a given signal in upstream DIC concentrations, alkalinity was adjusted to understand the influence of assumed alkalinity values on the simulation of carbonate equilibrium and the resulting simulation of pCO_2.



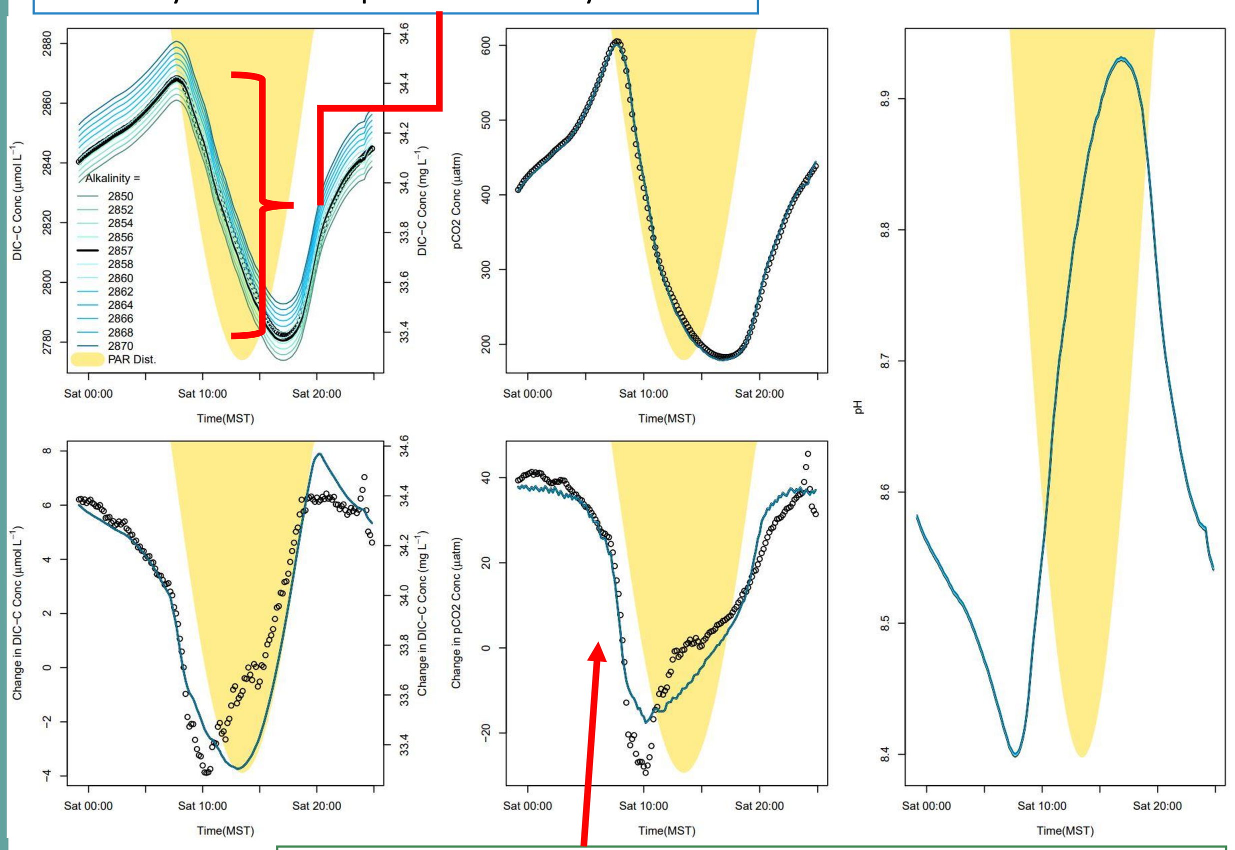
Higher alkalinity results in larger increases in dissolved inorganic carbon concentration over the reach due to decreased gas exchange.

Alkalinity has a strong influence on the estimate of pCO_2 from DIC, which in turn has a strong impact on the influence of gas exchange.

Alternative Alkalinity SA

Metabolism models were changed to assume a known upstream pCO_2 to further assess the choice of alkalinity on DIC metabolism estimates based on CO_2 concentrations.

Alkalinity has **direct effect on simulation of DIC** when an upstream pCO_2 is known. There is high variability seen in the predicted DIC dynamics.



Metabolism estimates from pCO_2 are not affected when upstream pCO_2 is known because the same alkalinity is used by the model to convert DIC concentrations back to pCO_2 concentration.

Conclusions

- A DIC:C fixation ratio between -0.4 and -0.24 (best fit at -0.32) is necessary for both DO and DIC models to provide the same estimates of metabolism.
- The magnitude of this ratio is much lower than the C:O photosynthetic quotient typically estimated for algal metabolism, and higher than the O:C PQ of 1.2 that "has been suggested to be widely accepted" (Reynolds, 2001).
- Alkalinity influence on the model when demonstrates the importance of alkalinity in linking DIC to pCO_2. When the upstream pCO_2 is known, the choice of alkalinity does not appear to be important for mathematical considerations of metabolism estimates based on CO_2.
- Further research on why stoichiometric ratios are so far from typical values and if variation in alkalinity over space or time causes error in the model predictions relative to observations is necessary to use DO and DIC together to estimate metabolism with confidence.

Acknowledgements

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