Evaluating the Variability of Gas Transfer Velocity in Mountain Streams as a Function of Stream Kinematics and CO_2 Mass Balance

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INTRODUCTION

Mountain streams comprise a large fraction of waterways worldwide and are known to be large contributors of greenhouse gases to the atmosphere. One of the challenges in accurately estimating CO_2 fluxes from surface waters in mountainous streams include the accurate estimation of the gas transfer velocity (K), which represents the rate of bidirectional gas exchange between surface water and atmosphere. Unfortunately, there are an overwhelming amount of conflicting methods to determine this variable that each provide vastly different values. Currently, there is little evidence supporting the use of any of these equations, or methods as a whole, which oftentimes are motivated by estimation of gas transfer velocity values, instead of experimental conclusions. We will present an in depth comparison between different methods for evaluating the gas transfer velocity of mountain streams. Accordingly, this comparison will be, to the best of our knowledge, the first of its kind in the high elevation, mountain stream environment of the Paramos in the Andes mountains.

METHODS

- Collected water velocity, flux, slope, dissolved CO2, and water depth at 35 distinct sites in one study reach
- Calculated a Gas Transfer Velocity using Equation (1) and (2)
- Correlation analysis confirmed by Two Sample Independent T- Test

Methods for Calculating K600

1) Gas transfer velocity equation based on kinematic variables.(Raymond et al. 2012)

$$K_{600} = (VS)^{.89\pm .020} X (D)^{.54\pm .030} X\, 5037 \pm 604$$

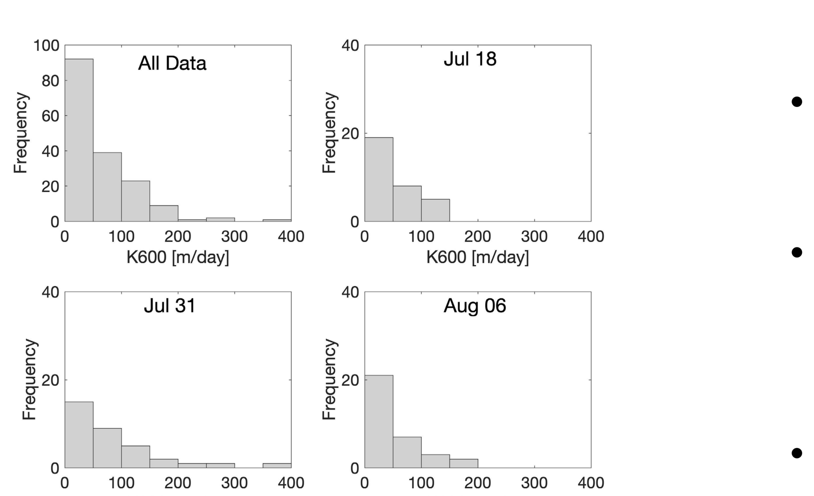
2) Gas transfer velocity equation based on mass balance. (Mcdowell and Johsnon 2018)

$$F_{CO_2} = K_{CO_2} * (pCO_{2\,(aq)} - pCO_{2\,(air)}) * K_H \quad (2)$$

V- Velocity (m s^{-1})
S- Slope (Unitless)
D- Depth (m)

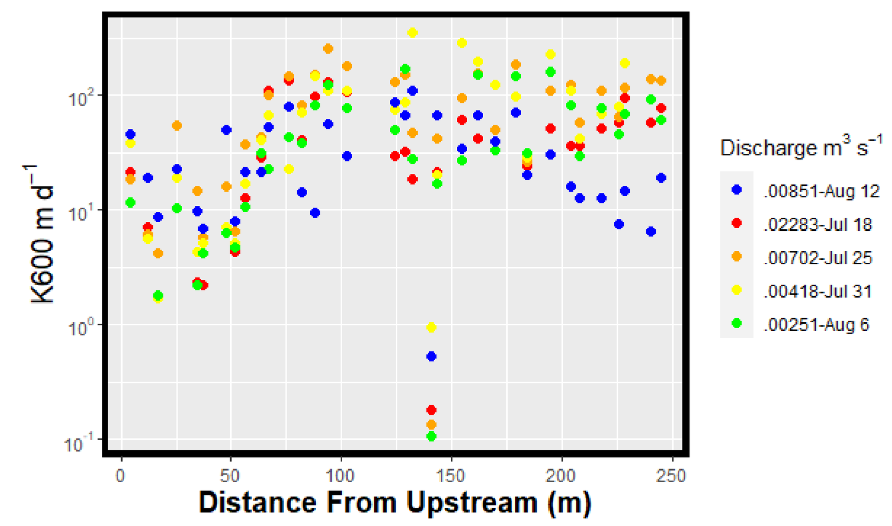
F_{CO_2} – Flux of $\boldsymbol{CO_2}$ (umoles m^{-2} s^{-1})
K_H –Henry's Constant (mol L^{-1} atm^{-1})
p $CO_{2\,(aq)}$ – Partial Pressure of CO_2 in water
p $CO_{2\,(air)}$ - Partial Pressure of CO_2 in air

Kinematic Gas Transfer Velocity



- Gas transfer velocity calculated based on equation (1) dubbed $\boldsymbol{K_{Kin\text{-}600}}$
- Majority of Values within 0 (m day^{-1}) to 50 (m day^{-1})
- More packed values at very high and very low discharge given in units of (m^3 s^{-1})
- Greater spread of observed values at intermediate discharge given in units of (m^3 s^{-1})

Spatial and Temporal Variation of $K_{Kin\text{-}600}$



This demonstrates that kinematically calculated gas transfer velocity scales accordingly with discharge, but can lack consistency as evidenced by July 18th and August 6th, where a larger discharge did not grant a larger calculated value of K_{600} average. As evidenced by figure 1, the greatest source of variability may not have been exhibited day to day, but between each synoptic site throughout the stream on one given day. Gas transfer velocity values steadily increase through the course of the stream, typically with values calculated on lower discharge days being the smallest.

Consistency and Correlation of $K_{Kin\text{-}600}$ Values Between Various Studies

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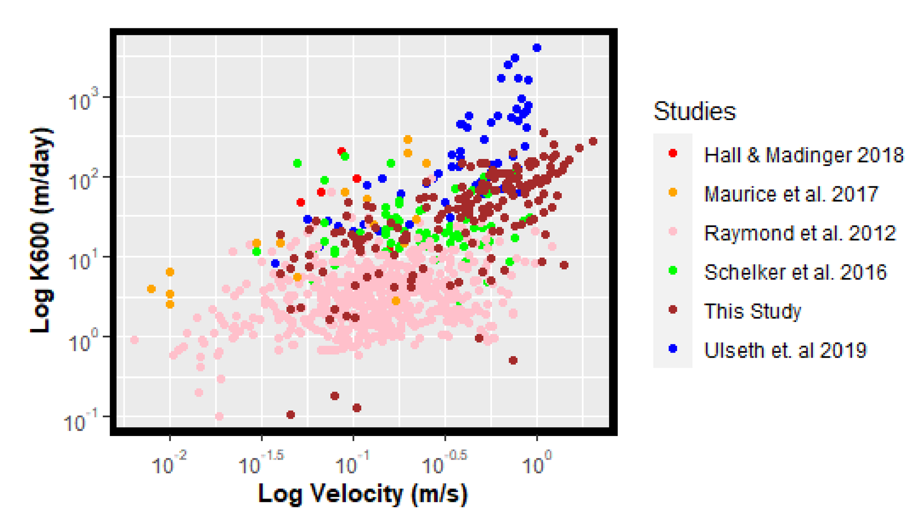
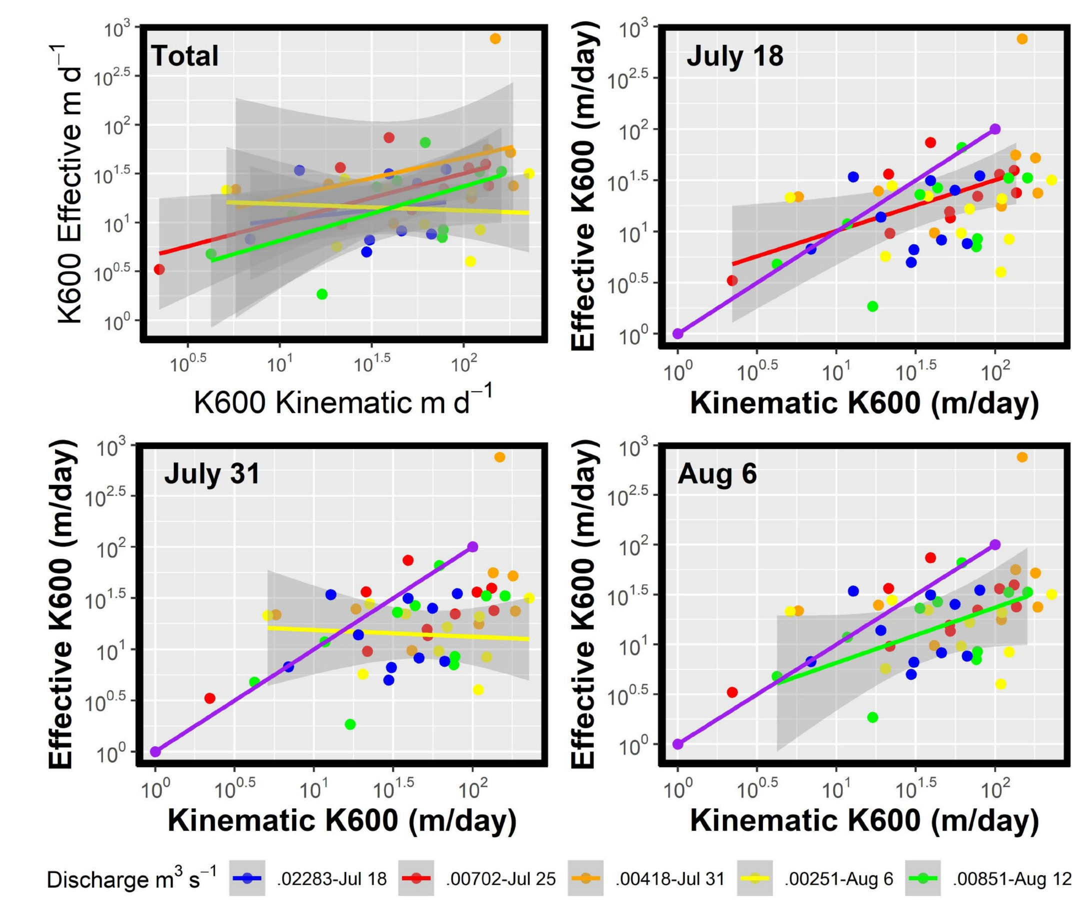


Ulseth et al. 2019, collected necessary data to calculate $K_{Kin\text{-}600}$ using a modified equation than our own equation (1), and tabulated values of the data from their study as well as four other studies focused on calculating the gas transfer velocity with a kinematic focus in montane environments. To this data, our group combined the measurements obtained from our synoptics. Based on equation (1), the water velocity measured at our site may have been a main determinant of the $K_{Kin\text{-}600}$ values calculated, instead of other kinematic variables such as water depth and slope of terrain.

3.4 Comparing K_{600} As A Function of Stream Kinematics and CO_2 Mass Balance



The comparisons illustrated in figure 5, portray the crux of this study. Demonstrated are panels with plots of gas transfer velocity calculated via equation (1) and equation (2) using data obtained at the same sites. This allows for a direct comparison between K values obtained using the variant methods. Not only do the values tend to have a positive relationship, their magnitude is of similar scale. As evidenced by panel 1, the vast majority of the points lie within the tens to hundreds magnitude. We ran a two sample T- test to identify the statistical correlation between the mean value of gas transfer velocity for both methods on all five synoptic days and in total. We found the degrees of freedom to be 70, and that our T- statistic (1.716) is less than the critical value at .05 significance level. We fail to reject the null hypothesis, and can assume that the means of the two data sets compare in magnitude.

SUMMARY

1. We suggest that there is a definitive correlation between stream metabolism and the kinematic environment of any given stream.
2. These effects are exaggerated in the high elevation terrains of mountainous streams.
3. Any full understanding of stream metabolism and the true effects of gas transfer velocity on gas exchange cannot solely focus on the stream dynamics, but also on a mass balance between the gas at the

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References:

1. Mcdowell, M. J.; Johnson, M. S. *Journal of Geophysical Research: Biogeosciences* **2018**, *123* (7), 2183.
2. Raymond, P. A.; Zappa, C. J.; Butman, D.; Bott, T. L.; Potter, J.; Mulholland, P.; Laursen, A. E.; Mcdowell, W. H.; Newbold, D. *Limnology and Oceanography: Fluids and Environments* **2012**, *2* (1), 41.
3. Ulseth, A. J.; Hall, R. O.; Canadell, M. B.; Madinger, H. L.; Niayifar, A.; Battin, T. J. *Nature Geoscience* **2019**, *12* (4), 259.