

Controls on Diffusive Fluxes of Methane and Carbon Dioxide in a Wetland in the California Delta

Emily Rose Gilson

ABSTRACT

Wetlands play an important role in global greenhouse gas cycles, producing or sequestering atmospheric gases including CH₄ and CO₂. The objective of this study was to determine how local and wetland-scale variables drive diffusion of CH₄ and CO₂ into the atmosphere from the water column in the Mayberry wetland in the California Delta. Between October 2011 and November 2012, I collected water samples from shallow, deep, and vegetated locations in the wetland and I measured concentrations of CH₄ and CO₂ in each sample. I combined concentration measurements with measurements of water temperature and wind speed in a model to calculate diffusive fluxes at each sampling location for each sampling day. CH₄ diffusive fluxes from the wetland ranged from 0.26722 nmol m⁻² s⁻¹ to 40.070 nmol m⁻² s⁻¹ and CO₂ diffusive fluxes ranged from 0.50437 umol m⁻² s⁻¹ to 3.7222 umol m⁻² s⁻¹. These fluxes follow large seasonal patterns. Although significant differences exist on some days between shallow and deep locations, the lack of trend in these differences suggests that water depth does not have a consistent influence on diffusive fluxes of CH₄ and CO₂. On the other hand, proximity to vegetation seems to be associated with high diffusive fluxes of CO₂ and low diffusive fluxes of CH₄. Wind speed is another important driver of CO₂ and CH₄ diffusive fluxes in this system. Diffusive fluxes of CH₄ and CO₂ are on the same order of magnitude as total fluxes, indicating that diffusive fluxes are a significant contributor to wetland emissions.

KEYWORDS

greenhouse gases, carbon cycle, water-air interface, vegetative cover, headspace equilibration

INTRODUCTION

Wetlands play an important role in global greenhouse gas cycles by producing or sequestering atmospheric gases including methane (CH_4) and carbon dioxide (CO_2). Over the past few centuries, steadily rising concentrations of atmospheric CH_4 and CO_2 have altered planetary energy dynamics, leading to climate change effects such as rising temperatures (Hansen et al. 2007). Wetlands may contribute to these changes because they are significant natural sources of CH_4 , accounting for at least 20% of total yearly global CH_4 emissions (Houghton et al. 2001, Ding and Cai 2007). Alternatively, wetlands may mitigate climate change because they generally act as carbon sinks on century-long time scales primarily by incorporating carbon in the form of plant biomass (Whiting and Chanton 2001, Mander et al. 2011). Whether wetlands act as sources or sinks for carbon-containing greenhouse gases depends on the relative rates and magnitudes of physical and biological processes which contribute to net fluxes of CH_4 and CO_2 .

Net flux is the sum of a number of distinct pathways by which CH_4 and CO_2 enter a wetland system or escape to the atmosphere (Fig. 1). Plant pathways contribute to the movement of both CH_4 and CO_2 in wetlands. Plants, whose biomass consists of carbon-containing sugars, release carbon into the soil when they decompose after they die (Mander et al. 2011). On the other hand, intracellular air space in plant tissue allows CH_4 to exit wetlands without passing through the water column (Morrissey et al. 1993, Ding and Cai 2007). CH_4 and CO_2 can also exit wetlands by moving through the water column. CH_4 escapes through the water column by both ebullition, isolated CH_4 bubbles, and diffusion, constant movement along a concentration gradient from soil to atmosphere (Strack and Waddington 2008). Likewise, CO_2 diffuses easily through the water column because it is water-soluble (Miller 2011). Across wetlands, net fluxes, and presumably their diffusive components, depend on local wetland characteristics.

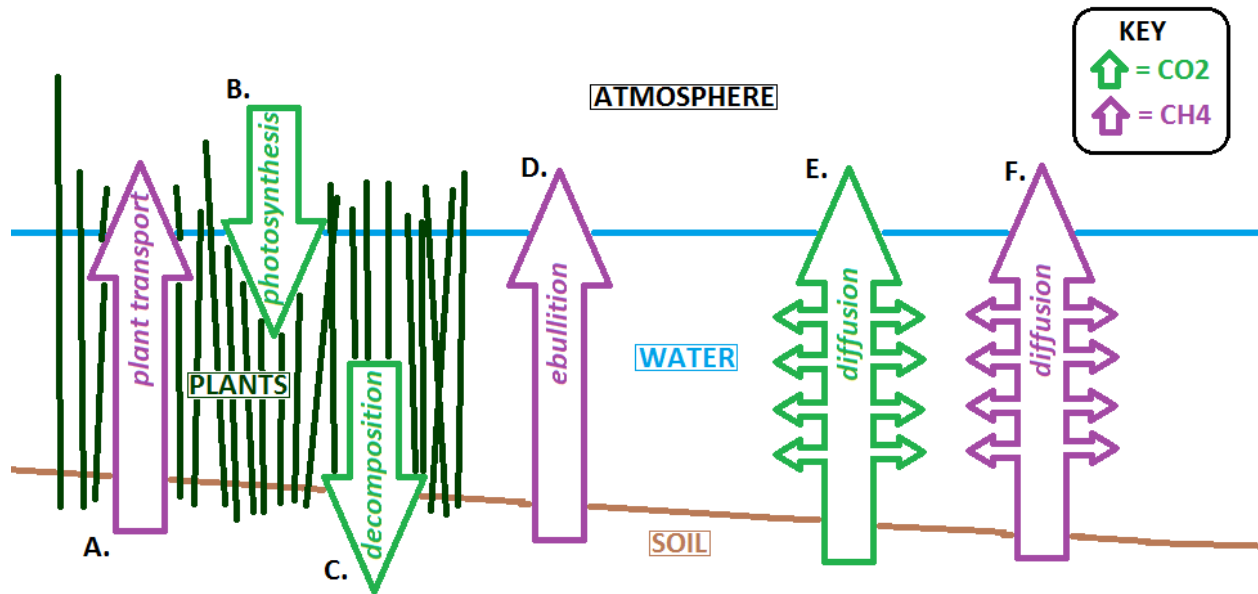


Fig. 1. Movement of CH₄ and CO₂ in a wetland ecosystem. Plant-mediated transport (A) and ebullition (D) move CH₄ directly from the soil to the atmosphere. Plants perform photosynthesis (B), which removes CO₂ from the atmosphere and stores the carbon as sugars in plants. When plants die, their biomass undergoes decomposition (C) and CO₂ is released in the soil. Taken together, photosynthesis and decomposition move CO₂ from the atmosphere to the soil. Diffusion of CH₄ (F) and CO₂ (E) refers to the constant movement of CH₄ and CO₂ through the water from regions of high concentration to regions of low concentration. Because CH₄ and CO₂ are produced and deposited in the soil by methanogenesis and decomposition respectively, the direction of diffusion is toward the atmosphere. Source: E.R. Gilson.

In wetlands, water depth and patterns of vegetative cover are two factors associated with net greenhouse gas flux and perhaps also with the diffusive component of net flux (Whiting and Chanton 2001, Herbst et al. 2011, Mander et al. 2011, Miller 2011). Increasing water depth and high plant density could increase diffusion of CH₄ and CO₂, respectively, because high CH₄ production in the anaerobic soil layer (Mander et al. 2011, Dai et al. 2012) and increased incorporation of CO₂ by plants (Mander et al. 2011) contribute to concentration gradients that drive diffusion. Other factors that control CH₄ and CO₂ production and transformation in the wetland can also affect wetland emissions. Soil aeration and temperature can inhibit or enhance production of CH₄ and CO₂, contributing to overall fluxes of these gases (Blodau and Moore 2002, McMillan et al. 2007, Herbst et al. 2011). The associations between net fluxes and wetland characteristics suggest that these factors also influence diffusion of CH₄ and CO₂ across the water-air interface of the wetland; however, it has yet to be experimentally determined

whether associations between diffusive fluxes and wetland depth and vegetation mirror those between net fluxes and these same characteristics.

The objective of this study was to determine how local and wetland-scale variables drive diffusion of CH₄ and CO₂ through the water column in the Mayberry wetland in the California Delta. First, I hypothesized that increasing water depth would be related to increased diffusive fluxes of CH₄ and CO₂ across the water-air interface. Second, I hypothesized that increasing proximity to vegetative cover would be related to increased diffusive flux of CO₂ and decreased diffusive flux of CH₄ across the water-air interface. Third, I hypothesized that additional variables including wind speed, aqueous concentration, and water temperature would impact diffusive fluxes of CH₄ and CO₂ from the wetland.

METHODS

Study site

My study site was the Mayberry wetland on Sherman Island in the California Delta (38°3'N, 121°46'W, Fig. 2). This wetland is a 300-acre site managed by the California Department of Water Resources (www.dwr.water.ca.gov) and the wetland conservation group Ducks Unlimited (www.ducks.org). The Mayberry wetland was created when a grassland pasture was flooded for this purpose in the summer of 2010 (J. Hatala, personal communication). Currently, the Mayberry wetland is a mosaic of deep and shallow water containing patches of tules (*Schoenoplectus acutus*) and cattails (*Typha latifolia* and *Typha glauca*).



Fig. 2. Location of the Mayberry wetland. The Mayberry wetland is on Sherman Island in the Sacramento-San Joaquin Delta in California. Source: U.S. Geological Survey National Map: Geographic Coordinate System, NAD 1983.

Sample collection

Between October 4, 2011 and November 29, 2012, I collected water samples from three locations across the wetland: one deep location in open water (water depth approximately 1.25 meters), one shallow location (water depth approximately 0.65 meters), and one location immediately next to clusters of plants (water depth approximately 1.25 meters). I chose my sampling locations using a sample of convenience because the locations needed to be easy to access without disturbing the wetland. The sampling locations were distributed across the wetland, away from locations where water enters the wetland, so the CH_4 and CO_2 concentrations in the samples accurately reflected wetland biogeochemistry. Each sampling location was representative of its location class (deep and open, shallow, or vegetated). I

collected samples between once a week and once a month over a period of 14 months to assess seasonal variability related to diffusive fluxes and wetland characteristics.

To collect samples, my lab-mates and I filled small vials with wetland water at each sampling location. While slowly walking forward through the wetland water, we submerged 30-milliliter glass vials at a full arm's length in front of our bodies so the samples were unaffected by disruption of wetland sediment by our footsteps. We filled the vials completely and capped them before removing them from the water. At each of the three sampling locations, we filled between one and five vials with water approximately 5 centimeters below the air-water interface. Though the number of vials collected at each location varied across the sampling season, the number of vials collected per site was always the same across the three sites on any given day. At the deep and shallow locations, we also collected vials of water from the bottom of the water column. These samples were taken at depths of approximately 0.75 meters below the air-water interface in the deep locations and approximately 0.10 meters above the substrate in shallow locations. Samples from the bottom of the water column were not used directly to calculate diffusive flux, but they informed us about the CH₄ and CO₂ gradients across the water column which provided information about the strength of vertical mixing. In total, I collected 5 sets of vials in each hour-long sampling event (deep channel surface, bottom of water column in the deep channel, shallow shelf surface, bottom of water column on the shallow shelf, and near vegetation).

Sample analysis

Once the samples were transported to the laboratory, I prepared to measure the concentrations of trace gases in each vial. We stored samples in a refrigerator at 5°C for between 20 and 26 hours before analysis. Refrigeration slowed microbe metabolism so the gas concentrations in the samples were not biologically altered. To prepare gas samples from the collected water samples, I pulled 20 milliliters of liquid from each wetland sample vial into a syringe, replacing the liquid with 20 milliliters of pure nitrogen gas to keep the pressure in the vial constant. I then drew 20 milliliters of pure nitrogen gas into the syringe so the syringe contained equal volumes of liquid sample and nitrogen gas. To ensure that the gases in the syringe liquid diffused to equilibrium across the boundary between the liquid and the nitrogen

gas, I shook the syringe for 60 seconds. Finally, I allowed the syringe to sit to equilibrate for 300 seconds.

To determine the concentrations of CO₂ and CH₄ in the equilibrated gas in the syringe, I injected the 20 milliliters of equilibrated gas from the syringe into a background stream of 410.49ppm CO₂/3.228ppm CH₄ gas flowing into a Los Gatos Research, Inc., Greenhouse Gas Analyzer (Los Gatos, California, USA). The Greenhouse Gas Analyzer recorded concentrations of CH₄, CO₂, and H₂O in the inflow stream at 1 Hertz (1 measurement per second). I repeated this injection process with each water sample and transferred the data from the Greenhouse Gas Analyzer output file to a Microsoft Excel file (Microsoft 2007). I wrote MATLAB (MATLAB R2011b) code which calculated the total concentrations of CH₄ and CO₂ in each injection of sample gas from the Microsoft Excel data file (Appendix A). Because the gas in the syringe was pure nitrogen initially, all CH₄ and CO₂ present in the injected gas sample originated in the liquid sample.

Calculation of concentrations of CH₄ and CO₂ in wetland water

I used Henry's Law (Eq. 1) to calculate the concentrations of CH₄ and CO₂ in liquid samples from their concentrations in injected syringe gas. Henry's Law is written:

$$C_l(X) = K_H * pX \quad (\text{Eq. 1})$$

where X is either CH₄ or CO₂, C_l(X) is the concentration of X in equilibrated syringe liquid (mol L⁻¹), K_H is the Henry's Law constant (mol L⁻¹ atm⁻¹), and pX is the partial pressure of X in the injected gas (atm) (Dixon and Kell 1989). I calculated Henry's Law constants, K_H, for CO₂ and CH₄ using established relationships between K_H and temperature (Weiss 1974, Rettich et al. 1981). I derived partial pressures, pX, from MATLAB-calculated concentrations of CO₂ and CH₄ in injected gas using the Ideal Gas Law. After calculating the concentrations of X in equilibrated syringe liquid, I calculated concentrations of X in the wetland water samples. Since all the CH₄ and CO₂ in both the injected gas and the equilibrated syringe liquid originated in the wetland water samples, the final step to calculate concentration of X in wetland water samples ([X]_{aq}, mol L⁻¹, Eq. 2) was a sum:

$$[X]_{\text{aq}} = C_l(X) + C_g(X) * V_g * V_l^{-1} \quad (\text{Eq. 2})$$

where $C_g(X)$ is the MATLAB-calculated concentration of X in injected gas (mol L^{-1}), V_g is the volume of injected gas (L), and V_l is the volume of equilibrated syringe liquid (L). $[X]_{\text{aq}}$ represented concentrations of species in the wetland water column at the locations from which the water samples came.

Calculation of piston velocity

Piston velocity, k , is a parameter in the equation for diffusive flux. Piston velocity represents the turbulent exchange of energy between the atmosphere and the water surface and can be estimated accurately with wind and temperature-based models. To account for the temperature dependence of k , I calculated the species-specific nondimensional Schmidt number (Sc , Eq. 3 & Eq. 4) for each sample day:

$$Sc(\text{CO}_2) = 1911.11 - 118.11 * T + 3.4527 * T^2 - 0.041320 * T^3 \quad (\text{Eq. 3})$$

$$Sc(\text{CH}_4) = 1897.8 - 114.28 * T + 3.2902 * T^2 - 0.039061 * T^3 \quad (\text{Eq. 4})$$

where T is the average water temperature ($^{\circ}\text{C}$) between 11:00am and 1:00pm on sampling days measured by field equipment (Wanninkhof 1992). The value of k also depends on the wind speed measured 10 meters above the water surface (U_{10} , m s^{-1}). I obtained wind speed data corresponding to each sampling event from the Gill WindMaster Pro 3D Sonic Anemometer (Serial: 000022, Gill Instruments Ltd, Lymington, Hampshire, UK) at the Mayberry wetland. Because the sonic anemometer measured wind speed 2 meters above the surface, I extrapolated U_{10} from this wind data using the log wind profile (Eq. 5) which describes the relationships between wind speeds at different heights from the surface:

$$U_{10} = \frac{U_m}{0.41 * \log\left(\frac{(10-d_0)}{z_{0m}}\right)} \quad (\text{Eq. 5})$$

where U_m is the measured wind speed (m s^{-1}), d_0 is the displacement height (m), and z_{0m} is the roughness length (m). The parameters d_0 and z_{0m} depend on wind direction and the height of the plant canopy and were calculated iteratively for each sample day. Generally, d_0 was 65% of the average height of the plant canopy and z_{0m} was 10% of the average height of the plant canopy. Once $Sc(X)$ and U_{10} were determined, I calculated k (m d^{-1} , Eq. 6) for each species (Matson and Harriss 1995).

$$k(X) = 0.45 * U_{10}^{1.6} * (Sc(X)/600)^{-0.5} \quad (\text{Eq. 6})$$

Calculation of diffusive flux

I used calculated concentrations and piston velocities to calculate diffusive fluxes at each sampling location for each sampling day. Diffusion from water to atmosphere depends on the difference between the concentrations of gases in the atmosphere and below the water surface and the piston velocity of the system. An equation for diffusive flux (Eq. 7) is:

$$F(X) = k(X) ([X]_{\text{aq}} - [X]_{\text{eq}}) \quad (\text{Eq. 7})$$

where $F(X)$ is diffusive flux of X ($\text{mol m}^{-2} \text{d}^{-1}$), $k(X)$ is piston velocity (m d^{-1}), and $[X]_{\text{aq}}$ is the aqueous concentration of the species in the top of the water column (mol L^{-1} or 10^3 mol m^{-3}). As noted above, I calculated $[X]_{\text{aq}}$ by summing the concentrations of X in the equilibrated syringe liquid and the injected gas. $[X]_{\text{eq}}$ is the equilibrium liquid concentration of the species corresponding to its partial pressure in the gas above the water (mol L^{-1} or 10^3 mol m^{-3}) (Cole et al. 2010). $[X]_{\text{eq}}$ is determined by multiplying the appropriate Henry's constant, K_H , by the atmospheric partial pressures of each species on each sample day between 11:00am and 1:00pm as measured by LI-7500 and LI-7700 open-path analyzers (LI-COR, Lincoln, Nebraska, USA).

Statistical analysis of flux variation with season

To determine the effects of time on wetland diffusive fluxes, I performed two repeated measures ANOVAs in which the repeated measures factor was time and the measurement

locations were the subjects. The response variables were the average calculated diffusive fluxes of CH₄ and CO₂ at each site on each day. The first null hypothesis was that there was no difference over time in the mean diffusive fluxes of CH₄ at shallow, deep, and vegetated locations. The associated alternative hypothesis was that there were differences between mean fluxes of CH₄ at these sites for at least two sampling days. The second null hypothesis was that there was no difference over time in the mean diffusive fluxes of CO₂ at shallow, deep, and vegetated locations. The associated alternative hypothesis was that there were differences between mean fluxes of CO₂ at these sites for at least two sampling days.

Statistical analysis of flux variation with location

To determine the effects of water table depth and vegetative cover on wetland diffusive fluxes, I performed four two-sample t-tests for each sample day. For each day, the first null hypothesis was that there was no difference in the mean diffusive fluxes of CH₄ at shallow and deep sites on a given day. The second null hypothesis was that there was no difference in the mean diffusive fluxes in CO₂ at shallow and deep sites on a given day. The third null hypothesis was that there was no difference in the mean diffusive fluxes of CH₄ at open water and vegetated sites on a given day. The fourth null hypothesis was that there was no difference in the mean diffusive fluxes of CO₂ at open water and vegetated sites on a given day. In all cases, my alternative hypotheses stated that differences in diffusive fluxes of CH₄ or CO₂ existed between deep and shallow or open and vegetated sites on a given day. I looked for significant differences between deep and shallow or open and vegetated sites on each sample day using a significance level of 0.05.

Statistical analysis of flux variation with concentration, wind, and surface temperature

To determine the relative impacts of the parameters in the flux equation on diffusive fluxes of CH₄ and CO₂, I examined graphs of each parameter against the fluxes at the deep open water site for the entire sampling season. The three primary parameters in the diffusive flux calculation are the concentration gradient, wind turbulence, and water surface temperature. I

initially plotted graphs (three for CH₄ flux and three for CO₂ flux) of each parameter as the independent variable and the associated flux as the dependent variable. If the graphs showed no relationship between the variables, I stopped the analyses. If the graphs showed linear trends between parameters and fluxes, I quantified the relationships using correlation coefficients.

Qualitative analysis of the relationship between CH₄ flux and dissolved oxygen

To further explore the relationship between measured fluxes and physical variables, I plotted the dependence of CH₄ flux at the deep open water site on dissolved oxygen levels in the wetland water. I acquired 30 minute average dissolved oxygen levels corresponding to my sample days from a CS511 dissolved oxygen sensor (Campbell Scientific, Logan, Utah, USA) near the deep wetland location. I averaged the dissolved oxygen levels between 11:00am and 1:00pm on these days. I then color-coded the plotted data points by the corresponding friction velocity to separate the effects of dissolved oxygen alone from the effects of wind-driven mixing.

Comparison of diffusive fluxes and total fluxes of CH₄ and CO₂

To determine the contribution of diffusion to total wetland emissions, I compared my calculated diffusive fluxes to net emissions values measured by the eddy covariance method (Baldocchi 2003). To eliminate effects of carbon exchange by plants during photosynthesis, I used averages of nighttime measurements of net CH₄ emissions and net CO₂ emissions from the wetland on the days on which I took my samples. I then recalculated diffusive fluxes of CH₄ and CO₂ using the concentration measurements from the collected water samples, but replacing the midday wind speed and temperature measurements with the nighttime averages of measurements on each day. I took this step to make the calculated diffusive fluxes and the measured net nighttime fluxes as comparable as possible. The result of dividing the nighttime diffusive fluxes by the nighttime net emissions indicates the proportion of total flux attributable to diffusion on each sample day.

RESULTS

Study site

Average midday air temperature at the Mayberry wetland varied from a high of 22.5°C during the summer to a low of 10.5°C in the winter (Table 1). Average midday atmospheric CO₂ partial pressures were highest during winter, when they were 4% greater than the summer partial pressures (Table 1). Average midday atmospheric CH₄ partial pressures were highest in the spring, when they were 6% higher than the lowest partial pressures which occurred in autumn. The variation of midday partial pressures of both CO₂ and CH₄ was very small in all seasons.

Table 1. Physical characteristics of the Mayberry wetland at midday (11:00am – 1:00pm) on days on which water samples were taken from the wetland. Table shows average values with measurement standard errors in parentheses.

| Season | Average air temperature (°C) | Average partial pressure of CO ₂ (atm) | Average partial pressure of CH ₄ (atm) |
|---------------------|------------------------------|---|---|
| Spring (3/21-6/21) | 17.9 (0.96) | 3.90E-4 (3.53E-6) | 1.93E-6 (7.94E-9) |
| Summer (6/21-9/21) | 22.5 (0.89) | 3.81E-4 (1.41E-6) | 1.94E-6 (2.05E-8) |
| Autumn (9/21-12/21) | 19.9 (1.20) | 3.92E-4 (3.93E-6) | 2.05E-6 (4.64E-8) |
| Winter (12/21-3/21) | 10.5 (0.57) | 3.96E-4 (5.53E-6) | 2.04E-6 (3.82E-8) |

Concentrations of CH₄ and CO₂ in wetland water

Concentrations of CO₂ and CH₄ in wetland water did not follow the same trends over time (Fig. 3). Using established empirical relationships and measured temperatures of liquid samples, I found that Henry's constants for CH₄ ranged from 0.0014 mol L⁻¹ atm⁻¹ to 0.0018 mol L⁻¹ atm⁻¹ and Henry's constants for CO₂ ranged from 0.0340 mol L⁻¹ atm⁻¹ to 0.0463 mol L⁻¹ atm⁻¹. Based on these Henry's constants and measurements of wetland samples, I found that the aqueous concentrations of CH₄ and CO₂ in the Mayberry wetland vary over time (Fig 3). At the shallow site, concentrations of CH₄ ranged from 252.18 nmol L⁻¹ to 2656.5 nmol L⁻¹ and concentrations of CO₂ ranged from 66.046 umol L⁻¹ to 225.49 umol L⁻¹. At the deep open water site, concentrations of CH₄ ranged from 218.46 nmol L⁻¹ to 1463.0 nmol L⁻¹ and concentrations of CO₂ ranged from 68.867 umol L⁻¹ to 228.79 umol L⁻¹. At the vegetated site, concentrations of

CH₄ ranged from 89.607 nmol L⁻¹ to 1101.9 nmol L⁻¹ and concentrations of CO₂ ranged from 112.87 umol L⁻¹ to 251.33 umol L⁻¹.

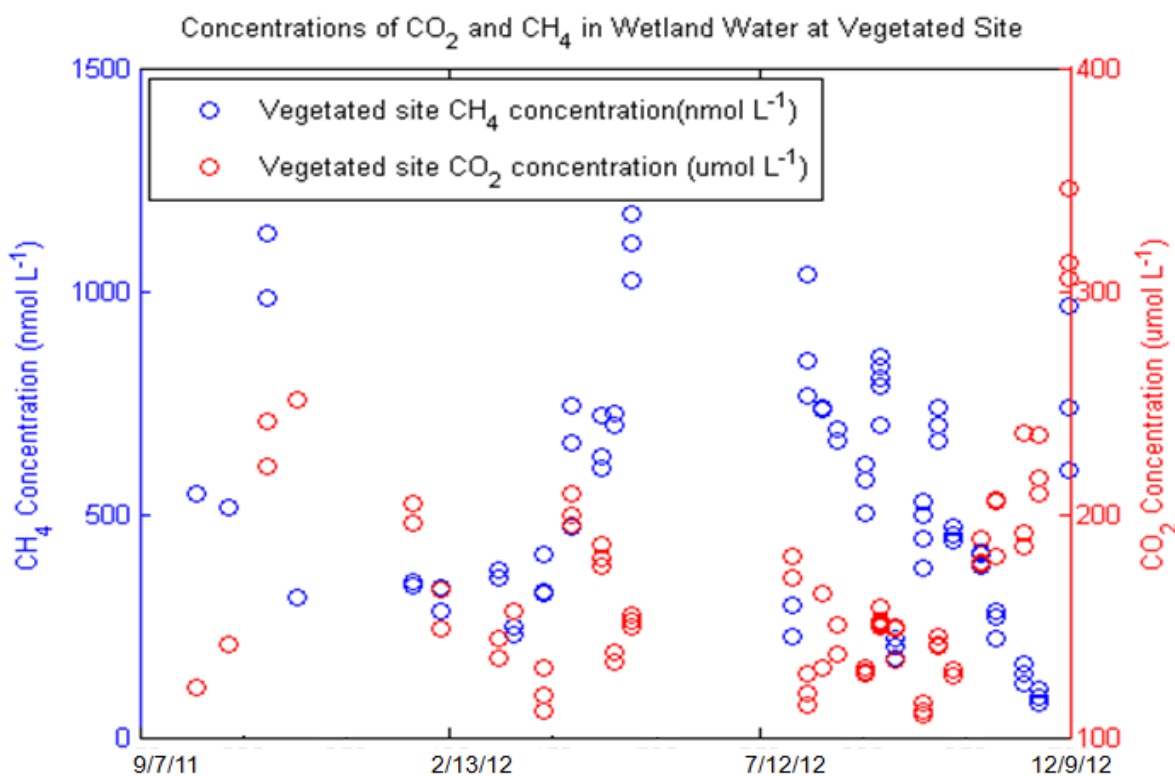


Fig. 3. Concentrations of CH₄ and CO₂ in vegetated site over time. The number of points per day represents the number of wetland water samples (between 1 and 5) collected on that day.

Piston velocity

Piston velocities vary throughout a single day by a factor of 10 as a result of different conditions during night and day. Between 11:00am and 1:00pm, piston velocities for CH₄ varied from 2.7694E-6 m s⁻¹ to 3.1254E-5 m s⁻¹ throughout the sampling season. Between 11:00am and 1:00pm, piston velocities for CO₂ varied from 2.7968E-6 m s⁻¹ to 3.1669E-5 m s⁻¹ throughout the sampling season.

Diffusive flux

CH₄ fluxes out of the wetland were more influenced by time of year than by location (Fig. 4). During the growing season in 2012, the shallow and deep open water sites both generally had higher diffusive fluxes of CH₄ than the vegetated site. During winter months, all CH₄ fluxes were less than approximately 5 nmol m⁻² s⁻¹. CH₄ fluxes at the shallow site varied from 0.83749 nmol m⁻² s⁻¹ to 40.070 nmol m⁻² s⁻¹. CH₄ fluxes at the deep open water site varied from 0.66805 nmol m⁻² s⁻¹ to 21.596 nmol m⁻² s⁻¹. CH₄ fluxes at the vegetated site varied from 0.26722 nmol m⁻² s⁻¹ to 19.834 nmol m⁻² s⁻¹.

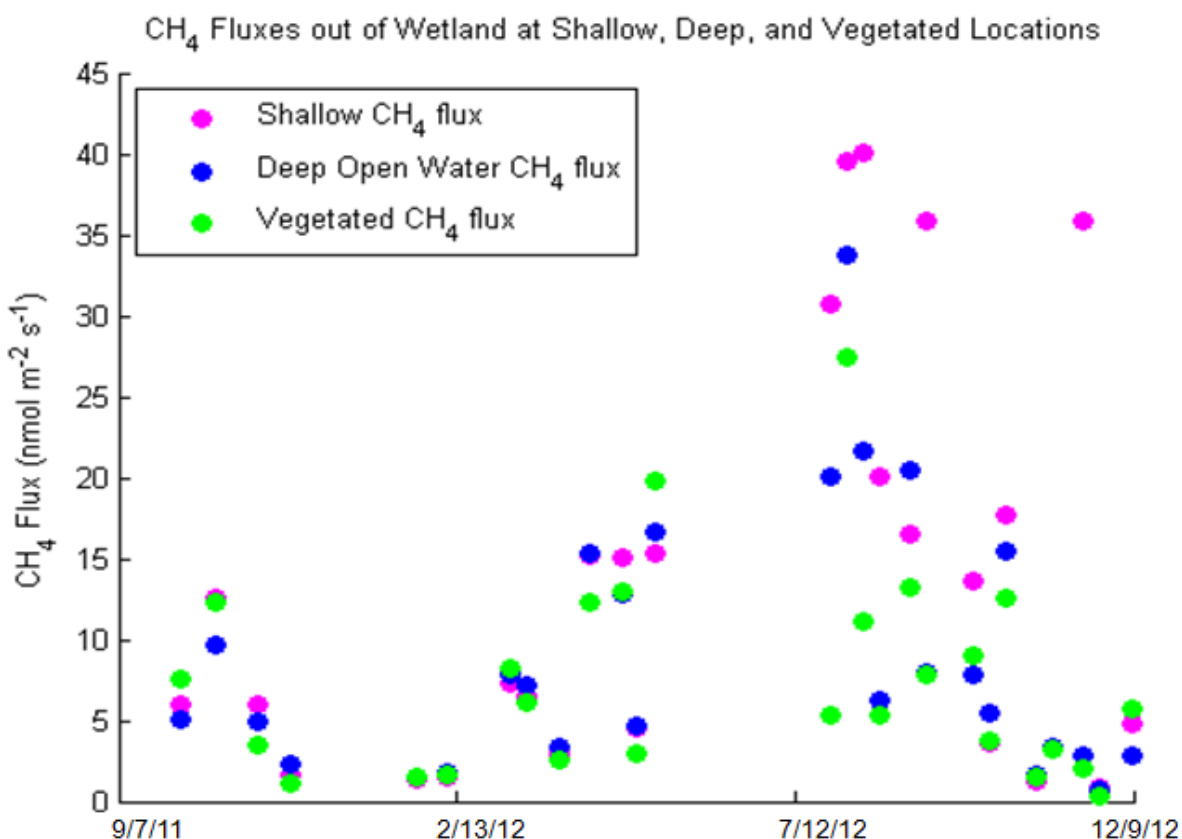


Fig. 4. Average daily CH₄ diffusive fluxes out of three wetland locations. Fluxes shown represent daily averages of samples taken from shallow, deep, and vegetated sites on days between 10/4/2011 and 11/29/2012.

CO₂ fluxes also varied throughout the year, but CO₂ fluxes at the three sites were generally similar on each sample day (Fig. 5). CO₂ fluxes at the shallow site varied from 0.54395 umol m⁻² s⁻¹ to 3.5110 umol m⁻² s⁻¹. CO₂ fluxes at the deep open water site varied from

0.57825 $\text{umol m}^{-2} \text{s}^{-1}$ to 3.5353 $\text{umol m}^{-2} \text{s}^{-1}$. CO_2 fluxes at the vegetated site varied from 0.50437 $\text{umol m}^{-2} \text{s}^{-1}$ to 3.7222 $\text{umol m}^{-2} \text{s}^{-1}$.

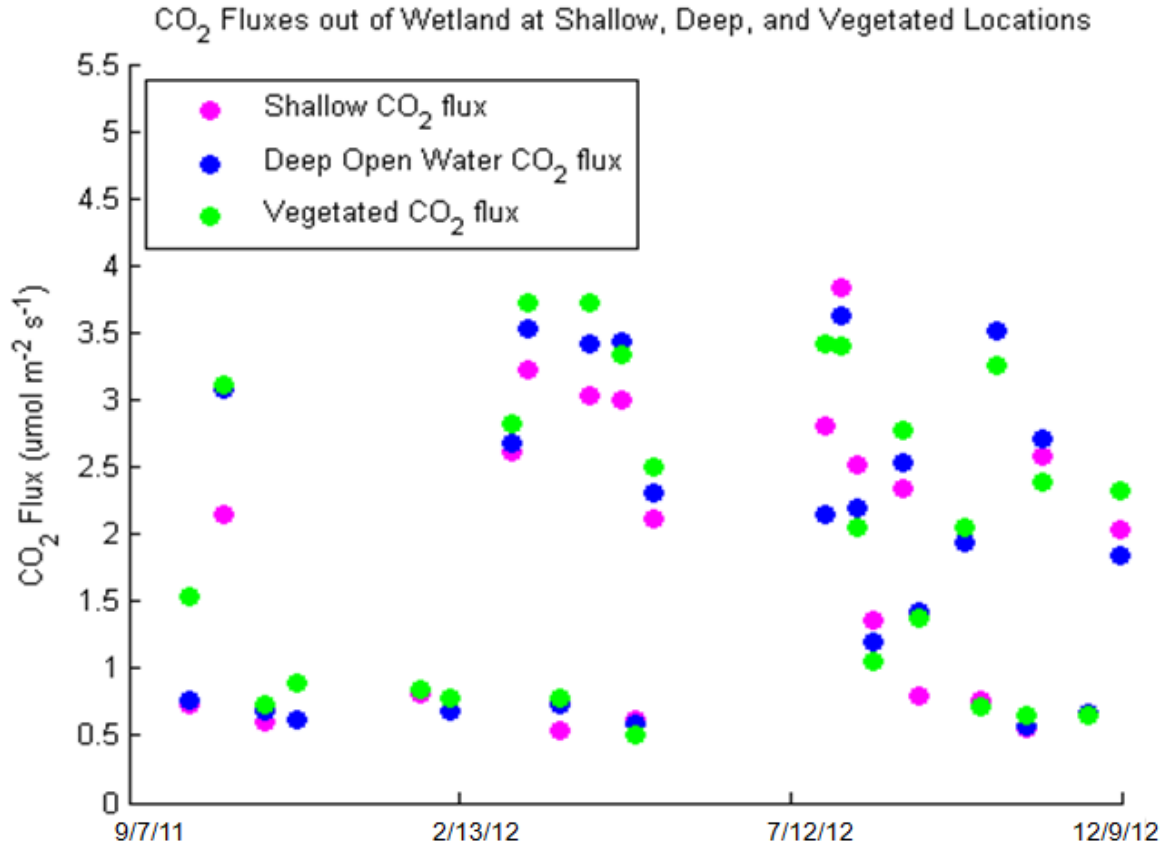


Fig. 5. Average daily CO_2 diffusive fluxes out of three wetland locations. Fluxes shown represent daily averages of samples taken from shallow, deep, and vegetated sites on days between 10/4/2011 and 11/29/2012.

Diffusive flux variation with season

Seasons influence the flux differences between the three wetland locations tested. Over the entire sampling period, time of year had a statistically significant effect on CH_4 fluxes ($F(27,54) = 3.44555$, $p < 0.05$) and on CO_2 fluxes ($F(27,54) = 2.03371$, $p < 0.05$).

Diffusive flux variation with location

CH₄ flux differed significantly between shallow and deep locations on 7 of the 25 sample days (11/8/2011, 8/30/2012, 9/6/2012, 9/20/2012, 10/18/2012, 11/8/2012, and 11/29/2012, $p < 0.05$, Appendix B). CO₂ flux differed significantly between shallow and deep locations on 9 of the 25 sample days (3/20/2012, 4/3/2012, 5/2/2012, 7/19/2012, 8/9/2012, 8/23/2012, 8/30/2012, 9/6/2012, and 11/8/2012, $p < 0.05$, Appendix C). 8/30/2012, 9/6/2012, and 11/8/2012 had significant differences between fluxes at shallow and deep locations for both gases.

CH₄ flux differed significantly between the open water and the vegetated areas on 8 of the 25 sample days (11/8/2011, 3/20/2012, 4/24/2012, 8/23/2012, 9/6/2012, 10/4/2012, 11/8/2012, and 11/29/2012, $p < 0.05$, Appendix D). 7 of these 8 significant differences occurred on days on which CH₄ fluxes in the open water location exceeded fluxes in the vegetated location. Even on days where significant differences did not exist between these two locations, average CH₄ fluxes were generally higher in the open water location than the vegetated location.

CO₂ flux differed significantly between open water and vegetated areas on 6 of the 25 sample days (5/2/2012, 7/19/2012, 8/23/2012, 9/6/2012, 10/18/2012, and 11/29/2012, $p < 0.05$, Appendix E). 5 of these 6 significant differences occurred on days on which CO₂ fluxes in the vegetated location exceeded fluxes at open water. Even on days where significant differences did not exist between these two locations, average CO₂ fluxes were generally higher in the vegetated location than the open water location. Only 08/23/2012, 9/6/2012, and 11/29/2012 had significant differences between fluxes at vegetated and open water locations for both gases.

Diffusive flux variation with concentration, wind, and temperature

Plots of diffusive fluxes of CH₄ in deep open water against parameters of the flux equation indicate that wind turbulence is the strongest driver of diffusive fluxes of CH₄, but that concentrations of CH₄ and water temperatures also affect fluxes. There is a strong linear trend between diffusive fluxes of CH₄ and friction velocity, a measure of wind turbulence at the surface of the water ($r^2 = 0.7641$, Fig. 6c). There is also a moderate linear trend between CH₄ concentration and CH₄ diffusive flux ($r^2 = 0.5468$, Fig. 6a). There is not a linear relationship

between water temperature and diffusive flux of CH₄, but the variation in flux increases as temperature increases (Fig. 6b).

Plots of diffusive fluxes of CO₂ in deep open water against parameters to the flux equation demonstrate that wind turbulence is also the strongest driver of diffusive fluxes of CO₂. There is a strong linear trend between friction velocity and diffusive flux ($r^2=0.8401$, Fig. 6f). There is no relationship between diffusive fluxes of CO₂ and CO₂ concentration or water temperature (Fig. 6d-e).

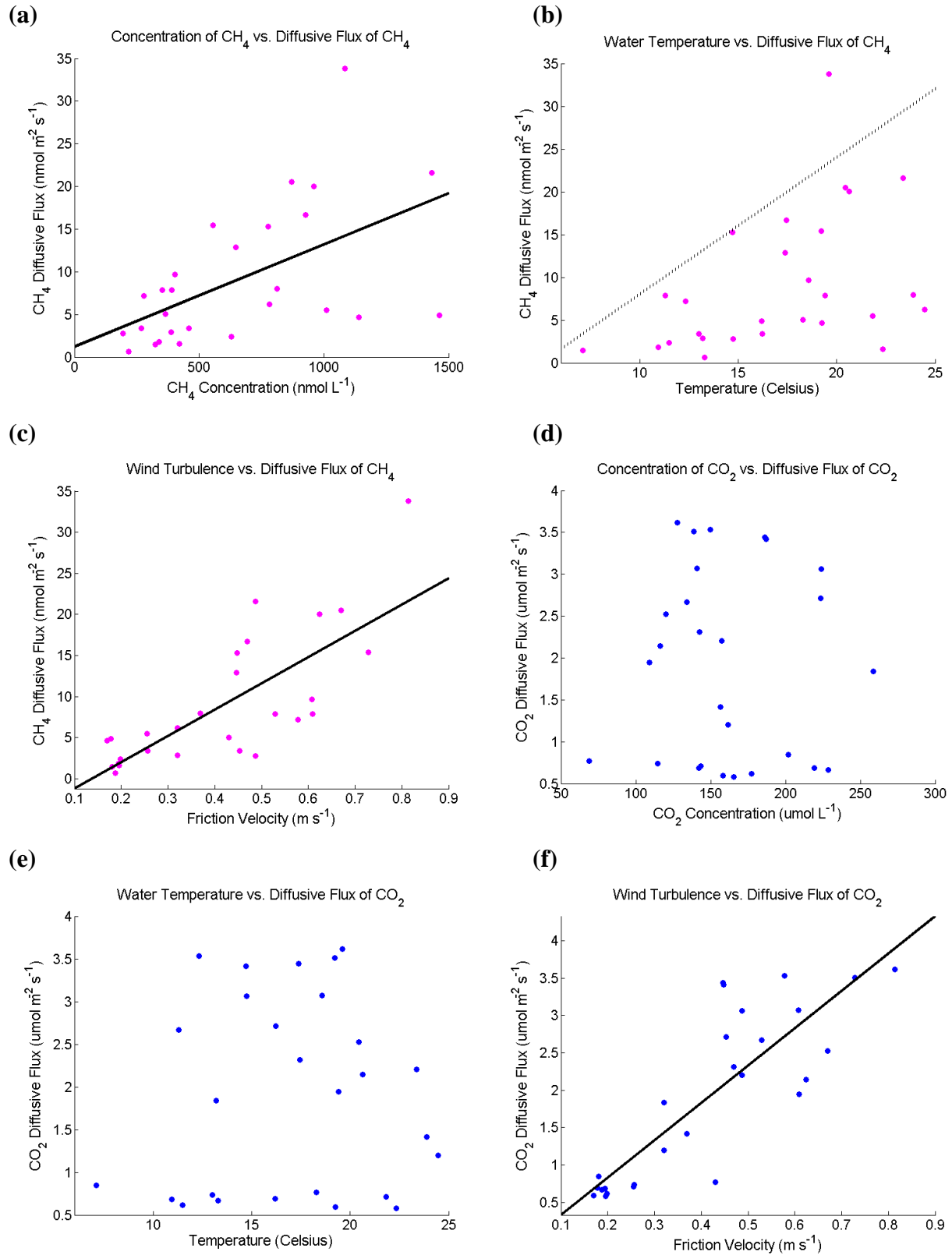


Fig. 6. Dependence of CO_2 and CH_4 diffusive fluxes on aqueous CO_2 and CH_4 concentrations, friction velocities, and water temperatures. All graphs show diffusive fluxes from the deep open water location.

Relationship between CH₄ diffusive flux and dissolved oxygen

Dissolved oxygen levels and CH₄ diffusive fluxes show a moderate linear relationship ($r^2=0.6523$, Fig. 7). Generally, higher dissolved oxygen levels occur at higher wind speeds.

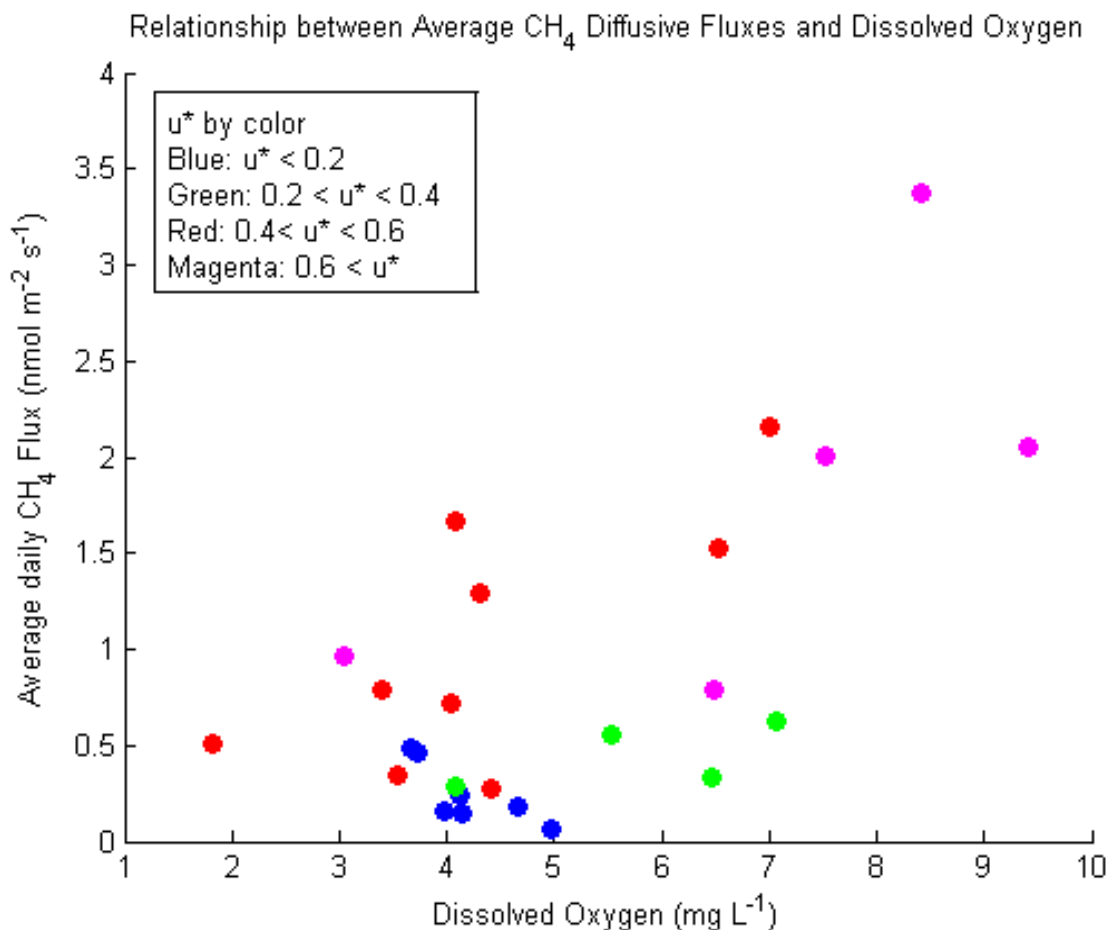


Fig. 7. Relationship between CH₄ diffusive fluxes, dissolved oxygen, and friction velocity (u^*). Friction velocity is measured in units of $m s^{-1}$. Note that dissolved oxygen generally increases with u^* .

Comparison of diffusive fluxes and total fluxes of CH₄ and CO₂

On about half (8 of 21) of the days for which I have CH₄ diffusive and total flux data, the ratio of diffusive flux of CH₄ to total flux of CH₄ was greater than 1. These ratios varied from 1.04 to 5.43 with one exceptional ratio of 683.53 (Fig. 8a). On about half (10 of 21) of the days for which I have CO₂ diffusive and total flux data, the ratio of diffusive flux of CO₂ to total flux of CO₂ was greater than 1, varying from 1.33 to 4.94 (Fig. 8b). When considering only the days

on which diffusive to total flux ratios were between 0 and 1, diffusive fluxes of CH_4 range from 1.0% to 95.4% of total flux with an average of 19.1%. On the same days, diffusive fluxes of CO_2 ranged from 13.1% to 93.9% of total flux with an average of 44.3%.

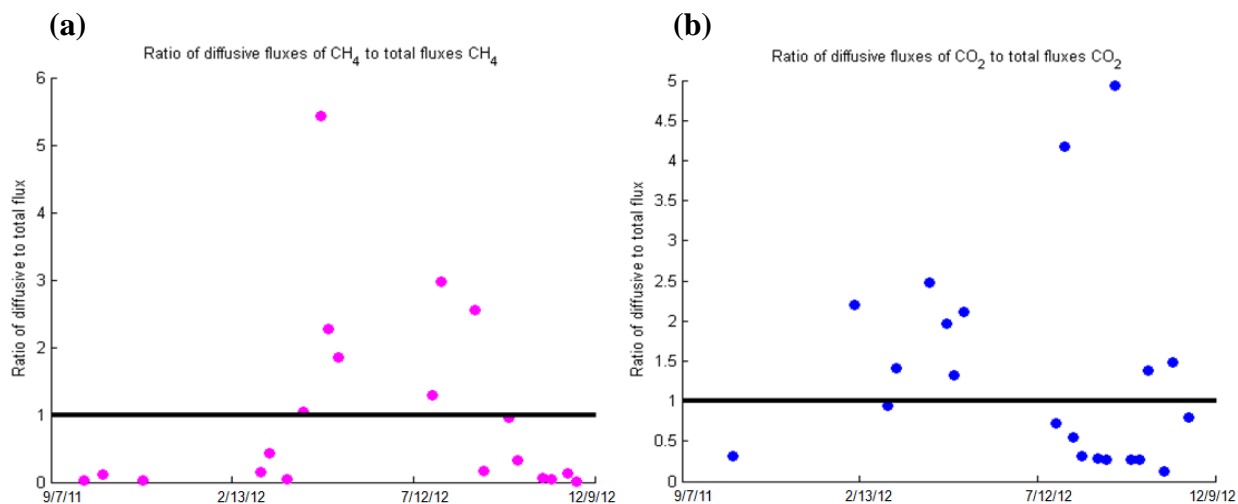


Fig. 8. Ratio of diffusive fluxes of CH_4 and CO_2 to total fluxes of CH_4 and CO_2 . A ratio of 1 indicates that the diffusive flux is equal to the total flux (i.e. diffusive flux accounts for all of the total flux). Ratios greater than 1 indicate that diffusive flux is greater than total flux; these high ratios are probably artifacts of the models I chose. Outliers with values greater than 2 standard deviations from the mean have been eliminated from these plots.

DISCUSSION

Quantifying the relationship between wetland characteristics and diffusive fluxes of CH_4 and CO_2 paints a more complete picture of the carbon cycle and provides important baseline information as politicians and industry discuss strategies for greenhouse gas emission reductions. This study determined that seasonal, wetland-scale variables had the largest influences on diffusive fluxes of both gases. In contrast to my first hypothesis, I found that CH_4 and CO_2 fluxes were not consistently different between deep and shallow field sites. My second hypothesis was supported by this study, with higher diffusive fluxes of CO_2 consistently occurring near vegetation and lower diffusive fluxes of CH_4 consistently occurring near vegetation. The primary physical driver of diffusive fluxes of CH_4 and CO_2 is wind turbulence, though concentration gradients also impact CH_4 fluxes. A positive linear relationship between CH_4 flux and dissolved oxygen indicates that CH_4 diffuses most when water is well-mixed.

Concentrations of CH₄ and CO₂ in wetland water

The lack of relationship between concentrations of CH₄ and CO₂ over time suggests that these gases are produced and released in wetlands by different biogeochemical processes. CO₂ is primarily added to wetland systems through photosynthesis, but can be released into the air or water by respiration of plant leaves and roots (Hatala et al. 2012). In flooded conditions, decomposition and respiration occur slowly with surges of CO₂ released following large water table fluctuations (Hatala et al. 2012). Perhaps some of the variability in CO₂ concentrations can be attributed to manipulation of the wetland water table. CH₄, on the other hand, is produced by soil methanogens in wetlands (Bossio et al. 2006) and is oxidized by methanotrophs particularly at low temperatures (Ding et al. 2004). I observed low concentrations of CH₄ during the winter months, which could be due to inhibition of methanogenesis at low temperatures (Ferry 1993).

In addition to production differences, transport and chemical processes can account for differences in concentrations of CH₄ and CO₂. Calculated Henry's constants for CH₄ ranged from 0.0015 mol L⁻¹ atm⁻¹ to 0.0017 mol L⁻¹ atm⁻¹ while Henry's constants for CO₂ ranged from 0.0354 mol L⁻¹ atm⁻¹ to 0.0458 mol L⁻¹ atm⁻¹. The difference in Henry's constants indicates that CO₂ is approximately 25 times more soluble in water than CH₄. In isolation, this difference only accounts for differences in magnitudes of concentration. However, different solubilities promote different interactions between CO₂ and CH₄ and various environmental variables in the air and the water (Wanninkhof et al. 2009). For example, low wind speeds might cause significant emissions of CH₄ while having a smaller effect on more soluble CO₂. The low covariance between CO₂ and CH₄ concentrations in the water over time demonstrates that CH₄ and CO₂ production and transport processes occur at different time scales.

Diffusive fluxes of CH₄ and CO₂ in wetland water

The similarity of flux trends among sites over time may imply that these gases are driven from the system by the same physical variables. Both CH₄ and CO₂ have higher diffusive fluxes in the growing season, the period in which the wetland has net uptake of carbon. This seasonal similarity suggests that the most important drivers of diffusive fluxes in the Mayberry wetland are shared physical drivers like wind and atmospheric stability that vary seasonally (Wanninkhof

et al. 2009). While these common forcing phenomena explain the general similarity in CH₄ and CO₂ flux trends, the trends certainly do not align perfectly. In addition to different temporal trends in production of these gases, surface films could complicate our understanding of common physical flux drivers. Surface films are layers on the wetland water surface that can interact with diffusing gases chemically, biologically, or physically (Happell et al. 1995). On one hand, surface films could act as a shared barrier to CO₂ and CH₄ fluxes; on the other hand, these films could enhance flux differences if their permeability is different for each gas (Happell et al. 1995, Matthews et al. 2003).

Controls of diffusive fluxes of CH₄ and CO₂

Season

The finding that seasons had a large effect on CH₄ and CO₂ diffusive fluxes suggests that variables with annual seasonal cycles are the most important controls on diffusive flux. Though much of the existing literature on greenhouse gas fluxes from wetlands averages fluxes over long timescales (Barber et al. 1988, Happell et al. 1995), significant differences by month or season exist (Belger et al. 2011, Mander et al. 2011). CH₄ fluxes in both shallow and deep sites were greatest during the summer months of July through September 2012. One variable that helps explain high summer fluxes is temperature. Water temperature, which varied from 5.76°C to 21.91°C at a height of 10cm above the soil, affects the rate of degassing from the water column with higher diffusive fluxes at higher temperatures (Ding and Cai 2007, Mander et al. 2011). Variations in water temperature can indirectly cause seasonal trends in gas fluxes because CH₄ and CO₂-producing microbes perform better at specific temperatures (Ferry 1993). With more summer microbial activity and plant growth, there are larger pools of CO₂ and CH₄ in the soil acting as sources of diffusing gases.

Location in wetland

Although significant differences exist on some days between shallow and deep locations, the lack of trend in these differences over time suggests that depth does not consistently affect

diffusive flux (Herbst et al. 2011). The days with significant differences were spread throughout the year indicating that growing season does not influence deep and shallow areas differently or that mixing in the wetland obscures initial differences. It is also interesting to note that average calculated diffusive fluxes on each sample day are not consistently greatest or least in either deep or shallow locations. The number of variables affecting diffusive flux is too great for flux differences to be seen when comparing only water depth over time (Blodau and Moore 2002).

On the other hand, vegetation seems to have a stronger influence on both CH₄ and CO₂ fluxes. There were generally higher diffusive fluxes of CH₄ in open water than in the vegetated location (Miller 2011). This trend could indicate that plants play a significant role in direct removal of CH₄ from wetlands. CH₄ can move through plant tissue directly from soil to air thus plants can remove CH₄ that otherwise might exit the wetland by diffusion (Morrissey et al. 1993). In the open water, stocks of CH₄ in the soil are not depleted by plant transport.

Fluxes of CO₂ at vegetated and open water locations demonstrate a trend opposite to fluxes of CH₄; vegetated areas generally had higher average fluxes of CO₂. This trend could be due to increased carbon inputs to the soil around vegetation patches from photosynthesis and decomposition of plants (Mander et al. 2011). In locations with more carbon inputs, there is more CO₂ in the soil to diffuse out of the wetland. Interestingly, the period between 7/12/12 and 12/9/12 had more variation in the location of highest flux. This increase in variability in the later months could be due to changes in the plant community (Miller and Fujii 2010). Since the wetland was restored in 2010, plant growth has occurred. Perhaps as plants spread across the wetland and deposit more total carbon in the system, proximity to plants affects CO₂ diffusive fluxes less. Diffusion of CH₄ is greatest in open water while diffusion of CO₂ is greatest near plants.

Concentration, wind, and water temperature

The linear trend between diffusive fluxes and wind speed indicates that turbulence is the most important driver of CO₂ and CH₄ diffusive fluxes in this system. Wind speed, surface water temperature, and concentration gradient are the three main parameters in the calculation of diffusive flux (Wanninkhof et al. 2009). I observed no relationship between CO₂ diffusive flux and temperature or CO₂ diffusive flux and CO₂ concentration, suggesting that temperature and

CO₂ concentration gradients have little effect on diffusion. A relatively strong linear trend between diffusive fluxes of both gases and wind speed suggests that physical turbulence drives diffusion (Sebacher et al. 1983, Wanninkhof et al. 2009).

The linear trend between diffusive flux of CH₄ and concentration of CH₄ in the wetland indicates that gradients in concentration are a second important driver of CH₄ diffusive flux in this system. The relationship between diffusive flux and concentration ($r^2=0.5468$) is somewhat weaker than the relationship between diffusive flux and wind speed ($r^2=0.7641$), but much more linear than the relationship between diffusive flux and temperature. The dependence of CH₄ flux on concentration makes physical sense because emissions of sparingly soluble gases like CH₄ are rate limited by molecular diffusion through water which depends on concentration gradients (Wanninkhof et al. 2009).

In the Mayberry wetland, diffusive fluxes of CH₄ remained below 8 nmol m⁻² s⁻¹ when average temperature was less than 14°C. These low fluxes are likely due to the inhibition of methanogenesis that occurs below 15°C (Ferry 1993). Less production of CH₄ results in lower diffusion of CH₄ because concentration gradients between water and air are weaker (Wanninkhof et al. 2009). As average daily temperatures increased, flux variability and maximum diffusive fluxes increased. These trends suggest that high temperature is necessary but not sufficient for high CH₄ diffusive fluxes (Ding and Cai 2007). Other factors, like the amount of dissolved oxygen, can control production of CH₄ at high temperatures (Herbst et al. 2011). Once temperatures are high and methanogenesis establishes strong concentration gradients, wind speed and turbulence can cause higher or lower fluxes (Wanninkhof et al. 2009).

Dissolved oxygen

Surprisingly, CH₄ diffusive flux is loosely positively associated with dissolved oxygen in the Mayberry wetland. CH₄ production generally peaks in anaerobic conditions, thus I expected to see higher CH₄ fluxes associated with lower dissolved oxygen (Blodau and Moore 2002, Belger et al. 2011). This unexpected result can be explained by considering how wind turbulence contributes to both dissolved oxygen and diffusive fluxes. Turbulence mixes the wetland water column, incorporating oxygen from the air. Turbulence also causes diffusion of CH₄ out of the water column (Wanninkhof et al. 2009). An examination of wind speed at the

Mayberry wetland demonstrated that both dissolved oxygen and diffusion increased generally with wind speed. These trends suggest that conditions of low dissolved oxygen do not persist for enough time to generate significant CH₄ concentration gradients and high diffusive fluxes.

Comparison of diffusive fluxes and total fluxes of CH₄ and CO₂

The finding that diffusive fluxes of CH₄ and CO₂ are on the same order of magnitude as total fluxes indicates that diffusive fluxes are a significant contributor to wetland emissions. Since diffusive flux is a component of total flux, the ratio of diffusive to total flux should be less than or equal to 1. Some of the ratios calculated were greater than 1, possibly due to incompatibility of the models I used to calculate diffusive flux and the total flux. The total flux values are averaged total fluxes for the entire wetland (Baldocchi 2003). Because the wetland includes vegetated areas with low wind turbulence and thus low total flux, the total actual flux is lower than it would be if the wetland were entirely open. The wind model which I use to calculate diffusive fluxes was built primarily for open lakes without vegetation to break up wind patterns (Matson and Harriss 1995). Although wind-based calculations of piston velocity are appropriate for wetlands (Matthews et al. 2003), use of a wind-based model generates the maximum diffusive fluxes for given concentrations of CH₄ or CO₂ based on the assumption that no vegetation attenuates wind across the wetland. Since the total measured fluxes do account for areas of the wetland sheltered from the wind, the total calculated flux can be lower than calculated diffusive flux.

The finding that diffusive flux, on average, is responsible for 19.1% of total CH₄ flux is comparable to the finding that diffusive fluxes account for 13%-33% of total fluxes of CH₄ in Florida marshes and mangrove ponds (Barber et al. 1988). In these Florida systems, total CH₄ fluxes exceeded diffusive fluxes by factors of 10 in areas of high ebullition (Barber et al. 1988). On about half (6 of 13) of the days when the ratio of diffusive CH₄ flux to total flux was between 0 and 1, total CH₄ fluxes at Mayberry wetland exceeded diffusive fluxes by factors greater than 10. It is possible that these days were days of high ebullition in the wetland. Ebullition in the wetland would increase the total flux without affecting samples taken to calculate diffusive fluxes because ebullition occurs so sporadically (Varadharajan and Hemond 2012).

One remarkable difference between diffusive and total flux occurred on 9/6/2012 (not shown on Fig. 8a) when the calculated diffusive flux was almost 700 times greater than the measured total flux. This difference could be an indication of ebullition at the sample location. If ebullition occurred during the sampling event, the measured concentration and thus calculated flux would have been high, but the measured average net flux would not have reflected this temporally distinct surge as strongly. These results indicate that both ebullition and diffusion are important CH₄ transport processes and that their relative importance varies over time (Whalen 2005).

Limitations and future directions

The scope of my study prevents me from making broad, wetland scale inferences. My samples were collected at 3 locations, so I cannot apply my conclusions to wetland areas that are very different from these sites. Another limiting factor is the recent restoration of the Mayberry wetland because the first few years since restorations are usually not typical of the years once a steady community is established (Miller 2011). In addition to questions about spatial variation, my study brings up questions of variability in measurement at a single location. It is possible that 3 replicate vials are not enough to capture the variability in concentration at one sample site on a sample day.

Limitations in spatial scale could be addressed by a future study that examines more locations, perhaps over a shorter sampling season. A study that accounts for the extreme heterogeneity of a wetland landscape could further explore the differences in flux by location.

Broader implications

My study shows that movement of gases in wetlands varies seasonally. There are large seasonal flux trends across the whole wetland and smaller flux trends within seasons at each location. Diffusive fluxes do not necessarily follow patterns of net fluxes, implying a more complex relationship between diffusion, ebullition, and plant transport than was previously acknowledged. Physical processes, such as wind, drive diffusion of CH₄ and CO₂. While depth

is unimportant in controlling diffusive fluxes, proximity to vegetation increases fluxes of CO₂ and decreases fluxes of CH₄.

In conclusion, I found that it is difficult to manage a wetland to minimize diffusive fluxes of greenhouse gases. Diffusive fluxes of these gases are closely intertwined with other natural wetland processes and limiting diffusive fluxes would require extensive manipulation that would destroy the integrity of the natural system. Though it does not offer insight into emission reduction strategies, this study advances the effort to locate and quantify sources of greenhouse gases.

ACKNOWLEDGEMENTS

Encouragement and expertise of members of Professor Dennis Baldocchi's Biometeorology Laboratory at UC Berkeley were critical in the conceptualization and execution of this project. I am grateful to Professor Baldocchi for welcoming me into his lab group for two years, giving me access high quality field and lab instruments, and sharing advice on everything from this project to graduate school programs. This research would have been impossible without the help of Jaclyn Hatala who spent hours helping me perfect my methods, proofreading, processing field data, and answering my questions and emails. I am grateful not only for the quantity of her assistance, but also for the superb quality of her analysis and insight. I also appreciate Joe Verfaillie's contributions including acquiring materials, writing a data collection program for the data logger, and fixing every lab-related problem imaginable. Many thanks to Sara Knox and Cristina Poindexter who collected field samples and helped me run them through the greenhouse gas analyzer when my undergraduate class schedule prevented me from taking trips to the Delta. This work was funded, in part, by the Sponsored Projects for Undergraduate Research in UC Berkeley's College of Natural Resources. On the writing and editing side, I very much appreciate thorough and thoughtful editing performed by Patina Mendez and Anne Murray. Thanks also to Toby Haas Walpert, Michelle Chang, Jeffrey Wong, Jenny Tang, Gabriella Vozza, and Robin Kim for peer editing many drafts of this thesis and to Attrace Chang for being a wonderful Environmental Sciences teammate. I appreciate Laura Gilson's willingness to teach me MATLAB tricks and her astute challenges to my methods when they were in the development stages. I thank Cindy Chen, Kelsey Udinski, and Sadie Symens for continual

encouragement. Finally, I thank Linda and Tom Gilson for their emotional support and especially for cheering me on at the Environmental Sciences Senior Thesis Symposium.

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APPENDIX A: MATLAB Code

```
%To calculate concentrations of CH4 and CO2 in wetland water from greenhouse
%gas analyzer output file and file containing measured volumes of each gas
%injection and the temperatures of the liquid following gas injection.
%This code analyzes samples from 8/10/2012
```

```
%Emily Gilson, 4/13/2012
```

```
%Before this program works:
```

```
%1. Make LGRoutput_dmonyr.csv
```

```
%2. Make TempAndVol_dmonyr.csv
```

```
%3. Look at plot and choose values for columnIndex and columnIndexEnd that
%limit the total bounds that will be examined in the peak-finding portion
%of the code.
```

```
dat =
```

```
importdata('C:\Users\Emily\Documents\Biometlab\LGRoutput_10aug12.csv','');
```

```
%load TempAndVol_dmonyr.csv file containing temp and volume information
```

```
measuredDat =
```

```
importdata('C:\Users\Emily\Documents\Biometlab\TempAndVol_10aug12.csv','');
```

```
%When MATLAB loads text files, it separates the numbers ('data') from the
```

```
%text ('colheaders') - this creates variables from the
```

```
%columns of data with the proper colheaders name
```

```
for i = 1:length(dat.colheaders)
```

```
    eval([dat.colheaders{i} ' = dat.data(:,i);']);
```

```
end
```

```
for i = 1:length(measuredDat.colheaders)
```

```
    eval([measuredDat.colheaders{i} ' = measuredDat.data(:,i);']);
```

```
end
```

```
%take a look at some plots first to make sure everything loaded properly
```

```
plot(CO2, '.')
```

```
%FIND THE START AND END BOUNDS OF THE PEAKS
```

```
%columnIndex tracks current index of the CO2 column in Excel file. Input
```

```
%values for columnIndex and columnIndexEnd based on where peaks start and
```

```
%end (observe the graph).
```

```
columnIndex = 50;
```

```
columnIndexEnd = 4000;
```

```
%peakIndex tracks current injection peak number whose interval bounds are
```

```
%being determined.
```

```
peakIndex = 1;
```

```
%pstart and pend hold the index used as the start and end bounds for each
```

```
%injection peak interval.
```

```
pstart = [];
```

```
pend = [];
```

```
%initBackground values are the background levels of CH4 and CO2 flowing
```

```
%through the LGR before peaks occur.
```

```
initBackgroundCO2 = mean(CO2(columnIndex:columnIndex+9));
```

```
initBackgroundCH4 = mean(CH4(columnIndex:columnIndex+9));
```

```
%runningBackground matrices track the background amounts of CO2 and CH4
```

```
%before each peak starts (in row 1) and after each peak ends (in row 2).
```

```

%The column index of runningBackground corresponds to the column index of
%pstart and pend.
runningBackgroundCO2 = zeros (2, 1);
runningBackgroundCH4 = zeros (2, 1);

%Loop through CO2 column in imported file to find peaks. We find the
%start and end points of peaks by finding places where the difference
%between consecutive means of 10 consecutive CO2 values exceeds a
%threshold. (The thresholds were determined by finding patterns in the data.)
while (columnIndex < length (CO2) -9) && columnIndex < columnIndexEnd
    meanPreviousTenCO2 = mean(CO2(columnIndex:columnIndex+9));
    columnIndex = columnIndex +1;
    meanCurrentTenCO2 = mean(CO2(columnIndex:columnIndex+9));
    %Loop until the difference between the mean of the previous ten values
    %and the mean of the next ten values exceeds a threshold. When it
    %does, the final value in the "meanCurrentTenCO2" is the first
    %value past the initial bound of the integral.
    while (abs(meanCurrentTenCO2 - meanPreviousTenCO2) < .5 && columnIndex <
        length(CO2) -9) && (columnIndex < columnIndexEnd)
        meanPreviousTenCO2 = meanCurrentTenCO2;
        columnIndex = columnIndex +1;
        meanCurrentTenCO2 = mean(CO2(columnIndex:columnIndex+9));
    end
    %When the initial bound of a peak is found, it is added to pstart
    if columnIndex < columnIndexEnd
        pstart(peakIndex) = columnIndex+7; %7 worked better than 8
        runningBackgroundCO2(1, peakIndex) = meanPreviousTenCO2;
        runningBackgroundCH4(1, peakIndex) = mean(CH4(columnIndex-
            1:columnIndex+8));
    end
    %Loop until the difference is less than a threshold and the values are
    %similar to the background value(has re-achieved stability). The first
    %value in "meanCurrentTenCO2" is the final bound of the integral.
    while (abs(meanCurrentTenCO2 - meanPreviousTenCO2) >= .35 ||
        (meanCurrentTenCO2 > 1.05*initBackgroundCO2)) && (columnIndex <
        columnIndexEnd)
        meanPreviousTenCO2 = meanCurrentTenCO2;
        columnIndex = columnIndex +1;
        meanCurrentTenCO2 = mean(CO2(columnIndex:columnIndex+9));
    end
    %When the final bound of a peak is found, it is added to pend
    if columnIndex < columnIndexEnd
        pend(peakIndex) = columnIndex;
        runningBackgroundCO2(2, peakIndex) =
            mean(CO2(columnIndex+1:columnIndex+10));
        runningBackgroundCH4(2, peakIndex) =
            mean(CH4(columnIndex+1:columnIndex+10));
        %Remove most recent pstart and pend if they are fake peak (values
        %differ by less than 40; most real peaks differ by at least 60).
        if (pend(peakIndex) - pstart(peakIndex)) < 40
            pstart(peakIndex) = [];
            pend(peakIndex) = [];
            runningBackgroundCO2(:,peakIndex) = [];
            runningBackgroundCH4(:, peakIndex) = [];
        else peakIndex = peakIndex +1;
        end
    end
end
end

```



```

end;

%Plot the pstart and pend points on the CO2 graph to make sure that each
%peak was correctly found.
hold on;
plot(pstart, CO2(pstart), 'r. ');
plot(pend, CO2(pend), 'r. ');
hold off;

%CALCULATE THE AREA OF EACH PEAK
%intpeak stores the result of integrating the CO2/CH4 curves for each peak
intpeakCO2 = nan(1,length(pstart));
intpeakCH4 = nan(1, length(pstart));
%intflow stores flow values for each interval. Row 1 is mean flow rate
%(mL/min). Row 2 is SD of flow rates. Row 3 is mean + SD. Row 4 is mean -
%SD. Row 5 is mean flow rate (L/s).
intflow = zeros(4, length(pstart));
%inttime stores the start times (row 1) and end times (row 2) that
%correspond to the initial and final bounds of each peak.
inttime = zeros (2, length(pstart));

for i=1:length(pstart) %loop over the number of peaks
    %integrate each peak - trapz is MATLAB's low-level integration command
    intpeakCO2(i) = trapz(StdTime(pstart(i):pend(i)),...
        CO2(pstart(i):pend(i)));
    intpeakCH4(i) = trapz(StdTime(pstart(i):pend(i)),...
        CH4(pstart(i):pend(i)));

    intflow(1, i) = mean(Flow_mL(pstart(i):pend(i)));%Mean flow (mL/min)
    intflow(2, i) = std(Flow_mL(pstart(i):pend(i)));%SD flow
    intflow(3, i) = intflow(1, i) + intflow(2, i);%Mean + SD
    intflow(4, i) = intflow(1, i) - intflow(2, i);%Mean - SD
    intflow(5, i) = intflow(1, i)/(60*1000);%Mean flow (L/s)
    inttime(1,i) = StdTime(pstart(i));%Start time
    inttime(2,i) = StdTime(pend(i));%End time
end

%CALCULATE PPM CONCENTRATIONS OF CH4 AND CO2 IN GAS FOR EACH PEAK
%Average the pre-peak and post-peak values of background CH4 and CO2 to
%determine the background levels of CH4 and CO2 for each specific peak.
avgBackgroundCO2 = mean(runningBackgroundCO2);
avgBackgroundCH4 = mean(runningBackgroundCH4);

R = 0.0821;

ppmCO2 = nan(1,length(intpeakCO2));
ppmCH4 = nan(1,length(intpeakCH4));
for i=1:length(ppmCO2)
    ppmCO2(i) =
        ((.041*R*Temp_K(i))/(Vol_L(i)*1))*((intflow(5,i)*intpeakCO2(i))-
        (intflow(5,i)*avgBackgroundCO2(i)*(inttime(2,i)-
        inttime(1,i)))+(Vol_L(i)*avgBackgroundCO2(i)));
    ppmCH4(i) =
        ((.041*R*Temp_K(i))/(Vol_L(i)*1))*((intflow(5,i)*intpeakCH4(i))-

```

```
(intflow(5,i)*avgBackgroundCH4(i)*(inttime(2,i)-  
inttime(1,i)))+(Vol_L(i)*avgBackgroundCH4(i));  
end
```

APPENDIX B: T-test Results Comparing CH₄ Fluxes at Shallow and Deep Sites**Table A1. Two-tail, two sample t-test assuming equal variance to assess significant differences between CH₄ fluxes at shallow and deep sites on sample days.** Means and standard deviations have units of mol m⁻² s⁻¹. Days with significant differences (p < 0.05) are bolded.

| | 11/8/2011 | | 1/17/2012 | | 1/31/2012 | | 2/28/2012 | | 3/6/2012 | | 3/20/2012 | | 4/3/2012 | |
|-------------|------------------|---------|-----------|---------|-----------|---------|-----------|---------|----------|---------|-----------|---------|----------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 6.0E-09 | 4.9E-09 | 1.4E-09 | 1.5E-09 | 1.6E-09 | 1.8E-09 | 7.4E-09 | 7.9E-09 | 6.5E-09 | 7.2E-09 | 3.0E-09 | 3.4E-09 | 1.5E-08 | 1.5E-08 |
| Std Dev | 1.5E-10 | 1.9E-10 | 2.0E-10 | 4.3E-11 | 2.1E-10 | 1.4E-10 | 1.6E-09 | 4.0E-10 | 5.5E-10 | 3.2E-10 | 2.7E-10 | 2.2E-10 | 1.2E-09 | 4.5E-10 |
| Deg Free | 2 | | 2 | | 2 | | 2 | | 2 | | 4 | | 4 | |
| t-statistic | 6.335 | | -0.631 | | -1.468 | | -0.426 | | -1.485 | | -1.816 | | -0.092 | |
| p-value | 0.024 | | 0.592 | | 0.280 | | 0.712 | | 0.276 | | 0.144 | | 0.931 | |

| | 4/17/2012 | | 4/24/2012 | | 5/2/2012 | | 7/19/2012 | | 7/26/2012 | | 8/2/2012 | | 8/9/2012 | |
|-------------|-----------|---------|-----------|---------|----------|---------|-----------|---------|-----------|---------|----------|---------|----------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 1.5E-08 | 1.3E-08 | 4.5E-09 | 4.7E-09 | 1.5E-08 | 1.7E-08 | 3.1E-08 | 2.0E-08 | 4.0E-08 | 3.4E-08 | 4.0E-08 | 2.2E-08 | 2.0E-08 | 6.2E-09 |
| Std Dev | 1.6E-09 | 2.0E-10 | 3.0E-10 | 2.7E-11 | 2.9E-09 | 1.8E-09 | 8.0E-09 | 4.7E-09 | 3.9E-09 | 1.8E-09 | 3.3E-10 | 1.6E-08 | 6.5E-09 | 7.6E-10 |
| Deg Free | 3 | | 4 | | 4 | | 2 | | 4 | | 2 | | 2 | |
| t-statistic | 1.922 | | -0.430 | | -0.714 | | 1.634 | | 2.327 | | 1.626 | | 2.990 | |
| p-value | 0.150 | | 0.689 | | 0.515 | | 0.244 | | 0.081 | | 0.245 | | 0.096 | |

| | 8/23/2012 | | 8/30/2012 | | 9/6/2012 | | 9/20/2012 | | 9/27/2012 | | 10/4/2012 | | 10/18/2012 | |
|-------------|-----------|---------|------------------|---------|----------|---------|------------------|---------|-----------|---------|-----------|---------|-------------------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 1.6E-08 | 2.1E-08 | 3.6E-08 | 8.0E-09 | 1.8E-08 | 5.8E-08 | 1.4E-08 | 7.9E-09 | 3.6E-09 | 5.5E-09 | 1.8E-08 | 1.5E-08 | 1.2E-09 | 1.6E-09 |
| Std Dev | 3.4E-09 | 4.3E-09 | 1.1E-08 | 5.5E-10 | 4.6E-09 | 4.7E-09 | 4.6E-09 | 6.6E-10 | 3.9E-10 | 2.1E-09 | 9.9E-10 | 1.3E-09 | 1.9E-10 | 1.8E-11 |
| Deg Free | 4 | | 8 | | 4 | | 8 | | 4 | | 4 | | 4 | |
| t-statistic | -1.278 | | 5.844 | | -10.557 | | 2.779 | | -1.489 | | 2.314 | | -3.311 | |
| p-value | 0.271 | | 0.000 | | 0.000 | | 0.024 | | 0.211 | | 0.082 | | 0.030 | |

| | 10/25/2012 | | 11/8/2012 | | 11/15/2012 | | 11/29/2012 | |
|-------------|------------|---------|------------------|---------|------------|---------|-------------------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 3.4E-09 | 3.4E-09 | 3.6E-08 | 2.8E-09 | 8.4E-10 | 6.7E-10 | 4.8E-09 | 2.9E-09 |
| Std Dev | 1.1E-10 | 2.5E-10 | 6.9E-09 | 2.1E-10 | 3.9E-10 | 3.0E-10 | 5.9E-10 | 2.2E-10 |
| Deg Free | 4 | | 4 | | 4 | | 4 | |
| t-statistic | -0.248 | | 8.299 | | 0.599 | | 5.236 | |
| p-value | 0.817 | | 0.001 | | 0.581 | | 0.006 | |

APPENDIX C: T-test Results Comparing CO₂ Fluxes at Shallow and Deep Sites

Table A2. Two-tail, two sample t-test assuming equal variance to assess significant differences between CO₂ fluxes at shallow and deep sites on sample days. Means and standard deviations have units of mol m⁻² s⁻¹. Days with significant differences (p < 0.05) are bolded.

| | 11/8/2011 | | 1/17/2012 | | 1/31/2012 | | 2/28/2012 | | 3/6/2012 | | 3/20/2012 | | 4/3/2012 | |
|-------------|-----------|---------|-----------|---------|-----------|---------|-----------|---------|----------|---------|------------------|---------|-----------------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 6.1E-07 | 6.9E-07 | 8.2E-07 | 8.5E-07 | 6.9E-07 | 6.9E-07 | 2.6E-06 | 2.7E-06 | 3.2E-06 | 3.5E-06 | 5.4E-07 | 7.4E-07 | 3.0E-06 | 3.4E-06 |
| Std Dev | 7.7E-08 | 3.3E-08 | 5.0E-08 | 1.4E-08 | 2.3E-08 | 3.1E-08 | 2.0E-07 | 1.3E-08 | 1.7E-07 | 2.2E-07 | 5.3E-08 | 5.6E-08 | 1.9E-07 | 1.3E-07 |
| Deg Free | 2 | | 2 | | 2 | | 2 | | 2 | | 4 | | 4 | |
| t-statistic | -1.356 | | -0.850 | | 0.026 | | -0.350 | | -1.544 | | -4.324 | | -2.832 | |
| p-value | 0.308 | | 0.485 | | 0.981 | | 0.760 | | 0.263 | | 0.012 | | 0.047 | |

| | 4/17/2012 | | 4/24/2012 | | 5/2/2012 | | 7/19/2012 | | 7/26/2012 | | 8/2/2012 | | 8/9/2012 | |
|-------------|-----------|---------|-----------|---------|-----------------|---------|------------------|---------|-----------|---------|----------|---------|-----------------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 3.0E-06 | 3.4E-06 | 6.2E-07 | 5.9E-07 | 2.1E-06 | 2.3E-06 | 2.8E-06 | 2.1E-06 | 3.8E-06 | 3.6E-06 | 2.5E-06 | 2.2E-06 | 1.4E-06 | 1.2E-06 |
| Std Dev | 4.7E-08 | 2.7E-07 | 8.9E-08 | 4.3E-08 | 5.8E-08 | 2.8E-08 | 1.9E-07 | 5.5E-08 | 8.4E-08 | 1.5E-07 | 3.6E-08 | 1.4E-07 | 1.8E-08 | 4.7E-08 |
| Deg Free | 3 | | 4 | | 4 | | 2 | | 4 | | 2 | | 2 | |
| t-statistic | -2.038 | | 0.499 | | -5.193 | | 4.622 | | 2.104 | | 3.041 | | 4.464 | |
| p-value | 0.134 | | 0.644 | | 0.007 | | 0.044 | | 0.103 | | 0.093 | | 0.047 | |

| | 8/23/2012 | | 8/30/2012 | | 9/6/2012 | | 9/20/2012 | | 9/27/2012 | | 10/4/2012 | | 10/18/2012 | |
|-------------|------------------|---------|------------------|---------|-----------------|---------|-----------|---------|-----------|---------|-----------|---------|------------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 2.3E-06 | 2.5E-06 | 8.0E-07 | 1.4E-06 | 2.7E-06 | 1.4E-05 | 2.0E-06 | 1.9E-06 | 7.6E-07 | 7.1E-07 | 3.5E-06 | 3.5E-06 | 5.5E-07 | 5.8E-07 |
| Std Dev | 8.2E-08 | 5.0E-08 | 1.1E-07 | 1.4E-07 | 3.6E-07 | 5.6E-07 | 9.5E-08 | 9.7E-08 | 1.5E-08 | 4.3E-08 | 8.8E-08 | 2.3E-07 | 5.1E-08 | 1.1E-08 |
| Deg Free | 4 | | 8 | | 4 | | 8 | | 4 | | 4 | | 4 | |
| t-statistic | -3.435 | | -7.962 | | -30.453 | | 1.673 | | 1.857 | | 0.012 | | -0.826 | |
| p-value | 0.026 | | 0.000 | | 0.000 | | 0.133 | | 0.137 | | 0.991 | | 0.455 | |

| | 10/25/2012 | | 11/8/2012 | | 11/15/2012 | | 11/29/2012 | |
|-------------|------------|---------|------------------|---------|------------|---------|------------|---------|
| | Shallow | Deep | Shallow | Deep | Shallow | Deep | Shallow | Deep |
| Mean | 2.6E-06 | 2.7E-06 | 1.8E-05 | 3.1E-06 | 6.6E-07 | 6.7E-07 | 2.0E-06 | 1.8E-06 |
| Std Dev | 1.3E-07 | 1.9E-07 | 1.8E-07 | 1.5E-07 | 1.1E-07 | 6.7E-08 | 2.2E-07 | 1.8E-07 |
| Deg Free | 4 | | 4 | | 4 | | 4 | |
| t-statistic | -0.952 | | 113.411 | | -0.128 | | 1.172 | |
| p-value | 0.395 | | 0.000 | | 0.904 | | 0.306 | |

APPENDIX D: T-test Results Comparing CH₄ Fluxes at Open and Vegetated Sites**Table A3. Two-tail, two sample t-test assuming equal variance to assess significant differences between CH₄ fluxes at open water and vegetated sites on sample days.** Means and standard deviations have units of mol m⁻² s⁻¹. Days with significant differences (p < 0.05) are bolded.

| | 11/8/2011 | | 1/17/2012 | | 1/31/2012 | | 2/28/2012 | | 3/6/2012 | | 3/20/2012 | | 4/3/2012 | |
|-------------|------------------|---------|-----------|---------|-----------|---------|-----------|---------|----------|---------|------------------|---------|----------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 4.9E-09 | 3.5E-09 | 1.5E-09 | 1.6E-09 | 1.8E-09 | 1.7E-09 | 7.9E-09 | 8.2E-09 | 7.2E-09 | 6.1E-09 | 3.4E-09 | 2.6E-09 | 1.5E-08 | 1.2E-08 |
| Std Dev | 1.9E-10 | 3.5E-10 | 4.3E-11 | 2.6E-11 | 1.4E-10 | 2.0E-10 | 4.0E-10 | 3.0E-10 | 3.2E-10 | 3.2E-10 | 2.2E-10 | 3.6E-10 | 4.5E-10 | 2.8E-09 |
| Deg Free | 2 | | 2 | | 2 | | 2 | | 2 | | 4 | | 4 | |
| t-statistic | 4.863 | | -2.728 | | 0.973 | | -0.947 | | 3.325 | | 3.192 | | 1.837 | |
| p-value | 0.040 | | 0.112 | | 0.433 | | 0.444 | | 0.080 | | 0.033 | | 0.140 | |

| | 4/17/2012 | | 4/24/2012 | | 5/2/2012 | | 7/19/2012 | | 7/26/2012 | | 8/2/2012 | | 8/9/2012 | |
|-------------|-----------|---------|------------------|---------|----------|---------|-----------|---------|-----------|---------|----------|---------|----------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 1.3E-08 | 1.3E-08 | 4.7E-09 | 2.9E-09 | 1.7E-08 | 2.0E-08 | 2.0E-08 | 5.4E-09 | 3.4E-08 | 2.7E-08 | 2.2E-08 | 1.1E-08 | 6.2E-09 | 5.4E-09 |
| Std Dev | 2.0E-10 | 1.2E-09 | 3.3E-10 | 8.0E-11 | 1.8E-09 | 1.3E-09 | 4.7E-09 | 1.1E-09 | 1.8E-09 | 4.4E-09 | 1.6E-08 | 3.7E-11 | 7.6E-10 | 1.5E-10 |
| Deg Free | 3 | | 3 | | 4 | | 2 | | 4 | | 2 | | 2 | |
| t-statistic | -0.099 | | 6.967 | | -2.443 | | 4.256 | | 2.332 | | 0.927 | | 1.525 | |
| p-value | 0.927 | | 0.006 | | 0.071 | | 0.051 | | 0.080 | | 0.452 | | 0.267 | |

| | 8/23/2012 | | 8/30/2012 | | 9/6/2012 | | 9/20/2012 | | 9/27/2012 | | 10/4/2012 | | 10/18/2012 | |
|-------------|------------------|---------|-----------|---------|-----------------|---------|-----------|---------|-----------|---------|------------------|---------|------------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 2.1E-08 | 1.3E-08 | 8.0E-09 | 7.8E-09 | 5.8E-08 | 3.4E-09 | 7.9E-09 | 9.0E-09 | 5.5E-09 | 3.8E-09 | 1.5E-08 | 1.3E-08 | 1.6E-09 | 1.5E-09 |
| Std Dev | 4.3E-09 | 1.3E-09 | 5.5E-10 | 5.8E-10 | 4.7E-09 | 4.0E-10 | 6.6E-10 | 1.4E-09 | 2.1E-09 | 2.1E-10 | 1.3E-09 | 4.4E-10 | 1.8E-11 | 5.6E-11 |
| Deg Free | 4 | | 8 | | 4 | | 8 | | 4 | | 4 | | 4 | |
| t-statistic | 2.835 | | 0.424 | | 20.186 | | -1.674 | | 1.366 | | 3.477 | | 2.121 | |
| p-value | 0.047 | | 0.683 | | 0.000 | | 0.133 | | 0.244 | | 0.025 | | 0.101 | |

| | 10/25/2012 | | 11/8/2012 | | 11/15/2012 | | 11/29/2012 | |
|-------------|------------|---------|------------------|---------|------------|---------|-------------------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 3.4E-09 | 3.3E-09 | 2.8E-09 | 2.0E-09 | 6.7E-10 | 2.7E-10 | 2.9E-09 | 5.8E-09 |
| Std Dev | 2.5E-10 | 4.0E-10 | 2.1E-10 | 2.9E-10 | 3.0E-10 | 4.9E-11 | 2.2E-10 | 1.4E-09 |
| Deg Free | 4 | | 4 | | 4 | | 4 | |
| t-statistic | 0.500 | | 3.532 | | 2.319 | | -3.475 | |
| p-value | 0.644 | | 0.024 | | 0.081 | | 0.025 | |

APPENDIX E: T-test Results Comparing CO₂ Fluxes at Open and Vegetated Sites**Table A4. Two-tail, two sample t-test assuming equal variance to assess significant differences between CO₂ fluxes at open water and vegetated sites on sample days.** Means and standard deviations have units of mol m⁻² s⁻¹. Days with significant differences (p < 0.05) are bolded.

| | 11/8/2011 | | 1/17/2012 | | 1/31/2012 | | 2/28/2012 | | 3/6/2012 | | 3/20/2012 | | 4/3/2012 | |
|-------------|-----------|---------|-----------|---------|-----------|---------|-----------|---------|----------|---------|-----------|---------|----------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 6.9E-07 | 7.3E-07 | 8.5E-07 | 8.4E-07 | 6.9E-07 | 7.7E-07 | 2.7E-06 | 2.8E-06 | 3.5E-06 | 3.7E-06 | 7.4E-07 | 7.9E-07 | 3.4E-06 | 3.7E-06 |
| Std Dev | 3.3E-08 | 5.0E-08 | 1.4E-08 | 2.9E-08 | 3.1E-08 | 6.9E-08 | 1.3E-08 | 1.4E-07 | 2.2E-07 | 1.9E-09 | 5.6E-08 | 7.7E-08 | 1.3E-07 | 1.4E-07 |
| Deg Free | 2 | | 2 | | 2 | | 2 | | 2 | | 4 | | 4 | |
| t-statistic | -1.052 | | 0.163 | | -1.620 | | -1.588 | | -1.199 | | -0.938 | | -2.767 | |
| p-value | 0.403 | | 0.886 | | 0.247 | | 0.253 | | 0.353 | | 0.401 | | 0.050 | |

| | 4/17/2012 | | 4/24/2012 | | 5/2/2012 | | 7/19/2012 | | 7/26/2012 | | 8/2/2012 | | 8/9/2012 | |
|-------------|-----------|---------|-----------|---------|-----------------|---------|------------------|---------|-----------|---------|----------|---------|----------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 3.4E-06 | 3.3E-06 | 5.9E-07 | 5.0E-07 | 2.3E-06 | 2.5E-06 | 2.1E-06 | 3.4E-06 | 3.6E-06 | 3.4E-06 | 2.2E-06 | 2.1E-06 | 1.2E-06 | 1.1E-06 |
| Std Dev | 2.7E-07 | 1.0E-07 | 5.4E-08 | 1.4E-08 | 2.8E-08 | 5.2E-08 | 5.5E-08 | 1.4E-07 | 1.5E-07 | 2.2E-07 | 1.4E-07 | 3.7E-07 | 4.7E-08 | 7.2E-08 |
| Deg Free | 3 | | 3 | | 4 | | 2 | | 4 | | 2 | | 2 | |
| t-statistic | 0.612 | | 2.189 | | -5.648 | | -12.124 | | 1.412 | | 0.536 | | 2.356 | |
| p-value | 0.584 | | 0.116 | | 0.005 | | 0.007 | | 0.231 | | 0.646 | | 0.143 | |

| | 8/23/2012 | | 8/30/2012 | | 9/6/2012 | | 9/20/2012 | | 9/27/2012 | | 10/4/2012 | | 10/18/2012 | |
|-------------|------------------|---------|-----------|---------|-----------------|---------|-----------|---------|-----------|---------|-----------|---------|-------------------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 2.5E-06 | 2.8E-06 | 1.4E-06 | 1.4E-06 | 1.4E-05 | 2.3E-06 | 1.9E-06 | 2.0E-06 | 7.1E-07 | 7.1E-07 | 3.5E-06 | 3.3E-06 | 5.8E-07 | 6.4E-07 |
| Std Dev | 5.0E-08 | 3.8E-08 | 1.4E-07 | 3.4E-08 | 5.6E-07 | 1.5E-07 | 9.7E-08 | 4.6E-08 | 4.3E-08 | 1.4E-08 | 2.3E-07 | 3.9E-08 | 1.1E-08 | 2.4E-08 |
| Deg Free | 4 | | 8 | | 4 | | 8 | | 4 | | 4 | | 4 | |
| t-statistic | -6.711 | | 0.573 | | 36.150 | | -2.133 | | 0.033 | | 1.843 | | -4.285 | |
| p-value | 0.003 | | 0.582 | | 0.000 | | 0.065 | | 0.976 | | 0.139 | | 0.013 | |

| | 10/25/2012 | | 11/8/2012 | | 11/15/2012 | | 11/29/2012 | |
|-------------|------------|---------|-----------|---------|------------|---------|-------------------|---------|
| | Open | Veg | Open | Veg | Open | Veg | Open | Veg |
| Mean | 2.7E-06 | 2.4E-06 | 3.1E-06 | 2.8E-06 | 6.7E-07 | 6.4E-07 | 1.8E-06 | 2.3E-06 |
| Std Dev | 1.9E-07 | 1.9E-07 | 1.5E-07 | 4.1E-07 | 6.7E-08 | 4.2E-08 | 1.8E-07 | 1.7E-07 |
| Deg Free | 4 | | 4 | | 4 | | 4 | |
| t-statistic | 2.142 | | 1.089 | | 0.499 | | -3.452 | |
| p-value | 0.099 | | 0.337 | | 0.644 | | 0.026 | |