Supplementary material for: Gareis J.A.L. & Lesack L.F.W. 2020. Ice-out and freshet fluxes of CO_2 and CH_4 across the air–water interface of the channel network of a great Arctic delta, the Mackenzie. *Polar Research 39*. Correspondence: Jolie A.L. Gareis, Department of Geography, Simon Fraser University, 8888 University Drive, Burnaby, V5A 1S6 BC, Canada. E-mail: jolieg@sfu.ca.

Estimates of gas transfer velocities in the Mackenzie River Delta

Calculating gas transfer velocities

Instantaneous gas flux rates (F-GAS) depend on two factors. The first is the gas concentration gradient in water relative to air (C_W relative to C_A), with positive gradients ($C_W > C_A$) indicating a net efflux out of the water (evasion) and negative gradients ($C_W < C_A$) indicating a net influx into the water (invasion). The second is the turbulent dissipation rate at the air–water interface, which is quantified as the gas transfer velocity (k_{GAS}) across this interface. These are used in the following equation to find the instantaneous flux:

$$F\text{-}_{GAS} = 10\ k_{GAS}\ (C_W - C_A)$$

Gas transfer velocities quantify the depth of the water column that equilibrates with the atmosphere per unit of time (Frankignoulle 1988; Wanninkhof et al. 2009). Gas transfer velocities are gas-specific but can be normalized using a Schmidt number of 600 (k_{600}, cm h^{-1}), which can be used to convert the k value for one gas to the k value for another gas. For example, k_{CO2} can be converted to k_{CH4} using the equations:

$$k_{600} = k_{CO2} * (600 / Sc\text{-}CO_2)^{-0.5}$$

$$k_{CH4} = k_{600} * (600 / Sc\text{-}CH_4)^{0.5} ,$$

where Sc-CO_2 and Sc-CH_4 are the temperature-dependent Schmidt numbers calculated according to the methods of MacIntyre et al. (1995) and Wanninkhof (1992), respectively.

The gas transfer velocity is often found for a system by monitoring changes in gas concentration over time in a closed headspace directly above the air-water interface (the floating chamber method, as in Frankignoulle 1988), thereby directly quantifying the rate at which the gas moves across this interface. For this study, however, conditions in the Mackenzie River and Delta at the time of sampling (moving ice in channels) and our method of accessing sampling sites (either by helicopter or commuter ferry) did not allow repeated direct measurements of a closed headspace over time. We were therefore required to use gas transfer velocities derived from the literature.

Methods used to estimate gas transfer velocities

We calculated k_{600} using a range of methods from the literature on gas fluxes in large rivers to examine the resulting differences in instantaneous flux rates and system-wide cumulative fluxes in the Mackenzie River Delta. From most to least conservative, the methods considered were:

(1) Using physical characteristics of the channel, as in Raymond et al. (2012). In this case, gas transfer coefficients were found using the equation:

$$k_{600} = (S * V * 2841) + 2.02 ,$$

where S is the slope of the river or channel (unitless), and V is the flow velocity ($m^3 s^{-1}$) calculated as:

$$V = e * Q^f ,$$

where Q is discharge ($m^3 s^{-1}$), e is a hydraulic coefficient (e = 0.19, as by Raymond et al. 2012), and f is a hydraulic exponent (f = 0.29, as by Raymond et al. 2012).

Since Q is not known for the outer delta sites due to backwater effects during the freshet (Beltaos 2012; Blackburn et al. 2015), it was approximated using flow split data from Morley (2012). Together, Reindeer and Langley channels carry approximately 50% of the delta outflow, which was assumed to be equal to the incoming Mackenzie River flow. Discharge in each channel was therefore assumed to be 25% of the Mackenzie River flow on that day.

(2) Following the recommendations of Raymond & Cole (2001). In their 2001 paper, Raymond & Cole found that unless the system is exceptionally shallow, has an average wind speed over 8 m s^{-1}, or has rapid tidal velocities, average k_{CO2} in riverine and estuarine systems generally falls in the range of 3 to 7 cm h^{-1}. None of these exceptions applied at our sampling sites, where depths were 8 m or greater, average daily wind speeds at the nearest Environment and Climate Change Canada (ECCC) meteorological station throughout May 2010 ranged from 2.8 to 5.7 m s^{-1} (Supplementary Fig. S1), and there was no tidal influence. The value of k_{600} was then found using these high and low limits and the standard equation:

$$k_{600} = k_{CO2} * (600 / Sc\text{-}CO_2)^{-0.5} ,$$

where Sc-CO_2 is the temperature-dependent Schmidt number calculated according to the methods of MacIntyre et al. (1995).

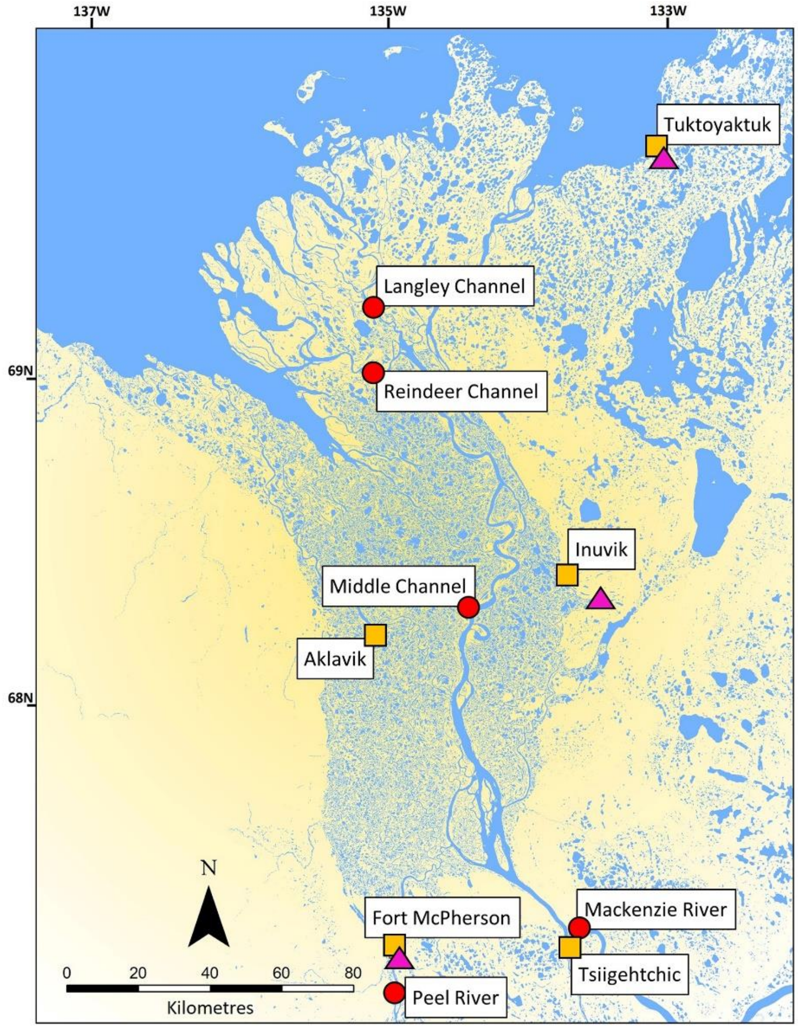
(3) Using wind speeds, as proposed by Alin et al. (2011). In this case, the gas transfer velocities were found using the equation:

$$k_{600} = 4.46 + (7.11 * u) ,$$

where u is the average daily wind speed (m s^{-1}) on the day of sampling, which was measured at the nearest ECCC meteorological station (Supplementary Fig. S1). These stations were within

100 km from the sampling sites (Supplementary Fig. S1b) and represented our best source of continuous wind speed data in this region of the western Arctic.

(a)



(b)

site	distance to nearest meteorological station (km)	station name	average wind speed, May 2010 (m s^{-1})
Mackenzie River	50	Fort McPherson	2.8
Peel River	9		
Middle Channel	38	Inuvik	3.5
Langley Channel	90	Tuktoyaktuk	5.7
Reindeer Channel	100		

Supplementary Fig. S1. (a) The Mackenzie Delta. Sampling sites are shown as red dots, towns as yellow squares, and ECCC meteorological stations as pink triangles. (b) Metadata for each site, including the distance (km) to the nearest ECCC meteorological station where wind speeds were continuously recorded throughout the study, the station name, and the average wind speeds at each station during the month of May 2010.

All further calculations of gas-specific transfer velocities (k_{CO2}, k_{CH4}) followed the methods presented in the main body of the paper. Gas transfer velocities, instantaneous flux rates, and cumulative delta-wide fluxes that were calculated using the methods described above are presented in Supplementary Table S1 and Supplementary Fig. S2.

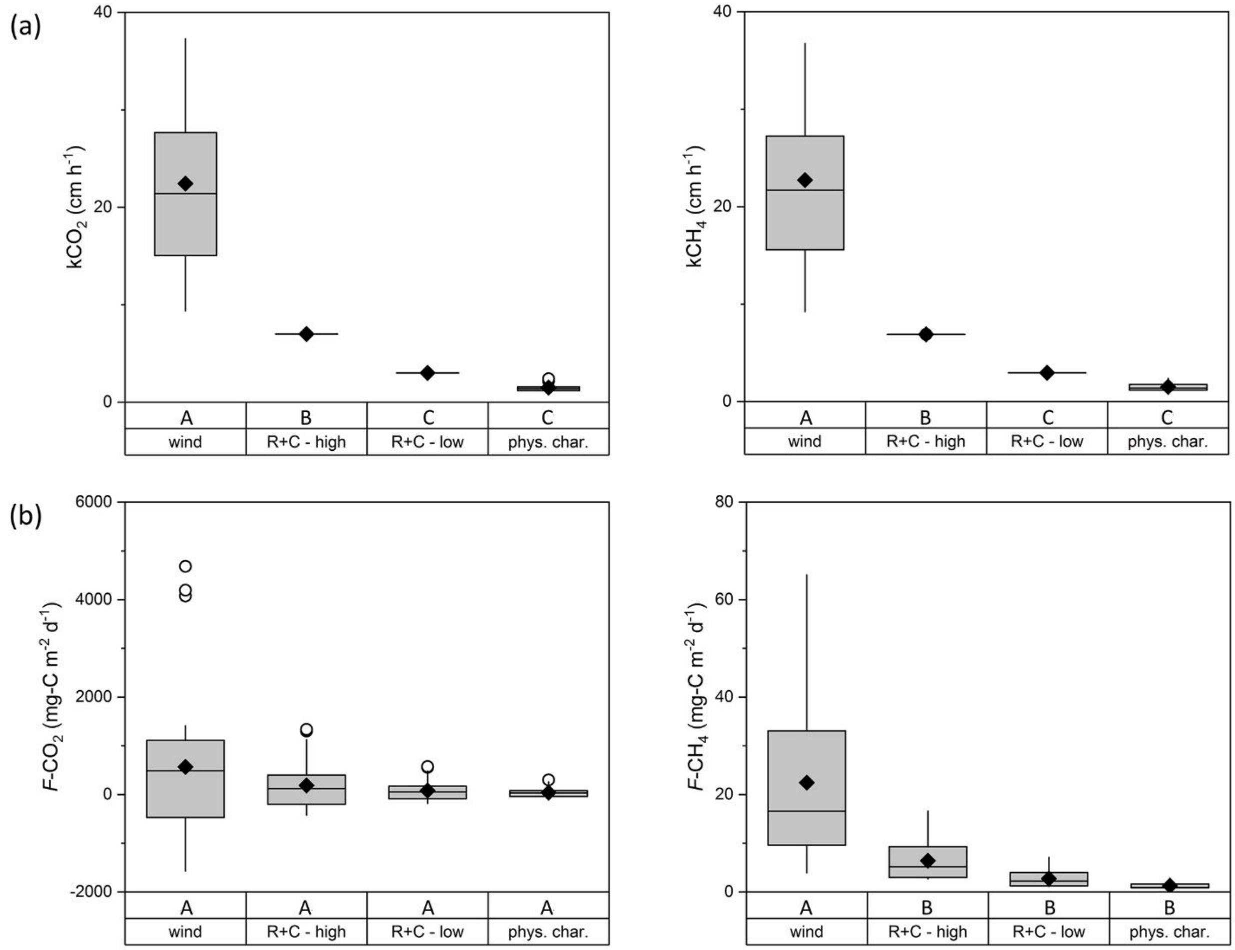
Supplementary Table S1. Estimated average fluxes of a) CO_2 and b) CH_4 at the air-water interface of the Mackenzie Delta channel network during the 2010 ice-out (May). Estimates were calculated for each delta transect and then summed to give delta-wide fluxes. Three methods were used to calculate gas transfer velocities (k_{600}, cm h^{-1}): (1) using physical characteristics of the channel (discharge and slope) as proposed by Raymond et al. (2012); (2) using upper and lower limits ([2] High and [2] Low, respectively) proposed by Raymond & Cole (2001); and (3) using wind speeds as proposed by Alin et al. (2011). Values in the boldface rows were presented as the low and high flux (*F*-GAS) estimates at the air–water interface of the delta-wide channel network in the main text of the paper. Fluxes generated using methods (1) and (3) are presented as extreme lower and upper estimates of cumulative delta-wide fluxes as controlled by the physical characteristics of the channels and wind, respectively.

(a) CO_2

	Inflow			Middle delta			Outer delta			Total flux (Gg-C)
	F-CO_2 (mg-C m^{-2} d^{-1})	area (km^2)	flux (Gg-C)	*F*-CO_2 (mg-C m^{-2} d^{-1})	area (km^2)	flux (Gg-C)	*F*-CO_2 (mg-C m^{-2} d^{-1})	area (km^2)	flux (Gg-C)	
(1)	20.6	325.646	0.2	22.7	889.993	0.6	9.3	528.647	0.2	1.0
(2) Low	**20.0**	**325.646**	**0.2**	**50.6**	**889.993**	**1.4**	**27.4**	**528.647**	**0.5**	**2.1**
(2) High	**48.0**	**325.646**	**0.5**	**118.7**	**889.993**	**3.3**	**65.1**	**528.647**	**1.1**	**4.8**
(3)	139.0	325.646	1.4	338.4	889.993	9.3	233.7	528.647	3.8	14.6

(b) CH_4

	Inflow			Middle delta			Outer delta			Total flux (Mg-C)
	F-CH_4 (mg-C m^{-2} d^{-1})	area (km^2)	flux (Mg-C)	*F*-CH_4 (mg-C m^{-2} d^{-1})	area (km^2)	flux (Mg-C)	*F*-CH_4 (mg-C m^{-2} d^{-1})	area (km^2)	flux (Mg-C)	
(1)	1.3	325.646	13.3	1.6	889.993	43.5	1.6	528.647	26.5	83
(2) Low	**2.6**	**325.646**	**26.3**	**3.4**	**889.993**	**93.0**	**4.1**	**528.647**	**66.5**	**186**
(2) High	**6.1**	**325.646**	**61.3**	**7.9**	**889.993**	**216.9**	**9.5**	**528.647**	**155.3**	**433**
(3)	15.3	325.646	154.4	20.6	889.993	568.5	42.3	528.647	693.7	1417



Supplementary Fig. S2. (a) Gas transfer velocities (k_{GAS}) and (b) instantaneous flux rates (*F*-GAS) for CO_2 (left) and CH_4 (right) in Mackenzie Delta channels during the 2010 freshet. Values were calculated using measured gas concentrations in water and the overlying atmosphere, and three different methods from the literature; one that used wind speeds (wind; Alin et al. 2011), one that proposed upper and lower limits (R+C – high and R+C – low, respectively) on the CO_2 gas transfer velocity (Raymond & Cole 2001), and one that used the physical characteristics of the channel (phys. char.; Raymond et al. 2012). Boxplots show medians and quartiles (boxes), averages (filled diamonds), 90% confidence intervals (whiskers) and ranges (hollow dots). In each graph, those sites accompanied by the same letter (shown below each boxplot) had mean values that were not significantly different from one another ($p > 0.05$) according to a one-way analysis of variance followed by a post-hoc Tukey HSD test.

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