



# Dissolved methane and carbon dioxide fluxes in Subarctic and Arctic regions: Assessing measurement techniques and spatial gradients



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## ABSTRACT

Here we use a portable method to obtain high spatial resolution measurements of concentrations and calculate diffusive water-to-air fluxes of CH<sub>4</sub> and CO<sub>2</sub> from two Subarctic coastal regions (Kasitsna and Jakolof Bays) and an Arctic lake (Toolik Lake). The goals of this study are to determine distributions of these concentrations and fluxes to (1) critically evaluate the established protocols of collecting discrete water samples for these determinations, and to (2) provide a first-order extrapolation of the regional impacts of these diffusive atmospheric fluxes. Our measurements show that these environments are highly heterogeneous. Areas with the highest dissolved CH<sub>4</sub> and CO<sub>2</sub> concentrations were isolated, covering less than 21% of the total lake and bay areas, and significant errors can be introduced if the collection of discrete water samples does not adequately characterize these spatial distributions. A first order extrapolation of diffusive fluxes to all Arctic regions with similar characteristics as Toolik Lake suggests that these lakes are likely supplying 0.21 and 15.77 Tg of CH<sub>4</sub> and CO<sub>2</sub> to the atmosphere annually, respectively. Similarly, we found that the Subarctic Coastal Ocean is likely supplying 0.027 Tg of CH<sub>4</sub> annually and is taking up roughly 524 Tg of CO<sub>2</sub> per year. Although diffusive fluxes at Toolik Lake may not be as substantial when comparing against present seep ebullition and spring ice-out values, warming in the Arctic may result in the increase of methane discharge and methane emissions to the atmosphere. Thus further work is needed to understand this changing environment. This study suggests that high spatial resolution measurement protocols, similar to the one used here, should be incorporated into field campaigns to reduce regional uncertainty and refine global emission estimates.

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## 1. Introduction

Numerous terrestrial and marine high latitude ecosystems harbor large reservoirs of carbon. Arctic permafrost soils, for example, are estimated to hold approximately 14% of the world's soil organic carbon (Zimov et al., 2006). The rise of surface air and seawater temperatures in response to both natural and anthropogenic climate changes has been almost twice as large in high latitude regions (Arctic and Subarctic) compared to the global average, a feature known as Arctic Amplification (Serreze and Francis, 2006). Temperature increases will enhance thawing, liberation, transport, and/or transformation of this carbon, thereby modulat-

ing global carbon cycles and the budgets of greenhouse gases, primarily carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) (e.g., Christensen et al., 2004; Zimov et al., 2006).

Several recent investigations have measured or modeled substantial CO<sub>2</sub> and CH<sub>4</sub> fluxes from Arctic and Subarctic regions highlighting the diverse nature of the fluxes, carbon source, and biogeochemical processes governing the release (e.g., Damm et al., 2008; Kessler et al., 2008; Ruppel, 2011; Schuur et al., 2013; Shakhova et al., 2010; Walter Anthony et al., 2012). For example, ubiquitous fluxes of CO<sub>2</sub> and CH<sub>4</sub> could be found due to the decomposition of organic matter in marine and lake sediments or from permafrost thaw (e.g., Wickland et al., 2006; Zimov et al., 1997). However, point sources have been associated with hydrocarbon seeps, methane clathrate decomposition, and groundwater discharge (e.g., Kling et al., 1991; Paytan et al., 2015; Ruppel, 2011; Shakhova et al., 2010; Walter Anthony et al., 2012).

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While greenhouse gas fluxes associated with ebullition and spring thaw have been shown to be significant sources to the atmosphere (e.g., Walter Anthony et al., 2012; Phelps et al., 1998), they likely represent smaller areas (point source emissions) or short-term fluxes. Diffusive fluxes of CO<sub>2</sub> and CH<sub>4</sub>, while conventionally viewed as being a fraction of the ebullition and spring-thaw flux, cover a much larger area and occur over the entire ice-free season. However, due to technological limitations and the relatively inaccessible nature of most Arctic and Subarctic aquatic environments, fundamental uncertainties exist in the diffusive CO<sub>2</sub> and CH<sub>4</sub> fluxes to the atmosphere. For example, due to the difficulty to access these environments, the standard protocol for sampling the dissolved concentrations of CO<sub>2</sub> and CH<sub>4</sub> in surface waters is to collect discrete samples (U.S. Environmental Protection Agency (EPA), 2007). This practice assumes that either the region is homogeneous or that the sampling adequately captures the average and the distribution of concentrations found in that environment. However, recent discoveries of significant greenhouse gas fluxes associated with seepage (Walter Anthony et al., 2012) and groundwater discharge (Kling et al., 1991; Paytan et al., 2015) suggest a more heterogeneous distribution of surface water CO<sub>2</sub> and CH<sub>4</sub> concentrations and thus diffusive fluxes that may be irregularly distributed around an aquatic environment; groundwater inputs would display elevated concentrations around the perimeter while seepage would input high concentrations of these gases at the location of these features. Understanding the distribution and magnitude of these fluxes is vital to accurately extrapolate fluxes from local to regional to global scales and improve estimates of atmospheric greenhouse gas budgets (Ciais et al., 2013).

In this article, we investigate the spatiotemporal distributions and diffusive fluxes of CO<sub>2</sub> and CH<sub>4</sub> in two diverse environments in Alaska: an Arctic lake (Toolik Lake) and a Subarctic coastal region (Kasitsna and Jakolof Bays). Toolik Lake (68°37'36"N, 149°35'56"W) represents a terrestrial Arctic lake overlaying continuous permafrost with recognized groundwater inputs (Dimova et al., 2015; Kling et al., 1991; Paytan et al., 2015). Kasitsna Bay (59°28'07"N, 151°33'11"W) and Jakolof Bay (59°26'49"N, 151°30'37"W) represent a marine Subarctic region with sporadic permafrost, where methane sources may originate from marine or terrestrial sources (Lecher et al., 2015). Collectively, these environments represent Arctic and Subarctic regions with the potential for both ubiquitous and point source emissions of CO<sub>2</sub> and CH<sub>4</sub>.

We used a new portable method to continuously measure CO<sub>2</sub> and CH<sub>4</sub> concentrations in surface waters as well as the atmosphere at a rate of approximately 1 Hz. This technique was recently used successfully on a research vessel (Du et al., 2014) and is applied here on jon boats (Toolik Lake) and small recreational fishing vessels (Kasitsna and Jakolof Bays). The goal of this research is to provide high-resolution spatial distributions of the water-to-air fluxes of CO<sub>2</sub> and CH<sub>4</sub> from two regionally contrasting sites so that (1) future field measurement campaigns can be designed to adequately capture the true greenhouse gas dynamics of these systems, (2) to provide an estimate of the errors introduced in regional emissions of CO<sub>2</sub> and CH<sub>4</sub> if extrapolations are performed ignoring spatial gradients of diffusive fluxes, and (3) to obtain first-order water-to-air fluxes from these systems. Nearly homogeneous distributions of dissolved surface water concentrations of these greenhouse gases would imply that gas concentrations in surface waters and fluxes to the atmosphere could be measured with a simple sampling strategy where discrete water samples are collected in vials at a limited number of sites; this simplified sampling strategy would be both welcomed and appreciated when working in these often inaccessible and logistically challenging environments. However, highly heterogeneous and irregular distributions would suggest that higher resolution

and more experimentally complex measurement systems would be necessary, such as used here and elsewhere (e.g., Du et al., 2014; Güllow et al., 2011).

The emission of CO<sub>2</sub> and CH<sub>4</sub> from thawing permafrost may become significant in the 21st century under naturally and anthropogenically driven climate change. These regions may serve as gas conduits for the transport of greenhouse gases to the atmosphere and exert a positive feedback on climate (Kling et al., 1991; Paytan et al., 2015; Shakhova et al., 2010; Walter et al., 2006); however, the magnitude of these emissions is still uncertain (Ciais et al., 2013). More intense sampling of Arctic lakes and high-latitude coastal areas is essential to accurately capture the distributions of the CO<sub>2</sub> and CH<sub>4</sub> dissolved in surface waters as well as to accurately determine fluxes, constrain global influences on atmospheric budgets, and predict climate changes.

## 2. Study areas

Methane and CO<sub>2</sub> emissions from an Arctic lake (Toolik Lake) and from two Subarctic coastal environments (Kasitsna and Jakolof Bays) in Alaska were investigated (Fig. 1). Toolik Lake was surveyed two consecutive summers (16 August 2011 and 24–25 July 2012), while Jakolof Bay was surveyed on 23 August 2011, and Kasitsna Bay on 19–20 July 2012. These two regions were selected for this study because of their contrasting sources of CH<sub>4</sub> and CO<sub>2</sub>. Toolik Lake (68°38'00"N, 149°36'15"W) is a multiple basin kettle lake located on the North Slope of Alaska with continuous permafrost underlying the entire lake's watershed. Toolik Lake has a surface area of 1.32 km<sup>2</sup>, an average depth of 7 m, and a maximum depth of 25 m (O'Brien et al., 1997). The main inlet to the lake enters from the south and provides 71% of the total water flow to the lake (O'Brien et al., 1997). A secondary inlet provides 9% of the water, and the remainder of the flow is accounted by ephemeral streams (O'Brien et al., 1997). Toolik Lake is oligotrophic (Whalen and Alexander, 1986) and characterized by CO<sub>2</sub> and CH<sub>4</sub> supersaturation (Kling et al., 1991). The excess of CO<sub>2</sub> and CH<sub>4</sub> has been linked to groundwater transport of dissolved carbon from the tundra (Kling et al., 1991; Paytan et al., 2015).

Kasitsna Bay (59°28'34"N, 151°33'31"W) and Jakolof Bay (59°26'49"N, 151°30'37"W) are located in the Kenai Peninsula in southern Alaska. Unlike Toolik Lake, watersheds around Kasitsna and Jakolof Bay are generally free of permafrost (Miller and Whitehead, 1999). These bays receive freshwater inputs from rivers draining a large portion of the Kenai Peninsula watershed and from glacial melting (Griffiths et al., 1982). An additional source of CH<sub>4</sub> to these bays could be methane produced from the coal bearing deposits known to exist in the Kenai Peninsula (Flores and Strieker, 1993). This CH<sub>4</sub> could be transported to coastal waters through groundwater (Dimova et al., 2015; Lecher et al., 2015). Large seasonal fluctuations in primary productivity and respiration have been observed for this region (Griffiths et al., 1982). Primary productivity and respiration are low in January and start to increase at the end of April, reaching a maximum in June and July. No previous studies on the CH<sub>4</sub> and CO<sub>2</sub> dynamics of this region have been published. Altogether, Toolik Lake, Kasitsna Bay, and Jakolof Bay represent Arctic and Subarctic environments with different geology and hydrology characteristics and possibly distinct sources of CH<sub>4</sub> and CO<sub>2</sub>.

## 3. Methods

### 3.1. Equipment

The partial pressures of dissolved and atmospheric CH<sub>4</sub> and CO<sub>2</sub> were continuously measured using a portable pCH<sub>4</sub>-pCO<sub>2</sub> system

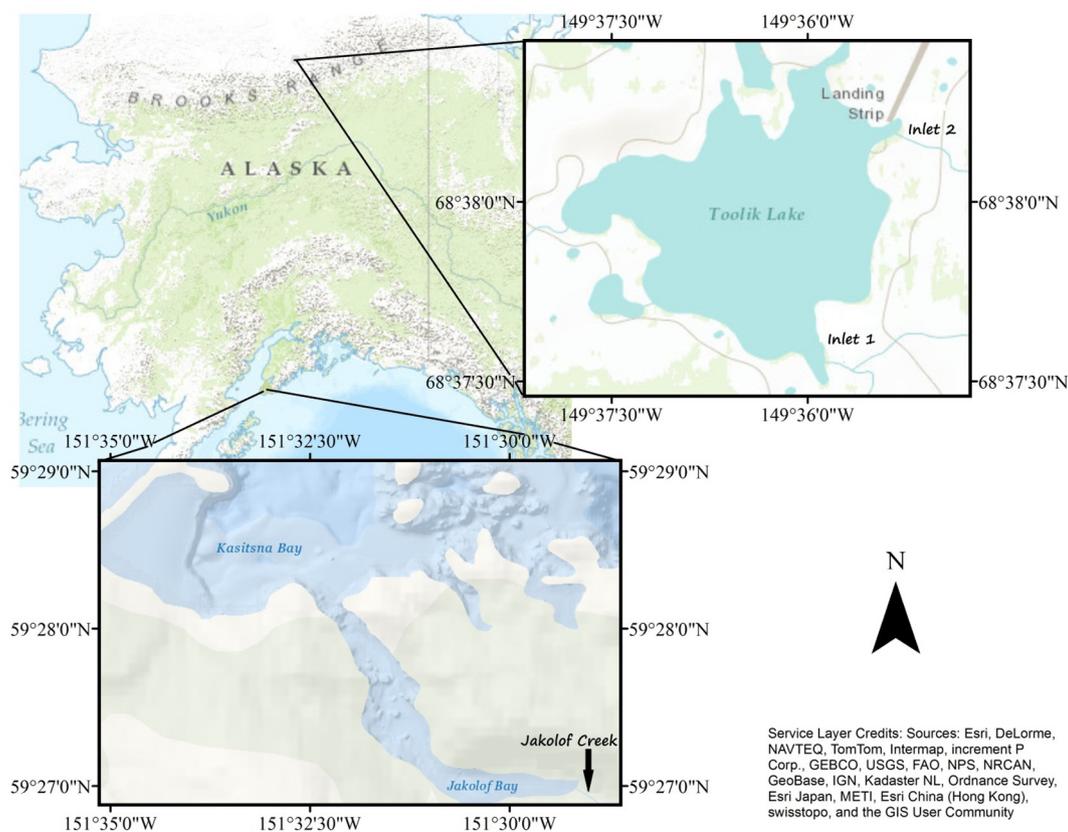


Fig. 1. Areas of study.

similar to that described previously (Du et al., 2014 and references therein), however, with a few slight modifications. A schematic of the system is shown in the supplemental material (Fig. S1). Surface water is drawn from an intake at approximately 0.5 m depth and distributed through a manifold to both a sonde measuring water temperature and salinity (YSI 600R-series sonde) and two Weiss-type equilibrators (Johnson, 1999). Under normal operation, the equilibrator has a sample stream flow rate of 4 to 6 L min<sup>-1</sup> and a headspace volume of 0.54 L. Surface water flows continuously into the equilibrators through hollow cone nozzles producing a fine spray of water and expediting the rate of equilibration between the dissolved and gaseous phases of CH<sub>4</sub> and CO<sub>2</sub>. The headspace inside the primary equilibrator is maintained at ambient pressure by a vent connected to a secondary equilibrator. The role of the secondary equilibrator is to prevent any gas exchange with ambient air; while the rate of gas loss from the main equilibrator was measured and determined to be minimal, the secondary equilibrator serves to supply pre-equilibrated headspace gas to the main equilibrator in the event of any gas loss. Atmospheric air is continuously pumped through a 0.63 cm-ID SynFlex tube mounted to the front of the boat to avoid contamination by exhaust gases. Atmospheric air and gas from the equilibrator headspace are pumped through water vapor condensers and Nafion dryers to remove water moisture, and then are alternately analyzed using a Cavity Ring-Down Spectrometer (CRDS) (Picarro Inc, G1301). The analysis routine used here was ~120 min continuous measurement of the equilibrator headspace followed by 10 min continuous measurement of bow air samples. The CRDS was calibrated daily in the field using four different reference gas standards obtained from Scott Specialty and Air Liquide (1.27, 2.06, 242, and 995 ppm for CH<sub>4</sub> and 382, 490, 1485, and 2219 ppm for CO<sub>2</sub>).

### 3.2. Calculating diffusive fluxes

The net water-to-air fluxes ( $F$ ) were calculated as:

$$F = k \cdot \alpha \cdot (p_{sw} - p_{atm}) \quad (1)$$

where  $k$  (m d<sup>-1</sup>) is the gas transfer velocity, and  $\alpha$  is the solubility of CH<sub>4</sub> or CO<sub>2</sub> in water calculated from surface water temperature and salinity (Weiss, 1974; Wiesenburg and Guinasso, 1979).  $p_{sw}$  is the equilibrium partial pressure of the gas in the surface water determined in the equilibrator headspace, and  $p_{atm}$  is the partial pressure of the gas in the atmosphere measured from the bow air.

The gas transfer velocity for the coastal ocean was calculated using the parameterization from Sweeney et al. (2007) since it is an improvement over the typical Wanninkhof (1992) equation:

$$K_w = 0.27(U_{10}^2)(Sc/660)^{-0.5} \quad (2)$$

$k$  is estimated as a function of the Schmidt number ( $Sc$ ) and wind speed ( $U$ ) at a reference height of 10 m. The Schmidt number is a dimensionless number and is calculated using third-order polynomial fits as described by Wanninkhof (1992). The gas transfer velocity for Toolik Lake was calculated according to Cole et al. (2010) which used four methods for estimating  $k$  in a series of small lakes. With the exception of Toolik Lake 2011, wind speeds were continuously measured during the survey at ~3 m above the water surface using an Airmar® weather station mounted to the ship. Wind speeds for Toolik Lake 2011 were taken from the weather monitoring station at Toolik Field Station. Wind speed was corrected to 10 m to match the reference height as described by Erickson (1993).

### 3.3. Equilibrator concentration correction

Even though the CRDS collects data at a rate of about 1 Hz, the time needed for a gas in the headspace of the equilibrator to reach equilibrium with the incoming water is different for gases with different solubilities. To describe the gaseous exchange process between the headspace and incoming water, the measured headspace gas concentration,  $C_e$ , at time,  $t$ , is expressed following the equation published by Johnson (1999):

$$C_e = \left( C_i - \frac{C_w}{\alpha} \right) e^{-\left(\frac{t}{\tau}\right)} + \frac{C_w}{\alpha} \quad (3)$$

where  $C_i$  is the initial gas concentration that is not at equilibrium,  $C_w$  is the gas concentration of the trace gas in the incoming water at equilibrium, and  $\tau$  is the equilibrator response time which describes the time interval in which the gas phase in the equilibrator declines or increases exponentially to  $1/e$  (36.8%) with respect to its starting value.  $\tau$  was experimentally evaluated in the lab following the procedures used by Johnson (1999). This experiment involved two steps. In the first step, the equilibrator was thrown into disequilibrium by rapidly flushing ( $5 \text{ L min}^{-1}$ ) a gas containing known concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  into the headspace of the equilibrator. In the second step, the flushing was terminated and the headspace was allowed to return to equilibrium. The response time was calculated by fitting the measured response to an exponential function and by rearranging equation (3):

$$\tau = -\frac{t}{\ln\left[\frac{(C_e - \frac{C_w}{\alpha})}{(C_i - \frac{C_w}{\alpha})}\right]} \quad (4)$$

This experiment was repeated six times using water with different temperatures to assess the effect of solubility on  $\tau$  (16, 31, and  $45^\circ\text{C}$ ) and by using gas standards from a range of concentrations (0, 1.7, 249, and 999 ppm of  $\text{CH}_4$  and 0, 365, 1513 and 2248 ppm of  $\text{CO}_2$ ). The response times when going from both high to low concentration waters and vice versa were simulated.

The mean equilibrator response time for methane was determined to be  $\tau = 4.53$  min for the exponential decay process (when simulating movement from high concentration waters to low concentration waters), and  $\tau = 2.51$  min in the scenario of increasing concentration (simulating movement from low concentration waters to high concentration waters; refer to Fig. S2). Previous studies have reported  $\tau$  values between 11 and 12 min for  $\text{CH}_4$  (Gülzow et al., 2011; Hu et al., 2012). The faster equilibrator response time in this study may be associated with the headspace volume, headspace analysis technique, water flow rate, or the type of spray nozzle that was used. Instead of using a nozzle, Gülzow et al. (2011) flowed seawater at  $0.5 \text{ L min}^{-1}$  into a  $0.07 \text{ L}$  headspace and then circulated the headspace air through a glass frit in the water to produce bubbles and decrease the equilibration time. The  $\tau$  values provided by Hu et al. (2012) were theoretically derived and are for an equilibrator with a  $19 \text{ L}$  headspace volume that was fitted with a showerhead and flow rates of  $13\text{--}20 \text{ L min}^{-1}$ .

Equation (3) is only applicable when the equilibrator vent flow is zero, i.e. when no ambient air is entering the equilibrator. Venting rates of ambient air into the equilibrator headspace were measured to be zero, indicating that no air was removed from the headspace. Furthermore, the use of a secondary equilibrator further ensures that no ambient air was entering the equilibrator. After  $\tau$  was determined, equation (3) was rearranged and solved for  $C_w$ :

$$C_w = \frac{\alpha(C_e - C_i e^{-\left(\frac{\Delta t}{\tau}\right)})}{1 - e^{-\left(\frac{\Delta t}{\tau}\right)}} \quad (5)$$

where  $\Delta t(t_{C_i} - t_{C_e})$  is the time difference between measurements assuming the dissolved gas concentration ( $C_w$ ) is constant during  $\Delta t$ . This is a reasonable assumption since our boat speed did not exceed  $1.5 \text{ m s}^{-1}$ .  $\tau$  is the measured equilibrator response time calculated using equation (4),  $C_i$  is the initial gas concentration that is not at equilibrium averaged over 1 min, and  $C_e$  is the next headspace gas concentration measured at time  $t_{C_e}$  averaged over 1 min. Equation (5) was used to translate the measured headspace concentrations ( $C_e$  and  $C_i$ ) into the true dissolved gas concentration ( $C_w$ ). This conversion was applied to the measured headspace from controlled laboratory calibrations and the data was averaged over 20, 50, and 100 s intervals. The 50 s average yielded the lowest errors and for this reason all the parameters were averaged over 1 min (Fig. S2).

The equilibrator response to changing  $\text{CO}_2$  concentrations in seawater is known to be quick (approximately 2 min for the exponential decay process Pierrot et al., 2009). The equilibrator's response time for  $\text{CO}_2$  from Pierrot et al. (2009) is about 2.3 times faster than those determined for  $\text{CH}_4$  in this study and 6 times faster than the time reported for  $\text{CH}_4$  in previous studies (Gülzow et al., 2011; Hu et al., 2012). Because of the faster equilibrator response time of  $\text{CO}_2$ , no concentration correction was applied to the  $\text{CO}_2$  data.

The uncertainty associated with the CRDS was calculated to be less than 1.6% ( $\pm 0.84$  ppm) based on least squares analyses with the standard gases. The uncertainty in calculating  $C_w$  was determined using data collected from the laboratory experiment measuring response times. The data corrected using equation (5) was compared to the true known value after the system was allowed to reach steady-state:

$$\text{Percent error} = \frac{|\text{corrected data} - \text{true value}|}{\text{true value}} \cdot 100 \quad (6)$$

The true value was defined as the point where the equilibrator headspace had reached equilibrium (i.e., where concentration plateaus). As depicted in Fig. S2, the largest errors occur when gas concentration in the water changes and the decaying/increasing trend begins. However, within 9 min this error is reduced to less than 30% for the exponential decay process and to less than 2% within 3 min when the concentration is increasing. When comparing to uncorrected data, it takes 14 min for the error to be reduced to less than 30% for the exponential decay process and 16 min must elapse for the error to be reduced to less than 2% when the concentration is increasing. These results show that the data is significantly improved when using equation (5) to correct the data; however the remaining uncertainty is not negligible (Fig. S2).

Despite the high sampling resolution of this experimental design (ca. 1 Hz), full-lake/bay coverage can only be achieved with interpolation. Several different interpolation methods were evaluated for accuracy and precision in terms of the mean error:

$$\text{ME} = \text{mean}(\text{true value} - \text{interpolated value}) \quad (7)$$

and the root-mean square error:

$$\text{RMSE} = \sqrt{\text{mean}[(\text{true value} - \text{interpolated value})^2]} \quad (8)$$

A bootstrapping assessment was performed using random subsampling validation. Roughly 2/3 of the measured data points were randomly selected and used for the actual interpolation while the remaining 1/3 were used for the error estimation. The procedure was repeated 1000 times with a new set of random samples selected each time to cross-validate the results. The obtained errors for 5 different interpolation techniques are shown in Table S1. While all five interpolation techniques were precise, the natural neighbor interpolation method yielded the most accurate values and thus was selected. The cubic interpolation technique showed to be inappropriate due to its high sensitivity to outliers.

**Table 1**Mean surface CH<sub>4</sub> and CO<sub>2</sub> concentrations with their respective standard deviation and standard deviation of the mean.

Study area	Mean surface concentration water	Mean interpolated surface water concentration	Area (km <sup>2</sup> )	Reference
<b>CH<sub>4</sub></b>				
	(nmol L <sup>-1</sup> )	(nmol L <sup>-1</sup> )		
Toolik Lake 2011	165.72 ± 92.62, 4.97	189.54 ± 100.31, 12.08	1.32	This study
Toolik Lake 2012	128.27 ± 51.02, 2.36	172.32 ± 98.87, 11.99	1.32	This study
Toolik Lake 1990	1100	n/a		Kling et al. (1992)
Kasitsna Bay 2012	5.32 ± 0.52, 0.03	8.16 ± 2.45, 0.48	4.70	This study
Jakolof Bay 2011	5.86 ± 0.74, 0.05	7.96 ± 0.99, 0.01	1.36	This study
<b>CO<sub>2</sub></b>				
	(ppm)	(ppm)		
Toolik Lake 2011	379.96 ± 40.54, 2.17	377.03 ± 44.02, 8.04	1.32	This study
Toolik Lake 2012	399.95 ± 50.44, 2.34	399.95 ± 50.44, 2.34	1.32	This study
Toolik Lake 75–89	1847 ± 239	n/a	1.32	Kling et al. (1991)
Kasitsna Bay 2012	206.75 ± 39.56, 2.03	257.84 ± 59.89, 9.35	4.70	This study
Jakolof Bay 2011	230.61 ± 4.01, 0.28	231.82 ± 2.95, 0.03	1.36	This study
Bering Sea Shelf	156–475	n/a	n/a	Borges (2005)

**Table 2**Mean CH<sub>4</sub> and CO<sub>2</sub> water-to-air fluxes with their respective standard deviation and standard deviation of the mean.

Study area	Mean flux	Total mean flux (mol d <sup>-1</sup> )	Mean interpolated flux	Mean interpolated emission (mol d <sup>-1</sup> )	Reference
<b>Flux CH<sub>4</sub></b>					
	(μmol m <sup>-2</sup> d <sup>-1</sup> )		(μmol m <sup>-2</sup> d <sup>-1</sup> )		
Toolik Lake 2011	116.36 ± 61.86, 3.32	153.60	112.80 ± 37.40, 0.36	148.90	This study
Toolik Lake 2012	126.87 ± 97.32, 4.53	167.6	126.04 ± 82.73, 0.80	166.37	This study
Toolik Lake 1990	550 (80–1020)	1342	n/a	n/a	Kling et al. (1992)
Kasitsna Bay 2012	0.5 ± 0.42, 0.02	2.37	0.58 ± 0.35, 0.42	2.72	This study
Jakolof Bay 2011	0.80 ± 0.77, 0.05	1.07	0.95 ± 0.65, 0.01	1.25	This study
Coastal Ocean	1.5 (1–20)	n/a	n/a	n/a	Rhee et al. (2009)
<b>Flux CO<sub>2</sub></b>					
	(mmol m <sup>-2</sup> d <sup>-1</sup> )		(mmol m <sup>-2</sup> d <sup>-1</sup> )		
Toolik Lake 2011	1.50 ± 1.49, 0.08	1980	1.37 ± 1.11, 0.01	1808	This study
Toolik Lake 2012	3.70 ± 4.02, 0.19	4884	3.13 ± 2.66, 0.03	4132	This study
Toolik Lake 1990	21 (–7–60)	46,048	n/a	n/a	Kling et al. (1992)
Kasitsna Bay 2012	–1.69 ± 1.26, 0.06	–7979	–1.94 ± 0.97, 0.01	–10,614	This study
Jakolof Bay 2011	–0.82 ± 0.78, 0.06	–1375	–0.95 ± 0.63, .01	–1245	This study
Coastal Ocean	–11.75	n/a	n/a	n/a	Borges (2005)

#### 4. Results

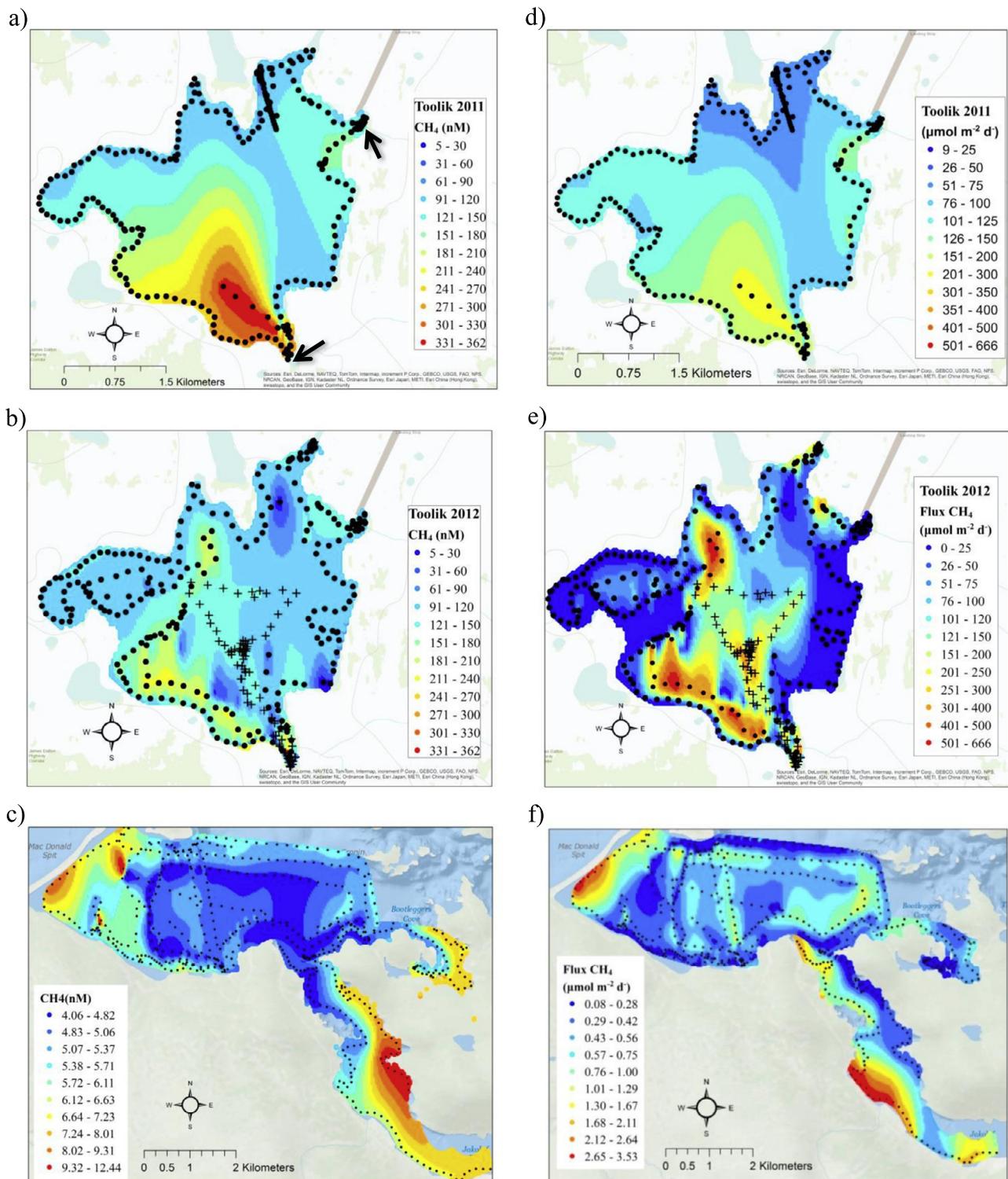
The results presented here are from detailed surveys and continuous measurements at each studied area. Since groundwater discharge has been shown to be a substantial point source of dissolved CO<sub>2</sub> and CH<sub>4</sub> to Toolik Lake (Kling et al., 1991; Paytan et al., 2015), the surface surveys focused on the littoral areas to quantify the spatial distribution of these hot spots as well as the center of the lake. In Toolik Lake, dissolved CH<sub>4</sub> concentrations ranged from 5 to 362 nM with mean water concentrations of 165.72 nM in 2011 and 128.27 nM in 2012 (Table 1). The mean atmospheric mixing ratios ranged from 2.15 to 2.49 ppm. Dissolved CO<sub>2</sub> partial pressure ranged from 304.53 to 588.24 ppm with mean values of 379.96 ppm in 2011 and 399.95 ppm in 2012 (Table 1). The mean atmospheric mixing ratio of CO<sub>2</sub> ranged from 315.97 to 357.73 ppm.

Dissolved CH<sub>4</sub> concentrations in Kasitsna and Jakolof Bays were up to two orders of magnitude lower than in Toolik Lake. The mean CH<sub>4</sub> concentration in Kasitsna Bay was 5.32 nM with values ranging from 2.03 to 7.23 nM (Table 1). The atmospheric mixing ratio of CH<sub>4</sub> ranged from 1.80 to 2.24 ppm. The mean surface dissolved CO<sub>2</sub> partial pressure in Kasitsna Bay was 206.75 ppm with values ranging from 157.84 to 361.34 ppm. The mean CH<sub>4</sub> concentration in Jakolof Bay was 5.86 nM with values ranging from 4.3 to 7.7 nM (Table 1). The atmospheric mixing ratio of CH<sub>4</sub> ranged from 2.20 to 2.24 ppm.

In Toolik Lake, mean water-to-air fluxes of CH<sub>4</sub> were 116.35 ± 61.86 (range: –0.03 to 334.67) μmol m<sup>-2</sup> d<sup>-1</sup> in 2011 and 126.88 ± 97.35 (range: –0.77 to 544.25) μmol m<sup>-2</sup> d<sup>-1</sup> in 2012 (Table 2).

Wind speeds were slightly higher in 2012 than in 2011 (2.71 ± 0.69 m/s in 2011 compare to 3.31 ± 2.17 m/s in 2012) and may explain the wider range of fluxes in 2012 (Fig. S3). Mean water-to-air fluxes of CO<sub>2</sub> were 1.50 ± 1.49 (range: –1.10 to 4.33) mmol m<sup>-2</sup> and 3.70 ± 4.02 (range: –0.19 to 26.19) mmol m<sup>-2</sup> d<sup>-1</sup> in 2012 (Table 2; Figs. 2 and 3). Extrapolating over the entire 1.3 km<sup>2</sup> lake surface, these estimates yield positive mean flux values, indicating that Toolik Lake is a net source of CH<sub>4</sub> and CO<sub>2</sub> to the atmosphere. This is consistent with previous studies which have reported greenhouse gas emissions from Arctic Lakes in Alaska (Kling et al., 1991; O'Brien et al., 1997; Walter Anthony et al., 2012). The survey in Toolik Lake 2011 did not include the interior of the lake; therefore the extrapolations for this year should be looked at as a first-order approximation.

Mean fluxes of CH<sub>4</sub> and CO<sub>2</sub> at Kasitsna Bay were 0.5 ± 0.42 (range: 0.002 to 3.68) μmol m<sup>-2</sup> d<sup>-1</sup> and –1.69 ± 1.26 (range: –6.45 to 0.22) mmol m<sup>-2</sup> d<sup>-1</sup>, respectively (Table 1). Mean fluxes of CH<sub>4</sub> and CO<sub>2</sub> at Jakolof Bay were 0.80 ± 0.77 (range: 0.07 to 3.07) μmol m<sup>-2</sup> d<sup>-1</sup> and –0.82 ± 0.78 (range: –2.79 to –0.1) mmol m<sup>-2</sup> d<sup>-1</sup>, respectively (Table 1). Small, positive CH<sub>4</sub> fluxes indicate that Kasitsna and Jakolof are weak sources of CH<sub>4</sub> to the atmosphere. This is consistent with what is known about coastal oceans (see Table 2) (Rhee et al., 2009; Scranton and Brewer, 1977). The highest efflux of CH<sub>4</sub> coincides with the highest wind speeds indicating that wind speeds may be governing the flux (Fig. S4). Negative fluxes of CO<sub>2</sub> indicate that this region is a sink of atmospheric CO<sub>2</sub>. Coastal oceans receive major inputs of organic matter and nutrients from land which enhance primary



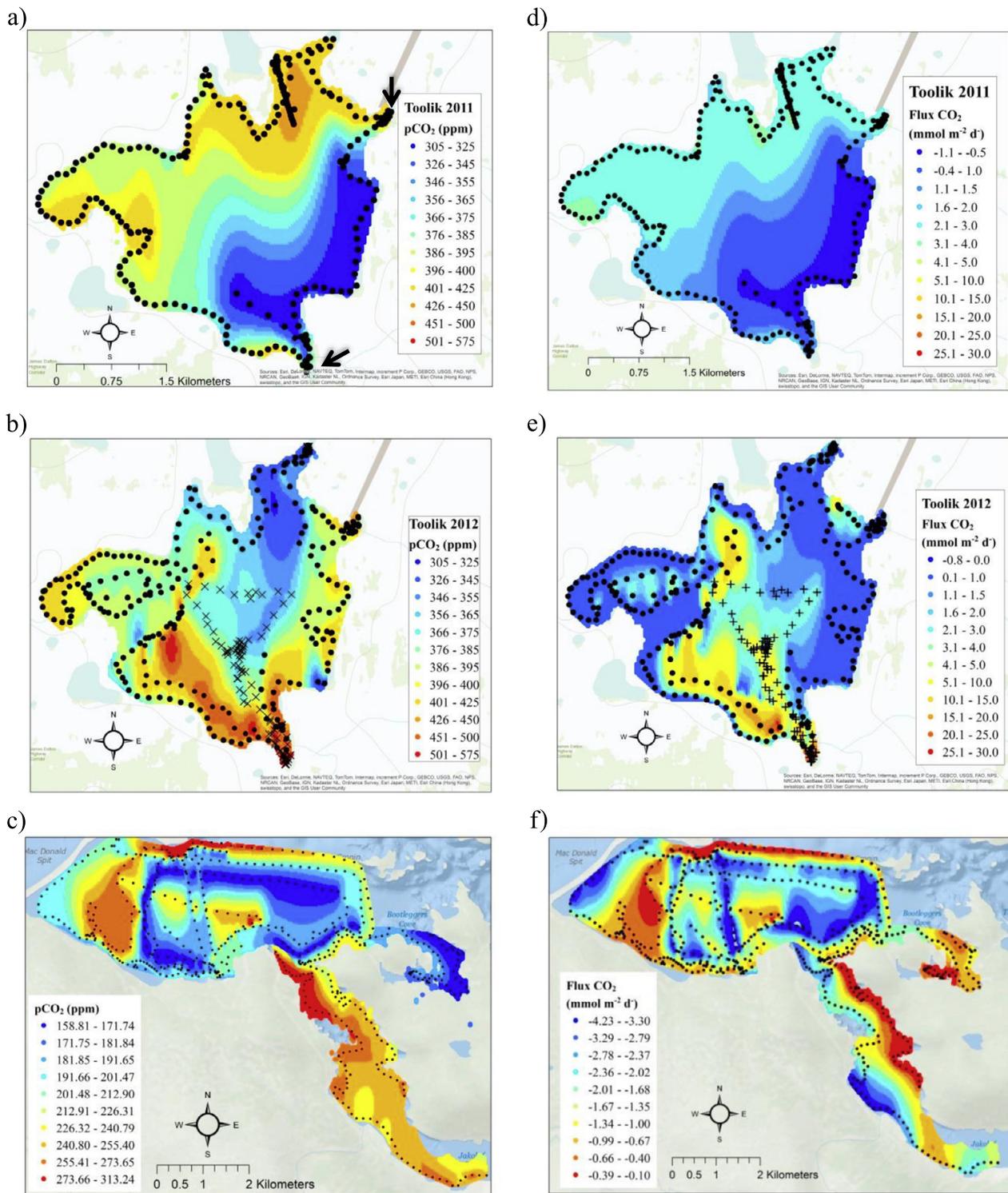
**Fig. 2.** Dissolved CH<sub>4</sub> concentrations in Toolik Lake in (a) 2011, (b) 2012, and in Jakolof and Kasitsna Bays 2012, 2011 (c). Water-to-air fluxes of CH<sub>4</sub> in Toolik Lake in (d) 2011, (e) 2012, and in Jakolof and Kasitsna Bays 2012 and 2011 (f). In Toolik Lake, the black dots denote the locations where measurements were taken on 16 August 2011 (a and d) and on 24 July 2012 (b and e), while the crosses denote samples measured on 25 July 2012. The arrows denote stream inlets. Jakolof Bay was surveyed on 23 August 2011 and Kasitsna Bay on 19–20 July 2012 (c and f).

productivity and atmospheric CO<sub>2</sub> uptake (Borges et al., 2005; Wollast, 1998).

## 5. Discussion

The goal of this research was to provide high-resolution spatial distributions of the diffusive water-to-air fluxes of CH<sub>4</sub> and CO<sub>2</sub>

from two regionally distinct sites so that (1) future field measurement campaigns can be designed to adequately capture the true greenhouse gas dynamics of these systems, (2) to provide an estimate of the errors introduced in regional emissions of CO<sub>2</sub> and CH<sub>4</sub> if extrapolations are performed ignoring spatial gradients of diffusive fluxes, and (3) to obtain first-order water-to-air fluxes from these systems.



**Fig. 3.** Dissolved CO<sub>2</sub> concentrations in Toolik Lake (a) 2011, (b) 2012, and in Jakolof and Kasitsna Bays 2012, 2011 (c). Water-to-air fluxes of CO<sub>2</sub> in Toolik Lake in (b) 2011, (d) 2012, and (f) Jakolof Bay and Kasitsna Bay 2012 and 2011. In Toolik Lake, the black dots denote the locations where measurements were taken on 16 August 2011 (a and d) and on 24 July 2012 (b and e), while the crosses denote samples measured on 25 July 2012. The arrows denote stream inlets. Jakolof Bay was surveyed on 23 August 2011 and Kasitsna Bay on 19–20 July 2012 (c and f).

### 5.1. Designing sampling strategies for future field campaigns

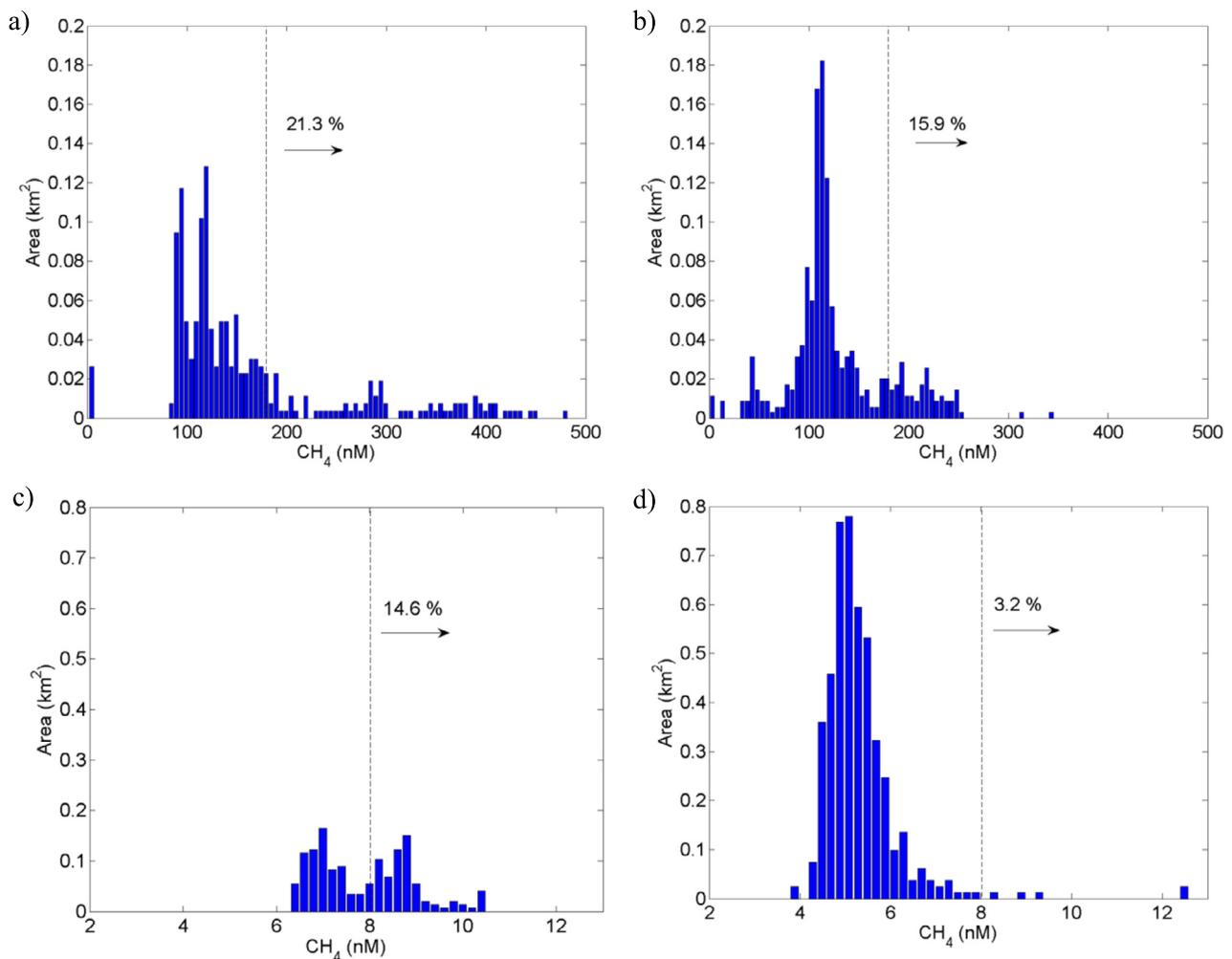
The distributions we measured were used to assess the uncertainty that might arise from the more common and logistically simple discrete sampling techniques. Traditional field sampling protocols for U.S. lakes suggests collecting 10 discrete samples (by filling and preserving vials of surface water): one near the center

of the lake and nine equally spaced from the center and around the lake (U.S. Environmental Protection Agency (EPA), 2007). To evaluate the percent error from following this protocol, we calculated the flux at the center of the lake and randomly selected nine measurements from around the perimeter of the lake. As one example, percent errors of 18% for CH<sub>4</sub> and 27% for CO<sub>2</sub> were calculated if the standard protocol was followed (see Table S2). It is worth

**Table 3**Comparing regional emissions of CH<sub>4</sub> and CO<sub>2</sub> from freshwater sources and the coastal ocean. All fluxes are diffusive unless otherwise stated.

Region	Permafrost coverage	Area (10 <sup>3</sup> km <sup>2</sup> )	Time of emission (d)	CH <sub>4</sub> flux (μmol m <sup>-2</sup> d <sup>-1</sup> )	CH <sub>4</sub> emission* (Tg yr <sup>-1</sup> )	CO <sub>2</sub> flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	CO <sub>2</sub> emission* (Tg C, yr <sup>-1</sup> )
<b>This study</b>							
Lakes – no hotspot	all types	1821 <sup>a</sup>	120	100	0.3	1.2	3
Lakes – mean	all types	1821 <sup>a</sup>	120	122	0.4	3	8
Lakes – only hotspot	all types	1821 <sup>a</sup>	120	544	1.9	39	102
<b>Other studies</b>							
NH Lakes	all types	1821 <sup>a</sup>	120	550 <sup>b</sup>	1.9	21 <sup>b</sup>	55
Lake Ebullition	all types	1821 <sup>a</sup>	120	11,794	15.5 <sup>c</sup>	n/a	n/a
Lake Spring Thaw	sporadic	135 <sup>a</sup>	10	83,126	1.8 <sup>d</sup>	n/a	n/a
Freshwater Sources	all types	n/a	n/a	n/a	19.3 <sup>e</sup>	n/a	151 <sup>g</sup>
<b>This study</b>							
Kasitsna Bay	discontinuous	7190 <sup>h</sup>	365	0.5	0.02	–2	–53
Jakolof Bay	discontinuous	7190 <sup>h</sup>	365	0.8	0.03	–0.8	–26
<b>Other studies</b>							
Coastal Ocean	n/a	7190 <sup>h</sup>	365	1.5 (1–2) <sup>i</sup>	0.7 (0.3–1) <sup>i</sup>	–5.2 <sup>h</sup>	–162 <sup>h</sup>
Global Ocean	n/a		365		1 (0.6–1.5) <sup>i</sup>	–1.21 <sup>h</sup>	–1930 <sup>h</sup>

\*Total CH<sub>4</sub> and CO<sub>2</sub> emissions were calculated for the time period of active flux (time of emission/yr). <sup>a</sup>Lake area was taken from Bastviken et al. (2011) for lakes north of 54°N. <sup>b</sup>These are averaged values from Kling et al. (1992), <sup>c</sup>Bastviken et al. (2011), <sup>d</sup>Phelps et al. (1998). Freshwater sources are defined as lakes, rivers and streams. <sup>e</sup>Freshwater CH<sub>4</sub> emissions were taken from Bastviken et al. (2011) and include ebullition and diffusive fluxes. <sup>g</sup>Emission of CO<sub>2</sub> from freshwater sources north of 50°N was taken from Aufdenkampe et al. (2011). <sup>h</sup>The coastal ocean area and flux were taken from Borges (2005) and were defined as the coastal region between 60°–90°N. <sup>i</sup>The averaged coastal flux of CH<sub>4</sub> was taken from Rhee et al. (2009).

**Fig. 4.** Histograms for dissolved CH<sub>4</sub> concentration for a) Toolik 2011, b) Toolik 2012, c) Jakolof 2011, and d) Kasitsna 2012.

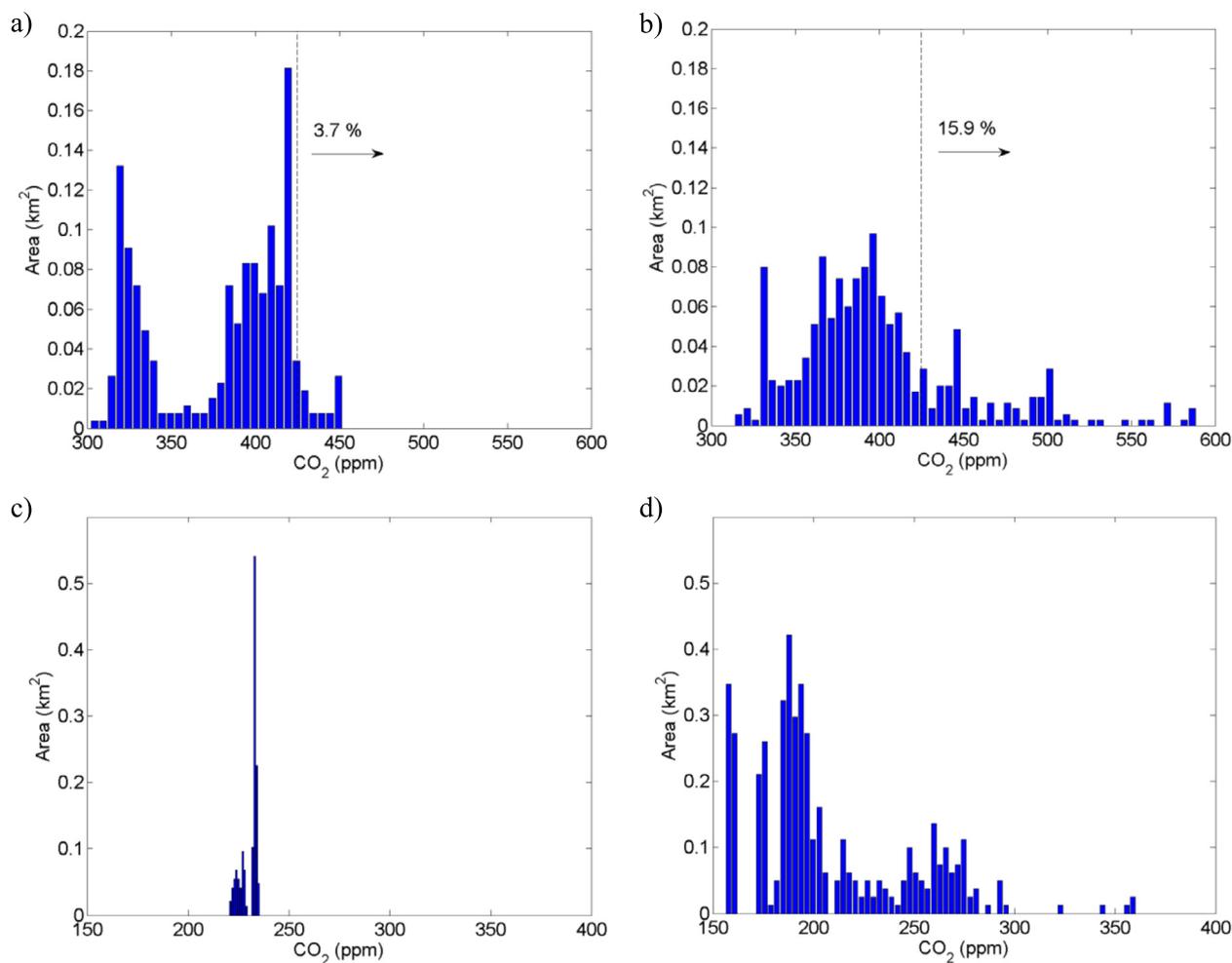


Fig. 5. Histograms of dissolved  $\text{CO}_2$  partial pressure for a) Toolik 2011, b) Toolik 2012, c) Jakolof 2011, and d) Kasitsna 2012.

noting that these are example calculations and very different percent errors will be determined if concentration hot-spots are not selected among the nine samples.

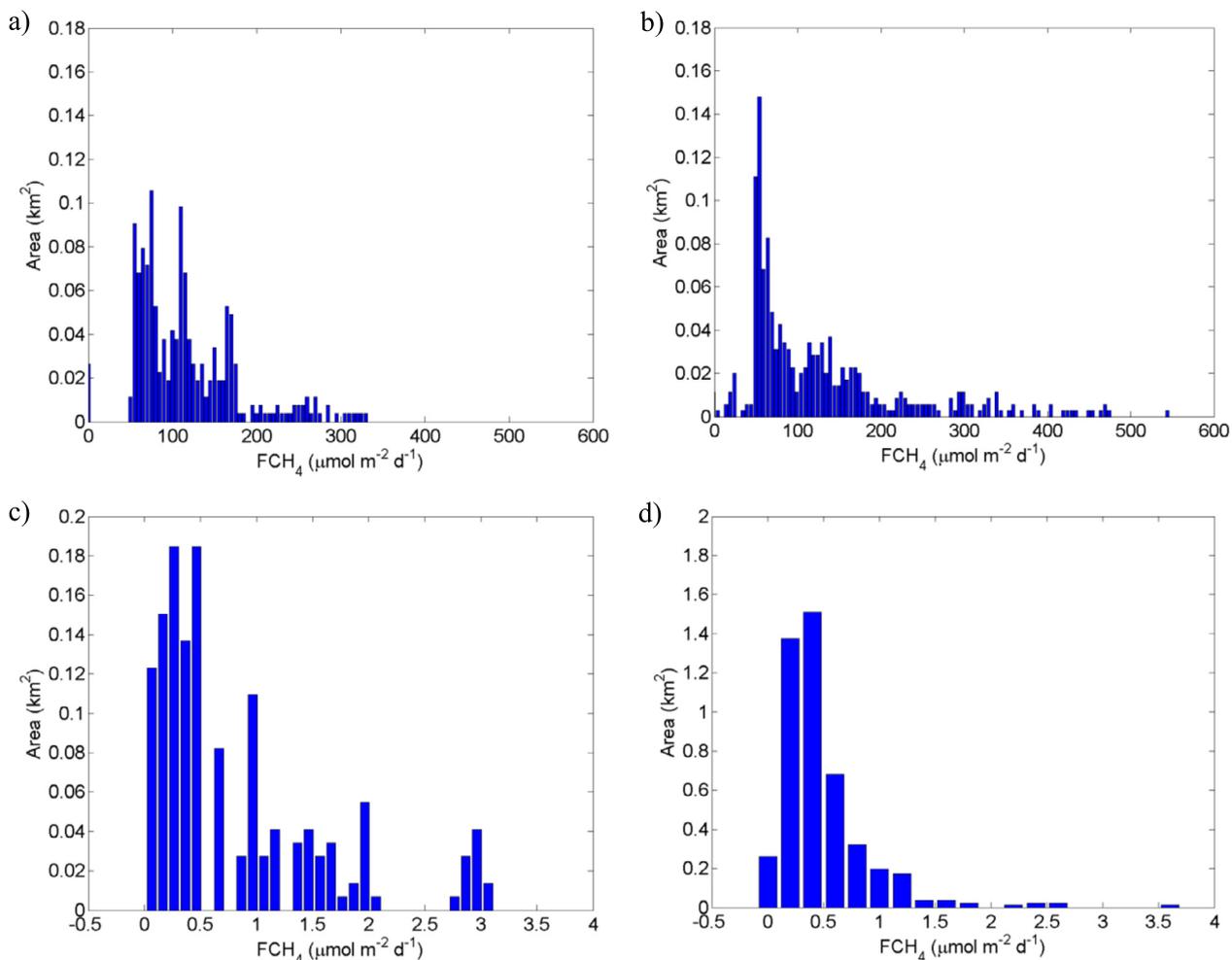
The distribution profiles of surface water concentrations and diffusive fluxes varied between regions and gases. The bimodal distribution of dissolved  $\text{CH}_4$  and  $\text{CO}_2$  in Toolik 2011 and Kasitsna 2012 suggests that there are multiple sources of dissolved  $\text{CH}_4$  and  $\text{CO}_2$ . Potential inputs of  $\text{CH}_4$  and  $\text{CO}_2$  to Toolik Lake could include groundwater discharge and in-lake respiration of terrestrial derived organic carbon (Kling et al., 1991, 1992). Other potential inputs of  $\text{CH}_4$  in Arctic Lakes comprise anaerobic methanogenesis in sediments or bottom waters, aerobic methanogenesis, and fossil (radiocarbon-free) sources. Anaerobic methanogenesis in sediments is an unlikely source as Toolik Lake is characterized by very low organic matter sedimentation rates and low dissolved oxygen consumption rates (Cornwell and Kipphut, 1992). Toolik Lake is also extremely oligotrophic, with primary production being co-limited by dissolved inorganic nitrogen and phosphorous (Whalen and Alexander, 1986) thus anaerobic methanogenesis of autochthonous material is also unlikely. This suggests that the  $\text{CH}_4$  emitted from Toolik Lake may be from a different origin. The highest dissolved concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  were observed in the southern and the northern areas of the lake in proximity to the stream inlets of the lake (Fig. 2 and Fig. 3) and coincident with areas of highest groundwater discharge (Dimova et al., 2015; Paytan et al., 2015). Thus, as suggested by previous studies, groundwater

is likely an important source of  $\text{CH}_4$  and  $\text{CO}_2$  in Toolik Lake (Kling et al., 1991; Paytan et al., 2015).

Sources of  $\text{CH}_4$  to the coastal ocean include: horizontal and vertical transport from seafloor sources (Sansone et al., 2001), river inputs (Abril and Borges, 2005), in situ methane production, zooplankton, and fecal pellets (Damm et al., 2008; Karl et al., 2008). Likewise, submarine groundwater discharge has been observed to be significant in coastal regions and could also contribute to the release of carbon into this coastal ocean (Bugna et al., 1996; Lecher et al., 2015; Moore, 2010). A study by Lecher et al. (2015) found that submarine groundwater discharge is a source of  $\text{CH}_4$  in Kasitsna Bay.

The data presented here shows that the concentration and flux of  $\text{CH}_4$  and  $\text{CO}_2$  in Toolik Lake, Kasitsna and Jakolof Bays are highly heterogeneous most likely due to local sources. The highest dissolved  $\text{CH}_4$  and  $\text{CO}_2$  concentration values were localized to areas where streams enter the lake and bays (Figs. 2 and 3). Similarly, areas of high  $\text{CH}_4$  and  $\text{CO}_2$  flux were not uniform but were instead constrained to smaller and irregular zones (Figs. 6 and 7). A further indication of significant variability is the standard deviation of our data which is of a similar order of magnitude as the mean (Table 2).

To assess the effect of such non-uniform fluxes on the overall estimates in these two study areas, we calculated the percent error if 1) hot-spots areas were omitted and if 2) only the highest flux value was measured and compared these values to the mean flux using all the data. Hot-spots areas were defined as areas with



**Fig. 6.** Histograms for water-to-air fluxes of  $\text{CH}_4$  for a) Toolik 2011, b) Toolik 2012, c) Jakolof 2011, and d) Kasitsna 2012. Please note the difference in y-axis for panels c) and d).

the highest concentrations of  $\text{CH}_4$  and  $\text{CO}_2$ . Gas concentrations in Toolik Lake were higher in 2012 than in 2011, thus to be consistent between years we chose the 2011 data to define our hot-spot areas (concentrations higher than 180 nM for  $\text{CH}_4$  and 425 ppm for  $\text{CO}_2$ ). For the coastal ocean, we defined hot-spot areas as areas with  $\text{CH}_4$  concentration higher than 8 nM. Since the coastal ocean was undersaturated with respect to  $\text{CO}_2$ , no hotspots errors were calculated. These calculations suggest that errors of 18% for  $\text{CH}_4$  and 24% for  $\text{CO}_2$  are obtained if hot-spots are ignored (see Table S2). Errors of over 346% for  $\text{CH}_4$  and 1000% for  $\text{CO}_2$  are obtained if only the highest flux value is assumed to be representative (Table 3).

Likewise, we can calculate the percentage of the Toolik Lake or bay area covered by hot-spots (as defined above). Our estimates indicate that hot-spots of dissolved  $\text{CH}_4$  concentrations were isolated covering 16% (in 2012) to 21% (in 2011) of the total lake area and less than 15% of the bay areas (Fig. 4). It should be pointed out that the hot-spots area for Toolik Lake 2011 may be overestimated as no data for the center of the lake is available. For dissolved  $\text{CO}_2$ , hot-spot areas were constrained to less than 16% of the total lake (Fig. 5).

To determine the significance of temporal variability between the surveys in 2011 and 2012, we selected those points with similar location within a 15 m radius. We calculated a temporal error of up 0.5% for diffusive fluxes of  $\text{CH}_4$  and 2.8% for diffusive fluxes of  $\text{CO}_2$ . At least to first-order, this suggests that spatial heterogeneity provides more variance than year-to-year differences.

Methane and  $\text{CO}_2$  fluxes measured in this study for Toolik Lake were about an order of magnitude lower than the fluxes published by Kling et al. (1991) and Kling et al. (1992) (Table 1 and Table 2), who calculated diffusive fluxes from discrete surface water concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  ( $n = 4$  to 11). While the source of the discrepancy could be due to undersampling, it could also be manifested in the different choice of gas exchange coefficients and atmospheric concentration measurements. Kling et al. (1991) and Kling et al. (1992) used globally averaged atmospheric concentrations, whereas the results presented here were recorded locally. Likewise, flux variability could arise from natural variations. As observed by Kling et al. (1992),  $\text{CO}_2$  fluxes at Toolik Lake showed significant inter-annual variations (fluxes ranged from 10.6 to 66.7  $\text{mmol m}^{-2} \text{d}^{-1}$  over 14 yr). To determine the potential cause of the discrepancy between our data and those published by Kling et al. (1992), we used the mean concentration values for  $\text{CH}_4$  and  $\text{CO}_2$  given in Kling et al. (1992) and our gas exchange coefficient to calculate diffusive fluxes. We obtained similar fluxes as those reported by Kling et al. (1.2 and 71  $\text{mmol m}^{-2} \text{d}^{-1}$  of  $\text{CH}_4$  and  $\text{CO}_2$ , respectively) suggesting that the different choice of gas exchange coefficients is not the source of difference. Since water concentrations were orders of magnitudes higher than atmospheric concentrations, varying atmospheric concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  did not drastically change the calculated diffusive fluxes suggesting that changing atmospheric concentrations was also not the source of the difference. However, if our sampling was restricted to only the regions of highest flux, the values pre-

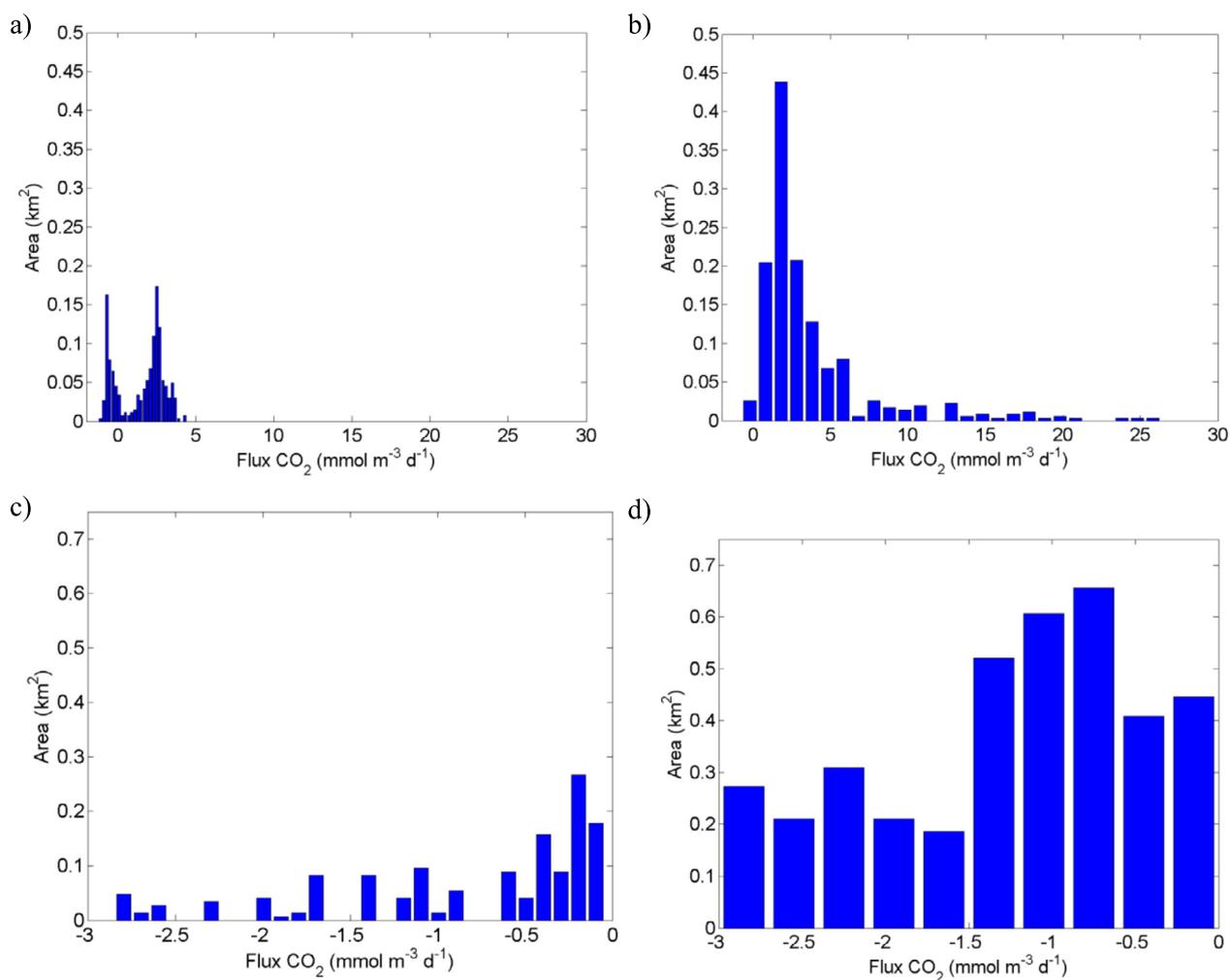


Fig. 7. Histograms for water-to-air fluxes of CO<sub>2</sub> for a) Toolik 2011, b) Toolik 2012, c) Jakolof 2011, and d) Kasitsna 2012.

sented here would be closer to those published by Kling et al. (1992) (20 to 30 mmol m<sup>-2</sup> d<sup>-1</sup>). Thus, the difference in fluxes between those presented here and Kling et al. (1992) may be due to the irregular spatial distribution in this environment, which is difficult to constrain with discrete samples (Figs. 4–7). Finally, no predictive distribution profiles were determined for the surface water concentrations (Figs. 4–5). Even though this technique may be more difficult to utilize in remote locations than collecting discrete water samples, it is our recommendation that high resolution sampling techniques be employed when possible to minimize uncertainties.

## 5.2. First-order assessment of Arctic and Subarctic diffusive fluxes

To assess the regional contribution of Arctic and Subarctic diffusive fluxes, we conducted a first-order extrapolation to coastal waters north of 60°N and to lakes north of 54°N (Table 3). The area for the coastal ocean was taken from Borges (2005), whereas the area for lakes was taken from Bastviken et al. (2011). For the Subarctic coastal ocean, if we assume 120 days of open water annually and that our average measured diffusive fluxes (Ave. CH<sub>4</sub> = 0.65 μmol m<sup>-2</sup> d<sup>-1</sup> and Ave. CO<sub>2</sub> = -1.3 mmol m<sup>-2</sup> d<sup>-1</sup>) are constant over this time period, we estimated that the Subarctic coastal ocean is supplying 0.027 Tg of CH<sub>4</sub> to the atmosphere. This is 4% of Subarctic coastal CH<sub>4</sub> emissions and 2.6% of the global CH<sub>4</sub> emissions. We also estimated that the coastal ocean is taking up approximately 40 Tg of C from the atmosphere annually as CO<sub>2</sub>.

This is 24% of Subarctic coastal CO<sub>2</sub> uptake and 2% of the global uptake (Table 3).

We conducted a similar extrapolation for northern high latitude lakes where we assume 120 days of open water annually and that our average measured diffusive fluxes (Ave. CH<sub>4</sub> = 122 μmol m<sup>-2</sup> d<sup>-1</sup> and Ave. CO<sub>2</sub> = 3 mmol m<sup>-2</sup> d<sup>-1</sup>) are constant over this time period. This first-order extrapolation indicates that diffusive fluxes from lakes north of 54°N are likely supplying 0.4 CH<sub>4</sub> and 8 Tg C as CO<sub>2</sub> to the atmosphere annually. These estimates suggest that Arctic lakes such as Toolik Lake contribute between 2.2% and 5% of the regional freshwater CH<sub>4</sub> and CO<sub>2</sub> emissions, respectively, or between 0.5% and 0.7% of the global freshwater CH<sub>4</sub> and CO<sub>2</sub> emissions, respectively (Table 3). These are small percentages when compared to other freshwater sources. However, if we used the flux values from Kling et al. (1992), which are of similar magnitude as the fluxes from hot-spot areas in this study, northern hemispheric lakes could be contributing 2 Tg of CH<sub>4</sub> and 55 Tg of C as CO<sub>2</sub> to the atmosphere annually (39% higher emissions for CH<sub>4</sub> and 60% higher emission for CO<sub>2</sub>). This translates to about an order of magnitude higher emissions and emphasizes the discrepancy that can be obtained if such lakes are not well characterized. While lakes such as Toolik Lake may be a small source of CH<sub>4</sub> and CO<sub>2</sub> to the atmosphere presently, warming in the Arctic may result in the expansion of the active layer which may increase methane discharge and methane emissions to the atmosphere (Paytan et al., 2015). Further investigations and continued

monitoring are needed to better understand and predict changes in this dynamic environment.

## 6. Conclusion

Here we determined high-resolution spatial distributions of dissolved concentrations and water-to-air fluxes of CO<sub>2</sub> and CH<sub>4</sub> from two different Alaskan field sites, Kasitsna and Jakolof Bays and Toolik Lake. The investigation presented here shows that these environments are highly heterogeneous and that the errors introduced from inappropriate sampling may be higher. Errors of up to 60% can be introduced in regional emission models if the spatial distributions of CH<sub>4</sub> and CO<sub>2</sub> in northern hemisphere lakes are not well characterized. This suggests that in order to produce more accurate regional models and capture the true dynamics of these systems, higher spatial resolution determinations requiring more experimentally complex measurements are needed to account for the heterogeneity of the sources.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2015.12.002>.

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