## Research Brief

# **Summer methane ebullition from a headwater catchment in Northeastern Siberia**

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# **Abstract**

Streams and rivers are active processors of terrestrial carbon and significant sources of carbon dioxide (CO<sub>2</sub>) and methane  $(CH<sub>4</sub>)$  to the atmosphere. Recent studies suggest that ebullition may represent a sizable yet overlooked component of the total CH<sub>4</sub> flux from these systems; however, there are no published CH<sub>4</sub> ebullition estimates for streams or rivers in subarctic or arctic biomes, regions that store vast quantities of vulnerable, old organic carbon in permafrost soils. We quantified CH<sub>4</sub> ebullition from headwater streams in a small arctic watershed in Northeastern Siberia. Ebullitive emissions were 0.64 mmol m<sup>-2</sup> d<sup>-1</sup>, which is lower than the global average but approximately 2 times greater than the pan-arctic diffusive  $CH<sub>4</sub>$  flux estimate reported in a recent synthesis of global freshwater  $CH<sub>4</sub>$ emissions. The high  $CO_2$ :CH<sub>4</sub> of sediment bubbles (0.52) suggests that methane emissions may currently be constrained by resource competition between methanogens and microbes using more efficient metabolic strategies. Furthermore, the magnitude and frequency of ebullition events were greater as temperatures increased, suggesting that ebullition from streams could become a more prominent component of the regional CH<sub>4</sub> flux in a warmer future.

**Key words:** Arctic, carbon dioxide, carbon emissions, ebullition, methane, rivers, Siberia, streams

# **Introduction**

Rivers and streams are important sites of terrestrial carbon (C) transport and processing (Cole et al. 2007, Battin et al. 2009) and have gained recognition as considerable sources of carbon dioxide  $(CO<sub>2</sub>)$  to the atmosphere (Aufdenkampe et al. 2011, Butman and Raymond 2011, Raymond et al. 2013). Their role in the global methane  $(CH<sub>4</sub>)$  cycle, however, remains uncertain, particularly in high-latitude environments (Bastviken et al. 2011) where permafrost soils store vast quantities of old organic C (Tarnocai et al. 2009, Hugelius et al. 2014). As the climate continues to warm and permafrost thaws, this C will be increasingly vulnerable to mineralization and transfer to the atmosphere as greenhouse gases, thereby perpetuating a potent positive feedback to anthropogenic climate warming (Schuur et al. 2008, 2013). Understanding the

factors regulating C metabolism in streams and rivers and the relative contribution of these systems to aquatic  $CH<sub>4</sub>$ emissions is therefore necessary to constrain flux estimates and predict future emissions from arctic and subarctic regions (Kirschke et al. 2013).

Gas flux estimates from streams and rivers typically emphasize diffusive emissions and overlook the contribution of ebullition (bubble mediated emission), which is the dominant pathway of  $CH<sub>4</sub>$  evasion from lakes (Bastviken et al. 2004). Recent studies in temperate and tropical streams and rivers suggest that ebullition may represent up to 80% of  $CH_4$  emissions from these systems, but data remain sparse (Baulch et al. 2011, Sawakuchi et al. 2014). Ebullition is both episodic and spatially variable and is often poorly quantified due to insufficient spatial coverage and/or brief measurement periods (Wik et al. 2013, Maeck et al. 2014). In lakes, the timing and magnitude of

ebullition events is often driven by landscape-level, meteorological factors such as falling hydrostatic pressure (Mattson and Likens 1990, Varadharajan and Hemond 2012) and energy inputs (Wik et al. 2014), but the factors driving these events in streams remain uncertain. Here we report the first estimate of  $CH<sub>4</sub>$  ebullition from streams north of 49°N and explore possible factors affecting the spatial and temporal patterns of ebullitive emissions.

## **Study site**

We studied stream reaches within the "Y3" catchment of the lower Kolyma River basin (Fig. 1) located near the Northeast Science Station in the town of Cherskiy, Russia. The Kolyma River is the fifth largest river draining into the Arctic Ocean, and its watershed is the world's largest underlain entirely by continuous permafrost. The Y3 watershed covers  $16.84 \text{ km}^2$  and extends from alpine to floodplain ecosystems (elevation: 18–275 m). The regional climate is dry, cold, and continental. Sampled streams drain boreal larch (*Larix cajanderi*) forests of varying density and large patches of dense, low-lying *Betula*, *Salix*, and *Vaccinium* shrubs. The watershed also contains 9 small lakes, one of which was the subject of 2 intensive studies of  $CH<sub>4</sub>$  ebullition (Zimov et al. 1997, Walter et al. 2006).

# **Methods**

We measured  $CH<sub>4</sub>$  and  $CO<sub>2</sub>$  ebullition from streams of the Y3 watershed for 40 d during July and August 2014 using inverted funnels affixed to wooden stakes to trap bubbles (Molongoski and Klug 1980). We deployed 24 funnel traps at sites chosen randomly along 6 accessible stream reaches (order 2–4) using a Geographic Information System (GIS). Accumulated gas volumes were recorded every 2–4 d. On 25 July and 13 August we collected sediment bubbles from sites adjacent to each trap (within 1 m) to analyze  $CO<sub>2</sub>$  and  $CH<sub>4</sub>$  content. Bubble samples were collected by stirring sediments to release bubbles and capturing them in a mobile version of our stationary bubble traps. Stirred bubbles were collected rather than those collected in our traps due to the potential for diffusion of component gases out of the trap (Crawford et al. 2014). Due to the shallow water depth of our streams (<1 m), we assumed that equilibration of erupted bubbles with the surrounding water column (McGinnis et al, 2006) was negligible and that stirred bubbles were representative of the true ebullitive flux (Crawford et al. 2014).

At each site, we collected one 10 mL gas sample and transferred it into a 24 mL serum vial pre-flushed with  $N<sub>2</sub>$ gas and sealed with thick butyl rubber stoppers. Samples were shipped to Fort Collins, Colorado, for analysis on a



**Figure 1.** Location of our study site, the Y3 watershed, and the spatial distribution of bubble traps.



for site-specific sediment metrics.



Los Gatos Research (Mountain View, CA) DLT-100 greenhouse gas analyzer (see Supplementary Methods). Prepared standards accompanied samples in shipment to evaluate potential leakage during transit. After accounting for the dilution resulting from our sampling procedure, we estimated daily molar fluxes of  $CH<sub>4</sub>$  and  $CO<sub>2</sub>$  according to the ideal gas law as:

$$
n = (P \times V) / (R \times T) \times X_{gas},
$$
 (1)

where n is the molar flux of a given gas, P is barometric pressure (atm), V is the rate of bubble release (L m<sup>-2</sup> d<sup>-1</sup>), R is the gas constant (L atm K<sup>-1</sup> mol<sup>-1</sup>), T is the sediment temperature at the time of bubble collection  $(K)$ , and  $X_{\text{gas}}$ is the mole fraction of  $CO<sub>2</sub>$  or  $CH<sub>4</sub>$  in collected bubbles.

We used Monte Carlo methods to calculate a constrained estimate of total ebullitive CO<sub>2</sub> and  $CH<sub>4</sub>$ fluxes from Y3 streams with quantified uncertainty (Baulch et al. 2011, Crawford et al. 2013, 2014). We created probability distributions of  $CO$ , and  $CH<sub>4</sub>$  fluxes by resampling  $(n = 10000)$  measured flux volumes, bubble compositions, and a probability distribution of stream area. The stream area distribution was created using Monte Carlo resampling as the product of stream length and a random survey of 96 stream widths measured throughout Y3 in late July 2014. Stream length was generated using a digital elevation model (DEM) derived from high-resolution  $(\leq 2 \text{ m})$  stereo-pair imagery obtained from the Polar Geospatial Center [\(www.pgc.umn.edu](http://www.pgc.umn.edu)) and validated by field observation. We assumed a 120 d open water season. Fluxes were reported as the mean of the resulting distribution, and error was quantified as a 95% confidence interval (CI).

To explore factors affecting ebullition events, we collected 3 cm diameter cores from the upper 10 cm of sediment at each site in early August to measure bulk density and organic matter (OM) content. Sediment OM was determined as percent loss on ignition (%LOI) by combusting samples at 450 °C for 4 h in a muffle furnace. We also measured sediment temperature using a type K thermocouple and thaw depth (distance between sediment surface and underlying permafrost) with a metal probe at each site, once monthly. To identify potential meteorological controls, we assessed the temporal consistency of ebullition events between sites by correlation, assuming that these landscape-level controls should affect all sites comparably, and fluxes between sites should therefore be positively correlated (Crawford et al. 2014).

Data distributions were described using Fisher-Pearson's coefficient of skewness (γ1) and the coefficient of excess kurtosis  $(\gamma_2)$ . Because our data were not normally distributed, significant differences in monthly bubble composition and sediment temperature were identified with a Wilcoxon signed-rank test. Relationships between sediment metrics and mean flux magnitude, cumulative flux, and bubble composition were explored using linear regression. All data were log-transformed to meet the assumptions of linear regression, as determined and confirmed using the *gvlma* package in R (Pena and Slate 2014). The sample size (n) for all statistical analyses was 24, unless otherwise noted.

#### **Results**

Volumetric bubble release rates were spatially and temporally variable (Fig. 2), ranging from 0 to 2420 mL m<sup>-2</sup> d<sup>-1</sup> with a mean of 83 mL m<sup>-2</sup> d<sup>-1</sup>. The distribution was skewed right with high kurtosis ( $\gamma_1 = 6.26$ ,  $\gamma_2 = 42.6$ ). Flux events were episodic, and the timing of these events was not consistent among sites, with most sites showing both positive and negative correlations with other sites (Supplementary Fig. S1). In general however, we observed an increase in the relative frequency and magnitude of bubble flux at 19 of 24 sites beginning in late July (Supplementary Fig. S2). Neither mean flux rates nor cumulative flux volumes were correlated with sediment bulk density, OM content, temperature, or thaw depth ( $p > 0.05$ ,  $R^2 < 0.1$ ).

The mean  $CH<sub>4</sub>$  mole fraction of sediment bubbles was 23.3% (range: 1.7–98%) and the distribution was highly skewed to the right ( $\gamma_1$  = 1.43,  $\gamma_2$  = 1.73). On average, CO<sub>2</sub> composed an additional 4.0% (range: 1.0–11.4%) of bubble component gas, and the distribution was also rightskewed ( $\gamma_1 = 1.03$ ,  $\gamma_2 = 0.36$ ). Mean bubble CO<sub>2</sub>:CH<sub>4</sub> was 0.52 (range: 0.02–2.48). While both bubble  $CO<sub>2</sub>$  content and sediment temperature were significantly higher in August compared to July ( $p < 0.001$ ; Fig. 3), neither bubble  $CH_4$  content nor  $CO_2:CH_4$  showed significant changes between July and August ( $p > 0.05$ ). Bubble composition was not correlated to sediment bulk density, OM content, or thaw depth (Table 1;  $p > 0.05$ ,  $R^2 < 0.1$ ).

Ebullitive CH<sub>4</sub> flux from Y3 streams was 0.64 mmol m<sup>-2</sup> d<sup>-1</sup> (95% CI: 0–5.82 mmol m<sup>-2</sup> d<sup>-1</sup>), and CO<sub>2</sub> was 0.13 mmol m−2 d−1 (95% CI: 0–1.14 mmol m−2 d−1). Median surface area of Y3 streams was  $0.135 \text{ km}^2$  (95% CI: 0.022–0.869 km<sup>2</sup>), which represents  $\sim$ 0.8% of the total watershed area. Scaling our fluxes to this area, we estimate that ebullition from streams contributes an additional 40 kg CO<sub>2</sub>-C (95% CI: 0–315 kg) and 186 kg CH<sub>4</sub>-C (95% CI: 0–1.51 Mg) to aquatic C emissions from the Y3 watershed during the open water season.

#### **Discussion**

Our study is the first to quantify ebullition from streams in the Arctic and is one of few stream ebullition studies conducted anywhere in the world. Mean ebullitive  $CH<sub>4</sub>$ flux from Y3 is lower than most other studies and 35% lower than the global average (Table 2). Ebullition from streams in this study represented  $\sim$ 13% of total aquatic  $CH<sub>4</sub>$  ebullition from the Y3 watershed, an area encompassing lakes that represent the largest lake  $CH<sub>4</sub>$  emissions in the literature by 1–3 orders of magnitude (Walter et al. 2006, Bastviken et al. 2011). While  $CH<sub>4</sub>$  ebullition from this study was lower than most other regions,  $CO<sub>2</sub>$  flux estimates were comparable to those of a temperate peatland stream (Crawford et al. 2014). Compared to diffusive emissions reported for Y3 and neighboring streams (Denfeld et al. 2013), however,  $CO<sub>2</sub>$  ebullition was negligible, constituting  $\leq 0.0002\%$  of the total CO<sub>2</sub> flux from streams.

The quantity of  $CH<sub>4</sub>$  in bubbles and the magnitude of  $CH<sub>4</sub>$  emissions may currently be constrained by sediment redox conditions. The high  $CO<sub>2</sub>:CH<sub>4</sub>$  of Y3 sediment bubbles compared to streams in other regions (Table 2) suggests that arctic stream sediments may be less reduced than in temperate and tropical streams (Schimel 1995).



**Figure 2.** Boxplots showing the flux volume distribution for each site. Thick, horizontal black lines represent median flux volumes; boxes represent the interquartile range (IQR); fences indicate 1.5×IQR; and open circles represent outliers.



**Figure 3.** Boxplots of (a) monthly sediment temperature at 15 cm depth, (b) monthly bubble CO<sub>2</sub> content, and (c) monthly CH<sub>4</sub> concentration. Thick, horizontal black lines represent median flux volumes; boxes represent the interquartile range (IQR); fences indicate 1.5×IQR; and open circles represent outliers.

<b>Region</b>	<b>Study</b>	Latitude	<b>Mean Volume</b> $(mL m^{-2} d^{-1})$	<b>Mean Mole</b> Fraction CH <sub>4</sub> $(\%$ )	$CO$ <sub>;</sub> $CH4$	<b>Mean Flux</b> (mmol m <sup>-2</sup> d <sup>-1</sup> )
Russian Arctic	This Study	69°N	83 $(\pm 18)$	$23.3(\pm 3.3)$	$0.52 (\pm 0.8)$	$0.64 (\pm 0.13)$
Temperate Germany	Maeck et al. 2013	49°N				0.04
Temperate <b>USA</b>	Crawford et al. 2014	$46^{\circ}$ N	123	22	0.08	1.25
Temperate Canada	Baulch et al. 2011	44°N	104	26	$0.01 - 0.07$ <sup>a</sup>	1.41
Amazon River and Tributaries	Sawakuchi et al. 2014	2°S				0.6
Agricultural Streams, New Zealand	Wilcock and Sorrell 2008	37°S		41	$0.03 - 0.3$ <sup>a</sup>	1.68
Global Average						0.94

Table 2. Comparison of ebullitive CH<sub>4</sub> emissions from streams and rivers of diverse ecoregions organized by latitude. Error is reported as standard error for our study (n = 48 for %CH<sub>4</sub> and CO<sub>2</sub>:CH<sub>4</sub>; n = 238 for Mean Volume and Mean CH<sub>4</sub> Flux).

<sup>a</sup> Range calculated as the minimum and maximum ratios from the range of  $CO_2$  and  $CH_4$  mole fractions reported.

"-" Indicates that data were not reported.

Accumulations of oxidized iron, Fe(III), which were common throughout reaches of Y3 during this study, lend qualitative support to this hypothesis because the presence of Fe(III) and alternative electron acceptors can inhibit methanogenesis in anoxic sediments (Roden and Wetzel 1996, Bodegom et al. 2004). These metabolic strategies produce  $CO<sub>2</sub>$ , which is relatively water soluble and does not readily nucleate bubbles (van Kesteren and van Kessel 2002). If sediment respiration was dominated by anaerobic CO<sub>2</sub> production, we would expect to see bubbles with both low  $CO<sub>2</sub>$  and  $CH<sub>4</sub>$  content and high  $CO<sub>2</sub>:CH<sub>4</sub>$ , as observed.

Sediment temperature may also regulate the rate of bubble production and emission. While barometric pressure is a driver of ebullition events in lakes (Mattson and Likens 1990, Varadharajan and Hemond 2012), variation in the timing of bubbling events across sites suggests that pressure changes were not the primary driver of bubbling in these streams during the time period of our study. Instead, we hypothesize that the magnitude and frequency of ebullition events depend on the rate of bubble production and growth within sediments. Bubble production rate is related to both respiration rate and the solubility of component gases (Fendinger et al. 1992, Boudreau 2012) and is therefore temperature dependent (Yvon-Durocher et al. 2012, 2014). While the size of our dataset and the length of our study do not permit us to quantitatively assess the role of temperature on bubble release rates in Y3, observed late-season increases in flux volume and frequency (Supplementary Fig. S2) corresponded to a period of warmer air, water, and sediment temperature. Noting the temperature dependence of  $CO<sub>2</sub>$ production in Y3 (Fig. 3), we suspect that this late-season increase is due to greater rates of sediment respiration and bubble production following ice-out and a sufficient sediment warm-up period (Maeck et al. 2013). Energy input, through its effect on sediment temperature and substrate availability, is a known driver of ebullition in lakes (Wik et al. 2014). We surmise that this may also be true in streams and recommend that future studies consider localized variation in energy flux due to riparian shading (Bott et al. 2006, Ball et al. 2010, Burrell et al. 2014) as a potential source of flux variability.

Ebullitive  $CH<sub>4</sub>$  emissions from streams are both regionally significant and sensitive to environmental change. In a recent global synthesis of freshwater  $CH<sub>4</sub>$ emissions (Bastviken et al. 2011), high-latitude stream emissions were extrapolated from a single study of diffusive emissions from the Kuparuk River in Northern Alaska (Kling et al. 1992). The flux estimate from this river (0.36 mmol m<sup>-2</sup> d<sup>-1</sup>) only accounted for diffusion and is  $\approx$  2 times less than the emissions we observed via ebullition, suggesting that ebullition could be a considerable component of  $CH<sub>4</sub>$  emissions from arctic streams and that the current pan-arctic estimate of  $CH<sub>4</sub>$  emissions from rivers and streams may be considerably underestimated. In addition, more recent diffusive estimates from boreal, subarctic, and arctic streams and rivers range from 0.63 to 15.8 mmol m−2 d−1 (Striegl et al. 2012, Crawford et al. 2013, Huotari et al. 2013, Lundin et al. 2013), lending further support to the importance of  $CH<sub>4</sub>$  emissions from

arctic streams to the regional and global  $CH<sub>4</sub>$  cycle. The Arctic is expected to continue warming throughout the next century at rates greater than the global average (Overland et al. 2014). If rates of ebullition are sensitive to temperature, as we hypothesize, the role of  $CH<sub>4</sub>$ ebullition from arctic streams may become more prominent in a warmer future.

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#### **Supplementary Material**

Supplementary Material is available for download via the Inland Waters website, https://www.fba.org.uk/journals/index.php/IW:

Supplementary Figure S1-2; Supplementary Table S1; Supplementary Methods.