Spatial and temporal heterogeneity of methane ebullition in lowland headwater streams and the impact on sampling design

Andrew L. Robison [1,2]* Wilfred M. Wollheim [1] Bonnie Turek [1] Cynthia Bova,[3] Carter Snay,[1] Ruth K. Varner [3]

[1]Department of Natural Resources and Environment, University of New Hampshire, Durham, New Hampshire
[2]Stream Biofilm and Ecosystem Research Laboratory, Ecole Polytechinque Fédérale de Lausanne, Lausanne, Switzerland
[3]Department of Earth Sciences, University of New Hampshire, Durham, New Hampshire

Abstract

Headwater streams are known sources of methane (CH_4) to the atmosphere, but their contribution to global scale budgets remains poorly constrained. While efforts have been made to better understand diffusive fluxes of CH_4 in streams, much less attention has been paid to ebullitive fluxes. We examine the temporal and spatial heterogeneity of CH_4 ebullition from four lowland headwater streams in the temperate northeastern United States over a 2-yr period. Ebullition was observed in all monitored streams with an overall mean rate of 1.00 ± 0.23 mmol CH_4 m^{-2} d^{-1}, ranging from 0.01 to 1.79 to mmol CH_4 m^{-2} d^{-1} across streams. At biweekly timescales, rates of ebullition tended to increase with temperature. We observed a high degree of spatial heterogeneity in CH_4 ebullition within and across streams. Yet, catchment land use was not a simple predictor of this heterogeneity, and instead patches scale variability weakly explained by water depth and sediment organic matter content and quality. Overall, our results support the prevalence of CH_4 ebullition from streams and high levels of variability characteristic of this process. Our findings also highlight the need for robust temporal and spatial sampling of ebullition in lotic ecosystems to account for this high level of heterogeneity, where multiple sampling locations and times are necessary to accurately represent the mean rate of flux in a stream. The heterogeneity observed likely indicates a complex set of drivers affect CH_4 ebullition from streams which must be considered when upscaling site measurements to larger spatial scales.

Streams and rivers contribute significantly to the global carbon cycle as sources of atmospheric carbon dioxide (CO_2) and methane (CH_4) (Cole et al. 2007; Drake et al. 2018). However, a comprehensive understanding of controls on emissions of these gases both spatially and temporally is needed to accurately scale to continental or global extents (Kirschke et al. 2013; Saunois et al. 2020). In particular, measurements of CH_4 dynamics in streams and rivers are scarce (Stanley et al. 2016), and as a result these ecosystems are rarely included in global CH_4 inventories (Butman et al. 2018).

*Correspondence: andrew.robison@epfl.ch

Additional Supporting Information may be found in the online version of this article.

Author Contribution Statement: A.L.R., W.M.W., B.T., and R.K.V. designed the study. A.L.R., B.T., C.B., and C.S. performed the field observations and laboratory analyses. A.L.R. analyzed the data with input from W.M.W. A.L.R. wrote the manuscript with input from all authors.

Observations of CH_4 concentrations and fluxes across studies suggest most streams are sources of CH_4 to the atmosphere (Stanley et al. 2016). However, almost all estimates of CH_4 emissions from streams ignore ebullitive, or bubble-mediated emissions despite studies showing ebullition can account for over 50% of the total CH_4 emitted (Baulch et al. 2011; Crawford et al. 2014). Daily rates of CH_4 ebullition from streams can vary over several orders of magnitude within a single river network, from near zero to over 100 mmol CH_4 m^{-2} d^{-1} (Zhang et al. 2020), but usually average less than 10 mmol CH_4 m^{-2} d^{-1} (Stanley et al. 2016). While attempts have been made to include diffusive CH_4 emissions from lotic ecosystems in global budgets, ebullitive fluxes remain too unconstrained to scale effectively (Saunois et al. 2020). Because small streams comprise the largest fraction of surface area within the global fluvial network (Downing et al. 2012), understanding ebullitive CH_4 emissions from these systems is essential to accurately include lotic ecosystems in the global CH_4 budget.

Generally, for ebullition to occur at a given location, the sediment must support CH_4 production and bubble formation. This entails both chemical parameters like availability

and lability of organic matter (OM) and reduced redox conditions, and physical conditions for bubble formation and release like porosity and hydrostatic pressure (Wik et al. 2018). Ebullition variability over monthly to seasonal periods appears to be driven mainly by temperature (Aben et al. 2017; Spawn et al. 2017). Spatial variability of ebullition is less constrained. For lentic systems, geomorphic characteristics like depth appear important (Wik et al. 2016*b*; Burke et al. 2019), where shallower water bodies typically exhibit higher rates of ebullition due to higher sediment temperature (Wik et al. 2014). In streams, sediment characteristics (e.g., OM content, sediment depth) appear to be the strongest predictors of spatial variability in CH_4 ebullition in streams, but results are not uniform across studies (Baulch et al. 2011; Crawford et al. 2014). Furthermore, streams and rivers exhibit characteristics that likely distinguish them from lentic ecosystems regarding ebullition (Stanley et al. 2016). For example, patterns of erosion or sedimentation caused by flow may promote bubble formation in specific patches (i.e., pools) and limit bubble formation in others (i.e., riffles; Sanders et al. 2007; Bodmer et al. 2020). Similarly, the impact of land use on streams can exacerbate these theoretical influences on CH_4 ebullition, including hydrologic disturbance, erosion, nutrient loading, and temperature (Walsh et al. 2005). While some analyses of the effects of land use on diffusive CH_4 concentrations and emissions from streams and rivers have been reported (Stanley et al. 2016), a similar analysis has yet to be done for ebullition. A recent study attributed high rates of CH_4 ebullition from urban streams to high levels of sediment organic carbon (Wang et al. 2021); however, benthic OM is not always elevated in urban streams (Meyer et al. 2005). In summary, these complex and interdependent set of controls have hindered our understanding of ebullitive fluxes in lotic ecosystems and highlight the need for further study of this emission pathway.

Ebullition monitoring in aquatic environments is most commonly done in limited temporal scope where floating chambers are deployed at a location for several hours during daylight on 1 d for one or a few occasions (Sawakuchi et al. 2014; Borges et al. 2015; Zhang et al. 2020). Moreover, many of these studies also rely on a single chamber to represent a stream or limit deployment of chambers to a specific area of the stream. Because of the stochastic nature of bubble releases, that is, bubbles are released intermittently and irregularly, studies that sample infrequently or in a single location will likely incorrectly estimate ebullitive flux depending on the time of year and the proclivity of the specific patch for ebullition. Studies have addressed the temporal and spatial sampling intensity required to accurately represent lakes (Wik et al. 2016*a*) and peatlands (Treat et al. 2007; Ramirez et al. 2017), but this has yet to be examined in lotic ecosystems.

We examined the links among CH_4 ebullition and physical (e.g., flow, temperature) and biogeochemical (e.g., sediment OM content) variables across four headwater streams, including two streams draining suburban landscapes. Our goal was to identify drivers of seasonal and spatial heterogeneity of CH_4 ebullition among and within streams. We expected patch rates of ebullition to increase with sediment OM content (Bodmer et al. 2020; Wang et al. 2021) and for ebullition to increase with temperature (Aben et al. 2017). We also examine the impact of sampling design (i.e., sampling duration and spatial extent) on estimations of mean annual ebullitive CH_4 flux to provide a framework for future investigations of ebullition in lotic ecosystems.

Methods

Ebullition was monitored at four headwater streams using stationary bubble traps. Traps were deployed at four patches within a 60 m reach in each stream and were visited at least once a week from June through October and collected gas was analyzed for CH_4 concentration. Two streams were monitored in 2018 and 2019 and two additional streams were monitored only in 2019. Environmental variables monitored as potential seasonal controls on ebullition included water temperature, barometric pressure, solar radiation, dissolved oxygen (D.O.), water depth, and discharge. Spatial variability was examined primarily at the patch scale, and included water depth, canopy cover, and sediment OM content, particle size, percent carbon, and percent nitrogen.
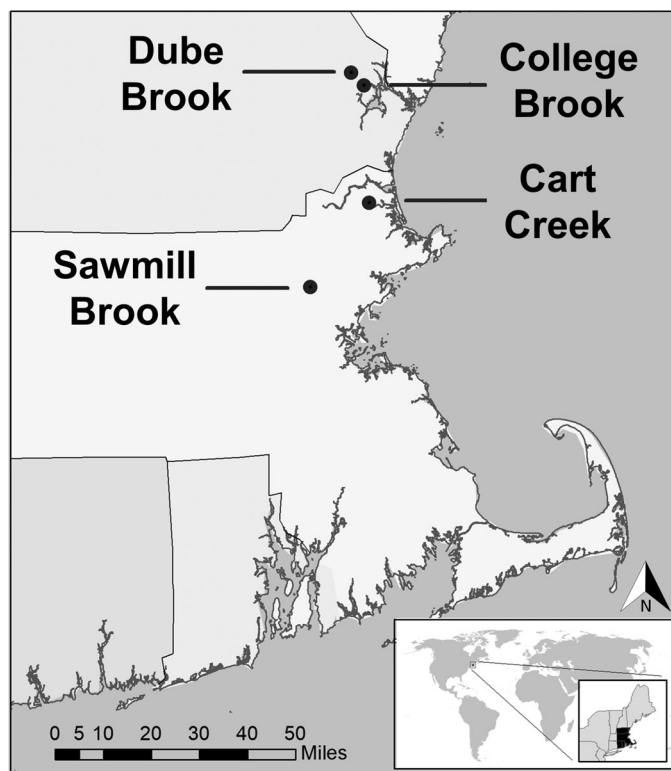

Fig. 1. Location of four study stream reaches in southeast New Hampshire and northeast Massachusetts.

Site description

Reaches within four headwater streams, each draining approximately 2–4 km^2 watersheds, were monitored in this study (Fig. 1). These streams are part of long-term monitoring efforts: two streams (Cart Creek and Sawmill Brook) are part of the Plum Island Ecosystems Long Term Ecological Research (PIE LTER; Morse and Wollheim 2014) in northeastern Massachusetts and two streams (College Brook and Dube Brook) are part of long-term monitoring in the Oyster River watershed (Wollheim et al. 2017) in southeastern New Hampshire. All streams are Strahler stream order one, except Sawmill Brook, which is a second-order system. The watersheds are located on the coastal lowland section of New England and are characterized by shallow relief (Baker et al. 1964).

As part of these monitoring efforts, basin characteristics, discharge, and some water quality variables are measured (Table 1). These watersheds were originally selected to represent distinct land use class, where Cart Creek and Dube Brook drain relatively undeveloped watersheds for coastal New England and are primarily covered by forests and wetlands. Sawmill Brook and College Brook drain suburban landscapes, and as a result, generally have higher background concentrations of nitrate and chloride. The two suburban streams are primarily characterized by sandy sediments, while the sediment in the two undeveloped streams has a higher fine particulate and OM content (Table 2). Reaches selected for ebullition monitoring were colocated with long-term monitoring locations and are generally representative of the larger stream systems. Each reach included various stream habitats (e.g., pools and riffles), which also correspond to changes in benthic substrates (e.g., fine sediments to cobbles).

Bubble trap construction, deployment, and sampling

Bubble traps were installed in each stream reach to estimate ebullitive CH_4 emissions (*see* Baulch et al. 2011; Crawford and Stanley 2016). The traps consisted of a 25-cm diameter plastic funnel fitted with a 60 mL plastic syringe and three-way stopcock, all sealed with water-tight sealant. To install a trap in the stream channel, a 1-m long steel stake was hammered into the stream bottom and a trap was affixed to the stake by plastic zip-ties. The traps were placed approximately halfway underwater so that the syringe remained above the water across most flow conditions while the funnel remained partially submerged (Fig. S1). The funnels could not move vertically, thus were adjusted across the monitoring period to follow baseflow conditions.

Locations for bubble trap deployment, hereafter referred to as patches, were selected for each stream. An initial patch near a long-term monitoring location for water quality was installed at each stream, and subsequent patches were distributed approximately every 10–15 m upstream or downstream. Four patches were located at Cart Creek, Dube Brook, and Sawmill Brook, and three patches were chosen at College Brook due to limited access to this stream. Patch selection avoided rocky substrate, which makes installation of our trap design unfeasible. This limitation accounted for less than 10% of each stream reach and the larger stream network, a feature of these relatively low-gradient systems. Traps were placed in established channels rather than in intermittently inundated portions of the sediments. No other preference for patch selection was made, and we assume the distribution of patches is representative of the stream reach apart from rocky substrates. Three traps were installed at each patch, approximately

Table 1. Location, watershed, and stream characteristics, and select mean water quality variables for the four streams during the study period. Standard deviations are shown in parentheses where relevant.

		Cart Creek	Sawmill Brook	College Brook	Dube Brook
Physical descriptors	Study period	2018–2019	2018–2019	2019	2019
	Latitude (°)	42.77	42.52	43.13	43.17
	Longitude (°)	−70.92	−71.18	−70.92	−70.97
	Area (km^2)	3.9	4.1	2.3	3.3
	Mean discharge (L s^{-1})	30.8	36.7	25.5	29.1
	Slope (m km^{-1})	2.1	1.7	1.9	1.4
	Mean reach depth (cm)*	14.5 (1.4)	11.9 (1.2)	7.2 (0.9)	7.7 (0.8)
	Mean reach width (m)*	2.78 (0.94)	2.83 (0.76)	1.94 (0.69)	2.23 (0.49)
	Riparian canopy cover (%)	73	76	71	21
	Mean annual temperature (°C)	9.9	10.6	9.7	10.1
Land cover	Forest (%)	57.0	13.7	20.8	59.4
	Developed (%)	10.7	72.8	68.7	7.9
	Wetland (%)	18.7	4.3	0.7	17.3
Stream chemistry	Nitrate (mg L^{-1})	0.1(0.1)	0.8(0.4)	0.7 (0.3)	0.2 (0.1)
	Chloride (mg L^{-1})	101(51)	190(112)	321 (193)	63 (29)
	DOC (mg L^{-1})	7.3(3.3)	4.6(2.0)	4.2 (2.3)	6.0 (2.9)

*Characteristics at baseflow conditions.

Table 2. Patch characteristics used in spatial analyses. Mean values are shown. OM indicates organic matter.

Stream	Patch	Canopy cover	Water depth	Depth to refusal	Sediment < 2 mm	Sediment OM content	Sediment C : N
		%	cm	cm	%	%	Ratio
Cart Creek	1	76.5	42.0	72.1	4.24	15.08	22.4
	2	64.7	78.5	36.2	6.36	14.70	19.5
	3	73.5	64.5	76.8	6.49	12.17	17.1
	4	70.6	34.0	6.5	8.70	19.47	21.5
Sawmill	1	76.5	51.0	78.2	0.03	0.77	32.9
Brook	2	76.5	38.9	39.0	0.10	2.82	41.4
	3	78.0	28.1	67.0	0.91	4.48	29.7
	4	73.5	46.0	27.0	4.40	5.80	39.4
Dube Brook	1	16.8	27.3	36.0	14.32	4.05	26.3
	2	21.2	33.2	28.4	12.85	4.31	17.0
	3	17.3	21.5	58.7	17.43	11.95	26.2
	4	34.7	18.1	22.8	1.13	5.75	32.9
College	1	76.5	17.6	67.5	0.04	0.53	32.1
Brook	2	73.5	9.0	33.5	0.72	1.48	35.1
	3	70.6	9.3	40.3	86.21	2.41	33.6

equally dispersed about 1 m apart (Fig. S1). Bubble traps were installed at Cart Creek and Sawmill Brook on 04 June 2018 and removed 05 November 2018. The metal stakes were left in place to maintain the same locations for 2019. Bubble traps were redeployed at Cart Creek and Sawmill Brook on 07 May 2019 and installed at College Brook and Dube Brook on 28 May 2019. Bubble traps were removed at all patches on 04 November 2019. Thus, two seasons of monitoring were performed at Cart Creek and Sawmill Brook, and one season at College Brook and Dube Brook.

Traps were filled with water initially (no headspace), and bubbles emitted from below each trap accumulated in the upper portion and attached syringe by displacing water. The volume of water displaced at each trap was recorded, indicating total ebullitive volume, and volumes larger than 5 mL were collected with an additional syringe and stored for analysis of greenhouse gas concentration (CH_4, CO_2, and nitrous oxide [N_2O]). Bubble traps were visited 1–2 times per week throughout the observation periods. Because of the inherent disturbance to the sediment imposed by trap installation, we discarded all measurements taken within 28 d of installation. Effort was made to minimize disturbance to the benthic substrate during sampling, including maintaining a maximum distance from the trap and approaching from downstream. Gas samples were either analyzed within 24 h or injected into evacuated glass vials closed with butyl rubber stoppers (30 mL nominal capacity) until analyzed. Gas collected from traps that were not visited for more than 3 d were not analyzed for concentration under the assumption the gases will undergo some equilibration with stream water over time, thereby underestimating the measured concentration (Wik

et al. 2013). The measured volumes of these samples are still considered accurate. Additional gas samples were collected at the beginning and end of each sampling season by disturbing the benthic sediment and collecting bubbles in a separate handheld bubble trap. These samples were used to increase the sample size of measured ebullitive gas concentrations used in flux calculations as described below. The gas concentrations measured in these samples did not significantly differ from samples collected in the traps. All traps were reset (i.e., filled with water) after observation. Measurements for broken or leaky traps were not made, and the traps were repaired or replaced.

Gas concentration analysis

All gas samples were analyzed in the Trace Gas Biogeochemistry Laboratory at the University of New Hampshire. Gas samples were always analyzed for CH_4, and when enough sample was available, for CO_2 and N_2O. The concentration in parts per million (ppmv) of CH_4 was determined by analysis with a Shimadzu Gas Chromatograph Flame Ionization Detector (Treat et al. 2007), CO_2 using an infrared gas analyzer (LI-6252 CO_2 infrared gas analyzer [IRGA]), and N_2O using a Shimadzu GC-8A with an electron capture detector. Methane was standardized using the average area response of 10 injections of a standard gas mixture (Maine Oxy, 1000 ppmv) to determine an instrument precision of analysis (Frolking and Crill 1994). For CO_2, an instrumentation response factor for the IRGA was identified by first using a linear regression analysis to determine the slope and *y*-intercept of the standard (Northeast Airgas, 980.9 ppmv). Triplicate standards were run by injecting incremental volumes of CO_2 standard gas (1, 3,

4, 5, and 10 mL; Treat et al. 2014). Finally for N_2O, triplicate injections of three standard gases (0.267, 0.638, and 1.98 ppmv) were used to develop a standard curve response.

Flux calculations

Not all collected ebullitive gas samples were analyzed for gas concentration (Table S1). To estimate the concentration of these samples, we implemented bootstrap resampling to assign concentration values (Treat et al. 2018). We randomly sampled from the population of analyzed gas concentrations (CH_4, CO_2, and N_2O) at a stream with replacement to assign a concentration to any nonmeasured sample volume. The concentration set used in this analysis includes those samples collected by physical disturbance to increase the sample size because no difference was detected in concentration between sets of samples. Because no patch within a stream exhibited a significantly different mean gas concentration in the ebullition gas, measured concentrations were pooled across each individual stream. College Brook, gas samples were limited and the entire set of measured concentrations across all streams was used (Table S1). Additionally, no seasonality was detected in the concentration data, thus no seasonal adjustment was implemented in the concentration assignment. For example, for an unanalyzed ebullitive gas sample at Cart Creek, a concentration of CH_4, CO_2, and N_2O would be assigned at random from the measured samples at Cart Creek. This sampling was repeated 1000 times and the resulting median concentration calculated for each missing ebullitive gas sample was used in analysis. The ebullitive flux was then calculated as the mass of each gas emitted per sampling area per unit time:

$$\text{Ebullitive flux} = \frac{\text{Gas concentration} \times \text{Volume captured}}{\text{Area of bubble trap} \times \text{Time since last measurement}}$$

(1)

A flux was calculated for each trap and gas for each observation period.

As a rough approximation of watershed-level ebullitive CH_4 emissions (mg CH_4 m^{-2} watershed area d^{-1}), we estimated the overall flux for each stream as the product of the average daily flux rate and the total stream surface area, normalized by watershed size as follows:

$$\text{Watershed flux} = \frac{\text{Mean ebullitive flux} \times \text{Benthic surface area}}{\text{Watershed area}},$$

(2)

where benthic surface area (km^2) is estimated using a product of stream lengths derived from 2 m digital elevation models and estimates of stream width from a survey of each stream (Table S2). Watershed flux is converted to mg CH_4 m^{-2} watershed area d^{-1} to compare with watershed carbon fluxes from streams in previous studies (Crawford et al. 2014; Butman

et al. 2018). This analysis assumes the ebullitive fluxes calculated for a reach is consistent throughout the entire stream.

Environmental parameters

Measured dynamic variables included stage height, water temperature, D.O., and photosynthetically active radiation (PAR) at all streams. Stage height was measured at 15-min intervals with HOBO water level data loggers (U20L-04; Onset) deployed at a fixed depth and corrected for barometric pressure. Water temperature and D.O. were measured at 15-min intervals with HOBO Dissolved Oxygen Logger (U26-001; Onset). PAR was measured continuously at the first patch in each stream by an Odyssey Integrating PAR sensor (Dataflow Systems PTY Limited). Discharge was calculated from continuous stage records using rating curves developed for each stream (Morse and Wollheim 2014; Wollheim et al. 2017). The accuracy of all stage-discharge rating curves was confirmed with measurements of discharge during the monitoring period of this study using an electromagnetic flow sensor (Marsh McBirney, Flo Mate) and the velocity-area method.

Patch level variables included canopy cover, water depth, sediment depth to refusal, sediment particle size, and sediment OM content. Canopy cover was estimated using a convex spherical densiometer (Forestry Suppliers, Model-C) at each patch within each stream. Water depth was found using the mean of 10 locations measured with a meter stick in each patch. Following Crawford and Stanley (2016), depth to refusal was measured during trap installation in 2019 as a means of approximating the depth of sediments overlying hard mineral sediments. Fifteen measurements were made at each patch, five measurements along three replicate channel cross-sections, and the average was used as the patch metric. Finally, sediment cores were collected near all patches in the summer of 2019 and separated into subsamples representing 5 cm depth intervals from 0 cm to the deepest collected sample (maximum sampling depth varied from 10 to 35 cm). To do this, a Multi Stage Soil Core Sampler (AMS), which consists of a stainless steel cylinder and a 5 cm diameter plastic liner, was driven into the stream sediments using a sliding weight stand (Wik et al. 2018). Sediment cores were located at least 1 m away from traps to minimize disturbance. Subsamples were analyzed for OM content by loss of mass on ignition. The percent of sediment smaller than 2 mm in diameter was determined by passing subsamples through a 2-mm sieve and weighing each fraction. Finally, sediment carbon and nitrogen content were measured on dry pulverized samples by elemental analysis using a Thermo FlashEA Series 1112 at the USDA Forest Service, Louis C. Wyman Forest Sciences Laboratory in Durham, NH.

Statistical analyses

All statistical analyses were performed in MATLAB and Statistics Toolbox Release 2020a (The MathWorks). All data used in this study are available on the PIE data portal (https://pie-

lter.ecosystems.mbl.edu/data). Following our focus on drivers of seasonal variation in ebullition rates and the inconsistent intervals of trap visits, we primarily examine the mean daily rate of ebullition over 2-week periods. This ensured at least two trap observations were made at each trap during each period. Issues with measurement timescales of ebullition have been discussed previously and generally emphasize the need to consider fluxes over timescales of weeks rather than days when considering seasonal drivers (Maeck et al. 2014; Wik et al. 2016a). The use of a mean daily flux is supported by our monitoring design, which provides continuous measurement during the monitoring period. However, because the measurements of ebullition exhibited high skewness and kurtosis (Table S3), we use the nonparametric Mann–Whitney U and Wilcoxon signed-rank test to for differences ($\alpha = 0.95$). Variability at the stream, patch, and trap scales is quantified by the interquartile range. Temporal environmental variables were also split into 2-week increments to align with ebullitive fluxes. Our sampling design precludes efforts to robustly analyze temporal variability over daily or shorter timescales, so we focus instead on seasonal drivers as represented by the average of these variables over the two-week increments. The relatively small geographic expanse of our study area favors this compilation as climatic patterns (e.g., temperature, precipitation) are very similar across all sites at the two-week timescale.

Statistical analyses focused on factors potentially driving ebullition. This includes mean water temperature (Wik et al. 2013), mean and maximum discharge (Shakhova et al. 2014), mean PAR (Burke et al. 2019), mean and minimum D.O. concentration (Crawford et al. 2014), minimum barometric pressure, and the maximum decline in discharge and barometric pressure (Tokida et al. 2007). These parameters are generally independent of one another, with the main exception of temperature and D.O. As such, we investigated temporal correlations between these variables and ebullitive CH_4 flux using simple linear regression. The effect of temperature on temporal variability of ebullitive CH_4 flux was further examined with a Q_{10} relationship:

$$Q_{10} = \left(\frac{R_2}{R_1}\right)^{\frac{10}{T_2 - T_1}} \tag{3}$$

where R is the rate of ebullition at temperature T, and 1 and 2 are two different temperature selections. The 2-week means of CH_4 ebullition rate at Cart Creek, Sawmill Brook, and Dube Brook were used in this analysis. College Brook was omitted as the ebullition rate was relatively constant near zero.

Simple linear regression was also used to analyze controls on spatial variation in ebullitive CH_4 flux. However, the environmental variables used in spatial analysis are highly correlated to one another; thus, we also used partial least squares (PLS) regression to investigate spatial variability. PLS regression is an alternative method to simple linear regression for

datasets with many colinear predictor variables and when the number of observations is small relative to the number of predictor variables (Wold et al. 1984; Carrascal et al. 2009; Nash and Chaloud 2011). PLS has been implemented in many biogeochemical studies where multivariate approaches are ideal (Sobek et al. 2003, 2007; Bodmer et al. 2020; Linkhorst et al. 2020). Our single response variable was the mean ebullitive rate of CH_4 flux from patches across all streams. Analyzing spatial variability at the patch scale, as opposed to the stream or trap scale, allows for analysis of spatial heterogeneity both within and among streams. Predictor variables included all variables in Table 2 as well as the mean percent carbon, mean percent nitrogen, and maximum OM content among sediment core layers. We include the maximum OM content under the hypothesis that specific layers within the sediment may be more amenable to CH_4 production, and this is best predicted by OM content (Crawford and Stanley 2016). Predictor variables were relativized by variable maximum to balance their contribution in the computation of the PLS model.

A Monte-Carlo cross-validation method was used to assess the predictive ability of the resulting PLS model. The PLS model was fitted with a sub-sample of data (calibration/validation ratio was set to 0.8 following Onderka et al. 2012), and the fitted models were then tested on the validation set. This process was repeated 500 times. The mean cross-validated goodness of prediction (Q^2) was then compared to the original model fit (R^2Y), where close alignment indicates the model is not overfitted. The contribution of each predictor variable to the model was then analyzed using variable importance in the projection (VIP), and categorized as highly (VIP > 1.0), moderately (0.8 < VIP < 1.0) or less influential (VIP < 0.8), following Eriksson et al. (2001).

Finally, we analyzed the effect of sampling effort, both temporally and spatially, on individual stream estimates of mean ebullitive CH_4 flux. We omitted College Brook from this analysis because ebullitive CH_4 flux was consistently near zero. We also focused on 2019 data only, when the number of sampling periods was similar across the three sites, 32 for Cart Creek and Sawmill Brook and 26 at Dube Brook. Following Wik et al. (2016a), we simulated sampling regimes in which an iterative number of traps (spatial) or sampling periods (temporal) were selected and the mean daily ebullitive flux of CH_4 was calculated and compared to the actual values. For each stream, we calculated the mean ebullitive CH_4 flux based on a single measurement period up to $n - 1$ periods, where n is the total number of sampling periods. Sampling periods in this analysis were individual measurements from each trap rather than the 2-week average. The mean sampling period is approximately 3 d. We also calculated the mean ebullitive CH_4 flux based on a single bubble trap up to $n - 1$ bubble traps, where n is the total number of bubble traps at the stream (12 at all three streams). Up to 100 randomly generated

combinations of days or traps were included for each possible number of days or traps, respectively.

Results

Ebullitive emissions

Ebullitive fluxes of CH_4 were observed at all streams and all patches (overall mean = 1.00 ± 0.23 mmol CH_4 m^{-2} d^{-1}); however, high variability was observed in typical flux rates between and within streams (Fig. 2; Table S4). Emissions of CO_2 and N_2O via ebullition were significantly less, with mean rates across all sampling sites of approximately 0.01 mmol CO_2 m^{-2} d^{-1} and nearly 0.00 mmol N_2O m^{-2} d^{-1} (Figs. S2 and S3). As such, we focus only on ebullitive CH_4 emissions. The highest and lowest overall mean daily ebullitive CH_4 flux at the stream scale was observed at the two streams draining more developed landscapes, Sawmill Brook (1.76 ± 0.32 mmol CH_4 m^{-2} d^{-1} in 2018) and College Brook (of 0.01 ± 0.00 mmol CH_4 m^{-2} d^{-1} in 2019), respectively (Table 1). Scaling the mean ebullitive CH_4 flux throughout the stream network, we calculate a mean flux of 4.8 ± 3.1 mg CH_4-C m^{-2} watershed area yr^{-1}, ranging from 0.1 ± 0.1 mg CH_4-C m^{-2} watershed area yr^{-1} at College Brook to 12.1 ± 8.5 mg CH_4-C m^{-2} watershed area yr^{-1} at Sawmill Brook.

Mean daily ebullitive fluxes for individual patches ranged from 5.10 ± 2.55 mmol CH_4 m^{-2} d^{-1} at the fourth Sawmill Brook patch in 2018, to less than 0.01 ± 0.00 mmol CH_4 m^{-2} d^{-1} at College Brook patches two and three. At all streams except College Brook, variability in ebullitive CH_4 flux is clear between patches (Fig. 2b). This difference was greatest comparing patches two (0.35 ± 0.10 mmol CH_4 m^{-2} d^{-1}) and four (5.10 ± 2.55 mmol CH_4 m^{-2} d^{-1}) at Sawmill Brook in 2018. The maximum observed flux at a single patch over any 2-week period was 9.40 ± 2.31 mmol CH_4 m^{-2} d^{-1} at the Sawmill Brook patch two in August 2019. At Cart Creek and Sawmill Brook, where 2 yr of observations were made, the rate of ebullition was relatively stable at the stream and patch level between years (Fig. 2a,b). At the stream scale, no significant difference was detected between years based on a Wilcoxon signed-rank test. At the patch scale, a significant change in the rate of CH_4 ebullition were only observed at fourth patch at Cart Creek, with a difference of 0.77 ± 0.24 mmol CH_4 m^{-2} d^{-1}. Thus, at seven of the eight patches, no significant difference was detected between years.

Variability was also observed between traps within patches; that is, differences in the rate CH_4 ebullition were found among individual traps at a single patch based on a Kruskal–Wallis test (Fig. 2c). At this scale, 4 of 15 patches had significant differences in trap-level rates of ebullition in 2019. At patches with mean rates of ebullition above 0.01 mmol CH_4 m^{-2} d^{-1}, this proportion increased to 4 of 11. The most extreme example of this is at the first patch at Sawmill Brook, where individual traps had ebullitive CH_4 flux rates of 0.43, 0.75, and 3.61 mmol CH_4 m^{-2} d^{-1} ($p = 0.01$).

Temporal and spatial controls on ebullition

Ebullitive CH_4 flux displayed a seasonal pattern, with the highest emissions in August (Fig. 3). Simple linear regression
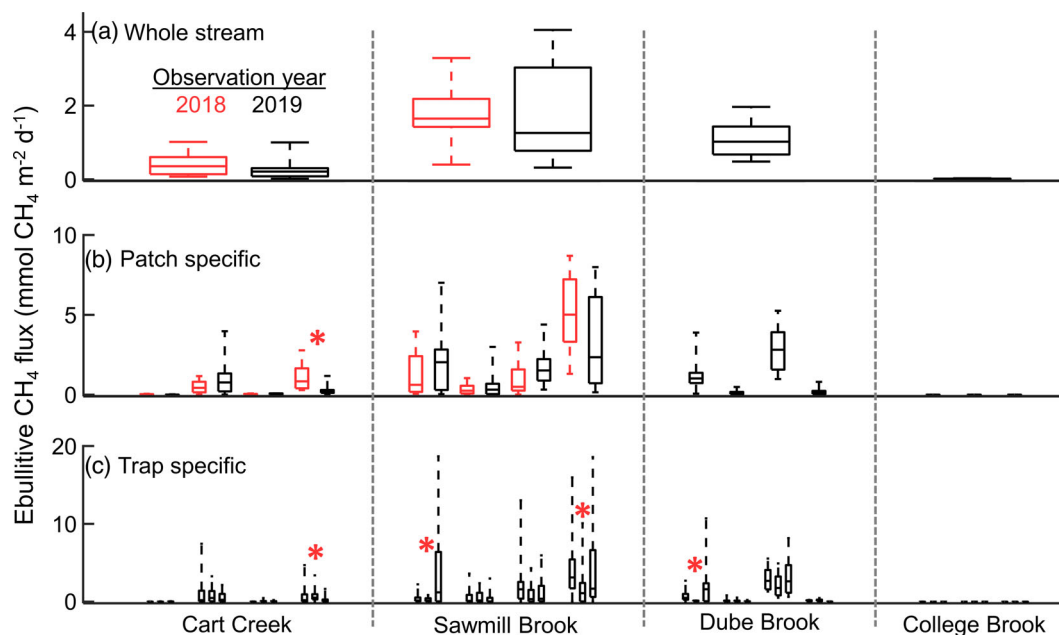

Fig. 2. Boxplots of observed ebullitive CH_4 fluxes at the scale of (**a**) the whole stream, (**b**) individual patches, and (**c**) individual traps with the 5th and 95th percentiles as the whisker extents. Red boxes represent fluxes from 2018 (only at Cart Creek and Sawmill Brook), while black boxes represent observations from 2019. Ebullitive fluxes at the trap scale (**c**) are shown for 2019 only. A single data point is the mean of all measured fluxes at the representative bubble traps for a 2-week period. Red asterisks mark comparisons where there is a significant difference in the mean ebullitive CH_4 flux between years (**a** and **b**) or traps (**c**) based on a Wilcoxon ranked sum or Kruskal–Wallis test, respectively.
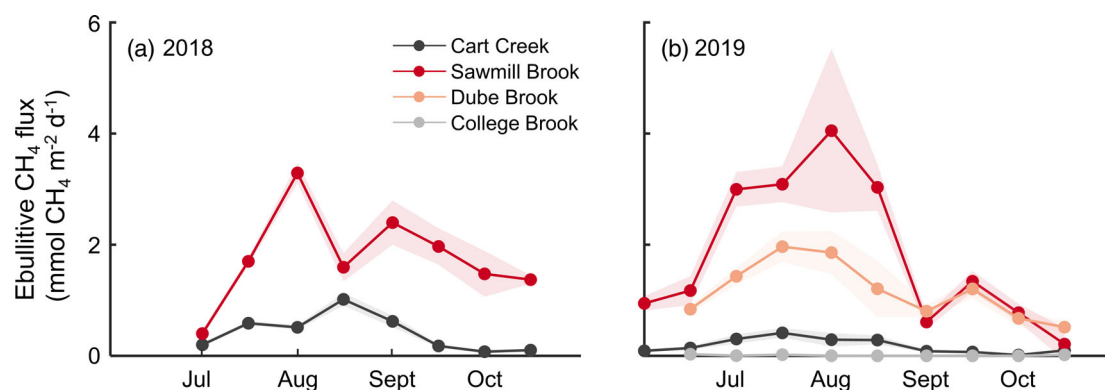
Fig. 3. Time series of ebullitive CH_4 flux. a) Cart Creek and Sawmill Brook were monitoried in 2018, and b) Dube Brook and College Brook were added 2019. The shaded areas denote ± 1 standard error.
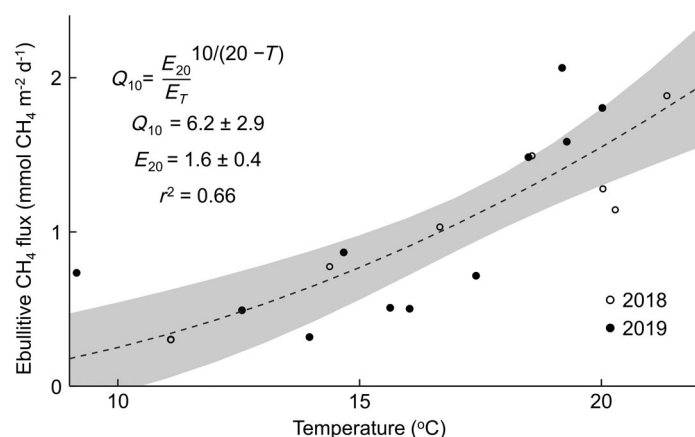

Fig. 4. Mean ebullitive CH_4 flux vs. mean water temperature across Cart Creek, Dube Brook, and Sawmill Brook fitted with the Q_{10} equation. Data points represent the mean of all ebullitive measurements during a 2-week period for 2018 (circles) when only Cart Creek and Sawmill Brook were monitored and 2019 (black dots) when Dube Brook was added. College Brook is omitted from this analysis because it had near-zero rate of ebullition across the entire observation period. The shaded area indicates the 95% confidence interval of the regression line.

indicated a significant positive relationship between CH_4 ebullition and both water temperature and D.O. percent saturation (Table S5). The percentage of variability in mean CH_4 ebullition across all streams averaged over 2-week intervals was explained more by mean water temperature ($r^2 = 0.63$, $p < 0.01$) than by mean D.O. percent saturation ($r^2 = 0.31$). The relationship between temperature and CH_4 ebullition results in a Q_{10} of 6.2 ± 2.9 (Fig. 4).

No single spatial variable explained the variability among patches well. However, the PLS analysis extracted two significant components which explained 46% of the variance ($R^2Y = 0.46$) with a relatively moderate predictive power ($Q^2 = 0.43$; Fig. 5). Based on VIP scores, mean sediment C : N, percent carbon, water depth, the maximum OM content were the most important predictor variables (Table S6). All these

variables positively correlated with ebullitive CH_4 flux on the second PLS axis, and all but water depth negatively correlated with ebullitive CH_4 on the first PLS axis. The sediment depth and canopy cover were the least influential predictor variables. Finally, and consistent with this high degree of temporal and spatial heterogeneity, our analysis of sampling effort suggests at least 20 sampling periods (approximately 60 d) and 10 traps are needed to accurately capture the variability of ebullition in these streams (Fig. 6).

Discussion

Ebullitive CH_4 fluxes from headwater streams

The data presented here add to a growing list of studies which highlight the prevalence of ebullitive CH_4 emissions from streams. The mean observed ebullitive flux across all sites of 1.00 mmol CH_4 m^{-2} d^{-1} is similar to the mean of 1.96 mmol CH_4 m^{-2} d^{-1} reported in a synthesis of fluvial systems (Stanley et al. 2016), and the range in fluxes observed in this study, 0.00–9.40 mmol CH_4 m^{-2} d^{-1}, falls within that reported as well (0.00–35.66 mmol CH_4 m^{-2} d^{-1}). Compared to lakes and ponds, the rate of CH_4 ebullition from these study streams is generally lower but within an order of magnitude (e.g., approximately 4.1 mmol CH_4 m^{-2} d^{-1}; Wik et al. 2016b). Emissions of CO_2 and N_2O via ebullition were negligible compared to CH_4, which follows previous studies in streams and rivers (Baulch et al. 2011).

The mean ebullitive CH_4 flux scaled to watershed area was 4.8 ± 3.1 mg CH_4-C m^{-2} watershed area yr^{-1}, which is lower than the 16.6 mg CH_4-C m^{-2} watershed area yr^{-1} calculated by Crawford et al. (2014) for streams in Wisconsin. Our lower rate is driven by a lower mean rate of CH_4 ebullition (1.00 mmol CH_4 m^{-2} d^{-1} in this study compared to 1.25 mmol CH_4 m^{-2} d^{-1}) and by the lower areal coverage of streams in this region (approximately 0.15% in this study compared to 0.5% in the Wisconsin study). Our estimate of ebullitive CH_4 emissions is low compared to the range of 4–1780 mg CH_4-C m^{-2} watershed area yr^{-1} reported for diffusive
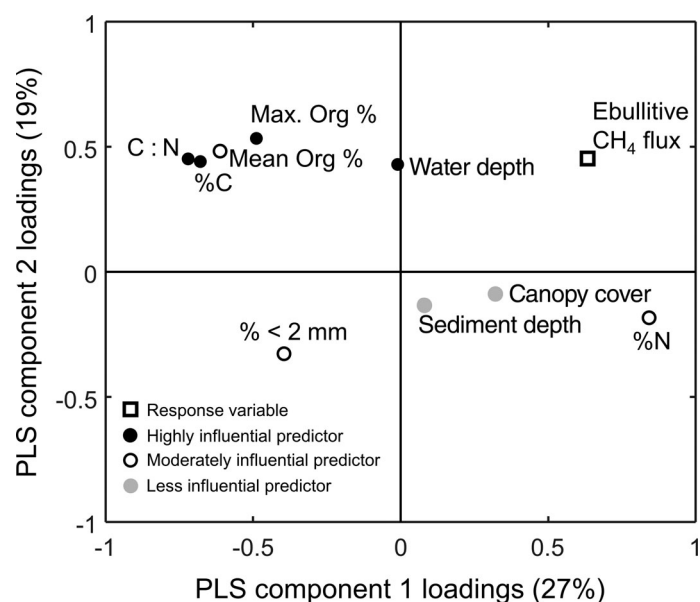
Fig. 5. A two-component partial least square (PLS) loading plot of ebullitive CH_4 flux showing the correlation structure of spatial variables. The graph depicts the correlation structures between the predictor variables and ebullitive CH_4 flux at the patch level. Variables situated along the same directional axis correlate with each other. Percentage values in the axis labels are the percent of ebullitive CH_4 flux variability explained at the patch scale by each component. Predictor variables correspond to those listed in Table 2.

CH_4 emissions from streams in the boreal landscape of Quebec, Canada (Hutchins et al. 2020), suggesting ebullition may be of lower magnitude than diffusive CH_4 emissions generally. Compared to the total carbon flux recently estimated for inland waters across North America (24 g C m^{-2} continental area yr^{-1}; Butman et al. 2018), the potential contribution of CH_4 ebullition to total carbon flux would be less than 1% based on this study. While we cannot exactly quantify the contribution of CH_4 ebullition to the carbon budget in this study, our comparison with literature values suggests ebullitive fluxes represent a minor loss term.

The rates reported here should be contextualized to these specific ecosystems. First, our stream level ebullition rates may represent the specific reaches monitored rather than the entire stream. It is possible specific reach characteristics (e.g., slope, depth) may promote CH_4 ebullition in certain reaches and hinder ebullition in others (Crawford et al. 2014). While we attempted to monitor representative reaches and patches, high levels of habitat heterogeneity make stream environments difficult to fully characterize (Poole 2002). While our site selections were made to minimize selection bias, it is not possible to examine how well the reaches represent the streams at large. Similarly, the relatively small size and shallow topography of these streams limits comparisons to larger rivers or steeper watersheds, where sediment and water depth are markedly different (Bodmer et al. 2020; Wang et al. 2021). As

attempts to scale riverine CH_4 emissions across watersheds at local to global scales continue (Butman et al. 2018; Hutchins et al. 2020), it will be critical to maintain this contextualization.

Temperature controls seasonal variability in ebullition

The strong temporal relationship between temperature and ebullitive CH_4 flux observed in this study has been highlighted in previous studies of streams and rivers (Wilkinson et al. 2015; Aben et al. 2017) and in freshwaters generally (Zhu et al. 2020). Our derived Q_{10} (6.2 ± 2.9) of CH_4 ebullition is well within the range of reported values in the literature (Duc et al. 2010; Inglett et al. 2012; Delsontro et al. 2016). This is a relatively important consideration for CH_4 ebullition given the strong response to temperature changes in contrast to other aquatic processes like denitrification ($Q_{10} \approx 2$; Seitzinger 1988). While our monitoring design did not include colder months, the assumption of lower ebullitive rates during colder periods appears robust (Aben et al. 2017). Extrapolating our mean daily ebullitive CH_4 flux over the entire year based on the Q_{10} relationship and a mean annual water temperature of 10°C (Table 1) results in an annual mean of 0.28 mmol CH_4 m^{-2} d^{-1}. This has important implications for streams in a warming climate (Hill et al. 2014), with the potential for a positive feedback in which increased temperatures lead to increased ebullitive CH_4 emissions from streams and rivers (Aben et al. 2017; Dean et al. 2018).

For streams with 2 yr of observations (Cart Creek and Sawmill Brook), we observed similar rates of CH_4 ebullition between the years at the stream and patch scale (Fig. 2a,b). While statistically insignificant differences were observed, the limited temporal scope of this analysis precludes strong statistical inferences of either annual stability or variability. Thus, longer-term monitoring of CH_4 ebullition in streams is warranted to explore either possibility. It is possible changes in temperature, hydrology, or solar input may drive differences in ebullition rates between years, as observed in lakes (Wik et al. 2014). Similarly, at the patch level, alterations in sedimentation rates could affect where in a stream reach ebullition occurs, as described in reservoirs (Hilgert et al. 2019). Thus, while CH_4 ebullition from the streams and patches presented here do not appear to change significantly within 2 yr, they may be temporally variable at longer timescales.

Variability of ebullition at multiple spatial scales

Spatial heterogeneity in CH_4 ebullition was observed at three scales: between streams, between patches at a stream, and within patches (Fig. 2). Differences between streams is common (Baulch et al. 2011; Zhang et al. 2020) and is suggested to result from differences in conditions for CH_4 production and bubble formation in sediments. These conditions are often a result of stream reach characteristics like slope or land use (Crawford et al. 2014). While the sample size of
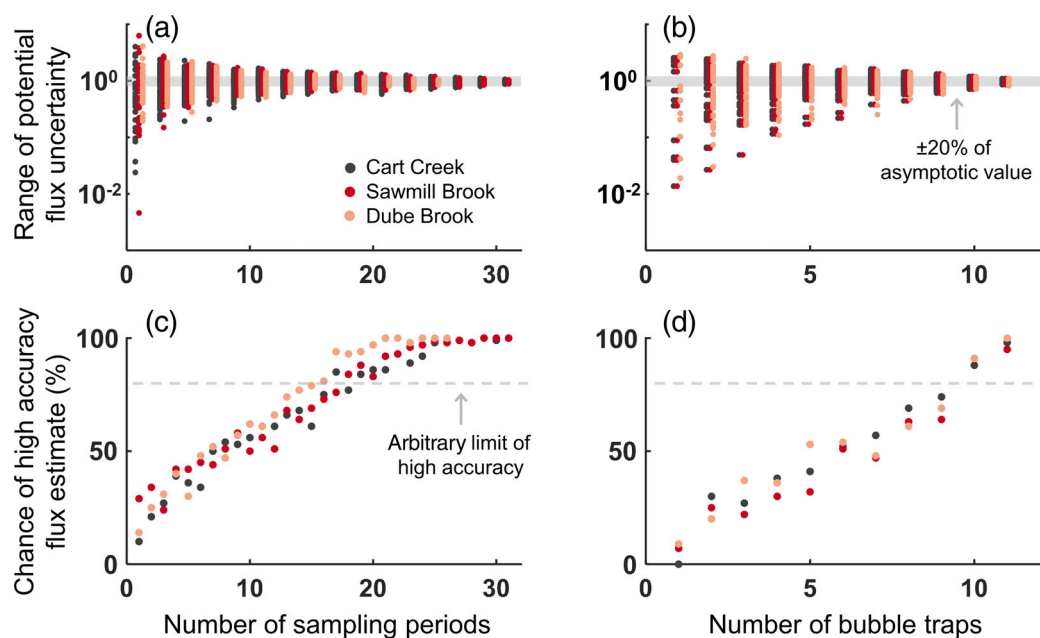
Fig. 6. Ranges in uncertainty and chances of high accuracy ebullitive CH_4 flux estimates vs. the number of (**a, c**) sampling days and (**b, d**) bubble traps. Cart Creek and Sawmill Brook each had 32 sampling days while Dube Brook had 27. All three streams had a total of 12 bubble traps. In panels (**a**) and (**b**), each point represents a simulated flux estimate based on a specified number of (**a**) sampling periods or (**b**) bubble traps, with the shaded area as ± 20% of the asymptotic ebullitive CH_4 flux. In panels (**c**) and (**d**), points indicate the likelihood of a high accuracy estimate (within 20% of the asymptotic ebullitive CH_4 flux) based on the subset of sampling c) days or d) traps. Analysis follows Wik et al. (2016*a*).

streams in this study is small, there was not a clear relationship between watershed land use and stream ebullition rates (Fig. 2). For example, the two streams draining developed landscapes (Sawmill Brook and College Brook) represent the highest and lowest observed mean ebullitive CH_4 emissions. It is also notable College Brook exhibited very low rates of CH_4 ebullition overall. Our spatial analysis does not provide a clear explanation for this; however, we expect the largely sandy nature of the sediment to be a contributing factor.

Patch variability of ebullitive CH_4 flux (Fig. 2b) is an important consideration when monitoring CH_4 ebullition in streams. Patch-scale differences in CH_4 ebullition have been observed in other stream and river systems, and have been related to sediment properties like OM content (Crawford et al. 2014) or sedimentation rates (Wilkinson et al. 2015). The lack of a single predictor variable in this study for spatial variability at the patch-scale at this scale suggests either a controlling variable was not measured (e.g., sedimentation rate, sediment bulk density) or patch-scale variability is driven by a complex set of variables. Indeed, our multivariate approach supports this latter hypothesis, where physical (water depth) and chemical conditions (OM content and quality) likely play interacting roles in influencing ebullition (Fig. 5). The strength of certain variables in our PLS analysis supports the findings of previous studies (Bodmer et al. 2020), where sedimentation (as inferred by percentage of sediment < 2 mm) and OM content are influential drivers of ebullitive spatial

heterogeneity. However, the relatively limited explanatory power of our PLS model (45% variance explained) suggests our ability to predict spatial variability remains limited, at least with respect to the measured variables.

Variability within patches can also be significant, indicating fine scale heterogeneity of CH_4 ebullition across the monitored streams (Fig. 2c). This variability may be caused by sediment properties that promote CH_4 production at microsites within the sediment (Bodmer et al. 2020) or from preferential paths for bubble movement out of the sediment (Delsontro et al. 2015), which we did not measure. Relatedly, some studies have found preferential sites for ebullition near aquatic edges (Bastviken et al. 2008; Holgerson and Raymond 2016). Characterizing sediment properties at this scale becomes difficult without critically altering the sediment during monitoring but post hoc analysis may allow for differentiation in these properties.

Spatial variability remains the largest uncertainty in lotic CH_4 ebullition. While this and previous studies have found a relatively similar and complex set of factors drive a large proportion of the spatial variability (Bodmer et al. 2020), these relationships are relatively weak to scale ebullition across space with high confidence. Key to reducing this uncertainty will be to expand measurement of ebullition in streams paired with detailed analyses of sediment properties (Hering et al. 2006). Examination of hyporheic exchange in relation to ebullition may be of particular interest, as the exchange of

water between stream surface water and the hyporheic zone can significantly affect oxygenation, microbial communities, and temperature (Briggs et al. 2013; Nelson et al. 2019). Moreover, the exchange of water may influence the ability of bubbles to form or emerge from the sediment (Wik et al. 2018).

Implications for stream ebullition monitoring design

The temporal and spatial heterogeneity described here has significant implications for the monitoring of ebullition in streams, and we can consider the impacts of differing monitoring designs on estimates of ebullitive CH_4 flux. Based on our simulations, at least 20 sampling periods (approximately 60 d) are required to accurately capture the variability of ebullition in these streams (Fig. 6a,c). Limitations imposed by infrequent sampling of ebullition have been demonstrated previously (Wik et al. 2016a). However, the robust sensitivity of CH_4 ebullition to temperature changes may provide a means of mitigating this need for many sampling periods. For example, a monitoring regime in which ebullition sampling efforts stretch over several weeks could theoretically be used to estimate annual rates of emissions by combining known Q_{10} relationships with water or sediment temperature records. However, confirming a robust Q_{10} relationship at a site would require a longer monitoring period initially.

Spatially, the range of uncertainty in the estimation of stream-level ebullitive CH_4 flux remains large until 10 traps are included in analysis (Fig. 6b,d). Previous studies have suggested similar numbers of traps are needed for accurate representation of lentic systems, where a minimum of 11 traps are necessary in lakes (Wik et al. 2016a) and 14 traps in peatlands (Ramirez et al. 2017). The larger area of these systems compared to the stream reaches of this study may indicate higher variability over smaller scales in streams. It is also possible our result of 10 traps is an artifact of our maximum sample size (12 traps). Thus, our results are best interpreted as a broad demonstration of the high level of spatial heterogeneity in ebullitive CH_4 fluxes from streams and indicate a need for consideration of this variation in designing monitoring programs. These simulations highlight potential drawbacks in commonly used ebullition monitoring designs in streams and rivers, which often rely on few measurement locations or times (Sawakuchi et al. 2014; Zhang et al. 2020). While the intended purpose of a study may require a different design to balance the spatial and temporal focus of a study, the conclusions presented here should be considered in study design and interpretation. When feasible, we suggest a robust examination of ebullition in streams and rivers should include a minimum of 10 sites sampled over 60 d.

Conclusion

CH_4 ebullition from four headwater streams was examined to constrain the temporal and spatial heterogeneity of this understudied carbon emission pathway. The rate of CH_4 emitted via ebullition across these streams is similar to other streams, rivers, and even lentic ecosystems (Stanley et al. 2016; Wik et al. 2016b). The prevalence of ebullition across streams of varying land use suggests this process should not be ignored as a potential source of aquatic CH_4. However, CH_4 ebullition appears to be a minor aquatic source of carbon on a landscape scale. Our analysis suggesting limited sampling of ebullition across space or time can lead to high uncertainty is critical in designing and interpreting studies of lotic CH_4 ebullition. For example, current methods that ignore temporal variability may overemphasize warmer periods and overestimate ebullitive CH_4 emissions from streams on an annual basis. The relatively high temperature sensitivity of CH_4 ebullition provides a pathway to scale emissions across time with fewer measurements and suggests feedback from a warming climate may be large in these ecosystems. Spatially, our results show a complex set of interacting drivers of CH_4 ebullition in stream ecosystems. While water depth and sediment OM content and quality appear to influence patch-level ebullition, this relationship is weak and does not permit robust scaling of ebullition across space. The lack of understanding of spatial heterogeneity is the principal factor inhibiting our ability to scale ebullitive CH_4 emissions with confidence, so studies that focus on spatial variability of ebullition are of utmost importance. Analysis of multiple sampling locations, including the chemical and physical characteristics of the sediment, will be critical to further constrain ebullition spatially and allow for scaling to larger areas. It may also be fruitful to expand beyond what has been studied and examine unique characteristics of fluvial systems, such as variable sedimentation rates and hyporheic exchange. Thus, novel approaches that intersect the disciplines of biogeochemistry, hydrology, geomorphology, and microbial ecology will be necessary to accurately include small streams in the global CH_4 budget.

References

Aben, R. C. H., and others. 2017. Cross continental increase in methane ebullition under climate change. Nat. Commun. **8**: 1–8. doi:10.1038/s41467-017-01535-y

Baker, J., H. Healy, and O. M. Hackett. 1964. Geology and ground-water conditions in the Wilmington-Reading area of Massachusetts. U.S. Government Printing Office.

Bastviken, D., J. J. Cole, M. L. Pace, and M. C. Van de Bogert. 2008. Fates of methane from different lake habitats: Connecting whole-lake budgets and CH_4 emissions. J. Geophys. Res. Biogeo. **113**: 1–13. doi:10.1029/2007JG000608

Baulch, H. M., P. J. Dillon, R. Maranger, and S. L. Schiff. 2011. Diffusive and ebullitive transport of methane and nitrous oxide from streams: Are bubble-mediated fluxes important? J. Geophys. Res. Biogeosci. **116**(G4): G04028. doi:10.1029/2011JG001656

Bodmer, P., J. Wilkinson, and A. Lorke. 2020. Sediment properties drive spatial variability of potential methane

production and oxidation in small streams. J. Geophys. Res. Biogeo. **125**: 1–15. doi:10.1029/2019JG005213

Borges, A. V., and others. 2015. Globally significant greenhouse-gas emissions from African inland waters. Nat. Geosci. **8**: 637–642. doi:10.1038/ngeo2486

Briggs, M. A., L. K. Lautz, D. K. Hare, and R. González-Pinzón. 2013. Relating hyporheic fluxes, residence times, and redox-sensitive biogeochemical processes upstream of beaver dams. Freshw. Sci. **32**: 622–641. doi:10.1899/12-110.1

Burke, S. A., M. Wik, A. Lang, A. R. Contosta, M. Palace, P. M. Crill, and R. K. Varner. 2019. Long-term measurements of methane ebullition from thaw ponds. J. Geophys. Res. Biogeo. **124**: 2208–2221. doi:10.1029/2018JG004786

Butman, D., and others. 2018. Chapter 14: Inland waters, p. 568–595. *In* Second state of the carbon cycle report. U.S. Global Change Research Program. doi:10.7930/SOCCR2.2018.Ch14

Carrascal, L. M., I. Galván, and O. Gordo. 2009. Partial least squares regression as an alternative to current regression methods used in ecology. Oikos **118**: 681–690. doi:10.1111/j.1600-0706.2008.16881.x

Cole, J. J., and others. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems **10**: 171–184. doi:10.1007/s10021-006-9013-8

Crawford, J. T., and E. H. Stanley. 2016. Controls on methane concentrations and fluxes in streams draining human-dominated landscapes. Ecol. Appl. **26**: 1581–1591. doi:10.1890/15-1330

Crawford, J. T., E. H. Stanley, S. A. Spawn, J. C. Finlay, L. C. Loken, and R. G. Striegl. 2014. Ebullitive methane emissions from oxygenated wetland streams. Glob. Chang. Biol. **20**: 3408–3422. doi:10.1111/gcb.12614

Dean, J. F., and others. 2018. Methane feedbacks to the global climate system. Rev. Geophys. **56**: 207–250. doi:10.1002/2017RG000559

Delsontro, T., L. Boutet, A. St-pierre, P. A. Giorgio, and Y. T. Prairie. 2016. Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity. Limnol. Oceanogr. **61**: S62–S77. doi:10.1002/lno.10335

Delsontro, T., D. F. Mcginnis, B. Wehrli, and I. Ostrovsky. 2015. Size does matter: Importance of large bubbles and small-scale hot spots for methane transport. Environ. Sci. Technol. **49**: 1268–1276. doi:10.1021/es5054286

Downing, J. A., and others. 2012. Global abundance and size distribution of streams and rivers. Inl. Waters **2**: 229–236. doi:10.5268/IW-2.4.502

Drake, T. W., P. A. Raymond, and R. G. M. Spencer. 2018. Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty. Limnol. Oceanogr.: Letters **3**: 132–142. doi:10.1002/lol2.10055

Duc, N. T., P. M. Crill, and D. Bastviken. 2010. Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments. Biogeochemistry **100**: 185–196. doi:10.1007/s10533-010-9415-8

Eriksson, L., E. Johansson, N. Kettaneh-Wold, and S. Wold. 2001. Multi- and megavariate data analysis: Principles and applications. Umetrics Academy.

Frolking, S., and P. Crill. 1994. Climate controls on temporal variability of methane flux from a poor ten in southeastern New Hampshire: Measurement and modeling. Glob. Bioceochem. Cycles **8**: 385–397.

Hering, D., R. K. Johnson, S. Kramm, S. Schmutz, K. Szoszkiewicz, and P. F. M. Verdonschot. 2006. Assessment of European streams with diatoms, macrophytes, macroinvertebrates and fish: A comparative metric-based analysis of organism response to stress. Freshw. Biol. **51**: 1757–1785. doi:10.1111/j.1365-2427.2006.01610.x

Hilgert, S., C. Vicente, S. Fernandes, and S. Fuchs. 2019. Redistribution of methane emission hot spots under drawdown conditions. Sci. Total Environ. **646**: 958–971. doi:10.1016/j.scitotenv.2018.07.338

Hill, R. A., C. P. Hawkins, and J. Jin. 2014. Predicting thermal vulnerability of stream and river ecosystems to climate change. Clim. Change **125**: 399–412. doi:10.1007/s10584-014-1174-4

Holgerson, M. A., and P. A. Raymond. 2016. Large contribution to inland water CO_2 and CH_4 emissions from very small ponds. Nat. Geosci. **9**: 222–226. doi:10.1038/ngeo2654

Hutchins, R. H. S., J. P. Casas-Ruiz, Y. T. Prairie, and P. A. del Giorgio. 2020. Magnitude and drivers of integrated fluvial network greenhouse gas emissions across the boreal landscape in Québec. Water Res. **173**: 115556. doi:10.1016/j.watres.2020.115556

Inglett, K. S., P. W. Inglett, K. R. Reddy, and T. Z. Osborne. 2012. Temperature sensitivity of greenhouse gas production in wetland soils of different vegetation. Biogeochemistry **108**: 77–90. doi:10.1007/s10533-011-9573-3

Kirschke, S., and others. 2013. Three decades of global methane sources and sinks. Nat. Geosci. **6**: 813–823. doi:10.1038/ngeo1955

Linkhorst, A., C. Hiller, T. DelSontro, G. M. Azevedo, N. Barros, R. Mendonça, and S. Sobek. 2020. Comparing methane ebullition variability across space and time in a Brazilian reservoir. Limnol. Oceanogr. **1–12**: 1623–1634. doi:10.1002/lno.11410

Maeck, A., H. Hofmann, and A. Lorke. 2014. Pumping methane out of aquatic sediments – ebullition forcing mechanisms in an impounded river. Biogeosciences **11**: 2925–2938. doi:10.5194/bg-11-2925-2014

Meyer, J. L., M. J. Paul, and W. K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. J. North Am. Benthol. Soc. **24**: 602–612. doi:10.1899/04-021.1

Morse, N. B., and W. M. Wollheim. 2014. Climate variability masks the impacts of land use change on nutrient export

in a suburbanizing watershed. Biogeochemistry **121**: 45–59. doi:10.1007/s10533-014-9998-6

Nash, M. S., and D. J. Chaloud. 2011. Partial least square analyses of landscape and surface water biota sssociations in the Savannah River basin. ISRN Ecol. **2011**: 1–11. doi:10.5402/2011/571749

Nelson, A. R., and others. 2019. Heterogeneity in hyporheic flow, pore water chemistry, and microbial community composition in an alpine streambed. J. Geophys. Res. Biogeosci. **124**: 3465–3478. doi:10.1029/2019JG005226

Onderka, M., S. Wrede, M. Rodný, L. Pfister, L. Hoffmann, and A. Krein. 2012. Hydrogeologic and landscape controls of dissolved inorganic nitrogen (DIN) and dissolved silica (DSi) fluxes in heterogeneous catchments. J. Hydrol. **450–451**: 36–47. doi:10.1016/j.jhydrol.2012.05.035

Poole, G. C. 2002. Fluvial landscape ecology: Addressing uniqueness within the river discontinuum. Freshw. Biol. **47**: 641–660. doi:10.1046/j.1365-2427.2002.00922.x

Ramirez, J. A., A. J. Baird, and T. J. Coulthard. 2017. The effect of sampling effort on estimates of methane ebullition from peat. Water Resour. Res. **53**: 4158–4168. doi:10.1111/j.1752-1688.1969.tb04897.x

Sanders, I. A., C. M. Heppell, J. A. Cotton, G. Wharton, A. G. Hildrew, E. J. Flowers, and M. Trimmer. 2007. Emission of methane from chalk streams has potential implications for agricultural practices. Freshw. Biol. **52**: 1176–1186. doi:10.1111/j.1365-2427.2007.01745.x

Saunois, M., and others. 2020. The global methane budget 2000–2017. Earth Syst. Sci. Data **12**: 1561–1623. doi:10.5194/essd-12-1561-2020

Sawakuchi, H. O., D. Bastviken, A. O. Sawakuchi, A. V. Krusche, M. V. Ballester, and J. E. Richey. 2014. Methane emissions from Amazonian Rivers and their contribution to the global methane budget. Glob. Chang. Biol. **20**: 2829–2840. doi:10.1111/gcb.12646

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. **33**: 702–724. doi:10.4319/lo.1988.33.4part2.0702, 4part2

Shakhova, N., and others. 2014. Ebullition and storm-induced methane release from the East Siberian Arctic Shelf. Nat. Geosci. **7**: 64–70. doi:10.1038/ngeo2007

Sobek, S., G. Algesten, A. K. Bergström, M. Jansson, and L. J. Tranvik. 2003. The catchment and climate regulation of pCO_2 in boreal lakes. Glob. Chang. Biol. **9**: 630–641. doi:10.1046/j.1365-2486.2003.00619.x

Sobek, S., L. J. Tranvik, Y. T. Prairie, P. Kortelainen, and J. J. Cole. 2007. Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. Limnol. Oceanogr. **52**: 1208–1219. doi:10.4319/lo.2007.52.3.1208

Spawn, S. A., and others. 2017. Summer methane ebullition from a headwater catchment in Northeastern Siberia. Inl. Waters **5**: 224–230. doi:10.5268/IW-5.3.845

Stanley, E. H., N. J. Casson, S. T. Christel, J. T. Crawford, L. C. Loken, and S. K. Oliver. 2016. The ecology of methane in streams and rivers: Patterns, controls, and global significance. Ecol. Monogr. **86**: 146–171. doi:10.1890/15-1027.1

Tokida, T., T. Miyazaki, M. Mizoguchi, O. Nagata, F. Takakai, A. Kagemoto, and R. Hatano. 2007. Falling atmospheric pressure as a trigger for methane ebullition from peatland. Global Biogeochem. Cycles **21**: 1–8. doi:10.1029/2006GB002790

Treat, C. C., A. A. Bloom, and M. E. Marushchak. 2018. Non-growing season methane emissions–a significant component of annual emissions across northern ecosystems. Glob. Change Biol. **24**: 3331–3343. doi:10.1111/gcb.14137

Treat, C. C., J. L. Bubier, R. K. Varner, and P. M. Crill. 2007. Timescale dependence of environmental and plant-mediated controls of CH_4 flux in a temperate fen. J. Geophys. Res. Biogeosci. **112**: 1–9. doi:10.1029/2006JG000210

Treat, C. C., W. M. Wollheim, R. K. Varner, A. S. Grandy, J. Talbot, and S. Frolking. 2014. Temperature and peat type control CO_2 and CH_4 production in Alaskan permafrost peats. Glob. Chang. Biol. **20**: 2674–2686. doi:10.1111/gcb.12572

Walsh, C. J., A. H. Roy, J. W. Feminella, P. D. Cottingham, P. M. Groffman, and R. P. Morgan II. 2005. The urban stream syndrome: Current knowledge and the search for a cure. J. N Am. Benthol. Soc. **24**: 706–723.

Wang, G., X. Xia, S. Liu, L. Zhang, S. Zhang, J. Wang, N. Xi, and Q. Zhang. 2021. Intense methane ebullition from urban inland waters and its significant contribution to greenhouse gas emissions. Water Res. **189**: 116654. doi:10.1016/j.watres.2020.116654

Wik, M., P. M. Crill, R. K. Varner, and D. Bastviken. 2013. Multiyear measurements of ebullitive methane flux from three subarctic lakes. J. Geophys. Res. Biogeo. **118**: 1307–1321. doi:10.1002/jgrg.20103

Wik, M., and others. 2018. Sediment characteristics and methane ebullition in three subarctic lakes. J. Geophys. Res. Biogeosci. **123**: 2399–2411. doi:10.1029/2017JG004298

Wik, M., B. F. Thornton, D. Bastviken, J. Uhlbäck, and P. M. Crill. 2016*a*. Biased sampling of methane release from northern lakes: A problem for extrapolation. Geophys. Res. Lett. **43**: 1256–1262. doi:10.1002/2015GL066501.Received

Wik, M., B. F. Thorton, D. Bastviken, R. MacIntyre, K. Varner, and P. M. Crill. 2014. Energy input is primary controller of methane bubbling in subarctic lakes. Geophys. Res. Lett. **41**: 555–560. doi:10.1002/2013GL058510.Received

Wik, M., R. K. Varner, K. W. Anthony, S. MacIntyre, and D. Bastviken. 2016*b*. Climate-sensitive northern lakes and ponds are critical components of methane release. Nat. Geosci. **9**: 99–105. doi:10.1038/ngeo2578

Wilkinson, J., A. Maeck, Z. Alshboul, and A. Lorke. 2015. Continuous seasonal river ebullition measurements linked to sediment methane formation. Environ. Sci. Technol. **49**: 13121–13129. doi:10.1021/acs.est.5b01525

Wold, S., A. Ruhe, H. Wold, and W. J. Dunn III. 1984. The collinearity problem in linear regression. The partial least squares (PLS) approach to generalized inverses. SIAM J. Sci. Stat. Comput. **5**: 735–743.

Wollheim, W. M., G. K. Mulukutla, C. Cook, and R. O. Carey. 2017. Aquatic nitrate rentention at river network scales across flow conditions determined using nested in situ sensors. Water Resour. Res. **53**: 9740–9756. doi:10.1002/2017WR020644

Zhang, L., and others. 2020. Significant methane ebullition from alpine permafrost rivers on the East Qinghai–Tibet plateau. Nat. Geosci. **13**: 349–354. doi:10.1038/s41561-020-0571-8

Zhu, Y., K. J. Purdy, Ö. Eyice, L. Shen, S. F. Harpenslager, G. Yvon-durocher, A. J. Dumbrell, and M. Trimmer. 2020. Disproportionate increase in freshwater methane emissions induced by experimental warming. Nat. Clim. Change **10**: 685–690. doi:10.1038/s41558-020-0824-y

Conflict of Interest

None declared.