

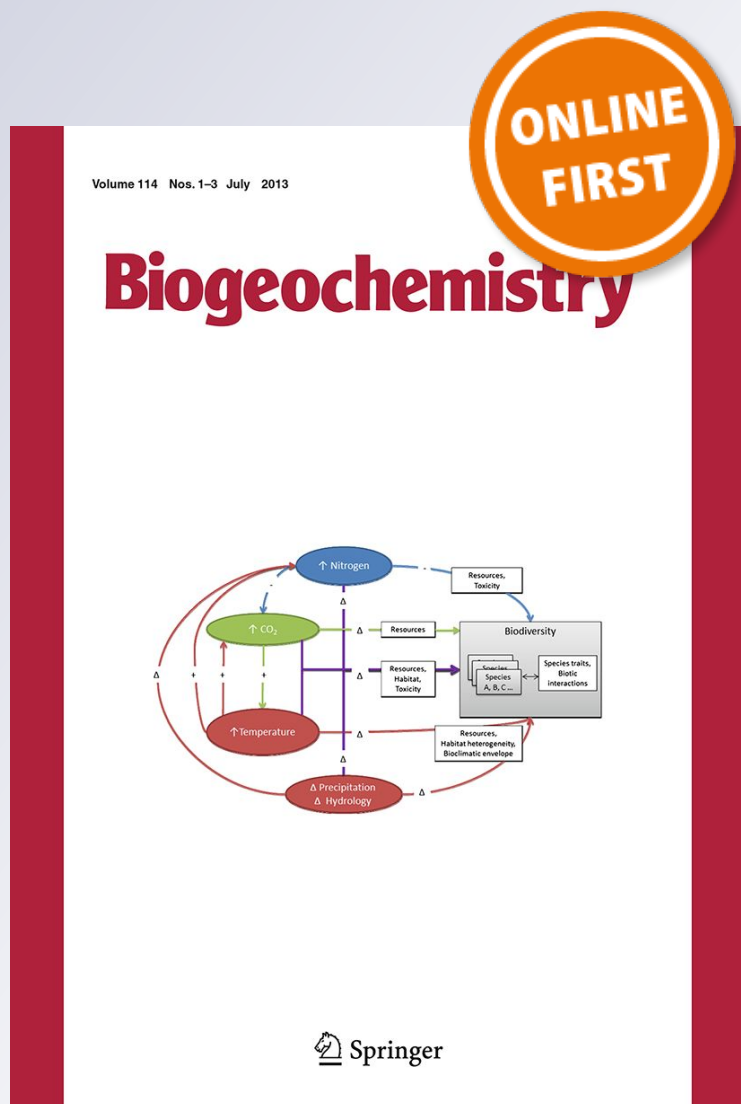
# *Methane and carbon dioxide dynamics within four vernal pools in Maine, USA*

**Lydia H. Kifner, Aram J. K. Calhoun,  
Stephen A. Norton, Kristine  
E. Hoffmann & Aria Amirbahman**

**Biogeochemistry**  
An International Journal

ISSN 0168-2563

Biogeochemistry  
DOI 10.1007/s10533-018-0467-5



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# Methane and carbon dioxide dynamics within four vernal pools in Maine, USA

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Received: 14 December 2017 / Accepted: 6 July 2018  
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**Abstract** Vernal pools are small, seasonal wetlands that are a common landscape feature contributing to biodiversity in northeastern North American forests. Basic information about their biogeochemical functions, such as carbon cycling, is limited. Concentrations of dissolved methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) and other water chemistry parameters were monitored weekly at the bottom and surface of four vernal pools in central and eastern Maine, USA, from April to August 2016. The vernal pools were supersaturated with respect to CH<sub>4</sub> and CO<sub>2</sub> at all sampling dates and locations. Concentrations of dissolved CH<sub>4</sub> and CO<sub>2</sub> ranged from 0.4 to 210 μmol L<sup>-1</sup> and 72–2300 μmol L<sup>-1</sup>, respectively. Diffusive fluxes of

CH<sub>4</sub> and CO<sub>2</sub> into the atmosphere ranged from 0.2 to 73 mmol m<sup>-2</sup> d<sup>-1</sup>, and 30–590 mmol m<sup>-2</sup> d<sup>-1</sup>, respectively. During the study period, the four vernal pools emitted 0.1–5.8 kg C m<sup>-2</sup> and 9.6–120 kg C m<sup>-2</sup> as CH<sub>4</sub> and CO<sub>2</sub>, respectively. The production fluxes (production rates normalized to surface area) of CH<sub>4</sub> and CO<sub>2</sub> ranged from -0.02 to 0.66 and 0.40–4.6 g C m<sup>-2</sup> d<sup>-1</sup>, respectively, and increased significantly over the season. Methane concentrations were best predicted by alkalinity, ortho-phosphate and depth, while CO<sub>2</sub> concentrations were best predicted with only alkalinity. Alkalinity as a predictor variable highlights the importance of anaerobic respiration in production of both gases. Our study pools had large concentrations and effluxes of CH<sub>4</sub> and CO<sub>2</sub> compared to permanently inundated wetlands, indicating vernal pools are metabolically active sites and may be important contributors to the global carbon budget.

Responsible Editor: Jack Brookshire.

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10533-018-0467-5>) contains supplementary material, which is available to authorized users.

L. H. Kifner · A. Amirbahman (✉)  
Department of Civil and Environmental Engineering,  
University of Maine, Orono, ME, USA  
e-mail: [ariaa@maine.edu](mailto:ariaa@maine.edu)

A. J. K. Calhoun · K. E. Hoffmann  
Department of Wildlife, Fisheries and Conservation  
Biology, University of Maine, Orono, ME, USA

S. A. Norton  
School of Earth and Climate Sciences, University of  
Maine, Orono, ME, USA

**Keywords** Carbon dioxide · Carbon cycling · Methane · Temporary wetlands · Vernal pools

## Introduction

The increase in concentrations of atmospheric methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) since the beginning of the Industrial Era has highlighted the importance of understanding the global carbon budget (IPCC 2013). Lakes and ponds are significant

components of global natural emissions of CH<sub>4</sub> and CO<sub>2</sub>. Approximately 3.7% of Earth's non-glaciated land surface is covered by water bodies > 0.002 km<sup>2</sup> (Verpoorter et al. 2014). Additionally, small ponds < 0.001 km<sup>2</sup>, make up ~ 8.6% of all freshwater surface area (Holgerson and Raymond 2016). Despite their small size, these water bodies have relatively large contributions of CH<sub>4</sub> and CO<sub>2</sub> emissions (Bastviken et al. 2004; Holgerson 2015; Kankaala et al. 2013; Raymond et al. 2013). Holgerson and Raymond (2016) estimated that although ponds < 0.001 km<sup>2</sup> make up < 10% of all freshwater surface area, they emit about 41% of total freshwater CH<sub>4</sub> and about 15% of total freshwater CO<sub>2</sub>. Globally, small water bodies comprise the majority of land-lake perimeter, an area with high productivity and biodiversity (Verpoorter et al. 2014). Small ponds have a large impact on global carbon emissions; however, as a result of their size, they are difficult to quantify and map, and are commonly excluded from global carbon budgets (Tiner et al. 2015; Verpoorter et al. 2014). Temporary wetlands are a subset of small ponds that do not have permanent standing water (also called vernal pools, seasonal wetlands, gilgais, or temporary pools; Calhoun et al. 2017).

Temporarily inundated wetlands are defined by varied hydrologic regimes that result in unique wetland ecosystem functions, such as increasing biodiversity by providing habitat for species adapted to waters with temporary hydroperiods (Calhoun et al. 2014, 2017; Zedler 2003). Additionally, temporarily inundated wetlands are biogeochemical hotspots for organic matter decomposition, denitrification, and water quality improvement through sediment retention and uptake of aquatic pollutants (Calhoun et al. 2017). Temporary wetlands have higher rates of these biogeochemical processes compared to adjacent upland ecosystems, primarily because of their high perimeter to area ratios, which enhance the rate of biogeochemical transformations (Calhoun et al. 2017; Capps et al. 2014; Marton et al. 2015). They have high terrestrial carbon content, varying seasonal dynamics, and mix more completely compared to larger water bodies. Water table fluctuations in vernal pools stimulate sediment microbial activity, resulting in a faster mineralization of organic matter (Corstanje and Reddy 2004; Rezanezhad et al. 2014). Temporary wetlands are common in the United States (e.g., Prairie Potholes, California vernal pools, northeastern

vernal pools) and globally (e.g., Mediterranean temporary ponds, rock pools, alpine seasonal ponds; Calhoun et al. 2017; Keeley and Zedler 1998).

Vernal pools are relatively small (generally < 0.002 km<sup>2</sup>; Calhoun et al. 2003) features in forested landscapes (Campbell Grant 2005; Zedler 2003). Reported densities in New England range from 0.1 to 49.5 pools per km<sup>2</sup> (Brooks et al. 1998; Calhoun et al. 2003; Faccio et al. 2013). Based on the highest densities, and using an average size of 0.001 km<sup>2</sup>, vernal pools could potentially make up to 4536 km<sup>2</sup> of the area in the State of Maine, USA. This is up to approximately 39% of the 11,750 km<sup>2</sup> of surface water, which translates to approximately 5% of Maine's total area of 91,633 km<sup>2</sup> (United States Geological Survey 2016). We present these numbers to highlight the potential importance of pool contributions to biogeochemical functions. We use the highest documented pool density to illustrate this point knowing that currently remote sensing methods result in considerable errors of omission (i.e., we typically miss 30% of the existing pools consistently in Maine remote sensing surveys). The existing literature is clear that pool density varies widely from region to region, may be very patchy in occurrence, and is not even predictable based on surficial deposits. However, it is worth noting that the potential contribution of these types of wetlands is considerable.

Vernal pools occur in a wide range of surficial glacial deposits and range in hydrogeomorphic setting from perched, precipitation-fed pools to pools strongly influenced by groundwater input and discharge (Calhoun et al. 2014; Wingham and Jordan 2003; Zedler 2003). They are typically at their highest water level in the spring, dry down by mid-summer, and re-fill in the autumn, while some dry on cycles longer than a year (Calhoun et al. 2014). Vernal pools in northeastern North America are amphibian breeding habitat and seasonal habitat for other wildlife. They have been widely studied as specialized breeding sites for species adapted to life in temporary waters (Faccio 2003; Semlitsch and Skelly 2007; Williams 1996).

Carbon cycling and greenhouse gas emissions have been evaluated in peatlands, lakes, and ponds (Bastviken et al. 2004; Holgerson and Raymond 2016; Huttunen et al. 2003; Lansdown et al. 1992; Rask et al. 2002); however, the role of seasonal wetlands, including vernal pools, in carbon dynamics is less known (Holgerson 2015). Vernal pool carbon

emissions may play a significant role in global carbon transformations, especially when considering their densities across the North American landscape. In the northeastern USA, carbon fluxes in and out of vernal pools in relation to their hydrology were studied in Rhode Island by examining the carbon budget throughout the pools (Ross 2017). The CH<sub>4</sub> and CO<sub>2</sub> production from vernal pools in Massachusetts with wet and dry conditions were explored in laboratory experiments (Kuhn 2015), where it was found that pools with frequent wet-dry cycles produce more CH<sub>4</sub> and CO<sub>2</sub> than those with stable hydroperiods. In this study, we examined dissolved carbon dynamics in four Maine vernal pools with different geologic substrates, from ice-off until dry down in 2016. The specific objectives of this study were to (1) quantify the dissolved concentrations and diffusive fluxes of CH<sub>4</sub> and CO<sub>2</sub> to the atmosphere; (2) identify environmental covariates of CH<sub>4</sub> and CO<sub>2</sub> emissions in vernal pools; and (3) estimate the carbon turnover by comparing leaf litter carbon inputs to carbon emissions.

**Methods**

**Study area**

We studied four vernal pools in Maine, USA (Fig. S1). The pools have varying underlying geology, dominant forest type, and canopy cover (Table 1). P1 and P2 are in urban settings in Bangor, Maine, ~ 200 m from surrounding areas of human activity and moderate landscape modification. P1 has no emergent aquatic vegetation, while P2 has emergent aquatic vegetation as the dominant cover. P3 is located in a minimally modified forested landscape located ~ 100 m from a gravel road used by logging and gravel trucks. Emergent aquatic vegetation occurs later in the season when the pool has partially dried down. P4 is located in a managed forest ~ 1 km from routine human activity or development, but ~ 10 m from a logging road. This site has no emergent aquatic vegetation. All sites have been logged but P1, P2, and P3 have not been cut for at least 25 years.

Spring 2016 was relatively dry. During the study period, Bangor, ME (near P1, P2, and P4) and Osborn, ME (near P3) received 6.1, 6.1, 9.2, and 13.2 cm of precipitation in April, May, June, and July, respectively. The 1981–2010 normal monthly precipitation

**Table 1** Geologic, forest, and hydrologic characteristics for four Maine vernal pools

Pool	Underlying geology	Dominant forest type	Canopy cover	Dry down (Julian day)	Max depth (m)	Max surf area (m <sup>2</sup> )	Max vol (m <sup>3</sup> )	Groundwater recharge rate (m/s)	Temp (°C)	Benthic temp (°C)
P1	Presumpscot Formation (marine silt/clay)	Deciduous	Closed	173	0.3	325	31	1.3 × 10 <sup>-6</sup> (1.1 × 10 <sup>-6</sup> – 1.5 × 10 <sup>-6</sup> )	17.4 (14–22)	12.3 (8–16)
P2	Presumpscot Formation	Shrub	Open	216	0.3	260	58	0	21.0 (15–30)	15.7 (10–21)
P3	Sand and gravel esker	Mixed	Open	209	1.5	2930	1930	4.6 × 10 <sup>-7</sup> (3.4 × 10 <sup>-7</sup> – 6.4 × 10 <sup>-7</sup> )	20.9 (10–31)	16.7 (8–26)
P4	Thin till	Deciduous	Closed	209	0.5	510	126	2.2 × 10 <sup>-7</sup> (9.9 × 10 <sup>-8</sup> – 3.0 × 10 <sup>-7</sup> )	14.3 (8–19)	11.5 (7–17)

Concentrations are reported as means, with range in parentheses. Maximum surface area, maximum volume, groundwater recharge rates, and benthic temperature are from Straka (2017). Groundwater recharge rates, and surface and benthic temperatures are from the study period, April–August 2016

was 9.2, 9.2, 9.6, and 8.8 cm in April, May, June, and July, respectively (National Weather Service 2017). Water depth in the pools was measured at all sampling dates as well as monitored continuously by Straka (2017). The four pools had varying hydroperiods. In 2016, P1 and P2 had estimated maximum volumes of 31 and 58 m<sup>3</sup>, respectively (Table 1). P3 was the largest of the pools, with an estimated maximum volume of 1930 m<sup>3</sup>, and P4 had an estimated maximum volume of 126 m<sup>3</sup> (Table 1). All four pools were at their greatest extent in March. P1 was dry by Julian day 173 (June 21st), P2 was dry by Julian day 216 (August 3rd), and P3 and P4 were dry by Julian day 209 (July 27th).

### Field and laboratory methods

Water in all pools was sampled at the deepest point, with the exception of P3, which was sampled at a depth of 1.25 m until later in the season when the deepest section was more accessible. Sampling locations were marked with a stake. Two lengths of Tygon<sup>TM</sup> tubing were attached to each stake, one fixed at ~ 5 cm from the bottom sediment of the pool (benthic samples), and one floating ~ 5 cm below the water surface. The floating tube was attached to a fishing bobber so that the tube inlet would fluctuate with the water level. Water was sampled through the tubes using a hand-held vacuum pump to avoid disturbing the pool sediments and water chemistry. Sample tubing was purged several times prior to taking samples for analysis.

Samples were collected from each pool at a minimum every 10 days from ice-out in late April until the pools dried completely in June or July. Aqueous samples for dissolved CO<sub>2</sub>, CH<sub>4</sub>, and nitrous oxide (N<sub>2</sub>O) were collected every week. Additional samples collected included chlorophyll *a* (chl *a*), dissolved organic carbon (DOC), sulfate (SO<sub>4</sub><sup>2-</sup>), dissolved oxygen (DO), ortho-phosphate (ortho-P), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), closed cell pH, and alkalinity. Details of sample collection and analysis are given in the Supplementary Material section. Samples from each pool were taken at approximately the same time of day to minimize variation caused by diurnal fluctuations. Immediately after collection, all samples were placed on ice in the dark prior to laboratory analysis.

Aqueous samples for CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O were collected directly from the tubing into a 60 mL syringe to prevent atmospheric air contamination and transported to the laboratory, where they were stored for no more than 5 h before gas extraction. The gases were extracted by injecting 30 mL of helium (He) gas into 30 mL of each water sample and shaking the sample vigorously for 5 min. The gas plus carrier He were then injected into a 25 mL crimp-sealed gas vial that had been previously flushed with He and then evacuated. We analyzed gas samples using gas chromatography on a Shimadzu GC-2014 with CTC AOC-5000 auto injector and three detectors (FID, ECD, TCD) within 4 weeks of collection at the University of New Hampshire Water Quality Analysis Laboratory. The water chemistry results are reported in Table 2.

Morphometric and hydrologic data (depth, surface area, pool volume, and groundwater recharge rate) are from Straka (2017). Hourly precipitation data are from National Weather Service precipitation data (National Weather Service 2017). Precipitation for the two weeks preceding the sampling day was considered.

### Gas flux calculations

The total gas concentrations in the samples were calculated by summing the extracted gas concentration in He and the residual dissolved gas in solution following extraction; the latter value was calculated using the Henry's Law:

$$CH_{4(gas)} \times K_H = CH_{4(aqueous)} \quad (1)$$

where  $K_H$  is the Henry's constant (Weisenberg and Guinasso 1979; Weiss 1974) adjusted for temperature.

The dissolved gas concentrations immediately below the water surface were then used to calculate the diffusive flux to the atmosphere:

$$F = k_{l,w}(C - C_s) \quad (2)$$

where  $F$  is the flux (mol m<sup>-2</sup> d<sup>-1</sup>),  $k_{l,w}$  is the mass transfer velocity across the water boundary layer (m d<sup>-1</sup>),  $C$  is the gas concentration (mol m<sup>-3</sup>) in the surface water sample, and  $C_s$  is the saturation gas concentration (mol m<sup>-3</sup>) calculated using the Henry's Law with the global atmospheric partial pressure (National Weather Service 2017) and the  $K_H$  values

**Table 2** Chemical characteristics for four Maine vernal pools April–August 2016

Pool	pH	DO (mg L <sup>-1</sup> )	Ortho-P (µg P L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (µg N L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (µg S L <sup>-1</sup> )	DOC (mgC L <sup>-1</sup> )	alk (µeq L <sup>-1</sup> )	chl <i>a</i> (µg L <sup>-1</sup> )
P1 benthic	5.1 (4.8–5.4)	2.3 (0.6–4.1)	54.1 (18–85)	130.1 (1–631)	1113.7 (25–4933)	13.4 (89–20)	88.6 (37–169)	10.3 (0–35)
P1 surface	5.1 (4.8–5.3)	3.8 (2.9–4.9)	40.5 (15–62)	31.0 (1–62)	1225 (45–4989)	13.0 (8–20)	65.5 (36–90)	12.6 (0–43)
P2 benthic	5.2 (4.9–5.9)	4.6 (0.7–7.3)	38.6 (15–107)	44.4 (4–222)	64.6 (12–171)	20.9 (14–29)	172.3 (56–296)	4.4 (0–20)
P2 surface	5.3 (4.9–5.9)	6.7 (3.6–10.3)	38.1 (11–121)	58.6 (11–314)	61.8 (9–181)	20.6 (13–29)	170.6 (99–261)	2.9 (0–8)
P3 benthic	4.9 (4.6–5.5)	5.8 (1.2–10.2)	121.5 (8–757)	345.1 (16–2944)	187.0 (28–330)	12.7 (6–20)	83.7 (23–339)	38.0 (0–190)
P3 surface	4.9 (4.4–5.7)	7.0 (3.3–10.2)	109.9 (9–229)	296.5 (6–882)	170.0 (64–298)	14.1 (6–29)	71.2 (24–328)	42.3 (1–176)
P4 benthic	5.0 (4.4–5.7)	2.4 (0.8–8.5)	96.1 (12–201)	121.7 (8–469)	209.5 (36–488)	33.0 (16–148)	357.2 (235–482)	8.3 (0–29)
P4 surface	5.3 (4.6–6.0)	4.4 (1.1–8.9)	73.3 (10–189)	99.6 (9–434)	244.5 (69–377)	19.3 (10–28)	271.5 (212–333)	4.5 (0–17)

Concentrations are means with range in parentheses

for the ambient water temperature (Weisenberg and Guinasso 1979; Weiss 1974).  $k_{l,w}$  was calculated using the equation (Schwarzenbach et al. 2003):

$$k_{l,w} = \left( \frac{Sc_i}{Sc_{CO_2,20}} \right)^{-a} k_{CO_2,20} \quad (3)$$

where  $Sc_i$ , the dimensionless Schmidt Number, is the ratio of the water kinematic viscosity to the diffusion coefficient of a gas in water, both of which vary with temperature;  $a$  is the constant that varies with wind velocity and is equal to 0.67 for a smooth water surface; and  $Sc_{CO_2,20}$  and  $k_{CO_2,20}$  are the Schmidt Number and the mass transfer velocity across the water boundary layer for CO<sub>2</sub> at 20 °C, respectively. A value of 0.56 m d<sup>-1</sup> was used for  $k_{CO_2,20}$  as the recommended value for the case where wind velocity 10 m above the surface is < 4.2 m s<sup>-1</sup> (Schwarzenbach et al. 2003). We assumed the surface wind velocity at all four sites to be negligible, because the recorded average daily wind speeds at the nearby weather stations were generally < 9.4 m s<sup>-1</sup> (Weather Underground 2017), and the closed (or nearly so at P3) canopy of the pools provided damping of the wind. The range of  $k_{l,w}$  values for CO<sub>2</sub> and CH<sub>4</sub> were 0.36–0.80 m d<sup>-1</sup> and 0.36–0.79 m d<sup>-1</sup>, respectively, for a water temperature range of 8–31 °C. Holgerson et al. (2017) determined  $k_{l,w}$  values ranging from 0.19 to 0.72 m d<sup>-1</sup> at 20 °C for pools with surface areas < 250 m<sup>2</sup> using propane gas injection. Their study also showed that wind speed averaging 0.3–0.4 m s<sup>-1</sup> was not a strong predictor of  $k_{l,w}$  in these pools.

#### Net production calculations

We used a mass balance approach to estimate the net production of CH<sub>4</sub> and CO<sub>2</sub> in each pool over the sampling period. Equation 4 expresses mass balance for a species in water by assuming a well-mixed pool (e.g., Schnoor 1996) and assumes that the calculated instantaneous fluxes are representative of fluxes between consecutive samplings:

$$\frac{d(VC)}{dt} = Q_{in}C_{in} - Q_{out}C_{out} - R_{ef} + R_P \quad (4)$$

where  $V$  is the average pool volume between two consecutive samples;  $C$  is the concentration of the gas in the pool;  $C_{in}$  and  $C_{out}$  (g C m<sup>-3</sup>) are the

concentration of the gas in the inflow and outflow, respectively, through groundwater or stream;  $Q_{in}$  and  $Q_{out}$  ( $\text{m}^3 \text{d}^{-1}$ ) are the flow rates of water in and out of the pool, respectively, through groundwater or stream;  $R_{ef}$  ( $\text{g C d}^{-1}$ ) is the diffusion rate of each gas into the atmosphere (obtained by multiplying the average weekly flux from Eq. 2 by the average weekly pool surface area); and  $R_p$  ( $\text{g C d}^{-1}$ ) is the net mass production rate of each gas. The left hand side of Eq. 4 expresses the mass of a carbon species accumulated in the pool water between two consecutive sampling periods. Zero order mass production fluxes ( $\text{g C m}^{-2} \text{d}^{-1}$ ) were calculated by dividing  $R_p$  by the average area of the pool in the period between samplings.

We did not collect gas samples in groundwater and overland inflow to the pools. Studying the hydrology of the same pools, Straka (2017) showed that in net, the pools recharged the groundwater (i.e.,  $Q_{out} > Q_{in}$ ). There was also no detectable overland flow to any of the pools during the sampling period. Consequently, in Eq. 4, the influence of inflow on the mass of gases carried into the pool ( $Q_{in}C_{in}$ ) was neglected. We accounted for the  $\text{CH}_4$  and  $\text{CO}_2$  export from the pools into groundwater using the groundwater recharge rates (Table S1; Straka 2017).

### Statistical analysis

We examined the relationship of  $\text{CH}_4$  and  $\text{CO}_2$  concentrations (independently) to the variables listed in Table 3. Methane and  $\text{CO}_2$  concentrations were checked for autocorrelation using the package “time-Series” in R (Wuertz et al. 2015) and were determined not to be autocorrelated. We found the mean of the benthic and surface measurements (except temperature) for predictor variables at each pool on each sampling occasion and plotted these against Julian date to check for outliers and linearity using Base R (R Core Team 2016) and the package “dplyr” (Wickham et al. 2017). We natural log transformed ortho-P,  $\text{NH}_4^+$ , chl *a* +1, volume, depth, surface area,  $\text{CH}_4$ , and  $\text{CO}_2$ . We scaled (z-scores) each variable and used the “Hmisc” package (Harrell et al. 2017) to produce a Pearson correlation matrix with p-values (Table 3). We discarded one of each pair of variables with an absolute value of  $r > 0.7$  (Dormann et al. 2013), choosing to retain the more directly measured or the more precise variable in each pair. We developed 14 additive a priori linear mixed effects models (with no

interactions) based on hypotheses about the effects of weather, seasonality, microbes, and general water chemistry parameters (Table 4) on  $\text{CH}_4$  and  $\text{CO}_2$  concentrations using the package “nlme” (Pinheiro et al. 2016). We used pool ID as a random effect on the intercept of each model (Zuur et al. 2009). We ranked  $\text{CO}_2$  and  $\text{CH}_4$  concentration models separately by AICc (Akaike's Information Criterion, adjusted for small sample size; Table 5). We used the “piecewiseSEM” package (Lefcheck 2015) to obtain marginal and conditional  $R^2$  values in order to determine the amount of variation explained by the fixed and the random factors (Nakagawa and Schielzeth 2013). We visibly inspected plots to examine the residuals for normality and homoscedasticity (Zuur et al. 2009). We estimated the  $\beta$  values of variables appearing in the top 0.9 cumulative models weight using model averaging with the “AICcmodavg” package (Mazerolle 2017). We examined the 85% confidence interval of each  $\beta$  estimate and considered the variables whose interval did not include zero to be important predictors (Burnham and Anderson 2002; Arnold 2010). We chose to use these 85% confidence intervals because they are a more appropriate match than 95% confidence intervals to the criterion of 2.0  $\Delta\text{AICc}$  (Arnold 2010).

## Results

### Pool chemistry

The temperature in the four pools (Table 1) increased in benthic ( $R^2 = 0.65$ ,  $p < 0.001$ ) and surface water ( $R^2 = 0.39$ ,  $p < 0.001$ ) samples over the season. The water chemistry of the four vernal pools varied throughout the season and among pools (Table 2). Notably, the pH of the four pools decreased ( $R^2 = 0.17$ ,  $p < 0.001$ ),  $\text{NH}_4^+$  concentrations increased ( $R^2 = 0.45$ ,  $p < 0.001$ ), and ortho-P concentrations increased throughout the season ( $R^2 = 0.39$ ,  $p < 0.001$ ). The chl *a* concentrations in the four pools suggest trophic levels ranging from oligotrophic to hypereutrophic throughout the wet season in 2016.



**Table 3** Pearson correlation coefficients between the natural logarithms of CH<sub>4</sub> and CO<sub>2</sub> concentration (mol L<sup>-1</sup>) and environmental variables for four Maine, USA, vernal pools April–August 2016

	pH	DO	Surf temp	Ben temp	ln (ortho-P)	ln(NH <sub>4</sub> )	SO <sub>4</sub>	DOC	alk	ln(1 + chl a)	Precip	ln(vol)	ln(depth)	ln(SA)	ln(CH <sub>4</sub> )	ln(CO <sub>2</sub> )
pH	1	-0.03	-0.47**	-0.6***	-0.5***	-0.39**	0.01	-0.07	0.15	-0.48***	-0.07	0.24	0.21	0.16	-0.03	-0.03
DO		1	0.07	0.09	-0.28	-0.13	-0.12	-0.24	-0.43**	0.29*	-0.1	0.36*	0.32*	0.36*	-0.18	-0.34*
Surf temp			1	<b>0.91***</b>	0.45**	0.5***	-0.23	0.38*	-0.06	0.38*	0.11	-0.46**	-0.52***	-0.44**	0.36*	0.04
Ben temp				1	0.58***	0.66***	-0.13	0.43**	0.01	0.39**	0.2	-0.51***	-0.58***	-0.49***	0.24	0.03
ln(ortho-P)					1	<b>0.84***</b>	-0.14	0.39**	0.43**	0.34*	0.22	-0.58***	-0.6***	-0.53***	0.35*	0.45**
ln(NH <sub>4</sub> )						1	-0.08	0.42**	0.4**	0.2	0.33*	-0.5***	-0.56***	-0.48***	0.35*	0.33*
SO <sub>4</sub>							1	-0.28	-0.15	-0.26	0.33*	-0.22	-0.12	-0.21	-0.14	0.09
DOC								1	0.63***	-0.09	0.07	-0.39**	-0.57***	-0.43**	0.39*	0.44**
alk									1	-0.25	0.2	-0.22	-0.31*	-0.26	0.52***	0.69***
ln(1 + chl a)										1	-0.13	-0.14	-0.1	-0.05	-0.08	-0.18
Precip											1	-0.16	-0.21	-0.17	0.28	0.25
ln(vol)												1	<b>0.97***</b>	<b>0.99***</b>	-0.44**	-0.46**
ln(depth)													1	<b>0.97***</b>	-0.47**	-0.47**
ln(SA)														1	-0.47**	-0.47**
ln(CH <sub>4</sub> )															1	-0.47**
ln(CO <sub>2</sub> )																1

Values of r between 0.7 and 1 are in bold

Significance: \* $p < 0.05$ , \*\* $p < 0.01$ , \*\*\* $p < 0.001$

**Table 4** A priori models based on hypotheses of conditions that might influence CH<sub>4</sub> and CO<sub>2</sub> concentrations in vernal pools in Maine, USA

Model number	Model name	Predictor variables
1	Weather global	Benthic temp + precip
2	Seasonality global	ln(depth) + pH + benthic temp
3	Seasonality sub1	ln(depth) + benthic temp
4	Seasonality sub 2	pH + benthic temp
5	Microbes global	pH + DO + benthic temp + DOC + SO <sub>4</sub> + ln(ortho-P) + alk
6	Microbe sub 1	pH
7	Microbe sub 2	ln(ortho-P) + DOC + SO <sub>4</sub>
8	Microbe sub 3	SO <sub>4</sub> + ln(ortho-P)
9	Microbe sub 4	Benthic temp + alk + pH
10	Microbe sub 5	Temp + DO
11	Water chem global	pH + DO + alk + ln(chl <i>a</i> + 1)
12	Water sub 1	alk + ln(chl <i>a</i> + 1)
13	Water sub 2	pH + alk
14	Water sub 3	DO + ln(chl <i>a</i> + 1)

Each model also included pool ID as a fixed effect on intercept. Models were ranked independently for CH<sub>4</sub> and CO<sub>2</sub> using AICc (i.e., ln(CH<sub>4</sub>) ~ pH was not compared to ln(CO<sub>2</sub>) ~ pH)

**Table 5** Linear mixed effect models for predicting CH<sub>4</sub> and CO<sub>2</sub> concentrations

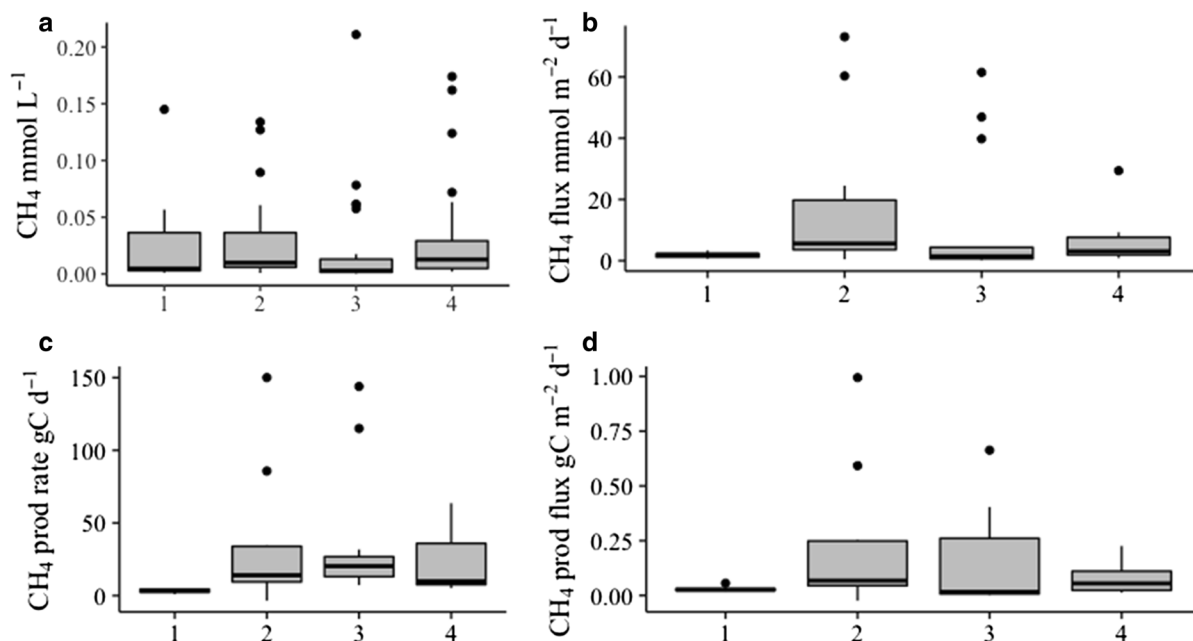
Model #	Model names	K	AICc	ΔAICc	AICc Wt	Cum Wt	R <sup>2</sup> Marg	R <sup>2</sup> Cond
13	Water sub 2 CH <sub>4</sub>	5	124.22	0	0.38	0.38	0.33	0.42
12	Water sub 1 CH <sub>4</sub>	5	124.48	0.27	0.34	0.72	0.32	0.42
9	Microbes sub 4 CH <sub>4</sub>	6	127.23	3.01	0.09	0.80	0.32	0.38
8	Microbes sub 3 CH <sub>4</sub>	5	127.84	3.62	0.06	0.87	0.17	0.32
3	Season sub 1 CH <sub>4</sub>	5	127.98	3.76	0.06	0.93	0.21	0.21
7	Microbes sub 2 CH <sub>4</sub>	6	129.89	5.67	0.02	0.95	0.17	0.29
1	Weather global CH <sub>4</sub>	5	130.67	6.45	0.02	0.96	0.14	0.29
13	Water sub 2 CO <sub>2</sub>	5	109.17	0	0.55	0.55	0.44	0.55
12	Water sub 1 CO <sub>2</sub>	5	110.27	1.10	0.31	0.86	0.43	0.54
9	Microbes sub 4 CO <sub>2</sub>	6	113.73	4.55	0.06	0.92	0.44	0.55
8	Microbes sub 3 CO <sub>2</sub>	5	113.96	4.78	0.05	0.97	0.21	0.51

Only models with ΔAICc < 7 are shown

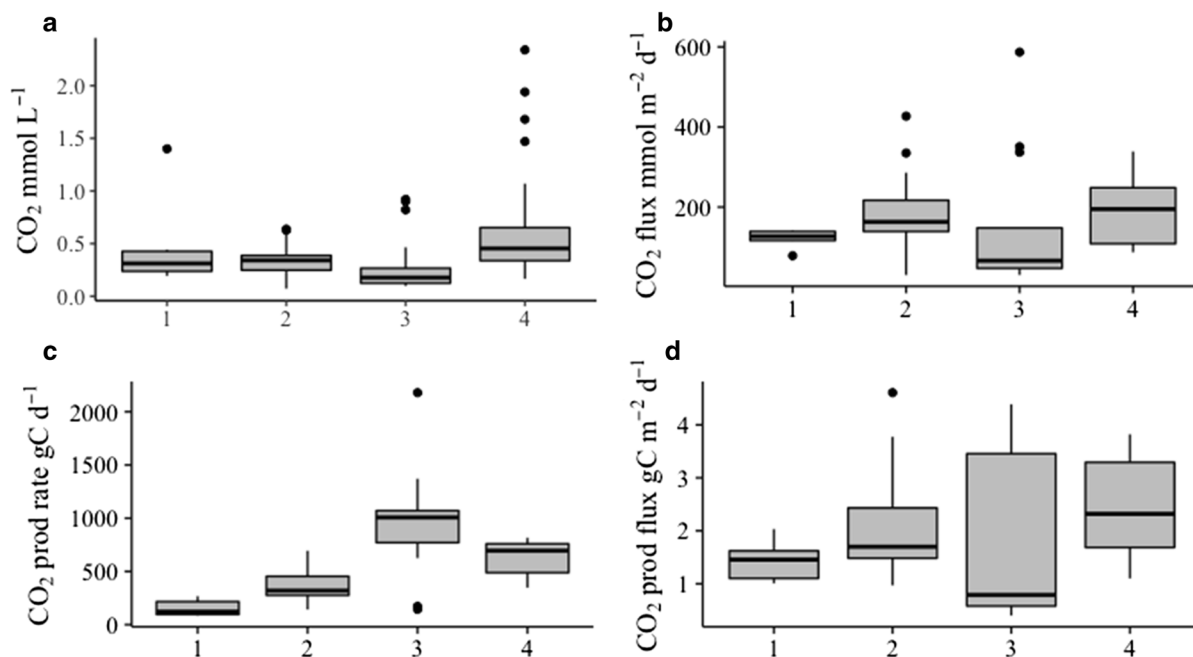
### Greenhouse gas concentrations and fluxes

Dissolved CH<sub>4</sub> concentrations ranged from to 0.39–210 μmol L<sup>-1</sup>, with an overall mean of 27 ± 4.6 μmol L<sup>-1</sup> (Fig. 1a). Methane was highly supersaturated, with 75% of the samples > 787-fold, and 25% > 5394-fold. The CH<sub>4</sub> concentrations had a weak but significant, positive relationship with time (R<sup>2</sup> = 0.09, *p* < 0.01). There were significant

temporal variations in dissolved CH<sub>4</sub> concentrations among sites (*p* < 0.05). Dissolved CO<sub>2</sub> concentrations ranged from 72 to 2300 μmol L<sup>-1</sup>, with an overall mean of 420 ± 42 μmol L<sup>-1</sup> (Fig. 2a). Carbon dioxide supersaturation was > tenfold for 75% of the samples and > 25-fold for 25%. The CO<sub>2</sub> concentrations had a weak but significant, positive relationship with time for individual pools (R<sup>2</sup> = 0.05, *p* < 0.05), and significant variations in



**Fig. 1** a–d a average concentrations, b flux to the atmosphere, c net production rate, and d net carbon production flux of CH<sub>4</sub> in four pools from April to August 2016



**Fig. 2** a–d a average concentrations, b flux to the atmosphere, c net production rate, and d net carbon production flux of CO<sub>2</sub> in four pools from April to August 2016

dissolved CO<sub>2</sub> concentrations among sites ( $p < 0.001$ ). Dissolved N<sub>2</sub>O concentrations were near

or below the detection limit ( $0.23 \mu\text{mol L}^{-1}$ ) at all pools throughout the entire sampling period.

The diffusive CH<sub>4</sub> flux in all pools ranged from 0.25 to 73.1 mmol m<sup>-2</sup> d<sup>-1</sup>, with a seasonal average of 10.8 ± 18.5 mmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 1b). The diffusive CO<sub>2</sub> flux in all pools ranged from 30 to 590 mmol m<sup>-2</sup> d<sup>-1</sup>, with a seasonal average of 170 ± 18.6 mmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 2b). The fluxes of both CH<sub>4</sub> and CO<sub>2</sub> increased over the season ( $R^2 = 0.34$ ,  $p < 0.001$  in Fig. S2b; and  $R^2 = 0.35$ ,  $p < 0.001$  in Fig. S3b, respectively).

#### Covariates of CH<sub>4</sub> and CO<sub>2</sub>

Our Pearson correlation matrix showed that both CH<sub>4</sub> and CO<sub>2</sub> concentrations correlated significantly positively with ortho-P, NH<sub>4</sub><sup>+</sup>, DOC, alkalinity, and each other (Table 3). They both correlated significantly negatively with depth, volume, and surface area. Further, CH<sub>4</sub> correlated significantly positively with temperature, and CO<sub>2</sub> correlated significantly negatively with DO. We also observed some collinearity in our other independent variables. We removed surface temperature from further consideration as it correlated positively with benthic temperature ( $r = 0.91$ ,  $p < 0.005$ ), NH<sub>4</sub><sup>+</sup> as it correlated positively with ortho-P ( $r = 0.84$ ,  $p < 0.005$ ), and both volume and surface area as they correlated positively with depth ( $r = 0.97$  and  $0.99$ ,  $p < 0.005$  for both relationships).

Our top models for predicting CH<sub>4</sub> concentrations ( $\Delta\text{AICc} < 7$ ) included those from each of the four categories (water chemistry, microbes, seasonality, and weather; Table 4). Our top models included Water sub 2 (model 13), Water sub 1 (model 12) and Microbes sub 4 (model 9), which together carried 80% of the cumulative model weight and shared the variable alkalinity (Table 5). Microbes sub 3 (model 8) and Season sub 1 (model 3) increased the cumulative model weight to 90% and were driven by other variables. With the exception of Season sub 1, the conditional  $R^2$  values were higher than marginal  $R^2$  values (Table 5), which we interpret as the random effect of pool ID explaining some of the variance. Plots of the residuals indicated normality and homogeneity. Model averaging indicated that the only important predictors of CH<sub>4</sub> concentrations were alkalinity ( $\beta = 0.63 \pm 0.18$  SE),  $\ln(\text{ortho-P})$  ( $\beta = 0.40 \pm 0.15$  SE), and  $\ln(\text{depth})$  ( $\beta = -0.48 \pm 0.17$  SE), as the confidence intervals for the  $\beta$  values of the

other variables included in the top 90% of model weight included zero (Table S2).

Only four models for predicting CO<sub>2</sub> concentrations were supported by the data with  $\Delta\text{AICc} < 7$  (Table 5). These models were the same as the top four models for predicting the CH<sub>4</sub> concentrations and represented categories in water chemistry and microbes but not seasonality or weather. The conditional  $R^2$  values were higher than marginal  $R^2$  values by a range of 0.09–0.30. We averaged the top three models and only alkalinity ( $\beta = 0.69 \pm 0.15$  SE) was an important predictor of CO<sub>2</sub> concentrations (Table S2).

#### Net production of CH<sub>4</sub> and CO<sub>2</sub>

We calculated the pool net C production rates and the production flux (pool net production rate/pool surface area) of CH<sub>4</sub> and CO<sub>2</sub> in the vernal pools with Eq. 4, using the calculated diffusive fluxes to the atmosphere, the change in mass over time within the pools, and the export through groundwater. The mass accumulation rates in the pool ( $d(\text{VC})/dt$ ) could be either positive (carbon mass in the form of CH<sub>4</sub> or CO<sub>2</sub> accumulated in the pool) or negative (mass left the pool). The mass outflow rates of CH<sub>4</sub> and CO<sub>2</sub> through groundwater ( $Q_{\text{out}}C_{\text{out}}$ ; Eq. 4) were always positive in P1, P3, and P4, and were zero in P2 because of the lack of downflow (Table 1). The diffusive rates ( $R_{\text{ef}}$ ; Eq. 4) of CH<sub>4</sub> and CO<sub>2</sub> escape to the atmosphere were always positive, a result of the supersaturation of the pools with respect to these gases. Net production rates ( $R_p$ ; Eq. 4) in the four pools ranged from  $-3.5$  to  $150$  g C d<sup>-1</sup> and  $85$ – $820$  g C d<sup>-1</sup> for CH<sub>4</sub> and CO<sub>2</sub>, respectively. The carbon production fluxes varied from  $-0.024$  to  $0.99$  g C m<sup>-2</sup> d<sup>-1</sup> and  $0.40$ – $4.6$  g C m<sup>-2</sup> d<sup>-1</sup> for CH<sub>4</sub> and CO<sub>2</sub>, respectively (Table 6). Most of the CH<sub>4</sub> and CO<sub>2</sub> that was produced left the pools through diffusion to the atmosphere; a significantly smaller fraction accumulated within the pools, and a negligible proportion left through groundwater (Table 6). Considering that vernal pools are net producers of CH<sub>4</sub> and CO<sub>2</sub>,  $C_{\text{in}}$  in Eq. 4 would be smaller than  $C_{\text{out}}$ , and as such, we believe that the groundwater contribution of these gases to the pools is insignificant compared to their diffusion to the atmosphere.

There were significant differences in CH<sub>4</sub> and CO<sub>2</sub> net production rates among sites (Figs. 1c, 2c;  $p < 0.01$ , and  $p < 0.001$ , respectively). The net

**Table 6** Mass accumulation rates ( $d(Vc)/dt$ ), groundwater output rates ( $Q_{out}C_{out}$ ), carbon evaporative rates ( $R_{ef}$ ), net production rates ( $R_p$ ), and carbon production fluxes of CH<sub>4</sub> and CO<sub>2</sub>

	$d(Vc)/dt$ (g C d <sup>-1</sup> )	$Q_{out}C_{out}$ (g C d <sup>-1</sup> )	$R_{ef}$ (g C d <sup>-1</sup> )	$R_p$ (g C d <sup>-1</sup> )	Carbon production flux (g C m <sup>-2</sup> d <sup>-1</sup> )
CH <sub>4</sub>					
P1	0.11 (– 1.1–0.86)	0.74 (0.12–1.4)	2.3 (0.91–4.1)	3.2 (0.97–4.7)	0.030 (0.019–0.056)
P2	0.60 (– 39–29)	–	31 (1.1–120)	31 (– 3.5 to 150)	0.20 (– 0.024–0.99)
P3	– 0.30 (– 2.8–2.6)	0.35 (0.093–1.2)	38 (8.8–140)	38 (7.3–140)	0.15 (3.0 × 10 <sup>-3</sup> –0.66)
P4	0.36 (– 3.0–5.4)	0.28 (0.024–0.79)	22 (5.3–65)	23 (5.2–64)	0.085 (0.013–0.23)
CO <sub>2</sub>					
P1	9.8 × 10 <sup>-3</sup> (– 4.0–6.6)	8.0 (4.1–10)	150 (79–260)	160 (85–270)	1.4 (1.0–2.0)
P2	– 0.89 (– 14–8.3)	–	360 (150–690)	360 (140–700)	2.2 (0.97–4.6)
P3	– 38 (– 140–22)	9.6 (4.5–17)	990 (140–2100)	960 (140–2200)	1.8 (0.40–4.4)
P4	– 2.0 (– 54–84)	5.8 (1.3–12)	620 (350–840)	620 (350–820)	2.4 (1.1–3.8)

Average values are reported with ranges in parentheses over the sampling season

production rate of CH<sub>4</sub> increased significantly over the season ( $R^2 = 0.19$ ,  $p < 0.01$ ), but the net production rate of CO<sub>2</sub> did not have a significant temporal trend. The net production flux accounts for the different surface area among the four pools and the changing surface area throughout the season. The CH<sub>4</sub> and CO<sub>2</sub> production fluxes increased significantly over the season ( $R^2 = 0.57$ ,  $p < 0.001$ , and  $R^2 = 0.49$ ,  $p < 0.001$ , respectively). There were no significant differences among pools in the production fluxes of CH<sub>4</sub> and CO<sub>2</sub> (Figs. 1d, 2d).

## Discussion

### CH<sub>4</sub> and CO<sub>2</sub> concentrations and fluxes

The CH<sub>4</sub> and CO<sub>2</sub> concentrations and fluxes in this study are of similar magnitude to those observed in Connecticut on small, temporary ponds with a similar sampling design (Holgerson 2015), but higher CH<sub>4</sub> than in the vernal pools in Massachusetts (Kuhn 2015). Vernal pools in Rhode Island emitted similar amounts of CH<sub>4</sub> during May and June, and similar amounts of CO<sub>2</sub> (Ross 2017). The fluxes of CH<sub>4</sub> and CO<sub>2</sub> from the vernal pools were 1–2 orders of magnitude larger than those from lakes (Bastviken et al. 2004; Casper et al. 2000; Huttunen et al. 2003; Kankaala et al. 2013; Rantakari and Kortelainen 2005). Salt marshes have CH<sub>4</sub> and CO<sub>2</sub> fluxes of the same order of magnitude as

those in our study pools (Chmura et al. 2011; Magenheimer et al. 1996). Our vernal pools have some of the highest documented concentrations and fluxes of CH<sub>4</sub> and CO<sub>2</sub> for ponds, lakes, and wetlands (Table 7).

The pools were supersaturated with respect to CH<sub>4</sub> and CO<sub>2</sub> across all surface samples and dates, indicating that all pools were emitting CH<sub>4</sub> and CO<sub>2</sub> across the air–water interface at all sampling events. The atmospheric fluxes in this study were estimated using Eqs. 2 and 3, which consider only diffusion across the water boundary layer. Due to the low solubility of CH<sub>4</sub> in water, ebullition can also be an important mechanism for its atmospheric emission. CH<sub>4</sub> ebullition can be especially important in water bodies with relatively shallow depths, such as vernal pools, because of the relatively low hydrostatic pressure (Bastviken et al. 2004; Casper et al. 2000; Coulthard et al. 2009; Fendinger et al. 1992; Huttunen et al. 2003; Whalen 2005). Methane can also be released from the sediment into the atmosphere through transport in emergent vegetation (Bastviken et al. 2004; Sebacher et al. 1985; Segers 1998; Whalen 2005). Therefore, the diffusive fluxes into the atmosphere estimated in this study are minimum values, especially for CH<sub>4</sub>.

Methane and CO<sub>2</sub> diffusive fluxes were estimated only during periods of inundation. After pool dry down, previously inundated sediment is exposed to air. However, there is little information on emissions from a dried vernal pool basin. Ross (2017) found that

**Table 7** Reported surface water CH<sub>4</sub> and CO<sub>2</sub> concentrations and emissions for a selection of ponds, wetlands, and lakes

Location	# sites	CH <sub>4</sub> conc ( $\mu\text{mol L}^{-1}$ )	CO <sub>2</sub> conc ( $\mu\text{mol L}^{-1}$ )	CH <sub>4</sub> emission ( $\text{mmol m}^{-2} \text{d}^{-1}$ )	CO <sub>2</sub> emission ( $\text{mmol m}^{-2} \text{d}^{-1}$ )	Source
Vernal pools, ME, USA	4	27.0 (0.4–211)	424 (71.8–2340)	10.8 (0.2–73.1)	167 (30.1–587)	Present study
Vernal pools, RI, USA	4			( $-1.4 \times 10^{-2}$ – $4.6 \times 10^{-2}$ )	(7.2–31.7)	Ross (2017)
Vernal pools, MA, USA	2	( $2.0 \times 10^{-2}$ –0.1)				Kuhn (2015)
Small temporary ponds, CT, USA	6	33.4 (21.0–58.9)	353.2 (273.3–553.4)	10.6 $\pm$ 0.13	100.6 $\pm$ 0.51	Holgerson (2015)
Prairie potholes, SK, CA	62			(0.1–3.8)		Badiou et al. (2011)
Lakes, ponds, & reservoirs, FI	9			( $9.0 \times 10^{-2}$ –8.3)	( $-1.8$ –73.0)	Huttunen et al. (2003)
Lakes, WI, USA & Sweden	24	(0.1–2.32)		( $2.2 \times 10^{-2}$ –4.1)		Bastviken et al. (2004)
Small lake, U.K.	1	1.3 (0.31–4.8)	132 (27–326)	(0–108.4)	(3.9–101.6)	Casper et al. (2000)
Lakes, FI	12	( $5.0 \times 10^{-3}$ –1787)	(11–2394)	( $8.2 \times 10^{-3}$ –1.1)	(5.8–65.2)	Kankaala et al. (2013)
Boreal lakes, FI	37				(5.5–19)	Rantakari and Kortelainen (2005)
Microtidal, macrotidal salt marsh NB and NS, CA	2			$2.9 \times 10^{-2} \pm 8.7 \times 10^{-2}$ , $5.3 \times 10^{-2} \pm 0.1$	$264.5 \pm 138.0$ , $217.1 \pm 109.6$	Chmura et al. (2011)
Salt marsh, NB, CA	52			0.1 (1.3 $\times$ $10^{-2}$ –0.7)	56.8 (6.8–84.1)	Magenheimer et al. (1996)
Temperate bog, WA, USA	1			6.1 (0.1–31.7)	216.7 (16.7–2000)	Lansdown et al. (1992)
Coastal meadow, fen, DK	2			$8.0 \times 10^{-3}$ , 0.4 (0.5–6.2)		Priemé (1994)
Boreal fen, SK, CA	1					Rask et al. (2002)
Drained, flooded rice paddy canopy, JP (nocturnal)	1				805.1 $\pm$ 137.5, 373.1 $\pm$ 117.8	Miyata et al. (2000)
Afternoon, night rice paddy canopy, JP (drained)	1			(6.5–7.0), (1.6–2.2)		Miyata et al. (2000)

Concentrations and emission fluxes are reported as means with range in parentheses when more than one location was included or multiple samplings of a location occurred. When fluxes are presented on a per year basis, they were converted to a per day basis, assuming equal flux for all 365 days

vernal pools emitted CO<sub>2</sub> continuously, but they only emitted CH<sub>4</sub> from the basins for two months of the year, and took up comparable amounts of CH<sub>4</sub> when they were dry for the other 10 months of the year. Methanogenesis may only occur in the saturated areas of the pools, and only during certain times of the wet-dry cycle. Vernal pools are dry and/or frozen for the majority of the year, and CH<sub>4</sub> and CO<sub>2</sub> emissions (positive or negative) during these times should be considered in an annual budget. Water table fluctuations in wetlands influence CH<sub>4</sub> and CO<sub>2</sub> production zones (Boon et al. 1997; Fromin et al. 2010; Kettunen et al. 1999). A higher water level generally leads to higher CH<sub>4</sub> emissions (Kettunen et al. 1996; Rask et al. 2002), and a lower one leads to higher CO<sub>2</sub> emissions (Fromin et al. 2010). Such behavior is also observed in soils and river sediments that are subject to wetting and drying cycles (e.g., Gómez-Gener et al. 2016; Rezaeezhad et al. 2014; Von Schiller et al. 2014).

#### Covariates of CH<sub>4</sub> and CO<sub>2</sub>

The primary covariates for CH<sub>4</sub> concentrations in this study were alkalinity, ortho-P, and depth; for CO<sub>2</sub> concentrations, the primary covariate was alkalinity (Tables 5 and S2; Fig. S4). That alkalinity is the primary predictor for both gases suggests that their concentrations were controlled by microbially-catalyzed processes in the sediment. Anaerobic processes of denitrification, dissimilatory NO<sub>3</sub><sup>-</sup> reduction to NH<sub>4</sub><sup>+</sup>, and iron (Fe), manganese (Mn), and SO<sub>4</sub><sup>2-</sup> reduction all increase alkalinity (Stumm and Morgan 1996). In general, aerobic respiration has little effect on alkalinity, unless CO<sub>2</sub> production by this process can mobilize significant cation concentrations in the sediment (Norton et al. 2001). A negative relationship between alkalinity and DO (Table 3) suggests anaerobic respiration as the source of alkalinity in the pools. Methanogenesis does not affect alkalinity; however, an increase in alkalinity via other sediment anaerobic activities suggests the presence of a low redox potential in the sediments leading to the onset of methanogenesis. In addition to generating CH<sub>4</sub> and CO<sub>2</sub>, anaerobic reactions result in the production of DOC and NH<sub>4</sub><sup>+</sup>, and release of P from the sediment (Stumm and Morgan 1996). Alkalinity is significantly and positively correlated with DOC, ortho-P, and NH<sub>4</sub><sup>+</sup> (Table 3).

Previous studies have shown that total P concentration is positively related to CH<sub>4</sub> concentration and emission in lakes, and have attributed this to the autochthonous production stimulating CH<sub>4</sub> production and emission (Bastviken et al. 2004; Huttunen et al. 2003; Rantakari and Kortelainen 2005). In addition to this mechanism, ortho-P release is brought about by the reductive dissolution of sediment Fe hydroxide that is common in anaerobic sediments (e.g., Boström et al. 1988; Amirbahman et al. 2003). Therefore, ortho-P as a covariate for CH<sub>4</sub> concentration highlights the importance of sediment anaerobic respiration in the production of greenhouse gasses.

Depth as a primary covariate of CH<sub>4</sub> concentration has a negative  $\beta$  value (Table S2). Depth is significantly and negatively correlated to temperature, ortho-P, NH<sub>4</sub><sup>+</sup>, DOC, and alkalinity, all parameters that are also related significantly and positively to CH<sub>4</sub> concentration (Table 3). In all of the pools, depth decreased consistently with time due to evaporation, leading to the concentration of all species.

The covariates of secondary importance to both gases were pH, chl *a*, temperature and SO<sub>4</sub><sup>2-</sup>. Even though these variables were in the top models, the confidence intervals of their  $\beta$  values included zero, and therefore, they only served to strengthen the relationship between the primary predictors and the gas concentrations.

Both gases correlated negatively with pH (Table 3); CO<sub>2</sub> is a weak acid, and therefore, its production reduces the pH (Stumm and Morgan 1996). Chlorophyll *a* correlated negatively with CO<sub>2</sub>, likely due to the consumption of CO<sub>2</sub> by the primary producers (Table 3). A negative relationship between CO<sub>2</sub> and Chl *a* has been observed previously (e.g., Holgerson 2015; Roehm et al. 2009). We observed a weak negative relationship between CH<sub>4</sub> and Chl *a*, likely driven by the strong correlation between CH<sub>4</sub> and CO<sub>2</sub> (Table 3). In contrast, previous studies have observed a positive relationship between CH<sub>4</sub> and Chl *a* (Bastviken et al. 2004; Holgerson 2015). Methane and CO<sub>2</sub> concentrations correlated positively with temperature (Table 3). The production and emission of greenhouse gases increase with temperature (Bansal et al. 2016; Brinson et al. 1981; Liikanen 2002; Marotta et al. 2014; Ross 2017; Whalen 2005; Yvon-Durocher et al. 2017) due to increase in the microbial activity.

Sulfate concentrations correlated negatively with  $\text{CH}_4$  and positively with  $\text{CO}_2$  concentrations (Table 3). Sulfate serves as an electron acceptor to the  $\text{SO}_4^{2-}$ -reducing bacteria leading to the production of  $\text{CO}_2$  and alkalinity. Sulfate-reducing bacteria also compete for labile organic substrate with methanogens, suppressing methanogenesis (Chmura et al. 2011; Segers 1998). A negative relationship between  $\text{SO}_4^{2-}$  and  $\text{CH}_4$  has been observed in prairie potholes and lakes (Badiou et al. 2011; Bansal et al. 2016; Liikanen 2002; Pennock et al. 2010). The  $\text{SO}_4^{2-}$  concentrations observed in our study, however, are at the lower end of the observed concentrations in these studies.

The between-pond variations were similar for  $\text{CH}_4$  and  $\text{CO}_2$ ; including the pond random effect increased the best model  $R^2$  by 11% in both cases. A similar improvement in the model  $R^2$  for the two gases after including the pond random effect is not surprising, because the production of both is related to sediment anaerobic respiration. Holgerson (2015) observed a more important between-pond effect for  $\text{CO}_2$  than  $\text{CH}_4$ ; the pond random effect increased the conditional  $R^2$  by 3% for  $\text{CH}_4$  and 37% for  $\text{CO}_2$ . In that study, precipitation was the primary predictor for  $\text{CH}_4$  concentrations, and given the uniform precipitation over the study area, little improvement in the model was observed after including the pond random effect. Similar to our study, the  $\text{CO}_2$  concentrations, however, were controlled by sediment anaerobic respiration.

#### Net production of $\text{CH}_4$ and $\text{CO}_2$

The net production rates of  $\text{CH}_4$  and  $\text{CO}_2$  in the four vernal pools were nearly all positive. The amount of  $\text{CH}_4$  and  $\text{CO}_2$  transported through groundwater flow was negligible compared to that transported into the atmosphere through diffusion (Table 6). The net production rate was dependent on pool area (i.e., a larger pool would produce more  $\text{CH}_4$  or  $\text{CO}_2$ ), but the production fluxes were not. Thus, varying pool area explains the differences in net production among pools. For example, the largest pool, P3, would produce more  $\text{CH}_4$  and  $\text{CO}_2$  than P1, but the production fluxes were not statistically different among the pools. The increase in carbon production fluxes as the summer progresses is attributed to rising temperatures and higher rates of decomposition within the pools. This mass balance approach allows for comparison of

$\text{CH}_4$  and  $\text{CO}_2$  production rates and fluxes among pools with fluctuating water levels and with varying sizes.

#### The role of vernal pools in carbon cycling

Determining a representative set of vernal pools in Maine is difficult, as the only commonality among these sites is that they all have seasonal hydroperiods; the other characteristics are challenging to generalize. If these pools are representative in Maine because of their diversity in hydroperiod, geology, and forest type, we can examine the potential large-scale impacts of vernal pools. The density of vernal pools across Maine ranges from 1.4 to 49.5 pools  $\text{km}^{-2}$  (Calhoun et al. 2003). Combining the range of calculated diffusive fluxes to the atmosphere in this study with the range of pool densities in Maine, we estimate that vernal pools in Maine could potentially emit from  $1.4 \times 10^{-4}$  to 12 Tg C of  $\text{CH}_4$  and 0.017 to  $5.3 \times 10^4$  Tg C of  $\text{CO}_2$  per year. Vernal pools and other temporary wetlands are widely distributed across northeastern landscapes and globally, and may constitute a large contribution to inland waters' carbon emissions. Small water bodies tend to have higher concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  than larger bodies of freshwater, and therefore, they can have a disproportionate effect with respect to their size on carbon emissions.

Carbon is the energy currency that moves through ecosystems (Fernandez 2008), and vernal pools are important for carbon transformations from leaf litter into nutrient forms that can be transferred to upland ecosystems. Leaf litter is the primary source of carbon for undisturbed vernal pools (Capps et al. 2014; Earl and Semlitsch 2013). Simmons et al. (1996) estimated an annual mean leaf litter mass input of  $301 \pm 33 \text{ g m}^{-2} \text{ year}^{-1}$ , corresponding to an estimated input of  $124 \pm 17 \text{ g C m}^{-2} \text{ year}^{-1}$ , to the forest floor in the region where our four vernal pool sites are located. These leaf litter fluxes were higher than those found in Acadia National Park, ME (Sheehan et al. 2006), but lower than other temperate deciduous forests (Morrison 1991; Nadelhoffer et al. 1983). Holgerson et al. (2016) reported 188–253  $\text{g m}^{-2} \text{ year}^{-1}$  of direct leaf input into five small ponds in mixed deciduous-coniferous forests in Connecticut, USA.

Applying the Simmons et al. (1996) mean estimate for litter flux, and assuming the maximum recorded



surface area of our four vernal pools in 2016, we estimate that 1400 kg of leaf litter (560 kg C) fell into our study sites in 2016. During the study period, each vernal pool emitted 0.14–5.8 kg C and 9.6–120 kg C of CH<sub>4</sub> and CO<sub>2</sub>, respectively, for a maximum total carbon export of 240 kg C from the four pools during the study period. Therefore, the estimated carbon flux from leaf litter into the pools is approximately twice as large as the maximum diffusive carbon flux from the pools. This disparity between carbon input and output from the pools may be explained by the carbon being transferred from wetlands to terrestrial environments in the form of biota (Gibbons et al. 2006). Additionally, wetlands sequester carbon in sediment, soil, and plant matter (Mitsch et al. 2013; Mitsch and Gosselink 2015; Lal 2008).

Vernal pools in this study have higher rates of decomposition, carbon mineralization, and nutrient cycling than ponds and other permanently inundated wetlands. High CH<sub>4</sub> and CO<sub>2</sub> emissions are a measure of a very metabolically active system. Vernal pools are important in the biochemical transformation of leaf litter into usable nutrient forms for aquatic and terrestrial fauna. As a result of the broad distribution of vernal pools and other temporary wetlands across the United States and around the globe, their contributions to carbon emissions are not insignificant. More research is needed to examine the carbon emissions in these pools after dry down and during ice cover, and to further quantify the amounts of terrestrial carbon output and storage.

**Acknowledgements** This research was funded by a National Science Foundation Coupled Natural Human Systems (CNH) Grant #1313627 to Aram Calhoun et al., and by a Maine Space Grant Consortium Graduate Research Fellowship. We thank Anthony Pawlicki, Kelli Straka, and Andrew Reeve for help in the field, laboratory, sharing ideas, and use of unpublished data. Constructive comments by two anonymous reviewers greatly improved the quality of the manuscript. This is Maine Agriculture and Forest Experiment Station Publication #3613.

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