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Drivers of carbon dioxide and methane supersaturation in small, temporary ponds

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Abstract Inland waters are an important component of the global carbon cycle, but there is a poor understanding of carbon dynamics in very small ponds. In this study, I evaluated the concentrations and drivers of carbon dioxide (CO_2) and methane (CH_4) in six small (<1000 m^2), temporary, forested ponds in Connecticut, USA. The six ponds were on average 19-fold supersaturated in CO_2 and 504-fold supersaturated in CH_4 relative to the atmosphere. For both gases, this level of supersaturation is among the highest reported for lentic freshwaters. The physical, chemical, and biological parameters in the ponds differ from larger lakes, and may explain the supersaturation. Specifically, the ponds have high terrestrial carbon loadings, are shallow, and polymictic, meaning much of the water is in contact with the carbon-rich sediments. Pond CO_2 concentrations were best predicted by a negative relationship with dissolved oxygen (DO), indicating that substantial respiration, likely from the sediments, drew down oxygen (O_2) and produced CO_2. The stoichiometric relationship between CO_2 supersaturation and O_2 undersaturation also implicates anaerobic respiration as a significant source of CO_2 production in the ponds. The high carbon, low oxygen, and shallow nature of small ponds were also prime for CH_4 supersaturation. Methane concentrations were best predicted by a negative relationship with precipitation, likely because precipitation increased pond depth, diluted dissolved organic carbon and gas concentrations, and increased DO. If the respiration of terrestrial carbon in small ponds is not accounted for in carbon budgets, current estimates of terrestrial net ecosystem productivity may be overestimated.

Keywords Carbon dioxide · Methane · Oxygen · Respiration · Small ponds · Temporary ponds

Introduction

Inland waters play an important role in the global carbon cycle. While estimated to comprise only 2.2–3.7 % of the earth's non-glaciated land area (Raymond et al. 2013; Verpoorter et al. 2014), inland waters process the same amount of carbon as both net terrestrial productivity and net oceanic uptake (Auffdenkampe et al. 2011; Battin et al. 2009). Yet, estimates of global carbon flux from inland waters are ridden with uncertainty (Raymond et al. 2013) and finer-scale studies are needed to determine carbon concentrations in global waters (Battin et al. 2009).

One source of uncertainty in global carbon budgets is the role of small ponds. The majority of studies on

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carbon cycling in lentic systems have focused on medium- to large-sized lakes. Yet the vast majority of ponds and lakes are small: over 90 % of all ponds and lakes are <0.01 km^2 (Downing et al. 2006; Verpoorter et al. 2014), not including very small ponds (0.0001–0.001 km^2) which could number as high as 3.2 billion and cover 0.8 million km^2 of surface area (Downing 2010). However, small ponds <0.1 km^2 are difficult to map (Lehner and Döll 2004) and even high-resolution satellite images cannot accurately identify ponds <0.002 km^2 (Verpoorter et al. 2014). Due to the uncertainty of their distribution, very small ponds (<0.001 km^2) remain difficult to assess in regional and global biogeochemical models, and are excluded.

Regardless of their areal extent, small ponds may be hotspots for carbon cycling. Small and shallow ponds receive high loadings of terrestrial dissolved and particulate organic carbon (DOC, POC) relative to their water volume, which increases respiration and carbon dioxide (CO_2) production (Hope et al. 1996; Kelly et al. 2001; Kortelainen et al. 2006; Rubbo et al. 2006). Methane (CH_4) concentrations also tend to be greater in small ponds because more water is in contact with anoxic sediments and shallow waters reduce the amount of CH_4 oxidation that occurs between the sediments and surface waters (Bastviken et al. 2004; Juutinen et al. 2009; Kankaala et al. 2013). As CH_4 has a global warming potential about 25 times higher than CO_2, its contribution to carbon budgets should not be overlooked (Bastviken et al. 2011).

Although small, shallow ponds are abundant and may be highly saturated with carbon gases, few studies have evaluated the concentrations, fluxes, and drivers of CO_2 and CH_4 in very small ponds. The studies that have done so indicate that small ponds (≤0.01 km^2) have some of the highest CO_2 and CH_4 concentrations in both boreal and temperate regions (Table 1). Due to their high concentrations of CO_2 and CH_4, is possible that carbon flux from small ponds <0.01 km^2 may match that of larger lakes on both a local (Abnizova et al. 2012) and a global (Torgersen and Branco 2008) scale.

Yet the paucity of studies on carbon dynamics in small ponds, particularly in temperate regions, limits our understanding of inland water carbon cycling. It is imperative to know both the concentrations and mechanisms driving CO_2 and CH_4 supersaturation in small freshwaters. As very small ponds have unique chemical, physical, and biological parameters, the drivers of carbon concentrations may differ from larger lakes. For instance, high carbon loading, shallow waters, and frequent mixing could lead to different mechanisms driving CO_2 and CH_4 production in small ponds compared to larger lakes. Furthermore, small pond carbon dynamics may be more sensitive than larger lakes to seasonal and annual variation, such as temperature changes and water availability. Carbon cycling provides valuable knowledge on pond and lake biology, which is important considering the vast majority of the world's ponds and lakes are very small. Additionally, understanding the drivers and concentrations of CO_2 and CH_4 in small ponds will inform local, regional, and global carbon budgets.

This study examines the carbon dynamics of six very small (<0.001 km^2), temporary ponds in Connecticut, USA across the open water season and across two years. The goals of the study were (1) to quantify the concentrations of CO_2 and CH_4 in small, temporary, and temperate ponds and (2) to identify the local drivers of CO_2 and CH_4 concentrations.

Methods

Study sites and sampling

I sampled six temporary ponds in 2013 and five of the six in 2014 (Long Pond was removed from study in 2014 for a whole-ecosystem experiment) (Table 2). The study ponds are located within the Yale Myers Forest, a 3,213-ha research forest in Tolland and Windham Counties, Connecticut, USA. The ponds are located in mixed deciduous-coniferous forest with minimal human disturbance. The forest composition surrounding the six ponds is primarily oak (*Quercus rubra*, *Q. alba*), red maple (*Acer rubrum*), Eastern hemlock (*Tsuga canadensis*), and pine (*Pinus resinosa*, *P. strobus*). The soil types are Charlton-Chatfield Complex (Blacksmith, E8, Quarry, Woodpile Ponds) and Hinckley gravelly sandy loam (Long, Atwood Ponds), with slopes ranging from 3 to 15 %, except for E8 Pond where surrounding slopes range from 15 to 45 % (U.S. Department of Agriculture NRCS 1996). Temporary ponds like these are abundant throughout northern and eastern North America, with one to thirteen ponds per km^2 of undeveloped forest (Brooks et al. 1998; Capps et al. 2014; Palik et al. 2003; Wu et al. 2014). In this region, ponds typically fill with autumnal rains, freeze over the

Table 1 Reported surface water CO_2 and CH_4 concentrations from small ponds ($\leq$0.01 km^2) globally

Reference	# Ponds	Study region	Surface area (km^2)	CO_2 conc. (μmol L^{-1})	CH_4 conc. (μmol L^{-1})
Barber et al. (1988)	1	Florida, USA	0.005		2.2
Bastviken et al. (2004)	4	Sweden; Wisconsin and Minnesota, USA	0.003–0.009		1.3 (0.3–2.3)
Casper et al. (2000)	1	United Kingdom	0.01	132.0	1.3
Hamilton et al. (1994)	22	Canada	0.00003–0.0015	136.8 (44.3–363.1)	6.2 (1.6–17.9)
Jonsson et al. (2003)	13	Sweden	0.007–0.01	33.2 (19.4–57.4)	
Kankaala et al. (2013)	5	Finland	0.0035–0.01	171.0 (81.0–313.0)	1.5 (0.7–2.6)
Kling et al. (1991)	2	Alaska, USA	0.001–0.002	43.1 (3.6–82.5)	
Laurion et al. (2010)	9	Canada	0.00002–0.0003	33.8 (4.8–116.6)	1.7 (0.1–3.9)
Natchimuthu et al. (2014)	1	Sweden	0.0012		1.3
Pelletier et al. (2014)	5	Canada	0.00013–0.0026	53.8 (41.6–82.4)	2.3 (0.5–6.7)
Repo et al. (2007)	1	Siberia	0.005	92	2.6
Riera et al. (1999)	2	Wisconsin, USA	0.0054–0.01	110.9 (79.6–142.2)	7.1 (3.9–10.2)
Smith and Lewis (1992)	1	Colorado, USA	0.01		1.0
This study	6	Connecticut, USA	0.0003–0.0008	352.3 (273.3–553.4)	33.4 (21.0–58.9)

Concentrations are direct measurements (from headspace equilibration) and are reported as means (range) when more than one pond was included in the study

winter, thaw in early spring, and dry by late summer or early fall, although hydroperiod is sensitive to precipitation events. Five of the six study ponds dried in 2013 (all but Woodpile Pond) and all ponds dried in 2014. All six ponds are shallow (<1 m), lack inlets and outlets, and have little emergent vegetation.

I sampled ponds for CO_2 and CH_4 concentrations biweekly from after ice-out in April until the ponds began to dry mid- to late-July. Dry date differed by ponds and among years, allowing up to 9 sampling rounds for each pond in 2013 and up to eight sampling rounds in 2014. In addition to gas concentrations, I measured depth, water temperature, percent dissolved oxygen (DO) (ProODO, Yellow Springs Instruments, Yellow Springs, Ohio, USA), pH, and conductivity (Waterproof Multiparameter PCS Testr 35, Oakton Instruments, Vernon Hills, Illinois, USA) biweekly. I also took biweekly samples for chlorophyll *a* from periphyton growing attached to glass slides (Periphyton Sampler, Wildlife Supply Company, Yulee, Florida, USA) and from surface water for phytoplankton. Once per month I took water samples to measure total dissolved nitrogen (TDN), total dissolved phosphorus (TDP), and dissolved organic carbon (DOC). Samples were taken from surface waters near Z_{max}. For gas concentrations, I took two samples at Z_{max} and in all but the smallest pond (Quarry Pond), I took two additional samples at either end of the pond to account for spatial variability.

Gas concentrations

Water samples were collected from 5 to 10 cm below the surface of the water using a peristaltic pump (Masterflex E/S Portable Sampler, Cole-Parmer, Vernon Hills, Illinois, USA). I collected water in glass BOD bottles, flushed at least twice by their volume while ensuring that no bubbles were produced. I then extracted 110 mL of water using a 140-mL plastic syringe with a three-way stopcock, also being careful to not produce bubbles. I immediately added 30 mL of N_2, and shook the syringe vigorously for two 2 min to ensure gas equilibrium. I then extracted 15 mL of headspace and stored it in a 12-mL evacuated vial (839 W Exetainer, Labco Limited, Lampeter, UK) until analysis.

Headspace concentrations of CO_2 and CH_4 were measured by gas chromatography with a flame ionization detector fit with a methanizer (Shimadzu GC2014, Kyoto, Japan) and calculated using standard curves. Concentrations of gases dissolved in water were corrected for dilution and calculated according to

Table 2 Physical, chemical, and biological characteristics of the six temporary ponds

Pond	Latitude	Longitude	SA (m^2)[a]	Zmax (cm)[b]	Temp. (C)	pH	Conductivity (μS/cm)	DO (%)	DOC (mg L^{-1})	Peri chl. a (μg cm^{-2})	Phyto chl. a (μg L^{-1})	TDP (μg L^{-1})	TDN (mg L^{-1})
Atwood	41.9652	−72.1523	459	37.0 (13–51)	12.3 (7.7–20.8)	5.7 (5.5–5.9)	20.6 (19.0–23.8)	31.6 (7.0–56.2)	7.1 (2.6–13.1)	49.5 (7.7–157.8)	13.8 (0.2–65.1)	47.3 (10.2–127.6)	0.43 (0.1–1.0)
Blacksmith	41.9549	−72.1236	604	37.8 (7–50)	13.2 (8.2–18.1)	5.6 (5.3–5.8)	28.6 (23.8–36.1)	25.3 (3.9–53.5)	20.9 (6.2–38.4)	231.4 (10.3–600.5)	2.2 (0.4–6.1)	82.8 (11.4–183.2)	0.95 (0.2–2.1)
E8	41.9632	−72.1500	604	47.14 (24–63)	12.4 (7.1–20.4)	5.2 (5.0–5.5)	27.8 (22.4–32.2)	41.0 (6.5–74.7)	11.2 (5.2–19.4)	27.4 (3.6–78.6)	3.1 (0.3–13.0)	27.0 (7.0–88.4)	0.44 (0.1–1.1)
Long	41.9668	−72.1509	847	45.75 (22–72)	14.8 (10.4–21)	5.9 (5.8–6.0)	36.9 (30.6–47.4)	20.6 (3.0–34.3)	13.2 (9.7–18.5)	221.2 (29.0–627.9)	19.7 (1.3–72.6)	104.2 (54.3–145.5)	0.69 (0.5–0.9)
Quarry	41.9434	−72.1287	298	57.7 (22–94)	14.0 (8.6–21.7)	6.8 (6.6–7.0)	75.4 (64.3–81.9)	50.8 (36.8–66.4)	3.7 (2.8–4.9)	58.7 (4.6–216.8)	4.7 (2.0–8.7)	10.5 (6.5–19.6)	0.18 (0.1–0.3)
Woodpile	41.9423	−72.1290	716	68.1 (22–92)	14.5 (9.0–22.2)	6.5 (6.4–6.8)	33.4 (23.2–41.2)	29.3 (6.1–65.1)	8.6 (6–10.6)	112.2 (38.2–192.9)	28.6 (1.2–66.5)	36.9 (13.4–65.4)	0.55 (0.3–0.8)

Values are means with ranges in parentheses

[a] SA is maximum surface area of the pond

[b] Zmax is depth at the deepest point in the pond

Henry's law using values for CO_2 from Weiss (1974) and for CH_4 from Wiesenburg and Guinasso (1979).

Water chemistry

Glass slides for periphyton chlorophyll *a* were scraped, rinsed with water, and the resulting periphyton-water slurry was filtered onto pre-combusted Whatman GF/F filters (Whatman, Brentford, UK) and frozen until analysis. Water samples for phytoplankton chlorophyll *a*, TDN, TDP, and DOC were pre-filtered through 150 μm mesh to remove zooplankton and debris. Water samples for phytoplankton chlorophyll *a* were then filtered onto pre-combusted Whatman GF/F filters (Whatman, Brentford, UK) and frozen until analysis. Periphyton and phytoplankton chlorophyll *a* was measured from the filters using a fluorometer (TD-700 Fluorometer, Turner Designs, Sunnyvale, California, USA) following Environmental Protection Agency Method 445.0.

Water samples for TDN, TDP, and DOC were filtered through pre-combusted Whatman GF/F filters (Whatman, Brentford, UK) and the filtrate was frozen until analysis. Concentrations of TDN and TDP were determined using a persulfate digestion and colorimetric standard methods (Clesceri et al. 1998) in conjunction with an auto-analyzer (Astoria2 Analyzer, Astoria-Pacific, Clackamas, Oregon, USA). Dissolved organic carbon was analyzed on a Shimadzu TOC 5000 auto-analyzer (Shimadzu Corporation, Kyoto, Japan).

Statistical analysis

For overall CO_2 and CH_4 concentrations, the two to four replicate samples were averaged for each pond at each sampling round. These biweekly measurements were used to estimate overall means for each gas ($n = 89$). To evaluate the saturation of each gas relative to the atmosphere, I used the average of monthly air concentrations from April through July for each year from the Mauna Loa Observatory, Hawaii, USA. The mean CO_2 air concentrations were 398.5 and 400.9 ppm and the mean CH_4 air concentrations were 1.824 and 1.837 ppm for 2013 and 2014, respectively. I then calculated relative saturation between the water and air for both gases in each pond for every sampling date.

To determine which environmental variables predicted gas concentrations, I created linear mixed-

Table 3 Pearson correlation coefficients between surface water gas concentrations (CO_2 and CH_4) and environmental variables measured in the six study ponds ($n = 40$ for all variables)

	Temp	Depth	pH	Cond	DO %	DOC_ln	Peri_ln	Phyto_ln	TDN_ln	TDP_ln	Precip_ln	CO_2_ln	CH_4_ln
Temp	1	−0.17	0.16	0.21	−0.63**	0.27	0.71**	0.34*	0.48**	0.50**	−0.47**	0.18	0.44**
Depth		1	0.32*	0.14	0.40**	−0.43**	−0.05	−0.02	−0.42**	−0.43**	0.50**	−0.37*	−0.13
pH			1	0.71**	0.09	−0.43**	0.05	0.46**	−0.18	−0.21	−0.03	−0.27	0.11
Cond				1	0.24	−0.42**	−0.06	0.11	−0.30	−0.34*	−0.03	−0.21	0.05
DO					1	−0.65**	−0.53**	−0.35*	−0.78**	−0.80**	0.58**	−0.49**	−0.41*
DOC_ln						1	0.38*	0.05	0.91**	0.82**	−0.45**	0.48*	0.24
Peri_ln							1	0.12	0.50**	0.58**	−0.10	0.25	0.27
Phyto_ln								1	0.27	0.25	−0.44**	−0.13	0.43**
TDN_ln									1	0.92**	−0.59**	0.46**	0.38*
TDP_ln										1	−0.49**	0.41**	0.26
Precip_ln											1	−0.30	−0.58**
CO2_ln												1	0.45**
CH4_ln													1

Significance of the coefficient denoted by asterisks: * $p < 0.05$, ** $p < 0.01$

effects models with pond as a random effect in R (R Version 3.1.2, R Core Team) using the "lme4" package (Bates et al. 2014). I evaluated the random-effects structure by comparing random intercepts for pond, random intercepts for pond with a correlated random slope for time, and random intercepts for pond with an uncorrelated random slope for time. The random intercept for pond was selected because it was most parsimonious and did not differ from the other models. Sampling year was not important in any model and was excluded.

Models were constructed using monthly estimates of gas concentrations and environmental variables because TDN, TDP, and DOC were only measured monthly ($n = 40$). The environmental variables included: temperature, depth, pH, conductivity, DO, DOC, periphyton chlorophyll *a*, phytoplankton chlorophyll *a*, TDN, TDP, and precipitation. Precipitation data was taken from a weather station in Willimantic, Connecticut, USA, about 24 km southwest of the study sites. The precipitation variable is the cumulative amount of precipitation occurring over 2 weeks prior to the sampling date. All environmental variables as well as response variables (CO_2 and CH_4) were evaluated for normality and the following variables were natural-log-transformed: CO_2, CH_4, DOC, periphyton chlorophyll *a*, phytoplankton chlorophyll *a*, TDN, TDP, and precipitation.

Models for CO_2 and CH_4 were first fit with all environmental variables and assessed for collinearity by calculating the variation inflation factor (VIF) and removing variables with a VIF ≥ 5. The variables removed included: TDN, TDP, and temperature. As TDN and TDP are highly correlated with DOC (Table 3) and can be considered proxies for DOC in lentic systems with high terrestrial inputs (Larsen et al. 2011), its removal should not mar model interpretation. Temperature and periphyton chlorophyll *a* are highly correlated (Table 3), meaning that if periphyton chlorophyll *a* is included in top models, it could also be interpreted as a possible temperature effect. Models were then fit with all remaining environmental variables (depth, pH, conductivity, DO, DOC, periphyton chlorophyll *a*, phytoplankton chlorophyll *a*, and precipitation). I built models by selectively removing one variable at a time using AICc model selection (Burnham and Anderson 2002). Once the top predictors were identified, I built the models back up adding in one variable at a time to ensure that I

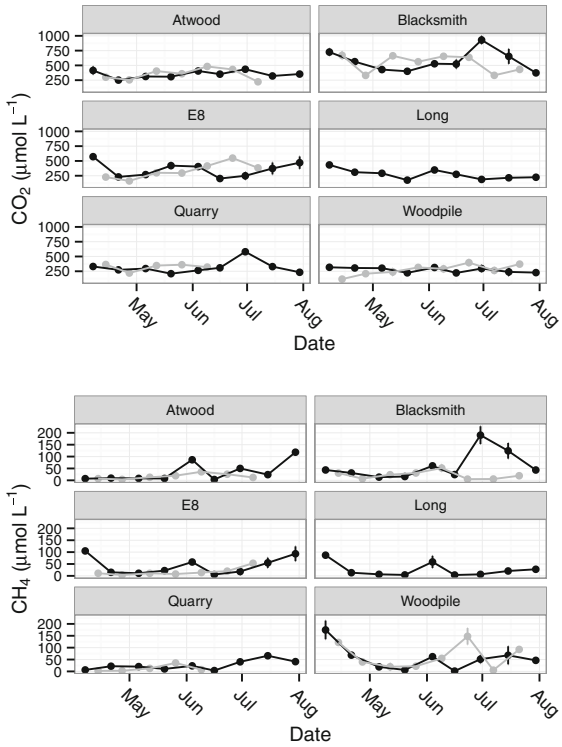

Fig. 1 Surface water CO_2 and CH_4 concentrations sampled from the six study ponds across 2013 (*black*) and 2014 (*gray*). *Error bars* represent standard error. For reference, the water–air equilibrium was on average 18.99 (±0.29 SE) µmol L^{-1} for CO_2 and 0.0727 (±0.0008 SE) µmol L^{-1} for CH_4 across both years

evaluated all possible best models. Top models are reported within two AICc of the best model (lowest AICc). I determined mixed model fit by calculating the marginal (variance associated with fixed effects) and conditional (variance associated with fixed and random effects) R^2 values (Nakagawa and Schielzeth 2013) using the "MuMIn" package in R (Barton 2014).

Results

Pond characteristics

The six temporary ponds exhibited high seasonal variability in physical, chemical, and biological parameters (Table 2). There were seasonal increases in temperature (linear regression, $F_{1,38} = 145.2$, $p < 0.001$, $R^2 = 0.79$), periphyton chlorophyll *a* ($F_{1,38} = 31.3$, $p < 0.001$, $R^2 = 0.44$), TDN ($F_{1,38} = 9.2$, $p = 0.004$, $R^2 = 0.17$), and TDP ($F_{1,38} = 14.7$, $p < 0.001$, $R^2 = 0.26$), and a seasonal decrease in DO ($F_{1,38} = 20.5$, $p < 0.001$, $R^2 = 0.33$). Notably, temperature ranged from 7.1 to 22.2 °C and trophic status ranged from oligotrophic to eutrophic within individual ponds (e.g. phytoplankton chlorophyll *a* range 0.2–65.1 µg L^{-1} in Atwood; TDP range 11.4–183.2 µg L^{-1} in Blacksmith). Dissolved oxygen was undersaturated at all sampling points, ranging from 3.0 to 74.7 %, indicating the ponds were net heterotrophic. There was also substantial between-pond variability (Table 2), with all of the environmental variables differing among ponds (ANOVA, $p < 0.01$) except for DO and temperature. Notably, DOC varied dramatically among ponds with maximum values ranging from 4.9 mg L^{-1} (Quarry Pond) to 38.4 mg L^{-1} (Blacksmith Pond).

CO_2 concentrations

Carbon dioxide concentrations were supersaturated across all ponds and all sampling dates, with an overall mean of 360.6 (±15.2 SE) µmol L^{-1} (7,716.6 ± 342.7 ppmv), equal to 19.3 (±0.9 SE) fold supersaturation (range 5.7–56.7 fold supersaturation) (Fig. 1). Across all ponds and all dates, 75 % of samples were >13-fold saturated and 25 % of samples were >22-fold saturated. The concentrations of CO_2 did not differ with time (linear regression, $F_{1,87} = 0.24$, $p = 0.62$, $R^2 = 0.009$), but concentrations did vary by pond (ANOVA, $F_{5,83} = 12.52$, $p < 0.001$) with Blacksmith Pond having significantly higher CO_2 concentrations than all other ponds (Tukey HSD, all $p < 0.05$), with all other ponds having similar concentrations (Tukey HSD, all $p > 0.05$).

CH_4 concentrations

Methane concentrations were supersaturated across all ponds and all sampling dates, with an overall mean of 35.7 (±4.1 SE) µmol L^{-1} (921.7 ± 107.0 ppmv), equal to 504.2 (±58.6 SE) fold supersaturation (range 19.0–2906.6 fold supersaturation) (Fig. 1). Across all ponds and dates, 75 % of samples were >105-fold saturated and 25 % of samples were >755-fold saturated. Methane concentrations had a weak, but significant, positive relationship with time ($F_{1,87} = 5.40$, $p = 0.02$, $R^2 = 0.05$) and were similar across all six ponds (ANOVA, $F_{5,83} = 1.83$ $p = 0.12$).

Table 4 Linear mixed-effects models for predicting surface CO_2 concentrations

Model	k	AICc	ΔAICc	R^2 marg.[a]	R^2 cond.[b]	Pond variance	Residual variance	Estimate intercept	Estimate DO	Estimate covariate 2	Estimate pond	Estimate residual
Null	0	26.81	–	0.00	0.36	0.044	0.077	5.74 (5.51, 5.96)	–	–	(0.10, 0.46)	(0.22, 0.36)
DO	1	14.29	0.00	0.23	0.60	0.046	0.050	6.02 (5.77, 6.26)	−0.008 (−0.01, −0.004)	–	(0.11, 0.46)	(0.18, 0.29)
DO + Phyto chl. a	2	15.46	−1.17	0.27	0.59	0.038	0.049	6.10 (5.83, 6.37)	−0.009 (−0.01, −0.005)	−0.038 (−0.10, 0.02)	(0.09, 0.43)	(0.18, 0.29)
DO + pH	2	15.50	−1.21	0.32	0.64	0.043	0.048	7.02 (5.30, 8.97)	−0.009 (−0.01, −0.005)	−0.168 (−0.49, 0.12)	(0.10, 0.45)	(0.18, 0.28)

Each model includes pond as a random effect. Estimates include 95 % confidence intervals in parentheses. Models within 2 AICc units of the best model are included

[a] R^2 marginal accounts for fixed effects

[b] R^2 conditional accounts for fixed and random effects

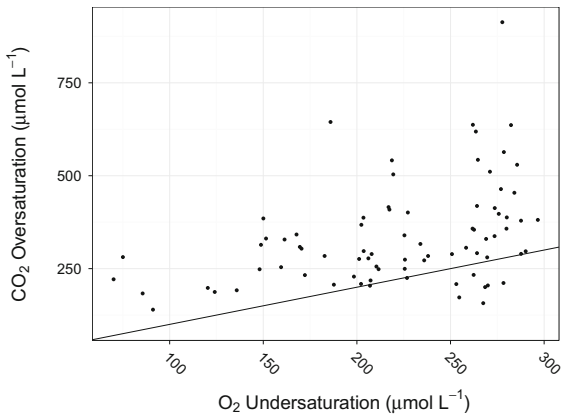

Fig. 2 Relationship between CO_2 oversaturation and O_2 undersaturation in the six ponds across the season (n = 78). The black line indicates a one-to-one relationship between CO_2 and O_2

Environmental predictors of CO_2

Concentrations of CO_2 negatively correlated with depth and DO, and positively correlated with DOC and TDP (Table 3). In the mixed-effects models, DO best predicted CO_2 concentrations, with phytoplankton chlorophyll *a* and pH being of secondary importance (Table 4). In the top model, DO explained 23 % of the variance, while between-pond variation explained an additional 37 %, highlighting the importance of variation among individual ponds.

To evaluate the relationship between CO_2 and DO further, I compared CO_2 oversaturation with oxygen (O_2) undersaturation using all seasonal data points where CO_2 and O_2 were both measured ($n = 78$) (Fig. 2). There was a significant positive relationship (linear regression, $F_{1,76} = 13.98$, $p < 0.001$, $R^2 = 0.14$), but this relationship began to break down as DO undersaturation increased. In other words, CO_2 saturation was more variable when DO was lower. Furthermore, the majority of the points fell above the one-to-one CO_2:O_2 ratio expected if CO_2 were only produced by aerobic respiration, indicating substantial anaerobic production of CO_2.

Environmental predictors of CH_4

Concentrations of CH_4 negatively correlated with DO and precipitation, and positively correlated with temperature and phytoplankton chlorophyll *a* (Table 3). In the mixed-effects models, precipitation was the best predictor of CH_4 concentrations, with periphyton chlorophyll *a*,

Table 5 Linear mixed-effects models for predicting surface CH_4 concentrations

Model	k	AICc	ΔAICc	R^2 marg.[a]	R^2 cond.[b]	Pond variance	Residual variance	Estimate intercept	Estimate precipitation	Estimate covariate 2	Estimate covariate 3	Estimate pond	Estimate residual
Null	0	129.53	–	0.00	<0.01	$1.7 * 10^{-15}$	1.26	2.73 (2.30, 3.09)	–	–	–	(0, inf)	(0.92, 1.42)
Precip	1	115.40	0	0.34	0.37	0.04	0.80	3.00 (2.58, 3.37)	−0.69 (−0.99, −0.39)	–	–	(0, 0.72)	(0.72, 1.15)
Precip + peri	2	115.55	−0.15	0.39	0.39	0.00	0.78	2.33 (1.45, 3.24)	−0.67 (−0.96, −0.37)	0.17 (−0.04, 0.38)	–	(0, 0.62)	(0.71, 1.12)
Precip + phyto	2	115.79	−0.39	0.38	0.39	0.01	0.78	2.74 (2.22, 3.22)	−0.58 (−0.91, −0.24)	−0.16 (−0.05, 0.37)	–	(0, 0.65)	(0.71, 1.12)
Precip + peri + depth	3	116.14	−0.75	0.42	0.42	0.00	0.74	2.55 (1.45, 3.64)	−0.79 (−1.13, −0.45)	0.17 (−0.03, 0.37)	0.01 (−0.003, 0.03)	(0, 0.48)	(0.70, 1.09)
Precip + peri + phyto	3	116.16	−0.76	0.42	0.42	0.00	0.74	2.65 (1.61, 3.69)	−0.56 (−0.88, −0.24)	0.16 (−0.04, 0.36)	0.15 (−0.05, 0.35)	(0, 0.58)	(0.70, 1.09)
Precip + depth	2	116.20	−0.81	0.38	0.38	0.00	0.80	3.26 (2.52, 4.00)	−0.81 (−1.16, −0.47)	0.01 (−0.004, 0.03)	–	(0, 0.58)	(0.72, 1.13)

Each model includes pond as a random effect. Estimates include 95 % confidence intervals in parentheses. Models within 2 AICc units of the best model are included

[a] R^2 marginal accounts for fixed effects

[b] R^2 conditional accounts for fixed and random effects

phytoplankton chlorophyll *a*, and depth being of secondary importance (Table 5). In the top model, precipitation explained 34 % of the variance, while between-pond variation only explained an additional 3 %.

Discussion

CO_2 and CH_4 concentrations

The concentrations of CO_2 and CH_4 in these small temporary ponds are among the most supersaturated for lentic waters globally. Cole et al. (1994) compared CO_2 concentrations among 1,835 lakes and found that the lower and upper 10 % of samples averaged 3.1-fold below and 16-fold above atmospheric equilibrium, respectively (range −175 to 57). In direct comparison, the lower and upper 10 % of samples in this study were 11.2 and 28.6-fold supersaturated. Until now, the highest reported CO_2 concentrations came from a study on 64 small (0.0002–0.2 km^2), forested ponds in Denmark, where 75 % of the samples were more than 6-fold saturated and 25 % were more than 16-fold saturated (Sand-Jensen and Staehr 2007). High CO_2 concentrations on the order of magnitude reported here have also been seen on the extreme ends of studies evaluating CO_2 in small wetland ponds in the Hudson Bay Lowlands (Hamilton et al. 1994) and lakes in New England (Lennon et al. 2006) and Finland (Kankaala et al. 2013). The temporary ponds studied here had CO_2 concentrations that were consistently some of the highest reported to date, suggesting the conditions in these ponds are prime for CO_2 production.

There have been fewer studies on CH_4 than CO_2 concentrations in ponds and lakes globally, but comparisons of available data indicate that the CH_4 concentrations in these study ponds were also among the highest reported. The range of CH_4 concentrations reported for ponds and lakes is substantial, with concentrations as low as 0.004 μmol L^{-1} in an Irish lake (Whitfield et al. 2011) up to 17.93 μmol L^{-1} in a Hudson Bay Lowland pond (Hamilton et al. 1994). The small wetland ponds found in the Hudson Bay Lowlands have, until now, had the highest reported concentrations of CH_4: 75 % of ponds were over 38-fold saturated and 25 % of ponds were over 110-fold saturated (Hamilton et al. 1994). Collectively, the CO_2 and CH_4 concentrations reported in this

study are exceptionally high across both time and space, indicating that small, temporary ponds are hotspots for CO_2 and CH_4 production.

Environmental predictors of CO_2

Carbon dioxide concentrations were best predicted by a negative relationship with DO, with phytoplankton chlorophyll *a* and pH of secondary importance. In many lakes, however, CO_2 concentrations are best predicted by a negative relationship with DOC (or TOC) (Hope et al. 1996; Jonsson et al. 2003; Kelly et al. 2001; Raymond et al. 2013; Roehm et al. 2009; Sobek et al. 2005). This is because for many lakes, allochthonous organic carbon is the largest source of CO_2 production (Karlsson 2007; McCallister and del Giorgio 2008). A closer inspection, however, shows most studies that reported DOC as predicting CO_2 did not evaluate the relationship between CO_2 and DO (but see Roehm et al. 2009). When DO is considered, many studies found a significant negative correlation between CO_2 and DO (Balmer and Downing 2011; Cole et al. 2010; Kankaala et al. 2013; Kortelainen et al. 2006; Rantakari and Kortelainen 2005; Roulet et al. 1997; Zhang et al. 2013). A few studies even found DO to be a better predictor of CO_2 concentrations compared to DOC (Kortelainen et al. 2006; Rantakari and Kortelainen 2005).

Whether DOC or DO better predicts CO_2 concentrations likely depends on the physical, chemical, and biological parameters of ponds and lakes. A high correlation between O_2 and CO_2 indicates substantial respiration, oftentimes from the sediments (Jonsson et al. 2003; Kortelainen et al. 2006; Rantakari and Kortelainen 2005; Roulet et al. 1997). The relationship between O_2 and CO_2 can be stronger in ponds and lakes with high DOC, likely because of high sedimentation of allochthonous carbon (Jonsson et al. 2003). The ponds studied here are strongly influenced by allochthonous carbon because they are small, with a high perimeter to edge ratio. Each year, the ponds receive between 188 and 253 g m^{-2} $year^{-1}$ of dry leaf litter (Holgerson, unpubl. data), providing an annually-renewed source of POC and DOC (Meyer et al. 1998). Because the ponds are shallow, much of the water is in contact with the sediments where the terrestrial carbon decomposes. Furthermore, sediment respiration can affect the entire water column due to overnight mixing that occurs on the scale of days to weeks (Holgerson, unpubl. data).

The large amount of terrestrial carbon settling at the bottom of the pond is likely responsible for high respiration rates, driving O_2 levels down and CO_2 concentrations up. Substantial anaerobic respiration also occurred in the ponds (Fig. 2), supporting the notion that sediment respiration could explain both O_2 and CO_2 concentrations. The importance of sediment respiration in driving CO_2 in small ponds is in contrast to water column DOC driving CO_2 in larger ponds and lakes. This is likely because in larger lakes, allochthonous inputs and the contribution of sediments are lower relative to water volume, and the water column stratifies isolating the effects of the sediments to the hypolimnion. The different conditions between small ponds and larger lakes likely explain why the drivers of surface water CO_2 differ with lake size.

The second and third top models for predicting CO_2 concentration included phytoplankton chlorophyll *a* and pH, respectively, as covariates of secondary importance to DO. The estimates for both phytoplankton chlorophyll *a* and pH overlapped with zero, illustrating that these variables are not individually important but do strengthen the relationship between DO and CO_2. Phytoplankton chlorophyll *a* negatively correlated with CO_2, which is intuitive, as increased primary production consumes more CO_2. Other studies have also seen a negative relationship between CO_2 and phytoplankton (Balmer and Downing 2011; Kosten et al. 2010; Larsen et al. 2011; Roehm et al. 2009), highlighting that CO_2 is affected by production in addition to respiration. The third top model included DO and pH, which also negatively correlated with CO_2. This relationship is most likely driven by increased CO_2 concentrations driving down pH (Wetzel 2001).

The random effect of pond significantly improved models of CO_2 concentration and increased the best model's R^2 value from 0.23 to 0.60 (Table 4), indicating substantial between-pond variation. Blacksmith Pond had the highest CO_2 concentrations while Long and Woodpile Ponds had the lowest. Perhaps geology, groundwater inputs, turbulent differences, or another environmental variable not measured here played a role in between-pond differences. It is worth noting that while groundwater can be an important source of CO_2 in some freshwater systems (Humborg et al. 2010), there are several indications that

groundwater is unlikely to play a major role in these ponds. First, the strong correlation between precipitation and depth (Table 3, $r = 0.50$) along with low conductivity (<82 μS/cm) indicate that these ponds are fed by precipitation and not groundwater (Brooks 2004, 2005; Palik et al. 2001; Yoshikawa and Hinzman 2003). Additionally, there were no spikes in conductivity as the ponds dried, indicating that more water was lost to seepage than to evaporation and that the ponds recharged groundwater rather than drawing from it (Schneider and Frost 1996). As such, groundwater likely provides minimal CO_2 inputs to these temporary ponds, but there could be variation among sites.

Year and sampling round had no significant effect on CO_2, suggesting that CO_2 concentrations in these ponds were similar inter- and intra-annually. Jonsson et al. (2003) also found no seasonal effect on CO_2 concentrations across 16 Swedish lakes, hypothesizing that there was little metabolic change and that frequent mixing minimized seasonal changes in CO_2 concentrations. In the ponds studied here, metabolic activity likely increased with temperature as exhibited by seasonal increases in periphyton chlorophyll *a*. I hypothesize that CO_2 concentrations remained steady due to both polymictic mixing and high sediment respiration throughout the season. It is also possible that anaerobic breakdown of DOC and POC shifted more toward methanogenesis seasonally, which could reduce sediment CO_2 production and mask any seasonal increases in CO_2 that would occur if O_2 were more available.

Environmental predictors of CH_4

The strongest predictor of CH_4 concentrations in these temporary ponds was precipitation, with periphyton chlorophyll *a*, phytoplankton chlorophyll *a*, and depth being of secondary importance. Increased precipitation was associated with decreased CH_4 concentrations, a contrast with other studies where precipitation increased with CH_4 (Natchimuthu et al. 2014) and CO_2 (Einola et al. 2011; Rantakari and Kortelainen 2005; Roehm et al. 2009) concentrations or flux. In those studies, increased precipitation was associated with increased DOC in lakes likely due to increased runoff from the landscape (Einola et al. 2011; Rantakari and Kortelainen 2005). In this study, however, precipitation negatively correlated with DOC (Table 3, $r = -0.45$). Precipitation events likely influence small ponds differently than larger lakes because of their particular characteristics. Specifically, the volume of these small and shallow ponds responded dramatically to precipitation events. For instance, 21.7 cm of rainfall occurred during the first 2 weeks of June 2013 and as a result, pond depth increased by an average of 23.5 (±7.7 SE) cm (range 5–50 cm). Most ponds (five of the six) are located in defined basins, which prohibited areal expansion and led to dramatic increases in depth. For instance, Quarry and Long Ponds more than doubled in depth whereas Blacksmith Pond, the only pond able to significantly expand in area, only increased by 5 cm in depth.

As precipitation dramatically increased depth but not area in five of the six ponds, the relative depth (depth to surface area ratio) increased, causing a dilution effect for many of the pond's biological and chemical parameters. Specifically, increased precipitation correlated with decreased DOC, phytoplankton chlorophyll *a*, TDP, TDN, and temperature, and increased DO (Table 3). Many of these effects could alter CH_4 production and concentrations. For instance, DO is negatively correlated with CH_4 concentrations as anoxic sediments or waters are required for methanogenesis (Bastviken et al. 2004; Juutinen et al. 2009; Kankaala et al. 2013). Methane concentrations are also affected by lake area and depth: small and shallow lakes have more water in contact with anoxic sediments, less opportunity for methane oxidation between the sediments and surface water, and a well-mixed water column that permits benthic CH_4 to reach the surface (Bastviken et al. 2004; Juutinen et al. 2009; Kankaala et al. 2013). Increased temperature also correlates with greater CH_4 concentrations as methanogenesis increases with temperature (Borrel et al. 2011; van Hulzen et al. 1999). Interestingly, precipitation led to lower DOC in these ponds, implying an internal source of DOC (e.g. through leaf litter breakdown) that builds up between precipitation events and overmatches any DOC inputs from runoff. Overall, precipitation events dilute the biological and chemical parameters in small ponds, ultimately lowering CH_4 concentrations. In addition to dilution, precipitation also increases gas exchange rates (Ho et al. 1997, 2000), allowing O_2 to enter ponds and increasing efflux of CO_2 and CO_2. The observed negative relationship between CH_4 concentrations and

precipitation was therefore likely a result of both dilution and increased gas exchange.

Models predicting CH_4 concentrations also suggest that periphyton chlorophyll *a*, phytoplankton chlorophyll *a*, and depth were of secondary importance. Periphyton chlorophyll *a* was not significantly correlated with CH_4, but did correlate highly with temperature, which was removed from models due to collinearity. As temperature correlated strongly with CH_4, it is possible that periphyton is acting as a surrogate for temperature in the model, a plausible link as temperature increases methane production (Borrel et al. 2011; van Hulzen et al. 1999). Phytoplankton chlorophyll *a* also positively correlated with CH_4 concentration, likely because phytoplankton biomass increased with temperature and decreased with precipitation. Additionally, algal biomass is very labile and could provide another source of organic matter for decomposition. Lastly, depth improved model predictions, but its estimate included zero. It is likely that the model derived strength from the correlation between depth and precipitation.

There was little between-pond variation in CH_4 concentrations and as such, the random effect of pond only increased the best model R^2 from 0.34 to 0.37 (Table 5). It is worth considering why between-pond variation was important for CO_2 and not for CH_4. Methane concentrations were likely driven by precipitation, which was similar across all ponds (and imputed as the same number in models). In contrast, CO_2 concentrations were likely driven by sediment respiration, which was more variable among dates and ponds. Random effects of year and sampling round did also not improve CH_4 models, indicating that concentrations were similar between years and season, with major changes driven by precipitation.

Small ponds and inland water carbon budgets

It is well known that small ponds are more saturated with CO_2 and CH_4 than larger lakes (Bastviken et al. 2004; Kankaala et al. 2013; Raymond et al. 2013); however, this study shows that these very small ponds (<1000 m^2) are among the most saturated reported. Using a gas exchange velocity k_{600} of 0.36 m day^{-1} calculated from a propane-addition study in four similar ponds in the study area (E. Farr, unpubl. data), these ponds emit on average 100.6 ($\pm$0.51 SE) mmol C m^{-2} day^{-1} from CO_2 and 10.6 ($\pm$0.13 SE) mmol C m^{-2} day^{-1} from CH_4. In terms of carbon dioxide equivalence (CO_2e), the contribution of CH_4 (4.26 g CO_2e m^{-2} day^{-1}) is comparable to the contribution from CO_2 (4.43 g CO_2 m^{-2} day^{-1}), indicating a similar greenhouse gas potential. It is important to note that this flux estimate does not include CH_4 ebullition, which can be significant in shallow and nutrient-rich ponds and lakes (Bastviken et al. 2004; Casper et al. 2000; Huttunen et al. 2003). Convective mixing could also increase gas exchange at night (Eugster et al. 2003; MacIntyre et al. 2010); however, diurnal patterns of gas exchange in very small ponds need further study.

These fluxes are among the highest reported for ponds and lakes globally, indicating that supersaturation compensates for a lower gas transfer velocity. Despite the high concentrations and fluxes of carbon from ponds small in surface area, ponds <1000 m^2 are excluded from global carbon budgets because they cannot be easily identified from satellite imagery, calling into question both the total number and total surface area of small ponds. Local and regional estimates of small, temporary ponds are limited, but suggest that small, temporary ponds are abundant. Capps et al. (2014) report that Orono, Maine, USA, a town of 50.76 km^2, has 0.09 km^2 of temporary ponds ($\sim$0.002 % surface area). A study using high-resolution light detection and ranging (LiDAR) data to map temporary ponds across 147.9 km^2 in southeastern Massachusetts, USA, identified 2,228 potential ponds comprising 3.8 km^2 of surface area ($\sim$2.59 % surface area) (Wu et al. 2014). There is an urgent need for future studies utilizing advancing technologies, such as LiDAR, to map the distribution of very small ponds.

Because small ponds are numerous with extremely high CO_2 and CH_4 concentrations, they could play an important yet overlooked role in local, regional, and global carbon budgets. Specifically, small ponds respire significant amounts of terrestrial carbon that if unaccounted for, could overestimate terrestrial net ecosystem productivity (NEP). In regional carbon budgets, the exclusion of surface waters can overestimate terrestrial NEP by 6–44 % (Buffam et al. 2011; Christensen et al. 2007; Jonsson et al. 2007). On a global scale, unaccounted respiration from very small ponds could overestimate the terrestrial carbon sink, as has been suggested for other inland waters (Bastviken et al. 2011; Battin et al. 2009; Raymond et al. 2013).

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References

Abnizova A, Siemens J, Langer M, Boike J (2012) Small ponds with major impact: The relevance of ponds and lakes in permafrost landscapes to carbon dioxide emissions. Glob Biogeochem Cycle 26:GB2041

Aufdenkampe AK, Mayorga E, Raymond PA, Melack JM, Doney SC, Alin SR, Aalto RE, Yoo K (2011) Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Front Ecol Environ 9:53–60

Balmer MB, Downing JA (2011) Carbon dioxide concentrations in eutrophic lakes: undersaturation implies atmospheric uptake. Inland Waters 1:125–132

Barber TR, Burke RA Jr, Sackett WM (1988) Diffusive flux of methane from warm wetlands. Glob Biogeochem Cycle 2:411–425

Barton K (2014) Package 'MuMIn'. R package version 1.0-7

Bastviken D, Cole J, Pace M, Tranvik L (2004) Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. Glob Biogeochem Cycle 18:GB4009

Bastviken D, Tranvik LJ, Downing JA, Crill PM, Enrich-Prast A (2011) Freshwater methane emissions offset the continental carbon sink. Science 331:50

Bates D, Maechler M, Bolker B, Walker S (2014) lme4: Linear mixed effects models using Eigen and S4. R package version 1.0-7

Battin TJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A, Tranvik LJ (2009) The boundless carbon cycle. Nat Geosci 2:598–600

Borrel G, Jézéquel D, Biderre-Petit C, Morel-Desrosiers N, Morel J-P, Peyret P, Fonty G, Lehours A-C (2011) Production and consumption of methane in freshwater lake ecosystems. Res Microbiol 162:832–847

Brooks RT (2004) Weather-related effects on woodland vernal pool hydrology and hydroperiod. Wetlands 24:104–114

Brooks RT (2005) A review of basin morphology and pool hydrology of isolated ponded wetlands: implications for seasonal forest pools of the northeastern United States. Wetl Ecol Manag 13:335–348

Brooks RT, Stone J, Lyons P (1998) An inventory of seasonal forest ponds on the Quabbin reservoir watershed, Massachusetts. Northeast Nat 5:219–230

Buffam I, Turner MG, Desai AR, Hanson PC, Rusak JA, Lottig NR, Stanley EH, Carpenter SR (2011) Integrating aquatic and terrestrial components to construct a complete carbon budget for a north temperate lake district. Glob Change Biol 17:1193–1211

Burnham KP, Anderson DR (2002) Model selection and multimodel inference: A practical information-theoretic approach. Springer, New York

Capps KA, Berven KA, Tiegs SD (2014) Modelling nutrient transport and transformation by pool-breeding amphibians in forested landscapes using a 21-year dataset. Freshw Biol. doi:10.1111/fwb.12470

Casper P, Maberly SC, Hall GH, Finlay BJ (2000) Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere. Biogeochemistry 49:1–19

Christensen TR, Johansson T, Olsrud M, Ström L, Lindroth A, Mastepanov M, Malmer N, Friborg T, Crill P, Callaghan TV (2007) A catchment-scale carbon and greenhouse gas budget of a subarctic landscape. Philos Trans R Soc A Math Phys Eng Sci 365:1643–1656

Clesceri LS, Greenberg AE, Eaton AD (eds) (1998) Standard methods for the examination of water and wastewater. American Public Health Association, Water Environment Federation, Washington

Cole JJ, Caraco NF, Kling GW, Kratz TK (1994) Carbon dioxide supersaturation in the surface waters of lakes. Science 265:1568–1570

Cole JJ, Bade DL, Bastviken D, Pace ML, Van de Bogert M (2010) Multiple approaches to estimating air-water gas exchange in small lakes. Limnol Oceanogr Methods 8:285–293

Downing JA (2010) Emerging global role of small lakes and ponds: little things mean a lot. Limnetica 29:9–24

Downing JA, Prairie YT, Cole JJ, Duarte CM, Tranvik LJ, Striegl RG, McDowell WH, Kortelainen P, Caraco NF, Melack JM, Middelburg JJ (2006) The global abundance and size distribution of lakes, ponds, and impoundments. Limnol Oceanogr 51:2388–2397

Einola E, Rantakari M, Kankaala P, Kortelainen P, Ojala A, Pajunen H, Mäkelä S, Arvola L (2011) Carbon pools and fluxes in a chain of five boreal lakes: a dry and wet year comparison. J Geophys Res Biogeosci 116:G03009

Eugster W, Kling G, Jonas T, McFadden JP, Wüest A, MacIntyre S, Chapin FS (2003) CO_2 exchange between air and water in an Arctic Alaskan and midlatitude Swiss lake: importance of convective mixing. J Geophys Res Atm 108:4362

Hamilton JD, Kelly CA, Rudd JWM, Hesslein RH, Roulet NT (1994) Flux to the atmosphere of CH_4 and CO_2 from wetland ponds on the Hudson Bay lowlands (HBLs). J Geophys Res 99:1495–1510

Ho DT, Bliven LF, Wanninkhof RIK, Schlosser P (1997) The effect of rain on air-water gas exchange. Tellus B 49:149–158

Ho DT, Asher WE, Bliven LF, Schlosser P, Gordan EL (2000) On mechanisms of rain-induced air-water gas exchange. J Geophys Res Oceans 105:24045–24057

Hope D, Kratz TK, Riera JL (1996) Relationship between PCO2 and dissolved organic carbon in northern Wisconsin lakes. J Environ Qual 25:1442–1445

Humborg C, Mörth C-M, Sundbom M, Borg H, Blenckner T, Giesler R, Ittekkot V (2010) CO_2 supersaturation along the aquatic conduit in Swedish watersheds as constrained by

terrestrial respiration, aquatic respiration and weathering. Glob Change Biol 16:1966–1978

Huttunen JT, Alm J, Liikanen A, Juutinen S, Larmola T, Hammar T, Silvola J, Martikainen PJ (2003) Fluxes of methane, carbon dioxide and nitrous oxide in boreal lakes and potential anthropogenic effects on the aquatic greenhouse gas emissions. Chemosphere 52:609–621

Jonsson A, Karlsson J, Jansson M (2003) Sources of carbon dioxide supersaturation in clearwater and humic lakes in northern Sweden. Ecosystems 6:224–235

Jonsson A, Algesten G, Bergström AK, Bishop K, Sobek S, Tranvik LJ, Jansson M (2007) Integrating aquatic carbon fluxes in a boreal catchment carbon budget. J Hydrol 334:141–150

Juutinen S, Rantakari M, Kortelainen P, Huttunen JT, Larmola T, Alm J, Silvola J, Martikainen PJ (2009) Methane dynamics in different boreal lake types. Biogeosciences 6:209–223

Kankaala P, Huotari J, Tulonen T, Ojala A (2013) Lake-size dependent physical forcing drives carbon dioxide and methane effluxes from lakes in a boreal landscape. Limnol Oceanogr 58:1915–1930

Karlsson J (2007) Different carbon support for respiration and secondary production in unproductive lakes. Oikos 116:1691–1696

Kelly CA, Fee E, Ramlal PS, Rudd JWM, Hesslein RH, Anema C, Schindler EU (2001) Natural variability of carbon dioxide and net epilimnetic production in the surface waters of boreal lakes of different sizes. Limnol Oceanogr 46:1054–1064

Kling GW, Kipphut GW, Miller MC (1991) Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. Science 251:298–301

Kortelainen P, Rantakari M, Huttunen JT, Mattsson T, Alm J, Juutinen S, Larmola T, Silvola J, Martikainen PJ (2006) Sediment respiration and lake trophic state are important predictors of large CO_2 evasion from small boreal lakes. Glob Change Biol 12:1554–1567

Kosten S, Roland F, Da Motta Marques DML, Van Nes EH, Mazzeo N, Sternberg LdSL, Scheffer M, Cole JJ (2010) Climate-dependent CO_2 emissions from lakes. Glob Biogeochem Cycle 24:GB2007

Larsen S, Andersen T, Hessen DO (2011) The pCO2 in boreal lakes: organic carbon as a universal predictor? Glob Biogeochem Cycle 25:GB2012

Laurion I, Vincent WF, MacIntyre S, Retamal L, Dupont C, Francus P, Pienitz R (2010) Variability in greenhouse gas emissions from permafrost thaw ponds. Limnol Oceanogr 55:115–133

Lehner B, Döll P (2004) Development and validation of a global database of lakes, reservoirs and wetlands. J Hydrol 296:1–22

Lennon JT, Faiia AM, Feng X, Cottingham KL (2006) Relative importance of CO_2 recycling and CH_4 pathways in lake food webs along a dissolved organic carbon gradient. Limnol Oceanogr 51:1602–1613

MacIntyre S, Jonsson A, Jansson M, Aberg J, Turney DE, Miller SD (2010) Buoyancy flux, turbulence, and the gas transfer coefficient in a stratified lake. Geophys Res Lett 37:L24604

McCallister SL, del Giorgio P (2008) Direct measurement of the d13C signature of carbon respired by bacteria in lakes: linkages to potential carbon sources, ecosystem baseline metabolism, and CO2 fluxes. Limnol Oceanogr 53:1204–1216

Meyer JL, Wallace JB, Eggert SL (1998) Leaf litter as a source of dissolved organic carbon in streams. Ecosystems 1:240–249

Nakagawa S, Schielzeth H (2013) A general and simple method for obtaining R2 from generalized linear mixed-effects models. Methods Ecol Evol 4:133–142

Natchimuthu S, Panneer Selvam B, Bastviken D (2014) Influence of weather variables on methane and carbon dioxide flux from a shallow pond. Biogeochemistry 119:403–413

Palik B, Batzer D, Buech R, Nichols D, Cease K, Egeland L, Streblow D (2001) Seasonal pond characteristics across a chronosequence of adjacent forest ages in northern Minnesota, USA. Wetlands 21:532–542

Palik BJ, Buech R, Egeland L (2003) Using an ecological land hierarchy to predict seasonal-wetland abundance in upland forests. Ecol Appl 13:1153–1163

Pelletier L, Strachan IB, Garneau M, Roulet NT (2014) Carbon release from boreal peatland open water pools: Implication for the contemporary C exchange. J Geophys Res Biogeosci 119:JG002423

Rantakari M, Kortelainen P (2005) Interannual variation and climatic regulation of the CO2 emission from large boreal lakes. Glob Change Biol 11:1368–1380

Raymond PA, Hartmann J, Lauerwald R, Sobek S, McDonald C, Hoover M, Butman D, Striegl R, Mayorga E, Humborg C, Kortelainen P, Durr H, Meybeck M, Ciais P, Guth P (2013) Global carbon dioxide emissions from inland waters. Nature 503:355–359

Repo ME, Huttunen JT, Naumov AV, Chichulin AV, Lapshina ED, Bleuten W, Martikainen PJ (2007) Release of CO2 and CH4 from small wetland lakes in western Siberia. Tellus B 59:788–796

Riera JL, Schindler JE, Kratz TK (1999) Seasonal dynamics of carbon dioxide and methane in two clear-water lakes and two bog lakes in northern Wisconsin, USA. Can J Fish Aquat Sci 56:265–274

Roehm CL, Prairie YT, del Giorgio PA (2009) The pCO_2 dynamics in lakes in the boreal region of northern Québec. Canada. Glob Biogeochem Cycle 23:GB3013

Roulet NT, Crill PM, Comer NT, Dove A, Boubonniere RA (1997) CO_2 and CH_4 flux between a boreal beaver pond and the atmosphere. J Geophys Res Atmos 102:29313–29319

Rubbo M, Cole J, Kiesecker J (2006) Terrestrial subsidies of organic carbon support net ecosystem production in temporary forest ponds: evidence from an ecosystem experiment. Ecosystems 9:1170–1176

Sand-Jensen K, Staehr P (2007) Scaling of pelagic metabolism to size, trophy and forest cover in small Danish lakes. Ecosystems 10:128–142

Schneider DW, Frost TM (1996) Habitat duration and community structure in temporary ponds. J N Am Benthol Soc 15:64–86

Smith LK, Lewis WM Jr (1992) Seasonality of methane emissions from five lakes and associated wetlands of the Colorado Rockies. Glob Biogeochem Cycle 6:323–338

Sobek S, Tranvik LJ, Cole JJ (2005) Temperature independence of carbon dioxide supersaturation in global lakes. Glob Biogeochem Cycle 19:GB2003

Torgersen T, Branco B (2008) Carbon and oxygen fluxes from a small pond to the atmosphere: temporal variability and the CO_2/O_2 imbalance. Water Resour Res 44:W02417

U.S. Department of Agriculture NRCS (1996) Soil survey (SSURGO) for the 7.5 minute quadrangle of Westford. In U.S. Department of Agriculture, Natural Resources Conservation Science, Fort Worth, Texas, USA

van Hulzen JB, Segers R, van Bodegom PM, Leffelaar PA (1999) Temperature effects on soil methane production: an explanation for observed variability. Soil Biol Biochem 31:1919–1929

Verpoorter C, Kutser T, Seekell DA, Tranvik LJ (2014) A global inventory of lakes based on high-resolution satellite imagery. Geophys Res Lett 41:6396–6402

Weiss RF (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar Chem 2:203–215

Wetzel RG (2001) Limnology: lake and river ecosystems. Academic Press, San Diego

Whitfield CJ, Aherne J, Baulch HM (2011) Controls on greenhouse gas concentrations in polymictic headwater lakes in Ireland. Sci Total Environ 410–411:217–225

Wiesenburg DA, Guinasso NL (1979) Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. J Chem Eng Data 24:356–360

Wu Q, Lane C, Liu H (2014) An effective method for detecting potential woodland vernal pools using high-resolution LiDAR data and aerial imagery. Remote Sens 6:11444–11467

Yoshikawa K, Hinzman LD (2003) Shrinking thermokarst ponds and groundwater dynamics in discontinuous permafrost near council, Alaska. Permafr Periglac Process 14:151–160

Zhang J, Jiang Y, Gao Y, Wu Y, Luo W, Zhou Z, Wang F (2013) CO2 emission from Dianshan Lake in summer, East China. Chin J Geochem 32:430–435