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### How to cite

FLURY, Sabine, MCGINNIS, Daniel Frank, GESSNER, Mark O. Methane emissions from a freshwater marsh in response to experimentally simulated global warming and nitrogen enrichment. In: Journal of geophysical research, 2010, vol. 115, n° G1. doi: 10.1029/2009JG001079

This publication URL: <https://archive-ouverte.unige.ch/unige:40695>

Publication DOI: [10.1029/2009JG001079](https://doi.org/10.1029/2009JG001079)

# Methane emissions from a freshwater marsh in response to experimentally simulated global warming and nitrogen enrichment

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Received 12 June 2009; revised 13 September 2009; accepted 1 October 2009; published 9 February 2010.

[1] We determined methane (CH<sub>4</sub>) emissions in a field enclosure experiment in a littoral freshwater marsh under the influence of experimentally simulated warming and enhanced nitrogen deposition. Methane emissions by ebullition from the marsh composed of *Phragmites australis* were measured with funnel traps deployed in a series of enclosures for two 3 week periods. Diffusive fluxes were estimated on the basis of measured CH<sub>4</sub> concentrations and application of Fick's law. Neither diffusive nor ebullitive fluxes of methane were significantly affected by warming or nitrate enrichment, possibly because variability both within and among replicate experimental enclosures was high. Average emission rates resulted primarily from ebullition (0.2–30.3 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>), which were 4 orders of magnitude higher than estimated diffusive fluxes and were of similar importance as the coarsely estimated advective methane transport through plants. Significant correlations between dissolved oxygen and dissolved methane and ebullition flux suggest that methane release from the sediment might feed back positively on methane production by reducing dissolved oxygen in the water column and oxygen flux into the sediment. Nitrate may have a similar effect. Extrapolation of our limited data indicates that total methane fluxes from vegetated littoral zones of temperate lakes may contribute 0.5%–7% of the global natural CH<sub>4</sub> emissions. These results emphasize the importance of freshwater marshes as sources of methane emissions to the atmosphere, even when they occupy only relatively small littoral areas. More detailed investigations are clearly needed to assess whether global warming and nitrogen deposition can have climate feedbacks by altering methane fluxes from these wetlands.

**Citation:** Flury, S., D. F. McGinnis, and M. O. Gessner (2010), Methane emissions from a freshwater marsh in response to experimentally simulated global warming and nitrogen enrichment, *J. Geophys. Res.*, 115, G01007, doi:10.1029/2009JG001079.

## 1. Introduction

[2] Natural wetlands cover only a relatively small area on a global scale (~6% of the land surface) [Thorsell *et al.*, 1997] but play a very important role for the global methane (CH<sub>4</sub>) flux to the atmosphere, contributing an estimated 88% of all natural CH<sub>4</sub> emissions [Intergovernmental Panel on Climate Change (IPCC), 2007]. Despite its low concentration in the atmosphere (1.77 ppm), CH<sub>4</sub> is a potent greenhouse gas since its climate forcing potential over a 100 year time span is ~23 times higher on a mass basis than

that of carbon dioxide (CO<sub>2</sub>) [IPCC, 2007]. The atmospheric concentration of CH<sub>4</sub> has more than doubled over the past 250 years. This is due to increased anthropogenic activities such as agriculture (i.e., cattle farming and rice cultivation), wastewater treatment, expansion of landfills, and operation of hydroelectric power plants involving hypolimnetic water release from reservoirs [IPCC, 2007; Joos and Spahni, 2008].

[3] Global warming and sustained atmospheric nitrogen (N) deposition may alter flux rates of CH<sub>4</sub> from wetlands to the atmosphere (Figure 1), thereby further exacerbating climate change [Brix *et al.*, 2001]. Increasing air temperatures are accompanied by warming of surface waters [IPCC, 2007; Livingstone and Lotter, 1998], which enhances metabolic processes [e.g., Davidson and Janssens, 2006; Van Meeteren *et al.*, 2007] and oxygen consumption in aquatic ecosystems. Decreased dissolved oxygen (DO) reduces oxygen diffusion into sediments, stimulating anaerobic processes such as methanogenesis and further increasing CH<sub>4</sub> emissions. In addition, warming may enhance methanogenesis both directly and indirectly through possible effects on organic matter supply by primary producers.

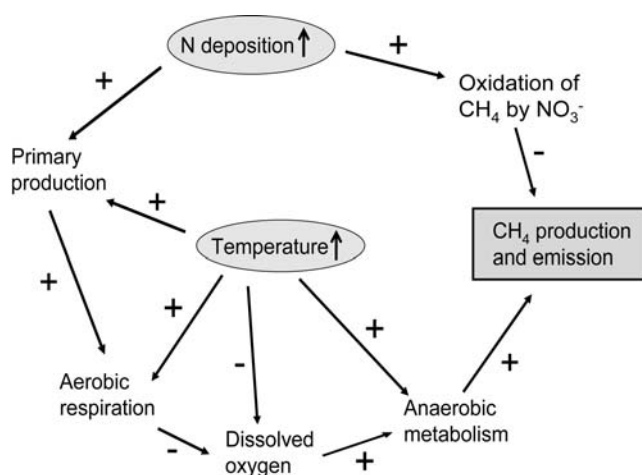
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**Figure 1.** Schematic showing various relationships between CH<sub>4</sub> dynamics and increased temperature and N deposition.

[4] Increased rates of atmospheric N deposition are another important component of global environmental change [Galloway *et al.*, 2008]. Because of industrial production of fertilizer and fertilizer application for growing crops [Galloway *et al.*, 2008], global atmospheric nitrate (NO<sub>3</sub><sup>-</sup>) deposition (wet and dry) has about doubled from pre-industrial time ( $7.38 \times 10^9$  kg yr<sup>-1</sup>) to the present ( $14.8 \times 10^9$  kg yr<sup>-1</sup>) and is predicted to increase to about  $19\text{--}25 \times 10^9$  kg yr<sup>-1</sup> by 2100 [Luo *et al.*, 2007]. Regional variation is large. Deposition of NO<sub>3</sub><sup>-</sup> at so-called hot spots in northwestern and central Europe and in northeastern North America ranges from  $\sim 12.0$  to  $15.7$  kg ha<sup>-1</sup> yr<sup>-1</sup>, compared to background values of  $0.16\text{--}1.6$  kg NO<sub>3</sub><sup>-</sup> ha<sup>-1</sup> yr<sup>-1</sup> [Luo *et al.*, 2007]. Like warming, increased nitrogen availability can stimulate methanogenesis and CH<sub>4</sub> emissions through increased supply rates of organic matter as a result of enhanced primary production (Figure 1) [Santruckova *et al.*, 2001]. However, laboratory experiments indicate that increased rates of N deposition may also reduce CH<sub>4</sub> emissions from sediments by amplifying the oxidation of CH<sub>4</sub> by NO<sub>3</sub><sup>-</sup> under anaerobic conditions [Islas-Lima *et al.*, 2004; Raghoebarsing *et al.*, 2006]. Therefore, the net effect of increased N deposition is not easily predicted.

[5] Freshwater wetlands dominated by emergent vegetation (i.e., freshwater marshes) are generally highly productive [Mitsch and Gosselink, 2007], and most of the produced biomass ultimately enters the pool of dead organic matter. High organic matter inputs, coupled with periodic or permanent flooding, strongly favor anaerobic microbial metabolism in the sediments of wetlands, with methanogenesis being the dominant process in fresh waters [Whiticar *et al.*, 1986]. There are three pathways by which CH<sub>4</sub> produced in wetland sediments is released into the atmosphere: (1) vertical diffusion into the water column and subsequently into the atmosphere, (2) ebullition (bubbling) from sediments, and (3) advective transport through aquatic vascular plants [Bastviken *et al.*, 2004; Brix *et al.*, 1996]. The relative importance of these pathways to CH<sub>4</sub> emissions depends on the presence of rooted plants, especially emergent macrophytes [Cheng *et al.*, 2007; Grünfeld and Brix, 1999; Juutinen *et al.*, 2003], and physical properties of the system

such as temperature, depth, and current patterns [Bastviken *et al.*, 2004; Joyce and Jewell, 2003; McGinnis *et al.*, 2006].

[6] In the present study, we assessed the response of two of the three CH<sub>4</sub> emission pathways, diffusion and ebullition, to experimentally simulated global warming and periodic enrichment with NO<sub>3</sub><sup>-</sup> in a freshwater wetland. We achieved this by determining CH<sub>4</sub> flux rates from enclosures placed within a littoral marsh composed of common reed (*Phragmites australis*). Enclosures were subjected to experimental warming and/or NO<sub>3</sub><sup>-</sup> enrichment, and CH<sub>4</sub> emissions from these enclosures were compared to those from both unmanipulated control enclosures and unenclosed control plots. We hypothesized that warming increases CH<sub>4</sub> emission as a result of stimulated methanogenesis in sediments. Additionally, our setup allowed us to test whether NO<sub>3</sub><sup>-</sup> enrichment has net negative or positive effects of CH<sub>4</sub> emission rates and whether any interactive effects occur between warming and NO<sub>3</sub><sup>-</sup> enrichment.

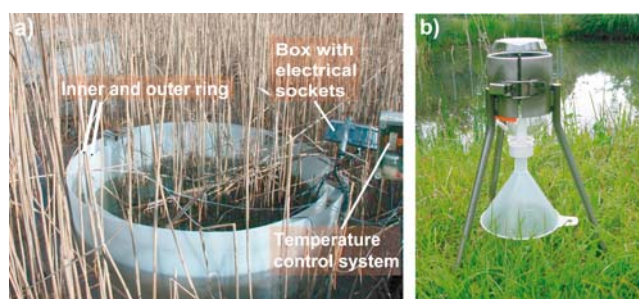
## 2. Methods

### 2.1. Study Site

[7] The experiment was conducted in a series of enclosures placed in a littoral marsh on the eastern shore of Lake Hallwil, Switzerland (46°54'N, 6°54'E). The lake is located on the Swiss Plateau at 449 m above sea level. Lake Hallwil is a eutrophic, postglacial moraine lake with a surface area of 10.2 km<sup>2</sup>, a volume of 0.292 km<sup>3</sup>, and a maximum depth of 48 m. The average depth is 28.6 m. A band of emergent wetland plants up to 20 m wide extends along parts of the shoreline. The dense, macroscopically homogenous vegetation is composed of common reed (*P. australis* (Cav.) Trin. ex Steud.), with a few isolated patches of common club-rush or bulrush (*Schoenoplectus lacustris* (L.) Palla) at the lake-ward edge. The density of live shoots in summer was determined to be  $34 \pm 23$  per m<sup>2</sup> (mean plus or minus standard deviation) [Buesing, 2002]. As the water table is regulated by a weir at the lake outlet, it normally fluctuates by  $<0.4$  m on an annual basis. As a result, the marsh remains submerged throughout the year. Wave action is significantly dampened within the reed stand, and wind speed, measured continuously 50 cm above the water surface with two Vortex pole mount anemometers with D2 rotors (Inspeed, Sudbury, Massachusetts, United States) that were connected to Pulse data loggers (MadgeTech, Inc., Contoocook, New Hampshire, United States), was always below the detection limit ( $1.3$  m s<sup>-1</sup>). The spatial extent of the littoral marsh derived from orthoimages (25 cm resolution, scale 1:5000, Geographic Information System of the Canton of Aargau, Aarau, Switzerland) using ArcMap 9.2 (Environmental Systems Research Institute Geoinformatik GmbH, Kranzberg, Germany) was 0.114 km<sup>2</sup>, corresponding to 1.1% of the total lake area. Information on water chemistry and other characteristics of the marsh is given by Buesing and Gessner [2006].

### 2.2. Experimental Design

[8] The experiment was performed using enclosures constructed with polypropylene rings 1.42 m in diameter and 1.2 m in height and pushed 20–30 cm into the sediment (Figure 2a). We installed 16 of these enclosures in spring 2004 in the center of the marsh, taking care not to damage

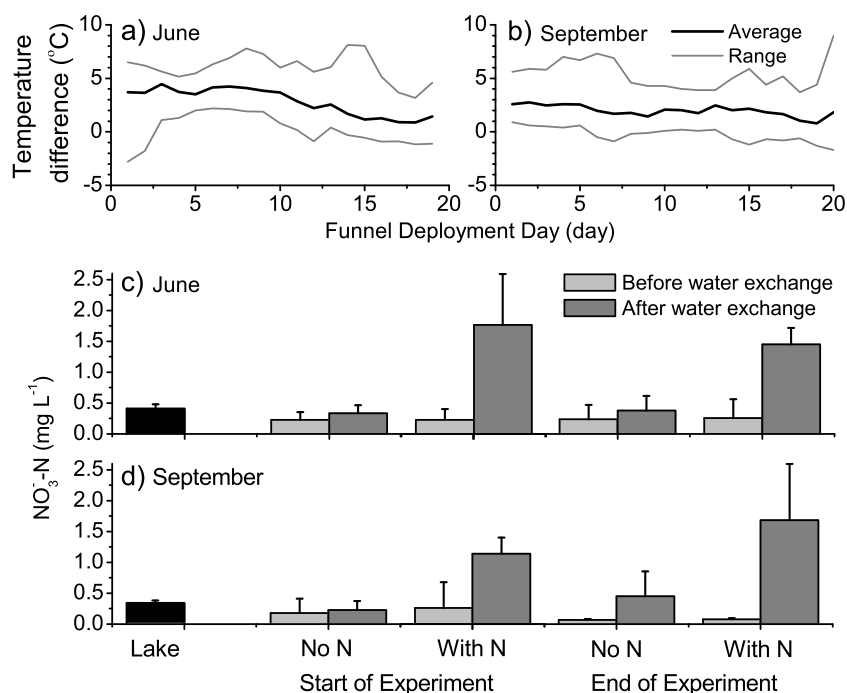


**Figure 2.** Photographs of (a) an enclosure in the littoral marsh studied in Lake Hallwil, Switzerland, and (b) a custom-made funnel trap used to estimate ebullition fluxes of  $\text{CH}_4$ . The purpose of the space between the outer and inner rings of the enclosures was to improve insulation.

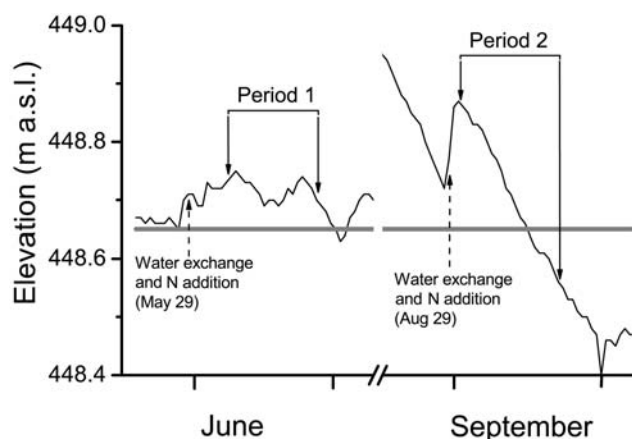
the vegetation. All enclosures were densely covered by *P. australis*. Our experimental design consisted of four blocks, each comprising four enclosures plus one unfenced control plot of equal size within the marsh. Enclosures were arranged in a row parallel to the shoreline at about 6 m distance from the shore. Measurements in spring and summer 2008 showed that no significant differences in shoot densities or heights existed either among blocks or among enclosures within blocks (M. O. Gessner and S. Grob, unpublished data, 2008). Two enclosures in each block were heated in an attempt to raise water temperature to  $4^\circ\text{C}$  above ambient lake temperature. This treatment will be referred to as H. Two control enclosures per block were kept at ambient lake temperature (0). In addition, there was one unfenced control plot per block referred to as L. Comparison of

the unheated and unenriched control enclosures with the unfenced control plots was intended to detect any possible enclosure artifacts. Calcium nitrate was added monthly to one each of the H and 0 enclosures. These enclosures are referred to as HN and 0N.

[9] Enclosures were heated with three to four outdoor aquarium heaters (300 W, JBL, Neuhofen, Germany). Aquarium pumps (EHEIM Universal Hobby Centrifugal Pump,  $300 \text{ L h}^{-1}$ , EHEIM GmbH & Co. KG, Deizisau, Germany) were connected to the heaters to achieve an even temperature distribution and to maintain a weak but constant water circulation, preventing strong chemical gradients within the water column. Microprocessor-based regulators (type FCR-13A, ROTH+CO.AG, Oberuzwil, Switzerland) controlled water temperature in individual enclosures. Temperatures were recorded every 30 min with submersible temperature loggers (Vemco Minilog 8-bit, VEMCO Division, AMIRIX Systems, Inc., Halifax, Nova Scotia, Canada; or StowAway TidbiT TBI32 loggers, Onset, Bourne, Massachusetts, United States) deployed on the sediment surface of all enclosures and the unfenced control plots. The average temperature difference between heated and corresponding unheated enclosures was  $2.9^\circ\text{C}$  in June and  $2.8^\circ\text{C}$  in September (Figures 3a and 3b). Pairs of enclosures occasionally showed either higher or lower differences at some point during measurements, sometimes by more than  $4^\circ\text{C}$ , but water temperatures in all but two of the heated enclosures were higher than in the corresponding unheated enclosures. In the two cases where warming during deployment of the traps failed, methane and other data were not used for subsequent analyses.



**Figure 3.** Average, minimum, and maximum temperature differences between heated and corresponding unheated enclosures in (a) June and (b) September 2007 and nitrate concentrations (mean plus or minus standard error) in enclosures before and after water exchange and nitrate addition during the two experimental periods in (c) June and (d) September 2007. With N indicates  $\text{NO}_3^-$  enriched enclosures, and No N indicates unenriched enclosures.



**Figure 4.** Water level of Lake Hallwil in June and September 2007 and schedule for measuring  $\text{CH}_4$  ebullition and  $\text{CH}_4$  concentration in the marsh water column. Funnel traps were installed on 6 June and 31 August in blocks 1 and 2 and 1 week later in blocks 3 and 4.

[10] Water within the enclosures was partly exchanged every fourth week to minimize enclosure artifacts. Water was exchanged for 20 min with two identical Marina pumps (KS 801/P,  $60 \text{ L min}^{-1}$ ) that simultaneously pumped water into and out of the enclosures. This ensured constant water levels in the enclosures during water exchange. Depending on the water level,  $\frac{1}{3}$  to  $\frac{1}{2}$  of the total enclosure water volume was exchanged. After each water exchange, nitrogen was added as  $\text{Ca}(\text{NO}_3)_2 \times 4 \text{ H}_2\text{O}$  dissolved in a small volume of deionized  $\text{H}_2\text{O}$ . The target concentration was 5 times the ambient  $\text{NO}_3^-$  concentration, resulting in a total added load of  $8.47 \text{ g N m}^{-2} \text{ yr}^{-1}$ . Amounts of nitrate to be added each month were estimated on the basis of lake water  $\text{NO}_3^-$  concentrations measured in previous years (average from 1997 to 2001).

[11]  $\text{NO}_3^-$  concentrations were routinely measured from water samples taken immediately before and after water exchange and  $\text{NO}_3^-$  additions. The samples were returned to the laboratory in a cooler and were immediately filtered through cellulose acetate filters ( $0.45 \mu\text{m}$ , Sartorius AG, Göttingen, Germany), and  $\text{NO}_3^-$  concentrations were determined spectrophotometrically (10 cm quartz cuvette, Hitachi U-2000 spectrophotometer, Portmann Instruments AG, Biel-Benken, Switzerland) with the nitrosalicylate method. Background nitrate concentrations averaged  $210\text{--}750 \mu\text{g L}^{-1}$  in unenriched enclosures and unfenced control plots and showed no significant difference between these two treatments at any time (Figures 3c and 3d). Monthly nitrate enrichment resulted in a threefold to eightfold increase in nitrate concentrations above ambient concentrations, similar to the targeted fivefold increase. However, the elevated concentrations in enriched enclosures dropped to almost background levels within a month or faster. Tracer experiments with fluorescein diacetate indicated that these declines in nitrate concentration were not due to dilution caused by hydrological exchange between enclosures and the marsh (A. Hammrich, personal communications, 2007). In September, DO concentration in the enclosures and unfenced control plots was measured in the field with a handheld Hq d40 oxygen probe (Hach Lange AG, Hegnau,

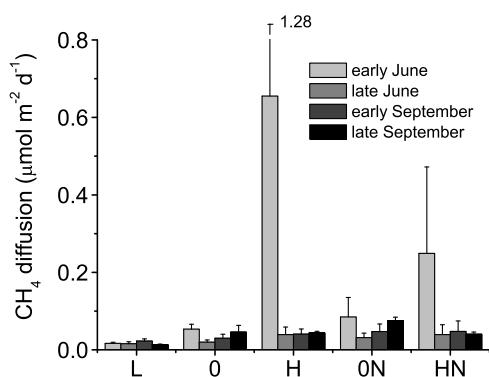
Switzerland) at the time when water samples were taken for dissolved  $\text{CH}_4$  analysis (see section 2.3).

### 2.3. Methane Emissions

[12]  $\text{CH}_4$  bubbles were captured with custom-designed funnel traps (Figure 2b). A polypropylene funnel (diameter, 12 cm) was connected directly with the funnel throat, which was pushed through a hole in the lid of a 500 mL polyethylene terephthalate (PET) bottle. The funnel trap was mounted on a tripod (wide end of the funnel facing the sediment) made of stainless steel. Three to four of these units were gently placed in each enclosure and unfenced control plot such that the lower rim of the funnel was 7 cm above the sediment surface. Similar designs of funnel traps have been used by Huttunen *et al.* [2001] and Casper *et al.* [2000], among others. Before each experiment the traps were completely filled with lake water. During installation of the traps, care was taken to preclude ebullition events and to prevent gas bubbles from entering the funnels. In June 2007, funnel traps were placed in enclosures 8 days after water exchange and  $\text{NO}_3^-$  additions (Figure 4). They were left in place to collect bubbles for 19 days. All funnel traps were then removed. In September, they were deployed again, this time 3 days after water exchange and  $\text{NO}_3^-$  addition, and were left in place for 20 days. Funnel traps were retrieved shortly before the next scheduled water exchange. For logistical reasons, blocks 1 and 2 were maintained (water exchange,  $\text{NO}_3^-$  addition) and sampled on 1 day, and blocks 3 and 4 were maintained exactly 1 week later.

[13] To collect gas samples, sample bottles were carefully unscrewed from the funnels and closed underwater with a screw lid lined with a silicon septum (Duran GmbH, Mainz, Germany). Care was taken not to trigger ebullition events during sampling. The bottle was retrieved, and a gas sample was drawn from the headspace with a gas-tight glass syringe (Poulten & Graf GmbH, Wertheim, Germany) connected to a two-way valve (miniature polytetrafluoroethylene body two-way valve, Sigma-Aldrich, Schnelldorf, Germany) with a Luer-Lok. The gas sample was then transferred to a PEWA-injection solution bottle (VWR International AG, Dietikon, Switzerland) filled with nitrogen gas ( $\text{N}_2$  5.0, PanGas, Dagmersellen, Switzerland). The total gas volume in the funnel trap was determined to the nearest 0.1 mL by weighing the remaining water and assuming a water density of  $1 \text{ g cm}^{-3}$ . The  $\text{CH}_4$  samples were returned to the laboratory and stored for up to 3 weeks at  $4^\circ\text{C}$  until analyzed by gas chromatography.

[14] Concentrations of  $\text{CH}_4$  dissolved in the enclosures and the open marsh water were measured on four occasions, i.e., each time when funnels for estimating ebullition fluxes were either deployed or retrieved (Figure 4). Water samples were taken with PEWA-injection solution bottles 15 cm below the water surface. Five to six pellets of potassium hydroxide were added to stop biological activity. The bottles were closed with butyl elastomer stoppers (Maagtechnik, Dübendorf, Switzerland), ensuring that no air bubbles were trapped in the sampling bottle. The samples were returned to the laboratory and were stored at  $4^\circ\text{C}$  until  $\text{CH}_4$  concentrations were analyzed by gas chromatography.  $\text{CH}_4$  concentrations in air were determined by flushing PEWA-injection solution bottles five times with a 50 mL plastic syringe filled



**Figure 5.** Diffusive fluxes from enclosures and unfenced control plots at four occasions between early June and late September 2007. L is unfenced control, 0 is ambient temperature, H is heated, ON is ambient temperature plus  $\text{NO}_3^-$  addition, and HN is heated plus  $\text{NO}_3^-$  addition. Error bars are standard errors ( $n = 3-4$ ).

with air taken just above the water surface within the reed stand.  $\text{CH}_4$  was then quantified by gas chromatography.

[15] Water samples for  $\text{CH}_4$  analyses were prepared by creating a 25 mL headspace in the sample bottles with  $\text{N}_2$ . The bottles were treated in an ultrasonic bath for 15 min to equilibrate gas concentrations between the headspace and water before withdrawing a gas sample from the headspace for  $\text{CH}_4$  quantification on an Agilent 6890N gas chromatograph (Agilent Technologies, Inc., Santa Clara, California, United States). The chromatograph was equipped with a JASValve autosampler (500  $\mu\text{L}$  sample loop, Joint Analytical Systems Benelux BV, Eindhoven, Netherlands), a Carboxen-1010 PLOT column (length, 30 m; inner diameter, 0.53 mm; Supelco, Bellefonte, Pennsylvania, United States), and a flame ionization detector. To analyze  $\text{CH}_4$  stripped from the water samples, temperature was kept constant at  $40^\circ\text{C}$  for 5 min and then was raised to  $120^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . For gas samples from the funnel traps and the atmospheric samples, the temperature was kept constant at  $100^\circ\text{C}$  for 4 min and then was raised to  $130^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . Hydrogen gas ( $\text{H}_2$  5.0, PanGas, Dagmersellen, Switzerland) was used as carrier gas at a flow rate of  $9 \text{ mL min}^{-1}$ . The  $\text{CH}_4$  retention time was 7.5 min for the method used for water samples and 4.4 min for the method used for gas samples from the funnel traps. The instrument was calibrated with standard  $\text{CH}_4$  at concentrations ranging from 100 to 10,100 ppm.

## 2.4. Data Analysis

[16] Ebullition gas flux ( $E$ ,  $\text{mmol m}^{-2} \text{ d}^{-1}$ ) was calculated as the amount of  $\text{CH}_4$  trapped in sample bottles divided by the funnel area and the time the gas traps were deployed in the field:

$$E = \frac{C_h + C_{w_t} - C_{w_0}}{tA}, \quad (1)$$

where  $C_{w_0}$  is the amount of dissolved  $\text{CH}_4$  in the bottle water at the beginning of the deployment,  $C_{w_t}$  is the amount of dissolved  $\text{CH}_4$  in the bottle water at the end of the deployment,  $C_h$  is the total amount of  $\text{CH}_4$  in the bottle headspace,  $t$  is the exposure time, and  $A$  is the funnel

surface area ( $0.0109 \text{ m}^2$ ). Changes in dissolved  $\text{CH}_4$  in the bottle water were accounted for in flux calculations because a fraction of the gas trapped may have redissolved during funnel deployment.

[17] Diffusive fluxes ( $F$ ,  $\text{nmol m}^{-2} \text{ s}^{-1}$ ) from the water to the atmosphere were estimated with Fick's law:

$$F = K_{\text{CH}_4, T}(C_w - \alpha C_a), \quad (2)$$

where  $K_{\text{CH}_4, T}$  [Engle and Melack, 2000] represents the piston velocity of  $\text{CH}_4$  in freshwater at temperature  $T$ ,  $C_w$  is the concentration of  $\text{CH}_4$  in water,  $C_a$  is the concentration of  $\text{CH}_4$  measured in air just above the water surface within the marsh, and  $\alpha$  is the Ostwald solubility for  $\text{CH}_4$  at temperature  $T$ . Calculation of piston velocity requires information on wind speed, which in the marsh was on average below detection limit during the entire experimental periods in June and September. Piston velocity was therefore calculated using the threshold value of our anemometer ( $1.3 \text{ m s}^{-1}$ ).

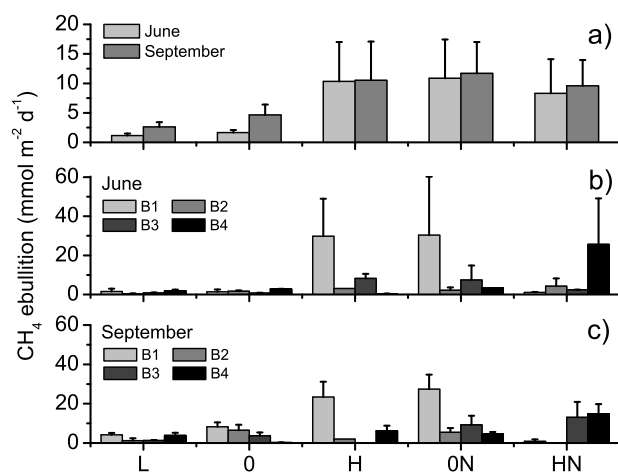
[18] To test for differences in methane emissions by ebullition and diffusion, repeated measures analysis of variance was used, with warming and N enrichment as factors and location (i.e., blocks 1 to 4) in the reed stand as a blocking factor. All analyses were performed with Systat 11 (Systat Software, Inc., Chicago, Illinois, United States). Samples from the unfenced control plots were separately compared with samples from the control enclosures to test for enclosure artifacts.

## 3. Results

### 3.1. Diffusive and Ebullition Fluxes of $\text{CH}_4$

[19] Diffusive fluxes calculated from dissolved  $\text{CH}_4$  concentrations in enclosures and unfenced control plots varied over nearly 3 orders of magnitude, with an overall range of  $0.004-2.6 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  (Figure 5). The highest values were recorded at the beginning of June, when emissions from heated enclosures were up to 10 times higher than those determined for other types of enclosures or subsequent sampling days ( $p < 0.05$ ). Concentrations were slightly, although not significantly ( $p = 0.08$ ), higher in control enclosures than in unfenced control plots, where flux rates were consistently the lowest. Variability was sometimes high among blocks for a given treatment, which reduced the statistical power to detect significant differences in diffusive  $\text{CH}_4$  emissions among warming and N enrichment treatments or among sampling days.

[20] Ebullition fluxes of  $\text{CH}_4$  to the atmosphere were found to be more than  $10^4$  times higher than diffusive fluxes, with  $0.2-30.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  of  $\text{CH}_4$  emitted from some of the enclosures (Figure 6). Average emissions from heated or N-enriched enclosures were 2–3 times higher than those from control enclosures. Virtually the same pattern and magnitude of ebullition fluxes were observed in June and September. However, because of large variability both within individual enclosures and among blocks for a given treatment, the differences apparent in Figure 6 were not significant. Estimated ebullition fluxes from the unfenced control plots were consistently the lowest, but, again, no significant difference was detected from fluxes deter-



**Figure 6.** (a) Ebullition fluxes of  $\text{CH}_4$  averaged across all four blocks and in individual enclosures in (b) June and (c) September 2007. L is unfenced control, 0 is ambient temperature, H is heated, ON is ambient temperature plus  $\text{NO}_3^-$  addition, and HN is heated plus  $\text{NO}_3^-$  addition. B1–B4 denote blocks 1–4, respectively. Error bars are standard errors ( $n = 2$ –4). No error bar means  $n = 1$  because of sample loss.

mined in control enclosures. However, variability among the control enclosures and especially among the unfenced control plots was notably lower than for the other enclosures.

[21] The  $\text{CH}_4$  content of gas samples collected from funnels in June ranged from about 3% to 70%, with about 80% of the samples containing between 10% and 40%  $\text{CH}_4$ . In September, the overall range of  $\text{CH}_4$  content in gas samples was similar, with about 80% of the samples having a  $\text{CH}_4$  content  $>30\%$ .

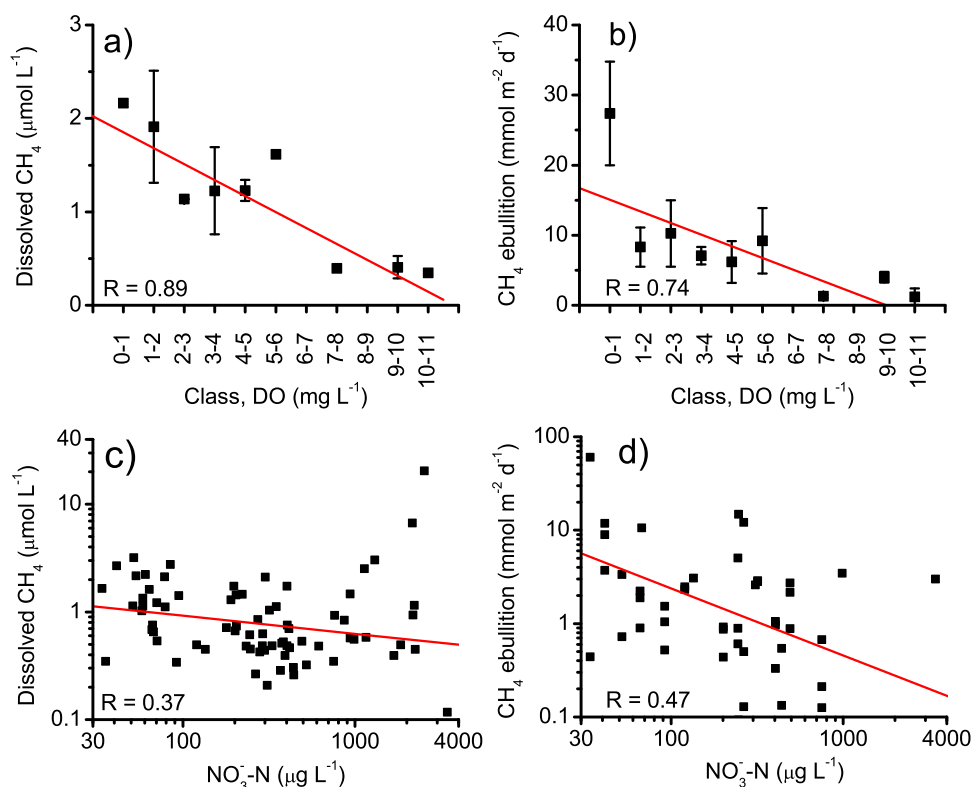
### 3.2. Relationships Between Methane, Oxygen, and Nitrate

[22] Negative correlations were found between water column DO (only data collected in September) and both dissolved  $\text{CH}_4$  (Figure 7a) and ebullition flux (Figure 7b). Furthermore, following log transformation of the variables, significant negative correlations were also found between concentrations of  $\text{NO}_3^-$  and dissolved  $\text{CH}_4$  (Figure 7c) and, in June, between  $\text{NO}_3^-$  concentration and ebullition flux (Figure 7d).

## 4. Discussion

### 4.1. Warming and Nitrogen Enrichment Effects

[23] Given clear evidence that rates of methanogenesis increase with temperature [e.g., Boon and Mitchell, 1995; Liikanen *et al.*, 2002b], we had expected significantly increased ebullition and diffusive fluxes of  $\text{CH}_4$  from our



**Figure 7.** Relationships between (a) dissolved  $\text{O}_2$  and  $\text{CH}_4$  concentration (class average plus or minus standard error,  $p < 0.01$ ), (b)  $\text{O}_2$  concentration and average ebullition flux (class average plus or minus standard error,  $p < 0.05$ ), (c)  $\text{NO}_3^-$  concentration and dissolved  $\text{CH}_4$  ( $p < 0.001$ ), and (d)  $\text{NO}_3^-$  concentration and average ebullition flux in June ( $p < 0.001$ ). Data in Figures 7a and 7b were combined in classes to smoothen patterns. Note logarithmic scales in Figures 7c and 7d.



heated enclosures. That no significant warming effect was detected is consistent, however, with results from an experiment with homogenized pond sediments incubated at 13°C and 20°C in the laboratory [Stadmark and Leonardson, 2007]. This lack of significant temperature effects in both studies could indicate that under some conditions methane production and subsequent emission are unresponsive to warming.

[24] A key to understanding this counterintuitive indifference to warming might lie in the very broad temperature optimum (16°C–27°C) observed for methanogens from lake sediments [Nozhevnikova *et al.*, 1997]. Water temperatures during our measurements in both June and September were indeed within the optimal range reported by Nozhevnikova *et al.* [1997]. However, whereas the profundal communities sampled in that study experience consistently low temperatures year-round (typically 4°C), methanogens in sediments of shallow temperate waters should have an evolved ability to respond to warming at elevated temperature as well. Therefore, alternative explanations may be more likely for our finding that CH<sub>4</sub> emission showed little sensitivity to warming. One possibility is that high variability both within individual enclosures and among replicate enclosures masked any warming effect. It could also be, however, that heat diffusion in the sediment was insufficient to stimulate methanogenesis or that factors other than temperature were limiting metabolic activity. For example, the carbon available in sediments may be too refractory for fermentative bacteria, which provide substrates for methanogens, to respond strongly to warming, thus indirectly limiting methanogenesis.

[25] Responses of CH<sub>4</sub> emissions to N enrichment are more difficult to interpret than responses to temperature changes because both stimulatory and inhibitory mechanisms could operate simultaneously. Lack of a significant response to N enrichment in our experiment could be due to an offset of positive and negative effects and/or insufficient statistical power because of high variability. Alternatively, it might be due to a true unresponsiveness of CH<sub>4</sub> emissions to NO<sub>3</sub><sup>-</sup> addition, as observed by Stadmark and Leonardson [2007] in laboratory experiments. An additional, quite likely reason for the lack of response to N enrichment in our study may be that the bulk of methanogenesis occurs in sediment layers inaccessible to the NO<sub>3</sub><sup>-</sup> supplied to the water column. The sediments of the studied marsh are fine grained, compact, and rich in organic matter, and they experience steep redox gradients at the surface [Buesing and Gessner, 2006]. Therefore, hydrological exchange of nitrate-rich surface water with surface pore water is likely slow, and any NO<sub>3</sub><sup>-</sup> penetrating the sediment would be quickly denitrified.

#### 4.2. Spatial Heterogeneity

[26] An intriguing finding of our study is the consistency of ebullition flux intensity within individual enclosures. In particular, average ebullition fluxes from the heated unenriched and the unheated enriched enclosures of block 1 were very high in both June and September (Figures 6b and 6c). If this is a general pattern, it may suggest that CH<sub>4</sub> ebullition was primarily controlled by spatially varying factors such as the physical structure of sediments [Boudreau *et al.*, 2005], availability of carbon [e.g., Stadmark and Leonardson, 2007], or sediment redox potential [Kludze *et al.*, 1993]

rather than by temperature and/or NO<sub>3</sub><sup>-</sup> enrichment. Regardless of the underlying factors, the spatial coherence of CH<sub>4</sub> ebullition fluxes we observed within individual enclosures suggests the presence of CH<sub>4</sub> seeps or vents within the marsh, similar to observations of permafrost thaw lakes in Siberia [Walter *et al.*, 2006].

#### 4.3. Methane, Dissolved Oxygen, and Nitrate in the Water Column

[27] Although the correlations we found between DO and both dissolved CH<sub>4</sub> and ebullition (Figures 7a and 7b, respectively) are not especially strong, they suggest that methane dynamics in the water column to some extent influenced oxygen regimes and/or vice versa. For example, Liikanen *et al.* [2002a] found in a laboratory experiment that CH<sub>4</sub> release from sediment decreased after incubation of the sediment with oxic lake water. Oxidation of dissolved CH<sub>4</sub> occurs particularly through the activity of methanotrophic bacteria [Bastviken *et al.*, 2002, 2008; Sweet's *et al.*, 1991]. Accordingly, Moosavi and Crill [1998] calculated that methanotrophs oxidized 78% of the total CH<sub>4</sub> production in a tundra wetland (wet sedge community). An associated effect of dissolved CH<sub>4</sub> oxidation in the aerobic water column is oxygen consumption, which could result in reduced oxygen fluxes into the sediment and induce a positive feedback to methane production.

[28] Significant negative correlations between NO<sub>3</sub><sup>-</sup> concentration and CH<sub>4</sub> concentration and, in June, ebullition (Figures 7c and 7d, respectively) suggest that nitrate might play a role similar to that of DO in the dynamics of dissolved CH<sub>4</sub>. This interpretation is in accordance with results from a laboratory experiment showing that anoxic NO<sub>3</sub><sup>-</sup> enriched surface water negatively affected CH<sub>4</sub> release from sediment cores [Liikanen *et al.*, 2002a]. Boon and Mitchell [1995] also observed a negative influence of NO<sub>3</sub><sup>-</sup> on methanogenesis in laboratory experiments with natural sediment communities. These negative relationships may have been caused by oxidation of CH<sub>4</sub> in the water column coupled with denitrification when extra NO<sub>3</sub><sup>-</sup> is available and oxygen levels are low [Islas-Lima *et al.*, 2004; Raghoebarsing *et al.*, 2006]. Such coupling of denitrification with CH<sub>4</sub> oxidation may be quantitatively important in water bodies where DO tends to become depleted and NO<sub>3</sub><sup>-</sup> concentrations are in the mg L<sup>-1</sup> range.

#### 4.4. Relative Importance of CH<sub>4</sub> Emission Pathways

[29] Estimated ebullition fluxes (0.2–30.3 mmol m<sup>-2</sup> d<sup>-1</sup>) were as much as 4 orders of magnitude higher than estimated diffusive fluxes (0.004–2.6 μmol m<sup>-2</sup> d<sup>-1</sup>), providing strong evidence, in spite of considerable spatial variability, that diffusive emission from our littoral marsh was negligible. However, ebullition is unlikely to be the only significant pathway of CH<sub>4</sub> emissions. Another potentially important process is advective transport through emergent marsh plants [Cheng *et al.*, 2007], which, even more than bubbles, circumvents passage of dissolved CH<sub>4</sub> through the water column where CH<sub>4</sub> is efficiently oxidized. While we did not directly measure CH<sub>4</sub> emission through plants, we estimated the average flux on the basis of the density of dead shoots in our marsh (mean plus or minus standard deviation of 34 ± 18 m<sup>-2</sup>) [Buesing, 2002], an average daily gas flow through efflux culms (i.e., mainly dead and broken culms) of



0.7 cm<sup>3</sup> culm<sup>-1</sup> min<sup>-1</sup> in another *P. australis* marsh at similar latitude during summer (only during 12 h of the day), and 8108 ppm CH<sub>4</sub> in the gas emitted from those culms [Brix *et al.*, 2001]. This resulted in an estimated advective CH<sub>4</sub> transport through plants of 5.5 mmol m<sup>-2</sup> d<sup>-1</sup> during summer. The magnitude of this approximation corroborates previous conclusions [e.g., Brix *et al.*, 2001] that advection through plants needs to be considered as an additional major pathway of CH<sub>4</sub> emissions from marshes. However, since both flux rates and gas composition can vary widely over space and time, this estimate is associated with important uncertainties [e.g., Kankaala *et al.*, 2003; Brix *et al.*, 2001].

[30] Extrapolated to a year, our data lead to a best estimate of total CH<sub>4</sub> emissions of 2.3 mol or 28 g C m<sup>-2</sup> yr<sup>-1</sup>, where 0.03 mmol result from diffusion, 1.28 mol result from ebullition, and 1.03 mol result from advection through plants. This extrapolation is based on average flux rates and the conservative assumption that ebullition and advection through plants occur only during 6 months of the year. The resulting estimate lies within the range calculated by Cao *et al.* [1996] for temperate wetlands (1.3–7.5 mol CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>) and represents an appreciable fraction of the 600 g C yr<sup>-1</sup> produced on average by emergent plant shoots in our marsh [Buesing and Gessner, 2006]. Given a total submerged marsh area of 0.114 km<sup>2</sup>, extrapolation to the entire aquatic reed stand of Lake Hallwil yields a total CH<sub>4</sub> flux of 265 kmol or 4.2 t CH<sub>4</sub> yr<sup>-1</sup>.

[31] Sizable CH<sub>4</sub> emissions from small littoral strips of lakes covered by emergent aquatic plants may be a fairly common phenomenon. For example, Juutinen *et al.* [2003] found that vegetated littoral zones contributed between 66% and 77% to the total CH<sub>4</sub> emission from boreal shallow lakes (mean depth 1.8–6.2 m). In this light, our estimated annual total flux from a littoral *P. australis* marsh might be extrapolated even to the total vegetated area of lakes in the temperate zone. If 1%–15% of a lake area is covered by plants [Bastviken *et al.*, 2004] and the total lake area in the temperate zone is  $\sim 2.58 \times 10^6$  km<sup>2</sup> [Lehner and Döll, 2004], then 1–14 Mt of CH<sub>4</sub> per year would be emitted from temperate vegetated littoral zones alone. This is equivalent to 0.5%–7% of the total natural global CH<sub>4</sub> emission (average of 199 Mt yr<sup>-1</sup> [IPCC, 2007]) and points to vegetated littoral zones of temperate lakes as globally significant sources of CH<sub>4</sub> emissions.

[32] Clearly, much more detailed investigations than presented here are needed to assess reliably to what extent global environmental change may cause climate feedbacks by altering methane fluxes from these wetlands. Given high variability of CH<sub>4</sub> fluxes both in space and time, greater temporal and spatial resolution and extent of measurements (over scales ranging from hours and decimeters to decades and continents) are crucial to constrain the possible range of average flux rates. Models that relate fluxes to site characteristics (vegetation structure, sediment grain size, organic carbon content of sediments, bioavailability of organic carbon, sediment temperature profiles, redox potentials, penetration depth of NO<sub>3</sub><sup>-</sup> into the sediment, etc.) have been successfully used to integrate data over space and time [Cao *et al.*, 1996; Dinsmore *et al.*, 2009; Potter, 1997]. Coupling such models of both ebullition fluxes and advective fluxes through plants with long-term data from field

experiments such as the one presented here would be an important step forward toward a solid assessment of the magnitude of changes in CH<sub>4</sub> emissions from wetlands resulting from global environmental change.

[33] **Acknowledgments.** We are grateful to Sabina Käppeli, Torsten Diem, Arne Hammrich, and Wenjing Xu for field and laboratory assistance, to the Eawag workshop for constructing funnel traps, to the Canton of Aargau for permission to access the field site, to the Fisheries Sports Club Hallwilersee-Meisterschwanden for access to electricity, and to Kevin A. Kuehn, Helmut Bürgmann, the anonymous reviewers, and Diane McKnight for constructive comments on earlier versions of the manuscript. This project was funded by the Swiss National Science Foundation (grant 3100A0-108441).

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