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Diel variation in lacunal CH_4 and CO_2 concentration and $\delta^{13}C$ in *Phragmites australis*

JEFFREY P. CHANTON[1,*], TIMOTHY J. ARKEBAUER[2], HARMON S. HARDEN[1] and SHASHI B. VERMA[3]
*[1]Department of Oceanography, Florida State University, Tallahassee, FL 32306-4320, USA; [2]Department of Agronomy, University of Nebraska, Lincoln, NE 68583-0817, USA; [3]School of Natural Resource Sciences, Center for Laser-Analytical Studies of Trace Gas Dynamics, University of Nebraska, Lincoln, NE 68583-0728, USA; *Author for correspondence (e-mail: jchanton@mailer.fsu.edu; phone: (850) 644-7493; fax: (850) 644-2581)*

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Abstract. We tested the hypothesis that the diurnal patterns of variation in lacunal gas concentrations and isotopic fractionation previously reported in a single plant genera (*Typha*) typified the patterns of all through-flow convective plants by extending our observations to *Phragmites australis* Cav. In daylight, *Phragmites* CH_4 transport is driven by internal pressurization which results in gas flow down young green culms and its exit from one year old dead brown culms. Flow rates of 10.4 ± 4.0 mL min^{-1} were measured in this study. At night, CH_4 is transported from the sediments to the atmosphere via the lacunal plant spaces by molecular diffusion. Within green culms, lacunal CH_4 concentrations varied by a factor of 1000, from 3% (parts by volume) pre-dawn to lows of 25 ppmv during midday. Methane in brown culms varied by a factor of 10 diurnally, from 5% pre-dawn to 0.3% at midday. Lacunal CO_2 concentrations varied similarly. Concentrations of both gases varied inversely with lacunal pressure. In green culms, large isotopic fractionations were observed in CH_4 and CO_2 in the morning and evening during transitions in gas transport mode and were associated with slight downward flows counter to the upward diffusion of these gases. Methane $\delta^{13}C$ as depleted as −100‰ was observed. In daylight, lacunal CH_4 was similar to or ^{13}C depleted relative to sedimentary and emitted CH_4 isotopic values, but at night lacunal CH_4 was ^{13}C enriched relative to sedimentary methane. Overall, the diurnal variations of CH_4 concentration and $\delta^{13}C$ value in *Phragmites* were similar to those observed in *Typha* and indicate that these patterns should be consistent in other convective-flow plants. Furthermore, our results demonstrate that the large isotopic fractionations found in aquatic plants can result solely from isotopic fractionation associated with gas transport.

Introduction

As wetlands and rice fields contribute about 40% of the global atmospheric burden of CH_4, a major portion of the biogenic CH_4 emitted to the atmosphere has passed through the lacunae of aquatic macrophytes. Plants serve as gas conduits, transporting 80–90% of CH_4 emitted from many wetlands through their aerchymous tissue (Schutz et al. 1991). The behavior of carbon gas concentrations and $\delta^{13}C$ in the lacunae is the subject of this paper.

Wetland macrophytes employ both active and passive modes of gas transport (Chanton and Whiting 1996). Passive transport is the sole gas transport mode found in plants such as *Carex rostrata* Stokes, *Oryza sativa* and *Peltandra virginica* L. and is molecular diffusion of gas molecules down a concentration gradient (Whiting and Chanton 1996). Active transport is the convective through-flow of gases from areas of high pressure to low pressure. The pressure gradient can be accomplished by either thermal transpiration (Dacey 1981a, 1981b; Grosse et al. 1991; Grosse 1996) or it can be induced from a humidity differential across the leaf boundary (Armstrong and Armstrong 1991; Armstrong et al. 1992; Brix et al. 1992, 1996; Armstrong et al. 1996a, 1996b). Gases enter areas of high pressure in the young green leaves and exit to the atmosphere through porous dead or senescent leaves (Dacey 1981a; Armstrong et al. 1992; Bendix et al. 1994).

Gas transport in *Typha latifolia* L., *Typha angustifolia* L., *Nymphaea odorata, Nuphar luteum* L., *Nelumbo nucifera* Gaertn., *Nymphoides pelata* Gmel. and *Phragmites australis* Cav. is dominated by convective through-flow transport in daylight (Armstrong and Armstrong 1991; Bendix et al. 1994; Brix et al. 1992, 1996; Dacey 1981a, 1981b; Grosse and Mevi-Schutz 1987; Mevi-Schutz and Grosse 1988; Tornbjerg et al. 1994). At night when these pressure gradients are absent, molecular diffusion is the primary transport mechanism (references above). However, small increases in CH_4 flux on windy nights have been contributed to Venturi-induced convection in *Phragmites australis* (Armstrong et al. 1992, 1996a; Brix et al. 1992; Kim et al. 1998a, 1998b).

It appears that the diurnal pattern of CH_4 emission from aquatic macrophytes is strongly influenced by the mode of gas transport. In aquatic plants having only diffusive transport only small variations in flux rate have been observed and attributed to changes in soil and water temperature (Whiting and Chanton 1996; Van Der Nat et al. 1998). But a dramatic increase in CH_4 emission rate during daylight has been observed in *Typha*, a convective transport plant (Chanton et al. 1993). In the *Phragmites* dominated Ballard's Marsh, the location of this study, diel variations in CH_4 emission varied by a factor of three, with a peak rate of 1000 $mg \cdot m^{-2} \cdot day^{-1}$ near midday and at night rates of approximately 300 $mg \cdot m^{-2} \cdot day^{-1}$ (Kim et al. 1998a, 1998b). Similar diurnal variations in emission have been observed in an artificial *Phragmites* system (Van Der Nat et al. 1998).

However, the CH_4 emission patterns for *Typha* and *Phragmites* are distinctly different. The *Typha* emission pattern is characterized by a sharp peak in mid morning and emissions are not closely correlated with PAR (Chanton et al. 1993; Whiting and Chanton 1996). In *Typha*, daylight switches on connective through-flow and elevated lacunal CH_4 is flushed, resulting in an emission peak. Following this peak, emission rate is similar to night time rates, suggesting that CH_4 flux is limited by gas transport across the root–shoot boundary as suggested by Kelker and Chanton (1997). The *Phragmites* daytime emission pattern is a more sustained peak which more closely follows PAR (Kim et al. 1998a, 1998b). In *Phragmites*, it appears that the more effective gas transport mechanism, through-flow convection, transports more CH_4 overall, whereas in *Typha*, the convection induced enhanced transport rate is more transitory.

In a comparison of two plant genera, *Typha* and *Peltandra*, lacunal CH_4 concentration was found to be affected by the gas transport mechanism (Whiting and Chanton 1996). In *Typha*, the lacunal concentrations were high in the pre-dawn and early morning hours and decreased rapidly at mid morning, staying low throughout the day. At night, CH_4 again accumulated in the culms. The rapid decrease in lacunal CH_4 concentrations in the morning is associated with the initiation of convective through-flow. Lacunal methane accumulates in the evening as convective transport becomes less active. In *Peltandra*, a passive transport plant, the lacunal concentration remained relatively constant over a 24 h period.

Lacunal CH_4 $\delta^{13}C$ patterns appear to vary with gas transport mode. In samples collected at midday, diffusive plants have lacunal CH_4 that is ^{13}C enriched relative to sedimentary CH_4 (Chanton and Whiting 1996). It has been hypothesized that this trend is due to the faster diffusion of the lighter isotope which is emitted from the plant more rapidly, leaving the residual lacunal CH_4 enriched in the heavier isotope. Experiments utilizing the injection of an ethane/propane mixture into plants were consistent with this hypothesis (Harden and Chanton 1994).

During active transport less isotopic fractionation is associated with bulk convective through-flow. During convective through-flow in Typha, lacunal CH_4 concentrations were observed to be low and similar in isotopic composition to sedimentary CH_4. At night, *Typha* exhibited a pattern similar to diffusive plants, with high lacunal CH_4 concentrations that were ^{13}C enriched relative to the sedimentary CH_4 (Chanton and Whiting 1996).

In this study, we will test the hypothesis that in active transport plants it is a general rule that lacunal gas concentration and $\delta^{13}C$ distribution vary diurnally. Our objective is to extend our *Typha* observations to *Phragmites*, a second plant known to exhibit convective flow. Observations in a single genera cannot be extrapolated to all other plants using convective flow; it is important to confirm that the conceptual model formed from observations of *Typha* holds in a second pressurized plant. Recently our paradigm that ^{13}C enrichment in plant lacunae should be attributed to gas transport processes has been questioned and attributed to plant associated methane oxidation (Tyler et al. 1997; Tyler and Bilek 2001; Bilek et al. 1999).

In *Phragmites* we expect to observe reductions in lacunal CH_4 and CO_2 concentration that are associated with the advent of convective through-flow in the morning and increases in lacunal CH_4 and CO_2 associated with cessation of flow at night when gas transport switches to molecular diffusion. We hypothesize that the isotopic patterns in *Phragmites* will appear similar to our results from *Typha* (Chanton and Whiting 1996). In daylight, we expect that lacunal CH_4 will appear similar to or ^{13}C depleted relative to sedimentary CH_4 isotopic values, but at night lacunal CH_4 will be ^{13}C enriched relative to sedimentary methane. Thus we hope to demonstrate clearly that variations in transport mechanism alone can cause significant isotopic fractionation of lacunal CH_4. Furthermore, we will examine gas flow in daylight in *Phragmites* through an ethane tracer experiment to aid in the interpretation of our results.

Methods

The field work for this study was conducted in June and July of 1996 at Ballard's Marsh in the Sandhills region of Nebraska, described in detail in Kim et al. (1998a, 1998b) and in Arkebauer et al. (2001). Ballard's marsh covers an area of ~2.5 km^2 and is typical of the many interdunal areas in the sandhills where the water table is near or above the ground surface. The marsh is dominated by 2–3 m tall *Phragmites australis*, which covers 70% of the surface. Water depth in the marsh is roughly 0.5 m. Plants are rooted in a 0.1 to 0.3 m layer of recent plant litter underlain by highly decomposed litter, organic materials and sand.

Briefly, CH_4 and CO_2 samples from within plant lacunae were collected with a syringe by inserting a needle within 5 cm below the water line on the plant. For each time point we collected 7 mL gas samples from 4 to 6 individual plants and we did not resample those sampled previously. Samples were transferred to evacuated vials sealed with butyl rubber stoppers and stored at 1–2 °C. Gas sampled by this technique has been shown to be representative of the actual lacunal gas pool (Chanton et al. 1992a). Calculations within this paper will show that the volume of a typical culm is roughly 13 mL, so while our samples may contain some methane from the rhizome or some outdoor air, they are primarily lacunal gas. Sedimentary gas was collected by stirring gas from the sediments and collecting it in evacuated vials sealed with butyl rubber stoppers. Bubble CH_4 has been shown to be representative of porewater CH_4 and sedimentary CH_4 in general (Chanton et al. 1992b). Methane emitted from plants was collected in light transparent chambers in daylight only. Methane and ethane concentrations were determined by flame ionization gas chromatography, and CO_2 concentrations were determined from the area of the peak on the GC-IRMS (Coupled gas chromatograph isotope ratio mass spectrometer, Finigan MAT, Delta S) chromatograms by comparing them to known standards. Chamber samples were run by cryogenic pre-concentration of CH_4 from air (Merritt and Hayes 1995) while lacunal CH_4 and sedimentary CH_4 were injected onto the GC directly. Samples of CH_4 were prepared for isotopic analysis by combusting CH_4 to CO_2 in a Finigan MAT combustion coupled to the GC-IRMS. Carbon dioxide was run similarly.

Stable isotope results are reported in the δ notation:

$$\delta^{13}C‰ = \left(\frac{R_{sample}}{R_{std}} - 1\right) \times 1000$$

where R_{sample} and R_{std} refer to the $^{13}C/^{12}C$ ratio of the sample and a known standard, Peedee Belemnite. Methane is depleted in ^{13}C, with values for biogenic CH_4 often ranging from −50 to −70‰ (Hoefs 1987).

Air flow speed and direction were determined by injecting ethane into green culms and by monitoring adjacent green and brown culms by withdrawing 1 mL samples at 1 min intervals. In a separate experiment to measure flow rate, green culms were cut just below the water line and interfaced with a short piece of plastic tubing to a mass flow meter from Omega Engineering (Stamford CT model FMA-5604).

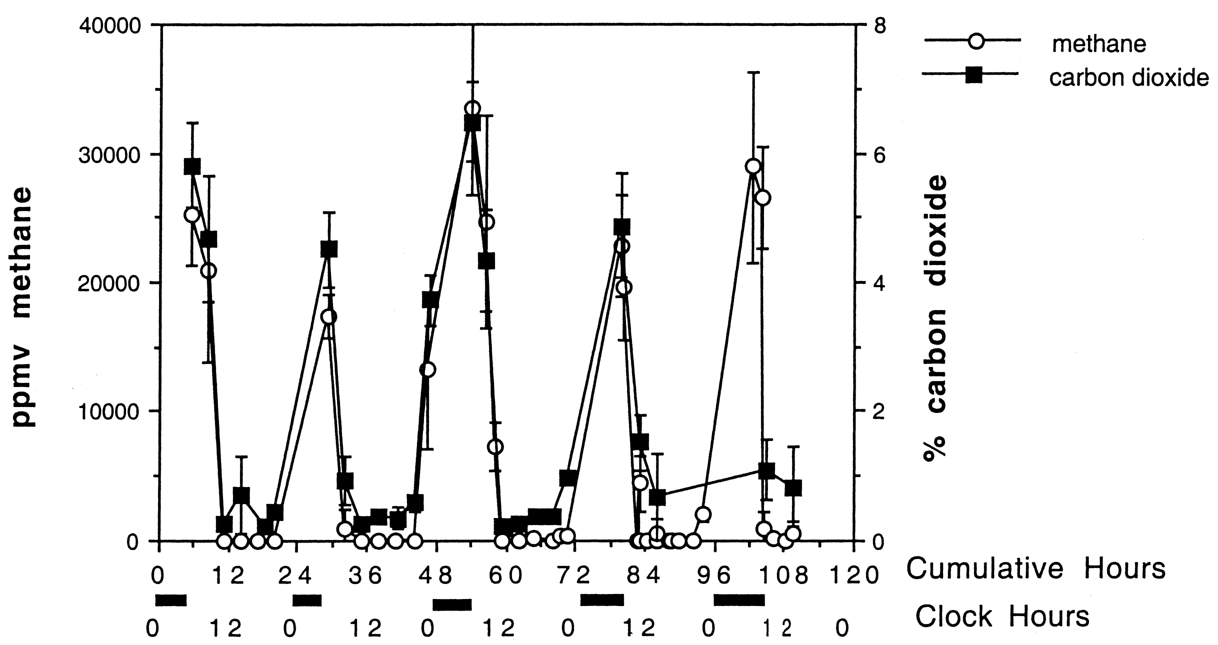
Culm pressure differentials between the inside of the culm and the ambient air were measured in the following manner. The culm was taped in two or three places to surrounding culms to hold it in an ambient-like position and then the culm was severed with a razor blade 3 to 5 cm above the water surface. The cut end was then connected to a pressure transducer (model CPFM, Furness Controls, Ltd., Bexhill, Sussex, UK) with a short length of plastic tubing. For further detail see Arkebauer et al. (2001).

Results and discussion

As hypothesized, lacunal CH_4 and CO_2 concentrations showed dramatic diurnal variation (Figures 1 and 2, Table 1). When pressurized (Arkebauer et al. 2001), brown culms contained greater concentrations of CH_4 and CO_2 relative to green culms at the 99% confidence interval (T-test). Significant differences in concentration were observed at the 99% confidence interval for pressurized versus diffusive transport in green culms for both gases. During diffusive transport lacunal gas concentrations were not different between the brown and green culms. Both CH_4 and CO_2 concentrations in green culms peaked just before dawn at 3% and 6% and had midday minima of approximately 25 ppm and 0.3%, respectively (Figure 1). Although the daily concentration minima were greater, CH_4 concentrations in brown culms exhibited a similar pattern, with a pre-dawn high of 5% and a full sun low of 0.3% (Figure 2). These changes in lacunal gas concentrations coincided with changes in lacunal pressure in green culms which increased from near 0 at pre-dawn to 1000 Pa during midday (Figure 3). When pressure was low, lacunal CH_4 concentrations were high and conversely when lacunal pressure was high lacunal CH_4 concentrations were low (Figure 3). The degree of pressurization was highly correlated with the incident PAR levels (Arkebauer et al. 2001).

Lacunal CH_4 concentration patterns in *Phragmites* were consistent with those observed in *Typha* (Chanton et al. 1993; Whiting and Chanton 1996). The concentrations in lacunae of both plants are higher at night. Under conditions of diffusive transport CH_4 accumulates until the elevated concentration gradient from lacunae to the atmosphere causes the flux out of the plant to match the flux from the rhizome to the lacunae. During the day, when the more efficient pressurized system is active, CH_4 is swept from the culms and concentrations remain low.

During full sun and associated lowered humidity, gas flows on the order of 10 mL/min were measured using a tracer and confirmed with a flow meter. Ethane injected into a green culm was observed exiting the adjoining brown culm within 2 min, and was exhausted 15–20 min after injection (Figure 4). A flow rate of 10 mL min^{-1} was calculated by estimating the volume of culm pathway and dividing by the time elapsed between the injection of ethane and its peak appearance in the brown culm. The pathway volume was estimated by measuring the culms lengths,



Green culm methane and carbon dioxide concentrations

Figure 1. Diel CH_4 (open circles) and CO_2 (closed squares) lacunal concentrations in green *Phragmites* culms. Higher concentrations were observed at night when molecular diffusion controlled gas transport occurs. Each time point represents a mean value of determinations from 4 to 6 individual culms. For every time point entirely new plants were sampled. Error bars represent the standard deviation of the mean. Dark bars represent night.

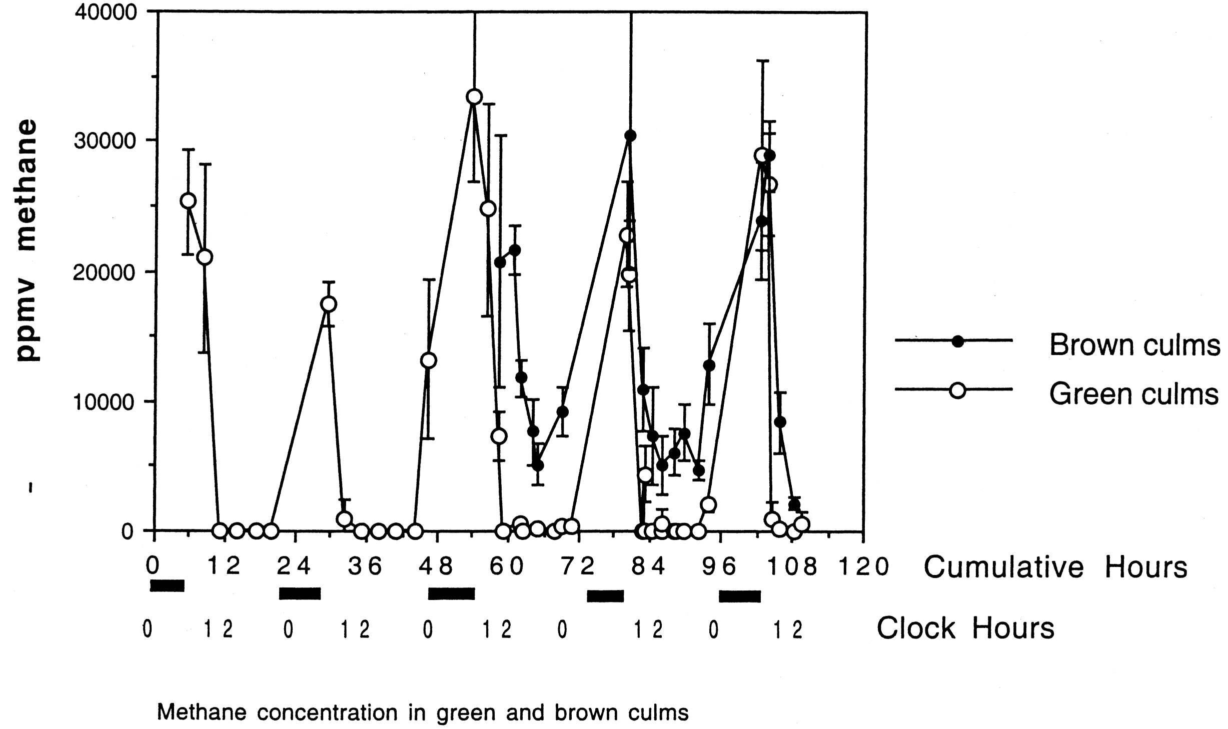


Figure 2. Comparison of diel lacunal CH_4 concentrations in brown (closed circle) and green (open circle) culms of *Phragmites australis*. With daylight, lowered humidity and the advent of pressurized through-flow convection, clean air is swept downward via green culms, flushing respiration products out of the brown culms. Prior to hour 60, samples were not collected from brown culms. Each time point represents a mean value of determinations from 4 to 6 individual culms. For every time point entirely new plants were sampled. Error bars represent the standard deviation of the mean. Dark bars represent night.

Table 1. Lacunal gas concentrations under conditions of pressurized and diffusive gas transport. Means reported in this table are averages of individual time point means, each of which consisted of four to six samples collected at each time point

Sample type	Mean, standard error, # time points
Methane, ppmv	
Pressurized green culms	52, 6, 21
Diffusive green culms	21844, 2212, 11
Pressurized brown culms	6336, 664, 10
Diffusive brown culms	20126, 2701, 8
Carbon dioxide, % by volume	
Pressurized green culms	0.53, 0.07, 17
Diffusive green culms	5.01, 0.04, 6
Pressurized brown culms	2.59, 0.63, 3
Diffusive brown culms	5.25, 0.88, 2

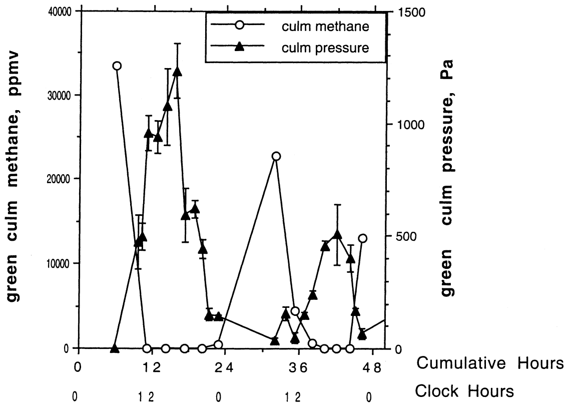


Figure 3. Lacunal CH_4 concentration (open circles) varied inversely with lacunal air pressure (closed triangles). When lacumae were pressurized, gas flows swept CH_4 from plant internal spaces. When pressures were low, diffusion was the dominant mechanism and CH_4 concentration was higher. Each time point represents a mean value of determinations from 4 to 6 individual culms. For every time point entirely new plants were sampled. Error bars represent the standard deviation of the mean. Uncertainty in methane concentration is reported in Figure 1.

and their inner diameter and using the equation: volume = $\pi h \cdot r^2$, where $r = 0.25$ cm and $h = 70$ cm. Node volume was neglected during this calculation so the volume is slightly overestimated. Ethane was only observed exiting from the brown culm that was paired with the injected green culm and not neighboring brown or green culms (data not shown). The ethane experiment demonstrates that air flows from the green culms down to the node where green and brown culm pairs meet and out the brown culm. Although the air pathways connect many culms, in this

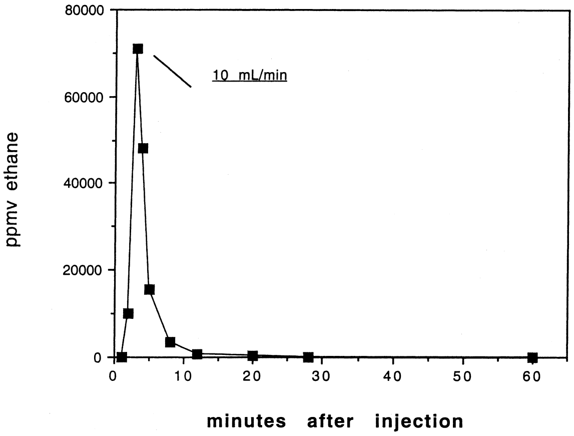


Figure 4. Ethane injected into a green culm was rapidly emitted from the paired brown culm. Ethane was not observed exiting neighboring brown culms, only the one paired with the injected green culm. A gas flow rate of 10 mL min^{-1} was calculated from the tracer transport rate and the plant length and volume. This rate compared very well with direct measurements of gas flow (see text).

case the air flow followed the path of least resistance and exited only from the nearest brown culm. This finding suggests a tight pairing of green and brown culms, in contrast to the depiction shown in Armstrong et al. (1996a, Figure 4).

The ethane experiment result compares well with direct measurements conducted with a flow meter which was interfaced to cut green culms with tygon tubing. The flow meter yielded rates of 10.4 ± 4.0 mL min^{-1} (n = 8 culms) during full sun. This result is similar to the rate of 4.8 ± 0.6 mL min^{-1} obtained by Brix et al. (1996).

The isotopic signature of green culm CH_4 changed dramatically with pressurization, going from a pre-dawn value of −55.9 ± 1.7‰ to values ranging from −81 to −100‰ at intermediate concentrations during the transition from diffusive to pressurized flow (Figures 5 and 6, Table 2). Similar extremely depleted lacunal isotopic values were observed in the evening during the cessation of gas flow as light levels fell and humidity rose. This transition can apparently last several hours (see Figure 5, between hours 84 and 96).

In brown culms, the CH_4 isotopic composition went from −53.6 ± 2.0‰ predawn to −62.6 ± 0.8‰ midday, similar to or ^{13}C depleted relative to the isotopic composition of sedimentary CH_4. Sedimentary CH_4 had an isotopic signature of −59.8 ± 1.7‰ similar to CH_4 emitted in daylight, −58.0 ± 1.6‰ (Table 2). In full sun, green culm lacunal CH_4 was about 25 ppm and had a δ^{13}C value of −61.8 ± 2.3. The isotopic composition of CO_2 behaved in a similar fashion to CH_4 (Bendix et al. 1994), exhibiting extremely depleted values during the transition from diffusive to pressurized flow and the reverse.

Except for the observations made during the transition in gas transport mode, the CH_4 stable isotope distribution pattern in *Phragmites* (Table 2) is similar to the diurnal pattern observed in *Typha* (Chanton and Whiting 1996). Daylight observa-

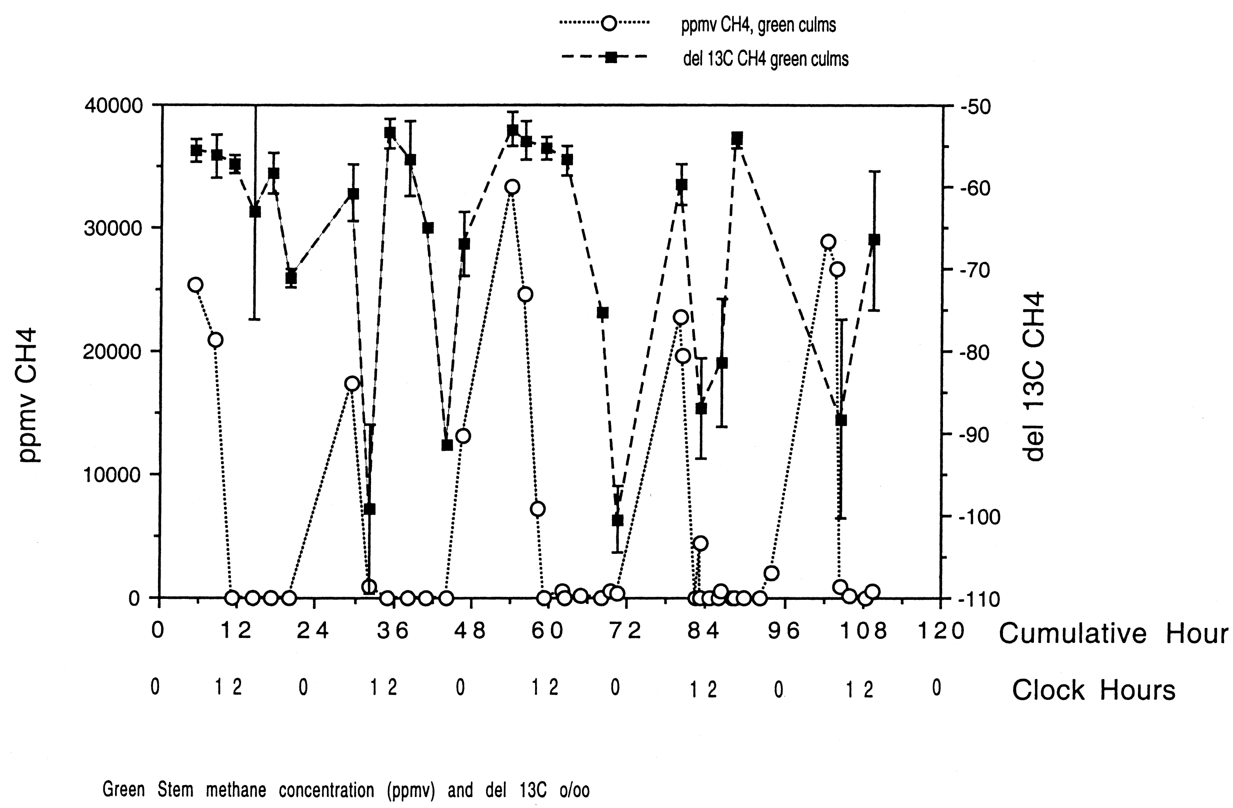
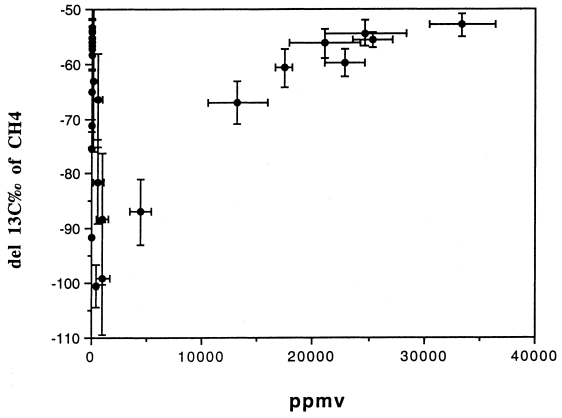
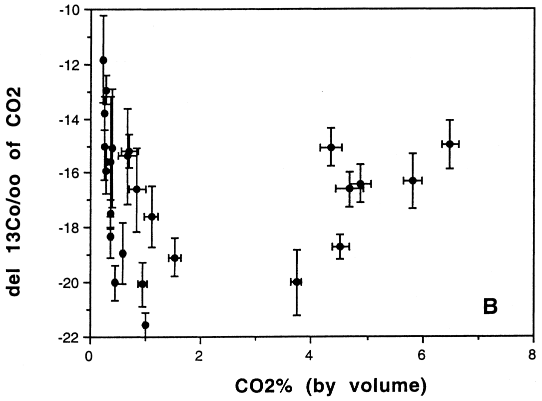


Figure 5. Green culm lacunal methane concentration (ppmv, open circles) and $\delta^{13}C‰$ (filled squares). Extremely depleted isotopic values were observed during times when methane concentration was changing most abruptly. Uncertainty in methane concentration is reported in Figure 1.



Culm gas-- del 13C of CH4 vs concentration



Culm gas-- del 13C of CO2 vs concentration

Figure 6. Isotopic composition of lacunal CH_4 (Panel A) and CO_2 (panel B) versus their concentration in green culms. At high concentrations gases were more ^{13}C enriched and were under the influence of molecular diffusion. With the advent of pressurization and convective downward flow in the green culms, CH_4 and CO_2 concentrations were reduced. During the transition to pressurized flow, CH_4 diffused upward against weakly flowing air, resulting in extreme isotopic fractionation. These fractionations occurred at concentrations intermediate between elevated ones found under diffusive flow and low ones found under convection.

tions are similar to additional convective plants, where values have only been obtained in daylight, to date (Table 3). In this overall data set, it may be stated that during the day when convective through-flow is active, both emitted and lacunal CH_4 are similar to or slightly depleted in isotopic composition relative to sedimentary CH_4. Molecular diffusion occurs concurrently with convective through-flow, accounting for the small degree of fractionation evident in the depleted culm lacu-

Table 2. Methane isotopic distribution patterns in *Phragmites australis* at Ballard's Marsh. The δ^{13}C of emitted and lacunal CH_4 is compared to the δ^{13}C of sedimentary CH_4. Lacunal CH_4 within culms is ^{13}C enriched relative to sedimentary CH_4 in darkness, but in the light the culm CH_4 is ^{13}C depleted or similar to sedimentary CH_4. Emitted CH_4 under sunlight was similar to sediment CH_4. No measurements were made of emitted methane at night

Methane sampled	δ^{13}C of CH_4 (‰)
Sediment CH_4	−59.8 ± 1.7
Emitted CH_4 under sunlight	−58.0 ± 1.6
CH_4 Brown culms, in darkness	−53.6 ± 2.0
CH_4 Green culms, in darkness	−55.9 ± 1.7
CH_4 Brown culms, in light	−62.6 ± 0.8
CH_4 Green culms, in light	−61.8 ± 2.3
CH_4 Green culms in transition	−81 to −100
From diffusive to pressurized flow	Concentrations 0.04 to 0.2%

nal CH_4 in daylight. Also, diffusion is the dominant transport process for gases from the sediment to the internal root gas spaces of the plants. At night, the convective through-flow is not active and *Phragmites* relies on molecular diffusion as the primary mode of gas transport. During this time, the CH_4 isotopic distribution pattern is similar to the pattern of diffusive transport plants. The culm lacunal CH_4 is ^{13}C enriched relative to sedimentary CH_4 (Tables 2 and 3).

In *Phragmites*, during the morning as humidity falls and the plants switch from diffusion to pressurized flow, and at evening during the reverse, lacunal CH_4 in the green culms became extremely depleted in ^{13}C relative to sedimentary CH_4 (Figures 5 and 6A). Laucunal CO_2 followed the same pattern (Figure 6B). As convective through-flow is activated, a flow of air develops from the green culms to the base and then out the brown culm. This downward air flow is counter to the upward diffusion of CH_4 and CO_2 from the rhizosphere through the green culm to the atmosphere, causing the extreme isotopic fractionation observed. At some point the downward flow of air becomes strong enough to flush this depleted CH_4 from the green culm. Similarly in the evening, flow becomes weaker and CH_4 and CO_2 diffuse upward against this weak flow, again resulting in large isotopic fractionations in green culms. Such large fractionations were not observed in brown culms, where air flows upward, in the same direction as diffusive transport. During the transition to convective flow or vice versa, weak downward air flow in green culms interacted with the upward diffusing CH_4 to cause a high degree of isotopic fractionation. Such large isotopic fractionations associated with the transition to pressurized flow have not been observed in other plants, primarily because until the advent of the GC-IRMS such detailed sampling was not possible.

We conclude that lacunal gas concentration and stable isotope distribution patterns vary diurnally in *Phragmites*. The patterns observed in *Phragmites* are consistent with the patterns observed in *Typha* and can now be extrapolated to other convective plants. Gas transport mode affects lacunal gas concentrations and stable isotopic distributions, resulting in clear differences between convective and diffu-

Table 3. Plant gas transport mode affects CH_4 isotopic distribution. All values reported were from samples collected in daylight. Sediment and lacunal values are generally means of three to four replicates except for *N. odorata*. Uncertainty given is the standard deviation of the mean. Emitted values are generally means of two measurements and estimates are half of the value's range

Plant	Sedimentary CH_4 $\delta^{13}C$ (‰)	Lacunal CH_4 $\delta^{13}C$ (‰)	Emitted CH_4 $\delta^{13}C$ (‰)
Convective through-flow transport			
Phragmites australis[a]	−59.8 ± 1.7	−62.6 ± 0.8	−58.0 ± 1.6
Nymphaea odorata[b]	−55.0	−55.4 ± 3.2	−59.9 ± 0.05
Typha domingenis [b]	−62.4 ± 0.3	−64.6 ± 2.2	−66.1 ± 1.2
Typha latifolia [b]	−61.6 ± 2.3	−61.7 ± 1.6	−60.6 ± 0.2
Diffusive transport			
Carex rostrata[c]	60.6 ± 1.9	−48.3 ± 1.4	−66.6 ± 2.5
Oryza sativa[d]	−60.2 ± 0.6	−53.4 ± 2.3	−65.5 ± 0.4
Peltandra virginica[e]	−57.1 ± 1.0	−51.4 ± 2.9	−65.0 ± 3.4
Pontederia cordata[f]	−52.9 ± 0.1	−44.4 ± 1.7	−56.1 ± 0.1
Sagittaria lancifolia[g]	−51.7 ± 0.3	−42.0 ± 0.2	−61.6 ± 0.3

[a] This study.
[b] Chanton and Whiting (1996).
[c] Chanton et al. (1992a).
[d] Chanton et al. (1997).
[e] Chanton et al. (1992b).
[f] Chanton and Dacey (1991).
[g] Gerard and Chanton (1993).

sive plants in daylight. At night they appear similar. The diurnal variations we have observed support our conclusion that isotopic fractionation of lacunal methane is caused by diffusion of gases through lacunal spaces towards the atmosphere. During convection this fractionation is reduced. However, during slow flow rates at the transition between convection and diffusion extreme fractionation results in green culms where flow direction is downward, counter to diffusion. Overall, our results indicate that significant isotopic fractionations may be induced from gas transport. Researchers may expect to find significant differences in the diurnal variation in methane emission between wetlands populated by active as opposed to passive transport plants. Isotopic fractionation varies between plant types, and these factors need to be considered when applying isotopic tracing for purposes such as calculating methane oxidation (Chanton et al. 1997).

Finally, some workers have attributed lacunal fractionation patterns to methane oxidation rather than to gas transport. In our opinion, these diurnal studies in convective plants demonstrate that lacunal fractionation should be attributed mainly to gas transport processes because at night the plants show ^{13}C enrichment in lacunal methane but in the day they do not.

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