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Cycling of Molecular Hydrogen in Subarctic Sweden

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ABSTRACT
Cycling of Molecular Hydrogen in Subarctic Sweden
by
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Over the past decade, significant atmospheric warming has caused organic-rich

permafrost to thaw thereby increasing the amount of soil carbon available for decomposition.

The release of greenhouse gases, such as methane (CH_4), is predicted to also increase, resulting

in a positive feedback cycle to our climate. Little is known however about the effect of

permafrost thaw on the release of molecular hydrogen (H_2) from wetland ecosystems. Vegetated

surfaces are thought to be sinks for atmospheric H_2. However, as permafrost soils thaw and

precipitation events become more frequent, resulting in an increase in inundated areas under

anoxic conditions, soils could quickly shift from a sink of atmospheric H_2 to a source.

This project focused on the effect of changes in soil moisture following precipitation

events on the consumption or release of H_2 in a subarctic mire in the discontinuous permafrost

region near Abisko, Sweden during July 2012. Different habitats were sampled using existing

soil gas profiling arrays, autochambers, and a sipper device. All sipper and soil gas profiling

array samples were analyzed with a reduced gas (HgO) detector for H_2 and a flame ionization

detector for CH_4. Methane data were collected at all sites and depths to better understand the

tight coupling between H_2 and CH_4. On July 14th and 15th, the site received record precipitation

(54.6 mm) for any 48 hour period. In a thawed *Carex*-dominated site, the concentration of H_2 in

porewater decreased substantially immediately after the precipitation and slightly more

throughout the following week indicating a significant dilution event. A similar effect was

observed in an *Eriophorum*-dominated site; however, the behavior of CH_4 at these two sites

differed in that CH_4 responded similarly to H_2 after the precipitation event at the *Carex* site, but

CH_4 increased following precipitation at the *Eriophorum* site. In contrast, depth profiles for both

soil gas sampling arrays in the intermediate permafrost *Sphagnum* site show a large increase in H_2 concentration one week after the storm, which may be explained by more rapid draining from the *Sphagnum* site or may correlate with a decrease in CH_4 at the site over this same time period.

1. Introduction:

Organic-rich permafrost in the Arctic and subarctic regions of the Northern Hemisphere is thawing as a result of significant warming over the past decade (IPCC, 2007; Callaghan *et al*., 2010). As these soils thaw, the pool of soil carbon available for decomposition is increasing, which may increase the release of methane (CH_4) and other greenhouse gases (GHGs). These GHGs increase atmospheric temperatures, so these soils contribute to a positive feedback cycle by thawing further. In addition, more intense precipitation events in the subarctic are causing soils to become wetter, increasing the frequency of anaerobic events (Callaghan *et al.*, 2010).

After CH_4, molecular hydrogen (H_2) is the second most abundant trace gas in the atmosphere with a globally averaged mixing ratio of approximately 530 parts per billion by volume (ppbv) (Novelli *et al.*, 1999). Molecular hydrogen is a significant element of tropospheric and stratospheric chemistry because of its abundance and its role as a secondary GHG in addition to providing insight into the trace gas cycles to which it is coupled, notably carbon monoxide (CO) (Ehhalt and Rohrer, 2009). However, it is currently unclear whether cycling of H_2 is impacted by the increased availability of carbon and frequency of anaerobic events due to the thawing of permafrost.

Soils are generally a sink for atmospheric H_2; however, thawing permafrost and wetter soil conditions may result in soils becoming a temporary source of H_2. Considering that soil uptake is currently the dominant H_2 sink process consuming/destroying up to 75% of global H_2, this could significantly alter the global distribution of H_2 (Ehhalt and Rohrer, 2009) and therefore our understanding of the cycling of other trace gas species in the atmosphere. The seasonal

minimum mixing ratio of H_2 is 70 ppb lower in the Northern Hemisphere than in the Southern Hemisphere because of the larger land mass present in the Northern Hemisphere (Novelli *et al.*, 1999). Wetter soil conditions increase the frequency of fermentation, the breakdown of organic matter under anaerobic conditions, which in turn increases production of H_2 (Eq. 1).

$$CH_2O + H_2O \rightarrow CO_2 + 2H_2 \text{ Eq. 1}$$
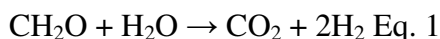
Although previous studies have failed to account for soil moisture or temperature, the highest H_2 uptake typically occurs in summer, when soils are warm and dry, suggesting that wetter soils will increase release of H_2 (Ehhalt and Rohrer, 2009).

The second most important sink of H_2 is reaction with the hydroxyl radical (OH) in the atmosphere (Eq. 2).

$$H_2 + OH \rightarrow H_2O + H \text{ Eq. 2}$$

As the concentration of H_2 increases, a resulting decrease in the average OH concentration could decrease the tropospheric oxidation capacity, a potential feedback to a warming climate. Understanding the H_2 cycling in different subarctic subhabitats can therefore provide information on the oxidizing capacity of the atmosphere and therefore residence time of GHGs (Novelli *et al.*, 1999).

This research focused on the effect of changes in soil moisture caused by precipitation events on the consumption or release of H_2 in permafrost ecosystems on Stordalen Mire in subarctic Sweden. Precipitation events can result in an increase in soil moisture causing temporary anoxia. This anoxia could switch these soils temporarily from a sink to a source of atmospheric H_2. As permafrost thaws and wetter soil conditions become more common, soils may become sources of H_2 more frequently, an unexpected feedback to climate change. The research question I addressed was:

Does an increase in soil moisture impact H_2 flux in permafrost thaw microhabitats?

By taking samples across multiple subhabitats and on different days surrounding a major rain event, it was possible to gain insight into the future behavior of soil hydrogen as the climate warms and permafrost thaws. The subhabitats considered represented different thaw regimes, allowing for a comparison between current soil H_2 levels and future levels with anticipated changes in vegetation and hydrology. Data on CH_4 and CO_2 were also considered to gain a more comprehensive understanding of H_2 cycling.

2. Site Description:

Stordalen Mire (68°22'N, 19°03'E) is located 12 km east of the Abisko Scientific Research Station (ANS) in subarctic Sweden. Within the past decade, subarctic Sweden has crossed the zero-degree temperature threshold (Callaghan *et al.,* 2010). The impacts of this transition on the landscape are visibly evident (Fig. 1), and significant changes have been observed in the ecosystem and its biogeochemistry that are expected to continue (Christensen *et al.,* 2004; Malmer *et al.,* 2005). Stordalen Mire is located in the region of the world most affected by climate warming (i.e. circumpolar regions), and there is a record of data spanning 100 years; consequently, it was an ideal site to perform research on the future behavior of soil H_2 (IPCC, 2007). Hydrogen in Stordalen mire had been studied as part of a Master's thesis in the summer of 2011, meaning that this work could be combined with that data to yield increased insight.

Fig. 1: Boardwalk on Stordalen Mire that is sinking due to thawing permafrost

Within the mire, the following four subhabitats were sampled (Fig. 2):

- Dry, permafrost dominated palsas covering 30% of the mire (Malmer *et al., 2005)*

- Mesic, intermediate, *Sphagnum* dominated permafrost sites covering 37% of the mire

- Wet, full summer-thaw, *Eriophorum* dominated sites covering 20% of the mire
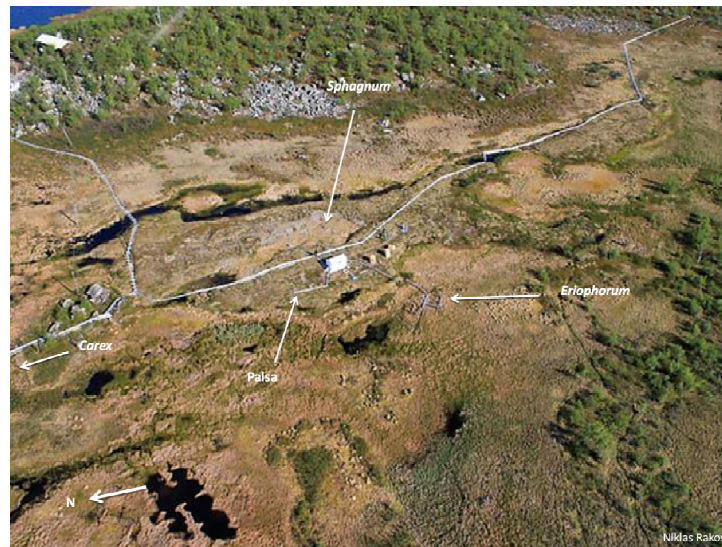
- Carex dominated sites covering about 2.6% of the mire

Fig. 2 Aerial view of Stordalen Mire showing all four subhabitats. Photo by Niklas Rakos

3. Methods:

3.1 Supply Preparation while at UNH:

Sixty ml and ten ml polypropylene syringes with polycarbonate stop cocks were used to collect gas samples in the field. The syringes were placed on the roof of Morse Hall prior to departure for Sweden for several days to expose them to sun because it is believed exposure of the polypropylene material to light can lead to hydrogen production. By exposing the syringes to ultraviolet light before storing samples in them, it was possible to minimize that potential bias.

Additionally, the syringes used for sipper sampling were labeled by subhabitat and depth to avoid the potential for cross-contamination between residue from a previous sample and the current sample. The syringes used for soil gas array measurements were labeled for high and low concentrations. Low concentration syringes were used for ambient samples, all samples from the Palsa site, the Red (+17 cm) and Yellow (+10 cm) sampling depths at the Sphagnum 1 site, and the Red (-3 cm) depth at the Sphagnum 2 site. All other soil gas sampling array measurements were stored in syringes designated for high concentration samples. A plastic sipper to collect porewater samples was constructed out of polypropylene to reduce the possibility of reaction between acidic water and a stainless steel sipper that could possibly generate H_2. The previous summer, a stainless steel sipper had been used.

3.2 Sampling at Stordalen:

To determine the effect of precipitation on H_2 consumption or release, soil gas sampling arrays were sampled and autochamber measurements were taken to determine where gas is produced in the soil and which gases are released to the atmosphere, respectively. Measurements were taken several times (3-4) each week to observe the effects of a variety of soil-moisture conditions on H_2 concentration. Samples were analyzed using a Flame Ionization Detector

(FID) to determine CH_4 concentrations and H_2 was determined using a Reduced Gas Detector (RGD) within 24 hours of sampling to minimize sample degradation.

In addition to analyzing the field samples, standard gases containing known samples of CH_4 and H_2 were analyzed on both the FID and RGD, respectively. On the RGD, three sets of standards were run. Before analyzing samples and at the end of running all samples, three 50000 ppb standards were run followed by three 1621.8 ppb standards. Halfway through analyzing samples another set of standards was run: three 1621.8 ppb standards, three 838.5 ppb standards, three 412.2 ppb standards, and three 50000 ppb standards. With adequate standards, it is possible to calculate hydrogen concentrations by fitting a curve to a plot of the standards. Once the best-fit curve is found, often a polynomial, it is possible to place the area measured by the RGD into the equation for x and determine the concentration of H_2 in each sample. It was necessary to determine a new polynomial for each day's standards. Due to lack of precision in the RGD when measuring low concentrations, several of the calculated H_2 concentrations, particularly those for Palsa, were negative. As it is impossible for a concentration to be negative, these values were not incorporated in the final analyses.

Concentrations of CH_4 were calculated after taking 12 standards with a known concentration of 1.872 ppm before and after running any samples. From each of these sets of 12, the highest and lowest standards were eliminated. The average of all 20 remaining standards was taken. Next, the known concentration of the CH_4 used for standards was determined to calculate the response factor. The area measured by the FID for each sample was then multiplied by the response factor to determine a concentration in the units of the standard gas.

Calculated concentrations in nM for H_2 and μM for CH_4 for soil gas sampling array samples were based on a Bunsen solubility constant at 8°C. For both H_2 and CH_4 the same equation (Eq. 3) was used.

$$C = \left(\frac{MR * \alpha * \left(\frac{1}{10^6}\right)}{R * T} \right) * 10^9 \; Eq.\,3$$

In this equation, C is the calculated concentration, MR is the concentration in ppm for CH_4 and ppb for H_2, α is the Bunsen solubility constant at 8 degrees Celsius, R is a constant with a value of 0.08205 L*mol/(K*atm), and T is the temperature in Kelvin. For this equation T is 281.15 K. For H_2, α is 0.01999 ml H_2/ml H_2O (Crozier and Yamamoto, 1974). For CH_4, α is 0.04579 ml CH_4/ ml H_2O (Yamamoto et al., 1974).

To convert sipper sample values to μM and nM, a different equation was used (Eq. 4).

$$C = \left(\frac{MR}{R * T} \right) * 1000 \; Eq.\,4$$

In this equation, C is the calculated molar concentration, MR is the concentration in ppm for CH_4 and ppb for H_2, R is the same constant of value 0.08205 L*mol/(K*atm), and T is the measured value at the field site that day in Kelvin.

3.3 Dissolved Soil Gas Samples:

Samples for H_2 analysis were taken from five arrays of soil gas profiling tubes (Fig. 3), installed in summer 2011 in four different subhabitats within Stordalen Mire: two in a *Sphagnum* habitat, two in an *Eriophorum* habitat, and one in a *Carex* dominated habitat. The soil gas profiling arrays were constructed from expanded polytetrafluoroethylene (PTFE) tubes, and samples were taken using a 10 ml polypropylene syringe drawn through PTFE microporous tubing. In order to avoid contamination of the potentially anoxic soil gas, a Mylar balloon filled with nitrogen (N_2) was attached to one end of the line. The stopcock on the balloon was opened

to the line before any sample could be taken, and the first 10 ml of sample were ejected before taking the 10 ml sample that would be analyzed at the lab. Analysis of the profile of H_2 concentrations allowed for determination of where in the soil gas is produced.
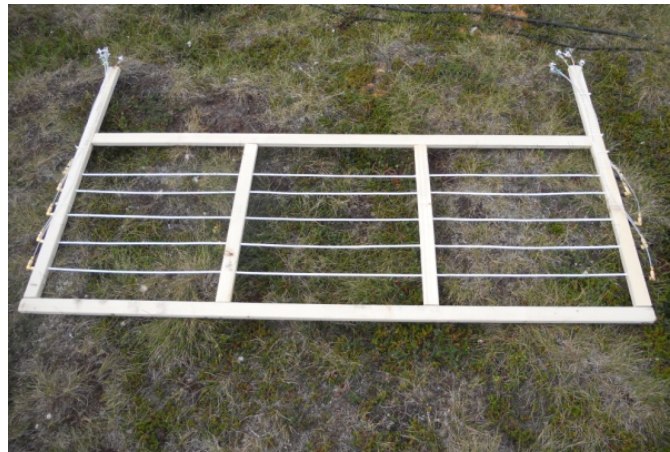

Fig. 3: Photo of soil gas sampling array (credit: Kaitlyn Steele)

A plastic sipper was used to measure the concentration of dissolved gases in the soil pore water in order to provide a comparison to the concentration profiles from the soil gas sampling arrays. These samples were taken with 60 ml polypropylene syringes. Immediately after collecting the sample, the syringes were shaken for two minutes to equilibrate the gas in the air and the water (McAullife, 1971). After equilibration, air from the samples was transferred to two 10 ml polypropylene syringes, which were used to inject five ml samples into the RGD and FID.

Samples were collected before, during, and after the large rain event of July 14th and 15th during which 54.6 mm of rain fell. Soil gas sampling array samples were collected on July 9th, 14th, 16th, 21st, and 26th. Sipper samples were taken on July 11th, 13th, 18th, 21st, and 26th. In order to create depth profiles, these values were placed in four categories: before the rain, during

the rain, after the rain, and one week after the rain. If more than one date were in a time period, the values were averaged over that time.

3.4 Autochamber Measurements:

Autochamber measurements (Fig. 4) were taken in three of the four subhabitats to determine the exchange of gases with the atmosphere. Three chambers are located in the permafrost-dominated, dry Palsa habitat; three are located in the intermediate permafrost habitat dominated by *Sphagnum*; two chambers sit in a full summer-thaw, wet habitat dominated by *Eriophorum*; and a final chamber is positioned on a Hummock site, which is a small area of raised ground dominated by dwarf shrubs. Manual syringe samples were taken to determine H_2 and CH_4 fluxes in the chambers. Autochamber measurements were taken on three occasions (7/20, 7/25, and 7/27) using 10 ml polypropylene syringes. Analysis for CO_2 was done as part of the autochamber measurements using a laser spectrometer. These data were available from Prof. Patrick Crill, Stockholm University.
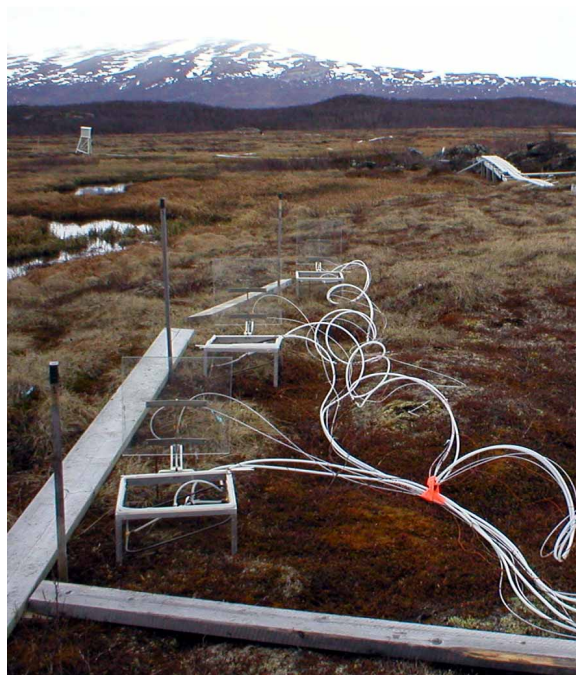

Fig. 4: Photo of autochambers in the Palsa site taken by Patrick Crill

For each autochamber, one ambient sample was taken before the chamber closed. After the chamber closure, four samples were taken at one minute intervals. The four concentrations were plotted versus time and a linear regression was fit. If the r^2 was 0.8 or higher, the sample was considered a good flux and included in an average flux calculation for the subhabitat. In order to calculate the fluxes of hydrogen and methane, the following equation was used:

$$\text{ppmv/ min or ppbv/min} * (\frac{\text{pressure}}{\text{R*temp}} * \text{molecular weight} * (\frac{\text{vol}}{\text{area}})) \text{ Eq. 1}$$

The standard deviation of fluxes for each site was calculated to determine the variability of the measurements over the sampling days. The flux of CO_2 was provided with the data set obtained from Prof. Patrick Crill, and averages were taken over the same time periods as for H_2 and CH_4.

3. 5 Tukey Kramer Analysis:

In order to determine whether or not there were significant statistical differences between sites, dates, and depths, a Tukey Kramer test was performed in JMP. The Tukey Kramer test determined if the means of samples were significantly different. The Tukey Kramer test was also performed to determine whether the autochamber flux of each gas differed among subhabitats.

4. Results:

4.1 Sipper Samples:

The region experienced record precipitation on July 14th and 15th (Fig. 5). Sipper samples showed a decrease in the concentration of H_2 at both the *Carex* and *Eriophorum* sites after the rain event at all depths measured; however, the *Eriophorum* site began to recover by the measurements taken on July 21st and July 26th. In fact, the concentrations at -30 cm and -40 cm were slightly higher than those on July 9th, before the rain event. At the *Sphagnum* site there was a decrease at the lower depths, but the higher depths actually showed an increase in H_2 concentrations after the storm. When considering concentrations at depth, there were not any

differences in H_2 concentrations at any of the three sites according to Tukey Kramer. There were not any differences in each site's H_2 concentration at any depth when all dates were considered.

Across all depths and vegetation types, it seems there was a drop in concentrations directly following the storm. Eventually, the systems began to recover. It seems as though the recovery was quickest at the *Sphagnum* site and slowest at the *Carex* site.

Overall, concentrations of H_2 and CH_4 demonstrate an initial decrease following the storm because the profiles observed on July 16th are the lowest. Over time, these concentrations seem to build back up toward pre-storm levels by July 21st and 26th.
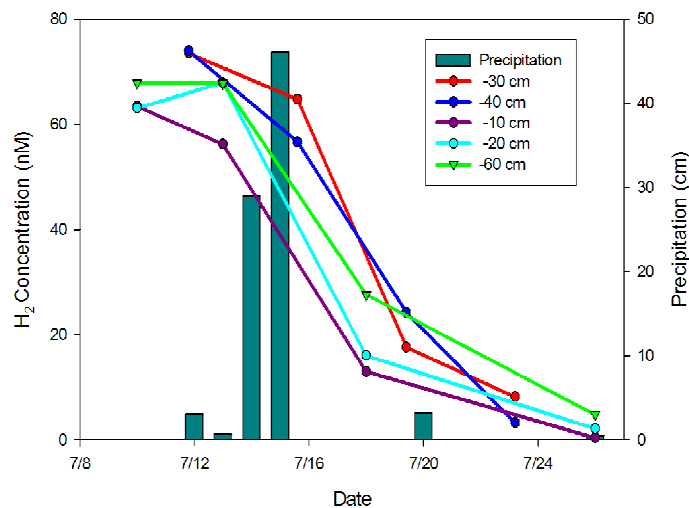

Fig. 5: Time series of H_2 concentration at each depth of the *Carex* sipper site plotted with precipitation data

4.2 Soil Gas Sampling Array:

The *Carex* site showed an increase from pre-rain levels (7/9) in the concentration of H_2 just after the storm on 7/14 (Fig. A5). By 7/16, there was a decrease in H_2 concentration that was eventually followed by a minor increase. The lowest depth's H_2 concentration on 7/21 and 7/26 exceeded that on 7/9.

Measurements from both *Eriophorum* soil gas sampling arrays demonstrated an increased H_2 concentration at after the rain event closer to the surface (Fig. A3). After the storm, concentrations at lower depths decreased before recovering to concentrations that were still below those on 7/9. At the middle depth, the concentration on 7/21 and 7/26 was substantially higher than that on 7/9.

The results from the *Sphagnum* soil gas sampling arrays demonstrate a stable H_2 concentration near the soil surface (Fig. A1). The lower depths showed a decrease after the rain event before increasing substantially to exceed pre-rain concentrations.

4.3 Autochamber:

Autochamber flux measurements showed that there was a net sink of H_2 at all but the hummock site (Fig. 6). Every site demonstrated a net sink of CO_2, and aside from the Palsa site, every site emitted some CH_4. Data were not available for autochamber H_2 concentrations before or during the storm, but these fluxes do provide information on the impact of different subhabitats on the release of trace gases. Statistical analysis using Tukey-Kramer demonstrated that the H_2 fluxes from the Hummock site were significantly different from the *Eriophorum* (p-value = 0.0404), and Palsa (p-value = 0.0473) sites, but the H_2 flux from the Hummock site did not vary significantly from the *Sphagnum* site (p-value = 0.0848). There were not any significant differences in H_2 flux among the Palsa, Eriophorum, and Sphagnum sites (p-values ranged from 0.3246 to 0.7809). When CH_4 emissions were considered, only the *Eriophorum* site differed significantly from the Palsa (p-value = 0.0005), *Sphagnum* (p-value = 0.0001), and *Eriophorum* (p-value = 0.0054) sites. Comparisons of CH_4 fluxes between Hummock and Palsa (p-value = 0.1501), *Sphagnum* and Palsa (p-value = 0.3057), and Hummock and *Sphagnum* (p-value = 0.5750) did not show any significant differences. Carbon Dioxide emissions showed the Palsa, *Eriophorum*, and Hummock sites to be significantly different from one another

(p-values ranging from 0.0002 to 0.0439), but the Palsa and *Sphagnum* sites were not
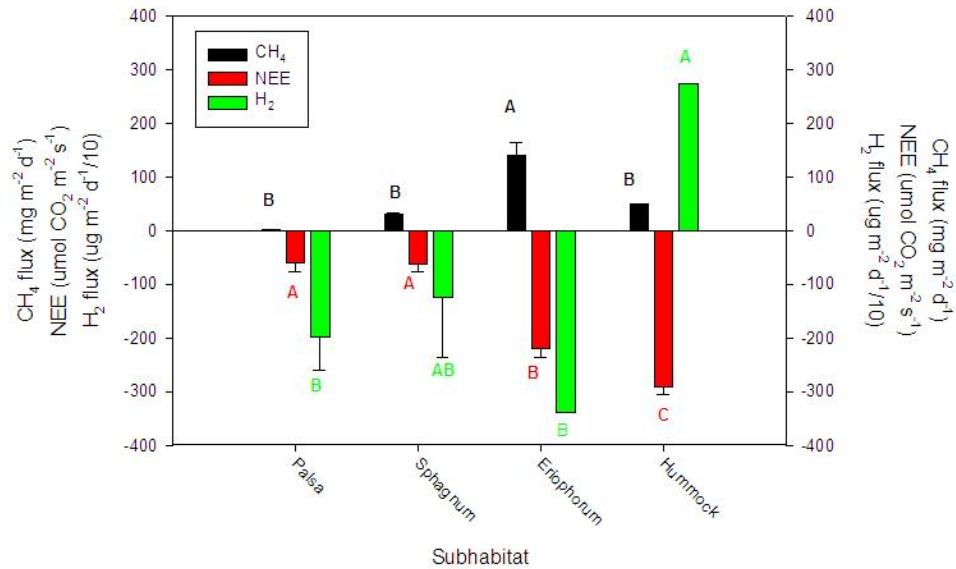
significantly different (p-value = 0.9990).

Fig. 6: Fluxes of Hydrogen, Methane, and Carbon Dioxide from autochambers located at each of 4 sites, showing standard deviation. Fluxes with the same letter indicate that differences are not statistically significant based on the Tukey-Kramer test.

5. Discussion:

An important factor in explaining the recovery times at different sites is the hydrologic

behavior of each site (Fig. 7). Under drier conditions, soil biogeochemistry is likely to explain

the behavior of these compounds at each site; however, considering the extreme magnitude of

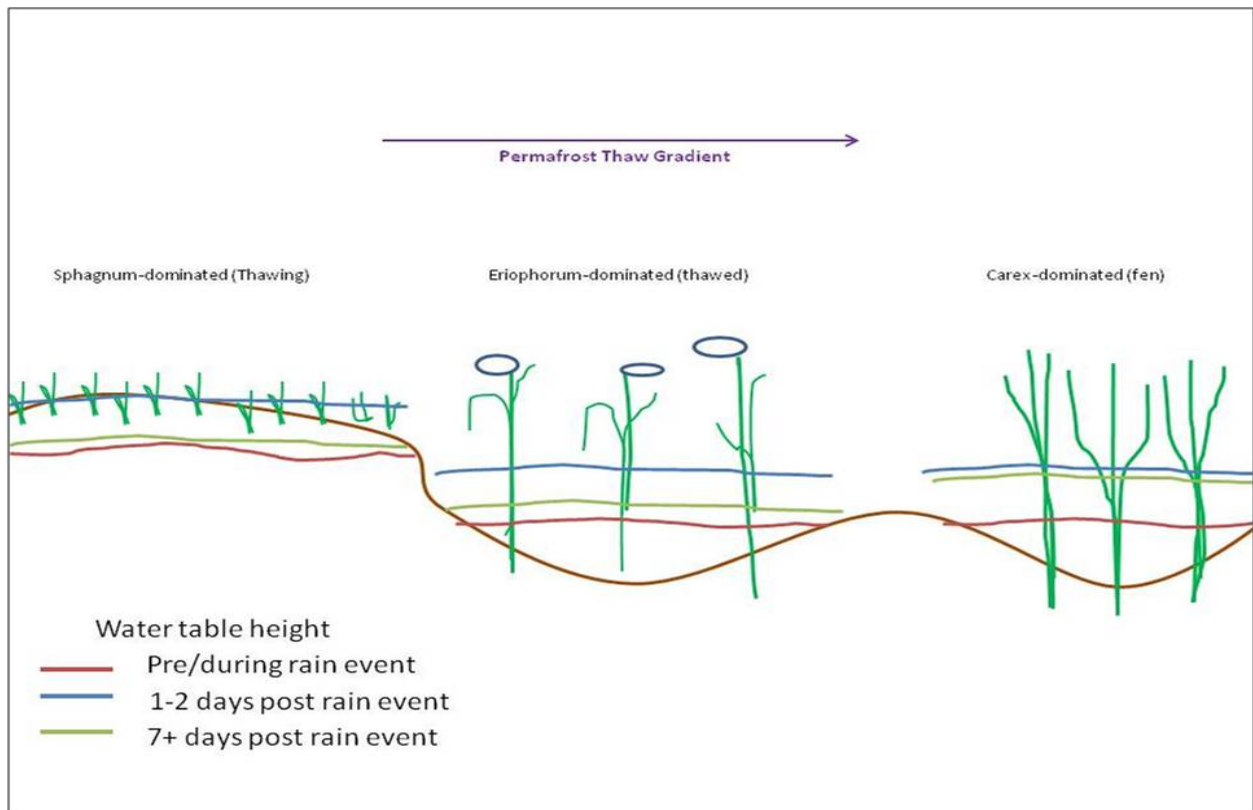this storm, it is likely that hydrology dominated H_2 behavior at all sites.

Fig. 7: Conceptual diagram of hydrologic response to precipitation event across *Sphagnum, Eriophorum,* and *Carex* subhabitats

Each of the three sites from which sipper and soil gas sampling array samples were drawn is characterized by significantly different hydrology (Fig. 7). The *Sphagnum* site is more elevated allowing it to drain quite quickly after a small rise in water table level immediately following the storm. The speed with which this site drains easily explains the rapid recovery of its soil H_2 concentrations. The *Eriophorum* site, which demonstrates an intermediate recovery time, does not drain as quickly as *Sphagnum* due to its lower elevation and larger drainage area, but it drains more rapidly than the *Carex* site. The *Carex* site is located in a fen-like portion of the mire where there is a relatively constant flow from Villasjon, a lake which has a large drainage area.

These results are important to our understanding of the release of trace gases from subarctic wetlands, particularly in response to extreme events. Further, these results add to those

taken during the summer of 2011 in building a longer-term record of H_2 behavior at Stordalen Mire. Comparison of autochamber results between 2011 and 2012 indicates that the fluxes are consistent for the Palsa, *Eriophorum*, and *Sphagnum* subhabitats. Given that the ninth autochamber was moved from a tussock to a hummock site, it is not possible to make an interannual comparison.

Although the results from this project and those from the summer of 2011 provide insight into soil H_2, the short time span during which data were collected means that additional data would substantially improve statistical analyses. A crucial improvement would be the addition of soil gas and sipper data from the Palsa site. During the summer of 2012, it was impossible to collect any soil gas sampler data because of a rupture in the soil that had not been repaired since the summer of 2011. Additionally, the sipper samples that were taken yielded negative concentration values, which are not possible due to a lack of precision in the RGD's reading of low concentrations. The establishment of a reintegration formula would eliminate this concern and provide Palsa data. In the interest of comparing data from all four subhabitats, the addition of autochamber measurements from the *Carex* site would allow for a better understanding of the differences in H_2 behavior between the *Carex* and *Eriophorum* sites.

Anyone working on soil H_2 at Stordalen mire in the future should consider the statistical tests he or she hopes to perform in devising a sampling plan. Because the Reduced Gas Detector has an injection interval of four minutes, do not expect to sample every day. Plan to sample three days per week and develop a sampling plan to collect all of the data necessary in that time. Be sure to run duplicate samples for each depth at each site as this will guarantee sufficient data for many of the statistical tests.

6. Conclusions:

Methane and H_2 concentrations decreased during the record rainfall event due to a flushing of the system by the large influx of freshwater.   After a certain amount of time, the system began to recover from this resetting of its biogeochemistry, and the concentrations built back up toward pre-precipitation levels. This information may be useful in models as it allows scientists to better understand the effects of this type of storm on the mire.

It is believed the hydrology and vegetation coverage of each site also produced differences in the behavior of soil H_2. For sites with less lateral flow of water, such as *Eriophorum*, the impact of the storm was less severe as the entire profile was flushed more quickly, allowing the concentration of H_2 to build back up at all depths after the storm in a relatively short period of time. In sites where lateral flow was sustained, such as *Carex*, it took much longer for the concentrations of H_2 to build back up after the freshwater influx from the rain event because the *Carex* site received freshwater from the surrounding lakes, meaning the soil was not drained to the point that H_2 concentrations could rebuild. The *Sphagnum* site showed a quicker recovery in the concentration of H_2 than the *Carex* site because it is extremely porous, meaning the freshwater influx drained quickly and H_2 concentrations were allowed to begin recovery earlier. By considering the fluxes to the atmosphere (Fig. 18), it was possible to gain an additional understanding of the relationship between all gases studied.

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Appendix A

Table A1: Depths in centimeters of soil gas sampling array measurements for each site. Asterisks indicate leaks.

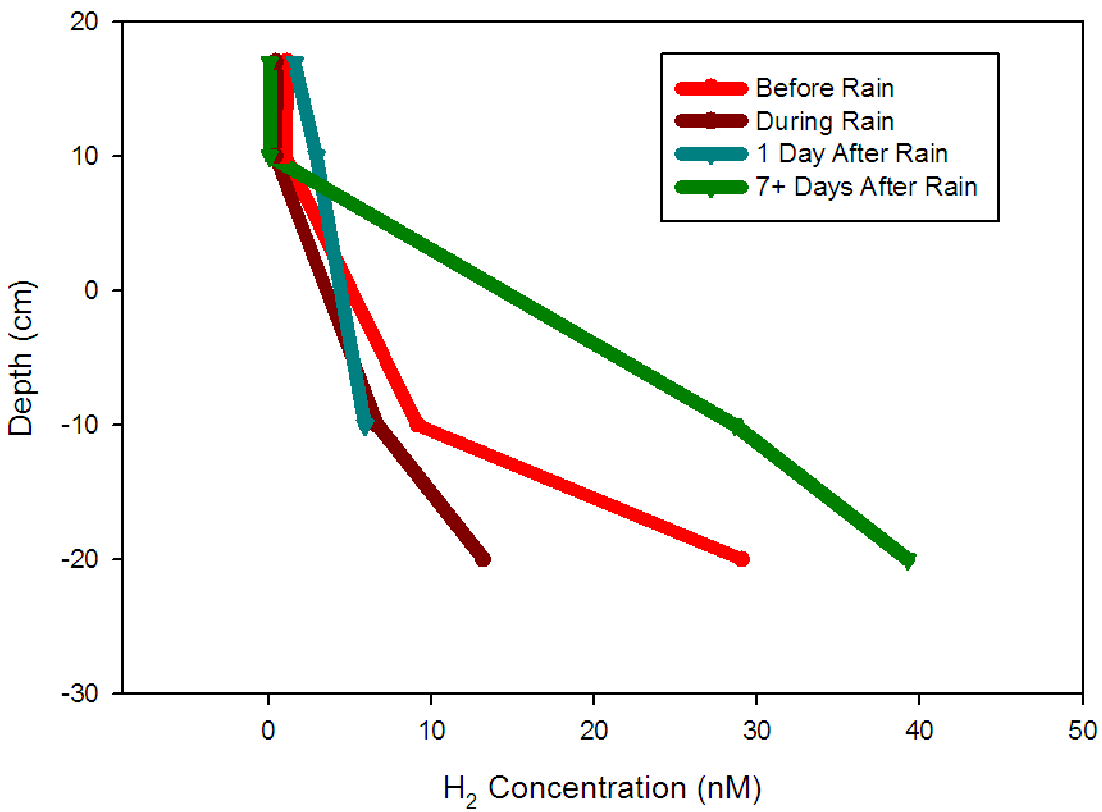|	Palsa	Sph 1	Eri 1	Sph2	Eri 2	Carex
Red	+2	+17	3	3	0	+7
Yellow	10	+10	10	15	7	3
Green	20	0*	20	25	17	13
Blue		10	30		27*	23
Clear		20	40		37	33*

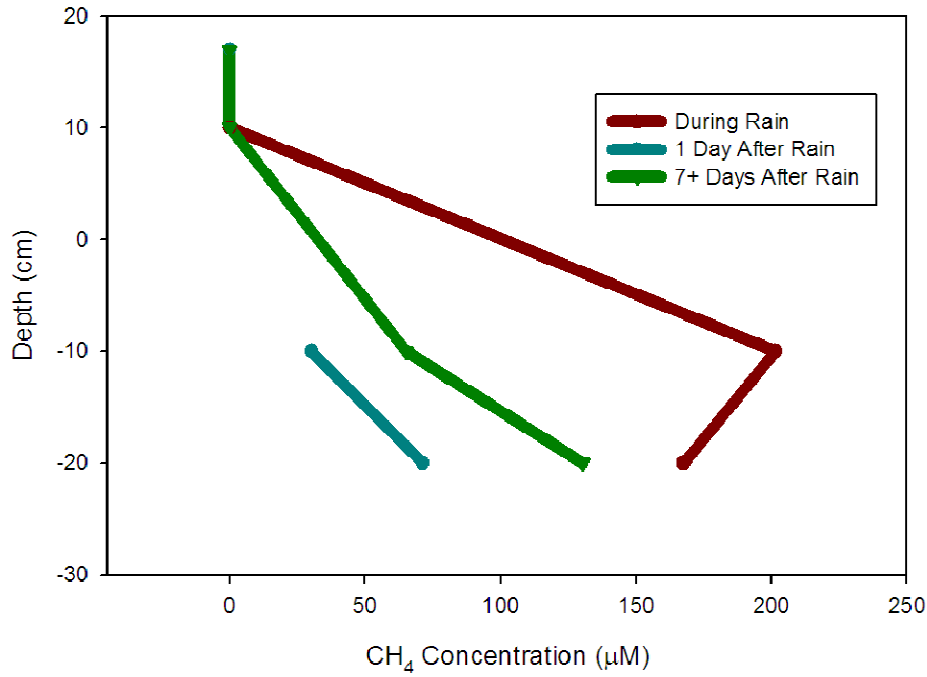Fig. A1: Soil Gas Sampling array H_2 depth profile at *Sphagnum* 1 site

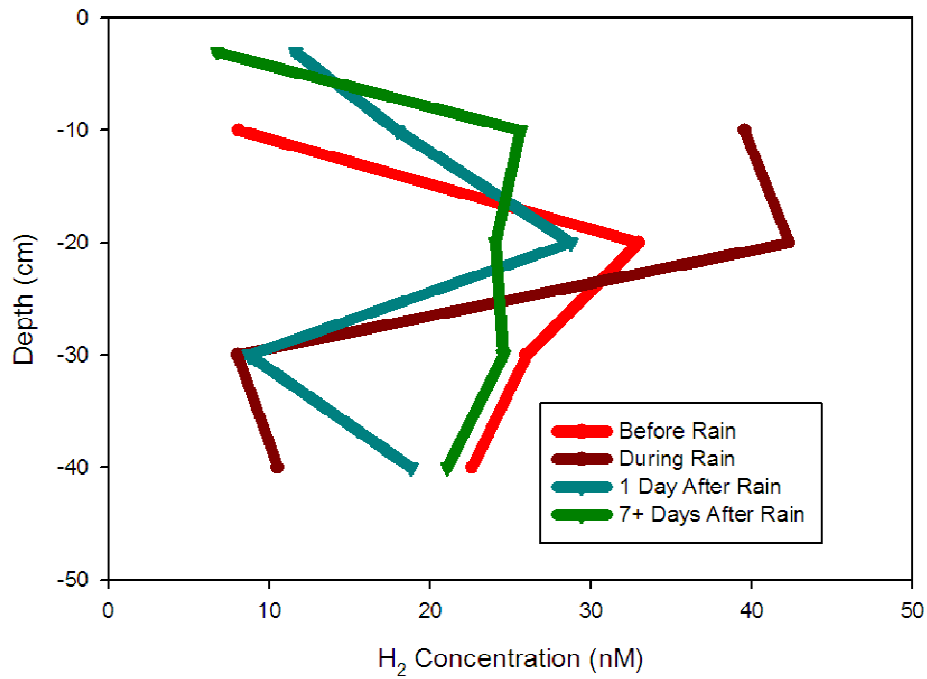Fig. A2: Soil Gas Sampling Array CH_4 depth profile at *Sphagnum* 1 site

Fig. A3: Soil Gas Sampling Array H_2 Depth profile at *Eriophorum* 1 site
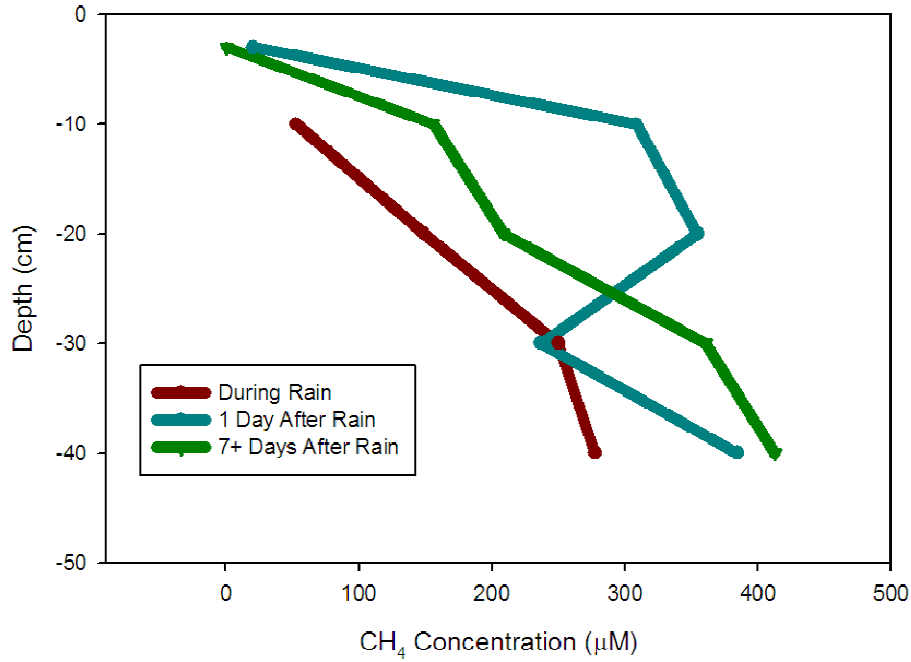
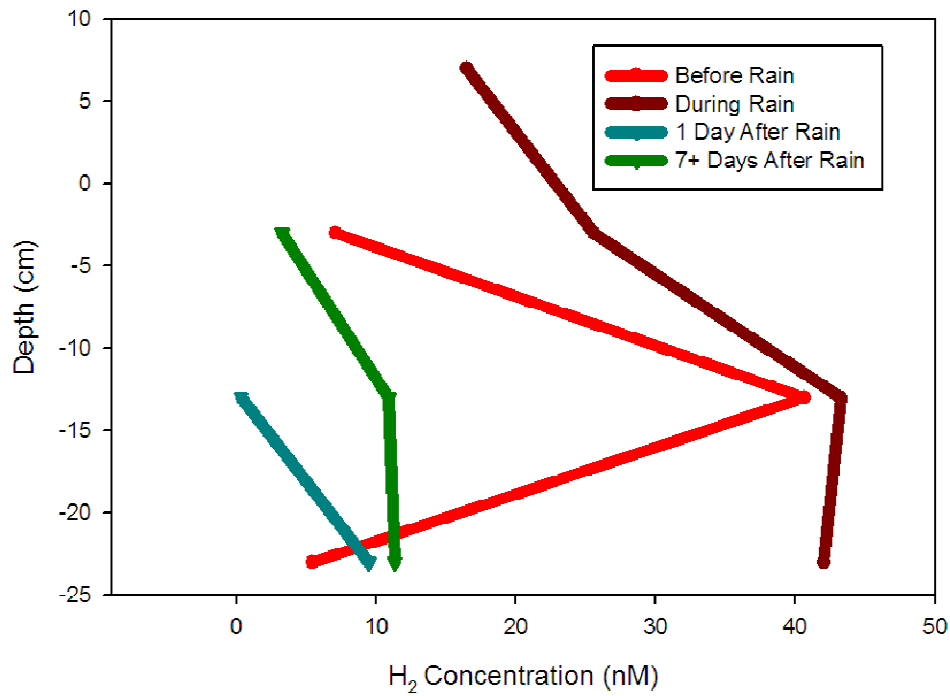Fig. A4: Soil Gas Sampling Array CH$_4$ depth profile at *Eriophorum* 1 site

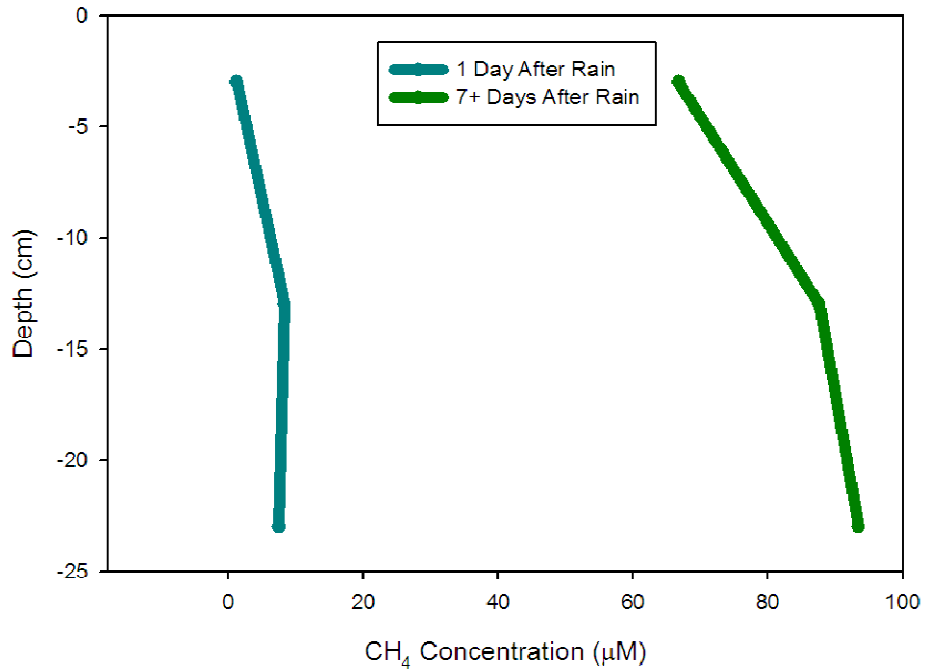Fig. A5: Soil gas sampling array H$_2$ depth concentration at *Carex* site

Fig. A6: Soil Gas sampling array CH_4 depth profile at *Carex* site

Table A2: Tukey Kramer comparison of H_2 and CH_4 sipper sample concentrations between depths at *Carex* site

Depth (cm)	H_2 on 7/10 and 7/13	H_2 on 7/18, 7/21 and 7/26	CH_4 on7/13	CH_4 on 7/18, 7/21, and 7/26	H_2 All Dates	CH_4 All Dates
-10	A	A	A	A	A	A
-20	A	A	A	A	A	A
-30	A	A	A	A	A	A
-40	A	A	A	A	A	A
-50	A		A		A	A

Table A3: Tukey Kramer comparison of H_2 and CH_4 sipper sample concentrations between depths at *Eriophorum* site

Depth (cm)	H_2 on 7/13	H_2 on 7/18, 7/21, and 7/26	CH_4 on 7/13	CH_4 on 7/18, 7/21, and 7/26	H_2 All Dates	CH_4 All Dates
-10	A	A	D	B	A	B
-20	A	A	C	A	A	A
-30	A	A	C	A	A	A
-40	A	A	B	A	A	A
-50	A	A	B	A	A	A
-60	A	A	A	A	A	A

Table A4: Tukey Kramer comparison of H_2 sipper sample concentrations across all sites at each depth

Depth (cm)	*Carex*	*Eriophorum*	*Sphagnum*
-10	A	A	A
-20	A	A	A
-30	A	A	
-40	A	A	
-50	A	A	
-60	A	A	

Table A5: Tukey Kramer comparison of CH_4 sipper sample concentrations across all sites at each depth

Depth (cm)	Carex	Eriophorum	Sphagnum
-10	A	A	A
-20	A	A	A
-30	A	A	
-40	A	B	
-50	A	A	
-60	A	B	

Table A6: Tukey Kramer comparison of Metal and Plastic sipper samples

Sample	Significant difference?
H_2 at -20 cm at *Eriophorum*	No
CH_4 at -20 at *Eriophorum*	No
H_2 at -20 at *Carex*	Yes
CH_4 at -20 at *Sphagnum*	No

Table A7: p-values for Tukey Kramer comparison of autochamber flux measurements. Asterisks indicate a significant difference at the 5% confidence level.

Level	-Level	H_2 p-value	CH_4 p-value	CO_2 p-value
Hummock	Eriophorum	0.0404*	0.0054*	0.0439*
Hummock	Palsa	0.0473*	0.1501	0.0002*
Hummock	Sphagnum	0.0848	0.5750	0.0002*
Sphagnum	Eriophorum	0.3246	0.0001*	0.0003*
Palsa	Eriophorum	0.5428	0.0005*	0.0003*
Sphagnum	Palsa	0.7809	0.3057	0.990