Cycling of Molecular Hydrogen in Subarctic Sweden

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ABSTRACT
Cycling of Molecular Hydrogen in Subarctic Sweden
by
Victoria Lynn Ward
University of New Hampshire, May 2013

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 14$^{th}$ and 15$^{th}$, 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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{4}, molecular hydrogen (H\textsubscript{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\textsubscript{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\textsubscript{2}; however, thawing permafrost and wetter soil conditions may result in soils becoming a temporary source of H\textsubscript{2}. Considering that soil uptake is currently the dominant H\textsubscript{2} sink process consuming/destroying up to 75\% of global H\textsubscript{2}, this could significantly alter the global distribution of H\textsubscript{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\textsubscript{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 \textit{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\textsubscript{2} (Eq. 1).

\[
\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2 \quad \text{Eq. 1}
\]

Although previous studies have failed to account for soil moisture or temperature, the highest H\textsubscript{2} uptake typically occurs in summer, when soils are warm and dry, suggesting that wetter soils will increase release of H\textsubscript{2} (Ehhalt and Rohrer, 2009).

The second most important sink of H\textsubscript{2} is reaction with the hydroxyl radical (OH) in the atmosphere (Eq. 2).

\[
\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \quad \text{Eq. 2}
\]

As the concentration of H\textsubscript{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\textsubscript{2} cycling in different subarctic subhabitats can therefore provide information on the oxidizing capacity of the atmosphere and therefore residence time of GHGs (Novelli \textit{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\textsubscript{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\textsubscript{2}. As permafrost thaws and wetter soil conditions become more common, soils may become sources of H\textsubscript{2} more frequently, an unexpected feedback to climate change. The research question I addressed was:

\textit{Does an increase in soil moisture impact H\textsubscript{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\textsubscript{2} levels and future levels with anticipated changes in vegetation and hydrology. Data on CH\textsubscript{4} and CO\textsubscript{2} were also considered to gain a more comprehensive understanding of H\textsubscript{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\textsubscript{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.
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 H₂. The previous summer, a stainless steel sipper had been used.

3.2 Sampling at Stordalen:

To determine the effect of precipitation on H₂ 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 H₂ concentration. Samples were analyzed using a Flame Ionization Detector.
(FID) to determine CH₄ concentrations and H₂ 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 CH₄ and H₂ 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 H₂ 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 H₂ 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 CH₄ 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 CH₄ 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 H₂ and µM for CH₄ for soil gas sampling array samples were based on a Bunsen solubility constant at 8°C. For both H₂ and CH₄ the same equation (Eq. 3) was used.

\[ C = \left( \frac{MR \times \alpha \times \left( \frac{1}{10^5} \right)}{R \times T} \right) \times 10^9 \text{ Eq. 3} \]

In this equation, \( C \) is the calculated concentration, \( MR \) is the concentration in ppm for CH₄ and ppb for H₂, \( \alpha \) 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 H₂, \( \alpha \) is 0.01999 ml H₂/ml H₂O (Crozier and Yamamoto, 1974). For CH₄, \( \alpha \) is 0.04579 ml CH₄/ml H₂O (Yamamoto et al., 1974).

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

\[ C = \left( \frac{MR}{R \times T} \right) \times 1000 \text{ Eq. 4} \]

In this equation, \( C \) is the calculated molar concentration, \( MR \) is the concentration in ppm for CH₄ and ppb for H₂, \( R \) 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 H₂ 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 (N₂) 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 H₂
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 14<sup>th</sup> and 15<sup>th</sup>
during which 54.6 mm of rain fell. Soil gas sampling array samples were collected on July 9<sup>th</sup>,
14<sup>th</sup>, 16<sup>th</sup>, 21<sup>st</sup>, and 26<sup>th</sup>. Sipper samples were taken on July 11<sup>th</sup>, 13<sup>th</sup>, 18<sup>th</sup>, 21<sup>st</sup>, and 26<sup>th</sup>. 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:

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

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 14$^{th}$ and 15$^{th}$ (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 21$^{st}$ and July 26$^{th}$. In fact, the concentrations at -30 cm and -40 cm were slightly higher than those on July 9$^{th}$, 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\textsubscript{2} concentrations at any of the three sites according to Tukey Kramer. There were not any differences in each site’s H\textsubscript{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 \textit{Sphagnum} site and slowest at the \textit{Carex} site.

Overall, concentrations of H\textsubscript{2} and CH\textsubscript{4} demonstrate an initial decrease following the storm because the profiles observed on July 16\textsuperscript{th} are the lowest. Over time, these concentrations seem to build back up toward pre-storm levels by July 21\textsuperscript{st} and 26\textsuperscript{th}.

![](image)

**Fig. 5:** Time series of H\textsubscript{2} concentration at each depth of the \textit{Carex} sipper site plotted with precipitation data

### 4.2 Soil Gas Sampling Array:

The \textit{Carex} site showed an increase from pre-rain levels (7/9) in the concentration of H\textsubscript{2} just after the storm on 7/14 (Fig. A5). By 7/16, there was a decrease in H\textsubscript{2} concentration that was eventually followed by a minor increase. The lowest depth’s H\textsubscript{2} concentration on 7/21 and 7/26 exceeded that on 7/9.
Measurements from both *Eriophorum* soil gas sampling arrays demonstrated an increased H₂ 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 H₂ 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 H₂ at all but the hummock site (Fig. 6). Every site demonstrated a net sink of CO₂, and aside from the Palsa site, every site emitted some CH₄. Data were not available for autochamber H₂ 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 H₂ fluxes from the Hummock site were significantly different from the *Eriophorum* (p-value = 0.0404), and Palsa (p-value = 0.0473) sites, but the H₂ flux from the Hummock site did not vary significantly from the *Sphagnum* site (p-value = 0.0848). There were not any significant differences in H₂ flux among the Palsa, Eriophorum, and Sphagnum sites (p-values ranged from 0.3246 to 0.7809). When CH₄ 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 CH₄ 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).

![Graph showing 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.](image)

**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 H₂ behavior at all sites.
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 $\text{H}_2$ 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.
References


Appendix A

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

<table>
<thead>
<tr>
<th></th>
<th>Palsa</th>
<th>Sph 1</th>
<th>Eri 1</th>
<th>Sph2</th>
<th>Eri 2</th>
<th>Carex</th>
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Fig. A1: Soil Gas Sampling array H₂ 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 CH₄ depth profile at *Eriophorum* 1 site

Fig. A5: Soil gas sampling array H₂ depth concentration at *Carex* site
Table A2: Tukey Kramer comparison of H$_2$ and CH$_4$ sipper sample concentrations between depths at Carex site

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>H$_2$ on 7/10 and 7/13</th>
<th>H$_2$ on 7/18, 7/21 and 7/26</th>
<th>CH$_4$ on 7/13</th>
<th>CH$_4$ on 7/18, 7/21, and 7/26</th>
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<th>CH$_4$ All Dates</th>
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Table A3: Tukey Kramer comparison of H\textsubscript{2} and CH\textsubscript{4} sipper sample concentrations between depths at *Eriophorum* site

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>H\textsubscript{2} on 7/13</th>
<th>H\textsubscript{2} on 7/18, 7/21, and 7/26</th>
<th>CH\textsubscript{4} on 7/13</th>
<th>CH\textsubscript{4} on 7/18, 7/21, and 7/26</th>
<th>H\textsubscript{2} All Dates</th>
<th>CH\textsubscript{4} All Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>A</td>
<td>A</td>
<td>D</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>-20</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-30</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-40</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-50</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-60</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

Table A4: Tukey Kramer comparison of H\textsubscript{2} sipper sample concentrations across all sites at each depth

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Carex</th>
<th><em>Eriophorum</em></th>
<th><em>Sphagnum</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-20</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-30</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-40</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-50</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-60</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

Table A5: Tukey Kramer comparison of CH\textsubscript{4} sipper sample concentrations across all sites at each depth

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Carex</th>
<th><em>Eriophorum</em></th>
<th><em>Sphagnum</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-20</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-30</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-40</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>-50</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>-60</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Significant difference?</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2} at -20 cm at <em>Eriophorum</em></td>
<td>No</td>
</tr>
<tr>
<td>CH\textsubscript{4} at -20 at <em>Eriophorum</em></td>
<td>No</td>
</tr>
<tr>
<td>H\textsubscript{2} at -20 at <em>Carex</em></td>
<td>Yes</td>
</tr>
<tr>
<td>CH\textsubscript{4} at -20 at <em>Sphagnum</em></td>
<td>No</td>
</tr>
</tbody>
</table>
Table A7: p-values for Tukey Kramer comparison of autochamber flux measurements. Asterisks indicate a significant difference at the 5% confidence level.

<table>
<thead>
<tr>
<th>Level</th>
<th>-Level</th>
<th>H2 p-value</th>
<th>CH4 p-value</th>
<th>CO2 p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hummock</td>
<td>Eriophorum</td>
<td>0.0404*</td>
<td>0.0054*</td>
<td>0.0439*</td>
</tr>
<tr>
<td>Hummock</td>
<td>Palsa</td>
<td>0.0473*</td>
<td>0.1501</td>
<td>0.0002*</td>
</tr>
<tr>
<td>Hummock</td>
<td>Sphagnum</td>
<td>0.0848</td>
<td>0.5750</td>
<td>0.0002*</td>
</tr>
<tr>
<td>Sphagnum</td>
<td>Eriophorum</td>
<td>0.3246</td>
<td>0.0001*</td>
<td>0.0003*</td>
</tr>
<tr>
<td>Palsa</td>
<td>Eriophorum</td>
<td>0.5428</td>
<td>0.0005*</td>
<td>0.0003*</td>
</tr>
<tr>
<td>Sphagnum</td>
<td>Palsa</td>
<td>0.7809</td>
<td>0.3057</td>
<td>0.990</td>
</tr>
</tbody>
</table>