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COMPOUND-SPECIFIC H AND C ISOTOPE MEASUREMENTS REVEAL NEW ASPECTS OF HOLOCENE HYDROLOGICAL AND CARBON CYCLES

Jonathan E. Nichols (*corresponding author*)
Lamont-Doherty Earth Observatory, 61 Route 9W, Palisades, NY 10964 USA
+1 (845) 365-8428; jnichols@ldeo.columbia.edu

Dorothy M. Peteet
Lamont-Doherty Earth Observatory, 61 Route 9W, Palisades, NY 10964 USA
+1 (845) 365-8420; peteet@ldeo.columbia.edu

Peter D. Isles
University of Vermont, Burlington, VT 05405 USA
+1 (802) 434-5953; Peter.Isles@uvm.edu

Yongsong Huang
Brown University, Department of Geological Science, 234 Brook St., Providence, RI 02912 USA; +1 (401) 863-3822; yongsong_huang@brown.edu

SUMMARY

We have developed several new approaches to quantitatively assess past changes in precipitation δD, evaporation, and methane release based on compound-specific hydrogen and carbon isotope ratios of biomarkers in ombrotrophic peatland sediments. Vascular plant leaf waxes record the δD of acrotelm water, which is little affected by evaporation, whereas *Sphagnum* leaf waxes record the δD of surface water, strongly affected by evaporation. The contrast in δD of water available to living *Sphagnum* and in the rooting zone of vascular plants can be used to estimate "*f*"—the fraction of water remaining after evaporation. The influence of peatlands on the concentrations of atmospheric methane is poorly understood. To constrain the relationships among methane release, vegetation type, and climate, we compare the $\delta^{13}C$ of biomarkers in several microhabitats in ombrotrophic peatlands. We use these compound-specific carbon isotope measurements to understand changes in the amount of methane-derived CO_2 incorporated by *Sphagnum* from symbiosis with methanotrophic bacteria.

KEYWORDS: hydrogen isotopes, carbon isotopes, organic geochemistry, evaporation, methane

INTRODUCTION

Stable isotope ratios of hydrogen, oxygen, and carbon are widely used as tracers of the hydrological and carbon cycles. During photosynthesis, plants use waters and carbon dioxide from the environment to produce biomass, often retaining the stable isotope ratio signature of these compounds with a predictable offset. As plant material is excellently preserved in obrotrophic peatlands, these environments are important recorders of the hydrological and carbon cycles in the regions in which they grow (Chambers et al., 2011).

Though the offset between stable isotope ratios of environmental water and CO_2 and plant biomass is often predictable, it may vary for different species or plant functional types and for different compounds produced by different biological processes (e.g., Loader et al., 2007). For this reason, we focus on using lipid biomarkers as archives of the hydrogen and carbon isotope ratios of hydrological and carbon cycle changes, as these compounds can be traced to specific groups of plants and specific production pathways.

In Part I, we constrain the hydrology of ombrotrophic peatlands using stable hydrogen isotope ratios of water, and constrain how changes in the hydrologic balance of the peatland are recorded in sedimentary lipids from *Sphagnum* and from vascular plants. We present results based on two sample groups, one is a suite of water samples collected from 18 peatlands in the Great Lakes region of the US, an the other is a transect of water and plant lipid samples collected from a transect across a single ombrotrophic peatland in coastal Maine, USA.

In Part II, we investigate the influences on the carbon isotope ratios of *Sphagnum* biomarkers with the goal of developing a proxy for changes in methane flux from peatlands. In general, plants utilizing the C3 photosynthetic pathway display a relatively constant offset between their biochemical products and atmospheric CO_2, which is little affected by environmental parameters, particularly in a peatland. *Sphagnum*, however, has an apparent biosynthetic enrichment that is highly variable, and is sensitive to several environmental factors. One factor often reported in literature is the water film thickness between the atmosphere and *Sphagnum* photosynthetic cells (Williams and Flanagan, 1996). When *Sphagnum* is wetter, the water film is thicker, and *Sphagnum* becomes less selective of the light isotope as diffusion of CO_2 through the water film becomes more difficult. More recently, however, a symbiotic methanotrophic bacterium was discovered to live within *Sphagnum* hyaline cells, providing very strongly isotopically depleted, methane-derived CO_2 as a photosynthate for the *Sphagnum* in which it lives (Raghoebarsing et al., 2005). The activity of these methanotrophic bacteria is another important influence on the carbon isotope ratios of *Sphagnum*. Here, we take advantage of this relationship to develop a proxy for changes in methane flux from peatlands.

METHODS

Samples

Two types of water samples were collected from 18 peatlands in the eastern Great Lakes region of the US and from a 36-station transect across as single peatland, The Great Heath, in coastal Maine, USA. The first is water squeezed from living *Sphagnum*, and the second is water from the acrotelm, sampled from a small trench dug in the peatland that was allowed to fill with water.

Peat monoliths for carbon isotope analysis were collected from Mer Bleue, a peatland near Ottawa, Ontario, Canada, using a 28cm diameter polyethylene cylinder driven into the peat surface and dug out.

Analytical Methods

Hydrogen isotope ratios of water samples are measured either by thermal conversion/elemental analysis-isotope ratio mass spectrometry (TC/EA-IRMS) or by cavity

ring-down spectroscopy (Nichols et al., 2010). Leaf waxes are extracted from plant material by sonication in hexane. *n*-Alkanes are obtained by silica gel chromatography. Carbon and hydrogen isotope ratios of leaf waxes are measured by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) (Nichols et al., 2010).

RESULTS AND CONCLUSIONS

Part I: Hydrogen isotopes of peatland waters as recorders of the hydrological cycle

In Part I of our study, we collected a suite of surface water samples from multiple peatlands and a transect across a single peatland to establish that the contrast in δD between water available to *Sphagnum* living at the surface and in the rooting zone of vascular plants can be used to estimate evaporation. Figure 1 is a schematic cross-section of a peatland showing these two different pools of water. Evaporation from peatland surfaces is limited to the uppermost portion of the peat (Price et al., 2009), The *Sphagnum* at the surface constricts as it dries, cutting off vapor transport from lower levels out to the atmosphere (Kim and Verma, 1996). This property of *Sphagnum* distinguishes peatlands from other types of soils. Because the drying surface layer seals off vapor transport, we expect that the δD of the water below the surface, in the acrotelm, will have the δD signature of precipitation (Hou et al., 2008; Nichols et al., 2009). Conversely, the *Sphagnum* water at the surface should be strongly affected by evaporation. We find in both the suite of Great Lakes region samples (Fig. 2), and in the transect samples (Fig. 3) support these hypotheses. Acrotelm waters plot near the meteoric water line, indicating that they are affected little by evaporation. The *Sphagnum* water samples plot along a slope that is much steeper than the meteoric water line, indicating they are strongly evaporated. We conclude that water used by vascular plants (i.e., acrotlem water) is representative precipitation, and that *Sphagnum* water can be used to estimate evaporation.

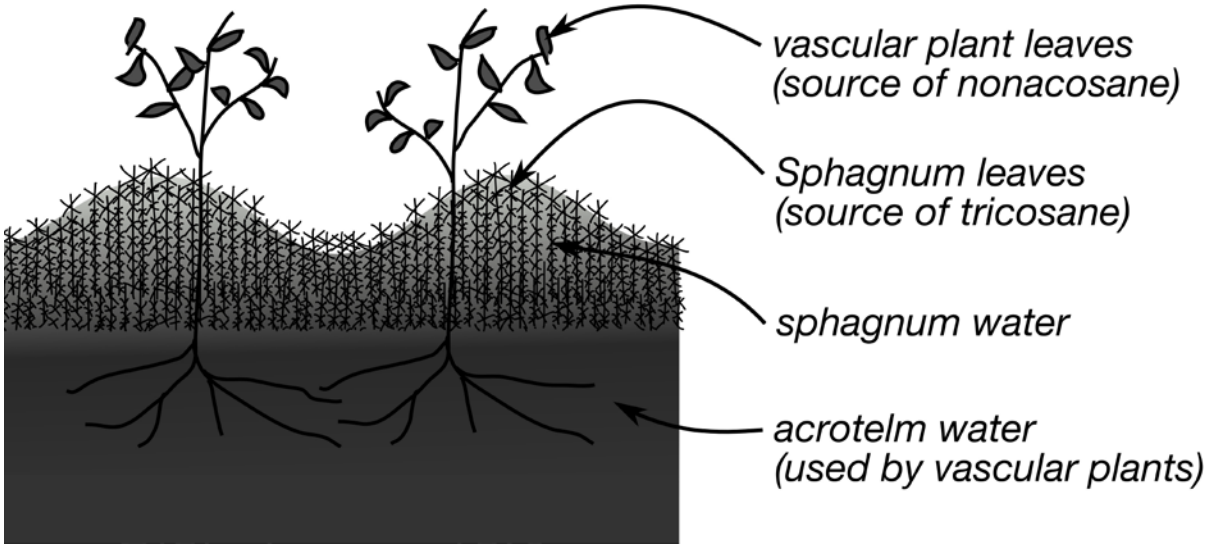

Figure 1: Schematic of a peatland showing the two water reservoirs discussed. The acrotelm contains water used by vascular plants. The other, referred to here as “sphagnum water,” is water trapped inside *Sphagnum* hyaline cells and between *Sphagnum* leaves.

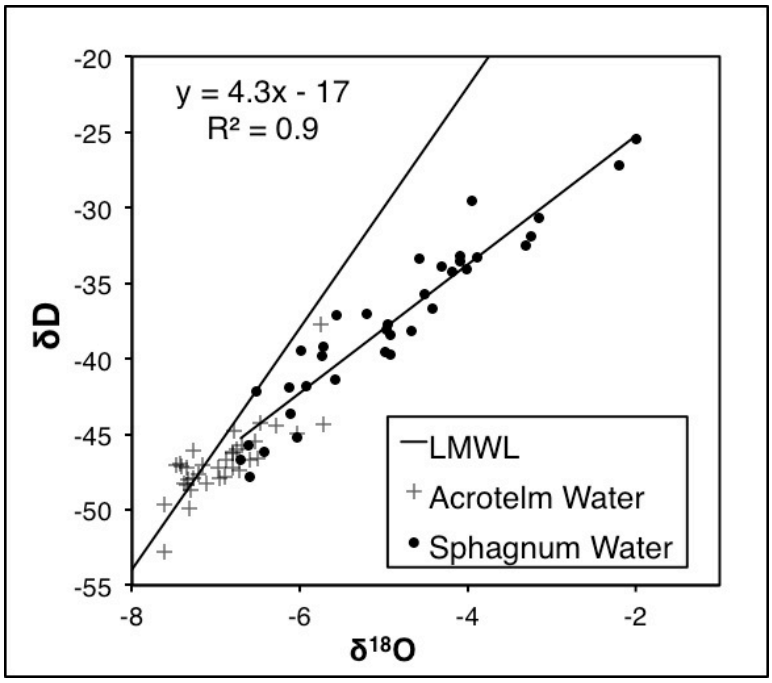

Figure 2: Water samples from a single peatland, The Great Heath, in coastal Maine, USA. The solid black line is the local meteoric water line. The crosses indicate samples from the acrotelm, while spots indicate water squeezed from Sphagnum capitula. The Sphagnum water is strongly affected by evaporation, while the acrotelm water shows little to no effect.

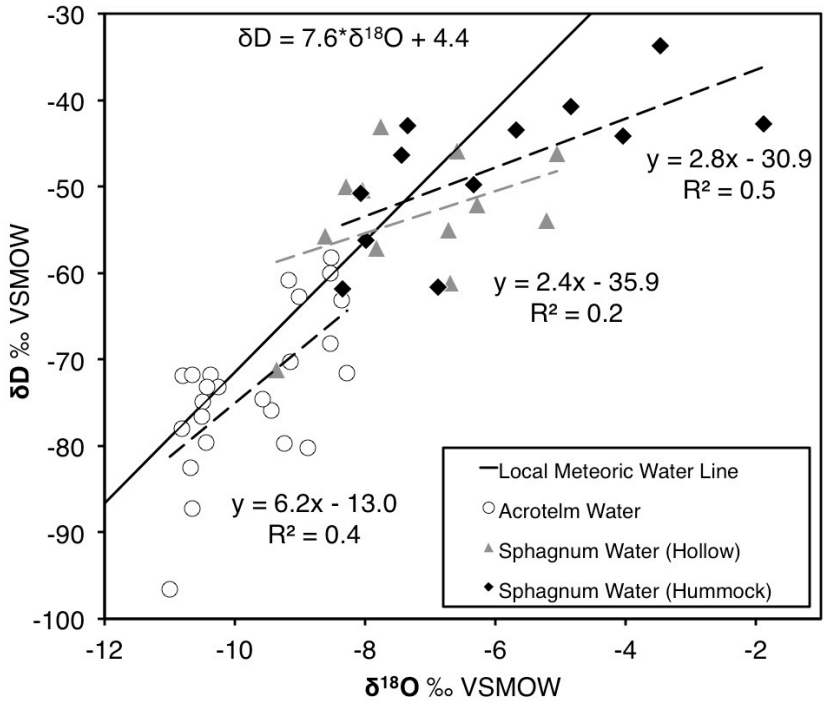

Figure 3: Water samples from a group of 18 peatlands in the Great Lakes region of the US. Black spots indicate samples from the acrotelms, while white and grey spots indicate water squeezed from sphagnum in hollow and hummock microhabitats respectively. While there is more scatter in this set of samples than in the set from a single peatland, it is still clear that sphagnum water is strongly evaporated, while acrotelm water clusters near the meteoric water line.

Using the data from these water samples, we developed a method to quantitatively reconstruct the fraction of water remaining after evaporation, f, from ombrotrophic peat bogs. We calculate this value using the hydrogen isotope enrichment between water used by *Sphagnum* and water used by vascular plants. *Sphagnum* water δD is reconstructed from measurements of sedimentary C_{23} *n*-alkane, a biomarker for *Sphagnum*, while acrotelm water δD is reconstructed from isotope ratio measurements of sedimentary C_{29} *n*-alkane, a biomarker for vascular plants. We then use a Rayleigh model (below) to estimate the amount of evaporation from the enrichment between these two water types (Nichols et al., 2010).

$$\ln f = \frac{\delta D_a - \delta D_s}{\varepsilon_k + \varepsilon^*}$$

where: δD_a = isotope ratio of acrotelm water (representing precipitation)
δD_s = isotope ratio of *Sphagnum* water
ε_k = kinetic enrichment factor = 3.125
ε^* = equilibrium enrichment factor = 86.731

Part II: Carbon isotopes of *Sphagnum* biomarkers

Previous studies have found that influence of methane release on the carbon isotopes of *Sphagnum* varies based on the microhabitat in which the *Sphagnum* grows (e.g. Markel et al., 2010). These studies include hummocks and hollows, but do not, however, typically include sedge tussocks. These are important microhabitats for the methane cycle, as sedges have arenchyma, which allow methane produced at depth to be released to the atmosphere efficiently. We analyzed carbon isotope ratios of *Sphagnum* and vascular plant leaf waxes (C_{23} *n*-alkane and C_{29} *n*-alkane respectively) from three peat monoliths sampled from three microhabitats, a dry, *Sphagnum magellanicum* dominated hummock, a moist, *Sphagnum capillifolium* dominated low lawn, and a moist, low lawn with abundant *Eriophorum vaginatum*, referred to here as the hummock, lawn, and tussock cores, respectively.

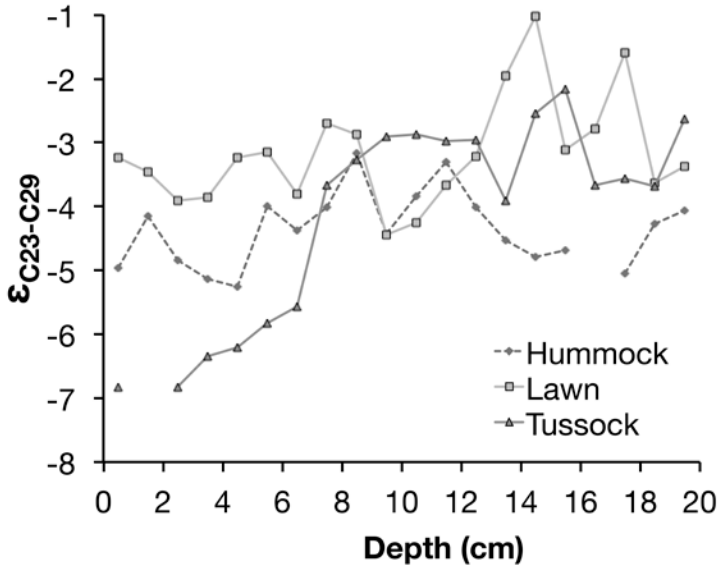

Figure 4: A plot of the enrichment factor between C23 n-alkane and C29 n-alkane. This enrichment represents the difference between the carbon isotope ratios of *Sphagnum* (producer of n-C23), which is affected by environmental parameters, and those of typical C3 vegetation (producers of n-C29), which are hypothesized to remain constant.

Carbon isotope values for vascular plant biomarkers, *n*-C_{29}, at all depths and at all sites averaged -33‰ ± 1.3, typical of C3 vegetation (Farquhar et al., 1989). Values for the $\delta^{13}C$ of *Sphagnum* biomarkers, *n*-C_{23}, were much more variable, and always depleted relative to *n*-C_{29}, showing the influence of methane-derived CO_2 in all three locations. By calculating an enrichment factor (ε) between the $\delta^{13}C$ of *n*-C_{23} and *n*-C_{29}, we can determine how much of the depletion of ^{13}C in *Sphagnum* leaf wax is due to factors other than C3 photosynthesis (i.e. water film thickness or contribution of respired methane). When plotted against depth, the enrichment factor between *n*-C_{23} and *n*-C_{29} exhibits no particular trend at the hummock or lawn sites, but at the tussock site, there is a strong stepwise depletion in carbon isotope ratios of *n*-C_{23} relative to *n*-C_{29} (Fig. 4).

The ages of these cores are not well constrained, but enough is known about the sedimentation rate from other studies of this peatland to estimate that the 20 centimeter monoliths represent approximately 40 years in total, with the upper 10 centimeters representing approximately 10 years (Talbot et al., 2010). Methane flux measuremnts made by the Fluxnet Canada program indicate an increase in methane release from the peatland since 2005, which could correspond with the strong decrease in $\delta^{13}C$ of *n*-C_{23} in the tussock microhabitat, indicating that this site may be the most sensitive to changes in methane flux. This is consistent with the observation that sedge tussocks are places where the most methane is released from Mer Bleue. We conclude that sedge tussock environments are the most promising locations for reconstructing past methane flux from peatlands using carbon isotope ratios of *Sphagnum* leaf waxes.

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