Response of carbon cycle to drier conditions in the mid-Holocene in central China

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The nature and extent to which hydrological changes induced by the Asian summer monsoon affected key biogeochemical processes remain poorly defined. This study explores the relationship between peatland drying and carbon cycling on centennial timescales in central China using lipid biomarkers. The difference between peat n-alkane $\delta^{2}$H and a nearby stalagmite $\delta^{18}$O record reveals that intervals of prominent peatland drying occurred during the mid-Holocene. Synchronous with these drier conditions, leaf wax $\delta^{13}$C values show large negative excursions, with the utilization of CO$_2$ respired from the peatland subsurface for plant photosynthesis being a possible mechanism. Crucially, successive drying events appear to have had a cumulative impact on the susceptibility of peat carbon stores to climate change. Concurrently, bacterially derived hopane $\delta^{13}$C values suggest the occurrence of enhanced methane oxidation during the drier periods. Collectively, these observations expand our understanding of how respiration and degradation of peat are enhanced during drying events.
Peatlands are a vast store of organic carbon and play a significant role in the global carbon cycle\textsuperscript{1,2}. The height of the water table in such environments is the primary influence on carbon degradation pathways and peatland carbon storage, exerting local control on redox conditions in the shallow subsurface\textsuperscript{3}. Hence, changes in peatland hydrology will impact carbon storage; for example, dry conditions associated with drought bring about depression of the water table, enhancing degradation of organic matter and release of CO\textsubscript{2} to the atmosphere\textsuperscript{4}. Because global warming is likely to produce more frequent and/or severe droughts in many regions\textsuperscript{5}, including in the monsoon region of China, it is crucial to better understand the relationship between hydrological change and the peatland carbon cycle across multiple timescales and particularly in regions expected to experience changing rainfall under future warming scenarios.

The hydrological impact on peatland carbon cycles, especially on varying timescales, continues to be debated. Even on annual timescales, the relationship between water-table lowering and soil organic carbon (SOC) dynamics in peatlands remains unclear; the conventional viewpoint is that drier conditions enhance SOC decomposition through the “enzyme latch” mechanism\textsuperscript{7}. In contrast, recent work proposed a new “iron gate” mechanism to interpret the negative relationship between water-table decline and SOC decomposition in settings with abundant iron\textsuperscript{8}. On longer timescales, our knowledge of how the peatland carbon cycle responds to drier conditions is even poorer, particularly in monsoon dominated regions\textsuperscript{9,10}. In East Asia, monsoon-mediated rainfall has varied both spatially and temporally since the late deglaciation\textsuperscript{9,10}, likely impacting the carbon cycle\textsuperscript{8}.

In this study, we examine the response of the carbon cycle in a central China peatland to hydrological change over the past 18 ky, but especially to dry intervals during the middle Holocene. During the mid-Holocene, pronounced drier conditions occurred commonly in Indian monsoon dominated regions\textsuperscript{11}. In eastern China, however, evidence for drier conditions during the mid-Holocene is limited, with most evidence coming from central China\textsuperscript{10,12}. The occurrence of such conditions in the middle Holocene in central China provides an opportunity to explore the relationship between paleohydrological conditions and the peatland carbon cycle.

The Dajiuhu peatland is a typical subtropical subalpine peatland in central China (Fig. 1)\textsuperscript{13}; and due to the monsoon-influenced climate, it was exposed to severe drying and flooding events\textsuperscript{12}. To reconstruct paleohydrological conditions, we determined the controls on hydrogen isotope compositions in modern pore water, plants, and peats; based on those constraints and radiocarbon chronology, we use the difference between Dajiuhu leaf wax hydrogen isotope compositions ($\delta^2$H\textsubscript{max}) and the nearby Sanbao stalagmite $\delta^{18}$O sequence\textsuperscript{14}, complemented by other biomarker indicators of vegetation and bacterial changes, to identify potential dry intervals in the Dajiuhu sequence over the past 18 ky. These records are then integrated with $\delta^{13}$C values for the same leaf waxes, as well as those of bacterially derived hopanes and carbon accumulation rates, to explore the response of peatland carbon cycle to drier conditions in the middle Holocene. Collectively, this study shows that the peatland carbon cycle is strongly sensitive to paleohydrological changes, expanding our understanding of how respiration and degradation of peat are enhanced during dry intervals.

Results

$\delta^2$H values of pore water and surface peat and modern plant lipids. The 1-year monitoring of pore water $\delta^2$H ($\delta^2$H\textsubscript{pw}) values in Dajiuhu reveals a clear depth pattern (Fig. 2). The $\delta^2$H\textsubscript{pw} values in the surface 30 cm are highly variable, whereas the $\delta^2$H\textsubscript{pw} values are stable at depths from 50 to 160 cm throughout the year. In 2015, the mean $\delta^2$H\textsubscript{pw} value in the upper 30 cm ($-46\%$; $n = 50$) was significantly different ($t$-test, $p < 0.0001$) from the mean $\delta^2$H\textsubscript{pw} value for 50–160 cm ($-56\%$; $n = 69$). Moreover, both the shallow and deep pore water mean $\delta^2$H\textsubscript{pw} values were enriched relative to the yearly averaged $\delta^2$H value ($-64\%$) of Dajiuhu precipitation derived from the model of Bowen et al.\textsuperscript{15}. Modeled annual $\delta^2$H values of precipitation must be considered cautiously when applied to a specific site, especially at higher altitude locations; however, the $\delta^2$H values of precipitation measured in June and July 2015 (Supplementary Table 1) are similar or even lower (avg. $-82\%$) than those estimated from models. Such a difference between the mean $\delta^2$H\textsubscript{pw} and the actual rainfall $\delta$D data clearly indicates that the $\delta^2$H values of pore water are affected by evaporation.

Peat-forming plants uptake peat water as the hydrogen source for lipid biosynthesis. Previous studies have shown that leaf wax $\delta^2$H values can be affected by various physiological and environmental factors, such as plant life forms, leaf wax production time and regeneration rate, and evapotranspiration\textsuperscript{16,17}. Leaf samples of dominant herb species (Carex argyi, Sanguisorba officinalis, Euphorbia esula) in Dajiuhu exhibited a mean $n$-C\textsubscript{29} $\delta^2$H ($\delta^2$H\textsubscript{29}) value of $-198\%$ and a mean $n$-C\textsubscript{31} $\delta^2$H value of $-191\%$ during the mature stage in 2010 (July–September). The root depths of these herb species range from 12 to 29 cm ($n = 50$ for each species). Assuming the mean $\delta^2$H value...
δ⁰H₂⁰ value of the surface 30 cm represents the annual average, the hydrogen isotope fractionation from the pore water to leaf wax n-C₂₉ alkane ε alk/p is −159‰. Such a ε alk/p value is larger than a previously calculated value based on surface soil samples in eastern China (−130‰ to −140‰)¹⁸, and the biosynthesis value of forbs (−113‰ ± 31‰)¹⁶. These differences could result from the response of ε alk/p to plant habitat conditions (e.g., relative humidity and its impact on evapotranspiration), seasonality of leaf wax production¹⁹, or differences among plant species¹⁶.

Peat deposits always have very high organic matter contents (normally >30%; Fig. 3). In such a terrestrial setting, in situ peat-forming plants contribute almost all long-chain n-alkanes to the underlying peat horizons²⁰, ²¹. Consistent with this, in Dajiuhu, the mean δ²H value (−204‰)²² in surface peats (n = 26) is indistinguishable from those of the plant leaves, indicating an isotopic signal inherited from leaves, without a significant alteration during early diagenesis. Collectively, these observations mean that sedimentary leaf wax δ²H values record those of the peat-forming plants, which in turn appear to be strongly governed by both evaporative and evaporational processes.

Fig. 3 Variations of TOC and n-alkane ratios in the ZK-5 peat core. a TOC. b ACL. c C₂₃/C₂₉ ratio. d Pₐ₉

δ¹³C values of C₂₉ alkane (δ₁³C) range from −22.5‰ to −30.9‰, which is 5-6‰ higher than those of the long-chain n-alkanes (Supplementary Table 4). These δ¹³C variations normally occur rapidly. For example, in the interval from 4.5 to 3.5 ky, the δ¹³C values decrease by 5% in 100–200 years. These variations are larger than those observed in other investigations of Holocene peat vegetation²⁹–³¹.

Hopane δ¹³C values in the peat core. Hopane concentrations in the ZK-5 core are high but variable. The distribution is dominated by the 17α,21β(H)-homohopane with an R-configuration at C-22 (C₃₁ αβ) (Supplementary Fig. 3), consistent with a previous study in Dajiuhu on a different core (ZK-3)³² and other investigations of peat deposits²⁹, ³⁰, ³¹. Throughout the whole 18 ky, the δ¹³C values of the C₃₁ αβ homohopane (δ¹³C₃₁αβ) range from −22.5‰ to −30.9‰, which is 5-6‰ higher than those of the long-chain n-alkanes (Supplementary Table 4). These isotopic signatures are consistent with previous reports from other peats²⁰, ²⁶, ³⁰, ³³, ³⁴. The 17β,21β(H)-norhopane (C₂₉ ββ) is also present but less abundant than the 17α,21β(H)-homohopane; it generally has lower and more variable δ¹³C values than the C₃₁ αβ hopane (Fig. 6). Over the whole 18 ky, the δ¹³C values of C₂₉ ββ (δ¹³C₂₉ββ) do not show any clear temporal trend, but are characterized by lower values from 15 to 11.5 ky and a highly variable interval from 9 to 3 ky (Fig. 5).

Discussion

In this study, to explore the relationship between peatland carbon cycle and drier conditions, we combine leaf wax hydrogen and carbon isotope analyses on the same compounds in the same samples, which minimize the influence of other factors, such as vegetation source and sedimentological leads and lags that will affect, for example, microbial biomarkers²⁸, ³⁵. Leaf wax δ²H values reveal both changes in water source on glacial–interglacial timescales and in response to Holocene dry intervals. During photosynthesis, terrestrial plants utilize soil water as their major H source, thereby recording the isotopic signatures of the source water, i.e., precipitation (δ²H). Leaf wax δ²H values are affected by additional factors, such as soil...
evaporation, and leaf transpiration, as well as plant-specific physiological and biochemical differences. In peat deposits, in situ peat-forming plants, especially herbaceous subaerial plants (C3 plants), are the predominant contributor of long-chain n-alkanes, which has also been confirmed by our previous study at Dajiuhu. Such an inference is further supported by the n-alkane ratios, which reveal a predominance of vascular plants rather than Sphagnum during much of the Holocene and especially the last 9 ky (Fig. 3). Moreover, where biomarkers indicate changes in peat-forming plant distributions (Fig. 3 and see below), they are not correlated with leaf wax δ2H values and certainly do not appear to be driving variations in those values. This likely reflects the narrower range of sources for the high-molecular-weight leaf waxes, C3 herb plants that generally exhibit a narrow range of apparent hydrogen isotope fractionation between source water and wax lipids. Thus, variations in plant life forms appear to be not an important control on δ2H variations in the ZK-5 δ2H sequence.

The broad match (r = 0.63, p < 0.001) between the ZK-5 δ2H sequence and the nearby Sanbao Cave (<50 km) δ18O carbonate record is consistent with vapor source being an important factor controlling the ZK-5 δ2H values on millennial timescales (Fig. 4). This inference is further supported by the first order similarity to the δ2H wax record from the Bengal Bay, an important vapor source for the East Asia region.

However, prominent differences exist between the Sanbao calcite δ18O and the ZK-5 δ2H records, exemplified by large variations in the Δδ2H between the two sites (determined by converting the former into meteoric δ2H values, Fig. 4), especially during the 7.4–3 ky interval. This indicates that factors other than vapor source control the δ2H variations at Dajiuhu. Relative humidity, via its influence on evaporation and/or evapotranspiration, is a likely factor. Peats are known to be particularly sensitive to changes in evaporative water balance, and therefore, it is unsurprising that the Dajiuhu sequence exhibits variability not observed for the Sanbao Cave (for more detailed discussion, please refer the Supplementary Note 1). This is supported by the modern vertical profile of δ2Hw values, in which the upper layers are seasonally variable and 2H-enriched relative to deeper sections (Fig. 2) and precipitation water, presumably due to evaporative enrichment.

An interval of relatively drier conditions in the mid-Holocene Dajiuhu sequence is further supported by biomarker indicators of vegetation (Fig. 3). Leaf wax indicators of peat vegetation change must be used with caution, but in the Dajiuhu peat sequence they exhibit significant changes that could reflect changes in the
relative importance of Sphagnum species (high $n$-C$_{29}$/n-C$_{23}$ ratios and high $P_{aq}$ indices), which tend to dominate under wetter conditions. Both indices are low over the past 9 ky and especially from 9 to 5 ky. This corresponds with but slightly precedes $\delta^2$H evidence for dry conditions, suggesting different climatic thresholds for vegetation change. Additional evidence for mid-Holocene aridity is provided by hopanoid abundances in the adjacent ZK-3 core (Supplementary Fig. 5). In the Dajiuhu peatland, hopanoids are mainly biosynthesized by aerobic bacteria, such that hopanoid concentrations serve as a proxy for water-table depth, i.e., high-hopanoid abundances are indicative of a deeper water table and aerobic conditions. High abundances are associated with high $\Delta\delta^2$H$_{29}$ values and low inferred relative humidity (Fig. 4), and both proxies indicate prolonged drier conditions at 11.6–10.6 ky, and 7–3 ky.

It is unclear if mid-Holocene drier conditions in the Dajiuhu peat sequence reflect a regional climate event and again we note that they are not documented in the Sanbao calcite $\delta^{18}$O record. However, a prolonged drying, and perhaps even drought, during the mid-Holocene has also been inferred from the IRM$_{soft-flux}$ in speleothems of central China. This proxy records the flux of soil-derived magnetic minerals and correlates with rainfall amount and intensity, and in particular ENSO-related storms. During 6.7–3.4 ky, IRM$_{soft-flux}$ exhibits lower values, suggesting drier conditions. A synthesis of paleoenvironmental investigations in the Poyang Basin, central China, also demonstrates drier conditions during 6.0–3.6 ka. Modeling further supports the conclusion that drier conditions prevailed in central China during the mid-Holocene. A review of the mid-Holocene dry climate was recently presented in Liu et al.

The drier conditions during the mid-Holocene in central China contrast with the proposed wet interval of 8–3 ky in the north and the south of China. A previous study interpreted such a spatial pattern as the influence of the western Pacific subtropical high (WPSH) and the associated ENSO variance. During the mid-Holocene, the west–east surface sea temperature gradient was strong, and thus the average position of WPSH would have moved north and west, such that the middle and lower reaches of the Yangtze River became dominated by downdraft. In fact, a similar mechanism has been proposed to interpret the negative relationship between precipitation in the middle and lower reaches of the Yangtze River and the summer monsoon intensity on decadal timescales.
In the middle Holocene, multiple strong but brief positive $\Delta$H shifts occurred (Fig. 4). The three most prominent $\Delta$H intervals (20–40%, centered at 7.2, 5.6, and 4.4 ky, correspond to high-hopanoid concentrations and inferred drier conditions12 (Fig. 4). The occurrence of prominent drier conditions in the middle Holocene provides an opportunity to explore the relationship between paleohydrological conditions and the peatland carbon cycle. The most direct evidence for this impact is documented by prolonged low carbon accumulation rates from about 9 to 3.5 ky (Fig. 5) in the ZK-5 core. This likely reflects a combination of decreased production and increased respiration, collectively leading to decreased carbon storage. The leaf wax and bacterial biomarker carbon isotopic signatures provide additional insights into changes in carbon cycling during the mid-Holocene dry interval. For C3 plants, leaf $\delta^{13}$C values are mainly governed by the air isotopic composition and isotopic discrimination during photosynthesis ($\varepsilon_p$)48. Over the last 18 ky, atmospheric CO2 $\delta^{13}$C has changed by <1‰28, far too low to account for the shifts observed here. Moreover, although CO2 concentrations have changed slightly and these affect $\varepsilon_p$ values, the effect is likely to have been small49, especially during the Holocene. Similarly, $\varepsilon_p$ is sensitive to water stress with dry periods associated with decreased $\varepsilon_p$ and, therefore, high plant $\delta^{13}$C values50. It is unexpected, therefore, that during the drier episodes of the mid-Holocene, leaf wax $\delta^{13}$C values always display negative excursions (Fig. 5). In addition, vegetation shifts inferred from palynological data51 or leaf wax distributions (Fig. 3) do not match the $\delta^{13}$C variations.

Consequently, we argue that some of the large shifts in leaf wax $\delta^{13}$C values record changes in peatland carbon cycling, in particular increased plant uptake of respired CO2 during dry intervals. Dry intervals can be associated with enhanced peat degradation5, and previous studies have proposed that reoxidation of microbially respired CO2 is an important mechanism to maintain the higher primary productivity in peat bogs52–54. Such respired CO2 will have $\delta^{13}$C values close to the $\delta^{13}$C values of bulk OM55 and much lower than that of atmospheric CO256. Each of the three Holocene positive $\Delta$H shifts is associated with a decrease in leaf wax $\delta^{13}$C values. Increased microbial respiration under warmer and drier climate conditions, by increasing the release of $^{13}$C-depleted CO2 available for photosynthesis56, 57, provides a mechanistic link between these observations. This is also consistent with the lower TOC contents and peat accumulation rates from 9 to 3.5 ky (Fig. 5). However, not all episodes of $^{13}$C depletion are associated with inferred drier intervals, indicating that the relationship between the two was likely nonlinear and/or that other factors govern some of the $\delta^{13}$C variability in the Dajiuhu peat.

Throughout the interval of inferred dry (but variable) conditions in the mid-Holocene, the amplitudes of the negative $\delta^{13}$Cexcursions become larger over time; consequently, a relatively minor positive $\Delta$H excursion at 3.4 ky is associated with a large 4.6‰ $\delta^{13}$C shift (Fig. 5). Such a pattern suggests that the supply of respired CO2 could be sensitive to the cumulative effect of drying cycles, rather than simply linearly responding to a single event. Fenner and Freeman5 observed an increase of carbon losses from peat exposed to climatic variation and suggested that severe drying and subsequent rewetting would destabilize peatland carbon stocks. More contemporary studies emphasize the importance of drying–rewetting on peatland carbon dynamics58. As such, the nonlinear coupling of leaf wax carbon and hydrogen isotope ratios suggests that multiple drying cycles led to destabilization of Dajiuhu peat stock and pulses of organic matter respiration on centennial–millennial scales.

The influence of drier conditions on peatland carbon cycling is further evidenced by the carbon isotope shifts of bacterially derived hopanes. The controls on hopane carbon isotopic compositions are complex33, but previous work on peats suggests that the balance between heterotrophic (including the carbon isotopic composition of different substrates) and methanotrophy is crucial59. This is likely true in Dajiuhu, where hopanoids are mainly biosynthesized by aerobic bacteria (based on analyses of sqhC genes12, 60). However, the C29 $\beta^\beta$ hopane is both more $^{13}$C-depleted and more isotopically variable than the two C31 hopane isomers (Fig. 6 and Supplementary Fig. 4).

Previous studies reveal that the carbon isotope offset between C31 $\alpha^\beta$ homohopane and leaf wax $n$-alkanes is commonly between 4 and 6‰29. Consistent with this, in the modern surface peats collected from Dajiuhu in July 2012, the C31 $\alpha^\beta$ homohopane is 6–7‰ enriched relative to the C29 $n$-alkane. This offset suggests that hopane-producing bacteria in acidic peats are probably heterotrophic and utilizing isotopically heavy carbohydrates as their major substrate29, 33. However, from the late glacial to the late Holocene, the $\delta^{13}$C values increase by 2–3% (Supplementary Fig. 4), whereas those of the leaf waxes decrease. This isotopic decoupling between the putative organic matter source and the consumer bacteria could arise from a number of factors, but we tentatively propose that it reflects the temperature control on substrate availability. Under cooler climatic conditions, we suggest that lower rates of respiration are associated with a reduced bias toward microbial assimilation of carbohydrates.

In contrast, $\delta^{13}$C values of the C29 $\beta^\beta$ hopane, while also being lower in the glacial interval than the Holocene, exhibit a depth profile dominated by profound variability from 9 to 3 ky (in fact,
the C₃₃ haptanes also exhibit stronger variability during this interval, although less pronounced than for the C₃₀ haptane). The dramatic variability appears to be broadly associated with the drier interval, with δ¹³C values decreasing by up to 10‰, to values as low as −40‰ (Fig. 5). The interval of lowest δ¹³C values is deeper than the drier interval and individual shifts are not directly correlated to shifts in δ¹⁸O; this is likely due to depth offset, due to bacteria living in subsurface layers. This would be especially true for transient dry events, which would allow haptanoid-producing bacteria to periodically thrive in aerated regions of deeper peat. Consequently, haptane carbon isotope signals appear to stratigraphically lead the dry events recorded by δ¹⁸O.

Shifts to such low δ¹³C values are difficult to explain via changes in organic matter sources (and in fact, in some cases, δ¹³C values are 4–6‰ lower than those of the n-alkanes), and instead likely reveal contributions from δ¹³C-depleted methanotrophic bacteria during dry intervals. An increased methanotroph contribution during a dry interval seems counter-intuitive, as a low water table is likely associated with reduced rates of methanogenesis; however, it is similar to findings from a recent study of the Hongyuan peat sequence, southwest China, which revealed very low diploptene δ¹³C values during a dry interval of the mid-Holocene. In that work, the low δ¹³C values were attributed to more diffuse flux of methane during dry intervals (as opposed to root-mediated transport), which could have facilitated growth of methanotrophs. Alternatively, the low δ¹³C values could arise from changes in the abundance of Sphagnum symbiotic methanotrophs, which are known to produce C₁₃ hopanes. However, such a possibility is not supported by the n-alkane ratios during the drier interval in the mid-Holocene, which reveal a low contribution from Sphagnum (Fig. 3). In addition, symbiotic methanotrophs associated with Sphagnum are more active in wetter conditions.

By integrating multiple isotope records, this work provides new evidence for Chinese drier intervals on centennial–millennial timescales, as well as direct evidence that these drier conditions impacted the peatland carbon cycle. The difference between peat leaf wax δD values and the nearby cave calcite δ¹⁸O record reveals that prominent drier intervals, centered at 7.2, 5.6, 4.4, and 3.4 ky, occurred during the mid-Holocene in central China. This conclusion is reinforced by an absence of Sphagnum species during this interval and elevated abundances of haptanoids of putative aerobic bacteria origin. Corresponding to these drier intervals, carbon accumulation rates are very low and leaf wax δ¹³C values decrease markedly, opposite to the expected effect of decreased moisture, suggesting an increase in photosynthetic assimilation by the bog vegetation of isotopically depleted CO₂ derived from microbial respiration within the peat. The magnitude of the leaf wax δ¹³C perturbations increases with successive drying cycles, indicating a cumulative effect of drier conditions on peatland carbon dynamics. At approximately the same time, carbon isotope ratios of bacterial biomarkers, especially those of C₂₉ ββ haptane, become much more variable, providing further evidence of a perturbed carbon cycle, which we attribute to changes in the dynamics of perturbed carbon production, flux, and consumption. Collectively, these processes resulted in a dramatic reduction in carbon accumulation rates, such that this work directly demonstrates that the peatland carbon cycle is sensitive to paleohydrological changes on long-term, centennial to millennial timescales.

Methods

Site description. Dajiuhu is a closed subalpine basin located in the middle reaches of the Yangtze River, central China. This basin has a mean elevation of 1730 m and a total area of 16 km². Since the late deglaciation, peat developed in this basin to a depth of 2–3 m. The modern dominant peat-forming plants include sedge species, S. officinalis, and Sphagnum palustre. Water in this basin is drained through the Da River. Climate in this region is controlled by the Asian monsoon, with hot-wet summers and cold-dry winters, mean annual precipitation of 1560 mm and mean annual temperature of 7.2 °C. This region is located at the transition from the eastern lowland to the western highland, making it particularly sensitive to climate changes.

AMS ¹⁴C dating and chronology. The chronology of ZK-5 is based on the ¹⁴C accelerator mass spectrometer (AMS) analyses of 20 organic sediments (Supplementary Table S1). AMS measurements were conducted at Beta AMS Lab (Miami, USA). Following the study of Zhou et al., the 90–300 μm fraction was sieved from the bulk samples, and then subjected to an acid–alkali–acid treatment before AMS analysis. The calendar age was calibrated using the clam age-depth model (Supplementary Fig. 6).

Lipid extraction and analysis. Freeze-dried peat samples were ground to pass a 60-mesh sieve (0.18 mm) and were ultrasonically extracted 6 × 10 min with dichloromethane/methanol (9:1, v/v). The apolar fraction was isolated by elution from a silica gel chromatographic column with hexane. Gas chromatography–mass spectrometry analysis for the apolar fraction was conducted with an Agilent 6890 gas chromatograph interfaced with an Agilent 5973 mass selective detector, with the instrumental conditions identical with the previous study. Compound-specific hydrogen isotope compositions of n-alkanes were determined using a Trace GC coupled with a Delta V Advantage isotope ratio mass spectrometer. To check the reliability of the δD determinations, an n-alkane suite (n-C₁₃, n-C₁₉, n-C₂₇, and n-C₃₁, alkane) and the Indiana A4 mixture with known δH values were analyzed in every two samples. Squalane (δD = 167‰) was used as the internal standard.

Standard deviation for hydrogen isotope analysis was better than ±5‰, based on at least duplicate analyses. Results are reported in the delta notation (‰) relative to the Vienna Standard Mean Ocean Water standard.

Compound-specific carbon isotope analysis was conducted using a Finnigan Trace GC attached to a Finnigan Delta Plus XP isotope ratio mass spectrometer, equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm). The injector temperature was set at 270 °C. The GC oven temperature was initially at 50 °C (held 1 min), then ramped to 220 °C at a rate of 10 °C min⁻¹, and then ramped to 300 °C at a rate of 2 °C min⁻¹ (held 2 min), followed by further ramped to 350 °C at a rate of 2 °C min⁻¹, and finally to 370 °C at a rate of 0.5 °C min⁻¹ (held 10 min). The hydrogen was used as the carrier gas (1.4 ml min⁻¹). The combustion oven was set at 950 °C. Instrument performance was verified before and after each sample run using an n-alkane standard mixture with known δ¹³C values (n-C₁₃–n-C₃₃, Indiana University). Reproducibility for specific compounds was better than ±0.5‰ (standard deviation), based on at least duplicate analyses. Results are reported in the delta notation (‰) relative to the VPDB standard.

Calculations of the n-alkane ratios. The ACL, CPI, and Pₚ were calculated using the following equations:

\[
ACL = \frac{21C_{21} + 23C_{22} + 25C_{23} + 27C_{27} + 29C_{29} + 31C_{31} + 33C_{33}}{C_{21} + C_{22} + C_{23} + C_{27} + C_{29} + C_{31} + C_{33}}
\]

(1)

\[
CPI = \frac{(C_{21} + C_{23} + C_{27} + C_{29} + C_{31}) + (C_{22} + C_{25} + C_{27} + C_{29} + C_{31}) + (C_{22} + C_{25} + C_{27} + C_{29} + C_{31})}{C_{22} + C_{24} + C_{26} + C_{28} + C_{30}}
\]

(2)

\[
P_{\mu} = \frac{C_{21} + C_{25}}{C_{23} + C_{27} + C_{29} + C_{31}}
\]

(3)

Sampling of water and δD analysis. Peat pore waters were obtained from Dajiuhu during five sampling trips in 2015. These samples were collected using a MacroRhizon soil moisture sampler (with a length of 10 cm and pore size of 0.2 μm; Rhizophere Research Products B.V., The Netherlands). The samplers were established at five different depths (0–10, 20–30, 50–60, 100–110, and 150–160 cm (except April, for which 150–160 cm was not collected)) at five locations. During June and July 2015, rainfall samples were collected using a 1000-ml flask, blocked with a ping-pong ball on the bottleneck. During water collection, olefin was added to prevent water evaporation.

The hydrogen isotopic compositions of the peat pore waters and rainfall were analyzed using an IWA-35 EP Liquid Water Isotope Analyzer (LGR, USA) at the State Key Laboratory of Biogeology and Environmental Geology. The analytical precision was better than 0.2‰ for δD and 0.6‰ for δ¹³C. Data for the batch of water samples collected in October 2015 have been published in Huang et al.
Total organic carbon concentration analysis. The peat samples were first freeze-dried and then ground to fine powder (<100 mesh) and homogenized. The total organic carbon concentration was measured on the Vario MICRO cube Element Analyzer.

Calculation of carbon accumulation rate. The method was followed reference 7:

\[ \text{Accumulation rate} = \frac{\text{mass of carbon}}{\text{area} \times \text{time}} \]

\[ \text{Accumulation rate} = \frac{\text{mass of carbon}}{\text{area} \times \text{time}} \]

where mass of carbon is the total mass of carbon in the peat sample, area is the area of the peat sample, and time is the time period over which the peat sample was collected.

Calculation of $\Delta \delta^{18}O$. The $\Delta \delta^{18}O$ values were calculated using the equation:

\[ \Delta \delta^{18}O = \delta^{18}O_{\text{water}} - \delta^{18}O_{\text{plant}} \]

where $\delta^{18}O_{\text{water}}$ is the oxygen isotope composition of water, and $\delta^{18}O_{\text{plant}}$ is the oxygen isotope composition of the plant material.

Data availability. The data that support the findings of this study are included in the supplementary information files.

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Author contributions

X.H., J.X., and Y.G. performed the field work; J.X. and X.H. conducted biomarker and water isotope composition measurement and analysis. S.X. and X.H. designed the project. The manuscript was written by X.H., R.D.P., R.P.E. and S.X. with contributions from all authors.

Additional information

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