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Paleoclimate significance of *n*-alkane molecular distributions and δ^2H values in surface peats across the monsoon region of China

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ABSTRACT

Leaf wax molecular distributions and isotopic values are generally considered paleohydrologic proxies. Here we evaluate the sensitivity of alkane chain length distributions and compound-specific hydrogen isotopic compositions (δ^2H_{alk}) in surface peats to environmental parameters across the monsoon region of China. The alkane average chain length (ACL), carbon predominance index (CPI) and δ^2H_{alk} values show relatively large variations in multiple samples from a single site, highlighting the complexity of the processes affecting these ratios at small spatial scales. Nonetheless, the site-averaged CPI values correlate significantly with the mean annual temperature ($r = -0.57$, $p(\alpha) < 0.001$) and precipitation ($r = -0.53$, $p(\alpha) < 0.001$), suggesting that climate is important to control CPI values, together with other influences. The large variation of δ^2H_{alk} values in a single peatland suggests that δ^2H_{alk} values may be affected by factors in addition to biosynthetic isotopic discrimination and the D/H ratio of the water available to the plants. It is interesting to note that the site-averaged δ^2H_{alk} values correlate poorly with the modeled yearly δ^2H_p values. In addition, the site-averaged apparent hydrogen isotope fractionation between C_{31} *n*-alkanes and precipitation correlates with mean annual temperature. Together, our results show a relatively complex spatial pattern of δ^2H_{alk} values in a single peatland or along a climate transection. Thus, we caution that δ^2H_{alk} values would be affected by a series of factors, including the growth season length, the lipid synthesis time, the plant life forms, and/or the hydrogen isotope discrimination during lipid biosynthesis. More study is clearly required to elucidate the major controllers.

1. Introduction

Paleohydrologic reconstructions are a major component of Quaternary paleoclimate change studies. During the past several decades, leaf wax hydrogen isotopic compositions have become established as a powerful paleohydrologic tool (e.g. Sachse et al., 2012 and references therein). Leaf wax δ^2H ratios generally reflect the isotopic compositions of local meteoric water (δ^2H_p), which is the major water source for plant photosynthesis, but they are also affected by other factors (e.g. plant life forms, evaporation; Sachse et al., 2012). Therefore, leaf wax δ^2H ratios in geological archives have the potential to reflect the δ^2H_p values of the past and the associated paleoenvironmental factors that may have modified them.

In low latitude areas, δ^2H_p ratios are mainly affected by the "amount effect" (Dansgaard, 1964), and therefore leaf wax δ^2H values are generally interpreted as recording the precipitation amount or the relative humidity (e.g. Tierney et al., 2008; Schefuß et al., 2011; Contreras-Rosales et al., 2014; Sarkar et al., 2015). In contrast, the "temperature effect" mainly controls δ^2H_p values in high latitude regions. Modern lake sediment investigations in western Europe (Sachse et al., 2004) and North America (Hou et al., 2007; Thomas et al., 2012; Shanahan et al., 2013) have confirmed that leaf wax δ^2H values could provide evidence of past temperature changes.

In the middle latitude regions, such as the monsoon region of China, leaf wax *n*-alkane δ^2H (δ^2H_{alk}) and *n*-alkanoic acid δ^2H ratios have been widely applied for paleoclimate reconstructions (Liu and Huang, 2005; Seki et al., 2009, 2011; Aichner et al., 2010; Li et al., 2013, 2015; Patalano et al., 2015; Yao et al., 2015; Günther et al., 2016; Rao et al., 2016; Thomas et al., 2016; Witt et al., 2016). However, some of the interpretations of the leaf wax δ^2H ratios in these studies are inconsistent. On centennial to millennial timescales, Liu and Huang (2005) interpreted δ^2H_{alk} ratios in a soil sequence from the Chinese Loess Plateau as reflecting the combined effects of aridity, temperature and monsoon intensity, the latter two factors controlling δ^2H_p values of the water available to plants. In a somewhat related fashion, Yao et al. (2015) concluded that the combined effects of evapotranspiration and rainfall amount were the primary factors affecting δ^2H_{alk} values of a 2000-year sediment record from Poyang Lake, China. However, Li et al.

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(2013) attributed changes in δ^2H_{alk} values in a Taiwan peat deposit as reflecting paleotemperature changes. Other studies (e.g. Aichner et al., 2010; Seki et al., 2011; Günther et al., 2013, 2016; Patalano et al., 2015; Jin et al., 2016) concluded that plant wax δ^2H values integrated multiple environmental factors, including the origin of the water vapor, temperature-influenced evaporation, and the amount of precipitation. Hence, further investigation of modern settings is important to elucidate the dominant controllers on leaf wax δ^2H ratios.

In the monsoon region of China, previous studies have mainly investigated leaf wax δ^2H ratios in modern soils for the purpose of paleoelevation reconstructions (Jia et al., 2008; Luo et al., 2011; Zhang and Liu, 2011; Bai et al., 2011, 2012, 2015). Some studies have elaborated on the relationship between leaf wax δ^2H ratios and environmental factors in surface lake sediments from the Tibetan Plateau (Mügler et al., 2008; Xia et al., 2008; Aichner et al., 2010; Günther et al., 2013; Liu et al., 2016). However, only a few studies to date have investigated leaf wax δ^2H values in modern soils and lake sediments in eastern China. As an example, Rao et al. (2009a) studied δ^2H compositions of long-chain *n*-alkanes across a climate gradient in eastern China (18°N–50°N) and concluded that δ^2H_{alk} values have the potential to record δ^2H_p.

Peatlands are waterlogged continental settings whose evolutions are closely associated with hydrologic conditions (Charman, 2002). Hence, this kind of archive is well-suited for paleohydrologic reconstructions based on leaf wax δ^2H values. Xie et al. (2000) pioneered this approach in their description of a two-century-long leaf wax δ^2H sequence from the Bolton Fell Moss, Cumbria, UK. Nichols et al. (2010) discussed the differences in hydrogen isotopic values of *Sphagnum* and vascular plant biomarkers in common cores from North American ombrotrophic peatlands. Schemmel et al. (2016) interpreted changes in plant wax δ^2H values from a peatland in Greece to reflect changing Eastern Mediterranean atmospheric circulation patterns during the 8.2 ka climatic event. In the monsoon region of China, Seki et al. (2009, 2011) used differences between δ^2H values of leaf waxes from submerged and subaerial plants to reconstruct the differences in Holocene paleoclimate changes in two areas of China.

Other than δ^2H_{alk}, several *n*-alkane ratios such as the carbon predominance index (CPI), average chain length (ACL), and the proportion of aqueous plants ratio (P_{aq}) have also been widely applied for paleoclimate reconstructions from peat deposits (e.g. Zhou et al., 2005; Nichols et al., 2006; Zheng et al., 2007; He et al., 2015; Ortiz et al., 2016). These alkane ratios will be affected by multi-factors, including vegetation community, temperature, and the relative humidity (RH; Rao et al., 2009b; Bush and McInerney, 2013; Freeman and Pancost, 2014). To date, no study has evaluated their utility in peat deposits through the investigation of modern processes.

In China, peatlands are mainly clustered in the northeast and southwest, with a few scattered in the vast eastern lowlands (Chai, 1981). Because of greater human impacts in the eastern lowlands, only a few subalpine peatlands remain in relatively pristine conditions. In this study, seven peatlands were selected across the monsoon region of China, all with relatively low amounts of human disturbance, to study the spatial variations of leaf wax δ^2H values. The aim was to learn more about how modern climate affects leaf wax molecular distributions and δ^2H values.

2. Materials and methods

2.1. Sampling

The seven peatlands selected for this study (Fig. 1; Table 1) are all located in the monsoon region of China, with a warm and wet summer and a cool and dry winter. In the climate zonation of China, all of the seven peatland sites are characterized as humid (Ding et al., 2013). For detailed information about the vegetation community in Zoigê, Hani, Dajiuhu and Shiwangutian, please refer to Huang et al. (2015). Vegetation at Zoigê is dominated by sedges (Zhao et al., 1999). The vegetation at the other sites is mostly *Sphagnum* spp. with varying proportions of sedges and other subaerial plants. In Yichun, vegetation is dominated by *Larix gmelini*, *Sphagnum* spp., *Ledum palustre*, *Vaccinium uliginosum*, and sedge spp. (Zhao et al., 1999).

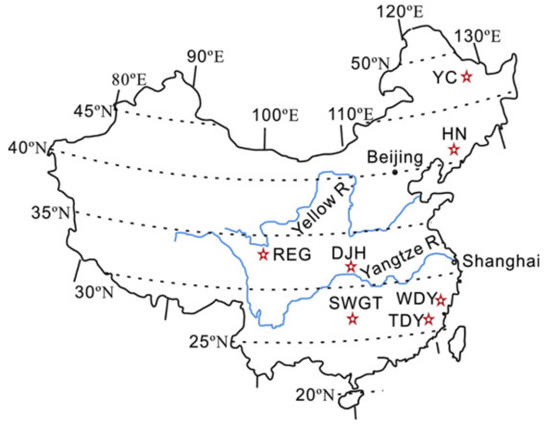

Fig. 1. Locations of the seven peatlands in the monsoon region of China mainland from which surface (0–2 cm) peat samples were collected.

In the six sites with abundant *Sphagnum*, peat samples were collected under living *Sphagnum* lawns. Surface samples (0–2 cm) from Dajiuhu were collected in July 2012 and from Hani, Zoigê and Shiwangutian in August 2013 as described in Huang et al. (2015). Surface samples (0–2 cm) were collected in Tiandouyang in October 2012, Wangdongyang in November 2012, and Yichun in July 2015. pH and oxidation-reduction potentials of peat water at each sampling site were measured using portable electrodes (Mettler Toledo, Swiss) for the six peatlands other than Yichun (Table 2), while the latter was done using a HQ 40d multi-parameter meter (Hach, U.S.A.). In this study, the water level was expressed as the depth from water surface to the peat surface (DWT-P) or to the moss top (DWT-M). In this case, the more positive values mean drier conditions, whereas more negative values mean wetter conditions. These details for Dajiuhu, Hani, Shiwangutian, and Zoigê have been presented in Huang et al. (2015).

During the field trip in October 2015, peat pore water samples were obtained from Dajiuhu. These samples were collected using a MacroRhizon soil moisture sampler (Rhizosphere Research Products B.V., Netherlands), with a ca. 10 cm porous section (0.2 μm in pore size). The sampling depths of five points were set as 0–10 cm, 20–30 cm, 50–60 cm, 100–110 cm, and 150–160 cm. The sampling depth of the other ten points was set at 0–10 cm.

2.2. Lipid extraction

The surface peat samples were first freeze-dried and then ground and sieved through an 80-mesh sieve (0.2 mm). About 0.5 g of the dried powdered peat was ultrasonically extracted 3× with dichloromethane/methanol (9:1, v/v) for 10 min. An internal standard of 5β(H)-cholane (Chiron, Norway) was added before extraction. After solvent removal under reduced pressure, the extract was fractionated into aliphatic and polar fractions using silica gel column chromatography, with *n*-hexane and methanol as elution solvents, respectively.

2.3. Instrumental analysis

The aliphatic fraction containing *n*-alkanes was analyzed in a Shimadzu GC-2010 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a DB-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The sample was injected in splitless mode with the injector temperature set at 300 °C. The initial oven temperature was 70 °C, which was held for 1 min, and then the oven was ramped to 210 °C at a rate of 10 °C min^{-1} and finally raised to 300 °C at a rate of