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Using $\delta D_{n\text{-alkane}}$ as a proxy for paleo-environmental reconstruction: A good choice to sample at the site dominated by woods

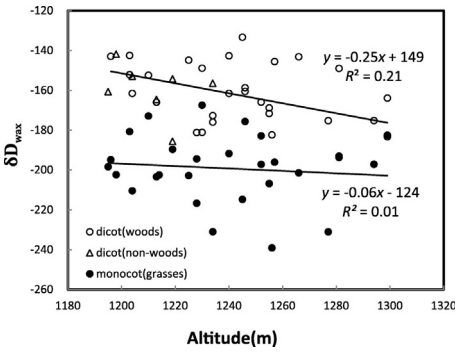
Jinzhao Liu [a,b,*], Zhisheng An [b], Zheng Wang [b], Huawu Wu [c]

[a] School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China
[c] Key Laboratory of Watershed Geographic Sciences, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China

HIGHLIGHTS

- We investigated plant and soil *n*-alkane δD values along different light slopes (sunny vs. cloudy) in different seasons (spring vs. autumn).
- Leaf wax $\delta D_{n\text{-alkane}}$ values were ca. 20‰ D-enriched in spring relative to autumn, whereas ca. 10‰ from the sunny slope relative to cloudy slope.
- Future sampling at a site dominated by woods is a good choice when *n*-alkane δD values are utilized for paleoenvironmental reconstruction.

GRAPHICAL ABSTRACT



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ABSTRACT

Some studies have demonstrated that leaf wax $\delta D_{n\text{-alkane}}$ values for a single species varied significantly with seasons. However, it is still not clear that the seasonality patterns of leaf wax $\delta D_{n\text{-alkane}}$ values in higher plants. Meanwhile, few efforts have been pursued to assess the effect of the light slopes (sunny vs. cloudy) on leaf wax $\delta D_{n\text{-alkane}}$ values. In this study, we systematically investigated plant wax $\delta D_{n\text{-alkane}}$ values and soil *n*-alkane δD values along different light slopes in different seasons (spring vs. autumn), as well as the relationship of *n*-alkane δD values between plant leaves and soil. We found that plant wax $\delta D_{n\text{-alkane}}$ values were D-enriched by ca. 20‰ in spring relative to autumn, and ca. 10‰ in the sunny slope than in the cloudy slope. Moreover, surface soil *n*-alkane δD values varied consistently with plant wax $\delta D_{n\text{-alkane}}$ values for different seasons and light slopes. More importantly, plant wax $\delta D_{n\text{-alkane}}$ values showed clear seasonal variations, but varied slightly with light slopes. The variations of plant wax $\delta D_{n\text{-alkane}}$ values can be recorded in soil *n*-alkane $\delta D_{n\text{-alkane}}$ values. In addition, we found that leaf wax $\delta D_{n\text{-alkane}}$ values in a majority of species differed significantly among woods, non-woods and grasses at a site. Therefore, we suggested a good choice to sample at the site dominated by woods when leaf wax $\delta D_{n\text{-alkane}}$ values are utilized as a proxy for the reconstruction of the paleoenvironment.

1. Introduction

Leaf wax, a major component of plant cuticle, forms at the interface between leaf and surrounding atmosphere (Hauke and Schreiber, 1998), which plays multiple physiological and ecological roles (Jetter

* Corresponding author at: School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, China.
E-mail address: liu.jin.zhao.am@stu.xjtu.edu.cn (J. Liu).

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and Schaffer, 2001) and provides a barrier against uncontrolled water loss, immoderate sunlight, and ultraviolet irradiation (Schreiber et al., 2001). Long chain alkanes (*n*-alkanes) with 27–35 carbons are biosynthesized as part of the cuticular leaf wax of terrestrial plants. They occur widely in leaves (Huang et al., 1995; Otto et al., 2005), soils and lacustrine sediments (Smith et al., 2007; Garcin et al., 2012), and can be easily extracted by chemical methods from plant leaves and sediments (Kahmen et al., 2011). Besides, they are resistant to microbial degradation (Bush and McInerney, 2013), and can keep the original isotope compositions stable for millions of years (Schimmelmann et al., 2006; Zhang and Liu, 2011; Osamu et al., 2012). Therefore, leaf wax *n*-alkanes are widely used for paleoenvironmental reconstruction.

Precipitation is provided as the only hydrogen source for most terrestrial plants (Sachse et al., 2006). A majority of studies have shown that leaf wax $\delta D_{n\text{-alkane}}$ values from modern plants and sediments are significantly correlated with precipitation δD values (Sachse et al., 2004; Liu et al., 2006; Liu and Yang, 2008; Collins et al., 2013). Leaf wax $\delta D_{n\text{-alkane}}$ values from plants or sediments can be an indicator of the intensity and origin of precipitation (Schefuss et al., 2005; Tierney et al., 2008). However, some recent studies have suggested that leaf wax $\delta D_{n\text{-alkane}}$ values from modern plants were significantly influenced by plant life forms based on ecosystem level, with grasses D-depleted vs. woody plants by 40–70‰ (Liu et al., 2006; Liu and Yang, 2008; Hou et al., 2007; Liu et al., 2015). More importantly, a reanalysis of an expanded database of available leaf wax $\delta D_{n\text{-alkane}}$ records in the Northern Hemisphere revealed that the difference in leaf wax $\delta D_{n\text{-alkane}}$ values among plant life forms (e.g., grasses, shrubs, trees, herbs, forbs, veins, ferns etc.) derived essentially from different plant taxonomic lineages (e.g., eudicots, monocots, gymnosperms) as a consequence of the biochemical level in higher plants (Liu et al., 2016). Additionally, light intensity, relative humidity (RH) and temperature have also been identified to have a modest effect on leaf wax $\delta D_{n\text{-alkane}}$ values (Baker, 1974; Giese, 1975; Kahmen et al., 2008). Therefore, the intensity and δD values of precipitation (manifested mainly by soil water as the water source) exert the first order of control on leaf wax $\delta D_{n\text{-alkane}}$ values, which are influenced by plant life forms, and some environmental factors (e.g., temperature, relative humidity, and light).

Previous studies have shown that leaf wax $\delta D_{n\text{-alkane}}$ values in single plants varied significantly on the order of 40‰ for *Spartina alterniflora* growing partially submerged in the seawater with a nearly unvarying isotopic composition (Sessions, 2006), and 20‰ for *Betula pendula*, *Populus tremuloides* and *Picea pungens* over the growing season although the isotopic composition of irrigated water remained relatively constant (Pedentchouk et al., 2008). Sachse et al. (2009) reported that two deciduous trees (i.e., *Acer pseudoplatanus* and *Fagus sylvatica*) in a temperate-humid climate exhibited large variations up to 40‰ on the short timescale of one week. Later, Sachse et al. (2010) showed that leaf wax $\delta D_{n\text{-alkane}}$ values from *Hordeum vulgar* in a field changed by ca. 20‰ during the period of two-month growing season, while source water (soil water) and leaf water varied by 40‰ over the same period. Recently, Tipple et al. (2013) observed that leaf wax $\delta D_{n\text{-alkane}}$ values in *Populus angustifolia* changed dramatically during leaf flush in the early growing season, and remained unchanged for the remainder of the growing season with constant source water. However, due to the lack of a systematical investigation of leaf wax $\delta D_{n\text{-alkane}}$ values from a majority of plant species in different seasons, it is still elusive whether leaf wax $\delta D_{n\text{-alkane}}$ values in higher plants show a clear seasonality, and how the soil *n*-alkane δD values are influenced by leaf wax $\delta D_{n\text{-alkane}}$ values from specific vegetation species?

In this study, we collected a great deal of plant materials and corresponding soil samples along different light slopes (sunny vs. cloudy) in different seasons (spring vs. autumn). To elucidate the variations of leaf wax $\delta D_{n\text{-alkane}}$ values from higher plants in different seasons and the relationship of *n*-alkane δD values between plant wax and soils, an observation of the δD values of plant wax and surface soil *n*-alkane in different seasons is necessary. Also, we investigated the effect of different light slopes on leaf wax $\delta D_{n\text{-alkane}}$ values in higher plants.

2. Materials and methods

2.1. Sampling

The study site Qiushui valley (36° 01′ N, 108° 06′ E; Fig. 1), in Heshui county in Gansu Province, is located in the middle of the Chinese Loess Plateau. The mean annual temperature is 7–10 °C with the mean annual precipitation 480–600 mm, which mainly occurs from July to September and contributes 58% to the annual total. Local precipitation shows an obvious unimodal distribution. Previous study suggested precipitation as the only source of water supply in the region (Lu, 2007).

We sampled materials from some dominant plants and the corresponding surface soil (0-5 cm) along different light slopes (sunny/cloudy; Fig. 1) in May (spring) and September (autumn), 2013. Plant leaf samples ($n = 37$ for spring; and $n = 28$ for autumn) and soil samples ($n = 12$ for the sunny slope; and $n = 14$ for the cloudy slope) were collected for δD determination. In different seasons, the dominant vegetation species vary dramatically along sunny or cloudy slopes (Table S1). To ensure the complete signal from the whole leaf, intact leaves were sampled in view of likely isotopic gradients within a leaf (Helliker and Ehleringer, 2000). All samples were immediately stored in a dry cooler (ca. 4 °C) in the field and transferred to the laboratory.

2.2. Soil water collection

Soil water was extracted by using the cryo-distillation devices (West et al., 2006). The extraction tube including soil samples was immerged in liquid N_2 for 5 min, then heated to 80 to 100 °C to allow evaporated water trapped in a U-tube submerged in liquid N_2. The extraction line was set at 0.02 mbar. Upon the finish of distillation, water in the U-tube trapper was collected in gas chromatography (GC) crimped cap vials (2 ml) and tightly sealed.

2.3. Lipid extraction

After plant and soil samples were oven dried at 40 °C in the laboratory, the soil samples (ca. 10 g) and plant leaf samples (ca. 2 g) were ultrasonically extracted (30 min × 3) with CH_2Cl_2/MeOH (9:1) at a 60 Hz vibrational frequency. The solvent was removed from the extract with a gentle N_2 stream and the *n*-alkane fraction was obtained using column chromatography (100–200 mesh silica gel) and elution with hexane.

2.4. Soil water analysis

Soil water were analyzed for δD values using a L2130-I isotope water analyzer (Picarro, Sunnyvale, CA, USA) at the Stable Isotope biogeochemistry Laboratory of the Institute of Earth Environment, Xi'an. Each sample was injected by six times, and the average of the last three measurements was adopted to calculate the raw value. Each sequence was calibrated using three different internal standards, which were periodically calibrated against the international Vienna Standard Mean Ocean Water (VSMOW). The Measurement precision for water δD analysis was 1‰.

2.5. Leaf wax and soil n-alkane hydrogen isotope analysis

The *n*-alkane fractions were analyzed using gas chromatography with an Agilent 6890 Series instrument equipped with a split injector, an Agilent HP1-ms column (60 m × 0.32 mm i.d., 0.25 μm film thickness) and a flame ionization detector (FID). For quantification, peak areas were compared with those from an external standard mixture (C_{21}–C_{33}, odd carbon numbers). The samples were injected in split mode, with a GC inlet temperature of 310 °C and a flow rate of