

Project report for “A critical examination on the climatic and environmental factors controlling the H isotopic fractionation between higher plant leaf waxes and precipitation”

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### **Research objectives:**

The main objective of the proposed research is to obtain values of the apparent hydrogen isotopic fractionation ( $\epsilon_{\text{wax-p}}$ ) between modern plant leaf waxes in aerosol, suspended solid and liquid particles in the atmosphere, and rainfall in the two highly contrasting climatic and environmental settings. As a collaborate research, the PI at Georgia Institute of Technology is responsible for collecting high quality aerosol and precipitation samples from the above two sites while the PI at Brown University examines the hydrogen isotopes in these samples. The results are critical when using leaf wax hydrogen isotopic data to reconstruct paleoclimatic records as  $\delta\text{D}$  values of plant leaf waxes represent a powerful and widely applicable proxy. Precipitation isotopic ratio has also been proposed to be one of the best proxies for quantitatively reconstructing continental paleoclimate. However, research is much needed for better understanding the hydrogen isotopic fractionation between leaf waxes and precipitation ( $\epsilon_{\text{wax-p}}$ ) under different climatic and environmental conditions. Therefore, we propose in this study to directly measure the  $\delta\text{D}$  values of leaf waxes from modern aerosol samples and precipitation samples from environments with different relative humidity including one site in Phoenix, Arizona and Atlanta, Georgia in the US. This is a preliminary research prior to fully examine samples from various sites globally and across significant vegetation and climate gradients.

### **Work carried out so far:**

Twenty-four hour PM<sub>2.5</sub> aerosol samples, particles with the aerodynamic diameter less than or equal to 10 micron, were collected using a high volume sampler at a flow rate of 1.13 m<sup>3</sup>/min (Thermo Scientific, Inc.) on the top of a building (20 m above

ground) at Georgia Institute of Technology during the summer of 2010. Simultaneous sampling of aerosol samples was carried out on the top of a 12-m high building on campus of Arizona State University by our collaborator, Prof. Matthew Fraser. Quartz fiber filters (8 x 10 inches) were prebaked for about 12 h at 550 °C in a muffle furnace before use to eliminate organics and water on the blank filter. Field blank was collected by placing the filters on the sampler for about five minutes without pumping air through. The sampler was placed at a reasonable height above ground to avoid impact from local emission sources. Thus, aerosol samples collected could capture a regional mean signal and be representative. Altogether, a total of 32 samples for each site were collected at a resolution of 2-3 samples per week from May 26 to August 6, 2010. In addition, three water samples were collected from irrigation water at Phoenix and about 15 precipitation samples were obtained in Atlanta, GA using a 2 mL vial filled with precipitation and avoiding air bubbles between the cap and precipitation samples. All the aerosol samples, irrigation water samples in Arizona and precipitation samples in Georgia were analyzed at Brown University for lipid compositions and hydrogen isotopic ratios by Prof. Yongsong Huang, the collaborative PI on this EAGER project. The information of site coordinates of Atlanta, Georgia and Phoenix, Arizona and other related information is given in Table 1.

#### **Brief summary of laboratory results by the collaborator at Brown University:**

With the aerosol samples provided by Georgia Institute of Technology in Atlanta and Arizona State University in Phoenix, the concentrations of *n*-alkanoic acids were first determined. The distributions of long chain *n*-alkanoic acids (>C<sub>20</sub>) from the two study sites are shown in Figure 1. A systematic chain length difference between Phoenix and Atlanta aerosol samples can be seen for *n*-alkanoic acids with the former dominated by C<sub>30</sub> homologue and the later by C<sub>24</sub>. Such a systematic difference is probably due to plants itself which may need to synthesize longer chain leaf waxes in dryer (and hotter) regions to reduce the water loss.

Compound-specific hydrogen isotopic ratios of leaf wax *n*-alkanoic acids at two study sites were determined and Figure 2 presents the fractionation factors of acids relative to precipitation (summer and annual mean). It was found from this study that the mean hydrogen isotopic fractionation between leaf waxes and precipitation is 20 (C28 and C30) to 40 per mil (C24) higher in Atlanta, GA than that in Phoenix, AZ. Some groups published several high profile papers in the past few years aiming to reconstruct paleohydrology using hydrogen isotopic ratios of plant leaf waxes extracted from sediments under a critical assumption that hydrogen fractionation between leaf waxes and precipitation is relatively constant under different climate conditions. Our results clearly shows that such an assumption has to be revisited and seriously considered as significant difference of hydrogen fractionation can be seen from sites with contrasting humidity.

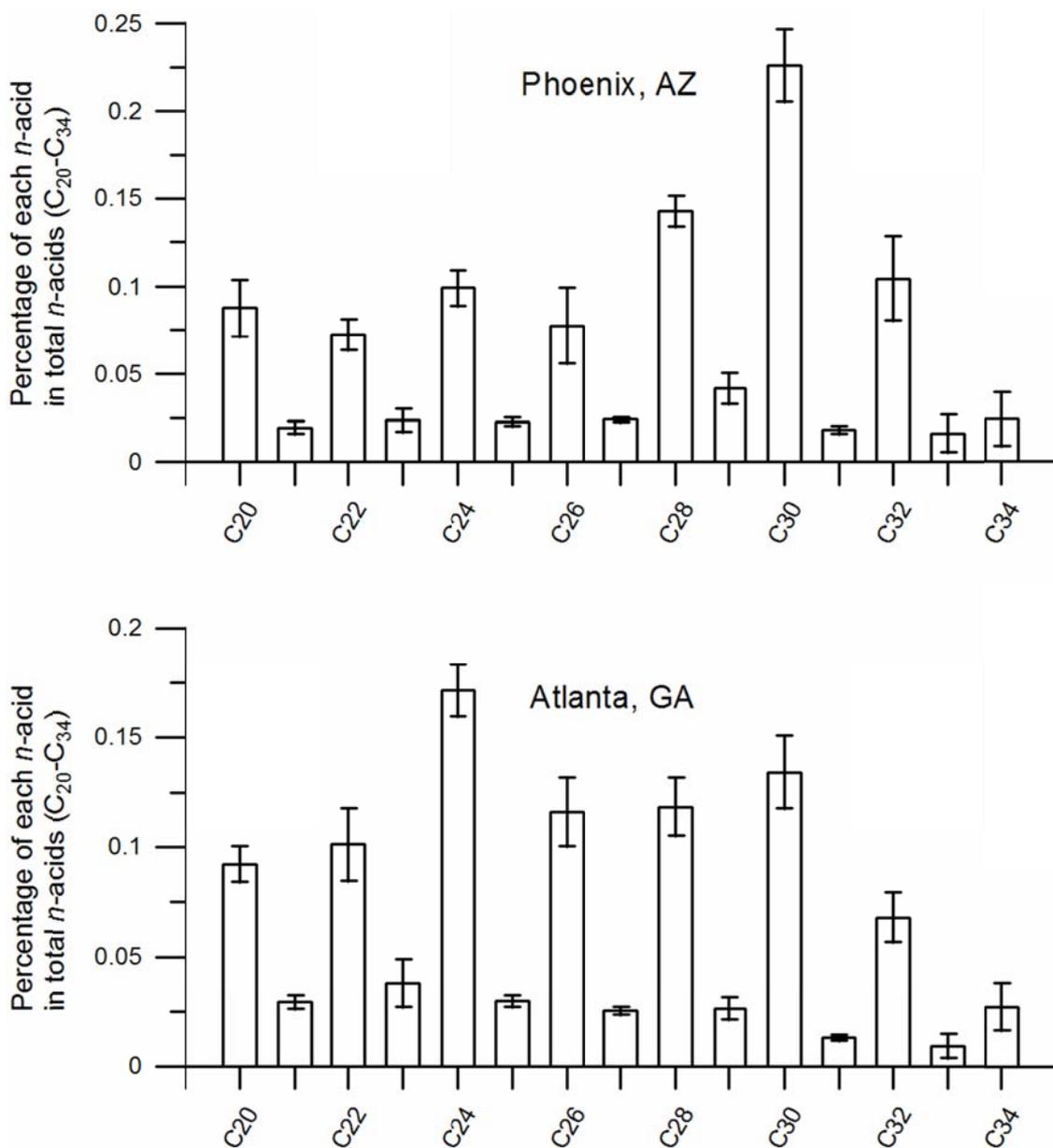


Figure 1. Average chain-length distributions of n-alkanoic acids in aerosols in both Atlanta, Georgia and Phoenix, Arizona (n=12 at each site and the error bars denote standard deviation).

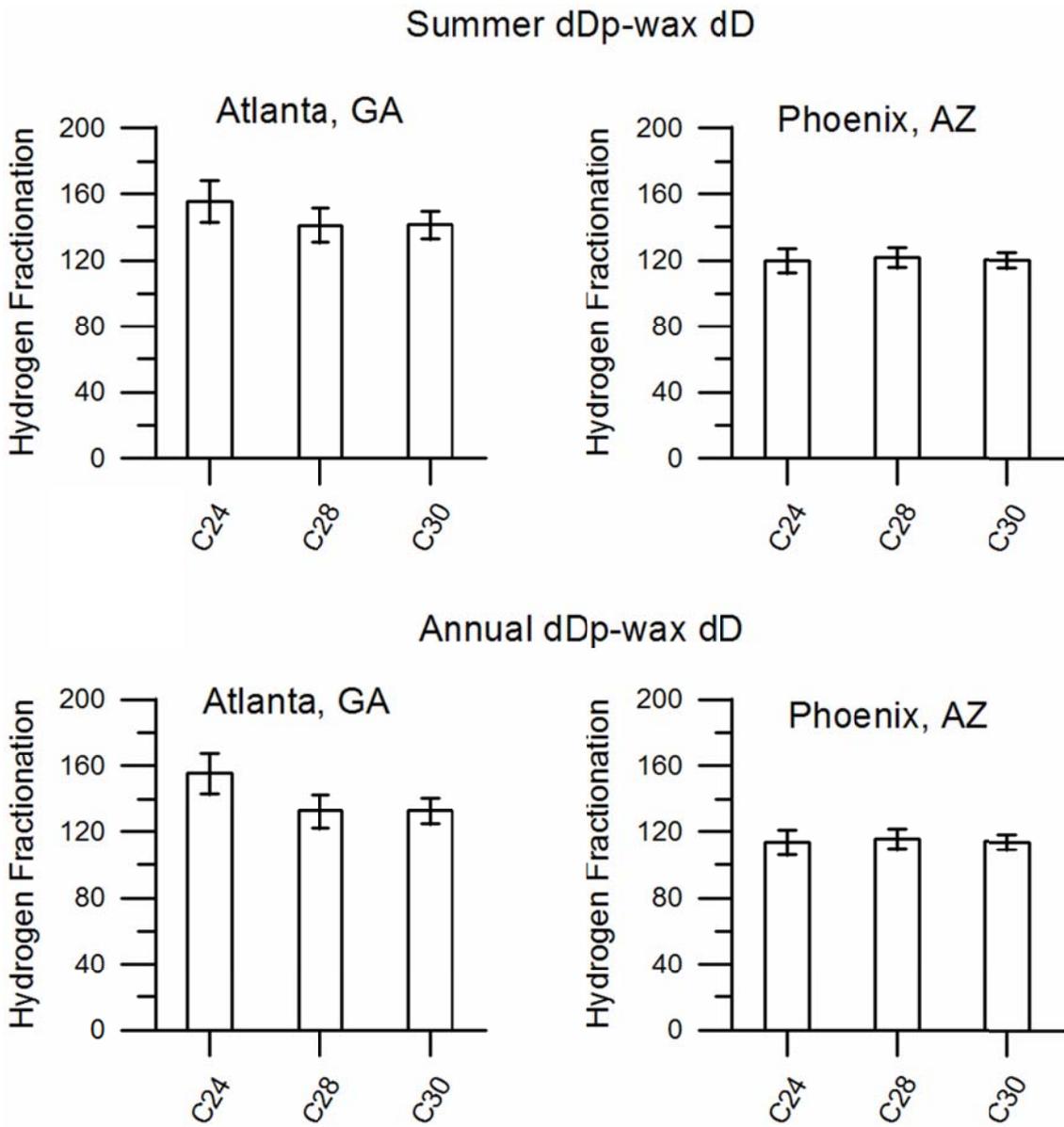


Figure 2. Hydrogen isotope fractionation between precipitation and leaf waxes.

Table 1. Hydrogen fractionation factors between precipitation  $\delta D$  and wax lipids  $\delta D$ .

<b>Sites</b>	<b>Atlanta, GA</b>	<b>Phoenix, AZ</b>
<b>Lat.</b>	31.51	33.5
<b>Long.</b>	-82.75	-112.1
<b><math>\delta D</math> in precipitation (May-Aug.)</b>	-19	-57
<b><math>\delta D</math> in precipitation (Annual mean.)</b>	-28	-63
<b>Fractionation between summer mean <math>\delta D_p</math> to <math>\delta D</math> of waxes (N=12)</b>		
	C <sub>24</sub> -acid*	120±7
	C <sub>28</sub> -acid*	122±6
	C <sub>30</sub> -acid *	120±5
<b>Fractionation between summer mean <math>\delta D_p</math> to <math>\delta D</math> of waxes (N=12)</b>		
	C <sub>24</sub> -acid*	113±7
	C <sub>28</sub> -acid*	115±6
	C <sub>30</sub> -acid*	114±5

\* hydrogen fractionation factors between two sites (GA and AZ) are significantly different based on 12 composite profiles for each site.