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Influence of salinity on hydrogen isotope fractionation in *Rhizophora* mangroves from Micronesia

S. Nemiah Ladd *, Julian P. Sachs

School of Oceanography, University of Washington, Box 355315, Seattle, WA 98195, USA

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Abstract

Hydrogen isotope ratios ($^2H/^1H$ or δ^2H) of plant leaf waxes typically covary with those of precipitation, and are therefore used as a proxy for past hydrologic variability. Mangroves present an important exception to this relationship, as salinity can strongly influence ^2H fractionation in leaf lipids. To better understand and calibrate this effect, δ^2H values of taraxerol and *n*-alkanes were measured in the leaves of *Rhizophora* spp. (red mangroves) from three estuaries and four brackish lakes on the Micronesian islands of Pohnpei and Palau, and compared to the δ^2H and $\delta^{18}O$ values of leaf water, xylem water and surface water. Net ^2H discrimination between surface water and taraxerol increased by $0.9 \pm 0.2‰$ per part per thousand (ppt^{-1}) over a salinity range of 1–34 ppt. Xylem water was always depleted in ^2H relative to surface water, and the magnitude of this depletion increased with salinity, which is most likely due to a combination of greater ^2H discrimination by roots during water uptake and opportunistic use of freshwater. Changes in the ^2H content of xylem water can account for up to 43% of the change in net taraxerol fractionation with salinity. Leaf water isotopes were minimally enriched relative to xylem water and there was not significant variability in leaf water enrichment with salinity, which is consistent with a Péclet-modified Craig–Gordon model of leaf water enrichment. As leaf water enrichment is therefore unlikely to be responsible for increased $^2H/^1H$ fractionation in mangrove leaf lipids at elevated salinities, the majority of this signal is most likely explained either by changes in biosynthetic fractionation in response to salt stress or by salinity influenced changes in the timing of water uptake and lipid synthesis.

1. INTRODUCTION

Hydrogen isotope ratios of plant leaf waxes are increasingly used as a proxy for past hydrologic variability (Sachse et al., 2012, and sources therein). This proxy is founded on the assumption that the hydrogen in leaf waxes and other plant lipids is derived from environmental water, and the observation that the δ^2H_{Lipid} values ($\delta^2H = (((^2H/^1H)_{sample}/(^2H/^1H)_{VSMOW}) - 1$; $\delta^2H = \delta D$) are highly correlated with local $\delta^2H_{Precipitation}$ values (Huang et al., 2004; Sachse et al., 2004, 2012; Hou et al., 2008; Polissar and Freeman, 2010). $\delta^2H_{Precipitation}$ values are determined by environmental parameters, including temperature, precipitation rate, and moisture source (Dansgaard, 1964; Craig and Gordon, 1965; Gat, 1996).

Leaf waxes and other lipids are typically very depleted in ^2H relative to the plant's source water (Sessions et al., 1999; Sauer et al., 2001; Chikaraishi and Naraoka, 2003; Sachse et al., 2012). The difference between δ^2H_{Lipid} values and δ^2H_{Water} values is expressed using the net fractionation factor, $\alpha_{Lipid-Water} = (^2H/^1H)_{Lipid}/(^2H/^1H)_{Water}$. The magnitude of $\alpha_{Lipid-Water}$ is sensitive to variables such as plant type (Liu et al., 2006; Smith and Freeman, 2006; Hou

* Corresponding author at: EAWAG Surface Waters Department, Seestrasse 79, 6047 Kastanienbaum, Switzerland. Tel.: +41 79 869 4345.

E-mail addresses: snladd@uw.edu (S.N. Ladd), jsachs@uw.edu (J.P. Sachs).

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et al., 2007), relative humidity (Feakins and Sessions, 2010; Kahmen et al., 2013a,b; Tipple et al., 2014), and light levels (Liu and Yang, 2008; Yang et al., 2009). In order to reliably use sedimentary δ^2H_{Lipid} values to infer information about past changes in climate, it is important to better understand causes of variability in $\alpha_{Lipid-Water}$, which can result in changes to δ^2H_{Lipid} values that are not solely driven by changes in $\delta^2H_{Precipitation}$ values.

Of particular importance for coastal sediments in the tropics and subtropics, the salinity of environmental water can influence $\alpha_{Lipid-Water}$ (Romero and Feakins, 2011; Ladd and Sachs, 2012). Salt tolerant mangrove trees are the dominant plant type in the intertidal zone of many low-latitude coastlines, and form highly productive ecosystems. As much as 30% of the total terrestrial carbon accumulating in modern subtropical and tropical coastal sediments is mangrove derived (Alongi and Mukhopadhyay, 2014). With so much of the plant material in such sediment coming from a mangrove source, it is important to fully determine the effect of salinity on hydrogen isotope fractionation.

The influence of salinity on $\alpha_{Lipid-Water}$ in leaf wax *n*-alkanes produced by *Avicennia marina* (gray mangroves) was previously investigated along a salinity gradient of 6–35 practical salinity units (PSU) in the Brisbane River Estuary in Queensland, Australia (Ladd and Sachs, 2012). A decrease in $\alpha_{Lipid-Water}$ of $1.5 \pm 0.3‰$ PSU^{-1} was observed for both nC_{31}- and nC_{33}-alkanes. Several hypotheses were proposed that could explain this relationship: (1) preferential exclusion of ^2H during water uptake, (2) increased compatible solute production, preferentially using relatively enriched H^+ from the pentose phosphate cycle, and leaving relatively depleted H^+ from recent photosynthesis available for incorporation into lipids, or (3) increased salt secretion at high salinity, which could decrease the δ^2H value of leaf water (δ^2H_{LW}) by creating a layer of isotopically depleted water hydrating the salt on the surface of leaves. Because intermediate xylem water and leaf water pools were not analyzed in the Brisbane River study, it was not possible to definitively exclude or support any of these hypotheses.

The results of the Brisbane River calibration were significant for two reasons. First of all, they demonstrated a potential pitfall of using δ^2H values of generic leaf waxes to reconstruct climate in coastal tropical settings where mangroves are present. Leaf wax *n*-alkanes are ubiquitous in vascular plants, and it is impossible to distinguish nC_{31}-alkanes in a sediment sample from a mangrove or terrestrial plant source. If local climate became more arid, one would expect the δ^2H_{Wax} values of terrestrial plants to increase, since $\delta^2H_{Precipitation}$ values increase with decreasing precipitation amount in the tropics (Dansgaard, 1964; Gat, 1996; Kurita et al., 2009; Conroy et al., 2013).

Although mangrove trees in the region would also be using isotopically enriched water, the salinity of that water would be expected to increase as less freshwater was delivered through rain. Since increased salinity results in more net discrimination against ^2H during lipid synthesis by mangroves (Ladd and Sachs, 2012), the δ^2H_{Wax} from mangroves could actually decrease in more arid conditions. In Brisbane, for example, *A. marina* growing at 35 PSU produced leaf wax lipids that were depleted by ~50‰ relative to trees growing at 6 PSU, even though the δ^2H_{Water} was enriched by ~15‰ (Ladd and Sachs, 2012). Opposing δ^2H_{Wax} responses to the same environmental shift would result in a muted signal in sediments that contain the molecular remains of both plant types. Relatively small δ^2H_{Wax} variability has in fact been observed in many coastal tropical records and could reflect this opposing hydrogen isotopic response (Tierney et al., 2010; Smittenberg et al., 2011).

While the inverse relationship between salinity and isotope fractionation in mangroves complicates the interpretation of δ^2H_{Wax} values in low-latitude coastal settings, it also forms the basis for quantitative reconstructions of both δ^2H_{Water} values and salinity. If the relationship between salinity and $\alpha_{Lipid-Water}$ observed in leaf waxes from the Brisbane River holds true for more mangrove-specific biomarkers, it will be possible to quantitatively reconstruct past salinity and δ^2H_{Water} values by measuring both δ^2H and $\delta^{13}C$ values in a single mangrove lipid, or by measuring δ^2H values of co-occurring lipids from phytoplankton and mangroves (Ladd and Sachs, 2012, 2013). The first of these strategies relies on the observation that $\delta^{13}C$ values of mangrove *n*-alkanes increase with increasing salinity, resulting in an independent measure of past salinity (Ladd and Sachs, 2013). The second approach is based on the observation that microalgae fractionate hydrogen isotopes less as salinity increases (Schouten et al., 2006; Sachse and Sachs, 2008; Sachs and Schwab, 2011; Chivall et al., 2014; Nelson and Sachs, 2014).

Required for both of these approaches is a robust calibration of the relationship between salinity and $\alpha_{Lipid-Water}$ for a mangrove specific lipid biomarker. Because the pentacyclic triterpenoid taraxerol is produced in high abundance by *Rhizophora* spp. mangroves (Killops and Frewin, 1994; Koch et al., 2003; Versteegh et al., 2004), and because it is relatively refractory and well preserved in sediment (Koch et al., 2003, 2005), it is a promising target compound. The primary goal of the present study was to assess the influence of salinity on net hydrogen isotope fractionation during the biosynthesis of taraxerol.

A related goal was to better understand the mechanisms by which isotopic fractionation occurs during lipid synthesis in mangroves. The only published study on the relationship between salinity and net H isotope fractionation in mangroves (Ladd and Sachs, 2012) presented δ^2H data from leaf wax *n*-alkanes and surface water (SW). This allowed $\alpha_{Lipid-SW}$ to be calculated, but left the fractionation associated with several intermediate steps unconstrained. These steps include potential discrimination against ^2H during water uptake (that is, depletion of xylem water (XW) relative to surface water or α_{XW-SW}), which is uncommon in most higher plants, but demonstrated to occur in halophytes (Lin and Sternberg, 1993; Ellsworth and Williams, 2007), enrichment of leaf water (LW) due to transpiration (α_{LW-XW}; Dawson et al., 2002; Kahmen et al., 2008), and biosynthetic fractionation during photosynthesis and lipid synthesis ($\alpha_{Lipid-LW}$). Analyzing δ^2H_{XW} and δ^2H_{LW} values,