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Lignin methoxyl hydrogen isotope ratios in a coastal ecosystem

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Abstract

Stable hydrogen isotope ratios of plant lignin methoxyl groups have recently been shown to record the hydrogen isotopic composition of meteoric water. Here we extend this technique towards tracing water source variations across a saltwater to freshwater gradient in a coastal, subtropical forest ecosystem. We measure the hydrogen isotopic composition of xylem water (δD_{xw}) and methoxyl hydrogen ($\delta D_{methoxyl}$) to calculate fractionations for coastal mangrove, buttonwood and hammock tree species in Sugarloaf Key, as well as buttonwoods from Miami, both in Florida, USA. Prior studies of the isotopic composition of cellulose and plant leaf waxes in coastal ecosystems have yielded only a weak correlation to source waters, attributed to leaf water effects. Here we find $\delta D_{methoxyl}$ values range from −230‰ to −130‰, across a 40‰ range in δD_{xw} with a regression equation of $\delta D_{methoxyl}$ ‰ = 1.8 * δD_{xw} − 178‰ ($R^2 = 0.48$, $p < 0.0001$, $n = 74$). This is comparable within error to the earlier published relationship for terrestrial trees which was defined across a much larger 125‰ isotopic range in precipitation. Analytical precision for measurements of δD values of pure CH_3I by gas chromatography–pyrolysis–isotope ratio mass spectrometry (GC–P–IRMS) is $\sigma = 6$‰ ($n = 31$), which is considerably better than for CH_3I liberated through cleavage with HI from lignin with $\sigma = 18$‰ ($n = 26$). Our results establish that $\delta D_{methoxyl}$ can record water sources and salinity incursion in coastal ecosystems, where variations sufficiently exceed method uncertainties (i.e., applications with δD excursions >50‰). For the first time, we also report yields of propyl iodide, which may indicate lignin synthesis of propoxyl groups under salt-stress.

1. INTRODUCTION

The hydrogen isotopic composition of methoxyl hydrogen on lignin polymers in plant tissues have recently been shown to record the hydrogen isotopic composition of precipitation (Keppler et al., 2007). The advantages of this technique are that only C bound H from methoxyl groups are sampled avoiding problems of H exchange in hydroxyl H. Furthermore the technique is rapid providing analytical advantages over other techniques including position-specific analysis of both δD (Epstein et al., 1976) and oxygen isotopes ($\delta^{18}O$) in cellulose (Sternberg et al., 2007a), as well as organic geochemical methods for isolation and analysis of plant leaf wax biomarkers in plants (Sessions et al., 1999) and sediments (Sachse et al., 2004). Each of these techniques finds useful application to paleoclimate reconstructions; however in applications to coastal saline environments each has faced challenges. Prior studies have found that source water signals are not uniquely recorded in saline environments: isotopic effects in the leaf lead to overprinting with a leaf water signal resulting in confounded signals recorded in both the oxygen isotopic composition of cellulose (Ellsworth et al., 2013) and in the hydrogen isotopic composition of plant leaf waxes (Romero and Feakins, 2011; Ladd and Sachs, 2012). The new lignin methoxyl δD approach has not yet been tested in a saline environment.

We have previously considered whether plant leaf waxes record spatial variations in source waters across a saltwater to freshwater gradient (Romero and Feakins, 2011). In that study we found that while the δD_{xw} decreased inland as expected, leaf water (δD_{lw}) displayed an inverse relationship. Leaf water was the dominant influence on δD_{wax}, but was

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attenuated by the initial xylem water gradient. In that study, it was suggested that δD_{lw} varied with inundation, recording a larger enrichment at the most inland sites, counteracting the source water effects (hypothesis a). Another study found a similar pattern in mangrove δD_{wax} across a salinity gradient in an Australian estuary, where δD_{wax} does not follow river water δD, but instead displays an inverse relationship with salinity (Ladd and Sachs, 2012). The authors give several hypotheses including (b) increased fractionation against D in the roots during water uptake, (c) increased relative humidity at the leaf surface due to secretion of salty brines, (d) water of hydration of leaf salts being incorporated in leaf water, or (e) increased contributions of isotopically depleted hydrogen from NADPH at high salinity (Ladd and Sachs, 2012). While xylem water was not directly measured in that study, elsewhere plant waters in mangroves, provide evidence that hypothesis (b), fractionation in the roots, is unlikely to be of sufficient magnitude, being <10‰ in a study of varied halophytes and xerophytes (Lin and Sternberg, 1994; Ellsworth and Williams, 2007). Another study proposed hypothesis (f) that salt alters the pathlength of leaf water flow and may lead to ^{18}O-depletion in saline environments relative to freshwater plants (Ellsworth et al., 2013). Although the effect of pathlength was observed in the oxygen isotope ratios of stem alpha cellulose ($\delta^{18}O_{cell}$) and phenylglucosazone ($\delta^{18}O_{pg}$), the same processes could apply to other leaf-based isotope proxies. Thus there are multiple competing hypotheses for the common problems affecting leaf-based isotope proxies and we cannot distinguish further between them here. Whatever the mechanism, the salinity-induced complications in the leaf water isotopic enrichment would ideally be circumvented in order to resolve source water signals with a plant-based proxy.

1.1. Lignin methoxyl hydrogen isotope approach

The lignin methoxyl hydrogen isotope approach has been tested on terrestrial tree wood sampled including species from Scandinavia to Yemen across a wide (125‰) isotopic range (Keppler et al., 2007). Like the nitration method for cellulose (Epstein et al., 1976), the methoxyl approach samples only non-exchangeable hydrogen on lignin. Lignin is formed in the xylem tissues and as such may avoid the complications that affect leaf-based isotopic proxies in saline environments (see Section 1). Analytical methods for measuring methoxyl hydrogen include cleavage of the methoxyl group with hydroiodic acid (HI) to yield methyl iodide (Keppler et al., 2007). The methyl iodide hydrogen isotopic ratio is determined by gas chromatography isotope ratio mass spectrometry (Greule et al., 2008). More recently, the method was refined with the addition of a cold trap before the IRMS to exclude HI generated during pyrolysis (Feakins et al., 2013) similar to an approach used for the analysis of chlorinated hydrocarbons (Chartrand et al., 2007). $\delta D_{methoxyl}$ values have been shown to do better than bulk wood δD in recording the δD of source waters in terrestrial trees in a global survey (Keppler et al., 2007) and tested against conventional techniques in an alpine ecosystem (Gori et al., 2013). Here we assess the potential of the $\delta D_{methoxyl}$ technique in application to a saline ecosystem for the first time.

Specifically we examine the prospects for the new lignin methoxyl hydrogen isotope technique to serve as a proxy of source water in a coastal ecosystem in South Florida including mangroves, and coastal hardwood hammocks. These two communities, which are characteristic of South Florida and Caribbean coastal regions, span a source water salinity gradient ranging from that of seawater (mangrove communities) to freshwater (hardwood hammocks). This study will allow us to test the potential of the new technique in saline environments.

1.2. Natural and anthropogenic influences on saltwater–freshwater gradients in coastal ecosystems

The coastal ecosystems in the Florida Keys have been affected by salt water intrusion associated with continued sea level rise exacerbated by diversion of freshwater inflows (Saha et al., 2011). In addition, periodic influxes of ocean water occur during tropical storms (Ross et al., 1994). As a result, rising salinity is pushing the boundary between saltwater tolerant mangroves and saltwater intolerant hammocks inland (Ross et al., 1994). The effects of sea level rise, however, are complex. Plant physiological behavior can affect the salinity of the soil and lead towards progression towards one of two stable states characterized by either freshwater or mangrove communities in close proximity, with hammock species depending on lenses of freshwater perched above the saline groundwater (Sternberg et al., 2007b). Satellites (Niedzielski and Kosek, 2011), tide gauges (Church and White, 2006) and proxy reconstructions (Gehrels et al., 2006) are all valued means of recording and reconstructing sea level rise (IPCC, 2007). However, mean sea level does not fully describe the impacts on an ecosystem. Coastal plants can modulate the flow of seawater and are prone to storm surges, leading to a variable freshwater to saltwater boundary. Furthermore freshwater diversion can cause a rise in salinity through processes that accelerate the local impacts of sea level rise (Saha et al., 2011). Water isotopic evidence can be helpful to trace actual water use by plants in ecosystems suffering the effects of sea level rise, freshwater inflow reductions, and perhaps increasing hurricane intensity (Emanuel, 2007).

The difference in the isotopic composition of ocean and freshwater (Sternberg et al., 1991) controls the isotopic composition of water available to plants. If that source water isotopic signal is not overprinted by leaf water processes such as transpiration and the pathway of water movement from the xylem to the leaf stomatal cavity (Barbour and Farquhar, 2003; as described in Section 1), then plant biochemicals may record the integrated signal of water accessed by the plant. Water sources may vary between adjacent trees of different species and during seasonal