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Origin and sedimentary fate of plant-derived terpenoids in a small river catchment and implications for terpenoids as quantitative paleovegetation proxies

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ABSTRACT

Tricyclic diterpenoids and non-steroid or non-hopanoid pentacyclic triterpenoids are almost exclusively taxon-specific terrestrial plant biomarkers produced by conifers and angiosperms, respectively. Due to this source specificity and their prevalence in the geologic record, these compounds are often used to reconstruct paleovegetation. However, the physical and chemical processes that influence the dispersal and fate of terpenoids in sedimentary archives are poorly constrained. Modern fluvial systems can be used as ancient river analogs to provide information on the utility of terrestrial plant terpenoids as paleovegetation proxies by defining their potential flux and identifying the processes that control their transport to, and deposition and degradation in, sediments. To determine if the contribution of terpenoids from vegetation is reflected in forested soil and river sediments and to constrain the dispersal of these compounds in fluvial systems, di- and triterpenoid concentrations in Miners River drainage basin (Upper Peninsula of Michigan, USA) were quantified. In the basin, evergreen conifers are less abundant than deciduous angiosperms, but yet contribute substantially more terpenoids to soils and river sediments when scaled for leaf litter production and present vegetation cover. The composition and relative concentration of di- and triterpenoids in source vegetation do not match those in soils and river sediments, suggesting that some process or processes result in the preferential removal of diterpenoids. While the soil and river sediment terpenoid concentration, corrected for differential terpenoid inputs, can closely predict the basin wide vegetation cover in Miners River drainage basin, the extent to which terpenoids can be used a paleovegetation proxy in other modern or geologic sediments remains unclear.

1. Introduction

Rivers transport a substantial amount of organic carbon (0.4 Gt C/yr) and thus provide an integral pathway for terrigenous plant matter dispersal and integration from land to lacustrine and marine sediments (McKee et al., 2004; Pancost and Boot, 2004). Terrigenous plant biomarkers are useful tools for studying organic matter (OM) in rivers because they are source-specific and remain relatively unchanged during transport and post-depositional processes (ten Haven and Rullkötter, 1988; Otto and Simoneit, 2001; Otto et al., 2002, 2003; Pancost and Boot, 2004). Due to this source specificity and sedimentary resilience, they can also be used as paleovegetation proxies in geologic settings where pollen and macrofossils are absent (e.g. Bechtel et al., 2003; Diefendorf et al., 2014).

Tricyclic diterpenoids and non-steroidal pentacyclic triterpenoids are terrestrial plant biomarkers synthesized almost exclusively by higher plants (conifers and angiosperms). Plant terpenoids have multiple roles in plant function, including defense against insect herbivory and plants must biosynthesize a diverse array of compound structures to maintain toxicity (Langenheim, 1994). Most conifers in North America today (Pinaceae and Cupressaceae) produce tricyclic diterpenoids (DTs) in the abietane and pimarane classes (e.g. Otto and Simpson, 2005), while angiosperms commonly produce triterpenoids (TTs) in the lupane, oleanane and ursane classes (e.g. Diefendorf et al., 2012; Fig. 1). On average, terpenoids account for 1–2% of dry leaf mass (Langenheim, 1994), but terpenoid synthesis varies between conifers and angiosperms and between leaf lifespans (deciduous vs. evergreen). Angiosperms produce terpenoids in greater concentration than conifers of the same leaf lifespan and evergreen taxa produce a higher concentration of terpenoids than deciduous taxa. This difference between taxonomic groups and leaf lifespans

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suggests that angiosperms and evergreen taxa may be over represented in sedimentary deposits (Diefendorf et al., 2012).

Terpenoids are common constituents of plant tissue (leaves, bark or roots) transferred to soils and sediments as plant debris decomposes (Langenheim, 1994). Terpenoids are subject to early alteration and degradation and only a small portion is transferred to sedimentary archives (Hedges and Prahl, 1993; Hautevelle et al., 2006; Jacob et al., 2007; Bechtel et al., 2008; Diefendorf et al., 2014).

Due to the widespread distribution of DTs and TTs in sediments and their qualitative reflection of major taxonomic groups, they are commonly used to infer paleovegetation in terrestrial, lacustrine and marine sediments (e.g. Bechtel et al., 2003, 2005; Pancost and Boot, 2004; Schouten et al., 2007). For more accurate paleovegetation reconstruction, differences in terpenoid production between major taxonomic groups are required (Diefendorf et al., 2012, 2014).

Few studies have evaluated whether DT/TT ratios in modern river systems reflect the surrounding plant community (Medeiros and Simoneit, 2008; Medeiros et al., 2012) and understanding the distribution of these compounds in fluvial systems is important for interpreting the geologic terpenoid record. Various taphonomic processes likely result in the leaves of some species entering river systems over others (Spicer, 1981; Burnham, 1989; Greenwood, 1991; Burnham et al., 1992; Ellis and Johnson, 2013) and differential preservation potential and water solubility of DTs vs. TTs may bias the terpenoid composition in rivers, thereby transferring it to the sedimentary record. Preferential alteration and degradation in the sedimentary archive will add additional complications (Wakeham et al., 1980; Hedges and Prahl, 1993). To explore terpenoid composition and concentration changes between source and transport, we used a small modern river system. The focus on terpenoids in the sedimentary record has been studied elsewhere (e.g. Diefendorf et al., 2014) and we instead focus here on the transfer of terpenoids from source vegetation to soils and into river systems to evaluate any bias in transport and early alteration/degradation. This provides an analog for testing the utility of DT/TT ratios as a quantitative paleovegetation proxy before terpenoids enter long term sedimentary archives.

2. Site description

The study focused on Miners River drainage basin (7044 ha) in Alger County of the Upper Peninsula of Michigan (MI; USA). This watershed includes Miners River, a small stream (13.4 km long), which drains into Lake Superior (Fig. 2; Handy and Twentner, 1985). The area was chosen because it is an entirely freshwater system, draining through a mixed conifer–angiosperm forest. The river discharge is highest in late spring and early summer and ranges from 0.4 m^3/s in August to 3.0 m^3/s in April (Handy and Twentner, 1985). The stream substrate consists mainly of bedrock, cobble and gravel. Fine grain sediments are deposited and accumulate in areas of low flow (Handy and Twentner, 1985). Theiver drains through Miners Lake, a small teardrop-shaped lake with a maximum depth of 4.0 m and average depth of 1.9 m. Several small groundwater springs are found along the river and lake (Loope, 2004).

The Upper Peninsula of MI experiences a cool continental climate, which is heavily influenced by Lake Superior. The average annual temperature is 5 °C and average annual precipitation 85.9 cm, 32% of which falls as snow (Mechenich et al., 2006). The underlying Cambrian sandstone and surficial Pleistocene and Holocene deposits control the topography of the region (Handy and Twentner, 1985). The regional soils derive from underlying sandstone units and glacial material and vary in their OM abundance (ca. 1–50%). Miners River drains through soils from the Munising–Stuben Association, a dominantly loamy soil underlain with sand, as well as the Kalkaska Association, a sandy, moderately well drained soil. The sandy subsoil of the Munising–Stuben Association prevents deep rooting by plants (Berndt, 1977).

The river drainage basin commonly has an assemblage of taxa for a temperate broadleaf angiosperm and conifer needle afforestation. The present plant community composition has been extensively mapped within the boundaries of Pictured Rocks National Lakeshore (Hop et al., 2010). Plant community is patchy and varies depending on substrate type, moisture gradient and drainage patterns (Read, 1975). Hardwood deciduous angiosperm forests, comprising *Acer rubrum*, *Acer saccharum*, *Acer spicatum*, *Alnus viridis*, *Alnus* spp., *Betula alleghaniensis* and *Fagus grandifolia* are the predominant vegetation of the Munising–Stuben Association, while evergreen conifers, including *Picea glauca*, *Pinus resinosa*, *Thuja occidentalis* and *Tsuga canadensis*, are prevalent on the Kalkaska Association (Berndt, 1977). Overall, the drainage basin broadly represents a forest community that is 14% needle leaf conifers, 80% broad leaf angiosperms and 6% other vegetation (herbaceous plants, grasses, sedges, etc.; Hop et al., 2010). Due to extensive logging of conifers in the late 1800s, the vegetation of the Upper Peninsula changed quite drastically and the forest has transitioned from a predominantly coniferous forest to the present day mixed conifer–angiosperm one (Frederick et al., 1977).

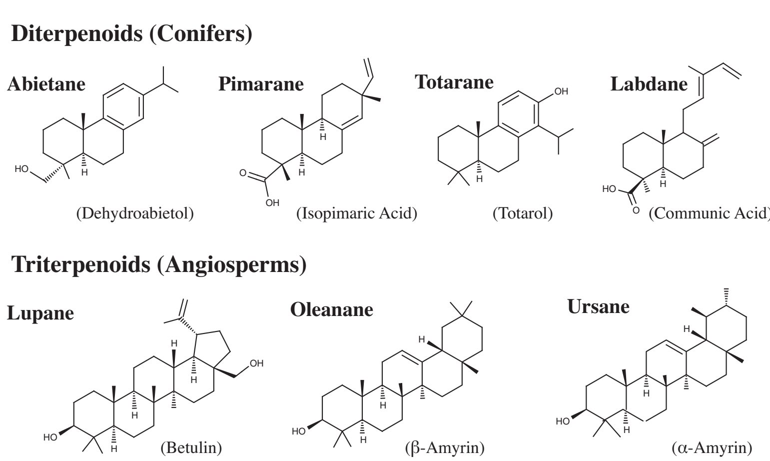

Fig. 1. DT and TT structures by compound class (classes in bold). Examples for compounds in each class are shown (names in parentheses).