Organic Geochemistry 121 (2018) 126–137

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Modelling leaf wax *n*-alkane inputs to soils along a latitudinal transect across Australia

S. Howard [a,*], F.A. McInerney [a], S. Caddy-Retalic [b,c], P.A. Hall [a], J.W. Andrae [a]

[a] University of Adelaide, Sprigg Geobiology Centre and School of Physical Sciences, Australia
[b] University of Adelaide, School of Biological Sciences, Australia
[c] University of Sydney, School of Life and Environmental Sciences, Australia

ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form 23 March 2018
Accepted 25 March 2018
Available online 29 March 2018

Keywords:
Leaf wax
n-Alkanes
Average chain length
Carbon preference index
Soils
Palaeoecology
Vegetation reconstruction

ABSTRACT

Leaf wax *n*-alkanes provide a valuable palaeoecological proxy, but their interpretation requires an understanding of the scale of temporal and spatial integration in soils. Leaf wax *n*-alkanes are continually deposited into soils directly from local plants as well as from more distant plants via wind or water transport. In addition, *n*-alkanes can persist in soils for thousands of years, and tend to decrease in age with shallower depth. To explore whether the uppermost soils reflect recent leaf fall inputs we compared surface soils and modern vegetation from 20 sites along a transect across Australia. At each site, the three most dominant plant species and a soil sample from the top 3 cm were analysed for *n*-alkane concentration, average chain length (ACL), proportional abundance of C_{33} and C_{29} (Norm33) and carbon preference index (CPI). Chain length distributions differ between trees and grasses, with a higher proportion of C_{29} in trees and C_{33} in grasses. Norm33 in soils correlates with proportional grass to tree cover across the transect. To model *n*-alkane inputs for each site, we calculated a predicted ACL, Norm33 and CPI using the dominant plants at that site, weighted by proportional species cover and *n*-alkane concentration. Predicted ACL, Norm33 and CPI inputs were generally higher than the soils, demonstrating that recent and local inputs do not dominate soil *n*-alkanes at our study sites. Thus, *n*-alkane distributions in surface soils do not correlate with local, current vegetation, but do correlate with proportional grass and tree cover, suggesting they provide a faithful record of large scale ecosystem structure.

1. Introduction

Plant waxes provide critical protection for leaves by limiting non-stomatal water loss from the leaf surface (Eglinton and Hamilton, 1967; Dodd and Poveda, 2003; Jetter and Riederer, 2016), protecting against damage from UV radiation (Shepherd and Wynne Griffiths, 2006; Koch et al., 2009), and resisting fungal infection and herbivory (Eigenbrode and Espelie, 1995; Banthorpe, 2006). Plant waxes contain a range of compounds, including long chain *n*-alkanes, which are non-polar, unbranched, straight-chain hydrocarbons (Eglinton and Hamilton, 1967; Banthorpe, 2006). Long chain-odd-numbered *n*-alkanes (C_{25}–C_{35}) are produced nearly exclusively as part of the waxes of terrestrial plants (Eglinton and Hamilton, 1967). Plants generally produce greater quantities of odd than even chain lengths due to synthesis by sequential elongation or condensation of a C_2 primer, where even-numbered fatty acid chains become decarboxylated to produce odd chain length alkanes (Khan and Kolattukudy, 1974; Shepherd and Wynne Griffiths, 2006). Higher plants produce different distributions of chain lengths that range from C_{25} to C_{35} (Sachse et al., 2004; Pu et al., 2011; Bush and McInerney, 2013). The majority of plant wax *n*-alkanes in soils and sediments should derive from leaves due to the high proportional biomass of leaves, and the high concentrations of *n*-alkanes in leaves relative to other plant organs (Gamarra and Kahmen, 2015). Roots can contribute *n*-alkanes to the soil directly, but their concentration is one or two orders of magnitude less than leaves and thus they are unlikely to be the dominant source of *n*-alkane signals in surface soils (Gamarra and Kahmen, 2015; Angst et al., 2016; Jansen and Wiesenberg, 2017). There is some evidence that insects also produce long-chain *n*-alkanes with an odd-over-even predominance, however their biomass is orders of magnitude less than that of terrestrial plants and their annual *n*-alkane production rate is unquantified, so their contribution to soils and sediments is considered negligible in comparison to plants (Chikaraishi et al., 2012).

Plant lipid biomarkers, such as leaf wax *n*-alkanes, are very common in the sedimentary record, compared to macrofossils

* Corresponding author.
E-mail address: sian.howard@adelaide.edu.au (S. Howard).

https://doi.org/10.1016/j.orggeochem.2018.03.013
0146-6380/

which are comparatively rare. Leaf wax *n*-alkanes are valuable recorders of past vegetation (Eglinton and Eglinton, 2008; Diefendorf and Freimuth, 2017) and can be distinguished from petroleum sources by their odd-over-even predominance (Eglinton and Hamilton, 1967; Yamamoto and Kawamura, 2010). However, to interpret the signatures preserved in sediments, we must understand how sedimentary leaf wax *n*-alkanes reflect the vegetation both temporally and spatially (Diefendorf and Freimuth, 2017).

Direct ^{14}C dating suggests that leaf wax *n*-alkanes can be pre-aged in soils for hundreds to thousands of years prior to remobilisation and transport to lacustrine and marginal marine sediments (Smittenberg et al., 2006; Drenzek et al., 2007; Douglas et al., 2014; Gierga et al., 2016), frequently resulting in highly time-averaged *n*-alkane accumulations. Once buried in sediments, *n*-alkanes can persist for millions of years and have been extracted from sediments from the Cretaceous–Paleogene boundary (Yamamoto et al., 2010), Paleocene–Eocene (Smith et al., 2007), Miocene (Huang et al., 2001) and Holocene (Schwark et al., 2002).

Although *n*-alkanes can persist for thousands of years in deeper subsoils and millions of years in buried sediments, analyses of modern soils demonstrates that more recent *n*-alkane inputs dominate near the soil surface (Angst et al., 2016). Direct ^{14}C dating of *n*-alkanes and soil organic carbon in soils and lake sediments shows increasing age with depth (Huang et al., 1996; Angst et al., 2016; Gierga et al., 2016). Makou et al. (2018) found ^{14}C dating of long, odd-chain *n*-alkanes in a surface soil indicated a pool of pre-aged *n*-alkanes attributed to erosional inputs from adjacent slopes, however the dominant chain length present in the soil, C_{27}, was modern in age and attributed to inputs of fresh leaf waxes from nearby beech trees. Therefore, surface soils appear to be the least time-averaged, and predominantly represent the most recent *n*-alkane inputs.

Leaf fall and breakdown of leaf litter represents direct *n*-alkane deposition to soils (Cranwell, 1981; Lichtfouse et al., 1998), resulting in soil *n*-alkane signatures representative of local sources. Previous work examining the relationship between chain length and biome type showed that the chain length distributions associated with the plants were similar to those in the soils of those respective biomes (Carr et al., 2014). However, leaf wax *n*-alkanes are also readily ablated and wind-dispersed, which would lead soil deposits to represent a regional catchment area (van Gardingen et al., 1991; Gao et al., 2012). Wind-blown *n*-alkanes can travel as far as between continents (Bendle et al., 2007; Yamamoto and Kawamura, 2010; Nelson et al., 2017) and are primarily deposited with particulate matter scrubbed from the atmosphere by precipitation (Meyers and Hites, 1982; Diefendorf and Freimuth, 2017). Similarly, water can transport leaf wax *n*-alkanes long distances via streams, rivers and runoff, either by moving fallen leaves or deposited particulate matter (Rouillard et al., 2016; Diefendorf and Freimuth, 2017). The relative importance of these processes in delivering *n*-alkanes to soils will determine whether soil records represent a regional or more localised vegetation sample (Jansen and Wiesenberg, 2017).

Here, we test the hypothesis that *n*-alkane distributions in surface soils correlate with *n*-alkane distributions of current local vegetation. We sampled a latitudinal transect across Australia to capture a climatically and ecologically diverse set of sites (Fig. 1). The continent-wide transect spans from monsoonal tropics in the north to arid desert in the centre, to the winter-wet Mediterranean climate zone in the south. The biomes sampled include tropical and subtropical grasslands, savannas and shrublands in the north; desert and xeric shrublands in the centre; and Mediterranean shrublands and woodlands in the south (Supplementary Table S1). At each site, we characterised the *n*-alkane abundance and distribution from the three most dominant plant species. At the vast majority of sites, the three dominant species represent the majority of the plant cover (Table 1). While it does not equate directly to biomass, dominant coverage provides us with a reasonable estimate of the dominant *n*-alkane contributors to the surface soils and improves on previous studies that sample plants without respect to their coverage in the landscape. Using the concentration and distribution of *n*-alkanes of the dominant vegetation to account for differences in production, we modelled their inputs to surface soils and compared them to the distributions measured from the soils (top 3 cm). The degree to which local and recent vegetation contributes to soil *n*-alkane signatures will determine how well our modelled inputs match our measured soil *n*-alkane distributions. This comparison provides a direct test of the hypothesis that the leaf wax *n*-alkane signals in surface soils are dominated by local and recent inputs rather than regional and/or long-term inputs. We also examined whether soil *n*-alkane distributions broadly reflect plant cover growth form (e.g., grasses vs trees) at each site. The results constrain the nature of delivery and turnover of *n*-alkane soils across a large and diverse transect, and provide bounds on the range of possible paradigms for the development of *n*-alkane records in soils.

2. Methods

2.1. Sample collection

Soil and plant samples were collected from 20 sites on a north-south transect across Australia (Fig. 1), using the AusPlots Rangelands survey methodology (White et al., 2012). These samples were collected by Australia's Terrestrial Ecosystem Research Network (TERN) and made available for this research. The sites monitored by TERN are permanent plots where baseline surveys of soils and vegetation are conducted as a source of ongoing and long-term ecosystem data for research (White et al., 2012). Sites analysed here were distributed through seven Australian bioregions (See Supplementary Table S1 for descriptions). A single surface soil sample from the middle of each site, taken from a maximum of 3 cm depth (total n = 20), was selected for analysis after having been air dried and stored in calico. Soils were sieved with 1000 and 250 μm sieves to remove large plant material, such as leaves, bark and roots. Particle size percentages were determined using mid-infrared particle size analysis.

Proportional plant species cover and growth form cover was determined from point intercept data obtained from the online Soils2Satellites portal (www.soils2satellites.org.au). At each one hectare site, 1010 points were assessed and all vegetation occurrences were recorded (White et al., 2012). The total number of occurrences for each species and growth form was divided by the total number of vegetation occurrences per site to determine the proportional species cover and growth form (trees, grasses, forbs and shrubs, inclusive of chenopods) cover at each site.

$$\text{Proportional species cover} = \frac{\text{number of species occurrences}}{\text{total vegetation occurrences}} \quad (1)$$

$$\text{Proportional growth form cover} = \frac{\text{number of growth form occurrences}}{\text{total vegetation occurrences}} \quad (2)$$

Leaves from the three most dominant plant species, in terms of proportional species cover, were selected for analysis from each site, except for one site from which the two most dominant were available (total n = 59). The leaves were placed in gauze bags and dried on silica gel. The total proportional species cover that the three most dominant plant species represent ranges from 42 to 99% (Table 1).