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Leaf wax *n*-alkane distributions in arid zone South African flora: Environmental controls, chemotaxonomy and palaeoecological implications

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ABSTRACT

The environmental controls on leaf wax *n*-alkane distributions and associated interpretation of such distributions in geological archives have long remained rather enigmatic. Studies of contemporary vegetation often conflate changing environmental conditions and species differences between biomes, making it difficult to assess the extent to which variation is driven by plant adaptation to prevailing environmental conditions and/or more fixed chemotaxonomic patterns. We present a case study of arid and semi-arid regions of South Africa that considers these issues. We anticipate that such conditions may impart strong controls upon leaf wax synthesis.

Leaf wax *n*-alkane data from 215 plants and 93 soils from the Succulent Karoo and Fynbos biomes of South Africa revealed yield and distributions to be highly variable. While many plants exhibited concentrations comparable with previous reports, several succulent plants produced *n*-alkane yield up to 100× the modal *n*-alkane concentration for their biome. The data demonstrate that, on average, leaf wax *n*-alkane distributions in the Succulent Karoo are different from those of the Fynbos biome, with the former associated with longer maximum chain length, less dispersed distributions and stronger odd numbered chain length preference. The patterns were closely mirrored in the soils. Average chain length was weakly correlated with climate and this is interpreted to be a function of multiple factors. We hypothesise that a key control is the shifting proportion of plant functional type between biomes, with a greater abundance of succulent growth forms in the more arid Succulent Karoo (which tended to produce longer and less dispersed *n*-alkane chain length distributions), differentiating this biome from the Fynbos, in which woody shrubs are more dominant. Inter-biome variability was also apparent, with some same taxonomic or functional groups common to both biomes tending to produce longer chain length *n*-alkane distributions under more arid conditions. There was, however, considerable individual plant variability and we observed both insensitivity to environmental conditions (i.e. consistent *n*-alkane distributions) and marked variability in chain length distributions.

A key finding is the high yield of *n*-alkanes from multiple succulent plants, many of which use the CAM photosynthetic pathway. Compound specific $\delta^{13}C/\delta D$ analyses (e.g. estimates of C_3 and C_4 biomass) for regions with potential succulent plant contributions should therefore be carried out cautiously.

1. Introduction

Leaf waxes comprise complex mixtures of fatty acids, *n*-alkanes (C_{21}–C_{35}), *n*-alkanols (C_{20}–C_{32}), aldehydes and wax esters, which form a protective barrier around plant leaves (Jenks and Ashworth, 1999). They are hypothesised to serve various specific functions, including internal water retention, external water repellence and protection from UV radiation and pathogens (Jenks and Ashworth, 1999; Shepherd and Griffiths, 2006). Wax abraded or ablated to the atmosphere is replaced throughout a plant's life (Conte et al., 2003), potentially very quickly (Gao et al., 2012). As a result, waxes

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are widely distributed in the environment and are commonly a component of atmospheric aerosols (Peltzer and Gagosian, 1989; Conte and Weber, 2002).

Leaf waxes are preserved in a range of sedimentary and geological contexts, and *n*-alkanes have attracted particular interest for palaeoenvironmental research as they are both relatively recalcitrant in the sedimentary context (i.e. high preservation potential) and amenable to compound specific stable carbon and hydrogen isotope analysis (e.g. Feakins et al., 2005; Schefuß et al., 2005; Sachse et al., 2012). Such data have been used to infer past changes in the abundance of plants using the C_3 and C_4 pathways (Collister et al., 1994; Boom et al., 2002) or to assess palaeo-hydrological change (e.g. Niedermeyer et al., 2010). Various studies have considered spatial, temporal and botanical patterns in the distributions of *n*-alkane homologues (i.e. the relative proportions of the different *n*-alkane homologues, usually C_{21}–C_{35}). Such patterns have also been considered in sedimentary contexts and used to infer palaeoenvironmental or palaeoecological change (inter alia, Poynter et al., 1989; Ficken et al., 2000; Schwark et al., 2002; Zhang et al., 2006; Bai et al., 2008).

Given the functions of leaf waxes, it is reasonable to assume that their synthesis is, at least to some extent, regulated and optimised by plants (Conte et al., 2003; Shepherd and Griffiths, 2006). However, the underlying significance of changes in *n*-alkane distributions is often not simple to interpret (Dodd and Afzal-Rafii, 2000; Bush and McInerney, 2013). In particular, the question of whether or not leaf wax distributions provide chemotaxonomic information has long been debated and there have been numerous attempts to link carbon chain length distributions to specific plant species, genera or plant functional type (Maffei, 1996), as well as different photosynthetic pathways (e.g. Rommerskirchen et al., 2006a). However, it remains rather unclear to what extent changes in leaf wax composition within palaeoenvironmental archives can be interpreted in terms of shifts in the relative proportions of different plant functional types or plant species and/or the response (i.e. adjustment in leaf wax composition) of a plant community to environmental conditions. For example, distinct shifts in *n*-alkane and *n*-alkanol chain length are seen in north–south transects in southwest Africa. They are associated with the transition from tropical rainforest to savannah (Vogts et al., 2009) and the pattern is mirrored in wax components transported offshore to the southeast Atlantic (Rommerskirchen et al., 2003; Vogts et al., 2012). However, resolving the processes driving such patterns, and thus the (palaeo)environmental significance of records obtained from the same area (e.g. Rommerskirchen et al., 2006b; Maslin et al., 2012), is difficult because the patterns in modern atmospheric aerosols conflate changing environmental conditions and changing plant species/functional type. A recent meta-analysis of *n*-alkane distributions from > 2000 specimens highlighted the great variability in leaf wax *n*-alkane production and distribution, suggesting that there is a need for caution when interpreting leaf wax distributions (Bush and McInerney, 2013). Comparative data concerning leaf wax concentration/production are less often reported (Bush and McInerney, 2013), but the importance of the issue for the interpretation of sedimentary archives has recently been demonstrated (Diefendorf et al., 2011).

Here we have built on such analyses to present a detailed case study that tracks patterns in leaf wax distribution within and between two arid zone biomes in South Africa. It was anticipated that, in arid environments, where stomatal conductance is low for a greater proportion of the time, water loss through the cuticle would be of increased significance (Shepherd and Griffiths, 2006). Hence, there would be environmental pressure for plants to optimise their wax composition (e.g. Macková et al., 2013). Drought adaptation is of further interest as the Succulent Karoo is renowned for an abundance of stem and leaf succulents, many of which utilise the crassulacean acid metabolism (CAM) pathway (Mooney et al., 1977; Rundel et al., 1999). Leaf wax distributions from CAM plants (which include > 10,000 angiosperm species and ca. 7% of vascular plants) have received relatively little study (cf. Maffei et al., 1997; Feakins and Sessions, 2010; Boom et al., 2014). Many terrestrial CAM plants are drought-adapted and have thick, waxy cuticles that potentially yield high leaf wax concentration (Eglinton et al., 1962; Maffei et al., 1997). In large parts of the Succulent Karoo, they are the dominant growth form/functional type and their contribution to, and influence on, various marine sedimentary archives in the region (e.g. Rommerskirchen et al., 2006a; Maslin et al., 2012), as well as emerging terrestrial palaeoenvironmental archives (Carr et al., 2010; Chase et al., 2012), is poorly defined.

We also sought to address a “scale gap” that exists between the analysis of individual plants (e.g. Maffei, 1996; Vogts et al., 2009; Bush and McInerney, 2013) and the integrated signals that characterise atmospheric aerosols (e.g. Huang et al., 2000; Vogts et al., 2012), lake basin sediments (Castañeda et al., 2009) and marine archives (Schefuß et al., 2005). This was achieved via the combined analysis of plant specimens and local soils sampled across the study area. There have been relatively few studies that directly link data from plants and associated soils (cf. Otto and Simpson, 2005), but soils are a potentially significant store and source of (reworked) wax, both to atmospheric aerosols (e.g. Poynter et al., 1989) – particularly in desert regions – and via runoff within catchments (Schefuß et al., 2005). This step is thus pertinent for the use of leaf wax component distributions in palaeoenvironmental reconstruction, not only in terms of understanding and assessing the influence of post-depositional diagenesis (e.g. Buggle et al., 2010), but also in terms of understanding the effect of differences in leaf wax production between plant species, genera or plant functional type.

We present a data set comprising 215 samples of modern plants and 93 soils from the Succulent Karoo and Fynbos biomes of southwest South Africa (Fig. 1). The environmental (climatic and edaphic) gradients in the region, as well as the occurrence of several cosmopolitan plant species throughout the study area allowed us to consider both biome-scale differences in leaf wax *n*-alkane distributions and some chemotaxonomic responses. Overall, the aims were to:

(i) Characterise the *n*-alkane leaf wax yield/concentration for contemporary plants and soils across the dryland biomes of South Africa.
(ii) Assess whether the major biomes/associated eco-regions/plant functional type in the sampling area produce characteristic *n*-alkane leaf wax concentrations and distributions.
(iii) Assess the extent to which comparable plant leaf wax signatures are preserved within the extractable lipids of the region’s soils.
(iv) Assess the significance of the results for application of leaf wax distributions as palaeoenvironmental proxies in southern Africa and for the interpretation of compound-specific stable isotope analysis.

2. Material and methods

2.1. Study area

The study area encompasses the Fynbos (part of the Cape Floristic Region; CFR) and Succulent Karoo biomes of South Africa (Fig. 1). Fynbos is a Mediterranean-type shrubland occupying ca. 90,000 km^2 at the southwest tip of South Africa. It exhibits some of the highest levels of plant diversity and endemism in the world (Goldblatt and Manning, 2002) and is characterised by