Reconstructing mid-Miocene vapor pressure deficit from leaf wax lipid molecular distributions

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Estimates of atmospheric moisture are critical for understanding the links and feedbacks between atmospheric CO_2 and global climate. At present, however, there are few quantitative moisture proxies that are applicable to deep time. Here, we present a new organic molecular proxy for atmospheric moisture derived from modern climate and leaf wax biomarker data from North and Central America. Specifically, we find that changes in the distribution of leaf wax *n*-alkanes, quantified by their Average Chain Length (ACL), is statistically related to mean annual vapour pressure deficit (VPD_{av}) enabling quantitative reconstruction of VPD from sedimentary *n*-alkanes. This relationship can be explained by both biological and physical parameters, such as a genetic pathway in plants regulating lipid production in response to osmotic stress, and differences in evaporation among alkane homologues due to variation in inter-molecule bonds. Further, we focus on *n*-alkanes extracted from soils in our modern calibration, rather than individual plant species, to ensure we capture a holistic 'ecosystem average' response to changes in atmospheric moisture over the period of soil formation.

To evaluate the performance of our new transfer function, we applied it to the Armantes section of the Calatayud-Daroca Basin in Central Spain spanning the Middle Miocene Climatic Optimum (MMCO) and the Middle Miocene Climate Transition (MMCT). Paleobiological studies have shown that Spain experienced drier, cooler conditions during the mid-Miocene, making it an ideal location to test our leaf wax biomarker-based VPD proxy. We observe a positive shift of ~3 ACL units in the Armantes sediments between 16.4 and 12.4 Ma. Applying our transfer function, we calculate that reconstructed VPD_{av} rises from 0.13 to 0.92 kPa during this interval, indicating a substantial drying through the MMCT. These data are consistent with fossil assemblages and mammalian stable isotope data, highlighting the utility of this new organic molecular tool for quantifying hydrologic variability over geologic timescales.