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Rapid atmospheric transport and large-scale deposition of recently synthesized plant waxes

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Abstract

Sedimentary plant wax $^2\text{H}/^1\text{H}$ ratios are important tools for understanding hydroclimate and environmental changes, but large spatial and temporal uncertainties exist about transport mechanisms from ecosystem to sediments. To assess atmospheric pathways, we collected aerosol samples for two years at four locations within a ~60 km radius in northern Switzerland. We measured *n*-alkane distributions and $^2\text{H}/^1\text{H}$ ratios in these samples, and from local plants, leaf litter, and soil, as well as surface sediment from six nearby lakes. Increased concentrations and ^2H depletion of long odd chain *n*-alkanes in early summer aerosols indicate that most wax aerosol production occurred shortly after leaf unfolding, when plants synthesize waxes in large quantities. During autumn and winter, aerosols were characterized by degraded *n*-alkanes lacking chain length preferences diagnostic of recent biosynthesis, and $^2\text{H}/^1\text{H}$ values that were in some cases more than 100‰ higher than growing season values. Despite these seasonal shifts, modeled deposition-weighted average $^2\text{H}/^1\text{H}$ values of long odd chain *n*-alkanes primarily reflected summer values. This was corroborated by *n*-alkane $^2\text{H}/^1\text{H}$ values in lake sediments, which were similar to deposition-weighted aerosol values at five of six sites. Atmospheric deposition rates for plant *n*-alkanes on land were ~20% of accumulation rates in lakes, suggesting a role for direct deposition to lakes or coastal oceans near similar production sources, and likely a larger role for deposition on land and transport in river systems. This mechanism allows mobilization and transport of large quantities of recently produced waxes as fine-grained material to low energy sedimentation sites over short timescales, even in areas with limited topography. Widespread atmospheric transfer well before leaf senescence also highlights the importance of the isotopic composition of early season source water used to synthesize waxes for the geologic record.

Keywords: Hydrogen isotopes; plant wax; *n*-alkanes; aerosol; sediment

1. Introduction

Plant waxes include a complex mixture of organic compounds that can be preserved in sediments on geologic timescales (Eglinton and Hamilton, 1967). Of these, *n*-alkanes are perhaps the most widely investigated. A number of approaches have been developed to quantify molecular distributions of *n*-alkanes in plants, sediments, oils, and rocks, and to use this information to extract information about past environmental conditions, biological sources, or diagenesis (see Bush and McInerney (2013) for a recent review).

Plant wax $\delta^2\text{H}$ values ($\delta^2\text{H} = (^2\text{H}/^1\text{H}_{\text{sample}})/(^2\text{H}/^1\text{H}_{\text{VSMOW}})-1$, in ‰, VSMOW - Vienna Standard Mean Ocean Water) have been developing as hydroclimate tracers over the past two decades (Sachse et al., 2012). These research efforts were largely motivated by empirical relationships between wax and precipitation $\delta^2\text{H}$ values, which can be used to understand moisture transport history (Dansgaard, 1964). $\delta^2\text{H}$ values of sedimentary plant waxes may be a highly useful tracer of precipitation isotope values, and fill an important gap in spatial coverage resulting from the limited geographic extent of other water isotope archives such as ice sheets, carbonate lakes, or cave deposits. However, applications are not yet optimized due to an incomplete mechanistic understanding of the signal transfer from precipitation to the plant and from the plant to the sediment (Sachse et al., 2012).

Interrogation of the relationship between source water and plant wax $\delta^2\text{H}$ values has identified important caveats to direct application of *n*-alkane $\delta^2\text{H}$ values as hydroclimate proxies. For example, transpiration can enrich biosynthetic source water $\delta^2\text{H}$ values at low to moderate humidity (Kahmen et al., 2013). The severity of this effect and the impact on $\delta^2\text{H}$ values of plant waxes varies between dicotyledonous trees and monocotyledonous grasses (Feakins and Sessions, 2010; Gamarra et al., 2016; Kahmen et al., 2013; Smith and Freeman, 2006). The timing of wax production is also important, and although some wax replacement may occur after initial leaf production, it is relatively clear that isotope values are largely set

during the major wax production period – either during initial leaf production for trees, or on a more continuous basis for grasses, which elongate over the course of a growing season (Freimuth et al., 2017; Kahmen et al., 2011; Sachse et al., 2015; Sachse et al., 2010; Tipple et al., 2013). For trees in temperate latitudes, source water is typically soil water during the major leaf formation period in the springtime, which is itself an integrated precipitation signal of the preceding months (Freimuth et al., 2017; Sachse et al., 2015; Tipple et al., 2013), while in the tropics the timing is linked to wet and dry season cycles (Ponton et al., 2014). Each of the aforementioned processes has potential to introduce a seasonal component to the climate signal recorded in sedimentary plant wax $\delta^2\text{H}$ values, the impacts of which may vary depending on how and when waxes are separated from living plants.

Plant wax transport mechanisms are the other key component for understanding sedimentary data (Sachse et al., 2012). Compound-specific radiocarbon studies have been especially informative here, and have demonstrated cases where the average ages of plant waxes in sediments were hundreds to thousands of years older than the surrounding matrix, and that these temporal offsets can vary with depth in sediment (Douglas et al., 2014; Eglinton et al., 1997; Kusch et al., 2010; Pearson and Eglinton, 2000; Smittenberg et al., 2004). These temporal offsets can be explained either by a consistently long residence time for plant waxes on land prior to sedimentation, or by mixing a small contribution of very old material with an otherwise contemporaneous source, with the relative importance of these likely varying over time and space. Improved understanding of the timescales over which plant waxes are transported to sediments is therefore key to improved interpretations of the climate signal preserved in sedimentary plant wax $\delta^2\text{H}$ values.

River transport is an important mechanism for transporting waxes to sedimentary settings, and studies have generally demonstrated that riverine waxes reflect the vegetation of regions through which they travel. However, certain environments may contribute

disproportionately to the exported signal, and erosion of older material can contribute to the transported plant wax composition (Galy et al., 2011; Häggi et al., 2016; Hemingway et al., 2016; Kusch et al., 2010; Ponton et al., 2014; Schefuß et al., 2016; Simoneit et al., 2017).

Plant waxes are also transported by wind (Simoneit et al., 1977). Waxes can be aerosolized from living plants through dust abrasion or by leaves rubbing together. They can also enter the atmosphere from wind action on soils or exposed sediments, or by burning fossil fuels, biomass, or cigarettes (Rogge et al., 1993). Similar to compounds in rivers, atmospheric plant waxes generally reflect the area through which they travel (Bendle et al., 2006; Nelson et al., 2017; Schefuß et al., 2003; Yamamoto et al., 2013). Non-urban studies have generally shown that atmospheric waxes over continents represent a regional footprint (tens to hundreds of km) rather than a highly localized or very large source region (Conte et al., 2003; Gao et al., 2014; Nelson et al., 2017).

Deposition of *n*-alkanes from aerosols occurs primarily through dry particle settling and wet deposition via precipitation scavenging, and varies by environment depending on source proximity and atmospheric conditions (Doskey, 2000; Gagosian and Peltzer, 1985; Zafirou et al., 1985). The relative importance of dry versus wet deposition also varies over space and time depending on weather, particle size, and depositional surface characteristics, with neither process consistently dominating (Feng, 2008). In remote marine settings atmospheric *n*-alkane deposition dominates over other mechanisms such as river transport (Gagosian and Peltzer, 1985). In continental lakes atmospheric *n*-alkane deposition has been considered negligible in some cases (Meyers and Hites, 1982). However, high atmospheric deposition rates responsible for more than 70% of total *n*-alkane accumulation from all transport pathways have been documented in lakes from very different settings including the Patagonian Steppe (Hockun et al., 2016) and temperate North America (Doskey, 2000). This implies that aerosols may be an important mechanism for transporting waxes to sediments

across diverse environments. Understanding the source areas, transport timescales, seasonal changes, and deposition patterns of plant wax aerosols are therefore all important yet poorly constrained processes for interpreting the sedimentary record.

The present study builds on previous work that showed that *n*-alkane distributions and $\delta^2\text{H}$ values in aerosols recovered from a forest in central Germany did not reflect local vegetation despite the close proximity to production sources in trees, and suggested that these aerosol *n*-alkanes reflected a regional source area on the order of tens to hundreds of km rather than a highly local (i.e. meter scale) source, or a signal from very long range transport over thousands of km (Nelson et al., 2017). Here we present results from an expanded sample set collected in a similar climate setting in Switzerland including above and below forest canopy, grassland, and high alpine environments to capture the regional spatial scale of tens to hundreds of km over which plant wax aerosols are likely integrated in a temperate latitude setting close vegetation sources.

The goals of this work were to quantify any seasonal changes in aerosol *n*-alkane distributions and $\delta^2\text{H}$ values in order to assess how these relate to changes in vegetation and how these are mixed with *n*-alkanes from other sources such as anthropogenic emissions. We also sought to evaluate how atmospheric deposition rates of *n*-alkanes change over these seasonal timescales, and whether deposition patterns reflect or deviate from the seasonal patterns in atmospheric concentrations. We also sought to improve understanding of the importance of atmospheric deposition for sediment accumulation in lakes within the study region. To achieve these objectives, we compared aerosol *n*-alkane distributions and $\delta^2\text{H}$ values among sites over twenty-two months of continuous recovery. We then used these data with meteorological records to model deposition, and to calculate deposition-weighted aerosol *n*-alkane $\delta^2\text{H}$ values. We then compared atmospheric deposition-weighted $\delta^2\text{H}$ values of *n*-alkanes to those recovered from surface sediments in six lakes in the same region to

determine whether the hydrogen isotope fingerprint of sedimentary *n*-alkanes would be consistent with a contribution from atmospheric deposition.

2. Material and Methods

2.1 Sampling schedule and site characteristics

Aerosol samples were collected from above and below the canopy of a mixed deciduous forest from the Swiss Canopy Crane at Hofstetten (47.4687°N, 7.5024°E, 575 m), from an intensively managed grassland research station at Chamau (47.2100°N, 8.4099°E, 395 m), and from the high altitude Jungfrauoch Sphinx Observatory (46.5475°N, 7.9850°E, 3466 m) (Fig. 1). All sites are independently managed, and meteorological records were compiled from on-site weather stations. Periodic data gaps were filled with data from nearby national weather stations (www.meteoswiss.ch) (Fig. A1). Continuous aerosol sampling was conducted from June 2014 to March 2016 at Chamau at ~2 week intervals during the spring, summer, and fall, and ~4 week intervals in the winter. Hofstetten sampling followed the same schedule, but did not begin until August 2014, and samples at the Jungfrauoch were recovered every ~4 weeks due to lower atmospheric plant wax concentrations at this site, and were not collected in the winter.

Plant samples were collected from Hofstetten during the growing seasons of 2014 and 2015 from the upper canopy. Sampled species were *Carpinus betulus* (European hornbeam), *Fagus sylvatica* (European beech), *Quercus petraea* (sessile oak), *Tilia platyphyllos* (largeleaf linden), *Larix decidua* (European larch), *Picea abies* (Norway spruce), and *Pinus sylvestris* (Scots pine), which dominate the canopy cover (Klein et al., 2016). Plants in the local vicinity of the aerosol sampler were also collected at Chamau, and included *Taraxacum officinale* (dandelion), *Trifolium repens* (white clover), and the dominant *Lolium multiflorum* (Italian ryegrass) (Merbold et al., 2014). End of season litter and soil samples were collected

in 2014 and 2015 from Chamau and Hofstetten. No plants or soils were present to collect at the Jungfrauoch. Lake sediments were collected during the spring of 2015 from Lake Soppen, Lake Mauen, Lake Greifen, Lake Rot, Lake Baldegg, and Lake Sarnen. These lakes span a range of surface and catchment areas and are surrounded by vegetation that is similar to that of the aerosol sample sites (Fig. 1; Table 1).

2.2 Sampling procedures

Aerosol samples were collected using high-volume filtration systems (Hi-Q Environmental Products Company, Inc., San Diego, CA, USA). Air was filtered at 1000 liters per minute onto EPM 2000 filters (retention efficiency of 99.95% of 0.3 μm size particles; Whatman GE, Little Chalfont, UK). Filters were wrapped in combusted aluminum foil, sealed in plastic bags, and frozen at -20°C until analysis. Leaf samples were collected from healthy, sun-exposed leaves in the upper canopy of the forest or grassland, while litter and soil samples were collected from the ground. Samples were oven-dried at 45°C and stored in dry paper bags or covered foil trays until analysis. Sediments were collected with a gravity corer, sectioned at 1 cm intervals, stored frozen at -20°C , and freeze-dried prior to analysis. Accumulation rates from each core were analyzed using a Ge Gamma Spectrometer (GCW3022-7500, Canberra, Meridian, CT, USA) on the 46.5 keV line for ^{210}Pb and the 661.7 keV line for ^{137}Cs activity. Lipid analyses were performed on the 0-1 cm samples.

2.3 Lipid extraction and purification

Aerosol, plant, litter, and soil samples were prepared in the Basel Stable Isotope Ecology Lab (BASIEL) at the University of Basel, Switzerland, while lake sediment samples were prepared in the Biogeochemistry Lab at the Swiss Federal Institute of Aquatic Science and Technology (Eawag), Kastanienbaum, Switzerland. Filters were extracted with two 20-

minute sonication cycles in 9:1 dichloromethane (DCM)/Methanol (MeOH), followed by one with hexane at 45°C in 40 mL glass vials. Plant, litter and soil were extracted similarly, but the samples were weighed first, and only the first two cycles were performed. A 5 α -androstane recovery standard was added to each sample before extraction, and aerosol samples received an additional *n*-C₃₆ standard. Lake sediments were extracted using 9:1 DCM/MeOH in a SOLVpro Microwave Reaction System (Anton Paar, Graz, Austria) at 70°C for five minutes. A 5 α -cholestane recovery standard was added to each sediment sample prior to extraction.

Total lipid extracts (TLEs) processed in Basel were dried under nitrogen, and hydrocarbon fractions were separated from TLEs using 1.5 g of silica gel (0.040 - 0.063 mm, 5% water deactivated) with 20 mL of hexane. Aerosol *n*-alkanes were further purified by urea adduction to remove branched and cyclic compounds. Extracts processed at Eawag were treated with copper to remove elemental sulfur, and saponified with 3 mL of 1N KOH in MeOH and 2 mL of nanopure H₂O for 3 hours at 70°C. Neutral compounds were extracted with hexane and hydrocarbons were then isolated by eluting from a 0.5 g/6 mL isolate silica gel column (Biotage, Uppsala, Sweden) with 4 mL of hexane, and further purified by urea adduction.

2.4 *n*-alkane quantification

A gas chromatography-flame ionization detector (GC-FID) (Trace 1310, Thermo Fisher Scientific, Waltham, MA, USA) was used to quantify *n*-alkane abundances. Samples were injected in hexane in splitless mode on a programmable temperature vaporization (PTV) inlet to a Zebron ZB-5 GC column (30 m x 0.25 mm x 0.25 μ m) with helium carrier gas at 1.1 mL min⁻¹. The GC oven was held at 60°C for 2 min, then ramped to 140°C at 12°C min⁻¹, then to 345°C at 6°C min⁻¹, then held for 15 min. Compounds were identified by retention time, and

original sample concentrations were calculated against the recovery standards for plant, litter, soil, and aerosol samples. Carbon Preference Index (CPI) values were calculated based on sample *n*-alkane distributions to quantify odd-over-even chain length preference (Bray and Evans, 1961). Concentrations of *n*-alkanes in air were based on the filtration volume, while concentrations in other samples were based on the dry sample mass.

2.5 Hydrogen isotope analyses

Hydrogen isotope analyses were performed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) on all aerosol *n*-alkanes for which adequate material was available. This required repeat analyses for some samples to achieve appropriate signal intensity for all compounds. Other sample types were not analyzed multiple times so for these only the major *n*-alkane values were determined. All samples were analyzed in Basel by injecting in hexane in splitless mode on a split/splitless inlet at 250°C to an Agilent (Santa Clara, CA, USA) DB-5 GC column (30 m x 0.25 mm x 0.25 µm) with helium carrier gas at 1.1 mL min⁻¹. The GC oven was held at 70°C for 3 min after injection, then ramped to 150°C at 10°C min⁻¹, then to 320°C at 4°C min⁻¹, then held for 10 min. Column effluent was pyrolyzed at 1420°C and δ²H values were measured on a Thermo Delta V Plus IRMS. The H₃⁺ factor was determined before each sample sequence (Sessions et al., 2001), and was always stable and lower than 4 ppm nA⁻¹. Three injections of an *n*-alkane standard (mix A4 or A6, Indiana University) were made at the beginning and end of each sequence and after approximately every six samples. These were done at different concentrations to bracket the range of permissible analyte peak sizes in samples. δ²H values of targeted analytes were calculated based on sequence-specific regressions between measured and known δ²H values in the standard mix. Samples were injected an average of 2.1 times, and the pooled analytical uncertainty of replicates was 1.5‰ (n = 850) (Polissar and D'Andrea, 2014). A quality control sample from oak leaves originally

collected in Berkeley, California, is analyzed in every instrument sequence in Basel to monitor long-term stability. The average $\delta^2\text{H}$ value of the major *n*-alkane in this sample, *n*-C₂₉, was $-142.7 \pm 3.6\text{‰}$ (*n* = 504) between 2014 and 2016.

2.6 End-member estimates

Estimates of relative contributions of degraded background aerosol sources to mixed distributions in samples were performed for *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) following Simoneit (1991). This assumes negligible production of even chain *n*-alkanes by plants and uses the average of concentration of the neighboring even carbon number homologs in a sample to estimate the background contribution. For any given odd carbon number *n*-alkane, the contribution from low CPI background material was therefore determined as: $C_{n(\text{background})} = (C_{n-1} + C_{n+1})/2$, where C_n indicates the concentration of an *n*-alkane of a given chain length, *n*, in a sample. Estimates of background $\delta^2\text{H}$ values were determined by averaging all available values from the same even carbon number homologs used in the background contribution estimate in a given sample, as well as the next shorter compound (i.e. C_{n-3}). This was done in order to calculate background values in more cases than would have otherwise been possible given the limited number of direct measurements of long chain even carbon number $\delta^2\text{H}$ values.

2.7 Back-trajectory analyses

Thirty-six hour air mass back trajectories were calculated at the location of each aerosol sampler (upper canopy sampler only at Hofstetten ca. 40 m) at hourly intervals using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Rolph, 2016; Stein et al., 2015) in order to compare regional transport histories among sites. Model runs used the National Center for Environmental Prediction (NCEP) Reanalysis data. Four back

trajectories were calculated per day concluding at 00:00, 06:00, 12:00, and 18:00, such that 28 trajectories were determined for each 7-day period at each site (Chamau, Hofstetten, and Jungfrauoch). Trajectories were determined for all intervals of aerosol sampling.

2.8 Atmospheric deposition modeling

Atmospheric deposition rates of *n*-alkanes were calculated from separate dry and wet deposition models that were each applied at the Chamau and Hofstetten sites, but not for the Jungfrauoch due to the discontinuous nature of the sample recovery, complex topography, and extreme weather conditions. Dry deposition velocities were calculated with a mechanistic model incorporating diffusion, turbulence, and inertial impaction for particles (Feng, 2008). The model description is available in Feng (2008), but in summary, deposition is calculated from particle diameter, wind speed, air temperature and pressure, and surface roughness.

Meteorological model inputs were obtained from the site stations (Fig. A1). Particle size distribution ranges for *n*-alkanes were not measured, so these were adapted from measurements in other European forests to define the relative contribution of six size fractions to the total sample (<0.5 μm , 0.5-0.96 μm , 0.96-1.5 μm , 1.5-3.0 μm , 3.0-7.2 μm , and >7.2 μm) (Kavouras and Stephanou, 2002). Surface roughness lengths of 0.027 m were used for grassland (Hansen, 1993) and 1.6 m for forest (Wieringa, 1993). The zero plane displacement was set at three-quarters of canopy height for forest (Kaimal and Finnigan, 1994) and two-thirds for grassland (Mölder et al., 1999). Dry particle settling velocities were modeled from 0.1 to 10 μm at 0.1 μm increments, and the mean velocity for each size category was used to calculate size-dependent fluxes. These were summed to total dry depositional flux (Dd) in $\text{pg cm}^{-2} \text{ s}^{-1}$:

$$Dd = \sum_{i=0.5\mu\text{m}}^{>7.2\mu\text{m}} C_{\text{alk-air}} * f_i * Vd_i$$

where $C_{alk-air}$ is the concentration of an individual n -alkane in air (pg cm^{-3}), f_i is the fractional contribution of a given size fraction, and Vd_i is the corresponding velocity (cm s^{-1}).

Wet deposition was calculated from measured n -alkane concentrations in air, precipitation rate, and a particle size-independent washout ratio of 2×10^5 (Wp ; $Wp = C_{alk-water}/C_{alk-air}$), taken from a review study (Jurado et al., 2005). Wet deposition (Dw) was calculated as ($\text{pg cm}^{-2} \text{ s}^{-1}$) $Dw = C_{alk-air} * Pre * Wp$, where Pre is precipitation (mm). Concentrations in precipitation were also calculated to compare against literature values ($C_{alk-water} = C_{alk-air} * Wp$).

Total atmospheric deposition (Dt) was determined from the sum of wet and dry deposition ($Dt = Dd + Dw$), and used to calculate monthly deposition in ng cm^{-2} , and deposition-weighted $\delta^2\text{H}$ values for each n -alkane at Chamau and Hofstetten. Annual rates were calculated from monthly totals for 2015, the only complete year of sampling. Many inputs used in the model lack published uncertainties so model products do not include propagated errors. To evaluate the sensitivity to input terms, model runs were conducted in which the precipitation washout ratio, air temperature, wind speed, particle density, surface roughness length, and datum displacement were set at values 20% higher, and 20% lower than the values assumed in the main experiments, and the effects of these changes were evaluated through the impact on the final annual deposition weighted aerosol $\delta^2\text{H}$ value calculations. All modeling and statistical analyses were performed using R (version 3.3.2) with RStudio (version 1.0.136).

3. Results

3.1 Aerosol samples

Atmospheric concentrations of n -alkanes were generally highest at the Chamau grassland, followed by the Hofstetten forest, followed by the high alpine Jungfrauoch, and seasonal

variability at each site was similar for each compound (Fig. 2; Electronic Annex (EA) 1). Middle chain length *n*-alkanes (*n*-C₂₃, *n*-C₂₄, *n*-C₂₅, *n*-C₂₆) were more abundant in the winter than in the summer in the grassland. This was also the case at the forest site, but concentrations were also generally much lower there. In contrast, concentrations of long chain odd carbon number *n*-alkanes typical of leaf waxes from higher plants (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) were highest in early to mid summer at both the grassland and forest, with one exception of a high concentration sample from late 2015 coinciding with a very strong wind event in the grassland (Figs. 2 and A1). The summertime maximum concentrations in long chain odd carbon number *n*-alkanes typical of higher plants (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) were larger in 2015 than in 2014, although it must be noted that sampling in 2014 did not start until mid/late summer. Minimal differences were observed between above and below canopy samples from the Hofstetten forest, but in some cases concentrations were higher above the canopy (Fig. 2). High alpine Jungfrauoch sampling was not possible in winter so the complete seasonal cycle was not captured. Summer and early autumn patterns were consistent with the grassland and forest sites, with greater concentrations of long odd chain *n*-alkanes than middle and even chain length *n*-alkanes, and overall declining concentrations throughout the season following an early/mid summer maximum.

Seasonal patterns were also present in the patterns of calculated contributions from fresh plant vs. degraded background sources to the total aerosol *n*-alkane pool for *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) (Fig. 3). At the Chamau grassland and high alpine Jungfrauoch in both years, the maximum concentrations of the inferred fresh plant end member occurred in the early growing season, or as early in the growing season as samples were collected given that sampling started after the growing season began in 2014. The same pattern held for the Hofstetten forest for 2015, but no such comparison was possible for 2014 because sampling there did not begin until the late growing season. In

contrast to the concentrations of the inferred fresh plant end member, the concentrations of the inferred degraded background end member showed a seasonal pattern that was generally characterized by higher values outside the growing season during the fall and winter (Fig. 3). However, in some cases the degraded background end member *n*-alkane concentrations did begin increasing near the end of the growing season (Fig. 3).

Seasonal patterns were also observed in aerosol $\delta^2\text{H}$ values of individual *n*-alkanes, which ranged from -214 to -79‰, and the seasonal patterns were more pronounced for odd than for even carbon number compounds (Fig. 4; EA1). $\delta^2\text{H}$ values of individual *n*-alkanes (Fig. 4) were lowest during the summertime, and coincided with high CPI values in samples (high odd-over-even chain length preference) (Fig. 4 color scale; EA1). Summertime minimum $\delta^2\text{H}$ values decreased slightly with increasing chain length for long chain odd carbon number *n*-alkanes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) and were more consistent among sites in summer than in fall and winter (Fig. 4). Fall/winter values from the Chamau grassland were higher than those from the Hofstetten forest, as were those from the high alpine Jungfrauoch to the extent that these samples were collected (Fig. 4). Minimal differences were observed between above and below canopy $\delta^2\text{H}$ values at Hofstetten (Fig. 4).

Background aerosol $\delta^2\text{H}$ value end member estimates for the main plant waxes, *n*-C₂₇, *n*-C₂₉, and *n*-C₃₁, were consistently ~100‰ (Fig. 5). Fresh aerosol $\delta^2\text{H}$ value end member estimates were similar to values measured during summer months when concentration estimates suggest a dominant contribution from fresh sources, but were lower and erratic during winter months, when background concentration estimates suggest little contribution from fresh material (Figs. 3 and 5).

3.2 Plant, litter, and soil samples

Concentrations of *n*-alkanes were higher for angiosperm-dicots than gymnosperms (Fig. 6, symbol size). Concentrations in grasses from Chamau (*Lolium multiflorum*; Italian ryegrass), increased from *n*-C₂₇ to *n*-C₃₁, and were intermediate between angiosperm-dicots and gymnosperm concentrations (Fig. 6; EA2). Tree *n*-alkane $\delta^2\text{H}$ values differed by species (Fig. 6; EA3), but were generally stable over the course of an individual season in contrast to values from grass samples, which increased throughout each summer (Fig. 6). Statistical tests of the slopes of $\delta^2\text{H}$ values over time in each year, and two sample t-tests for the difference between early and late season average values (before or after August 1st) for each plant functional type and *n*-alkane were significant ($p < .05$) only for the early/late season differences for monocot *n*-C₂₉ in 2014, and *n*-C₂₉ and *n*-C₃₁ in 2015, although such quantifications were limited by the level of sample replication in some cases.

End of season litter and soil $\delta^2\text{H}$ values were similar to those of the average plant values, and *n*-alkanes were present in equal or greater concentrations in litter compared to soils (Fig. 6). Comparisons of litter and soil $\delta^2\text{H}$ values with those of *n*-alkanes from plants (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) collected in the late growing season (August or after) at each site were conducted with two sample t-tests for all cases where data density allowed this. Out of these comparisons, the only significant difference ($p < .05$) was found between *n*-alkane $\delta^2\text{H}$ values from leaves and leaf litter at the Hofstetten forest site for *n*-C₂₉ in 2014. *n*-alkane $\delta^2\text{H}$ values from plants spanned a total range from -267 to -116‰, while litter varied between -215 and -161‰, and soils fell between -223 and -100‰ (EA3).

3.3 Back trajectories

Air mass back trajectories were similar between Chamau and Hofstetten in all seasons (Fig. 7). Individual trajectories from each site can be matched with the corresponding similar trajectory in the other site, and the spatial pattern of the highest trajectory densities at each

site are similar over equivalent intervals (Fig. 7). Jungfraujoch trajectories differed greatly from these, and indicated longer-range transport over a more dispersed area (Fig. 7). The areas of highest back trajectory density for the Chamau grassland and Hofstetten forest showed limited directional preference and were confined to a limited area in central Europe, although trajectory origins were also generally further from the sampling locations in winter seasons compared to summer seasons, with origins to the east. Long range transport originating from the east was common at the Jungfraujoch even during the summer months, with some trajectories indicating transport from areas as far away as Africa and Scandinavia (Fig. 7).

3.4 Aerosol deposition and source comparison

Modeled monthly atmospheric deposition rates of *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) at Chamau and Hofstetten were highest in the summer (Fig. 8; EA4), similar to the temporal atmospheric concentration patterns (Fig. 2). In winter, despite relatively high atmospheric concentrations (Fig. 2), deposition rates of middle and long-even chain length *n*-alkanes (*n*-C₂₃, *n*-C₂₄, *n*-C₂₅, *n*-C₂₆, *n*-C₂₈ and *n*-C₃₀) were much lower than those for odd long chain length *n*-alkanes with the exception of one high deposition event at Chamau in late 2015 (Fig. 8), coinciding with a strong wind event (Fig. A1). The highest deposition rates were determined for *n*-C₂₉ at the Hofstetten forest in July 2015, which occurred during a longer period of elevated deposition rates for long chain odd carbon number *n*-alkanes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) and overall lower aerosol *n*-alkane $\delta^2\text{H}$ values in summer beginning just after widespread leaf flush/unfolding (Fig. 8). Concentrations of *n*-alkanes in rain calculated from the washout ratio ranged from 0.2 to 8.9 $\mu\text{g L}^{-1}$, which is consistent with direct measurements on snow and rain from a similar climate and vegetation zone in southern Indiana, central North America, which ranged from 0.4 to 8 $\mu\text{g L}^{-1}$ (Meyers

and Hites, 1982), but much higher than concentrations measured in marine precipitation (Zafiriou et al., 1985).

Annual deposition in 2015 was highest for n -C₂₉ at Hofstetten, exceeding 90 ng cm⁻² yr⁻¹ (Fig. 9a; Table 2). Deposition rates were generally higher at both sites for odd than for even chain length n -alkanes, these odd/even differences were largest for long chain (>26) compounds, and were greater at Hofstetten than at Chamau (Fig. 9a). Accordingly, more even and middle chain length n -alkanes were deposited at Chamau (n -C₂₃, n -C₂₄, n -C₂₅, n -C₂₆, n -C₂₈) (Fig. 9a). These deposition rates were lower than accumulation rates in lake sediments in all cases for any given n -alkane, which varied from 26.0 to 667.8 ng cm⁻² yr⁻¹ overall, and from 105.8 to 667.8, 132.5 to 568.5, and 131.4 to 465.5 ng cm⁻² yr⁻¹ for n -C₂₇, n -C₂₉, and n -C₃₁, respectively (Fig. 9a; Table 2; EA5). Deposition-weighted aerosol $\delta^2\text{H}$ values were similar between sites, and while even chain length n -alkane $\delta^2\text{H}$ values were relatively consistent, odd chain length $\delta^2\text{H}$ values decreased with increasing chain length (Fig. 9b; Table 3; EA6). Deposition-weighted annual odd chain aerosol n -alkane $\delta^2\text{H}$ values were near the low end of values for individual aerosol samples (Fig. 9b), but were within the middle of the wide range of values for plants, and similar to or higher than litter and soil $\delta^2\text{H}$ values (Fig. 9b). Deposition-weighted aerosol $\delta^2\text{H}$ values of n -alkanes typical for higher plant waxes (n -C₂₇, n -C₂₉, n -C₃₁) were also similar but not identical to those from surface sediments from most sediment samples, and the similarities increased with increasing chain length (Fig 9b; Table 3; EA6 and 7). The exception was Lake Sarnen, where the sediment CPI value was less than 2, and the sediment $\delta^2\text{H}$ values were closer to the deposition weighted even chain length aerosol values (Fig. 9b). Sensitivity analysis results showed minimal impact on the annual deposition-weighted aerosol $\delta^2\text{H}$ values at either site (Fig. A2).

4. Discussion

4.1 Fresh plant waxes

Higher plant *n*-alkanes in temperate climates are dominated by *n*-C₂₇, *n*-C₂₉, *n*-C₃₁, and to a lesser extent, *n*-C₂₅ and *n*-C₃₃ (Bush and McInerney, 2013). High concentrations and low $\delta^2\text{H}$ values of *n*-C₂₇, *n*-C₂₉, and *n*-C₃₁ in aerosol samples with high CPI values at all sites in the summer shortly after widespread leaf production indicates rapid transfer of recently produced leaf waxes to the air (Figs. 2 and 4). Although this rapid transfer of recently produced leaf waxes to the air occurs each year, the exact timing and magnitude can change in response to variability in climate and phenology. For example, the earlier leaf formation period in Switzerland in 2014 compared to 2015 probably resulted in an earlier aerosol pulse that was already declining by the time sampling was initiated in that year, especially given that sampling at the forest site did not start until August (Fig. 2). Warmer and drier conditions in summer may have also resulted in a larger mass transfer of waxes to the atmosphere in 2015 as compared to 2014 due either to increased wax production in response to desiccation stress, increased loss to the atmosphere, or both (Fig. A1).

If plant species sampled from the Hofstetten forest and Chamau grassland can be regarded as broadly representative of similar areas throughout northern Switzerland, then some of the decrease in summertime aerosol $\delta^2\text{H}$ values of *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) that occurred with increasing chain length may indicate increasing relative proportion of waxes from monocot grasses, which produce *n*-alkanes with lower $\delta^2\text{H}$ values than those from trees (Figs. 4 and 6). This implies transport of aerosol *n*-alkanes from areas outside the immediate vicinity of the aerosol samplers, emphasizing a role for regional (tens to hundreds of km) transport processes (Conte et al., 2003; Nelson et al., 2017). Alternatively, decreasing summertime minimum $\delta^2\text{H}$ values with increasing chain length might indicate decreased contribution from a chemically degraded background with higher $\delta^2\text{H}$ values (Bai et al., 2017; Yamamoto and Kawamura, 2010). This possibility is

supported to some extent by decreasing summertime concentrations of the inferred degraded background *n*-alkane pool with increasing chain length, especially at the Chamau grassland (Fig. 3).

Summertime minimum $\delta^2\text{H}$ values of aerosol *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) at the Jungfrauoch were more similar to Hofstetten than Chamau (Fig. 4). This may suggest that trees more readily shed leaf wax *n*-alkanes to the atmosphere than grasses do, which is perhaps a function of the higher elevation of the tree canopy and increased wind exposure, or simply increased production of *n*-alkanes by trees compared to grasses (Fig. 6). If this is the case, it would partially explain how tree-derived waxes are overrepresented relative to those of grasses in some lacustrine sediments (Diefendorf and Freimuth, 2017).

Estimates of fresh end-member $\delta^2\text{H}$ values for the long chain odd carbon number *n*-alkanes typical of higher plants (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) were quite similar to the actual measured summer values in aerosol samples, in contrast to values measured from the winter (Fig. 5). Inferred fresh end member $\delta^2\text{H}$ values during the wintertime were in some cases lower than during the summer, which would be consistent with the expected changes in the $\delta^2\text{H}$ values of precipitation (Fig. 5). However, the very small inferred contribution from fresh material in this time of year cautions against interpreting this pattern (Fig. 3), especially given that most plants are not producing new leaves during the winter.

Similarities between $\delta^2\text{H}$ values from long chain odd carbon number *n*-alkanes recovered from litter and soil with those collected directly from plants in the late growing season (August or after) at each site suggests that even in cases where soils or leaf litter might be important sources of aerosols that they would still be representative of their location of origin (Fig. 6). However, aerosol production from waxes in litter and soil should be greater in fall than in the summer, after leaf senescence, which would more readily allow mobilization

by wind. Since aerosol *n*-alkane concentrations are highest in early summer shortly after leaf unfolding, it is unlikely that they are transferred to the air via a ground-first pathway, but rather that the major mechanism is direct transfer from leaves. Peak concentrations early in the growing season may indicate that outer waxes on new leaves may be more easily dislodged than on older leaves, or possibly transport associated with pollen dispersion which is also typically released in the investigated trees and grasses in the early spring.

4.2 Background *n*-alkanes

In contrast to long chain odd carbon number *n*-alkanes, even/middle chain length *n*-alkanes are not abundant in terrestrial vascular plants (Bush and McInerney, 2013). Instead, these are the major *n*-alkane constituents of chemically degraded sources that have lost the original odd-over-even chain length preference through diagenesis and cracking during thermal maturation, including gasoline, diesel, and other petrogenic products (Bai et al., 2017; Rogge et al., 1993). These sources can also contribute to the aerosol *n*-alkane pool, and studies in polluted urban settings confirm anthropogenic sources in many cases, with *n*-alkane distributions showing low CPI values, and maximum concentrations in the middle to short range (ca. *n*-C₂₄) (Bai et al., 2017; Rogge et al., 1993; Yamamoto and Kawamura, 2010). These values are consistent with the wintertime chain length distributions observed in aerosol *n*-alkanes from the Chamau grassland and Hofstetten forest (Fig. 2), and typical for petrogenic sources, including gasoline, diesel, and coal, which contain few *n*-alkanes longer than *n*-C₂₇ (Bai et al., 2017; Bai et al., 2014; Harvey et al., 2012; Rogge et al., 1993).

While *n*-alkane distribution patterns can distinguish degraded from recently produced material, $\delta^2\text{H}$ values of *n*-alkanes are less informative, as crude oils can span a range from at least ~ -70 to -240‰ according to a recent compilation (Yamamoto and Kawamura, 2010). The limited quantities of even chain length *n*-alkanes that are produced by plants do tend to

have higher $\delta^2\text{H}$ values than homologous odd carbon number compounds, which may relate to the use of propionate as a biosynthetic precursor instead of acetyl-CoA (Zhou et al., 2010). Although this could explain the higher $\delta^2\text{H}$ values of even carbon number aerosol *n*-alkanes in the present study, only a degraded source would also be compatible with the co-occurrence of low CPI values (Fig. 4) and a shift towards shorter chain length distributions (Fig. 2). Furthermore, wintertime odd chain length *n*-alkane $\delta^2\text{H}$ values were much higher than in summer (Fig. 4). This occurred when plants in the area of the present study were largely dormant, and further implies the existence of a degraded background that contains no odd over even chain length preference. Such a source would likely have consistent *n*-alkane $\delta^2\text{H}$ values among odd and even homologues, and in the absence of a large contribution from fresh plant material, could cause the $\delta^2\text{H}$ values of *n*-C₂₇, *n*-C₂₉, and *n*-C₃₁ to increase compared to summer values if the $\delta^2\text{H}$ value of this chemically degraded end member were more enriched than the local vegetation, as appears to be the case in this region.

The contribution from a degraded aerosol *n*-alkane end member would be expected to have a decreasing influence on the odd carbon number *n*-alkanes as chain length increased, given the previously described characteristics of petrogenic *n*-alkane chain length patterns which typically include few *n*-alkanes longer than *n*-C₂₇ (Bai et al., 2017; Bai et al., 2014; Harvey et al., 2012; Rogge et al., 1993). This is supported to some extent by the inferred background contribution to *n*-C₂₇, *n*-C₂₉, and *n*-C₃₁ in aerosols (Fig. 3), and the associated inferred $\delta^2\text{H}$ values (Fig. 5). Lower atmospheric concentrations of even and middle chain length *n*-alkanes in summer compared to winter at both Chamau and Hofstetten also shows that as fresh plant sources increase, there is a simultaneous decline in the chemically degraded sources, although the pattern at Chamau is more pronounced (Figs. 2 and 3). This indicates either reduced fossil fuel burning in summer, or atmospheric conditions that limit summertime middle and even chain length aerosol *n*-alkane dispersal. Differences in

fall/wintertime aerosol *n*-alkane concentrations and $\delta^2\text{H}$ values between sites also highlights the possible role of taller vegetation/trees as a background filter, as concentrations of *n*-C₂₄ and *n*-C₂₆ were never as high in the forest at Hofstetten as in the open grassland at Chamau (Fig.3), despite the sites sharing similar elevation and climate (Fig.1 and A1).

4.3 Regional transport effects

Air mass back trajectories from Chamau and Hofstetten were extremely similar, suggesting that any effects of long-range transport should be shared, and differ greatly from the Jungfraujoch (Fig. 7). However, the general annual cycles in the aerosol *n*-alkane distribution and hydrogen isotope data at all three sites were similar to the extent that the temporal coverage allows for comparison. These similarities indicate that long-range atmospheric transport processes were not the major factor controlling the aerosol *n*-alkane distributions and $\delta^2\text{H}$ values. At the same time, the large differences in local land cover in the immediate vicinity of the aerosol samplers among the high alpine, grassland, and forest sites indicates that processes occurring on this scale are also not dominant. Instead, and as previously suggested (Conte et al., 2003; Gao et al., 2014; Nelson et al., 2017), regional-scale processes on the order of tens to a few hundred km appear to be most important for controlling the distribution and $\delta^2\text{H}$ values of aerosol *n*-alkanes. This is the length scale over which transport characteristics at all three sites in the present study were most similar, which can therefore explain the general similarity between the aerosol *n*-alkane distribution patterns and $\delta^2\text{H}$ values at all sites. Such similarities despite large differences at other scales suggest that this pattern is likely consistent for most temperate climate continental zones close to production sources. The dominant role for regional transport processes on the order of tens to hundreds of km also explains why in some cases plant wax aerosols values do not directly match local vegetation (Conte et al., 2003; Nelson et al., 2017).

4.4 Transport and deposition

The relative importance of wet and dry particle deposition varies by location, meteorological conditions, and particle characteristics (Feng, 2008). For a given concentration of particles in the air, wet deposition scales with precipitation rate, while dry deposition scales with factors such as wind speed, air temperature, and the characteristics of the depositional surface, and each of these factors may therefore account for different rates of deposition for *n*-alkanes at Chamau and Hofstetten. One way in which the sites differ greatly from the perspective of atmospheric deposition is in surface roughness, which is orders of magnitude higher in a forest compared to a grassland and therefore promotes enhanced dry deposition (Hansen, 1993; Liu et al., 2016; Wieringa, 1993). While this may have some impact on direct comparisons between sites, it will have little bearing on the seasonal patterns at either location since these parameters were constant. Although deposition rates were modeled from concentration and meteorology data as opposed to being direct measurements, the models are published tools that were applied directly without modification (Feng, 2008; Jurado et al., 2005). Furthermore, modeling deposition from concentration data in this manner is the preferred approach for determining deposition from air pollution (Mohan, 2016), and the calculated *n*-alkane concentrations in rain are in close agreement with the limited number of measurements from previous work in temperate continental regions (Meyers and Hites, 1982). However, the potential for biases must also be acknowledged due to the assumptions regarding inputs such as surface roughness or particle concentration stability during sample accumulation. Nevertheless, the balance of information suggests that the calculated deposition rates should be broadly accurate, and sensitivity experiments suggest that the impact of changing input terms by $\pm 20\%$ has little consequence for the final predictions (Fig. A2).

Total atmospheric *n*-alkane deposition rates of long chain odd carbon number *n*-alkanes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) were higher in summer compared to winter (Fig. 8), and source distribution estimates suggest the summer aerosol load for these compounds is made up almost entirely of fresh material (Fig. 3). Together this indicates that the most important sources of long chain odd carbon number *n*-alkanes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) for atmospheric deposition were recently produced plant material. Across all *n*-alkanes the relative importance of fresh versus degraded sources varied with chain length, with middle chain length *n*-alkane deposition most affected by background signals due to lower production rates by plants (Bush and McInerney, 2013), and higher concentrations in fossil sources (Bai et al., 2017; Rogge et al., 1993).

Modeled annual deposition in 2015 at the forest and grassland sites ranged from 5 to 68% of accumulation rates for the corresponding *n*-alkane determined from lake sediments in the same area, but averaged about 20% (Fig. 9a; Table 2). Although these one-dimensional rates on land are much lower than lake accumulation rates, even these are non-negligible. Furthermore, post-depositional transport via surface runoff and rivers combined with sediment focusing within lakes will act to concentrate this mobile material in open lake depocenters. Aerosol *n*-alkanes are also likely contained within particle aggregates, which would add ballast and help promote sinking in water. Direct atmospheric deposition to water columns overlying sediments, as well as deposition near and in river systems may therefore explain how a sizeable component of the fine-grained mud and gyttja in lacustrine depocenters can contain abundant plant wax *n*-alkanes without long residence times on land. Unfortunately no parallel monitoring of the suspended particle load in rivers could be conducted in combination with the present study, but such paired plant, aerosol, and river sampling would be a logical target for future work.

Although large differences in *n*-alkane $\delta^2\text{H}$ values were observed among plant types, soils, and leaf litter at the locations investigated in this study, these did not translate into large differences in the deposition-weighted annual $\delta^2\text{H}$ values for *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) (Fig. 9b). Aerosols therefore seem to smooth out highly localized vegetation effects by sampling and integrating the signal at this regional scale. The similarities between the deposition-weighted annual $\delta^2\text{H}$ values of *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) and those from most surface sediments support the potential importance of atmospheric plant waxes in sedimentary records (Fig. 9b; Table 3). These similarities also increase with increasing chain length, which would be consistent with lower concentrations of degraded background material with increasing chain length, as might be expected from a fossil fuel source. The exception is Lake Sarnen, which yielded *n*-alkanes with a very low CPI value (<2), and $\delta^2\text{H}$ values that were generally much higher than those from deposition-weighted aerosols, with the exception of *n*-C₃₁ (Fig. 9b). This indicates contributions from degraded material resulting in an *n*-alkane signal that does not reflect local and recently synthesized waxes, as well as the decreasing importance of this type of effect with increasing chain length. To the extent that this is driven by human impact, these impacts would be expected to be less widespread in pre-industrial sediments.

4.5 Implications

The data from the present study suggests that atmospheric transport is an important process in temperate latitudes close to mixed forest and grassland production sources. While these results are likely transferrable to similar environmental zones, and support previous work on atmospheric *n*-alkane deposition to lakes in similar environments (Doskey, 2000), it must also be noted that the importance of atmospheric transport likely varies depending on vegetation, proximity to alternative sources, and atmospheric conditions.

Atmospheric *n*-alkane deposition from fresh plant sources, either on land followed by river transport or directly on lakes and coastal oceans, is likely the fastest mechanism for delivering plant waxes to sediments. This is offset by slower transport mechanisms that involve wind and river transport of leaf material after leaf fall, as well as after soil formation and erosion, which may take centuries to millennia in some cases. The relative contributions from each possible transport pathway will combine to produce the mixed sedimentary *n*-alkane pool, but the potentially large contribution from recently synthesized plant wax *n*-alkanes to sediments by wind illustrates how a climate signal may be rapidly incorporated in sediments.

The apparently higher deposition of local to regionally derived fresh plant wax aerosols and correspondingly lower background deposition at forested areas compared to other environments suggest that lakes in forested catchments may be preferred targets for paleoenvironmental research seeking to utilize sedimentary *n*-alkanes from plants (Fig. 9b). This regional scale interpretation is consistent with previous work on forest *n*-alkane aerosols (Nelson et al., 2017), and also suggests that changes in catchment vegetation over time will influence the spatial footprint of the area over which the sedimentary vegetation signal integrates. For example, a shift from forest to grassland or steppe might increase the source area of mean plant wax aerosol deposition or change the ratio between fresh and degraded source material. The area over which a sediment record integrates a vegetation signal will likely therefore partially depend on the characteristics of the surrounding vegetation, independent of the spatial extent of the surface runoff catchment area. For example, in a forested area the spatial footprint of the aerosol source region is likely limited to a few tens of km, while a lake in an open steppe or desert may receive atmospheric *n*-alkane deposition from source areas that are further away.

The observation that plant wax aerosols are produced in large quantities and rapidly deposited following leaf flush/unfolding highlights the importance of the climate conditions that influence the $\delta^2\text{H}$ value of these early season waxes. That is, the factors that affect the $\delta^2\text{H}$ values of springtime plant source water and leaf water. How the source water $\delta^2\text{H}$ values change by location and whether this is a precipitation, soil, or ground water signal is a separate question, but if large quantities of waxes are separated from leaves before leaf senescence, continued source water changes over the course of a season cannot influence the waxes that have already been lost to the air as fine grained and easily transported material.

Contributions of degraded *n*-alkane sources to sedimentary plant waxes are important to consider, but are also apparently easily assessed with CPI values. The results from the present study serve as a good reminder that CPI values should be used in a threshold capacity in interpretations of *n*-alkane data as a primary vegetation signal. However, the similarity of surface sediment *n*-alkane $\delta^2\text{H}$ values among sites for which CPI values are sufficiently high suggests that degraded sources may not substantially bias the $\delta^2\text{H}$ value of average local vegetation apart from extreme cases. This also suggests that while long chain *n*-alkanes from sediments may lack the sensitivity to resolve differences in microclimates between adjacent sites, this very same aspect may make them more amenable to producing robust regional composite records of large-scale circulation changes. At the same time, the potential for mixed *n*-alkane sources to contribute to the sedimentary signal, and for the relative importance of these to vary over time and by location also illustrates the importance of measuring multiple *n*-alkanes within each sediment sequence.

5. Conclusion

Plant wax aerosol samples were collected over a nearly two-year period at four sampling points in Switzerland, and samples of the surrounding vegetation, soil, and litter were also

collected for comparison. Distribution patterns and $\delta^2\text{H}$ values of *n*-alkanes in atmospheric waxes showed strong seasonal patterns that were highly consistent from year to year and site to site, reflecting mixing between vegetation and soils, and contributions from a degraded background. The aerosol depositional pattern of *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) generally reflected fresh production, and was therefore consistent with rapid widespread transport of waxes from vegetation to sediments. Deposition-weighted aerosol *n*-alkane $\delta^2\text{H}$ values were similar to those from surface sediments from nearby lakes, with the exception of Lake Sarnen, which was characterized by a CPI value lower than 2, highlighting how chain length distribution indices can be useful for identifying shifts in local vegetation and contributions from degraded background *n*-alkanes.

These results document the presence of a large pulse of *n*-alkanes to the atmosphere shortly after leaf unfolding, and demonstrate that this material has a molecular distribution pattern and $\delta^2\text{H}$ values indicative of recently synthesized material. This material is rapidly deposited from the atmosphere on timescales of weeks, even before the end of the growing season, and provides a process-based link between recent wax biosynthesis and fine-grained open water sedimentary leaf waxes. This study also shows how sedimentary plant wax $\delta^2\text{H}$ values in the right locations can capture an environmental signal that should be largely contemporaneous with deposition.

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Figure Captions

Figure 1: Location maps showing the forest (Swiss Canopy Crane, Hofstetten), grassland (ETH Grassland Site, Chamau), and high alpine (Sphinx Observatory, Jungfrauoch, 3466 m) aerosol sampling field sites, as well as the lake sites from which surface sediment was recovered. Top panel shows 1-km consensus land-cover product for biodiversity and ecosystem modeling land cover classifications (Tuanmu and Jetz, 2014). Evergreen, deciduous, needleleaf, broadleaf, and mixed forests are all indicated in green, and herbaceous, grassland, cultivated, and managed vegetation is indicated in brown. Other land-cover types are not shown. Bottom panel shows site elevation from the 30-arc second GTOPO30 digital elevation model from the United States Geological Survey.

Figure 2: Average aerosol *n*-alkane concentrations per cubic meter of air per sample from grassland (ETH Grassland Site, Chamau), forest (Swiss Canopy Crane, Hofstetten), and high alpine (Sphinx Observatory, Jungfrauoch, 3466 m) field sites. Background shading indicates the length of the growing season in each year and is equivalent on all panels. Growing season

was defined as the period between the mean leaf formation/unfolding date and mean 50% autumnal coloring/fall date for the four tree species used in calculating the Spring Index (www.meteoswiss.ch) for each year (2015 in blue, 2014 in green; species are *Aesculus hippocastanum* (chestnut), *Corylus avellana* (hazel bush), *Larix decidua* (larch), and *Fagus sylvatica* (beech tree). Data include all Swiss sites in the PEP725 database (n=135) (PEP725 Pan European Phenology Data. Data set accessed 2017-03-07 at <http://www.zamg.ac.at/pep725/>).

Figure 3: Estimates of degraded background and fresh plant material contributions to total measured aerosol *n*-alkane concentrations for the *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, and *n*-C₃₁). Background shading is as in figure 2.

Figure 4: Aerosol $\delta^2\text{H}$ values from all measured *n*-alkanes from grassland (ETH Grassland Site, Chamau), forest (Swiss Canopy Crane, Hofstetten), and high alpine (Sphinx Observatory, Jungfrauoch, 3466 m) field sites. Analytical errors are smaller than the symbols. Symbol fill color shows carbon preference index values from the whole *n*-alkane sample from which individual *n*-alkane $\delta^2\text{H}$ values were measured, and are therefore equivalent in all panels. Background shading is as in figure 2.

Figure 5: Estimates of degraded background and fresh plant material $\delta^2\text{H}$ values compared to measured values for *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁).

Background shading is as in figure 2.

Figure 6: Aerosol, plant, soil, and end-of season leaf litter *n*-alkane $\delta^2\text{H}$ values from *n*-alkanes typical for higher plant waxes (*n*-C₂₇, *n*-C₂₉, *n*-C₃₁) at grassland (ETH Grassland Site,

Chamau), forest (Swiss Canopy Crane, Hofstetten), and high alpine (Sphinx Observatory, Jungfrauoch, 3466 m) field sites. Aerosol values are repeated in each panel for a given n -alkane for direct comparison with other sources (gray symbols). Analytical errors are smaller than the symbols. Symbol shape indicates collection site. Symbol size indicates n -alkane concentration in dry sample material for plant, soil, and litter data (magenta symbols). Plants, soils and litter are not present at the Jungfrauoch. Background shading is as in figure 2.

Figure 7: Air mass back-trajectory plots for each aerosol sampling location grouped by season. Only trajectories that reached the site when air samplers were operating are shown, resulting in reduced data coverage for seasons at the start or end of a sampling period. All trajectories are 36-hours in duration, and sequential trajectories are offset by six hours such that four terminate per day at each sampling site. The color scale indicates trajectory density in high-density areas.

Figure 8: Modeled monthly total aerosol (wet + dry) n -alkane deposition rates for grassland (ETH Grassland Site, Chamau) and forest (Swiss Canopy Crane, Hofstetten) sites. Background shading is as in figure 2.

Figure 9: Total n -alkane deposition, and deposition-weighted $\delta^2\text{H}$ values compared to values from all other sample types. (A): Total n -alkane deposition in 2015 for each n -alkane from $n\text{-C}_{23}$ to $n\text{-C}_{31}$ compared to accumulation rates in the six sampled lake sediments. (B): Deposition-weighted average aerosol $\delta^2\text{H}$ values from Chamau and Hofstetten in 2015. These are compared to the distribution of all measured $\delta^2\text{H}$ values of aerosols, plants, end of season leaf litter, and soils from all sites (indicated by vertical colored bars in plot background). Surface sediment $\delta^2\text{H}$ values from six lakes in the Swiss Plateau are also shown on the

bottom panel (large circles), with symbol fill color indicating the carbon preference index value from the distribution of all *n*-alkanes in the given sample.

Figure A1: Meteorological data from 2014 and 2015 from grassland (ETH Grassland Site, Chamau), forest (Swiss Canopy Crane, Hofstetten), and high alpine (Sphinx Observatory, Jungfrauoch, 3466 m) sites. Wind speed (top row), precipitation (middle row; not recorded at Jungfrauoch), and temperature (bottom row). Missing data from Hofstetten and Chamau were filled with data from nearby meteoswiss stations (gray data) at Basel/Binningen, and Cham, respectively (www.meteoswiss.ch).

Figure A2: Sensitivity analysis results showing the impact of changing model input terms by $\pm 20\%$ on the final modeled annual deposition rate at each site. Overlapping $+20\%$ (red symbols) and -20% (blue symbols) appear purple, indicating minimal sensitivity.

Table 1: Location and characteristics of the six sampled lakes (data from <https://www.lakepedia.com/>).

Table 2: Annual accumulation and deposition rates (as shown in Fig. 9a) from the six sampled lakes and two aerosol sampling sites. Values for some compounds could not be determined in some lakes due to low concentrations, and are indicated in these cases by “n.d.”

Table 3: Measured surface sediment $\delta^2\text{H}$ values from the six sampled lakes compared to modeled annual deposition rates (as shown in Fig. 9b). More complete measurement statistics for the lake sediments are given in Electronic Annex (EA) 7). Values for some compounds

could not be determined in some lakes due to low concentrations, and are indicated in these cases by “n.d.”

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Figure A1

Figure A1: Meteorological data from 2014 and 2015 from grassland (ETH Grassland Site, Chamau), forest (Swiss Canopy Crane, Hofstetten), and high alpine (Sphinx Observatory, Jungfrauoch, 3466 m) sites. Wind speed (top row), precipitation (middle row; not recorded at Jungfrauoch), and temperature (bottom row). Missing data from Hofstetten and Chamau were filled with data from nearby meteoswiss stations (gray data) at Basel/Binningen, and Cham, respectively (www.meteoswiss.ch).

Figure A2

Figure A2: Sensitivity analysis results showing the impact of changing model input terms by $\pm 20\%$ on the final modeled annual deposition rate at each site. Overlapping +20% (red symbols) and -20% (blue symbols) appear purple, indicating minimal sensitivity.

Lake Name	Latitude	Longitude	Elevation (m)	Catchment Area (km ²)	Surface Area (km ²)	Average Depth (m)
Lake Sarnen	46.869	8.219	469	194	7	15
Lake Rot	47.070	8.314	419	3	0.37	7
Lake Greifen	47.354	8.672	439	195	8	7
Lake Mauern	47.171	8.076	522	4	0.41	4
Lake Baldegg	47.200	8.260	463	73	5	6
Lake Soppen	47.090	8.081	596	3	0.22	4

Location	Sample Type	Accumulation/Deposition Rate (ng cm ⁻² y ⁻¹)								
		<i>n</i> -C ₂₃	<i>n</i> -C ₂₄	<i>n</i> -C ₂₅	<i>n</i> -C ₂₆	<i>n</i> -C ₂₇	<i>n</i> -C ₂₈	<i>n</i> -C ₂₉	<i>n</i> -C ₃₀	<i>n</i> -C ₃₁
Lake Sarnen	sediment	573.4	493.1	555.1	427.7	667.8	428.7	568.5	267.2	465.5
Lake Rot	sediment	63.0	n.d.	95.1	n.d.	186.5	n.d.	242.1	n.d.	184.6
Lake Greifen	sediment	35.1	n.d.	52.7	n.d.	105.8	32.8	132.5	26.0	131.4
Lake Mauen	sediment	105.2	n.d.	115.9	n.d.	237.5	139.0	303.3	n.d.	199.7
Lake Baldegg	sediment	116.0	n.d.	118.2	n.d.	298.1	61.1	426.2	59.5	439.3
Lake Soppen	sediment	76.0	n.d.	115.4	n.d.	252.8	n.d.	266.1	n.d.	206.4
Hofstetten - forest	aerosol	1.2	3.8	11.2	6.5	54.8	5.6	90.5	1.8	53.3
Chamau - grassland	aerosol	11.0	39.9	59.2	51.4	61.8	30.1	44.6	1.8	21.5

Location	Sample Type	<i>n</i> -alkane $\delta^2\text{H}$ values (‰ VSMOW)								
		<i>n</i> -C ₂₃	<i>n</i> -C ₂₄	<i>n</i> -C ₂₅	<i>n</i> -C ₂₆	<i>n</i> -C ₂₇	<i>n</i> -C ₂₈	<i>n</i> -C ₂₉	<i>n</i> -C ₃₀	<i>n</i> -C ₃₁
Lake Sarnen	sediment	-109.7	-111.2	-118.2	-108.4	-132.7	-103.4	-142.4	-103.6	-197.6
Lake Rot	sediment	n.d.	n.d.	-172.4	n.d.	-186.4	n.d.	-200.0	n.d.	-196.9
Lake Greifen	sediment	n.d.	n.d.	n.d.	n.d.	-175.5	n.d.	-193.2	n.d.	-190.5
Lake Mauen	sediment	n.d.	n.d.	-178.7	n.d.	-188.2	n.d.	-200.2	n.d.	-196.1
Lake Baldegg	sediment	n.d.	n.d.	n.d.	n.d.	-176.1	n.d.	-199.7	n.d.	-197.6
Lake Soppen	sediment	n.d.	n.d.	n.d.	n.d.	-186.5	n.d.	-200.6	n.d.	-197.6
Hofstetten - forest	aerosol	-141.9	-128.0	-148.4	-128.9	-164.2	-124.2	-176.2	-122.7	-186.0
Chamau - grassland	aerosol	-126.6	-123.8	-127.0	-114.7	-142.6	-108.9	-169.2	-134.1	-191.4

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