Oxygen isotope analysis of levoglucosan, a tracer of wood burning, in experimental and ambient aerosol samples

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Abstract

Rationale Levoglucosan is formed from cellulose during biomass burning. It is therefore often used as a specific tracer to quantify the contribution of wood burning to the aerosol loading. The stable oxygen isotope composition ($\delta^{18}\text{O}$) of biomass is determined by the water cycle and varies regionally, and hence the $\delta^{18}\text{O}$ value of levoglucosan could help to identify source regions of organic aerosols.

Methods After solvent extraction of the organic fraction and concentration steps, a recently developed methylation derivatisation technique was applied on experimental (i.e. controlled wood burning experiments) and on ambient aerosol samples from Switzerland and Lithuania. The method achieves sufficient compound separation for isotope analysis in atmospheric particulate matter, enabling $\delta^{18}\text{O}$ analysis of levoglucosan by gas chromatography/pyrolysis – isotope ratio mass spectrometry (GC/Pyr-IRMS), with a precision better than 1.0 ‰ and an accuracy of 0.3 ‰.

Results The levoglucosan $\delta^{18}\text{O}$ released during controlled wood burning experiments was not significantly different from the cellulose $\delta^{18}\text{O}$, which implies very little or no isotope fractionation during wood burning under the given conditions. While $\delta^{18}\text{O}$ values of levoglucosan in Swiss samples were as expected for the source region, those in Lithuania were 1 - 4 ‰ lower than expected. This may be due to differences in vegetation (grass vs. wood) or burning conditions (high vs. low temperatures).

Conclusions Low oxygen isotope fractionation between cellulose and levoglucosan and clear differences in levoglucosan $\delta^{18}\text{O}$ values between the Swiss and Lithuanian ambient samples demonstrate that our new method is useful for source appointment studies on wood-burning derived aerosols.

Keywords: anhydrosugar, emission, fire, smoke, tree, water vapour

Introduction

Atmospheric particulate matter (PM) is relevant in both climate change and respiratory health problems^[1]. Its composition is often complex, with many structurally different compounds making up minor fractions of the bulk. The organic aerosol fraction, comprising a major part of atmospheric PM^[2], consists of a large number of different compounds. The chemical identity of those compounds can be indicative of sources. Therefore, a number of studies have resorted to compound-specific analyses to address the sources of atmospheric PM ^[3,4]. Some of those compounds are derived from biomass burning of wood and crop residues, creating high concentrations of organic aerosols that can be transported over long distances, potentially crossing national borders and causing health problems elsewhere. However, reliable tracers for detecting long-range transport of particles from biomass burning are currently still lacking.

Numerous studies in a wide range of scientific fields have shown that stable isotope ratios of carbon and oxygen in biologically-derived marker molecules (biomarkers) are a versatile tool to investigate biochemical pathways and origin of the biomarker in question^[5–7]. The stable isotope ratio of organic compounds depends on the isotope composition of the source, environmental conditions and specific (bio)chemical pathways and mechanisms that lead to the formation of the compound. The stable isotope composition of a compound that was sampled from soils or collected as aerosols after biomass burning can therefore be used to identify a source.

Carbon isotopes have so far been applied successfully in studies on organic aerosols^[5,8–13], in particular on levoglucosan in source apportionment studies ^[4,11]. Levoglucosan and other anhydrosugars can be highly abundant in PM samples and function as specific tracers for biomass/wood burning, or more specifically for the thermal decomposition of cellulose ^[14,15]. Sang et al.^[11], showed that levoglucosan from wood burning is slightly isotopically enriched in ¹³C compared to the parent material ($\delta^{13}\text{C}_{\text{holocellulose}} - \delta^{13}\text{C}_{\text{levoglucosan}} = -1.89\text{‰}$). This is in line with studies showing that the water soluble organic carbon fraction originating from wood burning in Zürich, Switzerland, was found to be enriched in ¹³C relative to other organic fractions^[16]. The C-

isotopic difference between sources is in a range of a few per mil and in principle an isotopic separation of this magnitude can be enough to distinguish between aerosol sources. However, the information that can be extracted from carbon stable isotope measurements is mainly limited to biochemical differences in carbon fixation (e.g., C3, C4, CAM plants) and to environmental impacts on plant physiology (e.g., weather, drought stress), while information on actual geographical location is restricted^[17].

Alternatively, the large degree of oxygenation of many organic aerosols, such as levoglucosan, makes ^{18}O an attractive candidate for additional isotopic studies on aerosols. The oxygen isotopes in biomass record a signal of the hydrological cycle^[18–20], providing information independent from the carbon cycle. The oxygen isotopic composition of water in the atmosphere is strongly influenced by the condensation temperature in clouds^[18] (the lower the temperature, the less H_2^{18}O in the water), and by the continental effect, i.e. the distance over which the moisture is transported away from the oceans into the continents (the more continental, the less H_2^{18}O in the water). The same mechanisms can be observed for air masses that are transported into high elevations of the mountains. This causes strong spatial $\delta^{18}\text{O}$ variability for precipitation water. Through studies on precipitation, soil water, and tree rings, the source $\delta^{18}\text{O}$ values for various regions are well known^[21–23]. The source water is taken up by plants where it experiences an ^{18}O -enrichment in leaf tissues due to transpiration^[19,20]. The magnitude of the leaf water enrichment depends mainly on atmospheric humidity, temperature, and plant physiological responses^[24]. The oxygen isotopic signal of leaf water equilibrates with atmospheric CO_2 ^[25], that is taken up and incorporated into plant organic matter during photosynthesis. Due to a rapid exchange of the oxygen in a carbonyl group of carbohydrates with the oxygen in the surrounding water^[26,27], a process that is known as the biosynthetic fractionation factor (ϵ_{O}), plant compounds such as cellulose are on average 27 ‰ enriched in ^{18}O compared to leaf water^[22,28,29]. Modelling studies that successfully reproduced regional patterns confirm that potential source $\delta^{18}\text{O}$ values can be predicted accurately from tree-ring cellulose^[30–32]. Thus far, studies on oxygen isotopes in atmospheric sciences have mainly

focused on CO, sulfates and phosphates^[6,33,34]. As far as we know, no study has yet reported compound-specific oxygen isotope ratios in organic aerosols. However, in order to use aerosol $\delta^{18}\text{O}$ data effectively, first a reproducible analytical method needs to be developed and second both the source and the aerosol $\delta^{18}\text{O}$ signal must be known to determine potential isotope fractionation during the emission process (i.e. wood/biomass burning). A better understanding of these isotope fractionation processes could significantly increase the explanatory power of isotope-based source apportionment studies. For instance, a multi-isotope approach with carbon and oxygen isotopes could facilitate the identification of the aerosol origin and the source of the burned biomass^[35–37]. In this study (1) we established a new protocol for $\delta^{18}\text{O}$ measurement of levoglucosan, taking advantage of a recently published methylation derivatisation method for carbohydrates^[38], which was already successfully applied on leaf carbohydrates^[27,39]; (2) we investigated isotope fractionation processes modulating $\delta^{18}\text{O}$ values of levoglucosan in a controlled wood burning experiment using beech and pine wood; (3) we determined oxygen isotope exchange between levoglucosan and ^{18}O -labelled water vapour and (4) $\delta^{18}\text{O}$ values of levoglucosan in ambient aerosol samples from Switzerland and Lithuania. To our knowledge this is the first dataset of compound-specific $\delta^{18}\text{O}$ values of levoglucosan in experimental and ambient samples.

Methods

Experimental setup

Controlled wood burning experiments:

Two types of wood with distinct different properties from two locations in Switzerland (Pine soft wood from the south side of the Alps, canton of Wallis, 2 experiments, and beech hard wood from the canton of Aargau, north of the Alps, 2 experiments) were burned in a cast-iron log-wood stove (Type Avant, 2009, Attika, Cham, Switzerland) ^[40]. Pine wood from Wallis was all taken from one tree from the Pfynwald area (46.30° N, 7.59° E), a valley with 550 mm precipitation per year and a mean annual temperature of 10.1 °C. Temperatures on the valley floor in this area often exceed 30

°C in summer. Beech wood from Aargau was obtained from one batch of fire wood of uniform age structure. Yearly precipitation in the canton Aargau is around twice as high as in the Pfynwald, with a mean annual temperature of 9.4 °C. Prior to the experiments the wood was left to dry under a roof in a ventilated space outside.

Controlled wood burning experiments were performed on dry and sunny days with low relative humidity (RH ~50%). Air supply during burning was kept similar by keeping the air inflow lever of the oven in the open position, ensuring maximum supply of oxygen. When wood burning was at maximum intensity, the exhaust was collected through a nozzle directly above a 3 m high chimney. Although wind speeds during the experiments were low, we observed some dispersion of the chimney exhaust, which potentially caused mixing of aerosol samples with ambient air. However, the nozzle was near the exhaust during the entire sampling time. Air collected by the nozzle was drawn through stainless steel tubing at a rate of 50 L min⁻¹ through quartz fibre filters (90 mm diameter) previously baked for 24 hours at 450 °C. Filters were subsequently packed in pre-baked aluminium foil and stored at -20 °C until extraction. Filters were dry after the sampling period, i.e. no condensation water was collected on the filters.

Oxygen isotope exchange experiment:

Several samples of 0.5 mg levoglucosan standard material in open silver capsules were placed in a 1-L desiccator for 72 h. The atmospheric humidity in the closed desiccator was fully saturated with ¹⁸O-depleted water ($\delta^{18}\text{O} = -367.4 \text{ ‰}$). All capsules were freeze-dried for 24 h, folded, and $\delta^{18}\text{O}$ values determined as described below for bulk samples.

Ambient samples:

Environmental samples from two locations in Europe were used for comparison. An alpine site in the south of Switzerland in the Magadino plain, close to the Lago Maggiore, (46.16° N, 8.93° E, 203 m a.s.l.) and about two kilometres outside of Cadenazzo, was chosen as a comparison site for

wood burning, since wood burning is a major source of heating in this area in winter ^[41,42]. Five samples that were collected on quartz fibre filters between 25 January and 12 March 2011 were used. Based on the location close to wood burning in the valley, photochemical ageing is not expected to have a significant influence on these samples.

The second sampling site was located in Lithuania, at the coastal Preila environmental pollution research station (55.92° N, 21.00° E) ^[43,44]. Two samples from March 2014 were collected on quartz fibre filters and chosen based on high particulate matter (PM10) loading events. These events have been linked to grass burning episodes in the Kaliningrad region (Russia), Belarus and the Ukraine ^[44].

Bulk wood and cellulose extraction and analysis

Wood samples were taken throughout the logs and homogenised using a ball mill (Mixer Mill MM200, Retsch, Haan, Germany). An aliquot of the milled and homogenised wood samples was transferred into teflon filter bags (Ankom Technology, Macedon, NY, USA) for cellulose extraction ^[45]. Briefly, lignin was removed in an ultrasonic bath for 24 h at 70 °C using a 2-L distilled water solution consisting of 24 g NaClO₂ and 8 mL acetic acid. The solution was renewed every 3 h and replaced by a 2-L solution with 72 g NaClO₂ and 8 mL acetic acid for overnight treatment. The samples were then washed in distilled water, soaked in a NaOH solution (150 g NaOH in 1 L water) for 45 min, neutralised with HCl solution (3 %) for 45 min in an ultrasonic bath, and washed in distilled water until a neutral pH was reached. Wood and cellulose extracts were dried at 50 °C and weighed into silver capsules (~1 mg), pyrolysed to CO at 1450 °C (PYRO-cube, Elementar, Langenselbold, Germany) and measured on a Delta Plus XP isotope ratio mass spectrometer (Thermo

Finnigan MAT, Bremen, Germany), which was linked to the pyrolysis unit by an open split ConFlo III interface (Thermo Finnigan MAT). Standard deviation (SD) of the mean for standard material was typically < 0.2 ‰. All $\delta^{18}\text{O}$ values in this article are expressed in ‰ using the “delta” notation:

$$\delta^{18}\text{O} (\text{‰}) = R_{\text{sample}}/R_{\text{standard}} - 1$$

where R_{sample} and R_{standard} are the $^{18}\text{O}/^{16}\text{O}$ ratio of the sample and the standard, respectively. All values are referenced to the VSMOW scale using international standards (benzoic acids 601 and 602, Vienna, Austria).

Organic extraction from filter samples

Filter pieces were transferred to teflon-coated centrifuge tubes and extracted four times in solvent mixtures of decreasing polarity: (1) Methanol (MeOH):dichloromethane (DCM) (2:1), (2) MeOH:DCM (1:2), (3, 4) DCM. Each step included 15 seconds vortexing followed by 15 minutes ultrasonication. Supernatants from all steps were merged and transferred to pre-baked glass tip flasks and the solvent was evaporated to several mL by rotary evaporation (water bath temperature 35 °C). Subsequently samples were transferred to 1.5 mL vials and divided in two for backup and further treatment.

Organic extract sample derivatisation

Total extracts were methylated according to a modified Purdie reaction, a derivatisation method that does not affect the compound $\delta^{18}\text{O}$ value by additional oxygen ^[38]. The extracts in MeOH:DCM were evaporated to dryness and redissolved in 1 mL acetonitrile (MeCN). 65 mg Ag_2O , 100 μL methyl iodide (MeI, Sigma-Aldrich, Buchs, SG, Switzerland) and 20 μL dimethyl sulfide (DMS, $(\text{CH}_3)_2\text{S}$, Merck, Zug, Switzerland) were added. To aid mixing and prevent formation of a hard pellet during derivatisation, two small glass beads were added. The reaction mixture was shaken in the dark for 24 hours, after which the vials were spiked with 50 μL MilliQ water, vortexed and centrifuged. The supernatant was then transferred to a new vial and concentrated as required for $\delta^{18}\text{O}$ analysis. Specificity of the reaction and analytical method was checked with pure standards of levoglucosan on a GC-quadrupole mass spectrometer (Thermo Fisher Scientific ISQ, Bremen, Germany), and only one product was found, showing that all three free OH-groups were

methylated.

Ag₂O for derivatisation was freshly prepared from silver nitrate to ensure optimal basicity for derivatisation. 15 g silver nitrate (AgNO₃, Sigma-Aldrich) and 3.5 g sodium hydroxide (NaOH, VWR, Dietikon, Switzerland) were dissolved separately in 100 mL MilliQ water (80–90 °C) and then mixed. The resulting brown precipitate (Ag₂O) was filtered under vacuum through a fritted glass filter (pore size of 40–100 µm; Winzer, Wertheim, Germany) and washed with 100 mL MilliQ water and 100 mL 99% ethanol. The remaining pellet was dried at 60 °C for 5 h, ground to a fine powder with a pestle and mortar and stored in a desiccator filled with silica gel in a light-impermeable vial, since Ag₂O is sensitive to light.

Initially also derivatisations with bis(trimethylsilyl)trifluoroacetamide (BSTFA) were carried out. These derivatisations, like the methylation reaction described above, also do not affect the δ¹⁸O value of the sample. However, the addition of silyl groups presents problems with the pyrolysis reactor and reactor lifetime was greatly reduced. Furthermore, methylated products have a lower mass and shorter retention time than trimethylsilyl derivatives, making them more amenable to IRMS analysis since with shorter GC retention times and consequently lower GC temperatures baseline interferences are less problematic. Finally, in case of planned ¹³C and ²H analyses, methylation adds fewer methyl groups than TMS-derivatisation does (1 vs. 3 per OH-group) to the molecule of interest, reducing the error in the calculation of the isotopic composition.

Identification of compounds and oxygen isotope measurements

Compound-specific stable oxygen isotope ratios were determined using GC/Pyr-IRMS (Trace GC Ultra, GC-IsoLink, and ConFlo IV coupled to a MAT253 isotope ratio mass spectrometer, all supplied by Thermo Fisher Scientific, Bremen, Germany). The split-splitless injector operated in splitless mode at 250 °C. We placed glass wool and glass beads in the injector liner to prevent precipitation of non-product derivatisation residues on the column. Methylated total extracts were separated by gas chromatography over a 60 m, 0.25 mm inner diameter, 0.25 µm film thickness

Semi-Volatiles capillary column (Zebron, Phenomenex, Torrance, CA, USA). Carrier gas (He 5.0 and better) flow was 1.4 mL min⁻¹ and the oven temperature programme consisted of 50 °C, 1 min isothermal, followed by 10 °C min⁻¹ to 120 °C, 4 °C min⁻¹ to 170 °C, 20 °C min⁻¹ to 290 °C and finally 15.5 min isothermal (42 minutes total GC time). With this we achieved appropriate compound separation for isotope analysis of anhydrosugars. Peak retention time of methylated levoglucosan was observed after 1153 s in both standards and samples (Fig. S1). After GC separation the sample was pyrolysed to CO at 1280 °C in a 32 cm platinum tube partly filled with Ni wires (Thermo Fisher Scientific) and $\delta^{18}\text{O}$ values determined from the ratio of m/z 30 to m/z 28. To ensure reducing conditions in the reactor, an auxiliary gas of He 6.0 with 1% H₂ 6.0 (Messer, Lenzburg, Switzerland) was added in continuous flow before the reactor^[38]. Regular tests of IRMS instrument linearity and stability demonstrated no significant isotopic variations. Three CO reference gas pulse injections both before and after the analysis in backflush mode showed a isotopic variation of $\leq 0.1\%$. The pyrolysis reactor was conditioned with one injection of 1 μL toluene, followed by multiple blank injections (with backflush on during the solvent peak retention time window) until a stable baseline level was reached with the m/z 30 background stabilising between 130 and 200 mV. The backflush flow that is directed backwards through the reactor towards the gas chromatograph was only interrupted for 100 s to allow $\delta^{18}\text{O}$ analysis of levoglucosan (Fig. S1). This reduces two separate potential negative effects on $\delta^{18}\text{O}$ measurements: 1) N₂O entering the ion source, which can lead to the formation of NO-ions, i.e. m/z 30, and 2) organic compounds other than levoglucosan entering the reactor and the isotope ratio mass spectrometer. The second issue was observed especially during the retention time window of polycyclic aromatic hydrocarbons present in the samples, which cannot be observed on m/z traces 28, 29 and 30, but do cause a local rise in the GC baseline. In addition, we found that a liquid N₂ trap after the pyrolysis reactor stabilises and improves the reproducibility of $\delta^{18}\text{O}$ values. With this set-up instrument drift was eliminated. Each sample was measured in triplicate and corrected for sample amount effects when necessary. The correction was based on a linear fit through raw $\delta^{18}\text{O}$

values from levoglucosan standards of different concentrations that were interspersed between the sample measurements. The difference between the raw $\delta^{18}\text{O}$ values of the standards and the regression was determined and added to the raw $\delta^{18}\text{O}$ values of the samples. Levoglucosan reference standard $\delta^{18}\text{O}$ values were determined on a PYRO-cube elemental analyser (Elementar) coupled to an isotope ratio mass spectrometer (as described above) and referenced to the VSMOW scale.

Results

$\delta^{18}\text{O}$ values of bulk wood, cellulose and levoglucosan in experimental and ambient samples

(1) Methylated levoglucosan could successfully be measured in a concentration range of around 250 $\text{ng } \mu\text{L}^{-1}$ to 2500 $\text{ng } \mu\text{L}^{-1}$ by GC/Pyr-IRMS (Fig. S1), with a standard deviation (SD) of the mean that was better than 1.0 ‰ and an accuracy of 0.3 ‰. Levoglucosan concentrations below 250 $\text{ng } \mu\text{L}^{-1}$ showed considerably stronger isotopic variations, representing the analytical detection limit.

(2) $\delta^{18}\text{O}$ values of bulk wood in samples that were used for the wood burning experiments were 5.4 ‰ (beech) and 6.1 ‰ (pine) lower than $\delta^{18}\text{O}$ values of cellulose, reflecting the influence of ^{18}O -depleted lignin (Fig. 1A, Table 1). No significant difference in $\delta^{18}\text{O}$ values between the tree species was found for bulk wood as well as cellulose. Furthermore, the wood was uniform in both species, with no significant difference in $\delta^{18}\text{O}$ values between samples from various parts of the wood. $\delta^{18}\text{O}$ values of cellulose were 30.0 ± 0.6 ‰ for the beech wood from the northern side and 30.5 ± 1.0 ‰ for the pine wood from southern side of the Alps. $\delta^{18}\text{O}$ values of levoglucosan from the wood burning experiments were 30.3 ± 0.3 ‰ for beech and 30.7 ± 1.4 ‰ for pine and thus not significantly different from $\delta^{18}\text{O}$ values of cellulose. The cellulose-levoglucosan isotope fractionation within both species therefore was not more than 0.4 ‰ and within one standard deviation of the $\delta^{18}\text{O}$ value of cellulose.

(3) The $\delta^{18}\text{O}$ value of levoglucosan that was treated with strongly ^{18}O -depleted water vapour was 1.1‰ lower compared to the control. Since maximum natural isotopic variations in water vapour are about twentyfold lower compared to the experimental effect, a potential oxygen isotope exchange of levoglucosan with atmospheric humidity is negligible.

(4) $\delta^{18}\text{O}$ values of levoglucosan in ambient samples from Magadino in southern Switzerland in 2011 were in the same range as those from the wood burning experiments, between 27.1 ‰ and 29.6 ‰, averaging around 28.4 ‰ (Fig. 1B, Table 2). $\delta^{18}\text{O}$ values of levoglucosan in ambient samples from Preila in Lithuania were clearly lower than those from the other locations, indicating differences in source and/or processes during combustion.

Discussion

Low cellulose-levoglucosan oxygen isotope fractionation during wood burning

Two wood materials were chosen for the wood burning experiments, originating from two separate locations. In both bulk wood and cellulose, the oxygen isotopic composition of the two wood types was very similar (Fig. 1A, Table 1), with an ^{18}O -enrichment of 5 ‰ and 6 ‰ in cellulose compared to bulk wood in beech and pine wood, respectively. This is similar to values reported by other studies^[45,46]. The $\delta^{18}\text{O}$ values of levoglucosan were not significantly different from the parent cellulose in both species. This is consistent with the small ^{13}C fractionation observed during biomass burning by other authors^[11] and suggests that at least under controlled burning conditions in an oven the source cellulose isotopic composition is largely retained in carbon and oxygen isotopes. In addition, the large isotopic difference between bulk wood and cellulose shows that cellulose extraction is important for studies comparing levoglucosan to potential source materials, as the analysis of bulk wood only could lead to an erroneous interpretation. Our results also indicate that the wood type (beech and pine in our study), and the accompanying difference in wood properties, has no influence on the oxygen isotope fractionation during wood burning. It is therefore possible to reconstruct the oxygen isotopic composition of the source cellulose from measurements

of primary emissions of levoglucosan from controlled wood burning.

Explanations for $\delta^{18}\text{O}$ values of levoglucosan in ambient samples

The aerosol samples from Magadino, southern Switzerland, were collected in winter, when local wood burning contributes significantly to the organic aerosol load in the area^[41]. These samples yielded $\delta^{18}\text{O}$ values of levoglucosan that were equal to or slightly lower than the primary emission samples of the wood burning experiments (Fig. 1B, Table 2). Based on the measured oxygen isotopic composition of levoglucosan between 27.1 ‰ and 29.6 ‰ and on the fact that we observed no isotope fractionation during controlled wood burning, it would thus follow that the source cellulose has a $\delta^{18}\text{O}$ value of 27 – 30 ‰, which is an expected range for trees growing in these parts of Switzerland^[47].

The aerosol samples collected at the Preila site in Lithuania reflect a high loading event in March 2014. Here, rather low $\delta^{18}\text{O}$ values were found. In contrast to the samples from Switzerland, the Lithuanian aerosols most likely did not have a local origin. 72-hour back trajectories, which model the atmospheric path of the air mass during the 3 days prior to its arrival at the sampling site, indicate that the air mass arriving at Preila had previously entrained emissions from large open grassland fires in the Kaliningrad region (Russia), Belarus and the Ukraine^[44]. A dominance of levoglucosan in the organic extracts of these samples supports a biomass burning origin. A meteorological high pressure system over the study area caused stagnant conditions and extended the aerosol residence time, leading to particularly high concentrations.

Based on literature data we can infer the oxygen isotopic composition of precipitation water in the potential source regions of Russia and Belarus. Compared to Switzerland the $\delta^{18}\text{O}$ value of precipitation water in the Belarussian source areas is expected to be around 2 - 3 ‰ lower^[48]. If the same relationship between $\delta^{18}\text{O}$ values of source water and cellulose holds for the biomass that was burned in the source area of this case study as for the trees from Switzerland (neglecting potential differences in leaf water isotopic enrichment due to transpiration), we would expect a $\delta^{18}\text{O}$ value of

cellulose, and by extension a $\delta^{18}\text{O}$ value of levoglucosan, of around 24 – 27 ‰ (i.e. 2 – 3 ‰ lower than in Switzerland). However, the Lithuanian levoglucosan $\delta^{18}\text{O}$ value was 1 to 4 ‰ lower than the expected range (20.1 and 23.3 ‰, Fig. 1B, Table 2). Two differences at the source of the aerosols, either the burned material (i.e. the grass vs. wood) or the fire conditions, may attribute to a lower $\delta^{18}\text{O}$ value of levoglucosan in the aerosols and are discussed in the following:

1. The isotopic relationship between $\delta^{18}\text{O}$ values of source water and carbohydrates such as cellulose is not necessarily the same for trees and for grasses^[27]. While the biosynthetic fractionation factor (ϵ_0) of tree-ring cellulose is often similar to the average ϵ_0 of 27 ‰ for plant compounds, the ϵ_0 of grass leaf cellulose can be much lower^[27,49]. Helliker & Ehleringer found in experiments under controlled conditions that ϵ_0 of grass leaf cellulose was dependent on relative humidity and that at low relative humidity (37 %, 24-h mean) ϵ_0 was below 20 ‰^[49]. Even above 90 % relative humidity the same authors found that ϵ_0 for cellulose was not higher than 25.5 ‰. This is most likely explained by the fact that cellulose is produced in less ^{18}O -enriched leaf water pools in the intercalary meristem of the grass leaf base^[27,49]. This less pronounced fractionation between leaf water and cellulose in grasses compared to trees results in lower grass cellulose $\delta^{18}\text{O}$ values, and ultimately lower levoglucosan $\delta^{18}\text{O}$ values. Thus, grass biomass burning in the Belarussian source area could partly explain why levoglucosan $\delta^{18}\text{O}$ values in Lithuanian samples were considerably lower than expected for this source region (Fig. 1B, Table 2).

2. Whereas the wood burning experiments were conducted under controlled conditions with uniformly high temperatures in a closed oven, the grassland burning that was the potential source for the Lithuanian levoglucosan was probably more heterogeneous and contained more water. As a consequence, the average burning temperature was likely lower. Schumacher et al.^[50] found that $\delta^{18}\text{O}$ values of CO_2 evolving from biomass burning decreased with lowering of the combustion temperatures. High combustion temperatures may therefore suppress isotope fractionations, while lower temperatures may lead to higher isotope fractionations, consistent with theoretical expectations. Whether levoglucosan follows the same trend as CO_2 , or perhaps an inverse trend, is

unclear, and must be the subject of future studies. In summary, temperature-dependent isotope fractionation processes might explain the lower $\delta^{18}\text{O}$ values of levoglucosan in the Lithuanian ambient samples compared to those from other samples (Figs. 1A, 1B).

In addition, environmental conditions and chemical reactions during transport could theoretically influence $\delta^{18}\text{O}$ values of levoglucosan in the air. In contrast to the controlled burning experiments and the Swiss ambient samples, the air mass that arrived at the Lithuanian field site was transported through the atmosphere for several days. We found that a potential oxygen exchange with atmospheric water vapour, which would change the $\delta^{18}\text{O}$ values during transport, is likely not a factor. Additionally, photo-oxidation of levoglucosan might play a role during long-distance transport of aerosol samples^[51,52]. However, it has been suggested that levoglucosan photo-oxidation proceeds through H-abstraction from the carbon atoms, subsequently oxidising the oxygen in the hydroxyl functional group to a carbonyl group^[53]. Since the O-atoms are not lost or exchanged, we expect that the influence of photo-oxidation is of minor importance here^[53,54].

Nevertheless, without samples of the original biomass that was burned, we cannot exclude the possibility that isotope fractionation took place during burning or transport, and it is important for future research that oxygen isotope studies on organic aerosols are done under controlled conditions. We conclude that the relatively low levoglucosan $\delta^{18}\text{O}$ values found at the Lithuanian compared to the Swiss station are likely a combined result of the differences in vegetation and burning conditions.

Conclusion

Methylation of levoglucosan in aerosol extract mixtures yielded complete methylation of all free OH-groups, ensuring one product only, leading to precise and accurate $\delta^{18}\text{O}$ measurements. The $\delta^{18}\text{O}$ values of levoglucosan from the wood burning experiments were not significantly different from the values of cellulose, indicating no or very small oxygen isotope fractionation under the controlled conditions, independent of the species (beech or pine). This suggests that oxygen

isotopes can be used as an ecological tracer of wood burning in the atmosphere.

This conclusion is supported by results of ambient samples from southern Switzerland, where aerosol levoglucosan $\delta^{18}\text{O}$ values were consistent with local vegetation. Aerosol samples from Lithuania yielded lower levoglucosan isotope values than aerosol samples from Swiss wood burning, which is partially consistent with the history of the air mass, having traversed regions with active biomass (grass) burning in Belarus and the Ukraine. In that region the biomass is expected to be ^{18}O -depleted compared to Switzerland due to differences in regional source water $\delta^{18}\text{O}$ values. Furthermore, cellulose derived from grass-type vegetation rather than wood, as well as low burning temperatures may cause an additional ^{18}O -depletion in levoglucosan. Thus, we show that on regional scales with a several per mil range in $\delta^{18}\text{O}$ values of precipitation water and cellulose, the $\delta^{18}\text{O}$ signal of the source water is ultimately transferred via biomass production and its burning to the levoglucosan in aerosols. $\delta^{18}\text{O}$ values of levoglucosan are therefore a potential tool to determine and confine the location of the emission source, e.g. to trace atmospheric pollution from illegal crop burning back to its source region.

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Tables

Table 1: $\delta^{18}\text{O}$ values in experimental samples from controlled wood burning experiments. Mean values and standard deviations of bulk wood, cellulose and levoglucosan of Swiss beech and pine samples are given (n = 2-8).

Compound	Beech	Pine
	$\delta^{18}\text{O} (\text{‰}) \pm 1 \text{ SD}$	$\delta^{18}\text{O} (\text{‰}) \pm 1 \text{ SD}$
Bulk wood	24.6 ± 0.5	24.4 ± 0.8
Cellulose	30.0 ± 0.6	30.5 ± 1.0
Levoglucosan	30.3 ± 0.3	30.7 ± 1.4

Table 2: $\delta^{18}\text{O}$ values of levoglucosan in ambient aerosol samples obtained from Magadino, Switzerland (CH, 2011) and from Preila, Lithuania (LTU, 2014). Mean values and standard deviations of triplicate measurements are given for each sample.

Magadino (CH)	
Date	$\delta^{18}\text{O}$ (‰) $\pm$ 1 SD
2011-01-25	29.4 ± 0.3
2011-02-12	29.6 ± 0.5
2011-02-14	27.5 ± 0.7
2011-02-15	28.5 ± 0.1
2011-03-12	27.1 ± 0.6
Preila (LTU)	
Date	$\delta^{18}\text{O}$ (‰) $\pm$ 1 SD
2014-03-09	20.1 ± 0.7
2014-03-10	23.3 ± 0.4

Figure captions

Fig. 1: A) $\delta^{18}\text{O}$ values of bulk wood, cellulose and levoglucosan in experimental pine (open circle) and beech (closed circle) samples from controlled wood burning experiments ($n = 2-8$). Mean values and standard deviations are given. B) $\delta^{18}\text{O}$ values of levoglucosan in ambient aerosol samples obtained from Magadino, Switzerland (CH, 2011) and from Preila, Lithuania (LTU, 2014). Mean values and standard deviations of triplicate measurements are given for each sample.