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# Stable Carbon Isotope Ratio Analysis of Anhydrosugars in Biomass Burning Aerosol Particles from Source Samples

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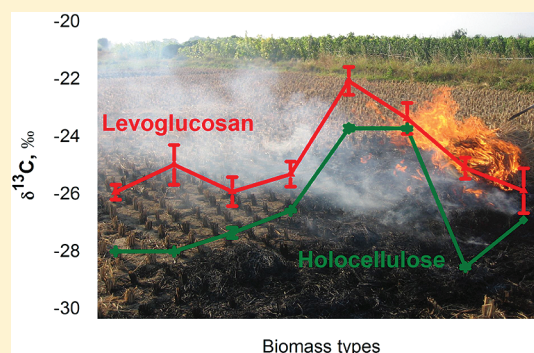
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**ABSTRACT:** A new method for stable carbon isotope ratio analysis of anhydrosugars from biomass burning aerosol particle source filter samples was developed by employing Thermal Desorption – 2 Dimensional Gas Chromatography – Isotope Ratio Mass Spectrometry (TD-2DGC-IRMS). Compound specific isotopic measurements of levoglucosan, mannosan, and galactosan performed by TD-2DGC-IRMS in a standard mixture show good agreement with isotopic measurements of the bulk anhydrosugars, carried out by Elemental Analyzer – Isotope Ratio Mass Spectrometry (EA-IRMS). The established method was applied to determine the isotope ratios of levoglucosan, mannosan, and galactosan from source samples collected during combustion of hard wood, softwood, and crop residues.  $\delta^{13}\text{C}$  values of levoglucosan were found to vary between  $-25.6$  and  $-22.2\text{‰}$ , being higher in the case of softwood. Mannosan and galactosan were detected only in the softwood samples showing isotope ratios of  $-23.5\text{‰}$  (mannosan) and  $-25.7\text{‰}$  (galactosan). The isotopic composition of holocellulose in the plant material used for combustion experiments was determined with  $\delta^{13}\text{C}$  values between  $-28.5$  and  $-23.7\text{‰}$ . The difference in  $\delta^{13}\text{C}$  of levoglucosan in biomass burning aerosol particles compared to the parent fuel holocellulose was found to be  $-1.89 (\pm 0.37)\text{‰}$  for the investigated biomass fuels. Compound specific  $\delta^{13}\text{C}$  measurements of anhydrosugars should contribute to an improved source apportionment.



## INTRODUCTION

Biomass burning is an important source of atmospheric trace gases and particulate matter impacting air quality and climate. It enhances levels of ozone and other trace gases relevant for the radiative balance of the atmosphere. In addition, biomass burning aerosol particles affect cloud formation and reflectivity.<sup>1–3</sup> The physical, chemical, and optical properties of biomass burning aerosol particles vary depending on fuel type, combustion phase, and meteorological conditions and might change rapidly during atmospheric transport.

A major chemical component found in biomass burning aerosol particles is levoglucosan, accompanied by its stereoisomers, mannosan and galactosan.<sup>4–7</sup> These anhydrosugars are highly polar and originate from thermal depolymerization of cellulose and hemicelluloses to monosaccharides, followed by a dehydration reaction. Because of its high atmospheric stability, with no decay over 10 days under acidic conditions as found in most atmospheric droplets,<sup>8</sup> levoglucosan is used as a marker for biomass burning processes. Combustion of other materials (e.g., fossil fuels), biodegradation or hydrolysis of cellulose does not produce any levoglucosan. However, uncertainties exist in the assessment of biomass burning contributions due to

analytical limitations and missing representative source profiles. Therefore, the effect of biomass burning on air quality and climate is still poorly constrained on regional and global scales.<sup>4,9–11</sup>

Schkolnik and Rudich<sup>12</sup> compared and evaluated methods for the quantification of levoglucosan by using aqueous phase or gas chromatography (GC). Ma et al.<sup>13</sup> described a novel method to quantify levoglucosan, mannosan, and galactosan in aerosol particles by using Thermo Desorption – Two-Dimensional Gas Chromatography – Mass Spectrometry (TD-2DGC-MS). Gaining volatile organic compounds (VOC) from aerosol particle filter samples by direct thermodesorption offers advantages over traditional techniques, which use solvent extraction, concentration, and derivatization. Direct thermodesorption requires less sample preparation, reduces the risk of sample contamination and is more sensitive. Yet GC separation of complex matrices containing polar

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compounds is very challenging for one-dimensional gas chromatography.

Information on concentration alone is often not enough to apportion nonmethane hydrocarbon (NMHC) sources or to investigate chemical and physical processes occurring from emission to observation. Using compound specific stable carbon isotope ratio measurements in volatile organic compounds (VOCs)<sup>14,15</sup> together with the isotopic hydrocarbon clock concept,<sup>16</sup> isotope ratio analysis has become a powerful tool for atmospheric research. It provides additional constraints on atmospheric budgets to better characterize emission sources and increase our understanding of physical and chemical processing of VOCs,<sup>17–19</sup> as well as secondary organic aerosol formation.<sup>20</sup> To this end, the isotope signature of chemical species at a specific point in time and space can be used to calculate the extent of chemical degradation or determine trace sources.

C3 and C4 plants possess very different isotopic signatures for the plant tissues, ranging from –32 to –20‰ against –17 to –9‰, respectively.<sup>21</sup> This difference exists because, in the carbon assimilation, the determining step is the dark photosynthetic carboxylation, in the case of C3 with a stronger discrimination against <sup>13</sup>CO<sub>2</sub>. Despite  $\delta^{13}\text{C}$  was found to be highly unlike in different plant organs and metabolites,<sup>21–26</sup> very small variations are observed within or among species belonging to the same photosynthetic type. As for isotopic studies on certain products of biomass burning, slight deviations between  $\delta^{13}\text{C}$  of low and high molecular *n*-alkanes were reported by O'Malley.<sup>27</sup> The isotopic composition of original biomass material was preserved in aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) resulting from the thermal decomposition of lignin. This conclusion was supported by Czapiewski et al.<sup>28</sup> They found yet other biomass burning products, whose isotopic composition strongly deviated from the parent plant tissue. Ethyne for instance was enriched in <sup>13</sup>C by 20–30‰, whereas methylchloride was on the contrary lighter than the plant carbon by 25‰.

No  $\delta^{13}\text{C}$  studies of the biomass burning markers levoglucosan, mannosan, and galactosan have been reported so far. The first goal of this work was to develop a reliable method for compound specific measurements of the isotopic composition of levoglucosan, mannosan, and galactosan. The three anhydrosugars were isotopically investigated in aerosol particle filter samples originating from the combustion of selected C3 plants, as typically used in domestic heating and cooking or for field waste disposal. The investigated plants can be divided into two main taxonomic classes, angiosperms (stalk plants and hardwoods) and gymnosperms, often referred to as softwoods.

The second goal was to investigate in a further step, whether levoglucosan has a source-specific isotopic signature and thus, can provide fingerprints for the type of burnt biomass. Additionally, we explored whether the isotopic composition of the other anhydrosugars gives more insight into the combustion process.

## MATERIALS AND METHODS

**$\delta^{13}\text{C}$  Analysis.** The stable carbon isotopic composition of a compound describes the ratio of the less abundant isotope of carbon, <sup>13</sup>C, to the more abundant isotope, <sup>12</sup>C. Instead of absolute isotope ratios, relative isotope ratio differences between sample and a known standard (delta values) are

reported.<sup>29</sup> The delta value represents the deviation of <sup>13</sup>R in the sample compared to a standard, expressed in per mil (‰):

$$\delta^{13}\text{C} = \delta^{13}\text{C}_{\text{P/STD}} = \left( \frac{R\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{P}}}{R\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{STD}}} - 1 \right) \cdot 1000\text{‰} \quad (1)$$

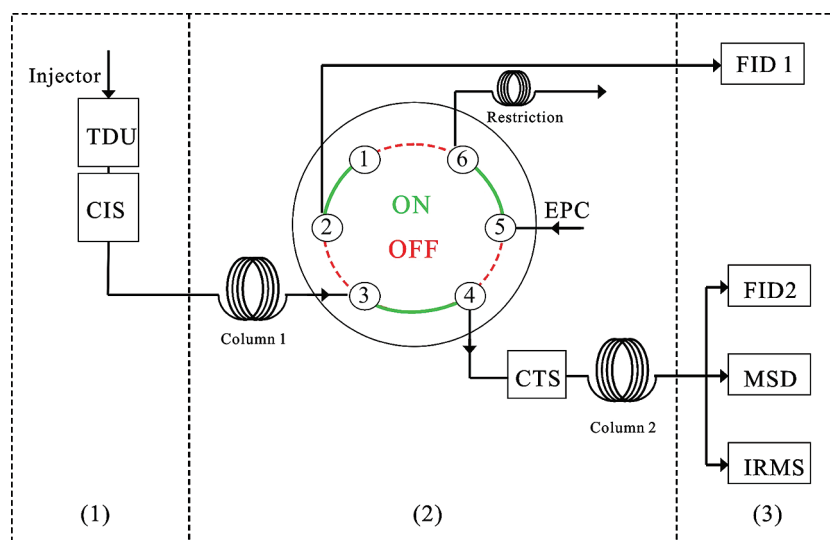
where  $R((^{13}\text{C})/(^{12}\text{C}))_{\text{P}}$  and  $R((^{13}\text{C})/(^{12}\text{C}))_{\text{STD}}$  are the absolute isotope ratios for the sample (P) and the working standard (STD), respectively.<sup>30</sup> As working standard for this study, high-purity CO<sub>2</sub> (Messer, 100%) was used. Its calibration against International Atomic Energy Agency (IAEA) standards (IAEA-CH6, IAEA-CH7, and USGS24) resulted in highly linearity with working standards Flukacell and Graphit VI ( $R^2 = 0.99991$ ). The <sup>17</sup>O correction was done using the algorithm described by Brand et al.<sup>31</sup> Final  $\delta^{13}\text{C}$  values are reported relative to the international reference Vienna Pee Dee Belemnite (VPDB).

**Source samples.** Source aerosol particle samples originating from combustion of typical crop residues – rice (*Oryza sativa*) straw, peanut (*Arachis hypogaea*), and mulberry (*Morus alba*) stalks – soft woods – China fir (*Cunninghamia lanceolata*) and Chinese red pine (*Pinus massoniana*) – and hard woods – Chestnut (*Castanea mollissima*) and Chinese Guger tree (*Schima superba*) – in field open fires or domestic stoves were collected during a measurement campaign in the Peal River Delta (PRD) region. Even though the PRD is one of the most developed areas in China, 30–40% of the total crop residues and wood production are used as energy source in the vast rural areas.<sup>32</sup>

The burning experiments for crop residues were conducted in Shixing County (SX), which mainly is a rice producing area. Wood burning experiments were carried out in Ruyuan County (RY), mainly covered by forest with typical local tree species, such as Chinese Guger tree, China fir, Chinese red pine. The stoves used for burning experiments are very common in rural Chinese households (found in 80% of cases<sup>33</sup>). These stoves contain one main and one auxiliary pot, with a bottom grate and a flue pipe.

The biomass burning procedures used for this study include domestic stove burning and field open burning. The former was conducted for all the biomasses mentioned above, while open burning was conducted only on rice straw. For domestic stove burning, water boiling tests<sup>34</sup> were done by heating a certain amount of water from room temperature to its boiling point. Stoves were fed with different types of fuel by local people to proceed in accordance to the commonly used practices. Sampling took place on the rooftop of the kitchen ca. 3–5 m away from the chimney under windless or faint wind weather conditions to ensure that enough aerosol particles could be collected on the filter. Under higher wind speed conditions (0.5–1.5 m s<sup>–1</sup>), samplers were moved into the smoke plume downwind of the source. For the field open burning of rice straw, samplers were set 5 m away from the piled burning material.

The total sampling time was chosen to start at smoke appearance until it disappeared and lasted ca. 40–60 min. Therefore, smoke particles generated in both smoldering and flaming stages were jointly collected. The sampler was a high flow impactor (100 L min<sup>–1</sup>, M131, MSP, Minnesota, USA) with six stages, collecting particles with aerodynamic diameters



**Figure 1.** Schematic diagram of the newly established TDU-2DGC-IRMS method consisting of a thermodesorption and cryo-trapping unit (1), a separation unit (2), and a detection unit (3).

of  $PM_{>10}$ ,  $PM_{10-2.5}$ ,  $PM_{2.5-1.4}$ ,  $PM_{1.4-1.0}$ ,  $PM_{1.0-0.44}$ , and  $PM_{0.44}$ . Design and operation principle of the cascade high flow impactor are given by Marple and Olson.<sup>35</sup> Aerosol particles were collected on 75 mm (the first to fifth stages) and 90 mm (the sixth stage) quartz microfiber filters (Whatman, Piscataway, NJ, USA), prebaked at 500 °C for 8 h. After sampling, the filters were stored in a freezer at −20 °C. Before and after sampling, all filters were conditioned for 24 h at constant temperature ( $23 \pm 1$  °C) and humidity (40%) and then weighed using an electronic balance.

**Cellulosic Parent Material Samples.** Plant residues and woods used in the above-described biomass burning experiments were milled into powder. Pure holocellulose (cellulose and hemicelluloses) for isotopic measurements was obtained in the Institute of Bio- and Geosciences of the Research Center Jülich by using a two-step method, which comprises solvent extraction for removal of tannins and resins, followed by wet oxidation for delignification.<sup>36</sup>

**Experimental Setup.** For compound specific isotopic measurements of aerosol particle filter samples, a setup consisting of a thermo-desorption/cryo-focusing unit (1), a separation unit (2), and a detection unit (3) was employed (Figure 1). To ensure optimal focusing of the analytes prior to separation, filter samples were thermodesorbed by using a Thermal Desorption Unit (TDU) (Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany), directly mounted onto a programmable-temperature-vaporizing – Cooled Injection System (CIS). The separation of the components was performed with a Gas Chromatograph (GC, Agilent 6890, Agilent Technologies Inc., Santa Clara, USA), equipped with two columns. The first nonpolar column (DB5-MS, 30 m length, 0.25 mm i.d., 1 μm film thickness, J&W Scientific, Folsom, USA) separates all chemical compounds by their volatility. The second midpolar column (RXI-624SilMS, 60 m length, 0.32 mm i.d., 1.8 μm film thickness, Restek, Bellefonte, USA) provides improved resolution and selectivity for polar compounds. A custom designed multi column switching system, including a six-way valve and a Capillary Trapping System (CTS) allowed selecting and trapping heart-cut windows containing compounds of interest from the first column eluate. Because the fast temperature changes inside the

CTS could damage the coating of the polar column, a retention gap (50 cm deactivated fused silica column, 0.32 mm i.d., 0.44 mm o.d., Chromatographie Service GmbH, Langerwehe, Germany) was integrated with the analytical column. The separated compounds were sent to three detectors: Flame Ionization Detectors (FID1 and FID2), a quadrupole Mass Spectrometer (MSD, PerkinElmer, Waltham, USA) to identify the chemical structure of the separated compounds and an Isotope Ratio Mass Spectrometer (IRMS, Delta-V Advantage, Thermo Electron GmbH, Bremen, Germany) to measure the stable carbon isotope ratios. The GC was linked to the IRMS through a combustion interface, where organic compounds were quantitatively oxidized at 1030 °C to CO<sub>2</sub> and water. After removal of water by a semipermeable trap (Nafion membrane), CO<sub>2</sub> was transferred via a continuous flow, open split device (Conflo-IV) to the IRMS for stable carbon isotope ratio measurements.

**Method.** The new TDU-2DGC-IRMS method was developed and tested by analyzing a levoglucosan/mannosan/galactosan standard mixture. Standard solutions of levoglucosan (1,6-anhydro-β-D-glucopyranose), mannosan (1,6-anhydro-β-D-mannopyranose) and galactosan (1,6-anhydro-β-D-galactopyranose) (Chromatographie Service GmbH, Langerwehe, Germany) were prepared by dissolving 10 mg of each compound in 10 mL methanol (99.9%, Merck KGaA, Darmstadt, Germany). Portions of 1000 μL of the standard solution were directly filled into small vials and stored at 4 °C until measurement.

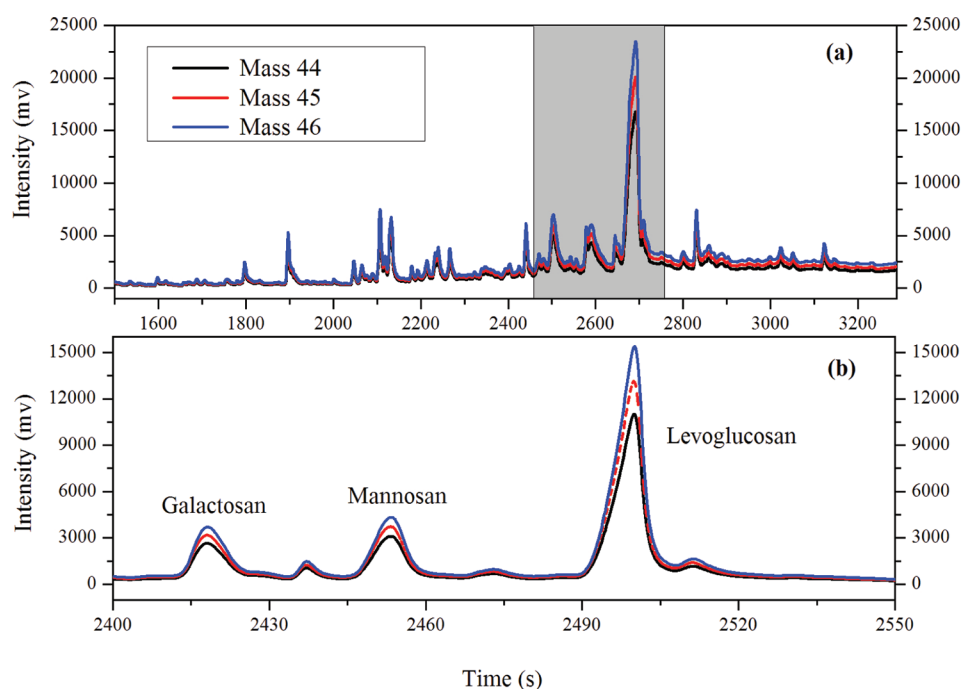
For standard analysis a small piece of quartz filter (ca. 0.2–0.3 cm<sup>2</sup>) was placed in a glass tube (60 mm, 4 mm i.d., preconditioned at 350 °C for 2 h) and inserted into the TDU. Thermal desorption of 1 μL aliquots of the standard mixture injected on the filter was achieved by ramping the TDU temperature from 25 to 340 °C at a rate of 720 °C min<sup>−1</sup>. The thermodesorbed analytes were flushed with helium at 50 mL min<sup>−1</sup> and trapped at −100 °C in the CIS operated in splitless mode. Subsequently, the mixture was transferred to the GC by heating the CIS to 340 °C at a rate of 720 °C min<sup>−1</sup>. Preliminary separation of the anhydrosugars occurred in the first column at a flow rate of 3 mL min<sup>−1</sup>. The temperature program of the GC oven included holding at 80 °C for 5 min,



**Table 1.**  $\delta^{13}\text{C}$  values of levoglucosan (Lev), mannosan (Man), and galactosan (Gal) in a standard mixture from compound specific measurements by the TDU-2DGC-IRMS and from isotope measurements of bulk anhydrosugars by EA-IRMS

method	sample mass/ $\mu\text{g}$ ( $n^a$ )	$\delta^{13}\text{C}/\text{‰}$		
		Lev	Man	Gal
TDU-2DGC-IRMS	1 (25)	$-23.22 \pm 0.39$	$-24.4 \pm 0.21$	$-26.70 \pm 0.42$
EA-IRMS	225 (3)	$-23.75 \pm 0.09$	$-24.77 \pm 0.02$	$-26.67 \pm 0.01$

<sup>a</sup>Number of data points.



**Figure 2.** Comparison of chromatograms for soft wood (Chinese red pine) burning aerosol particles without (a) and with heart-cutting (b), measured by the TDU-2DGC-IRMS. Signals of  $m/z$  44 (black,  $\text{CO}_2^+$ ), and isotopologues on  $m/z$  45 (red), and  $m/z$  46 (blue) are shown. Gray area in the chromatogram (a) indicates the heart-cut time window.

ramping at a rate of  $5\text{ }^\circ\text{C min}^{-1}$  to  $260\text{ }^\circ\text{C}$ , and holding for another 15 min.

The heart-cut time window was defined during the first measurement in which only column 1 was connected to the detectors. The chromatograms of compounds from column 1 were used to derive the retention times for the three anhydrosugars. A time window between 22 and 32 min was set as cutting time depending on oven temperature program, flow rate, and column dimensions. This selected part of the chromatogram was transferred to column 2.

Further measurements were carried out by using the developed heart-cutting procedure, which is controlled and programmable by the Gerstel Maestro software (isodat 3.0). From 0 to 22 min, the eluate from column 1 was directed to the FID1. After 22 min, the six-way valve was switched to transfer position for 10 min. The anhydrosugars eluting in this time window were totally trapped in the CTS at  $-100\text{ }^\circ\text{C}$  and later on sent to column 2 for complete separation. After the heart-cutting phase, the eluate from the column 1 was again entirely sent to FID1. At the same time, the anhydrosugars trapped in the CTS were transferred to column 2 by fast heating to  $260\text{ }^\circ\text{C}$  (at a rate of  $720\text{ }^\circ\text{C min}^{-1}$ ). The baseline-separated anhydrosugars were then sent to the detectors with 10–15% of the gas flow directed to the FID2 and MSD and the remainder part to the IRMS for isotope ratios measurements.

Parallel to the compound specific measurements, bulk stable carbon isotope composition of the total carbon (TC) in the solid anhydrosugars were performed using an elemental analyzer (Euro Vector, Hekatech GmbH, Wegberg, Germany) coupled to an IRMS (Delta-V Advantage, Thermo Electron GmbH, Bremen, Germany).  $\delta^{13}\text{C}$  obtained by employing TD-2DGC-IRMS against EA-IRMS are presented in Table 1. Within experimental errors,  $\delta^{13}\text{C}$  values derived from both analyses show good agreement, indicating that no isotopic fractionation occurs during the thermodesorption, cryo-trapping, and subsequent GC-separation of the anhydrosugar mixture.

After establishing the method in detail, source filter samples originating from combustion of different biomass fuels were isotopically analyzed with the same procedure. To this end, small pieces of the source filter were cut and placed into the TDU. The area of a filter cut was calculated according to the mixing ratio of levoglucosan and sampling volume, so that the total mass amount of levoglucosan on the filter portion was ca.  $1\text{ }\mu\text{g}$ .

Figure 2 shows the  $m/z$  44, 45, and 46 chromatograms obtained without (part a of Figure 2) and by employing the heart-cutting procedure (part b of Figure 2) for an aerosol particle filter sample from Chinese red pine combustion. In case of transferring all organic compounds on both columns and without trapping in the CTS (part a of Figure 2), the anhydrosugars, especially mannosan and galactosan, overlap

**Table 2.**  $\delta^{13}\text{C}$  Values of Detected Anhydrosugars in the Biomass Burning Source Samples Discretized on  $\text{PM}_{0.44}$ ,  $\text{PM}_{1.0-0.44}$ ,  $\text{PM}_{1.4-1.0}$ , and  $\text{PM}_{2.5-1.4}$ 

biomasses	anhydrosugars	$\delta^{13}\text{C}/\text{‰}^a$			
		$\text{PM}_{0.44}$ ( $n^b$ )	$\text{PM}_{1.0-0.44}$ ( $n^b$ )	$\text{PM}_{1.4-1.0}$ ( $n^b$ )	$\text{PM}_{2.5-1.4}$ ( $n^b$ )
rice straw (field open combustion)	Lev	$-25.72 \pm 0.44$ (4)	$-25.86 \pm 0.27$ (7)	$-25.60 \pm 0.49$ (2)	$-24.26 \pm 0.09$ (2)
rice straw	Lev	$-24.41 \pm 0.47$ (4)	$-25.06 \pm 0.88$ (6)	$-24.90 \pm 0.16$ (4)	$-23.56 \pm 0.29$ (2)
peanut stalk	Lev	$-25.68 \pm 0.64$ (4)	$-26.16 \pm 0.29$ (6)	$-25.20 \pm 0.60$ (2)	$-24.58 \pm 0.41$ (2)
mulberry stalk	Lev	$-25.24 \pm 0.55$ (5)	$-25.31 \pm 0.01$ (2)	$-24.60 \pm 0.70$ (3)	$-25.40 \pm 0.49$ (3)
China fir	Gal	N.D. <sup>c</sup>	$-25.74 \pm 0.56$ (4)	N.D. <sup>c</sup>	N.D. <sup>c</sup>
	Man	N.D. <sup>c</sup>	$-23.25 \pm 0.24$ (4)	N.D. <sup>c</sup>	N.D. <sup>c</sup>
	Lev	$-21.92 \pm 0.73$ (4)	$-21.92 \pm 0.37$ (8)	$-22.10 \pm 0.44$ (4)	$-22.60 \pm 0.35$ (2)
Chinese red pine	Gal	$-26.53 \pm 0.16$ (4)	$-25.61 \pm 0.74$ (5)	$-26.20 \pm 0.20$ (3)	$-26.05 \pm 0.06$ (2)
	Man	$-22.92 \pm 0.26$ (3)	$-23.47 \pm 0.78$ (3)	$-23.70 \pm 0.28$ (3)	$-23.69 \pm 0.40$ (2)
	Lev	$-23.51 \pm 0.49$ (4)	$-23.51 \pm 0.73$ (5)	$-23.10 \pm 0.68$ (3)	$-23.73 \pm 0.42$ (2)
chinese guger tree	Lev	$-25.41 \pm 0.27$ (3)	$-24.68 \pm 0.82$ (3)	$-24.90 \pm 0.20$ (2)	$-24.06 \pm 0.98$ (2)
Chestnut	Lev	$-25.68 \pm 0.49$ (5)	$-26.48 \pm 0.32$ (6)	$-25.78 \pm 0.44$ (4)	$-25.50 \pm 0.62$ (5)

<sup>a</sup>Mean value  $\pm$  standard deviation. <sup>b</sup>Number of data points. <sup>c</sup>Below detection limit.

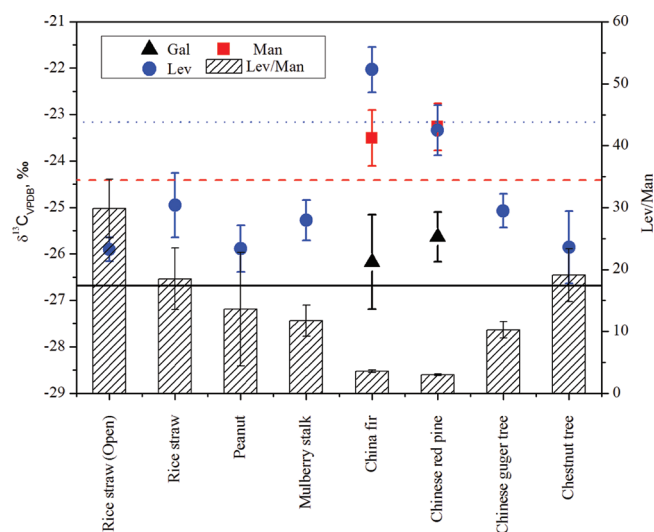
with other unresolved peaks (gray area). Contrary to this, when using the heart-cutting procedure, levoglucosan, mannosan, and galactosan are baseline separated, which is optimal for their isotope ratio measurements.

## RESULTS AND DISCUSSION

**Stable Carbon Isotope Composition of Anhydrosugars in Biomass Burning Source Samples.** Compound specific isotopic measurements were carried out for 144 source samples originating from different types of combustion of selected biomasses. The  $\delta^{13}\text{C}$  values, discretized for  $\text{PM}_{0.44}$ ,  $\text{PM}_{1.0-0.44}$ ,  $\text{PM}_{1.4-1.0}$ , and  $\text{PM}_{2.5-1.4}$  aerosol particle filter samples, are presented in Table 2 indicating no dependence of isotopic composition on size distribution of the collected particles. Levoglucosan, mannosan, and galactosan were not detected in  $\text{PM}_{10-2.5}$  and  $\text{PM}_{>10}$  samples, in accordance with Wang et al.,<sup>37</sup> who reported unimodal size distribution for biomass burning compounds accumulating in the fine mode at  $0.7\text{--}1.1\text{ }\mu\text{m}$ . Moreover, Krumal et al.<sup>38</sup> found comparable fractional abundances of total anhydrosugars from biomass burning in  $\text{PM}_1$  and  $\text{PM}_{2.5}$  aerosol particles (1.4 to 2.7% of the total PM mass). Therefore, fine mode sampling ( $\text{PM}_{2.5}$ ) of biomass burning products is recommended for isotopic analyses because optimal loading of anhydrosugars on filters is advantageous for IRMS sensitivity. The described method, finally aimed to be applied to ambient studies, is sensitive enough to measure levoglucosan concentrations higher than  $5.55\text{ ng m}^{-3}$ , which are commonly found in regions impacted by biomass burning (Pio et al.<sup>39</sup>).

Mean  $\delta^{13}\text{C}$  values of anhydrosugars measured in the different biomass samples are depicted in Figure 3 together with the corresponding levoglucosan to mannosan (Lev/Man) concentration ratios. Lev/Man ratios of 3–5 in the samples originating from fir and red pine combustion are typical for softwoods<sup>40</sup> serving as a diagnostic tool to differentiate between softwoods and stalk plants or hardwoods (with higher Lev/Man ratios of 13–30 and 8–18, respectively). These values indicate a high fraction of hemicelluloses beside cellulose in the parent plants, thus containing more mannose and galactose. Because of their higher abundance in the softwood biomass burning aerosol particles, mannosan and galactosan could be detected by the TD-2DGC-IRMS method in the softwood smoke samples.

Levoglucosan  $\delta^{13}\text{C}$  values of  $-25.6$  to  $-24.9\text{‰}$  were determined for stalk plants and hardwoods comparable to the



**Figure 3.** Mean  $\delta^{13}\text{C}$  values in four size ranges for levoglucosan (blue circles), galactosan (black triangles), and mannosan (red squares) together with the corresponding Lev/Man ratios (bars). The black line, red dashed line, and blue dotted line indicate the isotope ratios of galactosan, mannosan, and levoglucosan in the standard solutions. Rice straw (open) refers to the open field burning of rice straw; burning style of all other samples was domestic stove burning.

isotopic composition of most C3 plant tissues (on average  $-26.7\text{‰}$  as given by Rudolph et al.<sup>14</sup> or  $-26.4$  to  $-26.1\text{‰}$  as reported by O'Malley et al.<sup>27</sup>). The softwood samples showed higher levoglucosan  $\delta^{13}\text{C}$  values.  $\delta^{13}\text{C}$  of  $-22.2 \pm 0.5\text{‰}$  for China fir and  $-23.4 \pm 0.5\text{‰}$  for Chinese red pine were observed, corresponding to  $^{13}\text{C}$  enrichment by ca. 2.5‰. Mannosan showed similar isotopic composition of  $-23.5 \pm 0.6\text{‰}$  and  $-23.4 \pm 0.6\text{‰}$  for the China fir and Chinese red pine, respectively. Galactosan was lighter than levoglucosan and mannosan in softwood samples by 3‰. This might be explained by earlier thermal break up of galactosan from the hemicelluloses during the combustion process itself. Thermograms of natural biomasses show that hemicelluloses decompose already at  $498\text{--}598\text{ K}$ , whereas cellulose depolymerisation takes place at  $598\text{--}798\text{ K}$ .<sup>41,42</sup> The higher thermal stability of cellulose results from its crystalline structure, arising from the linear linkage within the polymer chain and the equatorial hydroxyl groups.<sup>43</sup> Most hemi-

celluloses from softwoods have a ramified structure, where xylose, glucose, and mannose make up the backbone polymer, whereas branches are made of galactose. As short side chains, galactose first leaves the macromolecules and is easily dehydrated because of its axial OH group in the saccharide ring. The isotopic fractionation of the three anhydrosugars could therefore be used to get more insight into the combustion process.

**Stable Carbon Isotope Composition of Holocellulose in the Parent Material.** Isotopic ratios of total carbon (TC) in parent holocellulose from each studied biomass, measured by EA-IRMS are presented in Table 3 together with the

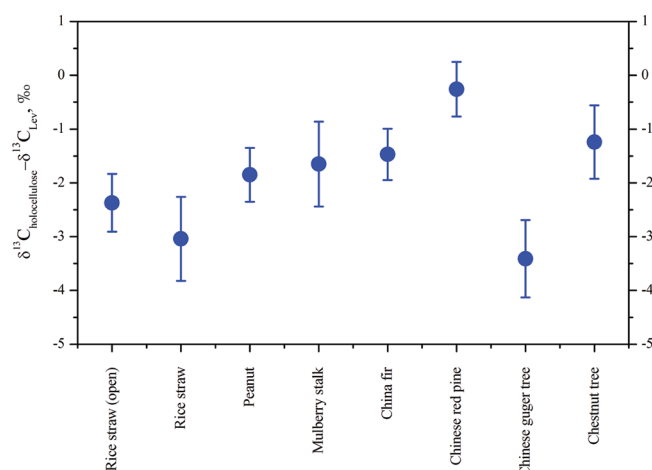
**Table 3.**  $\delta^{13}\text{C}$  Values of Parent Compound Holocellulose and Levoglucosan (Lev)

biomasses	$\delta^{13}\text{C}/\text{‰}$	
	holocellulose	Lev
rice straw (open)	$-27.97 \pm 0.08$	$-25.60 \pm 0.64$
rice straw	$-27.97 \pm 0.08$	$-24.93 \pm 1.03$
peanut	$-27.32 \pm 0.05$	$-25.47 \pm 0.71$
mulberry stalk	$-26.55 \pm 0.18$	$-24.90 \pm 0.75$
China fir	$-23.68 \pm 0.01$	$-22.21 \pm 0.48^a$
Chinese red pine	$-23.68 \pm 0.01$	$-23.42 \pm 0.51^a$
Chinese guger tree	$-28.52 \pm 0.03$	$-25.11 \pm 0.36$
chestnut tree	$-26.87 \pm 0.03$	$-25.63 \pm 0.68$

<sup>a</sup>Weighted mean  $\delta^{13}\text{C}$  values were calculated for the China Fir and Chinese Red Pine samples, in which mannosan and galactosan were detected, being  $-22.20 \pm 0.52\text{‰}$  and  $-23.62 \pm 0.36\text{‰}$ , respectively.  $\delta^{13}\text{C}_{\text{mean}} = (\delta^{13}\text{C}_{\text{Lev}} \times C_{\text{Lev}} + \delta^{13}\text{C}_{\text{Man}} \times C_{\text{Man}} + \delta^{13}\text{C}_{\text{Gal}} \times C_{\text{Gal}}) / (C_{\text{Lev}} + C_{\text{Man}} + C_{\text{Gal}})$ , where  $C_{\text{Lev}}$ ,  $C_{\text{Man}}$ , and  $C_{\text{Gal}}$  are mass concentrations with unit of  $\text{ng m}^{-3}$ .

corresponding isotopic ratios for levoglucosan.  $\delta^{13}\text{C}$  values of  $-28.5$  to  $-26.6\text{‰}$  were determined for the holocellulose extracted from stalk plants and hardwoods powder. In contrast,  $\delta^{13}\text{C}$  of  $-23.7\text{‰}$  was found for softwood holocellulose. The holocellulose of the softwood samples studied here was enriched in  $^{13}\text{C}$ , which lead to an enrichment of similar magnitude in the anhydrosugars in biomass burning aerosol particles. The isotopic composition of the combusted parent material thus influences the  $\delta^{13}\text{C}$  values of the biomass burning products.

The carbon isotope fractionation during the combustion (defined as  $\Delta = \delta^{13}\text{C}_{\text{holocellulose}} - \delta^{13}\text{C}_{\text{levoglucosan}}$ ) is depicted in Figure 4, having a mean value of  $-1.89 (\pm 0.37)\text{‰}$ . An explanation why the analyzed thermal decomposition products are isotopically heavier than the reactant might be that the pyrolysis process changes with increasing temperature. During the initial endothermic phase (below 473 K), gases such as  $\text{CO}_2$  and  $\text{CO}$  are mainly emitted. Depletion in  $^{13}\text{C}$  of these gases relative to the parent fuel translates into  $^{13}\text{C}$  enrichment of the remaining material. Volatile anhydrosugars, which arise subsequently at higher temperatures, could therefore carry higher  $\delta^{13}\text{C}$  values, and then partition into the particle phase. This fractionation was observed also by Widory,<sup>44</sup> who showed  $^{13}\text{C}$  depletion in the gases against enrichment in particles generated during the combustion of different types of fuels used in urban environments. Nevertheless, isotopic composition analyses of TC on filters as well as the emitted species in the gas phase are subject of future work, in order to better understand the reaction mechanisms.



**Figure 4.** Isotopic fractionation defined as difference between holocellulose  $\delta^{13}\text{C}$  and levoglucosan  $\delta^{13}\text{C}$  in the biomass burning source samples.

Moreover, parameters such as pyrolysis temperature or fuel moisture should be better monitored in future combustion experiments. Burning of other types of biomass originating from C4 plants should be explored as well.

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### Notes

The authors declare no competing financial interest.

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