Wood burning impact on PM10 in three Austrian regions

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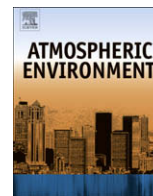TU Wien
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Wood burning impact on PM_{10} in three Austrian regions

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ABSTRACT

Anhydrosugars (levoglucosan, mannosan and galactosan) were investigated during one year in three Austrian regions at three types of sites (city-heavy traffic-impacted, city-residential and background) in order to assess the magnitude of the contribution of wood smoke to the particulate matter load and its organic fraction. The annually averaged concentrations of levoglucosan ranged from 0.12 to 0.48 $\mu g\, m^{-3}$. The levoglucosan concentration exhibited a strong annual cycle with higher concentrations in the cold season. The minor anhydrosugars had a similar annual trend, but their concentrations were lower by a factor of about 5 and about 25 in the cold season for mannosan and galactosan, respectively. Levoglucosan concentrations were higher at the inner-urban as compared to rural sites. The contribution of wood smoke to organic carbon and PM_{10} levels was calculated using a constant ratio of levoglucosan and OC, respectively PM_{10} as derived for fire wood typical for Alpine European regions [Schmidl, C., Marr, I.L., Caseiro, A.e, Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008a. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmospheric Environment 42, 126–141]. The estimated contribution of wood smoke-OC to the OC of PM_{10} ranged from one third to more than half in the cold season with higher contributions up to 70% in winter (December, January and February) in the smaller cities and the rural background. This indicates, that wood smoke is the predominant source of organic material at rural and small urban sites in central Europe. Consistently, wood smoke was an important contributor to PM_{10} during the cold season, with contributions of around 10% in the Vienna larger region and around 20% at rural sites in the densely forested regions of Salzburg and Styria during the winter months. In those regions residential sites exhibited highest relative wood smoke contents in PM_{10} during autumn (September till November), indicating the use of wood stoves for auxiliary heating in the transition of warm to cold season. Using the relationships between the different anhydrosugars the combustion of softwood was found to be dominant for the wood smoke occurrence in ambient air at the investigated sites. Potassium, a commonly used tracer for biomass burning, correlated well to levoglucosan, with a mass ratio of around 0.80 in the cold season.

1. Introduction

The impact of particulate matter (PM) on climate (e.g. IPCC, 2007) and public health (e.g. Chapman et al., 1997; Peden, 2005; Englert, 2004) is an environmental key concern. Therefore, an understanding of its source contributions is required in order to establish policies for reducing the emissions. A common technique to apportion the ambient particulate mass is to chemically characterise the aerosol for a set of compounds and to use them as tracers (e.g. Rogge et al., 1993; Sheffield et al., 1994; Schauer et al., 1996; Zheng et al., 2002).

There are quite different types of fire events which are of concern for the aerosol budget. Globally, the emphasis is on wild fires (forest, savanna etc.) and on biomass smoke from primitive use of biofuels (e.g. cooking in Africa and Asia countryside) (e.g. Bond et al., 2004). In Europe major biomass burning emissions are regionally from wild fires (in southern Europe) (e.g. Pio et al., 2008), agricultural fires (in eastern Europe, e.g. Stohl et al., 2007) and wood smoke from fireplaces and stoves (in central and northern Europe, e.g. Puxbaum et al., 2007). In the studies at the American Continent and in Scandinavia the wood smoke from fireplaces and stoves was identified as an important source of wintry fine particle levels, in particular at rural sites (Wolff et al., 1981; Ramdahl et al., 1984; Sexton et al., 1985; Freeman and Cattell, 1990; Schauer et al., 1996; Zheng et al., 2002; Khalil and Rasmussen, 2003). In these

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studies levoglucosan, retene, selected resin acids and syringoles were used as tracers for identifying wood smoke contributions to fine particulate levels. Recently, also the property of "brown carbon" has been elucidated to derive estimates for wood smoke contributions to ambient PM (Reisinger et al., 2008; Sandradewi et al., 2008).

Anhydrosugars, such as levoglucosan, mannosan and galactosan, are formed in pyrolysis process of cellulose and hemicellulose containing materials, and thus are important tracers for biomass burning emission (e.g. wood, straw, paper) (Shafizadeh, 1968, 1984). Levoglucosan was found to be the most abundant of the identified compounds in $PM_{2.5}$ emission of stoves and fireplaces burning wood, accounting for 3–30% of the fine particle organic compound mass emitted (100 ± 40 mg g^{-1} organic carbon) (Schauer et al., 2001; Fine et al., 2001, 2002). Schmidl et al. (2008a) studied the PM_{10} emissions of residential combustion of different kinds of wood commonly grown in central Europe and found similar results (4–15% levoglucosan emitted in PM). Levoglucosan has been studied not only in wood burning emission samples but also in the ambient air. Many studies have now detected its occurrence in biomass smoke-impacted plumes as well as in remote, rural, suburban and urban air samples (e.g. Schauer and Cass, 2000; Moreira dos Santos et al., 2002, 2004; Zheng et al., 2002; Gao et al., 2003; Graham et al., 2004; Fine et al., 2004a; Leithead et al., 2006; Ward et al., 2006; Puxbaum et al., 2007; Szidat et al., 2007; Lanz et al., 2008).

Favourable properties of levoglucosan as biomass combustion tracer are a reported good photochemical stability in the atmosphere (Locker, 1988, as cited by Simoneit, 2002) and in liquid phase (Fraser and Lakshmanan, 2000).

Levoglucosan derives from the D-glucose units of the holocellulose molecules (cellulose and hemicelluloses) when those undergo a pyrolysis process (Shafizadeh, 1968, 1984). The less investigated anhydrosugars mannosan and galactosan evolve in a similar way but from the mannose and galactose units of the biofuel's hemicellulose molecules (Otto et al., 2006), though they are not emitted in such high quantities. Recently, Schmidl et al. (2008a) have pointed out the potential of those substances for differentiating the contribution of hard and softwoods to the PM load. The ratio between levoglucosan and mannosan in the particulate emissions from the burning of woods commonly used in Austria (softwoods: spruce and larch, hardwoods: oak and beech) was found to be high for hardwoods (typically 14–15) and lower for softwoods (3.6–3.9). Briquettes from softwoods had a ratio of 2.5 (Schmidl et al., 2008a).

Here, through the concentration and the seasonal behaviour of the three major anhydrosugars emitted from wood burning, we investigate the impact of wood smoke on organic carbon and PM_{10} levels in three Austrian regions. Each region included three types of sites: a heavy traffic exposed site in a city, a residential site in a city, and a site not strongly impacted by city emissions. The three cities (Vienna, Graz, Salzburg) are capitals of Austrian counties. We investigate the relationships of the concentrations of the minor anhydrosugars to levoglucosan, and derive a predominance of softwood as wood smoke source at the three regions. Closeness to the access of wood as a fuel appears to influence the relative contents of wood smoke in PM_{10}.

2. Experimental

2.1. Sampling and sampling sites

Vienna is the largest and capital city of Austria with about 1.8 million inhabitants. Plains surround the city except in the West, where woody hills are present. Two sites with background

characteristics and two sites impacted by traffic were selected from the Vienna monitoring network for this campaign. Schafberg (SCH) and Lobau (LOB) are the two background sites. The former is located at the north-west end of the city, in a park-type residential area and the latter lies within the Donau Auen national park. Kendlerstrasse (KEN), alongside a busy street, and Rinnböckstrasse (RIN), close to a highway, are the traffic-impacted sites. The four sites are oriented in a NW-SE transect, which is the dominant wind direction. With this feature, one of the two city-fringe sites is expected to be upstream of and minimally influenced by the city PM production.

Graz (population around 288,000) is the second largest city of Austria and capital of the federated state of Styria. It is located some 200 km south of Vienna on the banks of the Mur River. The city lies south east of the Alps, which shield the city from prevailing westerly winds and gives the climate some Mediterranean influence. It is located in a basin with only one opening, to the south, which often gives the city's atmosphere stagnant characteristics. The sampling sites form a N–S transect, with two sites within the city, impacted by traffic (Don Bosco, DB and Graz Süd, GS, this last one with more residential characteristics), and one background site outside the city (Bockberg, BB).

Salzburg has around 150,000 inhabitants and is the fourth largest city in Austria. Salzburg is situated approximately 300 km West of Vienna. It lies along the Salzach River and is surrounded by mountains at the northern border of the Alps. The sampling site located at a roundabout at Rudolfsplatz (RU) is representative for highly traffic-impacted conditions. Lehen (LE) is another site located in the city-centre, though in a residential area and not as much impacted by road traffic. Anthering (AN) is a sampling site situated outside the city and representative for regional background conditions.

Approximately 750 m^3 of ambient air were sampled daily through 2004 using hi-vol samplers (DHA-80, DIGITEL elektronik AG, Hegnau, Switzerland) on quartz fibre filters (Pallflex™ 2500QAT-UP, 15 cm diameter, PALL life sciences, USA) for 24 h. The local authorities who run the sampling network conducted all the gravimetric measurements. Filters were weighed after and before sampling, and had been previously conditioned in a clean room with controlled temperature and humidity ($20\,^\circ C \pm 1\,^\circ C$; $50\% \pm 5\%$). For chemical analysis, aliquots from the daily samples were combined into pools of selected periods. Table 2 refers the total number of pools for each site.

2.2. Anhydrosugars

The method used in this work was described in detail by Caseiro et al. (2007). Sample aliquots were extracted in ultra pure water (Millipore, resistance of $18.2\,M\Omega\,cm^{-1}$) and the extracts were subsequently analysed using high pH anion exchange ion chromatography. The eluent was an alkaline solution (stepwise increase of NaOH concentration) so that the carbohydrates would behave as weak acids and ionize. Detection was done using pulsed amperometric detection, which is indicated for carbohydrates. The reproducibility at the mid calibration range was between 3 and 5%, recovery was between 95% and 108% and the detection limits were 3.6, 5.0 and 0.9 ng m^{-3} for levoglucosan, mannosan and galactosan, respectively. The whole procedure repeatability tested with a real sample was 3.5%.

Table 1
Detection and quantification limits for the three anhydrosugars.

	Levo	Manno	Galac
LOD (ng m^{-3})	4.5	6.1	1.1
LOQ (ng m^{-3})	13	18	3.3

Table 2
Number of analysed pools below the quantification limit and total number of pools.

	Levo	Manno	Galac	pools
RIN	0	10	11	52
KEN	3	12	12	52
SCH	1	12	12	51
LOB	0	19	13	48
DB	0	6	7	44
GS	0	8	9	44
BB	0	12	8	39
RU	0	11	6	39
LE	0	12	12	36
AN	0	16	13	40

2.3. Organic carbon and potassium

The determination of total carbon (TC) was done measuring the CO_2 evolved from the combustion, in oxygen and at 1000 °C, of all the material on the filter. Non-dispersive IR photometry (NDIR, Maihak) was used for this determination. The same apparatus was used to determine elemental carbon (EC), but the filters were previously heated at 340 °C so that it was free of all the organic matter (Cachier et al., 1989). Carbonate carbon (CC) was determined as the last form of carbon to be released as CO_2 in the thermo-optical gradient temperature method, at temperatures higher than 550 °C (Puxbaum, 1979; Schmid et al., 2001). Organic carbon (OC) was computed as the difference between TC and the sum of elemental and carbonate carbon (EC + CC).

Potassium was determined using cation chromatography (Schmidl et al., 2008a).

3. Results and discussion

3.1. Blank filters, detection and quantification limits

A set of 101 blank filters were analysed for the whole campaign. The three anhydrosugars considered in this work were not detected in any of those filters.

Therefore, the detection and quantification limits were calculated using the detection (LOD) and quantification (LOQ) limits of the method (Caseiro et al., 2007). The LOD is defined as three times the standard deviation of the lowest concentration standard. The LOQ is three times the LOD. Those limits (given in $\mu g\,mL^{-1}$) were applied to an average extraction volume (3 mL), an average filter portion (1/32) and an average sampled air volume (approximately 750 m^3). Results are reported in Table 1. Also, Table 2 reports the number of filter pools which were below the quantification limit for each compound and each site, as well as the total number of filter pools considered for the whole year. For calculation purposes, values below the LOD or the LOQ were set to ½ of the respective limit.

3.2. Levoglucosan, mannosan and galactosan annual averages

The annual average concentration for levoglucosan ranged from 0.12 (at the Viennese background sites SCH and LOB) to 0.48 $\mu g\,m^{-3}$ in the densely populated urban residential site in Graz, GS. Annual average concentrations were the lowest in Vienna (0.12–0.16 $\mu g\,m^{-3}$), and the highest in the Graz region (0.25–0.48 $\mu g\,m^{-3}$). Salzburg area had intermediate values (0.15–0.22 $\mu g\,m^{-3}$) (Table 3). Higher maximum values were also observed in the region of Graz, and lower in the region of Vienna, consistent with regional statistics of biomass fuel use for space heating in Austrian countries (e.g. fuel wood for space heating is used in 16% of houses and apartments in Styria, 13% in Salzburg and below 3% in Vienna; from: ÖSTAT Statistical yearbook for the Republic of Austria, 1997).

Mannosan and galactosan annual averages (Table 3) were around a factor of 4–7 and 11–24 lower than the respective levoglucosan values. Levoglucosan/mannosan and levoglucosan/galactosan ratios might change between the seasons, due to different emission patterns of the three anhydrosugars from the different types of combustion occurring in different seasons. Thus, we investigated in more detail the seasonal variation of those compounds.

3.3. Levoglucosan, mannosan and galactosan seasonal variation

At all sites, levoglucosan had a pronounced annual cycle with elevated concentrations in the cold and low ones in the warm season (Fig. 1). Winter average concentrations were around 6–8 times higher than summer (June till August) ones in the three experimental regions. The winter/summer ratio in Vienna (6.1–8.2) was more pronounced at the urban-fringe sites, and less important at the heavy traffic-impacted site. In Salzburg (ratios in the range

Table 3
Levoglucosan, mannosan (M.) and galactosan (G.) concentrations ($\mu g\,m^{-3}$), levoglucosan/mannosan and levoglucosan/galactosan ratios.[a]

		Vienna				Graz			Salzburg		
		RIN	KEN	SCH	LOB	DB	GS	BB	RU	LE	AN
Levoglucosan	average	0.16	0.14	0.12	0.12	0.41	0.48	0.25	0.22	0.21	0.15
	winter	0.24	0.23	0.22	0.19	0.74	0.86	0.45	0.30	0.33	0.25
	spring	0.06	0.06	0.05	0.05	0.18	0.22	0.16	0.07	0.07	0.06
	summer	0.04	0.03	0.03	0.02	0.09	0.10	0.08	0.05	0.05	0.03
	autumn	0.30	0.24	0.20	0.24	0.68	0.82	0.36	0.40	0.48	0.27
	winter/summer	6.1	7.6	8.2	8.0	8.4	8.2	5.8	5.9	6.9	8.1
Mannosan	average	0.044	0.038	0.024	0.018	0.102	0.114	0.037	0.04	0.037	0.027
	cold season	0.067	0.066	0.043	0.034	0.160	0.212	0.068	0.065	0.069	0.047
Galactosan	average	0.010	0.012	0.007	0.005	0.037	0.033	0.014	0.011	0.012	0.007
	cold season	0.02	0.022	0.013	0.01	0.07	0.063	0.025	0.018	0.024	0.012
	Levo/Manno	4.1 (5.6)	4.2 (5.7)	5.2 (6)	6.4 (7.5)	4.8 (4.6)	5.0 (6.4)	6.4 (7.7)	5.6 (5.8)	5.4 (5.7)	5.7 (6)
	Levo/Galacto	16 (18)	11 (22)	19 (21)	22 (30)	13 (18)	16 (58)	18 (22)	20 (25)	20 (28)	24 (24)

BQL – below quantification limit.
Winter is January, February and December; spring is March till May; Summer is June till August and autumn is September till November. The same terminology is used for the following tables.
Cold season: months from January till March and October–December.
[a] weighed average ratio for the months January, February and December. Into brackets: January–May and September–December (September was omitted at Vienna sites and at BB).
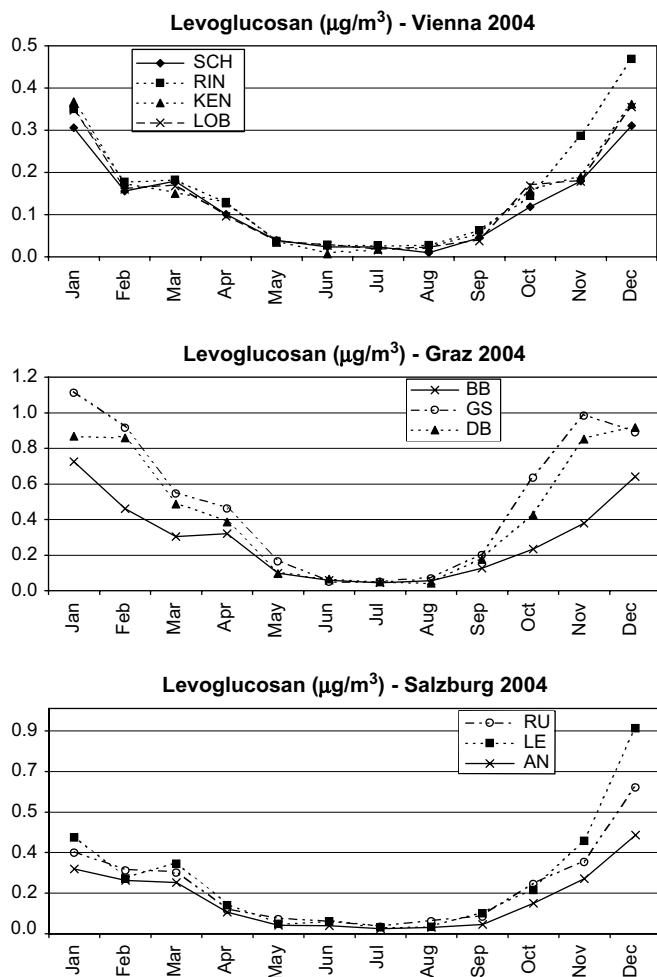
Fig. 1. Levoglucosan monthly averages for 2004 in Vienna, Graz and Salzburg.

Fig. 2. Mannosan monthly averages for 2004 in Vienna, Graz and Salzburg.

5.9–8.1) the same trend was observed, with a higher ratio at the rural site AN, an intermediate ratio at the urban site with residential characteristics LE and the lower ratio at RU, the site located nearby a traffic source. In the Graz region, winter/summer ratios were between 5.8 and 8.4, on the other hand, the difference was more accentuated at the city sites DB and GS (Table 3) and more moderate at the background site BB.

Both mannosan and galactosan had the same seasonal trend as levoglucosan. Mannosan concentrations were lower than levoglucosan ones (Figs. 2 and 3). Averages for the cold season (January–March and October–December) ranged from 35 to 68, 69 to 212 and 46 to 69 ng m^{-3} in the Vienna, Graz and Salzburg regions, respectively. Galactosan occurred in even lower levels, with cold season averages of 6–20 ng m^{-3} (Vienna), 24–70 ng m^{-3} (Graz) and 9–23 ng m^{-3} (Salzburg). The values found in Austria are comparable to those reported for Ghent by Zdráhal et al. (2002) and Pashynska et al. (2002). As for levoglucosan, concentration ranges were higher (about the double) in the Graz region. This is probably a consequence of the geophysical surroundings of the city, which are able to confer its atmosphere stagnant characteristics where the accumulation of particulate matter can be important. Though the seasonality is similar, at all sites except SCH and LOB the concentrations of mannosan and galactosan at the end of the year were clearly higher than at the beg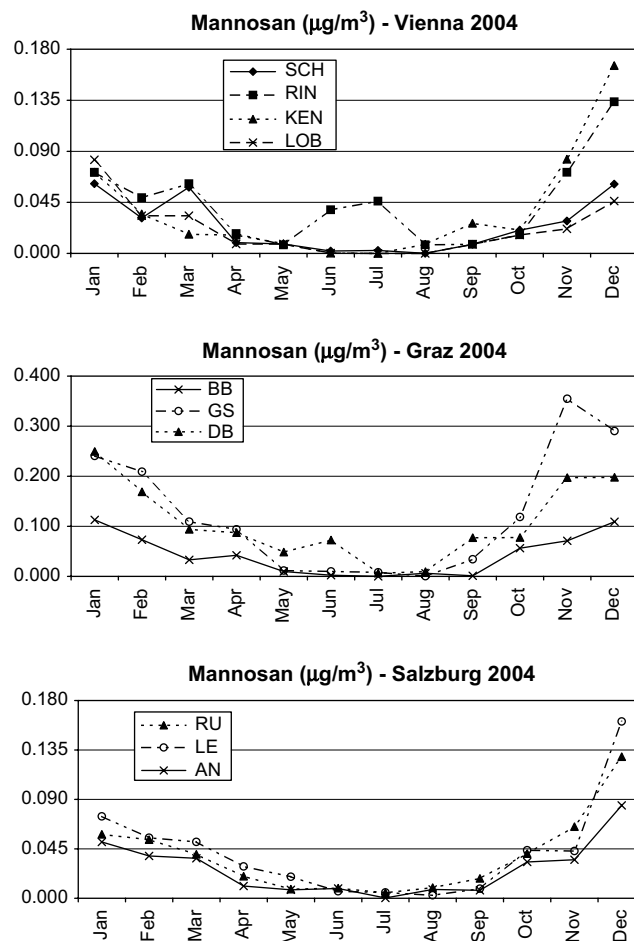inning. Indeed, the concentration in December is about the double of that in January. For levoglucosan, this feature was only observed for the city of Salzburg. Probably, a change in the types of wood burnt (e.g. for availability reasons), and not an increase in the quantity of wood burnt was the reason for such observations (Schmidl et al., 2008a).

The mannosan and galactosan concentrations from the warm season were frequently below the quantification limit. Therefore, those months were omitted in the following discussion.

3.4. Contribution of levoglucosan-C to OC

The average contribution of levoglucosan to the organic carbon (OC) load ranged between 1.3% (RIN and KEN) and 1.6% (SCH) in Vienna in 2004. Lower values were recorded in summer (less than half a percent on average) and higher values during the cold season (winter and autumn, around 2–3%). In the regions of Graz and Salzburg, the contributions were higher (1.7–2.8% in Graz, 1.6–2.7% in Salzburg). Seasonally, the contribution of levoglucosan to OC was also higher there: up to 5%, on average, in the cold season. Except for the region of Graz, where this trend is not as clear, it can be noted that the contribution of levoglucosan to OC is higher at the background sites, lower at the traffic-impacted sites and intermediate in the residential areas. This reveals the contribution of other sources to organic carbon at the urban sites and not a higher input from wood smoke at the background sites (see the wood smoke to PM load section).
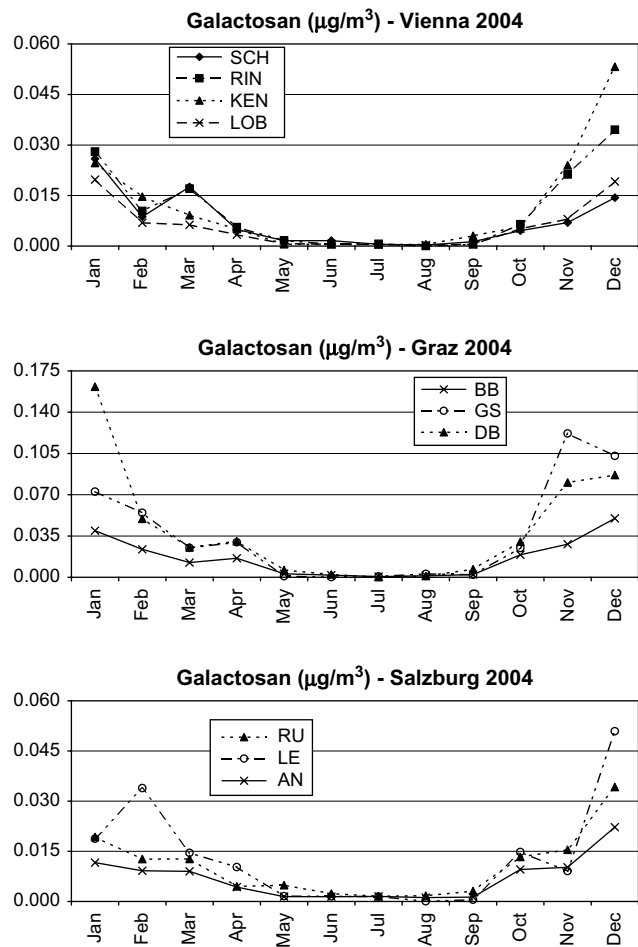
Galactosan (µg/m³) - Vienna 2004

Galactosan (µg/m³) - Graz 2004

Galactosan (µg/m³) - Salzburg 2004

Fig. 3. Galactosan monthly averages for 2004 in Vienna, Graz and Salzburg.

3.5. Contribution of wood smoke to OC, OM and PM

Using the factors derived by Schmidl et al. (2008a), it was possible to compute the relative contribution of wood smoke to the total OC, OM and PM load. The considered relationships were the following (levoglucosan and OC, OM and PM from wood smoke in mass per volume units):

$$\text{wood smoke OC} = \text{Levoglucosan} \times 6.1 \tag{1}$$

$$\text{wood smoke OM} = \text{Levoglucosan} \times 9.1 \tag{2}$$

$$\text{wood smoke PM} = \text{Levoglucosan} \times 10.7 \tag{3}$$

From the data presented in Schmidl et al., 2008a it can be derived, that for spruce as major representative of softwood, the conversion factor OC/levoglucosan (on a weight basis) is around 5, while for beech as a representative for hardwood it is around 12.

The value of 6.1 used in the submitted manuscript is for a 15% beech and 85% spruce mixture. Comparing with wood felling statistics in Austria (see Schmidl et al., 2008a) it can be seen that this value is a conservative one, because a lower contribution of hardwood than 15% is rather unlikely. A higher contribution of hardwood, however would shift our factor to far higher values. The highest assumed fraction of hardwood in small stoves (stoves with manual filling with logs) is 40%. This value is derived from a selling statistics of fuel wood from Austrian federal forests, which does not

include other sources. Based on analytical data from observed levoglucosan/mannosan ratios (shown later in the text) it appears that the fraction of softwood as source of the observed anhydrosugar levels is rather around 85% (for single events 75–95%). Thus we conclude, that the factor of 6.1 applied for a constant OC/levoglucosan ratio is correct due to the widespread use of spruce wood and derived products and the factor is conservative as it is derived for an observed estimate of softwood use, while selling statistics would demand for a factor 30% higher than 6.1.

From the uncertainty concerning the fuel mix and from the potential variation of the OC/levoglucosan ratio in different combustion conditions we derive, that the combined uncertainty will be not higher than −15% to +35%, due to the choice of the factor at the low side and a good knowledge about OC/levoglucosan ratios in fuel wood used in the regions studied.

The relationship to convert ambient OC into OM used was (Puxbaum et al., 2000, see discussion therein):

$$\text{OM}_{ambient} = \text{OC}_{ambient} \times 1.7 \tag{4}$$

Since this methodology is based on average values, it has some limitations. Indeed, in sites where the wood smoke impact is the strongest, it is possible that the average factors are not totally adequate and the calculated contribution to OC or OM may be beyond 100%. This was the case for one pool in LE and another one in GS. For statistical purposes, those values were set to 100%.

On a yearly average, wood smoke is a considerable source of organic carbon and organic matter in the ambient aerosol. About one fifth to one third of the annual OC and OM could be attributed to wood smoke (Table 4). In Vienna, wood smoke contributed 18–22% to the yearly OC and OM, with differences between sites being small, but with higher contributions at the urban-fringe sites. The differences between sites were not much more pronounced during the different seasons. In the other two regions, a gradient in the relative contribution of wood smoke can be observed: higher relative contributions occurred at the background sites (BB and AN) and lower at the traffic-impacted sites (DB and RU). The sites with densely populated residential characteristics (GS and LE) generally showed contributions close to those of the rural sites (GS and BB had similar figures). The relative contributions in Graz and Salzburg were higher than in Vienna: 19–38% of the annual particulate OC or OM load was found to originate in wood smoke (30–70% in winter). At all sites, maximum values ranged up to, or close to, 100%. For the residential and rural sites located in or around those two cities, wood smoke was an overwhelming contributor to OM (40–62% in the cold season), clearly higher than for the urban-fringe sites in Vienna, where the difference between sites, as well as the individual values, was not as high (Table 4). Still, though the annual averages and the contributions at the traffic-impacted sites are very similar, a difference between the Salzburg and Graz regions can be found for the residential and rural sites, with higher contributions in Salzburg. It is interesting that, in winter, background sites have the highest relative wood smoke-C to OC contributions, while for Salzburg and Graz, where the background sites are further away from the city borders, in autumn the residential sites within the cities show the higher relative wood smoke-C to OC contributions. This might be due to an increased use of supplementary wood stoves in addition to central heating.

On a yearly average basis, wood smoke contributed less to the PM load in Vienna (5.1–6.7%) than in the other cities (Graz: 8.9–13%; Salzburg: 7–12%) (Table 5). On absolute values, the concentration of wood smoke PM_{10} was the strongest in Graz (2.7–5.2 µg m⁻³), followed by Salzburg (1.7–2.3 µg m⁻³). The absolute values were the lowest in Vienna (1.3–1.7 µg m⁻³). Absolute contributions of wood smoke were higher in winter and autumn and the relative

Table 4
Contribution of levoglucosan and wood smoke to OC and OM.

		Vienna				Graz			Salzburg		
		RIN	KEN	SCH	LOB	DB	GS	BB	RU	LE	AN
Levo-C/OC (%)	average	1.3	1.3	1.6	1.5	1.7	2.8	2.7	1.6	2.4	2.7
	winter	2.3	2.3	2.7	2.9	2.8	3.0	4.4	2.5	4.5	5.1
	spring	1.1	1.3	1.7	1.5	1.6	2.6	3.2	1.2	1.9	2.4
	summer	0.4	0.2	0.4	0.4	0.6	1.1	1.0	0.5	0.7	0.7
	autumn	1.5	1.3	1.7	1.7	2.0	3.8	2.6	2.0	3.4	2.8
	winter/summer	6.0	10.7	6.6	6.9	4.8	2.9	4.6	4.8	6.3	7.2
WS-OC/OC (%)	average	18.0	17.7	22.1	20.9	23.4	37.7[a]	35.1	22.2	31.9	37.5
	winter	31.3	32.2	36.8	39.5	38.4	41.7	58.9	34.4	57.9	70.2
	spring	15.3	17.4	23.6	19.8	22.1	36.1	43.0	16.1	26.3	33.6
	summer	5.3	3.0	5.6	5.7	8.1	14.6[a]	13.1	7.1	9.7	9.77
	autumn	20.5	18.3	23.0	22.7	27.7	51.3	36.0	28.0	46.9	38.4
	winter/summer	6.0	10.7	6.6	6.9	4.8	2.9[a]	4.5	4.8	6.0	7.2
WS-OM/OM (%)	average	15.8	15.5	19.4	18.3	20.6	33.5	32.3	19.5	28.25	32.98
	winter	27.4	28.3	32.3	34.7	33.7	36.6	53.0	30.2	51.93	61.84
	spring	13.4	15.3	20.7	17.4	19.4	31.8	39.1	14.1	23.06	29.44
	summer	4.6	2.6	4.9	5.0	7.1	12.8	11.5	6.3	8.51	8.58
	autumn	18.0	16.0	20.2	19.9	24.5	45.9	31.9	24.5	41.16	33.73
	winter/summer	6.0	10.7	6.6	6.9	4.8	2.9	4.6	4.8	6.34	7.21

values above 100% were set to 100%.
[a] GS – no OC data for June.

contribution was on average 4.2 times stronger in winter than in summer (Table 5 and Fig. 4). In Vienna, the winter/summer difference in the relative contribution of wood smoke to the total PM load was slightly higher in the residential sites than in the traffic-impacted ones, in Salzburg it was clearly stronger and in Graz the ratios were fairly similar. The cold season relative contribution in Viennese residential sites (about 10%) was higher than in the traffic-impacted ones (about 8%). This tendency was also seen in the other cities, where the relative contribution of wood smoke at background and residential areas was stronger than at traffic-impacted sites: LE and AN: around 19%, DB: 14%; GS and BB: around 20%, RU: 11%.

Table 6 reports the concentration of wood smoke and PM_{10} during exceedance periods and non-exceedance periods for the cold season (January–March and October–December). It can be seen that the increase in the concentrations is always higher for PM_{10} than for wood smoke, except for DB, where the increase is equal. Thus, the relative contribution of wood smoke to PM_{10} increases, at most, as much as the total PM_{10}. This is an indication that other sources, or meteorological effects, such as accumulation, are responsible for the exceedance episodes. Secondary organic aerosol seems to be less important according to a study performed in a southern Alpine valley (Lanz et al., 2008).

3.6. Mannosan, galactosan and the differentiation between the soft and hardwood combustion contributions

At all sites, the correlation between the three anhydrosugars was high: all were above 0.8 and only 6 out of 30 below 0.9. Both mannosan and galactosan followed the same trend shown by levoglucosan, with lower concentrations at the background sites.

The average levoglucosan/mannosan ratios did not vary much when considering the period when wood burning is at its highest (January–February–December) or January–May/September(October)–December (Table 3).

The levoglucosan/mannosan ratio (weighed average) for the period January, February and December (winter, Table 3) was between 4.1 and 6.4. Following the findings by Schmidl et al. (2008a), this indicates that the use of biofuel is dominated by softwoods. In Austria, the main softwood sold for residential heating is spruce. In Vienna and in Graz, the ratio was slightly higher at the background sites, in Salzburg, the difference was very small (Table 3). This lower ratio at the city-centre sites might indicate the use of different biofuels. Indeed, briquettes from softwood have a levoglucosan/mannosan ratio of about 2.5 (Schmidl et al., 2008a), lower than for spruce logs of around 3.6. Due to availability reasons, it is possible that the share of hardwood in the

Table 5
Contribution of wood smoke (WS) to PM_{10} (%) and ambient wood smoke concentrations ($\mu g\,m^{-3}$).

		Vienna				Graz			Salzburg		
		RIN	KEN	SCH	LOB	DB	GS	BB	RU	LE	AN
WS/PM (%)	average	5.1	5.4	6.7	6.2	8.9	13	13	7	10	12
	winter	6.7	8.0	10.3	9.3	12.4	17.2	19.3	9.5	16.8	19.9
	spring	2.8	2.9	4.2	3.7	5.7	9.3	11.1	3.4	5.5	5.3
	summer	1.9	1.9	2.3	2.0	3.7	5.6	6.3	2.3	3.6	3.0
	autumn	8.8	8.6	10.1	10.6	15.0	23.4	19.0	11.6	20.8	17.9
	winter/summer	3.5	4.3	4.6	4.7	3.4	3.1	3.1	4.1	4.7	6.6
WS $\mu g\,m^{-3}$	average	1.7	1.5	1.3	1.3	4.4	5.2	2.7	2.3	2.2	1.7
	winter	2.5	2.5	2.3	2.1	7.9	9.2	4.8	3.2	3.5	2.7
	spring	0.7	0.6	0.6	0.6	1.9	2.4	1.7	0.8	0.8	0.6
	summer	0.4	0.3	0.3	0.3	0.9	1.1	0.8	0.6	0.5	0.3
	autumn	3.2	2.5	2.1	2.5	7.3	8.7	3.9	4.3	5.7	2.9
	winter/summer	6.1	7.6	8.2	8.0	8.4	8.2	5.8	5.9	6.5	8.1

Contribution of Wood Smoke to PM10 (%)
Vienna

Contribution of Wood Smoke to PM10 (%) Graz

Contribution of Wood Smoke to PM10 (%)
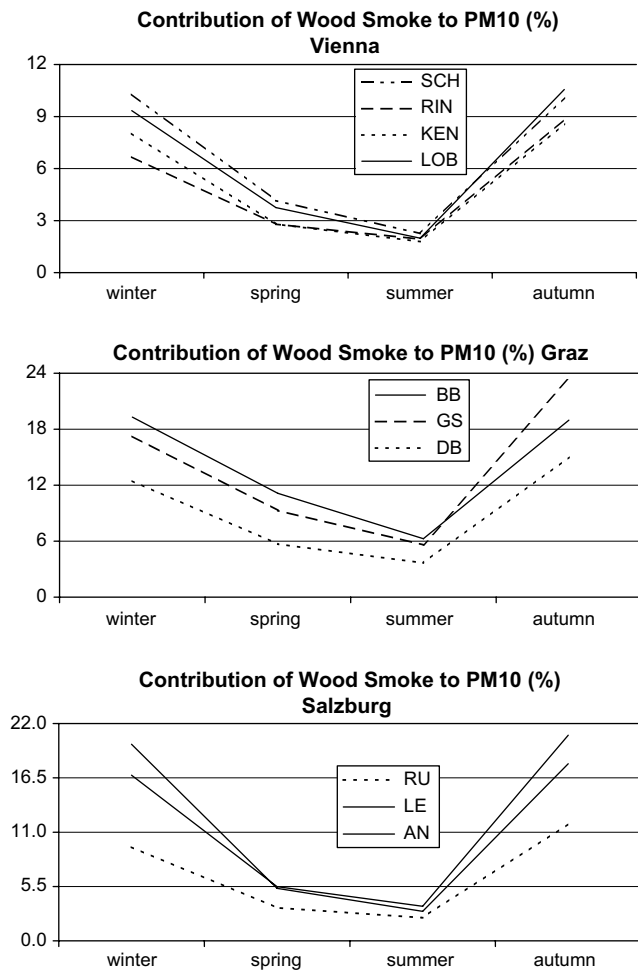**Salzburg**

Fig. 4. Contribution of wood smoke to PM_{10} in Vienna, Graz and Salzburg.

biofuels mix might be higher at the background sites than at the city sites.

Schmidl et al. (2008a) proposed the following equation to calculate the contribution of softwood burning to PM_{10} (in Austria,

softwood burned for residential heating is mainly spruce) using the levoglucosan/mannosan ratio:

$$\%\text{spruce} = \left(14.8 - R_{\text{levo/manno}}\right)/0.112 \qquad (5)$$

Using the ratio levoglucosan/mannosan for the months January, February and December given in Table 3 and equation (5), the spruce contribution in the biofuel mix burned was estimated to be in the range 75–95% at the three regions. According to the Austrian selling statistics burning wood sold in Austria consisted 59% of soft and 41% of hardwoods. The discrepancy may arise from the fact, that equation (5) was obtained for combustion in a ceramic stove, which is widely used in Austria but not the sole source of biomass emissions, and from a potential distortion of the statistics not accounting for private wood sources from forests and gardens. Thus, we think that softwood will be the major wood type used in Austria, with a contribution between the numbers obtained from the two evaluations (e.g. 60–85% in the mix). Further combustion tests with different types of stoves and wood types typical for Europe will be required, to evaluate with better accuracy the soft/hardwood contributions.

Galactosan concentrations happened to be low in relation to levoglucosan. The levoglucosan/galactosan winter average ratios ranged between 11–22, 13–18 and 20–24 in Vienna, Graz and Salzburg, respectively (Table 3). The same spatial trend is found as for the levoglucosan/mannosan ratios, with higher ratios at the background sites. As for the levoglucosan/mannosan ratio, it is not possible to observe a seasonal trend since many sample pools in summer had mannosan or galactosan levels below the quantification limit.

3.7. Comparison of levoglucosan and potassium

In the scope of the AQUELLA projects, other compounds commonly used for wood burning tracers have also been measured. One of them was potassium.

Potassium concentrations are reported in Table 7. Average concentrations ranged from 0.20 to 0.57 $\mu g\,m^{-3}$ and were clearly higher in Graz than in Salzburg or Vienna, as for levoglucosan and the other anhydrosugars. Despite the fact that potassium in particulate matter also has other sources than biomass burning (e.g. Schauer et al., 1999), its correlation to levoglucosan was high at all sites, with a range of $r = 0.7–0.9$ as determined from the pools' individual data (Fig. 5).

The average ratio of K/levoglucosan was 0.8–2.1 at the different sites for the whole year's pools. The ratio was in the

Table 6
PM_{10} and wood smoke (WS) concentrations ($\mu g\,m^{-3}$) for exceedance and non-exceedance periods during the cold season.

		Exceedance	Non-exceedance	Exceedance/non-exceedance
RIN	PM_{10}	65.0	29.8	2.2
	WS	4.5	2.1	2.1
KEN	PM_{10}	66.6	27.6	2.4
	WS	4.1	2.1	1.9
SCH	PM_{10}	60.9	22.8	2.7
	WS	4.6	2.0	2.3
LOB	PM_{10}	56.4	20.8	2.7
	WS	5.5	2.1	2.6
DB	PM_{10}	77.4	33.8	2.3
	WS	10.1	4.4	2.3
GS	PM_{10}	76.4	29.8	2.6
	WS	12.4	6.1	2.0
BB	PM_{10}	58.0	18.9	3.1
	WS	7.1	4.1	1.7
RU	PM_{10}	64.3	33.0	1.9
	WS	5.4	3.3	1.6
LE	PM_{10}	61.1	17.7	3.4
	WS	8.3	3.7	2.2
AN	PM_{10}	61.6	18.5	3.3
	WS	3.7	2.8	1.3

Table 7
Potassium concentrations (yearly averages, minima and maxima) and Potassium/levoglucosan ratios in the warm and cold seasons.

	K (year, $\mu g\,m^{-3}$)			K/Levo (warm)			K/Levo (cold)		
	min	avg	max	avg	stdev	correl	avg	stdev	correl
RIN	0.03	0.31	1.27	2.22	1.06	0.90	0.94	0.48	0.79
KEN	0.04	0.29	1.14	4.46	3.35	0.72	1.11	0.55	0.69
SCH	0.03	0.26	0.85	2.72	2.39	0.86	1.06	0.48	0.86
LOB	0.03	0.25	1.26	2.63	1.31	0.88	1.07	0.43	0.81
DB	0.08	0.51	2.79	1.81	1.38	0.99	0.69	0.32	0.78
GS	0.11	0.57	2.54	1.78	0.96	0.98	0.59	0.17	0.82
BB	0.05	0.37	1.20	2.50	3.70	0.80	0.78	0.31	0.85
RU	0.07	0.28	1.29	1.97	0.89	0.31	0.92	0.45	0.77
LE	0.07	0.30	1.24	2.56	1.68	0.70	0.87	0.43	0.76
AN	0.06	0.20	0.96	2.92	1.26	0.80	0.88	0.35	0.88
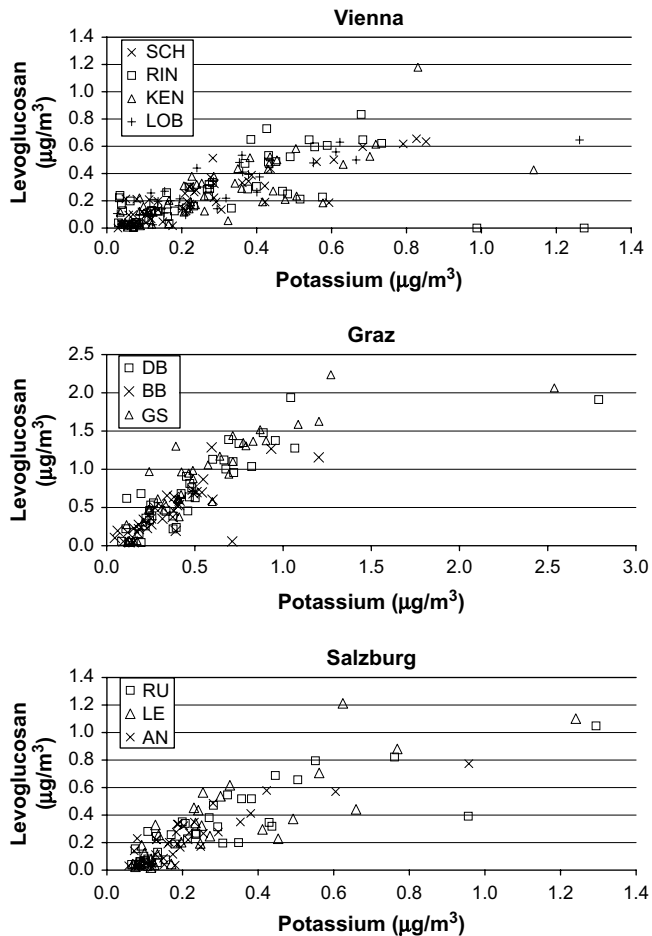
Fig. 5. Correlation between potassium and levoglucosan for 2004 in Vienna, Graz and Salzburg.

Table 8
Potassium/levoglucosan ratios from the recent literature.

		K/Levo	Reference
Wood stove – Austria	Hardwood	0.031–0.05	Schmidl
	Softwood	0.005–0.019	et al., 2008
Fireplace – NE US	Hardwood	0.068–0.103	Fine et al., 2001
	Softwood	0.114–0.171	
Fireplace – S US	Hardwood	0.017–0.230	Fine et al., 2002
	Softwood	0.119–0.138	
Fireplace – Midwest and W US	Hardwood	0.036–0.122	Fine et al., 2004b
	Softwood	0.014–0.192	
Wood stove – prevalent woods US	Hardwood	0.094–0.254	Fine et al., 2004c
	Softwood	0.026–0.038	
Fireplace – US	Pine	0.019	Schauer
	Oak	0.047	et al., 2001
	Eucalyptus	0.035	
Wood stove – US	Western hemlock	0.2	Hays et al., 2002
	various	0.02–0.04	
Asian biomass (wood stove)	Coconut leaves	1.09	Sheesley
	Rice straw	1.4	et al., 2003
	Cow dung	1.05	
	Biomass briquettes	0.14	
	Jackfruit branches	0.26	
Agricultural fires	Wheat straw	7.4	Hays et al., 2005
	Rice straw	0.084	
Biomass burning impacted ambient air, Amazonia	Pasture site	0.33	Graham
	Forest site	0.34	et al., 2002
Northern America, summer (wildfires period)	High-smoke	0.045–0.225	Ward et al., 2006
	Post-smoke	0.99–2.6	
Savannah fires	Directly over fire	0.93	Gao et al., 2003
	background	1.03	
Portugal, summer, $PM_{2.5}$, forest fires	Very intense fire period	3.6	Pio et al., 2008
	Baseline period	1.8	
	Fire input	8.7	
New Zealand, winter, PM_{10}	Ambient air	∼3	Wang et al., 2006

range 2–4.5 in the warm season and 0.6–1.1 in the winter season. The seasonal difference of the K/levoglucosan ratio reflects lower wood smoke emissions and the presence of potential other K sources, such as primary biogenic emissions and possibly meat grilling.

Schmidl et al. (2008a) found K/levoglucosan ratios of 0.005 and 0.05 for the major Austrian wood types beech and spruce, respectively, when burnt in a small ceramic stove ("tiled stove"). In US studies burning north American wood types in fireplaces (e.g. Fine et al., 2001, 2002) K/levoglucosan ratios were in the range of 0.017–0.23. Despite those low K/levoglucosan values from source (fireplaces, stoves, …) studies, authors have reported higher ratios from smoke-impacted or non smoke-impacted ambient aerosol (see Table 8), closer to what was found in this study. This means that a source of potassium is lacking. Recent studies have shown, however, that larger combustion units with higher combustion temperatures, as well as modern stoves and boilers operate a more complete combustion. The particulate emissions of those appliances consist predominantly of inorganic material (K-salts) and contain little OC (Valmari et al., 1998; Johansson et al., 2003; Schmidl et al., 2008b). Thus, the wintry K/levoglucosan ratio might originate mainly from the different types of wood combustion for space and water heating, with a currently unknown but assumedly weak influence from cooking and related activities. Also, some earth crust influence on the PM_{10} potassium load is possible.

4. Conclusions

- Levoglucosan yearly averages ranged from 0.12 to 0.48 $\mu g\,m^{-3}$. The sites in Graz showed higher concentrations compared to the other regions, while background sites, in general, evidenced slightly lower concentrations than urban sites.
- Levoglucosan showed a pronounced seasonal cycle. Concentrations were 6–8 times higher during the colder months.
- Annual averaged levoglucosan-C contributions to OC were lower in Vienna (1.3–1.6%) and higher in Graz and Salzburg (1.6–2.8%). There was a strong seasonality of the contribution of levoglucosan to OC with ratios between winter and summer in the range of around 3–11.
- The yearly average contributions of wood smoke to OC, OM and PM were in the ranges 18–38%, 16–34% and 5.1–13%, respectively. Values in the larger city, Vienna, were lower than in the regions of Graz and Salzburg. Contributions were generally lower at sites located closer to the denser populated city-centre. Cold season (winter and autumn) average contributions to OM were very high: 24–30%, 30–44% and 28–52% in Vienna, Graz and Salzburg, respectively. Thus making wood smoke the main contributor to the organic aerosol in the cold season and a major contributor to PM. For the residential and rural sites, the contribution of wood smoke to OM was overwhelming (close to or above 50% in the less populated cities). The

difference between the city-fringe sites and the city-centre sites in Vienna was not as marked as in the other two regions.

- From the uncertainty concerning the fuel mix and from the potential variation of the OC/levoglucosan ratio in different combustion conditions we derive, that the combined uncertainty for the wood smoke source contribution to OC will be not higher than −15% to +35%, due to the choice of the factor at the low side and a good knowledge about OC/levoglucosan ratios in fuel wood used in the regions studied.
- The relative contribution of wood burning to PM_{10}, in the cold season, does not increase during PM_{10} exceedance episodes. This is an indication that other sources, or meteorological factors (such as accumulation of particulate matter in a given area), are responsible for the occurrence exceedances.
- Mannosan and galactosan had a similar seasonal cycle as levoglucosan, and the correlation between the compounds were quite high. Their concentrations, however, were much lower than for levoglucosan.
- The ratios between levoglucosan and mannosan and between levoglucosan and galactosan showed a range of 4.1–6.4 and 11–22, respectively, in the periods where biomass burning is expected to be a strong source.
- The "best estimate" for the contribution of softwood in the mix of burned wood ranged between 60 and 85% for the three regions.
- Levoglucosan and potassium, another tracer for biomass burning, were well correlated at all sites. The ratios between those two species were rather below 1 in the cold season and around 3 in the warm season.

Acknowledgements

References

Bond, T.C., Streets, D.G., Yarber, K.F., Nelson, S.M., Woo, J.-H., Klimont, Z., 2004. A technology based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research 109 (D14203). doi:10.1029/2003JD003697.

Cachier, H., Bremond, M.-P., Buat-Ménard, P., 1989. Determination of atmospheric soot carbon with a simple thermal method. Tellus 41B, 379–390.

Caseiro, A., Marr, I.L., Claeys, M., Kasper-Giebl, A., Puxbaum, H., Pio, C.A., 2007. Determination of saccharides in atmospheric aerosol using anion-exchange high-performance liquid chromatography and pulsed-amperometric detection. Journal of Chromatography A 1171, 37–45.

Chapman, R.S., Watkinson, W.P., Dreher, K.L., Costa, D.L., 1997. Ambient particulate matter and respiratory and cardiovascular illness in adults: particle-borne transition metals and the heart–lung axis. Environmental Toxicology and Pharmacology 4 (3–4), 331–338.

Englert, N., 2004. Fine particles and human health a review of epidemiological studies. Toxicology Letters 149, 235–242.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the northeastern United States. Environmental Science and Technology 35, 2665–2675.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2002. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States. Environmental Science and Technology 36, 1442–1451.

Fine, P.M., Chakrabati, B., Krudysz, M., Schauer, J.J., Sioutas, C., 2004a. Diurnal variations of individual organic compound constituents of ultrafine and accumulations mode particulate matter in the Los Angeles basin. Environmental Science and Technology 38, 1296–1304.

Fine, P., Cass, G., Simoneit, B., 2004b. Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. Environmental Engineering Science 21, 387–409.

Fine, P., Cass, G., Simoneit, B., 2004c. Chemical characterization of fine particle emissions from the wood stove combustion of prevalent United States wood species. Environmental Engineering Science 21, 705–721.

Fraser, M.P., Lakshmanan, K., 2000. Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. Environmental Science and Technology 34, 4560–4564.

Freeman, D.J., Cattell, F.C.R., 1990. Wood burning as a source of atmospheric polycyclic aromatic hydrocarbons. Environmental Science and Technology 24, 1581–1585.

Gao, S., Hegg, D.A., Hobbs, P.V., Kirchstetter, T.W., Magi, B.I., Sadilek, M., 2003. Water-soluble organic components in aerosols associated with savanna fires in southern Africa: identification, evolution and distribution. SAF. Journal of Geophysical Research – Atmosphere 108 (D13), 27-1–27-16.

Graham, B., Mayol-Bracero, O.L., Guyon, P., Roberts, G.C., Decesari, S., Facchini, M.C., Artaxo, P., Maenhaut, W., Koll, P., Andreae, M.O., 2002. Water-soluble organic compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and GC-MS. Journal of Geophysical Research 107. doi:10.1029/2001JD000336.

Graham, B., Falkovitch, A.H., Rudich, Y., Maenhaut, W., Guyon, P., Andreae, M.O., 2004. Local and regional contributions to the atmospheric aerosol over Tel Aviv, Israel: a case study using elemental, ionic and organic tracers. Atmospheric Environment 38, 1593–1604.

Hays, M.D., Geron, C.D., Linna, K.J., Smith, D., Schauer, J.J., 2002. Speciation of gas-phase and fine particle emissions from burning of foliar fuels. Environmental Science and Technology 36, 2281–2295.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. Atmospheric Environment 39, 6747–6764.

Intergovernmental Panel on Climate Change Working Group 1, 2007. Fourth Assessment Report – Climate Change 2007: The Scientific Basis. Technical report, Intergovernmental Panel on Climate Change. Cambridge University Press, UK. Available from: http://ipcc-wg1.ucar.edu/wg1/wg1-report.html.

Johansson, L.S., Tullin, C., Leckner, B., Sjövall, P., 2003. Particle emissions from biomass combustion in small combustors. Biomass and Bioenergy 25, 435–446.

Khalil, M.A.K., Rasmussen, R.A., 2003. Tracers of wood smoke. Atmospheric Environment 37, 1211–1222.

Lanz, V.A., Alfarra, M.R., Baltensperger, U., Buchmann, B., Hueglin, C., Szidat, S., Wehrli, M.N., Wacker, L., Weimer, S., Caseiro, A., Puxbaum, H., Prevot, A.S., 2008. Source attribution of submicron organic aerosols during wintertime inversions by advanced factor analysis of aerosol mass spectra. Environmental Science and Technology 42, 214–220.

Leithead, A., Li, S.-M., Hoff, R., Cheng, Y., Brook, J., 2006. Levoglucosan and dehydroabietic acid: evidence of biomass burning impact on aerosols in the lower Fraser valley. Atmospheric Environment 40, 2721–2734.

Moreira dos Santos, C.Y., Almeida Azevedo, D., Radler Alquino de Neto, F., 2002. Selected organic compounds from biomass burning found in the atmospheric particulate matter over sugarcane plantation areas. Atmospheric Environment 36, 3009–3019.

Moreira dos Santos, C.Y., Almeida Azevedo, D., Radler Alquino de Neto, F., 2004. Atmospheric distribution of organic compounds from urban areas near a coal-fired power station. Atmospheric Environment 38, 1247–1257.

Otto, A., Gondokusumo, R., Simpson, M.J., 2006. Characterization and quantification of biomarkers from biomass burning at a recent wildfire site in Northern Alberta, Canada. Applied Geochemistry 21, 166–183.

Pashynska, V., Vermeylen, R., Vas, G., Maenhaut, W., Claeys, M., 2002. Development of a gas chromatographic/ion trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols. Journal of Mass Spectrometry 37, 1249–1257.

Peden, D.B., 2005. The epidemiology and genetics of asthma risk associated with air pollution. Journal of Allergy and Clinical Immunology 115 (2), 213–219.

Pio, C.A., Legrand, M., Alves, C.A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H., Sanchez-Ochoa, A., Gelencsér, A., 2008. Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period. Atmospheric Environment 42, 7530–7543.

Puxbaum, H., 1979. Thermo-Gasanalysator zur Charakterisierung von Kohlenstoff und Schwefelverbindungen in luftgetragenen Stäuben. Fresenius Zeitschrift für Analytische Chemie 298, 250–259.

Puxbaum, H., Rendl, J., Allabashi, R., Otter, L., Scholes, M.C., 2000. Mass balance of atmospheric aerosol in a South-African subtropical savanna (Nylsvley, May 1997). Journal of Geophysical Research 105, 20697–20706.

Puxbaum, H., Caseiro, A., Sanchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencser, A., Legrand, M., Preunkert, S., Pio, C., 2007. Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. Journal of Geophysical Research 112. doi:10.1029/2006JD008114.

Ramdahl, T., Schjoldager, J., Currie, L.A., Hanssen, J.E., Müller, M., Klouda, G.A., Alfheim, I., 1984. Ambient impact of residential wood combustion in Elverum, Norway. The Science of The Total Environment 38, 81–90.

Reisinger, P., Wonaschütz, A., Hitzenberger, R., Petzold, A., Bauer, H., Jankowski, N., Puxbaum, H., Chi, X., Maenhaut, W., 2008. Intercomparison of measurement techniques for black or elemental carbon under urban background conditions in

wintertime: influence of biomass combustion. Environmental Science and Technology 42, 884–889. doi:10.1021/es0715041.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environmental Science and Technology 27, 636–651.

Sandradewi, J., Prevot, A.S.H., Szidat, S., Perron, N., Alfarra, M.R., Lanz, V.A., Weingartner, E., Baltensperger, U., 2008. Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter. Environmental Science and Technology 42, 3316–3323.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmospheric Environment 30, 3837–3855.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emission from air pollution sources. 1. C1 through C29 organic compounds from meat charboiling. Environmental Science and Tecnology 33, 1566–1577.

Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. Environmental Science and Technology 34, 1821–1832.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emission from air pollution sources. 3. C1–C29 organic compounds from fireplace combustion of wood. Environmental Science and Tecnology 35, 1716–1728.

Schmid, H., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauck, T., Even, A., ten Brink, H.M., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., Puxbaum, H., 2001. Results of the "Carbon Conference" international aerosol carbon round robin, test stage I. Atmospheric Environment 35, 2111–2121.

Schmidl, C., Marr, I.L., Caseiro, A.e, Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008a. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmospheric Environment 42, 126–141.

Schmidl, Christoph, Bauer, Heidi, Puxbaum, Hans, 2008b. Chemical characterization of wood smoke particle emissions and its application to source apportionment. International conference on carbonaceous particles in atmosphere, August 12–14, Berkeley, USA.

Sexton, K., Liu, K.-S., Hayward, S.B., Spengler, J.D., 1985. Characterization and source apportionment of wintertime aerosol in a wood-burning community. Atmospheric Environment 19, 1225–1236.

Shafizadeh, F., 1968. Pyrolysis and combustion of cellulosic materials. Advances in Carbohydrate Chemistry 23, 419–474.

Shafizadeh, F., 1984. The chemistry of pyrolysis and combustion (489—529). In: Rowell, Roger M. (Ed.), The Chemistry of Solid Wood. The American Chemical Society, Washington D.C., U.S.A., ISBN 0-8412-0796-8.

Sheesley, R.J., Schauer, J.J., Chowdhury, Z., Cass, G.R., Simoneit, B.R.T., 2003. Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. Journal of Geophysical Research 108, 4285.

Sheffield, A.E., Gordon, G.E., Currie, L.A., Riederer, G.E., 1994. Organic, elemental, and isotopic tracers of air pollution sources in Albuquerque, NM. Atmospheric Environment 28, 1371–1384.

Simoneit, B.R.T., 2002. Biomass burning: a review of organic tracers for smoke from incomplete combustion. Applied Geochemistry 17, 129–162.

Stohl, A., Berg, T., Burkhart, J.F., Fjáraa, A.M., Forster, C., Herber, A., Hov, Ø., Lunder, C., McMillan, W.W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J., Tørseth, K., Treffeisen, R., Virkkunen, K., Yttri, K.E., 2007. Arctic smoke – record high air pollution levels in the European Arctic due to agricultural fires in eastern Europe in spring 2006. Atmospheric Chemistry and Physics 7, 511–534.

Szidat, S., Prévôt, A.S.H., Sandradewi, J., Alfarra, M.R., Synal, H.-.A., Wacker, L., Baltensperger, U., 2007. Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. Geophysical Research Letters 34, L05820.

Valmari, T., Kauppinen, E.I., Kurkela, J., Jokiniemi, J.K., Sfiris, G., Revitzer, H., 1998. Fly ash formation and deposition during fluidized bed combustion of willow. Journal of Aerosol Science 29, 445–459.

Wang, H., Kawamura, K., Shooter, D., 2006. Wintertime organic aerosols in Christchurch and Auckland, New Zealand: contributions of residential wood and coal burning and petroleum utilization. Environmental Science and Technology 40, 5257–5262.

Ward, T.J., Hamilton Jr., R.F., Dixon, R.W., Paulsen, M., Simpson, C.D., 2006. Characterization and evaluation of smoke tracers in PM: results from the 2003 Montana wildfire season. Atmospheric Environment 40, 7005–7017.

Wolff, G.T., Countess, R.J., Groblicky, P.J., Ferman, M.A., Cadle, S.H., Muhlbaier, J.L., 1981. Visibility-reducing species in the Denver «brouwn-cloud»-II. Sources and temporal patterns. Atmospheric Environment 15, 2485–2502.

Zdráhal, Z., Oliveira, J., Vermeylen, R., Claeys, Magda, Maenhaut, Willy, 2002. Improved method for quantifying levoglucosan and related monosaccharide anhydrides in atmospheric aerosols and application to samples from urban and tropical locations. Environmental Science and Technology 36, 747–753.

Zheng, M., Cass, G.R., Schauer, J.J., Edgerton, E.S., 2002. Source apportionment in the southeastern United States using solvent-extractable organic compounds as tracers. Environmental Science and Technology 36, 2361–2371.