



Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions

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Abstract

Woodsmoke samples derived from the combustion of beech, oak, spruce, larch and softwood briquettes in a closed stove have been collected and analysed so as to derive chemical profiles for ambient particulate matter (PM) source apportionment studies, for example, by CMB modelling. Trace metals, soluble ions, carbon species total carbon (TC), elemental carbon (EC) and organic carbon (OC), anhydrosugars, polar and non-polar trace organics, cellulose and humic-like substances (HULIS) have been measured. The inorganic and most organic components were not significantly different for the different woods, so that one profile could be derived for CMB modelling. The anhydrosugar levoglucosan was present in high concentrations, 4–15% w/w, and for the mix of woods important for Austria, one conversion factor can be used to derive the mass of woodsmoke from the levoglucosan concentration in ambient air. Mannosan is also a major component, 0.3–4% w/w, which, taken together with the levoglucosan content, permits estimates to be made of the proportion of hard- and softwood smoke to ambient PM.

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1. Introduction

Wood smoke is increasingly being seen as an important component of airborne particulate matter (PM), especially as the new short time standard

for PM₁₀—particles in ambient air, of 50 µg m^{−3}, set by the European Union (EU-Directive 1999/30/EG) is frequently violated in most urban regions in Europe. Finding effective measures to reduce these concentration levels requires detailed knowledge about the magnitudes of individual source contributions. Therefore the AQUELLA project was launched in Austria using a chemical mass balance (CMB)–receptor model as source apportionment technique (Watson, 1984; Schauer et al., 1996;

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Schauer and Cass, 2000). This model computes the best-fit linear combination of the chemical species profiles of primary particle emission sources, selected for a certain geographical area, that is needed to match the chemical composition of the ambient fine particle samples. Industrial and commercial production processes, combustion, traffic and agriculture can be mentioned as major primary sources of airborne fine PM.

This study focuses on domestic wood combustion which is thought to be a major source of particulate emissions in Europe north of the Alps. The aim was to characterise the emissions making up wood smoke in Austria and other mid-European Alpine regions, and to obtain a detailed chemical profile of the fine particles (PM₁₀) emitted from this source.

It may be argued that it would be easier and more straight forward to adopt profiles already published in the literature instead of launching a new research programme, especially since quite a big effort has been made on this issue in the United States (McDonald et al., 2000; Fine et al., 2001, 2002, 2004a, b) and in Scandinavia (Johansson et al., 2003; Hedberg et al., 2002). However, there are several reasons why it was necessary to make our own measurements in Austria.

Previous work (McDonald et al., 2000) has suggested that factors like the species of wood and the type of stove used can have a big influence on the particle emissions. More recently, Jordan and Seen (2005) have shown clearly that the type of stove is a more important variable than the air flow setting for a given stove. It was therefore necessary to establish smoke profiles for the wood types commonly used as fuel in Austria, and to do this using a wood-burning stove typical of those found in houses in the country in Austria.

Another problem which arises when profiles for wood smoke in the literature are compared is that they have been reported for different particle size fractions: while in the United States PM_{2.5} is the standard size fraction for aerosols, in Europe legislative limits are set for the PM₁₀ fraction.

A further difficulty concerns the presentation of the findings: some studies have focused on finding emission factors giving the mass of each component in the smoke per mass of wood burned without including the total mass of smoke solids (Oros and Simoneit, 2001), which is not helpful for CMB modelling. Further, a number of published profiles cannot be used for CMB modelling because they are based on one single burning test for each wood type.

Calculating a generalised chemical profile for wood smoke from such single-test results leads to big uncertainties, especially considering the high variability of particle emissions from wood combustion. Some reports focus on the VOCs in the emissions, rather than on the analysis of the particulate material (Olsson et al., 2003).

Last but not the least it is essential for CMB modelling that source profiles include the same components that are also determined in ambient aerosol samples. So, for use in Austrian source apportionment the analysed tracer set for the development of a wood smoke profile has to be the same as for the ambient samples in the AQUELLA project. This tracer set includes some species that were not common in earlier aerosol analysis and that were therefore missing in the earlier profiles. Examples for such components are glucose and cellulose, humic like substances (HULIS) and anhydrosugars like levoglucosan, mannosan and galactosan.

As an alternative to CMB modelling a macro-tracer model has been developed within the AQUELLA project which uses, for source apportionment, a numerical factor for each characteristic compound, in each of the source materials being considered, to estimate the contributions of individual sources to a given ambient particulate sample. Ideally, these are compounds that are known to be emitted by only one source. Levoglucosan has previously been recommended as a single tracer for the PM₁₀ source wood combustion (Simoneit et al., 1999). This anhydrosugar, which is formed during pyrolysis of cellulose (Shafizadeh, 1968), is emitted in large amounts during the burning of biomass and constitutes the most important organic species found in wood smoke particles. In addition, as it is a reasonably stable molecule and is specific to the burning of substances containing cellulose (Simoneit et al., 2004; Jordan et al., 2006), it therefore fulfils the important requirements for single tracers to be used for source apportionment.

Hence the objectives of this work were to establish chemical profiles for the emissions from combustion of wood types typical for Austria, with associated uncertainties, so as to be useful in CMB modelling, to calculate the relevant factors for the macro-tracer approach, and finally to look for tracers specific for wood types, to be able to distinguish between smoke from different types of wood, especially between hard- and softwoods. The selection of the stove model and the wood types for

testing should be representative for Austria and other Alpine regions of Europe.

2. Experimental

2.1. Wood selection

Not much information is available on wood species burned in domestic stoves in Austria. The [Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management \(2005\)](#) gives only some general information about the amounts of wood lumbered in the report “Holzeinschlag 2004.” In that year, 21.5% of wood felled in Austria was used as fuel. This number divides into 12.7% (59% of fuel wood) softwood and 8.8% (41% of fuel wood) hardwood (based on cubic metres). Additional information on the most common soft- and hardwood species was obtained from the [Austrian Forest Inventory 2000–2002](#) (Austrian Federal Forest Office), which includes statistical data on the numbers of trees, stocks and timber felled in Austrian forests for all common wood types.

The most common softwood in Austria is spruce (*Picea abies*) and the most common hardwood is beech (*Fagus sylvatica*). Low prices for these two wood types, resulting from the favourable supply situation, have resulted in their becoming the standard fuel wood types in Austria. Nevertheless, other wood types, larch and oak, were also tested in this study. Their use as fuel is mainly based on local availability. Especially in rural areas any kind of wood that can be easily obtained locally—from forests or farmers—is used for heating.

All wood samples selected for testing were obtained directly from local farmers. Storage time from felling to burning for each wood type was around 2 years except for oak which was stored for only 1 year. Detailed information about tested wood types, including scientific names, the number of tests and the water content, measured by following [DIN 52180 Part 1 \(1977\)](#), are listed in [Table 1](#).

2.2. Source tests

All tests were conducted on a domestic tiled stove (*Kachelofen*) built in 1994. This type of stove is typical for Austria, which is confirmed by the estimate of 450 000 such stoves existing in Austrian households (*Österreichischer Kachelofenverband*, personal communication) and of around 10 000 new stoves of this type built every year. They are used for heating, mainly during the winter months. Dimensions of the combustion chamber are 75 cm (length) × 45 cm (width) × 60 cm (height), resulting in a total volume of around 0.2 m³ (200 L). Combustion air enters through a grating in the bottom of the chamber. Hot exhaust gases and smoke are conducted through a double-S-shaped duct inside the stove, where they transfer their thermal energy to the brickwork of the stove before entering the chimney.

All wood types were burned as split logs of 30–50 cm in length and around 10 cm in diameter. Softwood briquettes were used in the typical cylindrical form 30 cm long and 10 cm in diameter with a 3 cm bore through the centre. For each test the combustion chamber was loaded with around

Table 1
Stock, felling, average moisture content and number of tests of selected wood types used for source tests ([Austrian Forest Inventory 2000–2002](#))

Wood type (class)	Scientific name	Austrian forest stock ^{a,b}		Timber felled in Austria ^a		Moisture content ^c	Number of tests
		% of total	% of class	% of total	% of class	% w/w	
Spruce (sw)	<i>Picea abies</i>	61.5	75.9	66.0	78.0	10	10
Larch (sw)	<i>Larix decidua</i>	6.7	8.3	4.9	5.8	11	3
Beech (hw)	<i>Fagus sylvatica</i>	9.3	57.4	6.7	56.5	11	8
Oak (hw)	<i>Quercus robur</i>	2.4	14.8	2.0	16.5	16	4
Briquettes (sw)						10	6

sw, softwood, hw, hardwood.

^aAll numbers are given as percent solid cubic metres.

^bStock values based on solid cubic metres in Austrian forests.

^cDetermination of moisture following [DIN 52180 Part 1 \(1977\)](#).

10 kg of wood and the fire was ignited with two pieces of lighter material (each 7 g) consisting of compressed softwood chips impregnated with paraffin oil as binder (sold under the name “Husch”).

The sampling port was positioned about 3 m above the stove and 4 m below the opening of the chimney to the outside air on the roof of the house. During each burning test three samples were taken. The first sampling period started 2 min after ignition of the fire, the second after 10 min and the last after 20 min. Each sample was collected over a period of exactly 60 s. Emission samples were taken from the centre of the chimney using a dilution sampler. A schematic of one sampling line is given in Fig. 1.

After leaving the chimney through the sampling probe the exhaust emissions were diluted with a 3-fold excess of air which had been dried and purified by passage through activated silica, then through activated carbon and finally through a HEPA filter. A critical orifice regulated the flow of the dilution air. The dilution ratio was lower than those reported in previous studies (Fine et al., 2001, 2002, 2004a, b) which were intended to allow organic vapours to condense before being sampled. It was felt that in the present experimental set-up, as the combustion products travel a long distance through the duct of the tiled stove and then up the chimney to the sampling point, the emission gases will be cooled down sufficiently that organic compounds of low volatility will by that point have condensed out. The temperature of sampling probe was generally below 60 °C which leads to a maximum sampling temperature of 30 °C if the dilution ratio of 1:3 is taken

into account. The residence time in the dilution system and PM₁₀ separator is around 0.2 s. We assume that all analytes in our study occur in the particulate state at these conditions.

After this dilution step the sampled air is drawn through a particle separator shown in Fig. 2 which retains particles with aerodynamic diameters greater than 10 µm. The sampling apparatus was built with two equal lines to be able to use two different filter types during the same sampling period. The separator is constructed as a single-stage impactor which reaches a separation efficiency of 50% for particles with 10-µm aerodynamic diameter at a flow of 3.2 m³ h⁻¹ (53.3 L min⁻¹). For particles with 8.1 µm aerodynamic diameter the separation efficiency is 33%, for 11.2 µm it is 66%. This leads to a calculated sigma of 0.97 (~1). It is constructed completely of anodized aluminium to keep the weight low and to avoid contamination of the samples. This separation step is followed by the sampling of particles simultaneously on two different filter types. One filter holder was loaded with quartz fibre filters (47 mm diameter, Pallflex—Tissuequartz, Pall Life Sciences) which were used for determination of organic tracers, carbon species, anhydrosugars, the ion analysis and for determination of total particulate mass. The second sampling train was equipped with mixed cellulose ester filters (47 mm diameter, GN4—Metrical membrane disc filters, Pall Life Sciences) which were used for inorganic analyses by XRF and ICP-OES. The volume flows of the two sampling lines were regulated by needle valves placed after the filter holders. Absolute volumes of sampled air

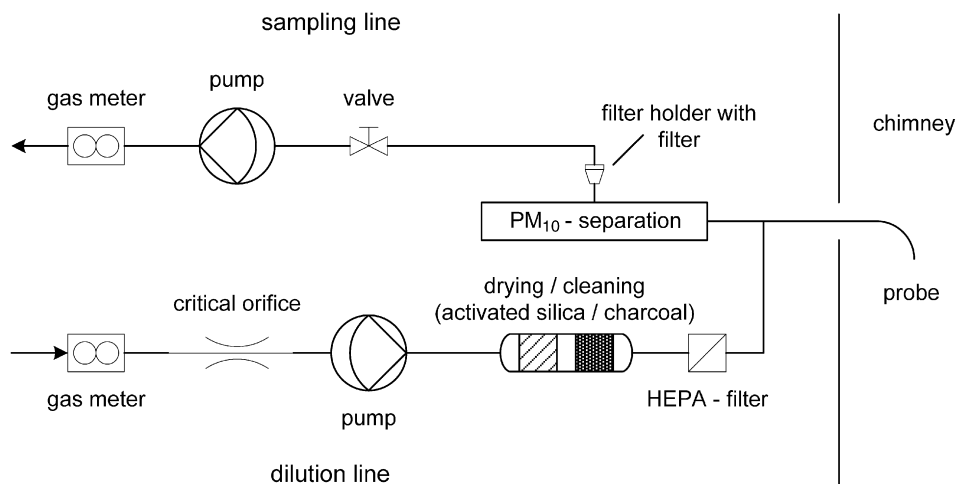


Fig. 1. Schematic drawing of on-line sampling equipment.

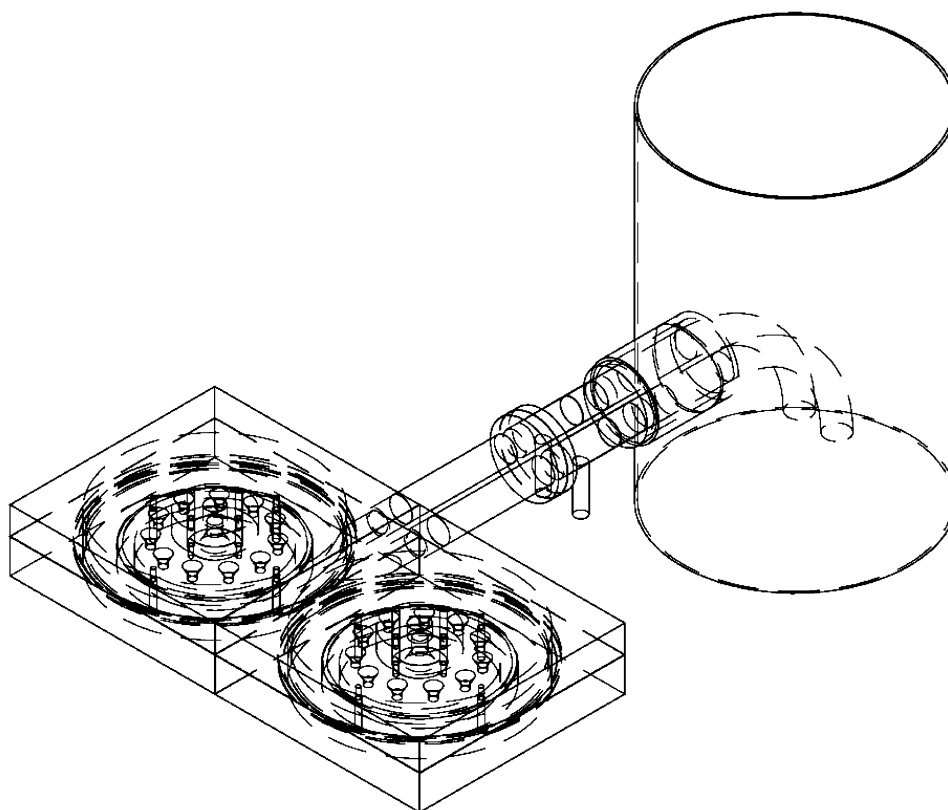


Fig. 2. Sampling probe and dual PM10 separation head with a one-stage-impactor.

(~53 L per sampling) and dilution air (~40 L per sampling) were measured with gas meters.

2.3. Analytical methods

2.3.1. Weighing and sample preparation

Gravimetric analysis was performed with a microbalance (Sartorius M5P with range up to 1 g reading to $\pm 0.5 \mu\text{g}$) after 48 h equilibration in an air-conditioned room ($20 \pm 1^\circ\text{C}$, $50 \pm 5\%$ r.h.). For analysis of ions and carbon species, small discs, with 8 or 10 mm diameter, were stamped out of the quartz tissue filters with steel punches. For the determination of trace metals by XRF and then by ICP, whole cellulose filters were used.

2.3.2. Anions

Anions were eluted from quartz tissue filters by washing with high purity water (Millipore Milli-Q Plus 185). After sonicating and centrifuging, the extract was analysed on an AS17A anion-exchange column, with an ASRS Ultra II auto-regenerating suppressor, and a model CD20 conductivity cell detector (the whole system from Dionex).

2.3.3. Cations

Cations were eluted by washing with the chromatography eluent, 0.1% v/v methane sulphonic acid. After sonication and centrifugation, the extract was analysed on a Dionex QIC ion chromatograph with a CS12A cation-exchange column, and a conductivity detector.

2.3.4. Cellulose

After elution of quartz fibre filters with a 0.05 M citric acid solution ($\text{pH} = 4.8$), extraction in an ultrasonic bath and saccharification to glucose through the action of two enzymes (a “*Trichoderma reesei*” cellulase and an “*Aspergillus niger*” cellobiase), cellulose was determined photometrically using a modified test-set (by Boehringer Mannheim GmbH/R-Biopharm). This method is described in detail elsewhere (Kunit and Puxbaum, 1996).

2.3.5. Carbon

TC—total carbon, was determined by combustion of all material on the filter, in oxygen, at 1000°C and measurement of the resulting CO_2 by non-dispersive IR photometry (NDIR, Maihak).

EC—elemental carbon, was determined in the same apparatus on material previously heated in oxygen at 340 °C to burn off the organic matter (Cachier et al., 1989) and additionally, as a check, it was also determined for a number of samples by the modified thermo-optical temperature gradient method (Puxbaum, 1979; Schmid et al., 2001).

CC—carbonate carbon, was determined by the thermo-optical temperature gradient method as the last form of carbon to be released as CO₂ at temperatures higher than 550 °C.

OC—organic carbon, was calculated as the difference TC—(EC + CC).

2.3.6. Humic like substances—HULIS

PM was extracted first with water, then with dilute alkali (0.06 mol L⁻¹ NaOH). Pre-concentration and clean-up of these separate extracts was achieved using SPE with a reversed phase (ISOLUTE C18), followed by a further clean-up step using an anion-exchange column (ISOLUTE SAX) in a flow-injection system. The organic material eluting was quantified by on-line TOC determination, with calibration based on oxalic acid solutions. The limit of detection (LOD) of this method is around 3 µg HULIS “C” absolute in the extract. A detailed description of this method is given elsewhere (Limbeck et al., 2005).

2.3.7. Anhydrosugars

The determination of levoglucosan and other anhydrosugars, including mannosan and galactosan was carried out by HPLC with electrochemical detection (ED40, Dionex). Compounds were separated on a CarboPac PA10 column using gradient elution with 1 mL min⁻¹ dilute sodium hydroxide, starting at 30 mM sodium hydroxide (88% Milli-Q water and 12% of 250 mM NaOH by volume) increasing to 40 mM. For the amperometric detection a gold working electrode was used. The analytical system was cleaned by rinsing with 250 mM NaOH for 5 min after every sample (Caseiro, et al., 2007).

2.3.8. Metals

Cellulose acetate filters have been analysed by a Philips X'Unique II (model 1480) wavelength-dispersive X-ray fluorescence spectrometer. The used system was equipped with a rhodium X-ray tube, operated at 50 kV and 40 mA. The XRF measurement method was optimised using aerosol-generated filter standards which were prepared in

our laboratory. For quality control the certified reference material NIST 2709 was used.

After XRF analysis cellulose acetate filters were digested in *aqua regia* with a little hydrofluoric acid, under pressure in sealed vessels in the microwave oven. The bulk of the acid was then removed by boiling off (from the open vessels), and the final solution was prepared in dilute hydrochloric acid (2% v/v). The sample digests were analysed by atomic spectroscopy—either plasma optical emission, or electrothermal atomic absorption (As, Sb).

2.3.9. Apolar organics

Organic trace components were extracted twice with 5 mL of cyclohexane. Prior to extraction the filter was spiked with deuterated recovery standards (tetracosane, benzo[a]pyrene). The combined extracts were evaporated to 200 µL and an internal standard (1-bromopentadecane) was added. Samples were then analysed by GC-MS using a HP-6890 gas chromatograph equipped with a pre-column of deactivated fused silica (1 m × 0.32 mm) and a capillary analytical column DB-5 MS (95% dimethyl-, 5% phenylsiloxane, 30 m × 0.25 mm ID × 0.25 µm film) running in splitless mode. Detection was carried out with a mass spectrometer HP-5973 (70 eV) in ion-scan mode.

2.3.10. Polar organics

The filters were spiked with internal standards (12-bromododecanoic acid, 1-bromopentadecane) to estimate the recoveries. For extraction the filter was sonicated twice with a mixture of 5 mL methanol and 150 µL acetone. In the following step organic acids were derivatised to methyl esters and extracted into cyclohexane. Analysis was carried out on a HP-5890 GC-MS, run with two capillary columns (95% dimethyl-, 5% phenylsiloxane, 30 m × 0.25 mm ID × 0.25 µm film) in splitless mode. The gas flow from one column was fed to a flame ionisation detector (FID) and that from the other column to a Hewlett-Packard mass spectrometer HP-5971-A (70 eV) running in ion-scan mode.

3. Results and discussion

3.1. Combustion characteristics and sampling protocol

The combustion process in a domestic stove does not run under steady-state conditions—there is an

initial relatively high smoke emission, lasting a few minutes, then follows a longer period of higher-temperature combustion with lower emissions. Different woods take longer to go through the initial phase, so the shapes of the curves (see Figs. 3(a) and (b)) depend on when the samples are collected in relation to the burning pattern. It should be pointed out that the lines fitted to these data points (each the average of many experimental data points) are binomial fits and that the exact shape (currently under investigation) is likely to be different, more like a skewed chromatographic peak.

For this reason three sampling points were chosen in the region of the high emission phase, which is confirmed by visual observations (no more visible flames after 30–40 min). From these data we found a high variability of the levoglucosan content in PM10 from combustion tests (Fig. 4).

The level of levoglucosan in the smoke is not constant, but tends to be less when there is less smoke, suggesting that as the temperature rises,

later in the burn, the volatile matter released during pyrolysis and gasification process is combusted more efficiently, and the recovered amounts of the anhydrosugars are less. Thus, for tests burning spruce, two-thirds of the samples were of low weight and with low levoglucosan content. Arithmetic averaging of the % content of levoglucosan for all 30 samples gave a result of 7.1%, compared to a result of 10.7% for the total recovered mass of levoglucosan over the mass of PM, and from Fig. 4 one can estimate that for the high-emission samples, the average would be around 14%. As the aim of this work was to establish an overall profile for “wood smoke,” it was decided to construct curves such as those in Fig. 3 and to integrate the amounts to get a more true impression of the overall emission of levoglucosan and then of the factor relating this marker to the total mass of PM. This gave, for spruce (PM curve as in Fig. 3(a)), a result of 9.6%, with a conversion factor of 10.4 for deriving wood smoke PM10 mass from levoglucosan.

Analyses for levoglucosan in wood smoke from all four woods except spruce (with PM curves as in Fig. 3(b)) yielded values by the integrated curve approach which were around 4–30% higher than those obtained by simply taking the ratio of the total mass of levoglucosan to total PM. The real curve in these cases should be much sharper and the fraction of the time when large samples, with high levels of levoglucosan would be found, should in fact be smaller. So, this integration method has been taken as an approximate validation and for estimation of uncertainties of the total mass ratio approach which was adopted for all the values reported in the following tables.

Concluding, we assume that by taking 30 samples from spruce and 24 samples from beech, all during the high emission phase of the burn, the error in the calculated average will be rendered small. To get information about uncertainties we compared two different averaging methods—the finally used mass ratio approach, with the method of integrating binomial fitted curves through the three data points. This second method leads to results for levoglucosan levels that are on average around 10% higher than with the mass ratio approach (range –10% to +30%). We therefore assume that an error of around 20% will be a good estimate for the uncertainty connected to our calculated values.

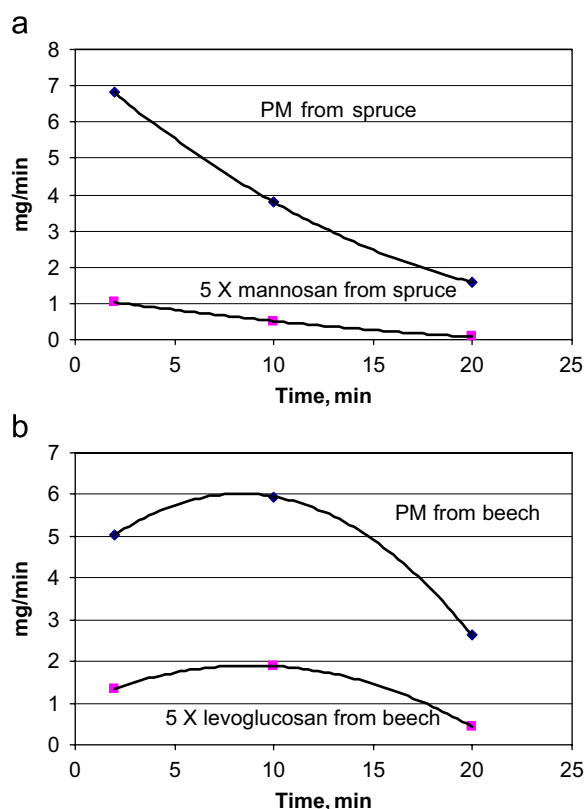


Fig. 3. (a) Emissions collected from burning spruce, as a function of time. (b) Emissions collected from burning beech, as a function of time.

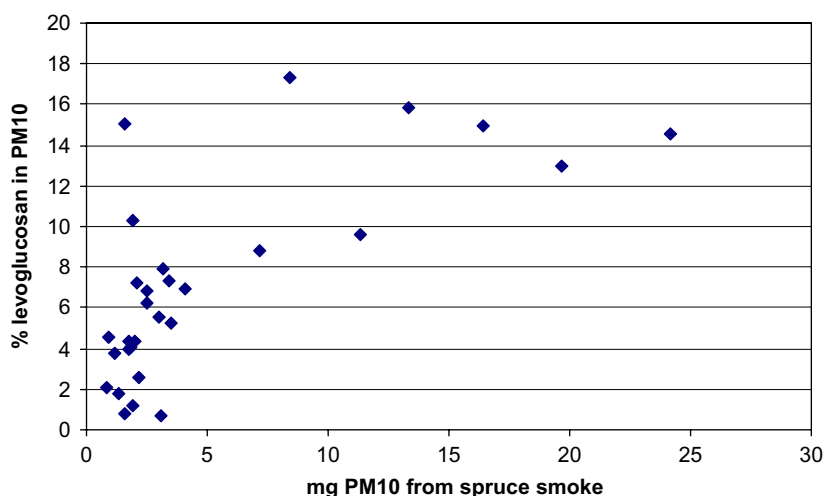


Fig. 4. Levoglucosan content of spruce smoke as a function of mass of PM10 emissions.

3.2. Anhydrosugars

Levoglucosan, mannosan and galactosan were found in high concentrations (0.2–15% w/w) in all wood smoke samples (Table 2). As expected the anhydrosugar levoglucosan, which has long been known as a by-product from the pyrolysis of cellulose (Shafizadeh, 1968), was the most abundant organic compound and was found in all analysed wood smoke samples. Average concentrations ranged from 4.1% in beech wood smoke to 15.1% of total particulate mass in larch wood smoke which is in general agreement with levoglucosan contents of 0.797–31.82% found for American tree species by Fine et al. (2001, 2002, 2004a, b). Applying a *t*-test leads to the conclusion that the concentration of levoglucosan in beech wood smoke (4.1%) is significantly different (at the 99% level) from that in the other three wood types (e.g. 10.7% in spruce, 10.1% in briquettes), but that the levels in spruce and larch (15.1%) are not different. When the relative proportions of beech and softwoods burned in Austria are taken into account, the change in the average levoglucosan level from that in spruce is not significant, so an average of all woods can be used.

Levoglucosan has been described as a tracer for biomass combustion in general—from any cellulosic material (Simoneit et al., 1999). In a previous study concerning the stability of levoglucosan, Simoneit et al. (2004) found no degradation due to acid-catalysed hydrolysis over 15 days under conditions simulating the aqueous chemistry of atmospheric droplets. However, as burning of farming waste in

the open air is not allowed in Austria, and is indeed rarely seen, we can conclude that the presence of levoglucosan in ambient PM in Austria must indicate burning of wood for domestic heating. This is supported by ambient values for sampling sites in Vienna which show levels in summer (May–September) $<0.05 \mu\text{g m}^{-3}$ compared to $0.2\text{--}0.5 \mu\text{g m}^{-3}$ in the remaining months of the year (Caseiro, personal communication). Johansson et al. (2003) mention that large-scale industrial furnaces consuming wood run at much higher temperatures and produce only small quantities of fly ash, and with very low OC levels. Our measurements on larger furnaces confirm this (BioComb project, continuously proceeding). Forest fires would also contribute something, but are not common in Austria. We can therefore conclude that levoglucosan can be used as a macrotracer for wood smoke PM in Austria.

Mannosan, a pyrolysis product from hemicelluloses, is the second most abundant anhydrosugar in the wood smoke samples and could be measured with confidence with standard error of mean (SEM) of 10–15% relative for beech and spruce. In this case, the difference between the concentrations in beech smoke (0.3%) and in spruce smoke (1.9%)—does allow one to distinguish between these two wood types. Even better, the two softwood types, spruce and larch, are similar, as are the two hardwood types, beech and oak (Table 2). These differences can be explained by the different mannose levels in the hemicelluloses of these wood types. In beech, mannose constitutes 0.9% of

polyoses while this sugar is highly abundant in spruce, accounting for 13.6% of the hemicelluloses (Fengel and Wegener, 2003).

Considering the ratio of levoglucosan to mannosan the difference between hard- and softwood types becomes even more marked. Hardwoods give high ratios, around 14–15, while softwoods give low ratios, 3.6–3.9 (Table 2). Softwood briquettes exhibit a ratio of 2.5 somewhat lower than the corresponding ratio for log wood. The experimental ratios are characterised by quite small uncertainties, typically 10% relative SEM. Therefore the proportion of soft- and hardwoods can be estimated from the levoglucosan to mannosan ratios in ambient PM by applying the following equation:

$$\% \text{ spruce} = (14.8 - R_{\text{levo/man}})/(0.112), \quad (1)$$

where $R_{\text{levo/man}}$ is the ratio of levoglucosan to mannosan concentration in ambient air; 0.112 the slope of the linear correlation between levoglucosan/mannosan ratios and contribution of spruce smoke to ambient wood smoke levels, calculated from levoglucosan/mannosan ratios in beech and spruce smoke: $(14.8 - 3.6)/100\%$.

We want to add that levoglucosan/mannosan ratios observed for PM collected at four different sites in Vienna, as well as at three in Salzburg, indicate fuel supply make-up values of 70–90% softwood by applying Eq. (1) (Caseiro, personal communication). Statistical data about fuel wood use in Austria indicate a 59% softwood–41% hardwood mixture (see Section 2.1). These numbers are gained by selling statistics of Austrian governmental forests and do not include the private use of “self-produced” wood and the vending of fuel wood by local farmers. We therefore can conclude that for private acquisition of fuel wood, which means using wood from one’s own forest or buying from local farmers, softwood is preferred—probably because of its low price and high availability.

Galactosan is the third important anhydrosugar in wood smoke. As the results in Table 2 show, very different concentrations of this sugar are to be found in the smoke from different woods (only spruce and briquettes coming close, as was expected). The level of galactosan in larch wood smoke is significantly higher than in all other wood types. However larch grows mainly in higher elevation regions of the Alps and is usually used for carpentry due to its weather durable properties. Thus larch wood is rarely seen as fuel wood. The applicability of galactosan for source apportionment depends on local burning habits and has to be explored further.

Glucose has been detected in the wood smoke, but at very low levels—typically one-hundredth of those of the levoglucosan. This is helpful to know, because the simple sugars are known to be components of soil dust (Simoneit et al., 2004) and could perhaps serve as markers for this source, without the complication of an additional input from wood smoke.

Considering these facts the results of this study suggest the use of levoglucosan as a tracer for wood burning in general and the levoglucosan to mannosan ratio to differentiate between hardwood and softwood smoke.

3.3. Other carbonaceous components

TC values lie in the range 63% (oak) to 75% (spruce) and are (except for oak) rather well defined, with $\text{SEM} < 3\%$, as the method gives good reproducibility and the numbers of samples were large (Table 2). TC in beech smoke is higher than for oak, and in spruce smoke is higher than for larch, all at the 99% confidence level, but the difference between beech and spruce, the two most important fuel woods for Central Europe, is just significant, and for practical

Table 2

Carbon species and anhydrosugars in wood smoke—% w/w \pm SEM (per set of tests)

	Beech	Oak	Spruce	Larch	Briquettes
TC	70.4 \pm 2.7	63.7 \pm 3.5	74.3 \pm 1.7	65.4 \pm 0.4	71.8 \pm 2.7
EC	19.1 \pm 7.0	15.0 \pm 1.3	20.6 \pm 6.1	9.8 \pm 2.8	31.0 \pm 7.0
OC	51.3 \pm 2.9	48.7 \pm 3.0	53.7 \pm 5.0	55.6 \pm 2.8	40.8 \pm 5.1
Levoglucosan	4.1 \pm 0.6	13.3 \pm 2.9	10.7 \pm 1.2	15.1 \pm 2.9	10.1 \pm 1.4
Mannosan	0.28 \pm 0.04	0.92 \pm 0.30	3.0 \pm 0.32	3.9 \pm 0.7	4.0 \pm 0.6
Galactosan	0.20 \pm 0.04	0.43 \pm 0.1	0.85 \pm 0.10	4.5 \pm 1.3	0.88 \pm 0.15
Levo/Man	14.8 \pm 2.2	14.4 \pm 2.7	3.6 \pm 0.35	3.9 \pm 0.1	2.5 \pm 0.2

purposes can be taken as the same, at $72 \pm 2\%$. Comparison with literature data (e.g. Hedberg et al., 2002; Fine et al., 2004a,b) seems not to be helpful, but as the method has been tested in inter-laboratory trials (Schmid et al., 2001), we have confidence in the quality of these values. In any case, the same methods are used for this characterisation of wood smoke and for the ambient PM samples for Austria.

Levels of EC cover a wider range, with mean values of 9.8% for larch, 21% for spruce, 19% for beech and 15% for oak, and are subject to much greater variability with SEM in the range 6–7%, for a given wood type. This spread of values is related to the complexity of the processes taking place during the determination of carbon, whether during the temperature programme of the TOT method, or during the isothermal burn-off stage of the Cachier method, which was used for EC for all samples tested. Comparison with EC results from the literature shows poor correspondence, but the marked differences between woods is common to other studies (e.g. Fine et al., 2004a,b). The EC value for spruce, and therefore also for the softwood briquettes, is significantly higher than the other EC values.

The OC fraction, calculated as the difference between TC and EC, accounts for around $52 \pm 4\%$ of particle mass ($n = 25$) for all the wood types as pieces, but for only 41% for the softwood briquettes. In the case of briquettes, the higher EC levels of around 31% of the total PM₁₀ as against around 20% average for beech and spruce, with a corresponding decrease in the level of OC from around 52% to only 40%, seem to indicate a significant influence of physical form of the fuel rather than of the wood type. Since briquettes are made of compressed wood chips, and disintegrate under the burning conditions, access of air to the fuel seems to be better than in the case of logs, and this could lead to a more efficient combustion process and to a higher degree of oxidation of the volatile organics. The interesting statistical analysis by McDonald et al. (2000) similarly suggested that differences in profiles could be found when the burning conditions were different, e.g. stove against fireplace.

CC was looked for using the TOT method, but was not seen. As K, Ca and Mg levels are very small, we can estimate that the CC must be less than 0.5% in the PM. It is to be expected that these components would remain in the ash and not be

carried up the chimney with the smoke, and these results bear this out.

3.4. Other components of wood smoke

Average particulate concentrations in wood smoke emissions and a number of inorganic components, expressed as percent w/w of the total PM₁₀ in the smoke, are listed in Table 3 for the different types of wood tested. The uncertainties, given as the standard errors of the means, to meet the requirements for the development of profiles for CMB modelling, are summarised in Table 4. It can be noted that the purely analytical uncertainties are much smaller.

3.4.1. Metals

In many previous studies concerning aerosol particulates, metal species were determined mainly because of the good availability of standard methods. Analysis of the wood smoke samples confirmed what has been reported before (Fine et al., 2004a,b) that concentrations of most metals are very low and are different from those for other particulate sources.

When one considers that different types of trees will take up metals from the soil to different extents, and that different soils will contain very different levels of trace metals of widely differing availability, then it is not surprising that the values for the trace metals in the wood smoke profiles do not show a close correspondence between results from other species of trees in other countries. In some cases, the differences may be due to procedural differences. Higher values for potassium in the North American profiles (Hildemann et al., 1991), however, may be ascribed to different emission conditions in different stoves and fire places. Compared to many other stoves, for instance, the one used in this study exhibits a high residence time of the flue gas in the ducts of the stove (see Section 2.2).

Table 4 summarises the uncertainties of the profile inorganic values. A statistical comparison of beech and spruce smoke profiles, based on 8 and 10 samples of each, respectively, gives t -values in the range 0.5–1.8, compared to 2.1, for 95% confidence that these values might be different, showing a significant difference only for zinc, with $t = 3.1$. However, because of the number of factors which can affect such values this element cannot be considered as a suitable tracer to distinguish between hardwood and softwood smoke. Thus we

Table 3

Average concentrations for inorganic species and some organic compounds in smoke from different wood types, with additional reference data

Compound	Analysis	Beech	Oak	Spruce	Larch	Briquettes	Ref. 1 ^a	Ref. 2 ^b
<i>Carbon species</i>								
Elemental carbon	T, TO	19.1	15.0	20.6	9.8	31.0	1.1–32.5	1.4–3.2
Organic carbon	T, TO	51.3	48.1	53.7	55.6	40.8	43.6–106.3	43.7–59.1
<i>Metals</i>								
Magnesium total	ICP-OES	0.056	0.084	0.073	0.052	0.093	NA	NA
Aluminum	XRF	0.015	0.041	0.023	0.027	0.011	NA	0.000–0.006
Silicon	XRF	0.042	0.24	0.062	0.19	0.126	0.0071–0.2	0.008–0.016
Titanium	ICP-OES	0.0026	0.0043	0.0070	0.0018	0.0058	NA	< LOD
Vanadium	ICP-OES	0.0013	< 0.0002	0.0012	0.0002	0.0027	NA	< LOD
Chromium	ICP-OES	0.035	0.038	0.035	0.026	0.052	NA	< LOD
Manganese	ICP-OES	0.0095	0.0083	0.0187	0.0090	0.0063	0.0026	< LOD
Iron	ICP-OES	0.042	0.170	0.052	0.025	0.045	NA	0.001
Cobalt	ICP-OES	< 0.003	< 0.003	< 0.003	0.0038	0.0034	NA	< LOD
Nickel	ICP-OES	0.0091	0.0093	0.0131	0.0010	0.0059	NA	< LOD
Copper	ICP-OES	0.065	0.0077	0.0196	0.0035	0.0175	0.0018	0.000–0.001
Zinc	ICP-OES	0.019	0.032	0.100	0.036	0.052	0.002–1.48	0.005–0.006
Arsenic	AAS	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	NA	< LOD
Strontium	ICP-OES	0.0014	0.0019	0.0017	0.0011	0.0033	0.0048	< LOD
Cadmium	ICP-OES	0.0019	< 0.001	0.0053	0.0021	0.0039	NA	0.000–0.002
Tin	ICP-OES	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	NA	0.000–0.001
Antimony	AAS	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	NA	0.000–0.004
Barium	ICP-OES	0.0026	0.0041	0.0038	0.0026	0.0047	NA	0.000–0.002
Lead	ICP-OES	0.0021	0.0120	0.0034	0.0020	< 0.001	0.008–0.019	< LOD
<i>Ionic species</i>								
Ammonium	IC	0.059	0.101	0.133	0.022	0.135	0.03–0.27	0.09–0.45
Sodium soluble	IC	0.022	0.038	0.032	0.0092	0.066	NA	0.09–0.18
Magnesium soluble	IC	0.0037	0.0100	0.0060	0.0046	0.0073	NA	NA
Potassium soluble	IC	0.213	0.414	0.160	0.073	0.189	0.159–2.74	0.277–0.809 ^d
Calcium soluble	IC	0.040	0.108	0.051	0.032	0.062	NA	NA
Carbonate ^c	TO	ND	ND	ND	ND	ND	NA	NA
Nitrate	IC	0.098	0.134	0.063	0.036	0.105	0.07–0.73	NA
Chloride	IC	0.073	0.196	0.163	0.047	0.113	0.04–1.32	0.20–1.70
Sulfate	IC	0.308	0.178	0.176	0.044	0.099	0.01–1.68	0.12–0.41
Formate ^e	IC	0.172	0.433	0.158	0.174	0.228	NA	NA
Acetate ^e	IC	0.64	1.48	0.53	0.62	0.44	NA	NA
Malonate	IC	0.019	0.067	0.0132	0.029	0.0025	NA	NA
Malate ^e	IC	0.143	0.35	0.098	0.151	0.117	NA	NA
Maleate	IC	0.016	0.024	0.0043	0.0101	0.0049	NA	NA
Oxalate	IC	0.106	0.28	0.087	0.117	0.086	NA	NA
<i>Anhydrosugars, sugars, cellulose</i>								
Levoglucosan	HPLC	4.10	13.3	10.7	15.1	10.1	0.797–31.82	NA
Mannosan	HPLC	0.28	0.92	3.0	3.9	4.0	0.114–9.157	NA
Galactosan	HPLC	0.20	0.43	0.85	4.5	0.88	ND–1.880	NA
Glucose	HPLC	0.011	0.0076	0.022	0.0013	0.0061	NA	NA
Fructose	HPLC	0.0018	0.0020	0.0008	0.0101	0.0010	NA	NA
Cellulose ^f	Enz-Ph	0.079	NA	0.079	NA	NA	NA	NA
HULIS	FI-DOC	2.63	5.84	1.14	0.57	3.02	–	–

All values given as % w/w.

T, thermal; TO, thermo-optical; ICP-OES, inductively coupled plasma–optical emission spectroscopy; XRF, X-ray fluorescence; AAS, atomic absorption spectroscopy; IC, ion chromatography; HPLC, high performance liquid chromatography; Enz-Ph, enzyme-photometric; FI-DOC, flow injection-dissolved organic carbon; LOD, limit of detection; ND, not detected; NA, not analysed.

^aRange of compound-concentrations from Fine et al. (2001, 2002, 2004a,b).

^bRange of compound-concentrations from Schauer et al. (2001).

^cNo signal at temperatures higher than 550 °C during thermo-optical analysis.

^dTotal potassium analysed with X-ray fluorescence.

^eQuantification uncertain because of overlapping peaks.

^fAnalysed in a mixed sample of beech and spruce smoke.

Table 4

Uncertainties of profile values for inorganic species—given as SEM, relative %

Uncertainty (%)	Species determined in PM10 profile
<5	TC
5–10	OC
10–20	Ba, Cr, Mg; acetate, formate, oxalate
20–40	EC, Ca(soluble), Fe, Mn, Pb, Zn; NH_4^+ , NO_3^- , SO_4^{2-}
40–60	Al, Si, Ni; K^+ , Cl^-
<LOD	As, Cd, Sr

can adopt one trace metals profile for wood smoke in general, and conclude that, for wood combustion smoke, metal species do not play an important role in defining a suitable profile for CMB modelling, but are helpful in allowing the model to reach a closer fit for ambient PM samples as the small contributions from the metals in wood smoke are still taken into account along with the higher levels found in e.g. road dust.

3.4.2. Extractable ions

Soluble ionic species are not major components of wood smoke (Table 3). As expected, the highest levels were observed for the potassium cation which is a major constituent of biomass ash. The abundances of ionic species in the Austrian wood smoke profiles are lower than in many previous studies (Fine et al., 2001, 2002, 2004a,b). The method of sampling used for this study could be one reason for that, because higher levels of ions are usually emitted with the fuel ash at the end of the burning process, while samples were taken at the beginning and in the middle of the burn because then the particulate emission levels are higher. There were no significant differences between beech and spruce smoke. Uncertainties are summarised in Table 4.

3.4.3. Trace organic compounds

Organic trace analyses were performed only for beech and spruce smoke samples to complete the chemical profiles for CMB modelling in Austria. Results of these analyses and additional reference data are presented in Table 5.

Their potential to be used as tracers for combustion of different wood types in ambient samples may be limited by their low concentrations in emissions

so that after mixing with ambient air in some cases the levels are close to or below the limits of detection. In principle, however, these organic compounds in wood smoke do offer a number of possible tracers for different wood types.

Typical substances found in spruce smoke are retene at around 0.03% of particle mass and abietic acid which accounted for around 0.8% of particle mass, and therefore was the most abundant trace organic component in spruce smoke. A comparison with ambient PM data showed for January and February, for which the samples were analysed soon after receipt, a good correlation between retene and levoglucosan, while for November and December, for which the samples had been left stored in the freezer for over a year, the disagreement is very marked. It would seem that retene is not so stable on the filters, even when stored at low temperatures.

Abietic acid (for spruce) averages 0.8% w/w in spruce woodsmoke and so we would expect it to be present in ambient PM samples. It is present, but the amounts measured do not correlate with the levoglucosan concentrations, as for retene. Syringol at around 0.4% was the most abundant trace organic component in beech smoke and represents a specific organic tracer for hardwood. All other organic tracers analysed in this study were present in smoke of both wood types or in a very low quantity, so that they are not suitable as specific tracers to distinguish between wood types.

Cellulose is the basic structural material for many plants, and is found in small amounts in wood smoke (around 0.08%, Table 3). It is much more important in other source materials, such as plant debris at up to 50% and in road dust at around 0.5%. The contribution of cellulose from wood smoke may therefore be notable in winter, but less so in summer, when the plant debris becomes the important contributor.

HULIS is a collective term for all those substances which behave chemically like the higher-molecular weight water-extractable components in soils. However, the fact that such material is detected in the small particle size fraction of PM10 samples means that soil dust is not the source and that these substances are present probably arising as secondary aerosol products as a result of photochemistry in the atmosphere (Gelencser, 2005). In wood smoke samples HULIS were found in notable concentrations of 0.57–5.84% of total particle mass.

Table 5

Results for organic trace compounds for beech and spruce smoke particles given as percent w/w and mg/g of organic carbon

Compound	Beech ^a		Spruce ^a		Fine et al. ^b
	% w/w	mg g ⁻¹ OC	% w/w	mg g ⁻¹ OC	
<i>Apolar tracers</i>					
Eicosane	0.0013	0.0254	0.0010	0.0180	0.026–0.15
Heneicosane	0.0017	0.0332	0.0004	0.0077	0.027–0.275
Docosane	0.0026	0.0507	0.0002	0.0044	0.033–0.47
Tricosane	0.0037	0.0722	0.0004	0.0080	0.036–0.309
Tetracosane	<0.00003	<0.0006	0.0029	0.0544	0.011–0.203
Pentacosane	<0.00003	<0.0006	0.0005	0.0099	0.015–0.221
Hexacosane	<0.00003	<0.0006	0.0012	0.0215	0.005–0.192
Heptacosane	<0.00003	<0.0006	0.0011	0.0213	0.026–0.22
Octacosane	<0.00004	<0.0008	<0.00004	<0.0007	0.007–0.052
Nonacosane	<0.00003	<0.0006	<0.00003	<0.0006	0.008–0.067
Triacontane	<0.00007	<0.0014	<0.00007	<0.0013	NA
Hentriacontane	<0.00007	<0.0014	<0.00007	<0.0013	NA
Dotriacontane	<0.00010	<0.0020	<0.00010	<0.0019	NA
Benzo[de]anthracen-7-one	0.0154	0.3012	0.0079	0.1466	NA
Retene	0.0035	0.0685	0.0285	0.5302	0.008–6.8
Benzo[e]pyrene	0.0131	0.2561	0.0088	0.1638	0.029–0.351
Indeno[cd]fluoranthene	<0.0001	<0.0002	<0.0001	<0.0002	0.01–0.133
Indeno[cd]pyrene	<0.00006	<0.0001	<0.00006	<0.0001	0.039–0.45
Benzo[ghi]perylene	0.0155	0.3020	0.0108	0.2007	0.025–0.271
Coronene	0.0078	0.1512	0.0049	0.0911	0.061–0.519
<i>Polar tracers</i>					
Hexanoic acid	0.0010	0.0186	0.0003	0.0053	NA
Octanoic acid	0.0049	0.0958	0.0013	0.0239	0.104–0.37
Nonanoic acid	0.0011	0.0212	0.0009	0.0161	0.045–0.109
Decanoic acid	0.0070	0.1374	0.0043	0.0792	0.055–0.245
Dodecanoic acid	<0.0002	<0.0004	0.0196	0.3648	0.088–0.414
Tetradecanoic acid	0.0376	0.7344	0.0430	0.8002	0.171–0.53
Hexadecanoic acid	0.1472	2.8712	0.0978	1.8211	1.032–5.522
Octadecenoic acid	0.1250	2.4382	0.1311	2.4403	0.861–24.12
Octadecadienoic acid	0.0901	1.7575	0.0940	1.7499	NA
Octadecanoic acid	0.0427	0.8320	0.0699	1.3005	0.25–2.567
Nonadecanoic acid	0.0297	0.5800	<0.0002	<0.0004	0.017–0.31
Eicosanoic acid	0.0378	0.7365	0.0446	0.8297	0.107–1.6
Heneicosanoic acid	0.0324	0.6327	<0.0002	<0.0004	0.033–0.401
Docosanoic acid	0.0887	1.7298	0.0626	1.1647	0.173–4.7
Tricosanoic acid	0.0311	0.6064	<0.0002	<0.0004	0.028–1.092
Tetracosanoic acid	0.1289	2.5149	0.0494	0.9199	0.166–9.876
Hexacosanoic acid	0.0307	0.5997	0.0200	0.3722	0.016–3.6
Octandioic acid	0.0231	0.4508	0.0071	0.1328	0.049–0.35
Nonandioic acid	0.0574	1.1202	0.0185	0.3438	0.092–0.749
Abietic acid	<0.0002	<0.0004	0.8054	14.9923	0.82–33
Syringol	0.4023	7.8471	<0.0002	<0.0004	0.04–15.35

^aAnalytical uncertainty was in the range of 5–10% rel.^bRange of compound-concentrations from Fine et al. (2001, 2002, 2004a, b).

3.5. Deriving the macro-tracer factors

As mentioned in the introduction the macro-tracer concept uses single chemical species for each source type to calculate their contribution to ambient values. Therefore the factors for calculating the mass

of an individual source material in an ambient PM sample need to be established experimentally. A suitable composite factor for Austrian woodsmoke is

$$F_W = 100 / \{c_{\text{beech}} \times 4.1 + c_{\text{oak}} \times 13.3 + c_{\text{spruce}} \times 10.7 + c_{\text{larch}} \times 15.1 + c_{\text{briquettes}} \times 10.1\}, \quad (2)$$

where F_W is the factor for converting levoglucosan to PM10 from wood smoke and c the relative contribution of wood type.

We calculate the factor F_W for two different cases:

In case 1 we use the information about wood types used for burning (59% softwood, 41% hardwood) and integrate the relative numbers for timber felled in Austrian forests to each of the classes “softwood” and “hardwood.” Further we assume 10% of spruce burned in the form of briquettes. This results in a beech/oak/spruce/larch/briquette combination of 32/9/50/4/5%. Applying Eq. (2), we obtain a F_W factor of 11.2.

In case 2 we omit larch and oak because they are not frequently used as fuel wood. Further, we assume 10% of the fuel used as briquettes. Considering levoglucosan/mannosan ratios found in ambient air at different sites in Austria (see Section 3.2) we calculate the factor for a combination of 20/70/10% (beech/spruce/briquettes) resulting in a F_W of 10.7.

The obtained F_W values of 10.7 and 11.2 for two different wood type scenarios are very close and describe the range expected for mid-European Alpine regions. However, based on personal observations case 2 appears closer to the common use of fuel wood in Austria.

4. Conclusions

A sampling device has been designed and constructed for collecting PM10 woodsmoke samples from a wood-burning stove, which has permitted many samples to be collected, from burning different woods (beech, oak, spruce, larch and softwood briquettes). Experience has demonstrated that, for future work, a higher degree of dilution with clean, filtered air would permit samples to be collected over a longer period, e.g. a complete burning cycle.

The comparison of chemical profiles from this study with literature data showed that while there were qualitative similarities, the concentrations of metals, for instance, could be quite different. Likewise, the values for OC and EC differed considerably from literature values, which has confirmed the need to establish in-house profiles for mid-European Alpine wood species and not to import profiles from other continents. The inorganic and most organic components were not significantly different for the different woods, so

that one profile could be derived for CMB modelling.

The choice of the combustion apparatus—open fireplace or closed wood stove—has been reported to make a big difference (McDonald et al., 2000). However, the suggestion that four different profiles can be derived to cope with different woods and different ways of burning them, could not be validated, as the variability of the emission data, even under carefully controlled conditions, was such as to render these suggested differences insignificant. In this connection, the large number of tests and of individual analyses carried out has been shown to be valuable and necessary, in agreement with Jordan and Seen's (2005) findings.

The anhydrosugars are shown to be important for characterising woodsmoke emissions. They also permit estimates to be made, from the analysis of ambient PM samples, of the contribution from wood smoke, based on the levoglucosan level, and of the make-up of the smoke as derived from hardwood or softwood, based on the levoglucosan to mannosan ratio. Numerical factors are provided.

For the Austrian wood smoke sources the use of a 20/70/10% combined profile of beech, spruce and briquettes smoke is recommended, both for CMB modelling and the macro-tracer concept. This recommendation is based on the available information on popularity of firewoods in Austria, which suggests that these two wood types constitute the most important fuel wood types. The numerical factor of levoglucosan to PM10 is then 10.7, derived from a weighted average levoglucosan content of the wood smoke of 9.3% w/w. Preliminary results from ambient air levoglucosan to mannosan ratios at Austrian sites confirm the validity of the combination of woods as used for deriving the F_W factor.

Attention is drawn to the fact that retene, sometimes suggested as a tracer for wood smoke, appears to have a limited stability on the filters and so should be used only with caution.

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References

- Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management, 2005. Holzeinschlag 2004. A 1010 Vienna.
- Austrian Forest Inventory, 2000–2002. Austrian Federal Forest Office, Seckendorf Gudent Weg 8, A 1131 Vienna, Austria. <<http://web.bfw.ac.at/i7/owei.owei0002>>.
- 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 anionexchange high-performance liquid chromatography and pulsed amperometric detection. *Journal of Chromatography A*, in press, doi:10.1016/j.chroma.2007.09.038.
- DIN 52180 Part 1, 1977. Prüfung von Holz; Probenahme, Grundlagen. Deutsches Institut für Normung, Berlin.
- Fengel, D., Wegener, G., 2003. Wood—Chemistry, Ultrastructure, Reactions. Verlag Kessel, Remagen, p. 108.
- Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterisation of fine particle emissions from 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 characterisation of fine particulate emissions from the fireplace combustion of woods grown in the southern United States. *Environmental Science and Technology* 36, 1442–1451.
- Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004a. Chemical characterisation of fine particulate emissions from the fireplace combustion of woods grown in the midwestern and western United States. *Environmental Engineering Science* 21, 387–409.
- Fine, P.M., Cass, G.C., Simoneit, B.R.T., 2004b. Chemical characterisation of fine particle emissions from the wood stove combustion of prevalent United States tree species. *Environmental Engineering Science* 21, 705–721.
- Gelencser, A., 2005. Carbonaceous Aerosols, vol. 30. Kluwer Academic Publishers, Amsterdam.
- Hedberg, E., Kristensson, A., Ohlsson, M., Johansson, C., Johansson, P.-A., Swietlicki, E., Vesely, V., Wideqvist, U., Westerholm, R., 2002. Chemical and physical characterisation of emissions from birch wood combustion in a wood stove. *Atmospheric Environment* 36, 4823–4837.
- Hildemann, L.M., Markowski, G.R., Cass, G.R., 1991. Chemical composition of emissions from urban sources of fine organic aerosol. *Environmental Science and Technology* 25, 744–759.
- Johansson, L.S., Tullin, C., Leckner, B., Sjövall, P., 2003. Particle emissions from biomass combustion in small combustors. *Biomass and Bioenergy* 25, 435–446.
- Jordan, T.B., Seen, A.J., 2005. Effect of airflow setting on the organic composition of woodheater emissions. *Environmental Science and Technology* 39, 3601–3610.
- Jordan, T.B., Seen, A.J., Jacobsen, G.E., 2006. Levoglucosan as an atmospheric tracer for wood smoke. *Atmospheric Environment* 40, 5316–5321.
- Kunit, M., Puxbaum, H., 1996. Enzymatic determination of the cellulose content of atmospheric aerosols. *Atmospheric Environment* 30, 1233–1236.
- Limbeck, A., Handler, M., Neuberger, B., Klatzer, B., Puxbaum, H., 2005. Carbon-specific analysis of humic-like substances in atmospheric aerosol and precipitation samples. *Analytical Chemistry* 77, 7288–7293.
- McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2000. Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science and Technology* 34, 2080–2091.
- Olsson, M., Kjällstrand, J., Petersson, G., 2003. Specific chimney emissions and biofuel characteristics of softwood pellets for residential heating in Sweden. *Biomass and Bioenergy* 24, 51–57.
- Oros, D.R., Simoneit, B.R.T., 2001. Identification and emission factors of molecular tracers in organic aerosols from biomass burning. Part 1: Temperate climate conifers. *Applied Geochemistry* 16, 1513–1544.
- Puxbaum, H., 1979. Thermo-Gasanalysator zur Charakterisierung von Kohlenstoff und Schwefelverbindungen in luftgetragenen Stäuben. *Fresenius Zeitschrift für Analytische Chemie* 298, 250–259.
- Schauer, J.J., Cass, G.C., 2000. Source apportionment of wintertime gas-phase and particle-phase 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 emissions from air pollution sources. 3. C1–C29 organic compounds from fireplace combustion of wood. *Environmental Science and Technology* 35, 1716–1728.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.C., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30, 3837–3855.
- 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., Hitznerberger, 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.
- Shafizadeh, F., 1968. Pyrolysis and combustion of cellulosic materials. *Advances in Carbohydrate Chemistry* 23, 419–474.
- Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning

- and atmospheric particles. *Atmospheric Environment* 33, 173–182.
- Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, K., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., Didyk, B.M., 2004. Sugars—dominant water-soluble organic compounds in soils and characterisation as tracers in atmospheric particulate matter. *Environmental Science and Technology* 38, 5939–5949.
- Watson, J.G., 1984. Overview of receptor model principles. *Journal of Air Pollution Control Association* 34, 619–623.