

Chemical characterisation of particle emissions from burning leaves

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ABSTRACT

Particulate matter emissions (PM₁₀) from open-air burning of dry leaves were sampled and analysed for a series of organic and inorganic species, including carbon fractions, anhydrosugars, humic-like substances (HULIS), water-soluble ions, metals and organic trace components. The study was performed to investigate whether open-air burning of leaves in rural areas is a potential source of high amounts of unexplained organic matter (OM) in ambient PM. Results of the carbon analysis indicated that the amount of OM, more than 90% of emitted PM₁₀, is significantly higher in smoke from leaves than from wood burning [Schmidl, C., Marr, I.L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008. Chemical characterization of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmospheric Environment* 42, 126–141, till now considered as the main combustion source of organic PM used in source apportionment. While the proportion of total carbon (TC), 67% of PM₁₀, is very similar to that in wood smoke, the make-up of the total carbon is different. In wood smoke, levels of elemental carbon (EC) equivalent to soot, of around 20% were found, however in leaf smoke EC was very low, between 0 and 10% depending on the analytical methodology. In addition chemical markers were identified that permit the discrimination of wood smoke from leaf smoke in ambient PM samples. In particular the levels of anhydrosugars, sugar alcohols, PAH and *n*-alkanes in leaf smoke differ significantly from those in wood smoke. The ratios of levoglucosan to galactosan and benzo[*a*]pyrene to tetracosane differ by an order of magnitude between smoke of leaf burning and that of typical mid-European firewood (Schmidl et al., 2008). Furthermore sugar alcohols were found in notable concentrations in leaf burning samples, which were not found in wood smoke. Complete chemical profiles for leaf burning as a particulate matter source are presented here, including organic trace compounds to be used in source apportionment studies either by the chemical mass balance (CMB) or the macrotracer approach.

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1. Introduction

The countries of the EU, and many other countries worldwide, have adopted air quality standards for PM₁₀ particulate matter in ambient air. In particular

the short time standard for PM₁₀ of 50 µg m⁻³, with an allowed 35 exceedances per year, set by the EU (EU-Directive 1999/30/EG) is violated in many densely settled regions all over Europe (Van Dingenen et al., 2004).

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For an effective reduction of the elevated PM levels a knowledge of the source contributions to the PM₁₀ levels is essential. Thus, most advanced aerosol source receptor models require the a priori knowledge of the composition of the major sources of the atmospheric aerosol (e.g. Schauer et al., 1996; Schauer and Cass, 2000; Watson, 1984).

An important source namely in rural areas in the cold season is biomass fuel combustion (Lanz et al., 2008). Source profiles for mid-European wood types have recently been reported (Schmidl et al., 2008). However, biomass combustion tracers, such as levoglucosan, have been found to exhibit non-negligible levels also during the warm season at rural European sites (Puxbaum et al., 2007). Candidates for the warm season sources of wood smoke tracers are forest fires (Pio et al., 2007; Ward et al., 2006), and combustion of garden, agricultural and forestry waste (e.g. Hays et al., 2002; Engling et al., 2006; Iinuma et al., 2007a). Common to all the above mentioned biomass combustion sources is the different composition of the biomass compared to that from wood combustion in stoves and fireplaces. Straw, foliar material and twigs exhibit a distinctly different chemical emission pattern compared to wood logs (e.g. Hays et al., 2004; Iinuma et al., 2007a; Ward et al., 2006), and tracer/PM relationships are also different for dung, straw, and foliar material, and small branches as compared to logs (Sheesley et al., 2003).

Although not allowed in many European countries, open-air combustion of garden waste – cut material and leaves – is very widespread, in particular during autumn and spring. In addition, agricultural fires from burning of field residues are common in the eastern European countries as can be seen by the MODIS fire pixel detection system (e.g. Lukács et al., 2007).

Here we report emission profiles from an open-air garden waste combustion experiment. Foliar material common in mid-European gardens has been burned as is common during autumn or spring garden cleaning. We find that EC/OC ratios are distinctly different for smoke from foliar material as compared to that from wood logs and that the galactosan/levoglucosan ratio can be used to discriminate between organic combustion emissions from foliar material and from wood log combustion.

2. Experimental

2.1. Source sampling

Source sampling of leaf burning smoke was performed in a garden in a small village in Lower-Austria. For the burning test heaps of dry leaves were formed with diameter around 1 m at the bottom and height 50 cm. A mixture of pear (*Pyrus communis*), walnut (*Juglans regia*) and birch (*Betulus pendula*) leaves with an average moisture content of 25% (dry basis) was used. All three wood types are very common in the backyards of rural regions in eastern Austria. For both tests a similar amount of fuel was applied ($\sim 0.13 \text{ m}^3$) and the mixture of leaf types was approximately in same volumetric parts (1:1:1)

according to personal communication to local inhabitants performing the burn. Sampling was performed using a commercial low-volume PM₁₀ sampling head (Digital AG, Switzerland) placed beside the heap directly in the smoke plume. After the separation of particles in the sampling head, working on the principle of a single-stage impactor, the sample gas was drawn through eight polycarbonate filter holders (Pall Life Sciences) running simultaneously in parallel, equipped with six quartz fibre filters (Tissuequartz 47 mm, Pall Life Sciences) and two mixed cellulose ester filters (GN-4 Metrical 47 mm, Pall Life Sciences). Quartz filters were used for organic analyses and determination of total particulate mass while cellulose ester filters were used for metal analyses with XRF and ICP-OES.

The gas flow through the filters was regulated and balanced with needle valves to give a total flow of $2.3 \text{ m}^3/\text{h}$, measured with a rotameter after the pump, which is the required flow for PM₁₀ sampling head. Total gas volumes were measured with dry gas meters. Each sample was taken over the whole burning process. Sampling was started just before ignition and concluded after complete burn down indicated by no further visible smoke emissions. Average sampling time was 45 min per sample.

2.2. Analytical methods

2.2.1. 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 ($20 \pm 1 \text{ }^\circ\text{C}$, $50 \pm 5\% \text{ r.h.}$). For analysis of ions and carbon species, small discs, with 8 or 10 mm diameter, were stamped out of the quartz fibre filters tissues with steel punches. For the determination of trace metals by XRF and then by ICP-OES, the whole cellulose ester filters were used.

2.2.2. 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).

2.2.3. Cations

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

2.2.4. Cellulose

After elution of quartz fibre filters with a 0.05 M citric acid solution (pH = 4.8), in an ultrasonic bath and hydrolysis 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 by Puxbaum and Tenze-Kunit (2003).

2.2.5. Carbon

TC – total carbon, was determined by combustion of all material on the filter, in oxygen, at 1000 °C and measurement of the resulting CO₂ 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). Additionally samples were analysed with a modified thermal-optical transmission, linear temperature program (TLT) method (Puxbaum, 1979, Method no. 9b in Schmid et al., 2001; Jankowski et al., 2008) and an integrating sphere method (Hitzenberger et al., 1996; Reisinger et al., 2008). Fig. 1 gives an example for results obtained from TLT analysis.

CC – carbonate carbon, was determined by the TLT – method as the last peak evolving from the decarboxylation of carbonates at temperatures higher than 550 °C.

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

BrC – brown carbon, was determined by an integrating sphere method mentioned by Reisinger et al. (2008) using a modification of the integrated sphere method for discriminating black and brown carbon.

2.2.6. Humic-like substances – HULIS

Particulate matter 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 solid phase extraction (SPE) with a size-exclusion solid phase (ISOLUTE C18), followed by a further clean-up step using an anion-exchange column (ISOLUE SAX) in a flow-injection system. The organic material eluting was quantified by on-line total organic carbon (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 by Limbeck et al. (2005).

2.2.7. Anhydrosugars

The determination of levoglucosan and other anhydrosugars including mannosan and galactosan was carried out by high performance liquid chromatography (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).

2.2.8. Metals

Cellulose acetate filters were analysed on a Philips X'Unique II (model 1480) wavelength-dispersive X-ray fluorescence (XRF) spectrometer. The 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 has been used.

After XRF – analysis cellulose acetate filters were digested in *aqua regia* with the addition of a 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 (for As, Sb) (Handler et al., 2008).

2.2.9. Apolar organics

Organic trace components were extracted with two 5 mL portions 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 gas chromatography/mass spectrometry (GC/MS) using a HP-6890 gas chromatograph connected to a HP-5973 mass spectrometer. The gas chromatograph was 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. The mass spectrometer was operated in the electron ionisation mode (70 eV) and in the ion-scan mode. A detailed description of the methodology is given in Kotianova et al. (2008).

2.2.10. 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 gas chromatography system, running with a capillary column (95% dimethyl-, 5% phenylsiloxane, 30 m × 0.25 mm ID × 0.25 µm film) in splitless mode. The gas chromatograph is connected to a Hewlett-Packard mass spectrometer HP-5971-A operated in the electron ionisation mode (70 eV) and in the ion-scan mode.

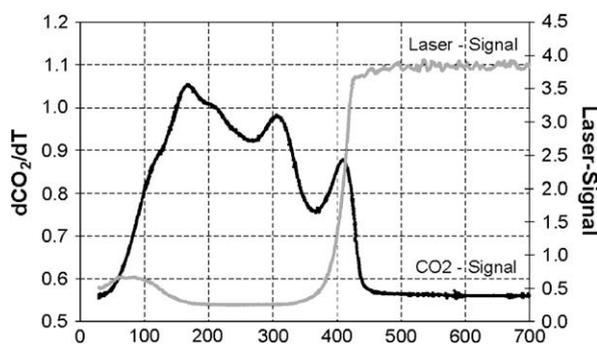


Fig. 1. Thermogram of leaf smoke sample.

3. Results and discussion

3.1. Carbon fractions

The total carbon (TC) levels in the samples collected from the two leaf-burning experiments were 67.8 and 66.5% of total PM₁₀, similar to results for the combustion of wood logs in small stoves and in fireplaces (Schauer et al., 2001; Fine et al., 2004b; Schmidl et al., 2008). Analysis of the carbon fractions OC and EC was done with two different methods: the method described by Cachier et al. (1989) using a two-step oxidation, and a thermo – optical analysis, using a laser transmission signal (TLT). While there are small quantitative differences, both methods give similar result (methods no. 9b and 17 in Schmid et al., 2001; “TOM-TU” and “Cachier” in Reisinger et al., 2008). Carbonaceous fractions in the samples consist mostly of organic carbon. EC levels, indicating soot, are in fact very small. Fig. 1 displays a TLT thermogram including the CO₂ and the laser signals for EC peak identification for a leaf-burning sample.

The thermogram shows high amounts of organic compounds, giving signals between 50 and 350 °C. The EC peak, indicated by a steep rise in the laser signal at around 400 °C, is relatively well separated from the organic fractions. The laser signal gives additional information about charring effects of organic compounds. In the case of the leaf-burning samples charring occurs at relatively low temperatures (~150 °C) leading to a decrease in the laser signal after an initial rise caused by the release of the more volatile organic compounds.

For correction of charring the laser signal is used to start the integration of the EC peak at that temperature where the laser signal reaches the same level as at the beginning of the analysis. For both samples this leads to very low soot contents lying at 5–10% of total carbon. EC analysis following the method by Cachier et al. (1989) gives lower amounts of 1–2% EC. This difference can be explained by the low oxidation temperature of biomass soot which causes a part of the biomass-EC to be removed during the 2 h pre-treatment at 340 °C (Cachier et al., 1989). No carbonate signals were observed, which, if present, would be expected to occur at 550–650 °C.

In addition, the samples were analysed with an optical integrating sphere method (Reisinger et al., 2008), which quantifies black and brown carbon. Results indicated no black carbon (BC) content in the leaf burning samples but high brown carbon amounts accounting for 18.5% of PM₁₀. It is well known in the EC/OC scientific community that results from carbon analysis are highly method-dependent (e.g. Schmid et al., 2001; Reisinger et al., 2008). We also observed differences between results from the methods used for EC, and for BC, in the analysis of the leaf smoke samples. EC (BC) levels reach 5–10% measured with TLT analysis compared to 0% from the integrating sphere method, with thermal method (Cachier et al., 1989) results (1–2%) lying in between. This mainly reflects the different analytical approaches using either thermal or optical properties of carbonaceous compounds. Considering this the importance of reporting the analytical methodology together with every result becomes obvious.

We conclude that all carbon analysis methods give high organic carbon contents (90–100% OC of TC and 86–99% OM of PM₁₀ respectively using a conversion factor OM/OC of 1.5) in leaf smoke samples which therefore have significant higher OC and OM values as wood combustion, the main combustion source in Austria (wood: 60–85% OC of TC, Schmidl et al., 2008). Burning of leaves may therefore result in regional short time increase of ambient organic matter levels that the presumption that high organic matter levels in ambient PM₁₀ may be due to burning of leaves especially in spring and in autumn, could be confirmed by the results from different carbon analysis methods. Organic matter, calculated as the difference between TC and EC multiplied with a factor of 1.5 (OC to OM conversion factor), could account for 86–99% of PM₁₀, since the EC value depended on the method used and lay in the range 1–10% of PM₁₀ (Schmidl et al., 2008).

3.2. Saccharides

Levoglucosan, mannosan and galactosan were found in notable concentrations (0.4–2% w/w) in both leaf combustion samples (Table 1). As expected levoglucosan, a major by-product from the pyrolysis of cellulose (Shafiqzadeh, 1968) and a specific marker for wood combustion in ambient PM samples (Simoneit et al., 1999; Jordan et al., 2006), was the most abundant organic compound. Compared to wood combustion smoke the levoglucosan emissions relative to PM tend to be a little lower in the leaf smoke samples. In a recent study concentrations of 4–15% levoglucosan in smoke PM of common mid-European wood types (Schmidl et al., 2008) were reported. In the same study mannosan, another anhydrosugar emitted during pyrolyses of cellulosic material, was found to be a useful compound for distinguishing between soft- and hardwood combustion. Mannosan is formed in the pyrolysis of hemicelluloses containing mannose, which occur mainly in conifers. Biomass smoke PM from conifers contains around five times higher concentrations of mannosan than smoke PM from deciduous trees (Schmidl et al., 2008). The mannosan level of around 0.4% found in leaf smoke PM₁₀ is very similar to that from hardwood log combustion reported by Schmidl et al. (2008).

Galactosan is the third important anhydrosugar usually found in biomass smoke. Like mannosan it is formed during pyrolysis of hemicelluloses. Concentrations of galactosan found in wood smoke are scattered over a wide range reaching from 0–1.9% of PM_{2.5} (Fine et al., 2001) to 0.2–4.5% of PM₁₀ (Schmidl et al., 2008). Mostly they are around 10–50 times lower than those of levoglucosan and one to three times lower than mannosan levels. In the case of leaf smoke, however, PM galactosan constitutes the second most abundant organic compound yielding 1.4–1.9% of the emitted PM₁₀ (see Table 1) and is even close to the levoglucosan concentrations. Expressed as a factor levoglucosan/galactosan the difference to wood smoke becomes even more apparent. In wood smoke this ratio was around 13 for mid-European wood types (recommended average from Schmidl et al., 2008) and even higher for North American wood types with factors of 20–50 (Fine et al., 2001, 2002, 2004a,b). In the leaf smoke samples

Table 1

PM10 emission concentrations of organic and inorganic compounds from leaf burning tests with additional reference data from wood combustion

Compound	Analysis	Burn1	Burn2	Wood ^a	Compound	Analysis	Burn1	Burn2	Wood ^a
<i>Carbon species</i>									
Elemental carbon	T	2.60	1.71	21.3	Brown carbon	IS	18.2	18.7	NA
Elemental carbon	TLT	6.40	10.5	NA	Organic carbon	T	65.2	64.8	51.9
Black carbon	IS	ND	ND	NA	Organic carbon	TLT	61.4	56.0	NA
<i>Metals</i>									
Calcium total	ICP-OES	0.143	0.378	NA	Nickel	ICP-OES	<0.0004	0.0002	0.0116
Magnesium total	ICP-OES	0.006	0.022	0.0716	Copper	ICP-OES	<0.0001	<0.0001	0.0285
Aluminium	XRF	0.011	0.024	0.0202	Zinc	ICP-OES	0.0251	0.0148	0.0790
Silicon	XRF	0.022	0.036	0.0644	Arsenic	AAS	<0.0010	<0.0015	<0.0010
Titanium	ICP-OES	<0.0001	<0.0001	0.0060	Strontium	ICP-OES	0.0002	0.0006	0.0018
Vanadium	ICP-OES	<0.0001	<0.0001	0.0014	Cadmium	ICP-OES	<0.0005	<0.0003	0.0045
Chromium	ICP-OES	0.0157	0.0380	0.0367	Tin	ICP-OES	0.0013	0.0034	<0.008
Manganese	ICP-OES	<0.0001	<0.0001	0.0156	Antimony	AAS	0.0005	0.0033	<0.001
Iron	ICP-OES	0.0079	0.0151	0.0493	Barium	ICP-OES	0.0003	0.0008	0.0037
Cobalt	ICP-OES	<0.0029	<0.0015	<0.003	Lead	AAS	0.0015	0.0025	0.0028
<i>Ionic species</i>									
Ammonium	IC	0.198	0.132	0.118	Sulfate	IC	0.211	0.225	0.195
Sodium soluble	IC	0.0050	0.0050	0.0334	Formate	IC	0.391	0.482	0.168
Magnesium soluble	IC	0.0120	0.0160	0.0057	Acetate	IC	0.238	0.217	0.543
Potassium soluble	IC	0.6200	0.8850	0.174	Malonate	IC	0.0170	0.0090	0.0133
Calcium soluble	IC	0.0550	0.0860	0.0499	Malate	IC	0.0680	0.0830	0.109
Carbonate	TLT	ND	ND	ND	Maleate	IC	0.205	0.233	0.0067
Nitrate	IC	0.0250	0.0190	0.0742	Oxalate	IC	0.0860	0.0870	0.0907
Chloride	IC	0.255	0.353	0.1400					
<i>Anhydrosugars, sugars, cellulose</i>									
Xylitol	HPLC	<0.001	<0.001	<0.001	Arabitolose	HPLC	0.0100	0.0170	<0.005
Arabitol	HPLC	0.138	0.142	<0.005	Galactose	HPLC	<0.01	<0.01	<0.01
Levoglucofan	HPLC	2.12	2.14	9.32	Glucose	HPLC	0.0130	0.0200	0.0182
Sorbitol	HPLC	0.230	0.270	<0.01	Mannose	HPLC	<0.01	0.0170	<0.005
Mannitol	HPLC	<0.005	0.008	<0.005	Fructose	HPLC	<0.01	0.0260	0.0010
Mannosan	HPLC	0.412	0.359	2.56	Sucrose	HPLC	<0.01	<0.01	<0.01
Galactosan	HPLC	1.45	1.93	0.723	Cellulose	Enz-Ph	0.194	0.331	0.0790
<i>Humic-like substances</i>									
HULIS	FI-DOC	21.2	18.5	1.63					
<i>Organic acids</i>									
Hexanoic acid	GC-MS	0.0146	0.0177	0.0004	Octadecanoic acid	GC-MS	0.164	0.172	0.117
Heptanoic acid	GC-MS	0.0321	0.0298	NA	Nonadecanoic acid	GC-MS	0.0328	0.0099	0.0059
Octanoic acid	GC-MS	0.0298	0.0280	0.0019	Eicosanoic acid	GC-MS	0.0712	0.0576	0.0388
Nonanoic acid	GC-MS	0.0221	0.0179	0.0009	Heneicosanoic acid	GC-MS	0.0227	0.0269	0.0065
Decanoic acid	GC-MS	0.0154	0.0141	0.0044	Docosanoic acid	GC-MS	0.0710	0.0612	0.0616
Undecanoic acid	GC-MS	0.0061	0.0060	NA	Tricosanoic acid	GC-MS	0.0288	0.0228	0.00622
Dodecanoic acid	GC-MS	0.0453	0.0408	0.0137	Tetracosanoic acid	GC-MS	0.0535	0.0494	0.0604
Tridecanoic acid	GC-MS	0.0047	0.0043	NA	Pentacosanoic acid	GC-MS	0.0160	0.0144	NA
Tetradecanoic acid	GC-MS	0.121	0.119	0.0376	Hexacosanoic acid	GC-MS	0.0615	0.0502	0.0201
Pentadecanoic acid	GC-MS	0.0171	0.0158	NA	Pentanedioic acid	GC-MS	0.0207	0.0306	NA
Hexadecanoic acid	GC-MS	0.547	0.519	0.0979	Nonanedioic acid	GC-MS	0.0306	0.0228	0.0244
Heptadecanoic acid	GC-MS	0.0144	0.0141	NA					
<i>Alkanes</i>									
Eicosane	GC-MS	0.0110	0.0081	0.0010	Hexacosane	GC-MS	0.0206	0.0341	0.0008
Heneicosane	GC-MS	0.0208	0.0155	0.0006	Heptacosane	GC-MS	+	+	0.0008
Docosane	GC-MS	0.0224	0.0262	0.0007	Octacosane	GC-MS	0.0313	0.0280	<0.0001
Tricosane	GC-MS	0.0380	0.0280	0.0010	Nonacosane	GC-MS	+	+	<0.0001
Tetracosane	GC-MS	0.0349	0.0335	0.0020	Triacontane	GC-MS	0.0488	0.0273	<0.0001
Pentacosane	GC-MS	0.0142	0.0437	0.0004	Hentriacontane	GC-MS	0.0417	+	<0.0001
<i>PAH</i>									
Benzo[de]anthracen-7-one	GC-MS	<0.005	<0.003	0.0086	Benzo[j]fluoranthene	GC-MS	0.0017	0.0015	NA
Retene	GC-MS	<0.001	<0.001	0.0207	Benzo[ghi]perylene	GC-MS	0.0014	0.0016	0.0107
Benzo[a]pyrene	GC-MS	0.0017	0.0024	NA	Dibenz[ah]anthracene	GC-MS	<0.002	<0.002	NA
Benzo[e]pyrene	GC-MS	0.0017	0.0018	0.0088	Coronene	GC-MS	0.0015	0.0015	0.0050
Benzo[k]fluoranthene+									
Benzo[b]fluoranthene	GC-MS	0.0034	0.0041	NA					

All values are given as % of total mass. List of abbreviations: T, thermal; TLT, thermal-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; ND, not detected; NA, not analysed; +, present but quantification not possible.

^a Recommended wood combination (70% spruce, 20% beech, 10% briquettes) values from Schmidl et al. (2008).

analysed the levoglucosan/galactosan ratios are 1.46 and 1.12 respectively. In source apportionment studies this difference in the levoglucosan/galactosan ratio may help to identify PM10 pollution events influenced by leaf burning emissions. A comparison of levoglucosan/galactosan ratios with reference data for other combustion sources and ambient data is shown in Table 2.

The sugar alcohols arabitol and sorbitol were found in relatively high concentrations in leaf smoke samples yielding around 0.14% (arabitol) and 0.25% (sorbitol) of the PM10. The former polyol is found in fungi, serving as storage-carbohydrate (Bauer et al., 2008), while the latter is found in the leaves and fruit of higher plants of the Rosaceae family (Lewis and Smith, 1967). Fungi are important micro-organisms involved in the decomposition processes of leaves and are together with algae constituents of lichens. Therefore, the abundance of arabitol and sorbitol in the leaf combustion PM is much higher than in log combustion. In the leaf combustion tests arabitol and sorbitol concentrations were in a comparable range to the anhydrosugar mannosan, which is not the case in smoke from wood log biomass, where levels of sugar alcohols usually are found to be very small, mostly under the limit of detection.

Glucose, a primary sugar, has also been detected in the leaf smoke samples, but at very low levels – around 1/100 of the levoglucosan concentrations.

Considering these facts the results of this study suggest the use of levoglucosan as a tracer for biomass burning in general and the levoglucosan to galactosan ratio together with arabitol and sorbitol concentrations to identify the

contribution of leaf burning on high organic matter levels in ambient air.

3.3. Humic-like substances (HULIS)

The term HULIS in aerosol chemistry is used for a class of substances behaving chemically, like the high molecular weight water-extractable components found in soils. The origin and formation pathways of such material are still under investigation, results from recent studies show that these substances arise as secondary aerosol products from atmospheric processes with volatile organic compounds (VOC) as precursors (Surratt et al., 2007, 2008; Iinuma et al., 2007b; Reinnig et al., 2008). However, as HULIS are also found in emissions from wood combustion (Schmidl et al., 2008) there may be a connection to this source, especially in winter. In leaf-burning samples analysed HULIS were found in very high concentrations, forming 18.5–21.2% of PM10, ten times higher than in wood combustion samples reported by Schmidl et al. (2008). This therefore verifies the assumption that beside the secondary formation path HULIS can also be emitted as primary particles.

3.4. Metals

As in particulate matter emitted from other incomplete combustion sources inorganic compounds do not play an important role in the chemical composition profile of leaf-burning samples. The most abundant metal species was calcium constituting 0.14–0.38% of PM10. All other metals found were only in very low concentrations, all lower than

Table 2

Comparison of selected compound ratios (OC/PM, OC/TC, levoglucosan/galactosan, benzo[a]pyrene/tetracosane) of different types of biomass smoke and ambient aerosols

Fuel type	Reference	OC/PM	OC/TC	Lev/Gal ^a	BaP/C24 ^a
<i>Foliar/agricultural fuels</i>					
Garden leaves	This study	0.65	0.97	1.3	0.06
Mixed hardwood forest foliage	Hays et al., 2002	0.79	0.98	n.a.	0.04
Other foliar fuels	Hays et al., 2002	0.69–0.83	0.94–0.99	n.a.	0.09–0.49
Grass, needles, duff	Engling et al., 2006	n.a.	n.a.	2.5–108	n.a.
Rice and wheat straw	Hays et al., 2005	0.26–0.69	0.70–0.98	n.a.	0.14–1.18
Agricultural/foliar fuels	Sheesley et al., 2003	0.48–0.56	0.81–0.99	25–36	n.a.
<i>Wood</i>					
Wood (logs and briquettes)	Schmidl et al., 2008	0.41–0.56	0.57–0.85	3.4–31	3.0 ^b
Wood (logs)	Engling et al., 2006	n.a.	n.a.	5.3–158	n.a.
Wood (logs)	Fine et al., 2004b	0.44–0.78	0.72–0.94	17–82	0.81–6.1
Wood (logs)	Fine et al., 2004a	0.67–1.0	0.71–0.99	14–84	0.69–5.2
Briquettes	Sheesley et al., 2003	0.55	0.98	35	n.a.
Wood (logs)	Fine et al., 2002	0.74–1.0	0.85–0.98	45–53	1.2–7.4
Wood (logs)	Fine et al., 2001	0.73–1.1	0.70–0.96	32–48	1.3–16
Wood (logs)	Schauer et al., 2001	0.44–0.59	0.94–0.98	n.a.	0.98
<i>Forest/biomass fires</i>					
Montana	Ward et al., 2006	n.a.	n.a.	9.5–16	n.a.
Maine	Medeiros et al., 2006	n.a.	n.a.	21–49	n.a.
Amazonia	Graham et al., 2002	n.a.	0.95	44–52	n.a.
<i>Austrian ambient data: Styria 2004 (three-site-averages)</i>					
Easter bonfire	Bauer et al., 2007	0.38	0.82	8.1	0.12
April average without bonfire	Bauer et al., 2007	0.17	0.63	23	0.45
Winter (DJF) average	Bauer et al., 2007	0.22	0.69	16	0.53

^a Lev, levoglucosan; Gal, galactosan; BaP, benzo[a]pyrene; C24, tetracosane; n.a., not available.

^b BaP not available, benzo[e]pyrene was used instead.

0.1%. Therefore metal levels in leaf smoke are in a similar range as in wood smoke so that they do not reveal any useful markers to distinguish between those particulate sources. Results from metal analyses are presented in Table 1.

3.5. Extractable ions

Just as in the case of metals, also ionic species are not major compounds in leaf smoke. Among the inorganic ions potassium was the most abundant with a relative concentration of 0.6–0.9% of PM₁₀, around a factor of 2 higher than the range found for smoke from wood log combustion (Schmidl et al., 2008). Organic ions, in particular formate, acetate and maleate, each accounting for more than 0.2% of PM₁₀, are relatively high compared to smoke from other combustion sources. However, their use for source apportionment may be limited to their poor atmospheric stability, their volatility and lack of information on their levels in particulates from some sources. In particular the low molecular weight organic acids generally occur predominantly in the gas phase (e.g. Keene et al., 1989).

3.6. Trace organic compounds

Organic trace analyses were performed to complete the chemical profiles for source apportionment studies using either the CMB or other tracer concepts. In both chromatograms – for carboxylic acids and for apolar organics – broadened and overlapping peaks as well as a rise in the baseline, in chromatography commonly referred to as and “unresolved complex mixture” (UCM), was observed (see Figs. 2 and 3). Originally this was described in the gas chromatography of petroleum (e.g. Fryzinger et al., 2003) and in emissions from combustion of petroleum products, such as traffic (Rogge et al., 1993). Furthermore Hays et al. described similar results for residential wood combustion (Hays et al., 2004) and for residential oil-fired boiler emissions (Hays et al., 2008). Nevertheless quantification of most organic tracers was possible even though the uncertainties are a little higher. Results are presented in Table 1.

Carboxylic acids were found in notable concentrations showing a typical pattern for samples from biological origin with high abundances for even carbon numbers and low abundances for uneven carbon numbers. Palmitic acid (hexadecanoic acid), indicated as peak number 11 in the total ion current (TIC) chromatogram shown in Fig. 2, was the most abundant compound constituting 0.53% of PM₁₀, followed by stearic acid (octadecanoic acid, peak number 13) with 0.17% and myristic acid (tetradecanoic acid, peak number 9) with 0.12%. These results are in good agreement with literature data for emissions from mixed hardwood forest foliage (MHFF) from Hays et al. (2002). Compared to Austrian data for woodstove emissions (Schmidl et al., 2008) organic acid levels in leaf smoke tend to be around a factor of 2–5 higher than in emissions from small stoves. Unsaturated carboxylic acids oleic (octadecenoic acid) and linoleic acid (octadecadienoic acid,) indicated as peaks 27 and 28 in Fig. 2 were also found to be elevated, but as they are co-eluting, resulting in overlapping peaks, quantification was not possible. Similar problems but in lower concentration ranges were observed for syringol, a hardwood

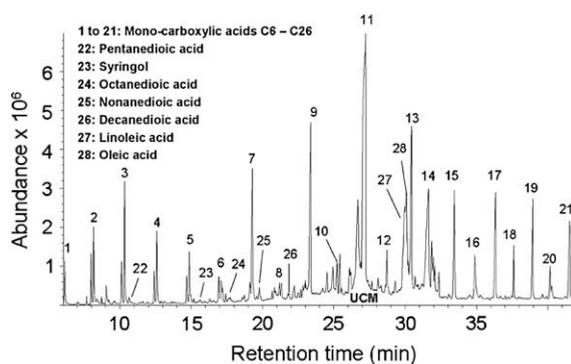


Fig. 2. GC-MS chromatogram (TIC) of carboxylic acids.

tracer, and the two dicarboxylic acids octanedioic and decanedioic acids (peak numbers 23, 24, 26 in Fig. 2).

Other apolar organic tracers, mainly *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs), were also determined in the leaf smoke samples (see Table 1). Different to smoke from other biomass combustion sources *n*-alkanes were found in much higher concentrations than were PAHs. The lower PAH levels are consistent with the results of low EC levels for those samples, in accordance with the structural relationship between soot and PAHs (e.g. Gelencser, 2004). In the chromatograms of apolar compounds the rise in the baseline due to the UCM is far more marked than in the chromatogram for polar compounds. As shown in Fig. 3 the UCM constitutes more than 90% of the total chromatogram area. Of the single analysed species C₂₃–C₂₅ each constituting around 0.03% of total PM₁₀, together with C₃₀ (around 0.04% of PM₁₀) were found to be most abundant. Heptacosane (C₂₇), nonacosane (C₂₉) and hentriacontane (C₃₁) also gave high signals (see Fig. 3) but were not quantified due to broadened peaks, probably resulting from co-eluting isomers. PAHs were found at much lower concentrations – more than one order of magnitude lower than *n*-alkanes – mostly constituting between 0.001 and 0.002% of PM₁₀. This gives another possibility for discriminating between leaf and wood smoke, where PAHs were found in noticeable concentrations (around 0.01% of PM₁₀) and *n*-alkanes levels were very low or below the limit of detection (Schmidl et al., 2008), a feature that may be

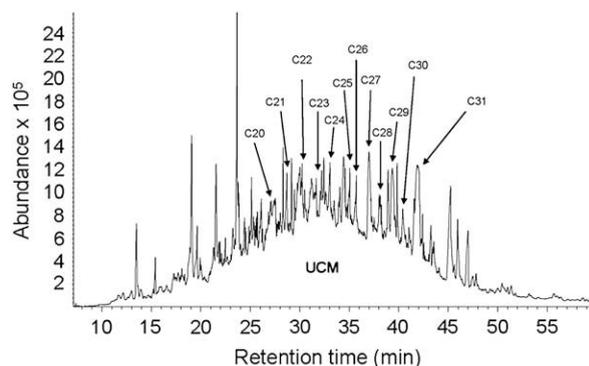


Fig. 3. GC-MS chromatogram (TIC) of apolar organic tracers.

scribed to the different temperatures reached in the oxidation zone in closed stoves (wood combustion) and open fires (leaves). At higher combustion temperatures *n*-alkanes seem to be less stable than PAHs. In addition it is important for source apportionment studies using the CMB model to know that besides road traffic, the main emitter, other combustion sources can also contribute significant amounts of *n*-alkanes to ambient PM levels. The PAH benzo[a]pyrene (BaP) and the *n*-alkane (C24) tetracosane represent typical compounds emitted by combustion sources (Fine et al., 2001; Hays et al., 2002). A comparison of BaP/C24 ratios for leaf burning with other combustion sources and ambient PM10 aerosol is presented in Table 2.

3.7. Comparison with ambient PM10 samples

In mid-Europe the predominant source of biomass smoke are appliances where the fuel is relatively well characterised (Schmidl et al., 2008). Open fires are not allowed, but are still observed on the countryside. On a few days (e.g. Holy Saturday before Easter, and summer solstice) the open fires are legal in Austria, thus we had “open access” to smoke from such burns.

Ambient PM10 samples data were compared for the winter average, the April average without bonfires and the average of bonfire days April 10–11, 2004 (averages from three sites in Styria) in Table 2. The ratio levoglucosan/galactosan dropped at three Styrian sites from 23 before and after to eight during the bonfires. While April average data without bonfire were comparable with winter averages for OC/PM, OC/TC, Lev/Gal, and BaP/C24; the results for the Easter bonfires showed an increase in relation to the other averages for the OC/PM, respectively OC/TC and a considerable decrease for Lev/Gal and BaP/C24 ratios; as expected for an increasing influence of leaf burning (Table 2).

4. Conclusions

This investigation has brought important information about differences in biomass smoke composition from burning leaves compared to combustion of wood in stoves. The chemical profiles for these fine particle sources seem to be sufficiently different that they can be used independently in source apportionment studies.

- The field test of open-air combustion of leaves was performed to represent burning of garden waste in mid-European gardens.
- Comparison of chemical profiles from this study with literature data showed best agreement with data been reported for smoke from mixed hardwood forest foliage litter (Hays et al., 2002) while there were quite big differences to other combustion emission sources. However, data for more compounds, notably for several saccharides, are reported here, which have not previously been mentioned for leaf smoke.
- Compared to emission profiles of mid-European wood types combusted in small stoves (Schmidl et al., 2008), the composition of leaf burning smoke shows higher

OC/TC ratios. The BaP/C24 and levoglucosan/galactosan ratios, however, are an order of magnitude lower in leaf smoke compared to wood smoke. Thus, OC/TC, Lev/Gal and BaP/C24 ratios may help to discriminate between biomass PM emissions from open-air burning of leaves and from burning of logs in small stoves.

- Levoglucosan occurs at lower concentrations in smoke from burning leaves compared to the levels found in wood smoke from small stoves, while the mannosan levels are similar for these two sources.
- Sugar alcohols typical for fungal biomass (arabitol) and leaf cells (sorbitol) were found in significant concentrations in the leaf smoke. As they are not common in wood smoke, they may also serve as tracers for leaf burning in ambient PM samples.
- In contrast to PM emissions from mid-European wood log combustion, the levels of *n*-alkanes were far higher, and of PAH far lower, in the leaf-burning smoke.
- Concentrations of organic acids were higher in leaf smoke than in wood combustion samples and exhibited the typical pattern for material from biogenic origin with high levels of even and low levels of uneven carbon number compounds.

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