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Chemical and physical characterization of emissions from birch wood combustion in a wood stove

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Abstract

The purpose of this study was to characterize the emissions of a large number of chemical compounds emitted from birch wood combustion in a wood stove. Birch wood is widely used as fuel in Swedish household appliances. The fuel load was held constant during six experiments.

Particles $<2.5\,\mu m$ in diameter were collected and the size distribution of the particles was measured. The results were compared to the size distribution in road traffic emissions. It could be seen that the number distribution differed between the sources. In traffic exhaust, the number of particles maximized at 20 nm, while the number distribution from wood burning ranged from 20 to 300 nm. The ratio K/Ca on particles was found to be significantly different in wood burning compared to road dust, range 30–330 for the former and 0.8 ± 0.15 for the latter. The source profile of common elements emitted from wood burning differed from that found on particles at a street-level site or in long-distance transported particles.

The ratio toluene/benzene in this study was found to be in the range 0.2–0.7, which is much lower than the ratio 3.6 ± 0.5 in traffic exhaust emissions.

Formaldehyde and acetone were the most abundant compounds among the volatile ketones and aldehydes. The emission factor varied between 180–710 mg/kg wood for formaldehyde and 5–1300 mg/kg wood for acetone. Of the organic acids analyzed (3,4,5)-trimethoxy benzoic acid was the most abundant compound. Of the PAHs reported, fluorene, phenanthrene, anthracene, fluoranthene and pyrene contribute to more than 70% of the mass of PAH. Of the elements analyzed, K and Si were the most abundant elements, having emission factors of 27 and 9 mg/kg wood, respectively.

Although fluoranthene has a toxic equivalence factor of 5% of benzo(a)pyrene (B(a)P), it can be seen that the toxic potency of fluoranthene in wood burning emissions is of the same size as B(a)P. This indicates that the relative carcinogenic potency contribution of fluoranthene in wood smoke would be about 40% of B(a)P.

Keywords: Particle size distribution; BTX; PAH; Wood combustion; Aldehydes; Ketones

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1. Introduction

In many areas throughout the world wood combustion is one of the most important sources of a large number of pollutants including benzene, toluene and xylenes (BTX), polycyclic aromatic hydrocarbons (PAHs), and particulate matter. Many of the substances released are classified as carcinogenic or have other serious health effects.

Today, every third Swedish home can be completely or partially heated by burning firewood. The Swedish emission of particles from wood combustion is estimated to be 8600–65,000 tons/yr, which can be compared to a total emission of 49,000–112,000 tons/yr (Areskoug et al., 2000). Wood combustion for residential heating can therefore be an important source of particles to the atmosphere but the uncertainty in estimated emissions can be at least one order of magnitude.

In Sweden, most wood combustion occurs in boilers constructed for multiple energy sources (oil, wood and electricity), and most of the residential furnaces used for wood burning are old installations from which emissions are several times larger than modern installations. According to an inventory of residential heating appliances in the city of Stockholm there are only about 60 furnaces for wood burning while there are several thousand installations for mixed energy sources (SRSA, 1998). Lately, wood stoves have increasingly come into use as an additional heating device, often in urban areas. In 1998, there were 38,000 fireplaces (stoves and the like) in Stockholm. The emission from small-scale wood stoves could be an important source of hydrocarbons and particulate matter in Stockholm and other large urban areas. However, there is very little data on emissions of pollutants from wood stoves.

The purpose of this work was to quantify and characterize the emission of hydrocarbons and particulate matter from a conventional wood stove. Birch wood was used as fuel throughout the samplings, since it is widely used as fuel in Swedish households. PAHs, BTX, organic acids, aldehydes and ketones were sampled and analyzed, as well as particle mass, number and size distribution, and elemental composition. Since the other main antropogenic source of most of the compounds reported here is road traffic emissions, the ratios of some key compounds are compared with the ratio found in traffic exhaust as measured in a road tunnel in central Stockholm.

2. Sampling and analysis

A commercial soapstone stove (Woodstock Fireview, USA, weight 220 kg, dimensions $0.72 \times 0.66 \times 0.51\,\mathrm{m}^3$) with a maximum fuel loading of 40 kg wood was used in the present investigation. The experimental sampling flow chart is schematically described in Fig. 1.

The flue gas air sampled from the duct was diluted with particle-free, dry compressed air (relative humidity $<5\%$). The dilution air had also passed through a charcoal filter to remove low-volatility hydrocarbons. The dilution air passed in a counter-flow arrangement through the outer concentric tube enclosing the sample flow tube. This meant that the sampled flue gases were gradually cooled to near room temperature, while the dilution air was heated to a temperature close to that of the flue gas itself. The point of dilution was placed immediately inside the hot flue gas pipe. For the occasions when particles were measured, the dilution ratio varied between 5 and 85, with typical values around 20–30.

The air flow rate through the stove was calculated by injecting sulfur hexafluoride (SF_6) as a tracer into the flue pipe at a controlled flow rate (E, g/h) about 1 m before the sampling point. The SF_6 concentration (C, g/m^3) was measured with a MIRAN 1B2 IR-spectrophotometer (Foxboro Instruments, Foxboro, MA, USA) and the total air flow rate (Afr, m^3/h) was then calculated as $\mathrm{Afr} = E/C$. A cyclone was used to remove particles $>2.5\,\mu\mathrm{m}$ in diameter, and the particle-associated measurements are therefore valid for PM2.5. The residence time of the sampled air in the sampling inlet (from the flue pipe to the flow splitter leading to the various instruments) was typically 2 s. The flow through the sampling equipment was held constant using mass flow controllers and the load of wood was held

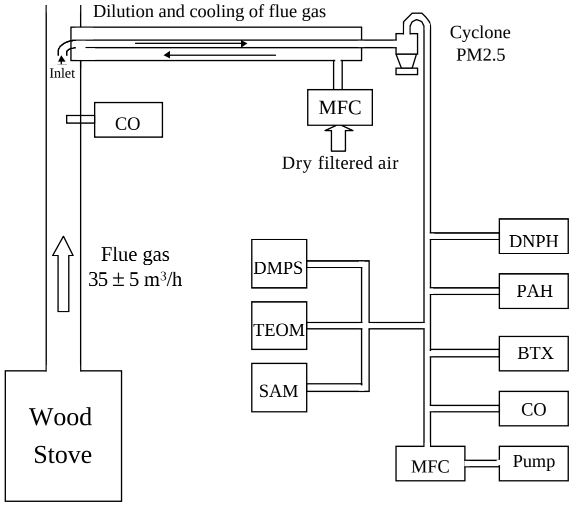


Fig. 1. Schematic illustration of experimental set-up. MFC—mass flow controller, DMPS—differential mobility particle sizer, TEOM—tapered element oscillating massbalance, SAM—stationary aerosol monitor. Sampling site for: DNPH, PAHs, BTXs and carbon monoxide (CO).

approximately constant, 5.8 ± 0.1 kg, during sample numbers 1–6. During sample number 7, the total load of wood was 7.3 kg.

The birch logs used in this experiment were 0.3 m long and weighed about 0.5 kg each with a moisture content of approximately 15% (Bes Bollmann moisture meter). Energy from dry birch wood is 18.3 MJ/kg dry wood. The wood burning cycle was initiated by lighting split-wood (500 g) and newspaper. A second wood load was inserted at 7 min (1022 ± 48 g), a third wood load at 17 min (2018 ± 42 g) and a fourth wood load at 45 min (2022 ± 82 g) after lighting the paper. Flue gas samples were collected during 90 min after lightning, excluding the first minute when paper was burning. Measurement methods, detection limits and sampling time of individual compound groups are shown in Table 1. The dilution was measured continuously as the ratio of the CO concentrations in the flue gases and the concentration in the diluted air. The dew point was measured in sampled, diluted air to control for condensation.

The flow through the sampling equipment was corrected to prevent break-through of volatile and semi-volatile compounds. Transport blanks were collected but had no influence on the results.

2.1. Aldehydes and ketones

Aldehydes and ketones were sampled for 30 + 60 min on 2,4-dinitrophenylhydrazine (Sep-Pak® DNPH-Silica Cartridges) (DNPH). The carbonyls react with the hydrazine and form the corresponding hydrazone, which was eluted with acetonitrile (ACN), tetrahydro furane (THF) and water, and analyzed by high-performance liquid chromatography (HPLC, Perkin-Elmer 200). The hydrazones were separated on a HYPERSIL C18-column and detected at 360 nm. The compounds were identified by retention time with authentic standards from SUPELCO.

2.2. Benzene, toluene and xylenes (BTX)

Benzene, toluene and xylene concentrations were determined with a BTX-monitor (CP-7001 BTX-Multi Component Monitor, Chrompack, The Netherlands), consisting of an adsorbent cold trap coupled to a gas chromatograph with a flame ionization detector for 30 + 60 min. Sample air is first collected on an adsorbent (Tenax GR) for 20 min and automatically desorbed by heating to 180°C. Desorption and analysis takes 10 min. The instrument has a precolumn (CP-Wax 52 CB Ultimetal 5 m × 0.53 mm; df 1.0 μm) and an analytical column (CP-Wax 52 CB Ultimetal 45 m × 0.53 mm; df 1.0 μm) and it was calibrated with two certified reference gas-mixtures (National Physical Laboratory, England). The detection limit is 0.1 $\mu g/m^3$ which corresponds to a minimum detectable emission factor of between 0.02 and 0.4 mg/kg wood depending on the dilution factor for the experiment (Table 1).

2.3. Polycyclic aromatic hydrocarbons (PAH)

Particulate PAH emission samples where collected on Munktell glass-fibre filters (MG 160, Munktell Filter, Sweden). Polyurethane Foam (PUF) plugs (75 mm diameter × 50 mm, 60 PPI; Specialplast AB, Sweden) were used for sampling the semi-volatile PAH. During each 90 min experiment sampling was made first during 30 min and then for 60 min. The PUF plugs were washed prior to use as described elsewhere (Westerholm et al., 1991). After sampling, the filter and PUF samples were combined and Soxhlet extracted with acetone (p.a.; Merck, Germany) (225 ml) for 12 h. No attempt was made to separate the analysis of the particle bound and semi-volatile PAH since the fractionation is expected to become very different as the flue gases enter the ambient atmosphere where environmental conditions are different compared to our air samples. The PAH results are therefore total PAH (particulate + semi-volatile PAH),

Table 1
Measurement methods, detection limits and sampling time of individual compound groups

	Instrument method	Detection limit (mg/kg wood)[a]	Sampling time (min)
BTXs	Chrompack	0.02–0.4	20
PM2.5	TEOM	0.1–1.3	Running 10
PAH	GC/MS	0.01–0.1	30 + 60
Aldehydes and ketones	DNPH HPLC	0.2–5	30 + 60
Organic acids	HPLC	0.1–1	30 + 60
Elements[b]	PIXE	<2	1

Ranges for detection limits are given to indicate maximum and minimum values for each substance group.

[a] Depends on dilution and amount of wood.

[b] Detection limits for individual elements are given in Table 8.

detection limit is shown in Table 1. The extract was evaporated under reduced pressure and stored at −18°C until analysis. The crude extracts were fractionated into two fractions before chemical analysis, as described by Alsberg et al. (1985) but using other solvent volumes. The PAH fraction was analyzed by gas chromatography-mass spectrometry (GC-MS), Table 1, for quantification as described in detail elsewhere (Westerholm et al., 2001). Prior to fractionation, internal standards were added (d_{10}-phenanthrene, d_{10}-pyrene, d_{12}-benz(a)-pyrene, picene, and 2,2′-binaphthyl) for quantification. A PAH standard mixture with internal standards was used for the determination of retention times and response factor calculations.

2.4. Organic acids

The samples were obtained from the crude extract used for PAH analysis, i.e. acetone was evaporated and the residue was diluted with water. The extract was analyzed using a HPLC (Table 1) (Perkin-Elmer 200) and the eluent used was a mixed mobile phase (33.5% ACN + 9.5% THF + 57% H_2O) at a flowrate of 0.7 ml/min. The column used was a DISCOVERY C18 ($250 \times 4.6\,mm^2$, 5 μm particles). Peaks were detected at 230 nm. The compounds were identified by retention times obtained with authentic standards (Fluka Aldrich Chemical Co.).

2.5. Particle mass

The PM2.5 mass was measured with a tapered element oscillating microbalance (TEOM, Series 1400a, Rupprecht & Patashnik Co., USA), Table 1. The operation of the TEOM relies on the change in eigenfrequency of an oscillating filter that is generated by the continuous accumulation of mass on the filter (Patashnick and Rupprecht, 1999). During our experiment the output was a 10 min running average value.

2.6. Elemental composition

PM2.5 samples were collected on filter strips at 5 l/min and analyzed with the proton-induced X-ray emission (PIXE) technique (Johansson and Campbell, 1988) for mass composition of the elements aluminum and heavier. The sampling time was 1 min every 10 min, Table 1.

2.7. Particle size distribution

A differential mobility particle sizer instrument (DMPS), similar to that of Wiedensohler et al. (1997), was used to determine the particle size distribution. The collected aerosols ranged between 3 and 920 nm in diameter. During this campaign, the time resolution of each size distribution was 10 min.

Median particle number concentrations (taken over consecutive 10 min periods after fire start-up excluding the first 10 min) varied between 1.5×10^7 and $8 \times 10^7/cm^3$. The transit time between the extraction of the sample flow from the flue gas pipe to the point of dilution in the inlet was typically 0.6 s. At an undiluted particle concentration of $10^8/cm^3$, particle coagulation in the inlet will only decrease the concentration by a few percent. The effect of coagulation on the measured size distribution is thus negligible. After dilution, coagulation is efficiently quenched and can be ignored. More important is the coagulation taking place in the flue pipe itself, when the flue gases are transported from the stove to the sampling inlet (a distance of approximately 1 m).

3. Results and discussion

As can be seen in Tables 2–4 and 7–8, the variations in the emissions observed in this study are large. In some cases the minimum and the maximum values differ by as much as a factor 100. The flow through the different equipments was corrected to prevent break-through of volatile and semi-volatile compounds. The emission rate is reported as mass/kg wood inserted. The flow through the stove and chimney varied between 20 and 50 m^3/h when the fire door was closed, which could explain some of the variation. Different combustion efficiency may explain the large variation seen in the emissions. The variation in supply of oxygen due to different sizes of the logs might influence the emissions, since it leads to different combustion conditions. During the course of the experiment more wood was inserted at specific time intervals. This is expected to lead to an increase in the emission during a few minutes right after new wood was inserted due to decreased burning efficiencies and incomplete combustion. No standard deviation is reported since it is unlikely that the samples are normally distributed.

3.1. Aldehydes and ketones

In Table 2, the emission factors for the aldehydes and ketones are shown. Formaldehyde and acetone are the most abundant compounds among the volatile ketones and aldehydes, with emission factors of 422 and 365 mg/kg wood, respectively. Another study (McDonald et al., 2000), where mixed hardwood (oak, cottonwood, birch and aspen) was combusted in a wood stove, showed comparable emissions for most of the compounds, except for propanal and butanal, for which they reported 10 and 30 times higher values, respectively. Schauer et al. (2001) combusted oak and eucalyptus and

Table 2
Emission factors from aldehydes, ketones and organic acids (mg/kg wood)

	mg/kg wood				Other ref.			
Compound	Average	Median	Max	Min	Mixed hardwood[a]	Oak	Pine	Eucalyptus
Aldehydes and ketones (number of samples=4)								
Formaldehyde	422	400	710	180	246	759[b]	1165[b]	599[b]
Acetaldehyde	86.3	72.9	157.4	42.0	360	823[b]	1704[b]	1021[b]
Acetone	366	84.2	1289	4.8	(+Propanal) 550	462[b]	749[b]	79[b]
Acrolein	15.7	14.2	29.6	4.7	46	44[b]	63[b]	56[b]
Propanal	7.6	6.4	14.5	3.1	96	153[b]	255[b]	155[b]
Crotonaldehyde	11.2	7.7	24.4	4.9		177[b]		198[b]
2-Butanon	8.3	6.7	19.0	<1.3		115[b]		77[b]
Methacrolein	1.8	0.7	5.5	<0.7		9[b]	23[b]	44[b]
Butanal	1.5	1.3	2.8	<0.7	36	62[b] (+isobutanal)	96[b]	31[b] (+isobutanal)
Benzaldehyde	12.2	4.5	37.1	2.9		16[b]	49[b]	21[b]
Cyklohexanon	10.3	9.7	17.0	4.8				
Isovaleraldehyde	42.8	37.9	76.0	19.3				
Valeraldehyde	1.1	1.3	2.2	<1.3				
o-Tolualdehyde			<1.3	<1.3				
p-Tolualdehyde	0.9	0.9	1.5	<0.7			12[b] (m+p)	27[b] (m+p)
Hexanal+DMBA[c]	34.6	34.6	62.5	6.8		110[b]		239[b]
Sum	1020.3	1050.4						
Organic acids (number of samples=7)								
Homovan+syring acid	9.1	6.2	37.8	1.4		38[d]	83[d,e]	
Vanillic acid	4.2	2.5	10.9	0.9		19[e]	65[e]	
Syringaldehyde	3.1	1.9	13.7	0.3		67[e], 33[b,f]	n.d.[e]	60[b,f]
Vanillin	4.8	3.0	23.9	0.1		2[e], 53[b,f]	29[e], 243[b,f]	53[b,f]
Veratric acid	2.8	1.8	12.6	0.3		19[e]	65[e]	
TMBA[g]	26.4	8.1	140	1.6		23[e]	n.d.[e]	
Guaiacol+o-vanillin	2.2	0.4	9.9	<0.4		172[b,h]	279[b,h]	183[b,h]
Anisic acid	38.1	0.6	230	<0.2		8[e]	4[e]	
Anisaldehyde	2.3	0.6	14.4	<0.6		n.d.[e]	0.7[e]	
Sum	92.7	35.9						

[a] McDonald et al. (2000). Mixed hardwood = Cottonwood, birch, aspen and oak.
[b] Schauer et al. (2001).
[c] 2,5-dimethyl benzaldehyde.
[d] Simoneit et al. (1993).
[e] Only homovan, syring acid n.d.
[f] Gas and particles.
[g] (3,4,5)-Trimethoxy benzoic acid.
[h] Only gvaiacol

recorded the highest emission factors for acetaldehyde, followed by formaldehyde (oak), heptanal (eucalyptus) and acetone (oak). The emissions of acetaldehyde, propanal, butanal were more than ten times higher than in this study, while emissions of other compounds were comparable. The ratio between formaldehyde and acetaldehyde may be used for characterization of sources. Anthropogenic emissions usually have a low ratio. McDonald et al. (2000) presented a ratio of 0.7 in emissions from burning of mixed hardwood. Measurements of emissions from motor vehicles in a road tunnel in Stockholm showed a ratio of 3 (in the range of 2–4) (Johansson et al., 2001). However, in our study of birch wood burning, the average ratio was about 5 (min. 3.3–max. 8.8) indicating variations up to an order of magnitude in anthropogenic sources. This may make it difficult to separate the effects of photochemistry from those of direct anthropogenic emissions (as suggested by Anderson et al. (1996)) on the concentrations of formaldehyde and acetaldehyde in ambient air.

Table 3
Emission factors from BTXs (mg/kg wood), number of samples = 7

	mg/kg wood				Other ref.	
Compound	Average	Median	Max	Min	Mixed hardwood[a]	Pine[b]
BTX						
Benzene	1500	1200	4000	170	1190 ± 875	383
Toluene	740	290	2900	37	320 ± 224	158
p-Xylene	100	44	420	< 1	(*m*+*p*)-Xylene	(*m* + *p*)-Xylene
m-Xylene	25	13	94	4.9	72	60
o-Xylene	20	11	67	3.5	27	18
Sum	2385	1558	7481	215		

[a] McDonald et al. (2000), Cottonwood, birch, aspen and oak.
[b] Schauer et al. (2001).

3.2. Organic acids

Of the organic acids analyzed, (3,4,5)-trimethoxybenzoic acid (TMBA) is the most abundant compound with an emission factor of 26 mg/kg wood (Table 2). A similar emission factor was found by Simoneit et al. (1993) for oak (23 mg/kg wood). Schauer et al. (2001) reported much higher emissions of syringylaldehyde, vanillin and guaiacol, both from oak and eucalyptus, than found in this study. The differences could be due to different types of appliances or different types of fuels.

3.3. Benzene, toluene and Xylene (BTX)

The emission of BTXs in this study (Table 3) is comparable with the BTXs reported by McDonald et al. (2000) for mixed hardwood. Approximately 1.5 g benzene/kg wood combusted is emitted according to our measurements, which is similar to the amount reported by McDonald et al. (1.2 g/kg).

The average toluene/benzene ratio was 0.4 (min. 0.2–max. 0.7), which is similar to the ratio found by McDonald et al. The emission ratio in wood burning differs from that in vehicle exhaust (Fig. 2), for which the toluene/benzene ratio was found to be 3.6 ± 0.5 (Johansson et al., 2001). The ratios of the xylenes to benzene were also higher for traffic emissions (Fig. 2).

3.4. PAH

PAH emissions reported include particulate and semivolatile PAHs, Table 4. There are several PAH compounds included in the PAH standard mix used as reference, which are emitted at very low levels, i.e. < 0.1 mg/kg wood. These are: 9-methylanthracene, 3,6-dimethylphenanthrene, 9,10-dimethylanthracene, 1-methylfluoranthene, benzo(b)naphto(1,2-d)thiophene, benso(k)fluoranthene, dibenz(a,h)anthracene and retene. Retene has been suggested as a marker for wood combustion of spruce (Ramdahl, 1983). It has also been detected when other types of fuels have been used, such as oak, eucalyptus and a mix of hardwood (cottonwood, birch and aspen) (McDonald et al., 2000; Schauer et al., 2001; Rogge et al. (1998)). Simoneit et al. (1993) did not detect retene during combustion of oak. In our study, no retene was detected. Retene has also been detected in traffic emissions (Johansson et al., 2001) and thus its use as a unique tracer for coniferous wood combustion may be questioned.

As can be seen in Table 4, the reported emissions of PAH vary considerably. The median values of our data for benzo(a)pyrene (B(a)P) is 1 mg/kg wood but the values ranged from 0.2 to 16 mg/kg wood. In comparison with a recent fireplace study by Schauer et al. (2001) our data is a factor 1.4–4 larger. With respect to fluoranthene, our data is a factor of approximately 1.3–2.5 larger. However, Schauer used pine, oak and eucalyptus as wood. This indicates that birch generates more PAH/kg wood than combustion of pine, oak or eucalyptus. The major emissions of PAH reported in Table 4 are fluorene, phenanthrene, anthracene, fluoranthene and pyrene, which contribute to more than 70% of the sum of PAH (Fig. 3a). The same compounds also dominate the emissions from motor vehicles, but in addition methylated anthracenes are emitted in large amounts (Johansson et al., 2001). Considering the relative contribution from single PAH compounds to the sum of PAH (Figs. 3a and b), the higher molecular weight PAHs, cyclopenta(cd)pyrene, benzo(ghi)perylene and coronene are typical for traffic emissions, but were of less importance for wood burning.

Table 5 lists PAH mean emissions calculated as B(a)P equivalents and percentual contribution of 11 PAHs to B(a)P equivalents using toxic equivalence factors (TEF) as introduced by Larsen and Larsen (1998). By using TEFs, the carcinogenic properties of the individual

Table 4
Emission factors of particulate and semi-volatile PAH (mg/kg wood), number of samples = 7

	mg/kg wood				Other ref.			
Compound	Average	Median	Max.	Min.	Mixed hardwood[b]	Oak	Pine	Eucalyptus[c]
PAH[a]								
Fluorene (Flu)	27.4	5.5	128.2	0.9	1.66	3.83[c]	4.4[c]	2.61
2-Methylfluorene (2-meFlu)	3.5	0.0	14.9	<0.1				
Dibenzothiophene[g]	0.5	0.1	2.6	<0.1				
Phenanthrene (Phe)	99.1	19.9	505.2	5.9	7.35	0.3[d], 9.26[c]	0.47[d], 16.4[c]	8.2
Anthracene (Ant)	19.3	3.2	102.0	0.8	1.43	0.057[d], 2.15[c]	0.051[d], 3.7[c]	1.76
3-Methylphenanthrene (3-MePhe)	2.9	1.0	11.3	0.2		1.04[c]	1.5[c]	0.80
2-Methylphenanthrene (2-MePhe)	3.4	1.2	13.0	0.2		1.40[c]	2.3[c]	1.0
2-Methylanthracene (2MeAnt)	1.3	0.4	5.0	<0.1		0.72[c]	1.4[c]	0.52
4H-Cyclopenta(def)phenanthrene (4HcpPhe)	6.3	1.4	29.8	0.3				
9-Methylphenanthrene (9-MePhe)	2.6	0.7	10.3	0.1		1.29[c]	2.0[c]	0.88
1-Methylphenanthrene (1-MePhe)	2.6	0.9	10.1	0.2	0.26	1.09[c]	2.8[c]	0.72
9-Methylanthracene			<0.1	<0.1				
2-Phenylnaphthalene (2-PheNa)	6.3	2.2	23.7	0.6				
3,6-Dimethylphenanthrene (3.6.diMePhe)			<0.1	<0.1				
3,9-Dimethylphenanthrene (3.9-diMePhe)	0.6	0.2	2.1	<0.1				
Fluoranthene (Fluo)	29.4	10.0	117.3	2.6	1.75	0.4[d], 4,81[c]	1.24[d], 7.0[c]	4.26
Pyrene (Py)	25.5	8.7	103.5	1.9	1.49	0.53[d], 3.63[c]	1.59[d], 5.7[c]	3.29
9,10-Dimethylanthracene			<0.1	<0.1				
1-Methylfluoranthene			<0.1	<0.1				
Benz(a)fluorene (B(a)Flu)	5.2	1.7	17.9	0.3				
Retene			<0.1	<0.1	0.02	0.11[d], 0.1[e], 2.3[c]	0.68[d],0.7[e], 9.9[c]	0.15
Benz(b)fluorene (B(b)Flu)	2.1	0.8	6.7	0.1	0.66[f]			
2-Methylpyrene (2-MePy)	2.0	0.4	6.7	0.1				
4-Methylpyrene (4-MePy)	2.1	0.7	7.0	0.1				
1-Methylpyrene (1-MePy)	2.1	0.7	6.7	0.1				
Benzo(ghi)fluoranthene (B(ghi)Fluo)	1.7	0.6	8.0	0.1		0.11[d], 0.47[c]	0.27[d], 0.9[c]	0.36
Benzo(c)phenanthrene	0.9	0.3	3.7	0.1				
Benzo(b)naphto(1,2-d)thiophene[g]			<0.1	<0.1				
Cyclopenta(cd)pyrene (Cp(c,d)Py)	4.0	0.7	20.2	0.1		0.23[d], 0.43[c]	0.72[d], 0.97[c]	0.35
Benzo(a)anthracene (B(a)Ant)	3.5	1.1	15.8	0.2	0.56	0.21[d], 0.63[c]	0.63[d], 1.2[c]	0.56
Chrysene (Chr)	4.1	1.4	17.8	0.3	0.35		1.1[c]	
3-Methylchrysene (3-MeChr)	0.5	0.1	2.0	<0.1				
2-Methylchrysene	0.2	0.1	0.6	<0.1				
6-Methylchrysene	0.1	0.0	0.5	<0.1				
1-Methylchrysene	0.3	0.1	0.9	<0.1				
Benzo(b)fluoranthene (B(b)Fluo)	6.1	1.9	26.0	0.3		0.21[d], 0.40[c]	0.53[d], 0.79[c]	0.33
Benzo(k)fluoranthene			<0.1	<0.1		0.26[d], 0.30[c]	0.51[d], 0.67[c]	0.29
Benzo(e)pyrene (B(e)Py)	1.8	0.6	7.6	0.1	0.14	0.13[d], 0.23[c]	0.30[d], 0.46[c]	0.21
Benzo(a)pyrene (B(a)Py)	3.6	1.0	16.0	0.2	0.2	0.23[d], 0.25[c]	0.62[d], 0.71[c]	0.30
Perylene	0.5	0.1	2.2	<0.1		0.038[d], 0.02[c]	0.12[d], 0.11[c]	0.02
Indeno(1,2,3-cd)fluoranthene	0.2	0.1	0.8	<0.1		0.15[d], 0.02[c]	0.35[d], 0.22[c]	0.01
Indeno(1,2,3-cd)pyrene (In(1,2,3-cd)Py)	3.6	1.0	13.0	0.2	0.08	0.047[d]	0.087[d], 0.52[c]	0.17
dibenz(a,h)anthracene			<0.1	<0.1		0.012[d]	0.079[d]	
Benzo(ghi)perylene (B(g,h,i)Per)	2.6	0.7	9.9	0.2	0.09	0.13[d]	0.032[d], 0.44[c]	0.17
Coronene (Cor)	1.6	0.5	6.1	0.1	0.03	n.d.[d]	n.d.[d]	
Sum	281.2	70.2	1282	16.4				

[a] Corresponding PAH abbreviation used in Fig. 3a and b within brackets.

[b] McDonald et al. (2000).

[c] Schauer et al. (2001).

[d] Rogge et al. (1998).

[e] Simoneit et al. (1993).

[f] Sum of benz(b)fluorene, benz(j)fluorene and benz(k)fluorene.

[g] A polycyclic aromatic heterocyclic containing one sulfur atom.

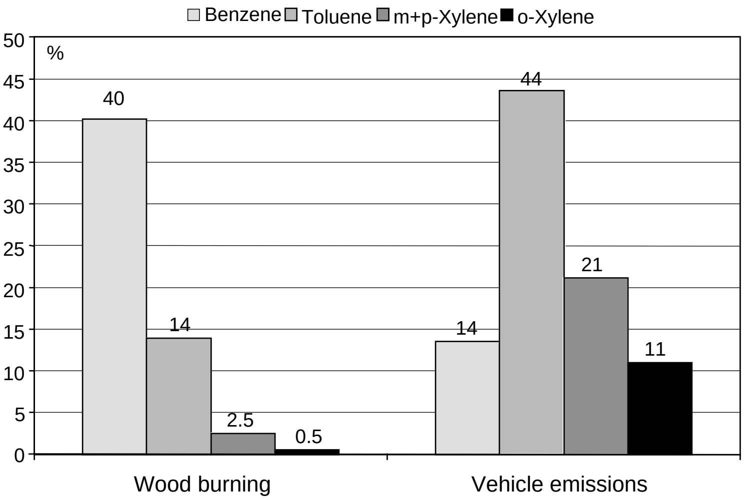


Fig. 2. Relative contribution of single BTX-compounds to total BTX wood burning and vehicle emissions (Road tunnel in Stockholm (Johansson et al., 2001)).

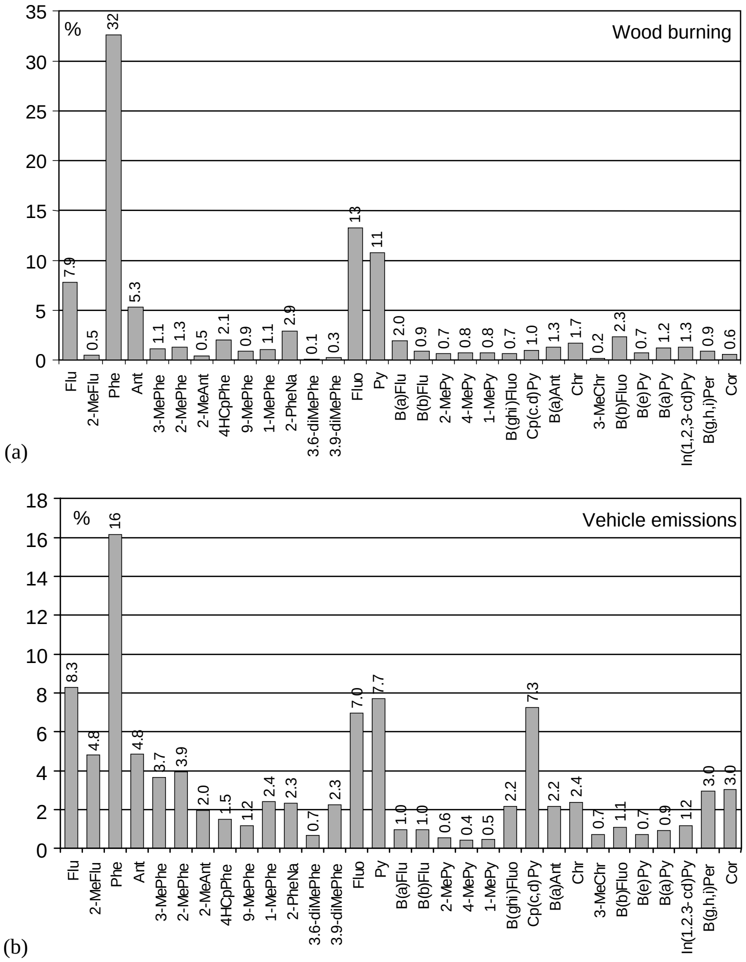


Fig. 3. (a) Relative average contribution of single PAH-compounds to total PAH for wood burning. PAH abbreviations used in the figure are identified in Table 4. (b) Relative average contribution of single PAH-compounds to total PAH in road traffic emissions (Westerholm, unpublished data). PAH abbreviations used in the figure are identified in Table 4.

Table 5
PAH emissions calculated as B(a)P equivalents and percentual contribution of 11 PAH to B(a)P equivalents

PAH	TEF[a]	Emission factor (EF) (mg/kg wood)	B(a)P eq. (%)[b]
Antracene	0.0005	19.3	0.3
Benzo(a)antracene	0.005	3.5	0.5
Benzo(a)pyrene	1	3.6	100
Benzo(k)fluorantene	0.1	0.1	0.3
Benzo(b)fluorantene	0.05	6.1	8.5
Benzo(ghi)perylene	0.02	2.6	1.4
Chrysene	0.03	4.1	3.4
Fluoranthene	0.05	29.4	41
Indeno(1,2,3cd)pyrene	0.1	3.6	10
Phenantrene	0.0005	99.1	1.4
Pyrene	0.001	25.5	0.7

[a] Toxic equivalence factors (TEF) obtained from Larsen and Larsen (1998).

[b] $B(a)P_{eq}(\%) = (X_{TEF}X_{EF}/B(a)P_{TEF}B(a)P_{EF})100$ where X is the individual PAH and EF is emission factor.

Table 6
Emissions from wood furnaces for residential heating, as compiled by Larnesjö et al. (2000), compared to the emission factors obtained in this study using a wood stove

	Wood furnace for residential heating		Wood stove for residential heating
	Traditional	Environmentally approved	Our study[a]
PAH (μg/MJ)	5000	74	4500 (18,000)
B(a)P (μg/MJ)	104	1.5	60 (230)

[a] Median value and average value given in brackets.

PAHs can be discussed (Table 5). Most important from a carcinogenic point of view is B(a)P, followed by fluoranthene. The relative carcinogenic potency contribution of fluoranthene in wood smoke is 40% of B(a)P. Calculating the relative carcinogenic potency using emissions reported by Schauer et al. (2001), fluoranthene in pine wood smoke would be about 60% of B(a)P. Corresponding values for oak and eucalyptus wood smoke emissions are 115% and 84%, respectively. This suggests that fluoranthene is as important a contributor to cancer risk as B(a)P in emissions from wood burning.

A comparison of the domestic burning of wood to that of oil shows that wood releases 1.5–104 μg B(a)P/MJ wood (environmentally approved, respectively, traditional furnace for residential wood burning) while oil releases <0.003 μg B(a)P/MJ (Larnesjö et al., 2000). In our measurements the emission was about 60 μg B(a)P/MJ wood burned (Table 6). The emission factor for total PAH is also presented in Table 6. It can be seen that both total PAH and B(a)P lie within the range of the data reported from other studies using wood boilers (per unit energy).

The emission of PAHs is dependent on the size of the appliance. In Figs. 4a and b the emission of the sum of PAH and B(a)P from this study is compared to emissions from other studies (Larnesjö et al., 2000). It can be seen that the smaller the appliance (i.e. maximum effect), the larger the emissions.

3.5. Particle measurements

The emission of PM2.5 varied considerably, as was also the case for the gases and PAHs. The emissions ranged from 0.1 to 2.6 g/kg wood burned with an average of 1.3 g/kg (Table 7). This is about a factor 4–10 times lower than those reported by Larson and Koenig (1993), Houck and Tiegs (1998) and McDonald et al. (2000) for different wood stoves and varying fuel types. Fireplace experiments with three different types of wood show the same range of emissions (Schauer et al., 2001) as in the present study.

About 5% (60 mg/kg) of the average PM2.5 is accounted for by the elements from Al to Pb. Larson and Koenig (1993) and Houck and Tiegs (1998) found about 1%.

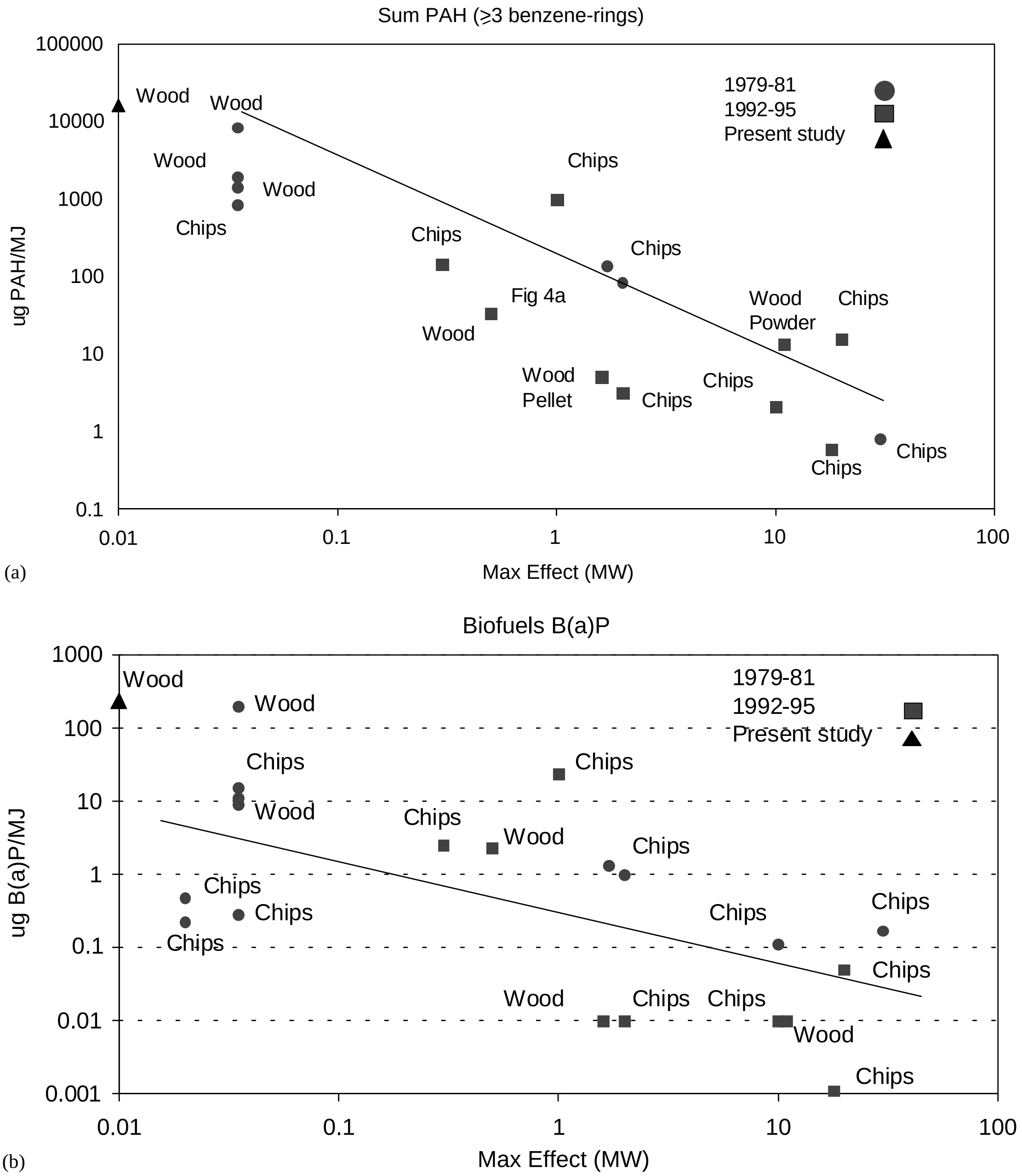


Fig. 4. (a) Emissions of PAH from power plants and household heating devices of different sizes, using biofuels. The larger emission of PAHs seen in our study is expected, since there is a connection between effect of the plant and the emission. (Larnesjö et al., 2000). (b) Emissions of B(a)P from power plants and household devices of different effects, using biofuels (Larnesjö et al., 2000).

The PM0.9 emission, as calculated from the DMPS system, was found to be comparable to the PM2.5 emission (Table 7). When calculating PM0.9 the particles are assumed to be spherical with a density of 1.0 g/cm^3. This is not an unreasonable assumption since the main fraction of the PM2.5 from wood burning is organic and elemental carbon (Larson and Koenig, 1993; Houck and Tiegs, 1998; Watson and Chow, 1994; Kleeman et al., 1999; Andreae and Merlet, 2001). On a closer examination, the fine particle mass fraction contains 40–60% organic carbon and 1.3–3.2% elemental carbon depending on wood type during fire place

Table 7
PM2.5 emissions and emissions calculated from DMPS (for particles smaller than 0.9 μm in diameter), number of samples = 6 (PM2.5 = 5)

Compound	Average	Median	Max.	Min.	Unit	Other ref.
Species						
PM2.5	1.3	1.5	2.6	0.10	g/kg wood	7–30[a]
PM0.9	1.3	0.74	6.2	0.029	g/kg wood	
Number (PM0.9)	4.22E + 14	3.79E + 14	9.68E + 14	1.29E + 13	#/kg wood	
Surface (PM0.9)	25.5	19.1	94.3	1.25	m^2/kg wood	

[a] Larson and Koenig (1993).

burning (Schauer et al., 2001). Schauer et al., also managed to extract about 50% of the organic particle mass fraction and found that levoglucosan and other sugars, guaiacols, syringols and phenols/acids were the dominant species. These compounds have dry densities from about 1.0 to 1.7 g/cm^3 (though data from all species is not available). As for the density of elemental carbon, values ranging from 1.0 to 2.0 g/cm^3 have been reported in the literature (McMurry and Zhang, 1991).

The small difference between PM2.5 and PM0.9 suggests that most particle mass should be found in PM0.9. Indeed, Fig. 5 indicates that the largest mass is found in particles around 500 nm. Measurements of Kleeman et al. (1999) from residential fireplaces, on the other hand, show that the largest mass emission is found between 100 and 200 nm particle diameter.

The average particle number emission reaches 4×10^{14}/kg (Table 7) and is highest during the first 20 min of the wood burning when wood insertion has been made three times (cf. Fig. 6a–c). A similar result was found in a birch study conducted with a 0.015 MW wood stove (Hueglin et al., 1997).

New particles in the size range below 50 nm can form from gas phase precursors during dilution and cooling of exhaust gases. This homogeneous nucleation of new particles has been shown to be dependent on the dilution ratio and the temperature of the diluting gas, controlling the vapor supersaturation ratios (Kittelson, 1998).

In the present study, the number concentrations were quite constant during the start-up phase for the smallest mode with a geometric mean diameter of 52 nm (Fig. 6), despite the fact that the dilution ratios varied quite substantially from one fire to the other. This seems to imply that the size distributions were not severely affected by the dilution ratios. The size-dependent concentrations were more variable for the intermediate and smoldering phases, while the geometric mean diameters of the two modes were stable around 26–28 nm and 125–129 nm, respectively (Fig. 6). Since the number concentrations of both modes varied substantially, it is likely that this variability was caused by changes in the combustion conditions between fires, and not by variations in the dilution ratios.

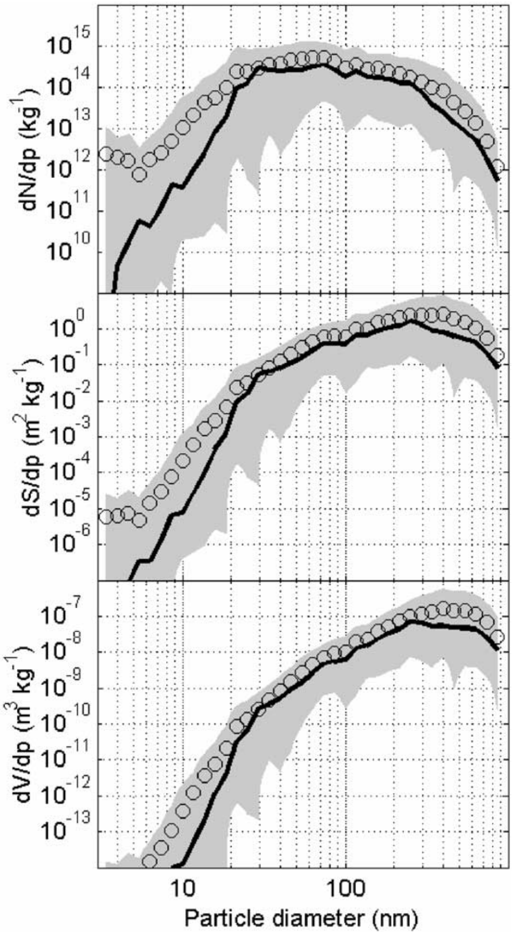


Fig. 5. Average (circles) and median number, surface and volume size distribution as function of particle diameter with data values between the 90- and 10-percentile covered by the gray area.

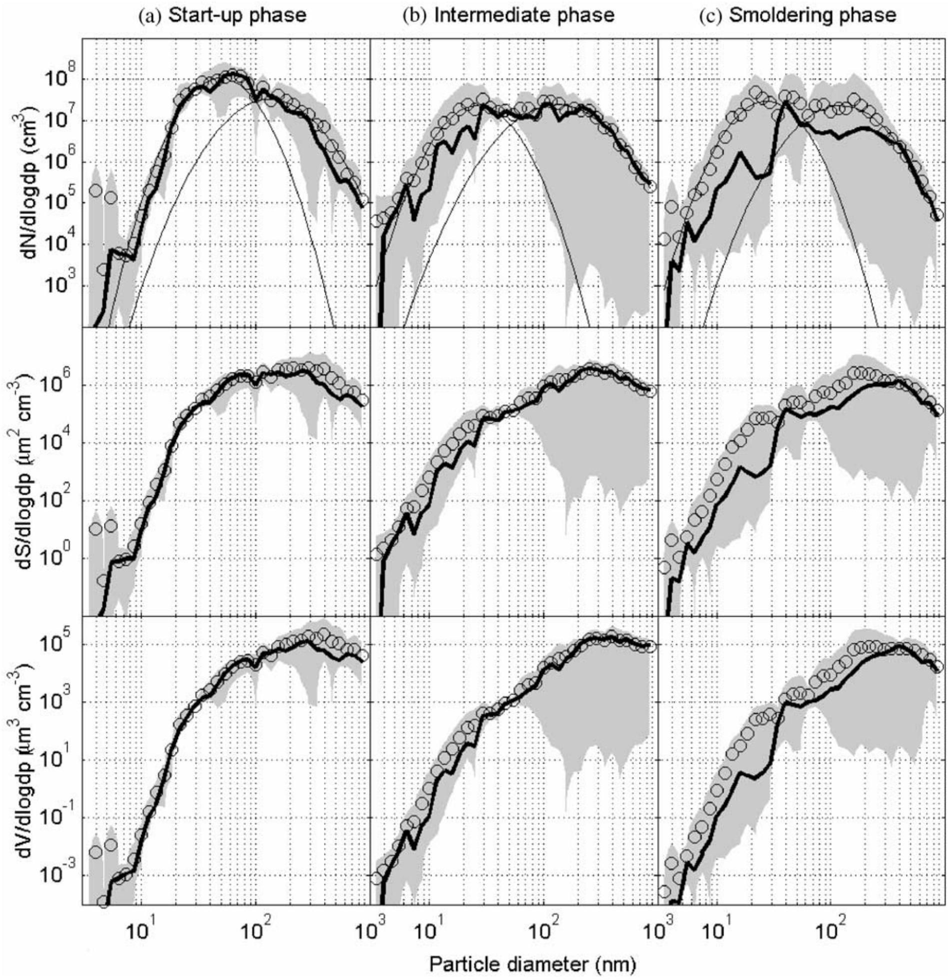


Fig. 6. Average (circles) and median number, surface and volume size distribution as function of particle diameter at different phases of the burning. Data values between the 90- and 10-percentile are covered by the gray area. Bimodal lognormal fittings of the number distribution is depicted with a thin line. (a) start-up phase (10–20 min), (b) intermediate phase (50–60 min), (c) smoldering phase (80–90 min).

In an experiment with wood chips in a 0.060 MW burner, Hueglin et al. (1997) also observed large variations in the size distributions during different stages of the wood burning cycle, with a continuous decrease in the count median diameter from around 300 to 50 nm as burning proceeds from the start-up phase to the burn-out phase. While their size distributions were basically unimodal, our measurements were bimodal (Fig. 6), with variable concentrations in both modes. One reason for this variation is the fact that wood was added to the fire four times in our study, mimicking a typical domestic wood burning cycle.

For small-scale appliances the particle emission ranges from about 800 to 5100 mg/MJ for different types of wood (Valenti and Clayton, 1998; Heyes, 2000; Karlsvik et al., 1992). Two other studies report total suspended particle mass (TSP) emissions as low as 10–50 mg/MJ for wood/pellet boilers and stoves, and 1000 mg/MJ for an old wood boiler (Tullin et al., 2000; Gustavsson et al., 2000). The emission from large biomass power plants is somewhat smaller and ranges from 250 to 1500 mg/MJ (TSP) (Heyes, 2000). The average PM2.5 particle emission from the wood stove in this study is 80 mg/MJ.

The maximum number of particles in road traffic emissions in Stockholm, Sweden, occurs at about 20 nm particle diameter (Johansson et al., 2001), while that for the wood stove exhaust reported here, range from 20 to 300 nm. If this difference in size distribution is typical and representative for ambient conditions, it might

Table 8
Emission factors of elements (mg/kg wood), number of samples = 7

Compound Elements	mg/kg wood					Other ref.	
	Average	Median	Max	Min	No. of times above det. limit		Min.–max.[a]
Al	<57.27	<45.14	<159.40	<5.91	0	5.71[b]	0.1–24
Si	9.27	6.23	38.32	0.37	7	0.8–0.9[c]	0.3–31
P	<11.21	<7.30	<33.70	<1.23	0	0.4–1.0[c]	
S	6.55	4.71	18.46	1.07	7	4.8–7.6[c]	0.1–29
Cl	5.71	5.37	10.56	0.81	7	15.36 (soluble)[b], 6.5–110[c]	0.7–21
K	27.37	25.24	60.26	4.67	7	26.3–68.8[c]	3–86
Ca	0.43	0.16	1.89	0.01	7		0.9–18
Ti	<1.89	<1.24	<5.67	<0.21	0		0.04–3
V	<1.28	<0.84	<3.86	<0.14	0		0.02–4
Cr	0.63	0.17	2.10	0.04	7		0.02–3
Mn	0.14	0.11	0.34	0.03	6		0.07–4
Fe	0.21	0.15	0.80	0.04	7		0.3–5
Co	0.03	0.01	0.16	0.00	7		
Ni	0.06	0.02	0.30	0.01	7		0.001–1
Cu	0.07	0.07	0.08	0.07	2		0.2–0.9
Zn	7.50	7.21	12.27	1.49	7	0.3–0.6[c]	0.7–8
Ga	<0.61	<0.53	<1.36	<0.08	0		
Ge	<0.69	<0.62	<1.49	<0.09	0		
As	<0.26	<0.26	<0.47	<0.04	0		
Se	0.01	0.01	0.02	0.00	2		
Br	0.19	0.09	0.86	0.02	7	0–1.1[c]	0.07–0.9
Rb	0.15	0.16	0.24	0.04	4		
Sr	<0.60	<0.43	<1.75	<0.07	0		
Zr	<0.86	<0.58	<2.58	<0.10	0		
Mo	0.64	0.43	1.64	0.07	4		
Cd	0.60	0.38	1.59	0.00	6		
Hg	<1.90	<1.64	<4.30	<0.26	0		
Pb	0.34	0.23	0.92	0.07	7		0.1–3
Sum	59.9	50.7	151	8.8			

[a] Larson and Koenig (1993).
[b] McDonald et al. (2000).
[c] Schauer et al. (2001).
Values denoted with a "less than"-sign denotes that the data was below this value and that this was the detection limit.

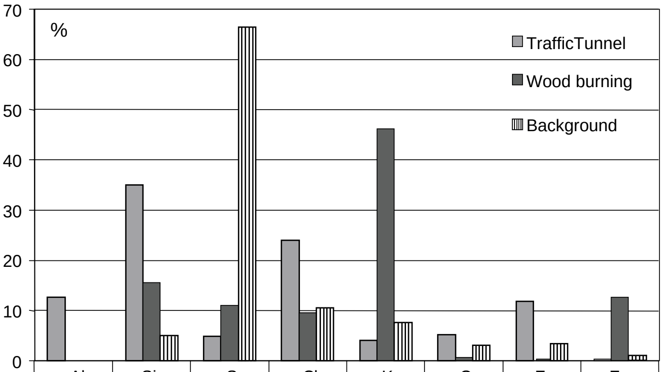
prove valuable when differentiating between wood burning and traffic exhaust contributions to ambient particle concentrations.

3.6. Elemental composition

Of the elements analyzed, K, Si, Zn, S and Cl contribute on average to 92% of the total PIXE mass. In general, all elements account for about 5% of the total PM2.5 mass with an emission of 60 mg/kg wood burned. K and Si have emission factors of 27.4 and 9.3 mg/kg wood, respectively (Table 8). Al, Ti and V were below detection limit in any sample, although they were found in the emissions reported by Larson and Koenig (1993). In our study, P was found below detection limit, while Schauer et al. (2001) found P in pine, oak and eucalyptus. The average and maximum emission factors for Cl found in our study were 5.7 mg/kg wood and 10.6 mg/kg wood, repectively. Schauer et al. (2001) reported emissions ranging from 6.5 mg/kg wood (oak) to 110 mg/kg wood (eucalyptus).

The source profile of elements from wood burning is very different from the source profile obtained in road dust (Johansson et al., 2001) and in background air (Swietlicki, unpublished data) (Fig. 7). It can be seen that the most pronounced elements for wood burning is K and Zn. Elements typically found in road dust are Al, Si, Ca and Fe. The long-distance transported particles are dominated by S.

From Fig. 7 it can also be seen that the ratio K to Ca is very different in background air where it is about 2 (in the range 1–4) and for wood burning where it is 64 (in



	Al	Si	S	Cl	K	Ca	Fe	Zn
Traffic Tunnel	13	35	5.0	24	4.1	5.3	12	0.4
Wood burning	<0.1	16	11	9.6	46	0.7	0.4	13
Background	0.1	5.1	66	11	7.7	3.2	3.5	1.1

Fig. 7. The relative contribution of elements analyzed with PIXE from different sources. The background site is influenced by long-distance transported particles. The minimum and maximum relative abundances for wood burning are displayed in the table below the figure.

the range 30–330). In particles derived from road traffic Ca is present in higher amounts than K (Johansson et al., 2001). The ratio of K to Ca is 0.8 ± 0.15 in traffic emissions.

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