

Domestic wood burning and PM_{2.5} trace elements: Personal exposures, indoor and outdoor levels

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Received 19 July 2004; received in revised form 4 January 2005; accepted 11 January 2005

Abstract

Personal exposures as well as indoor and outdoor levels of PM_{2.5} were measured with cyclones and impactors simultaneously in the winter of 2003 in a residential area where wood burning for domestic space heating is common. Twenty-four-hour samples from both wood-burning households (“wood burners”) and a reference group were analysed for mass and elemental concentration using energy dispersive X-ray fluorescence (EDXRF) and for black smoke (BS) concentration using an EEL 43 reflectometer. Wood-smoke particles made statistically significant contributions of K, Ca, and Zn for both personal exposure and indoor concentration, the median levels of these elements being 66–80% higher for the wood-burning group. In addition, Cl, Mn, Cu, Rb, and Pb were found to be possible markers of wood smoke, though levels of these were only significantly higher among the wood-burning group for either personal exposure or indoor concentrations. PM_{2.5} mass and S levels were not significantly elevated in wood burners, probably due to large variations in outdoor concentrations from long-distance transported air pollution. Personal exposure and indoor levels showed high correlations for all species, and the personal exposure levels were usually higher than or equal to the indoor levels. The associations between personal exposure and outdoor levels were generally weak except for outdoor S and PM_{2.5} levels that were both highly correlated with personal S exposure levels ($r_s > 0.8$).

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Keywords: Black smoke; Exposure assessment; Fine particles; X-ray fluorescence; Wood smoke markers

1. Introduction

The domestic use of wood stoves and fireplaces for heating and pleasure is quite common in many countries with cold climates. Wood burning as the main or supplementary space heating source in colder seasons has increased over the past decade. The increasing cost

of both fossil fuels and electricity has been an important factor driving this increased wood burning. Moreover, it has been government policy in many countries to promote a shift to renewable fuel consumption to decrease dependency on fossil fuels and on unsustainably produced electricity.

Wood burning affects ambient air concentrations of a number of gaseous and particulate pollutants. Many studies investigated the emissions from industrial and domestic biomass burning (Johansson et al., 2003;

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Pagels et al., 2003) and of their impact on ambient concentrations (McDonald et al., 2000). In parts of the US, where wood is the predominant heating fuel, wood burning contributes up to 80% of the total $PM_{2.5}$ concentrations in residential areas in the winter (McDonald et al., 2000). The adverse health effects of exposure to wood smoke are likely linked to the particulate phase, and include increased cardiovascular mortality, as well as asthma and other respiratory symptoms in adults and children (Boman et al., 2003).

Besides organic compounds, many different trace elements are present in wood, and the concentrations of these can differ greatly between various tree species (Harju et al., 1996; Harju et al., 1997; Saarela et al., 2002; Selin et al., 1993). In Scandinavia birch and spruce are the main types of wood burned.

Data on the presence of specific elements and their concentrations in wood-smoke particles are lacking. Some studies present data on wood-smoke particles in or just outside the chimney (Rau, 1989; Schauer et al., 2001). A recent study in Hagfors, Sweden (Johannesson et al., 2002), found a significant difference between an area where domestic wood burning was prevalent and an area where district heating was the norm in terms of mass concentrations of outdoor $PM_{2.5}$, median concentrations being 6.2 and $4.5 \mu\text{g m}^{-3}$, respectively. However, no previous studies estimating personal exposure to wood-smoke particles in residential areas were found.

The aim of the present study was to investigate the impact of domestic wood burning on personal exposure, indoor and outdoor levels of $PM_{2.5}$, trace elements and black smoke (BS). We compared the exposures and levels between wood burners and a reference group who live in a clearly defined area where wood burning is prevalent.

2. Material and methods

The study took place during 9 days in the period from 10th February to 12th March 2003 in a residential area ($400 \times 1100 \text{ m}$) in the Swedish town of Hagfors. This period was during winter in Sweden, when domestic space heating was necessary. The weather during the measurement period was typical of the season, with full snow cover and daily mean temperatures between -2° and -10°C . The wind speed was low, the daily mean being less than 3 m s^{-1} on all days, and the wind came from two main directions—southwest and north.

Hagfors is a small town of 5600 residents located at 60.03° North and 13.68° East. The residential area selected for the study is located in the north-eastern part of the town. Domestic wood burning is common in this area, and no major industries are located in the close vicinity (distance 6 km). Houses in the area are equally affected by the closest major road (3000 vehicles per

day) passing the western edge of the area. The local traffic within the area is limited.

The study was approved by the ethics committee at Göteborg University.

2.1. Study design, subjects, and background information

Personal and indoor 24 h samples were collected for each subject once during the study period. For each of these days also an outdoor 24 h sample was collected. The personal sampler was worn all day, and at night it was placed next to the stationary indoor sampler in the living room, owing to the noise of the pump. The outdoor measurements were made at a single location on the roof of a single car garage, belonging to one of the subjects, in the middle of the study area.

To avoid contamination from other possible sources (other than wood log burning) of the pollutants of interest, households heated by the combustion of other fuels, such as oil were excluded. Wood pellets were also excluded since the emissions are low compared to wood log emissions and not that common in Sweden (Johansson et al., 2004). The subjects were all non-smokers and cigarette smoking was not allowed in the homes during the 24 h sampling period.

Houses were selected based on information obtained from the local chimney sweeping register as to the type of heating system present in the subjects' homes. The participants were adults, in these houses, who were unlikely to have been exposed to the pollutants of interest in their occupations during the measurement period (e.g. people working at the local steel mill in Hagfors were thus only investigated on non-working days). Eighteen homes in the area with wood-burning appliances used daily were selected for the study, and in 14 of them (78%) one householder each (10 men and 4 women) agreed to participate in the study. Of these subjects ("wood burners"), 12 replenished their boilers regularly (median frequency, 3.5 times per day), the last two did not replenish themselves. For subjects living in homes with electrical heating or heat pumps (the reference group) the participation rate was 83% (one participant each from 10 of 12 households, 5 men and 5 women).

Prior to sampling, those involved in the study completed a questionnaire about their homes (dealing with, for example, age and type of boiler, presence of accumulator tank, type of firewood, firewood storage, frequency of fuel replenishment, total volume of wood burned, and type of ventilation system), occupation and work tasks. Of the 14 wood appliances, two were environmentally certified by the Swedish National Testing and Research Institute, and another three were equipped with accumulator tanks (i.e. a water tank used as a heat reservoir).

During the sampling period the subjects kept diaries in which they noted when they made fires, how much and what type of wood they burned, and if and when they replenished the firebox. They also recorded where they had been during the day and their activities at home and work. This information made it possible to determine activities likely to lead to PM exposure, thus influencing the results.

2.2. Aerosol sampling

Two different types of impactors were used for the outdoor sampling: one Sierra Andersen series 240, dichotomous virtual impactor that separates particles into two size ranges, coarse and fine particles (PM_{10–2.5} and PM_{2.5}, respectively); and one EPA-WINS impactor (PQ100 EPA-WINS Basel PM_{2.5} Sampler) for collecting PM_{2.5} particles. A flow rate of 16.71 min⁻¹ was used in both impactors. Identical sets of equipment were used for both personal exposure and indoor sampling: a GK2.05 (KTL) cyclone connected to a BGI 400S Personal Sampling Pump with a flow rate of 41 min⁻¹. Each person was equipped with an easily carried shoulder bag with the cyclone and pump attached to it. The cyclone was attached to the shoulder strap and placed near the breathing zone. The sampling was performed on 2–3 subjects per sampling day, including subjects from both groups except for one of the days.

Teflon filters of 37-mm (Pall Teflo, R2PJ037) were used in the dichotomous impactor and in the cyclones, and an equivalent 47-mm Teflon filter (Pall Teflo, R2PJ047) was used in the WINS impactor.

2.3. Analytical techniques

All the filters were weighed before and after exposure using a CAHN C-30 microbalance placed in a temperature- and humidity-controlled room. The filters were conditioned for at least 24 h before weighing. Sets of approximately 20 filters (including field blanks) were weighed twice. If the difference in the weight of a filter was greater than 2 µg, the procedure was repeated for the filter in question until a stable reading was obtained. The potential differences between the pre- and post-exposure weighing results arising from different air buoyancy levels in the balance room were accounted for by subtracting the differences between the pre- and post-exposure blank filter weights from the sampled mass of the exposed filters.

An energy dispersive X-ray fluorescence (EDXRF) spectrometer at the Department of Chemistry, Atmospheric Science, Göteborg University, Sweden (Öblad et al., 1982) was used to analyse the elemental composition of all filter samples. The EDXRF spectra were processed and quantified using the Quantitative X-ray Analysis System (QXAS) and the Analysis of X-ray spectra by

Iterative Least-square fitting (AXIL) (Bernasconi et al., 2000; Van Espen and Jansen, 1993). All samples were analysed using a live time of 1000 s, a tube voltage of 55 keV, a tube current of 25 mA, and a molybdenum secondary target. All filters were analysed using the same instrument settings.

Calibration of the EDXRF spectrometer was performed using 29 standards (MicroMatter Co., Eastsands, WA, USA) of suitable concentrations as well as a standard reference filter, NIST SRM1833, together covering a total of 30 elements. The calibration was verified using the standard reference filter, NIST SRM2783. The certified values and uncertainties as well as the measured values are available at <http://www.che.gu.se/atmsci/edxrf/lod.htm>.

Table 1 presents the limits of detection (LoD) as spectrometer limits expressed in ng cm⁻² and as airborne concentrations expressed in ng m⁻³, for the flow rates used in the different samplers, 16.7 and 41 min⁻¹, respectively. A randomly selected filter from the study was analysed 8 times and the mean value of the LoD is presented. The spectra were evaluated for net background area (NB) and the element's net peak area (NP), which were then applied to the International Union of Pure and Applied Chemistry (IUPAC) equation,

$$\text{LoD} = 3C \frac{\sqrt{\text{NB}}}{\text{NP}},$$

Table 1

Limits of detection (LoD) given as spectrometer limits (expressed in ng cm⁻²) and as airborne concentrations (expressed in ng m⁻³) for the flow rates used in the different samplers, 16.7 and 41 min⁻¹, respectively. A randomly selected filter from the study was analysed 8 times and the mean value of the LoD is presented.

Element	(ng cm ⁻²)	16.71 min ⁻¹ (ng m ⁻³)	41 min ⁻¹ (ng m ⁻³)
Si	320	86	370
S	44	12	51
Cl	12	3.1	13
K	4.3	1.1	4.9
Ca	2.0	0.55	2.3
Ti	0.93	0.25	1.1
V	0.73	0.20	0.84
Cr	0.67	0.18	0.77
Mn	0.62	0.17	0.71
Fe	0.74	0.20	0.85
Ni	0.23	0.063	0.26
Cu	0.23	0.062	0.26
Zn	0.40	0.11	0.46
Se	0.11	0.030	0.13
Br	0.13	0.034	0.15
Rb	0.094	0.025	0.11
Sr	0.075	0.020	0.086
Pb	0.26	0.069	0.30

where C is the certified concentration of the element of interest (de Vries and Vrebos, 1993). The standard filter, SRM1833 (certified concentrations for Si, K, Ti, Fe, Zn and Pb), was analysed multiple times daily over the analysis period to check the stability of the instrument. The relative standard deviations (RSD) were less than 3.5% for all the certified elements except for Si, which had an RSD of 8.8%.

After the elemental analysis the filters were examined for BS using an EEL 43 smoke stain reflectometer. Each filter was measured five times (in the centre and in each of the four main quadrants), and the average value was used in the calculations as described in the ULTRA study manual and data book (Götschi et al., 2002; Pekkanen et al., 2000). The reflectance of the filter was transformed into an absorption coefficient, a , according to the international standard, ISO9835, (1993) using the following equation:

$$a = \frac{A}{2V} \ln\left(\frac{R_0}{R_S}\right),$$

where A is the filter area (m^2), V is the sampled volume (m^3), R_0 is the average reflectance of field blanks, and R_S is the reflectance of the sampled filter. The absorption coefficient is expressed in the unit 10^{-5}m^{-1} .

2.4. Statistical analysis

The differences in elemental concentrations between wood burners and the reference group were assessed using the Wilcoxon rank-sum test for both personal exposure and indoor levels. The tests were performed one-sided since the only hypothesis was that the wood burners would display higher concentrations. Wilcoxon signed-rank tests (two-tailed) were performed on the differences in concentrations within the pairs of personal and indoor samples for the entire dataset, as well as for wood burners and the reference group separately. Correlations between personal exposures and indoor or outdoor levels were assessed using the Spearman rank correlation coefficient (r_s). Statistical calculations were made using the SAS System for Windows version 8.0, (SAS, 1999). Statistically significant refers to $p < 0.05$.

For values below LoD, the calculated value of the LoD divided by the square root of two was used in the statistical calculations (Hornung and Reed, 1990).

3. Results

A summary of the results for personal, indoor, and outdoor measurements is presented in Tables 2 and 3. The elements Ti, V, Cr, Ni, Se, and Sr have been omitted due to low detection frequency (<33%) for most households. Note that the indoor result for one wood burner was omitted because the boiler involved was placed in a separate shed and not in the main building.

The median *personal exposure* to $\text{PM}_{2.5}$ was $14.1 \mu\text{g m}^{-3}$ with a 95% confidence interval (CI) of $11.2\text{--}21.8 \mu\text{g m}^{-3}$ and to BS it was $0.80 \times 10^{-5} \text{m}^{-1}$ (95% CI $0.47\text{--}0.97 \times 10^{-5} \text{m}^{-1}$). When comparing wood burners and the reference group, the elemental concentrations of Cl, K, Ca, Cu, and Zn were found to be significantly higher among the wood burners (see Table 2). BS and Pb exposures were higher, but not significantly, among the wood burners. No significant differences were found for $\text{PM}_{2.5}$ mass or the other elements analysed in this study.

The median *indoor* concentration of $\text{PM}_{2.5}$ was $10.3 \mu\text{g m}^{-3}$ (95% CI $7.1\text{--}17.9 \mu\text{g m}^{-3}$) and of BS was $0.59 \times 10^{-5} \text{m}^{-1}$ (95% CI $0.31\text{--}0.88 \times 10^{-5} \text{m}^{-1}$). The indoor concentrations were significantly higher for wood burners than for the reference group for the elements K, Ca, Mn, Zn, and Rb, as shown in Table 2. The concentrations of BS and Cl, while not statistically significant, were higher for wood burners.

The correlations between personal exposure and indoor levels were generally good for the investigated species (mean $r_s = 0.71$, range $0.48\text{--}0.94$; $r_s > 0.7$ for $\text{PM}_{2.5}$, BS, S, K, Zn, Br, and Pb). The personal exposure levels were generally higher than were the corresponding stationary indoor levels, except for S, Cl, K, Br, and Rb where the levels were similar (see Tables 2 and 4). Personal exposures were significantly higher than the indoor levels for $\text{PM}_{2.5}$, BS, K, Ca, Mn, Fe, Cu, Zn, and Pb for the combined group of subjects (Table 4). For subjects living in houses heated with wood, personal exposures to $\text{PM}_{2.5}$, Ca, Mn, Fe, Cu, Zn, and Pb were significantly higher than the indoor levels, while personal exposure to Rb was significantly lower. In the reference group, personal exposures to BS, Ca, Mn, Fe, Cu, Zn, and Rb were higher than the indoor levels.

At the stationary *outdoor* location, the correlation between the two impactors was high for $\text{PM}_{2.5}$ mass ($r_s = 0.94$) and for most of the elements ($r_s \geq 0.7$), while it was lower for Ca and Cu, as shown in Table 3. The correlations between the outdoor levels and personal or indoor levels were generally weak or non-existent. The exceptions were outdoor S and $\text{PM}_{2.5}$ levels which were both highly correlated with personal S exposure and indoor S levels (outdoor S—personal S $r_s = 0.85$, outdoor S—indoor S $r_s = 0.82$, outdoor $\text{PM}_{2.5}$ —personal S $r_s = 0.86$ and outdoor $\text{PM}_{2.5}$ —indoor S $r_s = 0.82$).

4. Discussion

4.1. $\text{PM}_{2.5}$, BS and elements: exposure and concentrations

Comparing concentrations as measured by different studies can be complicated by different sampling techniques, sampling times, sites, and sampled species.

Table 2
Results from measurements of personal exposures and indoor levels

	Wood burners			Reference group			One-sided <i>p</i> -value ^a
	Median	Range	#>LoD	Median	Range	#>LoD	
<i>Personal exposure</i>							
PM _{2.5}	18	5.3–59	14	12	5.8–46	10	0.115
BS	0.97	0.32–3.0	14	0.74	0.24–0.96	10	0.053
S	880	<210–2000	8	650	<180–2400	6	0.500
Cl	200	140–470	14	160	120–280	9* ^c	0.036
K	240	88–550	14	140	89–360	9* ^c	0.024
Ca	76	36–530	14	43	26–98	10	0.033
Mn	4.8	<1.6–41	9	3.5	<1.6–7.1	6	0.250
Fe	64	22–280	13* ^b	49	14–150	10	0.139
Cu	8.9	<0.83–32	12* ^b	2.4	<0.86–28	6	0.016
Zn	38	18–130	14	22	8.4–67	10	0.033
Br	1.2	0.82–7.1	14	1.2	0.81–2.3	10	0.500
Rb	2.2	1.1–2.5	14	2.3	1.1–2.5	10	0.153
Pb	6.0	3.5–29	14	4.3	<1.7–7.9	9	0.060
<i>Indoor concentration</i>							
PM _{2.5}	12	3.9–61	13	9.5	2.9–53	10	0.278
BS	0.64	0.16–2.9	13	0.54	0.12–0.88	10	0.072
S	760	<140–2200	8	590	<160–2600	6	0.488
Cl	190	150–430	13	160	<83–340	8	0.091
K	200	72–600	13	120	70–410	9* ^c	0.026
Ca	44	17–200	13	25	10–49	9* ^c	0.044
Mn	2.6	<1.5–14	8	<1.7	<1.6–7.4	2	0.029
Fe	27	18–120	13	22	3.6–110	10	0.126
Cu	1.7	<0.81–34	7	<0.86	<0.80–7.2	2	0.102
Zn	25	10–100	13	15	7.1–76	10	0.039
Br	1.2	<0.81–9.5	12	1.2	<0.8–2.3	9	0.238
Rb	2.3	2.2–2.4	13	1.2	1.1–2.4	10	0.007
Pb	4.6	<0.84–10	12	3.0	<1.7–11	8	0.258

Median concentration, range, and number of samples above limit of detection (LoD) are presented. Units are $\mu\text{g m}^{-3}$ for PM_{2.5}, ng m^{-3} for the elemental concentrations, and 10^{-5} m^{-1} for black smoke (BS). An asterisk (*) denotes that one detected value was omitted due to a known major external non-wood-burning source.

^aWilcoxon rank-sum test for personal exposure and indoor levels, respectively. Significant *p*-values are marked in bold.

^bWelding copper pipes, occupational exposure.

^cUse of cleaning detergents at home.

Table 5 presents a summary of data pertaining to PM_{2.5} and BS compiled from some recently published studies and from the present study. Levels of PM_{2.5} reported by the present study are similar to those reported for Helsinki, New York, Birmingham—AL (winter levels), but clearly lower than the levels reported for Athens, Basel, Prague, and Amsterdam (Götschi et al., 2002; Janssen et al., 2000; Kinney et al., 2002; Lachenmyer and Hidy, 2000; Oglesby et al., 2000). The levels of BS found in Hagfors were lower than were reported in most of the other studies (Götschi et al., 2002; Janssen et al., 2000; Kinney et al., 2002): only one of the Helsinki studies (Götschi et al., 2002) presents similar levels. A possible reason for the reported differences in PM_{2.5} and BS levels is that the other studies were performed in

densely populated cities with high traffic intensities where combustion from diesel is a major contributor to BS (Cyrys et al., 2003).

Only two of the other studies presented in Table 5 (Kinney et al., 2002; Oglesby et al., 2000) present data on elemental concentrations, and the only elements analysed in all three studies are S, K, Ca, and Pb. Both outdoor levels and personal exposures were clearly lower in Hagfors than in Basel for these elements. Personal exposure to K was lower in New York, while similar levels of S and Ca were found; on the other hand, Pb exposure was higher in New York. For most elements, the associations between indoor concentrations and personal exposures found in New York displayed the same tendencies as were evident in Hagfors.

Table 3
Results from the centrally located stationary outdoor measurements

	Sierra Andersen impactor			WINS impactor			Sierra Andersen vs. WINS	
	Median	Range	#>LoD	Median	Range	#>LoD	Mean difference	Spearman correlation, r_s
PM _{2.5}	10	5.7–26	9	11	6.1–29	9	–0.87	0.94
BS	0.92	0.62–1.2	9	1.1	0.72–1.6	9	–0.21	0.70
S	1600	<140–4800	9	1400	<120–4200	8	220	0.99
Cl	49	27–200	7	75	<63–140	7	–7.4	0.81
K	130	82–230	9	140	80–200	9	0.46	0.88
Ca	19	5.1–36	9	11	4.7–17	9	7.3	0.57
Mn	5.3	0.80–21	9	3.3	<0.94–18	7	1.3	0.94
Fe	62	18–240	9	50	8.5–210	9	18	0.99
Cu	1.9	1.3–4.7	9	1.4	<0.47–3.3	7	1.1	0.62
Zn	44	18–220	9	57	16–180	9	6.1	0.95
Br	2.1	1.3–4.7	9	1.9	1.4–4.2	9	0.35	0.89
Rb	1.1	0.54–1.6	9	1.4	0.94–1.9	9	–0.33	0.73
Pb	7.8	2.4–17	9	8.5	3.3–16	9	–0.16	0.99

Median concentration, range, number of samples above limit of detection (LoD) and mean difference are presented. Units are, $\mu\text{g m}^{-3}$ for PM_{2.5}, ng m^{-3} for the elemental concentrations, and 10^{-5}m^{-1} for BS. All correlations are statistically significant.

Table 4

The difference in mean concentrations between personal exposure and indoor levels ($\mu\text{g m}^{-3}$ for PM_{2.5}, ng m^{-3} for the elemental concentrations, and 10^{-5}m^{-1} for BS) and corresponding p -values of the Wilcoxon signed-rank test

	All subjects		Wood-burners		Reference group	
	Mean difference	p -value	Mean difference	p -value	Mean difference	p -value
PM _{2.5}	4.81	0.001	6.60	0.021	2.23	0.084
BS	0.04	0.039	–0.02	0.638	0.14	0.010
S	34.68	0.148	–13.51	0.340	97.54	0.232
Cl	4.09	0.539	4.99	0.455	0.78	0.820
K	8.58	0.033	7.14	0.127	5.91	0.164
Ca	61.75	< 0.001	85.03	< 0.001	28.03	0.002
Mn	2.90	0.001	3.84	0.033	1.51	0.049
Fe	35.47	< 0.001	41.52	0.021	27.61	0.002
Cu	4.59	< 0.001	5.86	0.007	2.93	0.037
Zn	9.74	0.001	12.63	0.033	5.16	0.037
Br	–0.09	1.000	–0.30	0.623	0.15	0.516
Rb	–0.02	0.891	–0.41	0.013	0.48	0.047
Pb	1.84	0.009	2.97	0.002	0.23	0.700

Values are presented for all subjects as well as for wood burners and the reference group separately. Significant p -values are marked in bold.

4.2. Markers of wood smoke

The median differences between wood burners and the reference group for K, Ca, and Zn were 94, 34, and 16 ng m^{-3} , respectively, for personal exposures, and 83, 34, and 10 ng m^{-3} , respectively, for indoor levels. This

corresponds to a relative increase of 66–80% for these elements. In addition, Cl, Mn, Cu, and Rb showed significant differences in terms of personal exposure or indoor levels, while for BS the differences were nearly significant in both cases, and for Pb the differences were nearly significant for personal exposure. The relative

Table 5
A summary of some recent studies (mean value \pm standard deviation)

Measurement site	Personal PM _{2.5}	Personal BS	Indoor PM _{2.5}	Indoor BS	Outdoor PM _{2.5}	Outdoor BS	# of subjects	References
Hagfors, Sweden ^a	19.7 \pm 14.3	0.94 \pm 0.68	14.8 \pm 14.5	0.90 \pm 0.87	13.7 \pm 8.0	0.94 \pm 0.19	24	This study
Athens, Greece			35.6 \pm 29.4	2.92 \pm 2.50	37.3 \pm 27.4	3.30 \pm 2.56	43	Götschi et al. (2002)
Basel, Switzerland			21.0 \pm 16.7	1.37 \pm 0.58	19.3 \pm 11.5	1.39 \pm 0.51	41	Götschi et al. (2002)
Helsinki, Finland			9.5 \pm 6.1	0.78 \pm 0.46	10.5 \pm 7.1	0.97 \pm 0.44	82	Götschi et al. (2002)
Prague, the Czech Republic			34.4 \pm 28.7	2.74 \pm 0.81	27.3 \pm 10.4	2.98 \pm 1.30	20	Götschi et al. (2002)
New York, USA Winter ^a	17.0 \pm 6.8	1.65 \pm 0.70	20.9 \pm 16.9	1.62 \pm 0.78	11.9 \pm 3.8	1.94 \pm 0.91	46	Kinney et al. (2002)
New York, USA Summer ^a	18.5 \pm 17.7	1.71 \pm 0.61	19.0 \pm 21.5	1.66 \pm 0.62	13.6 \pm 4.5	1.79 \pm 0.71	46	Kinney et al. (2002)
Amsterdam, Netherlands ^a	24.3 \pm 25.7	1.73 \pm 0.78	28.6 \pm 41.8	1.84 \pm 0.74	20.6 \pm 4.0	1.79 \pm 0.28	37	Janssen et al. (2000)
Helsinki, Finland ^a	10.8 \pm 4.4	1.51 \pm 0.67	11.0 \pm 4.0	1.57 \pm 0.51	12.6 \pm 2.0	2.05 \pm 0.25	47	Janssen et al. (2000)
Birmingham, AL, USA, Winter	10.0 \pm 3.3		11.2 \pm 5.4		12.2 \pm 5.1		30	Lachenmyer and Hidy (2000)
Birmingham, AL, USA, Summer	18.6 \pm 6.4		16.1 \pm 5.7		26.5 \pm 9.5		30	Lachenmyer and Hidy (2000)
Basel, Switzerland ^a	17.5 \pm 13.0				17.7 \pm 7.1		20	Oglesby et al. (2000)

The data on PM_{2.5} are expressed in $\mu\text{g m}^{-3}$ and for black smoke (BS) in 10^{-5} m^{-1} .

^aNo exposure to cigarette smoke among the subjects.

increases for wood burners in both personal exposures and indoor levels of these species averaged 61%. All the above species are mentioned in the literature as being present in particles originating from burning wood (Harju et al., 1997; Hedberg et al., 2002; Moloi et al., 2002; Selin et al., 1993). The present study focused on the contribution of pollutants from wood burning in an area with mixed heating systems; the true contribution may be even larger, since the reference group was recruited from the same area, and thus could be indirectly affected by exposure to wood smoke. Ca and K are also present in soil. However, particles of crustal origin are mainly found in the coarse fraction and, therefore, it is less likely that they have affected our PM_{2.5} results. In addition there was full snow cover during the sampling period.

The lack of significant differences between wood burners and the reference group for S, a known marker of wood smoke, could be explained by the effect of the long-distance transport (LDT) of pollution. Sweden has no major anthropogenic sources of S. For instance, in Sweden the S content of fuel is < 10 ppm, much lower than the current European directive of 350 ppm. The additional S contributed by wood burning is small compared to the great variation in the contribution of S from air coming to Hagfors via LDT. The mean outdoor S concentration found in this study on days with a strong marine influence was 290 ng m⁻³; in contrast, the mean concentration of outdoor S was 3700 ng m⁻³ on days influenced by air originating from central Europe (see Section 4.4 below).

Pb is mentioned as being present in wood (Hedberg et al., 2002), and is enriched in wood by deposition from air pollution and uptake via the root system. However, after the ban of leaded fuel in vehicles, both atmospheric concentrations and the uptake of Pb have been reduced. For Pb, the difference in personal exposure between wood burners and the reference group was only nearly significant, while the difference was not at all significant for indoor levels. Since Pb correlated with S (indoors $r_s = 0.60$, outdoors $r_s = 0.82$), a substantial part of the measured exposure could be attributed to LDT.

The lack of significant differences between wood burners and the reference group for indoor levels of Cl (the difference was significant for personal exposure) and BS was unexpected. In Fig. 1, the BS concentration pattern shows that two clusters of wood burners can be identified, one in the midst of the reference group and one with higher concentrations. Note also (Fig. 1) that the indoor levels of BS for both wood burners and the reference group were independent of the outdoor concentrations, $r_s = 0.25$ and 0.28, respectively. The two clusters of wood burners were observed also to some extent for the wood-smoke related elements, Cl, K and Ca. For the personal exposure, similar clusters were found for, BS (see Fig. 1), K and Ca. The information

collected about the boilers and their use (age and type of boiler, presence of accumulator tank, type of firewood, firewood storage, frequency of fuel replenishment, total volume of wood burned, and type of ventilation system) could not explain these findings. Additional factors probably affect the presence of indoor wood smoke, such as differences in boiler efficiency, performance, and handling, and differences in the layout of the houses. Since Hagfors is a small town, the traffic intensity is low and therefore probably not the cause of the clusters. However, this study involves a limited number of subjects which makes it difficult to investigate the influence from different factors, e.g. boiler type, etc.

4.3. Personal exposures versus indoor concentrations

The differences between personal and indoor levels varied somewhat depending on the group (see Table 4). Personal exposure levels were higher for most elements, though this pattern could differ. Fig. 2 shows that

personal exposure levels of Ca are clearly higher than the corresponding indoor levels, while K and BS (see Fig. 1) shows an association close to unity. Similar relations as for Ca were noted for Cu, Fe, Mn, and PM_{2.5}. This might be explained by the substantial additional exposure experienced by some wood burners during fuel replenishment, or by activities in environments outside the home.

From the data in Table 5 the ratios between the mean personal exposures and mean indoor concentrations (*P/I*) for PM_{2.5} can be calculated; these range from 0.81 to 1.16, compared to 1.37 (mean of individual ratios 1.77) for Hagfors. The two studies that presented summer and winter values separately (Kinney et al., 2002; Lachenmyer and Hidy, 2000) both found higher ratios in the summer than in the winter — 0.97 vs. 0.81, and 1.16 vs. 0.89, respectively. Given that people tend to spend the majority of their time indoors the explanation for the higher ratio in Hagfors may be the addition of exposure to wood smoke during fuel replenishment, which is

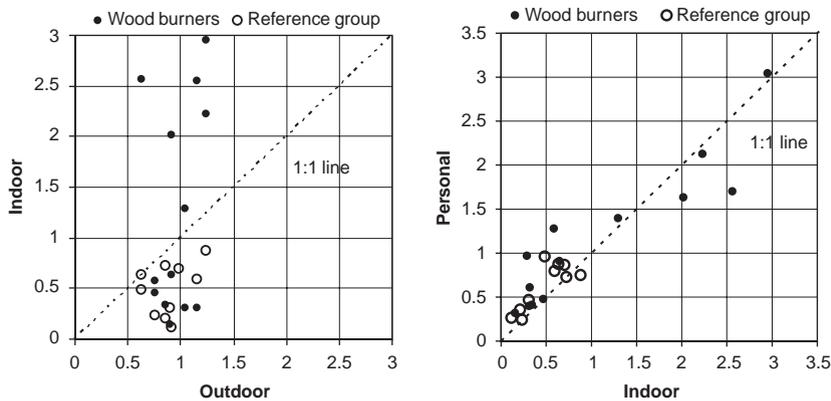


Fig. 1. Black smoke concentrations (in 10^{-5} m^{-1}) for wood burners and the reference group: indoors vs. outdoors and personal vs. indoors.

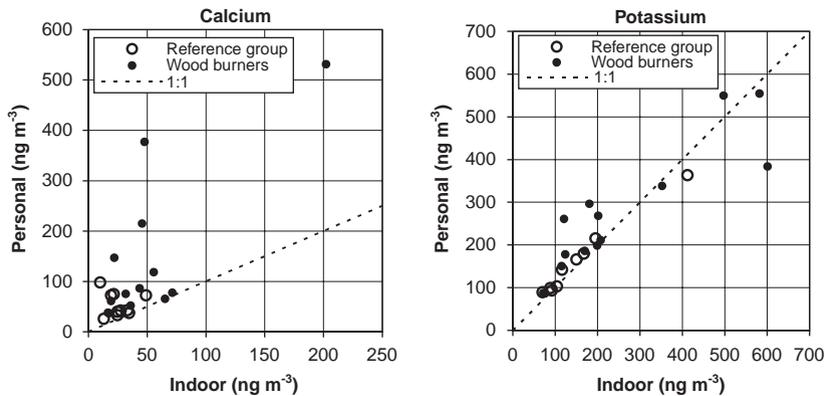


Fig. 2. Relations between personal exposure and indoor levels for two elements: Ca with a statistically significant difference, and K without.

supported by the fact that the mean individual P/I ratio is higher for wood burners compared to the reference group (2.05 vs. 1.41).

The correlations between personal exposure and indoor levels were generally high when analysing all subjects together; however, when analysing wood burners and the reference group separately the correlation for the latter was somewhat higher for most species. This seems logical, since additional exposure during fuel replenishment would have a larger effect on total personal exposure than on indoor levels, and thus decrease the correlation.

4.4. Outdoor levels and comparison to indoor levels and personal exposures

The overall high agreement between the two impactors was to be expected. The weaker agreement for Ca and Cu can be partly explained by the difference in the cut-off function between the Sierra Andersen and the WINS impactor. Since particles containing Ca (mainly of crustal origin) are normally greater than $1\ \mu\text{m}$ in aerodynamic diameter and Cu containing particles can exist in both the fine and the coarse fraction (Salma et al., 2001), sampling of particles around the $2.5\ \mu\text{m}$ cut-off size could influence the results.

Using the NOAA ARL HYSPLIT Model (Draxler and Rolph, 2003) 96-h air mass back trajectories were computed. Outdoor elemental concentrations were strongly affected by the route of the trajectories, and two typical air mass paths were dominant during the measurement period (see Fig. 3). One was a North Atlantic trajectory bringing in clean marine air (with high Cl levels), and the other was a trajectory route originating from Eastern Europe, and passing over Central Europe before turning northward towards Hagfors. The latter trajectory brought more polluted sulphur-rich air that also contained elevated concentrations of Pb and $\text{PM}_{2.5}$ (see Fig. 3). The high correlation

for S between outdoor and personal exposure found in the present study has also been shown in the study by Oglesby et al. (2000). For all other elements and $\text{PM}_{2.5}$ the correlations between the outdoor and personal or indoor levels were weak, thus measurements at a stationary outdoor location did not reflect the personal exposure.

Sulphur is a suitable element to use when calculating the penetration factor of fine outdoor particles. In this study the median S indoor/outdoor ratio (I/O) was 0.50 (95% CI of 0.38–0.59). Other studies have presented I/O ratios for S or sulphate ranging from 0.6 to 0.9 (Geller et al., 2002; Jones et al., 2000; Leaderer et al., 1999; Sarnat et al., 2002), somewhat lower values being found in winter than in summer. Sweden has longer seasons of colder weather than do most countries, and Swedish homes are better insulated with filtered ventilation systems that reduce the penetration factor. The strong influence of long-distance sources on the measured outdoor concentrations also affects the personal exposures and indoor levels, and this may mask the effect of some of the potential wood markers. However, most of the measurements were performed in parallel in the two groups.

5. Conclusions

Statistically significant contributions of wood burning to personal exposure and indoor concentrations have been shown for K, Ca, and Zn. Increases of 66–80% were found for these elements, which seem to be good wood-smoke markers. In addition, Cl, Mn, Cu, Rb, Pb, and BS were found to be possible wood-smoke markers, though not always to a statistically significant degree for personal exposure and indoor concentrations. For some of these elements subgroups of wood burners had clearly higher levels which could not be explained by the information available.

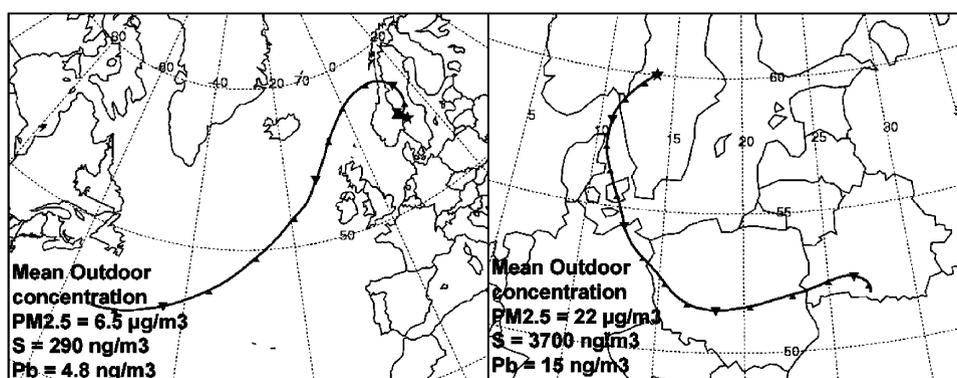


Fig. 3. Examples of two typical trajectory paths during the measurement period: to the left, a marine trajectory, and to the right an Eastern/Central European trajectory (representing 4 sampling occasions each).

Sulphur, one of the more typical elements mentioned as a wood-smoke marker, showed no relation to wood smoke in this study due to the large variations in outdoor concentrations from LDT air pollution. This was also the case for PM_{2.5} mass.

Personal exposures and indoor levels correlated well among the subjects for all investigated species, and personal exposures were generally higher than indoor levels. The correlations between the outdoor and personal or indoor levels were generally weak except for outdoor S and PM_{2.5} levels which were both highly correlated with personal S exposure and indoor S levels ($r_s > 0.8$).

There are few studies on wood smoke exposure in the general population. Further studies are needed, including also other substances and the influences of different factors.

Acknowledgements

This project was funded by the Swedish National Air Pollution and Health Effects Program (SNAP) and the Swedish Environmental Protection Agency. The authors also acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and for the READY website (<http://www.arl.noaa.gov/ready.html>) used in this publication. Thomas Götschi gave valuable comments on the draft manuscript.

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