Indoor and outdoor concentrations of $PM_{2.5}$ trace elements at homes, preschools and schools in Stockholm, Sweden

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Fine particles ($PM_{2.5}$) were sampled indoors and outdoors at 40 sampling sites; in ten classrooms in five schools, at ten preschools and 20 non-smoking homes, in three communities in Stockholm, Sweden, during nine 2-week periods. Each sampling site was sampled twice, once during winter and once during spring. The samples were analysed for elemental concentrations using X-ray fluorescence (XRF) spectroscopy. In all locations significantly higher outdoor concentrations were found for elements that are related to long-range transported air masses (S, Ni, Br and Pb), while only Ti was higher indoors in all locations. Similar differences for S, Br and Pb were found in both seasons for homes and schools. In preschools different seasonal patterns were seen for the long-range transported elements S, Br and Pb and the crustal elements Ti, Mn and Fe. The indoor/outdoor ratios for S and Pb suggest an outdoor $PM_{2.5}$ particle net infiltration of about 0.6 in these buildings. The community located 25 km from the city centre had significantly lower outdoor concentrations of elements of crustal or traffic origin compared with the two central communities, but had similar levels of long-range transported elements. Significant correlations were found between $PM_{2.5}$ and most elements outdoors (r_s=0.45–0.90). Copper levels were found to correlate well (r_s=0.64–0.91) to the traffic marker NO_2 during both winter and spring in all locations. Copper may be a suitable elemental marker for traffic-related aerosols in health studies in areas without other significant outdoor Cu sources.

Introduction

Air pollutants affect the health of humans globally. Long-term studies as well as short-term time series studies[1-4] have proven a causal link between exposure to air pollutants and adverse health outcomes[5]. The majority of these studies investigated the relationship between health outcomes (morbidity and/or mortality) and the concentrations of particles and gases. The mass concentrations of PM_{10} and/or $PM_{2.5}$ (particulate matter with an aerodynamic diameter <10 µm and <2.5 µm, respectively) were commonly measured outdoors at a fixed urban monitoring site.

Mass concentration is a rough measure since it is the sum of particles from numerous different sources (e.g. traffic, industries, wind-blown dust, sea spray and biomass burning) of both natural and anthropogenic origin. By chemical analysis of the particles additional information can be obtained. X-ray fluorescence (XRF) spectroscopy is a reliable, non-destructive technique for determination of trace elements, which requires no, or very limited, sample preparation. It can be used for a wide range of elements, from Si to U. Knowledge regarding particle composition and concentrations as well as the influence from different sources to ambient, indoor and personal exposure is needed to disentangle the causal relationships between PM components and health effects[6].

Children constitute a sensitive group, with airways not fully developed[7, 8]. The majority of children spend most of their time at home or at school/preschool and the concentrations at these localities are important for the time-weighted exposure of children. Both indoor and outdoor contributions should be considered since children often play outside. Two recent review articles [5, 9] conclude that fine particles, $PM_{2.5}$, have stronger relation to most health effects than PM_{10}. Concentration of $PM_{2.5}$ and its composition vary between cities and countries in ambient air[10]. and contribution of ambient sources to indoor $PM_{2.5}$ has been estimated to 23-67%[11, 12]. Schools and preschools have been sparsely investigated[13-18] and only two of these studies included trace elements[14, 16].

The aim of this study was to characterise and compare the indoor and outdoor fine particle ($PM_{2.5}$) trace element concentrations in different microenvironments (at homes, preschools and schools) relevant to children. The effects of season, degree of urbanisation (distance to city centre) and air exchange rates were also investigated. Another aim was to investigate the relation between the traffic marker NO_2 and levels of trace elements outdoors. The findings on $PM_{2.5}$ mass, $PM_{2.5}$ light absorption and NO_2 will be reported in detail elsewhere[19].

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Material and Methods

Study sites and measurement strategy

The study was conducted in Stockholm, Sweden, between 1 December 2003 and 1 July 2004 and was divided into nine 2-week periods. A total of 40 sampling sites were initially selected for the study: ten classrooms in five schools, and ten preschools and 20 homes. The sites were selected to represent local conditions, e.g. traffic intensity and population density. They were located in Stockholm city centre (Norrmalm), municipalities located about 10 km NW of the city centre (Solna and Sundbyberg) and a municipality situated about 25 km NW of the city centre (Järfälla), hereafter named "city centre", "suburban city area" and "background area". These areas are the same as in the Traffic-Related Air Pollution on Childhood Asthma (TRAPCA) study[20] and in the birth cohort (BAMSE)[21, 22]. Measurements were performed at eight to twelve sites in each 2-week period, incorporating the three microenvironments (homes, schools and preschools). At each site, two parallel 14-day samples were taken, one indoors and one outdoors. Measurements were performed in two different seasons (winter and spring/early summer). The winter season was from 1 December to mid-March, while the spring/early summer season (called "spring season" in this paper) was between the end of March and 1 July. Temperature and relative humidity were recorded both indoors and outdoors at each site.

Schools and preschools in the chosen areas were contacted by telephone. Those who were interested in participating in the study were visited. To be selected the schools and preschools were required to have a safe outdoor location for placement of the pump during the measurements, and possibilities to connect tubes (and cord) from the pump outside to the impactor in the classroom. The pump was placed outdoors because of the noise.

After the classrooms were selected, the school children's parents were asked to participate in the study and two families from every classroom were recruited. The children were 6–11 years old (i.e. no preschool children). The families had to be non-smoking, not use gas for cooking and have a balcony or some other safe place with electricity for the pump. Thus, no environmental tobacco smoke exposure occurred in any of the indoor environments.

Sampling and analysis

$PM_{2.5}$ sampling

$PM_{2.5}$ was sampled on Andersen 37 mm 2-µm pore size Teflon filters (Anderson Samplers Inc., Atlanta, GA, USA) with Harvard impactors[23] (Air Diagnostics and Engineering Inc., Harrison, ME, USA) using a flow rate of 10 l min^{-1} according to the standard operation procedure described in TRAPCA[24]. The pump units contained a vacuum pump, critical orifices to maintain the flow at 10 l min^{-1}, a timer and an elapsed time indicator (Institute for Risk Assessment, University of Utrecht, The Netherlands). The sampling flow rate was measured before and after each sampling, using a DryCal® DC-Lite Flowmeter (Bios International, Butler, NJ, USA). The mean flow rate at start-up was 10.2 l min^{-1}, (range 9.5-10.6 l min^{-1}) and at the end 10.2 l min^{-1} (range 8.7-10.8 l min^{-1}). Sample volume was calculated as the average flow rate multiplied by the elapsed time. Pairs of duplicate samples were collected during each measurement period, eight indoors and nine outdoors.

Table 1 Median limit of detection (LoD), expressed as airborne concentrations (in ng m^{-3}) measured at the homes of participating children.

Element	Limit of detection
S	60
K	5.7
Ca	3.5
Ti	1.9
V	1.5
Cr	1.1
Mn	0.83
Fe	0.65
Ni	0.65
Cu	0.58
Zn	0.50
Br	0.34
Pb	0.43

The sampling regimen aimed at characterising the air quality indoors and outdoors for those parts of normal weeks when the children were present in the measured microenvironment. In order to prevent overloading of the filter, timers were used to turn the pump on and off according to a schedule. At the homes of participating children the pump was turned on for 15 minutes every 2 hours both day and night for the whole 14-day period, while in schools it was turned on for 45 minutes every hour between 8 am and 4 pm. At preschools the pump was on for 30 minutes out of every hour between 8 am and 6 pm. Measurements at schools and preschools were not performed during Saturdays and Sundays. The sampling schedule gave mean sampling times of 43, 64, and 54 hours and mean sample volumes of 26 m^3, 39 m^3 and 33 m^3 at homes, schools and preschools, respectively. The figures are the same for both indoor and outdoor measurements.

Trace element analysis

The content of selected trace elements in the filters was analysed using an energy-dispersive X-ray fluorescence (EDXRF) spectrometer at the Department of Chemistry, Atmospheric Science, Göteborg University[25]. 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)[26, 27]. All samples were analysed using a livetime of 1,000 seconds, a tube voltage of 55 kV, a tube current of 25 mA, and a Mo secondary target. Calibration procedure and quality control followed the procedure presented in Molnár et al.[28]. The median limit of detection (LoD) for the different elements, expressed as airborne concentrations measured at participating children's homes, is presented in Table 1.

Table 2 Trace elemental concentrations for the total study, in ng m^{-3}, indoors and outdoors at the homes of participating children and at schools and preschools. N = number of samples and #>LoD = number of samples above the limit of detection.

	Homes							
	Indoor (N=28)				Outdoor (N=35)			
	Median	Mean	#>LoD	Range	Median	Mean	#>LoD	Range
S	330	400	24	81–920	580	610	35	140–1,500
K	120	170	28	35–560	84	91	35	36–210
Ca	70	76	28	31–170	33	40	35	8–100
Ti	8.0	9.0	28	3.6–27	5.7	6.7	34	1.4–18
V	2.5	3.1	23	0.9–12	3.0	3.5	30	0.7–6.2
Cr	<1.1[a]	1.3	12	0.5–2.3	<0.93[a]	1.0	6	0.3–2.0
Mn	2.2	2.2	25	0.7–4.7	2.6	2.9	35	0.9–5.6
Fe	57	70	28	17–190	89	94	35	13–250
Ni	0.99	1.1	19	0.3–3.5	1.3	1.4	33	0.4–2.7
Cu	9.3	13	28	2.5–38	3.6	4.2	34	0.3–14
Zn	14	16	28	6.9–38	16	18	35	7.0–38
Br	2.1	2.0	28	0.2–3.9	2.5	2.7	35	1.1–5.3
Pb	2.8	3.4	27	0.04–8.0	4.0	4.5	35	1.2–11
	Schools							
	Indoor (N=19)				Outdoor (N=19)			
	Median	Mean	#>LoD	Range	Median	Mean	#>LoD	Range
S	290	290	17	85–580	560	610	18	97–1,200
K	96	140	19	24–780	77	90	19	38–200
Ca	110	120	19	32–280	37	46	19	9.3–110
Ti	13	17	19	4.3–40	5.9	9.1	19	1.8–22
V	2.7	2.6	15	0.8–4.7	3.1	3.1	15	1.1–5.9
Cr	1.3	1.7	15	0.4–7.7	1.2	1.2	12	0.2–2.7
Mn	2.5	2.9	19	0.8–6	3.7	3.6	18	0.9–7.2
Fe	100	140	19	36–390	130	140	19	16–400
Ni	1.0	1.1	18	0.4–2	1.4	1.5	17	0.7–2.9
Cu	1.7	2.3	18	0.3–7	5.5	4.9	19	0.7–14
Zn	17	17	19	5.7–28	17	19	19	5.8–39
Br	1.3	1.3	19	0.5–2.5	2.4	2.5	18	1.4–4.3
Pb	2.5	2.5	17	0.39–5.3	4.1	4.6	18	1.3–10
	Preschools							
	Indoor (N=18)				Outdoor (N=20)			
	Median	Mean	#>LoD	Range	Median	Mean	#>LoD	Range
S	220	230	13	71–570	370	360	17	91–700
K	67	75	18	20–260	50	63	20	22–340
Ca	58	65	18	23–99	26	51	20	12–390
Ti	8.7	9.5	18	4.5–21	4.2	7.4	19	1.5–61
V	1.8	2.1	14	1.2–3.7	2.2	2.3	18	0.7–4.5
Cr	1.1	1.1	13	0.5–1.9	1.0	0.98	11	0.4–1.5
Mn	2.1	2.1	18	0.7–3.9	2.0	2.9	19	0.6–15
Fe	71	80	18	29–250	72	110	20	17–750
Ni	0.72	0.72	12	0.2–1.6	1.0	0.98	19	0.3–1.8
Cu	2.1	3.9	18	0.9–17	4.1	4.3	19	0.4–17
Zn	11	12	18	5.9–22	11	13	20	6.1–28
Br	1.3	1.2	18	0.4–2.4	1.6	1.8	20	1–3.7
Pb	1.7	1.8	17	0.64–5.5	2.0	2.6	20	1.1–6.8

[a] Where the median value is below the LoD for the element in question, the value is given with a < sign.

Duplicate samples were used to calculate the precision, expressed as the coefficient of variation (CV), for all the elements. This was <27% for all elements except Cu and Zn (CV 177% and 38%, respectively). For K, Mn, Fe, Ni, Br and Pb, the CVs were all <20%. The extremely high CV for Cu was caused by one pair of outdoor filters, which were responsible for 77% of the total variance for this element. Most likely, one of the filters was contaminated by brass since both the Cu and the Zn concentrations were highly elevated in the same filter while the other elements had equal concentrations for the pair. Excluding this filter pair, the CV for Cu and Zn dropped to 45% and 24%, respectively The CVs for the other elements were unaffected. This filter has not been used in any of the following analyses.

Analysis of $PM_{2.5}$ mass and NO_2

In addition to the elemental analysis, the filters were analysed gravimetrically for $PM_{2.5}$ mass. Nitric dioxide (NO_2) was sampled in parallel to $PM_{2.5}$ sampling, using diffusive samplers from the Swedish Environmental Research Institute (IVL). The NO_2 samples were analysed spectrophotometrically by the IVL [29].

Ventilation

The ventilation, determined as the air exchange rate, was evaluated using a sender-receiver tracer gas technique (using perfluorobenzene and perfluoromethylbenzene) and measuring the distribution of the ventilation and the total air infiltration rate[30]. Ventilation was measured day and night in the participating children's homes but only during daytime in schools and preschools. The placement of the trace gas emitter and the sampling tubes was done independently for each site by Pentiaq AB, Gävle, Sweden, who also prepared the tubes and performed the analyses.

Statistical analysis

Statistical calculations were performed using the SAS System for Windows, version 9.1[31]. Correlations between elemental concentrations in different microenvironments were assessed using the Spearman rank correlation coefficient (r_s) and differences between pairs of indoor and outdoor levels were calculated using the Wilcoxon signed rank test. For unpaired observations, Kruskal-Wallis or Wilcoxon rank sum test was used. Statistical significance refers to $p<0.05$ in two-tailed tests. Non-parametric tests were used, because in general the levels were not normally distributed. If the elemental concentration was below the LoD, the LoD divided by the square root of two was used in the calculations[32].

Results

Concentrations and differences between indoor and outdoor levels

A summary of the results for indoor and outdoor measurements in the investigated microenvironments is presented in Table 2. The median outdoor levels of most elements were similar for homes and schools, while preschools tended to have lower levels except for Cr, Ni and Cu which were similar. This general pattern was reproduced indoors, although some elements tended to deviate from the pattern. Median indoor Cu levels were higher in the homes of participating children than in other locations, and Fe tended to be higher in schools and preschools.

Significantly lower indoor than outdoor concentrations of S, Ni, Br and Pb were found in all locations, while Ti , K and Ca were higher indoors. However, only Ti was significantly higher indoors at all locations (Table 3). Schools also showed significantly lower indoor than outdoor concentrations of Cu. In addition to the general pattern, significantly lower indoor concentrations of V, Mn, Fe and Zn were also found in the participants' homes, while higher indoor concentrations were observed for K, Ca and Cu.

For S, Br and Pb, similar differences were found in both seasons for homes and schools, but some of the other differences between indoor and outdoor levels showed a seasonal pattern. At the preschools, significantly lower indoor than outdoor concentrations were found for S, Mn, Fe, Ni, Br and Pb only during the winter period. In schools, higher indoor concentrations were found for Ca and Ti although during spring the difference was not significant.

The mean $PM_{2.5}$ concentrations were about 8 μg m^{-3} both indoors and outdoors (range 3.3–19 μg m^{-3} and 3.2–26 μg m^{-3}, respectively). These results are discussed in detail elsewhere[19].

Spatial differences

The three different communities investigated, Norrmalm, Solna/Sundbyberg and Järfälla, represent the city centre, a suburban city area and a background area within the Stockholm metropolitan area. There were no statistically significant differences between the city centre and the suburban city area (not shown in table), but sampled sites in the city centre and in the suburban city area showed higher outdoor levels for all elements compared with sites in the background area, with similar differences for homes, schools and preschools (Table 4). For homes, most of these spatial differences were statistically significant, while only Cu showed statistically significant spatial differences for homes, schools and preschools. Homes in the two more central areas showed significantly higher outdoor levels of Ca, Mn, Fe, Ni, Cu and Zn compared with homes in the background area. For preschools in the two more central areas, significantly higher outdoor levels of elements of crustal origin (Ca, Ti and Fe) were found, similar to the findings for the homes.

Associations between outdoor trace elements and $PM_{2.5}$ or NO_2

Significant correlations were found between $PM_{2.5}$ mass and all elements except Cr in all microenvironments (Table 5). NO_2 by contrast, was significantly correlated only to Cu and Zn in all microenvironments. The associations between some elements (S, Cu and Zn) and NO_2 or $PM_{2.5}$ are presented in Fig. 1. Sulphur was highly correlated to $PM_{2.5}$ in all locations, while it was generally not correlated to NO_2. Similar results were also found for Ti, V, Ni, Br and Pb, with the exception for Ni and Pb at preschools, (not shown in the Figure). Copper levels showed a high and significant correlation with NO_2 in all microenvironments and for both seasons (not shown in Figure) while the correlations to $PM_{2.5}$ were moderate.

Table 3 Differences in mean concentration between indoor (I) and outdoor (O) levels, in ng m^{-3}, and corresponding p-values using the Wilcoxon signed-rank test. Significant p-values are marked in bold. N= number of samples.

	Homes					
	I-O total (N=28)		I-O winter (N=8)		I-O spring (N=20)	
	mean difference	p-value	mean difference	p-value	mean difference	p-value
S	-270	**<0.001**	-270	**0.008**	-270	**<0.001**
K	76	**0.048**	160	0.055	44	0.430
Ca	33	**<0.001**	34	**0.008**	33	**0.004**
Ti	1.9	**0.032**	2.6	**0.008**	1.6	0.430
V	-0.68	**0.001**	-0.66	0.109	-0.69	**0.006**
Cr [a]						
Mn	-0.79	**<0.001**	-0.47	0.078	-0.92	**0.001**
Fe	-30	**0.002**	-33	**0.039**	-29	**0.040**
Ni	-0.39	**<0.001**	-0.05	0.641	-0.53	**<0.001**
Cu	9.0	**<0.001**	12	**0.008**	7.8	**<0.001**
Zn	-3.1	**<0.001**	-4.0	**0.039**	-2.7	**0.005**
Br	-0.87	**<0.001**	-0.87	**0.016**	-0.87	**<0.001**
Pb	-1.5	**<0.001**	-1.6	**0.008**	-1.5	**<0.001**
	Schools					
	I-O total (N=19)		I-O winter (N=8)		I-O spring (N=11)	
	mean difference	p-value	mean difference	p-value	mean difference	p-value
S	-330	**<0.001**	-300	**0.023**	-340	**0.001**
K	33	0.225	100	0.078	13	0.700
Ca	68	**0.001**	74	**0.008**	68	0.067
Ti	7.6	**0.023**	5.9	**0.008**	8.9	0.123
V	-0.49	0.080	-0.33	0.461	-0.61	0.123
Cr	0.51	0.080	0.44	0.055	0.56	0.413
Mn	-0.70	0.096	-0.59	0.075	-0.75	0.365
Fe	-2.7	0.798	-17	0.313	7.2	0.765
Ni	-0.46	**0.003**	-0.45	**0.023**	-0.42	0.067
Cu	-2.7	**<0.001**	-2.7	**0.023**	-2.7	**0.007**
Zn	-2.2	0.258	-0.26	0.547	-2.9	0.320
Br	-1.2	**<0.001**	-1.1	**0.008**	-1.2	**0.001**
Pb	-2.1	**<0.001**	-2.0	**0.016**	-2.2	**0.007**
	Preschools					
	I-O total (N=18)		I-O winter (N=9)		I-O spring (N=9)	
	mean difference	p-value	mean difference	p-value	mean difference	p-value
S	-110	**0.001**	-170	**0.004**	-57	0.129
K	9.0	0.167	-8.3	0.910	26	**0.039**
Ca	9.7	0.060	-12	0.301	31	0.164
Ti	1.5	**0.030**	-3.9	0.734	6.9	**0.004**
V	-0.29	0.304	-0.51	0.203	-0.06	1.000
Cr	0.04	0.932	0.13	0.820	-0.04	0.652
Mn	-0.90	0.640	-2.40	**0.008**	0.63	0.098
Fe	-40	0.766	-120	**0.039**	39	0.098
Ni	-0.26	**0.018**	-0.31	**0.039**	-0.21	0.426
Cu	-0.63	0.246	-2.6	0.203	1.3	0.820
Zn	-1.4	0.347	-3.2	0.250	0.37	1.000
Br	-0.60	**<0.001**	-0.97	**0.004**	-0.24	0.055
Pb	-0.73	**0.009**	-1.2	**0.020**	-0.26	0.301

[a] Not analysed because fewer than 50% of samples were above the limit of detection (LoD).

Table 4 Mean differences, in ng m^{-3}, in outdoor concentrations between the city centre and the suburban city area versus the background area. Significant differences ($p<0.05$) using the Wilcoxon rank sum test are marked in bold.

	Homes		Schools		Preschools	
	City centre vs. Background	Suburban vs. Background	City centre vs. Background	Suburban vs. Background	City centre vs. Background	Suburban vs. Background
S	210	310	180	320	41	42
K	**45**	35	26	24	22	45
Ca	**43**	**22**	26	13	**22**	**67**
Ti	4.5	**3.0**	2.6	1.8	**4.4**	**8.9**
V	1.4	**1.7**	1.5	**2.3**	**1.3**	0.81
Cr	[a]	[a]	0.65	0.68	0.27	0.38
Mn	**1.8**	**1.5**	1.8	1.4	1.4	2.4
Fe	**101**	**75**	120	50	**93**	**142**
Ni	**0.70**	**0.73**	0.69	**0.84**	0.35	0.33
Cu	**3.9**	**3.8**	**7.1**	**3.1**	**3.8**	**5.1**
Zn	**8.6**	**7.9**	9.0	7.7	5.7	6.7
Br	0.94	**1.5**	0.62	0.93	0.20	0.12
Pb	2.0	**2.6**	1.4	1.5	1.4	**1.6**

[a] Not analysed because fewer than 50% of samples were above the limit of detection (LoD).

For Zn, similar associations with $PM_{2.5}$ and NO_2 were found except for homes where Zn had higher correlation to $PM_{2.5}$. Several more trace elements (K, Mn, Fe, Ni, Zn and Pb) were found to be highly correlated to NO_2 at preschools but not, or only weakly, to NO_2 at participating children's homes and in schools (Table 5).

The associations between $PM_{2.5}$ and trace elements were mostly similar for the two seasons. For NO_2, on the other hand, seasonal differences were found at preschools and homes, with significant correlations only in spring for many of the elements (data not shown).

Indoors, similar associations as outdoors were found between the trace elements and $PM_{2.5}$ mass while generally no associations were found for NO_2 (data not shown).

Infiltration and ventilation

The infiltration of outdoor particles indoors was evaluated for S and Pb since these two elements had no known indoor sources in our sampling locations. The infiltration was calculated as the ratio between matched indoor and outdoor concentrations for homes, schools and preschools separately.

The median infiltration ratios for S were 0.61, 0.53 and 0.69 for homes, schools and preschools, respectively (Table 6). Corresponding values for Pb were 0.70, 0.59 and 0.70. Winter period ratios were somewhat lower, mainly for homes and schools, for both S and Pb, while in the spring, higher ratios were found for preschools.

As described previously, the air exchange rate was measured by a tracer gas technique. The median air exchange rates for homes, schools and preschools were 0.6, 1.2 and 1.2, respectively. No significant associations were found between the air exchange rate and the infiltration for S or Pb at any location or season except for S at homes during winter (Fig. 2). The exchange rates at the homes (range 0.2–1.3) were evidently lower than for schools and preschools (0.4–3.5 and 0.3–5.8, respectively).

Discussion

In the present study the concentrations of 13 $PM_{2.5}$ trace elements indoors and outdoors in children's environments in Stockholm, Sweden were investigated. The main finding was that most elements showed lower levels indoors than outdoors, with only Ti showing consistently higher levels indoors than outdoors. The infiltration of $PM_{2.5}$ particles containing S and Pb was in the range of 0.4–0.9, depending on the microenvironment and season.

The results are discussed in relation to different pollution sources, seasons and locations. Apart from homes, children's environments (schools and preschools) have been sparsely investigated regarding trace elements. In the present study similar patterns were found for the three microenvironments regarding most trace elements. Significantly higher outdoor concentrations of S, Ni, Br and Pb were found in all locations. Outdoors, relatively high correlations were found between $PM_{2.5}$ and nearly all elements, while only Cu and Zn were significantly correlated to NO_2 in all microenvironments.

The sampling protocol was used to ensure both a spatial and seasonal mapping without the risk of filter overload. The limitation of this approach was that the sampling times in homes only captured 13% of the total time while in schools and preschools the figures were 75% and 50%, respectively.

Outdoor levels

The urban background levels of $PM_{2.5}$ in the Nordic countries are low in comparison with those in continental Europe[10, 33-37]. The levels in Stockholm are generally lower for S and Pb, and higher for Ti compared to reports from continental Europe [34, 38, 39] and the USA [40, 41]. For Ca, Fe, and Cu the levels are similar. The elemental levels in our study are generally in agreement with previous reports from Gothenburg[36] and Helsinki[34]. Sulphur levels are, however, lower in Stockholm (580 ng m^{-3}) than in Helsinki (1,400 ng m^{-3}) for the same

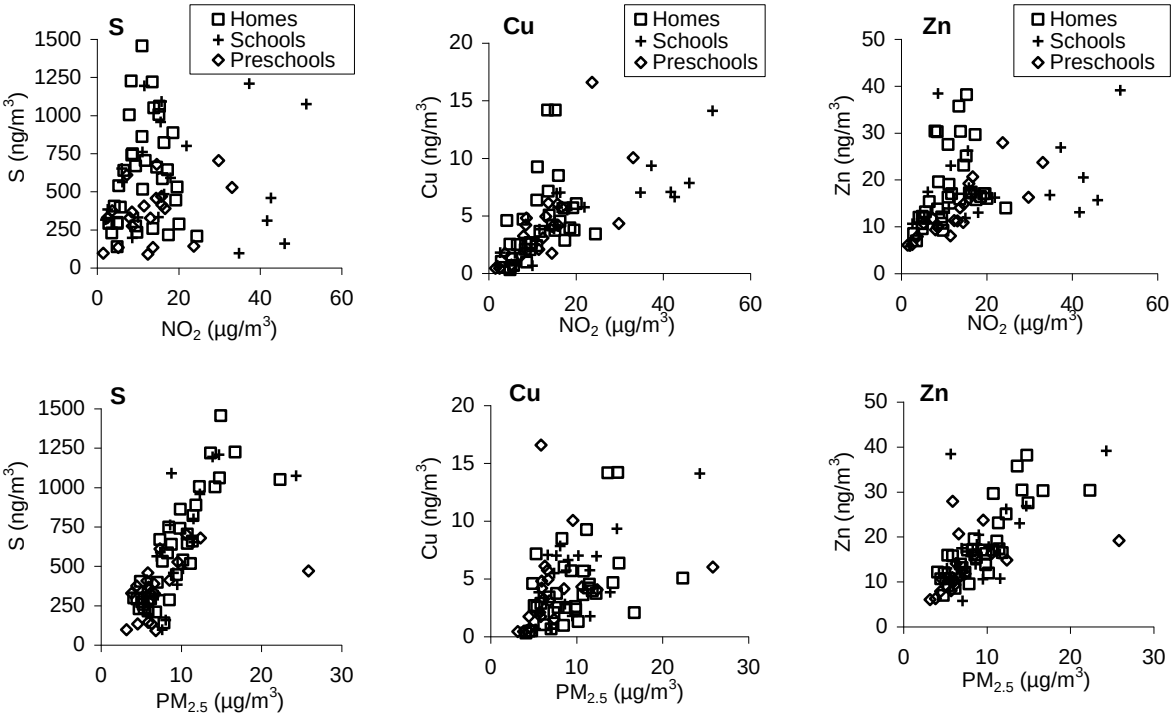

Fig. 1 Relations between outdoor levels of S, Cu and Zn, in ng m^{-3}, and NO_2 and $PM_{2.5}$, in µg m^{-3}.

period of the year. Stockholm and Helsinki are of comparable size, 1.2 and 0.9 million inhabitants, respectively, while Gothenburg has 0.6 million inhabitants. One explanation for the difference between Helsinki and Stockholm may be that Stockholm is less affected by long-range transported S from the Baltic countries and Russia[42]. Gothenburg showed somewhat lower S levels (460 ng m^{-3}) than did Stockholm, which could be due to the fact that the sampling in Gothenburg took place in spring and autumn. Also in keeping with previous reports[34, 36], we found Stockholm to have higher outdoor concentrations of Cu compared with both Gothenburg and Helsinki, and higher levels of Fe compared with Gothenburg. Stockholm's higher population density and traffic intensity may contribute, but different time periods and other local sources may also be important.

Indoor – outdoor differences

Very little has been published regarding indoor and outdoor concentrations of fine particle trace elements at schools and preschools. Our findings are in keeping with a recent study from a high school outside Los Angeles, CA, USA[16]. The concentrations, both indoors and outdoors, reported in that study were, however, higher than in the present study.

Generally, elements that are dominated by long-range transported air masses (S, Ni, Br and Pb) were found to have significantly lower concentrations indoors than outdoors in all microenvironments tested. Similar results for Br and Pb were seen in a previous study in homes in Gothenburg[36]. Only Ti was found to have significantly higher concentrations indoors than outdoors for all microenvironments. One likely indoor source of Ti is TiO_2, which is used as white pigment in paint[43].

The observed higher levels of Cu indoors compared with outdoors in the homes, but not in schools and preschools, may be due to cooking and frying[44] (using Cu-containing pots and frying pans) and electrical appliances (e.g. vacuum cleaners and hairdriers). Higher levels of Ca were found both at the participating children's homes and at schools (and preschools, although without statistical significance), which was probably caused by indoor resuspension of dust originating from ambient air and soil, and biological aerosols, as suggested in previous studies from countries such as the USA[45].

Table 5 Spearman correlation coefficients between outdoor measurements of trace elements and $PM_{2.5}$ or NO_2 in the three microenvironments. Significant correlations are marked in bold.

	Homes		Schools		Preschools	
	$PM_{2.5}$	NO_2	$PM_{2.5}$	NO_2	$PM_{2.5}$	NO_2
S	**0.85**	0.14	**0.74**	0.08	**0.56**	**0.45**
K	**0.90**	**0.39**	**0.86**	0.02	**0.72**	**0.71**
Ca	**0.67**	**0.45**	**0.68**	0.30	**0.46**	**0.47**
Ti	**0.59**	0.26	**0.51**	0.12	**0.49**	0.37
V	**0.84**	0.16	**0.45**	0.14	**0.73**	0.36
Cr	[a]	[a]	0.36	0.36	0.09	0.19
Mn	**0.78**	**0.41**	**0.74**	0.25	**0.66**	**0.84**
Fe	**0.68**	**0.65**	**0.74**	0.36	**0.70**	**0.75**
Ni	**0.85**	0.32	**0.61**	0.29	**0.60**	**0.53**
Cu	**0.51**	**0.64**	**0.45**	**0.91**	**0.56**	**0.80**
Zn	**0.83**	**0.52**	**0.46**	**0.47**	**0.75**	**0.90**
Br	**0.89**	0.27	**0.76**	0.26	**0.64**	0.37
Pb	**0.85**	0.24	**0.72**	0.24	**0.77**	**0.75**

[a] Not analysed because fewer than 50% of samples were above the limit of detection (LoD).

Table 6 Median ratios of the indoor infiltration of ambient particles, calculated for S and Pb for homes, schools and preschools for the whole study period as well as for winter and spring separately.

	Homes		Schools		Preschools	
	S	Pb	S	Pb	S	Pb
Both seasons	0.61	0.70	0.53	0.59	0.69	0.70
Winter	0.47	0.62	0.36	0.43	0.63	0.63
Spring	0.63	0.70	0.55	0.64	0.90	0.75

For the elements Mn and Fe, which are commonly found in resuspended dust, as well as Zn, from road traffic tire wear, statistically significantly lower indoor concentrations were found at homes, but not at schools and preschools. This may reflect the increased transport of soil dust on shoes indoors in schools and preschools in contrast to homes. In Sweden shoes are generally not worn indoors at home. In particular for preschools, however, the children tend to be outdoors a lot and frequently walk in and out, thus increasing the transport of soil dust particles to the indoor environment.

At homes and schools, the indoor-outdoor differences for the two seasons (winter and spring) were similar for all elements. For the preschools, on the other hand, the differences between seasons were more pronounced. The significantly lower indoor concentrations at preschools of the long-range transported elements S, Ni, Br and Pb during the winter season were not noticeable during spring, probably due to greater use of open doors and windows during the warmer period. The other elements that showed different patterns at preschools between the seasons were K, Ti, Mn and Fe. These elements changed from a higher mean outdoor concentration during winter to a higher mean indoor concentration during spring. Again, since preschool children often spend a large part of their days outdoors during the spring, often playing in the sandbox, they bring their sandy shoes and clothes indoors, which may increase the indoor concentrations of crustal material elements.

Spatial differences

For almost all elements, the outdoor concentrations in the two central areas were similar, while many elements at the background area were found to have a lower concentration. The effect was most pronounced for Fe and Cu (with fourfold increases in the central areas) and for Ca, Ti and Mn (with two- to threefold increases). The lower concentrations in the background area could be explained by the lower population density and the reduced traffic intensity. Less densely populated areas also have more green areas (private gardens and plantations) acting as deposition surfaces (i.e. particle traps), at the same time as there are fewer particle sources. Vehicles emit exhaust particles, produce particles through tire-road wear and increase the resuspension of settled particles. For homes and preschools, the elements having statistically higher concentrations in the two central areas were mainly of crustal and road wear origin, probably caused by emissions of resuspended road dust due to the higher traffic intensity. The elements that showed no or only weak, differences between areas were those that are strongly influenced by long-range transport. Similar results were seen in Cincinnati, OH, USA[46], where decreasing concentrations of a number of trace elements (Mn, Ni, Zn and Pb) from the city centre to a suburban and rural area were found.

Associations between outdoor trace elements and $PM_{2.5}$ or NO_2

Sulphur was found to be highly correlated to $PM_{2.5}$ but not to NO_2. Long-range transported pollution is a strong source for both S and $PM_{2.5}$, while NO_2 is of local traffic origin. High correlations between S and $PM_{2.5}$ have also been found in other studies[10, 28, 47]. Outdoor Cu was the only element that was significantly correlated to outdoor NO_2 in all microenvironments during both winter and spring, strongly suggesting that traffic is the source of outdoor Cu. Vehicle brakes are known to contain Cu[48-50], and therefore constitute a likely source of Cu. Several other studies from different parts of the world using various approaches have also shown that traffic is an important source of Cu [51-57]. Unfortunately, Cu does not seem to be a good candidate for monitoring the infiltration indoors of traffic-related particles, due to the presence of indoor sources in homes.

Most of the other elements correlated to NO_2 were traffic-produced, either directly (e.g. Zn from tire wear) or indirectly (e.g. Ca, Ti, Mn and Fe from resuspended road dust and road wear)[49]. These correlations to NO_2 were mainly seen during springtime at homes and preschools. The same elements were also correlated to $PM_{2.5}$ but in most cases in both seasons and in all microenvironments, suggesting a contribution also from non-traffic-related resuspension, i.e. wind-blown dust.

During winter conditions in Sweden the use of studded tires is common and sand and salt are routinely spread on streets to prevent accidents caused by skidding cars. In Stockholm about 75% of light vehicles use studded tires in winter[58]. During springtime, after the snow has melted, large amounts of particles are produced and resuspended when studded tyres are used on dry streets, and the streets are swept clean of excess sand and salt. This was reflected by the higher correlation between NO_2 (from traffic) and many elements (mainly crustal) during the spring compared with winter in our study, in support of the finding that street dust is an important source of airborne particulates during the spring months in Stockholm[59].

Infiltration and ventilation

The median value of the S infiltration was similar to that found in other studies[34, 36, 47, 60-63]. In the winter season the infiltration was lower, owing to the need for energy conservation in buildings in boreal regions. The calculated indoor-outdoor ratios were somewhat higher for Pb than for S in nearly all microenvironments regardless of season. A similar result was found by Long and Sarnat[61], who reported indoor-outdoor ratios of 0.74 and 0.81 for S and Pb, respectively. By contrast, Koistinen et al.[60] found a higher infiltration of S than of Pb for several seasons and Molnár et al.[36] found similar ratios for S and Pb. It has been shown that S particles are in the 0.2–1 µm size range[64, 65] while long-range transported Pb particles are around 0.5 µm[66]. Sulphur in the form of ammonium sulphate is hydroscopic and the mean relative humidity in Stockholm during the winter period was

about 90%, thus these particles will be larger. This may make the infiltration of Pb particles more effective.

The air exchange rates at the homes of the children in the present study were clearly lower compared with schools and preschools. The reason for the limited association between air exchange rate and infiltration in the present study is unclear. Most Swedish homes are tightly insulated and have non-mechanical (i.e. natural draught) ventilation driven by differences in indoor/outdoor air pressure. In winter, windows are kept shut and this was reflected by the low winter infiltration. On the other hand, schools commonly have filtered mechanical ventilation with higher air exchange rates. This feature with filtered air is reflected by the lower infiltration of outdoor particles in schools compared with the other microenvironments. Preschools have either natural or mechanical ventilation, but typically the doors to the playground are open during the spring season, permitting the children to freely move in and out. This situation favours a high outdoor-to-indoor transport of particles, reflected also for many of the crustal elements.

Implications for health studies

In this study we found high and consistent correlations between NO_2 and Cu outdoors for all microenvironments and over both seasons studied. This suggests that outdoor Cu may be a suitable elemental marker for traffic-related aerosols in health studies in areas without other significant outdoor Cu sources (e.g. certain industries or Cu roofs). Lead has traditionally been used as a marker of vehicle exhaust, but it is of less value today when most petrol is unleaded.

Other elements related to traffic are Zn from tire wear, and crustal elements from road wear. In Stockholm very high PM_{10} levels of resuspended road dust were reported by Norman and Johansson[58] during spring days with dry streets, and the present study showed the highest associations with NO_2 levels during spring. Presumably other Nordic cities share similar features. Toxicological studies have suggested that transition metals such as V, Cr, Mn, Fe, Ni, Cu and Zn are PM components with toxic potential[9]. A number of these elements are abundant during dry street conditions, but not when streets are wet. NO_2 levels, by comparison, are not dependent on the wetness of the streets. Therefore, studies of short-term health effects of trace elements should preferably be performed in spring when the contrast between days may be high for these elements.

Previous studies (in adult populations) have shown that personal exposures often are higher than indoor levels and also higher compared to outdoor levels except for elements dominated by outdoor sources [36, 38, 39, 67, 68]. Behaviour of adults and children are different and conclusions based on adult populations might not be valid for children and therefore more studies regarding children's exposure are warranted.

Conclusions

Significantly lower indoor concentrations of the elements S, Ni, Br and Pb, elements from long-range transported air masses, were found in all locations. Only Ti was significantly higher indoors in all locations, probably because of TiO_2 in paint pigment. Similar differences were found during both seasons for homes and schools. At preschools the infiltration of the long-range transported elements S, Br and Pb was lower in the winter than in spring, and also the crustal elements Ti, Mn and Fe had higher indoor concentrations during spring. There were spatial differences outdoors, with significantly lower concentrations of elements of crustal and traffic origin in the background area community. This shows the effect of differences in traffic intensity and green areas. Significant correlations were found between $PM_{2.5}$ and nearly all elements outdoors. Outdoors, Cu was found to correlate well with NO_2 during both winter and spring in all locations, making it a suitable marker for traffic. During springtime the correlations between NO_2 and resuspended elements were high, because of the release of accumulated road dust from winter sanding and increased road wear on days with dry surfaces. The infiltration of outdoor particles during winter was relatively low owing to tightly insulated buildings in this cold climate, while the higher spring values match results from temperate regions.

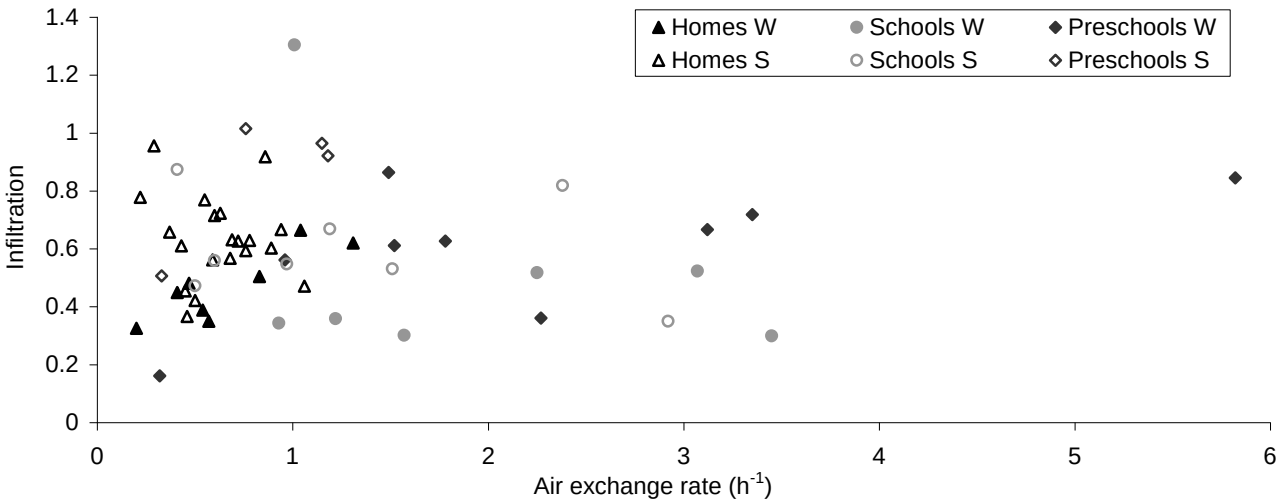

Fig. 2 Infiltration of ambient sulphur indoors (ratio between indoor and outdoor levels) as a function of air exchange rate for homes, schools and preschools. Winter (W) and spring (S) values are marked with filled and open symbols, respectively.

These results can probably be applicable for cities in regions of similar climate (i.e Northern parts of Europe and America) although absolute levels can differ. Differences in building constructions, indoor behaviour and features (e.g. carpeting), and local indoor and outdoor sources can, however, affect the results.

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